INORGANIC PHOSPHORS

COMPOSITIONS, PREPARATION AND OPTICAL PROPERTIES

The CRC Press
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William M. Yen
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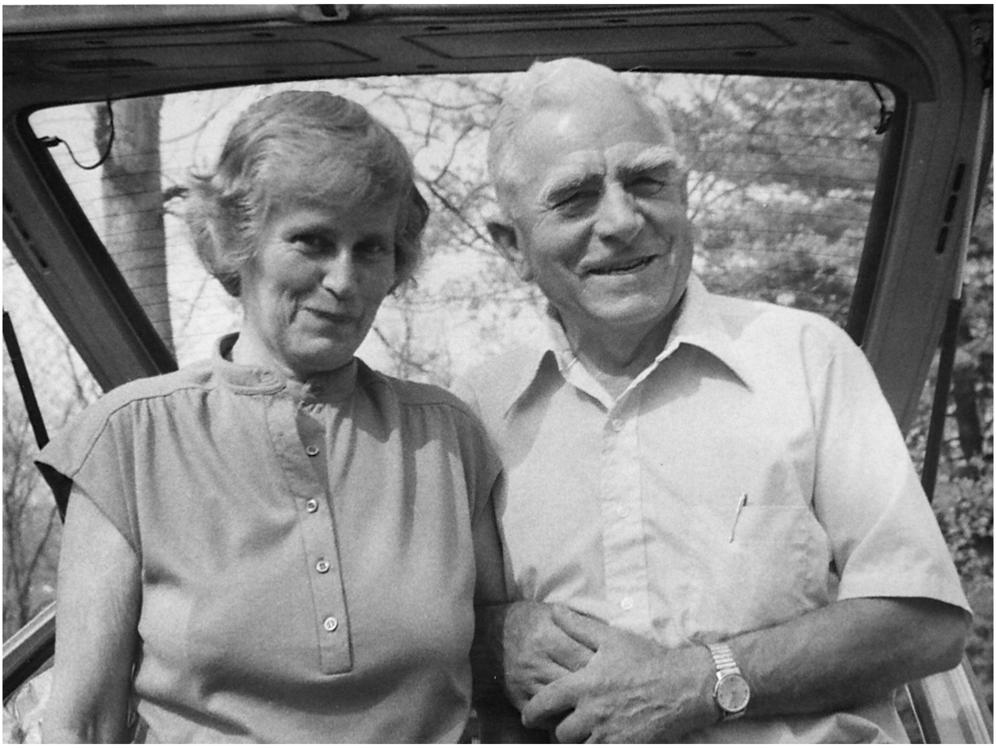

Willi and Renate Lehmann (circa 1970).

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Foreword

Willi Lehmann

It is a truism that all individuals are unique. However, in the case of the late Willi Lehmann this is true in the strongest sense possible. One often hears of a person with a "one-track" mind. That concept describes Willi perfectly. He was indeed one of a kind. As far as I know, he lived for and only thought about phosphors. He was a very oriented, strong willed and, yes, stubborn individual. It is my pleasure to have known him and have been his manager (in truth, no one "managed" Willi) for several interesting and productive years.

I knew very little about Willi's life in Germany. Fortunately, I was able to obtain a copy of an autobiography Willi wrote for his family and was able to learn something about his history. Bill Yen and I present a brief summary of Willi's life and times in Appendix III. I knew that he served in the German army during World War II, first on the Russian front and then on the Western front. It is difficult for me to conceive of him as a member of a military unit. He always had a very un-Germanic disregard for authority. This undoubtedly explains why, after working his way up to grade sergeant, he was "busted" back to private. I believe he objected to officers riding in comfortable first-class carriages while enlisted men rode in overcrowded second-class carriages. Another un-Germanic trait was that he disliked beer; he called it "seifewasser" (soapy water).

Willi was always resourceful (surely a good trait for a scientist). At the end of the war, after being captured by the French, he managed to escape and be recaptured by the Americans because he knew they treated their German captives better. While he was in POW camp a request came asking whether any prisoner could repair typewriters. Willi, who actually had no prior experience in this line, promptly volunteered and became a successful "typewriter mechanic" overnight. Also during his time as a prisoner he spent his spare time recalling and writing down the essentials of his previously studied elementary physics textbook. I suppose he "borrowed" the necessary paper and pencils from the offices where he repaired typewriters.

After the war Willi studied physics (I am not sure at what university) under Prof. Erich Krautz, who had an interest in luminescence. Later, Krautz became Director of Research at a branch of the Osram Lamp Co., located in Augsburg, near Munich. At that time, the Lamp Division of the Westinghouse Electric Corp., located in Bloomfield, New Jersey, had a patent and technical interchange agreement with Osram. On a visit to Augsburg, E.G.F. Arnott, Director of Research in Bloomfield, asked Prof. Krautz to recommend two of his former students who were interested in luminescence and would like to immigrate to the United States. Krautz recommended Willi Lehmann and Claus Haake, and both accepted the offer. This was probably in 1955, as Willi published his first American papers (*Phys. Rev.,* 101, 489; *J. Electrochem. Soc.,* 103, 667 and *Illum. Eng.,* 51, 684) in 1956. Willi remained with Westinghouse, first in Bloomfield and then in Pittsburg for many years, while Claus left after about 2 years to move to Arizona for reasons of his wife's health.

In 1956 I was Manager of the Phosphor Research Section of the Westinghouse Lamp Division and thus suddenly found myself responsible for two foreigners about whom I knew nothing. The situation was conceivably complicated by the fact that I was Jewish; I didn't know how they would react to me and vice versa. Fortunately, this never presented a problem. Both Willi and Claus turned out to be very diligent and skilled workers (Prof. Krautz would not have recommended dummies). Their knowledge of the English language was good, although Willi always spoke with a pronounced Germanic accent, probably because he spoke only German at home. (I must admit that while Willi worked for me I always edited his scientific papers before publication, but endeavored to leave them sounding like Willi.)

During those years in Bloomfield the attention of the Phosphor Section was directed primarily to electroluminescence, then in its infancy. I can truthfully say the best (brightest and longest lived) electroluminescent phosphors made anywhere in that era were made by Willi Lehmann. This activity, and that elsewhere, is summarized in my book, *Electroluminescence and Related Effects* (Academic Press, 1963). I was later made a fellow of the Institute of Electrical and Electronics Engineers (IEEE) and an Honorary Member of the Electrochemical Society for "leadership in the advancement of the science of luminescence." However, the work which resulted in these honors was primarily due to three outstanding members of the section: Willi Lehmann, William A. Thornton, and Anselm Wachtel. My effort was mainly that of support, coordination, and interpretation.

My approach to "management" of scientific activity was essentially minimalist, consisting of four steps: (1) hire the most capable and self-motivated people, (2) provide them with the necessary equipment and facilities, (3) point them in the directions of interest to the company, and (4) don't bother them, except for occasional encouragement and suggestions as to questions for which no one had an answer at the moment. This minimalist approach certainly worked well with Willi, who was never a "team player." I also learned that minor infractions of company rules could be overlooked unless they were officially brought to my attention: sometimes ignorance of events can be good.

Although trained as a physicist, Willi actually performed best as a self-taught chemist; he was more interested in making better phosphors than in explaining how or why they worked. He was always an enthusiastic worker. I remember one day Claus Haake stuck his head in my door and said, "Willi just made a three-gott-damn phosphor!" I said, "What does that mean?" Claus replied, "Well, when Willi has made a new sample and finds that it tests good, he says 'Gott damn!' Today he tested his latest sample and said, 'Gott damn! Gott damn! GOTT DAMN!'"

About 1963 both Willi and I transferred to the central Westinghouse Research Laboratories in Pittsburgh, but to different departments. I joined the Optical Physics Department, which was primarily concerned with lasers, and in 1969 became manager of the department. Willi went to the Solid State Physics Department, where he continued to work on phosphors, mainly for applications to fluorescent lamps and cathode-ray tubes. Nevertheless, we kept in frequent contact and he always put me on the distribution list for his research reports. It was during this period of his career that he organized the material for his *Phosphor Cookbook*.

Willi always maintained his independence and disregard for rules which seemed pointless to him. There were four types of scientific documents at Westinghouse: patent disclosures, papers to be published, summary research reports for internal use, and short research "memos." For some strange (probably historical) reason, memos had to be addressed to a particular individual, although they could have an extended distribution list. Once Willi (in Pittsburgh) apparently had trouble deciding to whom a certain memo should be addressed so in the proper place he wrote, "The Queen of England." Some unwitting secretary typed it up that way and sent it to his department manager for signature. Considerable consternation ensued, but Willi survived unscathed and hardly ruffled. For Willi, rules were usually meant for lesser beings; he had more important things (phosphors) to think about.

Willi retired from Westinghouse in about 1985 (the reason for my vagueness about dates is that Westinghouse is now defunct and I have no way of accessing company files). He went to live in Hendersonville, North Carolina, and apparently did consultation on electroluminescence for the Rogers Corp. in Connecticut. I am sorry to say that I lost contact with him after 1988.

I have learned since that Willi passed away in January 1993 and that he is survived by his wife Renate and four children, Caren, George, Hans, and Mary. All appear to be prospering and the family has given its approval to the belated publication of Willi's *Phosphor Cookbook* and *Phosphor Tables* he so carefully compiled nearly two decades ago.

When Willi Lehmann was alive and active he was one hell of a great phosphor maker. It was his obsession and sole occupation. He left many important published papers. In 1988 he wrote to inform me that he had been invited to contribute to a book entitled *Phosphors*. He enclosed a copy of his contribution, an extended collection of the main properties of about 300 of the best-known inorganic phosphors, with reference to the original publications. However, this book was never published. He said then, "My *Phosphor Tables* are completed and I don't like the idea of them going to waste." The present volume by Bill Yen and Marv Weber, which combines his *Phosphor Cookbook* and his *Phosphor Tables*, finally solves that waste problem. It will serve as a fitting and belated recognition of the valuable work this unusual individual contributed to the science of luminescence.

Henry Ivey
Coconut Creek, Florida
April 1, 2003

Preface

About a decade ago, one of us (WMY), in response to a federal broad agency announcement, initiated an effort to establish a baseline for the state of knowledge concerning the methodology for synthesis and the optical properties of a variety of phosphors used for display and other technical applications. Though for various reasons this effort ultimately turned futile, several members of the phosphor/luminescence community called my attention to an existing backlog of published and unpublished literature addressed to this subject. This resulted, for example, in our becoming aware of the existence of the *Phosphor Handbook* published in Japanese under the auspices of the Japan Phosphor Society and led to its eventual translation and publication as the *Phosphor Handbook*, a volume in the CRC Lasers and Optical Sciences and Technology Series.

In connection with efforts to establish a phosphor database, Ronald Petersen (of Motorola, at the time) first presented us with a copy of Willi Lehmann's opus (*Phosphor Cookbook*) on methods for synthesis and properties of over 200 phosphors. This report dates from the late 1970's and covered the majority of phosphors then in use. Dr. Lehmann, of course, was a principal in the development of many of the phosphors included in his cookbook. He later updated and extended this work in 1988 in his *Phosphor Tables* in which the phosphor properties of over 300 luminescent materials were summarized in tabular form. A copy of these tables, which was prepared for a publication that never appeared, was preserved and given to us by Dr. Henry Ivey. Henry had a close working relationship with Willi at Westinghouse as the Foreword to this volume attests.

The scholarship contained in the *Phosphor Cookbook* and the *Phosphor Tables* is quite remarkable and comprises a great deal of meticulous and careful work characterizing Willi Lehmann's career as a phosphor synthesizer. The list of materials presented in the compilations is large and the manuscripts preserve and summarize synthesis and optical data on most of the commonly used phosphors (as well as some less common ones). In the absence of any systematic database on phosphors, the two unpublished manuscripts represent a reasonably complete summary of the state of knowledge on phosphors up to the late 1980's.

Though it might be argued that the art of phosphors synthesis and characterization has advanced considerably since Lehmann's time, we believe that these contributions need to be preserved as part of the phosphor art. Thus, it appeared to us that the content of these two unpublished manuscripts fully deserved publication as a record, if nothing else, of past methodologies; these methodologies are often abandoned and forgotten but often need to be rediscovered and revived when circumstances warrant it. Almost all modern phosphors are synthesized by solid-state reactions at high temperatures. Updated versions of these techniques are presented in this volume along with other techniques such as sol–gel and combustion that have been developed in the past few decades.

This volume is divided into two parts. Most of the contents of Lehmann's *Phosphor Cookbook* and *Phosphor Tables* are preserved in the first part with either no or only slight changes in style and format. The phosphor data presented in Section 4 combine the results of both manuscripts. However, no composition or preparation information was included in the *Phosphor Tables*; thus such information is absent for many compounds. In the second part of the volume we have attempted to supplement Lehmann's work with additional developments including recent synthesis methods and new phosphors. Because of the plethora of phosphor compositions reported in recent decades, the listing is not exhaustive but rather representative of some of the more significant phosphors developed in recent years. We have restricted consideration to materials that are accessible in the open literature and have not included any recipes or description of phosphors that are proprietary. Only a relatively few phosphors have achieved commercial success. Section 8 presents a list of many commercial phosphor and scintillator materials and the peak wavelength of their emission. Finally, three appendices have been added. The first presents an historical perspective on phosphors; in the second a table of phosphors is arranged in order of emission wavelength as a guide in selecting phosphors for particular applications. The third gives a brief summary of Willi Lehmann's life.

It may be noted that the elements belonging to series such as the lanthanides (4f) have chemical behaviors that are nearly identical to each other. It follows that recipes for compounds doped with a certain ion of a series very likely will also be effective for other members of that series. Other considerations (such as ion sizes) will enter, so that the synthesis of any new compounds remains an area of experimentation; a good beginning point, however, would be with the procedures that are presented here. The preparation methods described in this volume generally entail the use of laboratory procedures which are normally encountered in solid-state chemistry and which expose the experimenter to the usual perils. As such, we emphasize that all normal safety precautions (fume hoods, eye protection, etc.) should be observed in the preparation and synthesis of the phosphors described in the volume.

The American Ceramic Society in collaboration with the National Institutes of Standards and Technology (NIST) has continued to publish and revise *Phase Diagrams for Ceramists* (Vols. I–VI) and the sequel *Phase Equilibrium Diagrams* (Vols. VII–XII); these volumes contain a great deal of material which is extremely useful in developing an understanding as to what can and cannot be synthesized. Much additional information on the synthesis and characterization of a phosphor or luminescent material information can be found in the aforementioned *Phosphor Handbook.*

In this effort we have benefitted from numerous comments, suggestions, and contributions from our Editorial Board. We are very appreciative of their help and that of Ron Petersen and Henry Ivey for having preserved the original manuscripts. We are also very thankful to the Lehmann family for giving their permission to use this material. We note with special appreciation the excellent work of Sergei Basun in preparing the many figures and the final manuscript, Sarah Dunning for typing the manuscript, Mike Caplinger and Jeff Deroshia for their computing assistance, and the valuable interactions with CRC Project Editor James McGovern and Development Manager Helena Redshaw.

We are aware that, as noted in the Foreword, Willi Lehmann was anxious to have the material that he had prepared with such care published in some form. We hope that the publication of *Inorganic Phosphors* serves to fulfill his wish. Indeed, this volume should be considered a tribute to this unusual individual and his contributions to the phosphor art.

William M. Yen
Athens, Georgia

Marvin J. Weber
Berkeley, California

April 2004

Further Readings

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The Editors

William M. Yen obtained his B.S. (Physics) degree from the University of Redlands, Redlands, California in 1956 and his Ph.D. in Physics from Washington University (St. Louis) in 1962. He served a term of 3 years (1962–1965) as a Research Associate at Stanford University under the tutelage of Professor A.L. Schawlow and accepted a faculty position at the University of Wisconsin—Madison in 1965. He was granted tenure at Wisconsin in 1968 and promoted to a full professorship in 1972; he retired from the Wisconsin system in 1990. In 1987 he was appointed to the Graham Perdue Professorship at the University of Georgia—Athens where he has established a research program in the properties of phosphors and other light-emitting materials.

Dr. Yen has been the recipient of a J.S. Guggenheim Foundation Fellowship (1979–1980), of a A. von Humboldt Senior U.S. Scientist Award (1985), and of a Senior Fulbright to Australia (1995). He has been appointed to Visiting Professorships at the University of Tokyo (1972), the University of Paris—South (1976), the Australian National University (1980, 1995), the Federal University of Pernambuco—Recife (1980), and the University of California—Santa Barbara (1982, 1985). He was also named by Washington University (St. Louis) as the first Edwin T. Jaynes Visiting Professor for the Fall of 2004. He has been a member of the technical staff at the AT&T Bell Telephone Laboratories (1966) and of the Laser Fusion Project at Lawrence Livermore Labs (1974–1975). Dr. Yen has been elected to fellowship in the American Physical Society, the Optical Society of America, the American Association for the Advancement of Science, and the Electrochemical Society.

Dr. Yen is the co-editor of the *Phosphor Handbook* published by CRC Press.

Marvin J. Weber received the A.B., M.A., and Ph.D. degrees in physics at the University of California, Berkeley. After graduation, Dr. Weber joined the Research Division of the Raytheon Co. where he was a Principal Scientist working in the areas of spectroscopy and quantum electronics. In 1966 to 1967 Dr. Weber was a Visiting Research Associate in the Department of Physics, Stanford University.

In 1973 Dr. Weber joined the Laser Program at the Lawrence Livermore National Laboratory where, as Head of Basic Materials Research and Assistant Program Leader, he was responsible for the physics and characterization of optical materials for high-power laser used in inertial confinement fusion research. From 1983 to 1985 he accepted a transfer assignment with the Office of Basic Energy Sciences of the U.S. Department of Energy in Washington, DC. Dr. Weber returned to the Chemistry and Materials Science Department at LLNL in 1986 and served as Associate Division Leader for condensed matter research and as spokesperson for the University of California/National Laboratories research facilities at the Stanford Synchrotron Radiation Laboratory. He is presently a scientist in the Department of Nuclear Medicine and Functional Imaging of the Life Sciences Division at the Lawrence Berkeley National Laboratory.

Dr. Weber is Editor-in-Chief of the multi-volume *CRC Handbook Series of Laser Science and Technology* and a Fellow of the American Physical Society, the Optical Society of America, and the American Ceramics Society. Among several honors, he is the recipient of the International Conference on Luminescence Prize, George W. Morey Award of the American Ceramics Society, and an Industrial Research IR-100 Award for research and development of fluorophosphate laser glass.

Editorial Board

Part 1:
Lehmann's Phosphor Cookbook and Phosphor Tables

Section 1: Introduction

Section 1

INTRODUCTION

The following is Willi Lehmann's introduction to his *Phosphor Cookbook*:

> The writer of this report has, during about 25 years of practical experience, prepared and tested roughly 2 × 10^4 individual samples of inorganic phosphors of various kinds. It is unavoidable in such work that many samples perform too poorly to be worth mentioning. Many others were just repetitions during optimizations, etc. of the same materials. What remains are relatively few. This report describes some 200 phosphors which are commercially in use already, which appear to have some potential to become commercially useful, or which are otherwise somehow "interesting" (to the writer, at least). Most of them are well known (more or less), but some are new and have never been mentioned anywhere else. The following tables give, for each phosphor, a brief description of how to prepare it and an equally brief description of its main properties. References to open publications or internal reports, where available, are added to help anyone wishing to know more about a particular material than these tables can give.
>
> The phosphor collection covered by this "cookbook" is not complete, of course. It will never be. It may anyway serve as a convenient guide for all occasional or professional users of phosphorus showing essentially what is available. Each one of the recipes is only a suggestion. It has been tried in this laboratory and it works, but it does not mean that a variation of the recipe does not work. In fact, the writer believes that most of the recipes still permit substantial improvements. It may remain to the individual phosphor chemist to work out such improvements.
>
> The professional phosphor chemist has often, only half jokingly, been referred to as "phosphor cook." Peculiarly, and despite of the fact that so many different phosphors are now available, there has been no phosphor cookbook before. To fill out this gap is the purpose of this report.

In the abstract to the report Lehmann expected that the cookbook would be useful as:

1. a survey of materials for which properties are available to the occasional user of phosphors,
2. a guide to help anyone new in the field in the successful preparation of phosphors,
3. a start for the experienced phosphor chemist in the improvement of known materials or in the development of new ones.

Most of the following two sections (with the exceptions of Sections 2.2 and 2.3) are predominantly taken verbatim from Lehmann's report.

Section 2: Phosphor Preparation

Section 2

PHOSPHOR PREPARATION*

The following methods are essentially the preparation procedures used by the writer (W. Lehmann) to make the phosphors described in this report. Many points probably are trivial to the professional phosphor chemist but they are certainly not so to the novice or to anyone preparing phosphors only once in a while.

Almost all good inorganic phosphors consist of a crystalline "host material" in which small amounts of certain impurities, the "activators" are dissolved. The activators are primarily responsible for the luminescence. Other impurities, the "co-activators," are necessary in some (not in all) cases to dissolve the activator impurities into the host crystal. Co-activators do not, or only to a very minor degree, participate in the luminescence process. Both activators and (if necessary) co-activators are diffused into the host crystal at elevated temperatures, the "firing." Even the final host material frequently is formed only during the firing by solid-state reactions between several starting materials. The firing temperature often is little below the melting temperature of the host material. If that is impractical because of excessively high-melting temperatures of the host material, the crystallization is facilitated at lower temperatures by addition of a "flux" (frequently a halide) to the raw mix before firing.

2.1 Starting Materials

Commercially available high-purity grade chemicals (e.g., analytical reagent grade, luminescent grade) are adequate to prepare most of the phosphors. Only sulfide-type phosphors are exceptions because they are sensitive to undesired impurities, sometimes down to the parts per million range. Sufficiently pure ZnS and CdS are available not to require additional purification for the preparation of ZnS-type phosphors. However, the chemicals needed to prepare CaS-type phosphors are not normally available in the required purity. Section 3 of this report describes some techniques that can be used to purify commercial compounds to prepare CaS-type phosphors.

The chemicals mentioned in the individual recipes are those that usually are the most readily available. They can frequently be exchanged with others. For instance, $CaCO_3$ can frequently be replaced by CaO, CaO_2, $Ca(NO_3)_2$, or $Ca(OH)_2$. Similarly, $MnCO_3$ can be replaced by MnO_2, MnO, MnS, $MnSO_4$, $Mn(C_2H_3O_2)_2$, and so on. What counts are only the necessary amounts of the particular chemical elements measured in moles, and that the used compounds decompose readily during the firing of the phosphor to provide the necessary building blocks to the final material.

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* This section is from W. Lehmann's *Phosphor Cookbook*.

2.2 Amounts

The recipes in this report are given in whole molar units to make them as clear as possible. Whenever such large amounts of phosphors are not needed or wanted, all amounts can be reduced by constant factors as long as the molar ratios between the individual components in the recipe are maintained. However, it is impractical to reduce the amounts to less than about 1 or 2 g of the final phosphor. The materials become poorly reproducible with such very small amounts.

The weightings of the starting materials are not very critical. Phosphor properties vary relatively little only with a variation of the starting material ratios. Roughly, the amounts of the chemicals involved in the formation of the host materials need to be weighed only within ±1% of the mentioned proportions, sometimes even within still wider tolerances. The smaller amounts of the activating chemicals involved are even less critical. Variations of ±10% of the mentioned activator concentrations normally have little effect on the performance of the final phosphor.

2.3 Mixing

Very thorough mixing of the starting materials before firing is extremely important for the successful preparation of a good phosphor. Some of the best methods are:

Slurrying The finely powdered starting materials are mixed into water, alcohol, or any other inert and volatile liquid to a uniform slurry. Water-soluble activator chemicals, etc. can be added dissolved in water. The slurry is dried and the dried material, which sometimes is a more or less hard crust, is powderized in a mortar as well as possible. This method has been used for most of the recipes of this report.

Wet Ball-Milling The slurry prepared above is ball-milled with porcelain pebbles for a time (about 1–2 hours) to ensure a moist thorough mix and, in particular, a breakup of all possible lumps in the slurry. The slurry is then dried in air and the dry material is mechanically powderized. This method is a bit cumbersome and it is impractical for small samples (a few grams); otherwise it is the most ideal.

Dry Ball-Milling The dry powder mix is ball-milled with porcelain pebbles for 1–2 hours. This method avoids the time-consuming drying of the slurry but it works only for powders, which stay free flowing all the time. Some materials (e.g., ZnO) are not free flowing and cannot be mixed this way.

Mortaring The dry powders are simply mixed by mortaring together to make the mix as uniform as possible. This method is least time-consuming and most practical for small samples but the mixes are less uniform down to the microscopic scale than any one prepared by the other methods. Corresponding non-uniformities of the final phosphor may be the result. Whenever such non-uniformities occur, firing not only once but also several times and mortaring every time in between can usually eliminate them. Several firing steps are appropriate in many cases for other chemical reasons.

2.4 Containers

The best container material for the preparation of most phosphors is clear quartz glass (silica). Only some materials (the alkali elements, in particular) react too badly with quartz glass at firing temperatures and are better fired in other container materials. Pure alumina serves fairly well in these cases.

Phosphor raw mixes not containing volatile (at firing conditions) constituents are best fired in open boats so that the charge is fully exposed to the desired atmosphere surrounding the material. Raw mixes which do contain volatile constituents (e.g., halides) are better fired in loosely covered containers permitting some contact with the surrounding atmosphere but still keeping at least some of the volatile part in the container. Capped silica tubes are widely used in our laboratory; they consist of two tubes each closed at one end and both loosely fitting into each other. Loosely covered crucibles are appropriate wherever alumina is the container material.

All these containers are placed near the closed ends of bigger firing tubes made of silica. Some typical arrangements are shown in Figure 1. Only these ends of the firing tubes are in the furnaces during firing.

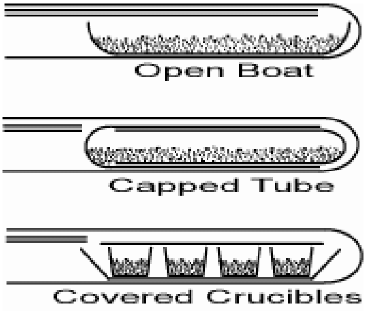

Figure 1 Schemata of different containers during phosphor firing.

2.5 Furnace

Phosphor firing requires an electric furnace permitting temperatures between about 500ºC and at least 1200ºC, better up to about 1400ºC. Any desired temperature should be maintained during firing by means of an automatic temperature controller to within ±20ºC or better. A simple on–off control is acceptable.

A reliable temperature control clearly is one of the weak points of phosphor preparation. The writer has yet to see a furnace whose temperature does not occasionally deviate from that indicated by the controller. The only way to eliminate this problem is frequent re-calibration of furnace and controller by means of a good thermocouple and a millivolt comparator.

2.6 Firing Atmospheres

The various phosphors are fired in different atmospheres depending on the materials and the desired reactions. Oxygen-dominated phosphors (oxides, silicates, phosphates, etc.) may be fired in oxidizing (air, O_2), inert (N_2, Ar), or reducing atmospheres (CO, forming gas, H_2, NH_3). Sulfurization of sulfide phosphors may be achieved by firing either in H_2S or in an inert gas loaded with CS_2. Many of these gases are interchangeable. It makes no difference, for instance, whether a phosphor is fired in N_2 or in Ar. Some arrangements used to handle the various gases in the firing tubes are shown in Figure 2 assuming the phosphor containers are both open boats.

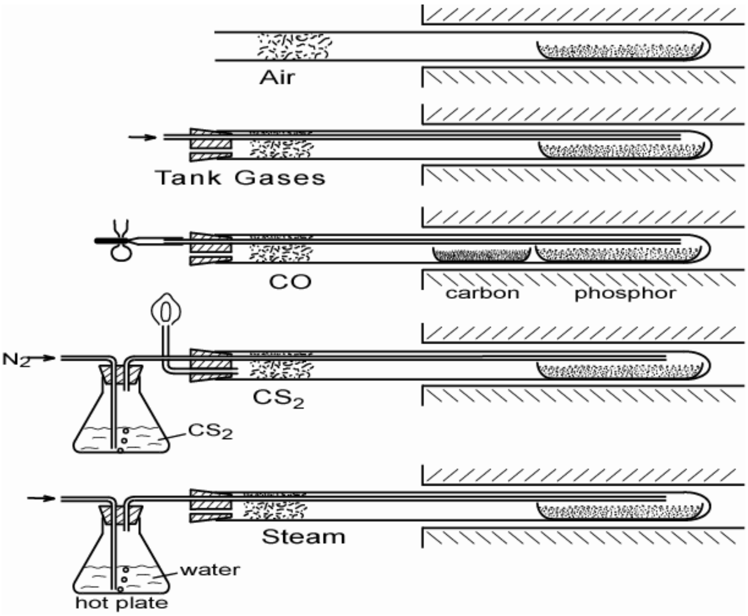

Figure 2 Schemata of different containers during phosphor firing.

Air Firing a phosphor in air requires nothing but the container in the firing tube whose open end is left open or, at most, closed by a bit of loose glass wool to prevent dust particles from drifting in during firing.

Gases from tanks (or other supplies) These can be piped into the firing tubes via long and thin gas inlet tubes (silica) reaching as far into the firing tubes as possible. The open ends of the latter are closed by ordinary rubber stoppers with two holes for gas inlet and outlet. The stopper is protected against radiant heat by a bit of loose glass wool in front of it. If the phosphor is fired in H_2 or in H_2S, it is extremely important first to flush all air out the firing tube with an inert gas (e.g., N_2) before admitting the final gas; otherwise the effect (explosion) will be spectacular when the firing tube enters the furnace. **Be extremely cautious!**

CO This gas is about the most convenient for firing an oxygen-dominated phosphor in a reducing atmosphere. Some carbon black is placed in a separate open container next to the phosphor container in the firing tube. The air is flushed out by plain O_2 and the gas inlet tube is then closed (*but leave the inlet open*). When the charge enters the furnace, some of the carbon black burns to CO in situ.

CS_2 An inert carrier gas (e.g., N_2) bubbles though a flask containing some liquid CS_2 in front of the firing tube. Do not heat the flask; the vapor pressure of the CS_2 is high enough at room temperature. Escaping unused CS_2 gas can be burned at the end of an outlet tube. As in cases of H_2 and H_2S, be very careful to flush all the air out the firing tube before admitting the CS_2-loaded gas.

Steam This arrangement resembles that used for CS_2. A carrier gas (air, N_2, etc.) bubbles through a flask containing some water in front of the firing tube. The vapor pressure of the water is too low at room temperature to have much effect, so it is necessary to heat the flask to gentle boiling. The tube connection between flask and firing tube should be as short and straight as possible; otherwise condensing liquid water might block the gas flow.

2.7 Treatments after Firing

Fired phosphors often (not always) are slightly sintered cakes that have to be powderized to obtain the desired fine powder. This powderizing usually is possible by gentle grinding or milling. Avoid all hard milling because it is likely to damage the phosphor. Phosphors coming out the furnace as badly sintered lumps indicate that something is wrong; most likely the firing temperature was too high.

Some phosphors require special washings after firing, usually to remove one or the other undesired residues (e.g., halides). Such cases are noted in the recipes of this report. Phosphors of recipes that do not mention a washing do not need it.

All phosphors should finally be screened to remove undesired big particles. A 200-mesh stainless steel sieve is adequate for most general purposes but some special applications may require finer screens. Some phosphors are free flowing and easily screened. Others tend to lump and are not screenable with any reasonable effort. Such materials can easily be made free flowing by addition of small amounts (roughly 1/10% by weight) of some additives like very fine SiO_2, Al_2O_3, Sb_2O_3, etc. Unfortunately there is no general rule to pick the best additive; to find one remains up to the ingenuity of the experimenter. Phosphors that stubbornly refuse to become free flowing with any additive can still be wet screened in a suspension in water, methanol, etc. However, this still requires subsequent drying, of course.

All phosphors that are not immediately used up for some application should be stored in **closed and labeled** containers. Closed containers obviously are necessary for any phosphor that is not completely stable in room air (e.g., CaO) but they are a good practice also for all others. Remember that good phosphors are precious materials.

Section 3: Purification of Some Starting Materials

Section 3

PURIFICATION OF SOME STARTING MATERIALS*

The normal purities (analytical reagent grade, luminescent grade, etc.) of commercially available starting materials are good enough to prepare almost every phosphor mentioned in this cookbook. Only some CaS-type phosphors are exceptions. Some impurities (e.g., Mn) show up in the CaS-type phosphors in concentrations as low as 1 ppm. Consequently, harmful impurities (mainly metals like Mn, Fe, etc.) in the starting materials are better kept below this level.

3.1 Carbonates (described using the example of $CaCO_3$)

Prepare two separate solutions.

Solution A: Dissolve 1 g-mole of $Ca(NO_3)\cdot 4H_2O$ (= 236 g) in about 1 liter water at room temperature. Add a few cubic centimeters of freshly prepared NH_4-sulfide solution; stir. Let stand overnight. Then filter through a milli-pore filter (0.45 µm pore size).

Solution B: Dissolve about 1.1 g-mole of the $(NH_4)_2CO_3$ (= 105 g) in 1 liter water at room temperature. The carbonate usually comes in big chunks which take considerable time to dissolve. It helps to crush the chunks but do not try to speed up the dissolution by heating. Do not filter this solution.

Slowly add solution A to B (or vice versa) while stirring. White $CaCO_3$ precipitates and some CO_2 develops.

Let settle.
Decant the excess liquid.
Wash the carbonate in de-ionized water several times (stir, let settle, decant).
Dry with methanol in filter funnel and then completely in open air.

Properties

Mg carbonate prepared in this way is of somewhat uncertain composition. It is best converted to MgO by heating in an open boat, air ~500–1000°C, for ~½ hour.

$CaCO_3$ precipitates and settles readily. It can be converted to CaO by firing in an open quartz boat, air, ~1000–1200°C, for ~½ hour.

$SrCO_3$ and $BaCO_3$ both precipitate in too fine particles which almost behave like a gel in the water and do not readily settle. Both are better prepared via the oxalates.

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* This section is from W. Lehmann's *Phosphor Cookbook*.

3.2 Sulfates (described using the example of $SrSO_4$)

Prepare two separate solutions.

Solution A: Dissolve 1 g-mole (= 212 g) of $Sr(NO_3)_2$ in about 1 liter water. Add a few cubic centimeters of freshly prepared NH_4 sulfide solution; stir. Let stand overnight. Then filter through a milli-pore filter (0.45 µm pore size).

Solution B: Dissolve about 1.1 g-mole of the $(NH_4)_2SO_4$ in 1 liter water. Add a few cubic centimeters of NH_4OH; stir. Filter through a milli-pore filter (0.45 µm pore size).

Slowly pour solution A into B (or vice versa) while stirring. White sulfate will precipitate.

Let settle.
Decant the excess liquid.
Wash in de-ionized water several times (stir, let settle, decant).
Dry with methanol in filter funnel over filter paper and then completely in open air.

Properties

Mg sulfate cannot be prepared in this way ($MgSO_4$ = epsom salt).

$CaSO_4$ precipitates as gypsum, $CaSO_4 \cdot 2H_2O$. It can be converted to the more stable anhydrite by heating in open boats, air ~500–1000ºC, for about ½ hour.

Sr and Ba sulfates precipitate immediately as anhydrous sulfates. $SrSO_4$ is still manageable but $BaSO_4$ tends to be of too fine particles which behave almost like a gel in the water and do not readily settle.

3.3 Oxalates (described using the example of BaC_2O_4)

Prepare two separate solutions.

Solution A: Dissolve 1 g-mole (= 273 g) of Ba-acetate, $Ba(C_2H_3O_2) \cdot H_2O$ in about 1 liter water at room temperature. Add a few cubic centimeters of freshly prepared NH_4 sulfide solution, stir. Let stand overnight. Then filter through a milli-pore filter (0.45 µm pore size).

Solution B: Dissolve about 1.1 g-mole (= 138 g) of oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, in 1 liter water at room temperature. Add NH_4OH to make the solution slightly alkalinic. Then filter through a milli-pore filter (0.45 µm pore size).

Slowly pour solution A into B (or vice versa) while stirring. White BaC_2O_4 will precipitate out and readily settles down.

Let settle.
Decant the excess liquid.
Wash in de-ionized water several times (stir, let settle, decant).
Dry with methanol in a filter funnel over filter paper and then completely in open air.

Properties

Mg oxalate precipitates as $MgC_2O_4 \cdot 2H_2O$. It converts completely to MgO by heating in an open boat, air, ~500ºC, ~ ½ hour.

Ca oxalate precipitates as $CaC_2O_4 \cdot H_2O$. It converts to $CaCO_3$ by heating in an open boat, air, ~500–1000°C, ~½ hour. Further conversion to SrO is not practically possible by firing in an open boat, H_2, ~1100ºC, ~1 hour.

Sr oxalate precipitates as $SrC_2O_4 \cdot H_2O$. It converts to $SrCO_3$ by firing in an open boat, H_2, ~1100°C, ~1 hour.

Ba-oxalate precipitates as BaC_2O_4 which can be converted to $BaCO_3$ by firing in an open boat, air, ~500–1000°C, ~½ hour. In contrast to $SrCO_3$, $BaCO_3$ is not as easily converted into the oxide by firing in H_2.

3.4 Sulfur

Dissolve ordinary precipitated (not sublimed) sulfur in as little CS_2 as possible.

Filter the solution though a dense paper filter. Black impurities (metal sulfides, etc.) will remain on the paper.

Pour the filtered solution into a clean flask; add the same amount (by volume) of pure acetone; stir or shake vigorously. Yellow sulfur will precipitate.

Wash the sulfur several times in acetone (stir, let settle, decant).

Dry in filter funnel over filter paper and then completely in open air.

Properties

This is a coarse yellow powder, sufficiently pure for all preparation work of sulfide-type phosphors.

Section 4: Phosphor Data

4.1 Description of Data
4.2 Simple Oxides
4.3 Silicates
4.4 Halosilicates
4.5 Phosphates
4.6 Halophosphates
4.7 Borates
4.8 Aluminates and Gallates
4.9 Molybdates and Tungstates
4.10 Miscellaneous Oxides
4.11 Halides and Oxyhalides
4.12 Sulfates
4.13 ZnS-Type Sulfides
4.14 CaS-Type Sulfides
4.15 Double Sulfides
4.16 Miscellaneous Sulfides and Oxysulfides

Section 4

PHOSPHOR DATA

4.1 Description of Data*

This section presents information about inorganic phosphors, either from Lehmann's *Phosphor Cookbook* or from Lehmann's *Phosphor Tables*. Almost all inorganic phosphors consist of a host material into which small amounts of an activator impurity have been dissolved. The chemical formula corresponding to the host crystal generally is well established but the crystal structure may not be available. The activation includes only the activator and its ionic state as far as it is known. Additional impurities (co-activators, etc.) are specified only in some cases where they have a strong effect on the final luminescence of the phosphor.

The phosphor composition and a brief description of the preparation conditions used by Lehmann are given in his *Phosphor Cookbook* but not in the *Phosphor Tables.* Optical properties summarize the emissions of the phosphors. The emission color is that as it appears to the human eye. Many emission spectra consist of diffuse bands extending over a certain range; others are complex in shape or consist of discrete (although sometimes somewhat diffuse) lines. The emission peak corresponds to the spectral position where the diffuse band has a maximum, to the spectral range of the main part of a complex emission, or to one or two strongest lines in case of line emission. The width corresponds only to band emission and indicates the width of the band at half of its peak intensity (full width at half maximum—FWHM). Both the peak and bandwidth frequently depend on preparation conditions and are reproducible only within about ±0.1 to 0.2 eV.

Because efficiencies obtained on poor phosphor samples are of limited usefulness, only observed efficiencies of the best samples known to Lehmann are shown. (Lehmann notes that one should keep in mind that an efficiency improvement of a phosphor, perhaps by using modified preparation conditions, is always a possibility that cannot be ruled out.)

Efficiencies under optical excitation, by either 365- or 254-nm ultraviolet (UV) — both the main emissions of a Hg discharge lamp — are given in Lehmann's *Phosphor Tables* in terms of quanta (i.e., the ratio of emitted light quanta over irradiated UV quanta). The symbols mean:

++ = efficiencies in the 50–100% range,
+ = efficiencies in the 10–50% range,
– = efficiencies below 10%.

The efficiencies by electron beam excitation in vacuum are described by the energy ratio (i.e., the ratio of emitted light energy over irradiated electron beam energy). In this instance the symbols mean:

++ = efficiencies of 10% or more,
+ = efficiencies in the 1–10% range,
– = efficiencies below 1%.

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*This subsection is adapted from W. Lehmann's *Phosphor Cookbook.*

The luminescence decay time is the time for the emission either to decay to 1/10 or to 1/e of its initial value.

The emission and absorption spectra measured by Lehmann are all for room temperature and for the activator concentrations shown. These concentrations are close to, but not necessarily at the optimum in every case. The absorption spectra indicate where the materials may be excited (no absorption—no emission). Too few excitation spectra were available to be included. All spectra are plotted on a quantum basis; that is, the abscissa is calibrated in electron volts (eV) rather than wavelength units because luminescence processes are quantum processes. It is also easier to compare the widths of approximately Gaussian-shaped emission bands plotted in eV than it is to compare the widths of very non-Gaussian-shaped bands plotted in wavelength units. The simple conversion between wavelength (in nanometers, nm) and quantum energy (in eV) is

$$(\mathrm{nm}) = 1240/(\mathrm{eV})$$

Using this conversion, the two optical wavelengths used for excitation correspond to:

365 nm — 3.40 eV
254 nm — 4.88 eV

Only the main references to original publications are given. Absence of a reference means that none is known.

4.2 Simple Oxides

The following host compounds and activators are included in this subsection:

$CaO:Bi^{3+}$
$CaO:Cd^{2+}$
$CaO:Cu^{+}$
$CaO:Eu^{3+}$
$CaO:Eu^{3+}, Na^{+}$
$CaO:Mn^{2+}$
$CaO:Pb^{2+}$
$CaO:Sb^{3+}$
$CaO:Sm^{3+}$
$CaO:Tb^{3+}$
$CaO:Tl^{+}$
$CaO:Zn^{2+}$
$ZnO:Al^{3+},Ga^{3+}$
$ZnO:Ga^{3+}$
$ZnO:S$
$ZnO:Se$
$ThO_2:Eu^{3+}$
$ThO_2:Pr^{3+}$
$ThO_2:Tb^{3+}$
$Y_2O_3:Bi^{3+}$
$Y_2O_3:Er^{3+}$
$Y_2O_3:Eu^{3+}$ (YOE)
$Y_2O_3:Ho^{3+}$
$Y_2O_3:Tb^{3+}$
$La_2O_3:Bi^{3+}$
$La_2O_3:Eu^{3+}$
$La_2O_3:Pb^{2+}$

$CaO:Bi^{3+}$

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
CaF_2	0.5	0.390
Bi_2O_3	0.01 (of Bi)	0.023

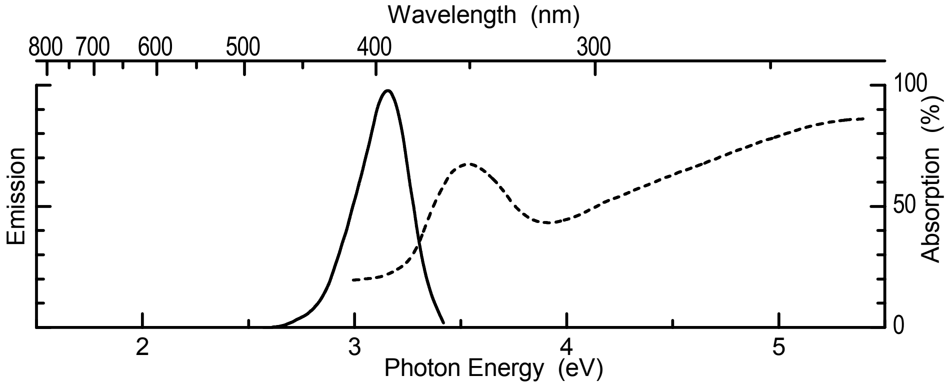
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, stagnant air, 1200ºC, 1 hour.
Powderize.
Store in well-closed container. Keep dry.

Optical Properties

Emission color: Violet + UV
Emission peak: 3.17 eV
Emission width (FWHM): 0.29 eV
Excitation efficiency by UV: ++ (3.4 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: 5%

Spectra



Remark

This phosphor is very sensitive to traces of Mn. Use only purest $CaCO_3$.

References

1. Lehmann, W., Calcium oxide phosphors, *J. Lumin.,* 6, 455 (1973).
2. Hughes, A.E., and Pells, G.P., Luminescence spectra of Bi^{3+} ions in MgO and CaO, *Phys. Status Solidi B,* 71, 707 (1975).
3. Yamashita, N., and Asano, A., Luminescence-centers of Ca(S,Se):Bi^{3+} and CaO:Bi^{3+} phosphors, *J. Phys. Soc. Jpn.,* 40, 144 (1976).

CaO:Cd^{2+}

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
CdO	0.3	0.385

Preparation

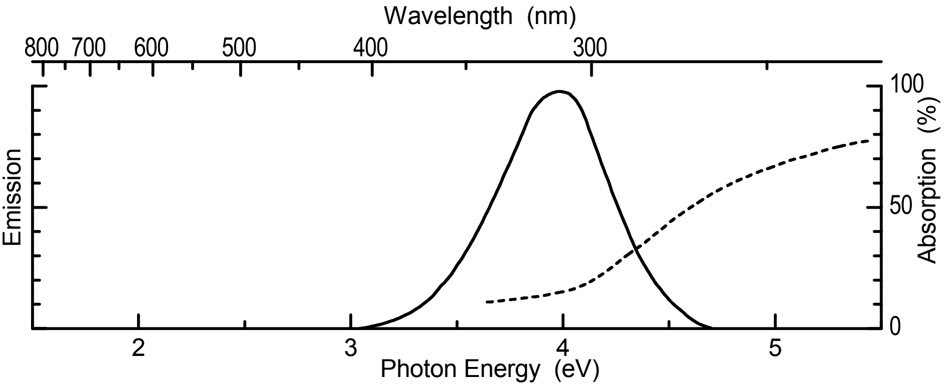
Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, stagnant air, 1200°C, 1 hour.
Powderize.
Store in well-closed container. Keep dry.

Optical Properties

Emission color: UV
Emission peak: Somewhat uncertain, may vary between about 3.90 and 4.00 eV

Emission width (FWHM): 0.63 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: 6–7%
Decay to 10% : Exponential, about 230 µsec

Spectra



References

1. Lange, H., *Tech. Wise. Abh. OSRAM Ges*., 10, 87 (1969).
2. Lehmann, W., Calcium oxide phosphors, *J. Lumin.,* 6, 455 (1973).

CaO:Cu$^+$

Structure: Cubic (NaCl)l

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
CaF_2	0.5	0.380
$CuSO_4{\cdot}5H_2O$	0.01	0.025

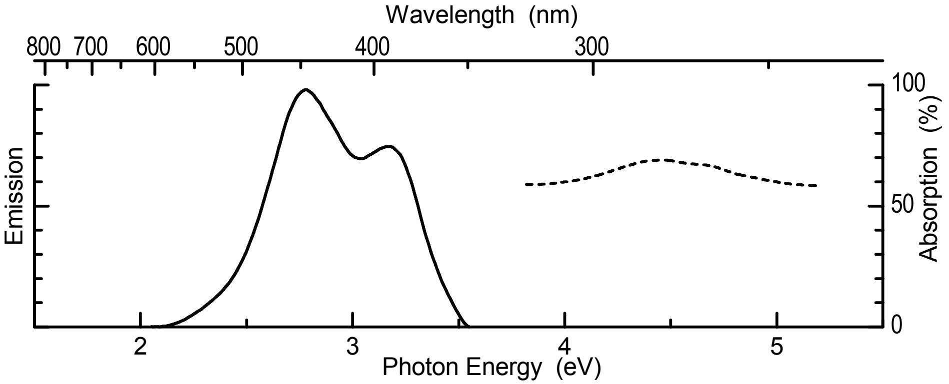
Preparation

Dissolve the copper sulfate in a little water; add solution to the $CaCO_3 + CaF_2$ mix.
Slurry in water.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, CO, 1200°C, 1 hour.
Powderize.
Store in well-closed container. Keep dry.

Optical Properties

Emission color: Bluish + UV
Emission peak: Two overlapping bands, ~2.77 and ~3.18 eV
Emission width (FWHM): 0.75 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: 2%

Spectra



Reference

1. Lehmann, W., Calcium oxide phosphors, *J. Lumin.,* 6, 455 (1973).

CaO:Eu^{3+}

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
CaF_2	1.5	1.2
Eu_2O_3	1.2 (of Eu)	2.1

Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.

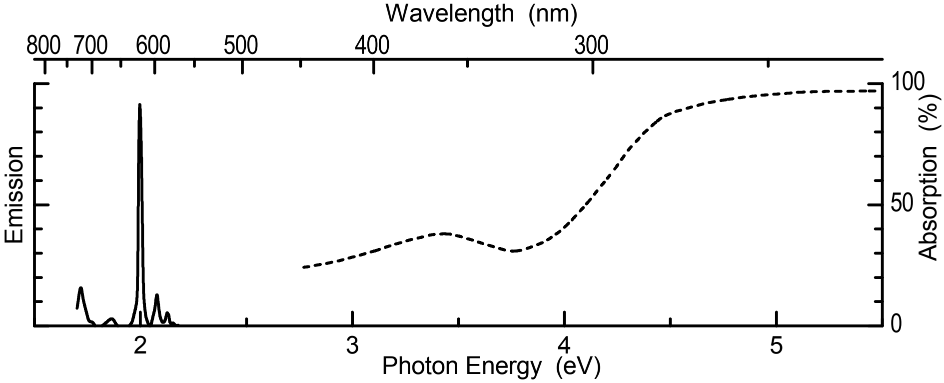
1. Fire in capped quartz tubes, N_2, 1200°C, 2 hours.
   Powderize.
2. Fire in open quartz boats, N_2 loaded with H_2O, 1200°C, 1 hour. After this firing, quench again to room temperature as quickly as possible.
   Powderize.
3. Fire in open quartz boats, stagnant air, 1200°C, ~20 min. After this firing, quench again to room temperature as quickly as possible.
   Powderize.

Store in well-closed container. Keep dry.

Optical Properties

Emission color: Red, slightly deeper red than that of YOE
Emission peak: Main line at 2.015 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV), can be sensitized for excitation at 3.40 eV by addition of Bi (see CaO:Bi^{3+})
Excitation efficiency by e-beam: Poor

Spectra



Remarks

1. The fluorine in the above recipe can be replaced by chlorine or bromine but a phosphor so prepared is badly hygroscopic probably because of leftover $CaCl_2$ or $CaBr_2$.
2. The phosphor reacts to a "bad" temperature range (~800–1100ºC) by greatly reduced efficiency. Top efficiency requires that the phosphor passes through this range as rapidly as possible after second and third firings.
3. The red Eu^{3+} emission shown in the preceding figure appears only if no alkali is present. Addition of Li, Na, or K (perhaps for charge compensation, $Li^+ + Eu^{3+} = 2Ca^{2+}$) causes the red line at 2.015 eV to appear.
4. This CaO:Eu^{3+} phosphor has been tested in fluorescent lamps. It performs very poorly.

References

1. Brauer, P., *Z. Naturforsch. Pt. A,* 6, 561 (1951), and Uber eu-ionen in erdalkalioxyden und erdalkali-sulfiden, *Z. Naturforsch. Pt. A,* 12, 233 (1957).
2. Lehmann, W., Calcium oxide phosphors, *J. Lumin.,* 6, 455 (1973).

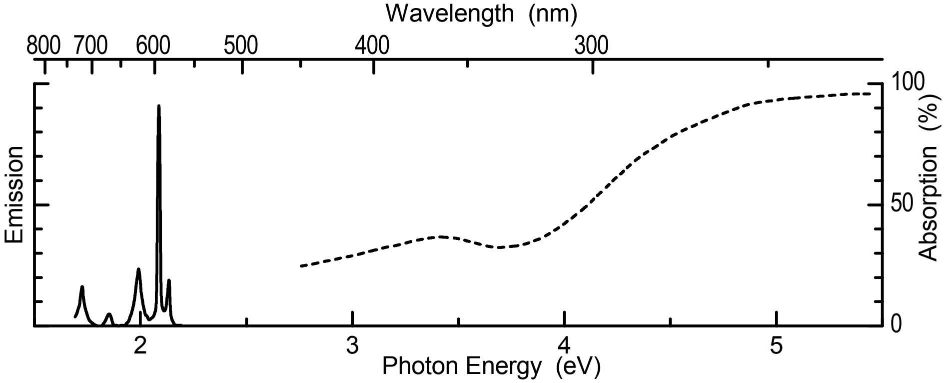
CaO:Eu^{3+}, Na^+

Structure: Cubic (NaCl)

Optical Properties

Emission color: Orange-yellow
Emission peak: 2.10 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



$CaO:Mn^{2+}$

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
CaF_2	0.5	0.390
$MnCO_3$	0.1	0.115

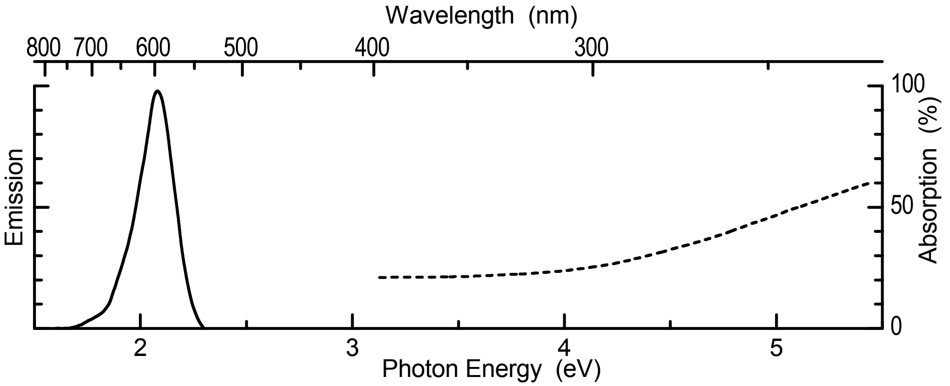
Preparation

Mix by slurrying in water.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, CO, 1200°C, 1 hour.
Powderize.
Store in well-closed container. Keep dry.

Optical Properties

Emission color: Orange-yellow
Emission peak: 2.07 eV
Emission width (FWHM): 0.20 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV); can be sensitized to respond to 4.88 eV by addition of Pb (see $CaO:Pb^{2+}$); can be sensitized to respond to 3.40 eV by addition of Bi (see $CaO:Bi^{3+}$)
Excitation efficiency by e-beam: 5%
Decay to 10%: Exponential, about 22 msec

Spectra



Remarks

1. The Mn concentration is not critical. Strong Mn^{2+} emission appears from about 1 ppm to 10% of Mn or Ca.
2. The phosphor must be fired in a reducing atmosphere; otherwise the Mn stays separate as MnO_2.

References

1. Ewles, J., and Lee, N., Studies on the concept of large activator centers in crystal phosphors. 1. Dependence of luminescent efficiency on concentration of activator size of luminescent centers, *J. Electrochem. Soc.*, 100, 392 (1953).

2. Sancier, K.M., Wise, H., and Fredericks, W.J., Luminescence of solids excited by surface recombination of atoms. 1. Luminescence spectra, *J. Chem. Phys., 37,* 854 (1962).
3. Hühninger, M., and Ruffler, A., *Techn. Wise. Abh. OSRAM Ges.*, 37, 41 (1963).
4. Lehmann, W., Calcium oxide phosphors, *J. Lumin.,* 6, 455 (1973).

CaO:Pb^{2+}

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
CaF_2	0.5	0.390
PbO	0.01	0.022

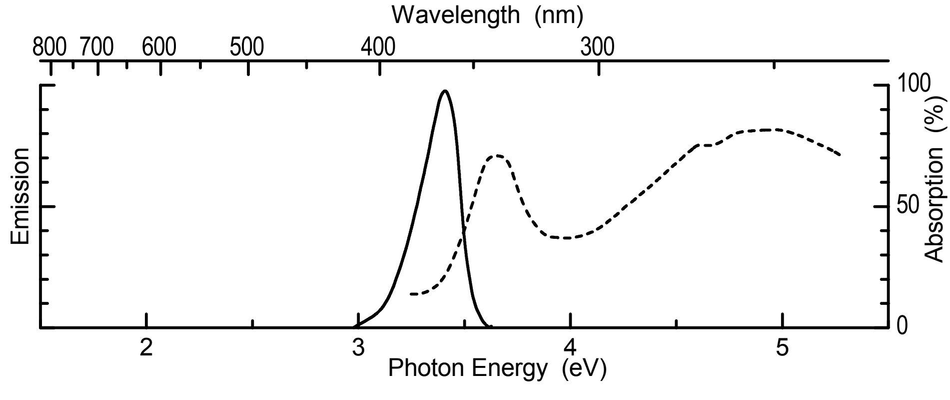
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, stagnant air, 1200ºC, 1 hour.
Powderize.
Store in well-closed container. Keep dry.

Optical Properties

Emission color: UV
Emission peak: 3.42 eV
Emission width (FWHM): 0.21 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: 10%

Spectra



Reference

1. Lehmann, W., Calcium oxide phosphors, *J. Lumin.,* 6, 455 (1973).

$CaO:Sb^{3+}$

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
Sb_2O_3	0.1 (of Sb)	0.145
$NaHCO_3$	1	0.840

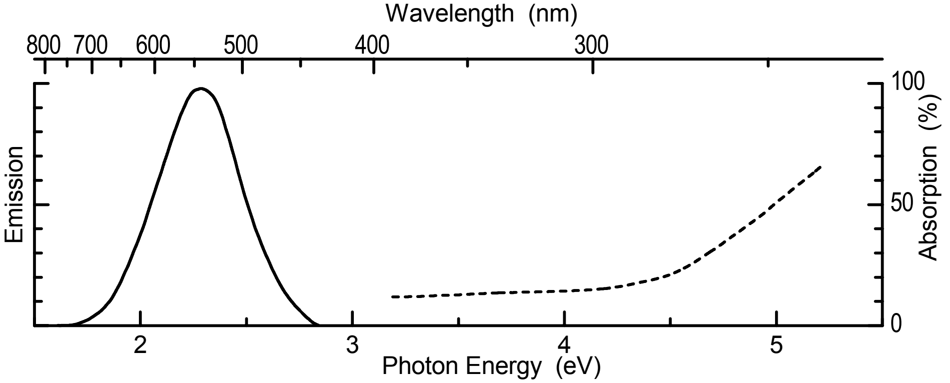
Preparation

Mix by slurrying in water.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, CO, 1200°C, 1 hour.
Powderize.
Store in well-closed container. Keep dry.

Optical Properties

Emission color: Yellow-green
Emission peak: 2.30 eV
Emission width (FWHM): 0.51 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV); can be sensitized for excitation by 4.88 and 3.40 eV UV by addition Bi (see $CaO:Bi^{3+}$)
Excitation efficiency by e-beam: Poor

Spectra



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2. Lehmann, W., Calcium oxide phosphors, *J. Lumin.,* 6, 455 (1973).

CaO:Sm^{3+}

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
CaF_2	0.5	0.380
Sm_2O_3	0.3 (of Sm)	0.520

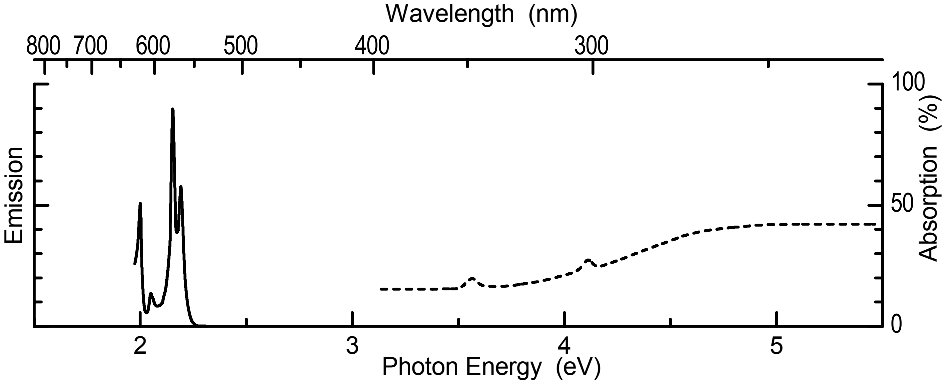
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, stagnant air, 1200ºC, 1 hour.
Powderize.
Store in well-closed container. Keep dry.

Optical Properties

Emission color: Orange-yellow
Emission peak: 2.00, 2.16, and 2.19 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV); can be sensitized to respond to 4.88 eV by addition of Pb (see CaO:Pb^{2+}); can be sensitized for 4.88 and 3.40 eV excitation by addition of Bi (see CaO:Bi^{3+})

Spectra



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2. Runciman, W.A., Atomic configurations in luminescent centres, *Br. J. Appl. Phys*., S78, Suppl. 4 (1955).
3. Witzmann, H., Herzog, G., and Wuntke, K., *Z. Phys. Chem. (Leipzig*), 225, 332 (1964).
4. Herzog, G., and Raths, R., Beitrag zur thermolumineszenz des samariumaktivierten calciumoxids, *Z. Phys. Chem. (Leipzig),* 228, 13 (1965).
5. Herzog, G., and Abel, W. ,Thermoluminescence of phosphors CaO-Sm and CaO-Bi (calcium oxide-samarium and-bismuth), *Z. Phys. Chem. (Leipzig),* 243, 33 (1970).
6. Lehmann, W., Calcium oxide phosphors, *J. Lumin.,* 6, 455 (1973).

CaO:Tb^{3+}

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
CaF_2	0.5	0.380
Tb_4O_7	1.5 (of Tb)	2.8

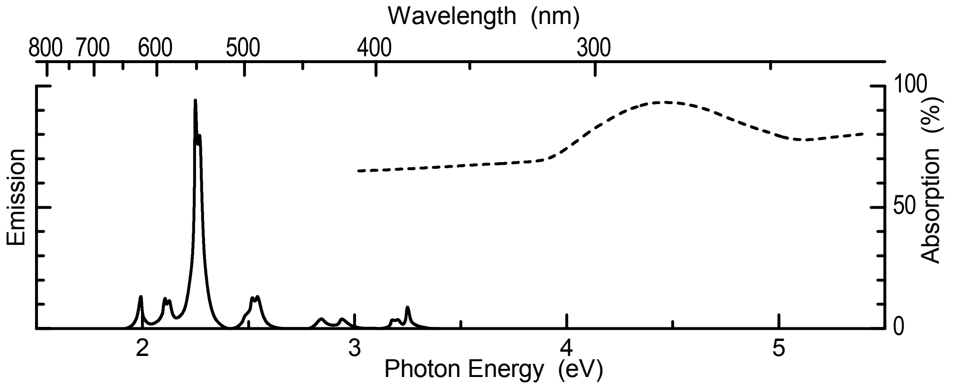
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, CO, 1200°C, 1 hour.
Powderize.
Store in well-closed container. Keep dry.

Optical Properties

Emission color: Pale green
Emission peak: Many lines; strongest near 2.26–2.28 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV); low because of dark body color
Excitation efficiency by e-beam:

Spectra



Reference

1. Lehmann, W., Calcium oxide phosphors, *J. Lumin.*, 6, 455 (1973).

CaO:Tl^{+}

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
CaO	100	56
TlOH	0.03	0.066
NH_4Cl	1	0.540

Preparation

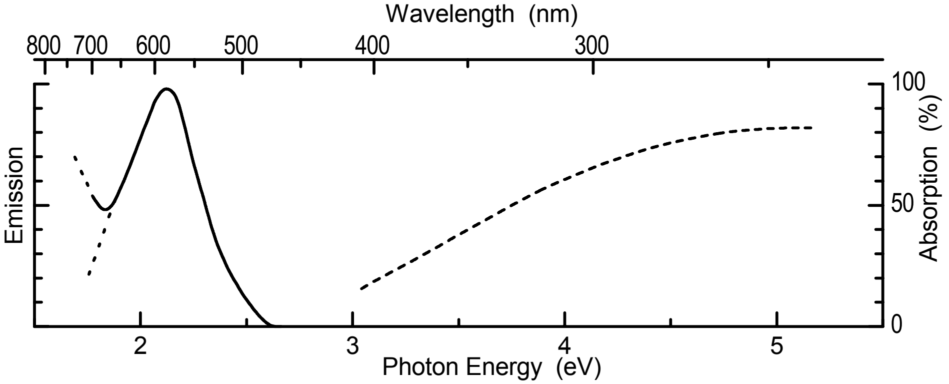
First mix only the CaO and NH_4Cl by dry grinding.

1. Fire in capped quartz tubes, N_2, 1200°C, 1 hour.
   Powderize.
   Now admit the TlOH by dry grinding.
2. Fire in capped quartz tubes, stagnant air, 1200°C, 1 hour.
   Powderize
   Store in well-closed container. Keep dry.

Optical Properties

Emission color: Pale yellow + IR
Emission peaks: 2.11 and 1.5 eV (IR)
Emission width (FWHM): 0.48 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: 3% (Including both bands)

Spectra



References

1. Anderson, H., Zur photoelektrischen messung geringer lumineszenzintensitaten, *Z. Phys. Chem. (Leipzig),* 227, 130 (1964).
2. Lehmann, W., Calcium oxide phosphors, *J. Lumin.,* 6, 455 (1973).

CaO:Zn^{2+}

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
CaF_2	0.5	0.390
ZnO	0.3	0.240

Preparation

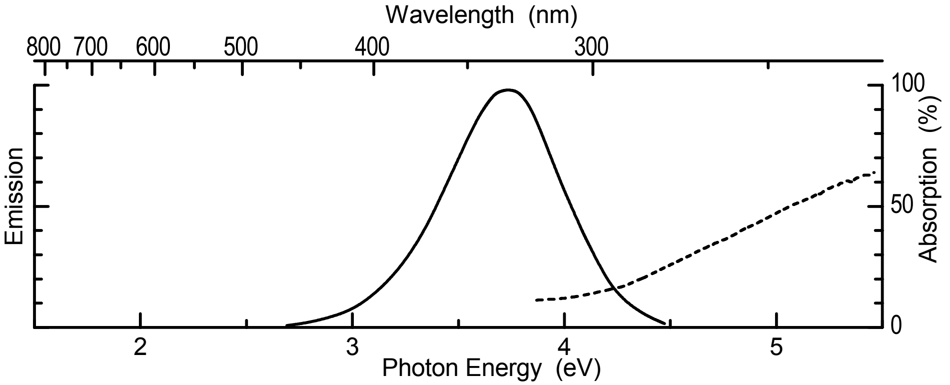
Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, stagnant air, 1200°C, 1 hour.

Powderize.
Store in well-closed container. Keep dry.

Optical Properties

Emission color: UV
Emission peak: Somewhat uncertain, varying between about 3.65 and 3.80 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: 10%
Decay to 10%: Exponential, about 300 μsec

Spectra



Reference

1. Lehmann, W., Calcium oxide phosphors, *J. Lumin.,* 6, 455 (1973).

ZnO:Al^{3+},Ga^{3+}

Structure: Hexagonal (wurtzite)

Optical Properties

Emission color: UV
Emission peak: 3.20 eV
Emission width (FWHM): 0.13 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +

References

1. Lehmann, W., Edge emission of n-type conducting ZnO and CdS, *Solid State Electron.,* 9, 1107 (1966).
2. Luckey, D., A fast inorganic scintillator, *Nucl. Instrum. Methods,* 62, 119 (1968); Luckey, D., Correction, *Nucl. Instrum. Methods,* 63, 358 (1968).

ZnO:Ga^{3+}

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnO	100	81
Ga_2O_3	0.3	0.280
$ZnCl_2$	1	1.4

Preparation

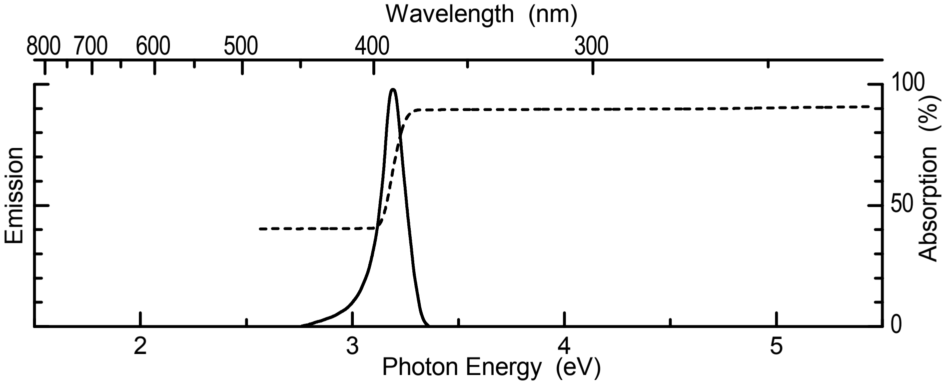
Mix by slurrying in water or methanol. Dry in air. Fire when dry.

1. Fire in capped quartz tubes, stagnant air, 1100°C, 1 hour.
   When cool, inspect under UV lamp. Material should be almost or completely dead. Remove any suspicious parts.
   Powderize. Screen through 200 mesh (stainless steel sieve OK).
2. Fire in open quartz boats, slowly flowing H_2, 800°C, 1 hour.
   When cool, inspect again under UV lamp. Material should show deep violet luminescence, nothing else. Remove all portions which look different.

Optical Properties

Emission color: Deep violet + UV
Emission peak: 3.195 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: 1–1.2%
Decay to 10%: Less than 1 nsec

Spectra



Remarks

1. This material is sensitive to traces of sulfur during preparation. Avoid all sulfur like the plague.
2. Phosphor has gray (not white) body color. It is thermally in a semi-stable state. Do not heat to greater than 300°C, except in H_2.

References

1. Lehmann, W., Edge emission of n-type conducting ZnO and CdS, *Solid State Electron.,* 9, 1107 (1966).
2. Luckey, D., A fast inorganic scintillator, *Nucl. Instrum. Methods,* 62, 119 (1968).
3. Luckey, D., Correction, *Nucl. Instrum. Methods*, 63, 358 (1968).

ZnO:S

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnO	100	81
S	~0.2	~0.064

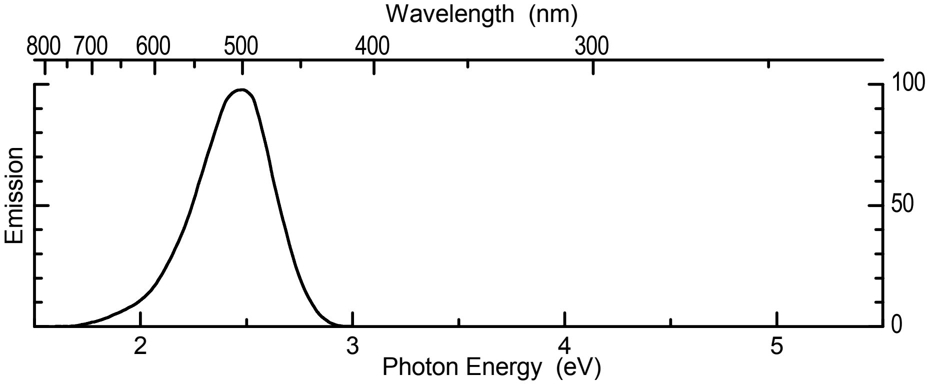
Preparation

Fire in capped tubes, CO, 900ºC, 1 hour.

Optical Properties

Emission color: Blue-green
Emission peak: 2.45 eV
Emission width (FWHM): 0.41 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV); ≈ 60%
Excitation efficiency by e-beam: +
Decay to 10%: In the 1–10 μsec range

Spectra



Remarks

1. This common bluish-green emission of ZnO is greatly enhanced by the addition of sulfur during firing.
2. The emission can be shifted towards blue by replacing 20% of the Zn by Mg, and towards yellow by replacing 10% of the Zn by Cd.

References

1. Thomsen, S.M., Sulfide in zinc-oxide luminophors, *J. Chem. Phys.*, 18, 770 (1950).
2. Smith, A.L., Zinc-magnesium oxide and zinc-magnesium sulfide phosphors, *J. Electrochem. Soc.*, 99, 155 (1952).
3. Lehmann, W., Zinc oxide and zinc-cadmium oxide phosphors, *J. Electrochem. Soc.,* 115, 538 (1968).

ZnO:Se

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnO	100	81
Se	~0.2	0.160

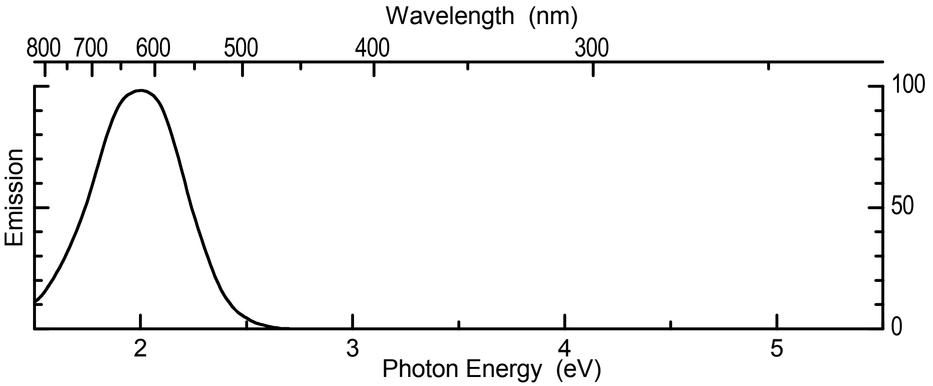
Preparation

Fire in capped quartz tubes, CO, 900ºC, 1 hour.

Optical Properties

Emission color: Orange
Emission peak: 1.98 eV
Emission width (FWHM): 0.51 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV); ≈ 50–60%
Excitation efficiency by e-beam: Afterglow tail observed into the millisecond range

Spectra



Remark

This material can be obtained also by “burning” (i.e., oxidizing) of ZnSe in air but the efficiency of this ZnO:Se is lower.

References

1. Markovski, L.Y., and Oshanskaya, N.S., *Optics and Spectr.,* 9, 40 (1960).
2. Lehmann, W., Zinc oxide and zinc-cadmium oxide phosphors, *J. Electrochem. Soc.*, 115, 538 (1968).

$ThO_2:Eu^{3+}$

Structure: Rutile

Composition

Ingredient	Mole %	By weight (g)
ThO_2	100	232
Eu_2O_3	1.5 (of Eu)	2.3
NH_4F	10	3.7

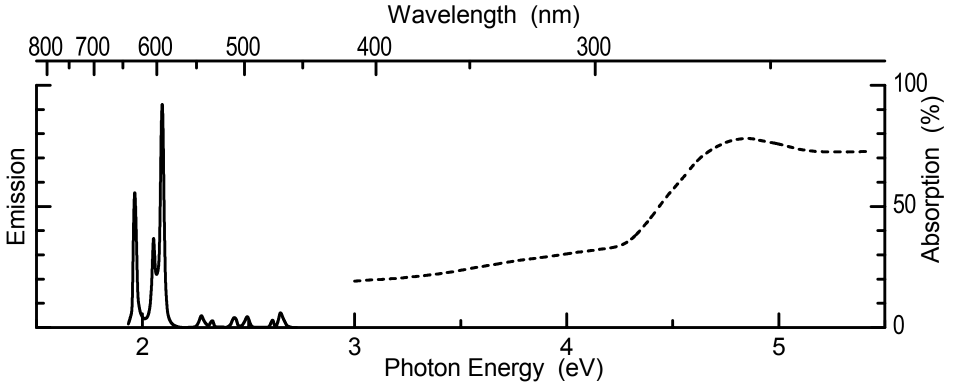
Preparation

Mix by slurrying in water.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, N_2, 1300°C, 1 hour.
Powderize.
Wash in concentrated nitric acid and then in water until neutral.
Dry.

Optical Properties

Emission color: Pinkish orange-red
Emission peak: Three strongest lines, 1.97, 2.04, and 2.095 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: 4%

Spectra



Remark

This phosphor has been proposed for X-ray excitation because of the high stopping power of ThO_2 for x-rays.

References

1. Fok, M.V., *Optika I Spektrosk.,* 2, 127 (1957).
2. Borchard, H.J., U.S. Pat., 3 408 303 (1968).

$ThO_2:Pr^{3+}$

Structure: Rutile

Composition

Ingredient	Mole %	By weight (g)
ThO_2	100	232
Pr_2O_3	0.2 (of Pr)	0.330
NH_4F	10	3.7

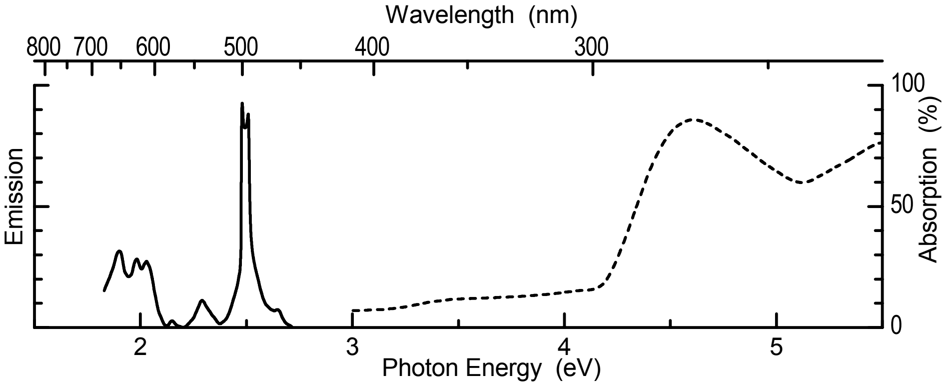
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, N_2, 1300ºC, 1 hour.
Powderize.
Wash in concentrated nitric acid and then in water until neutral.
Dry.

Optical Properties

Emission color: Blue-greenish white
Emission peak: Strongest lines: at 1.89, 2.48, and 2.52 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: 3%

Spectra



$ThO_2:Tb^{3+}$

Structure: Rutile

Composition

Ingredient	Mole %	By weight (g)
ThO_2	100	232
Tb_4O_7	0.2 (of Tb)	0.375
NH_4F	10	3.7

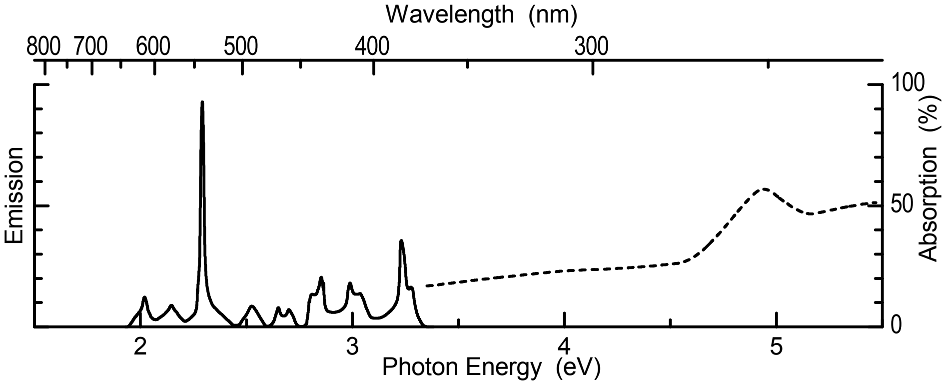
Preparation

Mix by slurrying in water.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, CO, 1300°C, 1 hour.
Powderize.
Wash in concentrated nitric acid and then in water until neutral.
Dry.

Optical Properties

Emission color: Bluish-greenish
Emission peak: Strongest at 2.285 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: 3%

Spectra



Remark

This phosphor has been proposed for X-ray excitation (high stopping power of ThO_2 for X-rays).

Reference

1. Borchard, H.J., U.S. Pat., 3 408 303 (1968).

$Y_2O_3:Bi^{3+}$

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	100 (of Y)	108
Bi_2O_3	0.1 (of Bi)	0.230
CaF_2	2.5	1.95

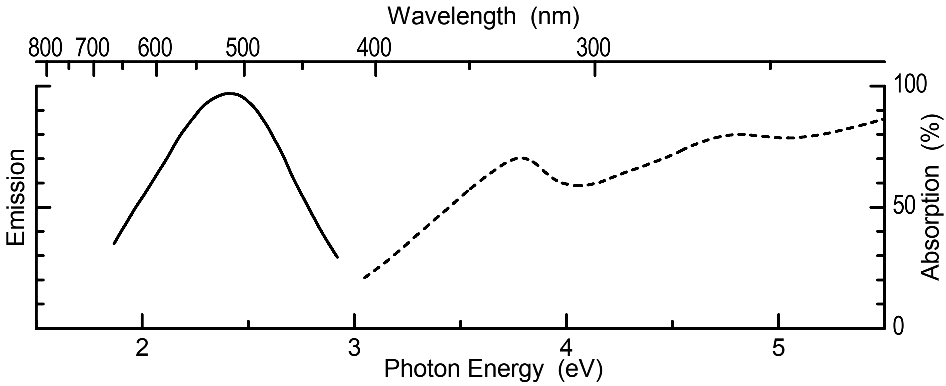
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, stagnant air, 1300°C, 1 hour.

Optical Properties

Emission color: Pale blue-greenish white
Emission peak: 2.35 and 3.00 eV, frequently only the 2.35 eV band showing up
Emission width (FWHM): 0.83 eV (for 2.35 eV peak)
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: Low in either case
Decay to 10%: ≈1 μsec

Spectra



Remark

The Bi^{3+} emission in Y_2O_3 is very poorly expressed. Sometimes it is difficult to recognize the bands in the very diffuse emission spectrum.

References

1. Datta, R.K., Luminescent behavior of bismuth in rare-earth oxides, *J. Electrochem. Soc.,* 114, 1137 (1967).
2. Toma, S.Z., and Palumbo, D.T., Luminescence of some bismuth-activated oxides, *J. Electrochem. Soc.,* 116, 274 (1969).
3. Blasse, G., and Bril, A., Investigations on BI^{3+}-activated phosphors, *J. Chem. Phys.,* 48, 217 (1968).
4. Boulon, G. et al., *Proc. Intern. Conf. Lumin.,* Leningrad, p. 530 (1972).

$Y_2O_3:Er^{3+}$

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	100 (of Y)	108
Bi_2O_3	0.1 (of Bi)	0.230
CaF_2	2.5	1.95

Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, stagnant air, 1300°C, 1 hour.

Powderize.

2. Fire in capped quartz tubes, stagnant air, 1300ºC, 1 hour.

Optical Properties

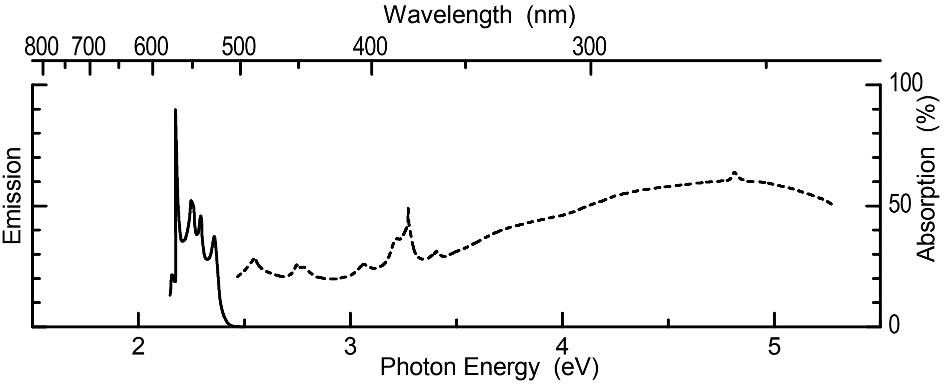
Emission color: Pale green

Emission peak: Strongest line at 2.206 eV

Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)

Excitation efficiency by e-beam: Efficiency not tested; is low for the visible part because of strong competition by IR emission

Spectra



Y_2O_3:Eu^{3+} (YOE)

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	100 (of Y)	108
Bi_2O_3	0.1 (of Bi)	0.230
CaF_2	2.5	1.95

Preparation

Mix by slurrying in water or methanol. Dry in air. Powderize when dry.

Fire in capped quartz tubes, stagnant air, 1300ºC, 1 hour. Powderize.

Fire in open quartz boats, air, 1300ºC, 1 hour.

Optical Properties

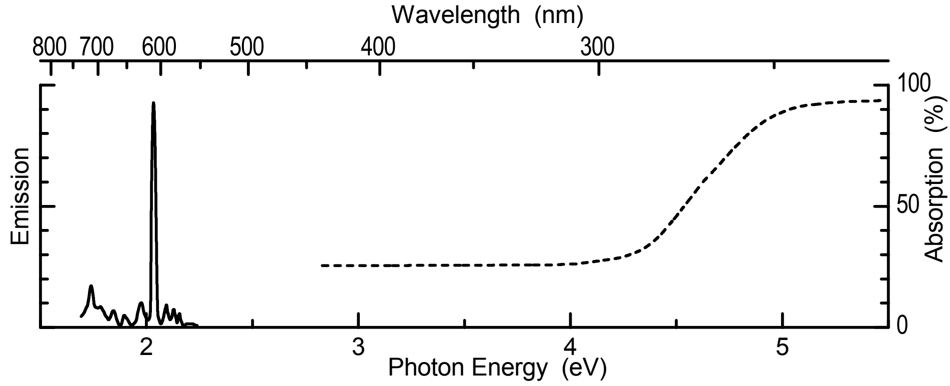
Emission color: Red

Emission peak: Strongest line at 2.03 eV

Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV); ≈ 80%

Excitation efficiency by e-beam: 7–8% (if Eu conc: = 3%, see below)

Spectra



Remarks

1. The above recipe gives a phosphor optimized for excitation by 4.88 eV. To obtain a phosphor optimized for e-beam excitation use only ½ of the above Eu concentration.
2. Sensitization by Bi causes excitability by 3.40 eV UV but reduces the efficiency for excitation by 4.88 eV UV.

References

1. Chang, N.C., Fluorescence and stimulated emission from trivalent europium in yttrium oxide, *J. Appl. Phys.,* 34, 3500 (1963).
2. Wickersheim, K.A., and Lefever, R.A., Luminescent behavior of the rare earths in yttrium oxide and related hosts, *J. Electrochem. Soc.,* 111, 47 (1964).
3. Ropp, R.C., Spectral properties of rare earth oxide phosphors, *J. Electrochem. Soc.*, 111, 311 (1964).
4. Ropp, R.C., Luminescence of europium in ternary system — A_2O_3-Gd_2O_3-Y_2O_3, *J. Electrochem. Soc.,* 112, 181 (1965).
5. Datta, R.K., Luminescent behavior of bismuth in rare-earth oxides, *J. Electrochem. Soc.,* 114, 1137 (1967).

Y_2O_3:Ho^{3+}

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	100 (of Y)	108
Bi_2O_3	0.1 (of Bi)	0.230
CaF_2	2.5	1.95

Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, stagnant air, 1300ºC, 1 hour. Powderize.
2. Fire in capped quartz tubes, stagnant air, 1300ºC, 1 hour.

Optical Properties

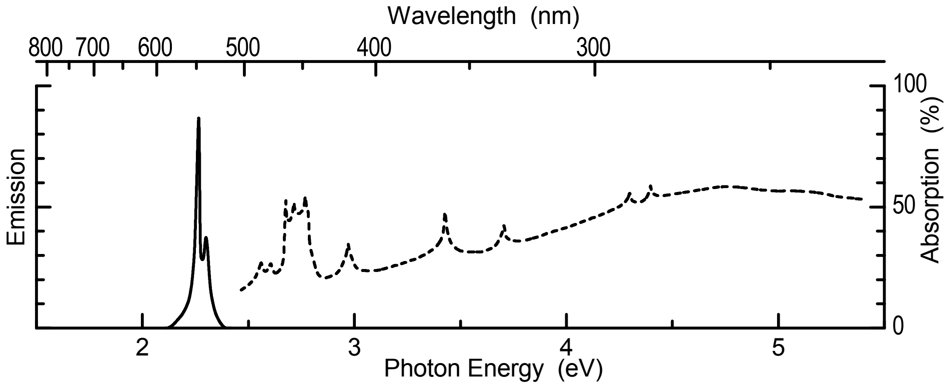
Emission color: Yellow-green

Emission peak: Two lines in the visible at 2.266 and 2.30 eV, plus many lines in the IR

Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)

Excitation efficiency by e-beam: Efficiency not tested; is low for the visible part because of the strong competition by IR emission

Spectra



Y_2O_3:Tb^{3+}

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	100 (of Y)	108
Bi_2O_3	0.1 (of Bi)	0.230
CaF_2	2.5	1.95

Preparation

Mix by slurrying in water or methanol.

Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, CO, 1300°C, 1 hour.
   Powderize.
2. Fire in capped quartz tubes, CO, 1300°C, 1 hour.

Optical Properties

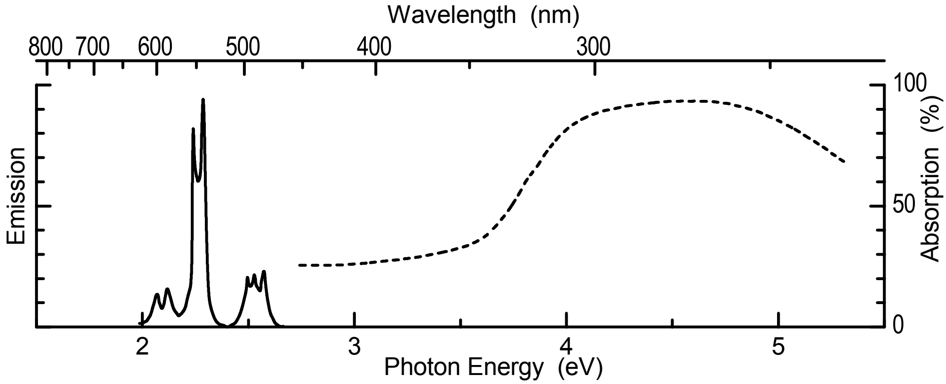
Emission color: Pale green

Emission peak: Strongest lines at 2.253 and 2.286 eV

Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Excitation efficiency by e-beam: 2–3% (if Tb conc. = 1%, see below)

Spectra



Remarks

1. The above recipe gives a phosphor optimized for excitation by 4.88 eV. To obtain a phosphor optimized for e-beam excitation use only 1% (instead of 2.5%) of Tb.
2. This phosphor must be fired in reducing atmosphere; otherwise Tb^{3+} oxidizes to Tb^{4+}.

Reference

1. Ropp, R.C., Spectral properties of rare earth oxide phosphors, *J. Electrochem. Soc.*, 111, 311 (1964).

La_2O_3:Bi^{3+}

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	100 (of Y)	163
Bi_2O_3	0.1 (of Bi)	0.230
CaF_2	2.5	1.95

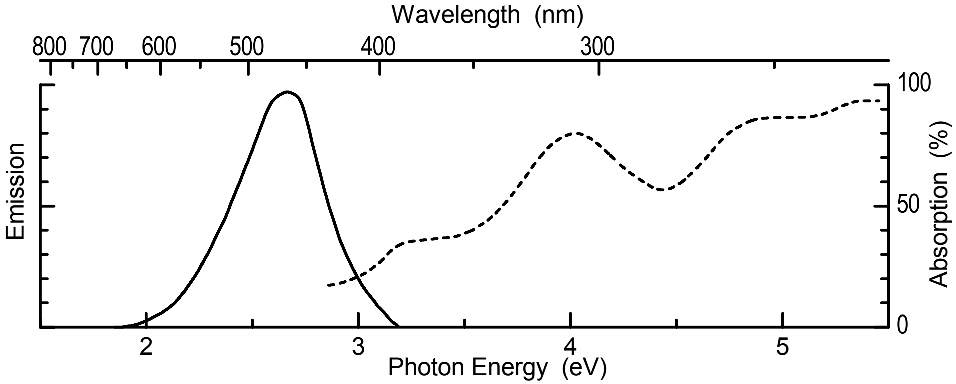
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, stagnant air, 1200°C, 1 hour.
Powderize.
Re-fire, same conditions as above.
Powderize.
Store in well-closed container.

Optical Properties

Color: Bluish
Emission peak: 2.67 eV
Emission width (FWHM): 0.49 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Decay to 1/e: 0.27 µsec

Spectra



References

1. Datta, R.K., Luminescent behavior of bismuth in rare-earth oxides, *J. Electrochem. Soc.,* 114, 1137 (1967).
2. Ropp, R.C., Luminescence of europium in ternary system — A_2O_3-Gd_2O_3-Y_2O_3, *J. Electrochem. Soc.,* 112, 124 (1965).
3. Bril, A., Wanmaker, W.L., and deLaat, C., Fluorescent properties of red-emitting europium-activated phosphors with cathode ray excitation, *J. Electrochem. Soc.,* 112, 111 (1965).

La_2O_3:Eu^{3+}

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	100 (of Y)	163
Bi_2O_3	0.1 (of Bi)	0.230
CaF_2	2.5	1.95

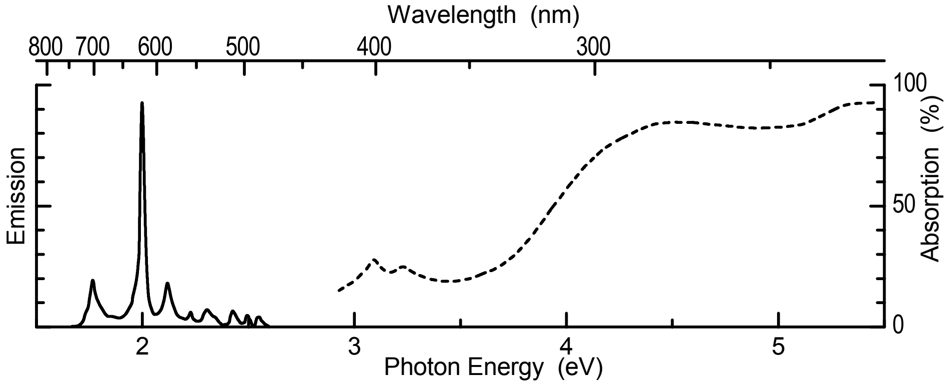
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, stagnant air, 1300ºC, 1 hour.
Powderize.
2. Fire in capped quartz tubes, stagnant air, 1300ºC, 1 hour.
Powderize.
Store in well-closed container.

Optical Properties

Emission color: Red
Emission peak: Strongest line at 1.985 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)

Spectra



References

1. Ropp, R.C., Spectral properties of rare earth oxide phosphors*, J. Electrochem. Soc.*, 111, 311 (1964).
2. Ropp, R.C., Luminescence of europium in ternary system — A_2O_3-Gd_2O_3-Y_2O_3, *J. Electrochem. Soc.,* 112, 181 (1965).
3. Bril, A., Wanmaker, W.L., and deLaat, C., Fluorescent properties of red-emitting europium-activated phosphors with cathode ray excitation, *J. Electrochem. Soc.,* 112, 111 (1965).
4. Barasch, G.E., and Dieke, G.H., Fluorescence decay of rare-earth ions in crystals, *J. Chem.. Phys.,* 43, 988 (1965).
5. Datta, R.K., Luminescent behavior of bismuth in rare-earth oxides, *J. Electrochem. Soc.,* 114, 1137 (1967).
6. Wickersheim, K.A., and Lefever, R.A., Luminescent behavior of the rare earths in yttrium oxide and related hosts, *J. Electrochem. Soc.,* 111, 47 (1964).
7. Chang, N.C., Fluorescence and stimulated emission from trivalent europium in yttrium oxide, *J. Appl. Phys.,* 34, 3500 (1963).

La_2O_3:Pb^{2+}

Structure: Cubic

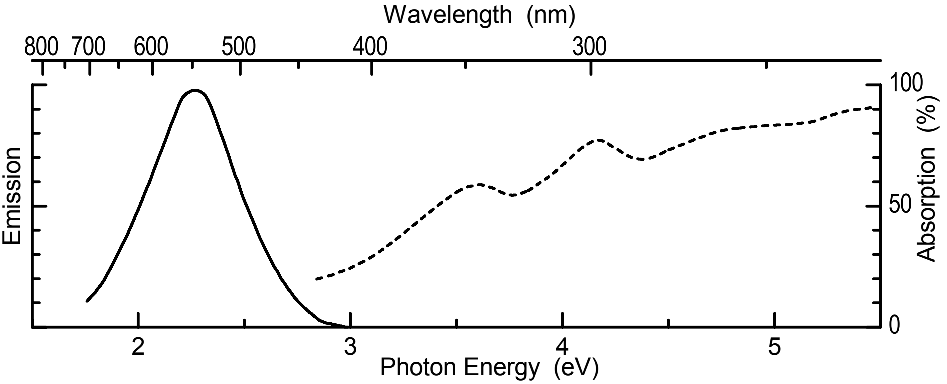
Composition

Ingredient	Mole %	By weight (g)
La_2O_3	100 (of Y)	163
Bi_2O_3	0.1 (of Bi)	0.230
CaF_2	2.5	1.95

Optical Properties

Emission color: Yellow-green
Emission peak: 2.27 eV
Emission width (FWHM): 0.51 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)

Spectra


Wavelength (nm)
800
700
600
500
400
300
Emission
100
50
0
Absorption (%)
2
3
4
5
Photon Energy (eV)

4.3 Silicates

The following host compounds and activators are included in this subsection:

$CaSiO_3$:Ce^{3+}
$CaSiO_3$:Eu^{2+}
$CaSiO_3$:Pb^{2+}
$CaSiO_3$:Ti^{4+}
$CaSiO_3$:Pb^{2+},Mn^{2+}
Be_2SiO_4:Mn^{2+}
Mg_2SiO_4:Mn^{2+}
Zn_2SiO_4:Mn^{2+}
Zn_2SiO_4:Mn^{2+},P
Zn_2SiO_4:Mn^{2+},As^{5+}
Zn_2SiO_4:Ti^{4+}
$(Zn+Be)_2SiO_4$:Mn^{2+}
Sr_2SiO_4:Eu^{2+}
$SrBaSiO_4$:Eu^{2+}
Ba_2SiO_4:Eu^{2+}
Ba_2SiO_4:Ce^{3+},Li^{+},Mn^{2+}
$BaSi_2O_5$:Eu^{2+}
$BaSi_2O_5$:Pb^{2+}
Y_2SiO_5:Ce^{3+}
$CaMgSi_2O_6$:Eu^{2+}
$CaMgSi_2O_6$:Eu^{2+},Mn^{2+}
$Ca_2MgSi_2O_7$:Eu^{2+}
$Ca_2MgSi_2O_7$
$Ca_2MgSi_2O_7$:Eu^{2+},Mn^{2+}
$Sr_2MgSi_2O_7$:Eu^{2+}
$Ba_2MgSi_2O_7$:Eu^{2+}
$BaMg_2Si_2O_7$:Eu^{2+}
$BaSrMgSi_2O_7$:Eu^{2+}
$Ba_2Li_2Si_2O_7$:Eu^{2+}
$Ba_2Li_2Si_2O_7$:Sn^{2+}
$Ba_2Li_2Si_2O_7$:Sn^{2+},Mn^{2+}
$MgSrBa_2Si_2O_7$:Eu^{2+}
$MgBa_3Si_2O_8$:Eu^{2+}
$MgSr_3Si_2O_8$:Eu^{2+},Mn^{2+}
$Sr_3MgSi_2O_8$:Eu^{2+}
$Ca_5B_2SiO_{10}$:Eu^{3+}
$Ca_3Al_2Si_3O_{12}$:Eu^{2+}
$LiCeBa_4Si_4O_{14}$:Mn^{2+}
$LiCeSrBa_3Si_4O_{14}$:Mn^{2+}

$CaSiO_3:Ce^{3+}$

Structure: Triclinic (pseudowollastonite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	97	97
SiO_2	100	100
TiO_2	1	0.80
CaF_2	2	1.56

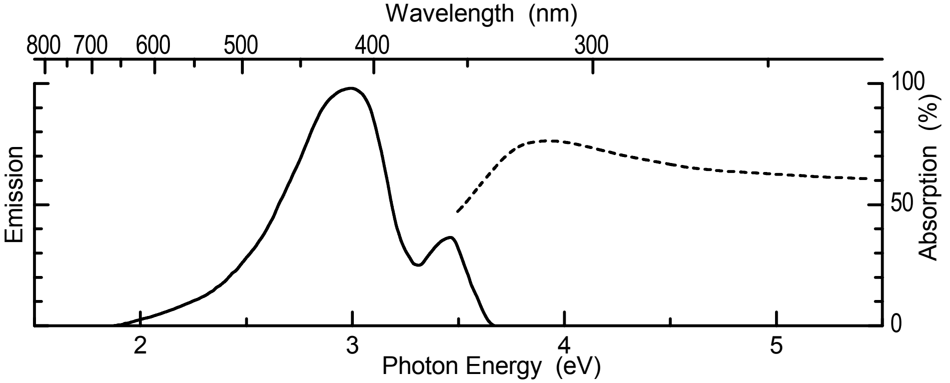
Preparation

Mix by slurrying in water.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, CO, 1100ºC, 1 hour.

Optical Properties

Emission color: Violet + UV
Emission peak: 3.00 eV, 3.42 eV
Excitation efficiency by UV: + (4.88 eV)
Excitation efficiency by e-beam: +

Spectra



Reference

1. Kröger, F.A., *Some Aspects of the Luminescence of Solids*, Elsevier, Amsterdam (1948).

$CaSiO_3:Eu^{2+}$

Structure: Triclinic (pseudowollastonite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	98	98
SiO_2	100	60
Eu_2O_3	0.1 (of Eu)	0.176
CaF_2	2	1.56

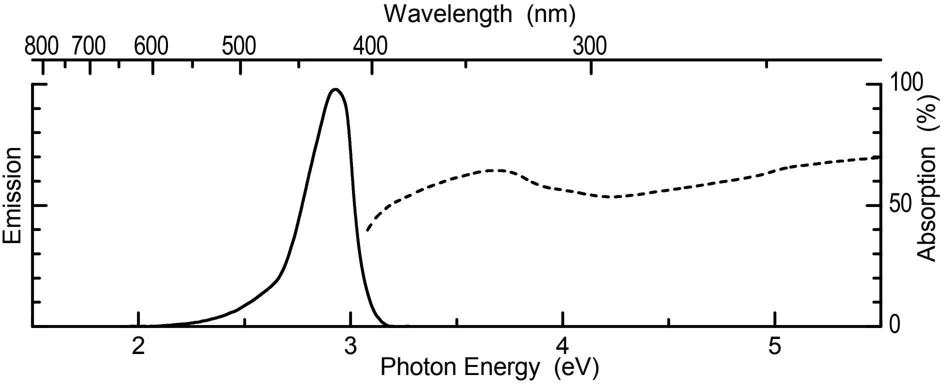
Preparation

Mix by slurrying in water.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, CO, 1100ºC, 1 hour.

Optical Properties

Emission color: Violet
Emission peak: 2.93 eV
Emission width (FWHM): 0.25 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)

Spectra



$CaSiO_3:Pb^{2+}$

Structure: Triclinic (pseudowollastonite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	97	97
SiO_2	100	60
PbO	1	2.23
CaF_2	2	1.56

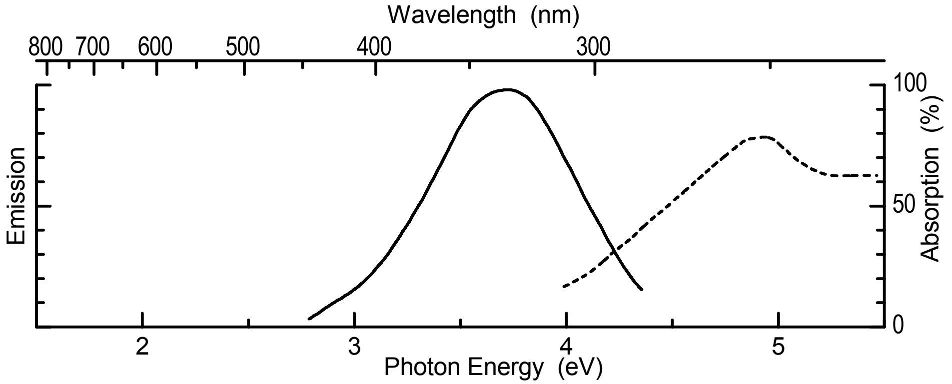
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, N_2, 1100º C, 1 hour.

Optical Properties

Emission color: UV
Emission peak: 3.70 eV
Emission width (FWHM): 0.87 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



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2. Schulman, J.H., Ginther, R.J., and Claffy, E.W., Note on the properties of calcium silicate phosphors, *J. Opt. Soc. Am.*, 43, 318 (1953).
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4. Bril, A., and Hoekstra, W., *Philips Res. Rep.*, 19, 269 (1964).
5. Hüniger, M., and Ruffler, H., *Tech. Wiss. Abh. OSRAM Ges.*, 8, 41 (1963).
6. Mooney, R.W., Optical properties of tin-activated and lead-activated calcium metasilicate phosphors, *J. Electrochem. Soc.*, 106, 955 (1959).
7. Harrison, D.E., and Hoffman, M.V., The calcium silicate Mn + Pb phosphor phase relationships and preparation, *J. Electrochem. Soc.*, 106, 800 (1959).
8. Nagy, R., Wei, C.K.L., and Wollentin, R.W., Calcium zinc silicate phosphor, *J. Electrochem. Soc.*, 99, 137 (1952).
9. Butler, K.H., *Fluorescent Lamp Phosphors*, Pennsylvania University Press, University Park (1980).
10. Lange, H., Die manganbanden und ihre trennung im lumineszenzspektrum von calciumsilikat (Mn,Pb), *Z. Phys.,* 139, 346 (1954).

$CaSiO_3:Ti^{4+}$

Structure: Triclinic (pseudowollastonite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	97	97
SiO_2	100	100
TiO_2	1	0.80
CaF_2	2	1.56

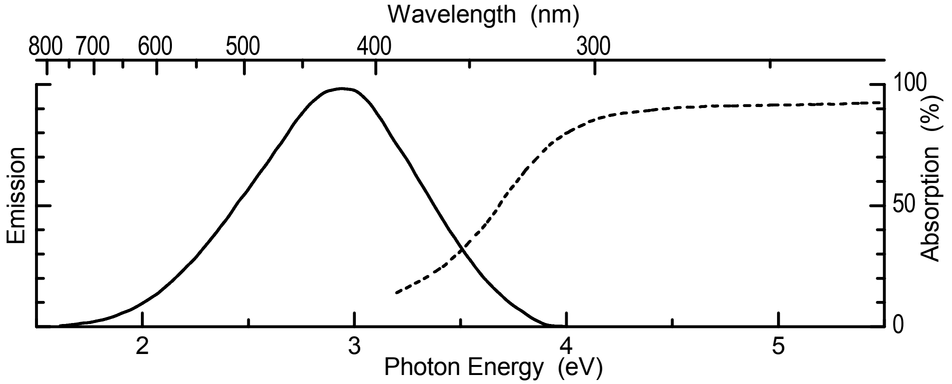
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, air, 1100°C, 1 hour.

Optical Properties

Emission color: Bluish
Emission peak: 2.93 eV
Emission width (FWHM): 0.92 eV
Excitation efficiency by UV: + (4.88 eV)

Spectra



$CaSiO_3:Pb^{2+},Mn^{2+}$

Structure: Triclinic (pseudowollastonite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	97.5	97.5
SiO_2	100	60
PbO	0.5	1.12
$MnCO_3$	2	2.3
CaF_2	2	1.56

Preparation

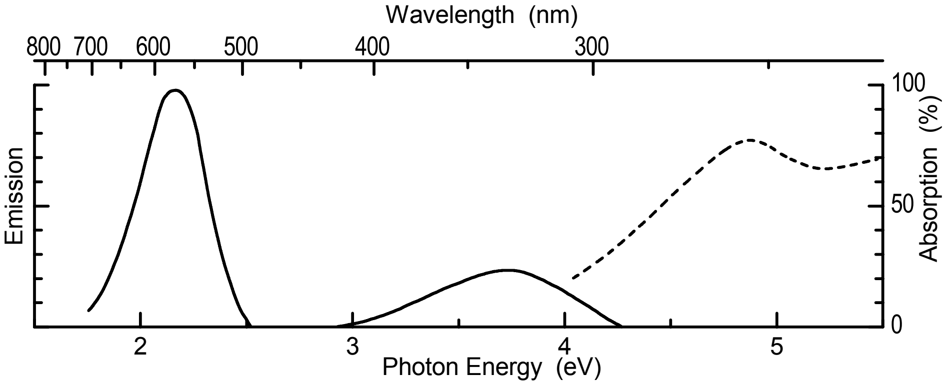
Mix by slurrying in methanol plus a few cubic centimeters water.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 1000°C, 1 hour.
   Powderize.
2. Fire in capped quartz tubes, CO, 1150°C, 1 hour.
   Powderize.
   Wash in water several times.
   Dry.

Optical Properties

Emission color: Orange
Emission peak: 2.17 eV
Emission width (FWHM): 0.42 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: 60% (estimated)
Decay to 10% : Slightly non exponential (≈ 35 msec) followed by a long but weaker afterglow tail extending into seconds

Spectra



Reference

1. Smith, A.L., Some new complex silicate phosphors containing calcium, magnesium, and beryllium, *J. Electrochem. Soc.*, 96, 287 (1949).

Be_2SiO_4:Mn^{2+}

Structure: Trigonal (phenakite)

Optical Properties

Emission color: Orange-red
Emission peak: 1.97 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Mg_2SiO_4:Mn^{2+}

Structure: Orthorhombic (forsterite)

Optical Properties

Emission color: Red
Emission peak: 1.88 eV
Emission width (FWHM): eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Zn_2SiO_4:Mn^{2+}

Structure: Trigonal (willemite)

Composition

Ingredient	Mole %	By weight (g)
ZnO	194	158
SiO_2	110	66
$MnCO_3$	6	6.9

Preparation

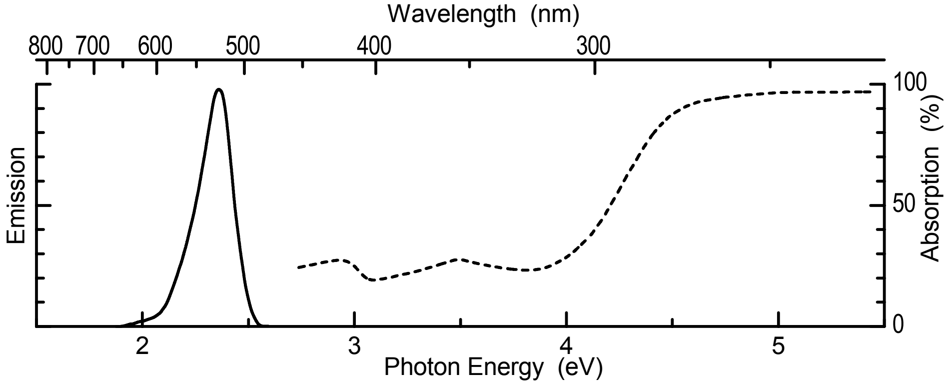
Mix by ball-milling in water about 2 hours.
Dry in air.
Powderize when dry.

1. Fire in open quartz containers, forming gas, 1200°C, 1 hour.
   Powderize by dry milling.
2. Fire in open quartz containers, air, 1200°C, 1 hour.

Optical Properties

Emission color: Green
Emission peak: 2.35 eV
Emission width (FWHM): 0.18 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV); 80–90%
Excitation efficiency by e-beam: 7%/+
Decay: Near exponential with time constant ~10 msec (22–25 msec to 1/10)

Spectra



Remarks

1. Very thorough mixing of the ingredients is essential.
2. Up to ~20% of the Zn can be replaced by Mg without visible effect of the Mg on the emission.
3. Parts or all of the Si can be replaced by Ge (but not by Sn).
4. Emission peak moves slightly to longer wavelength with increasing Mn concentration.
5. Efficiency for excitation by UV and by e-beam, and decay after excitation by e-beam pulse, depend on the Mn concentration used.

References

1. Leverenz, H.W., *An Introduction to Luminescence of Solids*, John Wiley & Sons, New York, and Chapman & Hall, London (1950).
2. Bull, C., and Garlick, G.F., The thermoluminescence characteristics of silicate phosphors activated by manganese and arsenic, *J. Electrochem. Soc.*, 98, 371 (1951).
3. Stevels, A.L.N., and Vink, A.T., *J. Lumin.,* 8, 443, (1974).
4. Segnit, E.R., and Holland, A.E., System MgO-ZnO-SiO_2, *J. Am. Ceram. Soc.,* 48, 409 (1965).
5. Bauer, G.T., Kinetics of X-ray irradiation-caused degradation of photoluminescence of some phosphors, *J. Electrochem. Soc.*, 123, 79 (1976).
6. Palumbo, D.T., and Brown, J.J., Electronic states of Mn^{2+}-activated phosphors. 1. Green-emitting phosphors, *J. Electrochem. Soc.*, 117, 1184 (1970).
7. Chang, I.F., and Shafer, M.W., Efficiency enhancement in manganese-doped zinc silicate phosphor with $AlPO_4$ substitution, *Appl. Phys. Lett.,* 35, 229 (1979).

8. Klick, C.C., and Schulman, J.H., On the luminescence of divalent manganese in solids, *J. Opt. Soc. Am.*, 42, 910 (1952).

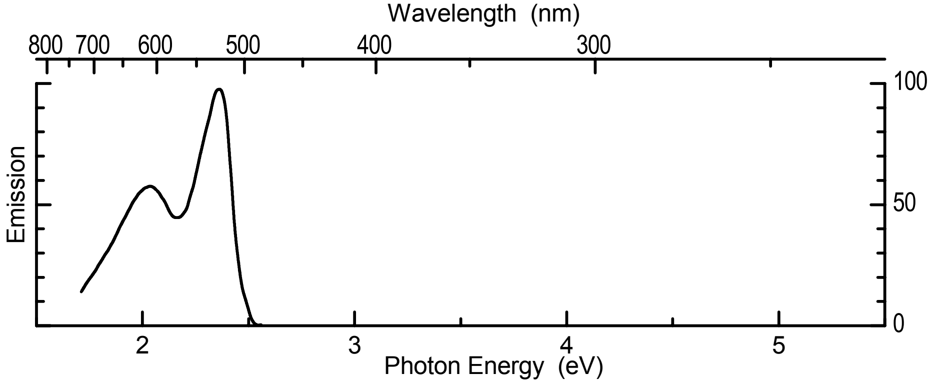
$Zn_2SiO_4:Mn^{2+},P$

Structure: Trigonal (willemite)

Optical Properties

Emission color: Green, orange
Emission peak: 2.04 and 2.35 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



$Zn_2SiO_4:Mn^{2+},As^{5+}$

Structure: Trigonal (willemite)

Composition

Ingredient	Mole %	By weight (g)
ZnO	200	163
$MnCO_3$	0.2	0.230
SiO_2^*	102	62.1
As_2O_3	0.02 (of As)	0.02

(* This requires extremely fine SiO_2, commercially available as “Silanox,” “Cab-O-Sil,” etc.)

Preparation

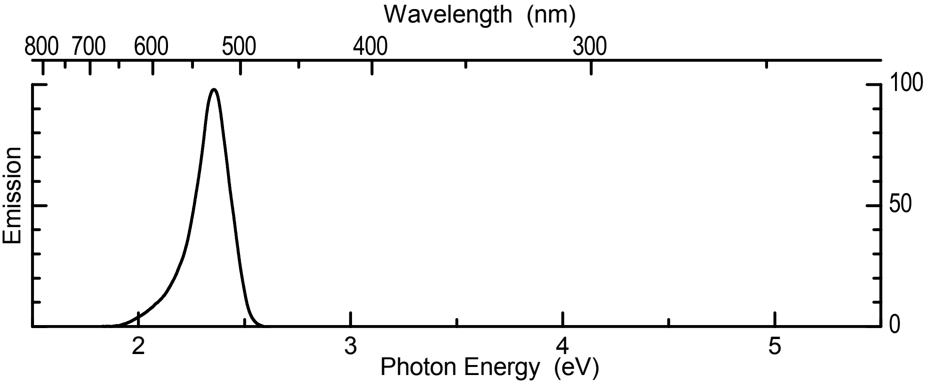
Mix by ball-milling in water about 2 hours.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, air, 1200ºC, 1 hour.

Optical Properties

Emission color: Green
Emission peak: 2.35 eV
Emission width (FWHM): 0.18 eV

Excitation efficiency by e-beam: 3–4%
Decay: Decay consisting of two subsequent branches, first branch near-exponential with time constant (to 1/e) ≈ 12 msec, later part non-exponential and extending to several seconds or longer

Spectra



Remarks

1. Very thorough mixing of the ingredients is important.
2. Ordinary silicic acid cannot be used for this phosphor (too coarse).
3. The afterglow due to As^{5+} appears only when the phosphor has been fired in oxidizing atmosphere.

References

1. Froelich, H.C., and Fonda, G.R., *J. Phys. Chem.,* 46, 878 (1942).
2. Bull, C., and Garlick, G.F., The thermoluminescence characteristics of silicate phosphors activated by manganese and arsenic, *J. Electrochem. Soc.*, 98, 371 (1951).

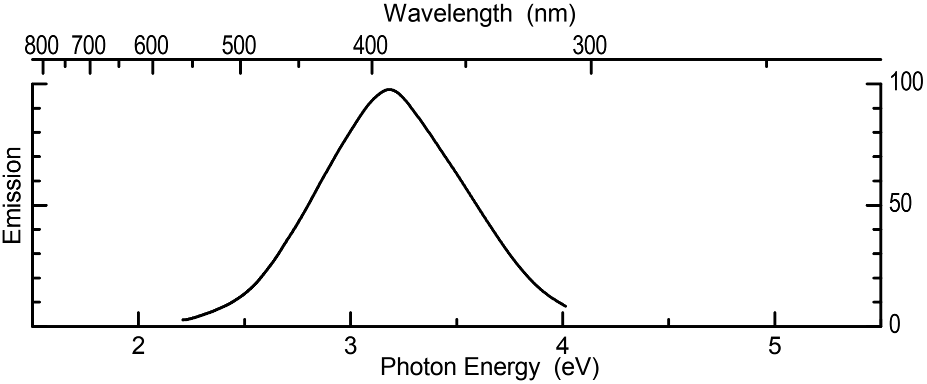
$Zn_2SiO_4:Ti^{4+}$

Structure: Trigonal (willemite)

Optical Properties

Emission color: Violet
Emission peak: 3.02 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Reference

1. Kröger, F.A., *Some Aspects of the Luminescence of Solids*, Elsevier, Amsterdam (1948), p.168.

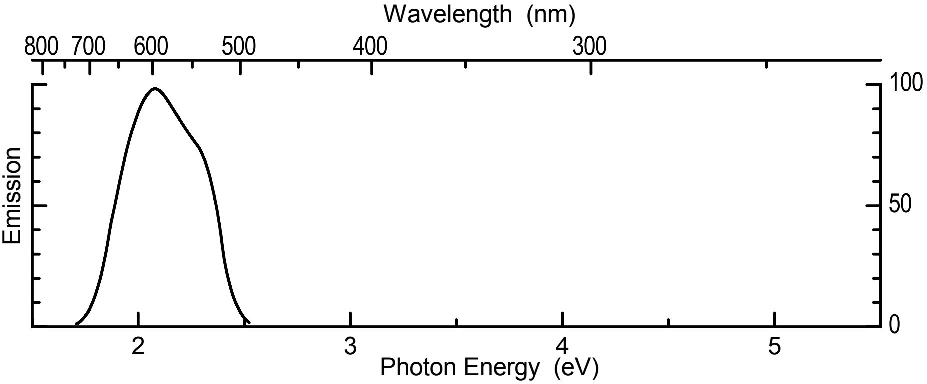
$(Zn+Be)_2SiO_4:Mn^{2+}$

Structure: Trigonal (willemite)

Optical Properties

Emission color: Green, orange
Emission peak: 2.04 eV, 2.35 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Reference

1. Butler, K.H., *Fluorescent Lamp Phosphors*, Pennsylvania University Press, University Park (1980), p. 244.

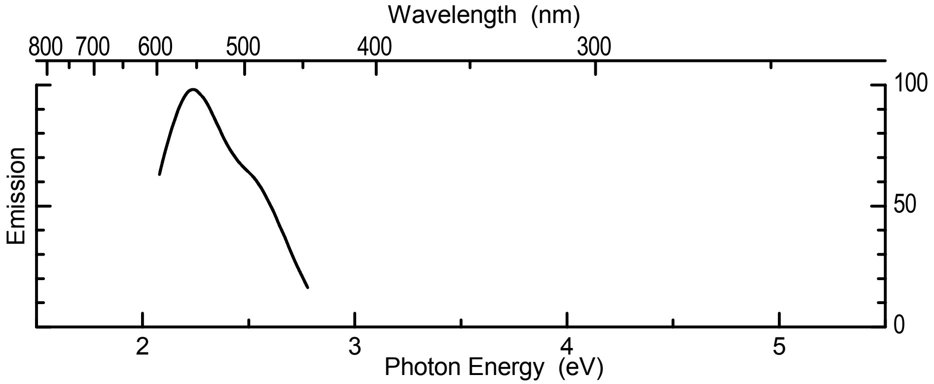
$Sr_2SiO_4:Eu^{2+}$

Structure: Orthorhombic

Optical Properties

Emission color: Green-yellow
Emission peak: 2.23 eV
Emission width (FWHM): 0.60 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Blasse, G. et al., Fluorescence of Eu2+ activated silicates, *Philips Res. Rep.*, 23, 189 (1968).
2. Blasse, G., and Bril, A., Characteristic luminescence, 1. The absorption and emission spectra of some important activators, *Philips Tech. Rev.*, 31, 304 (1970).

3 Barry, T.L., Equilibria and Eu^{2+} luminescence of subsolidus phases bounded by $Ba_3MgSi_2O_8$, $Sr_3MgSi_2O_8$, and $Ca_3MgSi_2O_8$, *J. Electrochem. Soc.*, 115, 733 (1968).

$SrBaSiO_4:Eu^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	98	145
$BaCO_3$	100	197
SiO_2	105	63
Eu_2O_3	2 (of Eu)	3.5
NH_4Cl	10	5.4

Preparation

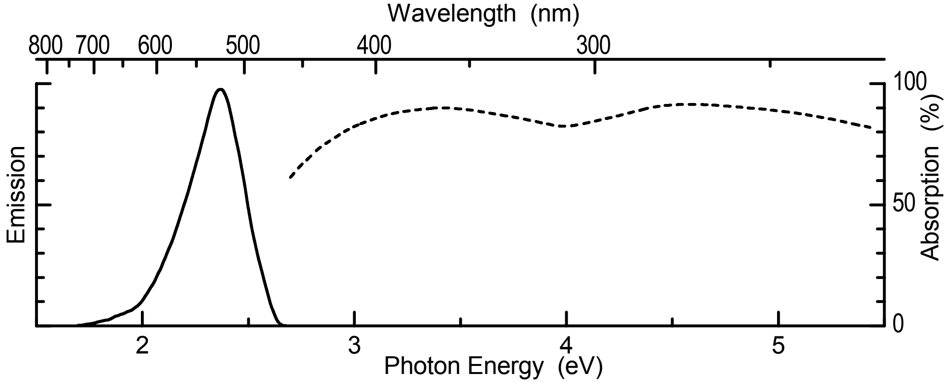
Mix by slurrying in water. Then ball-mill in water. Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, CO, 1100ºC, 1 hour. Powderize by dry milling.
   Add another 5.4 g NH_4Cl, mix by dry milling.
2. Fire in capped quartz tubes, CO, 1100ºC, 1 hour. Powderize.
   Wash in water several times (pH goes to ~10–12). Dry.

Optical Properties

Emission color: Yellow-green
Emission peak: 2.36 eV
Emission width (FWHM): 0.32 eV
Excitation efficiency by UV: ++ (4.88 eV) , + (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Remark

This phosphor is an intermediate between $Sr_2SiO_4:Eu^{2+}$ (yellow, stable in water) and $Ba_2SiO_4:Eu^{2+}$ (green, unstable) which are miscible in any ratio. The stability of $SrBaSiO_4:Eu^{2+}$ may not be good enough for use in lamps.

References

1. Barry, T.L., Equilibria and Eu^{2+} luminescence of subsolidus phases bounded by $Ba_3MgSi_2O_8$, $Sr_3MgSi_2O_8$, and $Ca_3MgSi_2O_8$, *J. Electrochem. Soc.,* 115, 733 (1968).
2. Barry, T.L,. Fluorescence of Eu^{2+}-activated phases in binary alkaline earth orthosilicate systems, *J. Electrochem. Soc.,* 115, 1181 (1968).

$Ba_2SiO_4:Eu^{2+}$

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	198	390
Eu_2O_3	2 (of Eu)	3.5
SiO_2	105	63
NH_4Cl	10	5.4

Preparation

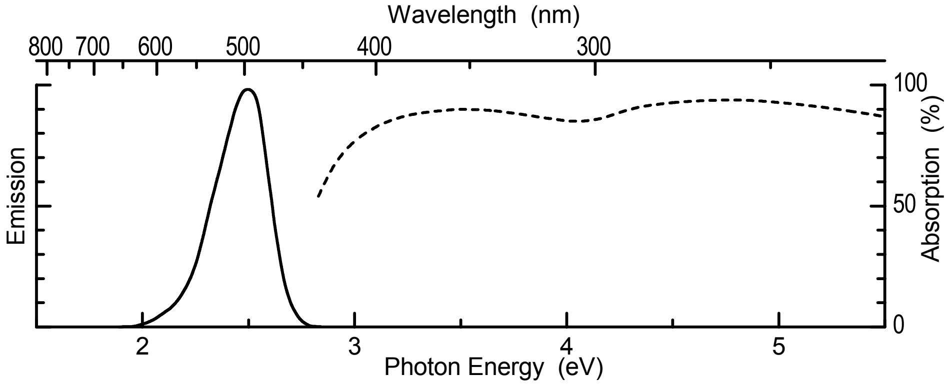
Mix by milling or grinding.

1. Fire in capped quartz tubes, CO, 1100ºC, 1 hour.
   Powderize by hard milling or grinding. Add another ~5.4 g NH_4Cl, mix well.
2. Fire in capped quartz tubes, CO, 1000ºC, 1 hour. Powderize.
   Wash in water (to remove leftover halide). Dry in air.
   Store in a well-closed container.

Optical Properties

Emission color: Blue-green
Emission peak: 2.44 eV
Emission width (FWHM): 0.28 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Remarks

1. Material is unstable in water.
2. Part or all of the Ba can be replaced by Sr causing increasing stability against water and shift of the emission towards yellow.

References

1. Blasse, G. et al., Fluorescence of Eu^{2+} activated silicates, *Philips Res. Rep.,* 23, 189 (1968).
2. Barry, T.L, Equilibria and Eu^{2+} luminescence of subsolidus phases bounded by $Ba_3MgSi_2O_8$, $Sr_3MgSi_2O_8$, and $Ca_3MgSi_2O_8$, *J. Electrochem. Soc.,* 115, 733 (1968), and Fluorescence of Eu^{2+}-activated phases in binary alkaline earth orthosilicate systems, *J. Electrochem. Soc.,* 115, 1181 (1968).

$Ba_2SiO_4:Ce^{3+},Li^+,Mn^{2+}$

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	75	148
SiO_2	50	30
CeO_2	10	17
Li_2CO_3	20 (of Li)	7.4
$MnCO_3$	5	5.8
NH_4Br	10	10

Preparation

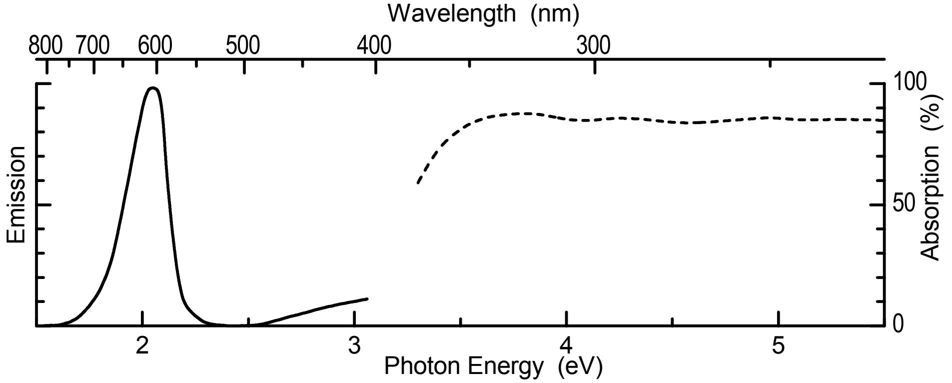
First mix by dry ball-milling or grinding only in the $BaCO_3$, SiO_2, and Li_2CO_3, CeO_2.

1. Fire in open quartz boats, H_2, 900ºC, 1 hour.
   Powderize.
   Now admit $MnCO_3$ and NH4Br by slurrying in methanol.
   Dry in air. Powderize when dry.
2. Fire in capped quartz tubes, N_2, 900ºC, 1 hour.
   Powderize.
3. Fire in open quartz boats, CO, 900ºC, 1 hour.

Optical Properties

Emission color: Orange-red
Emission peak: 2.015 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: Very poor

Spectra



Remarks

1. Phosphor is believed to be a modification of Ba_2SiO_4 (in which Mn^{2+} is non-luminescent) with 25% of Ba replaced by 10% Ce, 10% Li, and 5% Mn.
2. Emission changes color from orange-red at room temperature to yellow at 150ºC and whitish at 300ºC.
3. Partial replacement of Ba by Sr shifts the emission into somewhat deeper red, improves temperature stability of the emission, and improves chemical stability of the material. Such phosphor has been known as "triple silicate" in England.

References

1. McKeag, A.H., and Steward, E.C., The luminescent properties and crystal structure of some new phosphor systems, *Br. J. Appl. Phys.,* 4, 26 (1955).
2. McKeag, A.H., Temperature characteristics of barium strontium lithium silicate phosphors, *J. Electrochem. Soc.,* 105, 78 (1958).

$BaSi_2O_5:Eu^{2+}$

Structure: Orthorhombic

Optical Properties

Emission color: Blue-green
Emission peak: 2.46 eV
Emission width (FWHM): 0.50 eV
Excitation efficiency by UV: ++ (4.88 eV)
Excitation efficiency by e-beam: +

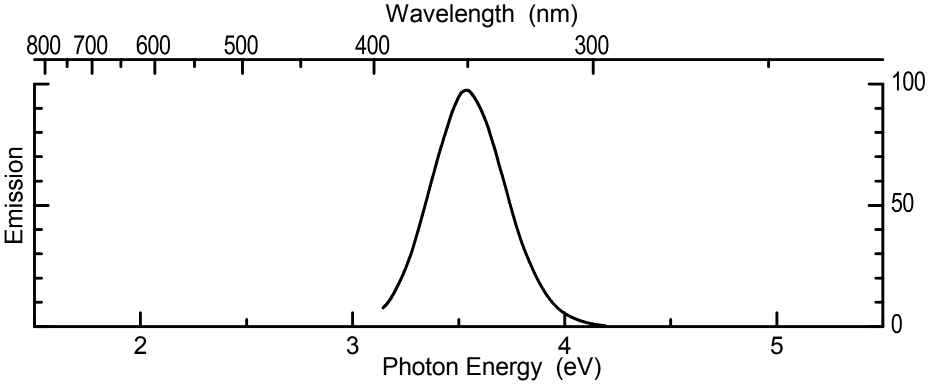
$BaSi_2O_5:Pb^{2+}$

Structure: Orthorhombic

Optical Properties

Emission color: UV
Emission peak: 3.54 eV
Emission width (FWHM): 0.39 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



References

1. Ropp., R.C., Phosphors based on rare earth phosphates fast decay phosphors, *J. Electrochem. Soc.,* 115, 531 (1968).
2. Butler, K.H., *Fluorescent Lamp Phosphors*, Pennsylvania University Press, University Park (1980), p. 169.

$Y_2SiO_5:Ce^{3+}$

Optical Properties

Emission color: Violet
Emission peak: 2.99 eV
Emission width (FWHM): eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +

$CaMgSi_2O_6:Eu^{2+}$

Structure: Monoclinic (diopside)

Composition

Ingredient	Mole %	By weight (g)
CaO	118	66
MgO	100	40
SiO_2	210	126
Eu_2O_3	2 (of Eu)	3.5
NH_4Cl	40	21.4

Preparation

Mix by slurrying in methanol plus a few cubic centimeters water.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 1000°C, 1 hour.

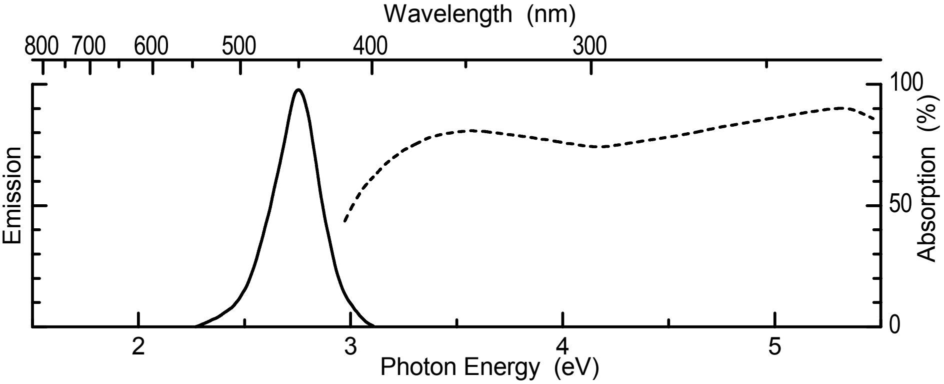
Powderize.

2. Fire in capped quartz tubes, CO, 1150ºC, 1 hour.
   Powderize.
   Wash in water several times.
   Dry.

Optical Properties

Emission color: Blue
Emission peak: 2.77 eV
Emission width (FWHM): 0.25 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV); 60% (estimated)

Spectra



Reference

1. Smith, A.L., Some new complex silicate phosphors containing calcium, magnesium, and beryllium, *J. Electrochem. Soc.*, 96, 287 (1949).

$CaMgSi_2O_6$:Eu^{2+},Mn^{2+}

Structure: Monoclinic (diopside)

Composition

Ingredient	Mole %	By weight (g)
CaO	114	64
MgO	100	40
SiO_2	210	126
Eu_2O_3	2 (of Eu)	3.5
$MnCO_3$	4	4.6
NH_4Cl	40	21.4

Preparation

First mix by slurrying in methanol plus a few cubic centimeters water.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 1000ºC, 1 hour.
   Powderize.
2. Fire in capped quartz tubes, CO, 1150ºC, 1 hour.
   Powderize.
   Wash in water several times.
   Dry.

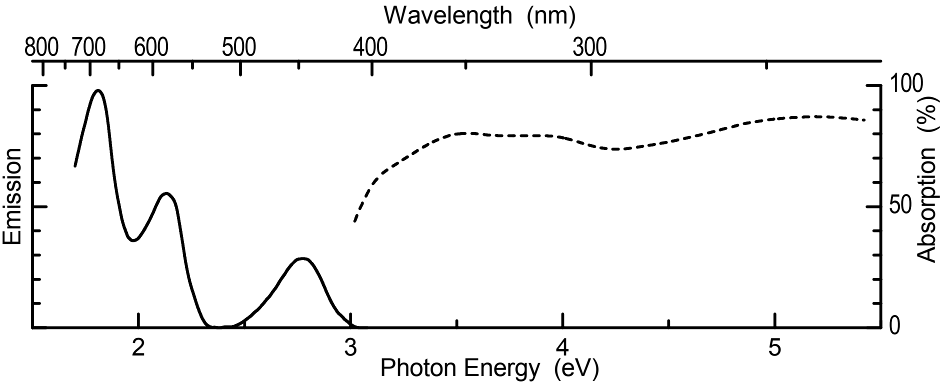
Optical Properties

Emission color: Reddish-purple.

Emission peak: 1.80 eV, 2.12 eV, 2.77 eV

Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV); ≈ 60% (estimated)

Spectra



$Ca_2MgSi_2O_7:Eu^{2+}$

Structure: Tetragonal (ackermanite)

Composition

Ingredient	Mole %	By weight (g)
CaO	200	112
MgO	100	40
SiO_2	210	126
Eu_2O_3	2 (of Eu)	3.5
NH_4Cl	40	21.4

Preparation

First mix by slurrying in methanol plus a few cubic centimeters water. Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 1000°C, 1 hour. Powderize.
2. Fire in capped quartz tubes, CO, 1150°C, 1 hour.

Optical Properties

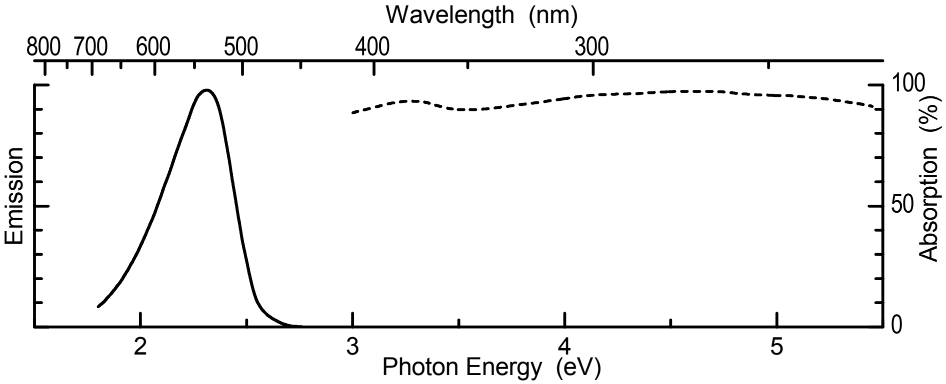
Emission color: Yellow-green

Emission peak: 2.29 eV

Emission width (FWHM): 0.37 eV

Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV); ≈ 25%

Spectra



$Ca_2MgSi_2O_7$

Structure: Tetragonal (ackermanite)

Optical Properties

Emission color: UV
Emission peak: 3.17 eV
Excitation efficiency by e-beam: +

$Ca_2MgSi_2O_7:Eu^{2+},Mn^{2+}$

Structure: Tetragonal (ackermanite)

Composition

Ingredient	Mole %	By weight (g)
CaO	205	115
MgO	100	40
SiO_2	210	126
Eu_2O_3	2 (of Eu)	3.5
$MnCO_3$	8	9.2
NH_4Cl	10	5.4

Preparation

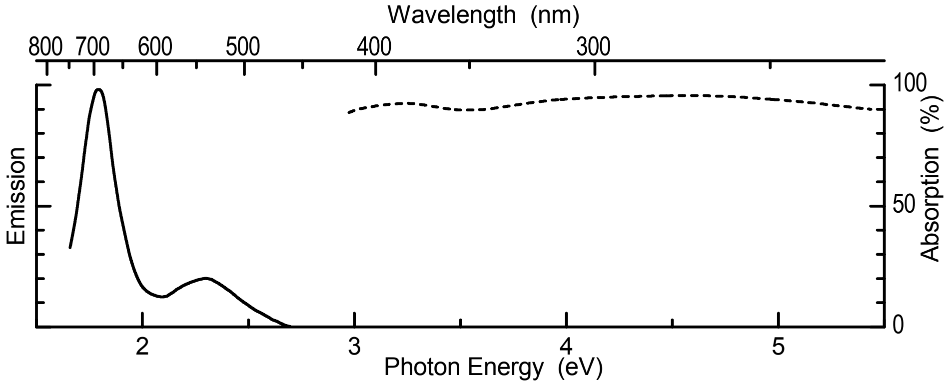
First mix by slurrying in methanol plus a few cubic centimeters water.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 1000°C, 1 hour.
   Powderize.
2. Fire in capped quartz tubes, CO, 1150°C, 1 hour.

Optical Properties

Emission color: Deep red plus weaker yellow-green
Emission peak: 1.80 eV, 2.29 eV
Emission width (FWHM): 0.21 eV
Excitation efficiency by UV: Excited by all UV plus visible blue

Spectra



References

1. Blasse, G., Wanmaker, W.L., and terVrugt, J.W., Some new classes of efficient Eu^{2+} activated phosphors, *J. Electrochem. Soc.,* 115, 673 (1968).
2. Blasse, G. et al., Fluorescence of Eu^{2+}-activated silicates, *Philips Res. Rep.*, 23, 189 (1968).

$Sr_2MgSi_2O_7:Eu^{2+}$

Structure: Tetragonal (ackermanite)

Composition

Ingredient	Mole %	By weight (g)
$SrCO_2$	187	276
SrF_2	10	12.6
MgO	100	40.3
SiO_2	210	126
Eu_2O_3	3 (of Eu)	5.3

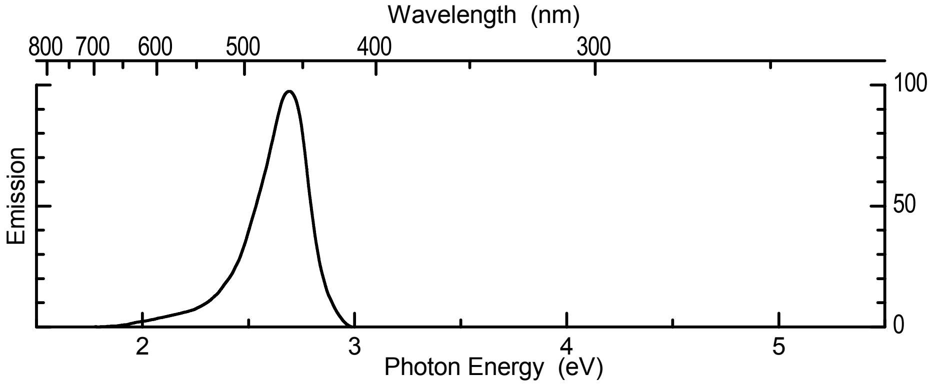
Preparation

Mix by ball-milling in methanol.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 1000°C, 1 hour.
   Powderize.
2. Fire in capped quartz tubes, CO, 1150°C, 1 hour.

Optical Properties

Emission color: Blue
Emission peak: 2.68 eV
Emission width (FWHM): 0.27 eV
Excitation efficiency by UV: + (4.88 eV)
Excitation efficiency by e-beam: +

Spectra



Reference

1. Blasse, G. et al., Fluorescence of Eu^{2+}-activated silicates, *Philips Res. Rep.*, 23, 189, (1968).

$Ba_2MgSi_2O_7$:Eu^{2+}

Structure: Tetragonal (melinite)

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	187	369
BaF_2	10	17.5
MgO	100	40.3
SiO_2	210	126
Eu_2O_3	3 (of Eu)	5.3

Preparation

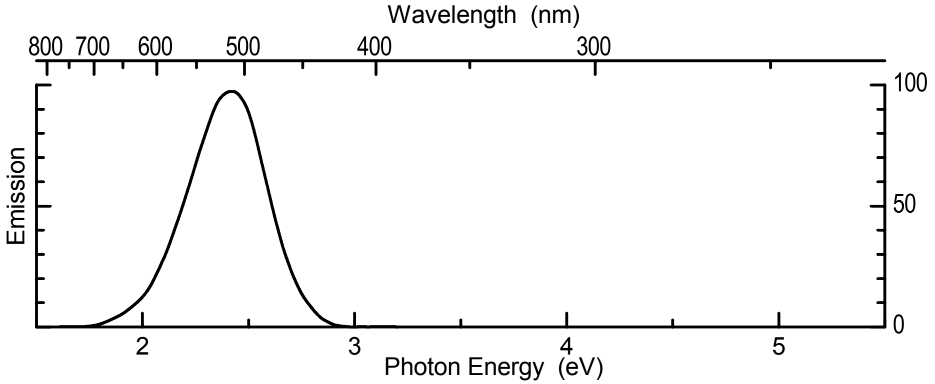
Mix by ball-milling in methanol.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 1000°C, 1 hour.
   Powderize.
2. Fire in capped quartz tubes, CO, 1100°C, 1 hour.

Optical Properties

Emission color: Blue-green
Emission peak: 2.42 eV
Emission width (FWHM): 0.41 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Blasse, G., Wanmaker, W.L., and terVrugt, J.W., Some new classes of efficient Eu^{2+} activated phosphors, *J. Electrochem. Soc.,* 115, 673 (1968).
2. Blasse, G., and Bril, A., Characteristic luminescence, 1. The absorption and emission spectra of some important activators, *Philips Tech. Rev.,* 31, 304 (1970).

$BaMg_2Si_2O_7$:Eu^{2+}

Structure: Tetragonal (melinite)

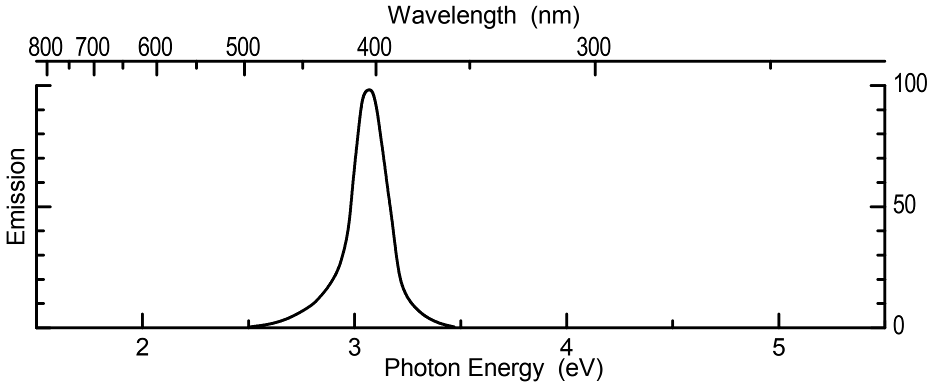
Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	187	369
BaF_2	10	17.5
MgO	100	40.3
SiO_2	210	126
Eu_2O_3	3 (of Eu)	5.3

Optical Properties

Emission color: Violet + UV
Emission peak: 3.10 eV
Emission width (FWHM): 0.19 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)

Spectra



Reference

1. Barry, T.J., Luminescent properties of Eu^{2+} and Eu^{2+} + Mn^{2+} activated $BaMg_2Si_2O_7$, *J. Electrochem. Soc.*, 117, 381 (1970).

$BaSrMgSi_2O_7$:Eu^{2+}

Structure: Ackermanite

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	90	177.6
$SrCO_3$	97	143.2
BaF_2	10	17.5
MgO	100	40.3
SiO_2	210	126
Eu_2O_3	3 (of Eu)	5.3

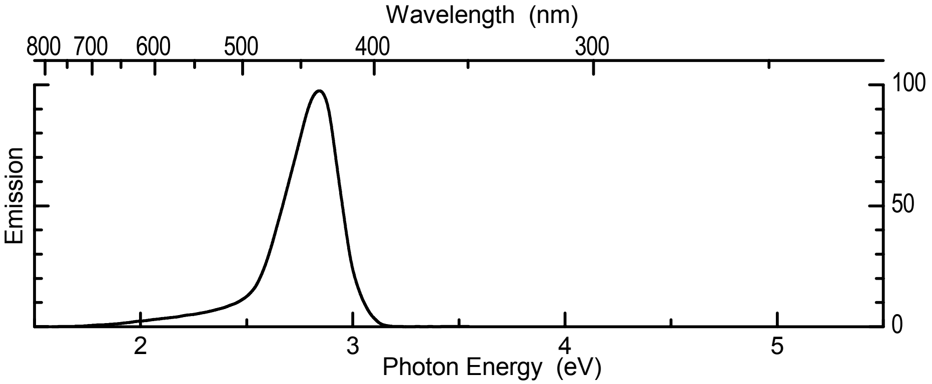
Preparation

Mix by ball-milling in methanol.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 1000ºC, 1 hour.
   Powderize.
2. Fire in capped quartz tubes, CO, 1100ºC, 1 hour.

Optical Properties

Emission color: Blue
Emission peak: 2.82 eV
Emission width (FWHM): 0.27 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Blasse, G., Wanmaker, W.L., and terVrugt, J.W., Some new classes of efficient Eu^{2+} activated phosphors, *J. Electrochem. Soc.,* 115, 673 (1968).
2. Butler, K.H., *Fluorescent Lamp Phosphors,* Pennsylvania University Press, University Park, (1980).
3. Blasse, G. et al., Fluorescence of Eu^{2+}-activated silicates, *Philips Res. Rep.*, 23, 189 (1968).

$Ba_2Li_2Si_2O_7:Eu^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	97	191
Li_2CO_3	110 (of Li)	41
SiO_2	110	66
Eu_2O_3	3 (of Eu)	5.3
NH_4Br	50	49

Preparation

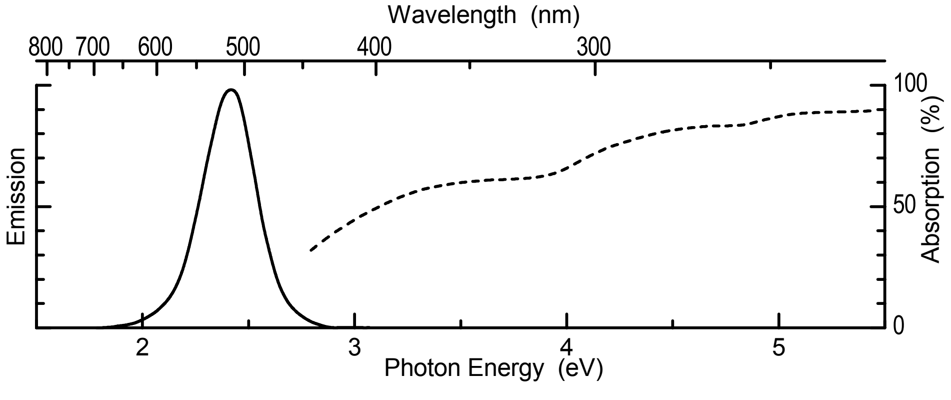
First mix all ingredients but the NH_4Br by dry grinding or milling .

1. Fire in open quartz boats, H_2, 850ºC, 1 hour.
   Now admit the NH_4Br by slurrying in methanol plus a few cubic centimeters water. Dry in air. Powderize when dry.
2. Fire in capped quartz tubes, N_2, 850ºC, 1 hour.
   Powderize.
3. Fire in open quartz boats, CO, 850ºC, 16 hours (overnight).
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Blue-green
Emission peak: 2.44 eV
Emission width (FWHM): 0.30 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV); excited by all UV

Spectra



Remarks

1. Phosphor is chemically unstable in water and deteriorates in moist air.
2. Gradual replacement of Ba by Sr causes rapid decrease of efficiency without visible change of color.

$Ba_2Li_2Si_2O_7:Sn^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	95	187
Li_2CO_3	110 (of Li)	41
SiO_2	110	66
SnO	5	6.8
NH_4Br	50	49

Preparation

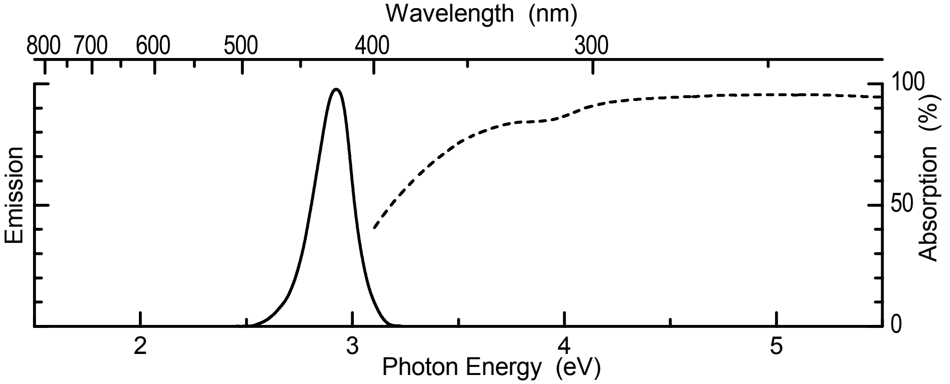
First mix by dry grinding or milling the $BaCO_3 + Li_2CO_3 + SiO_2$.

1. Fire in open boats, H_2, 850°C, 1 hour.
   Now admit the SnO + NH_4Br.
   Make slurry in methanol and stir to uniformity.
   Dry in air. Powderize when dry.
2. Fire in capped quartz tubes, N_2, 850°C, 1 hour.
   Powderize.
3. Fire in open quartz boats, CO, 850°C, ~16 hours (overnight).
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Violet
Emission peak: 2.89 eV
Emission width (FWHM): 0.22 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV); QE fairly high

Spectra



Remarks

1. Phosphor is chemically unstable in water and deteriorates even in moist air.
2. Part or all of the Ba can be replaced by Sr, causing a shift of the emission towards blue-green.
3. The Sn^{2+} emission sensitizes Mn^{2+} (see: $Ba_2Li_2Si_2O_7:Sn^{2+},Mn^{2+}$).

$Ba_2Li_2Si_2O_7:Sn^{2+},Mn^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	93.5	185
Li_2CO_3	110 (of Li)	41
SiO_2	110	66
SnO	5	6.8
$MnCO_3$	1.5	1.7
NH_4Br	50	49

Preparation

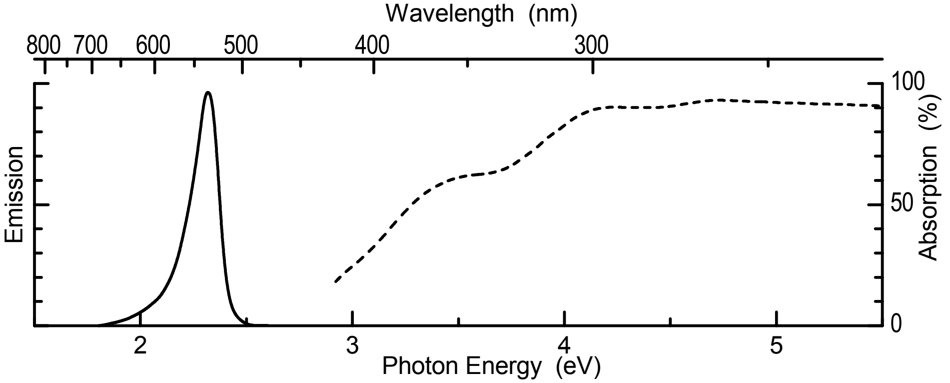
First mix by dry grinding or milling the $BaCO_3$ + Li_2CO_3 + SiO_2.

1. Fire in open boats, H_2, 850ºC, 1 hour.
   Now admit the SnO + $MnCO_3$ + NH_4Br.
   Make a slurry in methanol and stir to uniformity.
   Dry in air. Powderize.
2. Fire in capped quartz tubes, N_2, 850ºC, 1 hour.
   Powderize.
3. Fire in open quartz boats, CO, 850ºC, ~16 hours (overnight).
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Green
Emission peak: 2.32 eV
Emission width (FWHM): 0.16 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV); QE ≈ 60–70% (estimated)

Spectra



Remarks

1. Phosphor is chemically unstable in water and deteriorates even in moist air.
2. Increasing replacement of Ba by Sr causes gradual shift of the emission towards red, broadening and slight deformation of the emission band, and decreasing efficiency.

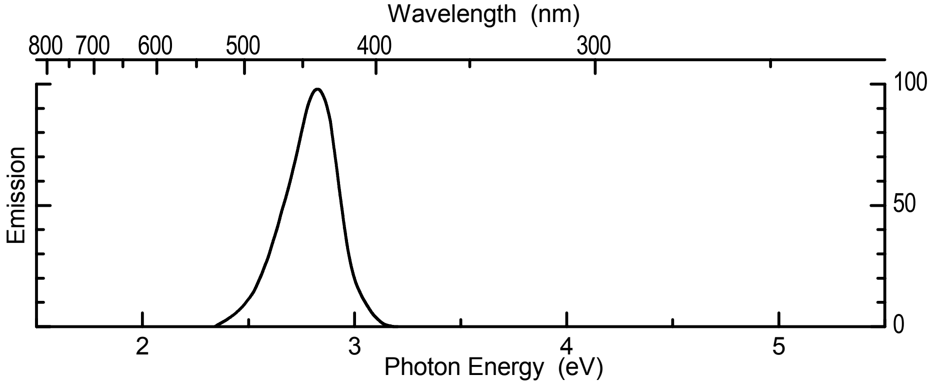
$MgSrBaSi_2O_7:Eu^{2+}$

Structure: Ackermanite

Optical Properties

Emission color: Blue
Emission peak: 2.82 eV
Emission width (FWHM): 0.27 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +

Spectra

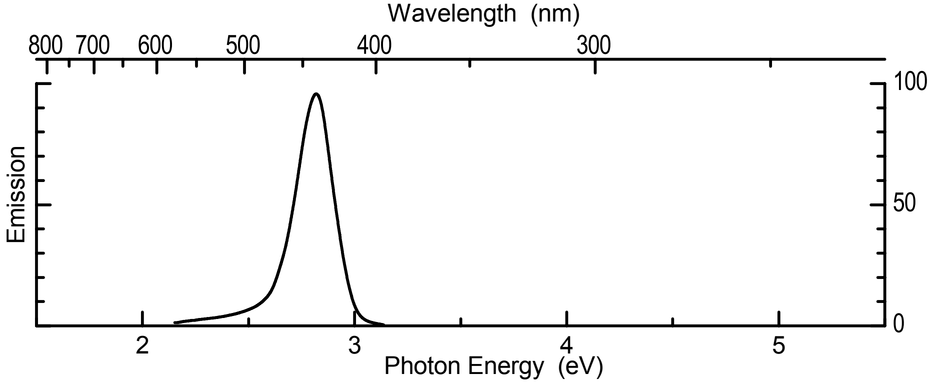


$MgBa_3Si_2O_8:Eu^{2+}$

Optical Properties

Emission color: Blue
Emission peak: 2.82 eV
Emission width (FWHM): 0.22 eV
Excitation efficiency by UV: ++ (4.88 eV)

Spectra



References

1. Barry, T.L., Equilibria and Eu^{2+} luminescence of subsolidus phases bounded by $Ba_3MgSi_2O_8$, $Sr_3MgSi_2O_8$, and $Ca_3MgSi_2O_8$, *J. Electrochem. Soc.*, 115, 733 (1968) and Fluorescence of Eu^{2+}-activated phases in binary alkaline earth orthosilicate systems, *J. Electrochem. Soc.*, 115, 1181 (1968).
2. Blasse, G. et al., Fluorescence of Eu^{2+} activated silicates, *Philips Res. Rep.*, 23, 189 (1968).

$MgSr_3Si_2O_8:Eu^{2+},Mn^{2+}$

Optical Properties

Emission color: Deep red
Emission peak: 1.82 eV
Excitation efficiency by UV: ++ (4.88 eV)

$Sr_3MgSi_2O_8:Eu^{2+}$

Structure: Ackermanite

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	295	435
MgO	100	40
SiO_2	206	124
Eu_2O_3	5 (of Eu)	8.8
NH_4Cl	30	16

Preparation

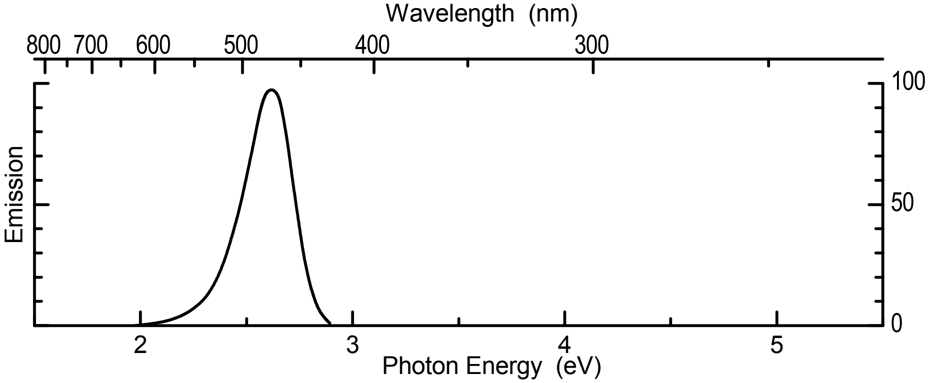
Mix by ball-milling in methanol about 1 hour.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 1000ºC, 1 hour.
   Powderize
2. Fire in capped quartz tubes, CO, 1100ºC, 1 hour.

Optical Properties

Emission color: Blue
Emission peak: 2.70 eV
Emission width (FWHM): 0.23 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV); QE ≈ 45%
Excitation efficiency by e-beam: $\eta \approx 3\%$
Decay: 0.2 μsec to 1/e

Spectra



References

1. Blasse, G. et al., Fluorescence of Eu^{2+}-activated silicates, *Philips Res. Rep.*, 23, 189 (1968).
2. Blasse, G., and Bril, A., Characteristic luminescence, 1. The absorption and emission spectra of some important activators, *Philips Tech. Rev.,* 31, 304 (1970).

$Ca_5B_2SiO_{10}:Eu^{3+}$

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
H_3BO_3	50	31
SiO_2	22	13.2
Eu_2O_3	5 (of Eu)	8.8

Preparation

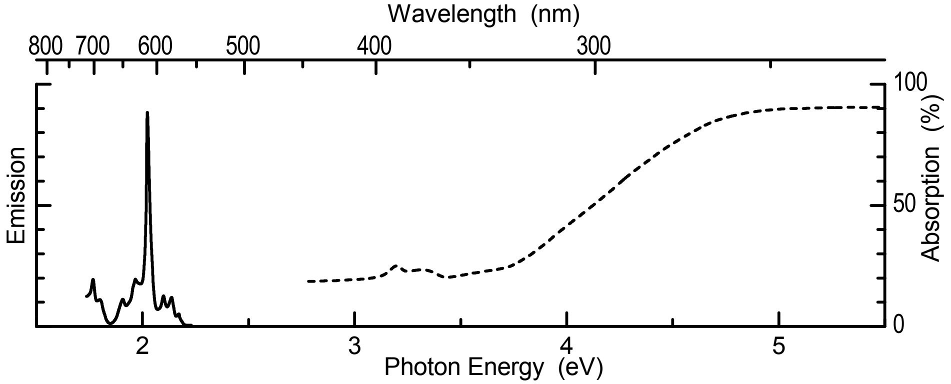
Mix by dry milling or grinding.

1. Fire in open quartz boats, air, 1100°C, 1 hour.
   Powderize by milling.
2. Fire in open quartz boats, air, 1200°C, 1 hour.
   Powderize.
3. Fire in open quartz boats, air, 1300°C, 1 hour.

Optical Properties

Emission color: Red
Emission peak: 2.03 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV); QE ≈ 50–60%
Excitation efficiency by e-beam: Poor

Spectra



Remark

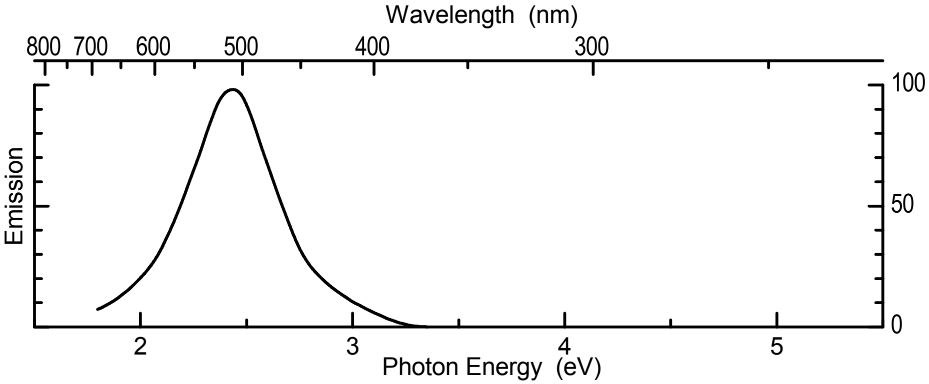
The chemical stability of this material is somewhat better than that of $CaO:Eu^{3+}$.

$Ca_3Al_2Si_3O_{12}:Eu^{2+}$

Optical Properties

Emission color: Pale bluish-green
Emission peak: 2.41 eV
Emission width (FWHM): 0.47 eV
Excitation efficiency by UV: Excited by all UV but low QE (≈ 20%)
Excitation efficiency by e-beam: Very poor, η ≈ 0.5%

Spectra

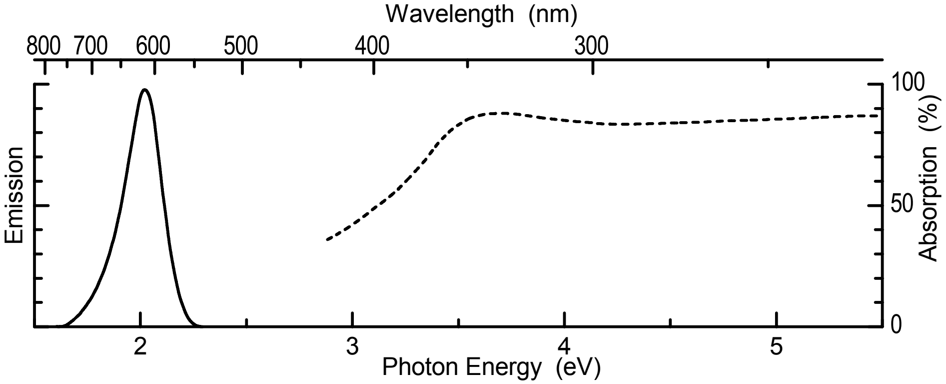


$LiCeBa_4Si_4O_{14}:Mn^{2+}$

Optical Properties

Emission color: orange–red
Emission peak: ~2.02 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra

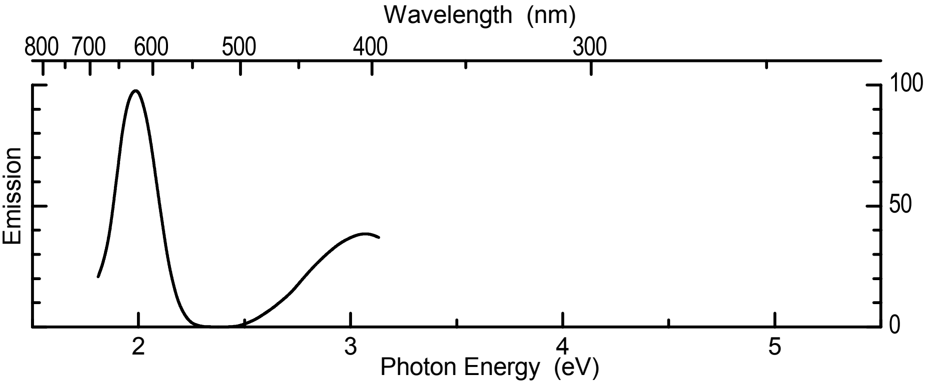


$LiCeSrBa_3Si_4O_{14}:Mn^{2+}$

Optical Properties

Emission color: Red
Emission peak: 1.99 eV
Emission width (FWHM): 0.23 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra


Wavelength (nm)
800
700
600
500
400
300
Emission
100
50
0
2
3
4
5
Photon Energy (eV)

4.4 Halosilicates

The following host compounds and activators are included in this subsection:

$LaSiO_3Cl:Ce^{3+}$
$LaSiO_3Cl:Ce^{3+},Tb^{3+}$
$Ca_3SiO_4Cl_2:Pb^{2+}$
$Ca_3SiO_4Cl_2:Eu^{2+}$
$Ba_5SiO_4Cl_6:Eu^{2+}$
$Sr_5Si_4O_{10}Cl_6:Eu^{2+}$

$LaSiO_3Cl:Ce^{3+}$

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	100 (of La)	163
SiO_2	160	96
CeO_2	20	34
NH_4Cl	120	64

Preparation

Mix by slurrying in water (NH_3 develops).
Dry in air. Powderize when dry.

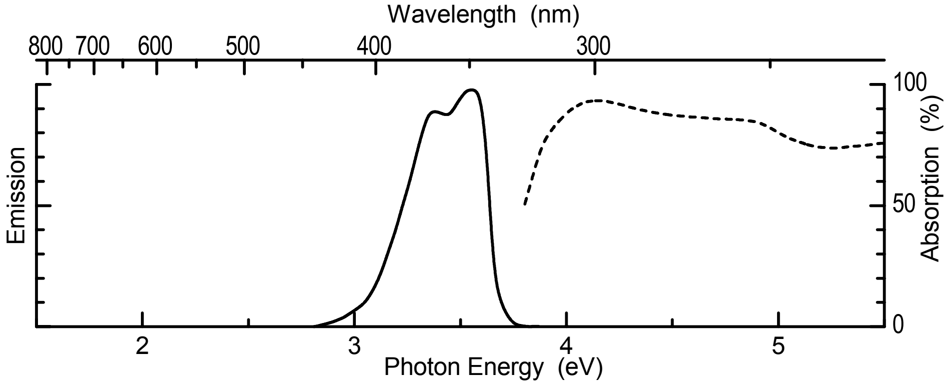
1. Fire in capped quartz tubes, N_2, 500°C, 1 hour. Powderize.
2. Fire in capped quartz tubes, N_2, 1200°C, 1 hour. Powderize.
3. Fire in open quartz boats, CO, 1200°C, 1 hour. Powderize.

Wash in water several times.
Dry in air.

Optical Properties

Emission color: UV
Emission peak: 3.35 and 3.56 eV
Excitation efficiency by UV: ++ (4.88 eV); QE ≈ 90%
Excitation efficiency by e-beam: $\eta \approx 5\%$

Spectra



Remarks

1. F or Br can replace the Cl in the above recipe, but Cl seems to perform best.
2. Replacement of La by Y is possible but gives somewhat poorer phosphors.

Reference

1. Lehmann, W., and Isaaks, T.H.J., Lanthanum and yttrium halo-silicate phosphors, *J. Electrochem. Soc.,* 125, 445 (1978).

$LaSiO_3Cl:Ce^{3+},Tb^{3+}$

Composition

Ingredient	**Mole %**	**By weight (g)**
La_2O_3	100 (of La)	163
SiO_2	180	108
CeO_2	20	34
Tb_4O_7	14 (of Tb)	26
NH_4Cl	130	60

Preparation

Mix by slurrying in water (NH_3 develops).
Dry in air. Powderize when dry.

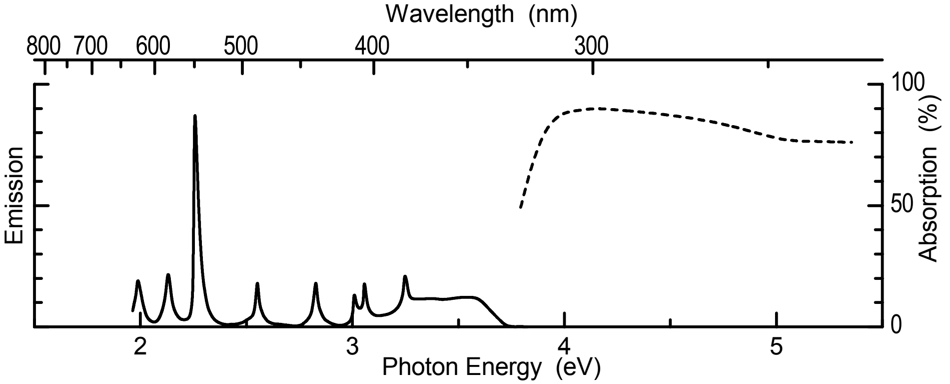
1. Fire in capped quartz tubes, N_2, ~500°C, ~1 hour. Powderize.
2. Fire in capped quartz tubes, N_2, 1200°C, 1 hour. Powderize.
3. Fire in open quartz boats, CO, 1200°C, 1 hour. Powderize.

Wash in water several times.
Dry in air.

Optical Properties

Emission color: Pale yellow-green
Emission peak: 2.29 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV); QE ≈ 80–90%
Excitation efficiency by e-beam: +/4%

Spectra



Remarks

1. The Cl in the above recipe can be replaced by F or Br but Cl seems to perform best.
2. Replacement of La by Y is possible but gives somewhat poorer phosphors.

Reference

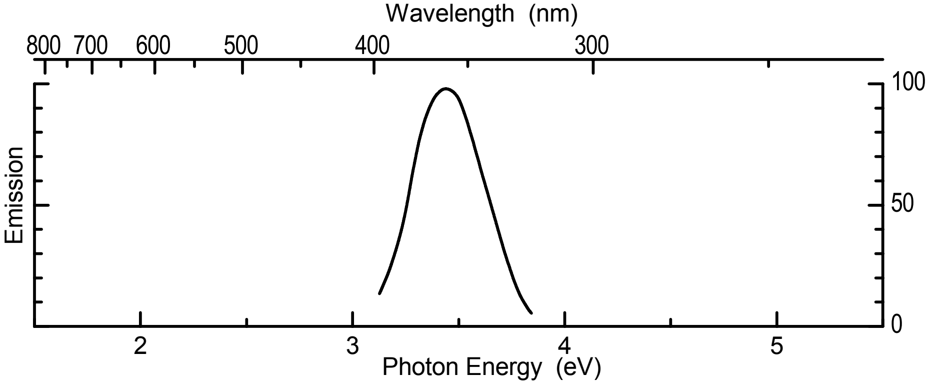
1. Lehmann, W., and Isaaks, T.H.J., Lanthanum and yttrium halo-silicate phosphors, *J. Electrochem. Soc.,* 125, 445 (1978).

$Ca_3SiO_4Cl_2$:Pb^{2+}

Optical Properties

Emission color: UV
Emission peak: 3.44 eV
Emission width (FWHM): 0.39 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Reference

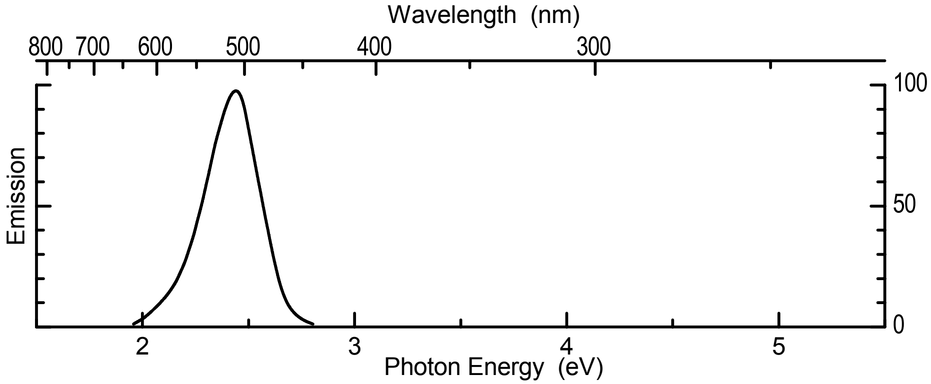
1. Wanmaker, W.L., and Verriet, J.G., Luminescence of phosphors with Ca_3SiO_4Cl, *Philips Res. Rep.*, 28, 80 (1973).

$Ca_3SiO_4Cl_2$:Eu^{2+}

Optical Properties

Emission color: Blue-green
Emission peak: 2.41 eV
Emission width (FWHM): 0.31 eV
Excitation efficiency by UV: + (4.88 eV), ++ (3.40 eV)

Spectra



Reference

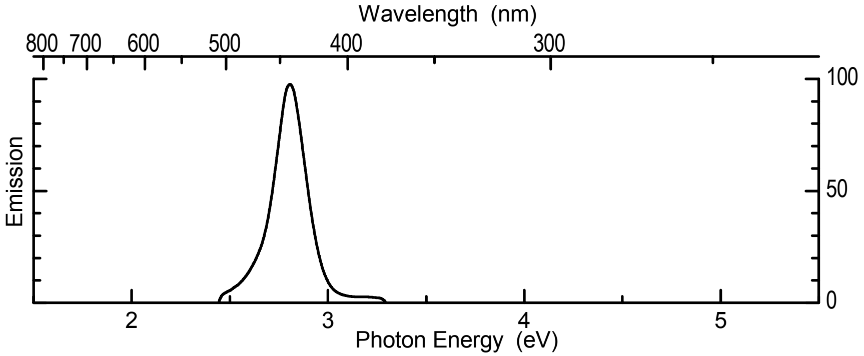
1. Wanmaker, W.L., and Verriet, J.G., Luminescence of phosphors with Ca_3SiO_4Cl, *Philips Res. Rep.*, 28, 80 (1973).

$Ba_5SiO_4Cl_6$:Eu^{2+}

Optical Properties

Emission color**:** blue
Emission peak**:** 2.82 eV
Emission width (FWHM)**:** 0.19 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Reference

1. Garcia, A, Latourette, B, and Fouassier, C., $Ba_5SiO_4Cl_6$:Eu, a new blue-emitting photo-luminescent material with high quenching temperature, *J. Electrochem. Soc.*, 126, 1734 (1979).

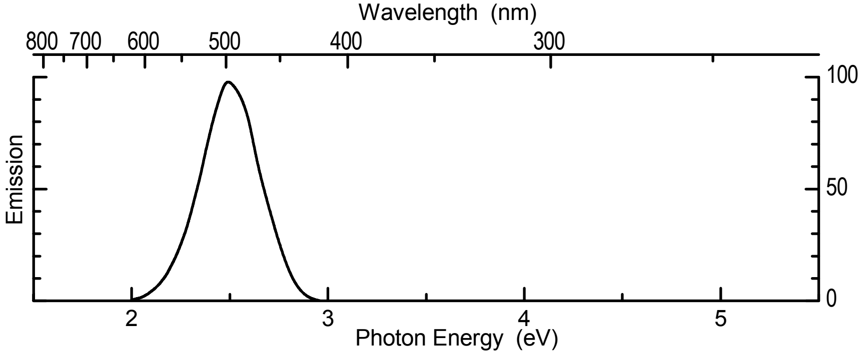
$Sr_5Si_4O_{10}Cl_6$:Eu^{2+}

Optical Properties

Emission color: Blue-green
Emission peak: 2.52 eV

Emission width (FWHM): 0.38 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



References

1. Burrus, H.L., Nicholson, K.P., and Rooksby, H.P., Fluorescence of Eu^{2+}-activated alkaline earth halosilicates, *J. Lumin.*, 3, 467 (1971).

4.5 Phosphates

The following host compounds and activators are included in this subsection:

$YPO_4:Ce^{3+}$
$YPO_4:Ce^{3+},Tb^{3+}$
$YPO_4:Eu^{3+}$
$YPO_4:Mn^{2+},Th^{4+}$
$YPO_4:V^{5+}$
$LaPO_4:Ce^{3+}$
$LaPO_4:Eu^{3+}$
$CaP_2O_6:Mn^{2+}$
$Sr_2P_2O_7:Sn^{2+}$
$Ca_2P_2O_7:Ce^{3+}$
$Ca_2P_2O_7:Eu^{2+},Mn^{2+}$
$Ca_2P_2O_7:Eu^{2+}$
$Li_2CaP_2O_7:Ce^{3+},Mn^{2+}$
$MgCaP_2O_7:Mn^{2+}$
$BaTiP_2O_7$
$MgSrP_2O_7:Eu^{2+}$
$MgBaP_2O_7:Eu^{2+}$
$MgBaP_2O_7:Eu^{2+},Mn^{2+}$
$\beta\text{-}Ca_3(PO_4)_2:Ce^{3+}$
$CaB_2P_2O_9:Eu^{2+}$
$\alpha\text{-}Ca_3(PO_4)_2:Sn^{2+}$
$\beta\text{-}Ca_3(PO_4)_2:Sn^{2+}$
$\alpha\text{-}Ca_3(PO_4)_2:Pb^{2+}$
$\alpha\text{-}Ca_3(PO_4)_2:Tl^{+}$
$\alpha\text{-}Ca_3(PO_4)_2:Ce^{3+}$
$\alpha\text{-}Ca_3(PO_4)_2:Eu^{2+}$
$\beta\text{-}Ca_3(PO_4)_2:Eu^{2+}$
$\beta\text{-}Ca_3(PO_4)_2:Eu^{2+},Mn^{2+}$
$\beta\text{-}Sr_3(PO_4)_2:Sn^{2+},Mn^{2+}(Al)$
$\beta\text{-}Sr_3(PO_4)_2:Sn^{2+}$
$\beta\text{-}Sr_3(PO_4)_2:Eu^{2+}$
$Ba_3(PO_4)_2:Eu^{2+}$
$Na_3Ce(PO_4)_2:Tb^{3+}$
$\beta\text{-}(Ca,Sr)_3(PO_4)_2:Sn^{2+},Mn^{2+}$
$ZnMg_2(PO_4)_2:Mn^{2+}$
$Zn_3(PO_4)_2:Mn^{2}$
$(Zn,Mg)_3(PO_4)_2:Mn^{2+}$
$Mg_3Ca_3(PO_4)_4:Eu^{2+}$
$MgSr_5(PO_4)_4:Sn^{2+}$
$MgBa_2(PO_4)_2:Sn^{2+}$
$CaSr_2(PO_4)_2:Bi^{3+}$
$MgBa_2(PO_4)_2:U$
$Sr_2P_2O_7:Eu^{2+}$

YPO_4:Ce^{3+}

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	97 (of Y)	110
Eu_2O_2	3 (of Eu)	5.2
H_3PO_4 solution, 85%	105 (of P)	64 ccm

Preparation

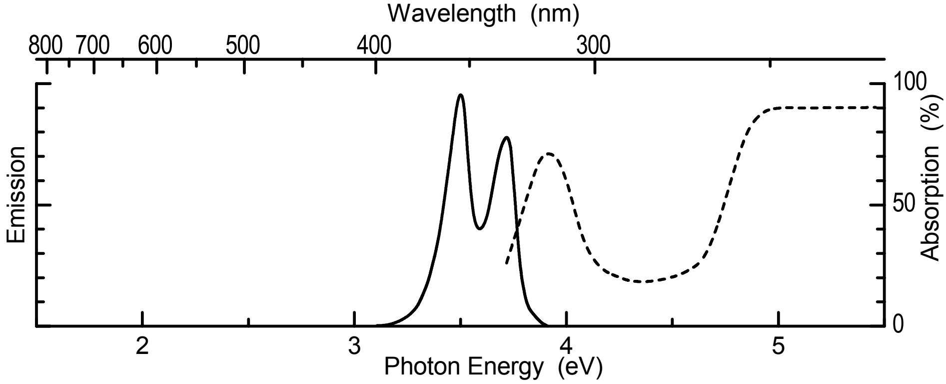
Make a thin slurry of Y_2O_3 and Eu_2O_3 in methanol. Slowly add the H_3PO_4 solution while stirring. Dry in air. Powderize when dry.

1. Fire in open quartz boats, N_2, ~500–600ºC, ~1 hour. Powderize. Add ~5 g of NH_4Cl; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, ~1300ºC, ~2 hours. Powderize.
3. Fire in open quartz boats, CO, 1300ºC, ~1 hour.

Optical Properties

Emission color: UV
Emission peak: 3.49 and 3.71 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: 2–3%
Decay: Near exponential decay, ~80 nsec to 1/10

Spectra



References

1. Blasse, G., and Bril, A., The absorption and emission spectra of some important activators, *Philips Tech. Rev.,* 31, 304 (1970).
2. Hoffman, M.V., Effect of thorium on Ce^{+3} phosphors, *J. Electrochem. Soc.,* 118, 1508 (1971).
3. Blasse, G., Ultraviolet-absorption bands of Bi^{3+} and Eu^{3+} in oxides, *J. Solid State Chem.,* 4, 52 (1972).
4. Bimburg, D., Robbins, D.R., Wright, D.R., and Jeser, J.P., CeP_5O_{14}, a new ultrafast scintillator, *Appl. Phys. Lett.*, 27, 67 (1975).
5. Mandel, G., Bauman, R.P., and Banks, E., Electronic transitions of rare earth ions in the infrared region, *J. Chem. Phys.,* 33, 192 (1960).

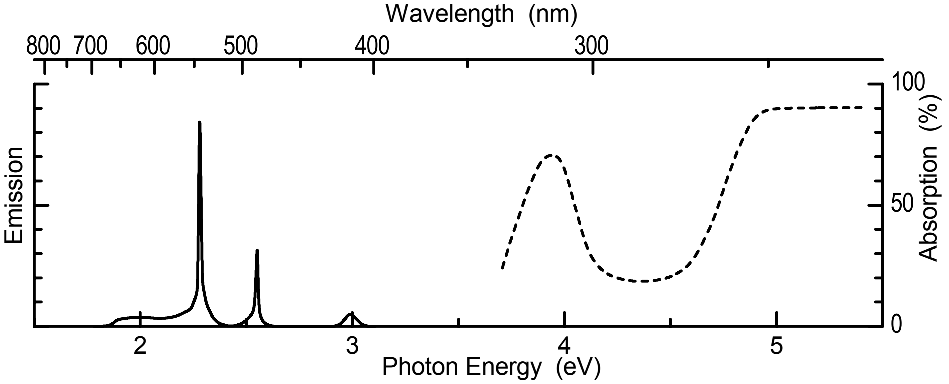
YPO$_4$:Ce^{3+},Tb^{3+}

Structure: Tetragonal

Optical Properties

Emission color: Green
Emission peak: 2.28 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



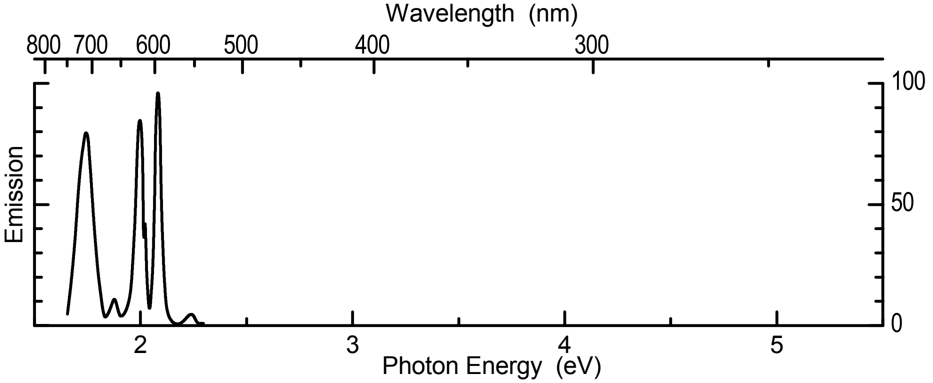
YPO$_4$:Eu^{3+}

Structure: Tetragonal

Optical Properties

Emission color: Orange-red
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Reference

1. Ropp, R.C., Phosphors based on rare earth phosphates. 1. Spectral properties of some rare earth phosphates, *J. Electrochem. Soc.*, 115, 841 (1968).

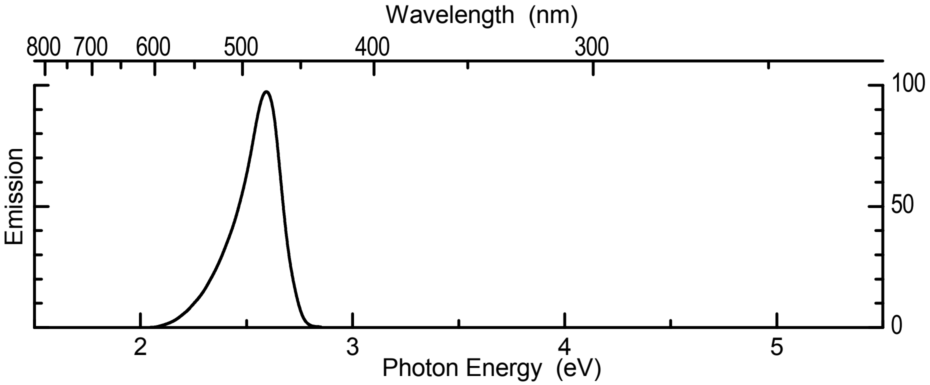
$YPO_4:Mn^{2+},Th^{4+}$

Structure: Tetragonal

Optical Properties

Emission color: Blue-green
Emission peak: 2.59 eV
Emission width (FWHM): 0.23 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



$YPO_4:V^{5+}$

Structure: Tetragonal

Optical Properties

Emission color: Blue
Emission peak: 2.99 eV
Emission width (FWHM): 0.56 eV
Excitation efficiency by UV: + (4.88 eV)

$LaPO_4:Ce^{3+}$

Structure: Monoclinic (monazite)

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	98 (of La)	160
CeO_2	2	3.44
NH_4Cl	10	5.4
H_3PO_4 solution, 85%	105 (of P)	64 ccm

Preparation

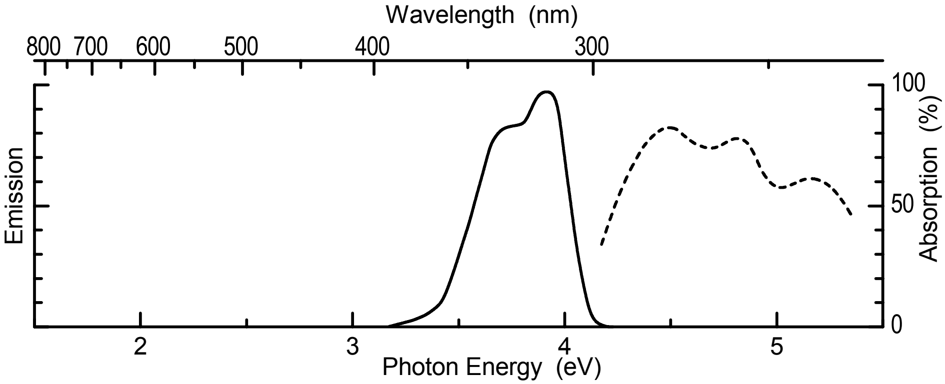
Make a slurry of La_2O_3, CeO_2 , and NH_4Cl in methanol.
Slowly add the H_3PO_4 solution while stirring.
Dry in air. Powderize when dry.

1 Fire in open quartz boats, N_2, 1250ºC, 2 hours.
Powderize.
2 Fire in open quartz boats, CO, 1250ºC, 1 hour.

Optical Properties

Emission color: UV
Emission peak: 3.67 and 3.94 eV
Excitation efficiency by UV: ++ (4.88eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Reference

1. Mandel, G., Bauman, R.P., and Banks, E., Electronic transitions of rare earth ions in the infrared region, *J. Chem. Phys.,* 33, 192 (1970).

$LaPO_4:Eu^{3+}$

Structure: Monoclinic (monazite)

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	95 (of La)	155
Eu_2O_3	5 (of Eu)	8.8
NH_4Cl	10	5.4
H_3PO_4 solution, 85%	105 (of P)	64 ccm

Preparation

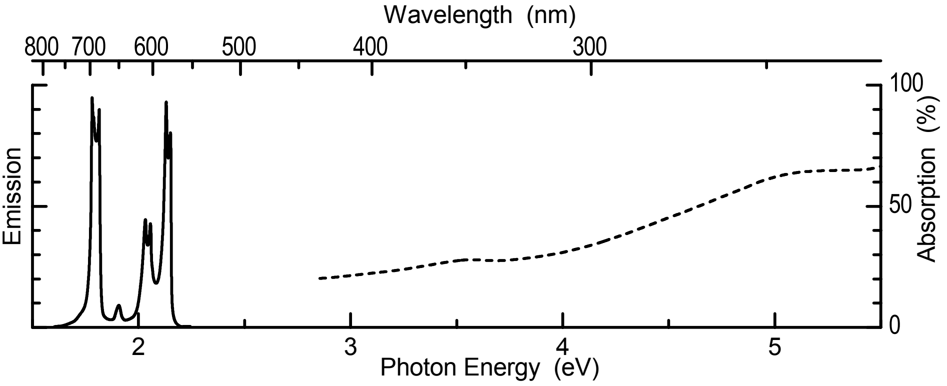
Make a slurry of La_2O_3, Eu_2O_3, and NH_4Cl in methanol.
Slowly add the H_3PO_4 solution while stirring.
Dry in air. Powderize when dry.

1. Fire in open quartz boats, N_2, 1250ºC, 2 hours.
   Powderize.
2. Fire in open quartz boats, air, 1250ºC, 1 hour.

Optical Properties

Emission color: Orange-red
Emission peak: Strongest lines are at 1.784, 1.815, 2.097, and 2.117 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra



Reference

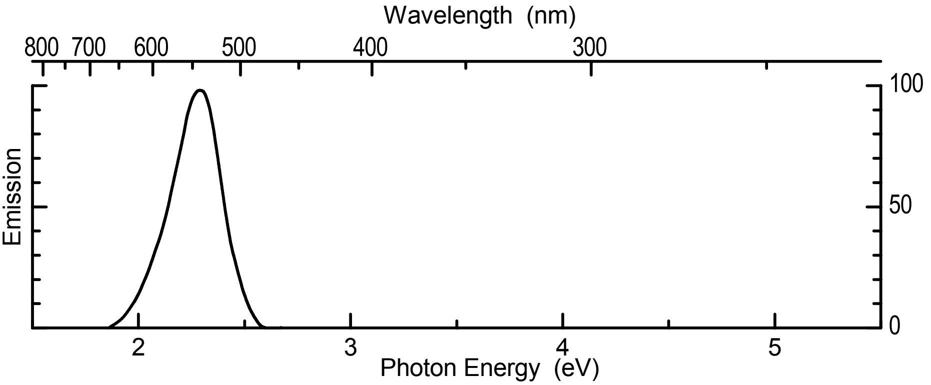
1. Wanmaker, W.L. et al., Luminescent properties of Eu-activated phosphors of type A_3BVO_4, *Philips Tech. Rev.,* 21, 270 (1966).

CaP_2O_6:Mn^{2+}

Optical Properties

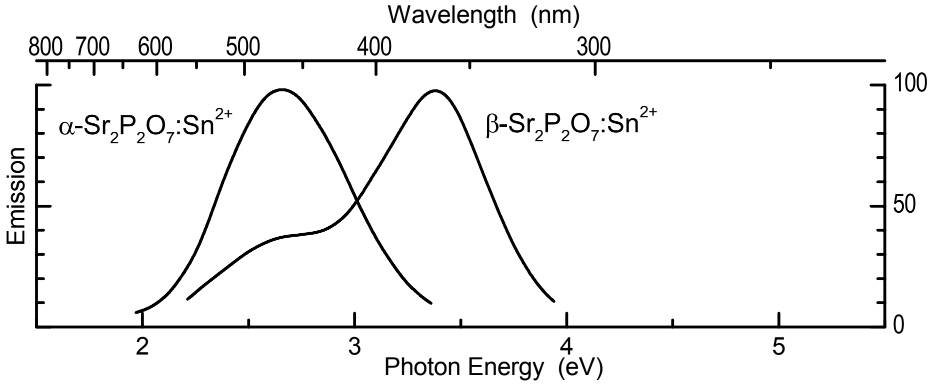
Emission color: Green
Emission peak: 2.30 eV
Emission width (FWHM): 0.29 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



$Sr_2P_2O_7:Sn^{2+}$

Spectra



Reference

1. Ropp., R.C., and Mooney, R.W., Tin-activated alkaline-earth pyrophosphate phosphors, *J. Electrochem. Soc.*, 107, 15 (1960).

$Ca_2P_2O_7:Ce^{3+}$

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
$CaHPO_4$	96	130
CeO_2	2	3.4
$NaHCO_3$	2	1.7
H_3PO_4-solution, 85%	6 (of P)	4.1 ccm

Preparation

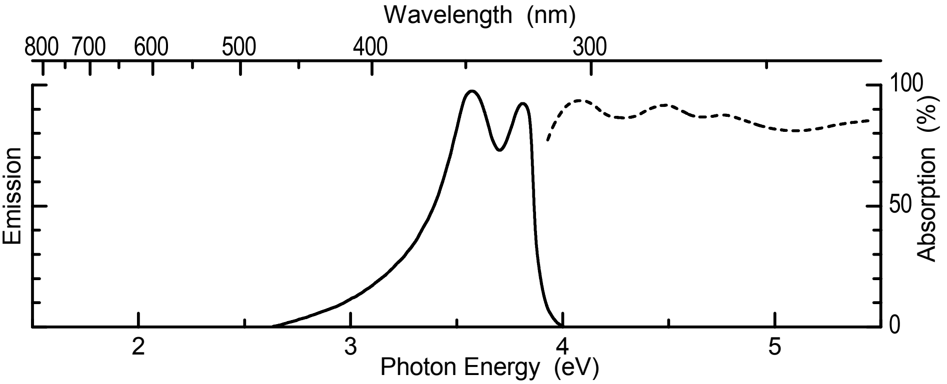
Make a slurry of $CaHPO_4$, CeO_2 , and $NaHCO_3$ in water or methanol.
Add the H_3PO_4 solution while stirring; stir to uniformity.
Dry in air. Powderize when dry.

1. Fire in open quartz boats, N_2, ~500–600°C, ~1/2 hour.
Powderize.
2. Fire in open quartz boats, CO, 1200°C, 1 hour.

Optical Properties

Emission color: Pale bluish (most of the emission in the UV)
Emission peaks: 3.60 and 3.83 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Reference

1. Ranby, P.W., Mash, D.H., and Henderson, S.T., The investigation of new phosphors, with particular reference to the pyrophosphates, *Br. J. Appl. Phys.,* Suppl. 4, 18 (1955).

$Ca_2P_2O_7$:Eu^{2+},Mn^{2+}

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
$CaHPO_4$	93	126
Eu_2O_3	2 (of Eu)	3.5
$MnCO_3$	5	5.75
H_3PO_4 solution, 85%	9 (of P)	6.1 ccm

Preparation

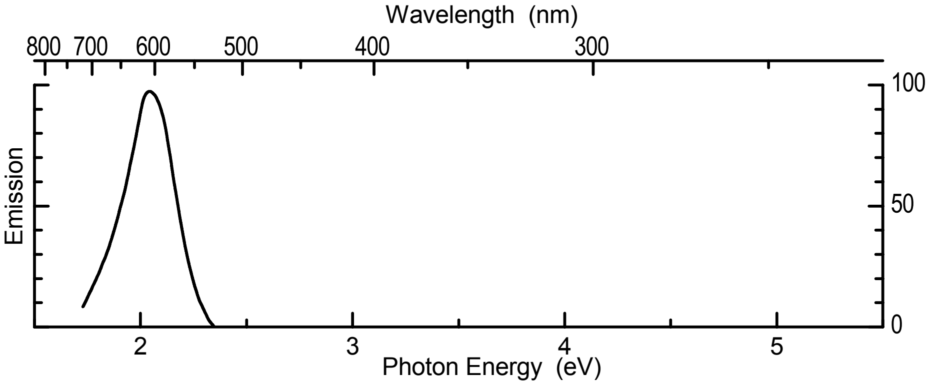
Make a slurry of $CaHPO_4$, Eu_2O_3 , and $MnCO_3$ in water or methanol.
Add the H_3PO_4 solution while stirring; stir to uniformity.
Dry in air. Powderize when dry.

1. Fire in open quartz boats, N_2, ~500–600°C, ~1 hour.
   Powderize.
2. Fire in open quartz boats, CO, 1200°C, 1 hour.

Optical Properties

Emission color: Pink-orange
Emission peak: Orange Mn^{2+} band at ~2.06 eV; Violet Eu^{2+} band at ~2.98 eV
Emission width (FWHM): 0.28 eV (Mn^{2+} band)
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



References

1. Kröger, F.A. et al., *J. Electrochem. Soc.,* 96, 132 (1949).
2. Kinney, D.E., Modified calcium pyrophosphate phosphors, *J. Electrochem. Soc.,* 102, 676 (1955).
3. Ranby, P.W., Mash, D.H., and Henderson, S.T., The investigation of new phosphors, with particular reference to the pyrophosphates, *Br. J. Appl. Phys.,* S18, Suppl. 4 (1955).
4. Ropp, R.C., Manganese-activated cadmium pyrophosphate phosphors, *J. Electrochem. Soc.,* 109, 569 (1962).

$Ca_2P_2O_7:Eu^{2+}$

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
$CaHPO_4$	98	133
Eu_2O_3	2 (of Eu)	3.5
H_3PO_4 solution, 85%	4 (of P)	2.7 ccm

Preparation

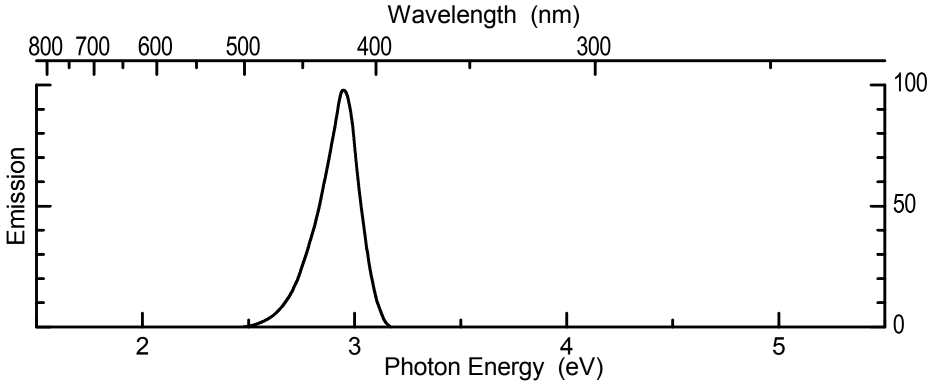
Make a slurry of $CaHPO_4$ + Eu_2O_3 in water or methanol.
Add the H_3PO_4 solution while stirring; stir to uniformity.
Dry in air. Powderize when dry.

1. Fire in open quartz boats, N_2, ~500–600°C, ~1 hour. Powderize.
2. Fire in open quartz boats, CO, 1200°C, 1 hour.

Optical Properties

Emission color: Violet
Emission peak: 2.96 eV
Emission width (FWHM): 0.19 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



References

1. Kröger, F.A. et al., *J. Electrochem. Soc.,* 96, 132 (1949).
2. Kinney, D.E., Modified calcium pyrophosphate phosphors, *J. Electrochem. Soc.,* 102, 676 (1955).
3. Ranby, P.W., Mash, D.H., and Henderson, S.T., The investigation of new phosphors, with particular reference to the pyrophosphates, *Br. J. Appl. Phys.,* S18, Suppl. 4 (1955).
4. Ropp, R.C., Manganese-activated cadmium pyrophosphate phosphors, *J. Electrochem. Soc.,* 109, 569 (1962).

$Li_2CaP_2O_7$:Ce^{3+},Mn^{2+}

Composition

Ingredient	Mole %	By weight (g)
Li_2CO_3	205 (of Li)	75.7
$CaHPO_4$	89	121
CeO_2	3	5.2
$MnCO_3$	5	5.75
H_3PO_4 solution, 85%	115 (of P)	70 ccm

Preparation

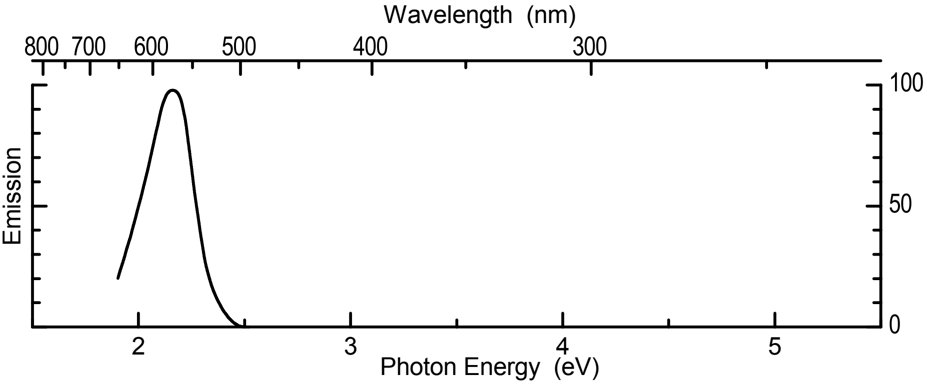
Make a slurry of $Li_2CO_3 + CaHPO_4 + CeO_2 + MnCO_3$ in methanol.
Add the H_3PO_4 solution while stirring (CO_2 develops).
Dry in air. Powderize when dry.

1. Fire in open quartz boats, N_2, ~500–600°C.
   Powderize.
2. Fire in open quartz boats, N_2, 700°C, 16 hours (overnight).

Optical Properties

Emission color: Greenish-yellow
Emission peak: 2.16 eV
Emission width (FWHM): 0.28 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



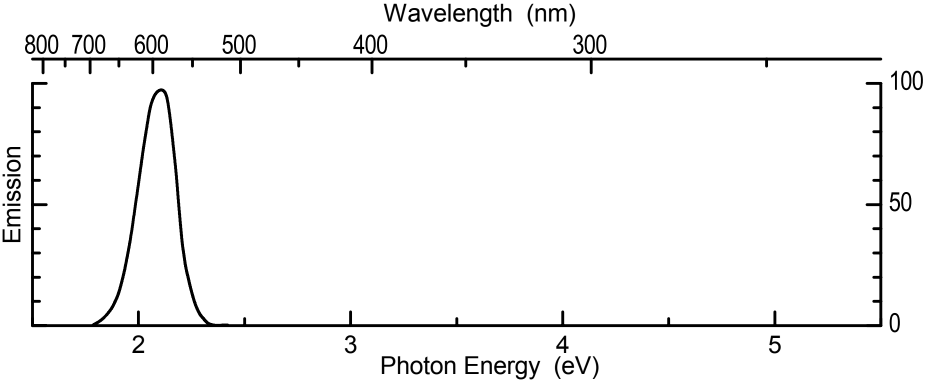
$MgCaP_2O_7:Mn^{2+}$

Structure: Monoclinic

Optical Properties

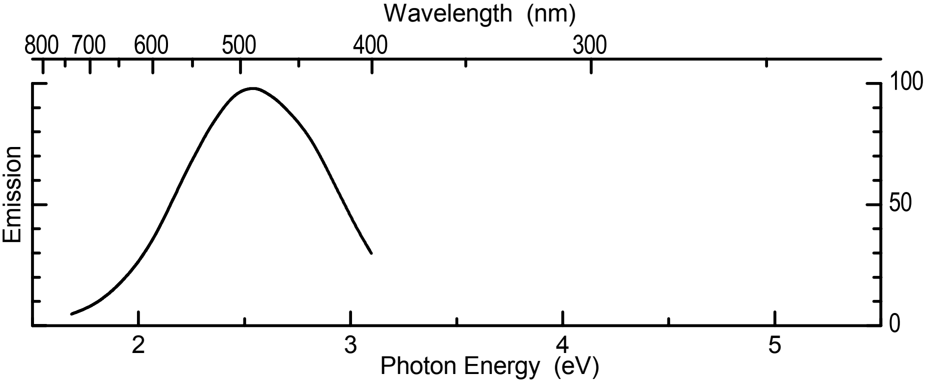
Emission color: Yellow
Emission peak: 2.12 eV
Emission width (FWHM): 0.20 eV

Spectra



$BaTiP_2O_7$

Spectra



Reference

1. Henderson, S.T., and Ranby, P.W., Barium titanium phosphate – a new phosphor, *J. Electrochem. Soc.*, 98, 479 (1951).

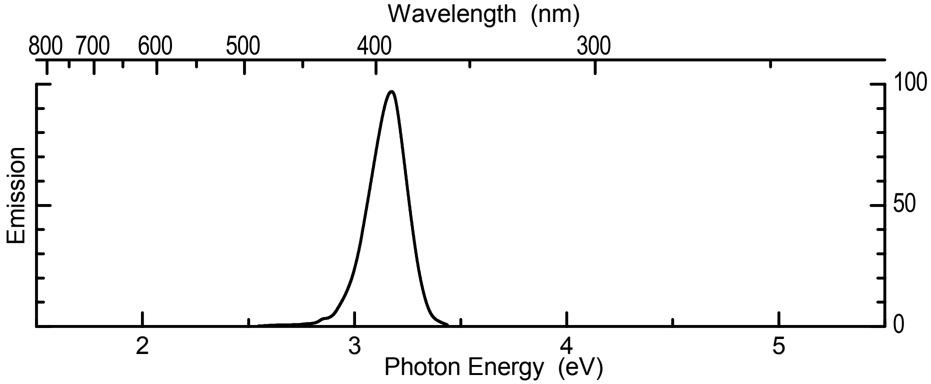
$MgSrP_2O_7:Eu^{2+}$

Structure: Monoclinic

Optical Properties

Emission color: Violet-UV
Emission peak: 3.16 eV
Emission width (FWHM): 0.20 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Hoffman, M.V., Eu^{+2} activation in some alkaline earth strontium phosphate compounds, *J. Electrochem. Soc.*, 115, 560 (1968).
2. Blasse, G., and Bril, A., The absorption and emission spectra of some important activators, *Philips Tech. Rev.*, 31, 304 (1970).

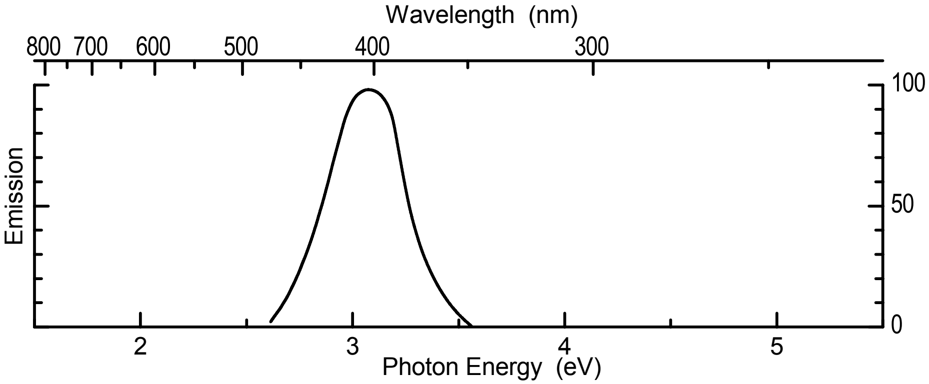
$MgBaP_2O_7:Eu^{2+}$

Structure: Monoclinic

Optical Properties

Emission color: Violet-UV
Emission peak: 3.04 eV
Emission width (FWHM): 0.35 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Reference

1. Lagos, C.C., Luminescence of divalent europium in BaO-MgO-P_2O_5 system, *J. Electrochem. Soc.*, 115, 1271 (1968).

$MgBaP_2O_7:Eu^{2+},Mn^{2+}$

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
$Mg_2P_2O_7$	90 (of Mg)	100
$Ba_2P_2O_7$	96 (of Ba)	215
Eu_2O_3	4 (of Eu)	7
$MnCO_3$	10	11.5
H_3PO_4-solution, 85%	19 (of P)	12.9 ccm

Preparation

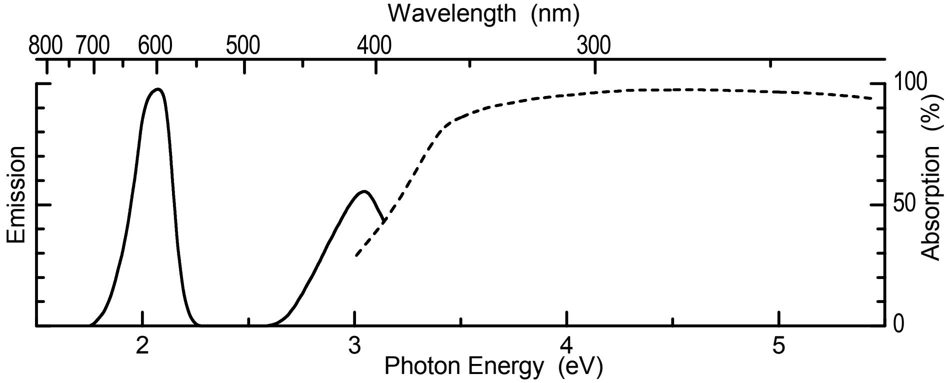
Make a slurry of $Mg_2P_2O_7$ + $Ba_2P_2O_7$ + Eu_2O_3 + $MnCO_3$ in water.
Add the H_3PO_4 solution while stirring.
Dry in air. Powderize when dry.

1. Fire in open quartz boats, N_2, 500–600ºC, 1 hour.
   Powderize.
2. Fire in open quartz boats, N_2, 950ºC, 2 hours.

Optical Properties

Emission color: Pinkish orange-red
Emission peak: Orange-red Mn^{2+} band at 2.07 eV, violet Eu^{2+} band at 3.06 eV
Emission width (FWHM): 0.18 eV (Mn^{2+} band)
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



β-$Ca_3(PO_4)_2$:Ce^{3+}

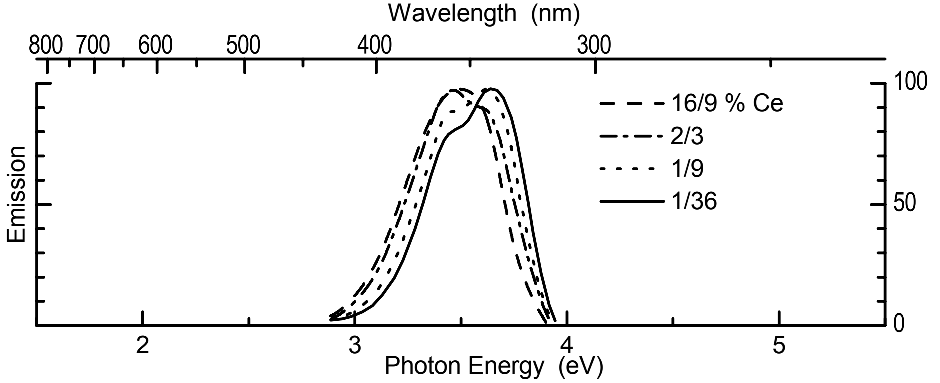
Structure: Trigonal

Optical Properties

Emission color: UV

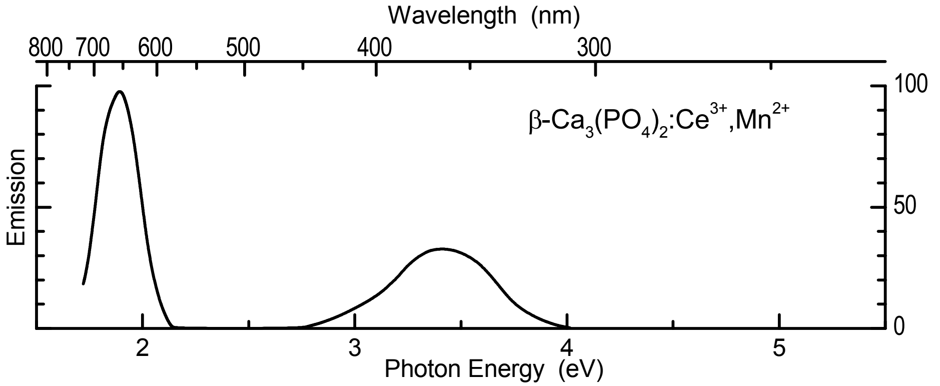
Excitation efficiency by UV: ++ (4.88 eV)

Spectra



Reference

1. Botden, T.P.J., Transfer and transport of energy by resonance processes in luminescent solids, *Philips Res. Rep.*, 7, 197 (1952).



Reference

1. Froelich, H.C., and Margolis, J.M., Calcium phosphate phosphor activated with cerium and manganese, *J. Electrochem. Soc.*, 98, 400 (1951).

$CaB_2P_2O_9:Eu^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$CaHPO_4$	98	134
H_3BO_3	200	124
Eu_2O_3	2 (of Eu)	3.5
$(NH_4)_2HPO_4$	106	140

Preparation

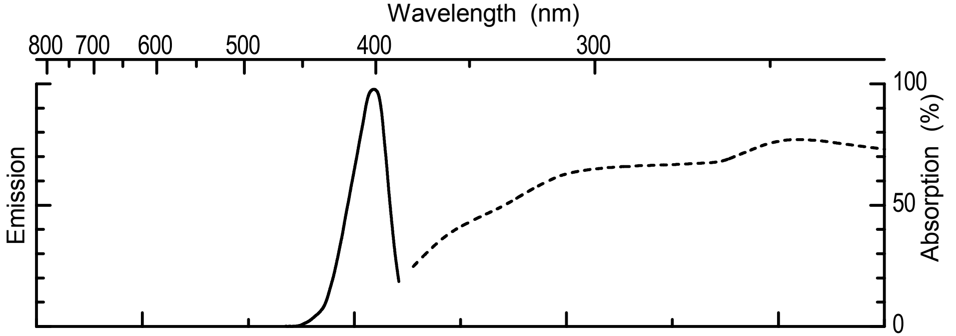
Make a slurry of the $CaHPO_4$ + Eu_2O_3 in methanol.
Dissolve the H_3BO_3 + $(NH_4)_2HPO_4$ together in a little water.
Add the solution to the slurry. Stir.
Dry in air. Powderize when dry.

1. Fire in open quartz boats, air, ~500–600°C, 1 hour.
   Powderize.
2. Fire in open quartz boats, N_2, 800°C, 1 hour.
   Powderize.
3. Fire in open quartz boats, CO, 1000°C, 1 hour.

Optical Properties

Emission color: Deep violet
Emission peak: 3.08 eV
Emission width (FWHM): 0.21 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



α-$Ca_3(PO_4)_2$:Sn^{2+}

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	10	10
$CaHPO_4$	75	90
SnO	1	1.35
$(NH_4)_2CO_4$	12	2

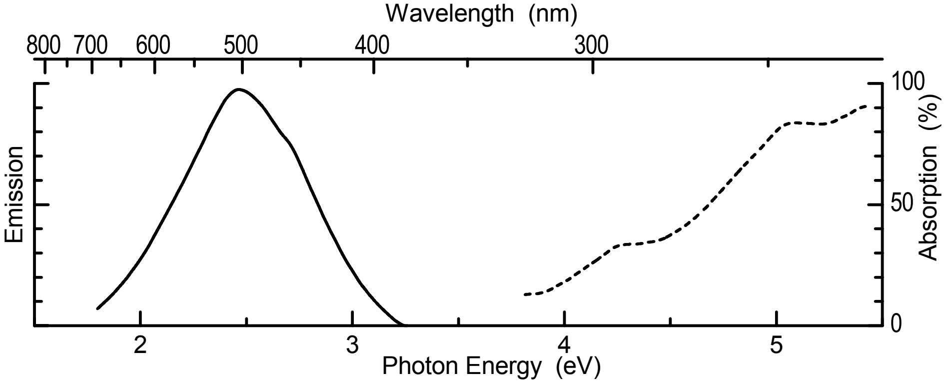
Preparation

Mix the $CaCO_3$ + $CaHPO_4$ + SnO by slurrying in methanol.
Dry in air. Powderize when dry.
Now add the crushed $(NH_4)_2CO_4$ by dry mixing.
Fire in capped quartz tubes, N_2, 1250°C, 1 hour.

Optical Properties

Emission color: Pale blue-green
Emission peak: 2.44 eV
Emission width (FWHM): 0.61 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Kröger, F.A., A proof of the associated-pair theory for sensitized luminophors, *Physica,* 15, 801 (1949).
2. Kreidler, E.R., Phase equilibria and tin-activated luminescence in system $Ca_3(PO_4)_2$-$Ba_3(PO_4)_2$, *J. Electrochem. Soc.,* 118, 923 (1971).

β-$Ca_3(PO_4)_2$:Sn^{2+}

Structure: Trigonal

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	5	5
$CaHPO_4$	75	90
SnO	5	6.75

Preparation

Mix by slurrying in water or methanol.

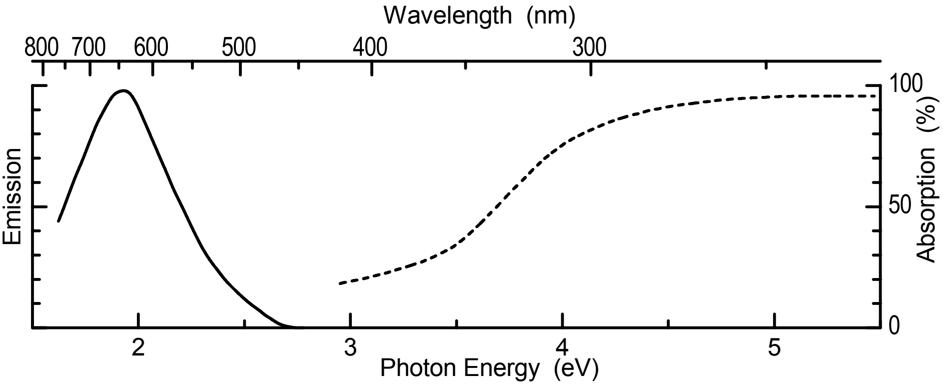
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 1100°C, 2 hours.
   Powderize by dry milling.
2. Fire in capped quartz tubes, CO, 1100°C, 2 hours.

Optical Properties

Emission color: Pale orange
Emission peak: 1.92 eV
Emission width (FWHM): 0.55 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



References

1. Kröger, F.A., A proof of the associated-pair theory for sensitized luminophors, *Physica,* 15, 801 (1949).
2. Kreidler, E.R., Phase equilibria and tin-activated luminescence in system $Ca_3(PO_4)_2$-$Ba_3(PO_4)_2$, *J. Electrochem. Soc.,* 118, 923 (1971).

α-$Ca_3(PO_4)_2$:Pb^{2+}

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	24	24
$CaHPO_4$	75	90
PbO	1	2.3

Preparation

Mix by slurrying in water or methanol.

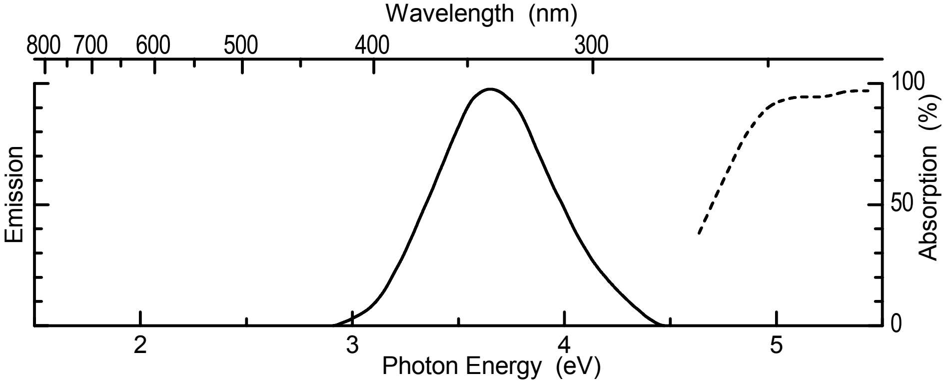
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, ~500°C, 1 hour.
   Powderize.
2. Fire in capped quartz tubes, CO, 1250°C, 1 hour.

Optical Properties

Emission color: UV
Emission peak: 3.68 eV
Emission width (FWHM): 0.64 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Reference

1. Clapp, R.H., and Ginther, R.J., Ultraviolet phosphors and fluorescent sun tan lamps, *J. Opt. Soc. Am.,* 37, 355 (1947).

α-$Ca_3(PO_4)_2$:Tl^+

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	22	22
$CaHPO_4$	75	90
TlOH	1	2.2
Al_2O_3	2 (of Al)	1

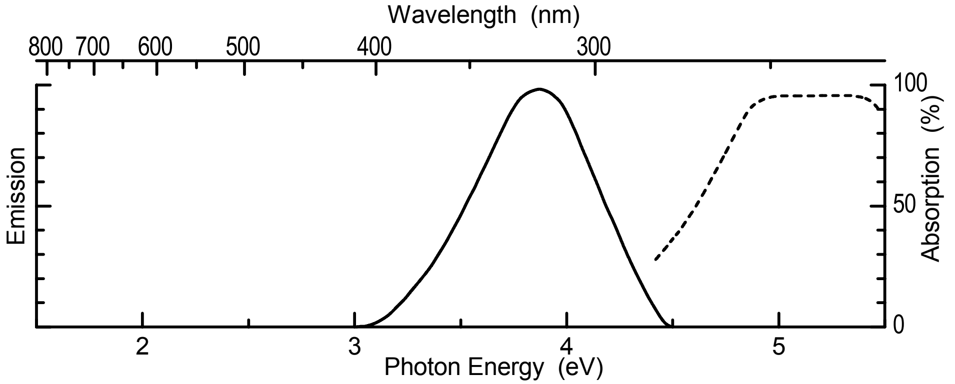
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, stagnant air, 1250°C, 1 hour.

Optical Properties

Emission color: UV
Emission peak: 3.88 eV
Emission width (FWHM): 0.66 eV
Excitation efficiency by UV**:** ++ (4.88 eV), – (3.40 eV)

Spectra



References

1. Froelich, H.C., New ultraviolet phosphors, *J. Electrochem. Soc.,* 91, 241 (1947).
2. Witzmann, H., and Buhrow, J., Ein neuer schwarzlichtphosphor, *Naturwissenschaften*, 49, 180 (1962).
3. Clapp, R.H., and Ginther, R.J., Ultraviolet phosphors and fluorescent sun tan lamps, *J. Opt. Soc. Am.,* 37, 355 (1947).
4. Bril, A., and Hoekstra, W., *Philips Res. Rep.,* 16, 356, (1961), and *Philips Res. Rep.,* 19, 296 (1964).

α-$Ca_3(PO_4)_2$:Ce^{3+}

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	15	15
$CaHPO_4$	75	90
CeO_3	5	17
$NaHCO_3$	5	8.4

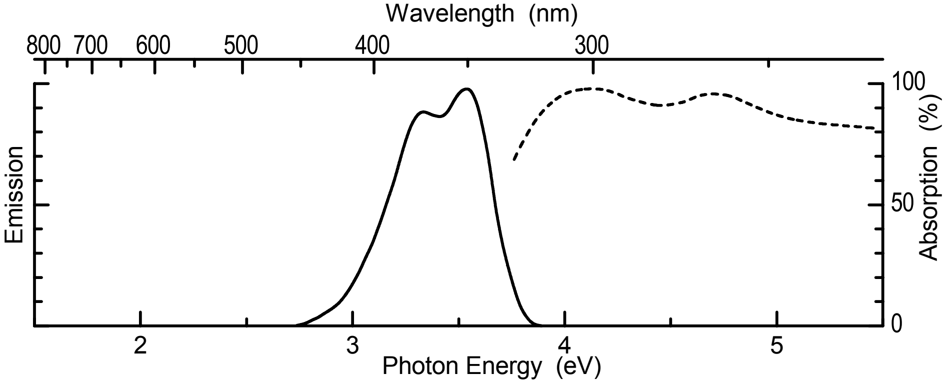
Preparation

Mix by slurrying in water.
Dry in air. Powderize when dry.
Fire in open quartz boats, CO, 1250°C, 1 hour.

Optical Properties

Emission color: UV
Emission peak: 3.33 eV, 3.57 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



References

1. Froelich, H.C., and Margolis, J.M., Calcium phosphate phosphor activated with cerium and manganese, *J. Electrochem. Soc.,* 98, 400 (1951).
2. Botden, T.P.J., Transfer and transport of energy by resonance processes in luminescent solids, *Philips Res. Rep.*, 7, 197 (1952).

α-$Ca_3(PO_4)_2$:Eu^{2+}

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	24	24
$CaHPO_4$	75	90
Eu_2O_3	1 (of Eu)	1.76

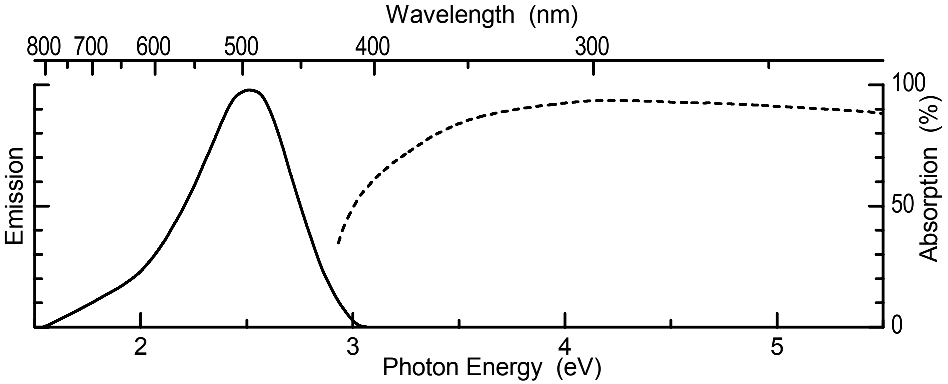
Preparation

Mix by slurrying in water.
Dry in air. Powderize when dry.
Fire in open quartz boats, CO, 1250°C, 1 hour.

Optical Properties

Emission color: Whitish blue-green
Emission peak: ~2.52 eV
Emission width (FWHM): 0.53 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Lagos, C.C., Luminescence of divalent europium in Ba-Ca, Ba-Sr, and Ca-Sr orthophosphate and pyrophosphate compositions, *J. Electrochem. Soc.,* 117, 1189 (1970).
2. McCauley, R.A., Hummel, F.A., and Hoffman, M.V., Phase equilibria and Eu^{2+}-activated, Tb^{3+}-activated, and Mn^{2+}-activated luminescent phases in CaO-MgO-P_2O_5 system, *J. Electrochem. Soc.,* 118, 755 (1971).

β-$Ca_3(PO_4)_2$:Eu^{2+}

Structure: Trigonal

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	24	24
$CaHPO_4$	75	90
Eu_2O_3	1 (of Eu)	1.76

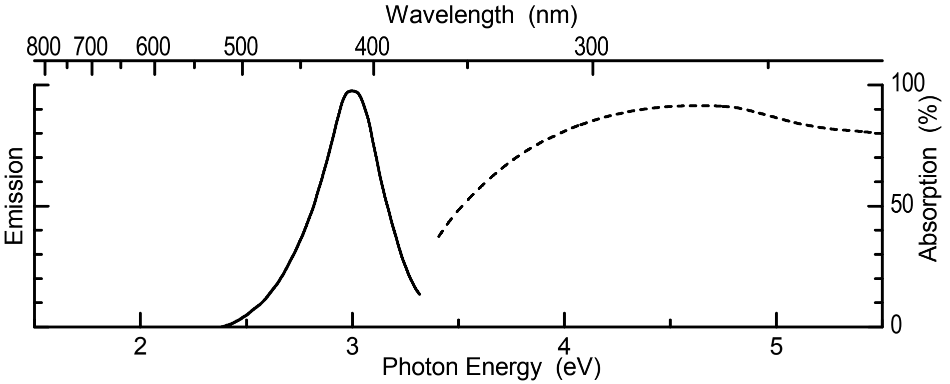
Preparation

Mix by slurrying in water.
Dry in air. Powderize when dry.
Fire in open quartz boats, CO, 1100°C, 2 hours.

Optical Properties

Emission color: Violet
Emission peak: 3.02 eV
Emission width (FWHM): 0.33 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Remark

This phosphor easily shows a weak green emission band due to the α-phosphate (see α-$Ca_3(PO_4)_2:Eu^{2+}$).

β-$Ca_3(PO_4)_2:Eu^{2+},Mn^{2+}$

Structure: Trigonal

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	19	19
$CaHPO_4$	75	90
Eu_2O_3	1 (of Eu)	1.76
$MnCO_3$	5	5.75

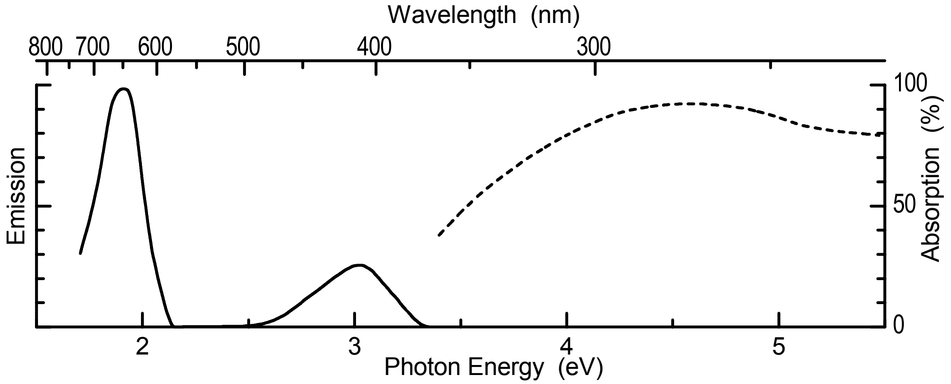
Preparation

Mix by slurrying in water.
Dry in air. Powderize when dry.
Fire in open quartz boats, CO, 1100°C, 2 hours.

Optical Properties

Emission color: Pinkish-red
Emission peak: ~1.91 eV (Mn^{2+} band), ~3.01 eV (Eu^{2+} band)
Emission width (FWHM): 0.24 eV (Mn^{2+} band)
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



β-$Sr_3(PO_4)_2$:Sn^{2+},Mn^{2+}(Al)

Structure: Trigonal

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	8	11.8
$SrHPO_4$	45	75.4
Al_2O_3	4 (of Al)	2
SnO	1.5	2
$MnCO_3$	1	1.15

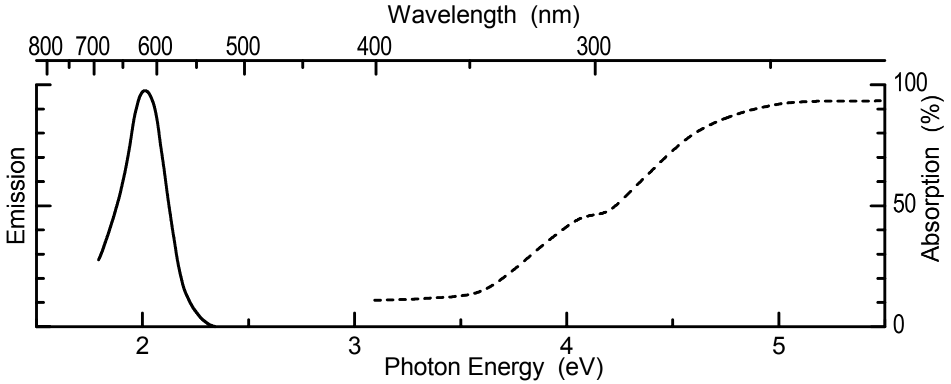
Preparation

Mix by ball-milling in water.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, CO, 1100ºC, 2 hours.

Optical Properties

Emission color: Orange-red
Emission peak: 2.02 eV
Emission width (FWHM): 0.25 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Remarks

1. This is a "tricky" phosphor, by no means yet understood or optimized.
2. Partial or complete replacement of Sr by Ca shifts the emission into deeper red.

References

1. Kröger, F.A., A proof of the associated-pair theory for sensitized luminophors, *Physica,* 15, 801 (1949).
2. Botden, T.P.J., Transfer and transport of energy by resonance processes in luminescent solids, *Philips Res. Rep.*, 7, 197 (1952).
3. Sarver, J.F., Hoffman, M.V., and Hummel, F.A., Phase equilibria and tin-activated luminescence in strontium orthophosphate systems, *J. Electrochem. Soc.,* 108, 1103 (1961).

β-$Sr_3(PO_4)_2$:Sn^{2+}

Structure: Trigonal

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	20	29.5
$SrHPO_4$	75	138
SnO	5	6.75

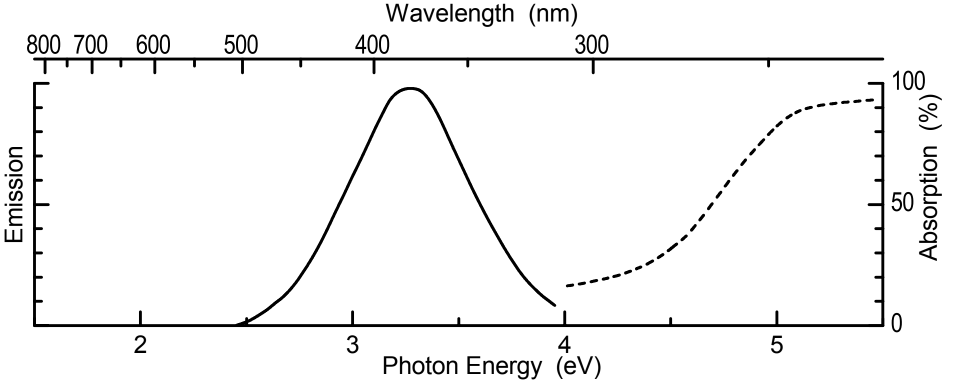
Preparation

Mix by slurrying in water.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, CO, 1100ºC, 2 hours.

Optical Properties

Emission color: Violet + UV
Emission peak: 3.28 eV
Emission width (FWHM): 0.66 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Reference

1. Botden, T.P.J., Transfer and transport of energy by resonance processes in luminescent solids, *Philips Res. Rep.*, 7, 197 (1952).

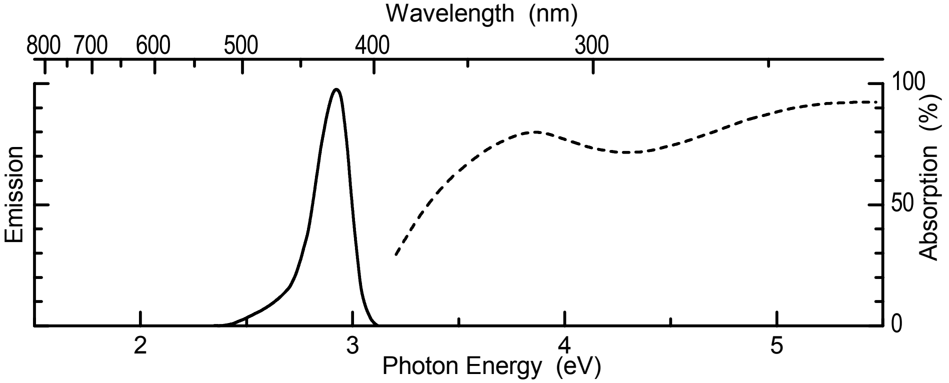
β-$Sr_3(PO_4)_2$:Eu^{2+}

Structure: Trigonal

Optical Properties

Emission color: Violet
Emission peak: 2.94 eV
Emission width (FWHM): 0.22 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)

Spectra



References

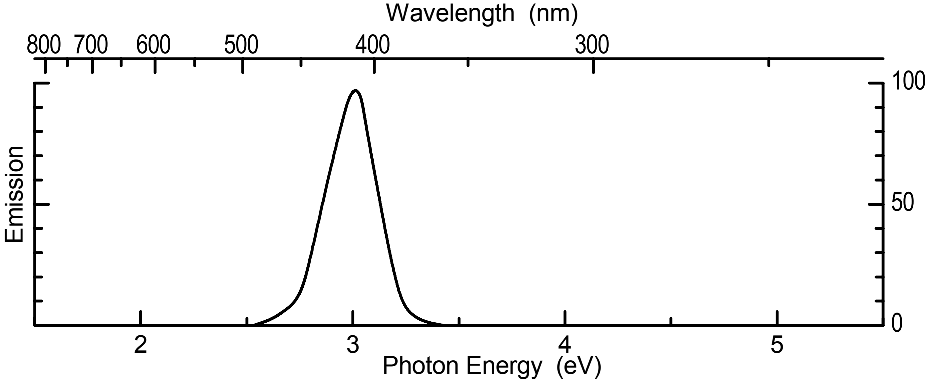
1. Lagos, C.C., Luminescence of divalent europium in Ba-Ca, Ba-Sr, and Ca-Sr orthophosphate and pyrophosphate compositions, *J. Electrochem. Soc.,* 117, 1189 (1970).
2. Hoffman, M.V., Eu^{+2} activation in some alkaline earth strontium phosphate compounds, *J. Electrochem. Soc.,* 115, 560 (1968).

$Ba_3(PO_4)_2$:Eu^{2+}

Optical Properties

Emission color: Violet
Emission peak: 2.99 eV
Emission width (FWHM): 0.25 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)

Spectra



Reference

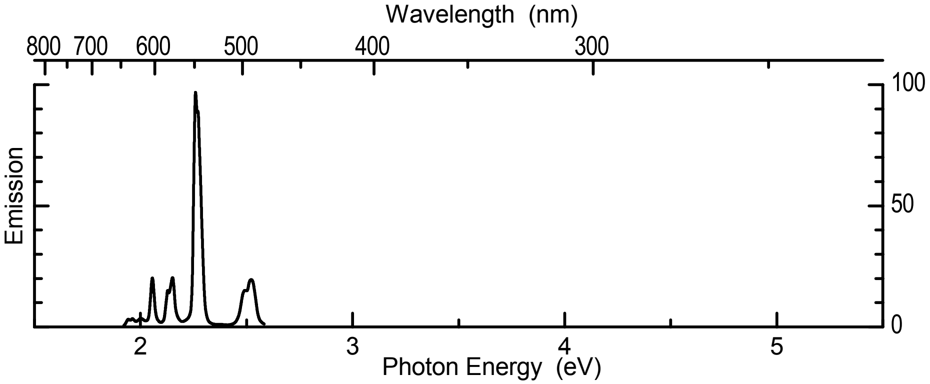
1. Lagos, C.C., Luminescence of divalent europium in Ba-Ca, Ba-Sr, and Ca-Sr orthophosphate and pyrophosphate compositions, *J. Electrochem. Soc.*, 117, 1189 (1970).

$Na_3Ce(PO_4)_2:Tb^{3+}$

Optical Properties

Emission color: Green
Emission peak: 2.27 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Reference

1. Fava, J. et al., Some new efficient luminophors with low-concentration quenching effects, *J. Lumin.*, 18/19, 389 (1979).

β-$(Ca,Sr)_3(PO_4)_2:Sn^{2+},Mn^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	50	50
$SrCO_3$	32	47
$SrHPO_4$	205	376
SnO	10	13.5
$MnCO_3$	3	3.45

Preparation

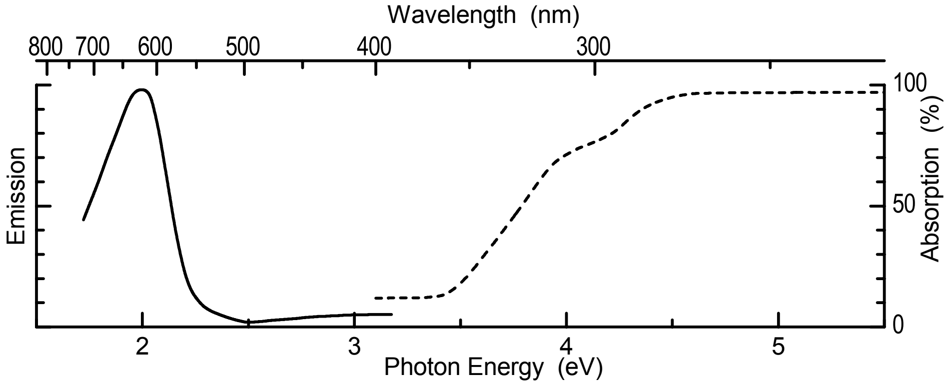
Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.

1. Fire in open quartz boats, N_2, 500–600ºC.
   Powderize.
2. Fire in capped quartz tubes, CO, 1150ºC, 2 hours.

Optical Properties

Emission color: Orange-red
Emission peak: 1.97 eV
Emission width (FWHM): 0.38 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Remarks

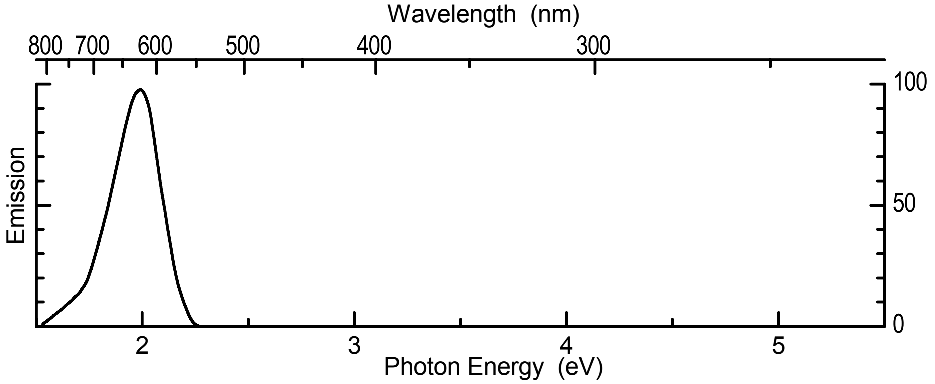
1. Increasing Mn concentration causes narrowing of the emission band but decreasing efficiency.
2. The β-phosphate structure is maintained from about Ca/Sr of 10/90 to 100/0. Increasing Ca/Sr causes a shift of the Mn^{2+} band into deeper red.

References

1. Butler, K.H., Alkaline earth orthophosphate phosphors, *J. Electrochem. Soc.*, 100, 250 (1953).
2. Koelmans, H., and Cox, A.P.M., Luminescence of modified tin-activated strontium orthophosphate, *J. Electrochem. Soc.,* 104, 442 (1957).
3. Mooney, R.W., Temperature dependence of fluorescence of tin-activated orthophosphates, *J. Electrochem. Soc.,* 105, 456 (1958).
4. Uehara, Y., Kobuke, Y., and Masuda, I., Copper-activated calcium orthophosphate and related phosphors, *J. Electrochem. Soc.*, 106, 200 (1959).
5. Wanmaker, W.L., and Bakker, C., Luminescence of copper-activated calcium and strontium orthophosphates, *J. Electrochem. Soc.,* 106, 1027 (1959).
6. Sarver, J.F., Hoffman, M.V., and Hummel, F.A., Phase equilibria and tin-activated luminescence in strontium orthophosphate systems, *J. Electrochem. Soc.,* 108, 1103 (1961).

$ZnMg_2(PO_4)_2:Mn^{2+}$

Spectra



$Zn_3(PO_4)_2:Mn^2$

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
ZnO	99	81
$MnCO_3$	1	1.15
H_3PO_4 solution	62 (of P)	47.6 ccm

Preparation

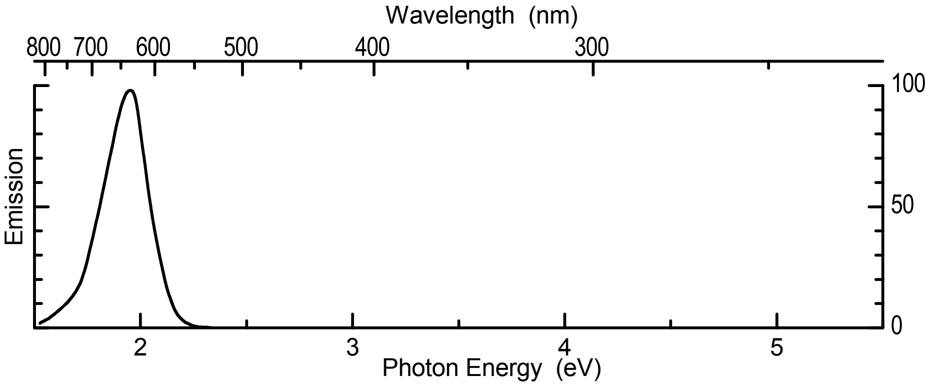
Make a thin slurry of ZnO + $MnCO_3$ in water or methanol. Stir to uniformity as well as possible. Slowly add the H_3PO_4 solution while stirring (slurry heats up). Ball-mill the slurry for about 1 hour. Dry in air. Powderize when dry.

1. Fire in open quartz boats, air, ~500°C, 1 hour. Powderize.
2. Fire in open quartz boats, air, 900°C, 1 hour. Powderize.
3. Fire in open quartz boats, air, 950°C, 2 hours.

Optical Properties

Emission color: Light red
Emission peak: 1.94 eV
Emission width (FWHM): 0.25 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: ~7–8%
Decay: Near-exponential decay, 30 msec to 1/10

Spectra



Remarks

1. This is strictly a catholuminescent phosphor. It cannot be sensitized to respond to 4.88 or 3.40 eV UV.
2. This phosphor has been used as the red component in early color TV picture tubes.

Reference

1. Sarver, J.S., Katnack, F.L., and Hummel, F.A., Phase equilibria and manganese-activated fluorescence in the system $Zn_3(PO_4)_2$-$Mg_3(PO_4)_2$, *J. Electrochem. Soc.*, 106, 960 (1959).

$(Zn,Mg)_3(PO_4)_2{:}Mn^{2+}$

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
ZnO	79	65
MnO	20	8.1
$MnCO_3$	1	1.15
H_3PO_4 solution	62 (of P)	46.7 ccm

Preparation

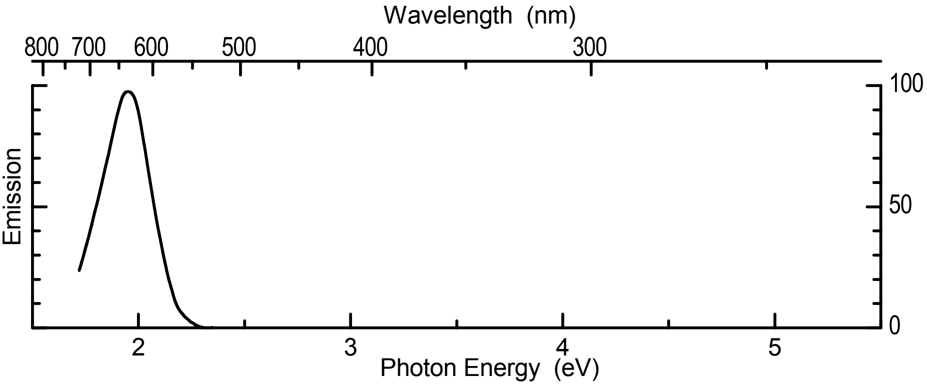
Make a thin slurry of ZnO + MgO + $MnCO_3$ in water or methanol.
Stir to uniformity. Slowly add the H_3PO_4 solution while stirring.
Crush forming phosphate by wet mortaring or milling.
Dry in air. Powderize when dry.

1. Fire in open quartz boats, air, ~500–600ºC, 1 hour. Powderize.
2. Fire in open quartz boats, air, 950ºC, 2 hours.

Optical Properties

Emission color: Light red
Emission peak: 1.96 eV
Emission width (FWHM): 0.27 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: ~6–8%
Decay**:** near-exponential decay, ≈ 100–1200 msec to 1/10

Spectra



Remarks

1. The 950ºC firing temperature is critical; 900ºC is too low; 1000ºC is too high.
2. This is strictly a catholuminescent phosphor. It cannot be sensitized for UV excitation.
3. The decay of this phosphor is significantly longer than that of $Zn_3(PO_4)_2{:}Mn^{2+}$ (~30 msec to 1/10).

Reference

1. Sarver, J.S., Katnack, F.L., and Hummel, F.A., Phase equilibria and manganese-activated fluorescence in the system $Zn_3(PO_4)_2$-$Mg_3(PO_4)_2$, *J. Electrochem. Soc.*, 106, 960 (1959).

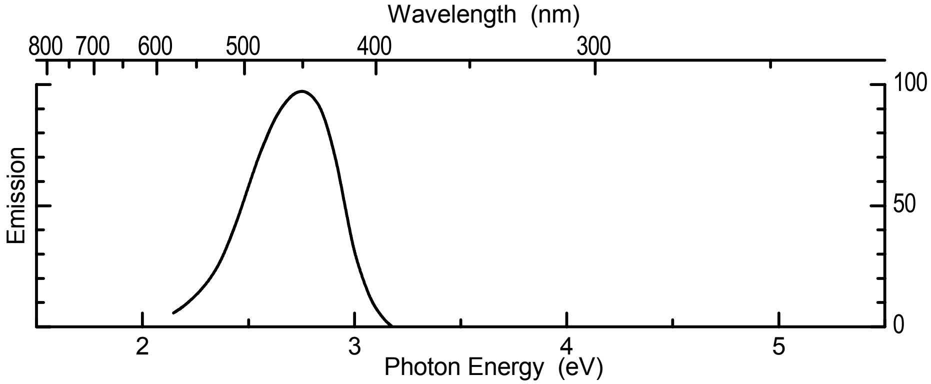
$Mg_3Ca_3(PO_4)_4:Eu^{2+}$

Structure: Monoclinic

Optical Properties

Emission color: Blue
Emission peak: 2.80 eV
Emission width (FWHM): 0.48 eV

Spectra



Reference

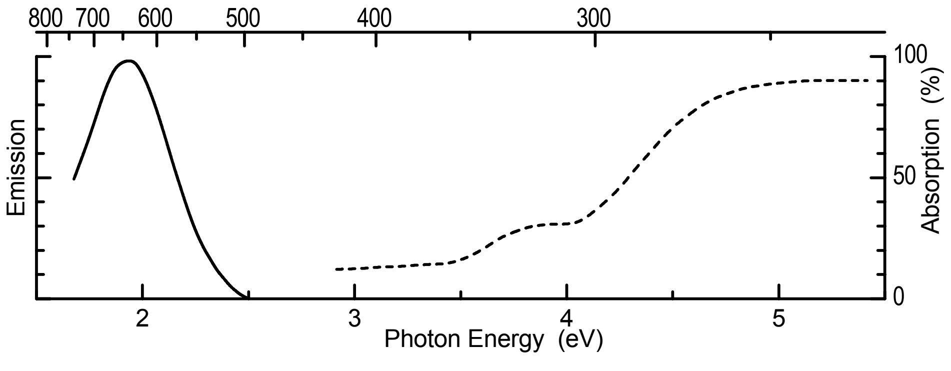
1. McCauley, R.A., Hummel, F.A., and Hoffman, M.V., Phase equilibria and Eu^{2+}-activated, Tb^{3+}-activated, and Mn^{2+}-activated luminescent phases in CaO-MgO-P_2O_5 system, *J. Electrochem. Soc.*, 118, 755 (1971).

$MgSr_5(PO_4)_4:Sn^{2+}$

Optical Properties

Emission color: Orange- red
Emission peak: 1.93 eV
Emission width (FWHM): 0.49 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra

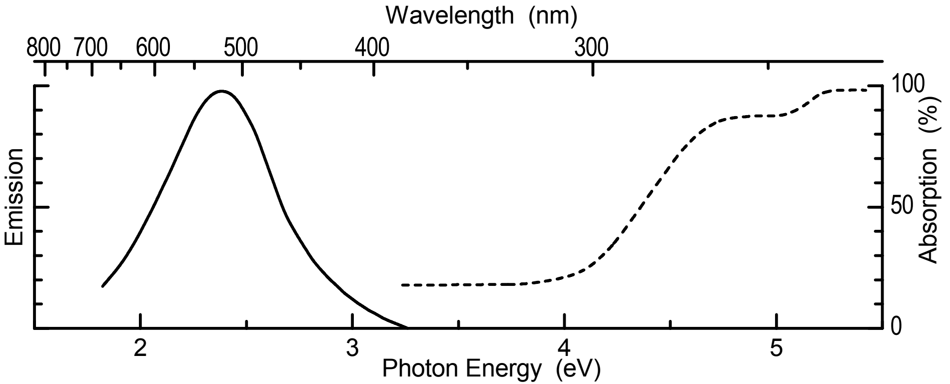


$MgBa_2(PO_4)_2:Sn^{2+}$

Optical Properties

Emission color: Greenish
Emission peak: 2.36 eV
Emission width (FWHM): 0.67 eV
Excitation efficiency by UV: ++ (4.88 eV)

Spectra

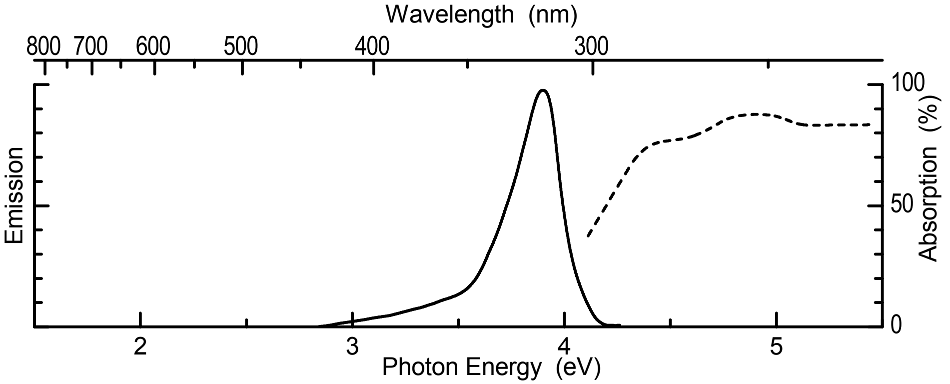


$CaSr_2(PO_4)_2:Bi^{3+}$

Optical Properties

Emission color: UV
Emission peak: 3.89 eV
Emission width (FWHM): 0.27 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra

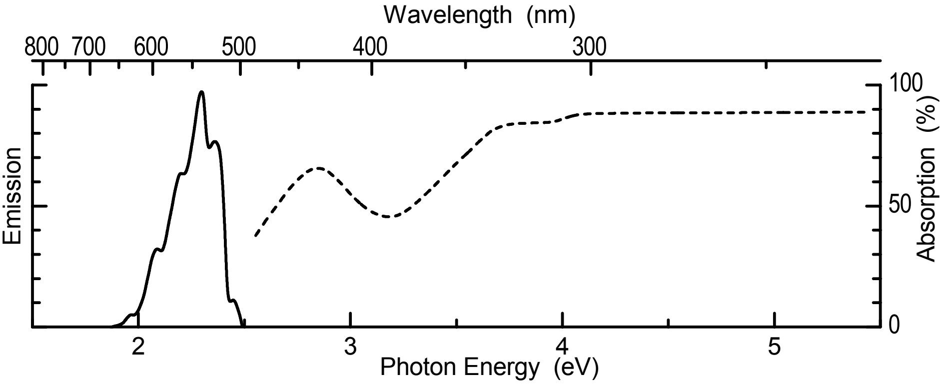


$MgBa_2(PO_4)_2:U$

Optical Properties

Emission color: Green
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: –

Spectra



$Sr_2P_2O_7:Eu^{2+}$

Optical Properties

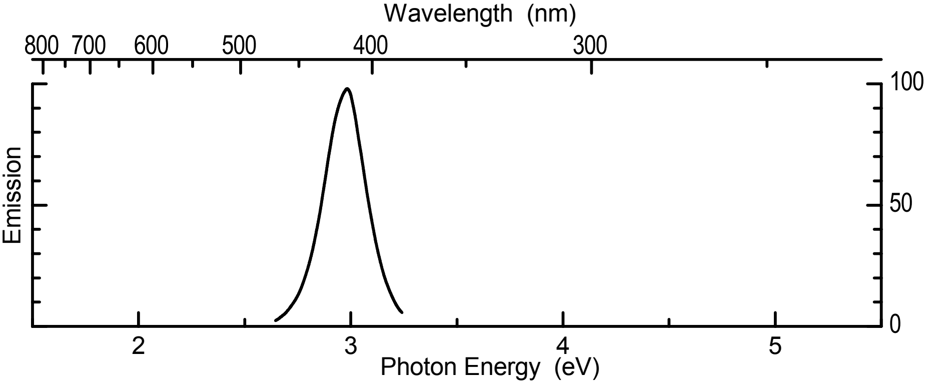
Emission color: Violet

Emission peak: 2.97 eV

Emission width (FWHM): 0.29 eV

Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Reference

1. Butler, K.H., *Fluorescent Lamp Phosphors*, Pennsylvania University Press, University Park (1980), p. 274.

4.6 Halophosphates

The following host compounds and activators are included in this subsection:

$Ca_5(PO_4)_3F:Mn^{2+}$
$Ca_5(PO_4)_3F:Sb^{3+}$
$Ca_5(PO_4)_3F:Sn^{2+}$
$Ca_5(PO_4)_3Cl:Eu^{2+}$
$Ca_5(PO_4)_3Cl:Mn^{2+}$
$Ca_5(PO_4)_3Cl:Sb^{3+}$
$Ca_5(PO_4)_3Cl:Sn^{2+}$
$Sr_5(PO_4)_3Cl:Eu^{2+}$
$Sr_5(PO_4)_3Cl:Mn^{2+}$
$Sr_5(PO_4)_3Cl:Sb^{3+}$
$Sr_5(PO_4)_3F:Mn^{2+}$
$Sr_5(PO_4)_3F:Sb^{3+}$
$Sr_5(PO_4)_3F:Sb^{3+},Mn^{2+}$
$Sr_5(PO_4)_3Cl:Eu^{2+},Pr^{3+}$
$Sr_5(PO_4)_3F:Sn^{2+}$
$Ba_5(PO_4)_3Cl:Eu^{2+}$
$Ba_5(PO_4)_3Cl:U$
$Ca_2Ba_3(PO_4)_3Cl:Eu^{2+}$

$Ca_5(PO_4)_3F:Mn^{2+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	140	140
$CaHPO_4$	400	360
CaF_2	50	39
$MnCO_3$	10	11.5

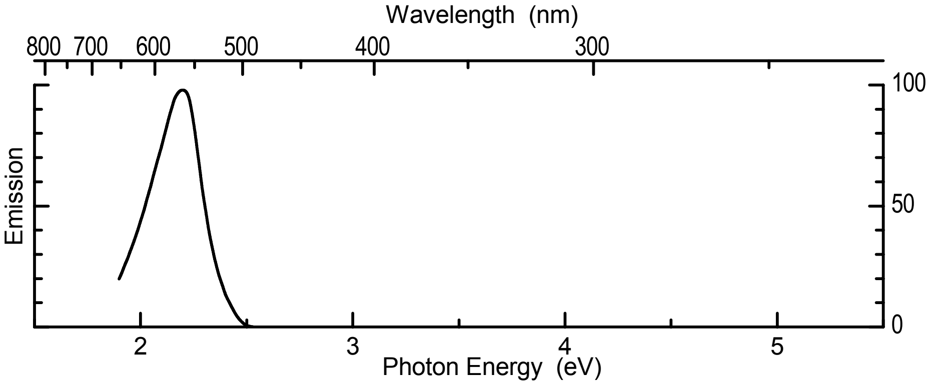
Preparation

Mix by ball-milling in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, N_2, 1100ºC, 1 hour.

Optical Properties

Emission color: Yellow
Emission peak: 2.17 eV
Emission width (FWHM): 0.28 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Remark

Can be sensitized for UV excitation by addition of Sn^{2+}, Sb^{3+}, or Ce^{3+}.

References

1. Jenkins, H.J., McKeag, A.H., and Ranby, P.W., Alkaline earth halophosphates and related phosphors, *J. Electrochem. Soc.,* 96, 1 (1949).
2. Alonso, P.J., and Alcala, R. Excitation-spectra and fluorescent lifetime measurements of Mn^{2+} in CaF_2 and $Ca_5(PO_4)_3F_2$, *J. Lumin.,* 22, 321 (1981).

$Ca_5(PO_4)_3F:Sb^{3+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	140	140
$CaHPO_4$	300	360
CaF_2	50	39
Sb_2O_3	10 (of Sb)	14.6

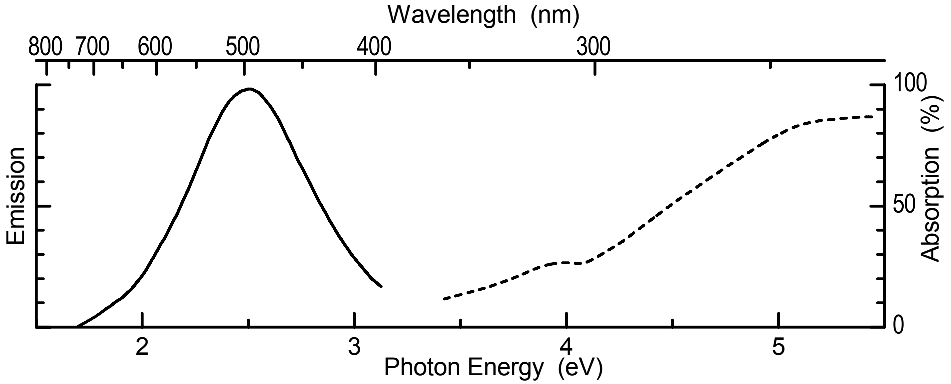
Preparation

Mix by ball-milling in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, N_2, 1100°C, 1 hour.

Optical Properties

Emission color: Pale blue-green
Emission peak: 2.50 eV
Emission width (FWHM): 0.70 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



References

1. Jenkins, H.J., McKeag, A.H., and Ranby, P.W., Alkaline earth halophosphates and related phosphors, *J. Electrochem. Soc.,* 96, 1 (1949).
2. Soules, T.F., Davis, T.S., and Kreidler, E.R., Molecular orbital model for antimony luminescent centers in fluorophosphate, *J. Chem. Phys.,* 55, 1056 (1971).
3. Soules, T.F. et al., Energy-transfer between antimony and manganese in fluorophosphate phosphors, *Phys. Rev. B,* 7, 1657 (1973).

$Ca_5(PO_4)_3F:Sn^{2+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	200	200
$CaHPO_4$	300	360
CaF_2	50	39
SnO	10	13.5

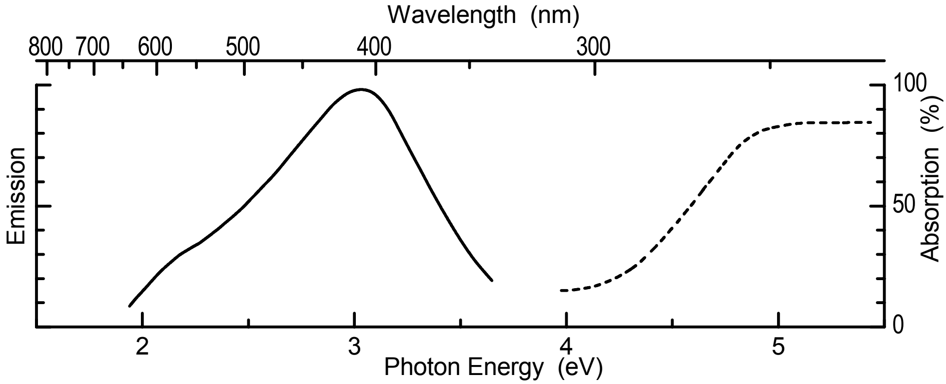
Preparation

Mix by ball-milling methanol plus a little water.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, N_2, 1100°C, 1 hour.

Optical Properties

Emission color: Pale bluish
Emission peak: 3.00 eV
Emission width (FWHM): ~0.9 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Reference

1. Jenkins, H.J., McKeag, A.H., and Ranby, P.W., Alkaline earth halophosphates and related phosphors, *J. Electrochem. Soc.,* 96, 1 (1949).

$Ca_5(PO_4)_3Cl:Eu^{2+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	200	200
$CaHPO_4$	300	360
NH_4Cl	120	64
Eu_2O_3	5 (of Eu)	8.8

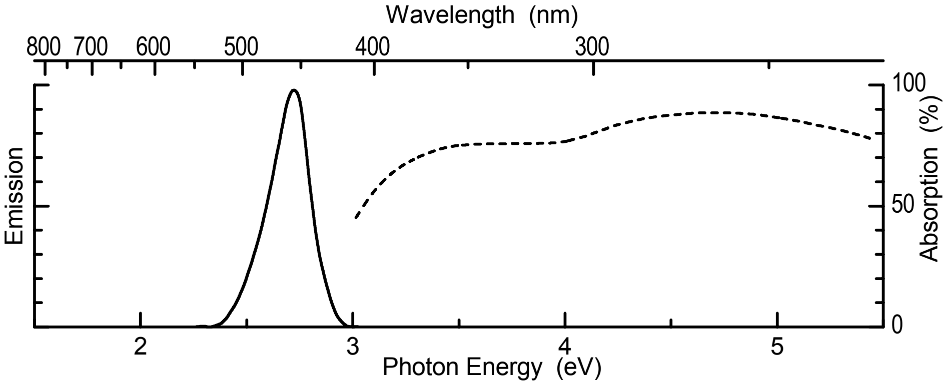
Preparation

Mix by ball-milling methanol plus a little water.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 1100° C, 1 hour.
Powderize.
Add 32 g NH_4Cl; mix by dry grinding or milling.
2. Fire in capped quartz tubes, N_2, 1100°C, 1 hour.
Powderize.
Wash in water several times.
Dry.

Optical Properties

Emission color: Blue
Emission peak: 2.72 eV
Emission width (FWHM): 0.23 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Reference

1. Wachtel, A., *Bloomfield Report,* BL-R-6-90102-29 (1968).

$Ca_5(PO_4)_3Cl:Mn^{2+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	200	200
$CaHPO_4$	300	360
NH_4Cl	120	64
$MnCO_3$	10	11.5

Preparation

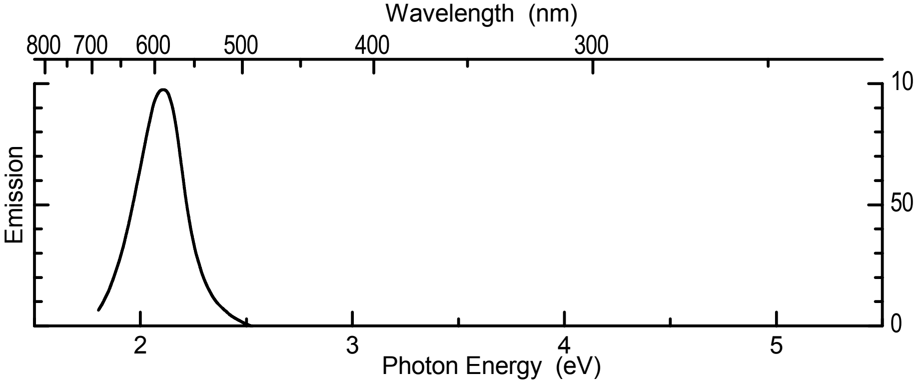
Mix by ball-milling methanol plus a little water.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 1100ºC, 1 hour.
   Powderize.
   Add 32 g NH_4Cl; mix by dry grinding or milling.
2. Fire in capped quartz tubes, N_2, 1100ºC, 1 hour.
   Powderize.
   Wash in water several times.
   Dry.

Optical Properties

Emission color: Orange-yellow
Emission peak: ~2.10 eV
Emission width (FWHM): 0.29 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)

Spectra



Remark

Can be sensitized for UV excitation by addition of Sn^{2+}, Sb^{3+}, Ce^{3+}, or Eu^{2+}.

Reference

1. Jenkins, H.J., McKeag, A.H., and Ranby, P.W., Alkaline earth halophosphates and related phosphors, *J. Electrochem. Soc.,* 96, 1 (1949).

$Ca_5(PO_4)_3Cl:Sb^{3+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	200	200
$CaHPO_4$	300	360
NH_4Cl	120	64
$MnCO_3$	10	11.5

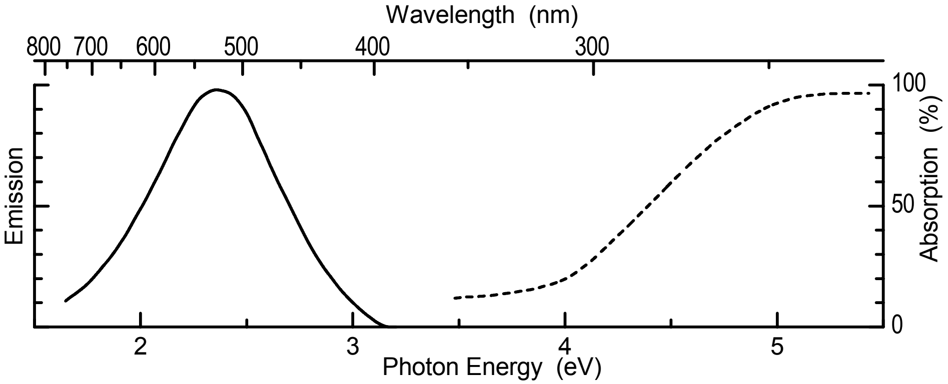
Preparation

Mix by ball-milling methanol plus a little water.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 1100ºC, 1 hour.
Powderize.
Add 32 g NH_4Cl; mix by dry grinding or milling.
2. Fire in capped quartz tubes, N_2, 1100ºC, 1 hour.
Powderize.
Wash in water several times.
Dry.

Optical Properties

Emission color: Pale whitish-green
Emission peak: 2.38 eV
Emission width (FWHM): 0.70 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Reference

1. Jenkins, H.J., McKeag, A.H., and Ranby, P.W., Alkaline earth halophosphates and related phosphors, *J. Electrochem. Soc.,* 96, 1 (1949).

$Ca_5(PO_4)_3Cl:Sn^{2+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	200	200
$CaHPO_4$	300	360
NH_4Cl	120	64
SnO	10	13.5

Preparation

Mix by ball-milling methanol plus a little water.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 1100°C, 1 hour.
Powderize.
Add 32 g NH_4Cl; mix by dry grinding or milling.
2. Fire in capped quartz tubes, N_2, 1100°C, 1 hour.
Powderize.
Wash in water several times.
Dry.

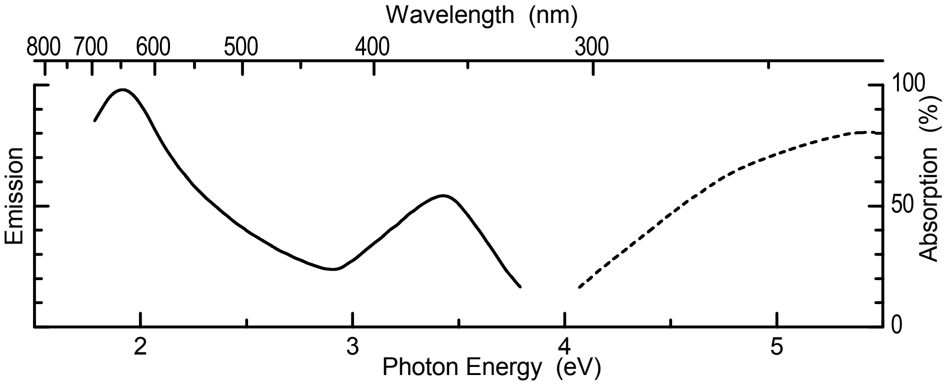
Optical Properties

Emission color: Pale pinkish-white

Emission peaks: Continuous distribution from the UV into the IR; the two peaks near 1.95 and 3.45 eV

Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



$Sr_5(PO_4)_3Cl:Eu^{2+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	200	295
$SrHPO_4$	300	550
NH_4Cl	120	64
Eu_2O_3	5 (of Eu)	8.8

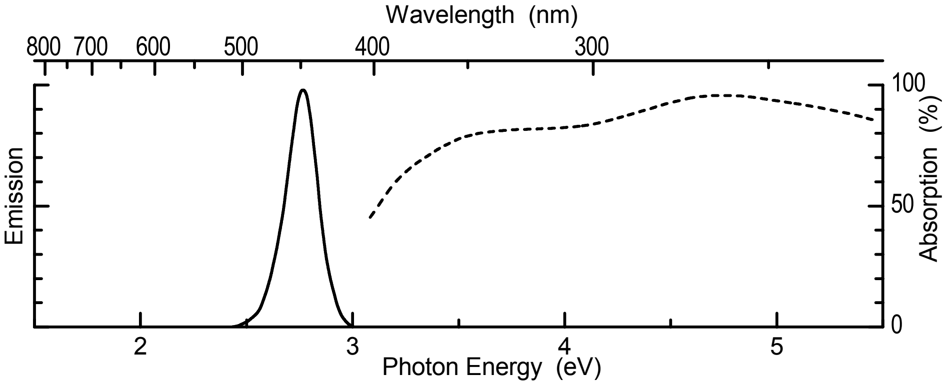
Preparation

Mix by ball-milling methanol plus a little water.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 1100°C, 1 hour.
Powderize.
Add 32 g NH_4Cl; mix by dry grinding or milling.
2. Fire in capped quartz tubes, N_2, 1100°C, 1 hour.
Powderize.
Wash in water several times.
Dry.

Optical Properties

Emission color: Blue
Emission peak: 2.75 eV
Emission width (FWHM): 0.19 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Reference

1. Wachtel, A., *Bloomfield Report,* BL-R-6-90102-29 (1968).

$Sr_5(PO_4)_3Cl:Mn^{2+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	200	295
$SrHPO_4$	300	550
NH_4Cl	120	64
$MnCO_3$	10	11.5

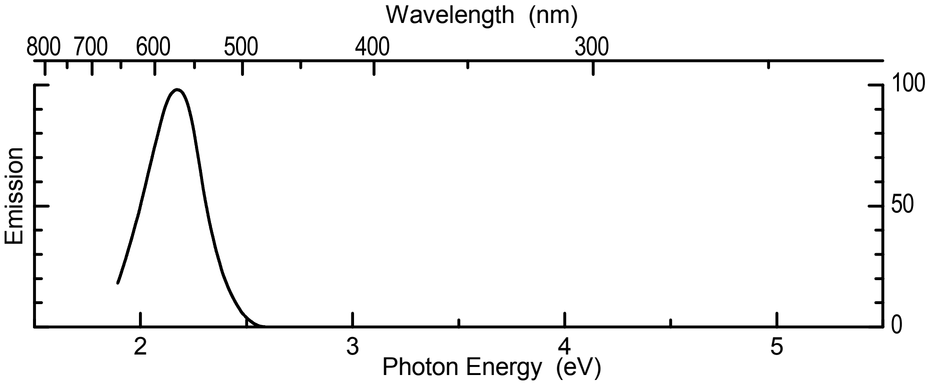
Preparation

Mix by ball-milling methanol plus a little water.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 1100°C, 1 hour.
Powderize.
Add 32 g NH_4Cl; mix by dry grinding or milling.
2. Fire in capped quartz tubes, N_2, 1100°C, 1 hour.
Powderize.
Wash in water several times.
Dry.

Optical Properties

Emission color: Yellow
Emission peak: 2.16 eV
Emission width (FWHM): 0.32 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)

Spectra



Remark

Can be sensitized for UV excitation by addition of Sn^{2+}, Sb^{3+}, Ce^{3+}, or Eu^{2+}.

Reference

1. Jenkins, H.J., McKeag, A.H., and Ranby, P.W., Alkaline earth halophosphates and related phosphors, *J. Electrochem. Soc.,* 96, 1 (1949).

$Sr_5(PO_4)_3Cl:Sb^{3+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	200	295
$SrHPO_4$	300	550
NH_4Cl	120	64
Sb_2O_3	10 (of Sb)	14.6

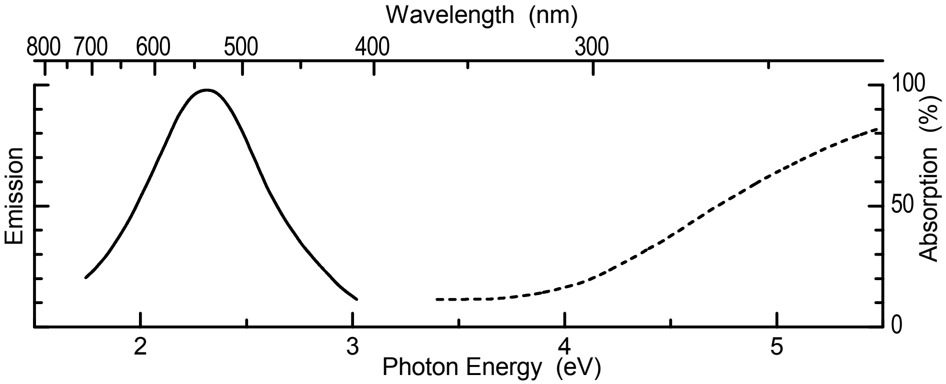
Preparation

Mix by ball-milling methanol plus a little water.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 1100ºC, 1 hour.
Powderize.
Add 32 g NH_4Cl; mix by dry grinding or milling.
2. Fire in capped quartz tubes, N_2, 1100ºC, 1 hour.
Powderize.
Wash in water several times.
Dry.

Optical Properties

Emission color: Whitish-green
Emission peak: ~2.31 eV
Emission width (FWHM): 0.68 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Reference

1. Jenkins, H.J., McKeag, A.H., and Ranby, P.W., Alkaline earth halophosphates and related phosphors, *J. Electrochem. Soc.,* 96, 1 (1949).

$Sr_5(PO_4)_3F:Mn^{2+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	200	295
$SrHPO_4$	300	550
SrF_2	50	63
$MnCO_3$	10	11.5

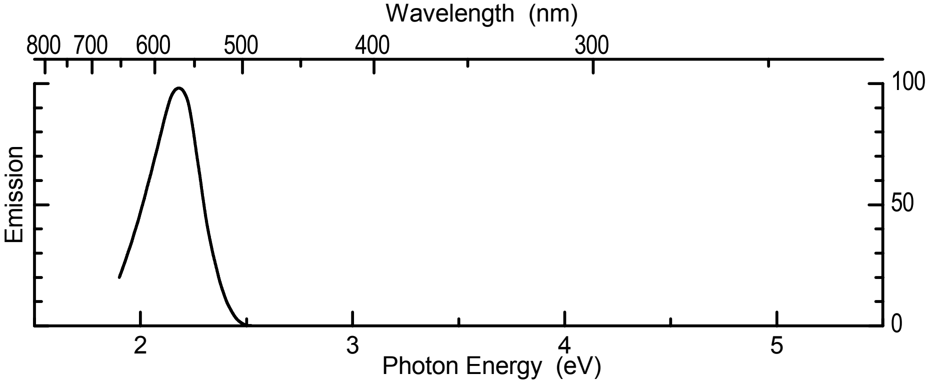
Preparation

Mix by ball-milling methanol plus a little water.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, N_2, 1100°C, 1 hour.

Optical Properties

Emission color: Yellow
Emission peak: ~2.17 eV
Emission width (FWHM): 0.28 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)

Spectra



Remark
Can be sensitized for UV excitation by addition of Sn^{2+}, Sb^{3+}, or Ce^{3+}.

Reference

1. Jenkins, H.J., McKeag, A.H., and Ranby, P.W., Alkaline earth halophosphates and related phosphors, *J. Electrochem. Soc.,* 96, 1 (1949).

$Sr_5(PO_4)_3F:Sb^{3+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	140	206
$SrHPO_4$	300	550
SrF_2	50	63
Sb_2O_3	10 (of Sb)	14.6

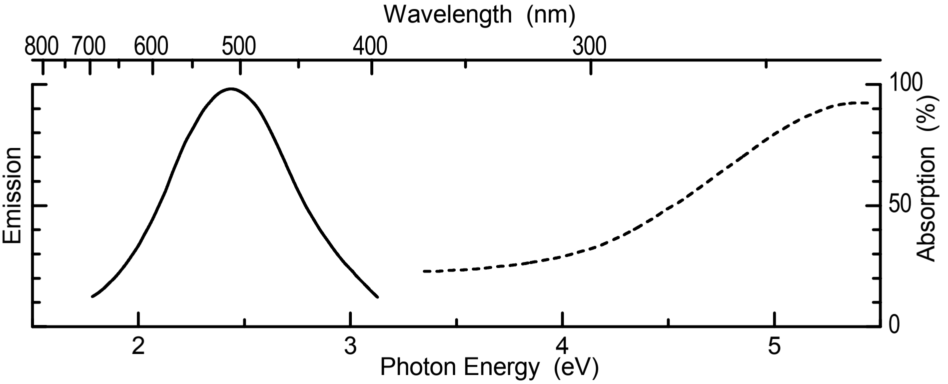
Preparation

Mix by ball-milling methanol plus a little water.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, N_2, 1100°C, 1 hour.

Optical Properties

Emission color: Pale whitish blue-green
Emission peak: ~2.43 eV
Emission width (FWHM): 0.75 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



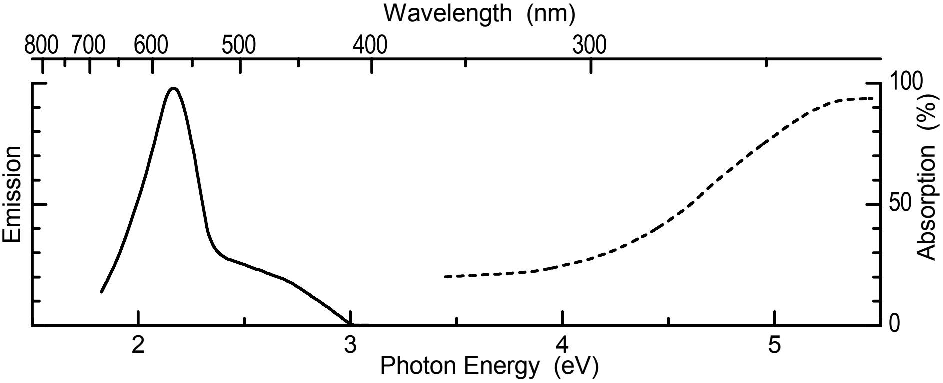
Reference

1. Jenkins, H.J., McKeag, A.H., and Ranby, P.W., Alkaline earth halophosphates and related phosphors, *J. Electrochem. Soc.,* 96, 1 (1949).

$Sr_5(PO_4)_3F:Sb^{3+},Mn^{2+}$

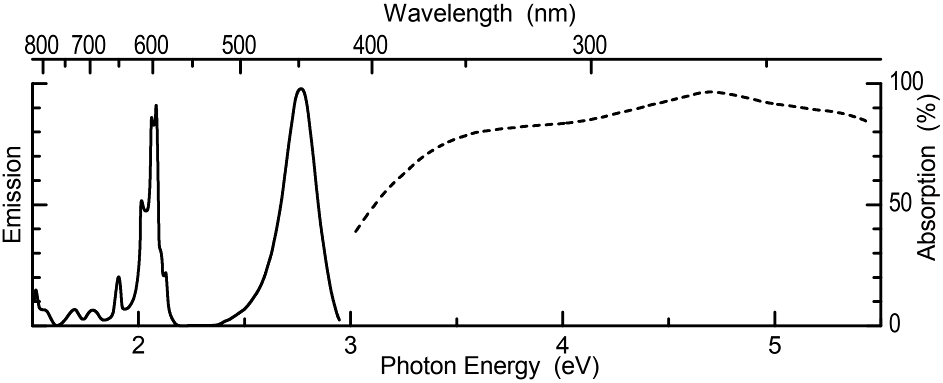
Structure: Hexagonal (apatite)

Spectra



$Sr_5(PO_4)_3Cl:Eu^{2+},Pr^{3+}$

Spectra



$Sr_5(PO_4)_3F:Sn^{2+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	140	206
$SrHPO_4$	300	550
SrF_2	50	63
SnO	10	13.5

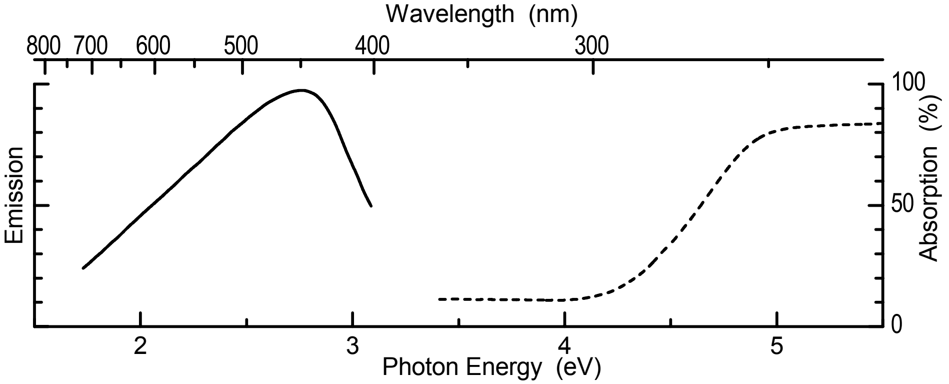
Preparation

Mix by ball-milling methanol plus a little water.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, N_2, 1100°C, 1 hour.

Optical Properties

Emission color: Bluish-white
Emission peak: ~2.75 eV
Emission width (FWHM): 0.75 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



$Ba_5(PO_4)_3Cl:Eu^{2+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	200	395
$BaHPO_4$	300	700
NH_4Cl	120	64
Eu_2O_3	5 (of Eu)	8.8

Preparation

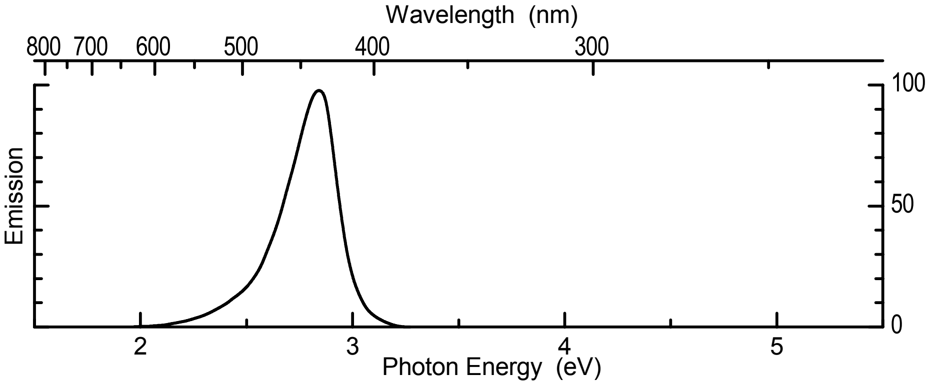
Mix by ball-milling methanol plus a little water.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 1000°C, 1 hour.
   Powderize.
   Add 32 g NH_4Cl; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1000°C, 1 hour.
   Powderize.
   Wash in water several times.
   Dry.

Optical Properties

Emission color: Violet-blue
Emission peak: ~2.84 eV
Emission width (FWHM): 0.28 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Reference

1. Wachtel, A., *Bloomfield Report,* BL-R-6-90102-29 (1968).

$Ba_5(PO_4)_3Cl$:U

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$BaHPO_4$	190	443
$BaCO_3$	150	295
NH_4Cl	120	64
$UO_2(C_2H_3O_2)_2$. $2H_2O$	10	42

Preparation

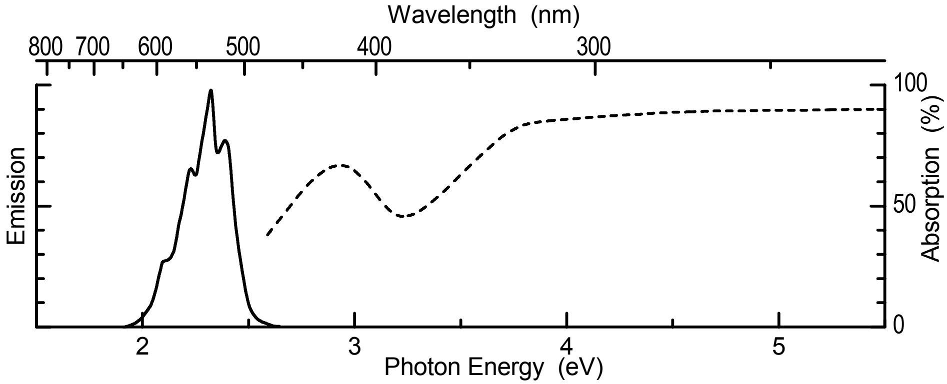
Make a slurry in methanol of $BaHPO_4$, $BaCO_3$, and NH_4Cl.
Dissolve the uranyl acetate in a little methanol, and add the solution to the slurry; stir to uniformity.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 850ºC, 1 hour.
   Powderize.
   Add 32 g NH_4Cl; mix by dry grinding or milling.
2. Fire in capped quartz tubes, N_2, 900ºC, 2 hours.
   Powderize.
   Wash in water several times (stir, let settle, decant).
   Dry.

Optical Properties

Emission color: Green
Emission peaks: 2.12–2.39 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV); QE ≈ 50%
Excitation efficiency by e-beam: Poor

Spectra



Reference

1. Anderson, J.T., and Wells, R.S., Luminescent barium and magnesium halophosphates, *J. Electrochem. Soc.,* 98, 414 (1951).

$Ca_2Ba_3(PO_4)_3Cl:Eu^{2+}$

Structure: Hexagonal (apatite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	200	200
$BaHPO_4$	300	700
NH_4Cl	120	64
Eu_2O_3	5 (of Eu)	8.8

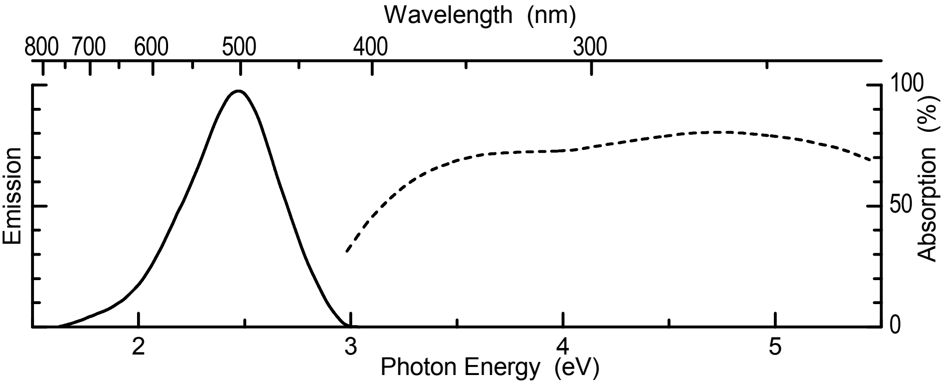
Preparation

Mix by ball-milling in methanol plus a little water.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 1100°C, 1 hour.
Powderize.
Add 3.2 g NH_4Cl; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1100°C, 1 hour.
Powderize.
Wash in water several times.
Dry.

Optical Properties

Emission color: Pale blue-green
Emission peak: 2.46 eV
Emission width (FWHM): 0.49 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Reference

1. Wachtel, A., *Bloomfield Report,* BL-R-6-90102-29 (1968).

4.7 Borates

The following host compounds and activators are included in this subsection:

$YBO_3:Ce^{3+}$
$YBO_3:Eu^{3+}$
$LaBO_3:Eu^{3+}$
$\beta\text{-}SrO\cdot 3B_2O_3:Pb^{2+}$
$\beta\text{-}SrO\cdot 3B_2O_3:Pb^{2+},Mn^{2+}$
$SrO\cdot 3B_2O_3:Eu^{2+},Cl$
$\alpha\text{-}SrO\cdot 3B_2O_3:Sm^{2+}$
$MgB_2O_4:Mn^{2+}$
$MgYBO_4:Eu^{3+}$
$CaB_2O_4:Mn^{2+}$
$CaB_2O_4:Pb^{2+}$
$CaYBO_4:Bi^{3+}$
$CaYBO_4:Eu^{3+}$
$CaLaBO_4:Eu^{3+}$
$ZnB_2O_4:Mn^{2+}$
$Ca_2B_2O_5:Mn^{2+}$
$LaAlB_2O_6:Eu^{3+}$
$CaLaB_3O_7:Ce^{3+},Mn^{2+}$
$SrB_4O_7:Eu^{2+}(F,Cl,Br)$
$SrB_4O_7:Pb^{2+}$
$SrB_4O_7:Pb^{2+},Mn^{2+}$
$Cd_2B_6O_{11}:Mn^{2+}$
$YAl_3B_4O_{12}:Ce^{3+}$
$YAl_3B_4O_{12}:Bi^{3+}$
$YAl_3B_4O_{12}:Eu^{3+}$
$YAl_3B_4O_{12}:Eu^{3+},Cr^{3+}$
$YAl_3B_4O_{12}:Th^{4+},Ce^{3+},Mn^{2+}$
$YAl_3B_4O_{12}:Ce^{3+},Tb^{3+}$
$LaAl_3B_4O_{12}:Eu^{3+}$
$BaB_8O_{13}:Eu^{2+}$
$SrB_8O_{13}:Sm^{2+}$
$Ca_2B_5O_9Cl:Eu^{2+}$
$Ca_2B_5O_9Cl:Pb^{2+}$
$Ca_2B_5O_9Br:Eu^{2+}$
$Sr_2B_5O_9Cl:Eu^{2+}$
$CaYB_{0.8}O_{3.7}:Eu^{3+}$
$Ca_2La_2BO_{6.5}:Pb^{2+}$
$YAl_3B_4O_{12}:Ce^{3+},Mn^{2+}$

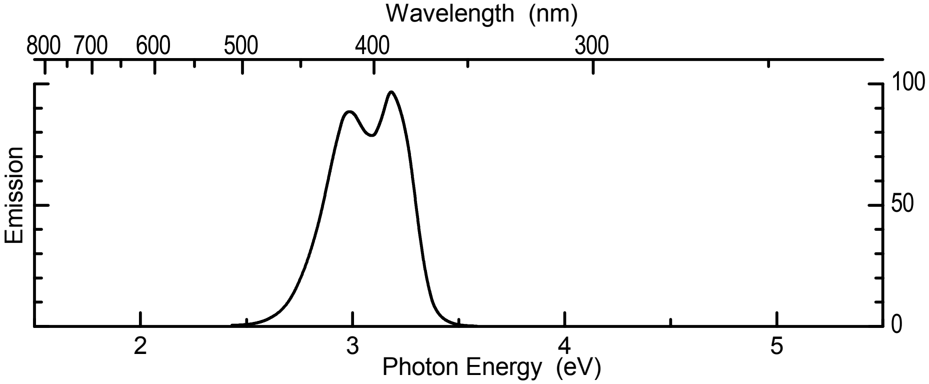
$YBO_3:Ce^{3+}$

Structure: Vaterite

Optical Properties

Emission color: Violet-UV
Emission peak: 3.00 and 3.22 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



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1. Blasse, G., and Bril, A., The absorption and emission spectra of some important activators, *Philips Tech. Rev.,* 31, 304 (1970).
2. Avella, F.J., Sovers, O.J., and Wiggins, C.S., Rare earth cathodoluminescence in $InBO_3$ and related orthoborates, *J. Electrochem. Soc.,* 114, 613 (1967).
3. Blasse, G., and Bril, A., Fluorescence of Eu^{3+}-activated sodium lanthanide titanates, *J. Chem. Phys.,* 48, 3652 (1968).
4. Blasse, G., Bril, A., and Poorter, J.A.D., Radiationless transitions in Eu^{3+} center in $LaAlO_3$, *J. Chem. Phys.,* 53, 4450 (1970).
5. Blasse, G., Ultraviolet-absorption bands of Bi^{3+} and Eu^{3+} in oxides, *J. Solid State Chem.,* 4, 52 (1972).
6. Bril, A., Blasse, G., and de Poorter, J.A., Fast-decay phosphors, *J. Electrochem. Soc.*, 117, 346 (1970).

$YBO_3:Eu^{3+}$

Structure: Vaterite

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	92 (of Y)	104
Eu_2O_3	8 (of Eu)	14
H_3BO_3	105	65

Preparation

Mix by dry grinding or milling.

1. Fire in open quartz boats, air, ~500°C, 1 hour.

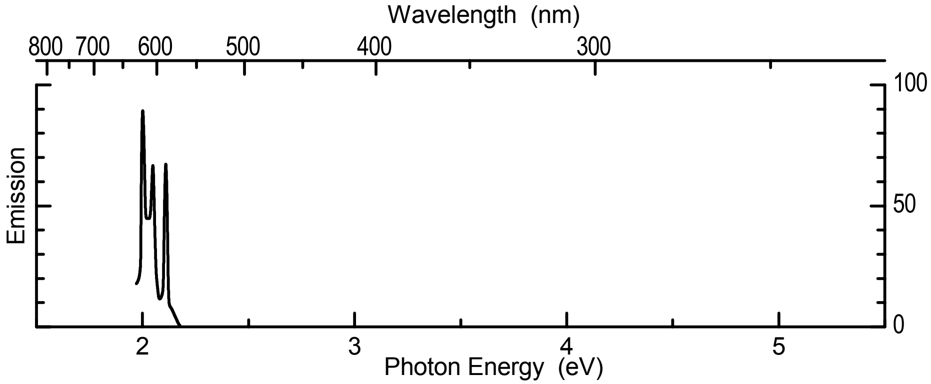
Powderize.

2. Fire in open quartz boats, air, 1000°C, 1 hour.
   Powderize.
3. Fire in open quartz boats, air, 1250°C, 1 hour.

Optical Properties

Emission color: Red-orange
Emission peaks: 1.98–2.10 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra



References

1. Avella, F.J., Sovers, O.J., and Wiggins, C.S., Rare earth cathodoluminescence in $InBO_3$ and related orthoborates, *J. Electrochem. Soc.,* 114, 613 (1967).
2. Veenis, A.W., and Bril, A., Fine structure in the low temperature luminescence of Zn_2SiO_4:Mn and $Mg_4Ta_2O_9$:Mn, *Philips J. Res*., 33, 124 (1978).

$LaBO_3:Eu^{3+}$

Structure: Orthorhombic (aragonite)

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	92 (of La)	150
Eu_2O_3	8 (of Eu)	14
H_3BO_3	105	65

Preparation

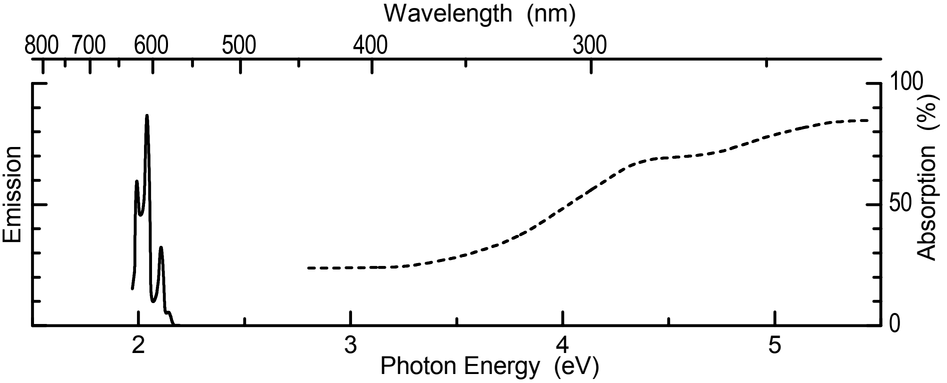
Mix by dry grinding or milling.

1. Fire in open quartz boats, air, ~500°C, 1 hour.
   Powderize.
2. Fire in open quartz boats, air, 1000°C, 1 hour.
   Powderize.
3. Fire in open quartz boats, air, 1150°C, 2 hours.

Optical Properties

Emission color: Light red
Emission peaks: 1.995, 2.02, and 2.10 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra



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1. Avella, F.J., Sovers, O.J., and Wiggins, C.S., Rare earth cathodoluminescence in $InBO_3$ and related orthoborates, *J. Electrochem. Soc.,* 114, 613 (1967).
2. Bril, A., and Wanmaker, W.L., Fluorescent properties of some europium-activated phosphors, *J. Electrochem. Soc.,* 111, 1363 (1964).

β-SrO·$3B_2O_3$:Pb^{2+}

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	99	146
PbO	1	2.3
H_3BO_3	600	370
NH_4Cl	5	2.7

Preparation

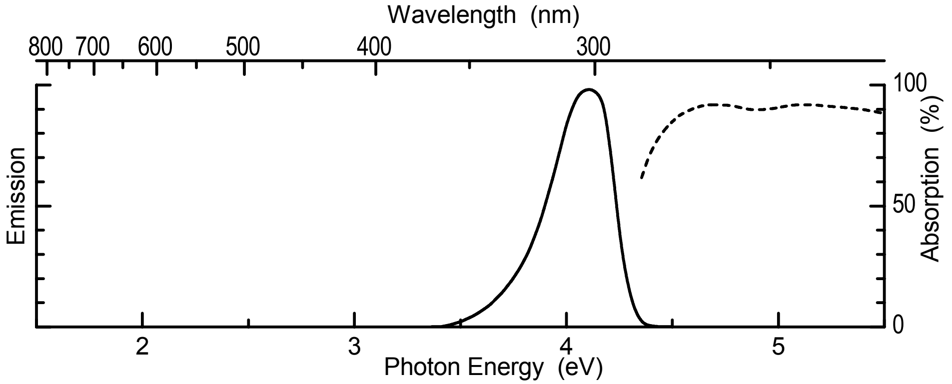
Mix by dry grinding or milling.

1. Fire in capped quartz tubes, air. Place into cold furnace, go slowly up with temperature to 600°C, and then take out.
   Powderize.
2. Fire in capped quartz tubes, N_2 , 700ºC, 2 hours.
   Powderize.
3. Fire in capped quartz tubes, N_2 , 700ºC, 16 hours (overnight).

Optical Properties

Emission color: UV
Emission peak: 4.09 eV
Emission width (FWHM): 0.33 eV
Excitation efficiency by UV: + (4.88 eV)

Spectra



References

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2. Witzmann, H., and Schreiber, H., Zur lumineszenz kupfer- und kupferbleiaktivierter strontiumboratphosphore, *Naturwissenschaften*, 49, 181 (1962).
3. Witzmann, H., Müller, R., and Semisch, G., Boratluminophore MIT UV-emission, *Naturwissenschaften,* 43, 580 (1956).
4. Witzmann, H., and Treichler, W., Zur uv-emission bleiaktivierter strontium-boratluminophore, *Naturwissenschaften,* 45, 542 (1958).
5. Witzmann, H., and Müller, R., *Z. Phys. Chem. (Leipzig),* 211, 307 (1959).
6. Witzmann, H., and Treichler, W., *Z. Phys. Chem. (Leipzig),* 212, 205 (1959).

β-$SrO{\cdot}3B_2O_3$:Pb^{2+},Mn^{2+}

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	98	180
PbO	1	2.28
$MnCO_3$	1	1.15
H_3BO_3	600	372
NH_4Cl	5	2.7

Preparation

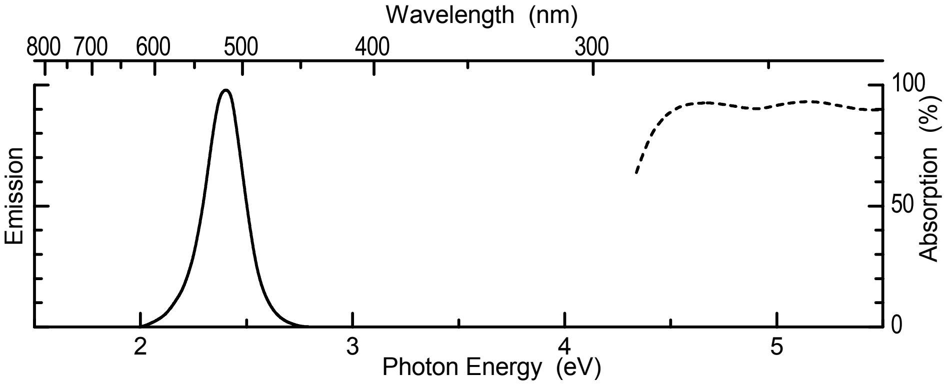
Mix by dry grinding or milling.

1. Fire in capped quartz tubes, air. Place into cold furnace, go slowly up with temperature to 600°C, and then take out. Powderize.
2. Fire in capped quartz tubes, N_2 , 700ºC, 2 hours. Powderize.
3. Fire in capped quartz tubes, N_2 , 700ºC, 16 hours (overnight).

Optical Properties

Emission color: Bluish-green
Emission peak: 2.41 eV
Emission width (FWHM): 0.22 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV); QE ≈ 45–50%

Spectra



Reference

1. Witzmann, H., and Schreiber, H., Zur lumineszenz kupfer- und kupferbleiaktivierter strontiumboratphosphore, *Naturwissenschaften*, 49, 181 (1962).

$SrO{\cdot}3B_2O_3{:}Eu^{2+},Cl$

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	98	180
Eu_2O_3	2 (of Eu)	3.5
H_3BO_3	620	384
NH_4Cl	50	27

Preparation

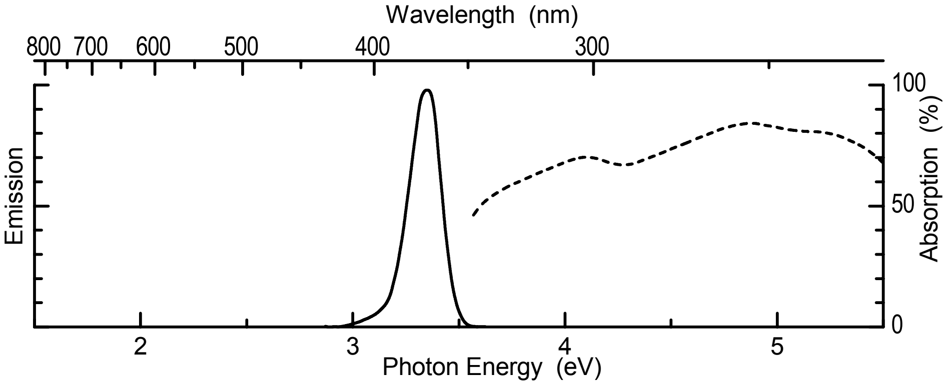
Mix all ingredients but the NH_4Cl by dry grinding or milling.

1. Fire in open quartz boats, air, ~500ºC, ½ hour.
   Powderize.
2. Fire in open quartz boats, N_2 , 700ºC, 1 hour.
   Add the above NH4Cl; mix by dry grinding.
   Powderize.
3. Fire in capped quartz tubes, CO , 850ºC, 4 hours.
   Powderize.
   Wash in water several times.
   Dry.

Optical Properties

Emission color: UV
Emission peak: 3.37 eV
Emission width (FWHM): 0.16 eV
Excitation efficiency by UV: ++ (4.88 eV)

Spectra



Remarks

1. The exact chemical formula of this material is still unknown.
2. The Cl in this recipe can be replaced by F or Br.

α-$SrO\cdot 3B_2O_3$:Sm

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	99	146
Sm_2O_3	1 (of Sm)	1.74
H_3BO_3	600	370

Preparation

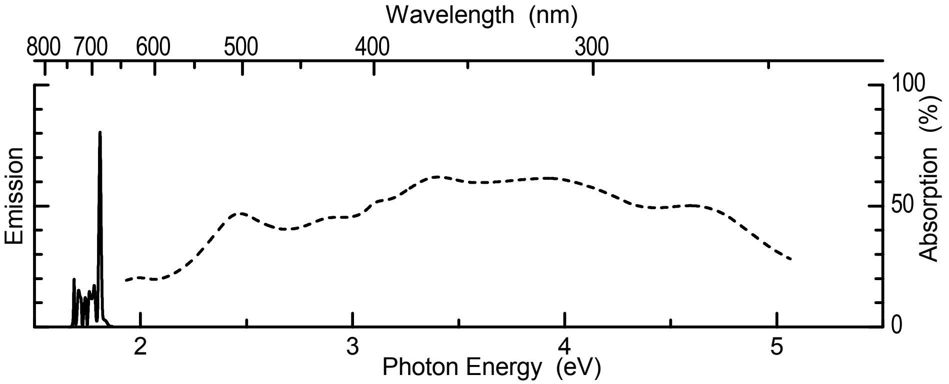
Mix by dry grinding or milling.

1. Fire in open quartz boats, air. Place into cold furnace, go slowly up with temperature to 600ºC, and then take out.
   Powderize.
2. Fire in open quartz boats, N_2, 800ºC, 1 hour.
   Powderize.
3. Fire in open quartz boats, CO, 900ºC, 4 hours.

Optical Properties

Emission color: Deep red
Emission peak: 1.812 eV
Excitation efficiency by UV: ++ (3.40 eV); QE ≈ 60% (estimated)

Spectra



$MgB_2O_4:Mn^{2+}$

Composition

Ingredient	Mole %	By weight (g)
MgO	98	40
$MnCO_3$	2	2.3
H_3BO_3	205	127

Preparation

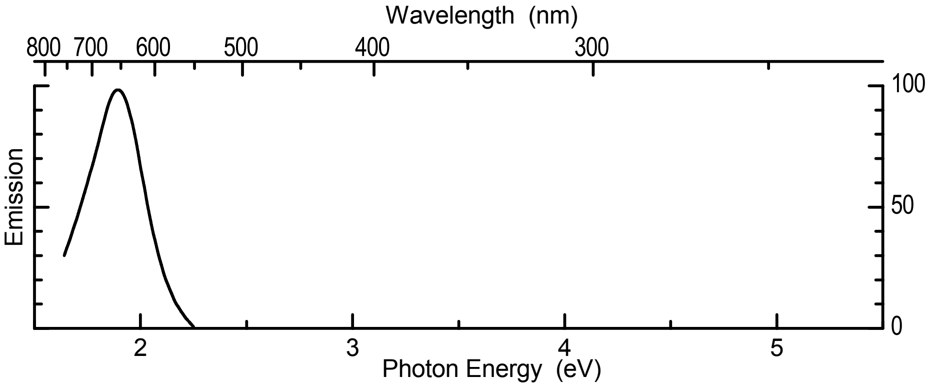
Mix by dry grinding or milling.

1. Fire in open quartz boats, N_2, ~500°C. Powderize.
2. Fire in open quartz boats, N_2, 700°C, 1 hour. Powderize.
3. Fire in open quartz boats, N_2.
   For α-structure, fire 2 hours at 1000°C.
   For β-structure, fire 4 hours at 850°C.

Optical Properties

Emission color: Red
Emission peak: 1.88 eV, 2.11 eV (see remark)
Emission width (FWHM): 0.32 eV, 0.39 eV (see remark)
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Remarks

1. This material comes in two different modifications, the high-temperature α-phase, and the low-temperature β-phase. Peak position depends on modification.
2. It can be sensitized for UV excitation by addition of $Ce^{3+} + Li^{+}$.

Reference

1. Ranby, P.W., U.S. Pat., 3 014 817 (1961).

$MgYBO_4:Eu^{3+}$

Composition

Ingredient	Mole %	By weight (g)
MgO	100	40.3
Y_2O_3	95 (of Y)	107
Eu_2O_3	5 (of Eu)	8.8
H_3BO_3	205	63.2

Preparation

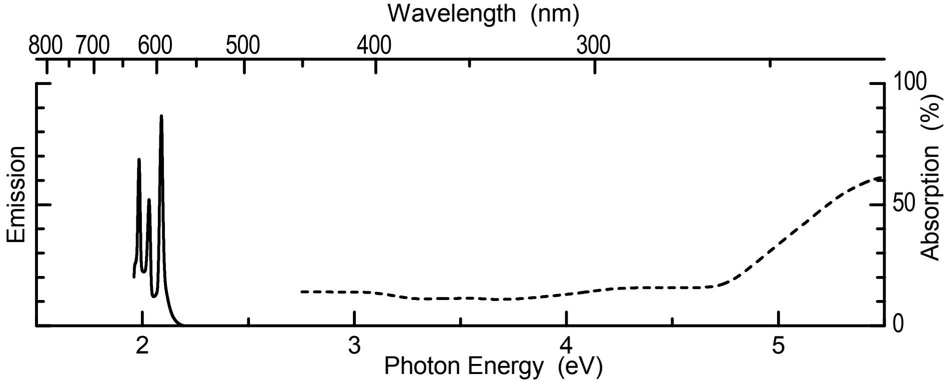
Mix by dry grinding or milling.

1. Fire in open quartz boats, air, ~500°C.
   Powderize.
2. Fire in open quartz boats, air, 1000°C, 1 hour.
   Powderize.
3. Fire in open quartz boats, air, 1200°C, 1 hour.

Optical Properties

Emission color: Orange-red
Emission peaks: 1.985, 2.035, and 2.098 eV
Excitation efficiency by UV: + (4.88 eV); QE ≈ 25–30%

Spectra



$CaB_2O_4:Mn^{2+}$

Structure: Orthorhombic

Optical Properties

Emission color: Green
Emission peak: 2.34 eV
Emission width (FWHM): 0.23 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Reference

1. Witzmann, H., Buhrow, J., and Müller, K., Zum emissionsvermogen blei-mangan-aktivierter kalziumboratphosphore ($CaO \cdot B_2O_3$-Pb,Mn), *Naturwissenschaften,* 51, 103 (1964).

$CaB_2O_4:Pb^{2+}$

Optical Properties

Emission color: UV
Emission peak: 3.82 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Reference

1. Witzmann, H., Buhrow, J., and Müller, K., Zum emissionsvermogen blei-mangan-aktivierter kalziumboratphosphore($CaO \cdot B_2O_3$-Pb,Mn), *Naturwissenschaften,* 51, 103 (1964).

$CaYBO_4:Bi^{3+}$

Composition

Ingredient	Mole %	By weight (g)
CaCO	100	100
Y_2O_3	99 (of Y)	112
Bi_2O_3	1 (of Bi)	2.3
H_3BO_3	105	65

Preparation

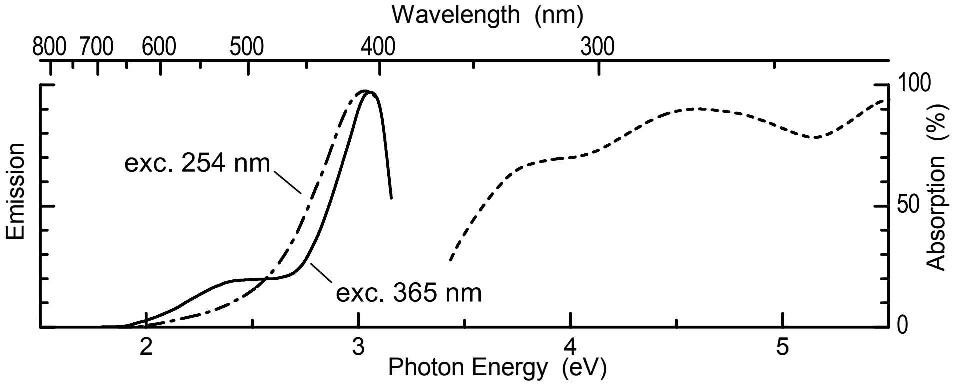
Mix by dry grinding or milling.

1. Fire in open quartz boats, air, ~500°C, ½ hour.
   Powderize.
2. Fire in capped quartz tubes, N_2, 1000°C, 1 hour.
   Powderize.
   Add 2 g of NH_4Cl; mix by dry grinding.
3. Fire in capped quartz tubes, N_2, 1200°C, 1 hour.

Optical Properties

Emission color: Blue
Emission peak: 2.99 eV (for UV 4.88 eV), 3.02 eV (for UV 3.40 eV)
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra



Remark

1. Peak position seems to depend on the excitation.

$CaYBO_4:Eu^{3+}$

Composition

Ingredient	Mole %	By weight (g)
CaCO	100	100
Y_2O_3	97 (of Y)	110
Eu_2O_3	3 (of Eu)	5.3
H_3BO_3	105	65

Preparation

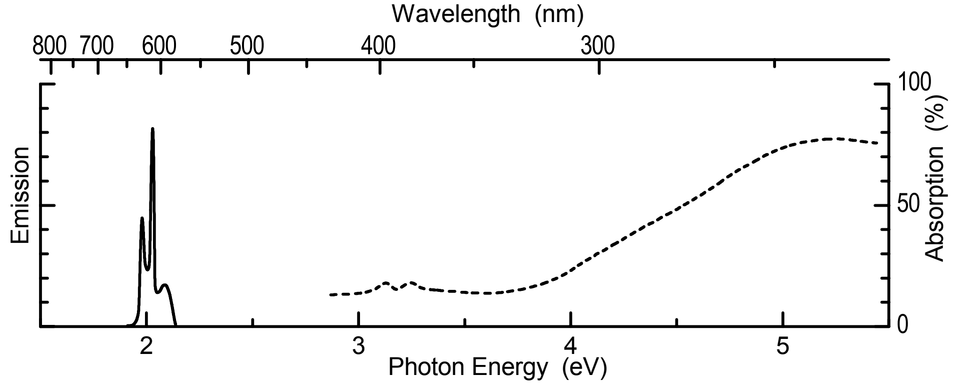
Mix by dry grinding or milling.

1. Fire in open quartz boats, air, ~500ºC, ½ hour.
   Powderize.
2. Fire in open quartz boats, air, 1000ºC, 1 hour.
   Powderize.
3. Fire in open quartz boats, air, 1200ºC, 1 hour.

Optical Properties

Emission color: Light red
Emission peak: 2.04 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Reference

1. Blasse, G., Ultraviolet-absorption bands of Bi^{3+} and Eu^{3+} in oxides, *J. Solid State Chem.,* 4, 52 (1972).

$CaLaBO_4:Eu^{3+}$

Composition

Ingredient	Mole %	By weight (g)
CaCO	100	100
La_2O_3	90 (of La)	146.7
Eu_2O_3	10 (of Eu)	17.6
H_3BO_3	102	63.2

Preparation

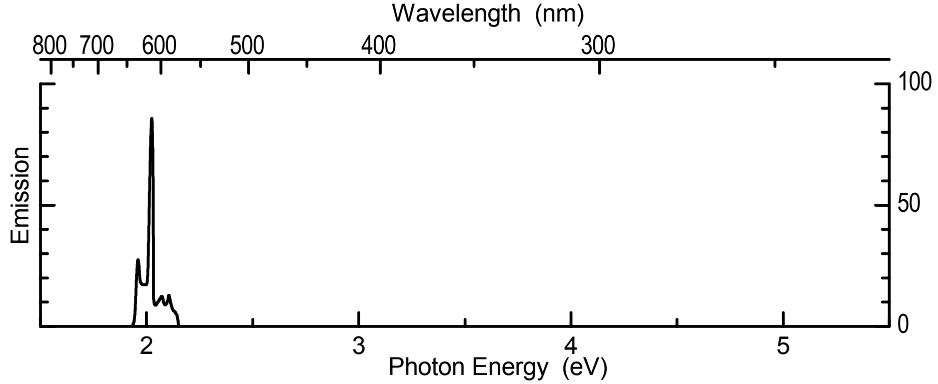
Mix by dry grinding or milling.

1. Fire in open quartz boats, air, ~500°C. Powderize.
2. Fire in open quartz boats, N_2, 1000°C, 1 hour. Powderize.
3. Fire in open quartz boats, N_2, 1200°C, 1 hour. Powderize.
   Add 5 g of NH_4Cl; mix by dry grinding.
4. Fire in capped quartz tubes, N_2, 1200°C, 16 hours (overnight).
   Powderize.
   Wash in water several times. Dry.

Optical Properties

Emission color: Light red
Emission peak: 2.03 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Remarks

1. This phosphor is somewhat discolored and less efficient if fired in air or oxygen.
2. Spectrum resembles that of YOE.

Reference

1. Blasse, G., Ultraviolet-absorption bands of Bi^{3+} and Eu^{3+} in oxides, *J. Solid State Chem.,* 4, 52 (1972).

$ZnB_2O_4:Mn^{2+}$

Composition

Ingredient	Mole %	By weight (g)
ZnO	97	79
$MnCO_3$	3	3.5
H_3BO_3	205	127

Preparation

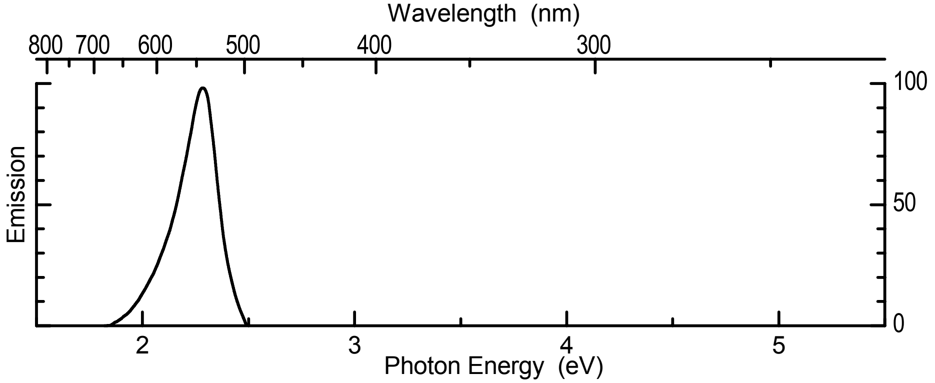
Mix by dry grinding or milling.

1. Fire in open quartz boats, air, ~500ºC. Powderize.
2. Fire in open quartz boats, air, 700ºC, 1 hour. Powderize.
3. Fire in open quartz boats, air, 900ºC, 2 hours.

Optical Properties

Emission color: Yellow-green
Emission peak: 2.29 eV
Emission width (FWHM): 0.21 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +/4–5%
Decay: Exponential decay, about 26 msec to 1/10

Spectra



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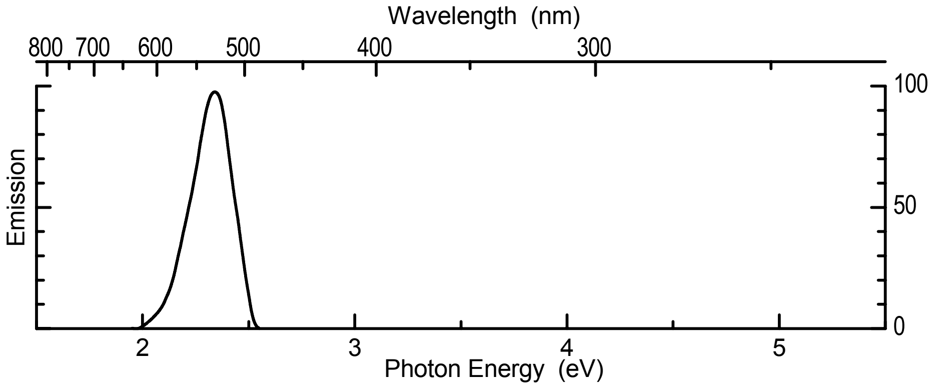
1. Kröger, F.A., *Some Aspects of Luminescence of Solids*, Elsevier, Amsterdam (1948).
2. Strange, J.W., and Henderson, S.T., Cathodo-luminescence. 1. Growth and decay processes, *P. Phys. Soc. London,* 58, 369 (1946).
3. Randall, J.T., *Proc. R. Soc.,* A170, 272 (1939).
4. Harrison, D.E., and Hummel, F.A., Phase equilibria and fluorescence in the system zinc oxide-boric oxide, *J. Electrochem. Soc.,* 103, 491 (1956).
5. Terol, S., and Otero, M.J., Anhydrous zinc borate as a host crystal in luminescence, *Z. Naturforsch. Pt. A*, 16, 920 (1961).

$Ca_2B_2O_5:Mn^{2+}$

Spectra



$LaAlB_2O_6:Eu^{3+}$

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	92 (of La)	150
Eu_2O_3	8 (of Eu)	14
Al_2O_3	100 (of Al)	51
H_3BO_3	205	127

Preparation

Mix by dry grinding or milling.

1. Fire in open quartz boats, air, ~500ºC. Powderize.
2. Fire in open quartz boats, air, 1000ºC, 1 hour. Powderize.
3. Fire in open quartz boats, air, 1200ºC, 1 hour.

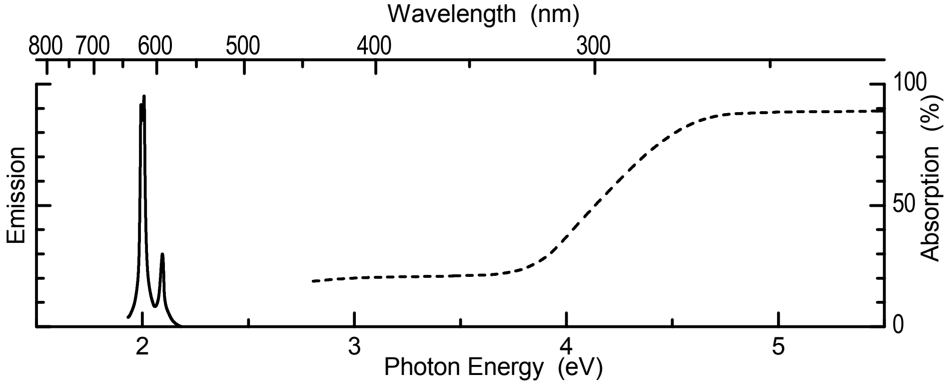
Optical Properties

Emission color: Light red

Emission peaks: Two overlapping lines at 2.015 and 2.205 eV, additionally a weaker line at 2.10 eV

Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



$CaLaB_3O_7:Ce^{3+},Mn^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	95	95
La_2O_3	98 (of La)	160
$MnCO_3$	5	5.8
CeO_2	2	3.4
H_3BO_3	310	192

Preparation

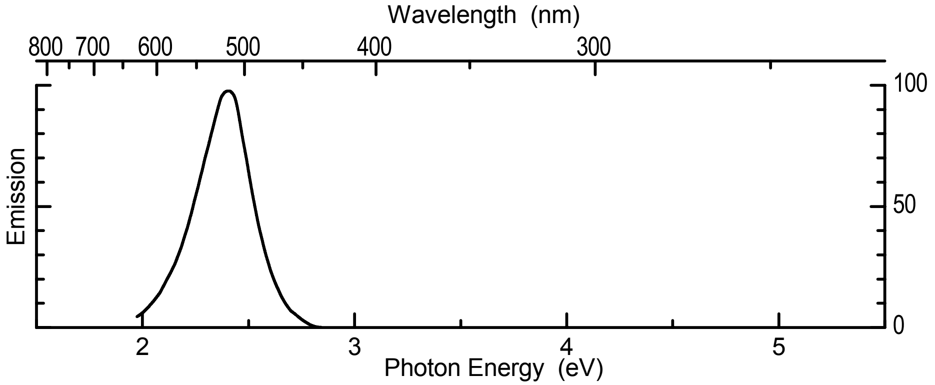
Mix by dry grinding or milling.

1. Fire in open quartz boats, air, ~500ºC.
   Powderize.
2. Fire in open quartz boats, N_2, 700ºC, 1 hour.
   Powderize.
3. Fire in open quartz boats, CO, 900ºC, 2 hours.

Optical Properties

Emission color: Green
Emission peak: 2.40 eV
Emission width (FWHM): 0.29 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra

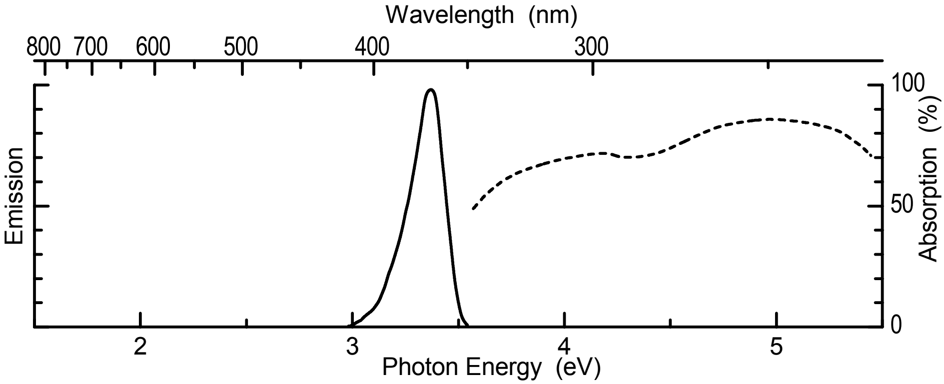


$SrB_4O_7:Eu^{2+}(F,Cl,Br)$

Optical Properties

Emission color: UV
Emission peak: 3.37 eV
Emission width (FWHM): 0.16 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Reference

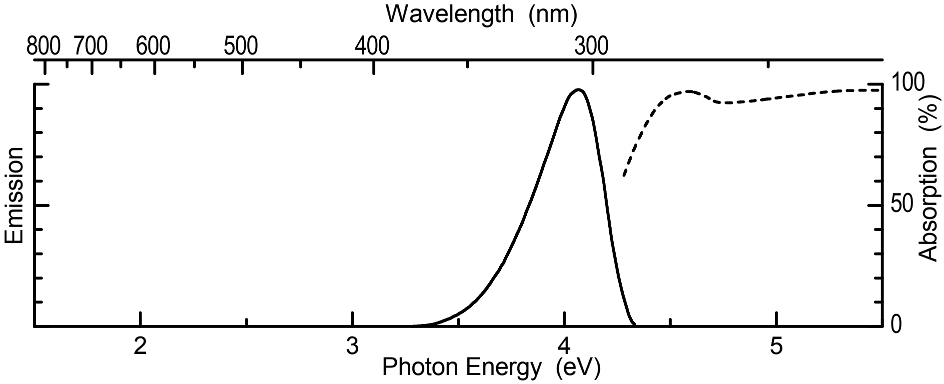
1. Machida, K., Adachi, G., and Shiokawa, J., Luminescence properties of Eu(II)-borates and Eu^{2+}-activated Sr-borates, *J. Lumin.,* 21, 101 (1979).

$SrB_4O_7:Pb^{2+}$

Optical Properties

Emission color: UV
Emission peak: 4.09 eV
Emission width (FWHM): 0.34 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



References

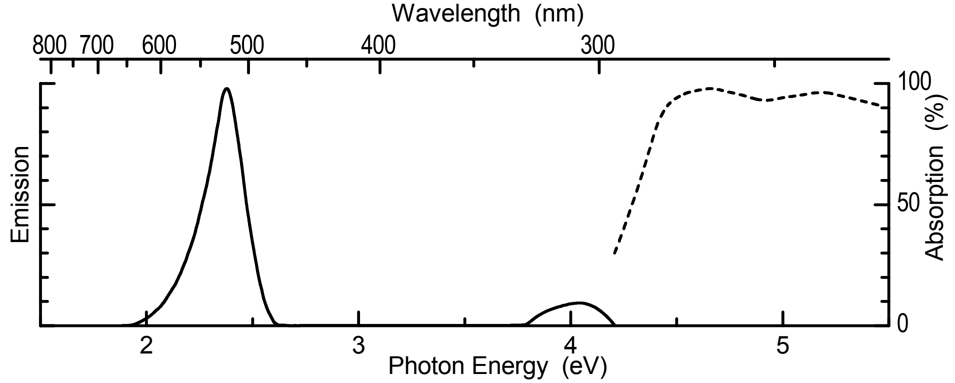
1. Witzmann, H., and Schreiber, H., Zur lumineszenz kupfer- und kupferbleiaktivierter strontiumboratphosphore, *Naturwissenschaften*, 49, 181 (1962).
2. Witzmann, H., Müller, R., and Semisch, G., Boratluminophore MIT UV-emission, *Naturwissenschaften,* 43, 580 (1956).

SrB_4O_7:Pb^{2+},Mn^{2+}

Optical Properties

Emission color: Blue-green
Emission peak: 2.42, 4.03 eV
Emission width (FWHM): 0.22 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



References

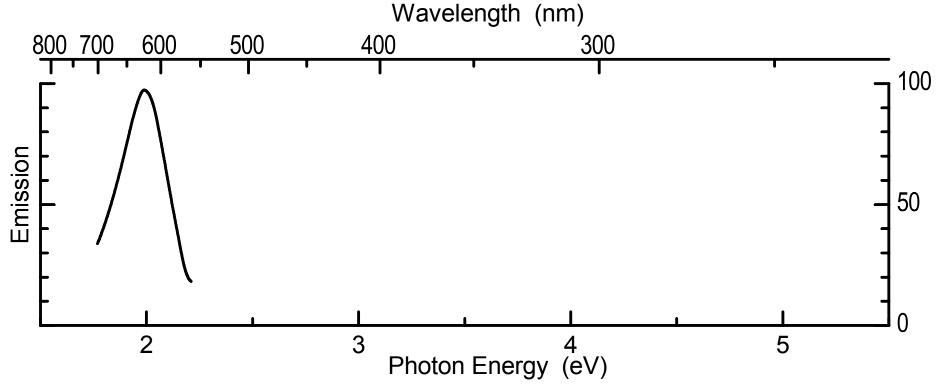
1. Witzmann, H., and Schreiber, H., Zur lumineszenz kupfer- und kupferbleiaktivierter strontiumboratphosphore, *Naturwissenschaften*, 49, 181 (1962).
2. Witzmann, H., Müller, R., and Semisch, G., Boratluminophore MIT UV-emission, *Naturwissenschaften,* 43, 580 (1956).

$Cd_2B_6O_{11}$:Mn^{2+}

Optical Properties

Emission color: Yellow-green
Emission peak: eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Harrison, D.E., and Hummel, F.A., Phase equilibria and fluorescence in the system zinc oxide-boric oxide, *J. Electrochem. Soc.,* 103, 491 (1956).
2. Hummel, F.A., and Subbarao, E.C., The system cadmium oxide-boric oxide. 2. Fluorescence, *J. Electrochem. Soc.,* 104, 616 (1957).

$YAl_3B_4O_{12}:Ce^{3+}$

Structure: Trigonal (huntite)

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	90 (of Y)	102
CeO_2	10	17.2
Al_2O_3	300 (of Al)	153
H_3BO_3	410	254

Preparation

Mix by dry grinding or milling.

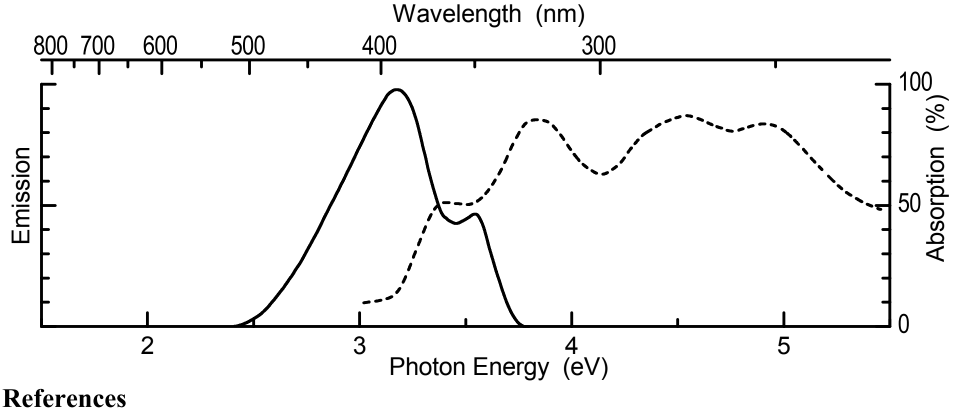
1. Fire in open quartz boats, air, ~500ºC. Powderize.
2. Fire in open alumina crucibles, N_2, 900ºC, 1 hour. Powderize.
3. Fire in open alumina crucibles, CO, 1100ºC, 1 hour. Powderize.
4. Fire in open alumina crucibles, CO, 1200ºC, 1 hour. Powderize.

Wash in hot water several times. Dry.

Optical Properties

Emission color: Blue-violet + UV
Emission peaks: 3.20 and 3.57 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



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2. Blasse, G., Bril, A., and Poorter, J.A.D., Radiationless transitions in Eu^{3+} center in $LaAlO_3$, *J. Chem. Phys.,* 53, 4450 (1970).

3. Blasse, G., Ultraviolet-absorption bands of Bi^{3+} and Eu^{3+} in oxides, *J. Solid State Chem.,* 4, 52 (1972).
4. Danielmeyer, H.G., Efficiency and fluorescence quenching of stoichiometric rare-earth laser materials, *J. Lumin.,* 12, 179 (1976).
5. Takahashi, T., and Yamada, O., Cathodoluminescent properties of yttrium terbium aluminum borate $Y_{1-x}Tb_x Al_3B_4O_{12}$ phosphors, *J. Electrochem. Soc.,* 124, 955 (1977).

$YAl_3B_4O_{12}:Bi^{3+}$

Structure: Trigonal (huntite)

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	99.7 (of Y)	113
Bi_2O_3	0.3 (of Bi)	0.700
Al_2O_3	300 (of Al)	153
H_3BO_3	410	254

Preparation

Mix by dry grinding or milling.

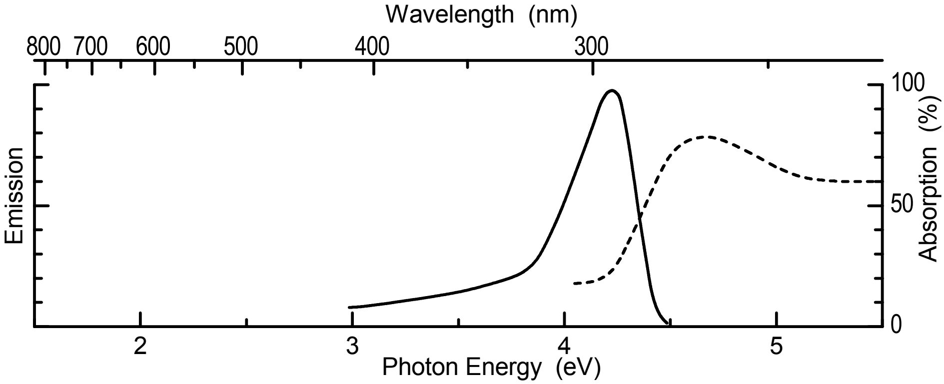
1. Fire in open quartz boats, air, ~500ºC, 1 hour. Powderize.
2. Fire in open alumina crucibles, air, 900ºC, 1 hour. Powderize.
3. Fire in open alumina crucibles, air, 1100ºC, 1 hour. Powderize.
4. Fire in open alumina crucibles, air, 1200ºC, 1 hour. Powderize.

Wash in hot water several times. Dry.

Optical Properties

Emission color: UV
Emission peak: 4.20 eV
Emission width (FWHM): 0.33 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra



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4. Blasse, G., and Bril, A., Photoluminescent efficiency of phosphors with electronic transitions in localized centers, *J. Electrochem. Soc.,* 115, 1067 (1968).
5. Kellendonk, F., van Os, M.A., and Blasse, G., Luminescence of bismuth in yttrium aluminum borate, *Chem. Phys. Lett.,* 61, 239 (1979).

$YAl_3B_4O_{12}$:Eu^{3+}

Structure: Trigonal (huntite)

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	90 (of Y)	102
Eu_2O_3	10 (of Eu)	17.6
Al_2O_3	300 (of Al)	153
H_3BO_3	410	248

Preparation

Mix by dry grinding or milling.

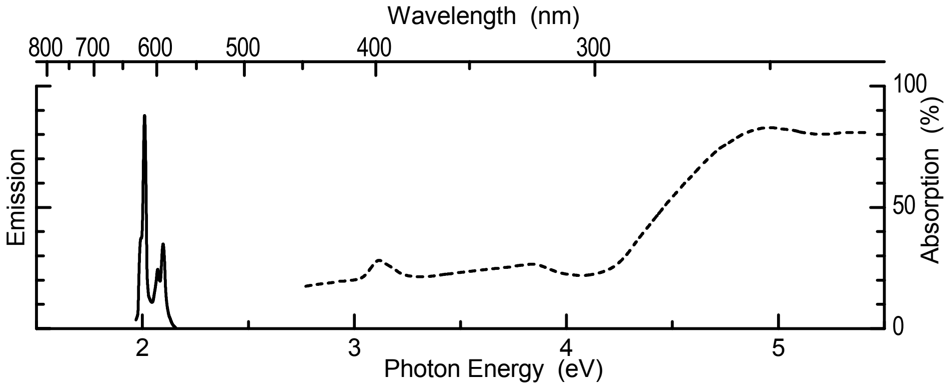
1. Fire in open quartz boats, air, ~500°C, 1 hour. Powderize.
2. Fire in open alumina crucibles, air, 900°C, 1 hour. Powderize.
3. Fire in open alumina crucibles, air, 1100°C, 1 hour. Powderize.
4. Fire in open alumina crucibles, air, 1200°C, 1 hour. Powderize.

Wash in hot water several times. Dry.

Optical Properties

Emission color: Red
Emission peaks: 2.01 and 2.035 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



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3. Takahashi, T., and Yamada, O., Cathodoluminescent properties of yttrium terbium aluminum borate Y_1-X TbX$Al_3B_4O_{12}$ phosphors, *J. Electrochem. Soc.,* 124, 955 (1977).

$YAl_3B_4O_{12}:Eu^{3+},Cr^{3+}$

Structure: Trigonal (huntite)

Optical Properties

Emission color: Deep red
Emission peak: 1.77 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Reference

1. Blasse, G., and Bril, A., Some observations on Cr^{3+} fluorescence in huntite structure, *Phys. Status Solidi,* 20, 551 (1967).

$YAl_3B_4O_{12}:Th^{4+},Ce^{3+},Mn^{2+}$

Structure: Trigonal (huntite)

Emission color: green
Emission peak: 2.31 eV
Emission width (FWHM): 0.23 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

$YAl_3B_4O_{12}:Ce^{3+},Tb^{3+}$

Structure: Trigonal (huntite)

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	80 (of Y)	90.4
CeO_2	10	17.2
Tb_4O_7	10 (of Tb)	18.7
Al_2O_3	300 (of Al)	153
H_3BO_3	410	254

Preparation

Mix by dry grinding or milling.

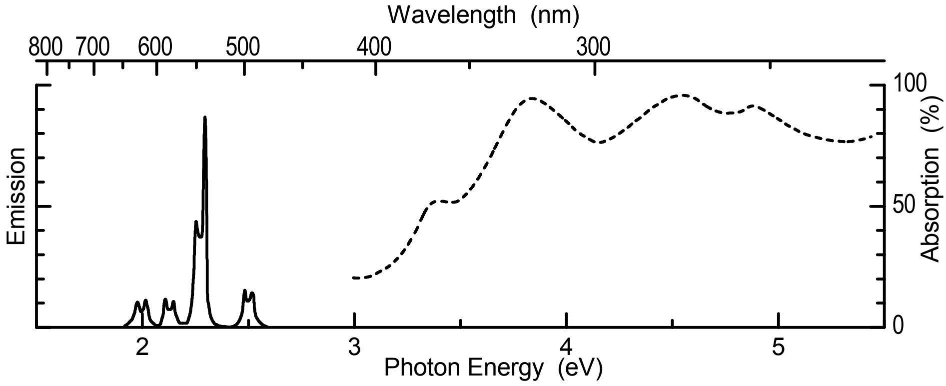
1. Fire in open quartz boats, air, ~500ºC, 1 hour. Powderize.
2. Fire in open alumina crucibles, N_2, 900ºC, 1 hour. Powderize.
3. Fire in open alumina crucibles, CO, 1100ºC, 1 hour. Powderize.
4. Fire in open alumina crucibles, CO, 1200ºC, 1 hour. Powderize.

Wash in hot water several times.
Dry.

Optical Properties

Emission color: Green
Emission peak: 2.29 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



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3. Blasse, G., and Bril, A., Fluorescence of Eu^{3+}-activated lanthanide oxyhalides LnOX, *J. Chem. Phys.,* 46, 2579 (1967); and Study of energy transfer from Sb^{3+}, Bi^{3+}, Ce^{3+} to Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, *J. Chem. Phys.,* 47, 1920 (1967).

$LaAl_3B_4O_{12}$:Eu^{3+}

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	90 (of La)	147
Eu_2O_3	10 (of Eu)	17.6
Al_2O_3	300 (of Al)	153
H_3BO_3	410	254

Preparation

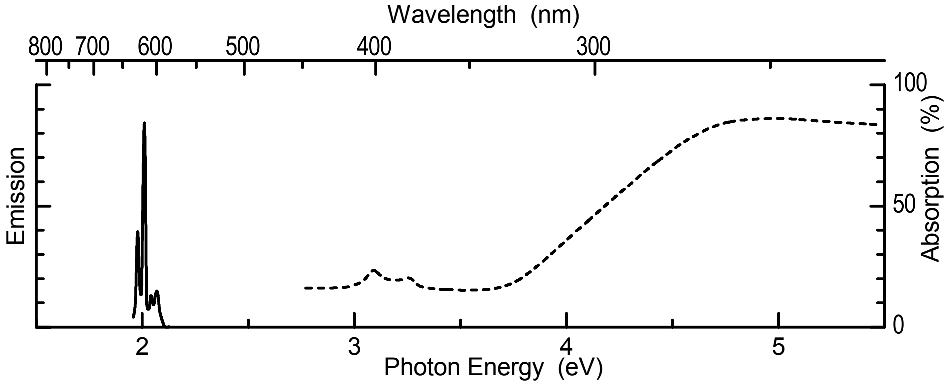
Mix by dry grinding or milling.

1. Fire in open quartz boats, air, ~500°C.
   Powderize.
2. Fire in open quartz boats, air, 900°C, 1 hour.
   Powderize.
3. Fire in open quartz boats, air, 1200°C, 2 hours.

Optical Properties

Emission color: Red
Emission peak: 2.005 and 2.020 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra

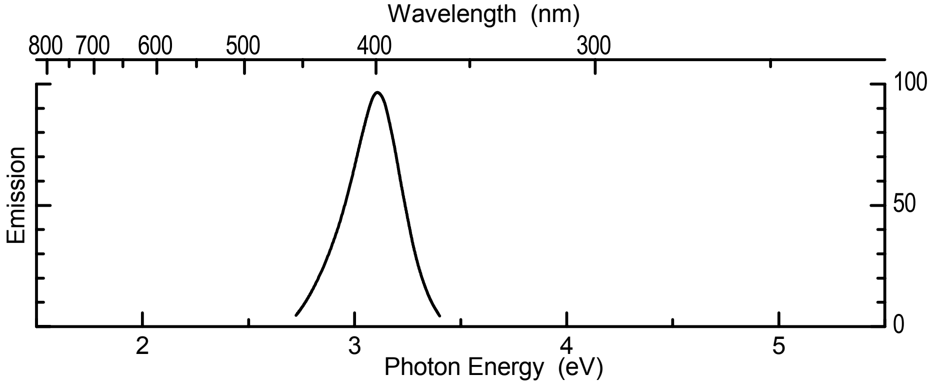


$BaB_8O_{13}:Eu^{2+}$

Optical Properties

Emission color: Violet–UV
Emission peak: 3.10 eV
Emission width (FWHM): 0.28 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: –

Spectra



Reference

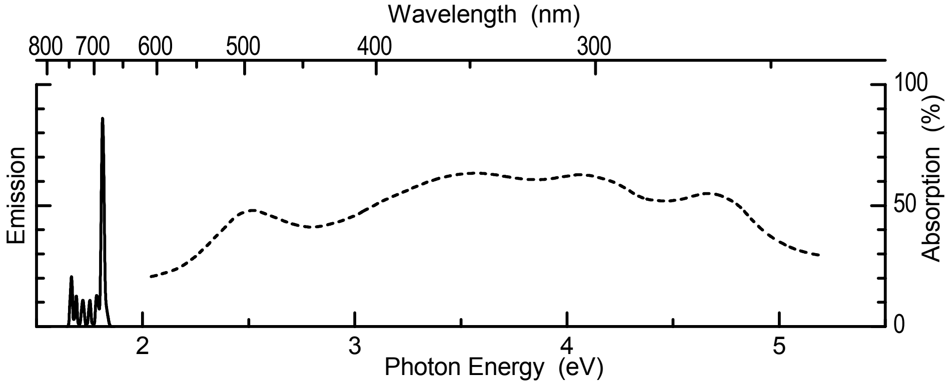
1. Blasse, G., Bril, A., and deVries, J., Fluorescence of Eu^{2+}-activated barium octaborate, *J. Electrochem. Soc.,* 115, 977 (1968).

SrB_8O_{13}:Sm

Optical Properties

Emission color: Deep red
Emission peak: 1.81 eV
Excitation efficiency by UV: + (4.88 eV), ++ (3.40 eV)

Spectra



Reference

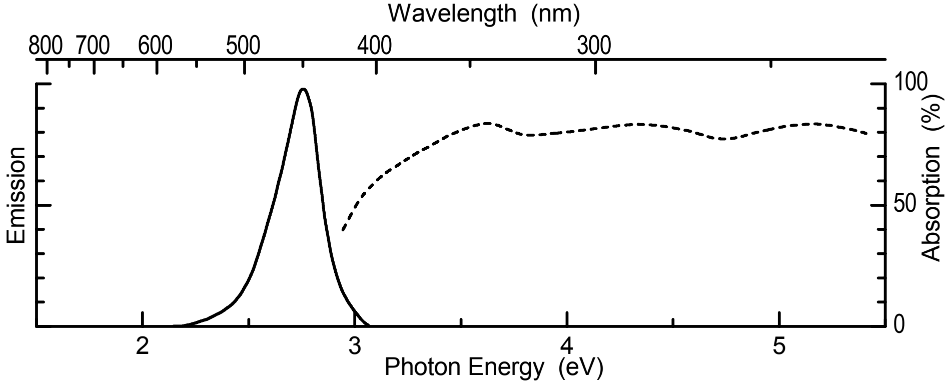
1. Chenot, C.F., U.S. Pat., 3 657 141 (1972).

$Ca_2B_5O_9Cl:Eu^{2+}$

Optical Properties

Emission color: Blue
Emission peak: 2.74 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



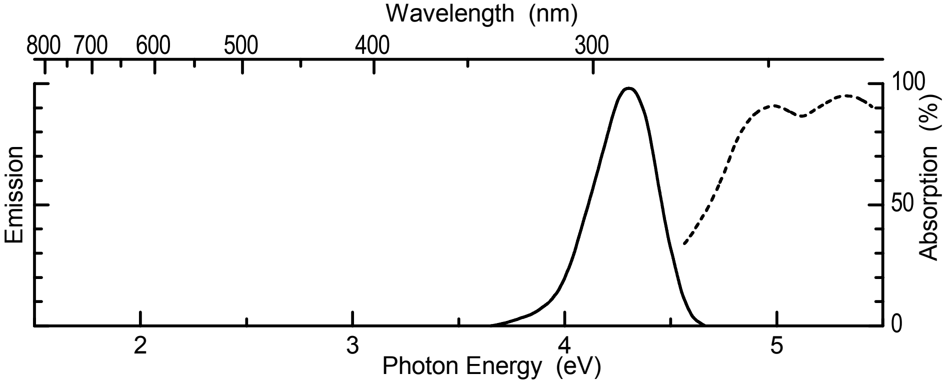
$Ca_2B_5O_9Cl:Pb^{2+}$

Optical Properties

Emission color: UV
Emission peak: 4.31 eV

Emission width (FWHM): 0.34 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra

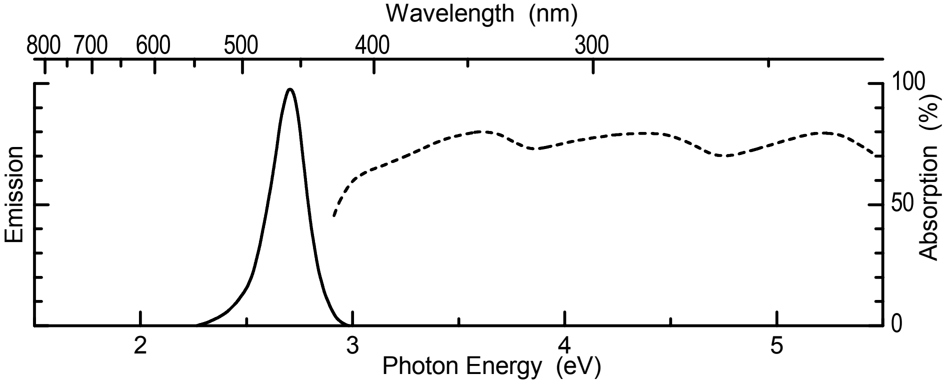


$Ca_2B_5O_9Br:Eu^{2+}$

Optical Properties

Emission color: Blue
Emission peak: 2.74 eV
Emission width (FWHM): 0.20 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra

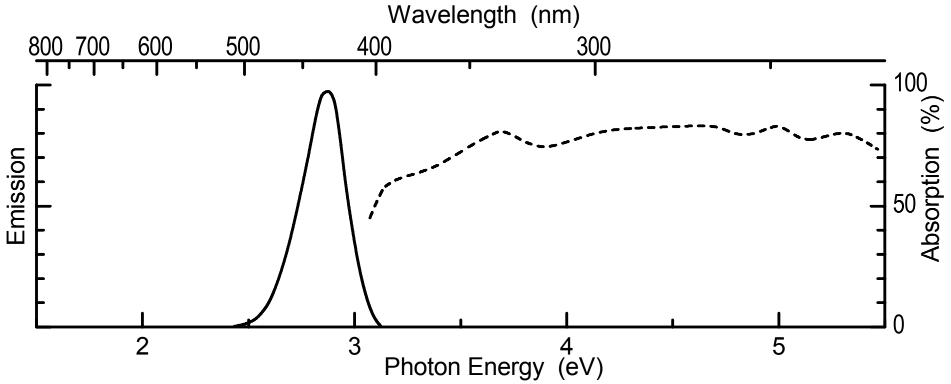


$Sr_2B_5O_9Cl:Eu^{2+}$

Optical Properties

Emission color: Blue-violet
Emission peak: 2.92 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra

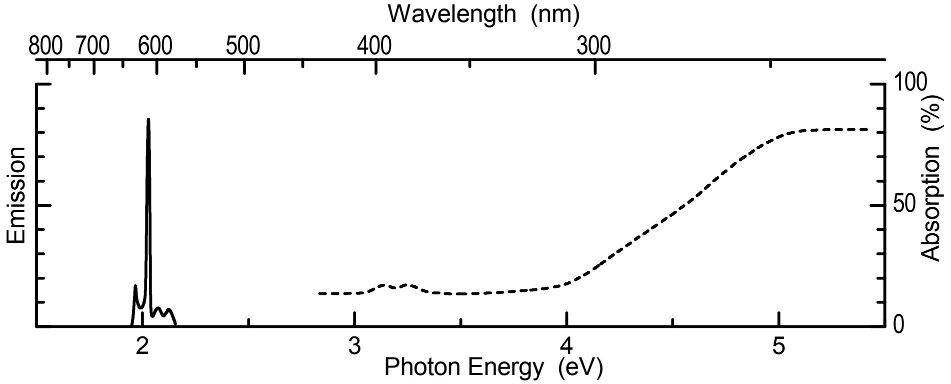


$CaYB_{0.8}O_{3.7}:Eu^{3+}$

Optical Properties

Emission color: Red
Emission peak: 2.03 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Reference

1. Lehmann, W., U.S. Pat., 4 202 794 (1980).

$Ca_2La_2BO_{6.5}:Pb^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	198	198
La_2O_3	200 (of La)	326
PbO	2	4.6
H_3BO_3	105	65

Preparation

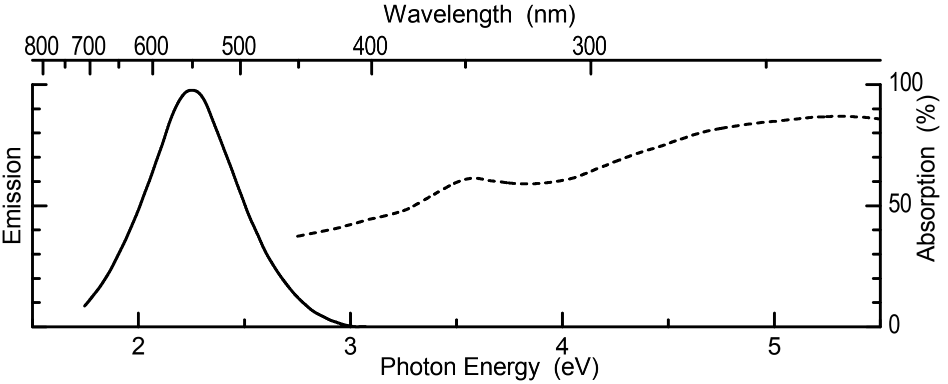
Mix by dry grinding or milling.

1. Fire in open quartz boats, air, ~500ºC.
   Powderize.
2. Fire in capped quartz tubes, N_2, 1000ºC, 1 hour.
   Powderize.
3. Fire in capped quartz tubes, N_2, 1200ºC, 1 hour.

Optical Properties

Emission color: Pale yellow-green
Emission peak: 2.28 eV
Emission width (FWHM): 0.48 eV
Excitation efficiency by UV: + (4.88 eV), ++ (3.40 eV)

Spectra

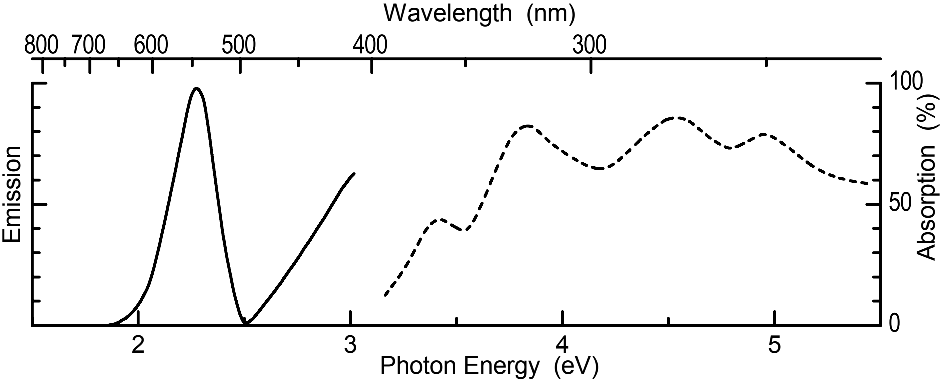


Remark

The formula of this peculiar material is still uncertain but the mole ratio Ca-La-B in the formula is close to 2:2:1

$YAl_3B_4O_{12}:Ce^{3+},Mn^{2+}$

Spectra



4.8 Aluminates and Gallates

The following host compounds and activators are included in this subsection:

$LiAlO_2:Fe^{3+}$
$LiAlO_2:Mn^{2+}$
$YAlO_3:Ce^{3+}$
$YAlO_3:Eu^{3+}$
$YAlO_3:Sm^{3+}$
$YAlO_3:Tb^{3+}$
$LaAlO_3:Eu^{3+}$
$LaAlO_3:Sm^{3+}$
$MgAl_2O_4:Mn^{2+}$
$MgGa_2O_4:Mn^{2+}$
$CaAl_2O_4:Mn^{2+}$
$CaAl_2O_4:Eu^{2+}$
$ZnAl_2O_4:Mn^{2+}$
$ZnGa_2O_4:Mn^{2+}$
$CaGa_2O_4:Mn^{2+}$
$CaGa_4O_7:Mn^{2+}$
$SrAl_2O_4:Eu^{2+}$
$BaAl_2O_4:Eu^{2+}$
$CaAl_4O_7:Pb^{2+},Mn^{2+}$
$LiAl_5O_8:Fe^{3+}$
$LiAl_5O_8:Mn^{2+}$
$Y_4Al_2O_9:Eu^{3+}$
$Y_3Al_5O_{12}:Ce^{3+}$
$KAl_{11}O_{17}:Tl^{+}$
$KGa_{11}O_{17}:Mn^{2+}$
$BaMgAl_{10}O_{17}:Ce^{3+}$
$Y_3Al_5O_{12}:Eu^{3+}$
$BaMgAl_{10}O_{17}:Eu^{2+}$
$BaMgAl_{10}O_{17}:Eu^{2+},Mn^{2+}$
$Ca_{0.5}Ba_{0.5}Al_{12}O_{19}:Ce^{3+},Mn^{2+}$
$SrAl_{12}O_{19}:Eu^{2+},Mn^{2+}$
$SrGa_{12}O_{19}:Mn^{2+}$
$SrAl_{12}O_{19}:Ce^{3+},Mn^{2+}$

$LiAlO_2:Fe^{3+}$

Structure: NaCl

Composition

Ingredient	Mole %	By weight (g)
Li_2CO_3	101 (of Li)	37.4
Al_2O_3	100 (of Al)	51
$Fe(NO_3)_3 \cdot 9H_2O$	0.6	2.4
LiF	2	0.520

Preparation

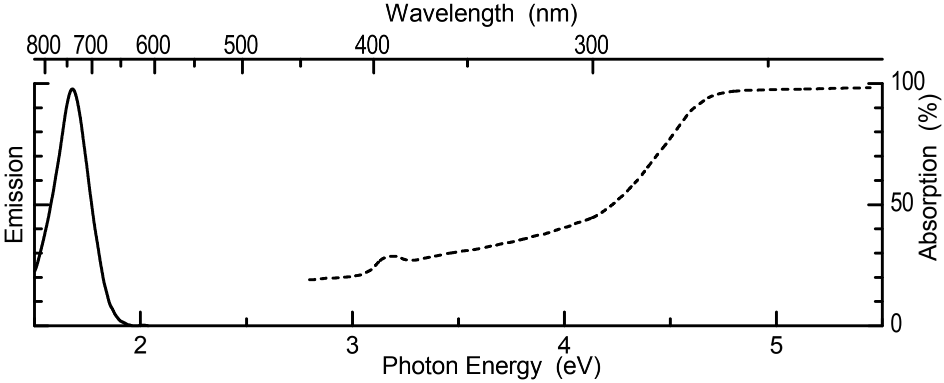
Dissolve iron nitrate in a little water; add solution to the mixture of other ingredients. Stir to uniformity. Dry in air. Powderize when dry.

1. Fire in covered alumina crucibles, air. Place crucibles into a cold furnace, go slowly up with temperature to 900ºC, and then take out. Powderize.
2. Fire in covered alumina crucibles, air, 1250ºC, 2 hours. Powderize.
   Wash in diluted acetic acid (~10%), and then in water until neutral. Add a solution of about 3 g $Al(NO_3)_3{\cdot}9H_2O$ in little water; stir to uniformity.
   Dry in air. Powderize when dry.
3. Fire in open quartz boats, air, 1250ºC, 1 hour.

Optical Properties

Emission color: Very deep red + IR
Emission peak: 1.67 eV
Emission width (FWHM): 0.20 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



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1. Hummel, F.A., and Sarver, J.F., The cathodoluminescence of Mn^{2+} activated and Fe^{3+} activated magnesium aluminate spinel, *J. Electrochem. Soc.*, 111, 252 (1964).
2. Palumbo, D.T., Electronic states of Fe^{3+} in $LiAl_5O_2$ and $LiAl_5O_8$ phosphors*, J. Lumin.,* 4, 19 (1971).
3. Rabatin, J., Luminescence of iron-activated lithium meta-gallate, *J. Electrochem. Soc.,* 125, 920 (1978).
4. Lehmann, W., and Watchtel, A., U.S. Pat., 3 857 054 (1974).
5. Kamiya, S., and Mizuno, H., *Phosphor Handbook*, CRC Press, Boca Raton, FL, Fig. 46, p. 422 (1998).
6. Van Broekhoven, J., Infrared emitting fluorescent lamp and applications, *J. Illum. Eng. Soc.,* 3, 234 (1974).
7. Stork, W.H.J., and Pott, G.T., Studies of compound formation on alkali-gamma-aluminum oxide catalyst systems using chromium, iron, and manganese luminescence, *J. Phys. Chem.,* 78, 2496 (1974).

$LiAlO_2$:Mn^{2+}

Structure: NaCl

Composition

Ingredient	Mole %	By weight (g)
Li_2CO_3	99 (of Li)	36.6
Al_2O_3	499 (of Al)	254
$MnCO_3$	2	2.3

Preparation

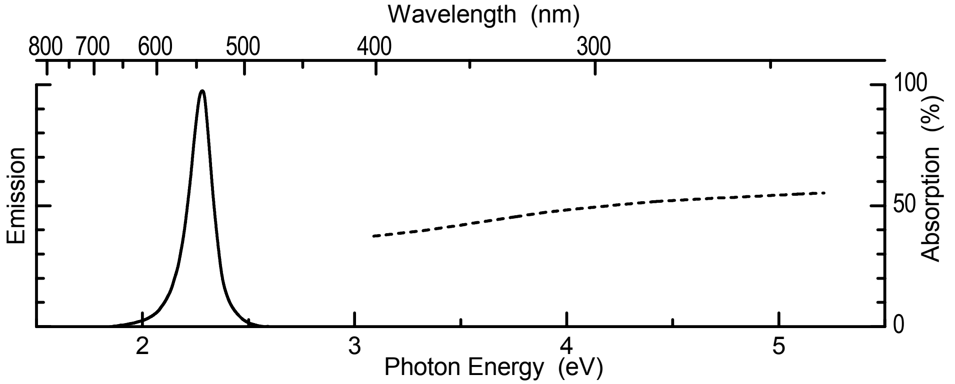
Mix by slurrying in methanol. Dry in air. Powderize when dry.

1. Fire in covered alumina crucibles, N_2, 1200°C, 1 hour. Powderize.
2. Fire in open quartz boats, CO, 1250°C, 2 hours.

Optical Properties

Emission color: Green
Emission peak: 2.375 eV
Emission width (FWHM): 0.15 eV
Excitation efficiency by UV: no sensitizer known to obtain response to this UV
Excitation efficiency by e-beam: ~6–8%
Decay to 10% (or 1/e, as given): Non-exponential decay, 1/10-time in the 10 msec range; long and strong phosphorescence

Spectra



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1. Jaffe, P.M., Cathodoluminescence spectra and coordination of Mn^{2+}, Fe^{3+}, and Cr^{3+} in $BeTaLiAl_5O_8$, *J. Electrochem. Soc.,* 115, 1203 (1968).
2. Stork, W.H.J., and Pott, G.T., Studies of compound formation on alkali-gamma-aluminum oxide catalyst systems using chromium, iron, and manganese luminescence, *J. Phys. Chem.,* 78, 2496 (1974).

$YAlO_3$:Ce^{3+}

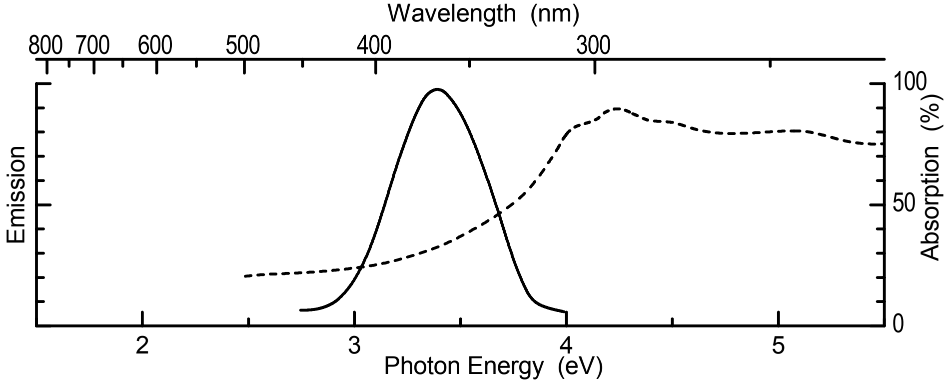
Structure: Orthorhombic

Optical Properties

Emission color: UV
Emission peak: 3.40 eV
Emission width (FWHM): 0.5 eV

Excitation efficiency by UV: + (4.88 eV)
Excitation efficiency by e-beam: +

Spectra



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1. Weber, M.J., Optical-spectra of Ce^{3+} and Ce^{3+}-sensitized fluorescence in $YAlO_3$, *J. Appl. Phys.,* 44, 3205 (1973).
2. Takeda, T. et al., Fast decay UV phosphor $YAlO_3$-Ce, *J. Electrochem. Soc.*, 127, 438 (1980).

$YAlO_3:Eu^{3+}$

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	94 (of Y)	83.6
Al_2O_3	100 (of Al)	51
Eu_2O_3	6 (of Eu)	10.6
H_3BO_3	10	6.2

Preparation

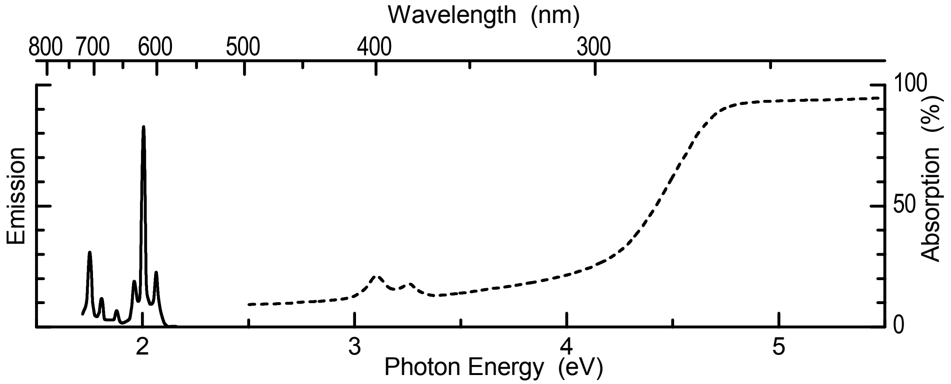
Mix by dry grinding or milling.

1. Fire in covered alumina crucibles, air, 1000ºC, 1 hour.
   Powderize.
2. Fire in covered alumina crucibles, air, 1300ºC, 4 hours.

Optical Properties

Emission color: Light red
Emission peaks: 1.785 – 2.015 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Remark

Q yield (UV excitation) is about the same as that of YOE.

$YAlO_3:Sm^{3+}$

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	98 (of Y)	110
Sm_2O_3	2 (of Sm)	3.6
Al_2O_3	100 (of Al)	51
CaF_2	10	7.8

Preparation

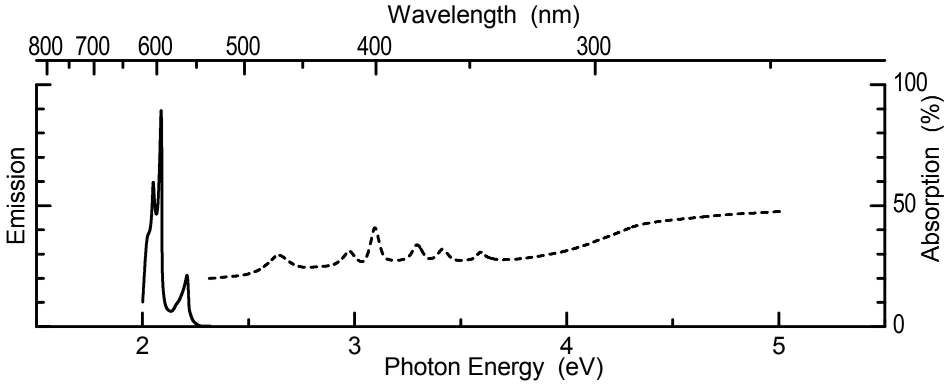
Mix by dry grinding or milling.

1. Fire in covered alumina crucibles, air, 1300ºC, 1 hour.
   Powderize.
2. Fire in covered alumina crucibles, air, 1300ºC, 4 hours.

Optical Properties

Emission color: Orange-yellow
Emission peaks: 2.008–3.06, 2.197 eV; strongest line at ~2.06 eV
Excitation efficiency by UV: − (4.88 eV), − (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



$YAlO_3$:Tb^{3+}

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	90 (of Y)	102
Tb_4O_7	10 (of Tb)	18.7
Al_2O_3	100 (of Al)	51
CaF_2	10	7.8

Preparation

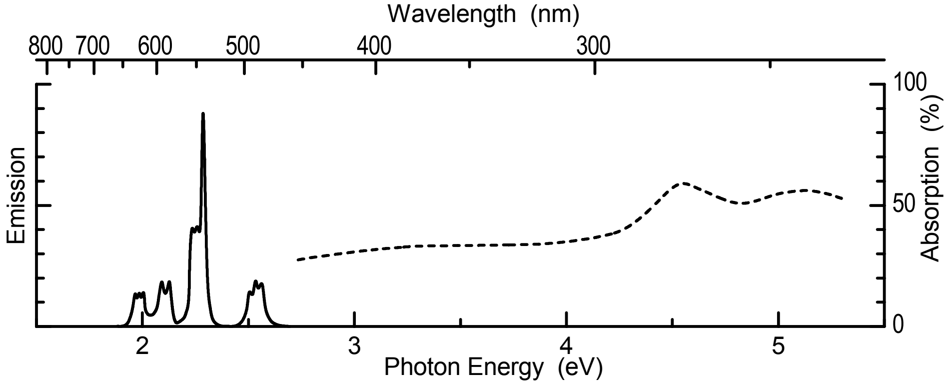
Mix by dry grinding or milling.

1. Fire in covered alumina crucibles, CO, 1300ºC, 1 hour.
   Powderize.
2. Fire in covered alumina crucibles, CO, 1300ºC, 4 hours.

Optical Properties

Emission color: Pale green
Emission peaks: Typical Tb^{3+} lines, strongest line at ~2.283 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: + (better than Y_2O_3:Tb^{3+})

Spectra



$LaAlO_3$:Eu^{3+}

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	94 (of La)	130.6
Al_2O_3	105 (of Al)	53.6
Eu_2O_3	6 (of Eu)	10.6
H_3BO_3	20	12.4

Preparation

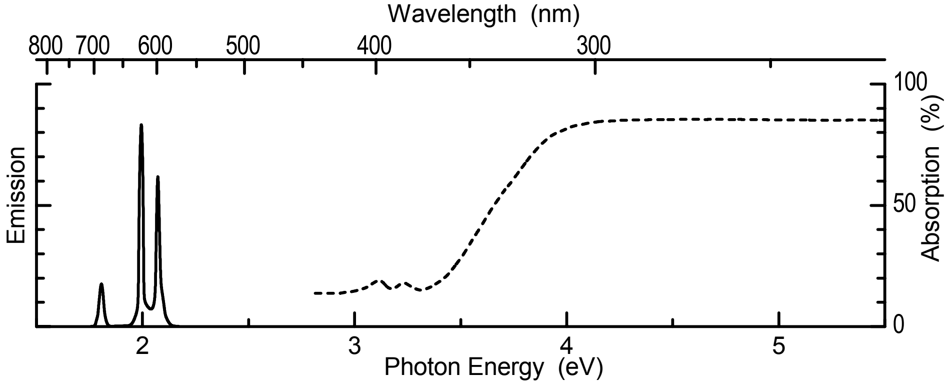
Mix by dry grinding or milling.

1. Fire in covered alumina crucibles, air, 1000ºC, 1 hour. Powderize.
2. Fire in covered alumina crucibles, air, 1300ºC, 4 hours.

Optical Properties

Emission color: Orange-red
Emission peaks: 2.01–2.10 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Remark

Q yield (UV excitation) is about ~75% of YOE.

Reference

1. Blasse, G., and Bril, A., Characteristic luminescence, 1. The absorption and emission spectra of some important activators, *Philips Tech. Rev.,* 31, 304 (1970).

LaAlO$_3$:Sm^{3+}

Structure: Trigonal

Composition

Ingredient	Mole %	By weight (g)
La$_2$O$_3$	100 (of La)	139
Al$_2$O$_3$	105 (of Al)	53.6
Sm$_2$O$_3$	0.2 (of Sm)	0.300
H$_3$BO$_3$	20	12.4

Preparation

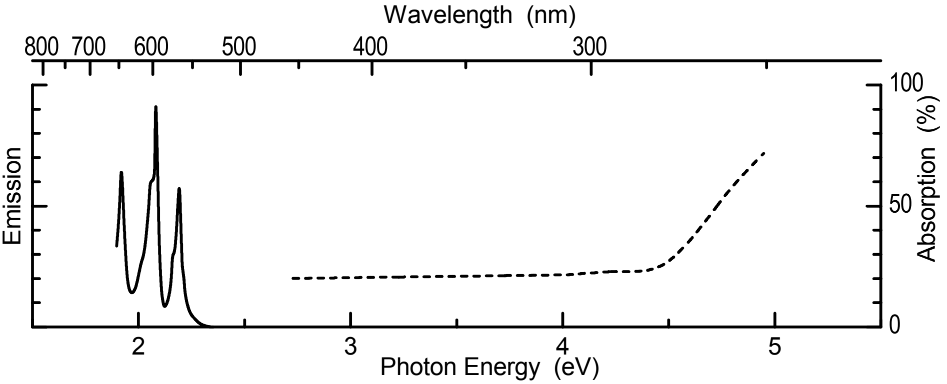
Mix by dry grinding or milling.

1. Fire in covered alumina crucibles, air, 1000ºC, 1 hour. Powderize.
2. Fire in covered alumina crucibles, air, 1300ºC, 4 hours.

Optical Properties

Emission color: Yellow
Emission peaks: 1.925–2.20 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra



$MgAl_2O_4$:Mn^{2+}

Structure: Tetragonal (spinel)

Composition

Ingredient	Mole %	By weight (g)
MgO	98	39
$MnCO_3$	1	1.15
Al_2O_3	210 (of Al)	107
MgF_2	1	0.620

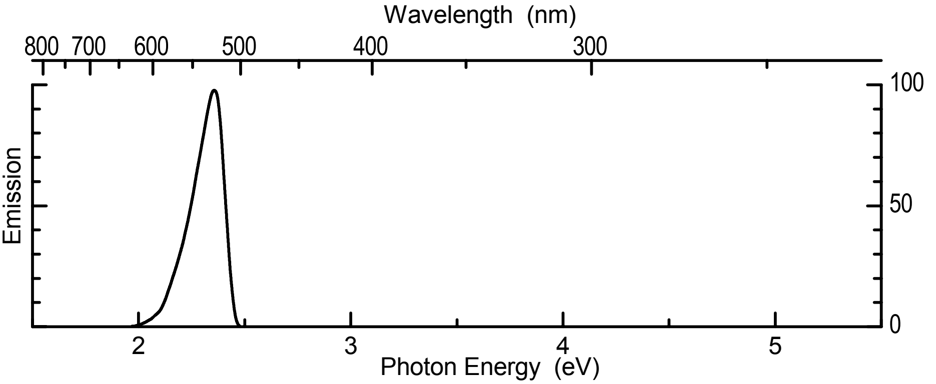
Preparation

Mix by dry ball-milling.
Fire in covered alumina crucibles, CO, 1250ºC, 2 hours.

Optical Properties

Emission color: Green
Emission peak: 2.36 eV
Emission width (FWHM): 0.16 eV
Excitation efficiency by UV: no sensitizer known to obtain response to this UV
Excitation efficiency by e-beam: +/~7–8%
Decay**:** Slightly non-exponential decay, ≈ 20 msec to 1/10

Spectra



Remark

Reducing the Mn concentration from 1 to 0.2% reduces the efficiency of cathodoluminescence to ~4% and increases the 1/10 decay time to ~40 msec.

References

1. Kröger, F.A., *Some Aspects of Luminescence of Solids*, Elsevier, Amsterdam (1948).
2. Hummel, F.A., and Sarver, J.F., The cathodoluminescence of Mn^{2+} activated and Fe^{3+} activated magnesium aluminate spinel, *J. Electrochem. Soc.*, 111, 252 (1964).
3. Lehmann, W., *Res. Rep.,* 78-5F4-ZSIBM-R1 (1978).

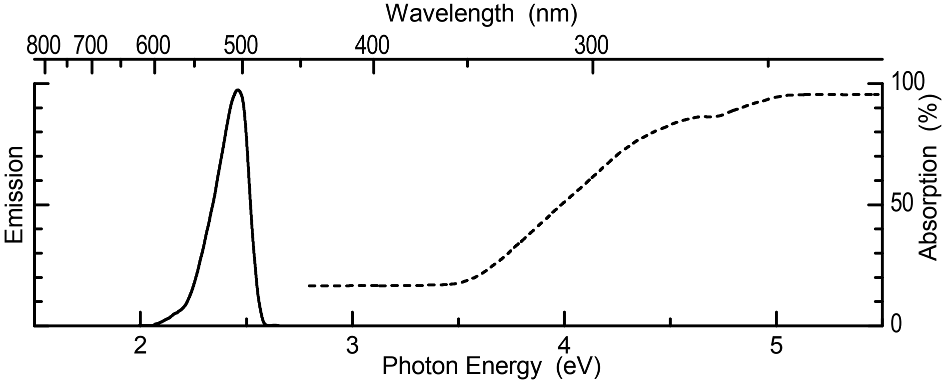
$MgGa_2O_4:Mn^{2+}$

Structure: Tetragonal (spinel)

Optical Properties

Emission color: Blue-green
Emission peak: 2.46 eV
Emission width (FWHM): 0.15 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



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1. Palumbo, D.T., and Brown, J., Electronic states of Mn^{2+}-activated phosphors. 1. Green-emitting phosphors, *J. Electrochem. Soc.,* 117, 1184 (1970).
2. Brown, J., Manganese-activated luminescence in $MgO-Al_2O_3-Ga_2O_3$ system, *J. Electrochem. Soc.,* 114, 245 (1967).
3. Wanmaker, W.L., terVrugt, J.W., and deBres, J.G.M., Luminescence of manganese-activated aluminiu-substituted magnesium gallate, *Philips Res. Rep.,* 22, 304 (1967).
4. Wanmaker, W.L., terVrugt, J.W., and Verlijsdonk, J.G., Luminescence of Mn^{2+}-activated spinels in $MgO-Li_2O-ZnO-Ga_2O_3-Al_2O_3$ system, *Philips Res. Rep.*, 25, 108 (1970).
5. Opstelten, J.J., Radielovic, D., and Wanmaker, W.L., Choice and evaluation of phosphors for application to lamps with improved color rendition, *J. Electrochem. Soc.*, 120, 1400 (1973).

$CaAl_2O_4:Mn^{2+}$

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	93	93
Al_2O_3	200 (of Al)	102
$MnCO_3$	2	2.3
CaF_2	5	3.9

Preparation

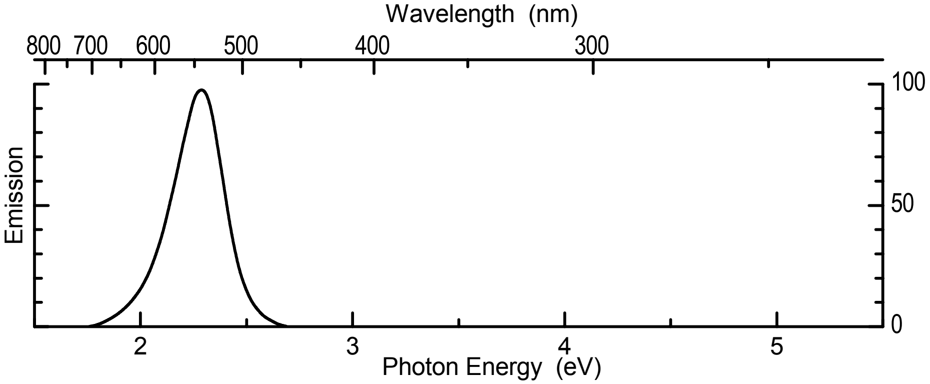
Mix by slurrying in water.
Dry in air. Powderize when dry.

1. Fire in covered alumina crucibles, CO, 1300ºC, 1 hour.
   Powderize.
2. Fire in open quartz boats, CO, 1200ºC, 1 hour.
   Wash in a solution of 20 g NH_4Cl in 1 liter of water and then several times in plain water.

Optical Properties

Emission color: Yellow-green
Emission peak: 2.28 eV
Emission width (FWHM): 0.27 eV
Excitation efficiency by UV: no sensitizer known to obtain response to this UV
Excitation efficiency by e-beam: ~ a few percent

Spectra



$CaAl_2O_4:Eu^{2+}$

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	98	98
Al_2O_3	210 (of Al)	107
Eu_2O_3	2 (of Eu)	3.5
NH_4Cl	10	5.4

Preparation

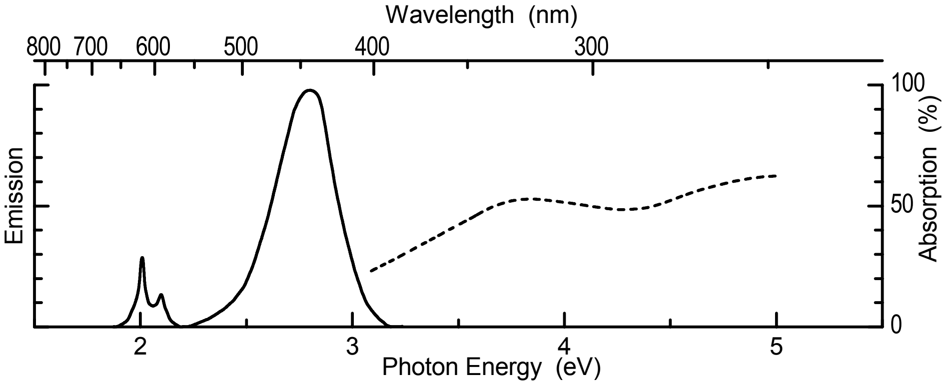
Mix by ball-milling in water.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, CO, 1200ºC, 1 hour.
   Powderize.
2. Fire in open quartz boats, CO, 1200ºC, 1 hour.
   Wash in a solution of ~20 g NH_4Cl in 1 liter of water and then several times in plain water.

Optical Properties

Emission color: Deep blue
Emission peak: Single Eu^{2+} band. 2.80 eV
Emission width (FWHM): 0.34 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: ≈ 1%
Decay: ~1 μsec to 1/10

Spectra



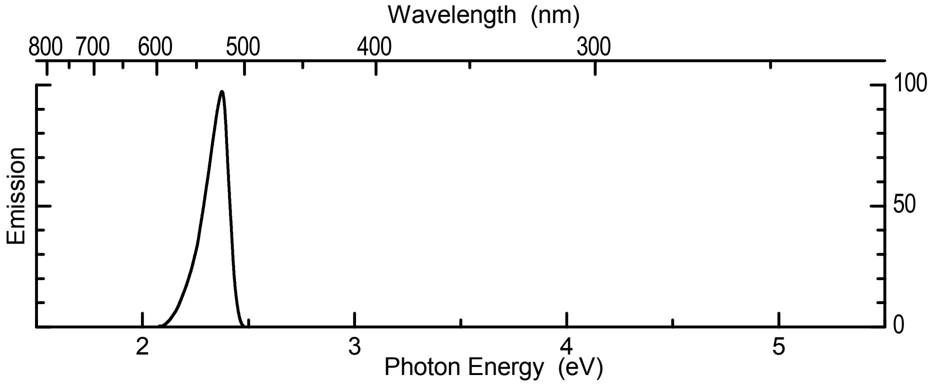
$ZnAl_2O_4:Mn^{2+}$

Structure: Tetragonal (spinel)

Optical Properties

Emission color: Blue-green
Emission peak: 2.41 eV
Emission width (FWHM): 0.13 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



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1. Leverenz, H.W., *An Introduction to Luminescence of Solids,* John Wiley & Sons, New York (1949).
2. Strange, J.W., and Henderson, S.T., Cathodo-luminescence. 1. Growth and decay processes, *P. Phys. Soc. London,* 58, 369 (1946).

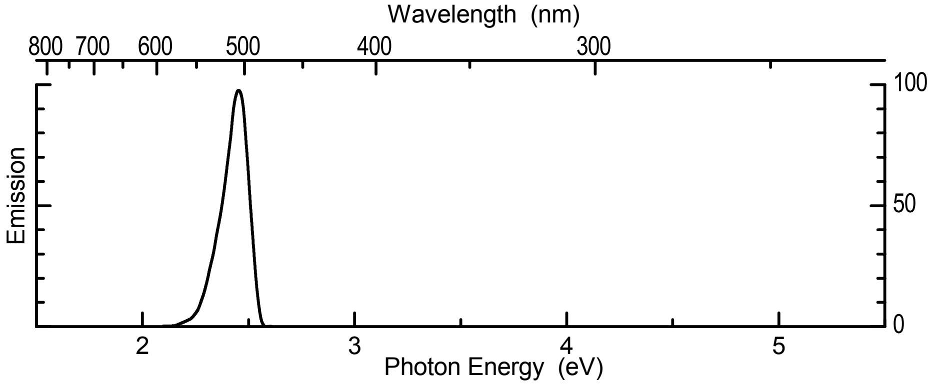
$ZnGa_2O_4$:Mn^{2+}

Structure: Cubic (gahnite)

Optical Properties

Emission color: Blue-green
Emission peak: 2.47 eV
Emission width (FWHM): 0.13 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



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2. Wanmaker, W.L., terVrugt, J.W., and Verlijsdonk, J.G., Luminescence of Mn^{2+}-activated spinels in MgO-Li_2O-ZnO-Ga_2O_3-Al_2O_3 system, *Philips Res. Rep.*, 25, 108 (1970).
3. Wanmaker, W.L., and terVrugt, J.W., Luminescence of gallates, *J. Electrochem. Soc.*, 116, 871 (1969).

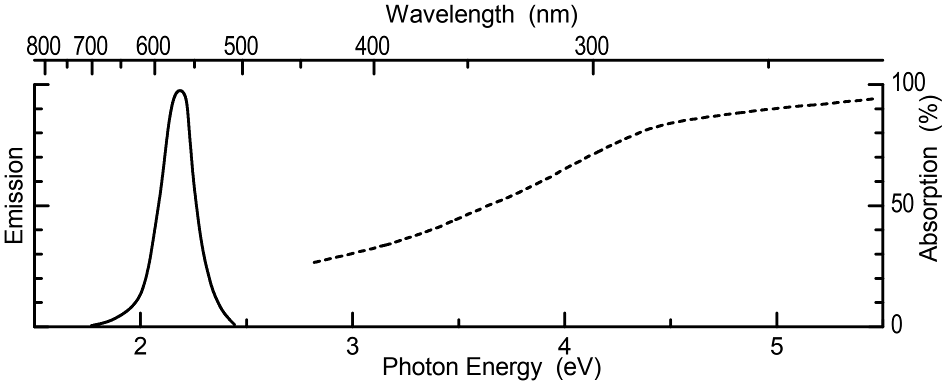
$CaGa_2O_4:Mn^{2+}$

Structure: Monoclinic

Optical Properties

Emission color: Yellow-green
Emission peak: 2.19 eV
Emission width (FWHM): 0.21 eV

Spectra



Reference

1. Brown, J.J., Can. Pat., 821 468 (1970).

$CaGa_4O_7:Mn^{2+}$

Optical Properties

Emission color: Yellow
Emission peak: 2.10 eV
Emission width (FWHM): 0.21 eV

Reference

1. Brown, J.J., Can. Pat., 821 468 (1970).

$SrAl_2O_4:Eu^{2+}$

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	98	145
Al_2O_3	210 (of Al)	107
Eu_2O_3	2 (of Eu)	3.5
NH_4Cl	10	5.4

Preparation

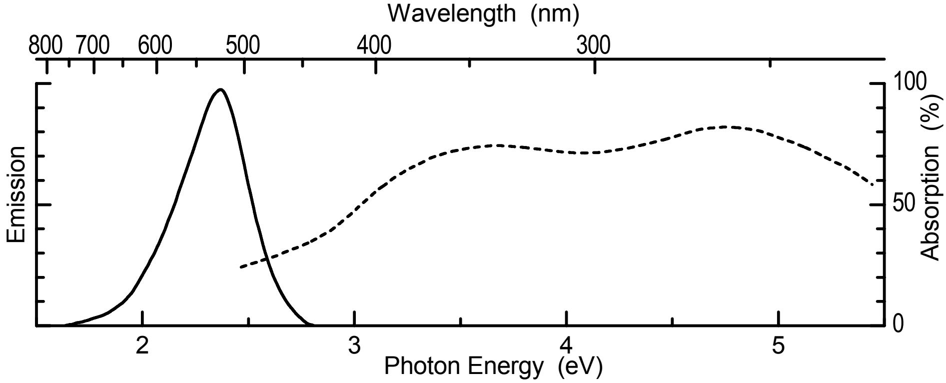
Mix by ball-milling in water.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, CO, 1200ºC, 1 hour.
   Powderize.
2. Fire in open quartz boats, CO, 1200ºC, 1 hour.
   Wash in a solution of ~20 g NH_4Cl in 1 liter of water and then several times in plain water.
   Dry.

Optical Properties

Emission color: Green
Emission peak: 2.37 eV
Emission width (FWHM): 0.34 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +/~1.5%
Decay: ~2 μsec to 1/10

Spectra



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2. Palilla, F.C., Levine, A.K., and Tomkus, M.R., Fluorescent properties of alkaline earth aluminates activated by divalent europium, *J. Electrochem. Soc.,* 115, 642 (1968).
3. Blasse, G., Wanmaker, W.L., and terVrugt, J.W., Some new classes of efficient Eu^{2+} activated phosphors, *J. Electrochem. Soc.,* 115, 673 (1968).
4. Abbruscato, V., Optical and electrical properties of $SrAl_2O_4$-Eu^{2+}, *J. Electrochem. Soc.,* 118, 930 (1971).

$BaAl_2O_4:Eu^{2+}$

Structure: Hexagonal

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	98	193
Al_2O_3	210 (of Al)	107
Eu_2O_3	2 (of Eu)	3.5
NH_4Cl	10	5.4

Preparation

Mix by ball-milling in water.

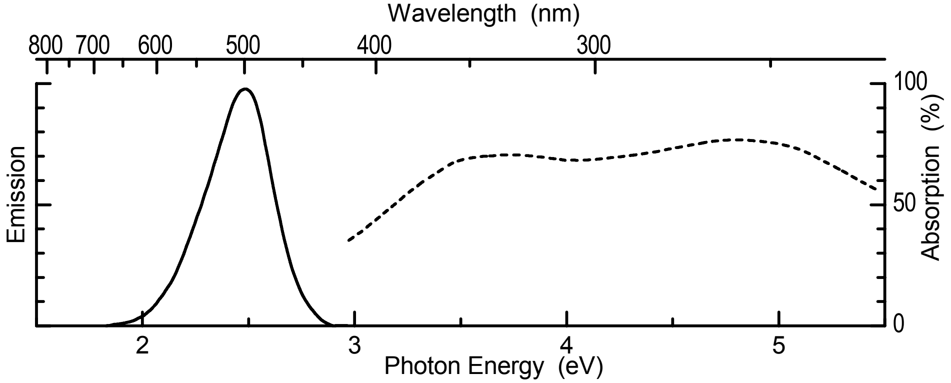
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, CO, 1200ºC, 1 hour.
   Powderize.
2. Fire in open quartz boats, CO, 1200ºC, 1 hour.
   Wash in a solution of ~20 g NH_4Cl + 20 ccm NH_4OH in 1 liter of water and then several times in diluted ammonium hydroxide.
   Dry.

Optical Properties

Emission color: Blue-green
Emission peak: 2.47 eV
Emission width (FWHM): 0.35 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



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2. Blasse, G., Wanmaker, W.L., and terVrugt, J.W., Some new classes of efficient Eu^{2+} activated phosphors, *J. Electrochem. Soc.,* 115, 673 (1968).
3. Blasse, G., and Bril, A., Phosphors based on lanthanide oxysulphates (Ln_2SO_6), *Philips Res. Rep.*, 23, 461 (1968).

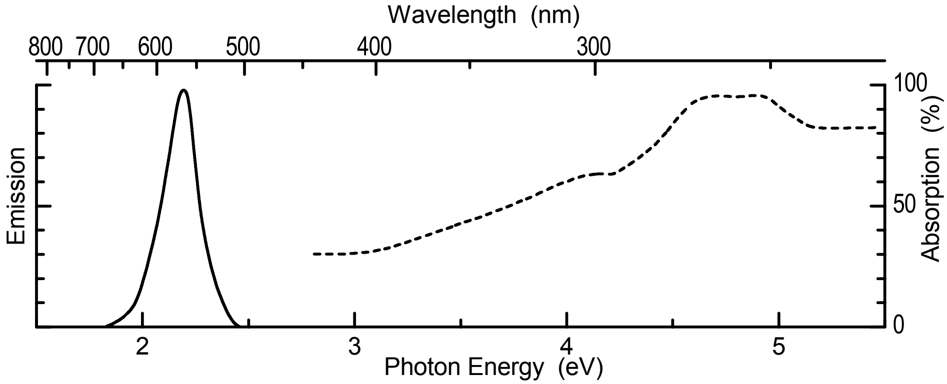
$CaAl_4O_7:Pb^{2+},Mn^{2+}$

Structure: Monoclinic

Optical Properties

Emission color: Yellow
Emission peak: 2.20 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



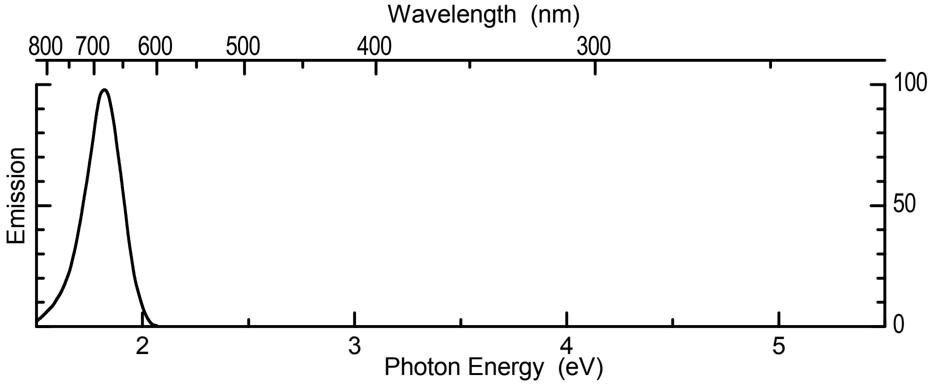
$LiAl_5O_8:Fe^{3+}$

Structure: Cubic (spinel)

Optical Properties

Emission color: Very deep red
Emission peak: 1.82 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



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2. Melamed, N.T., Viccaro, P.J., Barros, F.D.S. et al., Optical properties of Fe^{3+} in ordered and disordered $LiAl_5O_8$, *Phys. Rev. B5,* 3377 (1972).
3. Neto, J.M., Abritta, T., Barros, F.D. et al., A comparative-study of the optical-properties of Fe^{3+} in ordered $LiGa_5O_8$ and $LiAl_5O_8$, *J. Lumin.*, 22, 109 (1981).

$LiAl_5O_8:Mn^{2+}$

Structure: Cubic (spinel)

Composition

Ingredient	Mole %	By weight (g)
Li_2CO_3	99 (of Li)	36.6
Al_2O_3	499 (of Al)	254
$MnCO_3$	2	2.3

Preparation

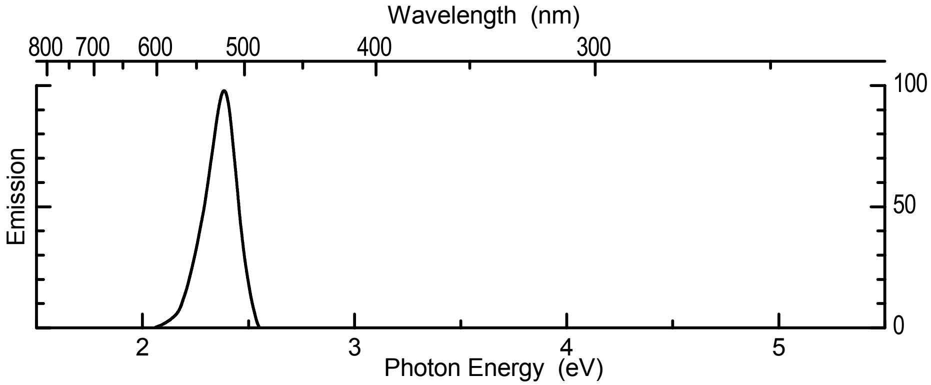
Mix by slurrying in methanol.
Dry in air. Powderize when dry.

1. Fire in open alumina crucibles, N_2, 1200ºC, 1 hour.
   Powderize.
2. Fire in open quartz boats, CO, 1250ºC, 2 hours.

Optical Properties

Emission color: Green
Emission peak: 2.38 eV
Emission width (FWHM): 0.15eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +/~6–8%
Decay: Non-exponential decay, 1/10 time in the 10 msec range; long and strong phosphorescence

Spectra



Reference

1. Jaffe, P.M., Cathodoluminescence spectra and coordination of Mn^{2+} Fe^{3+} and Cr^{3+} in $BeTaLiAl_5O_8$, *J. Electrochem. Soc.,* 115, 1203 (1968).

$Y_4Al_2O_9$:Eu^{3+}

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	95 (of Y)	84.5
Al_2O_3	50 (of Al)	25.5
Eu_2O_3	5 (of Eu)	8.8
H_3BO_3	10	6.2

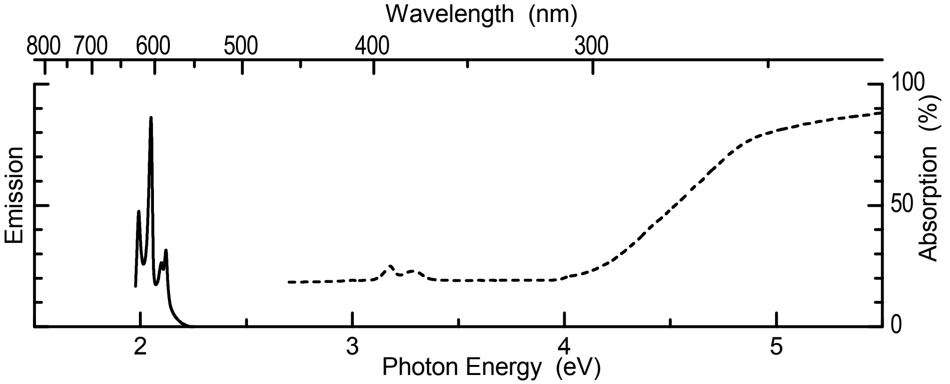
Preparation

Mix by dry grinding or milling.
1. Fire in covered alumina crucibles, air, 1000ºC, 1 hour.
   Powderize.
2. Fire in covered alumina crucibles, air, 1300ºC, 4 hours.

Optical Properties

Emission color: Light red
Emission peaks: Mainly three lines about 1.975, 2.03 eV, and 2.10 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



$Y_3Al_5O_{12}$:Ce^{3+}

Structure: Cubic (garnet)

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	35.5 (of Y)	40
Al_2O_3	62.5 (of Al)	32
CeO_2	2	3.44
NH_4Cl	5	2.7

Preparation

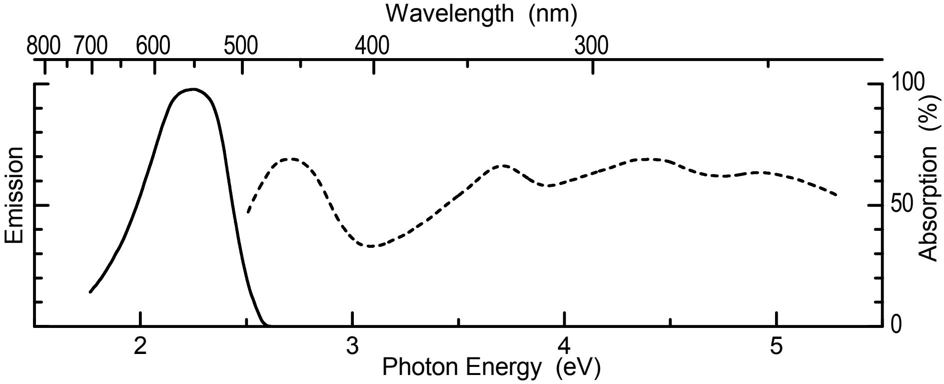
Mix by slurrying in water.

1. Fire in capped quartz tubes, CO, 1300ºC, 1 hour. Powderize.
   Add another 2.7 g NH_4Cl; mix by dry grinding.
2. Fire in capped quartz tubes, 1300ºC, 2 hours. Powderize.
3. Fire in open quartz boats, CO, 1300ºC, 1 hour.

Optical Properties

Emission color: Yellow-green
Emission peak: 2.37 eV
Emission width (FWHM): ~0.45 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +/~2%

Spectra



References

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2. Blasse, G., Bril, A., and Poorter, J.A.D., Radiationless transitions in Eu^{3+} center in $LaAlO_3$, *J. Chem. Phys.,* 53, 4450 (1970).
3. Blasse, G., and Bril, A., Gibbons, E.F. et al., Ce^{3+} activated $Y_3Al_5O_{12}$ and some of its solid-solutions, *J. Electrochem. Soc.,* 120, 278 (1973); and Gibbons, E.F. et al., Some factors influencing luminous decay characteristics of $Y_3Al_5O_{12}$ - Ce^{3+} , *J. Electrochem. Soc.,* 120, 835 (1973).
4. Tien, T.Y. et al., Ce^{3+} activated $Y_3Al_5O_{12}$ and some of its solid-solutions, *J. Electrochem. Soc.,* 102, 278 (1973).
5. Sang, E., The signal generation mechanism in bistable storage-scan converters, *SID Digest*, 104 (1973).

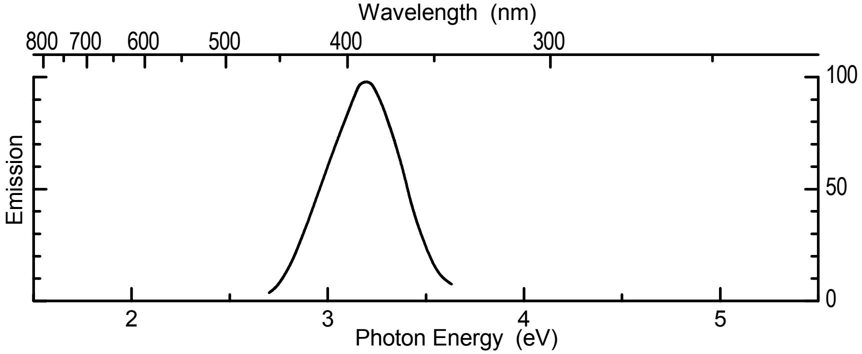
$KAl_{11}O_{17}$:Tl^+

Structure: Aluminate

Optical Properties

Emission color: Violet + UV
Emission peak: 3.14 eV
Emission width (FWHM): 0.49 eV
Excitation efficiency by UV: ++ (4.88 eV)

Spectra



References (see below)

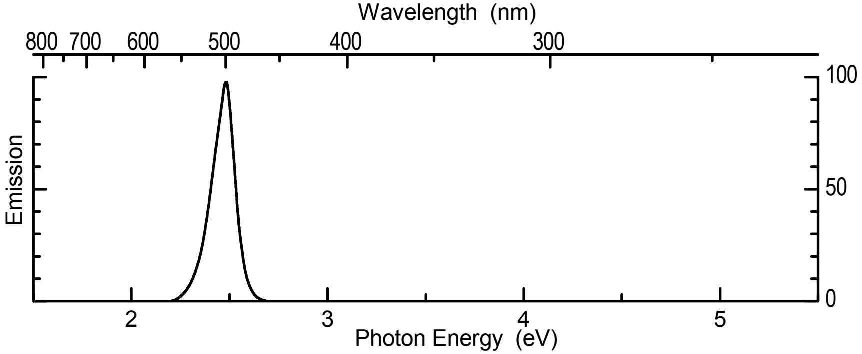
$KGa_{11}O_{17}:Mn^{2+}$

Structure: Aluminate

Optical Properties

Emission color: Blue-green
Emission peak: 2.49 eV
Emission width (FWHM): 0.14 eV

Spectra



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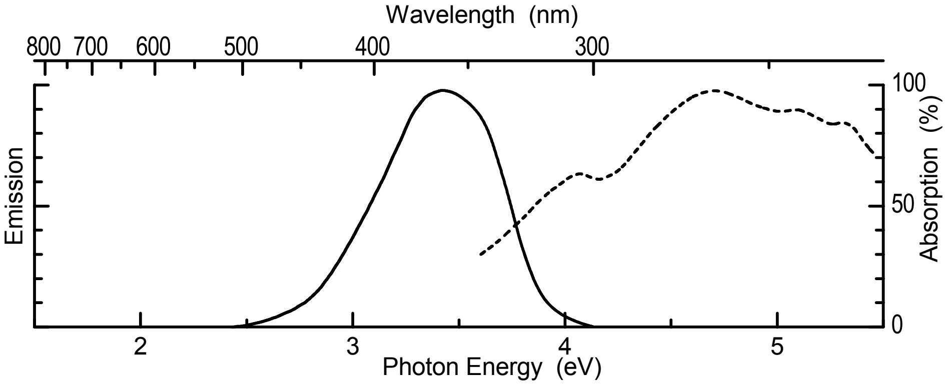
$BaMgAl_{10}O_{17}:Ce^{3+}$

Structure: Aluminate

Optical Properties

Emission color: UV
Emission peak: 3.40 eV
Emission width (FWHM): 0.65 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



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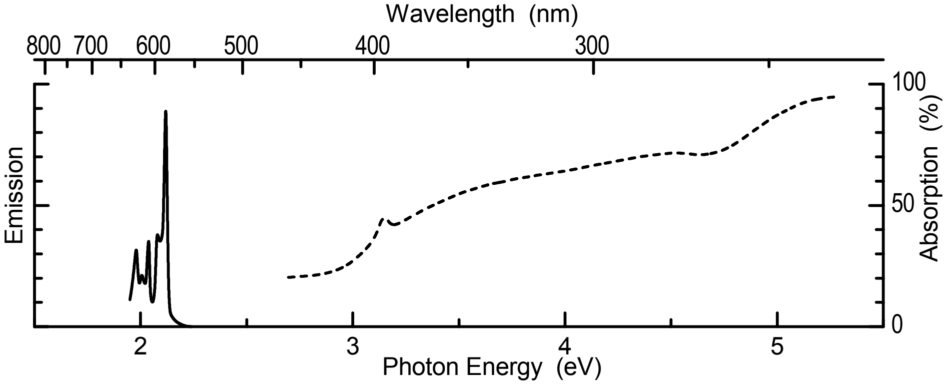
$Y_3Al_5O_{12}$:Eu^{3+}

Structure: Cubic (garnet)

Optical Properties

Emission color: Orange-yellow
Emission peak: 2.10 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra



$BaMgAl_{10}O_{17}:Eu^{2+}$

Structure: Aluminate

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	80	158
MgO	100	40
Al_2O_3	1050 (of Al)	536
Eu_2O_3	10 (of Eu)	17.6
BaF_2	10	17.5

Preparation

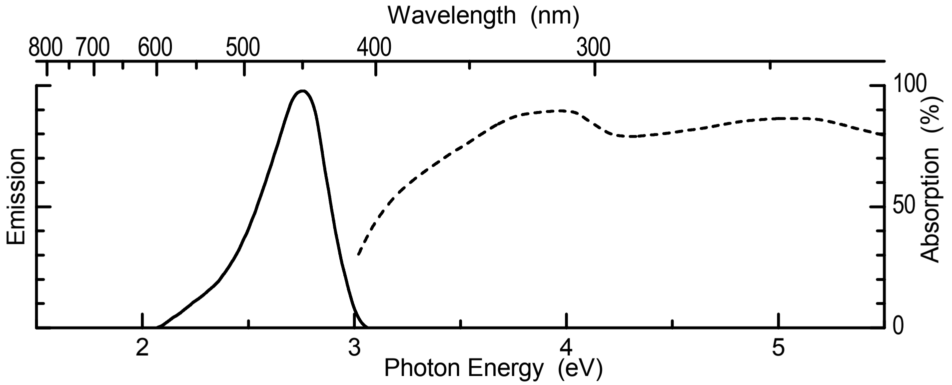
Mix by ball-milling in methanol.
Dry in air. Powderize when dry.

1. Fire in covered alumina crucibles, N_2, 1250ºC, 1 hour. Powderize.
2. Fire in open quartz boats, forming gas, 1250ºC, 1 hour.

Optical Properties

Emission color: Blue
Emission peak: 2.77 eV
Emission width (FWHM): 0.34 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



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$BaMgAl_{10}O_{17}$:Eu^{2+},Mn^{2+}

Structure: Aluminate

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	80	158
MgO	70	28.2
Al_2O_3	1050 (of Al)	536
Eu_2O_3	10	17.6
$MnCO_3$	24	27.6
BaF_2	10	17.5

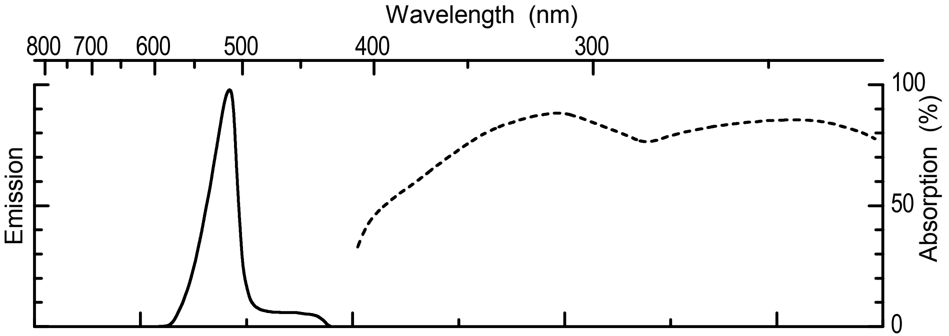
Preparation

Mix by ball-milling in methanol.
Dry in air. Powderize when dry.
1. Fire in open quartz boats, 500–600°C, ½ hour.
2. Fire in covered alumina crucibles, CO, 1250°C, 1 hour. Powderize.
3. Fire in open quartz boats, forming gas, 1250°C, 1 hour.

Optical Properties

Emission color: Bluish-green
Emission peak: 2.40 eV
Emission width (FWHM): 0.13 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Remark

This phosphor retains its high efficiency to several 100°C. It may be useful for color correction in arc lamps.

References

1. Stevels, A.L.N., and Schrama, A.D.M., Vapor-deposited CSi-Na layers. 1. Morphologic and crystallographic properties, *Philips Res. Rep.*, 29, 340 (1974).
2. Stevels, A.L.N., and Schrama, A.D.M., *J. Electrochem. Soc.,* 123, 691 (1974).

$Ca_{0.5}Ba_{0.5}Al_{12}O_{19}$:$Ce^{3+}$,$Mn^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	25	25
CaF_2	10	7.8
$BaCO_3$	35	69
Al_2O_3	1210 (of Al)	617
CeO_2	30	51.6
$MnCO_3$	24	27.6

Preparation

Mix by ball-milling in methanol.

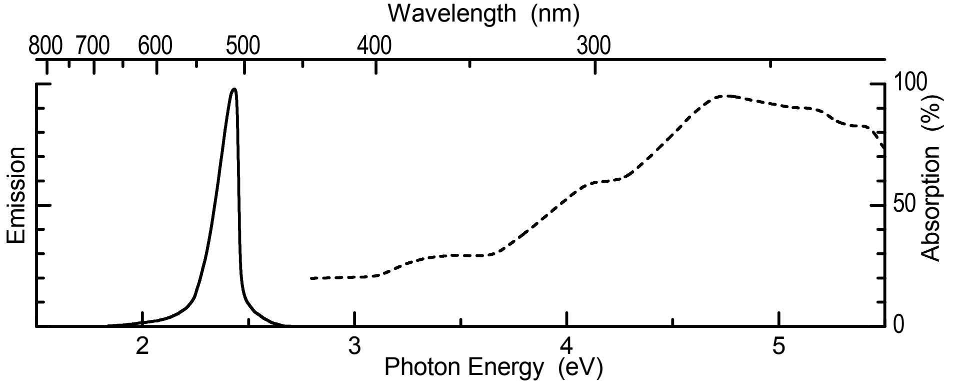
Dry in air. Powderize when dry.

1. Fire in open quartz boats, N_2, ~500–600°C, ~½ hour.
2. Fire in covered alumina crucibles, CO, 1250°C, 1 hour.
   Powderize.
3. Fire in open quartz boats, forming gas, 1250°C, 1 hour.

Optical Properties

Emission color: Bluish-green
Emission peak: 2.41 eV
Emission width (FWHM): 0.125 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: ~2–2.5%
Decay: Near-exponential decay, ~15 msec to 1/10

Spectra



Remarks

1. This phosphor retains its high efficiency up to several 100°C.
2. This phosphor is sensitive to lamp-lehring conditions but very stable once it is in the lamp.

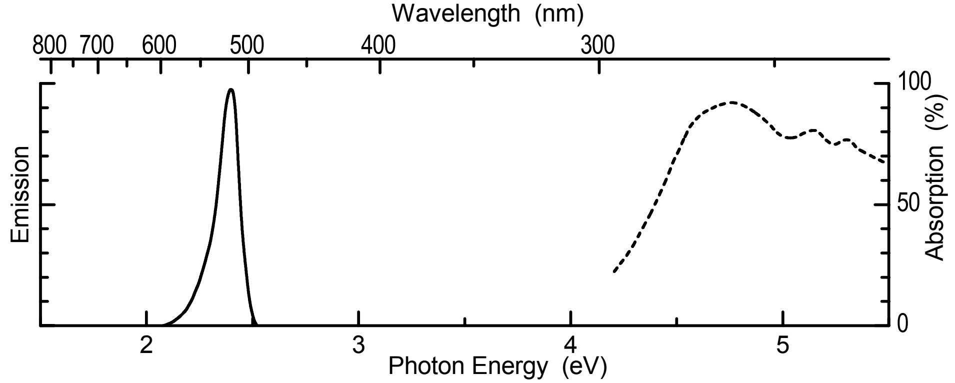
Reference

1. Stevels, A.L.N., and Verstegen, J.M.P.J., Eu^{2+}-Mn^{2+} energy-transfer in hexagonal aluminates, *J. Lumin.,* 14, 207 (1976).

$SrAl_{12}O_{19}:Eu^{2+},Mn^{2+}$

Structure: Aluminate

Spectra



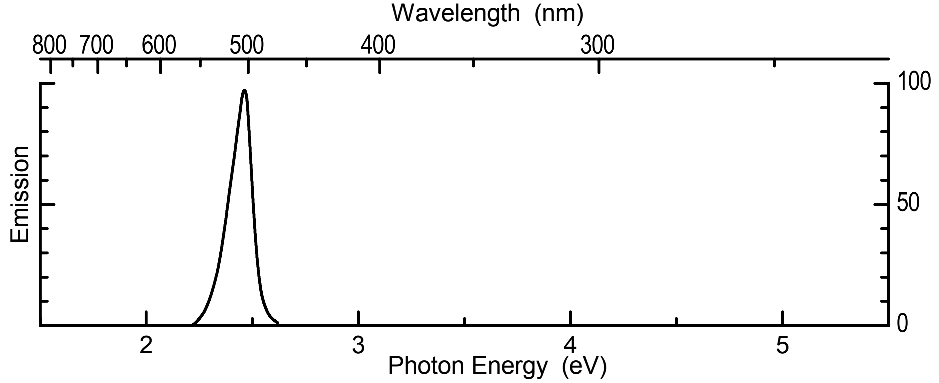
$SrGa_{12}O_{19}:Mn^{2+}$

Structure: Aluminate

Optical Properties

Emission color: Blue-green
Emission peak: 2.47 eV
Emission width (FWHM): 0.12 eV
Excitation efficiency by e-beam: +

Spectra



References

1. Verstegen, J.M., Survey of a group of phosphors, based on hexagonal aluminate and gallate host lattices, *J. Electrochem. Soc.,* 121, 1623 (1974).
2. Verstegen, J.M.P.J., Somerdijk, J.L., and Bril, A., Luminescence of $LiBaF_3:Eu^{2+}$, *J. Lumin.,* 10, 411 (1975).

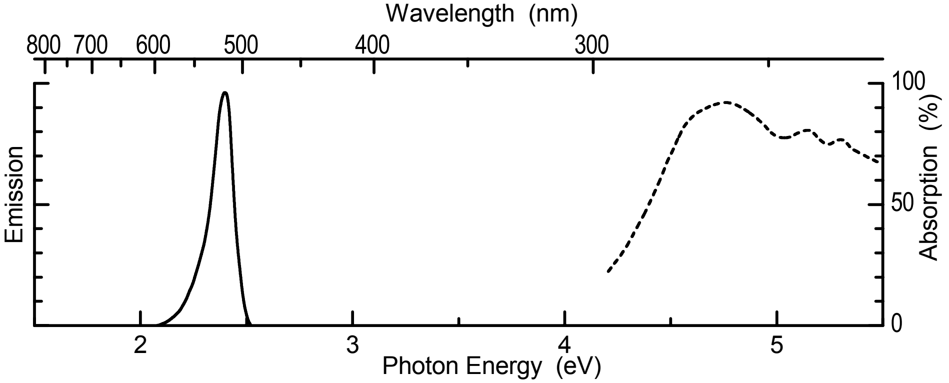
$SrAl_{12}O_{19}:Ce^{3+},Mn^{2+}$

Structure: Aluminate

Optical Properties

Emission color: Green
Emission peak: 2.39 eV
Emission width (FWHM): 0.14 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Reference

1. Stevels, A.L.N., and Verstegen, J.M.P.J. Eu^{2+}-Mn^{2+} energy-transfer in hexagonal aluminates, *J. Lumin.,* 14, 207 (1976).

4.9 Molybdates and Tungstates

The following host compounds and activators are included in this subsection:

$CaMoO_4$
$CaMoO_4$:Eu^{3+}
$SrMoO_4$:U
$MgWO_4$
$CaWO_4$
Ca_3WO_6:U
Sr_3WO_6:U
Ba_3WO_6:U
$La_2W_3O_{12}$:Eu^{3+}

$CaMoO_4$

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
MoO_3	98	141

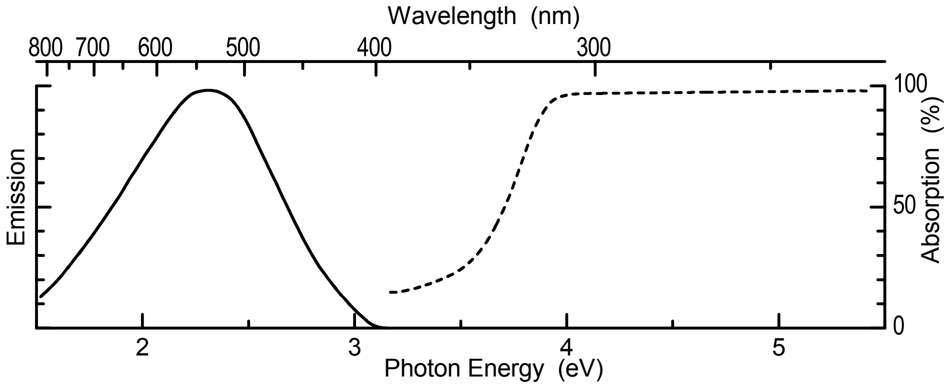
Preparation

Mix by dry grinding or milling.
1. Fire in open quartz boats, air, 1000°C, 1 hour.
   Powderize.
2. Fire in open quartz boats, air, 1100°C, 1 hour.

Optical Properties

Emission color: Pale yellow-green
Emission peak: ~2.34 eV
Emission width (FWHM): ~0.82 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra



$CaMoO_4:Eu^{3+}$

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	90	90
Eu_2O_3	5 (of Eu)	8.8
$NaHCO_3$	5	4.2
MoO_3	105	151

Preparation

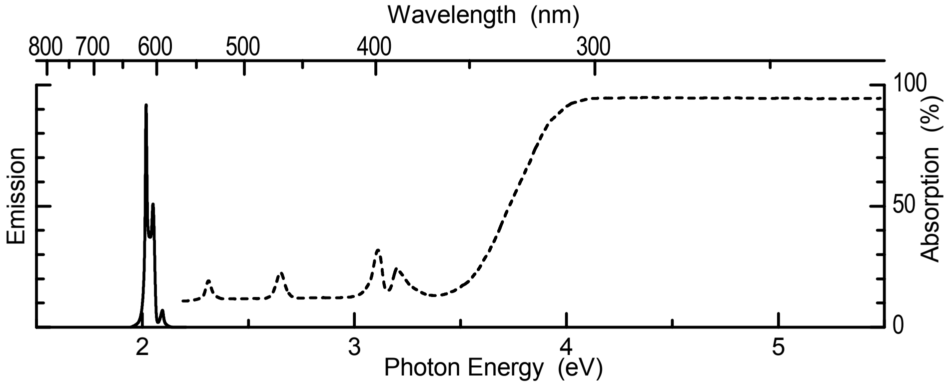
Mix by dry grinding or milling.

1. Fire in open quartz boats, air, 1000ºC, 1 hour.
   Powderize.
2. Fire in open quartz boats, O_2, 1100ºC, 1 hour.
   Powderize.
   Wash in a strong solution of NaOH (or KOH) in water and then several times in plain water until neutral.
   Dry.

Optical Properties

Emission color: Red
Emission peaks: ~2.02 and ~2.03 eV
Excitation efficiency by UV: ++ (4.88 eV)
Excitation efficiency by e-beam: ~0.5–1%

Spectra



$SrMoO_4:U$

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	100	148
MoO_3	105	151
$UO_2(NO_3)_2 \cdot 6H_2O$	0.2	1
Li_2CO_3	2 (of Li)	0.740

Preparation

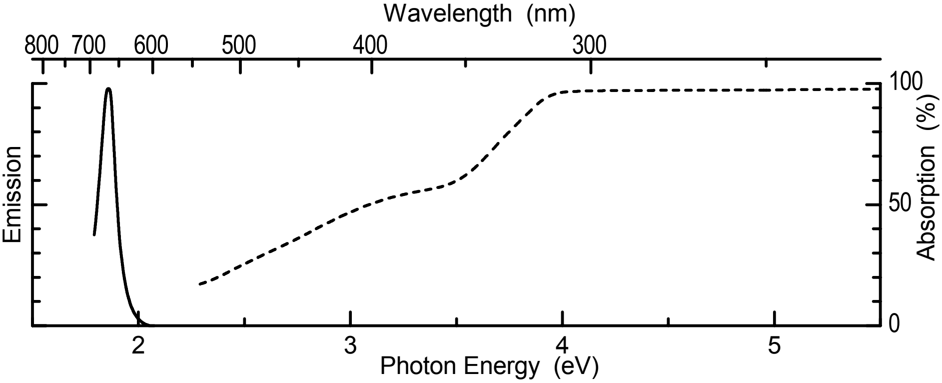
Dissolve the U-nitrate in a little methanol; add this solution to the other ingredients.
Add methanol to make a uniform slurry.
Dry in air. Powderize when dry.

1. Fire in open quartz boats, air, 800°C, 1 hour.
   Powderize.
2. Fire in open quartz boats, O_2, 1000°C, 2 hours.
   Powderize.
   Wash in a strong solution of NaOH (or KOH) in water and then several times in plain water until neutral.
   Dry.

Optical Properties

Emission color: Deep red
Emission peak: ~1.875 eV
Excitation efficiency by UV: – (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: −

Spectra



$MgWO_4$

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
MgO	120	48
WO_3	100	232

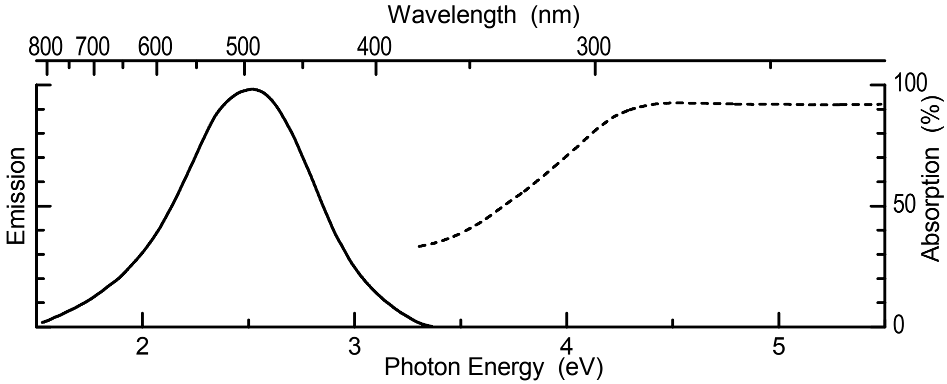
Preparation

Mix by slurrying in water.
Dry in air. Powderize when dry.
Fire in open quartz boats, O_2, 1200°C, 16 hours (overnight).

Optical Properties

Emission color: Blue-greenish white
Emission peak: 2.50 eV
Emission width (FWHM): 0.75 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: ~2.5%
Decay: Near-exponential decay, ~20 µsec to 1/10

Spectra



CaWO$_4$

Structure: Tetragonal (scheelite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	105	105
WO_3	100	232

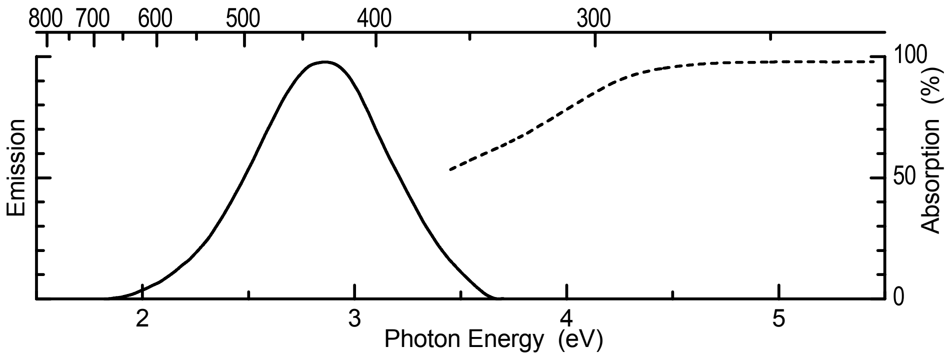
Preparation

Mix by slurrying in water.
Dry in air. Powderize when dry.
Fire in open quartz boats, O_2, 1200ºC, ~16 hours (overnight).

Optical Properties

Emission color: Pale blue
Emission peak: 2.87 eV
Emission width (FWHM): 0.77 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: ~2–2.5%
Decay: Near-exponential decay, ~10 μsec to 1/10

Spectra



Remark

This material is completely intersoluble with CaMoO$_4$ in any proportion.

References

1. Kröger, F.A., *Some Aspects of Luminescence of Solids*, Elsevier, Amsterdam (1948).
2. Cook, J.R., Photoconductivity in calcium tungstate, *P. Phys. Soc. London. B,* 68, 148 (1955).
3. Gobrecht, H., and Weiss, W., Lumineszenzuntersuchungen an uran-aktivierten erdalkaliwolframaten und erdalkalimolybdaten, *Z. Phys.*, 140, 139 (1955).
4. Grasser, R., and Scharmann, A., Luminescent sites in $CaWO_4$ and $CaWO_4$:Pb crystals, *J. Lumin.,* 12, 473 (1976).

Ca_3WO_6:U

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	300	300
WO_3	100	232
$UO_2(NO_3)_2{\cdot}6H_2O$	0.2	1
Li_2CO_3	2 (of Li)	0.740

Preparation

Dissolve the U-nitrate in a little methanol; add this solution to the other ingredients. Add methanol to make a uniform slurry.

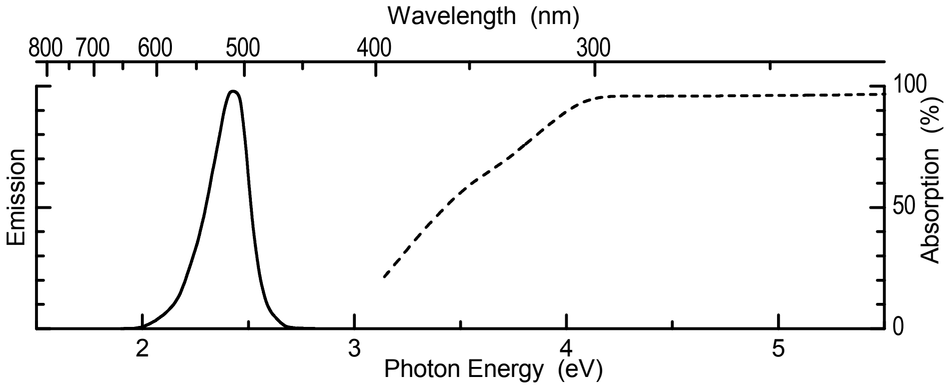
Dry in air. Powderize when dry.

1. Fire in open quartz boats, air, 900°C, 1 hour.
   Powderize by grinding or milling.
2. Fire in open quartz boats, O_2, 1200°C, 2 hours.

Optical Properties

Emission color: Green
Emission peak: 2.41 eV
Emission width (FWHM): 0.23 eV
Excitation efficiency by UV: – (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: –

Spectra



Remark

U is non-luminescent in $CaWO_4$.

References

1. Kröger, F.A., *Some Aspects of Luminescence of Solids*, Elsevier, Amsterdam (1948).
2. Garlick, G.F.J., and Gibson, A.F., The luminescence of photo-conducting phosphors, *J. Opt. Soc. Am.,* 39, 935 (1949).
3. Gobrecht, H., and Weiss, W., Lumineszenzuntersuchungen an uran-aktivierten erdalkaliwolframaten und erdalkalimolybdaten, *Z. Phys.*, 140, 139 (1955).

Sr_3WO_6:U

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	300	443
WO_3	100	232
$UO_2(NO_3)_2 \cdot 6H_2O$	0.2	1
Li_2CO_3	2 (of Li)	0.740

Preparation

Dissolve the U-nitrate in a little methanol; add this solution to the other ingredients. Add methanol to make a uniform slurry.

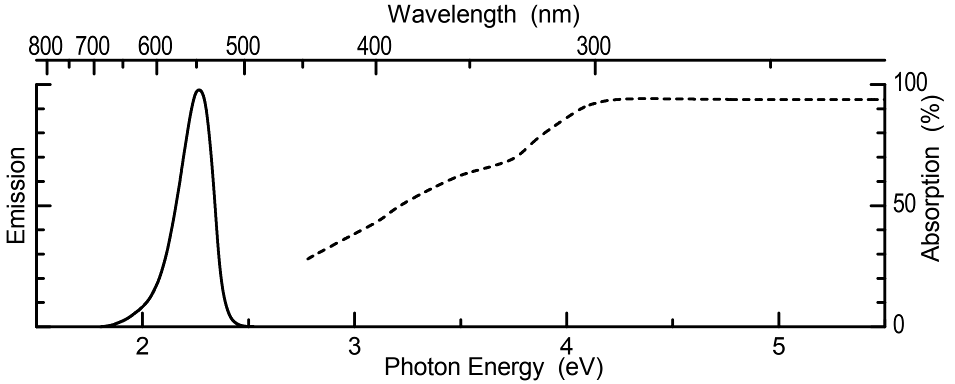
Dry in air. Powderize when dry.

1. Fire in open quartz boats, air, 900°C, 1 hour.
   Powderize by grinding or milling.
2. Fire in open quartz boats, O_2, 1000°C, 2 hours.

Optical Properties

Emission color: Yellow-green
Emission peak: 2.25 eV
Emission width (FWHM): 0.19 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: Poor

Spectra



Remark

U is non-luminescent in $SrWO_4$.

Reference

1. Gobrecht, H., and Weiss, W., Lumineszenzuntersuchungen an uran-aktivierten erdalkaliwolframaten und erdalkalimolybdaten, *Z. Phys.*, 140, 139 (1955).

Ba_3WO_6:U

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	300	592
WO_3	100	232
$UO_2(NO_3)_2{\cdot}6H_2O$	0.2	1
Li_2CO_3	2 (of Li)	0.740

Preparation

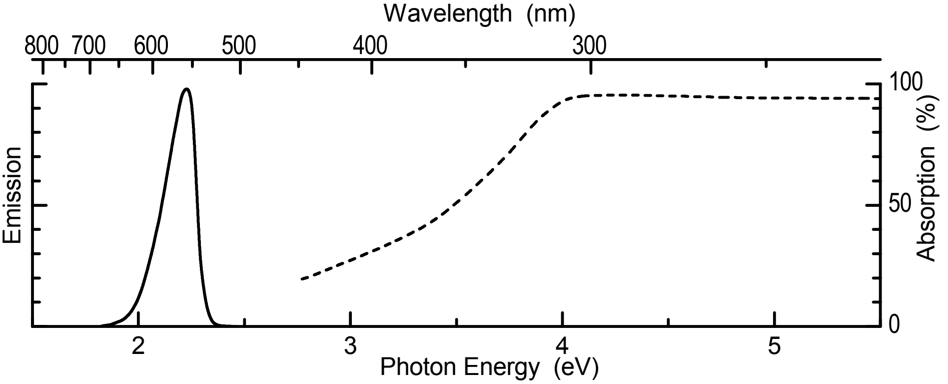
Dissolve the U-nitrate in a little methanol; add this solution to the other ingredients.
Add methanol to make a uniform slurry.
Dry in air. Powderize when dry.

1. Fire in open quartz boats, air, 900ºC, 1 hour.
   Powderize by grinding or milling.
2. Fire in open quartz boats, O_2, 1000ºC, 2 hours.

Optical Properties

Emission color: Green-yellow
Emission peak: 2.20 eV
Emission width (FWHM): 0.17 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: Poor

Spectra



Remark

U is non-luminescent in $BaWO_4$.

References

1. Gobrecht, H., and Weiss, W., Lumineszenzuntersuchungen an uran-aktivierten erdalkaliwolframaten und erdalkalimolybdaten, *Z. Phys.*, 140, 139 (1955).
2. Alberda, R.H., and Blasse, G., Luminescence in a new garnet phase with hexavalent metal-ions, *J. Lumin.,* 12–13, 687 (1976).

$La_2W_3O_{12}:Eu^{3+}$

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	190 (of La)	310
Eu_2O_3	10 (of Eu)	17.6
WO_3	300	696

Preparation

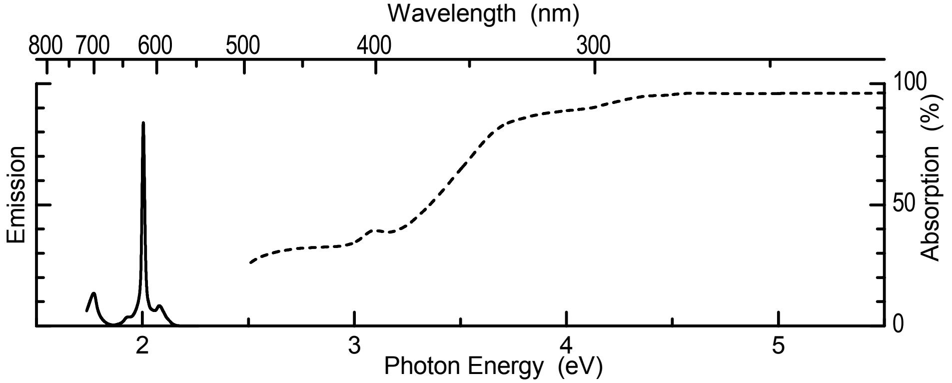
Mix by dry grinding or milling.

1. Fire in open quartz boats, air, 1000ºC, 1 hour.
   Powderize.
2. Fire in open quartz boats, air, 1100ºC, 1 hour.

Optical Properties

Emission color: Red
Emission peak: Strongest line at 2.018 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra



4.10 Miscellaneous Oxides

The following host compounds and activators are included in this subsection:

$LiInO_2:Eu^{3+}$
$LiInO_2:Sm^{3+}$
$LiLaO_2:Eu^{3+}$
$NaYO_2:Eu^{3+}$
$CaTiO_3:Pr^{3+}$
$CaGeO_3:Mn^{2+}$
$Mg_2TiO_4:Mn^{4+}$
$Zn_2GeO_4:Mn^{2+}$
$YVO_4:Eu^{3+}$
$LaVO_4:Eu^{3+}$
$YAsO_4:Eu^{3+}$
$LaAsO_4:Eu^{3+}$
$Ca_5(VO_4)_3Cl$
$Mg_8Ge_2O_{11}F_2:Mn^{4+}$
$CaY_2ZrO_6:Eu^{3+}$
$Mg_3SiO_3F_4:Ti^{4+}$

$LiInO_2:Eu^{3+}$

Structure: tetragonal

Composition

Ingredient	Mole %	By weight (g)
In_2O_3	98 (of In)	136
Eu_2O_3	2 (of Eu)	3.5
Li_2CO_3	101 (of Li)	37.4

Preparation

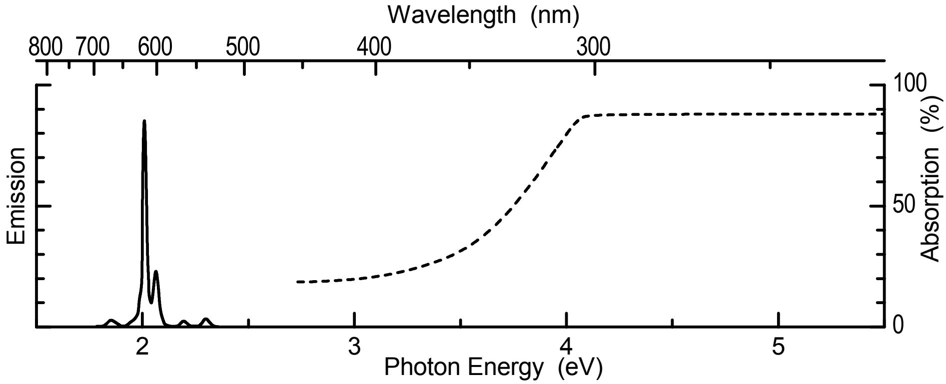
Mix by slurrying in methanol.

1. Fire in open alumina crucibles, air, 700ºC, 1 hour.
   Powderize.
2. Fire in open alumina crucibles, air, 950ºC, 1 hour.

Optical Properties

Emission color: Red
Emission peaks: 2.03 eV and 2.08 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV); weakly excited at 4.0 eV
Excitation efficiency by e-beam: ~5%

Spectra



Reference

1. Blasse, G., and Bril, A., On Eu^{3+} fluorescence in mixed metal oxides. 5. Eu^{3+} fluorescence in rocksalt lattice, *J. Chem. Phys.,* 45, 3327 (1966).

$LiInO_2:Sm^{3+}$

Structure: tetragonal

Composition

Ingredient	Mole %	By weight (g)
In_2O_3	99.7 (of In)	138
Sm_2O_3	0.3 (of Sm)	0.520
Li_2CO_3	101 (of Li)	37.4

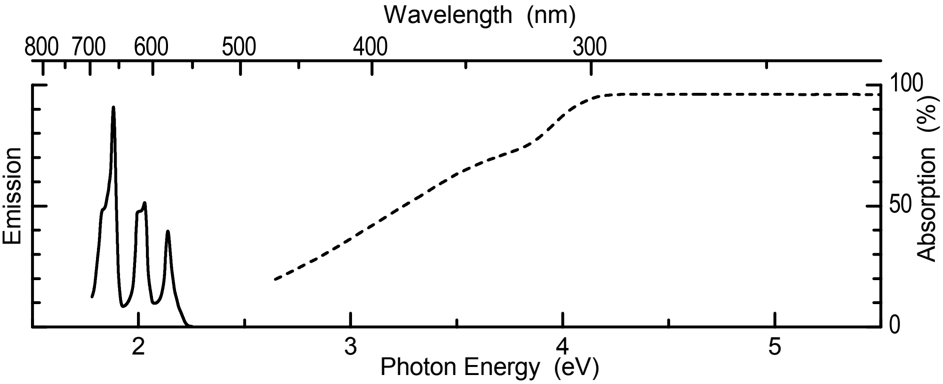
Preparation

Mix by slurrying in methanol.
Dry in air. Powderize when dry.
1. Fire in open alumina crucibles, air, 700ºC, 1 hour.
Powderize.
2. Fire in open alumina crucibles, air, 950ºC, 1 hour.

Optical Properties

Emission color: Orange
Emission peaks: 1.85–2.15 eV
Excitation efficiency by UV: + (4.88 eV), − (3.40 eV)
Excitation efficiency by e-beam: ~5%

Spectra



$LiLaO_2:Eu^{3+}$

Structure: tetragonal

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	95 (of La)	155
Eu_2O_3	5 (of Eu)	8.8
Li_2CO_3	101 (of Li)	37.4

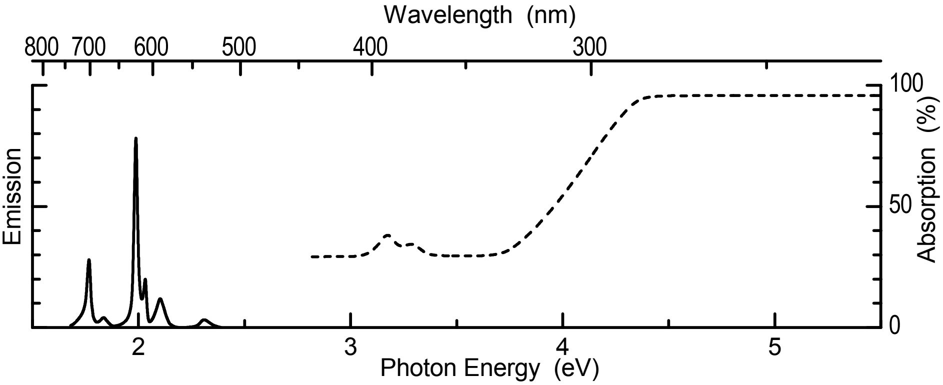
Preparation

Mix by slurrying in methanol.
Dry in air. Powderize when dry.
1. Fire in open alumina crucibles, air, ~600ºC.
   Powderize.
2. Fire in open alumina crucibles, air, 1000ºC, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Red
Emission peaks: 1.775–2.02 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: ~1%

Spectra



Remarks

1. This material is difficult to prepare; the reaction between Li_2CO_3 and La_2O_3 apparently does not go to completion.
2. This phosphor is slightly hygroscopic.

Reference

1. Blasse, G., and Bril, A., On Eu^{3+} fluorescence in mixed metal oxides. 5. Eu^{3+} fluorescence in rocksalt lattice, *J. Chem. Phys.,* 45, 3327 (1966).

$NaYO_2$:Eu^{3+}

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	95 (of Y)	108
Eu_2O_3	5 (of Eu)	8.8
$NaHCO_3$	101	85

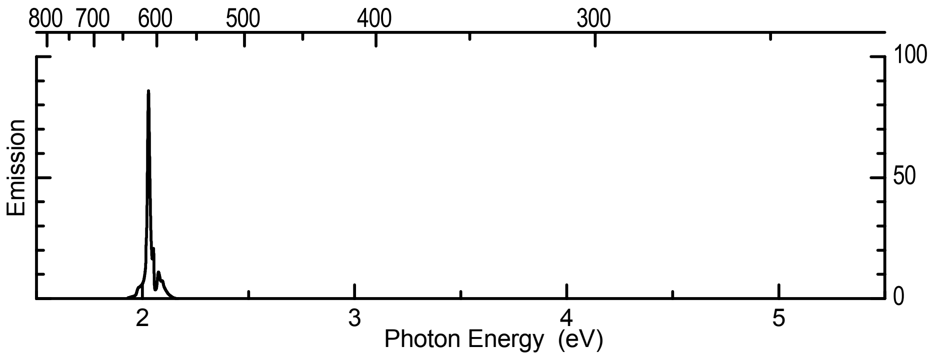
Preparation

Mix by slurrying in methanol.
Dry in air. Powderize when dry.
1. Fire in open alumina crucibles, air, ~600ºC, ½ hour.
Powderize.
2. Fire in open alumina crucibles, air, 900ºC, 1 hour.
Powderize.
Store in a well-closed container.

Optical Properties

Emission color: Red
Emission peak: 2.025 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra



Remarks

1. This material is difficult to prepare; the reaction between Na_2O and Y_2O_3 apparently does not go to completion.
2. This phosphor is slightly hygroscopic.

Reference

1. Blasse, G., and Bril, A., On Eu^{3+} fluorescence in mixed metal oxides. 5. Eu^{3+} fluorescence in rocksalt lattice, *J. Chem. Phys.,* 45, 3327 (1966).

$CaTiO_3$:Pr^{3+}

Structure: Cubic (perovskite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
Pr_3O_4	1	1.64
TiO_2	100	80

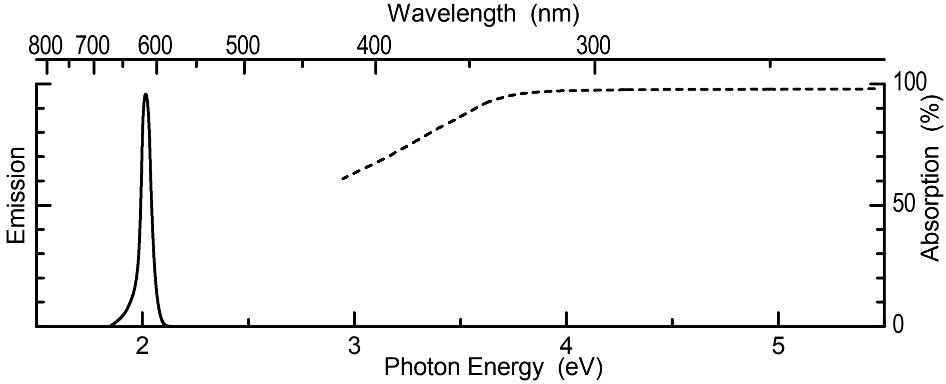
Preparation

Mix by slurrying in methanol.
Dry in air. Powderize when dry.
1. Fire in open quartz boats, air, 1300ºC, 1 hour.
Powderize by grinding or milling.
2. Fire in open quartz boats, air, 1300ºC, 1 hour.

Optical Properties

Emission color: Red
Emission peak: 2.025 eV
Emission width (FWHM): 0.05 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)

Spectra



Remark

The efficiency of this phosphor is not likely improvable because of:

(a) much "dead" absorption of the Ti^{4+}-ion in the UV,
(b) most likely an appreciable amount of emission in the IR.

$CaGeO_3:Mn^{2+}$

Structure: Orthorhombic (wollastonite)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	98	98
$MnCO_3$	2	2.3
GeO_2	105	110
NH_4Br	2	2

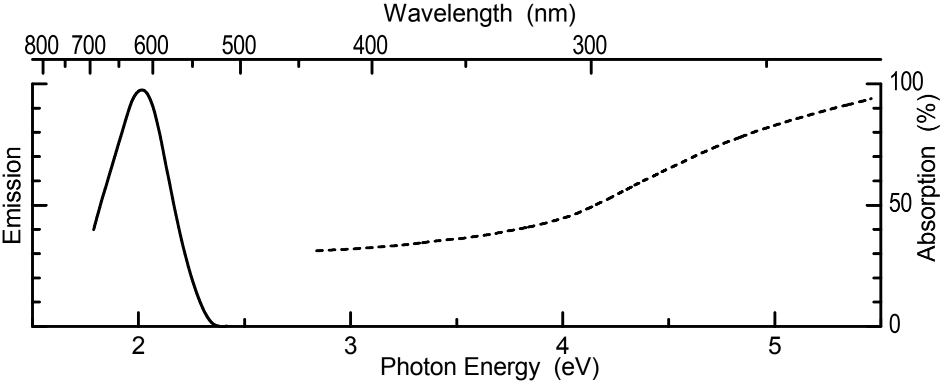
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in capped quartz tubes, CO, 1150ºC, 2 hours.

Optical Properties

Emission color: Orange
Emission peak: 2.01 eV
Emission width (FWHM): 0.30 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Remark

The excitation efficiency of QE ~50–60% under 4.88 eV was observed without addition of a sensitizer to the phosphor. Attempts to improve this efficiency by addition of various other impurities failed.

Reference

1. Koelmans, H., and Verhagen, C.M.C., The fluorescence of binary and ternary germanates of group-II elements, *J. Electrochem. Soc.,* 106, 677 (1959).

$Mg_2TiO_4:Mn^{4+}$

Structure: Cubic (spinel)

Composition

Ingredient	Mole %	By weight (g)
MgO	300	121
TiO_2	99	79
$MnCO_3$	1	1.15

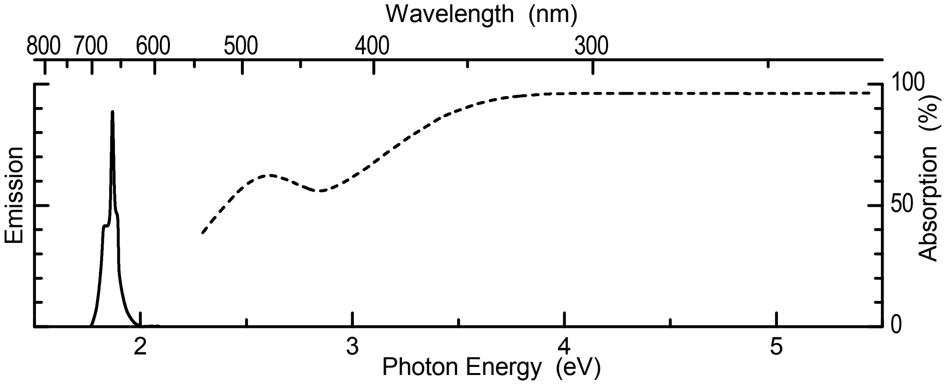
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
1. Fire in open quartz boats, air, 1300°C, 1 hour.
   Powderize by grinding or milling.
2. Fire in open quartz boats, O_2, 570°C, ~16 hours (overnight).

Optical Properties

Emission color: Deep red
Emission peak: 1.885 eV
Excitation efficiency by UV: – (4.88 eV), + (3.40 eV)

Spectra



Reference

1. Kröger, F.A., *Some Aspects of Luminescence of Solids*, Elsevier, Amsterdam (1948).

$Zn_2GeO_4:Mn^{2+}$

Structure: Tetragonal (willemite)

Composition

Ingredient	Mole %	By weight (g)
ZnO	90	73.2
MgF_2	5	3.1
$MnCO_3$	5	5.8
GeO_2	55	57.5

Preparation

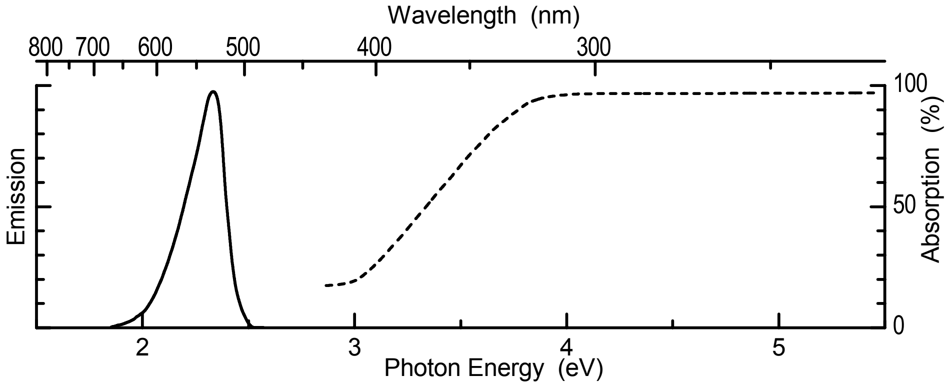
Mix by slurrying in water. Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, CO, 1100°C, 1 hour.
   Powderize by grinding or milling.
2. Fire in open quartz boats, water steam, 1000°C, 1 hour.

Optical Properties

Emission color: Green
Emission peak: 2.31 eV
Emission width (FWHM): 0.20 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: + Comparable to that of Zn_2SiO_4:Mn^{2+}

Spectra



Remarks

1. The emission of this phosphor is thermally quenched a little above room temperature.
2. This material forms solid solutions with Zn_2SiO_4:Mn^{2+} in all proportions.

References

1. Bube, R.H., and Larach, S., Luminescence and trapping in phosphors containing gallium, *J. Chem. Phys.*, 21, 5 (1953).
2. Palumbo, D.T., and Brown, J.J., Electronic states of Mn^{2+}-activated phosphors. 1. Green-emitting phosphors, *J. Electrochem. Soc.,* 117, 1814 (1971).
3. Schulman, J.H., Ginther, R.J., and Claffy, E.W., Manganese-activated zinc beryllium germanate phosphors, *J. Electrochem. Soc.,* 96, 57 (1949).

YVO_4:Eu^{3+}

Structure: Tetragonal (xenotime)

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	95 (of Y)	107
Eu_2O_3	5 (of Eu)	8.8
NH_4VO_3	110	129

Preparation

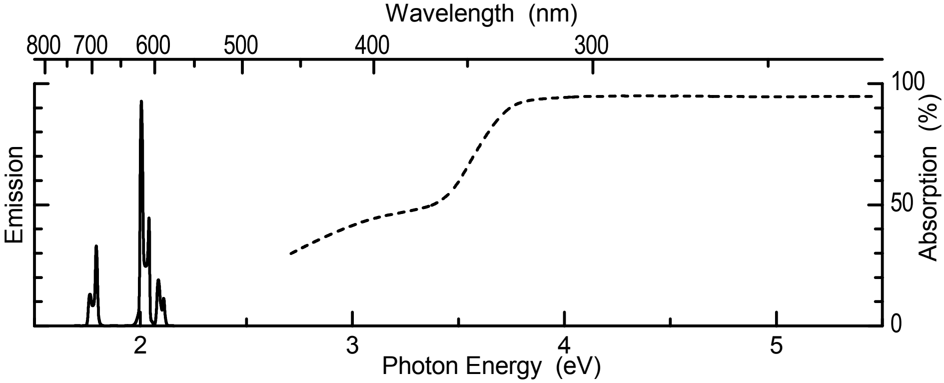
Mix by dry grinding or milling.

1. Fire in open quartz boats, air, 1000°C, 1 hour.
   Powderize.
2. Fire in open quartz boats, air, 1200°C, 1 hour.
   Powderize.
   Wash in a strong solution of NaOH (or KOH) in water and then several times in plain water.
   Dry.
3. Fire in open quartz boats, air, 1200°C, 1 hour.

Optical Properties

Emission color: Red
Emission peak: 2.00 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV); efficiency of 3.40 eV excitation improving considerably with increasing temperature
Excitation efficiency by e-beam: +/7%

Spectra



Remarks

1. Part of the V can be replaced by P.
2. This phosphor has been used for color correction of Hg arc lamps.
3. Optical absorption, and efficiency of luminescence, for 3.40 eV excitation can be somewhat improved by addition of Bi.

References

1. van Uitert, L.G. et al., Role of F-orbital electron wave function mixing in concentration quenching of Eu^{3+}, *J. Chem. Phys.,* 36, 702 (1962).
2. O'Connor, J.R., Unusual crystal-field energy levels and efficient laser properties of YVO_4 - Nd, *Appl. Phys. Lett.,* 9, 407 (1966).
3. Palilla, F.C., Levine, A.K., and Rinkevics, M., Rare earth activated phosphors based on yttriuum orthovanadate and related compounds, *J. Electrochem. Soc.,* 112, 776 (1965).
4. Toma, S.Z., Mikus, F.F., and Mathers, J.E., Energy transfer and fluorescence processes in Bi^{3+} and Eu^{3+} activated YVO_4, *J. Electrochem. Soc.,* 114, 953 (1967).
5. Ropp, R.C., Spectra of some rare earth vanadates, *J. Electrochem. Soc.,* 115, 940 (1968).
6. Levine, A.K, and Palilla, F.C., New highly efficient red-emitting cathodoluminescent phosphor (YVO_4 - Eu) for color television electron beam excitation, *Appl. Phys. Lett.,* 5, 118 (1964).

7. Palilla, F.C., and Levine, A.K., YVO_4-Eu- a highly efficient red-emitting phosphor for high pressure mercury lamps, *Appl. Optics,* 5, 1467 (1966).
8. Levine, A.K., and Palilla, F.C., YVO_4-Eu a new highly efficient phosphor for color television, *Electrochem. Technol.,* 4, 16 (1966).
9. Brixner, L.H., and Abramson, E., On luminescent properties of rare earth vanadates, *J. Electrochem. Soc.*, 112, 70, (1965).
10. Datta, R.K., Bismuth in yttrium vanadate and yttrium europium vanadate phosphors, *J. Electrochem. Soc.,* 114, 1057 (1967).
11. Blasse, G., and Bril, A., Characteristic luminescence, 1. The absorption and emission spectra of some important activators, *Philips Tech. Rev.,* 31, 304 (1970).

$LaVO_4:Eu^{3+}$

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	95 (of La)	155
Eu_2O_3	5 (of Eu)	8.8
NH_4VO_3	110	129

Preparation

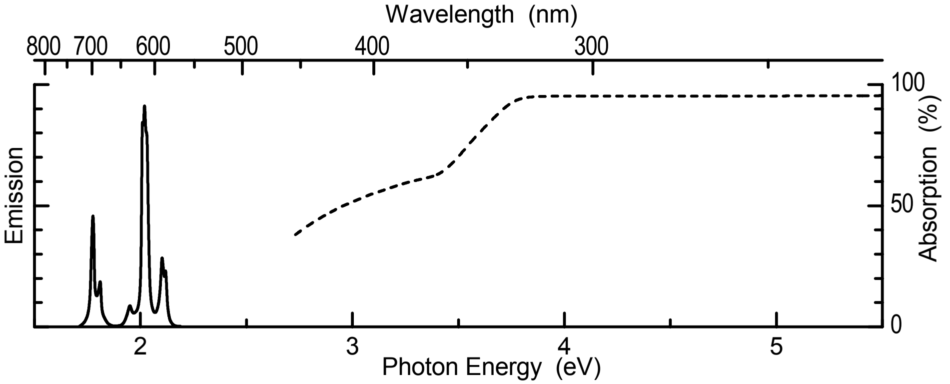
Mix by dry grinding or milling.

1. Fire in open quartz boats, air, 900ºC, 1 hour.
   Powderize.
2. Fire in open quartz boats, air, 1100ºC, 1 hour.
   Powderize.
   Wash in a strong solution of NaOH (or KOH) in water and then several times in plain water.
   Dry.
3. Fire in open quartz boats, air, 1100ºC, 1 hour.

Optical Properties

Emission color: Red
Emission peaks: 1.773–2.115 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)

Spectra



References

1. Wanmaker, W.L. et al., Luminescent properties of Eu-activated phosphors of type A_3BVO_4, *Philips Res. Rep.,* 21, 270 (1966).
2. Aia, M.A., Structure and luminescence of phosphate-vanadates of yttrium gadolinium lutetium and lanthanum, *J. Electrochem. Soc.*, 114, 367 (1967).

$YAsO_4$:Eu^{3+}

Structure: Tetragonal (xenotime)

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	95 (of Y)	107
Eu_2O_3	5 (of Eu)	8.8
As_2O_3	100 (of As)	75

Preparation

Mix by slurrying in 30% H_2O_2.

Gently heat up while stirring until reaction (boiling) indicates formations of H_3AsO_4.

Dry in air. Powderize when dry.

1. Fire in open quartz boats, air, ~500°C.
   Powderize.
2. Fire in open quartz boats, air, 1200°C, 1 hour.

Optical Properties

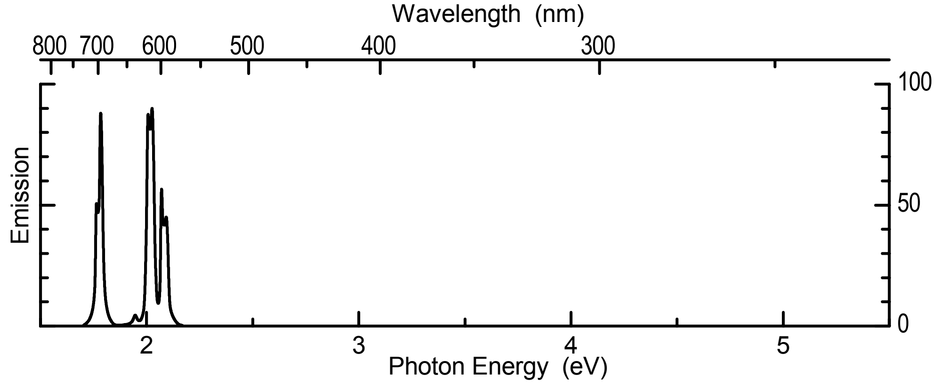
Emission color: Red

Emission peaks: 1.76–2.09 eV

Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)

Excitation efficiency by e-beam: +

Spectra



Remarks

1. This phosphor becomes excitable by 4.88 and by 3.40 eV UV upon replacement of some As by V.
2. The material forms solid solutions with YVO_4:Eu^{3+} in all proportions.

Reference

1. Wanmaker, W.L., et al., Luminescent properties of Eu-activated phosphors of type A_3BVO_4, *Philips Res. Rep.,* 21, 270 (1966).

$LaAsO_4:Eu^{3+}$

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	95 (of La)	155
Eu_2O_3	5 (of Eu)	8.8
As_2O_3	100 (of As)	75

Preparation

Mix by slurrying in 30% H_2O_2.

Gently heat up while stirring until reaction (boiling) indicates formations of H_3AsO_4.

Dry in air. Powderize when dry.

1. Fire in open quartz boats, air, ~500°C.
   Powderize.
2. Fire in open quartz boats, air, 1000°C, 1 hour.

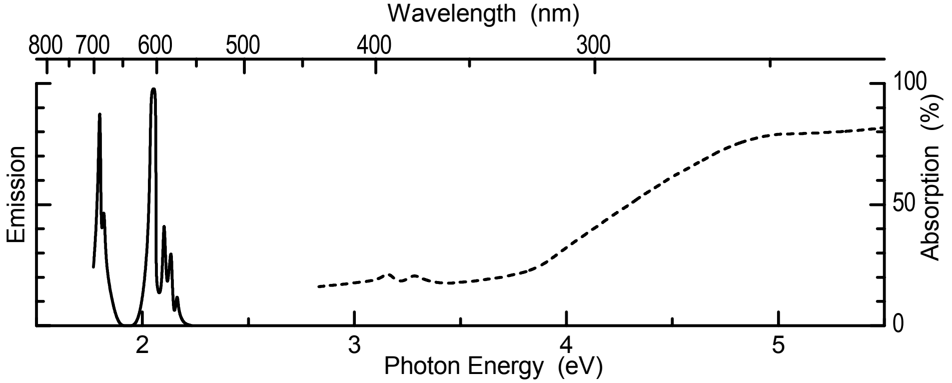
Optical Properties

Emission color: Red

Emission peaks: 1.785–2.149 eV

Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra



Remarks

1. This material becomes excitable by 3.40 eV UV upon replacement of a few percent of the As by V.
2. The material forms solid solutions with $LaVO_4$ in all proportions.

$Ca_5(VO_4)_3Cl$

Structure: Apatite

Composition

Ingredient	Mole %	By weight (g)
CaO	500	280
NH_4VO_3	200	234
NH_4Cl	200	107

Preparation

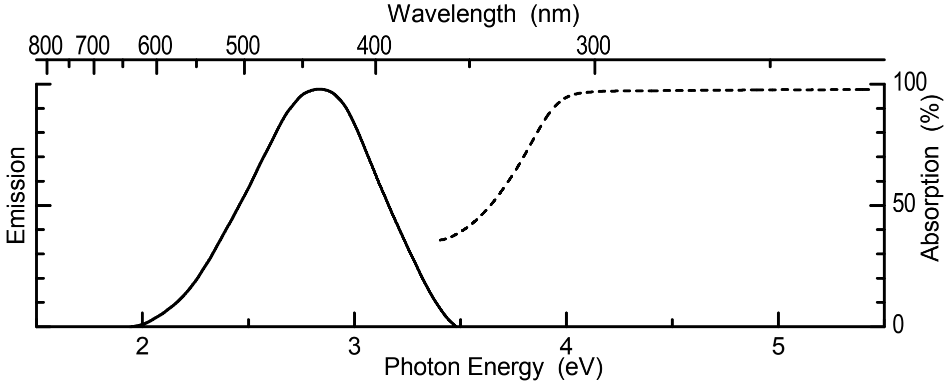
Mix by dry grinding or milling (some NH_3 develops).

1. Fire in capped quartz tubes, air, ~500ºC, 16 hours (overnight). Powderize.
2. Fire in capped quartz tubes, air, 1000ºC, 1 hour.

Optical Properties

Emission color: Bluish
Emission peak: 2.85 eV
Emission width (FWHM): 0.73 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra



Remarks

1. This phosphor requires a deficiency of V and an excess of Cl in the preparation.
2. The luminescence of this phosphor is due to the vanadate. Other impurities were tested as prospective activators but are either dead (Mn, Tb, Ho) or very poorly luminescent (Eu^{3+}).

Reference

1. Aia, M.A., and Lublin, P., Blue luminescence in calcium chlorovanadates, *J. Electrochem. Soc.,* 113, 1331 (1966).

$Mg_8Ge_2O_{11}F_2$:Mn^{4+}

Composition

Ingredient	Mole %	By weight (g)
MgO	700	282
MgF_2	100	62
$MgCO_3$	8	9.2
GeO_2	192	201

Preparation

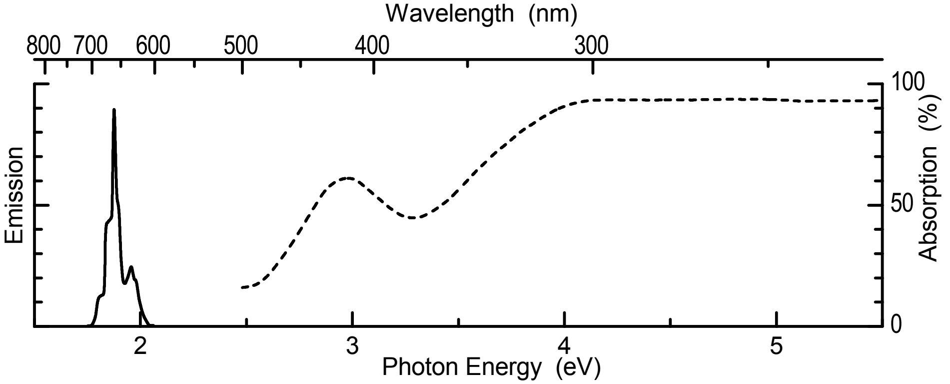
Mix by dry ball-milling.

1. Fire in capped quartz tubes, air, 1200°C, 2 hours.
   Powderize by dry ball-milling.
2. Fire in open quartz boats, air, 1200°C, ~16 hours (overnight).

Optical Properties

Emission color: Deep red
Emission peak: 1.88 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)

Spectra



Remarks

1. The exact formula of this material is still uncertain. The above formula is only that of the raw mix; some parts (mainly Ge fluoride) sublimes out during firing.
2. This phosphor has been used for color correction of Hg arc lamps.

References

1. Thorington, L., Temperature dependence of the emission of an improved manganese-activated magnesium germanate phosphor, *J. Opt. Soc. Am.,* 40, 579 (1950).
2. Kemeny, G., and Haake, C.H., Activator center in magnesium fluorogermanate phosphors, *J. Chem. Phys.,* 33, 783 (1960).

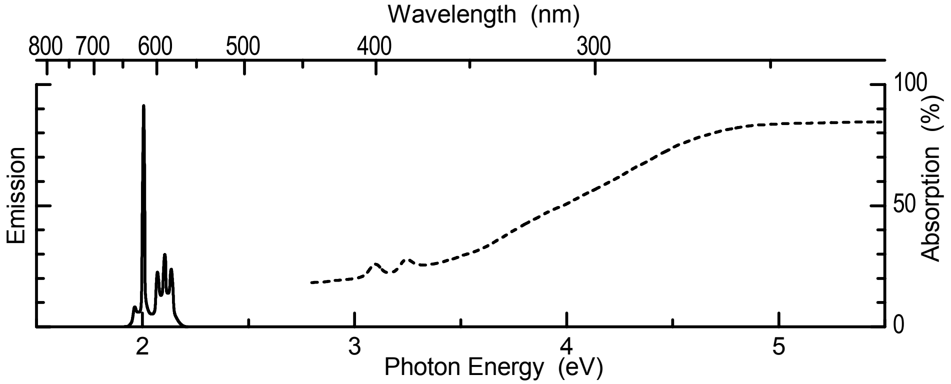
CaY_2ZrO_6:Eu^{3+}

Structure: Perovskite

Optical Properties

Emission color: Red
Emission peak: 2.01 eV
Excitation efficiency by UV:++ (4.88 eV), – (3.40 eV)

Spectra

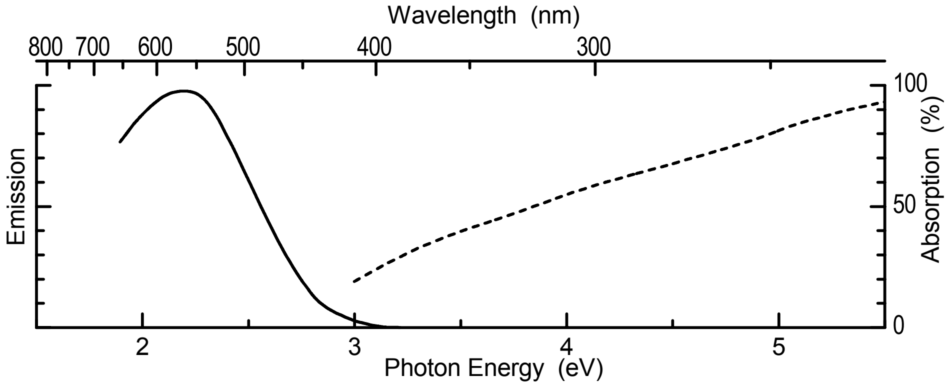


$Mg_3SiO_3F_4$:Ti^{4+}

Optical Properties

Emission color: whitish-yellow
Emission peak: 2.15 eV
Excitation efficiency by UV:++ (4.88 eV), – (3.40 eV)

Spectra



4.11 Halides and Oxyhalides

The following host compounds and activators are included in this subsection:

MgF_2:Mn^{2+}
CaF_2:Ce^{3+}
CaF_2:Eu^{2+}
CaF_2:Mn^{2+}
CaF_2:Ce^{3+},Mn^{2+}
CaF_2:Ce^{3+},Tb^{3+}
CaF_2:U
$CaCl_2$:Eu^{2+} in SiO_2
$CaCl_2$:Eu^{2+},Mn^{2+} in SiO_2
$CaBr_2$:Eu^{2+} in SiO_2
CaI_2:Eu^{2+} in SiO_2
CaI_2:Eu^{2+},Mn^{2+} in SiO_2
SrF_2:Eu^{2+}
$SrCl_2$:Eu^{2+} in SiO_2
$Sr(Cl,Br,I)_2$:Eu^{2+} in SiO_2
ZnF_2:Mn^{2+}
$Ba_xSr_{1-x}F_2$:Eu^{2+}
YF_3:Mn^{2+}
YF_3:Mn^{2+},Th^{4+}
$KMgF_3$:Eu^{2+}
$KMgF_3$:Mn^{2+}
$LiAlF_4$:Mn^{2+}
K_2SiF_6:Mn^{4+}
YOBr:Eu^{3+}
YOCl:Ce^{3+}
YOCl:Eu^{3+}
YOF:Eu^{3+}
YOF:Tb^{3+}
LaOF:Eu^{3+}
LaOCl:Bi^{3+}
LaOCl:Eu^{3+}

MgF_2:Mn^{2+}

Structure: Tetragonal (sellaite)

Composition

Ingredient	Mole %	By weight (g)
MgF_2	99	62
$MnCO_3$	1	1.15

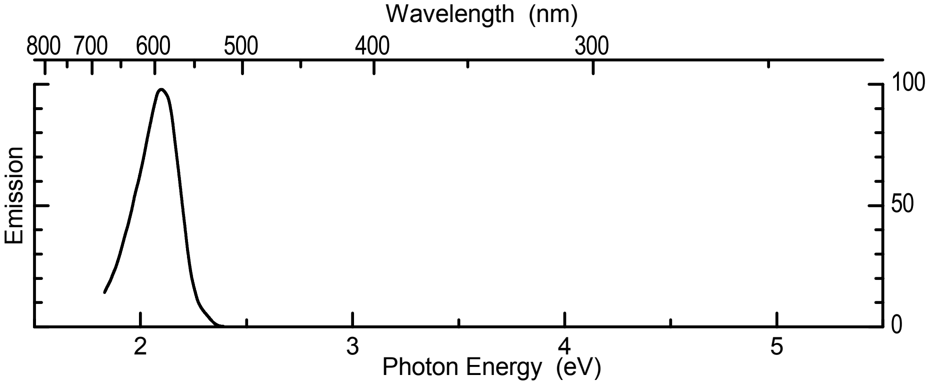
Preparation

Mix by slurrying in methanol.
Add ~2 g of NH_4F (dissolved in a little water) and ~2–3 ccm of HF acid; stir to uniformity.
Dry. Powderize.
Fire in capped quartz tubes, N_2, 900°C, 1 hour.

Optical Properties

Emission color: Orange-yellow
Emission peak: 2.10 eV
Emission width (FWHM): 0.25 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV).
Excitation efficiency by e-beam: +/~25%
Decay: Exponential, about 200 msec to 1/10

Spectra



Remark

No sensitizer is known to permit excitation by these UV wavelengths.

References

1. Klasens, H.A., Zalm, P., and Huysman, F.O., The manganese emission in AbF_3 compounds, *Philips Res. Rep.,* 8, 441 (1953).
2. Smith, A.L., New manganese-activated fluoride phosphors, *J. Electrochem. Soc.,* 101*,* 189 (1954).
3. Williams, F.E., and Eyring, H., The mechanism of the luminescence of solids, *J. Chem. Phys.,* 15, 289 (1947).
4. Bräunlich, P., Hanle, W., and Scharmann, A., Zur thermolumineszenz von MgF_2-Mn, *Z. Naturforsch. Pt. A*, 16, 869 (1961).

CaF_2:Ce^{3+}

Structure: Cubic (fluorite)

Composition

Ingredient	Mole %	By weight (g)
CaF_2	90	70
CeF_3	5	9.85
AlF_3	5	4.2

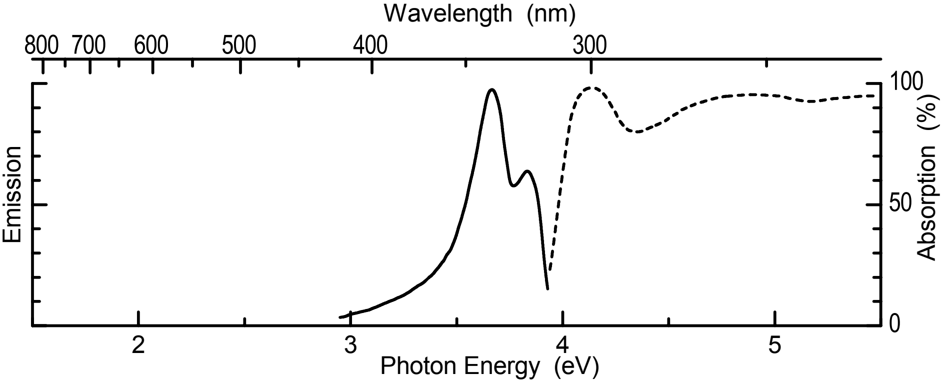
Preparation

Start with plain CaF_2 and pre-fire it in open quartz boats, air, 1000°C, 1 hour.
Make a slurry of the CaF_2 + CeF_3 + AlF_3 in methanol.
Add ~1–2 ccm HF acid; stir to uniformity. Dry; powderize.
Add ~2–3 g of iodine, mix by dry grinding.
Fire in capped quartz tubes, N_2, 1000°C, 1 hour. Powderize.

Optical Properties

Emission color: UV
Emission peak: 3.68 eV, 3.88 eV
Excitation efficiency by UV: ++ (4.88 eV), − (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Kröger, F.A., and Bakker, J., *Physica*, 8, 628 (1941).
2. Ginther, R.J., Luminescence of K_4MnCl_6 and KCl (Pb + Mn), *J. Electrochem. Soc.,* 98, 74 (1951).
3. Loh, E., Ultraviolet absorption spectra of Ce^{3+} in alkaline-earth fluorides, *Phys. Rev.,* 154, 270 (1967).
4. Schlesinger, M., and Whippey, P.W., Investigations of 4f–5d transitions of Ce^{+3} in CaF_2, *Phys. Rev.,* 171, 361 (1968).
5. Leach, R., Energy transfer and sensitization in single crystal phosphors*, J. Electrochem. Soc.*, 105, 27 (1958).

$CaF_2:Eu^{2+}$

Structure: Cubic (fluorite)

Composition

Ingredient	Mole %	By weight (g)
CaF_2	100	70
Eu_2O_3	0.2 (of Eu)	0.350

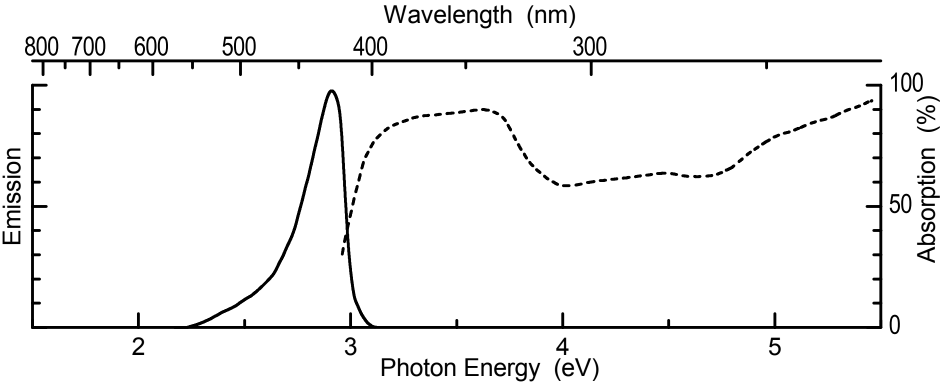
Preparation

Mix by slurrying in methanol (in a plastic container).
Add ~2 ccm HF acid; stir to uniformity.
Dry; powderize.
Add ~2–3 g of iodine; mix by dry grinding.
Fire in capped quartz tubes, N_2, 800°C, 1 hour.
Powderize.

Optical Properties

Emission color: Violet
Emission peak: 2.93 eV
Emission width (FWHM): 0.22 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Remark

This material can be sensitized for better UV excitation with 4.88 eV by addition of Ce (see CaF_2:Ce^{3+}).

References

1. Amster, R.L., Photosensitization of terbium fluorescence by europium in CaF_2, *J. Electrochem. Soc.,* 117, 791 (1970).
2. Amster, R.L., and Wiggins, C.S., Spectroscopic identification of europium-oxygen complexes in calcium fluoride, *J. Electrochem. Soc.,* 116, 68 (1969).

CaF_2:Mn^{2+}

Structure: Cubic (fluorite)

Composition

Ingredient	Mole %	By weight (g)
CaF_2	99	77
$MnCO_3$	1	1.15

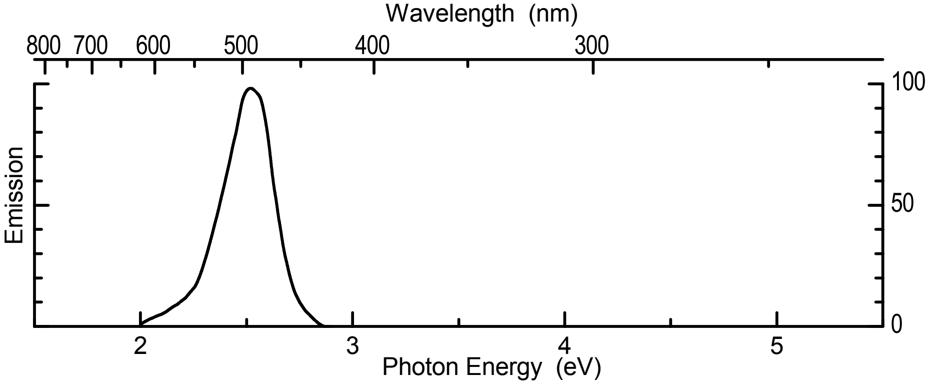
Preparation

Mix by slurrying in methanol (in a plastic container).
Add ~2 ccm HF acid; stir to uniformity.
Dry; powderize.
Add ~2–3 g of iodine; mix by dry grinding.
Fire in capped quartz tubes, N_2, 800°C, 1 hour.
Powderize.

Optical Properties

Emission color: Blue-green
Emission peak: 2.50 eV
Emission width (FWHM): 0.29 eV
Excitation efficiency by UV: − (4.88 eV), − (3.40 eV)
Excitation efficiency by e-beam: +/1.5%
Decay**:** Near-exponential decay, 45 msec to 1/10

Spectra



Remarks

1. This material can be sensitized for better UV excitation by 3.40 eV with addition of Eu (see CaF_2:Eu^{2+}).
2. The material can be sensitized for better UV excitation by 4.88 eV with addition of Ce (see CaF_2:Ce^{3+}).
3. The emission shifts to lower energy (= longer wavelength) with increasing Mn concentration.
4. Mn concentrations below 1% give somewhat longer decay times, up to ~60 msec to 1/10.

References

1. Klasens, H.A., Zalm, P., and Huysman, F.O., The manganese emission in AbF_3 compounds, *Philips Res. Rep.,* 8, 441 (1953).
2. Smith, A.L., New manganese-activated fluoride phosphors, *J. Electrochem. Soc.,* 101*,* 189 (1954).
3. Garlick, G.F.J., and Sayer, M., Decay of cathodoluminescence and nonradiative processes in manganese activated phosphors, *J. Electrochem. Soc.,* 109, 678 (1962).
4. Ginther, R.J., and Kirk, R.D., *J. Electrochem. Soc.,* 104, 365 (1967).
5. Schmid, W.F., and Mooney, R.W., The thermoluminescence of CaF_2-Mn, *J. Electrochem. Soc.* 110, 340 (1963).

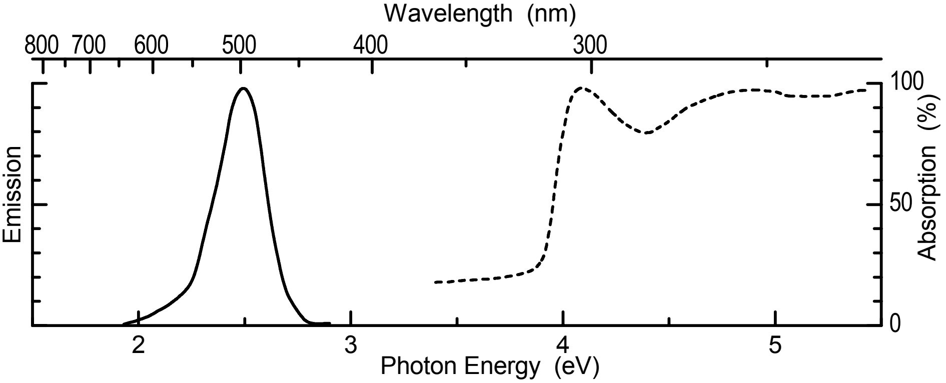
$CaF_2:Ce^{3+},Mn^{2+}$

Structure: Cubic (fluorite)

Optical Properties

Emission color: Blue-green
Emission peak: 2.50 eV
Emission width (FWHM): 0.35 eV
Excitation efficiency by UV: ++ (4.88 eV), − (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Kröger, F.A., and Bakker, J., *Physica*, 8, 628 (1941).
2. Ginther, R.J., Luminescence of K_4MnCl_6 and KCl (Pb + Mn), *J. Electrochem. Soc.,* 98, 74 (1951).

$CaF_2:Ce^{3+},Tb^{3+}$

Structure: Cubic (fluorite)

Composition

Ingredient	Mole %	By weight (g)
CaF_2	80	62
CeF_3	5	9.85
TbF_3	10	21.6
AlF_3	5	4.2

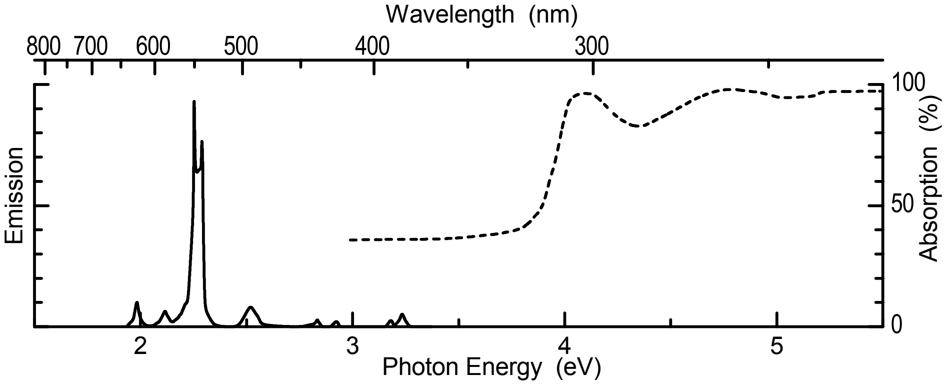
Preparation

Start with plain CaF_2 and pre-fire it in open quartz boats, air, 1000°C, 1 hour.
Make a slurry of all the above ingredients in methanol.
Add ~2 ccm HF acid; stir to uniformity.
Dry; powderize.
Add ~2–3 g of iodine; mix by dry grinding.
Fire in capped quartz tubes, N_2, 1000°C, 1 hour.
Powderize.

Optical Properties

Emission color: Pale green
Emission peaks: 2.26–2.28 eV
Excitation efficiency by UV: ++ (4.88 eV), − (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Remark

UV excitation is almost exclusively determined by the Ce^{3+} absorption (see CaF_2:Ce^{3+}).

Reference

1. Amster, R.L. Photosensitization of terbium fluorescence by europium in CaF_2, *J. Electrochem. Soc.,* 117, 791 (1970).

CaF_2:U

Structure: Cubic (fluorite)

Composition

Ingredient	Mole %	By weight (g)
CaF_2	100	78
$UO_2(NH_3)_2 \cdot 6H_2O$	0.1	0.500
LiF	1	0.260

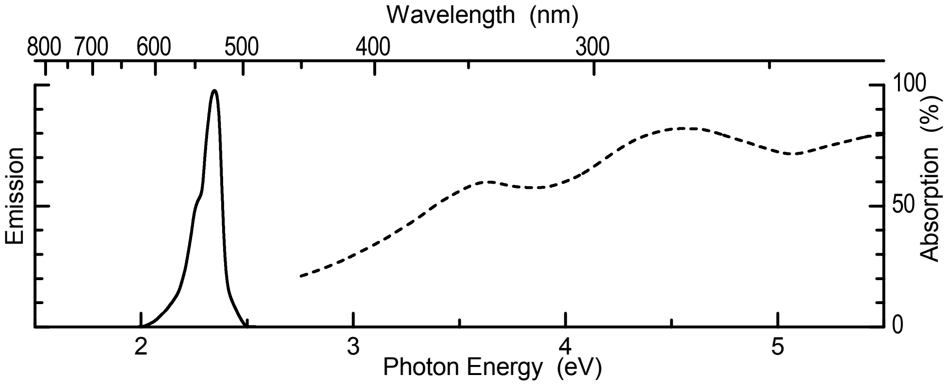
Preparation

Dissolve the uranyl nitrate in a little methanol; add solution to the CaF_2 + LiF mix.
Make a slurry of in methanol; stir to uniformity.
Dry; powderize.
Fire in open alumina crucibles, air, 1000ºC, 1 hour.
Powderize.

Optical Properties

Emission color: Green
Emission peak: 2.345 eV
Emission width (FWHM): 0.11 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: Very poor

Spectra



References

1. Gorlich, P., Karras, H., and Lehmann, R., Uber die optischen eigenschaften der erdalkalihalogenide vom flussspat-typ(I), *Phys. Status Solidi.,* 1, 387 (1961).
2. Gorlich, P., Karras, H., and Lehmann, R., Uber die optischen eigenschaften der erdalkalihalogenide vom flussspat-typ(II), *Phys. Status Solidi.,* 1, 551 (1961).
3. Nicholas, J.V., Luminescence of hexavalent uranium in CaF_2 and SrF_2 powders, *Phys. Rev.,* 155, 151 (1967).

$CaCl_2$:Eu^{2+} in SiO_2

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
CaO	7.6	4.3
Eu_2O_3	1 (of Eu)	1.76
NH_4Cl	17.5	9.4
SiO_2	100	60

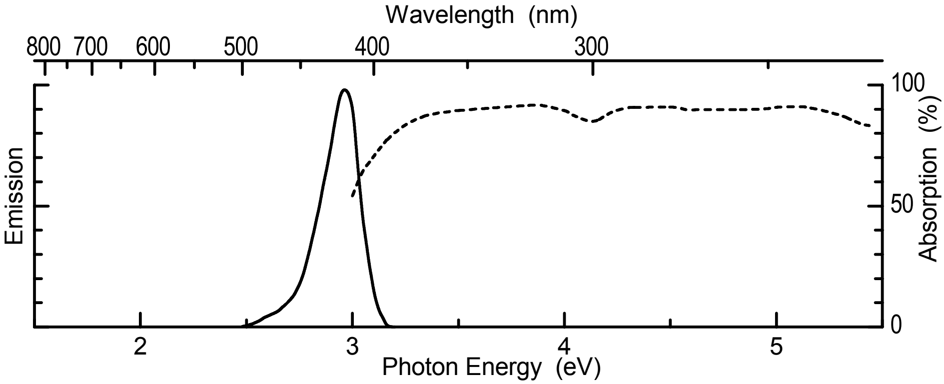
Preparation

Mix by slurrying in methanol, plus a little water.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 1000ºC, 1 hour.
Powderize.
Add the above amount of NH_4Cl once again; mix by dry grinding.
2. Fire in capped quartz tubes, CO, 1000ºC, 1 hour.
Powderize.
Wash in water several times.
Dry.

Optical Properties

Emission color: Blue-violet
Emission peak: 2.97 eV
Emission width (FWHM): 0.195 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: −

Spectra



Reference

1. Lehmann, W., Heterogeneous halide-silica phosphors, *J. Electrochem. Soc.*, 122, 748 (1975).

$CaCl_2:Eu^{2+},Mn^{2+}$ in SiO_2

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
CaO	7.5	4.2
NH_4Cl	20	10.7
Eu_2O_3	1 (of Eu)	1.76
$MnCO_3$	1	1.15
SiO_2	100	60

Preparation

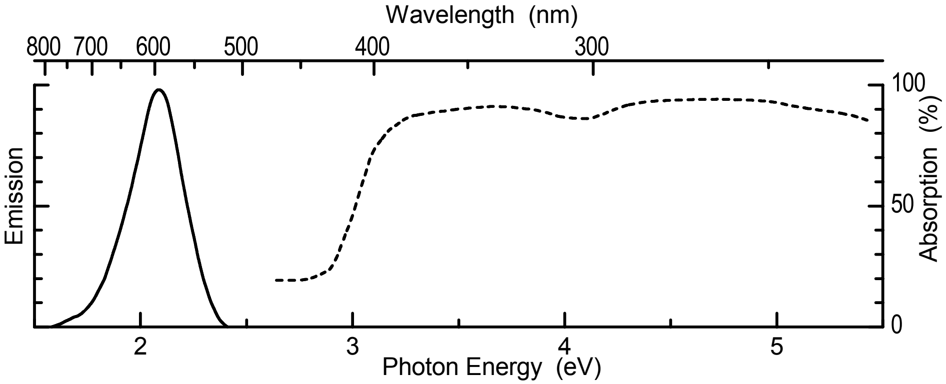
Mix by slurrying in methanol, plus a little water.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 900°C, 1 hour. Powderize.
   Add the above amount of NH_4Cl once again; mix by dry grinding.
2. Fire in capped quartz tubes, CO, 1000°C, 1 hour. Powderize.
   Wash in water several times. Dry.

Optical Properties

Emission color: Yellow
Emission peak: 2.09 eV
Emission width (FWHM): 0.30 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: −

Spectra



Remarks

1. The Cl in this recipe can be replaced by Br.
2. The emissions of $CaCl_2:Eu^{2+}$, Mn^{2+} and $CaBr_2:Eu^{2+}$, Mn^{2+} are identical.

Reference

1. Lehmann, W., Heterogeneous halide-silica phosphors, *J. Electrochem. Soc.*, 122, 748 (1975).

$CaBr_2:Eu^{2+}$ in SiO_2

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
CaO	7.6	4.3
Eu_2O_3	1.2 (of Eu)	2.1
NH_4Br	17.5	17.2
SiO_2	100	60

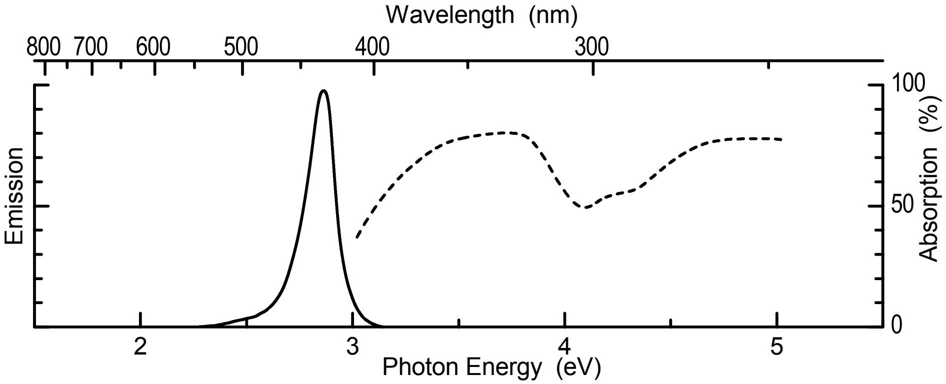
Preparation

Mix by slurrying in methanol, plus a little water.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 900°C, 1 hour.
Powderize.
Add the above amount of NH_4Br once again; mix by dry grinding.
2. Fire in capped quartz tubes, CO, 1000°C, 1 hour.
Powderize.
Wash in water several times.
Dry.

Optical Properties

Emission color: Blue
Emission peak: ~2.865 eV
Emission width (FWHM): 0.18 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: −

Spectra



Reference

1. Lehmann, W., Heterogeneous halide-silica phosphors, *J. Electrochem. Soc.*, 122, 748 (1975).

$CaI_2:Eu^{2+}$ in SiO_2

Composition

Ingredient	Mole %	By weight (g)
CaO	6	3.4
CaF_2	3	2.34
Eu_2O_3	2 (of Eu)	3.5
NH_4I	20	29
SiO_2	100	60

Preparation

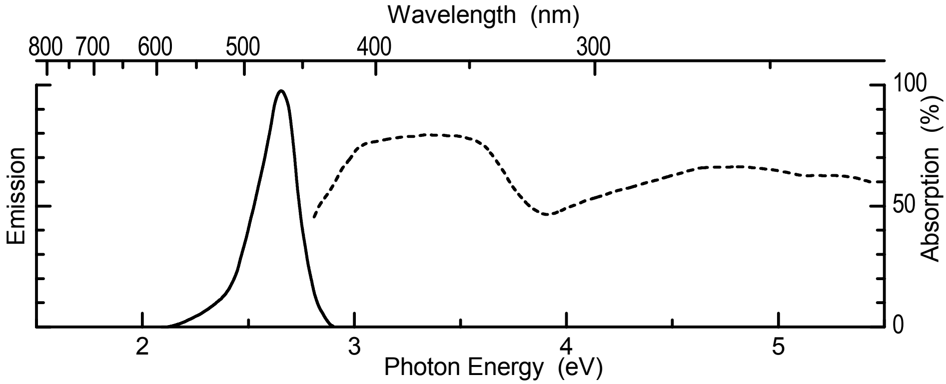
Mix by slurrying in methanol, plus a little water.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 900°C, 1 hour. Powderize.
   Add the above amount of NH_4I once again; mix by dry grinding.
2. Fire in capped quartz tubes, CO, 1000°C, 1 hour. Powderize.
   Wash in water several times. Dry.

Optical Properties

Emission color: Light blue
Emission peak: 2.67 eV
Emission width (FWHM): 0.21 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: −

Spectra



Remark

This phosphor is sensitive to even very small traces of Mn which causes a red emission band (see $CaI_2:Eu^{2+},Mn^{2+}$).

Reference

1. Lehmann, W., Heterogeneous halide-silica phosphors, *J. Electrochem. Soc.*, 122, 748 (1975).

$CaI_2:Eu^{2+},Mn^{2+}$ in SiO_2

Composition

Ingredient	Mole %	By weight (g)
CaO	7	3.9
CaF_2	1	0.78
Eu_2O_3	0.65 (of Eu)	1.14
$MnCO_3$	0.1	0.115
NH_4I	15	21
SiO_2	100	60

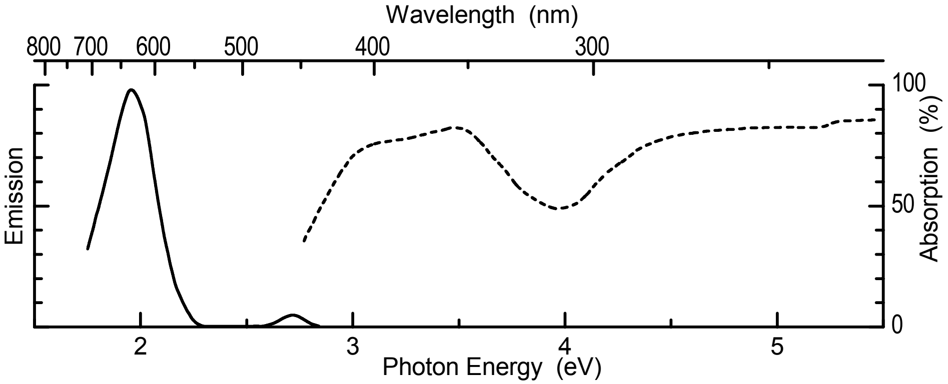
Preparation

Mix by slurrying in methanol, plus a little water.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 900°C, 1 hour.
Powderize.
Add the above amount of NH_4I once again; mix by dry grinding.
2. Fire in capped quartz tubes, CO, 1000°C, 1 hour.
Powderize.
Wash in water several times. Dry.

Optical Properties

Emission color: Light red, slightly pinkish hue
Emission peak: 1.95 eV, additionally a weak Eu^{2+}-emission band at 2.70 eV
Emission width (FWHM): 0.29 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: –

Spectra



Reference

1. Lehmann, W., Heterogeneous halide-silica phosphors, *J. Electrochem. Soc.*, 122, 748 (1975).

$SrF_2:Eu^{2+}$

Structure: Cubic (fluorite)

Optical Properties

Emission color: Violet
Emission peak: 2.95 eV
Emission width (FWHM): 0.30 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +

Reference

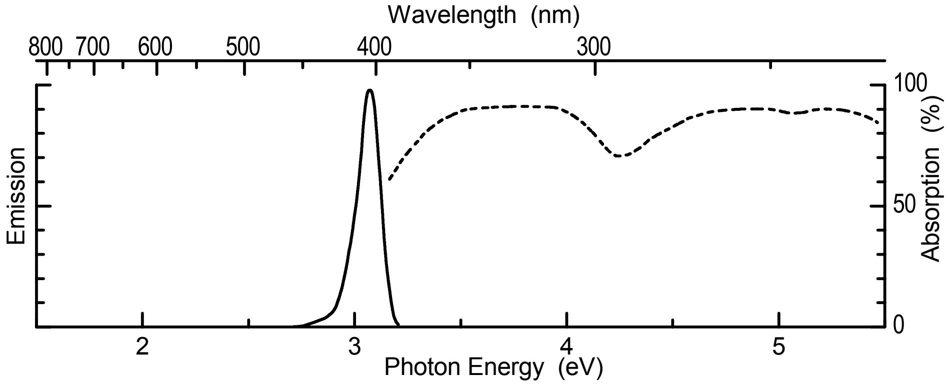
1. Chenot., C.F., Can. Pat., 896 453 (1972).

$SrCl_2:Eu^{2+}$ in SiO_2

Optical Properties

Emission color: Violet
Emission peak: 3.06 eV
Emission width (FWHM): 0.12 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: −

Spectra



Reference

1. Lehmann, W., Heterogeneous halide-silica phosphors, *J. Electrochem. Soc.*, 122, 748 (1975).

$Sr(Cl,Br,I)_2:Eu^{2+}$ in SiO_2

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
SrO	8	8.3
Eu_2O_3	1.5 (of Eu)	2.6
NH_4Cl	17.5	9.4
SiO_2	100	60

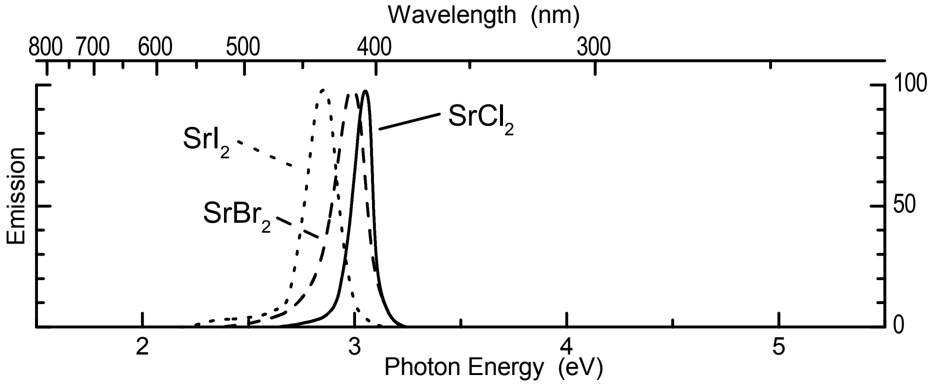
Preparation

Mix by slurrying in methanol, plus a little water.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 900°C, 1 hour. Powderize.
   Add the above amount of NH_4I once again; mix by dry grinding.
2. Fire in capped quartz tubes, CO, 1000°C, 1 hour. Powderize.
   Wash in water several times. Dry.

Optical Properties

Emission color: Violet
Emission peaks: Peak position depending on the used halide; for $SrCl_2$ is at ~3.06 eV, for $SrBr_2$ at ~3.015 eV, and SrI_2 at ~2.865 eV.
Emission width (FWHM): Width also depending on used halide; for $SrCl_2$ is 0.175 eV, for $SrBr_2$ is 0.16 eV, and for SrI_2 is 0.12 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: −

Spectra



Remark

The Cl in this recipe can be replaced by Br or I.

Reference

1. Lehmann, W., Heterogeneous halide-silica phosphors, *J. Electrochem. Soc.*, 122, 748 (1975).

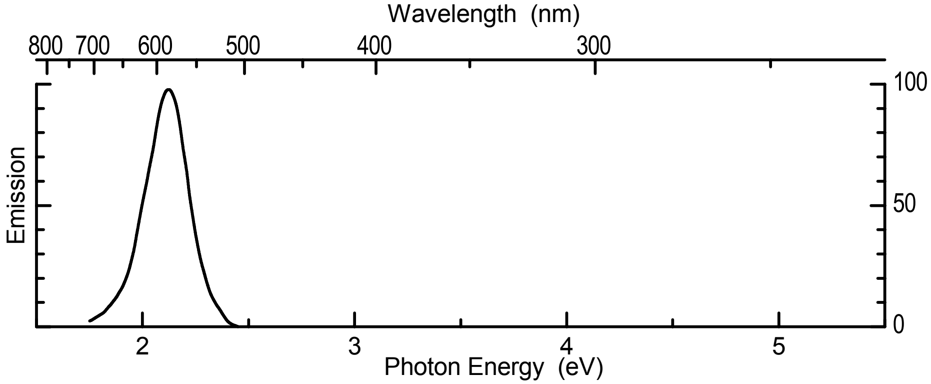
$ZnF_2:Mn^{2+}$

Structure: Tetragonal

Optical Properties

Emission color: Orange-yellow
Emission peak: 2.12 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: − (4.88 eV), − (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Leverenz, H.W., *An Introduction to Luminescence of Solids,* John Wiley & Sons, New York (1949).
2. Klasens, H.A., Zalm, P., and Huysman, F.O., The manganese emission in ABF_3 compounds, *Philips Res. Rep.,* 8, 441 (1953).

3. Smith, A.L., New manganese-activated fluoride phosphors, *J. Electrochem. Soc., 101,* 189 (1954).
4. Johnson, P.D., and Williams, F.E., Energy levels and rate processes in the thallium activated potassium chloride phosphor, *J. Chem. Phys.,* 20, 124 (1952).
5. Johnson, J.S., and Williams, F.E., Thermoluminescence of manganese-activated zinc fluoride phosphors, *J. Opt. Soc. Am.,* 39, 709 (1949).
6. Fonda, G.R., and Studer F.J., Optical properties of zinc fluoride phosphors, *J. Opt. Soc. Am.,* 38, 1007 (1948).
7. Studer, F.J., and Rosenbaum, J., The phosphorescence decay of halophosphates and other doubly activated phosphors, *J. Opt. Soc. Am.*, 38, 1007 (1948).

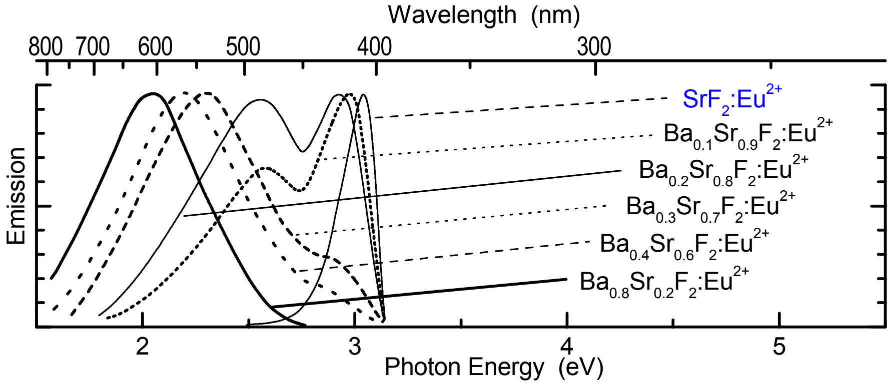
$Ba_xSr_{1-x}F_2:Eu^{2+}$

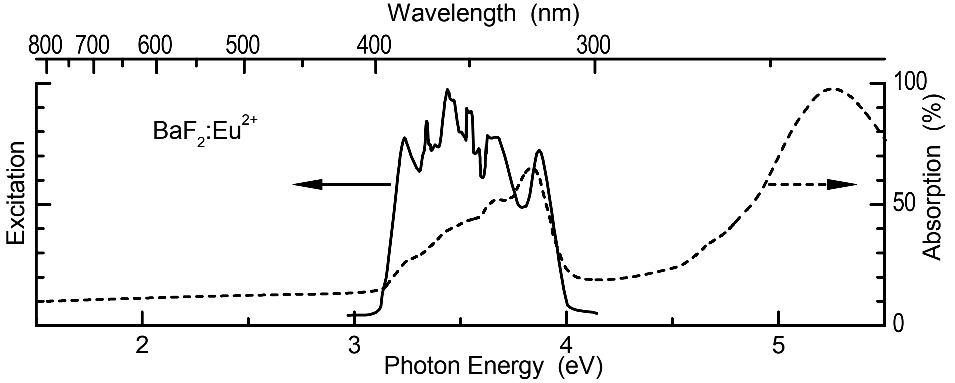
Structure: Cubic (fluorite)

Optical Properties

Emission color: varies with composition from yellow to blue
Emission peak: varies with composition from 2.04 to 3.04 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +

Spectra





References

1. Chenot., C.F., Can. Pat. 896 453 (1972).
2. Mou, W.F., and McClure, D.S., Photoionization and trapping of electrons in the system BaF_2:Eu:Sm, *Phys. Rev. B,* 47 no.17, 11031–11038 (1993).

3. Reut, E.G., Study on characteristics of wideband luminescence of Eu and Yb ions in crystals with fluorite structure, *Opt. Spektr.*, 45, 518 (1978) [*Opt. Spectrosc.* (USSR) 45, 290 (1978)].
4. Reut, E.G., Nature of luminescence of bivalent Eu and Yb ions in fluorite-type crystals, *Opt. Spektr.*, 40, 99 (1976) [*Opt. Spectrosc.* (USSR) 40, 55 (1976)].
5. Kaplyansky, A.A., and Feofilov, P.P., Spectra of divalent rare earth ions in crystals of alkali-earth fluorides. 2. Europium and Ytterbium, *Opt. Spektr.*, 13, 235 (1962) [*Opt. Spectrosc.* (USSR) 13, 129 (1962)].

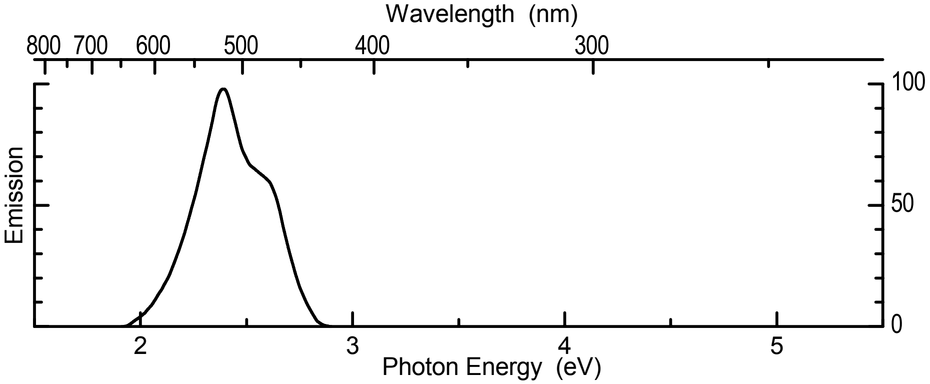
$YF_3:Mn^{2+}$

Structure: Orthorhombic

Optical Properties

Emission color: Greenish
Emission peaks: 2.38 and 2.60 eV
Excitation efficiency by UV: − (4.88 eV), − (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



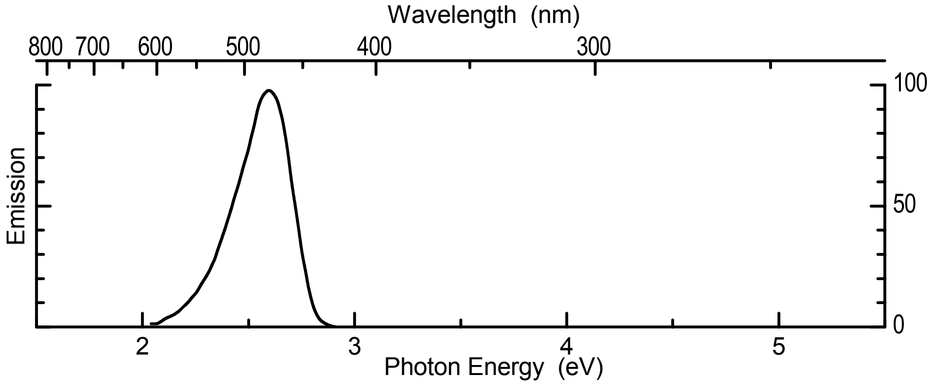
$YF_3:Mn^{2+},Th^{4+}$

Structure: Orthorhombic

Optical Properties

Emission color: Light blue
Emission peak: 2.60 eV
Emission width (FWHM): 0.29 eV
Excitation efficiency by UV: − (4.88 eV), − (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



KMgF$_3$:Eu^{2+}

Structure: Cubic (perovskite)

Optical Properties

Emission color: UV
Emission peak: 3.42 eV
Excitation efficiency by UV: + (4.88 eV), − (3.40 eV)
Excitation efficiency by e-beam: −

References

1. Sommerdijk, J.L., and Bril, A., Divalent europium luminescence in perovskite-like alkaline-earth alkaline fluorides, *J. Lumin.,* 11, 363 (1976).
2. Seo, H.J., Moon, B.K., and Tsuboi, T., Two-photon excitation spectroscopy of $4f^7 \rightarrow 4f^7$ transitions of Eu^{2+} ions doped in a KMgF$_3$ crystal, *Phys. Rev. B*, 62, no. 19, 12688–12695 (2000).
3. Ellens, A., Meijerink, A., and Blasse, G., ^{6}I emission and vibronic transitions of Eu^{2+} in KMgF$_3$, *J. Lumin*., 59, 293 (1994).

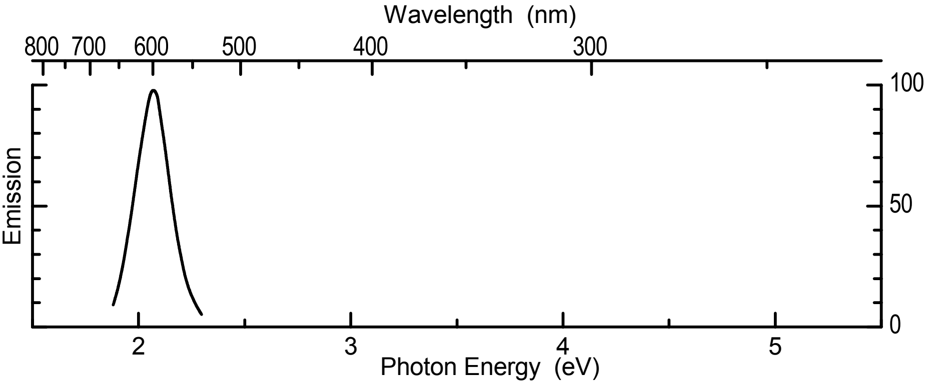
KMgF$_3$:Mn^{2+}

Structure: Cubic (perovskite)

Optical Properties

Emission color**:** Orange
Emission peak: 2.08 eV
Emission width (FWHM): 0.18 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Reference

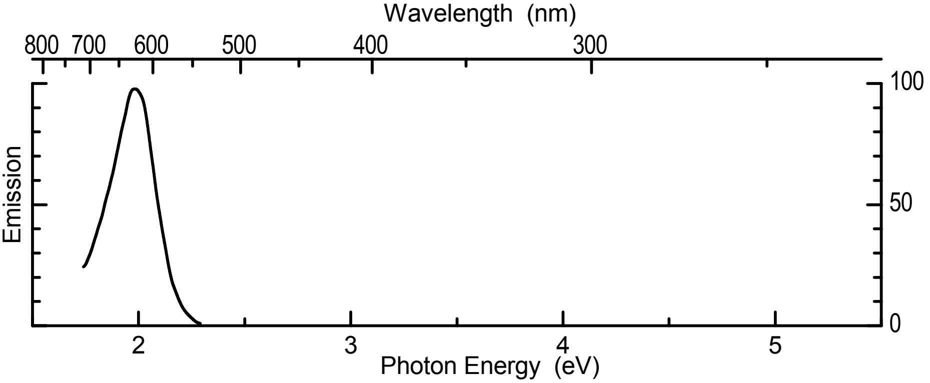
1. Kurtz, R.J., Cathodoluminescent characteristics of Mn-activated $KMgF_3$, *J. Electrochem. Soc.*, 109, 18 (1962).

$LiAlF_4:Mn^{2+}$

Optical Properties

Emission color: Red
Emission peak: 1.99 eV
Emission width (FWHM): 0.26 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



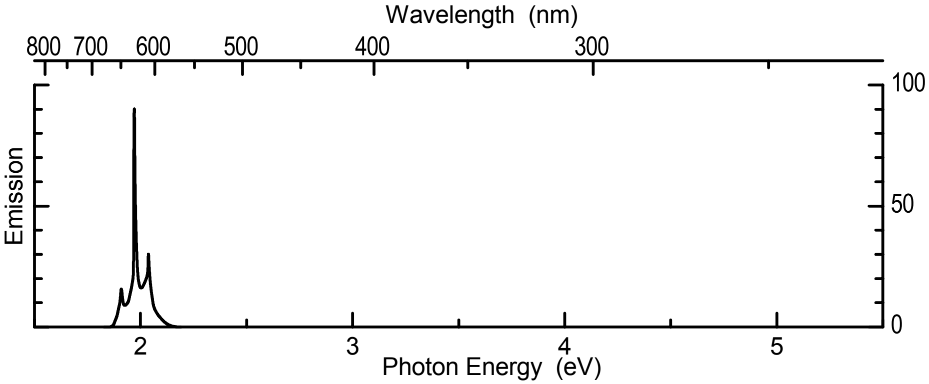
$K_2SiF_6:Mn^{4+}$

Structure: Cubic

Optical Properties

Emission color: Red
Emission peak: 1.97 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Reference

1. Paulusz, A.G., Efficient Mn(IV) emission in fluorine coordination, *J. Electrochem. Soc.*, 120, 942 (1973).

YOBr:Eu^{3+}

Structure: Rhombohedral

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	95 (of Y)	107.4
Eu_2O_3	5 (of Eu)	8.8
NH_4Br	110	108

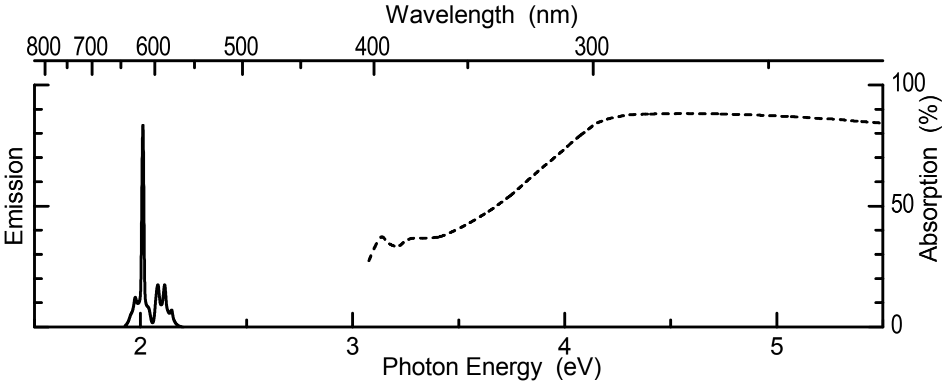
Preparation

Make a suspension of all ingredients in water.
Boil down to dry (slowly, to let the conversion of Y_2O_3 to YOBr take place).
Powderize.
1. Fire in capped quartz tubes, N_2, ~500ºC, ½ hour.
   Powderize.
2. Fire in capped quartz tubes, N_2, 1100ºC, 1 hour.
   Powderize.
   Wash in water several times.
   Dry.

Optical Properties

Emission color: Red
Emission peaks: 1.967–2.150 eV; main line at 1.996 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)

Spectra



Remarks

1. This phosphor is hygroscopic. Keep dry.
2. This phosphor is difficult to prepare. It tends either to be partly reduced (forming Eu^{2+}, blue emission) or to be partly oxidized (liberating brown bromine).

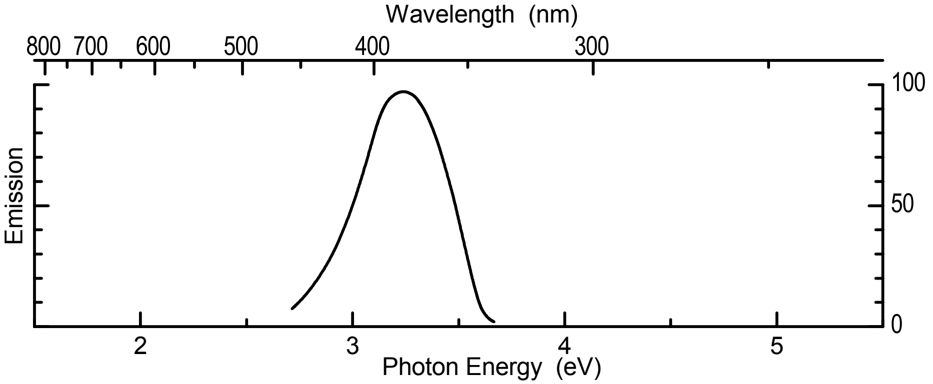
YOCl:Ce^{3+}

Structure: Rhombohedral (matlockite)

Optical Properties

Emission color: Violet − UV
Emission peak: 3.24 eV
Emission width (FWHM): 0.47 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Blasse, G., and Bril, A., and Poorter, J.A.D., Fast-decay phosphors, *J. Electrochem. Soc.,* 117, 346 (1970).
2. Blasse, G., and Bril, A., Photoluminescent efficiency of phosphors with electronic transitions in localized centers, *J. Electrochem. Soc.,* 115, 1067 (1968).
3. Blasse, G., and Bril, A., Characteristic luminescence, 1. The absorption and emission spectra of some important activators, *Philips Tech. Rev.,* 31, 304 (1970).

$YOCl:Eu^{3+}$

Structure: Rhombohedral (matlockite)

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	95 (of Y)	107.4
Eu_2O_3	5 (of Eu)	8.8
NH_4Cl	110	59

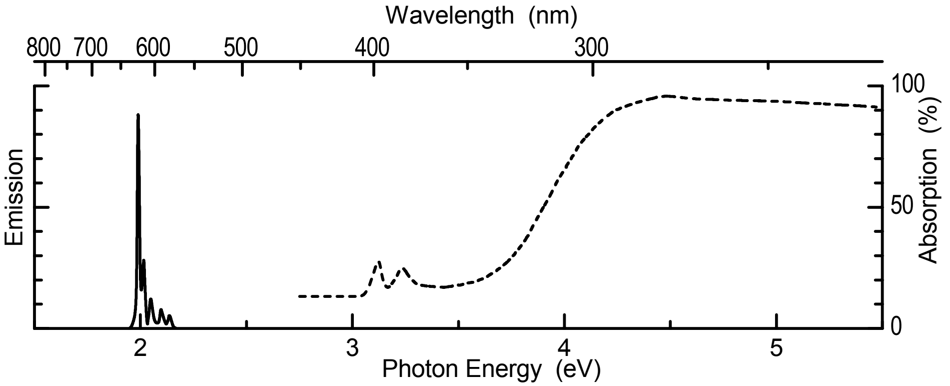
Preparation

Make a suspension of all ingredients in water.
Boil down to dry (slowly, to let the conversion of Y_2O_3 to YOCl take place).
Powderize.
1. Fire in capped quartz tubes, N_2, ~500°C, ½ hour.
Powderize.
2. Fire in capped quartz tubes, N_2, 1100°C, 1 hour.
Powderize.
Wash in water several times.
Dry.

Optical Properties

Emission color: Red
Emission peaks: 1.97–2.14 eV; main peak at 2.00 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: −

Spectra



Remark

This phosphor is hygroscopic. Keep dry.

Reference

1. Blasse, G., and Bril, A., Broad band UV excitation of Sm^{3+}-activated phosphors, *Phys. Lett.,* 23, 440 (1966).

YOF:Eu^{3+}

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	64 (of Y)	72.3
Eu_2O_3	2 (of Eu)	3.5
YF_3	34	49.6

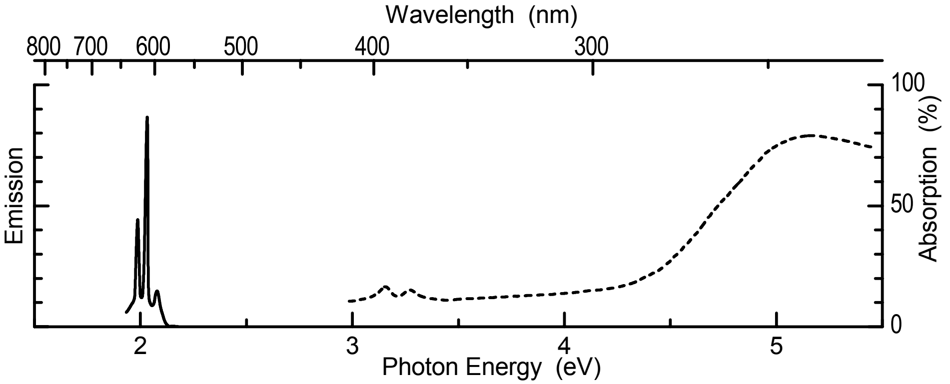
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
1. Fire in capped quartz tubes, N_2, 1000°C, 1 hour.
   Powderize.
2. Fire in capped quartz tubes, N_2, 1200°C, 1 hour.

Optical Properties

Emission color: Light red
Emission peaks: 1.977, 2.038, and 2.105 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: −

Spectra



Reference

1. Blasse, G., and Bril, A., Broad band UV excitation of Sm^{3+}-activated phosphors, *Phys. Lett.,* 23, 440 (1966).

YOF:Tb^{3+}

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	61 (of Y)	69
Tb_4O_7	5 (of Tb)	9.4
YF_3	34	49.6

Preparation

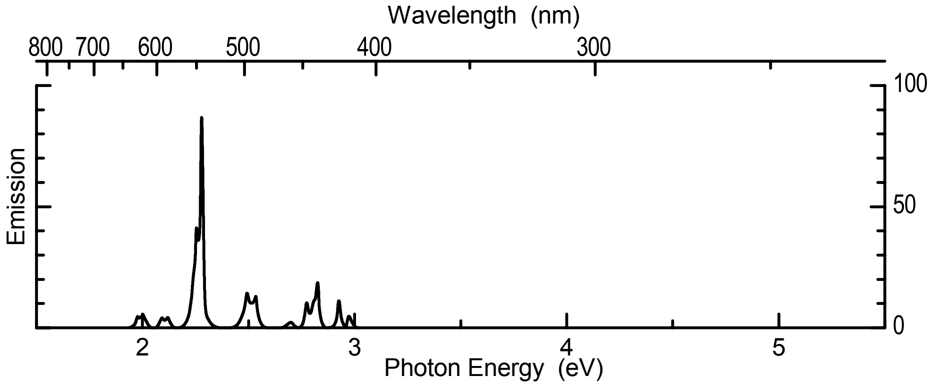
Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 1000°C, 1 hour.
   Powderize.
2. Fire in capped quartz tubes, N_2, 1200°C, 1 hour.

Optical Properties

Emission color: Pale green
Emission peaks: 1.982–2.993 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +/4–5%

Spectra



Remark

UV excitation is very poor (too little absorption) and can probably be improved by addition of Ce^{3+}.

LaOF:Eu^{3+}

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	61 (of La)	99.4
Eu_2O_3	5 (of Eu)	8.8
LaF_3	34	66.6

Preparation

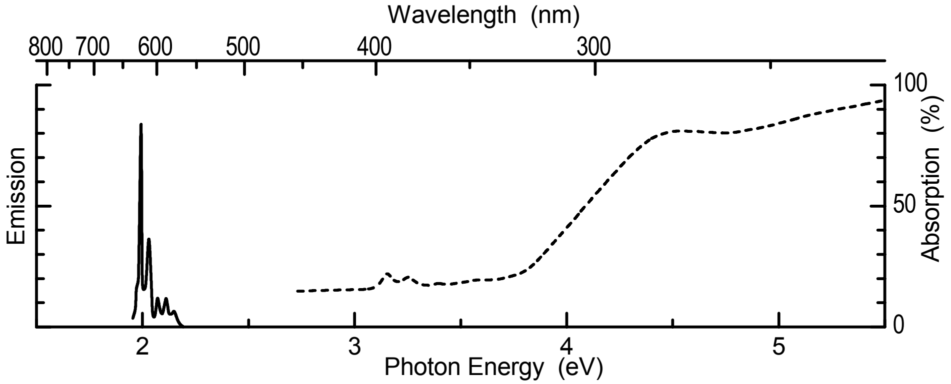
Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.

1. Fire in capped quartz tubes, N_2, 1000°C, 1 hour.
   Powderize.
2. Fire in capped quartz tubes, N_2, 1200°C, 1 hour.

Optical Properties

Emission color: Red
Emission peak: 1.981–2.145 eV; main line at 1.981 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)

Spectra



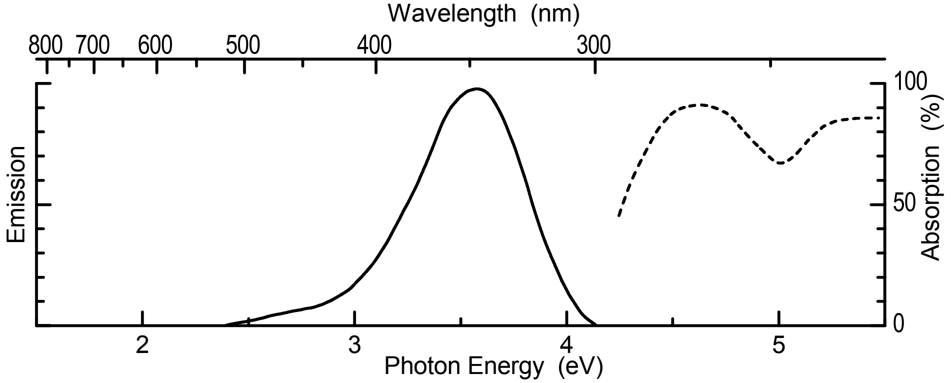
LaOCl:Bi^{3+}

Structure: Rhombohedral (matlockite)

Optical Properties

Emission color: UV
Emission peak: 3.56 eV
Emission width (FWHM): 0.58 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Blasse, G., and Bril, A., Investigations on BI^{3+}-activated phosphors, *J. Chem. Phys.,* 48, 217 (1968).
2. Boulon, G. et al., *Proc. Int. Conf. Phys*., 48, 217 (1968).
3. Jaquier, B., Photoluminescence processes in LaOCl-Bi and YOCl-Bi, *J. Lumin.,* 10, 95 (1975).

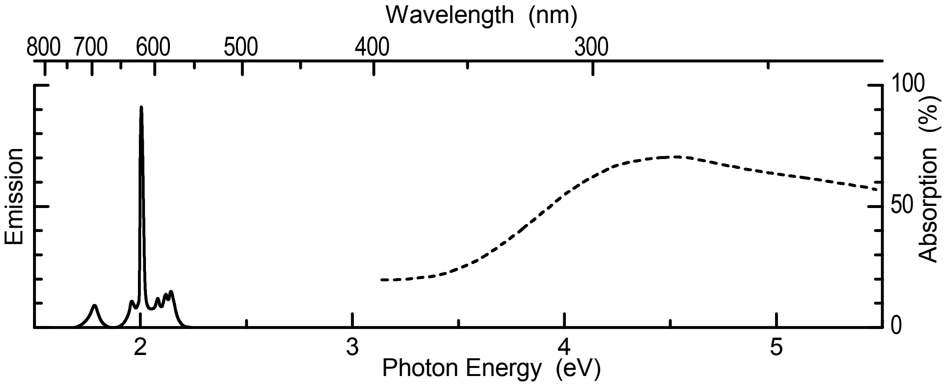
$LaOCl:Eu^{3+}$

Structure: Rhombohedral (matlockite)

Optical Properties

Emission color: Light red
Emission peak: 2.02 eV
Excitation efficiency by UV: + (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: –

Spectra



Reference

1. Blasse, G., and Bril, A., Characteristic luminescence, 1. The absorption and emission spectra of some important activators, *Philips Tech. Rev.,* 31, 304 (1970).

4.12 Sulfates

The following host compounds and activators are included in this subsection:

$MgSO_4{:}Eu^{2+}$
$MgSO_4{:}Pb^{2+}$
$CaSO_4{:}Eu^{2+},Mn^{2+}$
$CaSO_4{:}Pb^{2+}$
$CaSO_4{:}Bi$
$CaSO_4{:}Ce^{3+}$
$CaSO_4{:}Ce^{3+},Mn^{2+}$
$CaSO_4{:}Eu^{2+}$
$SrSO_4{:}Bi$
$SrSO_4{:}Ce^{3+}$
$SrSO_4{:}Eu^{2+},Mn^{2+}$
$SrSO_4{:}Eu^{2+}$
$BaSO_4{:}Ce^{3+}$
$BaSO_4{:}Eu^{2+}$
$MgBa(SO_4)_2{:}Eu^{2+}$
$Mg_2Ca(SO_4)_3{:}Eu^{2+}$
$Mg_2Ca(SO_4)_3{:}Eu^{2+},Mn^{2+}$
$Mg_2Sr(SO_4)_3{:}Eu^{2+}$

$MgSO_4{:}Eu^{2+}$

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$MgSO_4$	97	117
Eu_2O_3	3	5.3
$(NH_4)_2SO_4$	~10	13.2
NH_4Cl	1	0.540

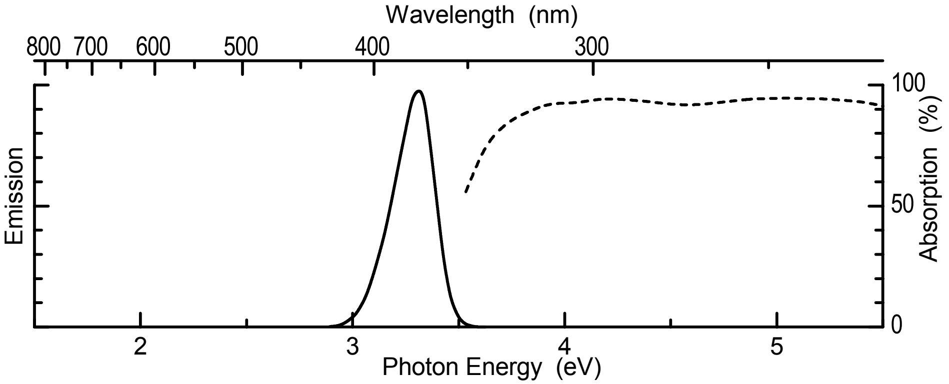
Preparation

Mix by dry grinding or milling.
Fire in capped quartz tubes, N_2, 1000ºC, 1 hour.
Powderize.
Store in well-closed containers.

Optical Properties

Emission color: UV
Emission peak: 3.31 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)

Spectra



Remark

$MgSO_4$ (epsom salt) is water soluble. Keep dry.

$MgSO_4:Pb^{2+}$

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$MgSO_4$	97	117
PbO	3	56.7
$(NH_4)_2SO_4$	~10	13.2
NH_4Cl	1	0.540

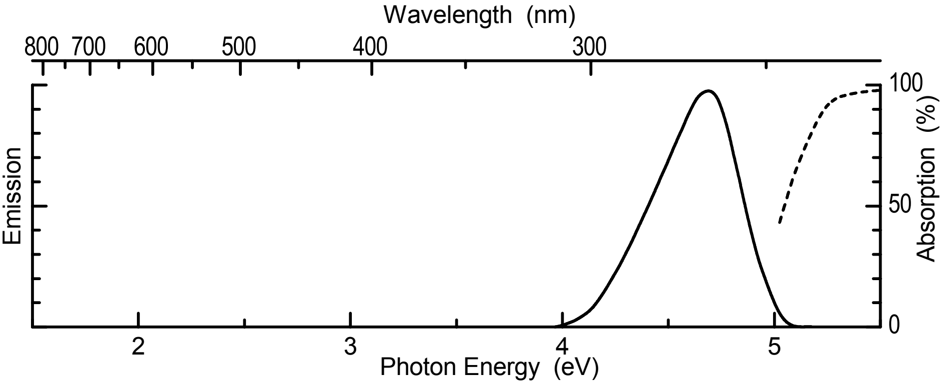
Preparation

Mix by dry grinding or milling.
Fire in capped quartz tubes, N_2, 1000ºC, 1 hour.
Powderize.
Store in well-closed containers.

Optical Properties

Emission color: UV
Emission peak: 4.65 eV
Emission width (FWHM): 0.46 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)

Spectra



Remarks

1. This material is excited only by UV of ~240 nm or shorter and apparently is fairly efficient.
2. $MgSO_4$ (epsom salt) is water soluble. Keep dry.

$CaSO_4:Eu^{2+},Mn^{2+}$

Structure: Orthorhombic (anhydrite)

Composition

Ingredient	Mole %	By weight (g)
$CaSO_4$	90	123
Eu_2O_3	5 (of Eu)	8.8
$MnCO_3$	5	5.75
$(NH_4)_2SO_4$	~10	13.2

Preparation

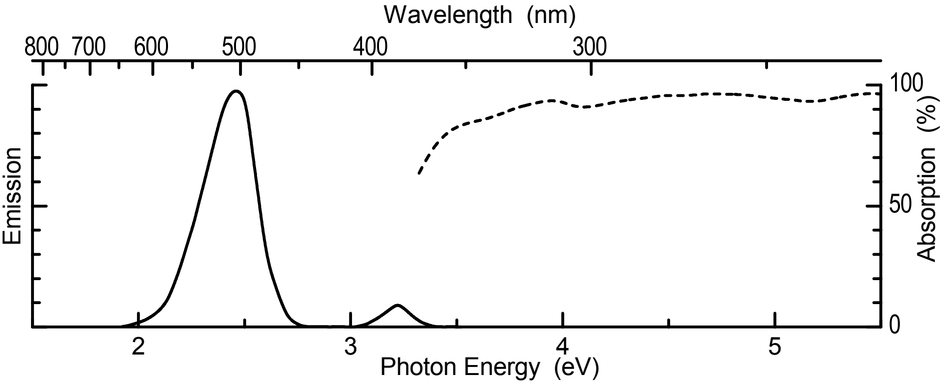
Mix by dry grinding or milling.

1. Fire in capped quartz tubes, N_2, 900°C, 1 hour.
   Powderize.
   Add ~5 g of NH_4Br and ~10 g of $(NH_4)_2SO_4$; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 800°C, ½ hour.
   Powderize.
   Wash in water several times.
   Dry.

Optical Properties

Emission color: Bluish-green
Emission peak: 2.42 eV (Mn^{2+}), 3.20 eV (Eu^{2+})
Emission width (FWHM): 0.30 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +/1%

Spectra



Remark

The spectral positions of the Mn^{2+}-emission band depends on the Mn concentration used, shifting to blue-green for 1% Mn and to yellow-green for 10% Mn.

$CaSO_4$:Pb^{2+}

Structure: Orthorhombic (anhydrite)

Composition

Ingredient	Mole %	By weight (g)
$CaSO_4$	98	133
CaF_2	1	0.780
PbO	1	2.23
$(NH_4)_2SO_4$	~5	6.6

Preparation

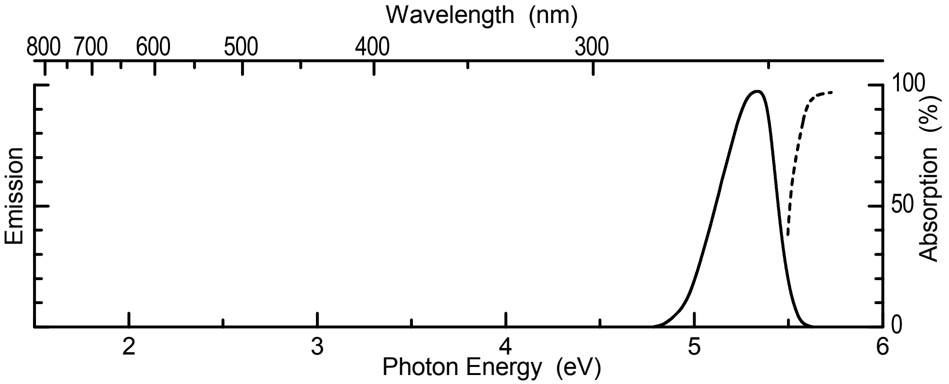
Mix by dry grinding or milling.

1. Fire in capped quartz tubes, N_2, 950ºC, 1 hour.
   Add another 6.6 g of $(NH_4)_2SO_4$. Mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1000ºC, 1 hour.
   Powderize.
   Add 5 g of NH_4Cl. Mix by dry grinding.
3. Fire in capped quartz tubes, N_2, 1050ºC, 1 hour.
   Powderize.
   Wash in water several times. Dry.

Optical Properties

Emission color: UV
Emission peak: 5.33 eV
Emission width (FWHM): 0.33 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Remarks

1. This phosphor is excited only by UV of ~220 nm or shorter and is fairly efficient.
2. It discolors in fluorescent lamps because of (probably) undissolved $PbSO_4$ dissociation to PbO.

$CaSO_4$:Bi

Structure: Orthorhombic (anhydrite)

Composition

Ingredient	Mole %	By weight (g)
$CaSO_4$	98	118
Bi_2O_3	1 (of Bi)	2.3
Na_2SO_4	5 (of Na)	3.5
$(NH_4)_2SO_4$	~5	6.6

Preparation

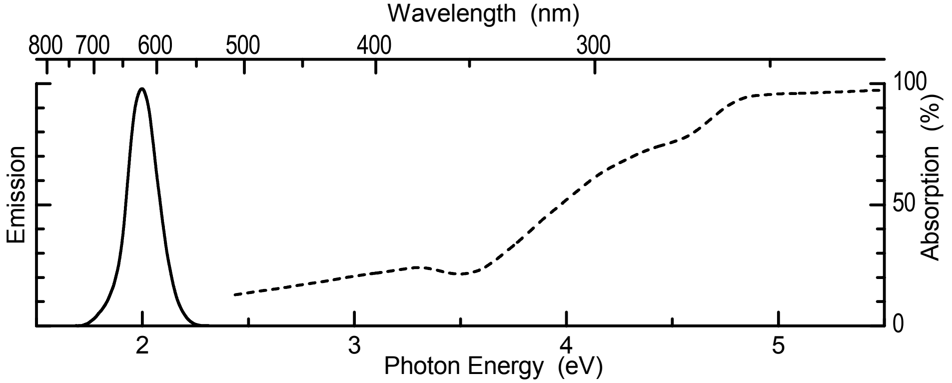
Mix by dry grinding or milling.

1. Fire in covered alumina crucibles, N_2, 900ºC, 1 hour.
   Add another 5–6 g of $(NH_4)_2SO_4$; mix by dry grinding.
2. Fire in covered alumina crucibles, N_2, 950ºC, 1 hour.
   Powderize.
   Wash in water several times. Dry.

Optical Properties

Emission color: Light red
Emission peak: 2.02 eV
Emission width (FWHM): 0.16 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +/0.7%

Spectra



Remark

The nature of this red emission is still unknown: It is not likely to be due to Bi^{3+} but it may possibly be due to Bi^{5+} substituting for S^{6+}.

Reference

1. Kröger, F.A., et al., Bismuth as activator in fluorescent solids, *J. Electrochem. Soc.,* 96, 132 (1949).

$CaSO_4:Ce^{3+}$

Structure: Orthorhombic (anhydrite)

Composition

Ingredient	Mole %	By weight (g)
$CaSO_4$	94	128
CeO_2	3	5.2
Na_2SO_4	5 (of Na)	3.6
$(NH_4)_2SO_4$	~10	13.2

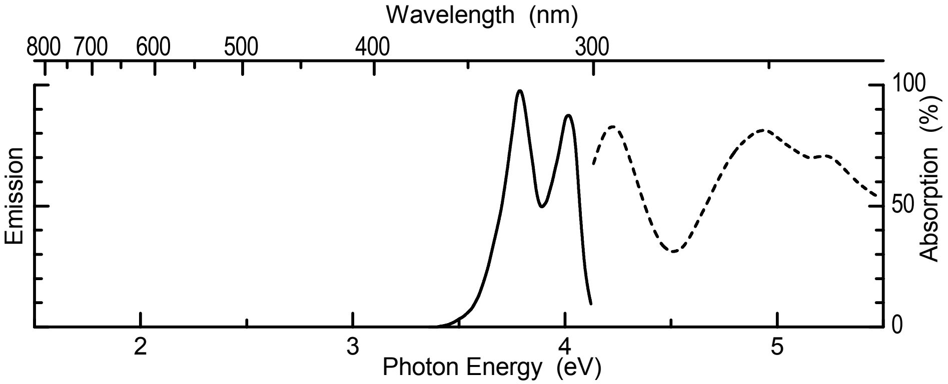
Preparation

Mix by dry grinding or milling.
1. Fire in covered alumina crucibles, N_2, 900°C, 1 hour.
   Powderize.
   Add above amounts of Na_2SO_4 and $(NH_4)_2SO_4$ once again; mix by dry grinding.
2. Fire in covered alumina crucibles, N_2, 900°C, 1 hour.
   Powderize.
   Wash in water several times.
   Dry.

Optical Properties

Emission color: UV
Emission peak: 3.79 eV, 4.01 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



$CaSO_4$:Ce^{3+},Mn^{2+}

Structure: Orthorhombic (anhydrite)

Composition

Ingredient	Mole %	By weight (g)
$CaSO_4$	88.5	121
CeO_2	2.5	4.3
$MnCO_4$	6	6.9
$(NH_4)_2SO_4$	~10	13.2

Preparation

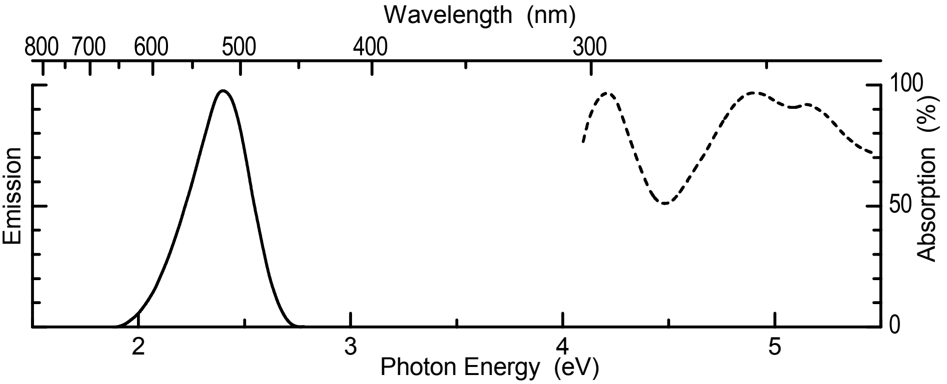
Mix by dry grinding or milling.

1. Fire in capped quartz tubes, N_2, 1000°C, 1 hour.
   Powderize.
   Add ~10 g of $(NH_4)_2SO_4$; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 800°C.
   Powderize.
   Add ~2 g of Li_2SO_4 and ~6 g of $(NH_4)_2SO_4$; mix by dry grinding.
3. Fire in capped quartz tubes, N_2, 700°C.
   Powderize.
   Add ~6 g of $(NH_4)_2SO_4$; mix by dry grinding.
4. Fire in capped quartz tubes, N_2, 700°C.
   Powderize.
   Wash in water several times. Dry.

Optical Properties

Emission color: Yellow-green
Emission peak: 2.35 eV
Emission width (FWHM): 0.36 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



References

1. Rudolf, J., and Ruffler, H., *Tech. Wiss. Abh. OSRAM Ges.,* 7, 232 (1958).
2. Rabatin, J., *Electrochem. Soc. Meeting,* Washington, DC, Abstr. 157 (May 1976).

$CaSO_4:Eu^{2+}$

Structure: Orthorhombic (anhydrite)

Composition

Ingredient	Mole %	By weight (g)
$CaSO_4$	99	135
Eu_2O_3	1 (of Eu)	1.76
$(NH_4)_2SO_4$	~5	6.6

Preparation

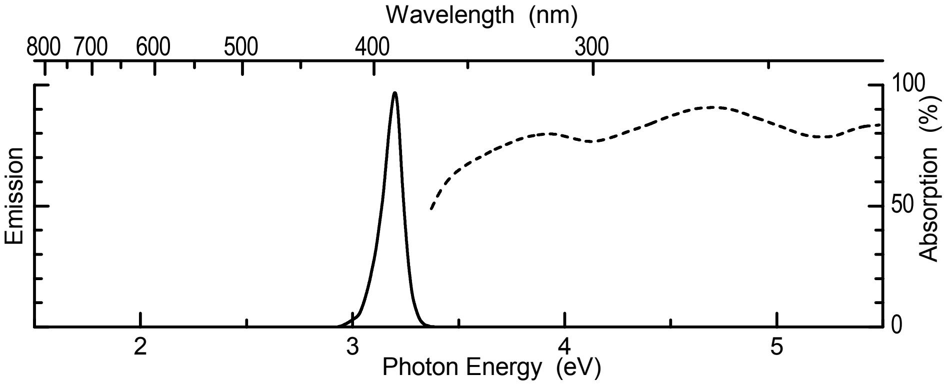
Mix by dry grinding or milling.

1. Fire in capped quartz tubes, N_2, 950ºC, 1 hour. Powderize.
   Add another 6.6 g of $(NH_4)_2SO_4$; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 950ºC, 1 hour. Powderize.
   Add 5 g of NH_4Cl; mix by dry grinding.
3. Fire in capped quartz tubes, N_2, 1000ºC, 1 hour. Powderize.
   Wash in water several times. Dry.

Optical Properties

Emission color: Very deep violet
Emission peak: 3.20 eV
Emission width (FWHM): 0.12 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +/4%
Decay**:** Near-exponential decay, about 1.1 µsec to 1/10

Spectra



Remark

This $CaSO_4$ phosphor is stable in water.

References

1. Wachtel, A., U.S. Pat., 3 669 897 (1971).
2. Dixon, R.L., and Ekstrand, K.E., Thermoluminescence of rare earth activated $CdSO_4$, $SrSO_4$ and $BaSO_4$, *J. Lumin.,* 8, 383 (1974).
3. Luckey, D., Germ. Pat., 2 051 240 (1971).

$SrSO_4$:Bi

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$SrSO_4$	98	180
Bi_2O_3	1 (of Bi)	2.3
Na_2SO_4	5 (of Na)	3.5
$(NH_4)_2SO_4$	~5	6.6

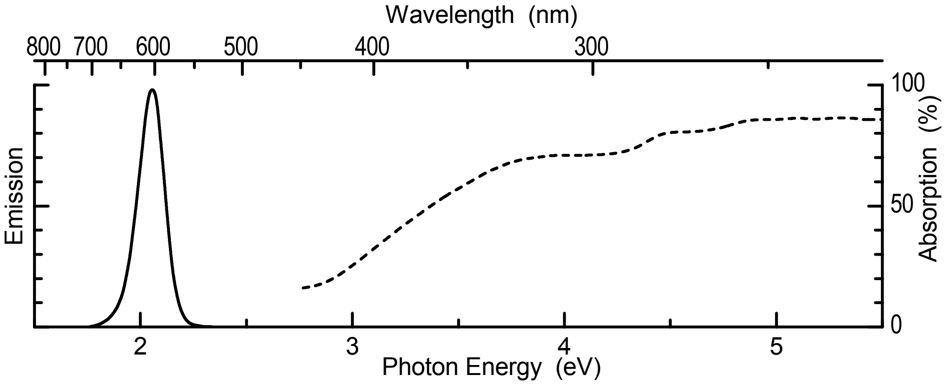
Preparation

Mix by dry grinding or milling.
1. Fire in covered alumina crucibles, N_2, 900°C, 1 hour.
Powderize.
Add another 5–6 g of $(NH_4)_2SO_4$; mix by dry grinding.
2. Fire in covered alumina crucibles, N_2, 950°C, 1 hour.
Powderize.
Wash in water several times. Dry.

Optical Properties

Emission color: Orange-red
Emission peak: 2.04 eV
Emission width (FWHM): 0.15 eV
Excitation efficiency by UV: – (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +/1–1.5%

Spectra



Remark
The nature of this emission is still unknown: It is not likely to be due to Bi^{3+} but it may possibly be due to Bi^{5+} substituting for S^{6+}.

Reference

1. Kröger, F.A. et al., Bismuth as activator in fluorescent solids, *J. Electrochem. Soc.,* 96, 132 (1949).

$SrSO_4$:Ce^{3+}

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$SrSO_4$	94	173
CeO_2	3	5.2
Na_2SO_4	5 (of Na)	3.6
$(NH_4)_2SO_4$	~10	13.2

Preparation

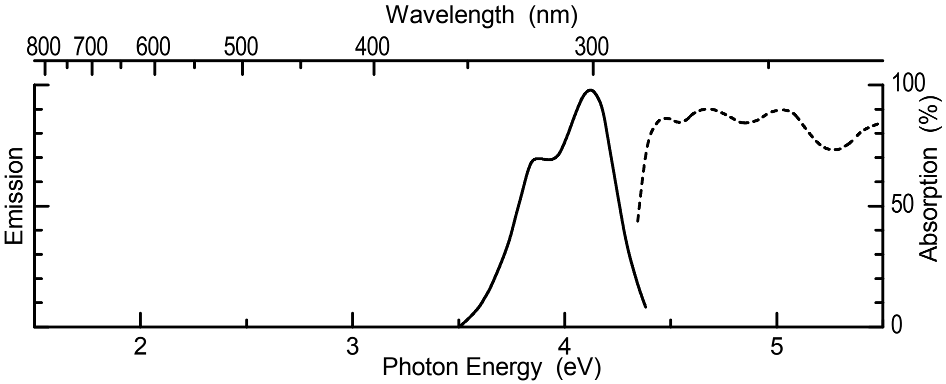
Mix by dry grinding or milling.

1. Fire in covered alumina crucibles, N_2, 900°C, 1 hour. Powderize.
   Add the above amounts of Na_2SO_4 and $(NH_4)_2SO_4$ once again; mix by dry grinding.
2. Fire in covered alumina crucibles, N_2, 900°C, 1 hour. Powderize.
   Wash in water several times. Dry.

Optical Properties

Emission color: UV
Emission peak: 3.89 and 4.11 eV (Two overlapping bands)
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



$SrSO_4$:Eu^{2+},Mn^{2+}

Structure: Orthorhombic

Optical Properties

Emission color: Orange
Emission peak: 2.19 eV
Emission width (FWHM): 0.29 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

$SrSO_4$:Eu^{2+}

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$SrSO_4$	98	180
Eu_2O_3	2 (of Eu)	3.5
SrF_2	1	1.26
$(NH_4)_2SO_4$	~5	6.6

Preparation

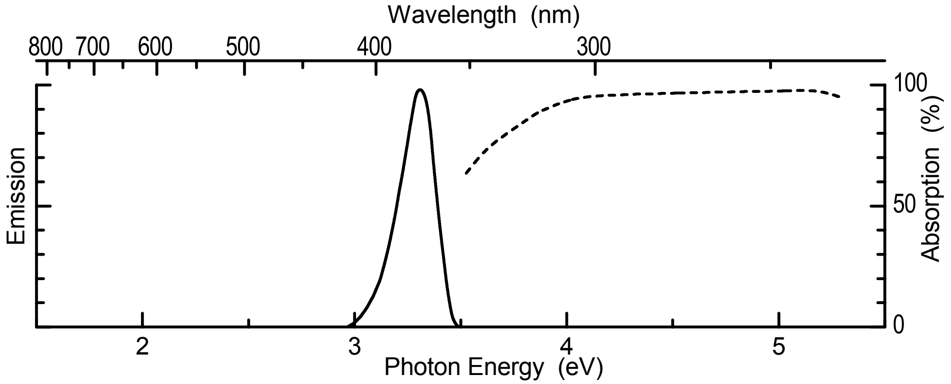
Mix by dry grinding or milling.

1. Fire in capped quartz tubes, N_2, 900°C, 1 hour. Powderize.
   Add another 6.6 g of $(NH_4)_2SO_4$; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 900°C, 1 hour. Powderize.
   Add 5 g of NH_4Cl; mix by dry grinding.
3. Fire in capped quartz tubes, 800°C, 1 hour. Powderize.
   Wash in water several times. Dry.

Optical Properties

Emission color: UV
Emission peak: 3.30 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +/5%
Decay: Near-exponential decay, about 5 μsec to 1/10

Spectra



References

1. Wachtel, A., U.S. Pat., 3 669 897 (1971).
2. Dixon, R.L., and Ekstrand, K.E., Thermoluminescence of rare earth activated $CdSO_4$, $SrSO_4$ and $BaSO_4$, *J. Lumin.,* 8, 383 (1974).
3. Luckey, D., Germ. Pat., 2 051 240 (1971).

$BaSO_4$:Ce^{3+}

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$BaSO_4$	94	173
CeO_2	3	5.2
Na_2SO_4	5 (of Na)	3.6
$(NH_4)_2SO_4$	~10	13.2

Preparation

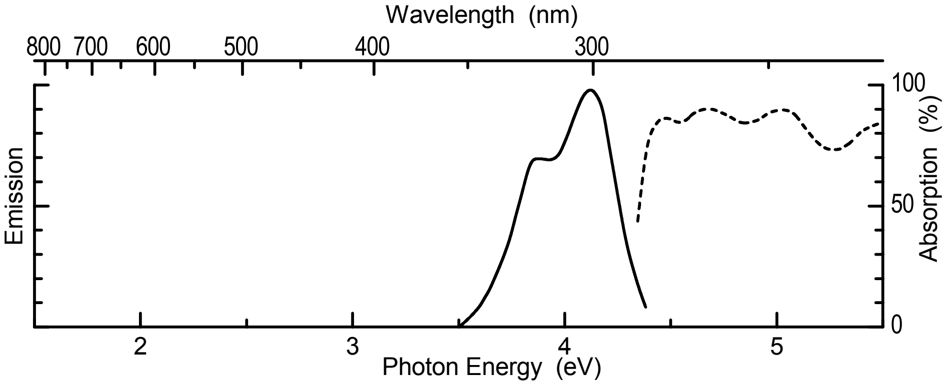
Mix by dry grinding or milling.

1. Fire in covered alumina crucibles, N_2, 900°C, 1 hour.
   Powderize.
   Add the above amounts of Na_2SO_4 and $(NH_4)_2SO_4$ once again; mix by dry grinding.
2. Fire in covered alumina crucibles, N_2, 900°C, 1 hour.
   Powderize.
   Wash in water several times.
   Dry.

Optical Properties

Emission color: UV
Emission peak: 3.89 eV, 4.11 eV (Two overlapping bands)
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



$BaSO_4$:Eu^{2+}

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$BaSO_4$	98	180
Eu_2O_3	2 (of Eu)	3.5
SrF_2	1	1.26
$(NH_4)_2SO_4$	~5	6.6

Preparation

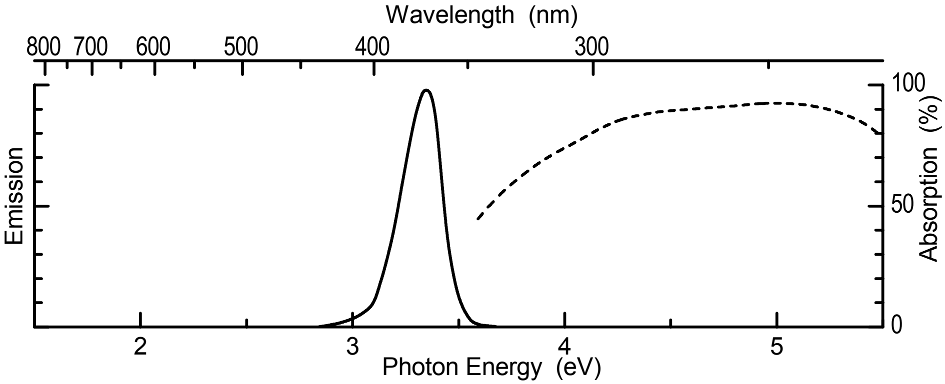
Mix by dry grinding or milling.

1. Fire in capped quartz tubes, N_2, 900ºC, 1 hour.
   Powderize.
   Add another 6.6 g of $(NH_4)_2SO_4$; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 900ºC, 1 hour.
   Powderize.
   Add 5 g of NH_4Cl; mix by dry grinding.
3. Fire in capped quartz tubes, 800ºC, 1 hour.
   Powderize.
   Wash in water several times. Dry.

Optical Properties

Emission color: UV
Emission peak: 3.30 eV
Emission width (FWHM): 0.21 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +/5%
Decay: Near-exponential decay, about 5 µsec to 1/10

Spectra



Reference

1. Luckey, D., Germ. Pat., 2 051 240 (1971).

$MgBa(SO_4)_2$:Eu^{2+}

Structure: KAl $(SO_4)_2$

Composition

Ingredient	Mole %	By weight (g)
$MgSO_4$	100	120
$BaSO_4$	94	219
Eu_2O_3	6 (of Eu)	10.6
$(NH_4)_2SO_4$	~10	13.2

Preparation

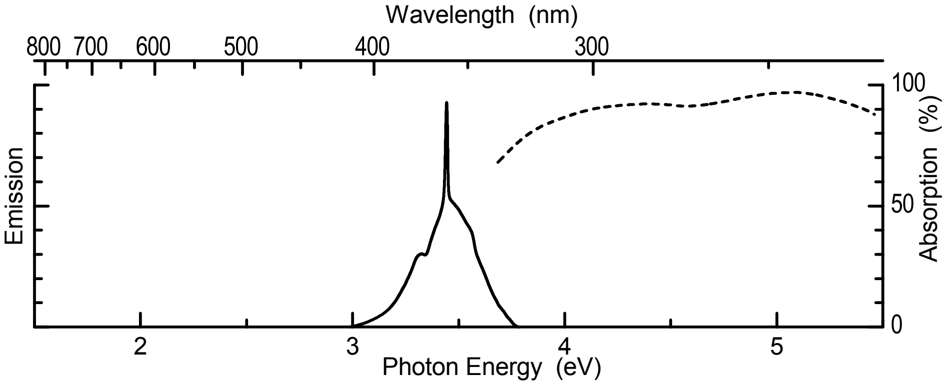
Mix by dry grinding or milling.

1. Fire in capped quartz tubes, N_2, 900°C, 1 hour. Powderize.
   Add ~10 g of $(NH_4)_2SO_4$; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1100°C, 1 hour. Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: UV
Emission peak: Main peak at 3.455 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Remark

This material decomposes in contact with water or in moist air.

References

1. Ryan, F.M. et al., Fine-structure in optical-spectra of divalent europium in alkaline-earth sulfates, *J. Electrochem. Soc.,* 121, 1475 (1974).
2. Blasse, G., VanDenHeuvel, G.P.M., and Stegenga, J., Luminescence of barium magnesium-sulfate, *J. Solid State Chem.,* 17, 439 (1976).
3. Blasse, G., and VanDenHeuvel, G.P.M., Crystal-structure of barium magnesium-sulfate, *J. Inorg. Nucl. Chem*., 38, 876 (1976).
4. Sakaguchi, M. et al., Thermoluminescence characteristics of binary sulfate phosphors, *J. Electrochem. Soc.,* 124, 1272 (1977).

$Mg_2Ca(SO_4)_3$:Eu^{2+}

Composition

Ingredient	Mole %	By weight (g)
$MgSO_4$	200	240
$CaSO_4$	94	128
Eu_2O_3	6 (of Eu)	10.6
$(NH_4)_2SO_4$	~10	13.2

Preparation

Mix by dry grinding or milling.

1. Fire in capped quartz tubes, N_2, 900°C, 1 hour.

   Powderize.

   Add ~5 g of NH_4Br, and ~10 g of $(NH_4)_2SO_4$; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 950°C.

Optical Properties

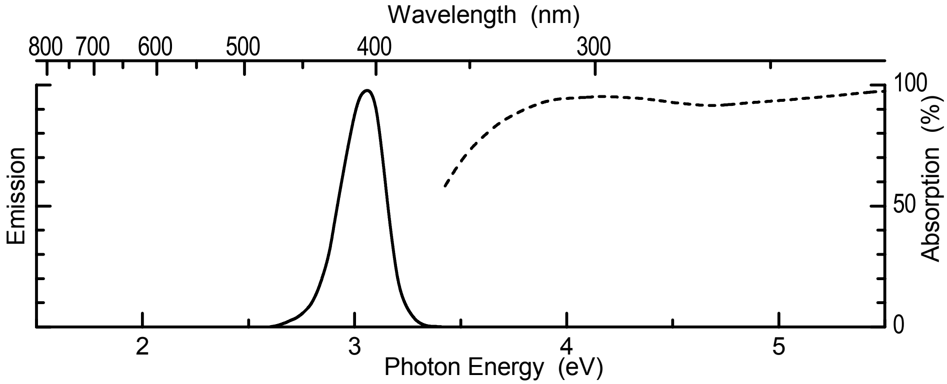
Emission color: Violet

Emission peak: 3.06 eV

Emission width (FWHM): 0.28 eV

Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Remark
This material decomposes in contact with water or in moist air. Keep dry.

$Mg_2Ca(SO_4)_3:Eu^{2+},Mn^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$MgSO_4$	200	240
$CaSO_4$	87	119
Eu_2O_3	5 (of Eu)	8.8
$MnCO_3$	8	9.2
$(NH_4)_2SO_4$	~10	13.2

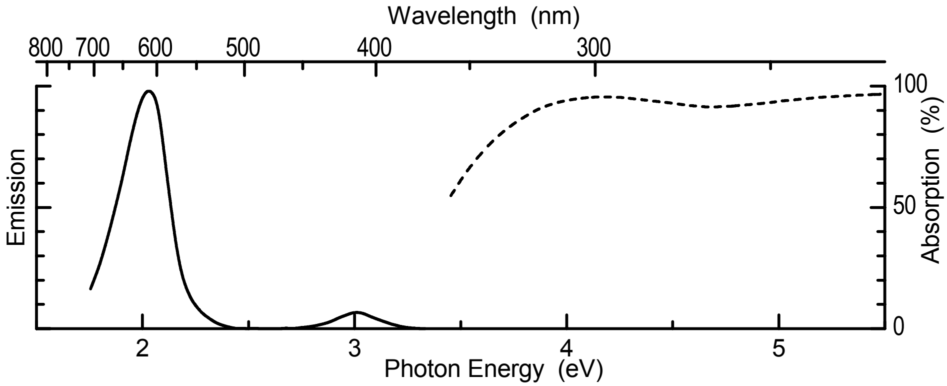
Preparation

Mix by dry grinding or milling.
1. Fire in capped quartz tubes, N_2, 900ºC, 1 hour.
Powderize.
Add ~5 g of NH_4Br, and ~10 g of $(NH_4)_2SO_4$; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 950ºC.

Optical Properties

Emission color: Orange-red
Emission peak: 2.01 eV (Mn^{2+}), 3.06 eV (Eu^{2+})
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Remark

This material decomposes in contact with water or in moist air. Keep dry.

$Mg_2Sr(SO_4)_3$:Eu^{2+}

Composition

Ingredient	Mole %	By weight (g)
MgO	200	240
$SrSO_4$	94	173
Eu_2O_3	6 (of Eu)	10.6
$(NH_4)_2SO_4$	~10	13.2

Preparation

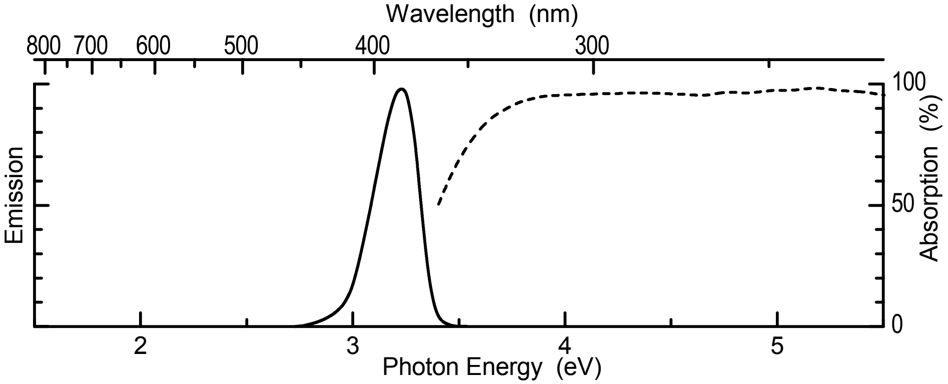
Mix by dry grinding or milling.

1. Fire in capped quartz tubes, N_2, 900°C, 1 hour.
   Powderize.
   Add 10 g of $(NH_4)_2SO_4$; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1100°C, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Barely visible deep violet
Emission peak: 3.21 eV
Emission width (FWHM): 0.23 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)

Spectra



Remark

This material decomposes in contact with water or in moist air.

4.13 ZnS-Type Sulfides

The following host compounds and activators are included in this subsection:

- ZnS:Ag^{+},Cl^{-}
- ZnS:Au,In
- ZnS:Cl^{-}
- ZnS:Cu,Sn
- ZnS:Cu^{+},Al^{3+}
- ZnS:Cu^{+},Cl^{-}
- ZnS:Eu^{2+}
- ZnS:Mn^{2+}
- ZnS:Mn^{2+},Te^{2+}
- ZnS:P
- ZnS:P^{3-},Cl^{-}
- ZnS:Pb^{2+}
- ZnS:Pb^{2+},Cl^{-}
- ZnS:Pb,Cu
- ZnS:Sn^{2+}
- ZnS:Sn,Ag
- ZnS:Sn^{2+},Li^{+}
- ZnSe:Cu^{+},Cl
- CdS:Ag^{+},Cl^{-}
- CdS:In
- ZnS-CdS:Cu,I
- ZnS-CdS (25-75)
- ZnS-CdS (50-50)
- ZnS-CdS (75-25)
- ZnS-CdS:Ag,Br,Ni
- ZnS-CdS:Ag^{+},Cl
- ZnS-CdS:Cu,Br long life
- ZnS-CdS:Cu,Br high brightness
- ZnS-ZnTe:Mn^{2+} 98-2

ZnS:Ag^{+},Cl^{-}

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	100	98
$AgNO_3$	0.3	0.050
NH_4Cl	5	2.5

Preparation

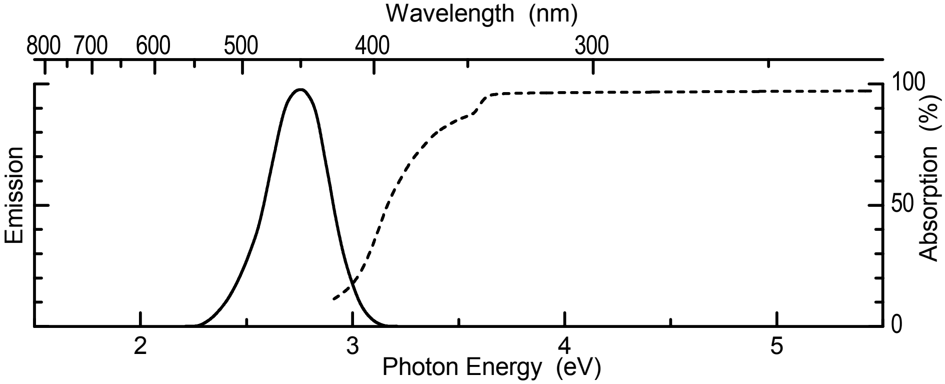
Dissolve the $AgNO_3$ and the NH_4Cl separately, each in a little water.
Make a slurry of the ZnS in water or methanol.
First add the silver solution, stir, then add the NH_4Cl solution, and stir again.
Dry in air. Powderize when dry.

Add ~2–3 g of sulfur.
Fire in capped quartz tubes, N_2, 1100°C, 1 hour. Powderize.
Wash in water several times (to remove leftover halide). Dry.

Optical Properties

Emission color: Blue
Emission peak: 2.80 eV
Emission width (FWHM): 0.34 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: ++
Decay: Non-exponential decay in the microsecond range

Spectra



Remarks

1. The chlorine in the above recipe may be replaced by bromine.
2. This phosphor corresponds to the commercial P-22B.

References

1. Leverenz, H.W., *An Introduction to Luminescence of Solids,* John Wiley & Sons, New York (1949).
2. Shionoya, S., in *Luminescence of Inorganic Solids,* Goldberg, P., Ed., Academic Press, New York (1966).

ZnS:Au,In

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	100	98
Au metal	0.005	0.010
In_2O_3	0.002 (of In)	0.0023
NH_4Cl	5	2.5

Preparation

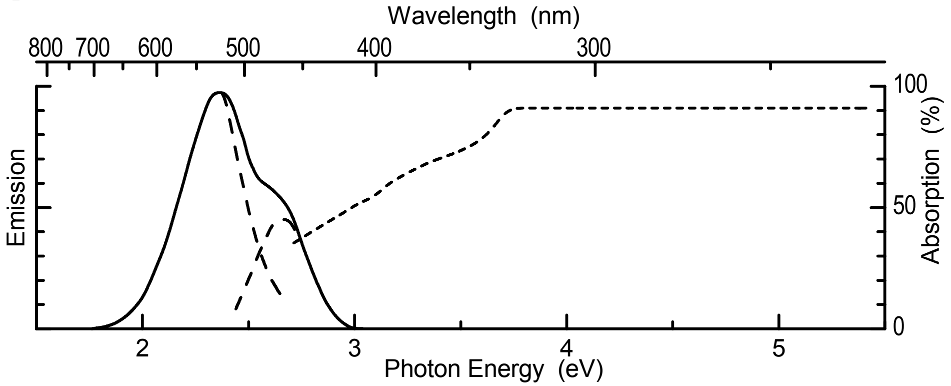
Dissolve the gold in a very little amount of aqua regia.
Add this solution to the ZnS. Make a slurry in methanol. Dry. Powderize.

1. Fire in open quartz boats, H_2S, 900ºC, 1 hour.
   Powderize.
   Add the dry NH_4Cl and about 2–3 g of sulfur; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1200ºC, 1 hour.
   Powderize. Make a slurry of the phosphor in methanol.
   Dissolve the In_2O_3 in a little nitric acid, add the solution to the slurry, stir, dry, and powderize.
   Add about 2–3 g of sulfur.
3. Fire in capped quartz tubes, N_2, 900ºC, 1 hour.
4. Fire in open quartz boats, H_2S, 900ºC.

Optical Properties

Emission color: Blue-green, long afterglow
Emission peaks: 2.34 eV, 2.67 eV
Emission width (FWHM): 0.34 eV (First peak)
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Remark

The green phosphorescence of this phosphor after excitation by UV or by e-beam is visible for several hours in the dark.

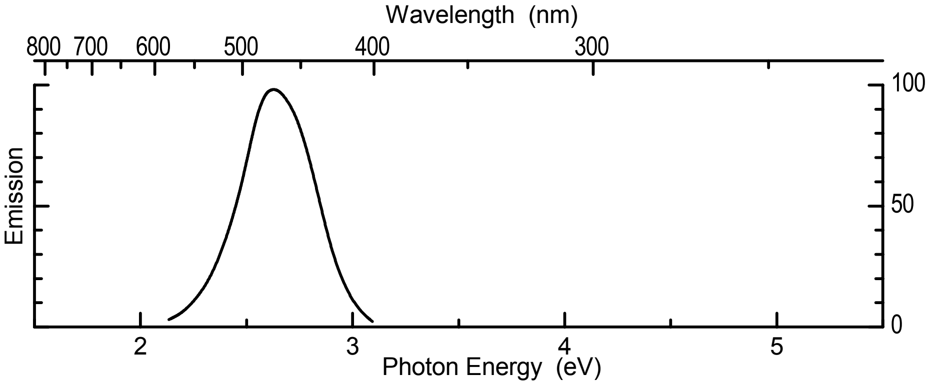
$ZnS:Cl^-$

Structure: Cubic, hexagonal (wurtzite)

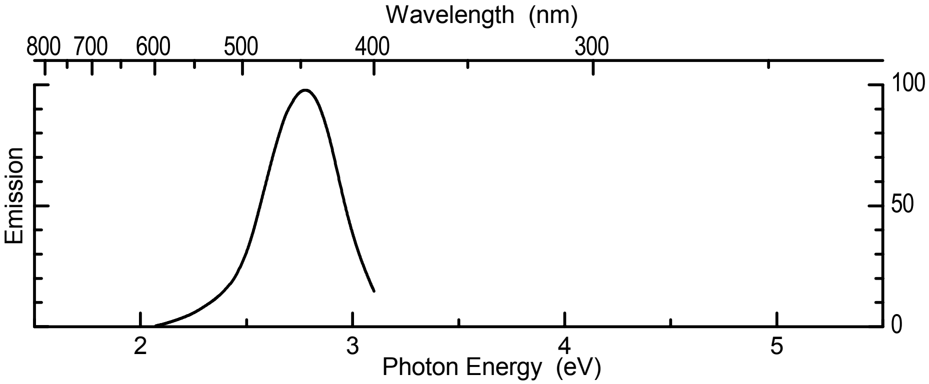
Optical Properties

Emission color: Blue
Emission peak: 2.70 eV
Emission width (FWHM): 0.50 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: ++

Spectra (cubic)



Spectra (hexagonal)



References

1. Leverenz, H.W., *An Introduction to Luminescence of Solids,* John Wiley & Sons, New York (1949).
2. Shionoya, S., in *Luminescence of Inorganic Solids,* Goldberg, P., Ed., Academic Press, New York (1966).

ZnS:Cu,Sn

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	100	98
SnS	0.1	0.150
$Cu(C_2H_3O_2)_2 . H_2O$	0.001	0.002

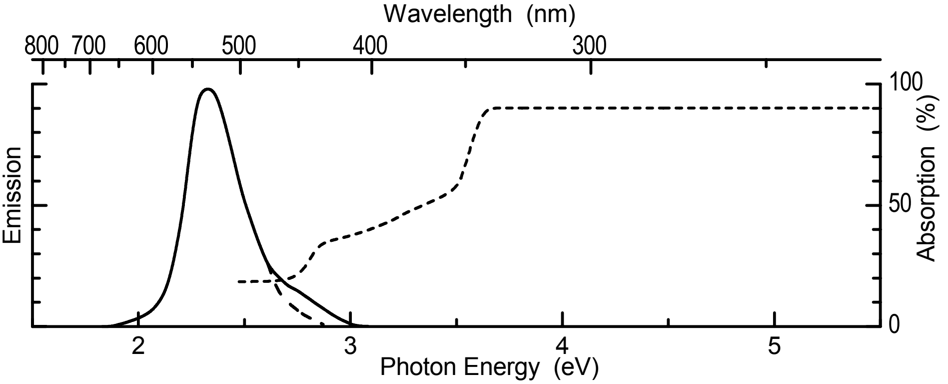
Preparation

Dissolve the copper acetate in a little water; add solution to the ZnS + SnS mix.
Make a slurry in water or methanol.
Dry. Powderize.
Add ~2–3 g of sulfur.
Fire in capped quartz tubes, N_2, 1150°C, 1 hour.

Optical Properties

Emission color: Green
Emission peak: 2.41 eV
Emission width (FWHM): 0.32 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Remarks

1. Irradiation of near-IR during excitation by 3.40 eV UV causes strong quenching of the green emission.
2. This phosphor is much more sensitive to IR than the fairly well-known ZnS:Cu,Co phosphor.

$ZnS:Cu^+,Al^{3+}$

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	100	98
$Cu(C_2H_3O_2)_2 . H_2O$	0.001	0.002
$AlCl_3$	0.3	0.400

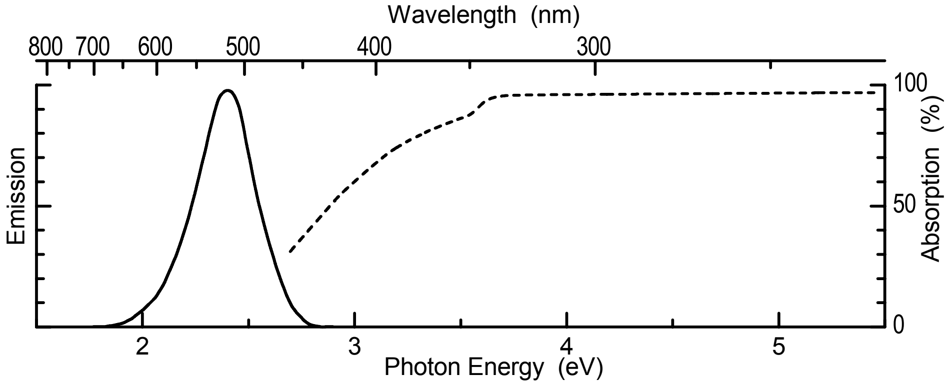
Preparation

Dissolve the copper acetate and the aluminum chloride together in a little water.
Add solution to the ZnS mix.
Add enough water or methanol to make a uniform slurry.
Dry. Powderize.
Add ~2–3 g of sulfur.
Fire in capped quartz tubes, H_2S, 1100°C, 1 hour.
Wash in water several times (stir, let settle) to remove left over chloride. Dry.

Optical Properties

Emission color: Green, long afterglow tail.
Emission peak: 2.38 eV
Emission width (FWHM): 0.32 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: ++
Decay: Non-exponential decay in the microsecond range

Spectra



Remarks

1. The chlorine in the above recipe may be replaced by bromine.
2. This phosphor corresponds to the P-31 cathodoluminescent phosphor.

References

1. Kröger, F.A., *Some Aspects of Luminescence of Solids*, Elsevier, Amsterdam (1948).
2. Gool, W., and Cleiren, A.P., *Philips Res. Rep.,* 15, 238 (1960).

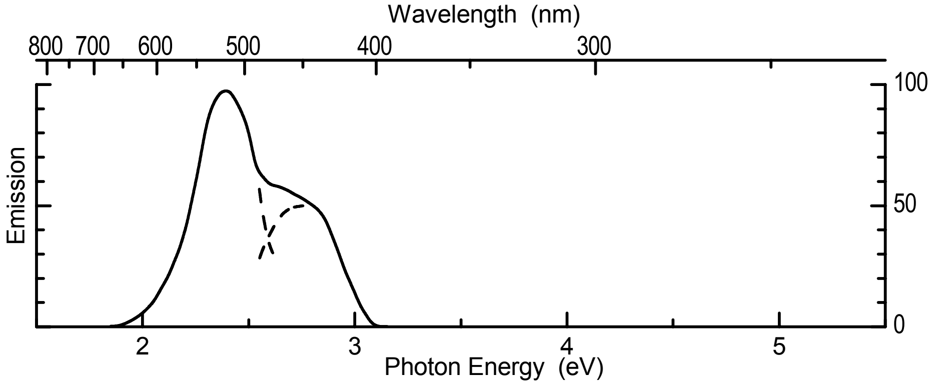
$ZnS:Cu^+,Cl^-$

Structure: Cubic (zinc blende)

Optical Properties

Emission color: Blue + green
Emission peak: 2.34 eV, 2.79 eV
Emission width (FWHM): 0.33 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: ++

Spectra



Reference

1. Leverenz, H.W., *An Introduction to Luminescence of Solids,* John Wiley & Sons, New York (1949).

ZnS:Eu^{2+}

Composition

Ingredient	Mole %	By weight (g)
ZnS	100	98
Eu_2O_3	0.03 (of Eu)	0.053

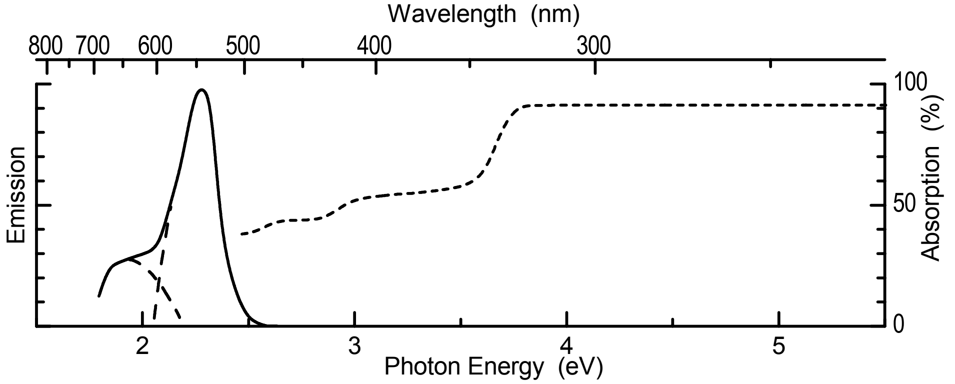
Preparation

Mix by slurrying in water or methanol.
Dry. Powderize.
Add ~2–3 g of sulfur.
1. Fire in open quartz boats, H_2S, 1100ºC, 1 hour.
   Powderize.
2. Fire in open quartz boats, H_2S, 1100ºC, 1 hour.

Optical Properties

Emission color: Yellow-green
Emission peak: 2.25 eV; Weaker band at 1.95 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: Poor

Spectra



ZnS:Mn^{2+}

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	99	97
$MnCO_3$	1	1.15
NH_4Cl	1	0.540

Preparation

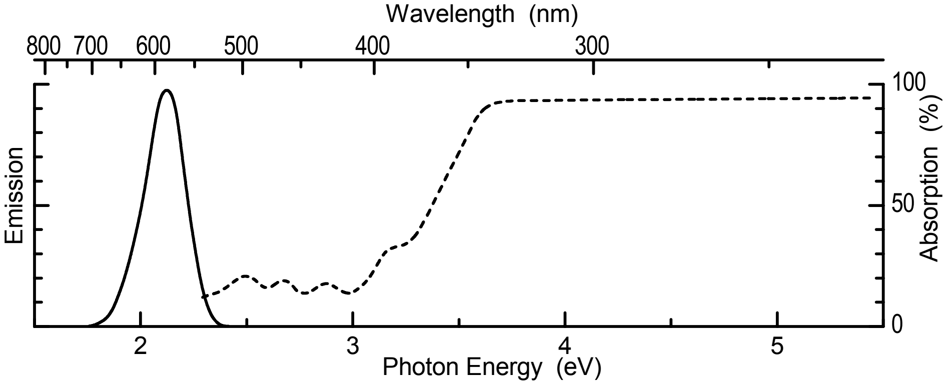
Mix by slurrying in water or methanol.
Dry. Powderize.

Add ~2–3 g of sulfur.
Fire in capped quartz tubes, N_2 or H_2S, 1100°C, 1 hour.

Optical Properties

Emission color: Orange-yellow
Emission peak: 2.13 eV
Emission width (FWHM): 0.21 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +/5%
Decay: Exponential, ~1 msec to 1/10

Spectra



Remarks

1. The emission shifts slightly to lower energy (= longer wavelength) with increasing Mn concentration.
2. This material is remarkable for its strong triboluminescence.

References

1. Leverenz, H.W., *An Introduction to Luminescence of Solids,* John Wiley & Sons, New York (1949).
2. Shionoya, S., in *Luminescence of Inorganic Solids,* Goldberg, P., Ed., Academic Press, New York (1966).

ZnS:Mn^{2+},Te^{2+}

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	94	92
$MnCO_3$	3	3.5
ZnTe	3	5.8
NH_4Br	2	2

Preparation

First mix only ZnS + $MnCO_3$ + NH_4Br (not yet the ZnTe).
Make a slurry in water.

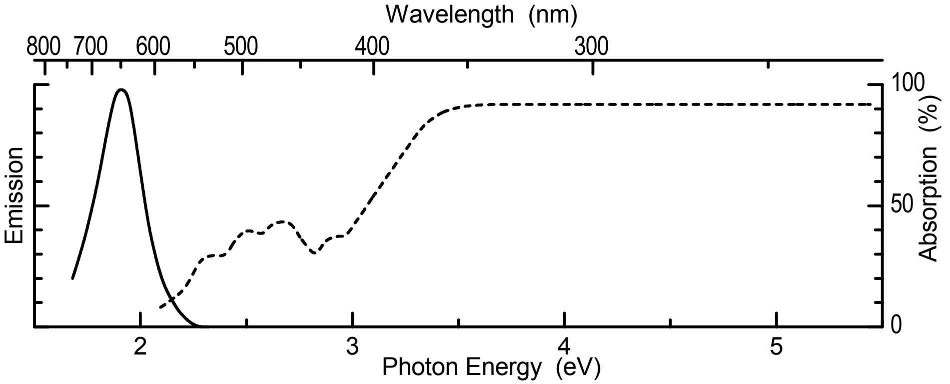
Dry in air. Powderize when dry.
Add ~2–3 g of sulfur.

1. Fire in capped quartz tubes, N_2, 900ºC, 1 hour.
   Now admit the ZnTe; mix by milling or grinding.
2. Fire in capped quartz tubes, N_2, 1200ºC, 1 hour. Powderize.
   Wash in a solution of a few percentage of Br in methanol and then several times in plain methanol.

Optical Properties

Emission color: Red
Emission peak: 1.92 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Remarks

1. This phosphor has been developed by A. Wachtel.
2. This material is remarkable for its strong triboluminescence (red).

Reference

1. Smirnova, R.I., and Pron, G.F., Effect of tellurium on luminescence properties of zinc sulfide luminors, *Opt. Spectrosc.-USSR,* 23, 67 (1967).

ZnS:P

Composition

Ingredient	Mole %	By weight (g)
ZnS	100	98
Zn_3P_2	0.4 (of P)	0.385
NH_4Cl	0.5	0.270

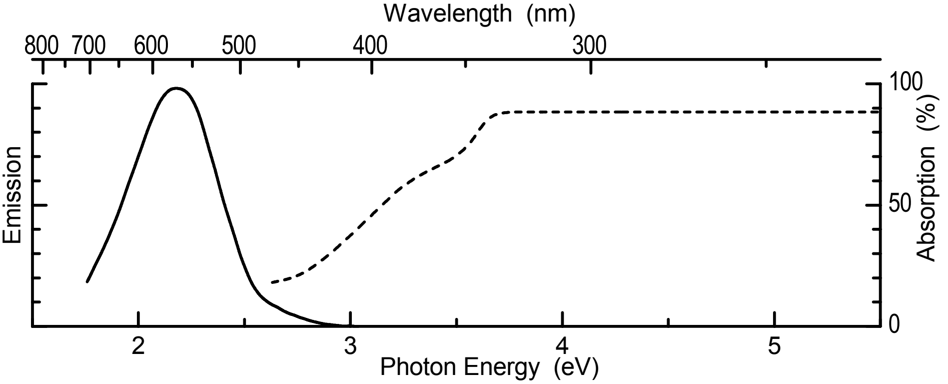
Preparation

Mix by dry grinding.
Fire in capped quartz tubes, H_2, 1100ºC, 1 hour.

Optical Properties

Emission color: Pale yellow
Emission peak: 2.14 eV
Emission width (FWHM): 0.50 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +/5%; Long afterglow tail

Spectra



Remarks

1. Spectral positions of the emission band depends on the P concentration. It shifts to a lower energy (= longer wavelengths) with increasing P.
2. Phosphor is poorly reproducible because of high volatility of Zn_3P_2 at firing temperature. The amount of P retained in the phosphor after firing certainly is much lower than the amount added.

Reference

1. McKeag, A.H., and Ranby, P.W., New zinc sulfide phosphors activated by phosphorus, *J. Electrochem. Soc.,* 96, 85 (1949).

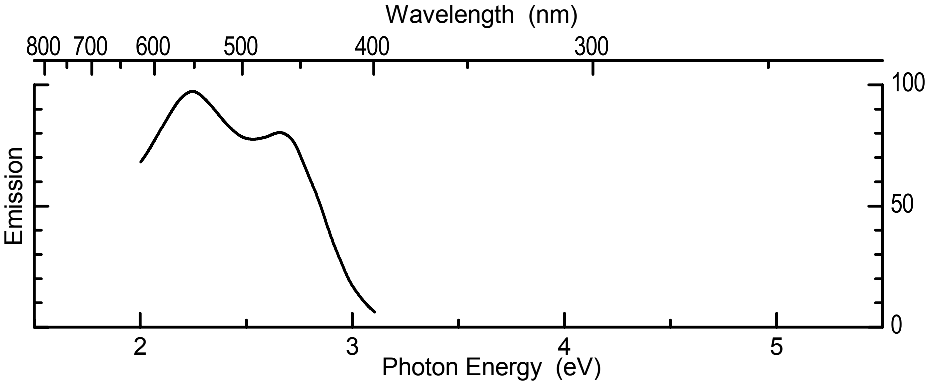
ZnS:P^{3-},Cl^{-}

Structure: Hexagonal (wurtzite)

Optical Properties

Emission color: Yellowish
Emission peak: 2.24, 2.66 eV
Emission width (FWHM): 0.50 eV
Excitation efficiency by UV: + (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Reference

1. McKeag, A.H., and Ranby, P.W., New zinc sulfide phosphors activated by phosphorus, *J. Electrochem. Soc.,* 96, 85 (1949).

ZnS:Pb^{2+}

Structure: Hexagonal (wurtzite)

Optical Properties

Emission color: Orange
Emission peak: 1.98 eV
Emission width (FWHM): 0.40 eV
Excitation efficiency by UV: − (4.88 eV), + (3.40 eV)

Reference

1. Fonda, G.R., Preparation and characteristics of zinc sulfide phosphors sensitive to infrared, *J. Opt. Soc. Am.,* 36, 382 (1946).

ZnS:Pb^{2+},Cl^{-}

Structure: Hexagonal (wurtzite)

Optical Properties

Emission color: Greenish
Emission peak: 2.54 eV
Emission width (FWHM): 0.40 eV
Excitation efficiency by UV: – (4.88 eV), ++ (3.40 eV)

References

1. Leverenz, H.W., *An Introduction to Luminescence of Solids,* John Wiley & Sons, New York (1949).
2. Fonda, G.R., Preparation and characteristics of zinc sulfide phosphors sensitive to infrared, *J. Opt. Soc. Am.,* 36, 382 (1946).

ZnS:Pb,Cu

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	100	98
$Pb(NO_3)_2$	0.1	0.330
$Cu(C_2H_3O_2)_2$	0.001	0.002

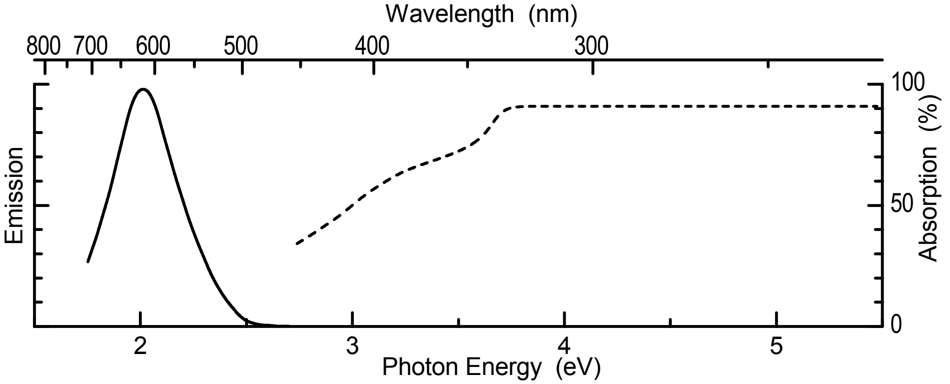
Preparation

Dissolve the lead nitrate and copper acetate together in a little water; add the solution to the ZnS.
Make a uniform slurry with water or methanol. Dry. Powderize.
Add ~2–3 g of sulfur.
Fire in capped quartz tubes, N_2, 1100°C, 1 hour.

Optical Properties

Emission color: Whitish orange during excitation, orange afterglow
Emission peak: 1.99 eV
Emission width (FWHM): 0.40 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Remarks

1. This phosphor is readily excited by UV and shows a long afterglow after excitation.
2. When the afterglow has decreased to a low level, irridation of near-IR causes a strong orange emission (stimulation).

Reference

1. Fonda, G.R., Preparation and characteristics of zinc sulfide phosphors sensitive to infrared, *J. Opt. Soc. Am.,* 36, 352 (1946).

$ZnS:Sn^{2+}$

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	99	97
SnS	1	1.5
Sulfur		~2–3

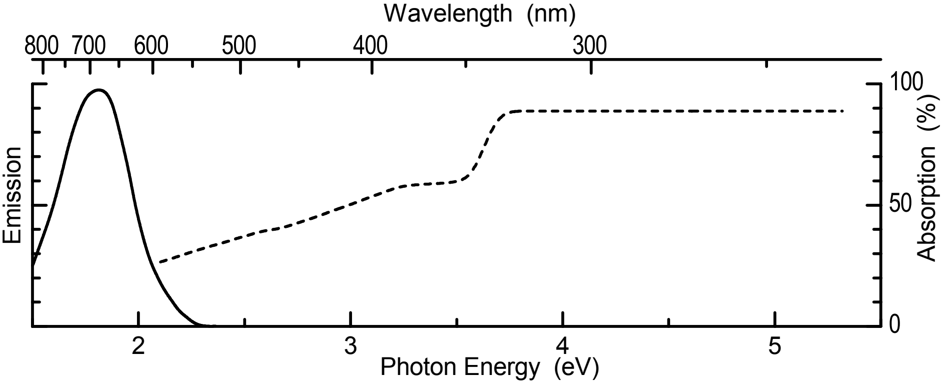
Preparation

Mix by dry grinding.
Fire in capped quartz tubes, N_2, 1150°C, 1 hour.

Optical Properties

Emission color: Red
Emission peak: 1.80 eV
Emission width (FWHM): 0.40 eV
Excitation efficiency by UV: + (4.88 eV), ++ (3.40 eV)

Spectra



Reference

1. Kulaszewcz, S., *Acta Phys. Polonica A,* 45, 499 (1974).

ZnS:Sn,Ag

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	100	98
SnS	0.1	0.150
$AgNO_3$	0.01	0.017

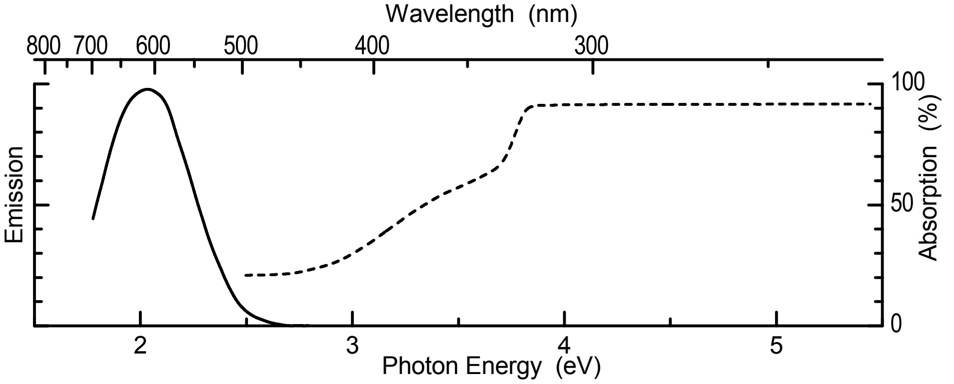
Preparation

Dissolve the $AgNO_3$ in a little water. Add the solutions to the ZnS + SnS.
Make a slurry in water or methanol.
Dry in air. Powderize when dry.
Admit ~2–3 g of sulfur.
Fire in capped quartz tubes, N_2, 1150°C, 1 hour.

Optical Properties

Emission color: Pale yellow
Emission peak: 1.99 eV
Emission width (FWHM): 0.50 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)

Spectra



Remarks

1. The Ag in the above recipe can be replaced by Li.
2. In contrast to ZnS:Cu,Sn, this phosphor shows only little response (stimulation) to irradiated IR.

Reference

1. Wachtel, A., ZnS-Sn,Li phosphor, *J. Electrochem. Soc.,* 105, 432 (1958).

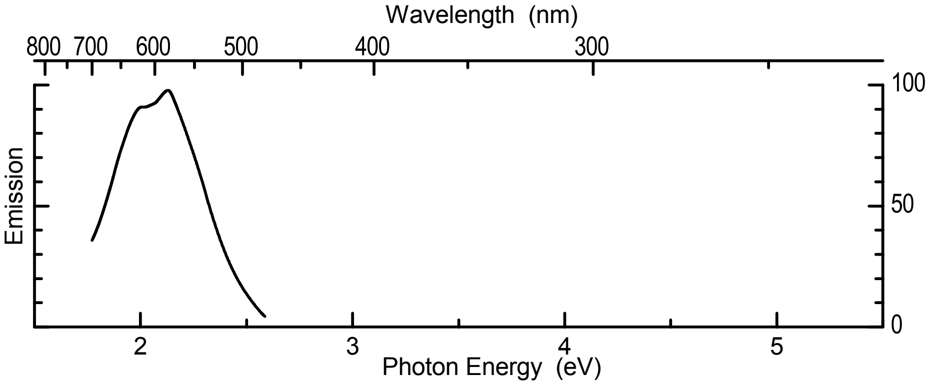
$ZnS:Sn^{2+},Li^{+}$

Structure: Hexagonal (wurtzite)

Optical Properties

Emission color: Orange
Emission peak: 1.99, 2.12 eV
Emission width (FWHM): 0.50 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Reference

1. Wachtel, A., ZnS-Sn,Li phosphor, *J. Electrochem. Soc.,* 105, 432 (1958).

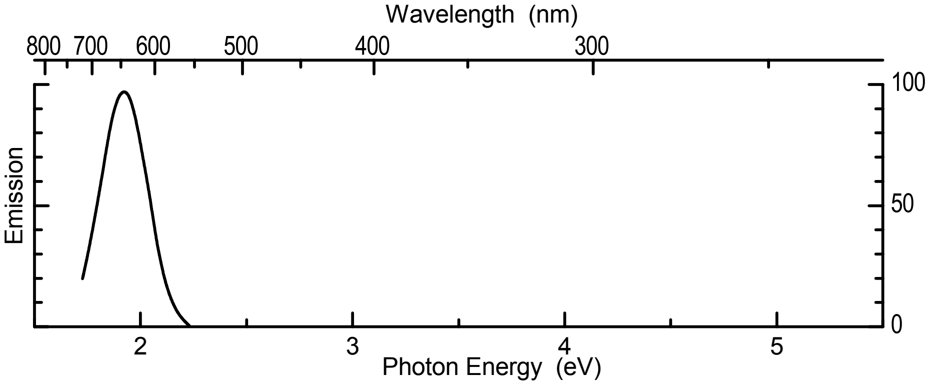
ZnSe:Cu^+,Cl

Structure: Cubic (zinc blende)

Optical Properties

Emission color: Red
Emission peak: 1.92 eV
Emission width (FWHM): 0.30 eV
Excitation efficiency by UV: − (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: ++

Spectra



References

1. Leverenz, H.W., *An Introduction to Luminescence of Solids,* John Wiley & Sons, New York (1949) p. 202.
2. Morehead, F.F., Luminescence in ZnS, Se Cu, Cl, *J. Phys. Chem. Solids,* 24, 37 (1963).

$CdS:Ag^+,Cl^-$

Structure: Hexagonal (wurtzite)

Optical Properties

Emission color: IR
Emission peak: 1.55 eV
Emission width (FWHM): 0.34 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: ++

Reference

1. Leverenz, H.W., *An Introduction to Luminescence of Solids,* John Wiley & Sons, New York (1949).

CdS:In

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
CdS	100	145
In_2O_3	0.1 (of In)	0.139

Preparation

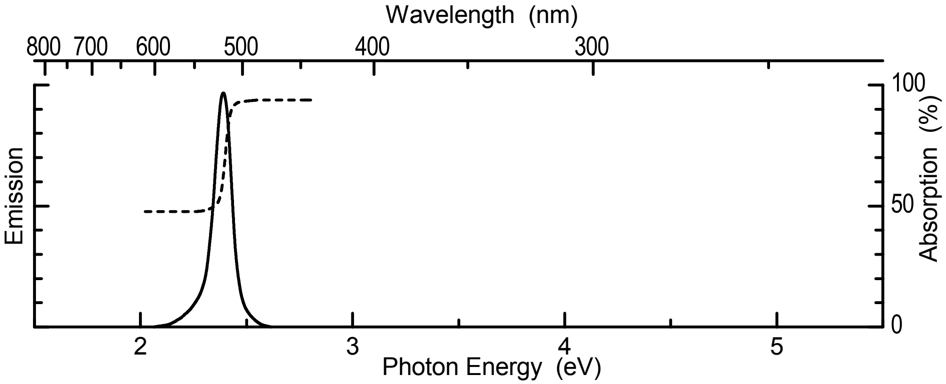
Dissolve the In_2O_3 in a little nitric acid. Add the solutions to the CdS.
Make a slurry in methanol. Dry. Powderize. Add ~2–3 g of sulfur.

1. Fire in capped quartz tubes, H_2S, 900°C, 1 hour.
   When cool, inspect under UV lamp. Material should be uniformly red luminescent.
   Remove all parts which look different. Powderize.
2. Fire in open quartz boats, H_2, 500°C.
   Inspect again under UV lamp. Material should now be uniformly green.

Optical Properties

Emission color: Green
Emission peak: 2.39 eV
Emission width (FWHM): 0.08 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +
Decay to 10%: Less than 1 nsec

Spectra



Remarks

1. This phosphor is thermodynamically in an unstable state. Do not heat up (except only in H_2) to more than about 250°C.
2. Phosphor has limited use in CR tubes for extremely fast display.

Reference

1. Lehmann, W., Edge emission of n-type conducting ZnO and CdS, *Solid State Electron.,* 9, 1107 (1966).

ZnS-CdS:Cu,I

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	98	95.4
CdS	2	2.9
$Cu(C_2H_3O_2)_2 . H_2O$	0.5	2.9
NH_4I	2	2.9

Preparation

Dissolve the Cu acetate and the NH_4I separately, each in a little water.
Make a slurry of the ZnS + CdS in methanol.
Add the Cu solution, stir, then add the NH_4I-solution, and stir. Dry. Powderize.
Screen through a medium-fine cloth sieve.
Add ~3−4 g of sulfur. Mix well.

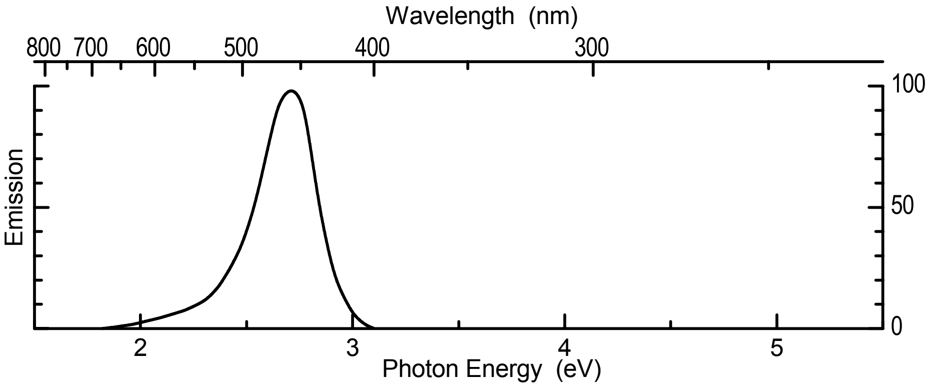
1. Fire in capped quartz tubes, N_2, 800°C, 1 hour. Powderize.
2. Fire in open quartz boats, N_2, 650°C, 1 hour. After this firing, pull the hot boat with the phosphor out of the furnace into open air and quench rapidly down to room temperature by blowing cold air against it. Powderize.

Boil briefly in a solution of about 10 g NaOH (or KOH) + 10 g NaCN (or KCN) in 1 liter of water.
Wash in plain water several times until neutral.
Dry with methanol in a filter funnel and then in open air.
Screen through 200 mesh or finer.

Optical Properties

Emission color: Blue
Emission peak: 2.72 eV
Emission width (FWHM): 0.33 eV

Spectra



Reference

1. Leverenz, H.W., *An Introduction to Luminescence of Solids,* John Wiley & Sons, New York (1949).

ZnS-CdS (25-75)

Structure: Wurtzite

Optical Properties

Emission color: Deep red
Emission peak: 1.78 eV
Emission width (FWHM): 0.35 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: ++

ZnS-CdS (50-50)

Optical Properties

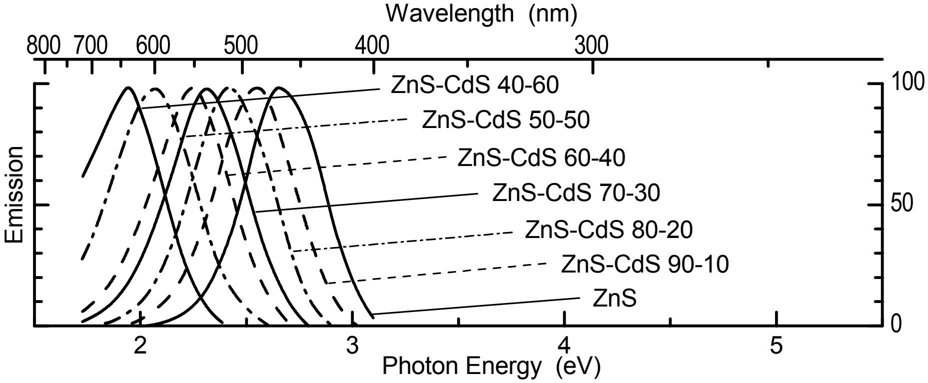
Emission color: Orange
Emission peak: 2.06 eV
Emission width (FWHM): 0.35 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: ++

ZnS-CdS (75-25)

Optical Properties

Emission color: Green
Emission peak: 2.38 eV
Emission width (FWHM): 0.35 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: ++

Spectra



Reference

1. Leverenz, H.W., *An Introduction to Luminescence of Solids,* John Wiley & Sons, New York (1949).

ZnS-CdS:Ag,Br,Ni

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	96	93.5
CdS	4	5.8
$Cu(C_2H_3O_2)_2$. H_2O	0.8	1.6
NH_4Br	0.7	0.686

Preparation

Make a slurry of the ZnS + CdS in methanol.

Dissolve the Cu acetate and the NH_4Br together in a little water. Add the solution to the slurry, stir. Dry. Powderize.

Screen through a medium-fine cloth sieve.

Add ~3–4 g of sulfur. Mix well.

1. Fire in capped quartz tubes, H_2S, 800°C, 45 minutes. Powderize.
2. Fire in open quartz boats, N_2, 700°C, 1 hour.

Optical Properties

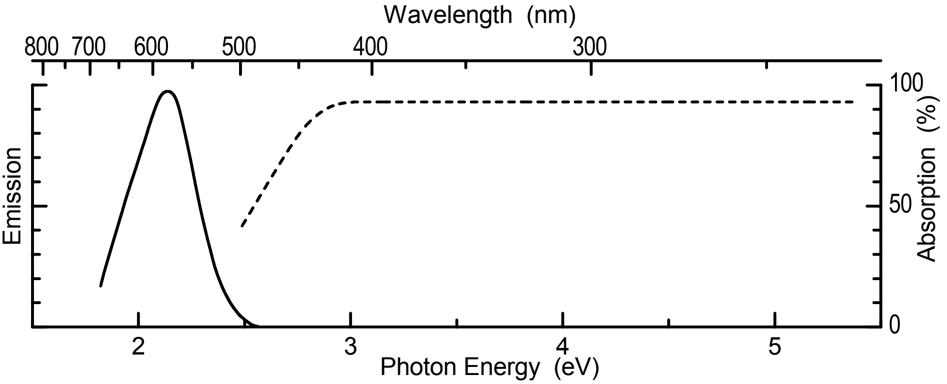
Emission color: Orange-yellow

Emission peak: 2.13 eV

Emission width (FWHM): 0.37 eV

Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Remarks

1. The emission intensity increases sharply super-linearly with increasing excitation intensity and decreases with increasing temperature: The best obtained temperature response is about 20% per degree Centigrade near room temperature.
2. This phosphor is good for thermal imaging.

Reference

1. Nail, N.R., Urbach, F., and Pearlman, D., New observations on superlinear luminescence, *J. Opt. Soc. Am.*, 39, 690 (1949).

$ZnS\text{-}CdS{:}Ag^+,Cl$

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS + CdS	100	
$AgNO_3$	0.03	0.050
NH_4Cl	5	2.5

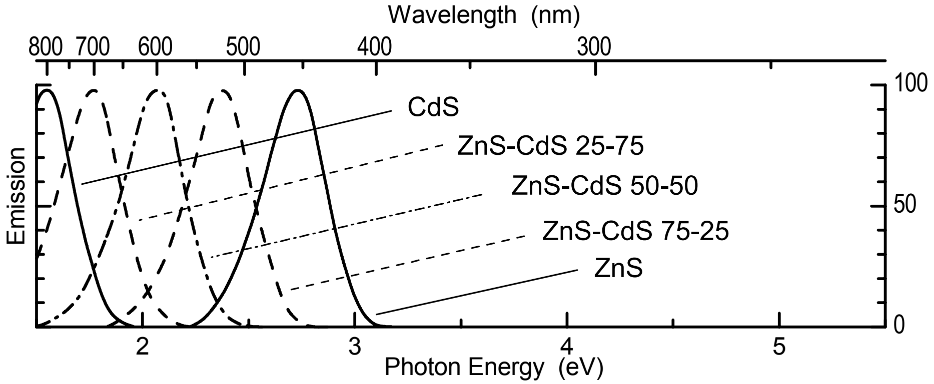
Preparation

Dissolve the $AgNO_3$ and the NH_4Cl separately, each in a little water.
Make a slurry of the ZnS + CdS of the desired ratio in water or methanol.
First add the silver solution; stir. Then add the NH_4Cl solution; stir again.
Dry. Powderize.
Add ~2–3 g of sulfur. Mix well.
Fire in capped quartz tubes, N_2, 1100°C, 1 hour.
Wash in water several times (to remove leftover halide).
Dry.

Optical Properties

Emission peak: Peak position depending on the ZnS/CdS ratio
Emission width (FWHM): ~0.35 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: 20%
Decay to 10%: Non-exponential afterglow in the microsecond range

Spectra



Remarks

1. Chlorine in the above recipe may be replaced by bromine.
2. The phosphor of ZnS/CdS ≈ 72/28 is commercial P-22G.

Reference

1. Leverenz, H.W., *An Introduction to Luminescence of Solids,* John Wiley & Sons, New York, 1949.

ZnS-CdS:Cu,Br long life

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	96	93.5
CdS	4	5.8
$Cu(C_2H_3O_2)_2 . H_2O$	0.8	1.6
NH_4Br	0.7	0.686

Preparation

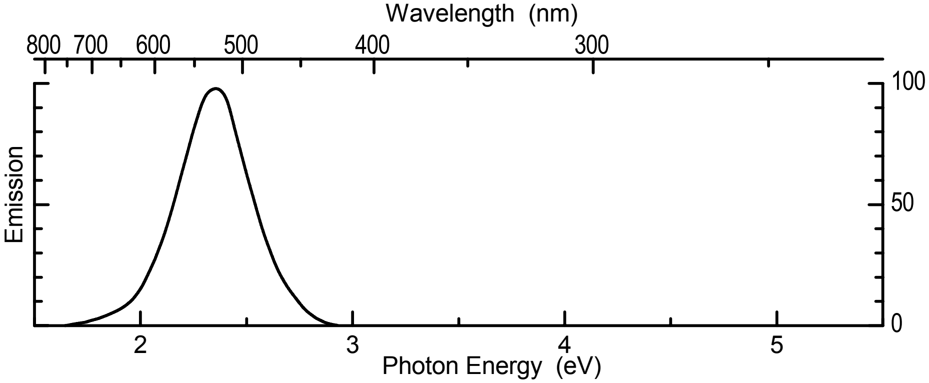
Make a slurry of the ZnS + CdS in methanol. Dissolve the Cu acetate and the NH_4Br together in a little water, add the solution to the slurry, and stir. Dry. Powderize. Screen through a medium-fine cloth sieve. Add ~3–4 g of sulfur. Mix well.

1. Fire in capped quartz tubes, H_2S, 800°C, 45 minutes. Powderize.
2. Fire in open quartz boats, N_2, 700°C, 1 hour. After this firing, pull the hot boat with the phosphor out of the furnace into open air and quench rapidly down to room temperature by blowing cold air against it. Powderize.
   Boil briefly in a solution of about 10 g NaOH (or KOH) + 10 g NaCN (or KCN) in 1 liter water. Wash in plain water several times until neutral.
   Dry with methanol in a filter funnel and then in open air.
3. Fire the same as 2. Firing includes rapid quenching.
   Boil again in cyanide solution as above. Wash in plain water several times until neutral. Dry with methanol in a filter funnel and then in open air.
   Screen through 200 mesh or finer.

Optical Properties

Emission color: Green
Emission peak: 2.35 eV
Emission width (FWHM): 0.35 eV

Spectra



Remark

The zero-hour brightness of this phosphor is ~½ of that of the one on the previous page.

ZnS-CdS:Cu,Br high brightness

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	96	93.5
CdS	4	5.8
$Cu(C_2H_3O_2)_2$. H_2O	0.3	0.600
NH_4Br	0.7	0.686

Preparation

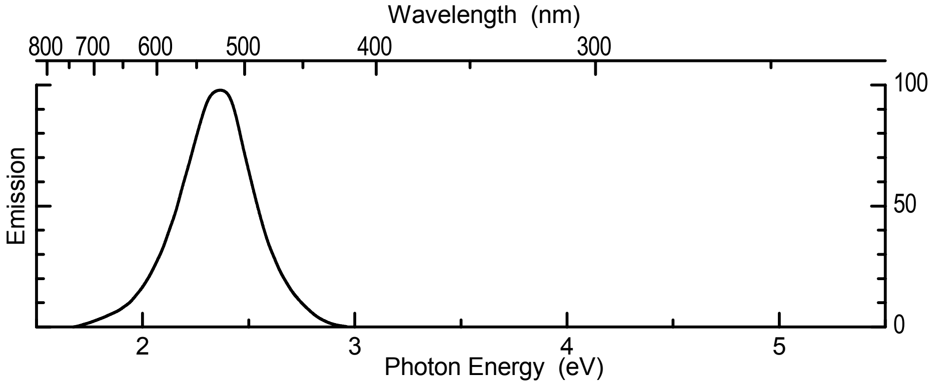
Make a slurry of the ZnS + CdS in methanol. Dissolve the Cu acetate and the NH_4Br together in a little water, add the solution to the slurry, and stir. Dry. Powderize. Screen through a medium-fine cloth sieve. Add ~3–4 g of sulfur. Mix well.

1. Fire in capped quartz tubes, H_2S, 800ºC, 45 minutes. Powderize.
2. Fire in open quartz boats, N_2, 650ºC, 1 hour. After this firing, pull the hot boat with the phosphor out of the furnace into open air and quench rapidly down to room temperature by blowing cold air against it. Powderize. Boil briefly in a solution of about 10 g NaOH (or KOH) + 10 g NaCN (or KCN) in 1 liter of water. Wash in plain water several times until neutral. Wash in about 2 liters of 10% H_2O_2 solution at room temperature for about 2 hours while stirring. Wash in plain water. Dry with methanol in a filter funnel and then in open air. Screen through 200 mesh or finer.

Optical Properties

Emission color: Green
Emission peak: 2.35 eV
Emission width (FWHM): 0.38 eV

Spectra



Remarks

1. This phosphor has been developed for high zero-hour brightness; its half-life under steady 5 kHz excitation is much shorter than that of the phosphor on the next page.
2. The H_2O_2 wash is an idea by Wachtel, A., U.S. Pat., 3 165 476 (1965).

ZnS-ZnTe:Mn^{2+} 98-2

Structure: Hexagonal (wurtzite)

Optical Properties

Emission color: Red
Emission peak: 1.92 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Reference

1. Smirnova, R.I., and Pron, G.F., Effect of tellurium on luminescence properties of zinc sulfide luminors, *Opt. Spectrosc.-USSR,* 23, 67 (1967).

4.14 CaS-Type Sulfides

The following host compounds and activators are included in this subsection:

$MgS:Eu^{2+}$
$CaS:Bi^{3+}$
$CaS:Bi^{3+},Na$
$CaS:Ce^{3+}$
$CaS:Cu^{+},Na^{+}$
$CaS:Eu^{2+}$
$CaS:Mn^{2+}$
$CaS:La^{3+}$
$CaS:Pb^{2+},Cl$
$CaS:Pb^{2+}$
$CaS:Pb^{2+},Mn^{2+}$
$CaS:Pr^{3+},Pb^{2+},Cl$
$CaS:Sb^{3+}$
$CaS:Sb^{3+},Na$
$CaS:Sm^{3+}$
$CaS:Sn^{2+}$
$CaS:Sn^{2+},F$
$CaS:Tb^{3+}$
$CaS:Tb^{3+},Cl$
$CaS:Y^{3+}$
$CaS:Yb^{2+}$
$CaS:Yb^{2+},Cl$
$SrS:Ce^{3+}$
$SrS:Cu^{+},Na$
$SrS:Eu^{2+}$
$SrS:Mn^{2+}$
BaS:Au,K

$MgS:Eu^{2+}$

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
MgO	100	0.040
Eu_2O_3	0.1 (of Eu)	0.176
NH_4Cl	2	1

Preparation

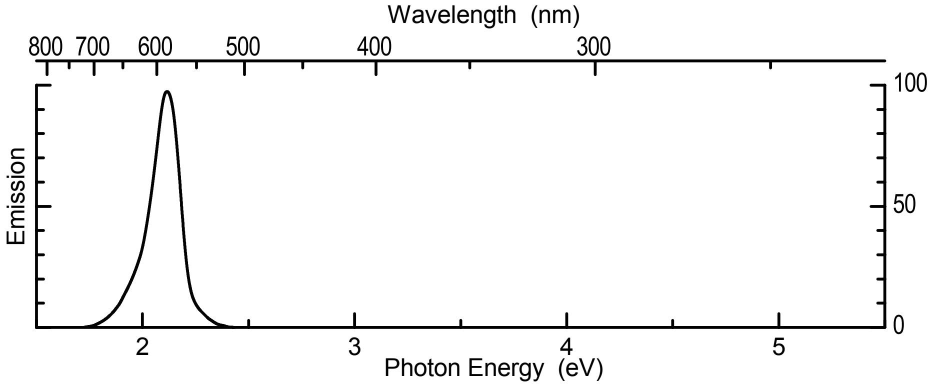
First mix only the MgO and Eu_2O_3.

1. Fire in open quartz boats, N_2 loaded with CS_2, 800ºC, 1 hour.
   Powderize.
   Admit above amount of NH_4Cl and also 2–3 g of sulfur; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1200ºC, 1 hour.
   Powderize.
   Store in a well-closed container. Keep dry.

Optical Properties

Emission color: Orange-yellow
Emission peak: 2.11 eV
Emission width (FWHM): 0.15 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +/8%

Spectra



Reference

1. Kasano, H., Megumi, K., and Yamamoto, H., Cathodoluminescence of $Ca_{1-x}Mg_xS$-Eu, $Ca_{1-x}Mg_xS$-Ce, *J. Electrochem. Soc.,* 131 (1953).

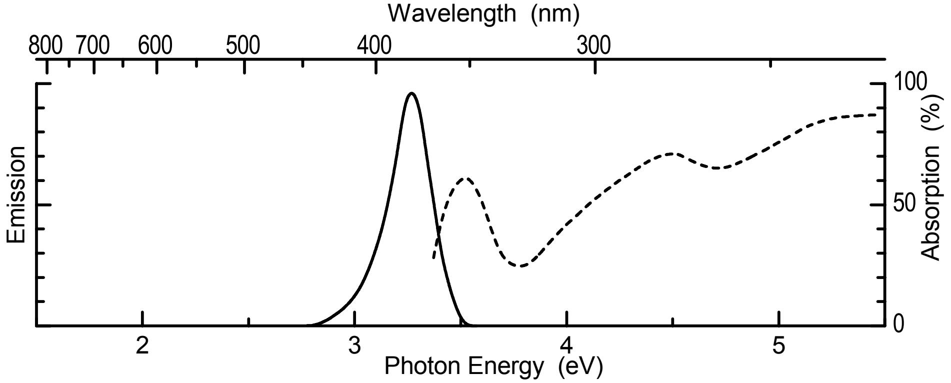
CaS:Bi^{3+}

Structure: Cubic (NaCl)

Optical Properties

Emission color: Near UV
Emission peak: 3.27eV
Emission width (FWHM):0.21 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).
2. Lehmann, W., and Ryan, F.M., Fast cathodoluminescent calcium sulfide phosphors, *J. Electrochem. Soc.,* 119, 275 (1972).
3. Ellervee, A.F., Luminescence of Pb^{2+} and Bi^{3+} centers in alkali-earth sulfides and oxides, *Phys. Status Solidi B,* 82, 91 (1977).
4. Garlick, G.F.J., and Mason, D.E., Electron traps and infrared stimulation of phosphors, *J. Electrochem. Soc.,* 96, 90 (1949).
5. Yamashita, N., and Asano, S., Luminescence-centers of Ca(S,Se):Bi^{3+} and CaO:Bi^{3+} phosphors, *J. Phys. Soc. Jpn.,* 40, 144 (1976).

CaS:Bi^{3+},Na

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
Bi_2O_3	0.03 (of Bi)	0.70
$NaHCO_3$	0.5	0.420

Preparation

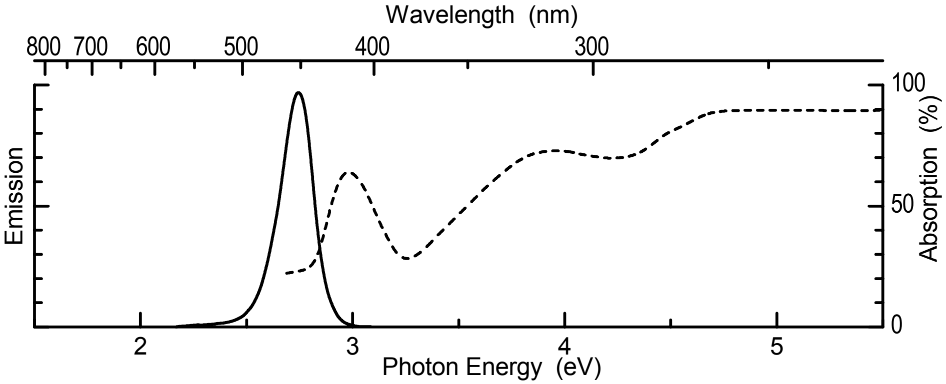
Start from purest $CaCO_3$. Convert it to CaS by one of the following methods:

1. Fire in open quartz boats, H_2S, 1100ºC, 1 hour.
   Powderize.
   Add the above amounts of Bi and Na, and also ~ 2–3 g of sulfur; mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1200ºC, 1 hour.
   Powderize.
3. Fire in capped quartz tubes, stagnant air, 1200ºC, 1 hour.
   Store in a well-closed container.

Optical Properties

Emission color: Blue
Emission peak: 2.77 eV
Emission width (FWHM): 0.18 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: 4–5%
Decay: Non-exponential decay in the microsecond range; long afterglow tail extending into seconds

Spectra



Remarks

1. Preparation required purest starting materials. Luminescent-grade $CaCO_3$ is not pure enough. Contamination by Mn as low as 1 ppm will cause appearance of the yellow Mn^{2+} emission.
2. Na in above recipe can be replaced by Li but Na seems to have a slight edge over it.

References

1. Garlick, G.F.J., and Mason, D.E., Electron traps and infrared stimulation of phosphors, *J. Electrochem. Soc.,* 96, 90 (1949).
2. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).
3. Lehmann, W., and Ryan, F.M., Fast cathodoluminescent calcium sulfide phosphors, *J. Electrochem. Soc.,* 119, 275 (1972).
4. Yamashita, N., and Asano, S., Luminescence-centers of Ca(S+Se):Bi^{3+} and CaO:Bi^{3+} phosphors, *J. Phys. Soc. Jpn.,* 40, 144 (1976).
5. Ellervee, A.F., Luminescence of Pb^{2+} and Bi^{3+} centers in alkali-earth sulfides and oxides, *Phys. Status Solidi B,* 82, 91 (1977).

CaS:Ce^{3+}

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
CeO_2	0.05	0.086

Preparation

Mix well.

1. Fire in open quartz boats, 1100°C, first 1 hour in N_2 and then 1 hour in H_2S.
   Powderize.
   Add about 2–3 g of sulfur.
   Admit about 1–2 g of NH_4Cl by dry grinding or milling.
2. Fire in capped quartz tubes, N_2, 1200°C, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Green

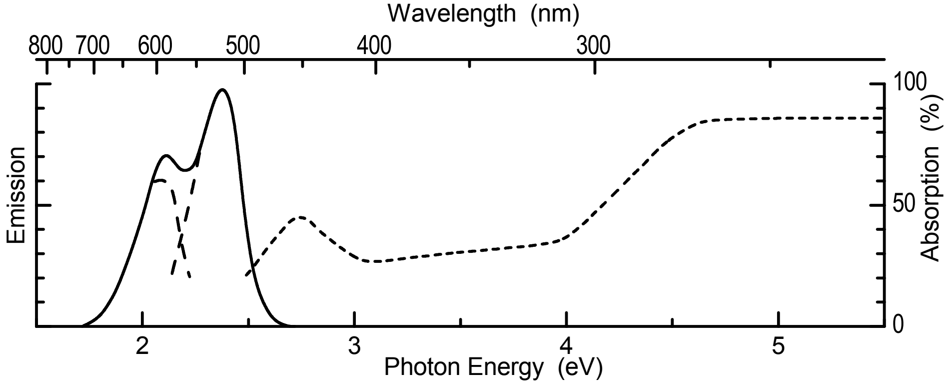
Emission peak: 2.13 eV, 2.38 eV

Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Excitation efficiency by e-beam: ++/20%

Decay to 10%: Non-exponential decay in the microsecond range; phosphor showing no color change and little saturation up to the highest current densities

Spectra



Remarks

1. Phosphor can be sensitized for efficient excitation by 3.40 eV by addition of Pb (see CaS:Pb^{2+}).
2. Decay time after excitation by an e-beam pulse can be reduced to ~200 nsec (1/10 of original) by addition of Co.
3. Phosphor has a slightly greenish body color due to the combined action of the blue absorption band and the green emission.
4. Cl in the above recipe can be replaced by F, Br, or I.
5. The distance between the two emission bands (in eV) cannot be changed but the exact positions of the bands depend slightly on the used Ce concentration.
6. This phosphor is efficiently luminescent up to ~300ºC.
7. This phosphor or modifications of it have found applications in CR tubes and for correction in arc lamps.

References

1. Lehmann, W., Optimum efficiency of cathodoluminescence of inorganic phosphors, *J. Electrochem. Soc.,* 118, 1164 (1971).
2. Lehmann, W., and Ryan, F.M., Fast cathodoluminescent calcium sulfide phosphors, *J. Electrochem. Soc.,* 119, 275 (1972).
3. Lehmann, W., and Ryan, F.M., Cathodoluminescence of CaS-Ce^{3+} and CaS-Eu^{2+} phosphors *J. Electrochem. Soc.,* 118, 477 (1971).
4. Okamoto, F., and Kato, K., Preparation and cathodoluminescence of CaS-Ce and $Ca_{1-x}Sr_xS$-Ce phosphors, *J. Electrochem. Soc.,* 130, 432 (1983).

CaS:Cu^+,Na^+

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
$Cu(C_2H_3O_2)_2 \cdot H_2O$	0.15	0.300
$NaHCO_3$	1.5	1.25

Preparation

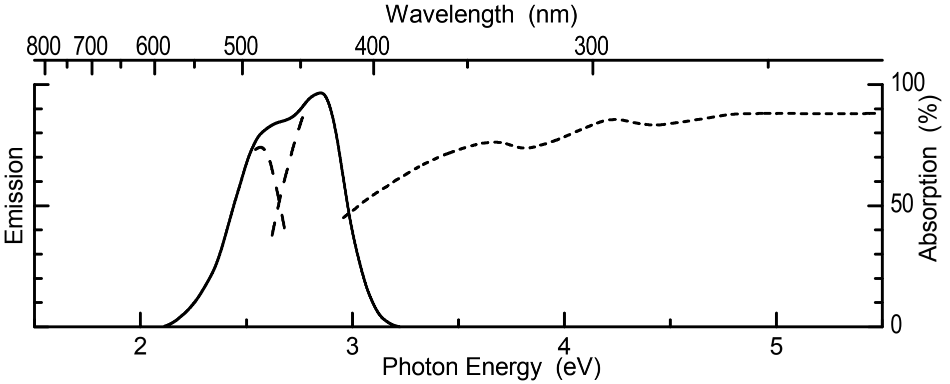
Dissolve the copper acetate in a little water; add solution to the $CaCO_3$.
Make a uniform slurry in water or methanol. Dry. Powderize.

1. Fire in open quartz boats, H_2S, 1100ºC, 1 hour. Powderize.
   Add 800 mg of $NaHCO_3$ plus ~ 2–3 g of sulfur. Mix by dry grinding.
2. Fire in covered alumina crucibles, H_2, 1000ºC, 1 hour.
   Powderize. Store in a well-closed container.

Optical Properties

Emission color: Light blue
Emission peak: 2.55 eV, 2.83 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: ++/16%
Decay: Non-exponential decay, 100 sec to 1/10; phosphor showing much less saturation at the high beam current than P-11

Spectra



Remarks

1. Halides are not co-activators in CaS:Cu (in contrast to ZnS:Cu).
2. The relative heights of the two emission bands depend on the preparation conditions.
3. Na in the above recipe can be omitted or be replaced by Li or K. The peak positions of the two emission bands depend on the alkali used (if any).

References

1. Wachtel, A., CaS-Cu,Eu electroluminescent phosphors, *J. Electrochem. Soc.,* 107, 199 (1960).
2. Lehmann, W., Alkaline earth sulfide phosphors activated by copper, silver, and gold, *J. Electrochem. Soc.,* 117, 1389 (1970).

CaS:Eu^{2+}

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
Eu_2O_3	0.05 (of Eu)	0.088
NH_4Cl	~2	~1

Preparation

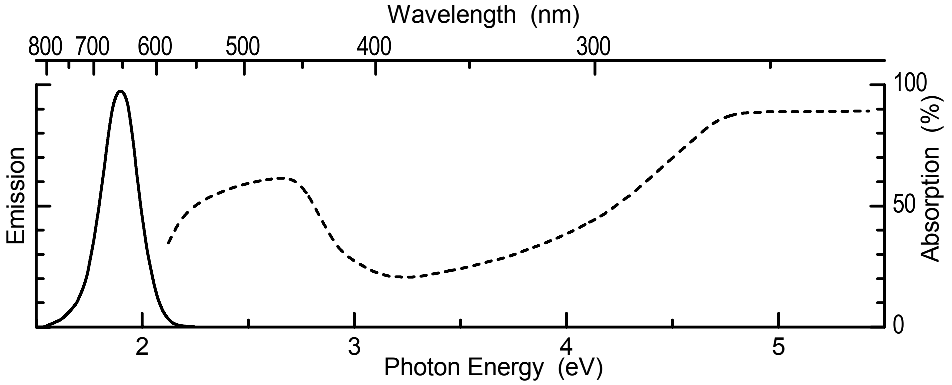
Mix the $CaCO_3$ and the Eu_2O_3.

1. Fire in open quartz boats, 1100°C, first 1 hour in N_2 and then 1 hour in H_2S.
   Powderize.
   Add the above amount of NH_4Cl, also ~ 2–3 g of sulfur.
   Mix by dry grinding.
2. Fire in capped quartz tubes, H_2, 1200°C, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Red
Emission peak: 1.91 eV
Emission width (FWHM): 0.20 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: ++/10% (can be improved to ~16% by the addition of Ce, see CaS:Ce^{3+}, Cl).
Decay: Non-exponential decay in the microsecond range

Spectra



Remarks

1. Phosphor can be sensitized for excitation by 3.40 eV by addition of Sn (see CaS:Sn,F) or by pB (see CaS:Pb).
2. Decay time after excitation by an e-beam pulse can be reduced to ~300 nsec by addition of Co.
3. This phosphor has a very characteristic pink body color due to the combined actions of the broad blue to yellow absorption band and the red fluorescence.
4. Cl in the above recipe can be replaced by F, Br, or I.

5. The emission peak position depends slightly upon the used Eu concentration.
6. Partial or complete replacement of the Ca by Sr causes the emission to sift to higher energy (= shorter wavelength).
7. This phosphor is efficiently luminescent up to ~300ºC.
8. This phosphor or modifications of it have found applications in CR tubes and for correction in arc lamps.

References

1. Lehmann, W., Optimum efficiency of cathodoluminescence of inorganic phosphors, *J. Electrochem. Soc.,* 118, 1164 (1971).
2. Lehmann, W., and Ryan, F.M., Cathodoluminescence of CaS-Ce^{3+} and CaS-Eu^{2+} phosphors *J. Electrochem. Soc.,* 118, 477 (1971).
3. Brauer, P. *Z. Naturforsch. Pt. A,* 6, 561 (1951), and Uber eu-ionen in erdalkalioxyden und erdalkali-sulfiden, *Z. Naturforsch Pt A,* 12, 233 (1957).
4. Jaffe, P.M., and Banks, E., Oxidation states of europium in the alkaline earth oxide and sulfide phosphors, *J. Electrochem. Soc.,* 102, 518 (1955).
5. Lehmann, W., and Ryan, F.M., Fast cathodoluminescent calcium sulfide phosphors, *J. Electrochem. Soc.,* 119, 275 (1972).
6. Wachtel, A., CaS-Cu,Eu electroluminescent phosphors, *J. Electrochem. Soc.,* 107, 199 (1960).

CaS:Mn^{2+}

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
$MnCO_3$	0.1	0.115
NH_4Cl	~2	~1

Preparation

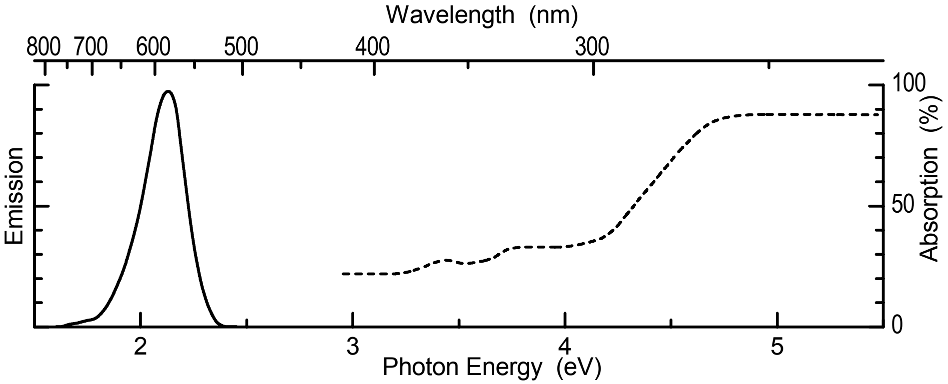
Mix the $CaCO_3$ and the $MnCO_3$.

1. Fire in open quartz boats, H_2S, 1100ºC, 1 hour.
   Powderize.
   Add the above amount of NH_4Cl, and ~ 2–3 g of sulfur.
   Mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1200ºC, 1 hour.
   Powderize.
3. Fire in open quartz boats, H_2S, 1100ºC, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Yellow
Emission peak: 2.11 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: ++/16%
Decay**:** Near-exponential decay with ~8 msec to 1/10

Spectra



Remarks

1. The Cl in the above recipe is not a co-activator. It serves only as a flux and can be replaced by F, Br, or I.
2. The Mn concentration is not critical, the Mn^{2+} emission is fairly strong between about 1 ppm and 5% of Mn/Ca.
3. The emission peak position depends slightly on the Mn concentration used.
4. Partial (up to 10%) replacement of the Ca by Mg shifts the emission from yellow to orange-red. Partial or complete replacement of Ca by Sr shifts it towards green (see $SrS:Mn^{2+}$).

References

1. Shionoya, S., and Era, K., Sensitization by bismuth of the luminescence of manganese and samarium in calcium sulfide phosphors, *B. Chem. Soc. Jpn.,* 30, 518 (1957).
2. Levshin, V.L., and Mikhaylin, V.V., Paper 111, *Intern Conf. Lumin.,* Budapest (1966).
3. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).
4. Lehmann, W., Optimum efficiency of cathodoluminescence of inorganic phosphors, *J. Electrochem. Soc.,* 118, 1164 (1971).

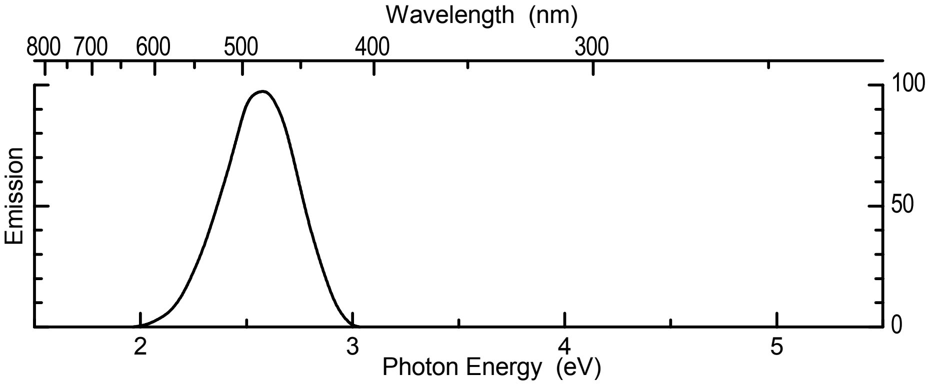
$CaS:La^{3+}$

Structure: Cubic (NaCl)

Optical Properties

Emission color: Blue-greenish
Emission peak: 2.55 eV
Emission width (FWHM): 0.42 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Reference

1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).

CaS:Pb^{2+},Cl

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
PbO	0.02	0.045
NH_4Cl	3	1.5

Preparation

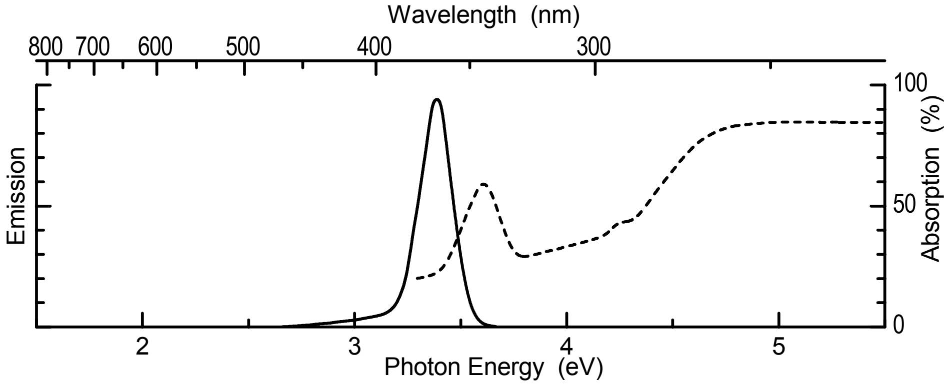
Start from purest $CaCO_3$. Convert to CaS by one of the following methods

1. Fire in open quartz boats, H_2S, 1100°C, 1 hour.
   Powderize.
   Add ~1g of NH_4Cl, and ~ 2–3 g of sulfur.
   Mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1200°C, 1 hour.
   Powderize.
   Add the above amount of PbO, another 2 g of NH_4Cl, and ~ 2–3 g of sulfur.
   Mix by dry grinding.
3. Fire in capped quartz tubes, N_2, 1200°C.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Near-UV
Emission peak: 3.39 eV
Emission width (FWHM): 0.22 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: 15–17%
Decay: Non-exponential decay in the microsecond range; decay to be shortened to about 250 nsec (to 1/10) by addition of a trace of cobalt

Spectra



Remarks

1. Preparation requires purest starting materials. Normal luminescent-grade $CaCO_3$ is not pure enough. Contamination by Mn as low as 1 ppm will cause appearance of the yellow Mn^{2+} emission.
2. The NH_4Cl in the above recipe can be replaced by NH_4Br. Fluoride is much less effective.
3. This phosphor has limited application as UV emitter in CR tubes.

References

1. Lehmann, W., Optimum efficiency of cathodoluminescence of inorganic phosphors, *J. Electrochem. Soc.,* 118, 1164 (1971); and Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).
2. Lehmann, W., and Ryan, F.M., Fast cathodoluminescent calcium sulfide phosphors, *J. Electrochem. Soc.,* 119, 275 (1972).
3. Ellervee, A.F., Luminescence of Pb^{2+} and Bi^{3+} centers in alkali-earth sulfides and oxides, *Phys. Status Solidi B,* 82, 91 (1977).

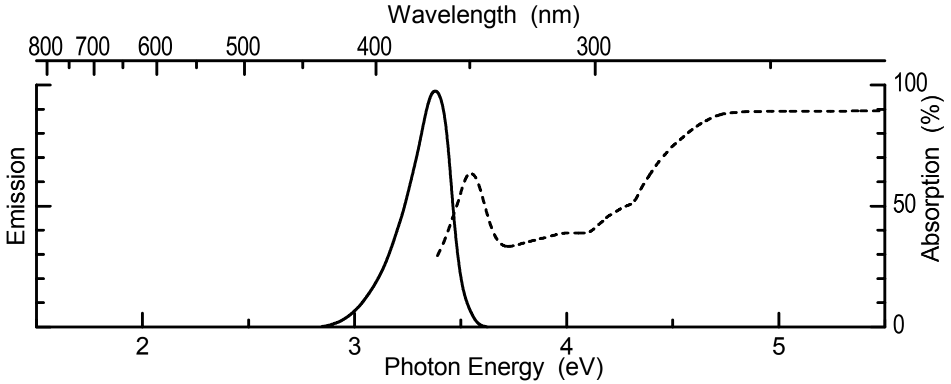
$CaS:Pb^{2+}$

Structure: Cubic (NaCl)

Optical Properties

Emission color: UV
Emission peak: 3.39 eV
Emission width (FWHM): 0.22 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: ++

Spectra



References

1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).
2. Lehmann, W., Optimum efficiency of cathodoluminescence of inorganic phosphors, *J. Electrochem. Soc.,* 118, 1164 (1971).
3. Lehmann, W., and Ryan, F.M., Fast cathodoluminescent calcium sulfide phosphors, *J. Electrochem. Soc.,* 119, 275 (1972).
4. Ellervee, A.F., Luminescence of Pb^{2+} and Bi^{3+} centers in alkali-earth sulfides and oxides, *Phys. Status Solidi B,* 82, 91, (1977).

$CaS{:}Pb^{2+},Mn^{2+}$

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
$MnCO_3$	0.5	0.575
PbO	0.3	0.670
NH_4Cl	2	~1

Preparation

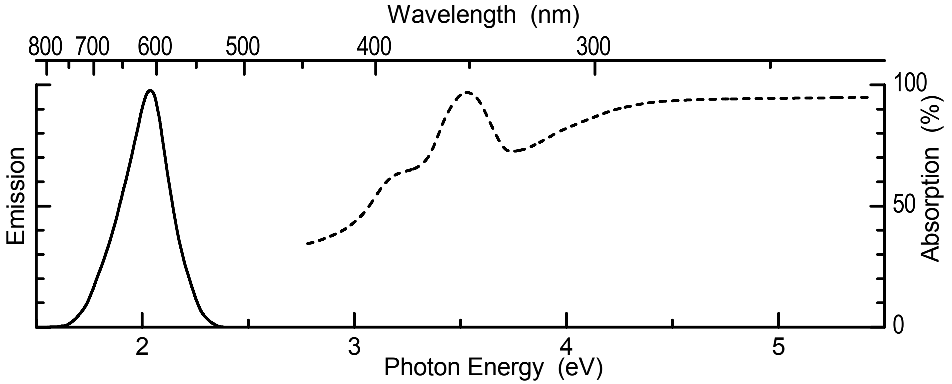
First mix only the $CaCO_3$ and $MnCO_3$.

1. Fire in open quartz boats, H_2S, 1100ºC, 1 hour.
   Powderize.
   Add the above amounts of PbO and NH_4Cl, and also ~ 2–3 g of sulfur.
   Mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1200ºC, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Red-orange (not the yellow of $CaS{:}Mn^{2+}$ without Pb)
Emission peak: 2.04 eV
Emission width (FWHM): 0.28 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)

Spectra



Remark
The Mn^{2+} emission shifts to lower energy (+ longer wave lengths) with increasing Pb concentration.

$CaS:Pr^{3+},Pb^{2+},Cl$

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
Pr_2O_3	0.1	0.165
PbO	0.02	0.045
NH_4Cl	~2	~1

Preparation

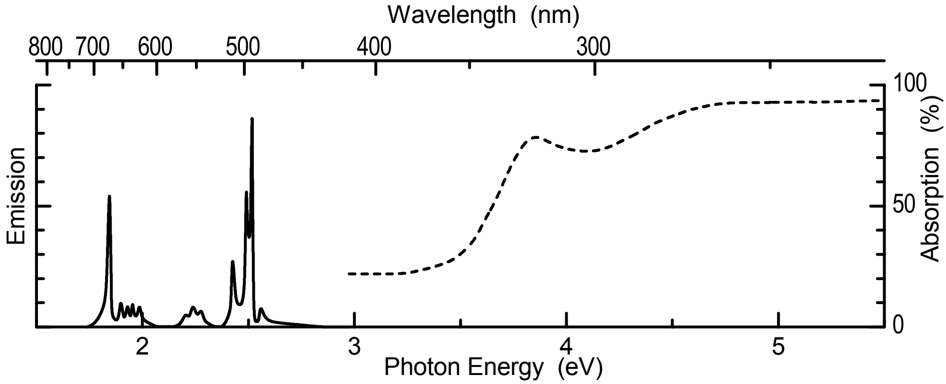
First mix only the $CaCO_3$ and $MnCO_3$.

1. Fire in open quartz boats, H_2S, 1100ºC, 1 hour. Powderize.
   Add the above amount of NH_4Cl and also ~ 2–3 g of sulfur.
   Mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1200ºC, 1 hour.
   Add the above amount of PbO and also ~ 2–3 g of sulfur. Mix by dry grinding.
3. Fire in capped quartz tubes, H_2, 1100ºC, 1 hour. Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Pale greenish-pink
Emission peak: 1.85 eV, 2.50 eV; mainly two line groups in the blue-green and in the red, respectively; also present (not shown in figure below) a strong line at 1.05 eV in the IR
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Decay**:** Exponential decay, about 0.5 msec to 1/10

Spectra



Remark
The intensity ratio of the two visible line groups is very sensitive to the details of the preparation and excitation.

Reference

1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).

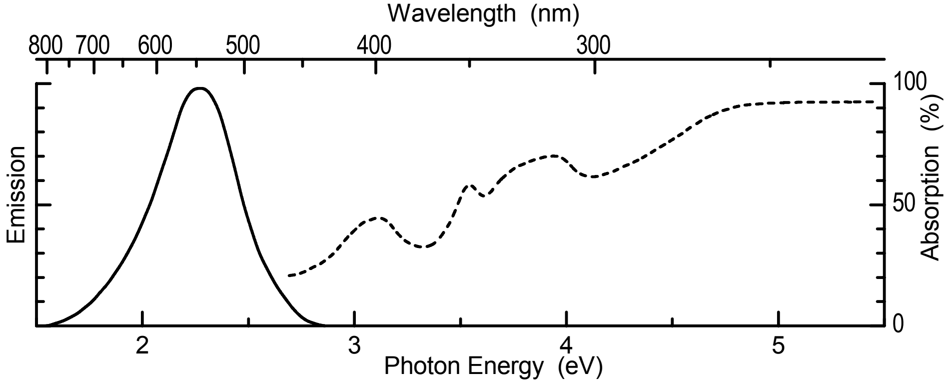
CaS:Sb^{3+}

Structure: Cubic (NaCl)

Optical Properties

Emission color: Yellow-green
Emission peak: 2.27 eV
Emission width (FWHM): 0.44 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: ++

Spectra



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1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).

2. Lehmann, W., Optimum efficiency of cathodoluminescence of inorganic phosphors, *J. Electrochem. Soc.,* 118, 1164 (1971).
3. Yamashita, N., Luminescence centers of Ca(S-Se) phosphors activated with impurity ions having s-2 configuration. 1. Ca(S-Se)-Sb^{3+} phosphors, *J. Phys. Soc. Jpn.,* 35, 1089 (1973).

CaS:Sb^{3+},Na

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
Sb_2O_3	0.1 (of Sb)	0.145
$NaHCO_3$	1	0.840

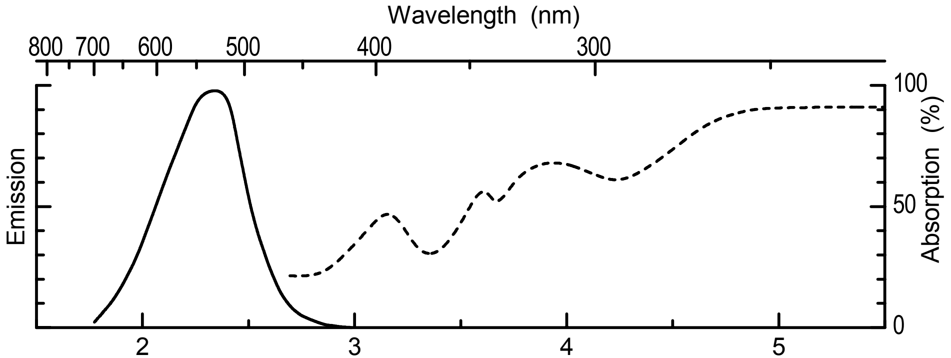
Preparation

1. Fire (purest $CaCO_3$ only) in open quartz boats, H_2S, 1100ºC, 1 hour.
   Powderize.
   Add the above amount of Sb_2O_3 + $NaHCO_3$, and also ~ 2–3 g of sulfur.
   Mix by dry grinding.
2. Fire in covered alumina crucibles, N_2, 1300ºC, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Yellow-green
Emission peak: 2.27 eV
Emission width (FWHM): 0.44 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: 18%
Decay: Exponential decay (~1.5 μsec to 1/10) followed by a long but weak phosphorescence tail

Spectra



References

1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).
2. Lehmann, W., Optimum efficiency of cathodoluminescence of inorganic phosphors, *J. Electrochem. Soc.,* 118, 1164 (1971).
3. Yamashita, N., Luminescence centers of Ca (S-Se) phosphors activated with impurity ions having s-2 configuration. 1. Ca(S-Se)-Sb^{3+} phosphors, *J. Phys. Soc. Jpn.,* 35, 1089 (1973).

CaS:Sm^{3+}

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
Sm_2O_3	0.01 (of Sm)	0.0175
Na_4Cl	~2	~1

Preparation

First mix only the $CaCO_3$ and Sm_2O_3.

1. Fire in open quartz boats, 1100°C, first in N_2, ~ 1 hour and then in H_2S for 1 hour.
   Powderize.
   Add the above amount of Na_4Cl and also ~ 2–3 g of sulfur.
   Mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1200°C, 1 hour.
   Powderize.
3. Fire in open quartz boats, H_2S, 1100°C, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

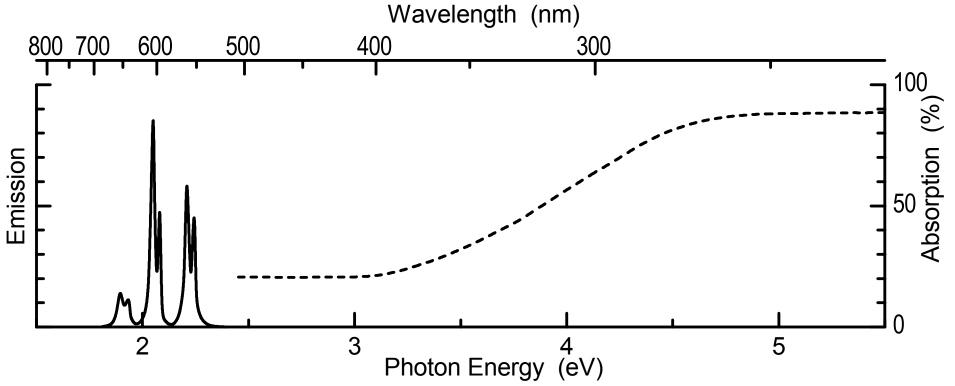
Emission color: Orange-yellow

Emission peak: Strongest lines at 2.04, 2.07, 2.20, and 2.23 eV; also present (not shown in figure below) two strong lines at 1.34 and 1.38 eV

Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Decay: Exponential decay, ~10 msec to 1/10

Spectra



Remark

Phosphor can be sensitized for excitation by 3.40 eV UV by addition of Sn (see $CaS:Sn^{2+}$).

Reference

1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).

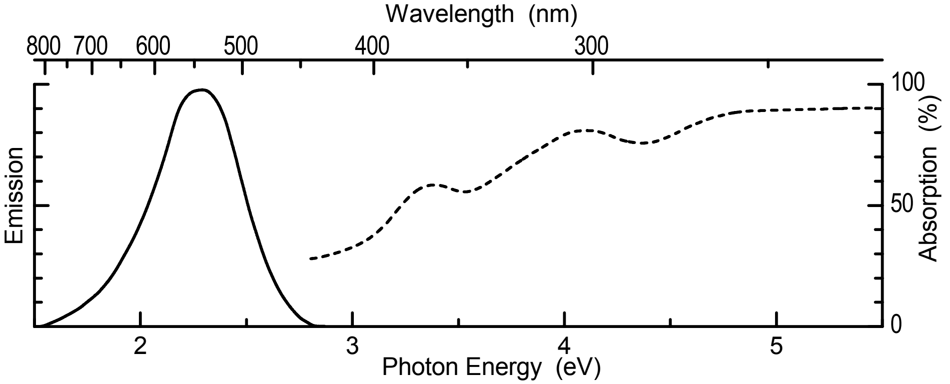
$CaS:Sn^{2+}$

Structure: Cubic (NaCl)

Optical Properties

Emission color: Yellow-greenish
Emission peak: 2.30 eV
Emission width (FWHM): 0.50 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).
2. Yamashita, N., and Asano, S., ESR of 2s ½-state centers in $CaS:Sn^{3+}$, $CaSe:Sn^{3+}$ and $CaSe:Pb^{3+}$, *J. Phys. C Solid State,* 9, L65 (1976).
3. Yamashita, N., and Asano, S., Luminescence-centers of $Ca(S:Se):Sn^{2+}$ phosphors, *J. Phys. Soc. Jpn.,* 41, 536 (1976).

$CaS:Sn^{2+},F$

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
SnS	0.1	0.135
CaF_2	0.5	0.390

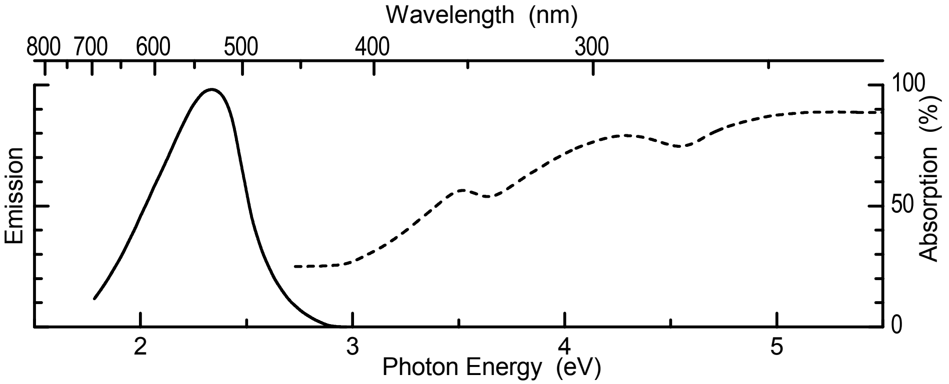
Preparation

1. Fire in plain $CaCO_3$ in open quartz boats, H_2S, 1100ºC, 1 hour.
   Powderize.
   Add the above amount of SnS and CaF_2 and about 2–3 g of sulfur.
   Mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1200ºC, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Pale yellow-green
Emission peak: 2.30 eV
Emission width (FWHM): 0.50 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: ~4%
Decay: Non-exponential decay of about 1 msec to 1/10

Spectra



References

1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).
2. Yamashita, N., and Asano, S., Esr of 2s ½-state centers in CaS:Sn^{3+}, CaSe:Sn^{3+} and CaSe:Pb^{3+}, *J. Phys. C Solid State,* 9, L65 (1976).
3. Yamashita, N., and Asano, S., Luminescence-centers of Ca(S,Se):Sn^{2+} phosphors, *J. Phys. Soc. Jpn.,* 41, 536 (1976).

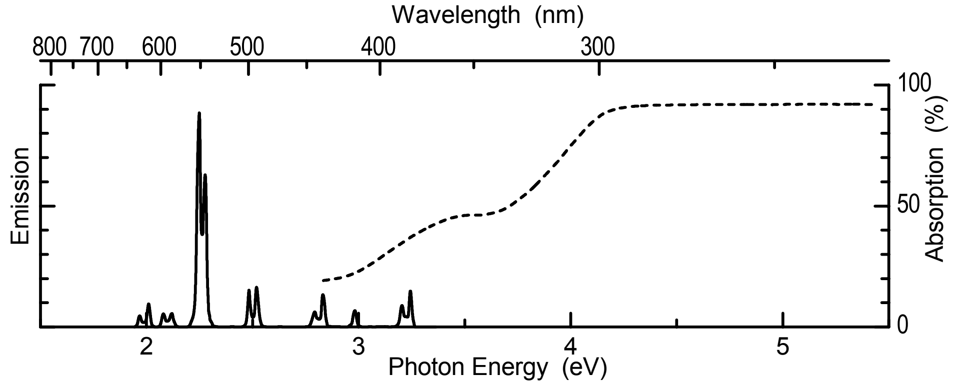
CaS:Tb^{3+}

Structure: Cubic (NaCl)

Optical Properties

Emission color: Green
Emission peak: 2.26–2.29 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Reference

1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).

CaS:Tb^{3+},Cl

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
Tb_4O_7	0.1 (of Tb)	0.187
NH_4Cl	~2	~1

Preparation

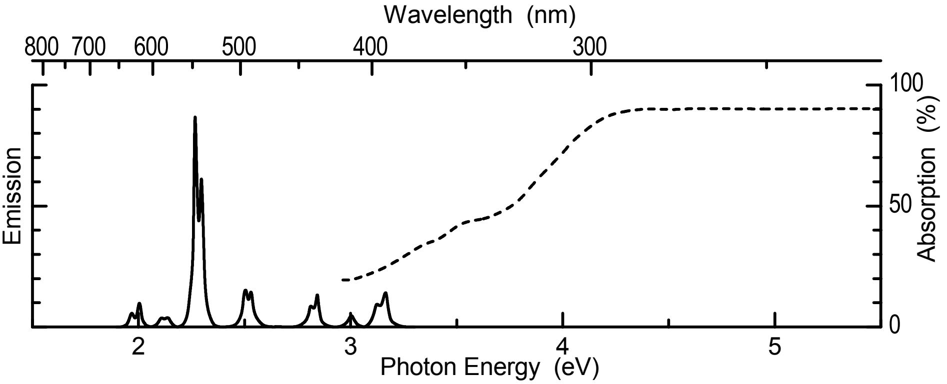
Mix the $CaCO_3$ and the Tb_4O_7.

1. Fire in plain $CaCO_3$ in open quartz boats, H_2S, 1100°C, 1 hour.
   Powderize.
   Add the above amount of NH_4Cl, also ~ 2–3 g of sulfur.
   Mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1200°C, 1 hour.
   Powderize.
3. Fire in capped quartz tubes, N_2, 1200°C, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Pale green
Emission peak: Strongest lines a doublet at 2.26 and 2.29 eV.
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)
Excitation efficiency by e-beam: Relatively poor
Decay: Exponential decay, ~ 3.6 msec to 1/10

Spectra



Reference

1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).

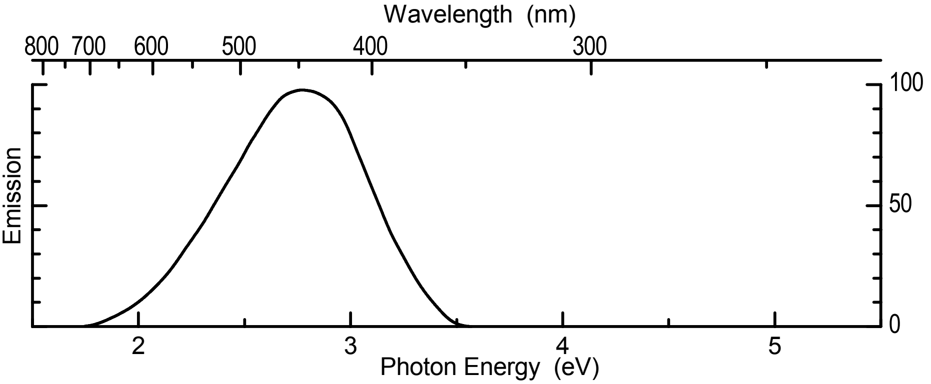
CaS:Y^{3+}

Structure: Cubic (NaCl)

Optical Properties

Emission color: Bluish
Emission peak: 2.80 eV
Emission width (FWHM): 0.78 eV
Excitation efficiency by UV: ++ (4.88 eV), – (3.40 eV)

Spectra



Reference

1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).

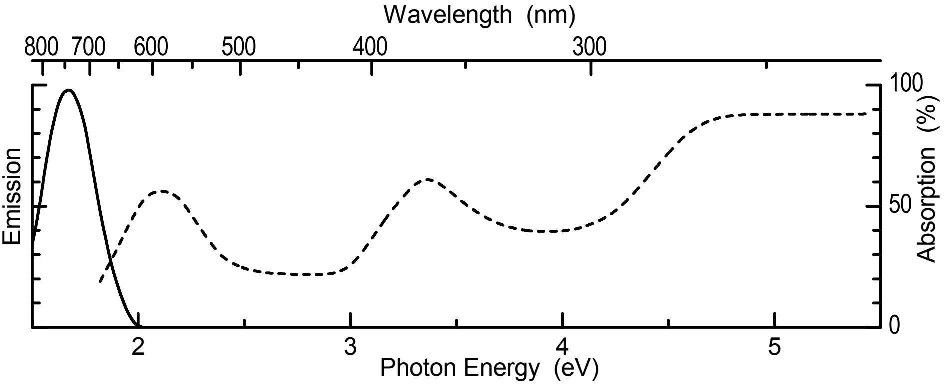
CaS:Yb^{2+}

Structure: Cubic (NaCl)

Optical Properties

Emission color: IR
Emission peak: 1.66 eV
Emission width (FWHM): 0.30 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Spectra



Reference

1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).

CaS:Yb^{2+},Cl

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	100
Yb_2O_3	0.1 (of Yb)	0.197
NH_4Cl	~ 2	~ 1

Preparation

Mix the $CaCO_3$ and the Tb_4O_7.

1. Fire in plain $CaCO_3$ in open quartz boats, H_2S, 1100ºC, 1 hour.
   Powderize.
   Add the above amount of NH_4Cl and also ~ 2–3 g of sulfur.
   Mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1200ºC, 1 hour.
   Powderize.
3. Fire in capped quartz tubes, N_2, 1200ºC, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Very deep red

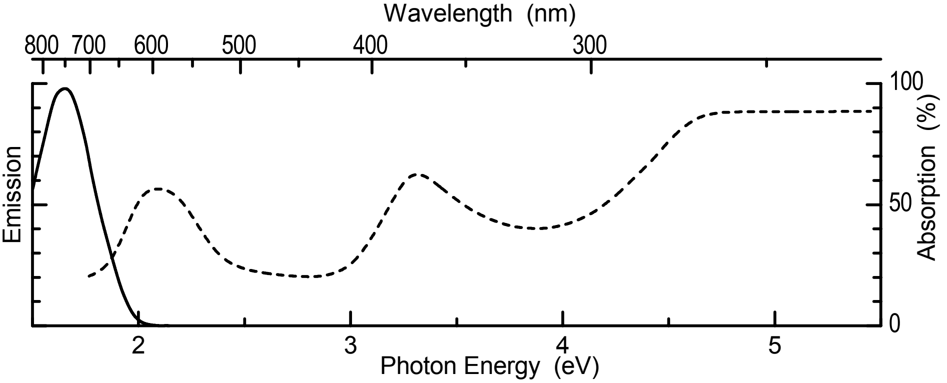
Emission peak: 1.66 eV

Emission width (FWHM): 0.30 eV

Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)

Decay: Non-exponential decay in the 20–50 μsec range

Spectra



Reference

1. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.,* 5, 87 (1972).

$SrS:Ce^{3+}$

Structure: Cubic (NaCl)

Optical Properties

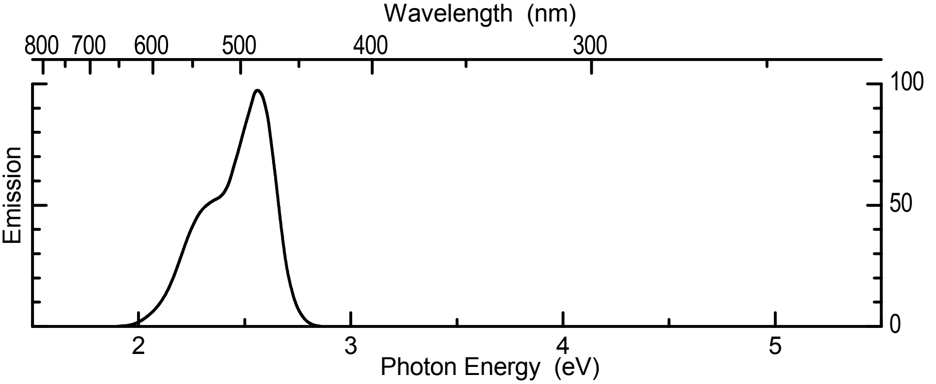
Emission color: Blue-green

Emission peak: 2.20 eV, 2.47 eV – or 2.3 eV, 2.56 eV in cathodoluminescence

Excitation efficiency by UV: + (4.88 eV)

Excitation efficiency by e-beam: +

Spectra



Reference

1. Okamoto, F., and Kato, K., Preparation and cathodoluminescence of CaS-Ce and $Ca_{1-x}Sr_xS$-Ce phosphors, *J. Electrochem. Soc.,* 130, 432 (1983).

SrS:Cu$^+$,Na

Structure Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	100	148
$CuSO_4 \cdot 5\ H_2O$	0.1	0.250
$NaHCO_3$	2	1.68

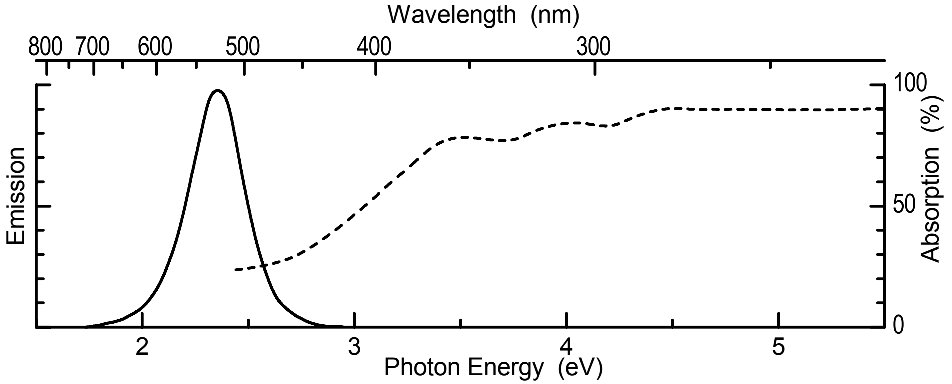
Preparation

Dissolve the copper sulfate and the $NaHCO_3$ together in a little water; add this solution to the $SrCO_3$.
Make a uniform slurry in water or methanol. Dry; powderize.
Fire in open alumina boats, H_2S, 1200°C, 1 hour. Powderize.
Store in a well-closed container.

Optical Properties

Emission color: Green
Emission peak: 2.33 eV
Emission width (FWHM): 0.31 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: ++/ Very efficient
Decay: Non-exponential decay in the 10 μsec range followed by long phosphorescence

Spectra



Remarks

1. Na in the above recipe cannot be replaced by other alkalies.
2. This phosphor shows exceptionally long and strong phosphorescence after excitation by UV.

Reference

1. Lehmann, W., Alkaline earth sulfide phosphors activated by copper, silver, and gold, *J. Electrochem. Soc.,* 117, 1389 (1970).

$SrS:Eu^{2+}$

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	100	148
Eu_2O_3	0.1 (of Eu)	0.176
NH_4Cl	2	1

Preparation

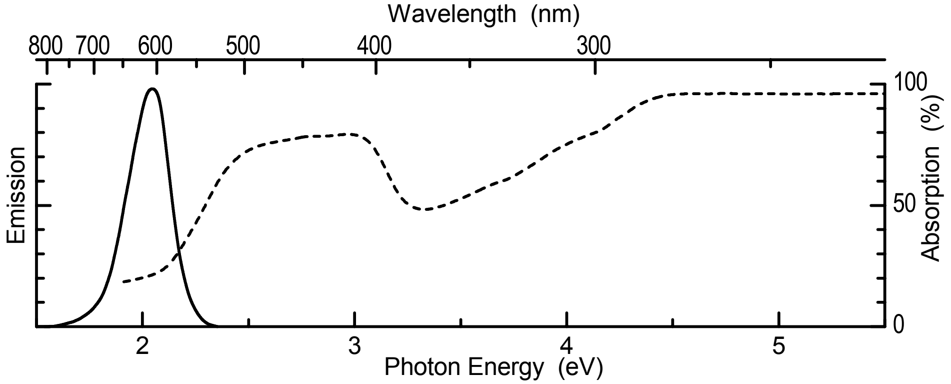
First mix only the $SrCO_3$ + Eu_2O_3.

1. Fire in open quartz boats, H_2S, 1100ºC, 1 hour. Powderize.
   Add the above amount of NH_4Cl, also ~ 2–3 g of sulfur.
   Mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1100ºC, 1 hour. Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Orange-red
Emission peak: 2.00 eV
Emission width (FWHM): 0.26 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +
Decay: Decay in the microsecond range

Spectra



Remarks

1. The Cl in the above recipe may be replaced by F, Br, or I.
2. The characteristic orange body color of this phosphor is caused by the blue to green absorption band and by the orange-red emission excited by ambient light.
3. This phosphor can be sensitized for efficient 3.40 eV excitation by addition of ~0.03 mol% of Pb.

$SrS:Mn^{2+}$

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	100	148
$MnCO_3$	0.1	0.115
NH_4Cl	1	0.540

Preparation

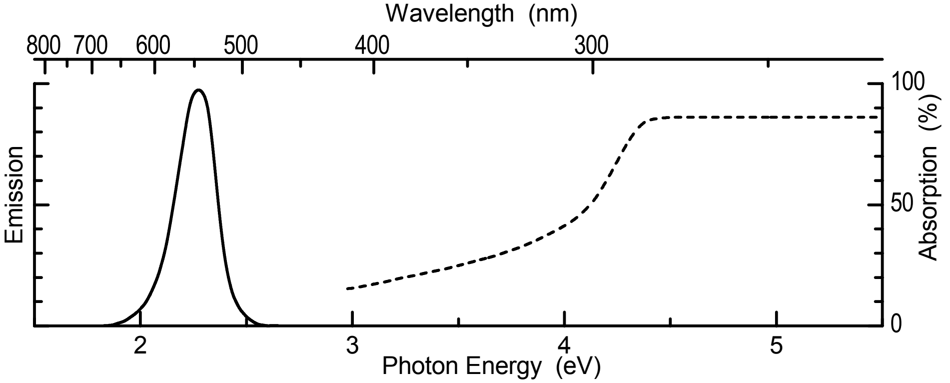
First mix only the $SrCO_3$ + $MnCO_3$.

1. Fire in open quartz boats, H_2S, 1100ºC, 1 hour.
   Powderize.
   Add the above amount of NH_4Cl and also ~ 2–3 g of sulfur.
   Mix by dry grinding.
2. Fire in capped quartz tubes, N_2, 1100ºC, 1 hour.
   Powderize.
3. Fire in open quartz boats, H_2S, 1000ºC, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Yellow-green
Emission peak: 2.28 eV
Emission width (FWHM): 0.23 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +/Fairly efficient
Decay: Exponential decay requiring ~4 msec to 1/10

Spectra



Remark

Phosphor can be sensitized for efficient 3.40 eV excitation by addition of ~0.03 mol% of Pb. This also shifts the emission band peak to ~2.245 eV.

Reference

1. Sorge, O., Thesis, Technical University of Berlin (1959).

BaS:Au,K

Structure: Cubic (NaCl)

Composition

Ingredient	Mole %	By weight (g)
$BaSO_4$	100	233
Au-metal	0.1	0.197
K_2CO_3	1 (of K)	0.690

Preparation

Dissolve the Au in a little (as little as possible) aqua regia and the K_2CO_3 in a little water. Make a slurry of the $BaSO_4$ in water or methanol.
Add both solutions; stir to uniformity; dry and powderize.

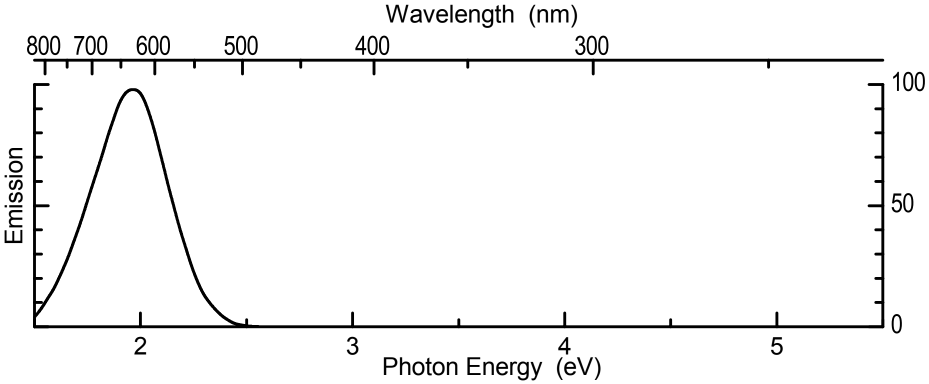
1. Fire in open alumina boats, H_2S, 900ºC, 1 hour. Powderize.
2. Fire in open alumina boats, H_2, 700ºC, 1 hour. Powderize.

Store in a well-closed container.

Optical Properties

Emission color: Orange-red
Emission peak: 1.93 eV
Emission width (FWHM): 0.38 eV
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Remarks

1. This material is very hygroscopic. Do not, under any circumstances, let it come into contact with water.
2. Replacement of K in the above recipe by Li, Rb, Cs, F, or P gives slightly different emission spectra. Replacement of K by Na gives near-dead material.

Reference

1. Lehmann, W., Alkaline earth sulfide phosphors activated by copper, silver, and gold, *J. Electrochem. Soc.,* 117, 1389 (1970).

4.15 Double Sulfides

The following host compounds and activators are included in this subsection:

$CaGa_2S_4$:Ce^{3+}
$CaGa_2S_4$:Eu^{2+}
$CaGa_2S_4$:Mn^{2+}
$CaGa_2S_4$:Pb^{2+}
$ZnGa_2S_4$:Mn^{2+}
$ZnBa_2S_3$:Mn^{2+}

$CaGa_2S_4$:Ce^{3+}

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	98	98
Ga_2O_3	200 (of Ga)	187
CeO_2	1	1.7
$NaHCO_3$	1	0.840

Preparation

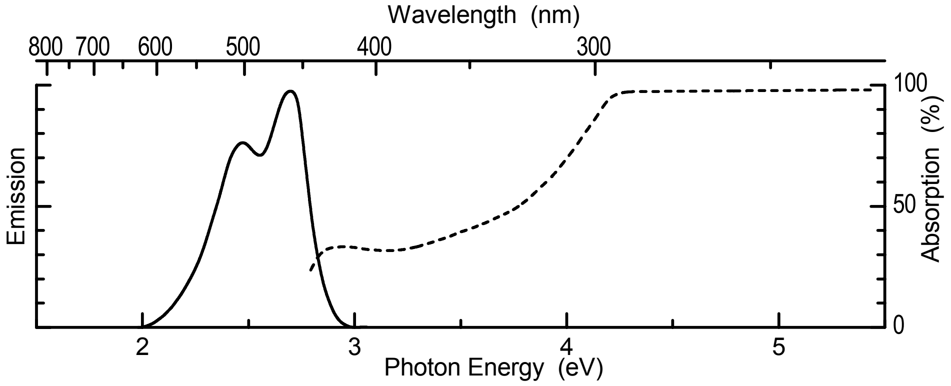
First mix only $CaCO_3 + Ga_2O_3 + CeO_2$.

1. Fire in open quartz boats, H_2S, 800ºC, 1 hour.
   Powderize.
2. Fire in open quartz boats, N_2, 800ºC, 1 hour.
   Powderize.
   Add the above amount of $NaHCO_3$ and also ~2–3 g of sulfur.
   Mix by dry grinding.
3. Fire in covered alumina crucibles, N_2, 800ºC, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Bluish
Emission peaks: Two overlapping bands ~2.42 and 2.68 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: 4.5%

Spectra



Remark

This phosphor is slightly unstable in water.

Reference

1. Peters, T.E., and Baglio, J.A., Luminescence and structural properties of thiogallate phosphors Ce^{+3} and Eu^{+2}-activated phosphors, *J. Electrochem. Soc.,* 119, 230 (1972).

$CaGa_2S_4:Eu^{2+}$

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	99	99
Ga_2O_3	200 (of Ga)	187
Eu_2O_3	1 (of Eu)	1.76

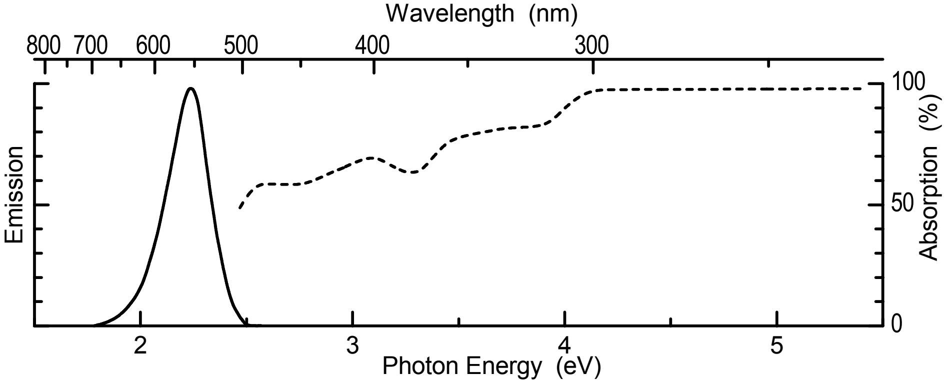
Preparation

Mix by slurrying in water, dry, and powderize.
1. Fire in open quartz boats, H_2S, 800ºC, 1 hour.
   Powderize.
2. Fire in open quartz boats, N_2 bubbling through CS_2, 800ºC, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Yellow-green
Emission peak: 2.22 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: 7%

Spectra



Remark
This phosphor is slightly unstable in water.

References

1. Peters, T.E., and Baglio, J.A., Luminescence and structural properties of thiogallate phosphors Ce^{+3} and Eu^{+2}-activated phosphors, *J. Electrochem. Soc.,* 119, 230 (1972).
2. Donohue, P.C., and Hanlon, J.E., Synthesis and photoluminescence of MIIM2III(S,Se)$_4$, *J. Electrochem. Soc.,* 121, 137 (1974).

$CaGa_2S_4:Mn^{2+}$

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	98	98
Ga_2O_3	200 (of Ga)	187
$MnCO_3$	2	2.3

Preparation

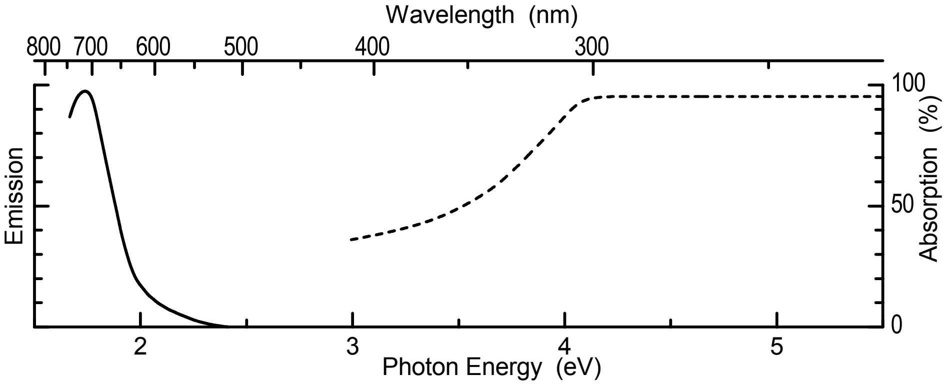
Mix by slurrying in water.
Dry in air. Powderize when dry.

1. Fire in open quartz boats, H_2S, 900ºC, 2 hours.
   Powderize.
2. Fire in open quartz boats, N_2 loaded with CS_2, 800ºC, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Deep red
Emission peak: 1.74 eV
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Remark

This phosphor is slightly unstable in water.

$CaGa_2S_4:Pb^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	99	99
Ga_2O_3	200 (of Ga)	187
PbO	1	2.2

Preparation

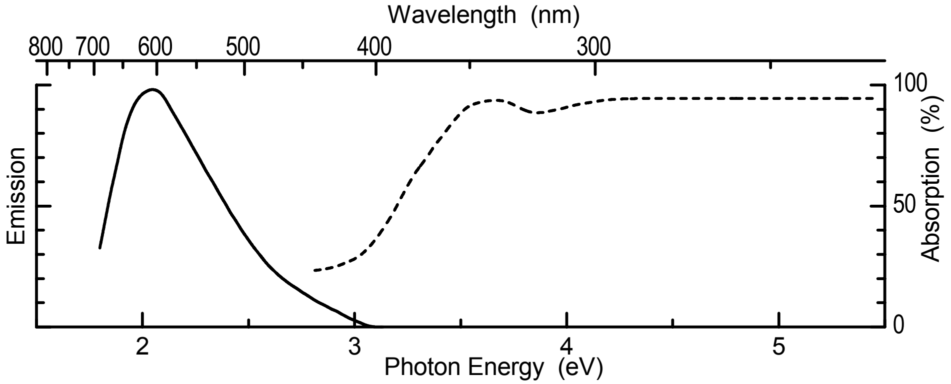
First mix only $CaCO_3$ + Ga_2O_3.

1. Fire in open quartz boats, H_2S, 800°C, 1 hour.
   Powderize.
2. Fire in open quartz boats, N_2 bubbling through CS_2, 800°C, 1 hour.
   Add the above amount of PbO and also ~2–3 g of sulfur.
   Mix by dry grinding.
3. Fire in capped quartz tubes, N_2, 800°C, 1 hour.
   Powderize.
   Store in a well-closed container.

Optical Properties

Emission color: Pale whitish-yellow
Emission peak: 2.03 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: 3.5%

Spectra



Remark

This phosphor is slightly unstable in water.

$ZnGa_2S_4$:Mn^{2+}

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
ZnS	98	96
Ga_2O_3	200 (of Ga)	187
$MnCO_3$	2	2.3

Preparation

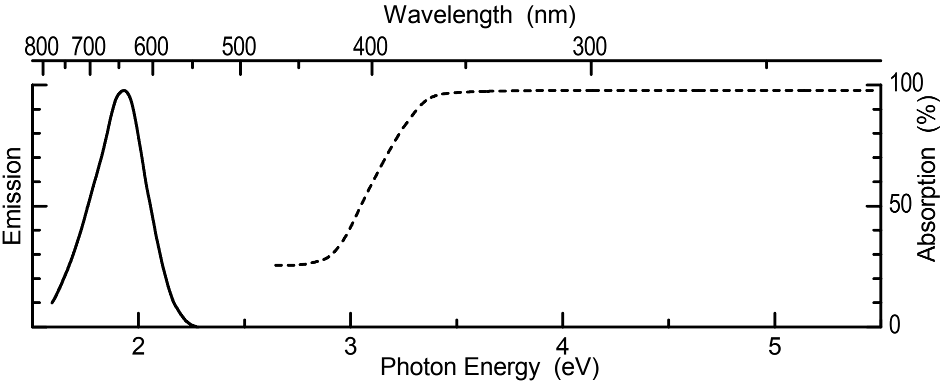
Mix by slurrying in water, dry, and powderize.

1. Fire in open quartz boats, H_2S, 1000ºC, 1 hour.
   Powderize.
2. Fire in open quartz boats, N_2 bubbling through CS_2, 800ºC, 1 hour.
   Powderize.
3. Fire in open quartz boats, H_2S, 1100ºC, 1 hour.
   Powderize.

Optical Properties

Emission color: Red
Emission peak: 1.92 eV
Emission width (FWHM): 0.30 eV
Excitation efficiency by UV: ++ (4.88 eV), ++ (3.40 eV)
Excitation efficiency by e-beam: 4%
Decay: Exponential decay, about 18–20 msec to 1/10

Spectra



Reference

1. Bird, G., Vecht, A., and Smith, P.J.F., *Electrochem. Soc. Meeting,* San Francisco, Abstr. 92 (May 1974).

$ZnBa_2S_3:Mn^{2+}$

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
ZnS	98	96
$BaCO_3$	200	275
$MnCO_3$	2	2.3

Preparation

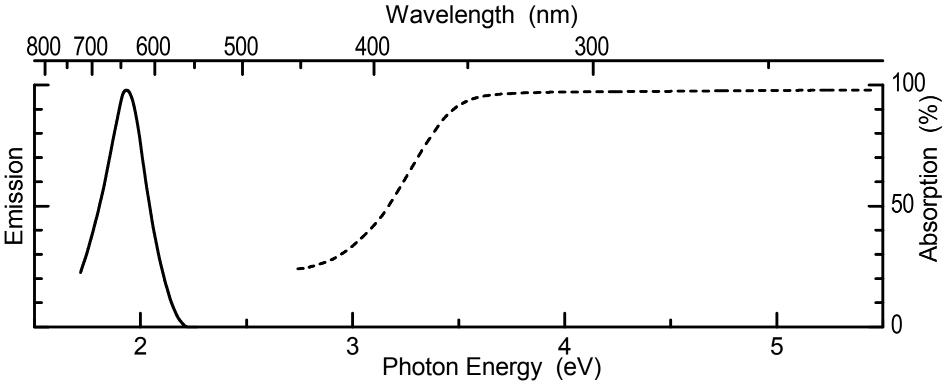
Mix by slurrying in water, dry, and powderize.

1. Fire in open quartz boats, H_2S, 800ºC, 1 hour. Powderize.
2. Fire in open quartz boats, H_2, 700ºC, 1 hour. Powderize.

Optical Properties

Emission color: Red
Emission peak: 1.935 eV
Emission width (FWHM): 0.24 eV
Excitation efficiency by UV: ++ (3.40 eV)
Excitation efficiency be e-beam: +

Spectra



Remark

This phosphor has been used for DC-EL by A. Vecht.

References

1. Vecht, A., Electroluminescent displays, *J. Vac. Sci. Technol.,* 10, 789 (1973).
2. Vecht, A. et al., *Electrochem. Soc. Meeting,* San Francisco, Abstr. 93 (May 1974).

4.16 Miscellaneous Sulfides and Oxysulfides

The following host compounds and activators are included in this subsection:

$SrAl_2S_4:Eu^{2+}$
$SrGa_2S_4:Pb^{2+}$
$BaAl_2S_4:Eu^{2+}$
$SrGa_2S_4:Ce^{2+}$
$SrGa_2S_4:Eu^{2+}$
$BaGa_2S_4:Ce^{3+}$
$BaGa_2S_4:Eu^{2+}$
$Y_2O_2S:Eu^{3+}$
$Y_2O_2S:Tb^{3+}$
$Gd_2O_2S:Tb^{3+}$

$SrAl_2S_4:Eu^{2+}$

Optical Properties

Emission color: Blue-green
Emission peak: 2.50 eV
Emission width (FWHM): 0.21 eV
Excitation efficiency by UV: + (4.88 eV)
Excitation efficiency by e-beam: +

Reference

1. Donohue, P.C., and Hanlon, J.E., Synthesis and photoluminescence of MIIM2III(S,Se)$_4$, *J. Electrochem. Soc.,* 121, 137 (1974).

$SrGa_2S_4:Pb^{2+}$

Optical Properties

Emission color: Orange
Emission peak: 2.04 eV
Emission width (FWHM): 0.51 eV
Excitation efficiency by e-beam: +

Reference

1. Peters, T.E., Luminescence properties of thiogallate phosphors. 3. Red and white emitting phosphors for flying spot scanner applications, *J. Electrochem. Soc.,* 122, 98 (1975).

$BaAl_2S_4:Eu^{2+}$

Optical Properties

Emission color: Light blue
Emission peak: 2.61 eV
Emission width (FWHM): 0.31 eV
Excitation efficiency by UV: + (3.40 eV)
Excitation efficiency by e-beam: +

Reference

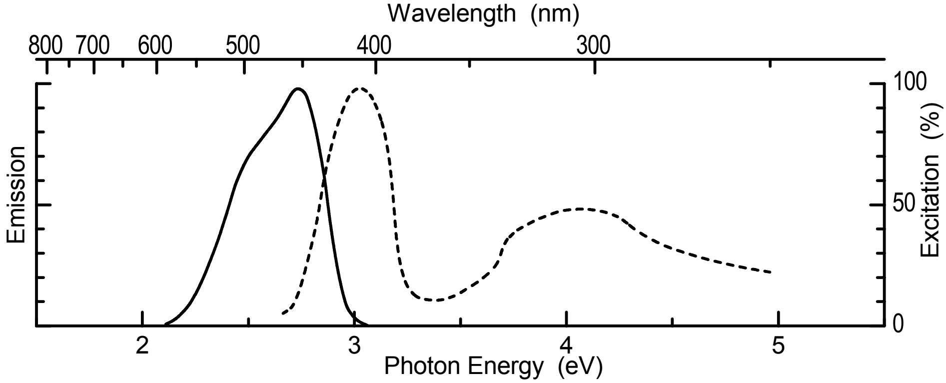
1. Donohue, P.C., and Hanlon, J.E., Synthesis and photoluminescence of MIIM2III(S,Se)$_4$, *J. Electrochem. Soc.,* 121, 137 (1974).

$SrGa_2S_4:Ce^{3+}$

Optical Properties

Emission color: Blue-green
Emission peak: 2.53 eV, 2.73 eV
Excitation efficiency by UV: + (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

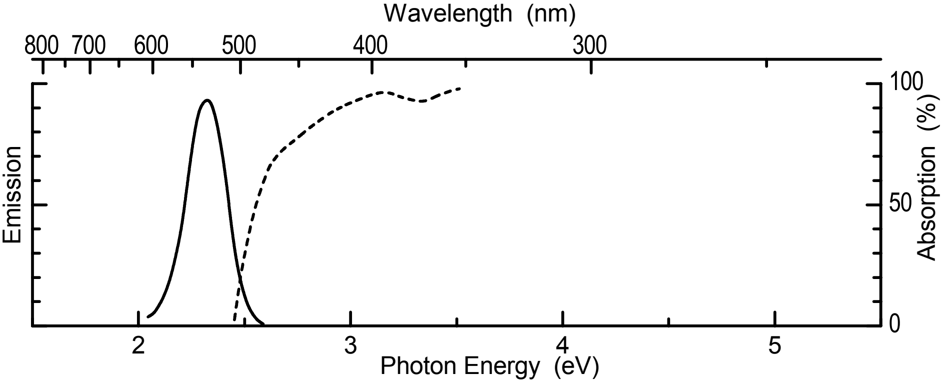
1. Peters, T.E., and Baglio, J.A., Luminescence and structural properties of thiogallate phosphors Ce^{+3} and Eu^{+2}-activated phosphors, *J. Electrochem. Soc.,* 119, 230 (1972).
2. Peters, T.E., Luminescence properties of thiogallate phosphors. 3. Red and white emitting phosphors for flying spot scanner applications, *J. Electrochem. Soc.,* 122, 98 (1975).

$SrGa_2S_4:Eu^{2+}$

Optical Properties

Emission color: Green
Emission peak: 2.31 eV
Emission width (FWHM): 0.20 eV
Excitation efficiency by UV: ++ (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



Reference

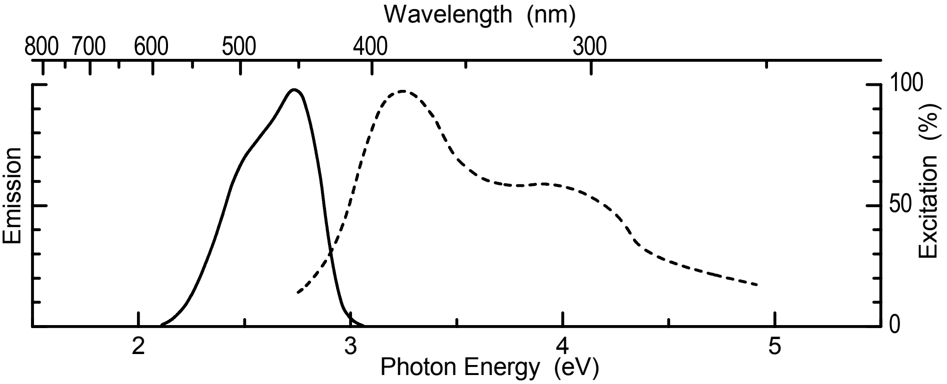
1. Peters, T.E., and Baglio, J.A., Luminescence and structural properties of thiogallate phosphors Ce^{+3} and Eu^{+2}-activated phosphors, *J. Electrochem. Soc.,* 119, 230 (1972).
2. Donohue, P.C., and Hanlon, J.E., Synthesis and photoluminescence of MIIM2III$(S,Se)_4$, *J. Electrochem. Soc.,* 121, 137 (1974).

$BaGa_2S_4:Ce^{3+}$

Optical Properties

Emission color: Blue-green
Emission peak: 2.53 eV, 2.73 eV
Excitation efficiency by UV: + (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

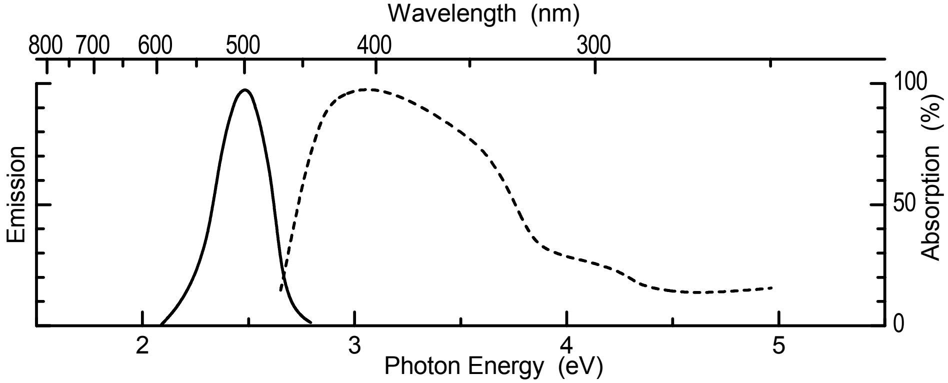
1. Peters, T.E., and Baglio, J.A., Luminescence and structural properties of thiogallate phosphors Ce^{+3} and Eu^{+2}-activated phosphors, *J. Electrochem. Soc.,* 119, 230 (1972).
2. Donohue, P.C., and Hanlon, J.E., Synthesis and photoluminescence of MIIM2III$(S,Se)_4$, *J. Electrochem. Soc.,* 121, 137 (1974).

$BaGa_2S_4:Eu^{2+}$

Optical Properties

Emission color: Blue-green
Emission peak: 2.52 eV
Excitation efficiency by UV: ++ (3.40 eV)
Excitation efficiency by e-beam: +

Spectra



References

1. Peters, T.E., and Baglio, J.A., Luminescence and structural properties of thiogallate phosphors Ce^{+3} and Eu^{+2}-activated phosphors, *J. Electrochem. Soc.,* 119, 230 (1972).
2. Donohue, P.C., and Hanlon, J.E., Synthesis and photoluminescence of MIIM2III(S,Se)$_4$, *J. Electrochem. Soc.,* 121, 137 (1974).

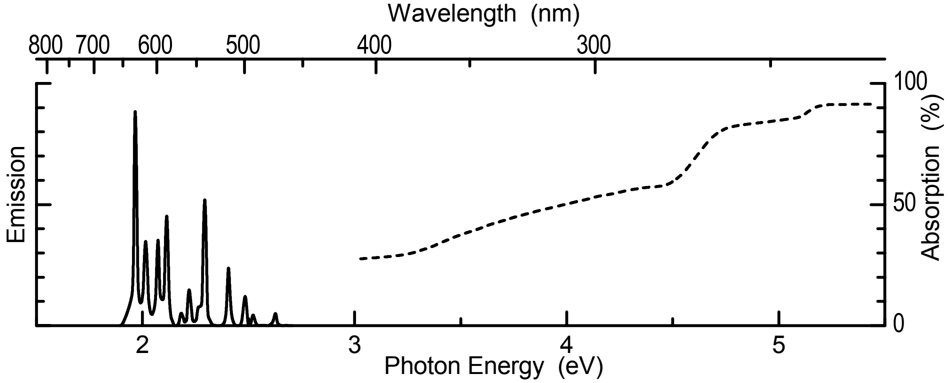
$Y_2O_2S:Eu^{3+}$

Structure: Trigonal

Optical Properties

Emission color: Orange to red (lines)
Excitation efficiency by UV: ++ (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: ++

Spectra



References

1. Royce, M.R., U.S. Pat., 3 418 246 (1968).
2. Ozawa, L., Preparation of Y_2O_2S:Eu phosphor particles of different sizes by a flux method, *J. Electrochem. Soc.,* 124, 413 (1977).
3. Fonger, W.H., and Struck, C.W., Energy loss and energy storage from the Eu^{3+} charge-transfer states in Y and La oxysulfides, *J. Electrochem. Soc.,* 117, 118 (1970).

$Y_2O_2S:Tb^{3+}$

Optical Properties

Emission color: Blue-green
Excitation efficiency by UV: + (4.88 eV), + (3.40 eV)
Excitation efficiency by e-beam: ++

$Gd_2O_2S:Tb^{3+}$

Optical Properties

Emission color: Green
Emission peak: 2.26–2.29 eV
Excitation efficiency by UV: + (4.88 eV), − (3.40 eV)
Excitation efficiency by e-beam: ++

Section 5:
Preparation of Phosphor Screens

Section 5

PREPARATION OF PHOSPHOR SCREENS*

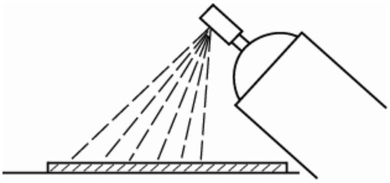
The following are examples of how to deposit inorganic phosphor powders in thin and uniform layers onto flat surfaces (usually glass). These methods have been tested and used in this laboratory. They are useful but certainly not the only ways of preparing phosphor screens.

5.1 Phosphor Screens by Brushing

This method gives excellent, thin but dense, phosphor layers. It is especially good for small screens. The method is quick and easy and has been extensively used in the laboratory.

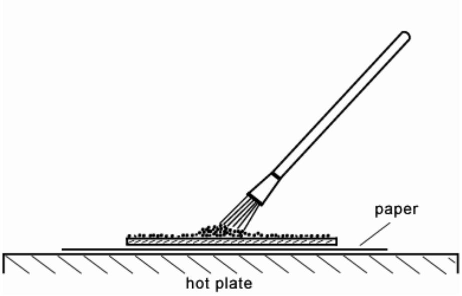
Procedure

Place the clean substrate (glass, etc.) on a horizontal surface.
Spray a layer of Krylon-Clear (out of a spray can) onto the substrate. Keep nozzle of the spray can about 5–10 cm over the substrate and spray enough to have the liquid laquer uniformly flowing over the area. Try to keep the laquer as uniform in thickness as possible.



Let dry in air.

Place the substrate, the lacquer up, onto a piece of white paper and some of the phosphor to be coated onto the dry lacquer layer.
Now place all onto an electric hot plate with a flat metal top.
Heat up the hot plate to a temperature where the paper under the substrate just about turns brown. Simultaneously, move the phosphor over the lacquer with a soft hair brush. The lacquer becomes tacky when hot and coats quickly with a very dense yet thin phosphor layer.



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* This section is from W. Lehmann's *Phosphor Cookbook.*

Take the screen off the hot plate; let cool down. Lacquer becomes solid.

Wipe excess loose phosphor particles off with a soft paper tissue.

The screen is now ready for most applications. The phosphor adheres very tightly to the substrate and is not easily damaged.

In some cases, however, the organic layer underneath of the phosphor layer cannot be tolerated. It can easily be burned out by heating in the open air, 400ºC, for a few minutes. Afterwards, the phosphor will still stick to the substrate but the layer is much softer and easier damaged by accidental touching.

Reference

1. Lehmann, W., U.S. Pat., 2 798 821 (1954).

5.2 Phosphor Screens by Settling in a Kasil Solution

This method gives somewhat less dense (macroscopically) layer than brushing but permits tight thickness control and is easily used for large screens. It is widely in use to prepare phosphor screens for cathode-ray tubes.

Procedure

Clean the glass to be coated. Place it in a sufficiently large beaker, face up.

Prepare two stock solutions.

Solution A: K-silicate solution in water, 3% solids
Solution B: 1 g Sr acetate, $Sr(C_2H_3O_2)_2$, in 1 liter water

Pour solution A into the beaker to 20–40% of the volume.

Screen the phosphor through a fine sieve immediately before use (this is an important point).

Weigh the amount of phosphor to give the desired layer of thickness, grams per square centimeter, over the area of the beaker opening. About 5–10 mg/cm^2 usually is sufficient for most phosphors and purposes.

Pour solution B, a volume equal to that of A, into a glass cylinder; add the weighed amount of phosphor; close the upper end of the cylinder with one hand and shake vigorously. Then pour the suspension quickly to the solution A in the beaker.

Cover the beaker and let stand for about 1–24 hours.* The phosphor settles down during this time and the phosphor layer reacts with the silicate of the solution. Small amounts of this reaction product, or of Sr silicate from the reaction between parts A and B, will bind the phosphor to the substrate.

Decant the excess liquid.

Cautiously (as not to damage the still soft phosphor layer) rinse the screen several times in water.

Dry in air.

* Best reaction times depend on the material. Zn_2SiO_4 phosphors give well-adhering screens after 1–2 hours. ZnS-type phosphors react slower and have to stand overnight or longer.

Reference

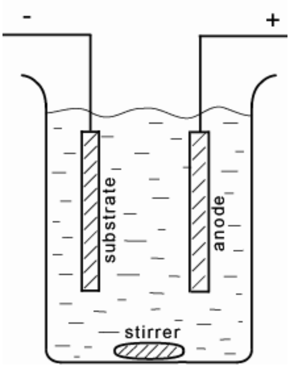
1. Vosburgh, K.G., Swank, R.K., and Houston, J.M., *Adv. Electr. Electron. Phys.*, 43, 205 (1977).

5.3 Phosphor Screens by Cathaphoretic Deposition

This method is used to prepare dense layers of fine-particled phosphors for high-resolution cathode ray screens.

Procedure

Coat the glass surface to be coated with a very thin, optically transparent gold layer by evaporation in a vacuum.
Provide a solution of 200 mg MG$(NO_3)_2 \cdot H_2O$ in 1 liter methanol. Pour this solution into a beaker and add a few grams of the phosphor. Keep the solution in suspension by stirring (magnetic stirrer).
Insert the Au-coated substrate and an inert anode (Pt, carbon, etc.) into the upper part of the beaker. Distance anode–cathode a few centimeters.



Apply about 100–150 V DC (subtrate = negative). Current should be about 5–10 mg/cm^2. A very uniform and compact phosphor layer will stick to the substrate within about 10–30 sec. Longer times give thicker but less uniform layers.
Turn off voltage and stirrer; let the excess phosphor settle. Then take the screen cautiously out of the solution (the phosphor adheres to the substrate even in the absence of any additional binder).
Rinse briefly in water.
Wash briefly in a solution of about 10 g NaOH (or KOH) + 10 g NaCN (or KCN) in 1 liter water to dissolve the Au film which is no longer needed.
Rinse again in water and then in methanol.
Dry.

Reference

1. Grosso, P.F., Rutherford, R.E., and Sargent, D.E., Electrophoretic deposition of luminescent materials, *J. Electrochem. Soc.,* 117, 1456 (1970).

5.4 Filming of Phosphor Screens

Phosphor layers in commercial CR tubes are backed by a thin metallic Al film which the exciting electrons penetrate to reach the phosphor particles. The Al film provides an optically reflecting rear layer (thus enhancing the output brightness of the tube) and protects the phosphor against damage by ion bombardment from unavoidable gas residues in the tube.

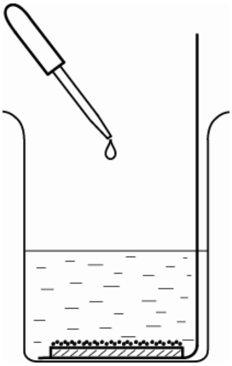
Procedure

Place the phosphor screen, face up, into a beaker on a metal carrier to permit easy lifting out again. Add water to cover the screen.

Provide a solution of:

50 ccm ethyl cellulose in amyl acetate (commercial cellulose binder),
65 ccm propyl acetate,
30 ccm isopropyl alcohol,
2 ccm octyl acetate.

With an eye dropper, drop 1–5 drops (depending on the surface area) of the above filming solution onto the water in the beaker.



The solution will quickly spread over the whole water surface. The solvent evaporates within about 20–30 sec, leaving behind a solid, very thin film of ethyl cellulose floating on the water.

Carefully lift screen out.

Let dry in air. The cellulose now forms a very thin solid film touching only the tops of the phosphor particles. It prevents the Al during the subsequent vacuum deposition to penetrate in between the particles.

Deposit the Al film by evaporation in vacuum.

Heat the screen in open air to about 300–400ºC for a few minutes.

The cellulose film will burn out leaving behind a shiny Al film.

Part 2:
Additional Developments

Section 6: Phosphor Synthesis

Section 6

PHOSPHOR SYNTHESIS

6.1 Alternative Preparation Methods*

The traditional way of preparing phosphors has been by the mix and fire techniques detailed in the earlier sections. In this method, the reactants are mixed thoroughly either in dryness or in suspension; the mixture is then heated or fired under an appropriate atmosphere. To ensure the proper reactivity between the constituents of the phosphor, the reactants are generally granular with radii in the micrometer range. To further facilitate the reaction and to improve the crystallinity of the luminescent materials, flux agents or molten salts are often added to provide a more interactive medium for the reaction. The use of an interaction medium often results in lower reaction temperatures and allows for the optimization of the grain size of the luminophores being synthesized.

A suitable flux increases the reactivity of the constituents by dissolving at least one of the reactants and provides a medium to incubate the crystallization of the phosphor. There are two types of fluxes which are used, volatile and non-volatile. The volatile flux often reacts with the starting material and leaves the reaction mixture spontaneously, through either decomposition or evaporation. Commonly used fluxes include NH_4Cl, NH_4Br, AlF_3, and boric acid. The amounts used are typically small, on the order of few mole percent. Molten salts are used as non-volatile fluxes and generally do not react with the starting materials. As the name denotes, these fluxes are always in the form of a melt. Large amounts of the salts are used (up to 30% by weight of the phosphor material); they generally do not leave the reaction mixture and must be removed by washing with water or other appropriate solvents. Examples of salts used for this purpose are Na_2MoO_4, $Na_2B_4O_7$, Na_2SiO_3, and $Na_4P_2O_7$.

Reactivity can also be improved by choosing starting materials which are unstable in controlled circumstances. Such reactants include the carbonates and the hydroxides which decompose with the emission of CO_2 or H_2O upon heating the mixture. This results in a more reactive mixture, as the interactive specific surface of the remaining elements increases in these processes.

A wet co-precipitation method is also being used. In these processes, the starting materials are dissolved in a solvent, come into contact with each other on an atomic or ionic level, and then co-precipitate forming an intimately commingled starting mixture. As an example, $Y(NO_3)_3$ and $Tb(NO_3)_3$ dissolved in water can be precipitated by the addition of a 2-to-1 solution of oxalic acid dissolved in hot water. The oxalates obtained in the precipitate can be converted to oxides by heating at a relatively low temperature of 800ºC. Alternatively, the oxides can also be dissolved directly in hot diluted nitric acid to obtain a treatable precipitate. This method is used in cases in which an insoluble salt can be identified for each of the reaction constituents. Other routes for co-precipitation can involve sulfates or hydroxides.

The method of spray drying can also be used to synthesize luminescent materials. In this method, the reactants are first dissolved in a solvent, preferably water. Droplets of this solution are then injected into a gas stream and are heated as they are transported downstream. The steam heating results in a very fast evaporation of the solvent or water. As a result, an intimate reaction mixture is formed and deposited downstream from the flow.

The various methods described above pose the advantage of assuring a better and more homogeneous admixture of the reactants to be used in the synthesis and of generally requiring a lower temperature to achieve this synthesis.

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* The above section was kindly provided by Cees Ronda.

6.2 Combustion Synthesis of Phosphors*

Beginning in the late 1980's, combustion synthesis has been investigated as a method to produce homogeneous, crystalline, fine oxide powders, as an alternative to time-consuming solid-state reaction and sol–gel processing techniques.[1–3] The method produces rapid, exothermic, self-sustaining reactions resulting from the appropriate combination of oxidizers (e.g., metal nitrates, ammonium nitrate, or ammonium perchlorate) and an organic fuel (e.g., urea, carbohydrazide, or glycine). For combustion to occur, it is necessary that a large amount of heat be released during the formation of the products. The reaction of aluminum nitrate, $Al(NO_3)_3$, and carbohydrazide, CH_6N_4O, to form aluminum oxide, Al_2O_3, is an example of a highly exothermic reaction, having a negative enthalpy of reaction ($\Delta H_{rxn} = -3800$ kJ/mol).

Later in the mid-1990's, several research groups began to investigate the use of combustion synthesis for oxide phosphor preparation[4–6] and found it to be a technique of interest for phosphor synthesis in general. For oxide phosphors, the advantages of combustion synthesis are in its ability to produce well-crystallized, fine particle size powders rapidly without extensive high temperature ($\geq 1500^\circ$C) annealing and mechanical separation (e.g., grinding and milling) steps. Grinding has often been implicated in the degradation of luminescent emission intensity through the creation of surface defects that quench the luminescence.

A composition of metal nitrates and fuel in which the fuel reacts completely with all of the metal nitrates in the mixture, so that no residues remain in the product material, is known as a stoichiometric ratio or composition. Equation 1 is an example of a stoichiometric combustion reaction of yttrium nitrate, aluminum nitrate, and carbohydrazide to form yttrium aluminum garnet, $Y_3Al_5O_{12}$ (YAG).

$$3YN_3O_9 + 5AlN_3O_9 + 15CH_6N_4O \rightarrow YAG(s) + 42N_2(g) + 15CO_2(g) + 45H_2O(g) \qquad (1)$$

When complete combustion occurs, the only gaseous products, N_2, CO_2, and H_2O, are released and no residuals are left in the synthesized YAG material.

The stoichiometry of metal nitrate-fuel mixtures is expressed in terms of the elemental stoichiometric coefficient, Φ_e, that is the ratio of the oxidizing to reducing components of the metal nitrate-fuel precursor mixture and is defined as:

$$\Phi_e = \frac{\Sigma(\text{coefficient of oxidizing elements in specific formula}) \times \text{valency}}{(-1)\,\Sigma(\text{coefficient of reducing elements in specific formula}) \times \text{valency}} \qquad (2)$$

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*This section was kindly provided by L.S. Rohwer.

The coefficients of the oxidizing and reducing elements are obtained from the balanced chemical equation for the combustion reaction of metal nitrates and a fuel, as noted below. The mixture is stoichiometric when $\Phi_e = 1$; it is fuel lean when $\Phi_e > 1$, and fuel rich when $\Phi_e < 1$. Stoichiometric mixtures are reported to produce maximum energy.

The oxidizer/fuel molar ratio required for a stoichiometric mixture ($\Phi_e = 1$) is determined by summing the total oxidizing and reducing valencies in the oxidizer compounds and dividing by the sum of the total oxidizing and reducing valencies in the fuel compounds. In these calculations, oxygen is considered to be the only oxidizing element and has a positive valence while carbon, hydrogen, and metal cations are considered to be reducing elements and have a negative valence. Nitrogen is considered to be neutral. For example, in Equation 1, $Y(NO_3)_3$ and $Al(NO_3)_3$ are oxidizers and the reducing agent is CH_6N_4O. For $Y_3Al_5O_{12}$ synthesized using carbohydrazide fuel, the metal nitrate to carbohydrazide molar ratio is given by:

$$\frac{\frac{3}{8}[1\,Y\times(-3)]+[3\,N\times 0]+[9\,O\times 2]\}+\frac{5}{8}\{[1\,Al\times(-3)]+[3\,N\times 0]+[9\,O\times 2]\}}{(-1)\times\{[1\,C\times(-4)]+[6\,H\times(-1)]+[4\,N\times 0]+[1\,O\times 2]\}}=\frac{15}{8}=1.875 \qquad (3)$$

Thus, the metal nitrate to carbohydrazide molar ratio = 1.875 is needed to obtain $\Phi_e = 1$ and complete combustion of all components.

Combustion reactions are initiated in a muffle furnace or on a hot plate at temperatures of 500°C or less; these temperatures are clearly much lower than the temperature at which crystallization of the desired phase takes place during conventional processing. In a typical reaction, the precursor mixture of de-ionized water, metal nitrates, and fuel boils, dehydrates, decomposes, and ruptures into a flame after about 3–5 minutes. The resultant product appears as a porous foam. The chemical energy released during the exothermic reaction between the metal nitrates and fuel can rapidly heat the system to a high temperature (>1800°C) and sustain that high temperature in the absence of an external heat source. Thus, the target phase(s) can be achieved with significantly reduced external energy input.

The type of fuel and the fuel to oxidizer ratio affect the adiabatic flame temperature, T_f. The fuel alters the energetics and exothermicity of the reaction, and provides a method to increase or decrease the adiabatic flame temperature. The flame temperature can also be increased by adding excess oxidizer such as ammonium nitrate, or by adjusting the fuel to oxidizer molar ratio so $\Phi_e = 1$. Hess' law can be used to approximate the adiabatic flame temperature for a combustion reaction:

$$T_f = T_o + \frac{\Delta H_r - \Delta H_p}{C_p} \qquad (4)$$

where ΔH_r and ΔH_p are the enthalpies of formation of the reactants and products, respectively, and C_p is the heat capacity of products at constant pressure.

Powders obtained from combustion reactions with urea or carbohydrazide fuels are luminescent in the as-synthesized state. Combustion reactions using glycine fuel yield amorphous powders or ash which must be annealed to produce crystalline luminescent powders. The photoluminescence emission spectra of YAG:Cr phosphors produced with carbohydrazide, urea, and glycine fuels followed by a heat treatment in air at 1300°C for 1 hour show the effect of flame temperature on the luminescent properties. The maximum flame temperatures during reactions with carbohydrazide, urea, and glycine were 1825, 1780, and 1210°C, respectively. The photoluminescence intensity increases for powders obtained from reactions that reached higher flame temperatures. This is an indication that certain properties of the resulting powders, such as crystallite size or and degree of disorder of the local environment at the activator ions, are affected by the flame temperature of the reaction.

The flame temperature is also controlled by the fuel to oxidizer ratio of the particular fuel used. The integrated photoluminescence intensity is a maximum for reactions at or near stoichiometry.

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6.3 Preparation of Phosphors by Sol–Gel Techniques*

6.3.1 Introduction

Phosphors used for most emissive display devices are in the form of powders. The quality of the displays depends on the nature of the powders used; fine and uniform powders with good crystallinity are generally preferred. This is especially true in low-voltage applications such as in the field emission displays of current interest. In these devices, lower energy electrons do not penetrate into phosphor grains very deeply, and in order to maintain efficiency the size of phosphor grains has to be reduced to reflect this fact. The grain size of phosphors prepared via solid-state chemical reactions depends on the temperature and the length of the sintering process. Lower temperature and shorter sintering periods give rise to smaller grain size particles, but both the crystallinity and grain uniformity are poor if the treatment parameters are such as not to allow the chemical reaction to be completed.

To resolve this problem, wet methods of preparation are often used; in the wet method, aqueous solutions of specific constituent metallic salts are employed. The addition of a $NH_4(OH)$ or oxalic acid causes the metallic hydroxides or oxalates to precipitate from the mixture; in these cases, the ingredients of the precipitate are in contact with each other at a molecular level and an efficient chemical reaction normally occurs.

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*This section was kindly provided by W. Jia.

The sol–gel method of phosphor preparation is regarded as a wet method. A kind of metal-organic compounds, known as alkoxides of metals, is used as precursors. These metal-organic alkoxides either are in liquid form or are soluble in certain organic solvents. Through the use of the appropriate reagents, the processes hydrolysis and gelation can be induced to produce homogeneous gels from the mixture of alkoxides. To obtain powder or ceramic samples, the gels can be baked, sintered, and powderized as in other traditional methods. The sol–gel method is advantageous inasmuch as thin films or coatings of the phosphor can be formed on substrates directly and/or the sol–gel can be molded into designated forms.

The sol–gel technique presents the following advantages:

(a) High homogeneity of the chemical composition of the materials produced occurs. Molecule-level-homogeneous multi-component materials can be obtained. Because of the better homogeneity, contributions to the optical spectra of these materials from inhomogeneous sources are generally expected to be smaller than those encountered in unordered systems.

(b) High uniformity of doping ions distribution exists. No "local" concentration quenching will occur because of impurity clustering, and higher doping concentration becomes possible.

(c) Processing temperature can be very low. This allows the doping of fragile organic and biological molecules into porous inorganic materials and the fabrication of organic–inorganic hybrid materials.

(d) The microstructure (porosity and size of pores) of the materials can be controlled. Nano-scale uniform pores can be obtained at intermediate processing temperature while high-density materials can be produced with higher annealing temperature.

(e) Thin films and multi-layers coatings of sol–gel materials can be readily prepared by spinning or dipping methods during the gelation period.

(f) The sol–gel procedures produce little unintentional contamination. No milling and grinding are needed; for example, processes are known to contaminate samples. Fluxes, such as B_2O_3, H_3BO_3, and NH_4Cl, which are commonly used in ceramic technology and contaminate the end products, are no longer needed. In cases where phosphor powders are prepared by the sol–gel method, powderizing may be used and trace of foreign particles can be mix in. This "contamination" does not enter into the lattice and will not affect the intrinsic optical properties of the phosphor.

The technique has the following disadvantages:

1. The drying and annealing processes have to be slow and deliberate; otherwise cracks and striations will appear in the samples.
2. It is difficult to completely remove the residual hydroxyls from the sol–gel materials. To get rid of these organic groups, samples have to be annealed above 1000°C and this may produce undesirable side effects.

The sol–gel method has been widely used to prepare a number of phosphors[10-12] for displays and other materials that are of technical importance. For example, Willi Lehmann reported in 1975 that very efficient luminescence was observed in, what he called, heterogeneous materials, such as SiO_2:CaX_2-Eu^{2+}/Mn^{2+} (where X = Cl, Br, or I), prepared by a solid-state reaction.[13] These materials are similar to those found in the nanoclusters in SiO_2 which have been developed recently via the sol–gel method described in the first section.[14-17] There are two ways to prepare such nanophosphor composites: (a) Alkoxide solutions of the phosphor are prepared from the appropriate precursors and then blended into the sol of SiO_2 (or other matrixes); the geletion process then proceeds as before. (b) Nanophases can be obtained by phase aggregation from doped SiO_2 or other matrices during thermal treatments. Different nanophosphor embedded glasses have been fabricated with this method. These materials are transparent and can be used for displays and laser devices.[18,19]

6.3.2 Sol–gel techniques

The sol–gel method is a chemical technique that uses metal alkoxides for the synthesis and production of glasses or ceramics through a series of chemical processes, including hydrolysis, gelation, drying, and thermal treatment. The sol–gel technique was developed as early as 1864; T. Graham[1] prepared gels of silica from aqueous salts, while M. Ebelmen[2] obtained silica gels from metal alkoxides. The potential of the sol–gel process was not appreciated until 1980, when it was "rediscovered" and found to be very useful in synthesizing various materials of practical importance, such as optical glasses and solid-state laser materials. Since then the method has received considerable attention and has been investigated extensively.[3]

In general, a sol is defined as a colloid of solid particles suspended in a liquid; the particles consist of dense oxide or polymetric clusters formed by the precursors and reagents. A gel, on the other hand, is a composite substance consisting of a continuous solid skeletal structure which results from the gelation of the sol; the gel forms cells which encapsulate colloidal liquids. This solute can be driven from the gel through thermal treatment, and a solid glass or ceramic is produced in this way. As an example, the procedure for the preparation of doped SiO_2 sol–gel glasses is described; similar procedures are applicable to other oxide compounds.

1. Preparation of precursor solutions

The initial raw materials for sol–gel preparations consist of metal alkoxides either in solid or in liquid form (Table 1); an alkoxide is a metalorganic compound, in which a hydrogen atom belonging to the hydroxyl (OH) group on an alcohol is replaced by a metal atom. Since the sol–gel method is a wet chemical method, a proper solvent is needed to convert solid alkoxides, if used, into liquid form. Some alkoxide solutions are commercially available (see Table 1). Doping or activator ions are introduced through either using another alkoxide solution or an aqueous solution of the doping ions. These liquid mixtures of the metal alkoxides are stirred for an extended period, on the order of several hours. To stimulate hydrolysis, a mixture of water to alcohol to HCl with pH ~2–5 is added.

Because the chemical–physical processes involved are similar for all metal alkoxides, we use silicon alkoxides as an illustrative example for the preparation of sol–gel materials, silicate-related materials in this case. For these matrices, TMOS (tetramethoxysilane, $Si(OCH_3)_4$, liquid) or TEOS (tetraethoxysilane, $Si(OC_2H_5)_4$, liquid) are commonly used. They react readily but are not soluble in water; a solvent such as MeOH (methanol) or EtOH (ethanol) is normally used to produce the precursor solution.

2. Hydrolysis [3,4]

A mixture of water, alcohol, and hydrochloric acid (HCl) is prepared so that it has a pH in the range of 2–5; HCl acts as a catalyst in this process. This acidic solution is added slowly (dropwise) into the precursor alkoxide mixture. The reaction of alkoxides with water is called hydrolysis; in hydrolysis, a hydroxyl (OH) group attaches itself to the metal atom by replacing the alkoxide group (OR) in the TMOS or TEOS. A typical reaction goes as:

$$(OR)_3\text{-Si-OR} + H_2O \rightarrow (OR)_3\text{-Si-OH} + ROH$$

Here R stands for the alkyl (alkylic radical), C_nH_{2n+1}; R=CH_3 for TMOS; and R=C_2H_5 for TEOS. Hydrolysis can occur with any one of the (OR) groups of the molecule. If the sol–gels are to be doped, an aqueous solution containing the doping ion/ions is also blended in during the hydrolysis step.

Table 1. Commonly used metal alkoxides and recommended solvents for solids

Name	Chemical Formula	Solvents
aluminum isopropoxide	$Al(OC_3H_7^i)_3$	isopropanol
aluminum *n*-butoxide	$Al(OC_4H_9^n)_3$	*n*-butanol
aluminum *sec*-butoxide	$Al(OC_4H_9^s)_3$	liquid
barium ethoxide	$Ba(OC_2H_5)_2$	ethanol
barium isopropoxide	$Ba(OC_3H_7^i)_3$	isopropanol
bismuth isopropoxide	$Bi(OC_3H_7^i)_3$	isopropanol
calcium ethoxide	$Ca(OC_2H_5)_2$	ethanol
calcium methoxide	$Ca(OCH_3)_2$	methanol
cerium isopropoxide	$Ce(OC_3H_7^i)_3$	isopropanol
copper ethoxide	$Cu(OC_2H_5)_2$	ethanol
dysprosium isopropoxide	$Dy(OC_3H_7^i)_3$	toluene-isopropanol
erbium isopropoxide	$Er(OC_3H_7^i)_3$	toluene-isopropanol
gadolinium isopropoxide	$Gd(OC_3H_7^i)_3$	toluene-isopropanol
gallium isopropoxide	$Ga(OC_3H_7^i)_3$	liquid
germanium methoxide	$Ge(OCH_3)_4$	liquid
germanium ethoxide	$Ge(OC_2H_5)_4$	liquid
germanium isopropoxide	$Ge(OC_3H_7^i)_4$	liquid
lanthanum isopropoxide	$La(OC_3H_7^i)_3$	isopropanol
lead isopropoxide	$Pb(OC_3H_7^i)_2$	isopropanol
magnesium methoxide	$Mg(OCH_3)_2$	methanol
magnesium ethoxide	$Mg(OC_2H_5)_2$	ethanol
manganese isopropoxide	$Mn(OC_3H_7^i)_2$	isopropanol
praseodymium isopropoxide	$Pr(OC_3H_7^i)_3$	toluene-isopropanol
tetraethoxysilane (TEOS)	$Si(OC_2H_5)_4$	liquid
tetramethoxysilane (TMOS)	$Si(OCH_3)_4$	liquid
strontium isopropoxide	$Sr(OC_3H_7^i)_2$	isopropanol
titanium(iv) ethoxide	$Ti(OC_2H_5)_4$	liquid
titanium(iv) methoxide	$Ti(OCH_3)_4$	methanol
titanium(iv) isopropoxide	$Ti(OC_3H_7^i)_4$	liquid
tungsten(vi) ethoxide	$W(OC_2H_5)_6$	ethanol
tungsten(vi) isopropoxide	$W(OC_3H_7^i)_6$	isopropanol
yttrium isopropoxide	$Y(OC_3H_7^i)_3$	isopropanol
zinc isopropoxide	$Zn(OC_3H_7^i)_2$	isopropanol
zirconium *n*-propoxide	$Zr(OC_3H_7^n)_4$	*n*-propanol
zirconium *n*-butoxide	$Zr(OC_4H_9^n)_4$	*n*-butanol

3. Gelation [3,4]

With the proper thermodynamic conditions, gelation occurs. Gelation is a continuous process in which two partially hydrolyzed molecules begin to connect and intertwine with each other with the release (condensation) of water when in a water solution:

$$(OR)_3\text{-Si-OH} + \text{HO-Si-}(OR)_3 \rightarrow (OR)_3\text{-Si-O-Si-}(OR)_3 + H_2O$$

Alcohol, ROH, is released when an alcohol solution is employed:

$$(OR)_3\text{-Si-OR} + \text{HO-Si-}(OR)_3 \rightarrow (OR)_3\text{-Si-O-Si-}(OR)_3 + ROH$$

ROH is an alcohol: $ROH=C_2H_5OH$ for TEOS and CH_3OH for TMOS.

With continuing gelation, larger structures are produced by polymerization; chains of polymers can cross-link to form three-dimensional clusters. Small clusters suspended in the liquid constitute the sol. Through the gelation process, these clusters begin to grow by combining with monomers or other clusters while releasing or condensing water or alcohols. Different metal alkoxides can also coalesce to form "compound" clusters.

Several factors affect the rate of sol and gel formation including the temperature; the relative concentration of the alkoxide precursors, water, and solvent; and the pH of the total admixture. In most cases, sol–gel synthesis is carried out at room temperature, though both the sol and gel formation rates are known to increase with increasing temperature. Because water and alkoxysilanes are immiscible, a common solvent such as alcohol is also normally used as a homogenizing agent.

In our example, silica gels prepared at low pH (<3) and low water content (less than 4 mol% water per mole of alkoxide) produce primarily linear polymers with low cross-link density. Additional cross-links form during gelation and the polymer chains become increasingly entangled. Silica gels prepared under more normal condition (pH ≈5–7) and/or higher water contents produce highly branched clusters which behave as discrete species; these clusters link together during gelation. At still higher pH and excess water content, colloidal silica is formed. Links between clusters keep on multiplying until a giant cluster forms that spans the vessel; during gelation, the viscosity and the elastic modulus of the solution increase rapidly. The final spanning cluster forms a skeletal framework which encloses cells containing the liquid phase (water or alcohol) and defines the gel phase. The solid network retards the escape of the liquid and prevents structural collapse.

4. Aging and drying

Aging leads to changes in the structure and other properties of the gel. That is through further condensation, dissolution, and re-precipitation of monomers or oligomers. Syneresis or spontaneous shrinkage of the network of the gel takes place as bond formation or attraction between clusters induces a contraction of the network and expulsion of liquid from the pores.

Drying by evaporation under normal conditions gives rise to pressure within the pores that causes shrinkage of the gel network. Pressure gradients develop through the volume of the gels, so that the networks are compressed more at the surfaces than in the bulk. If the gradients are too large, this may cause cracking of the sample.

After shrinkage stops, further evaporation drives the meniscus of the liquids into the bulk and the rate of evaporation decreases. The resulting dried gel is called a xerogel. Xerogels are useful in the preparation of dense ceramics and are also interesting because of their high porosity and large surface area; these materials are useful as phosphors, catalytic substrates, filters, and vapor sensors.[5,6]

5. Annealing and porosity control

Additional treatment of the sol–gel is required to produce pore-free ceramic materials; sintering at high temperatures results in densification driven by interfacial energy considerations. By heating, the gel constituents move by viscous flow or diffusion in such a way as to reduce the solid–vapor interfacial areas and hence reduce porosity. Removal of organics takes place by endothermic carbonization near 200°C, followed by exothermic oxidation at temperatures between 300 and 400°C. For the silicate system of our example, the exothermic process is suppressed if the gels are heated under inert conditions, where oxidation is prevented. The temperature interval 400–525°C represents a region where considerable skeletal densification occurs with little associated weight loss. Structural relaxation, a process by which free excess volume is removed by diffusive motion of the network, is the predominant shrinkage mechanism in this temperature interval. The condensation (water or alcohol) and pyrolysis reactions that occur during heating liberate a large volume of gas that can generate high pressures. Because of low permeability of the small pores in the network, this may cause cracking when the samples are heated between room temperature and 400°C. At 800°C, there is partial densification of the sol–gel; by 900°C, the gel is completely densified leaving only a trace of silanols (Si-OH).

6. Techniques for other materials

Techniques to prepare other oxide and nitride compounds are similar to those used for SiO_2.[6] As an example, to make Al_2O_3, $Al(OC_4H_9)_3$ (see Table 1) can be used. Hydrolysis can be conducted at 80°C with 1 mol of aluminum *sec*-butoxide, 100 mol of H_2O, and 0.07 mol of HCl. Alumina sols, then wet gels, and then dried gels can be obtained through the procedures of hydrolysis, gellation, and drying, as described above.[7] Monolithic transparent γ-alumina results when an annealing temperature of 500ºC is used; the alumina becomes α-phase when annealed at 1200°C.[7]

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Section 7: Other Phosphor Data

Section 7

OTHER PHOSPHOR DATA

Information about the following additional phosphors and their properties has been kindly provided (in Lehmann's format) by Edith Bourret-Courchesne, Luis Carlos, Takashi Hase, Dongdong Jia, Weiyi Jia, Willi Lehmann (posthumously), Yoh Mita, Shinji Okamoto, Shozo Oshio, Madis Raukas, Cees Ronda, Yoshitaka Sato, Lauren E. Shea-Rowhler, Masaaki Tamatani, and Hajime Yamamoto.

7.1 Oxides

The following host compounds and activators are included in this subsection:

$Bi_4Ge_3O_{12}$
$CaTiO_3$:Eu^{3+}
$CaTiO_3$:Pr^{3+}
$Gd_3Ga_5O_{12}$:Cr^{3+}
$GdNbO_4$:Bi^{3+}
$K_2La_2Ti_3O_{10}$:Eu
$LuTaO_4$:Nb^{5+}
$SrIn_2O_4$:Pr^{3+},Al^{3+}
SrY_2O_4:Eu^{3+}
$SrTiO_3$:Pr^{3+},Al^{3+}
$SrTiO_3$:Pr^{3+}
$Y(P,V)O_4$:Eu
Y_2O_3:Ce
Y_2O_3:Eu (YOE)
Y_2O_3:Eu^{3+}
Y_2O_3:Tb^{3+}
Y_2O_3:Ce^{3+},Tb^{3+}
Y_2O_2S:Eu
$(Y,Gd)_2O_3$:Eu^{3+}
$YTaO_4$
$YTaO_4$:Nb^{5+}
YVO_4:Dy^{3+}
$ZnGa_2O_4$
$ZnGa_2O_4$:Mn^{2+}
ZnO:Bi^{3+}
ZnO:Zn
ZnO:Ga, Ultrafast
ZnO-CdO:Ga, Ultrafast
Zn_2SiO_4:Mn

$Bi_4Ge_3O_{12}$

Structure: Cubic

Preparation

Grow the crystals of $Bi_4Ge_3O_{12}$ from stoichiometric melts, using Czochralski method.

Use a platinum crucible, atmospheric environment, and radio frequency induction heating.

The growth atmosphere has to be oxygen; otherwise the Pt crucible will be attacked.

Optical Properties

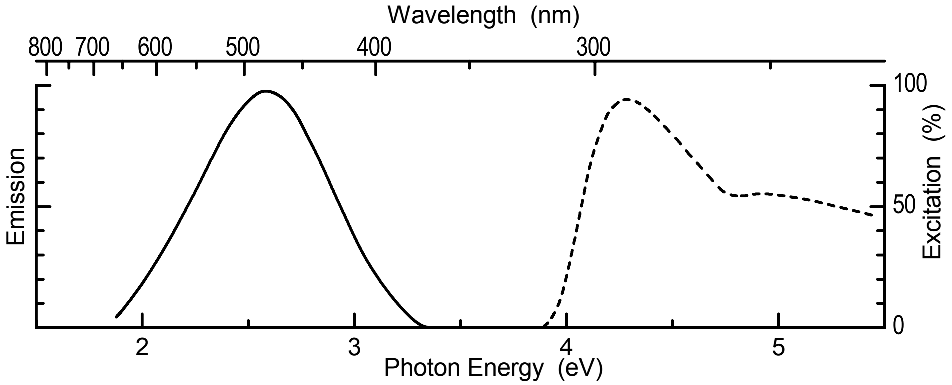
Emission peak: 485 nm

Excitation efficiency by UV: – (3.40 eV), ++ (4.88 eV)

Excitation efficiency by e-beam: +

Decay to 1/e: 0.3×10^{-6} s

Spectra



Remarks

1. This contribution is from Hajime Yamamoto.
2. The melting point of the single crystal is 1044°C.
3. The crystals will only be really colorless when the raw materials Bi_2O_3 and GeO_2 have a high purity.
4. The other growth technique of the horizontal Bridgman–Stockbarger method is now popular to prevent growths forming a core.

References

1. Weber, M.J., and Monchamp, R. R., Luminescence of $Bi_4Ge_3O_{12}$: Spectral and decay properties, *J. Appl. Phys.*, 44, 5495 (1973).
2. Blasse, G., and Grabmaier, B.C., *Luminescent Materials*, p. 179, Springer-Verlag, Heidelberg, (1994).
3. Rossner, W., and Grabmaier, B.C., Phosphors for X-ray detectors in computed tomography, *J. Lumin.*,48, 29 (1991).

$CaTiO_3:Eu^{3+}$

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	10.01
TiO_2	100	7.98
Eu_2O_3	1	0.352
B_2O_3	3	0.209

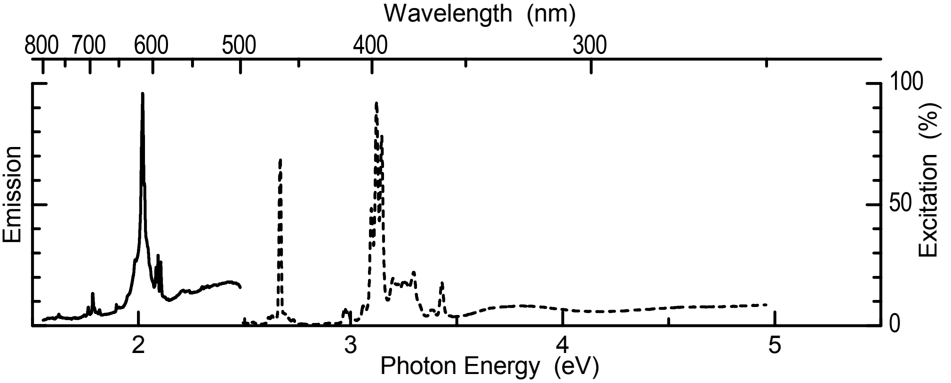
Preparation

Mix by dry grinding or milling.
Press into pellets.
1. Fire in air, 1000°C, 1 hour.
Powderize.
Grind and press into pellets again.
2. Fire in open quartz boats, air, 1300°C, 3 hours.

Optical Properties

Emission color: Red
Emission peak: 612 nm
Excitation efficiency by UV: + (3.40 eV), – (4.88 eV)

Spectra



Remarks

1. This contribution is from Weiyi Jia.
2. This compound is known as calcium titanate.

Reference

1. Rivera, I., Master Degree Thesis, University of Puerto Rico—Mayaguez (2001).

$CaTiO_3:Pr^{3+}$

Structure: Orthorhombic.

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	10.01
TiO_2	100	7.98
$Pr(NO_3)_3.6H_2O$	0.5	0.313
B_2O_3	3	0.209

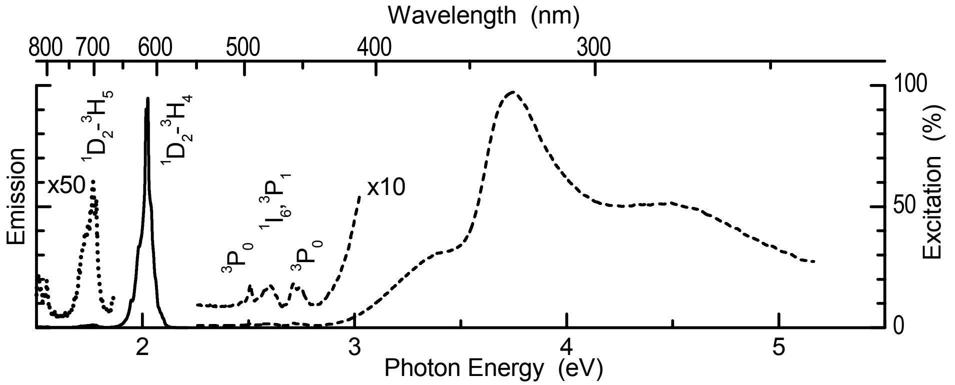
Preparation

Mix by dry grinding or milling.
Press into pellets.
1. Fire in air, 1000°C, 1 hour.
Powderize.
Grind and press into pellets again.
2. Fire in open quartz boats, air, 1300°C, 3 hours.

Optical Properties

Emission color: Red
Emission peak: 612 nm
Excitation efficiency by UV: + (3.40 eV), + (4.88 eV)

Spectra



Remarks

1. This contribution is from Weiyi Jia.
2. This compound is also known as calcium titanate.

References

1. Rivera, I. et al., Proceedings of the Second National Student Conference of NASA URC-SC 2000, Nashville, 180 (2000).
2. Jia, W., Xu, W., Rivera, I. et al., Effects of compositional phase transitions on luminescence of $Sr_{1-x}Ca_xTiO_3:Pr^{3+}$, *Solid State Commun.,* 126, 153 (2003).

$Gd_3Ga_5O_{12}:Cr^{3+}$

Structure: Cubic (garnet)

Composition

Ingredient	Mole %	By weight (g)
Gd_2O_3	37.5	100
Ga_2O_3	62.5	86.2
Cr_2O_3	0.5	0.6

Preparation

Combine the proper amounts of the oxides with some nitric acid to form a precipitate. Stir well and add the NH_4OH solution. Wash with water to remove the NH_4Cl by-product and excess NH_4OH. Dry in air.

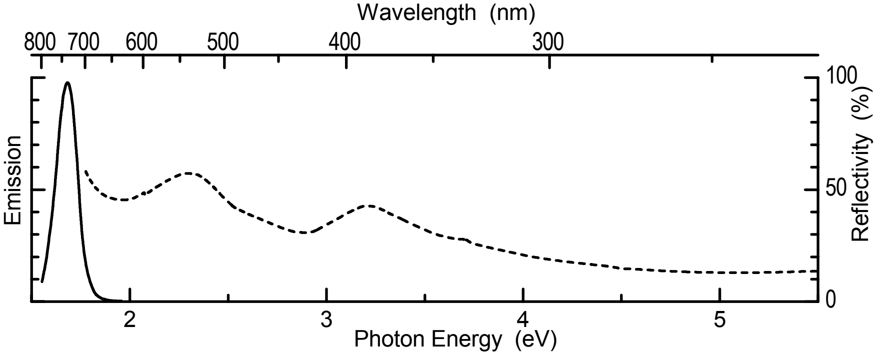
1. Fire in air, 900°C for an hour or more. Ball-mill the powder with a grinding media and a liquid vehicle, such as water or methanol.
2. Fire in flowing O_2, 1500–1550°C, 2 hours.

Co-doping with a small amount of Ce reduces the afterglow.

Optical Properties

Emission color: Red
Emission peak: 730 nm
Excitation efficiency by UV: – (3.40 eV), + (4.88 eV)
Excitation efficiency by e-beam: +
Decay to 1/e: 0.17×10^{-3} sec

Spectra



Remark

This contribution is from Hajime Yamamoto.

References

1. Greskovich, C., and Duclos, S., Ceramic scintillators, *Annu. Rev. Mater. Sci.*, 27, 69 (1997).
2. Rossner, W., Bodinger, H., Leppert, J., and Grabmaier, B.C., The conversion of high energy radiation to visible light by luminescent ceramics, *IEEE Trans. Nucl. Sci.*, 40, 376 (1993).
3. Blasse, G., Grabmaier, B.C., and Ostertag, M., The afterglow mechanism of chromium-doped gadolinium gallium garnet, *J. Alloys Ingredients*, 200, 17 (1993).
4. Petermann, K., and Huber, G., Broad band fluorescence of transition metal doped garnets and tungstates, *J. Lumin.,* 31/32, 71 (1984).

$GdNbO_4$:Bi^{3+}

Structure: Tetragonal (scheelite)

Composition

Ingredient	Mole %	By weight (g)
$Gd_2(C_2O_4)_3 \cdot 10H_2O$	41.51	15.701
Nb_2O_5	56.98	6.646
Bi_2O_3	1.51	0.350

Preparation

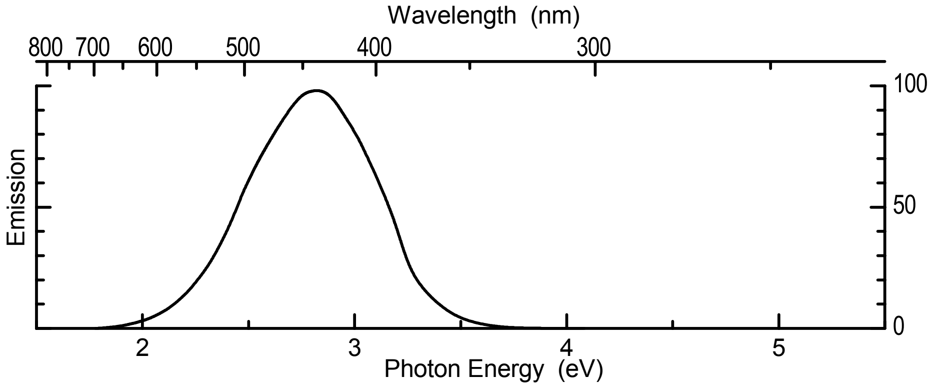
Mix by slurrying in acetone or by dry blende.

1. Fire in covered crucible, air, 600–800°C, 1 hour.
   Dry in air. Powderize when dry.
2. Fire in covered crucible, air, 1350–1650°C, 3 hours.
   Store in a well-sealed container.

Optical Properties

Emission color: Blue
Emission peak: 430 nm
Excitation efficiency by UV: Broad range, suitable for 2537 Å
Excitation efficiency by e-beam: Good

Spectra



Remarks

1. This contribution is from Madis Raukas.
2. This phosphor has a general formula of $Gd_{1-x}Bi_xNbO_4$ and per above ingredients yields a stoichiometry with x = 0.03.

Reference

1. Grisafe, D.A., and Fritsch, C.W., U.S. Pat., 3 767 589 (1973).

$K_2La_2Ti_3O_{10}$:Eu

Structure: Layered perovskite

Composition

Ingredient	Mole %	By weight (g)
K_2CO_3	23.06	6.63
TiO_2	57.72	9.59
La_2O_3	19.03	12.90
Eu_2O_3	0.19	0.141

Preparation

Mix stoichiometric amounts in a paint shaker for 30 minutes with about 20 mol% of excess potassium carbonate to compensate for losses due to volatilization.

Fire in covered alumina crucibles, air, increasing from 700°C to 1100°C, over 3 hours.

Fire in covered alumina crucibles, air, 1100°C, 24 hours.

Fire in covered alumina crucibles, air, 700°C, 2 hours.

Cool to room temperature.

Powderize.

Fire in covered alumina crucibles, air, 1100°C, 24 hours.

Washed in de-ionized water.

Filter, dry at 130°C, and screen through a 325-mesh stainless steel sieve.

Optical Properties

Emission peaks: Lines at 594, 617, and 702 nm.

Excitation efficiency by UV: + (3.40 eV), + (4.88 eV)

Excitation efficiency by e-beam: Characteristic emission at about 1.1 fL level under focused 15 kV/ 8 μA excitation

Remarks

1. This contribution is from Madis Raukas.
2. This phosphor in general formulation of $K_2La_2Ti_3O_{10}$:Eu is another example of materials belonging to intercalation ingredients.
3. The described composition yields a concentration of 0.02 mol Eu per mole of phosphor.
4. Good electroluminescent properties result when this phosphor is intercalated with conductive polymers or metals.

References

1. Qi, R.Y., Karam, R.E., Reddy, V.B., and Cox, J.R., U.S. Pat., 5 567 351 (1996).
2. Qi, R.Y., and Karam, R.E., U.S. Pat., 5 658 495 (1997).
3. Reddy, V.B., Karam, R.E., and Northrop, S.K., U.S. Pat., 5 489 398 (1996).
4. Qi, R.Y., and Karam, R.E., U.S. Pat., 5 531 926 (1996).
5. Reddy, V.B., and Karam, R.E., Northrop, S.K., and Zhang, Y., U.S. Pat., 5 531 928 (1996).

$LuTaO_4:Nb^{5+}$

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
Lu_2O_3	—	—
Ta_2O_5	—	—

Preparation

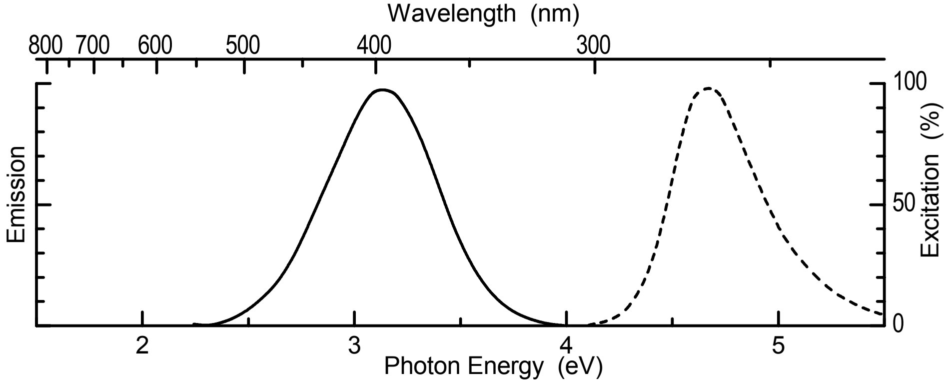
Mix stoichiometric quantities of the Lu_2O_3 and Ta_2O_5.

1. Fire in alumina containers, air, 1200°C, 8–10 hours.
   Ball-mill, using a Freon solvent as grinding medium.
2. Fire in alumina containers, either by itself or in the presence of 50% Li_2SO_4, air, 1250°C, 10–14 hours.
   In the cases where flux is used, leach with water.
   Wash in methanol.
   Dry at 130°C.

Optical Properties

Emission color: Violet
Emission peak: 394 nm
Excitation efficiency by UV: − (3.40 eV), + (4.88 eV)
Excitation efficiency by e-beam: +

Spectra



Remark

This contribution is from Masaaki Tamatani.

Reference

1. Brixner, L.H., and Chen, H.Y., On the structural and luminescent properties of the M' $LnTaO_4$ rare earth tantalates, *J. Electrochem. Soc.*, 130, 2435 (1983).

$SrIn_2O_4:Pr^{3+},Al^{3+}$

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	99.8	147.33
In_2O_3	200 (of In)	277.64
Pr_6O_{11}	0.2 (of Pr)	0.340
$Al(OH)_3$	5	3.900

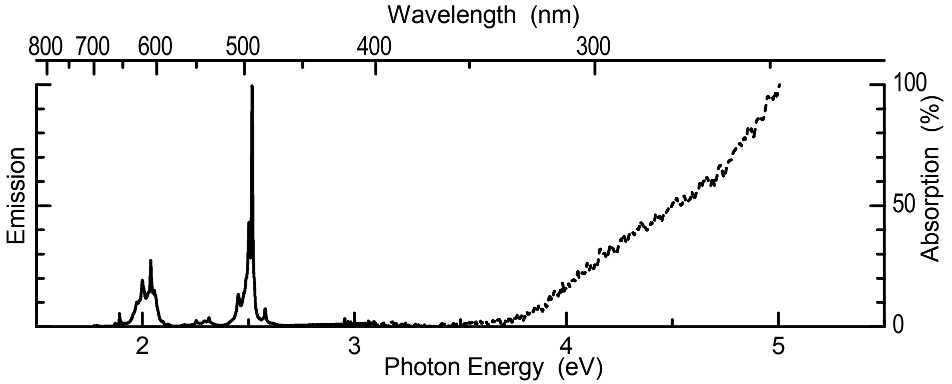
Preparation

Mix by slurrying in ethanol.
Dry in air.
Fire in aluminum crucibles, stagnant air, 1250°C, 3 hours.
Powderize.
Store in air.

Optical Properties

Emission peak: 2.517 eV
Emission width (FWHM): 0.007 eV
Excitation efficiency by UV: – (3.40 eV), ++ (4.88 eV)
Excitation efficiency by e-beam: ++ (10eV–1 keV)
Decay to 1/e: ~10 µsec

Spectra



Remark

This contribution is from Shinji Okamoto.

$SrY_2O_4:Eu^{3+}$

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	100	10
Y_2O_3	100	15.3
Eu_2O_3	1	0.238
H_3BO_3	6	0.251

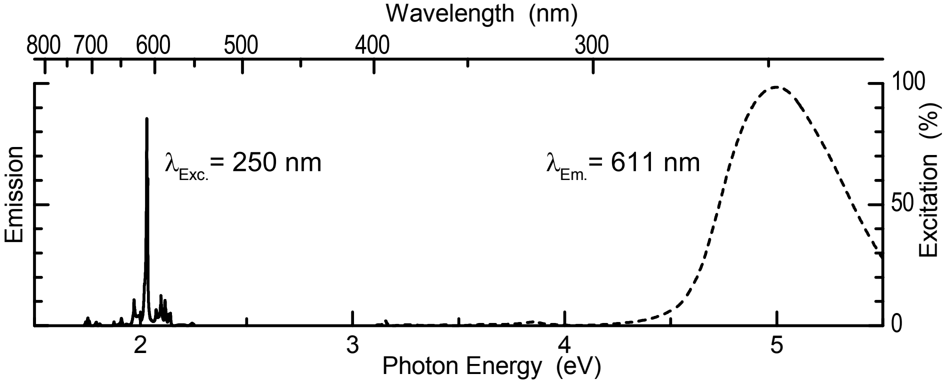
Preparation

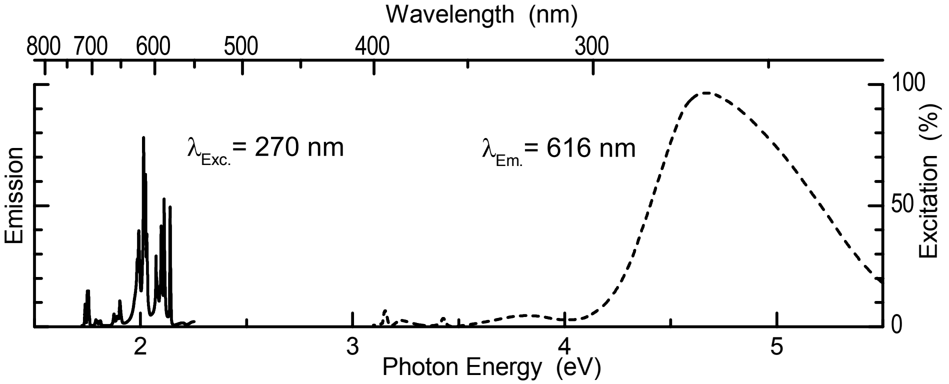
Mix by grinding in a mortar for 30 minutes.
Press into pellets with a hydraulic press machine at 40,000 psi.
1. Fire in air, 1000°C, 2 hours.
Powderize by dry ball-milling.
Press into pellets again.
2. Fire in air, 1350°C, 3 hours.

Optical Properties

Emission color: Red
Emission peak: 611 nm
Excitation efficiency by UV: ++ (2.88 eV), ++ (3.40 eV)

Spectra





Remark

This contribution is from Weiyi Jia.

References

1. Videa, M., Xu, W., Geil, B. et al., High Li^+ self-diffusivity and transport number in novel electrolyte solutions, *J. Electrochem. Soc.,* 148, A1352 (2001).
2. Park, S.J., Park, C.H., Yu, B.Y. et al., Structure and luminescence of SrY_2O_4:Eu, *J. Electrochem. Soc.,* 146, 3903 (1999).

$SrTiO_3:Pr^{3+},Al^{3+}$

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	99.8	147.33
TiO_2	100	79.879
Pr_6O_{11}	0.2 (of Pr)	0.340
$Al(OH)_3$	5–30	3.900–23.401

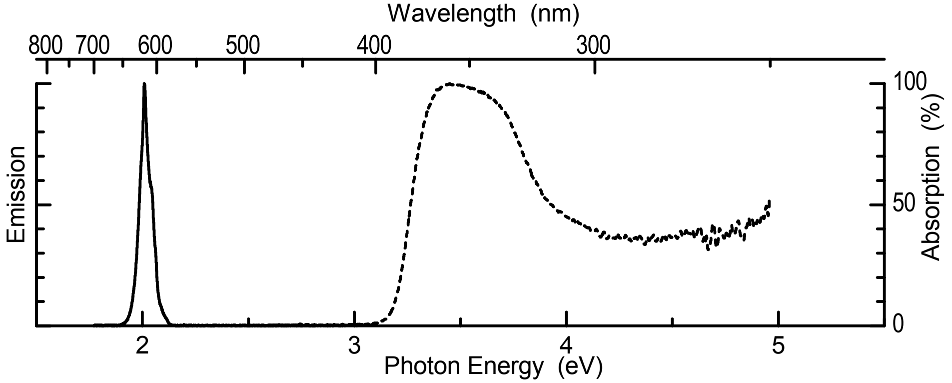
Preparation

Mix by slurrying in ethanol.
Dry in air.
Fire in aluminum crucibles, stagnant air, 1300°C, 2 hours.
Powderize.

Optical Properties

Emission peak: 2.009 eV
Emission width (FWHM): 0.064 eV
Excitation efficiency by UV: – (3.40 eV), ++ (4.88 eV)
Excitation efficiency by e-beam: ++ (10 eV–1 keV)
Decay to 1/e: ~100 µsec

Spectra



Remark

This contribution is from Shinji Okamoto.

References

1. Itoh, S., Toki, H., Tamura, K., and Kataoka, F., A new red-emitting phosphor, $SrTiO_3:Pr^{3+}$, for low-voltage electron excitation, *Jpn. J. Appl. Phys.*, 38, 6387 (1999).
2. Okamoto, S., and Yamamoto, H., Characteristic enhancement of emission from $SrTiO_3:Pr^{3+}$ by addition of group-IIIb ions, *Appl. Phys. Lett.*, 78, 655, (2001).

$SrTiO_3:Pr^{3+}$

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	100	10.00
TiO_2	100	5.41
$Pr(NO_3)_3.6H_2O$	0.5	0.212
B_2O_3	3	0.142

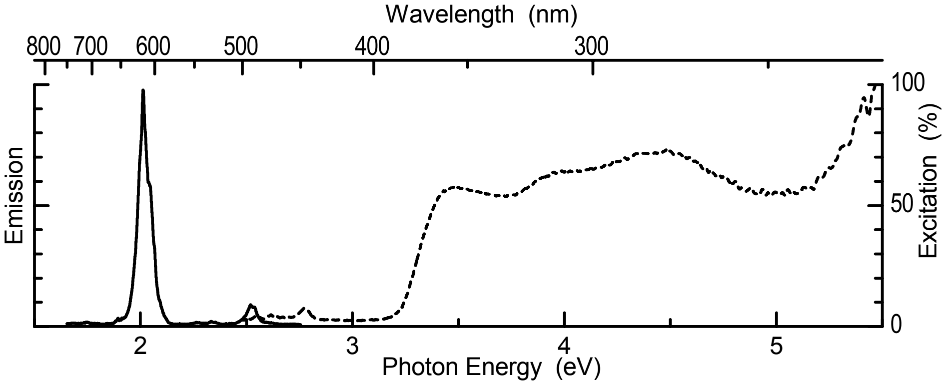
Preparation

Mix by dry grinding or milling.
Press into pellets.
1. Fire in air, 1000°C, 1 hour.
Powderize.
Grind and press into pellets again.
2. Fire in open quartz boats, air, 1300°C, 3 hours.

Optical Properties

Emission color: Red
Emission peak: 615 nm
Excitation efficiency by UV: ++ (3.40 eV), ++ (4.88 eV)

Spectra



Remarks

1. This contribution is from Weiyi Jia.
2. This compound is also known as strontium titanate.

Reference

1. Jia, W., Xu, W., Rivera, I. et al., Effects of compositional phase transitions on luminescence of $Sr_{1-x}Ca_xTiO_3:Pr^{3+}$, *Solid State Commun.,* 126, 153 (2003).

$Y(P,V)O_4:Eu$

Structure: Xenotime

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	48	104.8
Eu_2O_3	2	7.0
NH_4VO_3	35	40.9
$(NH_4)_2HPO_4$	65	85.8

Preparation

Dry-blend all ingredients and place in a capped quartz or alumina crucible.

1. Fire in 700°C, for 2 hours. Cool and lightly mortar to break aggregates.
2. Fire in 1150°C, for 2 hours. Cool and break up aggregates.
3. Fire in 1150°C, for an additional 2 hours.

Cool and slurry the powder in 2 wt% $(NH4)_2CO_3$ solution. Decant with water until neutral. Dry in air, 200°C.

Optical Properties

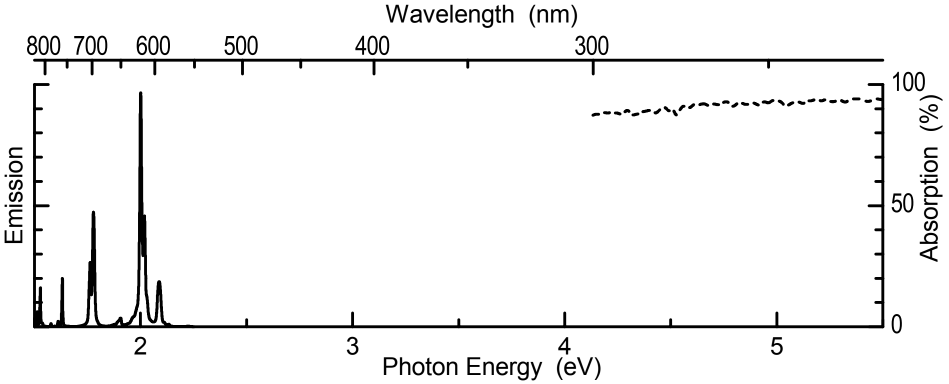
Emission color: Red

Emission peak: 619 nm

Excitation efficiency by UV: ++ (3.40 eV), + (4.88 eV), ++ (8.40 eV)

Excitation efficiency by e-beam: +

Spectra



Remark

This contribution is from Takashi Hase.

References

1. Wanmaker, W.L., and Verlijsdok, J.G., U.S. Pat., 3 417 027 (1968).
2. Japanese Patent Disclosure (Kokai), 50 67782 (1975); 51 114388 (1976).
3. Wanmaker, W.L., Bril, A., Vrugt, J.W.T., and Broos, J., *Proc. Int. Conf. Luminescence.*, Budapest, 9–16 (1966).
4. Wanmaker, W.L., Verlijsdok, J.G., and Bres, G.C.M., U.S. Pat., 3 647 708 (1972).

Y_2O_3:Ce

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
$Si(OEt)_4$	100	—
$Y(OC_3H_7i)_3$	7	—
$CeCl_3$ (aq.)	1	—
ethanol, water and HCl (pH = 7) 1:2:3		certain amount

Preparation

Stir ingredients.

After 20 minutes, add the $CeCl_3$ solution dropwise, into a small container such as cuvettes. Cover the cuvette with paraffin film with a pin hole in the center as a outlet of vapor.

Place the wet gel in an oven at 40°C for one or two weeks to obtain transparent dry gels.

Annealing in N_2 + 5% H_2 gas flow at 500–900°C to remove residual water, ethanol, or other organic groups created and entrapped in the gels during gellation process.

Optical Properties

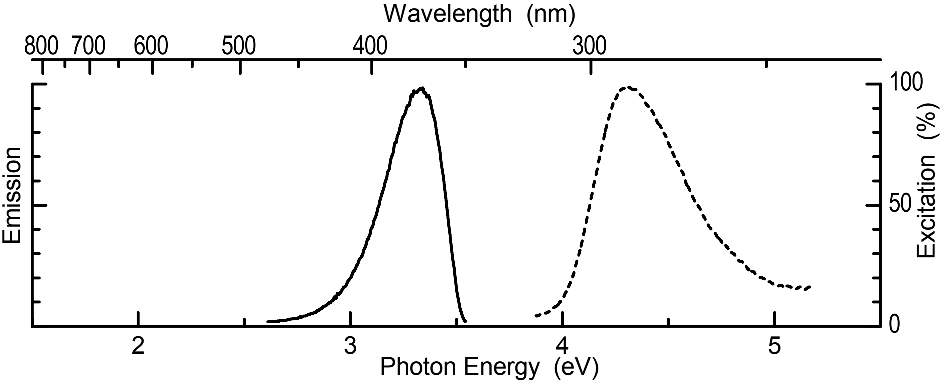
Emission color: Violet (Ce^{3+})

Emission peak: 375 nm

Emission width (FWHM): 30 nm

Excitation efficiency by UV: ++ (3.40 eV), ++ (4.88 eV)

Spectra



Remark

This contribution is from Weiyi Jia.

Nanoclusters embedded in SiO_2 glasses

Reference

1. Jia, W. et al., Photoluminescence of Y_2O_3:Ce^{3+},Tb^{3+} nanoclusters embedded in SiO_2 sol-gel glasses, *Mater. Sci. Eng. C,* 572, 55 (2001).

Y_2O_3:Eu (YOE)

Structure: Cubic

Composition

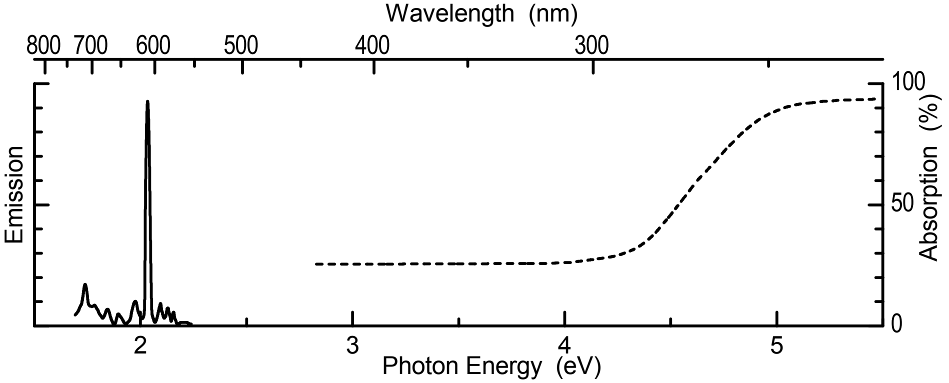
Ingredient	Mole %	By weight (g)
Y_2O_3	94 (Y)	108
Eu_2O_3	6 (Eu)	10.5
CaF_2	2.5	1.95

Preparation

Mix by slurrying in water or methanol and dry in air.
Powderize.
Firing should occur in air, at a temperature of about 1300°C for at least 1 hour.

This phosphor is used in fluorescent lamps and also in projection television tubes. It can also be used in plasma display panels. It can be sensitized for excitation at 365 nm using Bi, however, with reduced efficiency at 254 nm.

Spectra



Remark

This contribution is from Cees Ronda.

$Y_2O_3:Eu^{3+}$

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
$Si(OEt)_4$	92.6	100
$Y(OC_3H_7i)_3$	6.5	8.95
$EuCl_3{\cdot}6H_2O$	0.9	1.58

ethanol, water, and HCl (pH = 2.5) 1:2:3

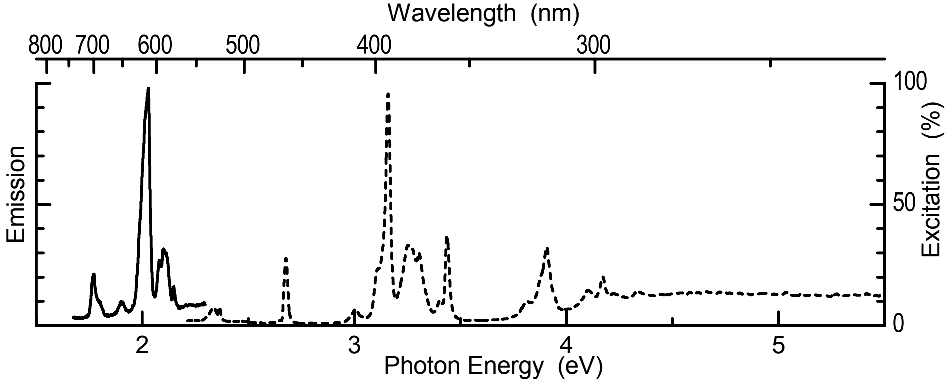
Preparation

Dissolve europium chloride in 2–3 g of distilled water. Blend it into the ethanol/water/HCl mix. Mix the Si and Y solutions and stir for 20 minutes with a magnetic stirring device. Put the $EuCl_3$/water/ethanol/HCl solution into the Si/Y mixture dropwise while stirring. Pour the resulting mixture into a small container with a cover, allowing slow evaporating of the excess or resulted water and ethanol. A wet gel will result. The wet gel is dried at low temperatures (45°C) for one or two weeks in an oven, to obtain transparent dry gels. Anneal the dry gel in air at 500–1000°C to remove residual water, ethanol, or other organic radicals.

Optical Properties

Emission color: Red
Emission peak: 612 nm
Emission width (FWHM): 30 nm
Excitation efficiency by UV: Weakly excited at 3.87 eV
Excitation efficiency by e-beam: Weakly excited by cathode rays

Spectra



Remark

This contribution is from Weiyi Jia.
Y_2O_3 nanoclusters embedded in SiO_2 glasses.

References

1. Jia, W., Liu, H., Feofilov, S.P., Meltzer, R., and Jiao, J., Spectroscopic study of Eu^{3+}doped and Eu^{3+},Y^{3+} codoped SiO_2 sol-gel glasses, *J. Alloys Ingredients*, 11, 311 (2000).
2. Jia, W. et al., Photoluminescence of Eu^{3+}:Y_2O_3 nanoclusters embedded in SiO_2 glass, *Mater. Res. Soc. Symp. Proc.*, 271, 519 (1998).

Y_2O_3:Tb^{3+}

Composition

Ingredient	Mole %	By weight (g)
$Si(OEt)_4$	92.6	100
$Y(OC_3H_7i)_3$	6.5	8.95
$TbCl_3.6H_2O$	0.9	1.8
ethanol, water, and HCl (pH = 7) 1:2:3		certain amount

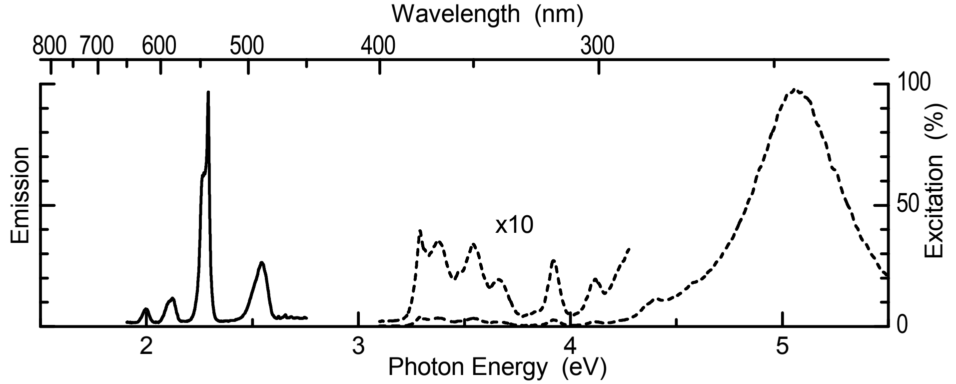
Preparation

Dissolve terbium chloride in 2–3 g of distilled water. Blend it into the ethanol/water/HCl mix. Mix the Si and Y solutions and stir for 20 minutes with a magnetic stirring device. Put the $TbCl_3$/water/ethanol/HCl solution into the Si/Y mixture dropwise while stirring. Pour the resulting mixture into a small container with a cover, allowing slow evaporating of the excess or resulted water and ethanol. A wet gel will result. The wet gel is dried at low temperatures (45°C) for one or two weeks in an oven, to obtain transparent dry gels. Anneal the dry gel in air at 500–1000°C to remove residual water, ethanol, or other organic radicals.

Optical Properties

Emission color: Green
Emission peak: 543 nm; Minor peaks at 495, 585, and 621 nm
Emission width (FWHM): 30 nm
Excitation efficiency by UV: ++ (3.40 eV), ++ (4.88 eV)

Spectra



Remark

This contribution is from Weiyi Jia.
Nanoclusters embedded in SiO_2 glasses.

Reference

1. Jia, W. et al., Photoluminescence of $Y_2O_3:Ce^{3+,}Tb^{3+}$ nanoclusters embedded in SiO_2 sol-gel glasses, *Mater. Sci. Eng. C,* 572, 55 (2001).

$Y_2O_3:Ce^{3+},Tb^{3+}$

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
$Si(OEt)_4$	91.8	100
$Y(OC_3H_7i)_3$	6.4	8.95
$TbCl_3$•$6H_2O$	0.9	1.61
$CeCl_3$•$6H_2O$	0.9	1.53

ethanol, water, and HCl (pH = 7) 1:2:3

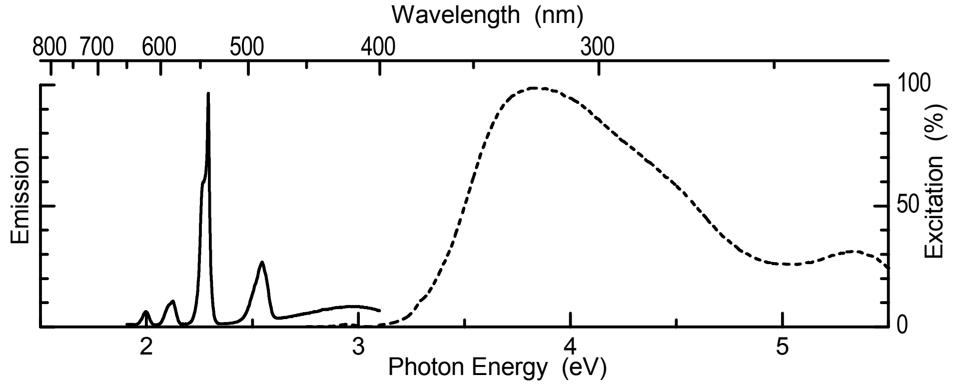
Preparation

Dissolve cerium and terbium chlorides in 2–3 g of distilled water. Blend it into the ethanol/water/HCl mix. Mix the Si and Y solutions and stir for 20 minutes with a magnetic stirring device. Put the Ce-$TbCl_3$/water/ethanol/HCl solution into the Si/Y mixture dropwise while stirring. Pour the resulting mixture into a small container with a cover, allowing slow evaporating of the excess or resulting water and ethanol. A wet gel will result. The wet gel is dried at low temperatures (45°C) for one or two weeks in an oven, to obtain transparent dry gels. Anneal the dry gel in air at 500–1000°C to remove residual water, ethanol, or other organic radicals.

Optical Properties

Emission color: Violet (Ce^{3+})
Emission peak: 543 nm
Emission width (FWHM): 30 nm
Excitation efficiency by UV: ++ (3.87 eV), ++ (5.39 eV)
Excitation efficiency by e-beam: Weakly excited by cathode rays

Spectra



Remark

This contribution is from Weiyi Jia.
Nanoclusters embedded in SiO_2 glasses.

Reference

1. Jia, W. et al., Photoluminescence of Y_2O_3:Ce^{3+},Tb^{3+} nanoclusters embedded in SiO_2 sol-gel glasses, *Mater. Sci. Eng. C*, 572, 55 (2001).

Y_2O_2S:Eu

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	94 (Y)	110
Eu_2O_3	3 (Eu)	5.3
Na_2CO_3	100	53
S	300	96

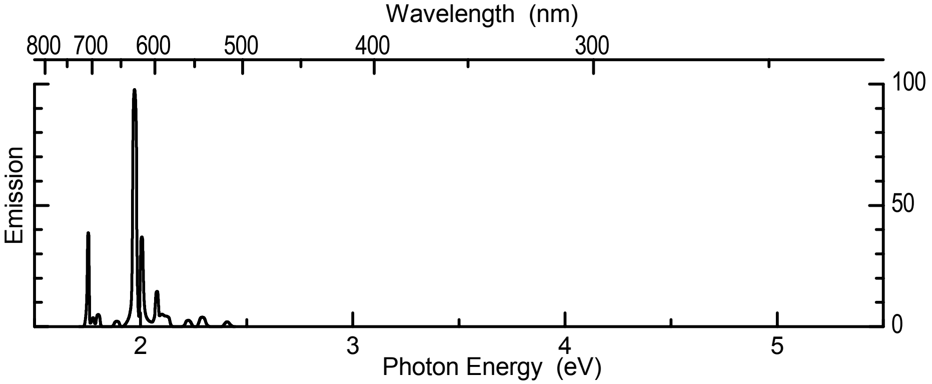
Preparation

Mix the rare-earth oxides by slurrying in water or methanol and dry in air. After drying, the mixture should be powdered in mortar. Subsequently, mix the rare earth mixture with Na_2CO_3 and S by dry mixing.

Firing should occur in air in a vessel with a well-closing lid, at a temperature of about 1100°C for a few hours.

After cooling down, the reaction product has to be washed a few times with water to remove residual flux.

Spectra



Spectrum from the *Phosphor Handbook*, CRC Press, Boca Raton, FL, Fig. 38, p. 478 (1998).

Remark

This contribution is from Cees Ronda.

$(Y,Gd)_2O_3:Eu^{3+}$

Structure: Cubic

Preparation

Oxidize the co-precipitated oxalate at about 800°C.

Preferably, if either the sintering or hot-pressing processes are subsequently used to produce the ceramic scintillator, the powder should be de-agglomerated.

Die or isostatically press the powder into powder compacts, using pressures up to about 300 MPa.

The $Y_{1.34}Gd_{0.60}Eu_{0.06}O_3$ compacts can be densified into transparent ceramics by either vacuum sintering at 1800°C or hydrogen-gas sintering at 1800–1900°C.

Optical Properties

Emission color: Red

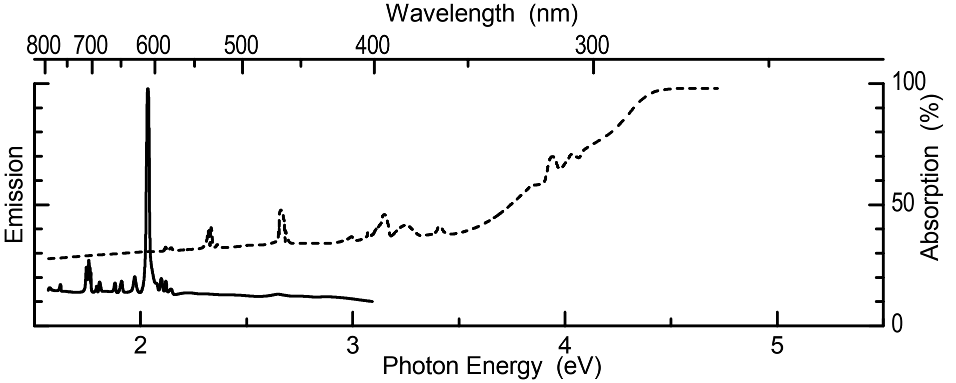
Emission peak: 610 nm

Excitation efficiency by UV: − (3.40 eV), ++ (4.88 eV)

Excitation efficiency by e-beam: +

Decay to 1/e: 1×10^{-3} sec

Spectra



Remarks

1. This contribution is from Hajime Yamamoto.
2. Co-doping of a small amount of Pr reduces the afterglow.
3. The sintered samples can be annealed in an oxygen-rich atmosphere to reduce the concentration of point defect/impurity-charge states in the host lattice.

Reference

1. Greskovich, C., and Duclos, S., Ceramic scintillators*, Annu. Rev. Mater. Sci.*, 27, 69 (1997).

YTaO$_4$

Structure: Monoclinic

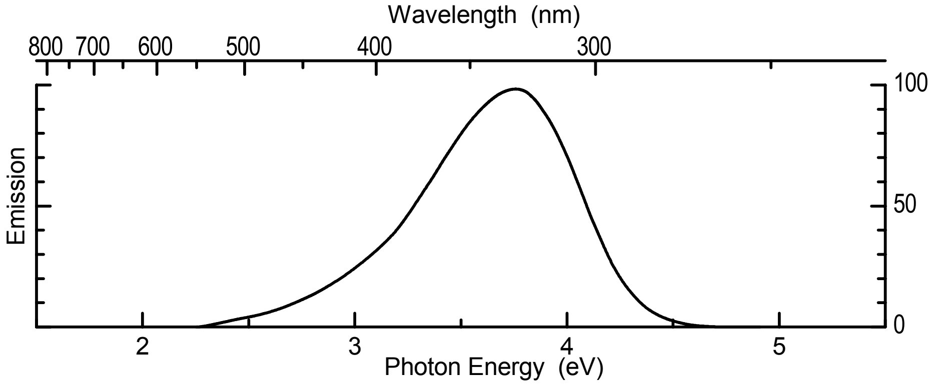
Preparation

Stoichiometric quantities are mixed Y_2O_3, Ta_2O_5.
Fire in capped alumina tubes, air, 1200°C, 8–10 hours.
Powderize with a Freon solvent as the grinding medium.
Fire in capped alumina tubes, either by itself or in the presence of 50% Li_2SO_4, 1250°C, 10–14 hours.
In the cases where a flux is used, leach with water and follow by methanol rinsing.
Dry in air, 130°C.

Optical Properties

Emission color: UV
Emission peak: 330 nm
Excitation efficiency by UV: – (3.40 eV), – (4.88 eV)
Excitation efficiency by e-beam: +

Spectra



Remarks

1. This contribution is from Masaaki Tamatani.
2. The use of a flux in the synthesis of M'-$YTaO_4$ not only allows the growth of 4–12 µm single crystals but also assists greatly in the formation of the compound (see Ref. 2).

References

1. Brixner, L.H., and Chen, H.Y, On the structural and luminescent properties of the M' $LnTaO_4$ rare earth tantalates, *J. Electrochem. Soc.*, 130, 2435 (1983).
2. Issler, S.L., and Torardi, C.C., Solid state chemistry and luminescence of X-ray phosphors, *J. Alloys Ingredients*, 229, 54 (1995).

$YTaO_4:Nb^{5+}$

Structure: Monoclinic

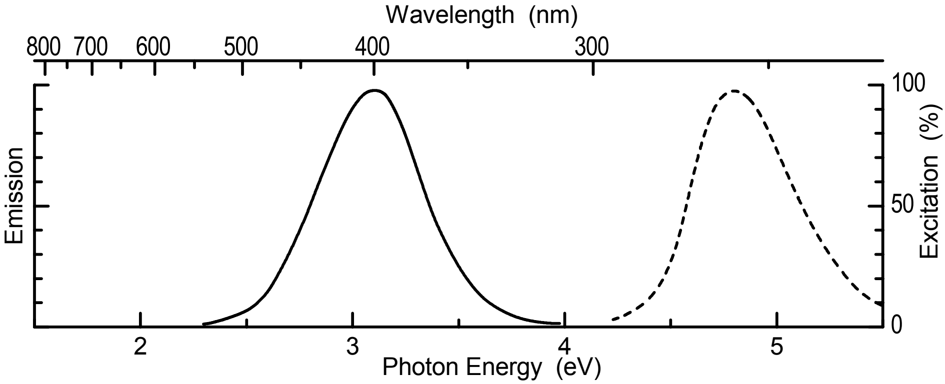
Preparation

Stoichiometric quantities are mixed Y_2O_3, Ta_2O_5, Nb_2O_5.
Fire in capped alumina tubes, air, 1200°C, 8–10 hours.
Powderize with a Freon solvent as the grinding medium.
Fire in capped alumina tubes, either by itself or in the presence of 50% Li_2SO_4, 1250°C, 10–14 hours.
In the cases where a flux is used, leach with water and follow by methanol rinsing.
Dry in air, 130°C.

Optical Properties

Emission color: Blue
Emission peak: 410 nm (x-ray excitation 2% Nb)
Excitation efficiency by UV: – (3.40 eV), ++ (4.88 eV)
Excitation efficiency by e-beam: +

Spectra



Remarks

This contribution is from Masaaki Tamatani.

Reference

1. Brixner, L.H., and Chen, H.Y., On the structural and luminescent properties of the M' $LnTaO_4$ rare earth tantalates, *J. Electrochem. Soc.*, 130, 2435 (1983).

$YVO_4:Dy^{3+}$

Structure: Tetragonal (zircon)

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	17.15	70.0
NH_4VO_3	82.80	175.0
Dy_2O_3	0.05	0.321

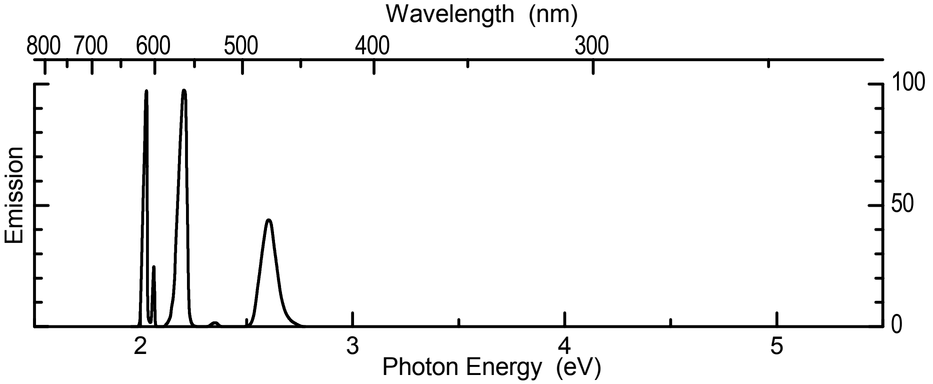
Preparation

Blend the materials thoroughly and fire in an open quartz crucible for 2 hours at 1700°C. Cool slightly and wash with a hot solution of 15 % NaOH. Rinse with deionized water until neutral. Dry in air and powderize.

Optical Properties

Emission color: Yellowish-green
Emission peak: Two strong dysprosium peaks at 480 and 570 nm
Excitation efficiency by UV: Suitable for 2537 and 3650 Å

Spectra



Remarks

1. This contribution is from Madis Raukas.
2. This recipe yields a phosphor containing 0.28 mol% of Dy^{3+}, which is optimum for excitation with mercury discharge lamps.
3. Other rare-earth elements (Pr, Sm, Eu,, Er, Tm, and alike) can be added up to a half of the activator content. By including such elements or combinations thereof, the emission characteristics can be adjusted.

References

1. Faria, S., and Palumbo, D.T., U.S. Pat., 3 555 337 (1968).
2. Ballman, A.A., Linares, R.C., and van Uitert, L.G.G., U.S. Pat. 3 152 085 (1964).
3. Thompson, G.L., U.S. Pat., 3 322 682 (1967).

$ZnGa_2O_4$

Structure: Cubic (spinel)

Composition

Ingredient	Mole %	By weight (g)
ZnO	50	8.14
Ga_2O_3	50	18.7
Li_3PO_4 (Flux)	—	—

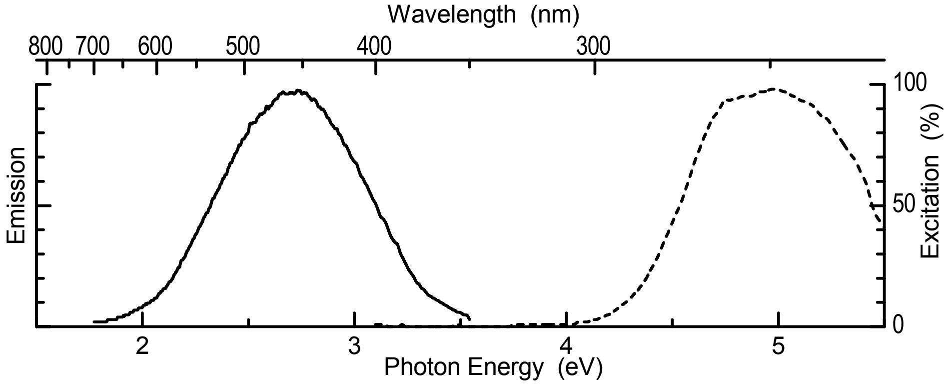
Preparation

Mix by slurrying in water or ethanol.
Dry in air. Powderize when dry.
Fire in capped quartz crucibles, stagnant air, 1200°C, 3 hours.
Powderize.
Wash with diluted nitric acid to remove excess flux.
Re-fire in $H_2 + N_2$ atmosphere, 1100°C, 1 hour.
Powderize.

Optical Properties

Emission color: Blue
Emission peak: 460 nm
Emission width (FWHM): 137 nm
Absorption edge: 270 nm (4.4 eV)
Excitation efficiency by e-beam: 0.7 lm/W or higher at 30 V DC

Spectra



Remark
This contribution is from Sato Yoshitaka.

Reference

1. Itoh, S. et al., The $ZnGa_2O_4$ phosphor for low-voltage blue cathodoluminescence, *J. Electrochem. Soc.*, 138, 1509 (1991).

$ZnGa_2O_4:Mn^{2+}$

Structure: Cubic (spinel)

Composition

Ingredient	Mole %	By weight (g)
ZnO	48	8.14
Ga_2O_3	50	18.7
$MnSO_4$	2	0.15
Li_3PO_4 (Flux)		

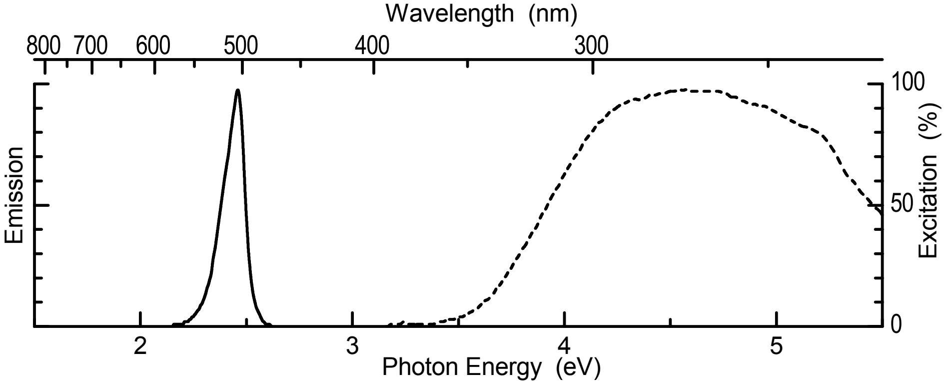
Preparation

Mix by slurrying in water or ethanol
Dry in air. Powderize when dry.
Fire in capped quartz crucibles, stagnant air, 1200°C, 3 hours.
Powderize.
Wash with de-ionized water.
Add solution of Mn^{2+} ion, mix, and vaporize moisture by warming.
Re-fire in $H_2 + N_2$ atmosphere, 1100°C, 1 hour.
Powderize.

Optical Properties

Emission color: Green
Emission peak: 505 nm
Emission width (FWHM): 25 nm
Absorption edge: 270 nm (4.4 eV)
Excitation efficiency by e-beam: 1.0 lm/W or higher at 30 V DC

Spectra



Remark

This contribution is from Yoshitaka Sato.

References

1. Toki, H. et al., *Proceedings of Japan Display'92*, (1992).
2. Toki, H., Kataoka, Y., Morimoto, K., and Itoh, S., $ZnGa_2O_4$:Mn green cathodoluminescent phosphors for VFDs, *Tech. Digest Jpn. Display,* 421 (1992).

ZnO:Bi^{3+}

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnO	97.6	10
Bi_2O_3	2.4	1.43

Preparation

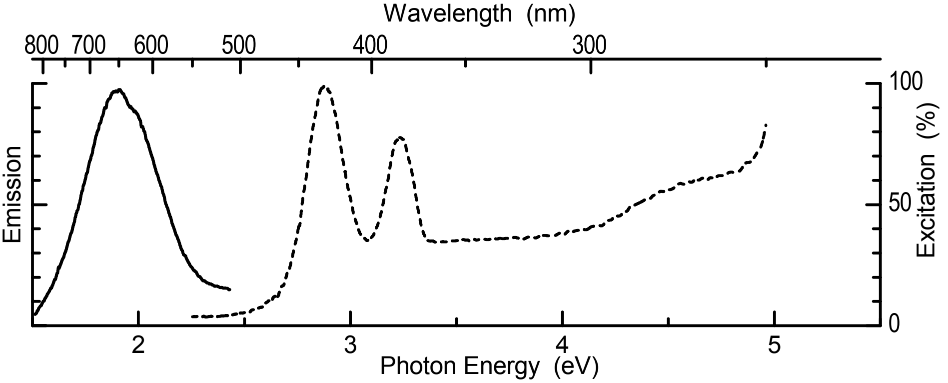
Mix by dry grinding.
1. Fire in air, 800ºC, 1 hour.
2. Fire in capped quartz tubes, stagnant air, 1120ºC, 2 hours.

Store in well-sealed container.

Optical Properties

Emission color: Red
Emission peak: 645 nm
Emission width (FWHM): 3540 cm^{-1}
Excitation efficiency by UV: ++ (3.26 eV), ++ (4.88 eV)

Spectra



Remark

This contribution is from Weiyi Jia.

Reference

1. Mosquera Vargas, E., Master Degree Thesis, University of Puerto Rico—Mayaguez (2003).

ZnO:Zn

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnO	100	158

Preparation

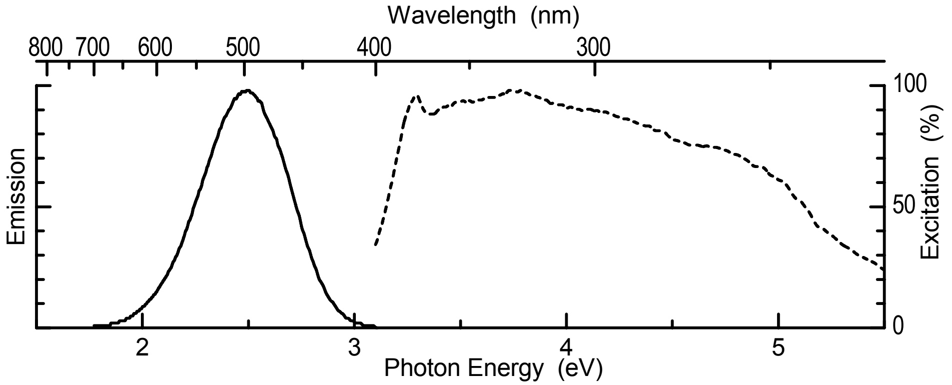
Fire in capped quartz crucibles in reduced atmosphere at 1000°C, 1 hour. Powderize.

.

Optical Properties

Emission color: Green
Emission peak: 505 nm
Emission width (FWHM): 0.4 eV
Absorption edge: 388 nm (300 K)
Excitation efficiency by e-beam: 16 lm/W or higher

Spectra



Remark

This contribution is from Yoshitaka Sato.

ZnO:Ga, Ultrafast

(Type WL-1201)

Composition

Ingredient	Mole %	By weight
ZnO	100	81 g
Ga_2O_3	0.3 (of Ga)	0.280 g
$ZnCl_2$	about 1 (not critical)	1.7 g

Preparation

Mix ZnO and Ga_2O_3 porcelain dish, add alcohol to make a uniform slurry. Dissolve the $ZnCl_2$ in a little water, add solution to above mix, stir to uniformity, and dry at room temperature or at moderate heat (e.g., over night). Then add a little water to make the raw mix slightly moist.

1. Fire in loosely capped quartz glass tubes (about half full, not more), stagnant air, 1100ºC, 1 hour. When cool, inspect under UV lamp. Material should be completely dead. Remove suspicious parts and powderize the rest..
2. Fire in open quartz boats, slowly flowing H_2, 800ºC, one-half hour. Cool while in H_2 (Important!). Inspect again under UV lamp. The bulk of the material should show deep violet luminescence (just at the limit of visibility). Remove all parts that look different. In case the material does not show the violet luminescence at all, repeat the last firing step at about 100ºC higher temperature.

Properties

Body color: Gray
Particles: About in the 5–10 μm size range
Emission: Narrow band in the near-UV with a tail extending into the visible violet
Peak about 3.195 eV (=388 nm)
Excitation by UV: By all UV shorter than about 380 nm
Excitation by e-beam: Energy—$\eta \approx$ 1–1.2%, decay < 1 nsec

Remarks

1. The $ZnCl_2$ in the above recipe can be replaced by about 1.1 g of NH_4Cl, or by about 1 ccm of concentrated HCl acid.
2. This phosphor is sensitive to traces of sulfur. Avoid all sulfur like the plague.
3. This phosphor is in a frozen-in semistable state. Do not heat higher than about 300ºC except in pure hydrogen.

References

1. Lehmann, W., Edge emission of n-type conducting ZnO and CdS, *Solid State Electron.,* 9, 1107 (1966) and U.S. Patent 3583929 (issued June 1971).
2. Luckey, D., A fast inorganic scintillator, *Nucl. Instr. Meth,* 62, 119 (1968).
3. Derenzo, S.E., Weber, M.J., Klintenberg, M.K., Temperature dependence of the fast, near-band-edge scintillation from CuI, HgI_2, PbI_2, ZnO:Ga and CdS:In, *Nucl. Instr. Meth.* A 486, 214 (2002).
4. Lehmann, W., Zinc oxide and zinc-cadmium oxide phosphors, *J. Electrochem. Soc.,* 115, 538 (1968).

The above recipe was provided by W. Lehmann during a visit to the Lawrence Livermore National Laboratory in 1987.

ZnO-CdO:Ga, Ultrafast

Composition

Ingredient	Mole %	By weight
ZnO	90	73 g
CdO	10	11.2 g
Ga_2O_3	0.3 (of Ga)	0.280 g
$ZnCl_2$	about 1 (not critical)	1.7 g

Preparation

Mix ZnO + CdO + Ga_2O_3 in a porcelain dish, add alcohol to make a uniform slurry. Dissolve the $ZnCl_2$ in a little water, add solution to above mix, stir to uniformity, and dry at room temperature or at moderate heat (e.g., over night). Then add a little water to make the raw mix slightly moist.

1. Fire in loosely capped quartz glass tubes (about half full, not more), stagnant air, 1100ºC, 1 hour. When cool, inspect under UV lamp. Material should be completely dead. Remove suspicious parts and powderize the rest..
2. Fire in open quartz boats, slowly flowing H_2, 800ºC, one-half hour. Cool while in H_2 (Important!). Inspect again under UV lamp. The bulk of the material should be violet luminescent (if it does not, repeat the last firing step at about 100ºC higher temperature). (just at the limit of visibility). Remove any parts (if preaent) that look different.

Properties

Body color: Yellowish-gray
Particles: About in the 5–10 µm size range
Emission: Narrow band, peak about 413 nm. Color: violet
Excitation by UV: By all UV shorter than about 400 nm
Excitation by e-beam: Energy—$\eta \approx$ 1–1.2%, decay < 1 nsec

Remarks

4. 10% CdO is the limit of solid solubility. Do not add more.
5. The CdO in the above recipe can be replaced by 17.2 g $CdCO_3$.
6. The $ZnCl_2$ in the above recipe can be replaced by about 1.1 g of NH_4Cl, or by about 1 ccm of concentrated HCl acid.
7. This phosphor is sensitive to traces of sulfur. Avoid all sulfur like the plague.
8. This phosphor is in a frozen-in semistable state. Do not heat higher than about 300ºC except in pure hydrogen.

References

5. Lehmann, W., Edge emission of n-type conducting ZnO and CdS, *Solid State Electron.,* 9, 1107 (1966) and U.S. Patent 3583929 (issued June 1971).
6. Luckey, D., A fast inorganic scintillator, *Nucl. Instr. Meth,* 62, 119 (1968).
7. Lehmann, W., Zinc oxide and zinc-cadmium oxide phosphors, *J. Electrochem. Soc.,* 115, 538 (1968).

The above recipe was provided by W. Lehmann during a visit to the Lawrence Livermore National Laboratory in 1987.

Zn_2SiO_4:Mn

Composition

Ingredient	Mole %	By weight (g)
ZnO	194	158
SiO_2	110	66
$MnCO_3$	6	6.9

Preparation

Mix by ball-milling or magnetic stirring in water or an alcohol and dry in air. Powderize.

Firing should occur in reducing atmosphere at a temperature of about 1150–1250°C for at least an hour.

The efficiency of this material (e-beam and (V)UV excitation) depends on the Mn^{2+} concentration. Higher Mn^{2+} concentrations adjust to a shorter decay time. The quantum efficiency drops less fast than the emission decay time. The emission band shifts to lower energy with increasing Mn^{2+} concentration, due to magnetic interactions lifting the spin selection rule.

This phosphor is used in plasma display panels and fluorescent lamps. It has been used in monochromic computer monitor tubes and projection television tubes (mixed with other green phosphors).

Remark

This contribution is from Cees Ronda.

Reference

1. Ronda, C., and Amrein, T., Evidence for exchange induced luminescence in Zn_2SiO_4:Mn, *J. Lumin.* 69, 245 (1996).

7.2 Silicates

The following host compounds and activators are included in this subsection:

$Ba_2MgSi_2O_7:Eu^{2+}$
$CaMgSi_2O_6:Eu^{2+}$
$Ca_2MgSi_2O_7:Eu^{2+},Mn^{2+}$
$Ca_3MgSi_2O_8:Eu^{2+}$
$Ca_3Al_2Si_3O_{12}:Ce^{3+}$
$Ca_3Al_2Si_3O_{12}:2\%Ce^{3+}$
$SrMgSi_2O_6:Eu^{2+}$
$Sr_2MgSi_2O_7:Eu^{2+}$
$Sr_3MgSi_2O_8:Eu^{2+}$

$Ba_2MgSi_2O_7:Eu^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	39.84	10.00
MgO	19.92	1.367
SiO_2	39.84	4.00
Eu_2O_3	0.40	0.120
H_3BO_3	1.6	0.16

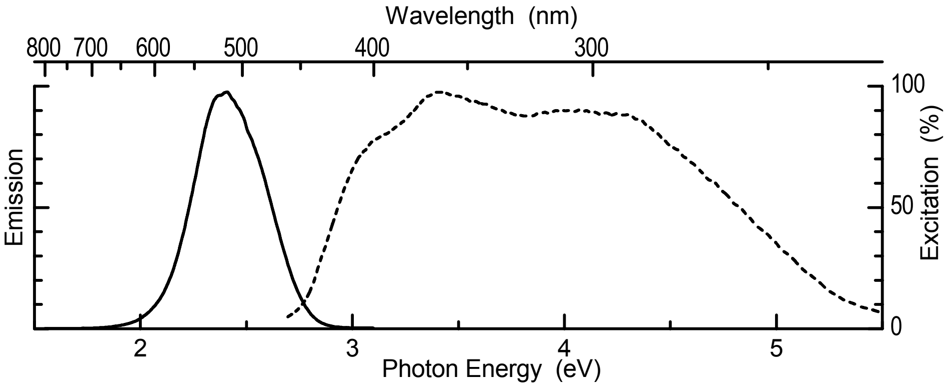
Preparation

Mix and grind. Pre-sinter at 900°C in N_2 for 2 hours. Powderize and grind. Sinter at 1300°C in N_2 + 5% H_2 gas flow for 3 hours. H_3BO_3 serves as flux.

Optical Properties

Emission color: Light blue.
Emission peak: 515 nm
Excitation efficiency by UV: Excited by UV from 240 to 440 nm.

Spectra



Remark

This contribution comes from Weiyi Jia.

Reference

1. Blasse, G., Wanmaker, W.L., terVrugt, J.W., and Bril, A., Fluorescence of Eu^{2+}-activated silicates, *Philips Res. Rep,* 23, 189 (1968).
2. Blasse, G., and Bril, Characteristic luminescence, 1. The absorption and emission spectra of some important activators, A., *Philips Tech. Rev.*, 31, 304 (1970).

$CaMgSi_2O_6:Eu^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	24.87	10.00
MgO	24.87	4.04
SiO_2	49.75	12.00
Eu_2O_3	0.51	0.36
H_3BO_3	2	0.48

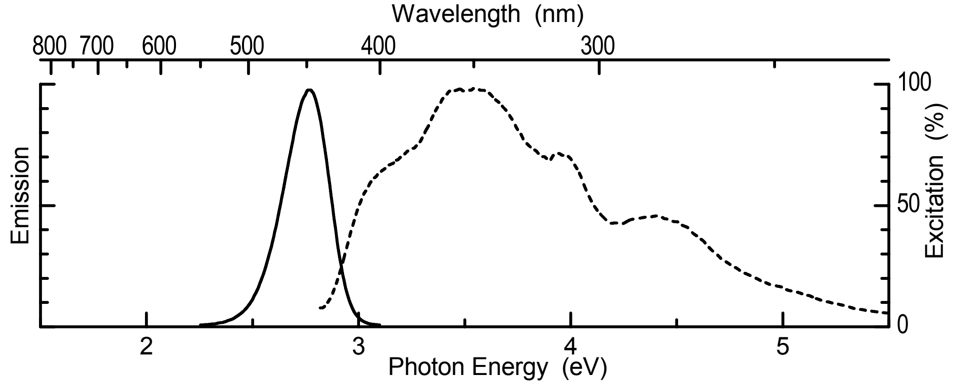
Preparation

Mix and grind. Pre-sinter at 800°C in N_2 for 2 hours. Powderize and grind. Sinter at 1250°C in N_2 + 5% H_2 gas flow for 3 hours. H_3BO_3 serves as flux.

Optical properties

Emission color: Blue
Emission peak: 448 nm
Excitation efficiency by UV: Excited by UV from 250 to 460 nm

Spectra



Remark

This contribution comes from Weiyi Jia.

References

1. Jia, W., Unpublished data.
2. Smith, A.L., *J. Electrochem. Soc.*, 96, 287 (1949).

$Ca_2MgSi_2O_7:Eu^{2+},Mn^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	39.68	10.00
MgO	19.84	1.367
SiO_2	39.68	4.00
Eu_2O_3	0.40	0.120
MnO	0.40	0.071
H_3BO_3	1.58	0.16

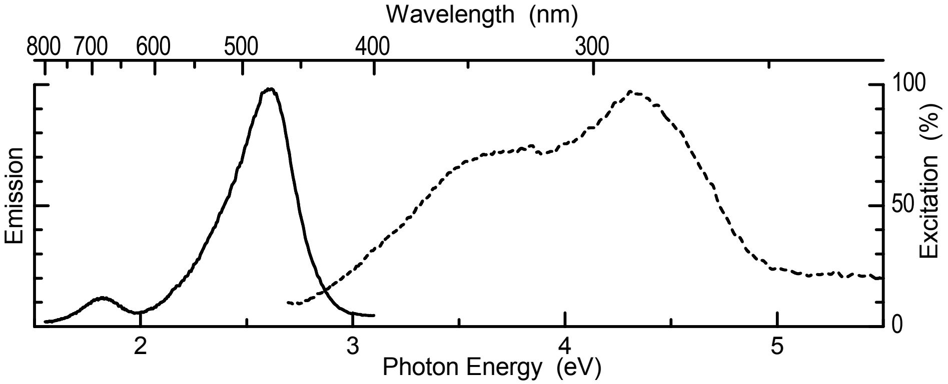
Preparation

Mix and grind. Pre-sinter at 900°C in N_2 for 2 hours. Powderize and grind. Sinter at 1300°C in N_2 + 5% H_2 gas flow for 3 hours. H_3BO_3 serves as flux.

Optical properties

Emission color: Whitish blue-green
Emission peak: Two peaks at 490 and 680 nm, respectively
Excitation efficiency by UV: Excited by UV from 260 to 420 nm

Spectra



Remark

This contribution comes from Weiyi Jia.

Reference

1. Jia, W., Unpublished data.

$Ca_3MgSi_2O_8:Eu^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	49.83	10.00
MgO	16.61	1.367
SiO_2	33.22	4.00
Eu_2O_3	0.34	0.120
H_3BO_3	1.33	0.16

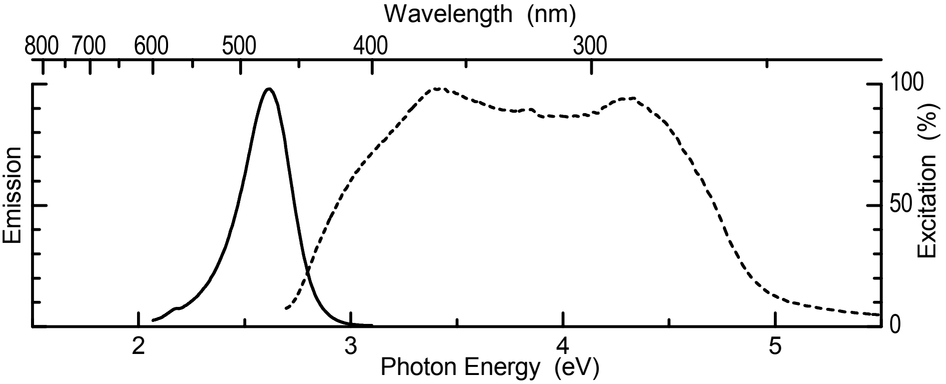
Preparation

Mix and grind. Pre-sinter at 900°C in N_2 for 2 hours. Powderize and grind. Sinter at 1350°C in N_2 + 5% H_2 gas flow for 3 hours. H_3BO_3 serves as flux.

Optical properties

Emission color: Light blue
Emission peak: 480 nm
Excitation efficiency by UV: Excited by UV from 250 to 440nm

Spectra



Remark

This contribution comes from Weiyi Jia.

Reference

1. Jia, W., Unpublished data.

$Ca_3Al_2Si_3O_{12}:Ce^{3+}$

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	300	10
Al_2O_3	100	3.40
SiO_2	300	6
Ce_2O_3	1	0.11
H_3BO_3	5	0.103

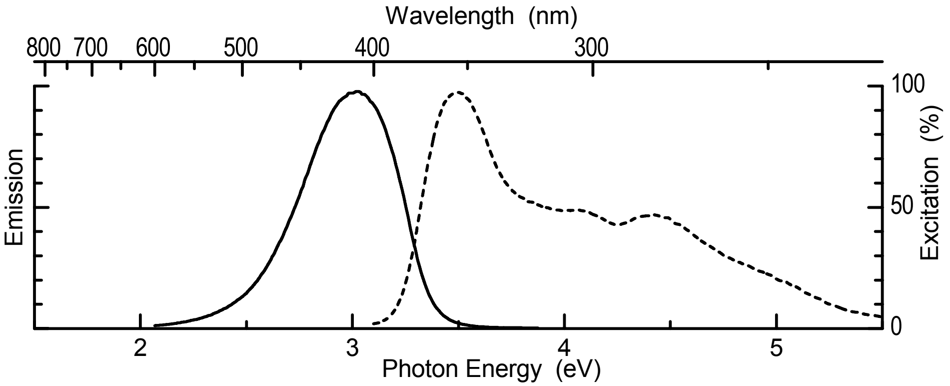
Preparation

Mix by grinding in a mortar for 30 minutes.
Press into pellets with a hydraulic press machine at 40,000 psi.
1. Fire in air, 900°C, 2 hours.
   Powderize by dry ball-milling.
   Press into pellets again.
2. Fire in 95%N_2 + 5% H_2, 1200°C, 3 hours

Optical Properties

Emission color: Violet
Emission peak: 410 nm
Excitation efficiency by UV: ++ (2.88 eV), ++ (3.40eV)

Spectra



Remark

This contribution is from Weiyi Jia.

Reference

1. Jia, W., Unpublished data.

$Ca_3Al_2Si_3O_{12}$:2%Ce^{3+}

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	300	10.00
Al_2O_3	100	3.40
SiO_2	300	6.00
Ce_2O_3	1	0.110
H_3BO_3	5	0.103

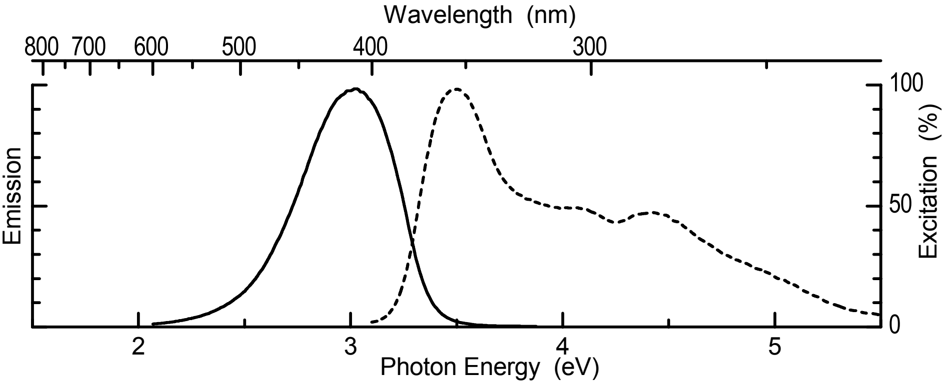
Preparation

Mix by dry grinding in a mortar for 30 minutes.
Press into pellets with a hydraulic press machine at 40,000 psi.
1. Fire in air, 900°C, 2 hours.
Powderize.
Grind and press into pellets again.
2. Fire in 95%N_2 + 5% H_2, 1200°C, 3 hours

Optical Properties

Emission color: Violet
Emission peaks: 280 and 355 nm
Excitation efficiency by UV: ++ (3.40 eV), ++ (4.88 eV)

Spectra



Remarks

1. This contribution is from Weiyi Jia.
2. This compound is also known as calcium aluminum silicate.

Reference

1. Jia, W., Unpublished data.

$SrMgSi_2O_6:Eu^{2+}$

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	24.87	10.00
MgO	24.87	2.74
SiO_2	49.75	8.14
Eu_2O_3	0.51	0.238
H_3BO_3	2	0.325

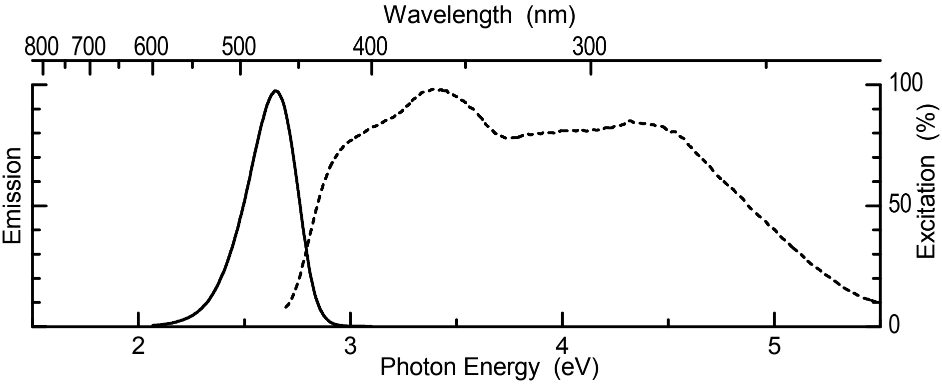
Preparation

Mix and grind. Pre-sinter at 700°C in air for 2 hours. Powderize and grind. Sinter at 1050°C in N_2 + 5% H_2 gas flow for 3 hours. H_3BO_3 serves as flux.

Optical properties

Emission color: Deep blue
Emission peak: 470 nm; Strong afterglow
Excitation by UV: Excited by UV from 240 to 450 nm.

Spectra



Remark
This contribution comes from Weiyi Jia.

Reference

1. Jia,W., Unpublished data.

$Sr_2MgSi_2O_7$:Eu^{2+}

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	39.84	10.00
MgO	19.92	1.369
SiO_2	39.84	4.072
Eu_2O_3	0.4	0.119
H_3BO_3	1.6	0.163

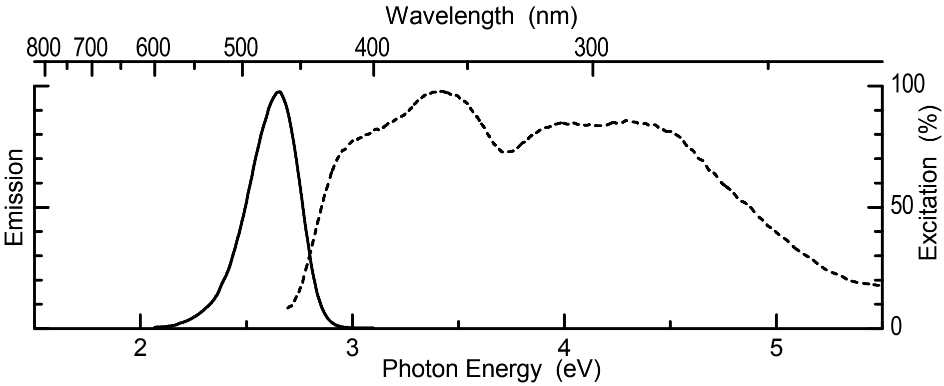
Preparation

Mix and grind. Pre-sinter at 800°C in air for 2 hours. Powderize and grind. Sinter at 1200°C in N_2 + 5% H_2 gas flow for 3 hours. H_3BO_3 (B_2O_3) serves as flux.

Optical properties

Emission color: Blue
Emission peak: 470 nm
Excitation by UV: Excited by UV from 250 to 450 nm

Spectra



Remark
This contribution comes from Weiyi Jia.

References

1. Jia,W., Unpublished data.
2. Blasse, G., Wanmaker, W.L., terVrugt, J.W., and Bril, A., Fluorescence of Eu^{2+}-activated silicates, *Philips Res. Rep*, 23, 189 (1968).

$Sr_3MgSi_2O_8$:Eu^{2+}

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	49.83	10.00
MgO	16.61	0.912
SiO_2	33.22	2.715
Eu_2O_3	0.34	0.079
H_3BO_3	1.33	0.108

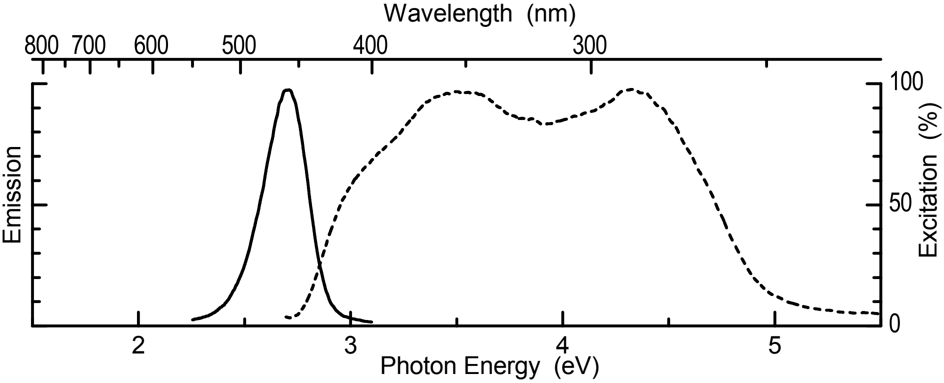
Preparation

Mix and grind. Pre-sinter at 800°C in air for 2 hours. Powderize and grind. Sinter at 1200°C in N_2 + 5% H_2 gas flow for 3 hours. H_3BO_3 (B_2O_3) serves as flux.

Optical properties

Emission color: Light blue
Emission peak: 470 nm
Excitation by UV: Excited by UV from 250 to 450 nm

Spectra



Remark

This contribution comes from Weiyi Jia.

Reference

1. Blasse, G., Wanmaker, W.L., terVrugt, J.W., and Bril, A., Fluorescence of Eu^{2+}-activated silicates, *Philips Res. Rep.*, 23, 189 (1968).
2. Blasse, G., and Bril, A., Characteristic luminescence, 1. The absorption and emission spectra of some important activators, *Philips Tech. Rev.*, 31, 304 (1970).

7.3 Phosphates, Halophosphates, and Borates

The following host compounds and activators are included in this subsection:

$(Y,Gd)BO_3$:Tb
$(Y,Gd)BO_3$:Eu
β-$Ca_2P_2O_7$:Sn,Mn
$Sr_2B_5O_9Cl$:Eu
$Sr_wF_xB_4O_{6.5}$:Eu^{2+}
$Sr_wF_xB_yO_z$:Eu^{2+},Sm^{2+}

$(Y,Gd)BO_3$:Tb

Structure: Pseudovaterite

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	23	51.9
Gd_2O_3	23	83.4
Tb_4O_7	2	15.0
H_3BO_3	139	85.9

Preparation

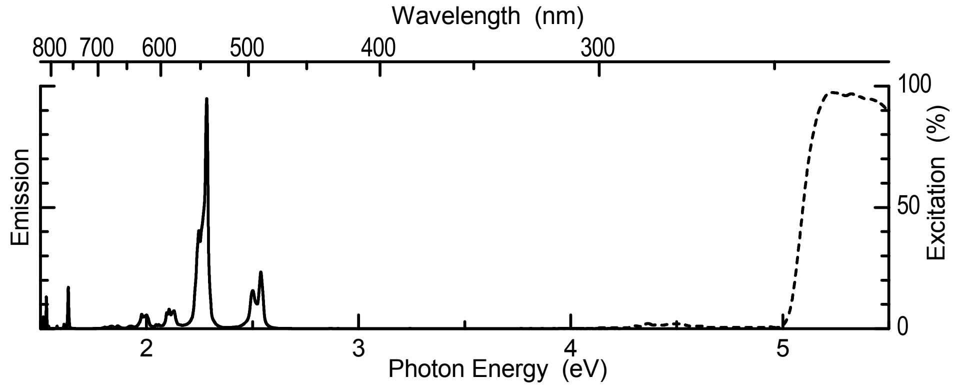
Dry blend ingredients.
1. Fire in capped quartz tubes, air, 400–500°C, 2 hours.
2. Fire in capped quartz tubes, reducing atmosphere, 1100°C, 2 hours.

Lightly mortar.
Slurry powder in boiling 10% HCl for 30 minutes.
Decant with boiling water until neutral.
Dry at 110°C.

Optical Properties

Emission color: Green
Emission peak: 544 nm
Excitation efficiency by UV: − (3.40 eV), ++ (4.88 eV), ++ (8.40 eV)

Spectra



Remark

This contribution is from Takashi Hase.

References

1. Japanese Patent Disclosure (Kokai), 52 133 091 (1977).
2. Hoshina, T., Sony Research Center Reports, *Supplement*, 92 (1983).
3. Wyckoff, R.W.G., *Crystal Structure*, 2nd ed., Interscience, New York: (1964).
4. Avella, F.J., Sovers, O.J., and Wiggins, C. S., Rare earth cathodoluminescence in $InBO_3$ and related orthoborates, *J. Electrochem. Soc.*, 114, 613 (1967).

$(Y,Gd)BO_3$:Eu

Structure: Pseudovaterite

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	32	72.2
Gd_2O_3	15	54.4
Eu_2O_3	3	10.6
H_3BO_3	130	80.4

Preparation

Mix by dry blend.

1. Fire in capped quartz tubes or alumina crucibles, air, 400–500°C, 2 hours.
2. Fire in capped quartz tubes or alumina crucibles, air, 1100°C, 2 hours.

Powderize. Slurry in boiling 10% HCl for 30 minutes. Wash by decanting in boiling water until neutral. Dry in air, 110°C.

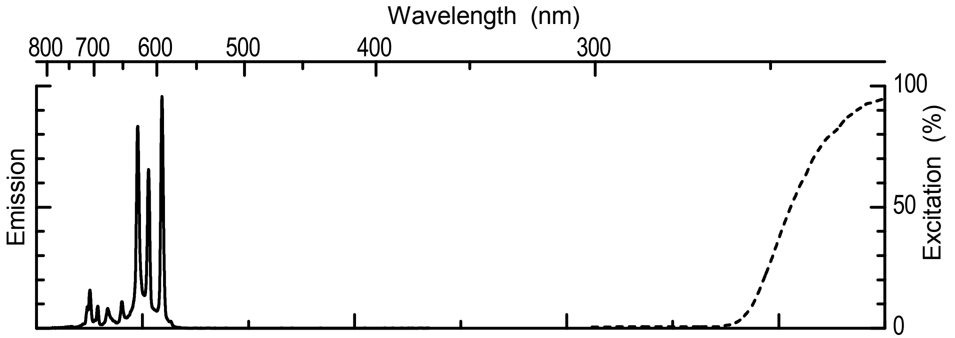
Optical Properties

Emission color: Red

Emission peak: 619 nm

Excitation efficiency by UV: – (3.40 eV), ++ (4.88 eV), ++ (8.40 eV)

Spectra



Remark

This contribution is from Takashi Hase.

References

1. Japanese Patent Disclosure (Kokai), 52 54690 (1977).
2. Koike, J., Okada, K., and Yokozawa, M. *NHK Giken Geppo*, 22, 176 (1979).
3. Wyckoff, R.W.G., *Crystal Structure*, 2nd ed., Interscience, New York (1964).
4. Bril. A., and Wanmaker, W.L., Fluorescent properties of some europium-activated phosphors, *J. Electrochem. Soc.*, 111, 1363 (1964).
5. Avella, F.J., Sovers, O.J., and Wiggins, C.S., Rare earth cathodoluminescence in $InBO_3$ and related orthoborates, *J. Electrochem. Soc.*, 114, 613 (1967).
6. Chadeyron, G., Arbus, A., Fournier, M.T., and Cousseins, D.Z., Influence of the synthesis method on the luminescent properties of the vaterite-type YBO_3-Eu^{3+}, *Cr. Acad. Sci. II.,* 320, 199 (1995).
7. Avella, F.J., U.S. Pat., 3 394 084 (1968).

β-$Ca_2P_2O_7$:Sn,Mn

Composition

Ingredient	Mole %	By weight (g)
$CaHPO_4$	81.04	18.92
$SrHPO_4$	8.32	0.73
$Sn_2P_2O_7$	0.28	0.20
$MnCO_3$	7.05	1.39
$(NH_4)_2HPO_4$	9.31	2.11

Preparation

Mix by shaking with six ½ in. nylon balls in a plastic jar on a paint mixer for ½ hour.

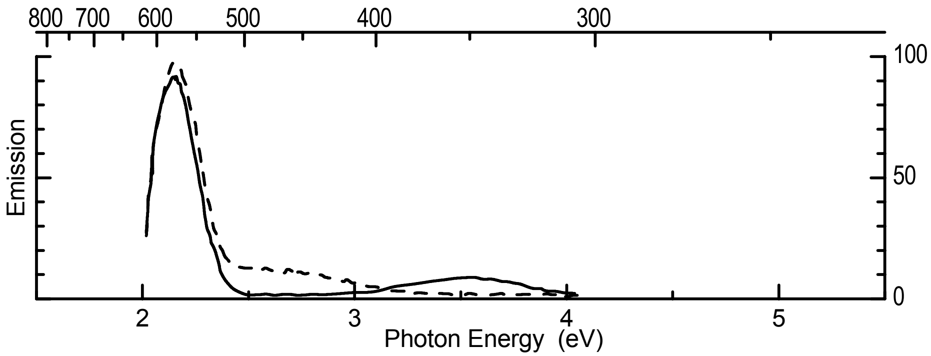
Dry in air. Powderize when dry.

1. Fire in alumina trays, 99.5% N_2/0.5%H_2, 625°C, ~½ hour.
   Eliminate the H_2
2. Fire in alumina trays, N_2, 1200°C, 1 hour.
   Cool in N_2.

Optical Properties

Emission color: Orange-red
Emission peaks: 350 and 575 nm
Emission width (FWHM): 72 nm (For the latter peak)
Excitation efficiency by UV: ++ (3.40 eV), + (4.88 eV)
Excitation by e-beam: Weakly excited

Spectra



Remarks

1. This contribution is from Madis Raukas.
2. Firing temperature should not exceed 1250°C to prevent formation of α-pyrophosphate.
3. Exhibits very strong triboluminescence or mechanoluminescence.

References

1. Henderson, S.T., *Proc. R. Soc. A*, 173, 323 (1939).
2. Ranby, P.W., Mash, D.H., and Henderson, S.T., The investigation of new phosphors, with particular reference to the pyrophosphates, *Brit. J. Appl. Phys.*, S18, 18 (1955).
3. Pappalardo, R.G., and Peters, T.E., U.S. Pat., 4 772 417 (1988).

$Sr_2B_5O_9Cl$:Eu

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	26.33	8.85
$SrCl_2$	27.42	9.91
Eu_2O_3	0.55	0.44
B_2O_3	45.71	7.25

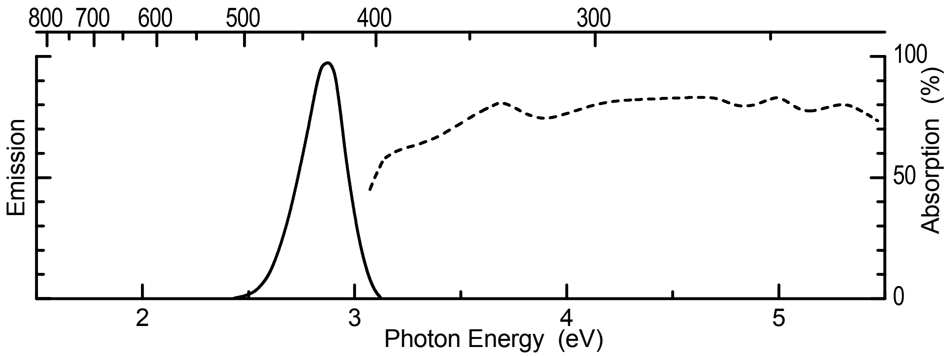
Preparation

Dry blend ingredients.
Fire in molybdenum trays, (99.5 N_2:0.5 H_2), 1025°C, 2 hours.
Cool.
Wash in hot water.
Dry.

Optical Properties

Emission color: Bluish-white body
Emission peak: 425 nm
Emission width (FWHM): 30 nm
Excitation efficiency by UV: ++ (3.40 eV), ++ (4.88 eV)
Excitation efficiency by e-beam: Weakly excited by cathode rays

Spectra



Remark

This contribution is from Madis Raukas.

Reference

1. Peters, T.E., and Baglio, J., Luminescence and structural properties of alkaline earth chloroborates activated with divalent europium, *J. Inorg. Nucl. Chem.,* 32, 1089 (1970).

$Sr_wF_xB_4O_{6.5}$:Eu^{2+}

Composition

Ingredient	Mole %	By weight (g)
$Sr(NO_3)_2$	10.00	63.49
SrF_2	9.77	61.30
H_3BO_3	80.11	247.36
Eu_2O_3	0.12	2.11

Preparation

Dissolve Eu_2O_3 powder in dilute nitric acid solution and $Sr(NO_3)_2$ and boric acid in warm water (80°C). Combine these two solutions.

Form a 1:1 solution of acetone and ammonium hydroxide and add to the above solution slowly while stirring vigorously. A fine white precipitate will result and form a slurry.

Cool the slurry to below 20°C, filter, and dry the precipitate in air.

Blend the precipitate with half the SrF_2 and grind.

Place in an open quartz crucible and fire in air at 800°C for 1 hour.

Cool, blend, and grind with the remainder of the SrF_2 into a fine powder. Fire for 2 hours at 890°C in a flow of H_2 in N_2 gas in the same open crucible. Cool and re-grind.

Optical Properties

Emission color: UV

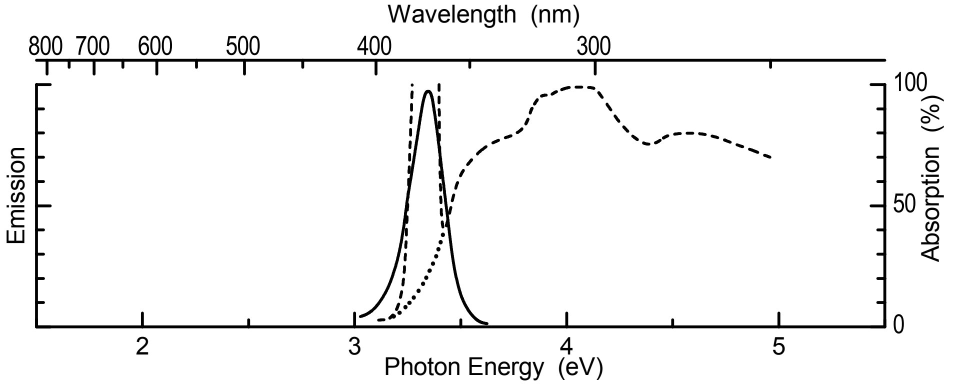
Emission peak: 370 nm

Emission width (FWHM): About 20 nm

Excitation by UV: In a broad range up to about 360 nm

Excitation by e-beam and x-rays: Good excitation by cathode rays

Spectra



Remarks

1. This contribution is from Madis Raukas.
2. This is a Eu-sensitized, IR-emitting phosphor, which is used in high- and low-pressure discharge lamps as well as in CRTs. The most efficient version has been determined to be $Sr_{0.96}F_{0.62}B_4O_{6.5}$:$Eu_{0.029}$.

References

1. Chenot, C.F., U.S. Pat., 3 649 550 (1972).
2. Chenot, C.F., U.S. Pat., 3 448 056 (1969).

$Sr_wF_xB_yO_z$:Eu^{2+},Sm^{2+}

Composition

Ingredient	Mole %	By weight (g)
$Sr(NO_3)_2$	10.09	126.98
SrF_2	5.43	40.58 g
H_3BO_3	84.12	309.20
Eu_2O_3	0.25	5.28
Sm_2O_3	0.11	2.09

Preparation

Dissolve Eu_2O_3 and Sm_2O_3 powders in dilute nitric acid solution and $Sr(NO_3)_2$ and boric acid in warm water (90°C). Combine these two solutions. Form a 1:1 solution of acetone and ammonium hydroxide and rapidly add to the above solution while stirring vigorously. A fine white precipitate will result and form a slurry. The slurry is kept at 80°C for about 2 hours and is cooled to ambient temperature. The resultant is filtered and dried in air. Blend the precipitate with SrF_2 and grind. Place in an open quartz crucible and fire in air at 900°C for 1–2 hours. Cool, blend, and grind into a fine powder. Fire for 2 hours at 900°C in a flow of H_2 in N_2 gas in the same open crucible. Cool and re-grind.

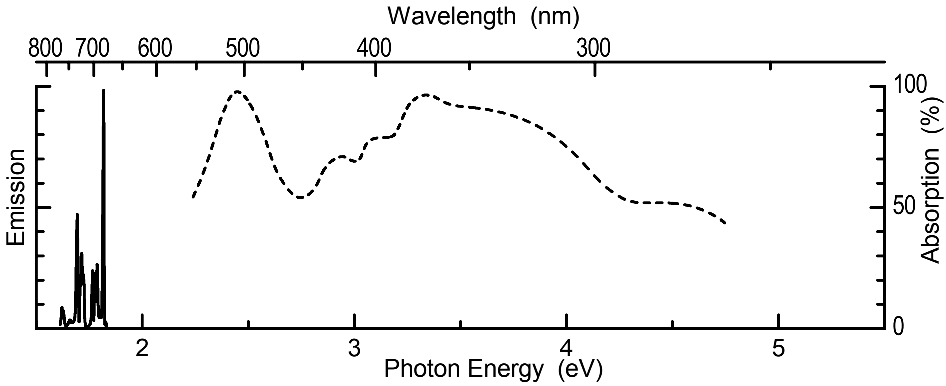
Optical Properties

Emission color: Narrow red and IR

Emission peaks: 684, 693, 697, 703, 723, 725 and 732 nm

Excitation by UV: in broad ranges 250–280, 300–390 nm with additional peaks at 395, 420, and 502 nm due to Sm^{2+}

Spectra



Remarks

1. This contribution is from Madis Raukas.
2. This is a Eu-sensitized, IR-emitting phosphor, which is used in high- and low-pressure discharge lamps as well as CRTs. The most efficient is $Sr_{0.96}F_{0.62}B_4O_{6.5}$:$Eu_{0.029}$,$Sm_{0.011}$.

References

1. Chenot, C.F., U.S. Pat., 3 649 550 (1972).
2. Chenot, C.F., U.S. Pat., 3 693 006 (1972).
3. Chenot, C.F., U.S. Pat., 3 448 056 (1969).

7.4 Aluminates

The following host compounds and activators are included in this subsection:

$BaMgAl_{10}O_{17}$:Eu,Mn (BAM:Mn)
$BaMgAl_{10}O_{17}$:Eu (BAM)
$CaAl_2O_4:Tb^{3+}$
$CaAl_4O_7:Ce^{3+}$
$CaTi_{0.9}Al_{0.1}O_3:Bi^{3+}$
$CaYAlO_4:Eu^{3+}$
$MgCeAl_{11}O_{19}:Tb^{3+}$
$SrAl_4O_7:Eu^{3+}$
$Sr_xBa_yCl_zAl_2O_{4-z/2}:Mn^{2+},Ce^{3+}$
$Y_3Al_5O_{12}$:Ce
$Y_3Al_5O_{12}:Ce^{3+}$
$Y_3Al_5O_{12}:Mn^{4+}$
$Y_3Al_5O_{12}:Cr^{3+}$

$BaMgAl_{10}O_{17}$:Eu,Mn (BAM:Mn)

Composition

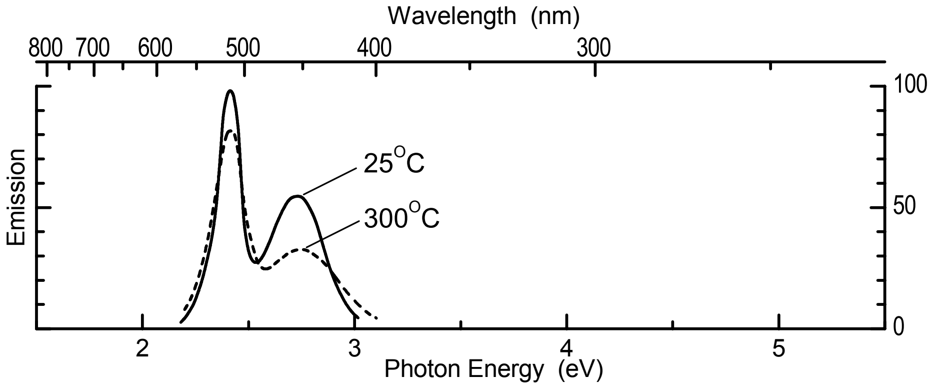
Ingredient	Mole %	By weight (g)
$BaCO_3$	80	158
MgO	70	28.2
Al_2O_3	1050 (Al)	536
Eu_2O_3	10 (Eu)	17.6
$MnCO_3$	30	34.5
BaF_2	10	17.5

Preparation

Mix by ball-milling or magnetic stirring in an alcohol and dry in air. Powderize.
Fire in a reducing atmosphere at a temperature of about 1200–1500°C for at least 1 hour. Powderize.

This phosphor can be used in plasma display panels and is in use in fluorescent lamps. The phosphor remains efficient to high temperatures.

Spectra



Spectra were provided by Madis Raukas.

Remark
This contribution is from Cees Ronda.

$BaMgAl_{10}O_{17}$:Eu (BAM)

Composition

Ingredient	Mole %	By weight (g)
$BaCO_3$	80	158
MgO	100	40
Al_2O_3	1050 (Al)	536
Eu_2O_3	10 (Eu)	17.6
BaF_2	10	17.5

Preparation

Mix by ball-milling or magnetic stirring in an alcohol and dry in air.
Powderize
Fire in reducing atmosphere at a temperature of about 1200–1500°C for at least 1 hour.
This phosphor is used in plasma display panels and in fluorescent lamps. The phosphor remains efficient to high temperatures.

Remark
This contribution is from Cees Ronda.

$CaAl_2O_4:Tb^{3+}$

Structure: Hexagonal

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	10
Al_2O_3	100	10.2
Tb_2O_3	1	0.366
B_2O_3	2	0.139

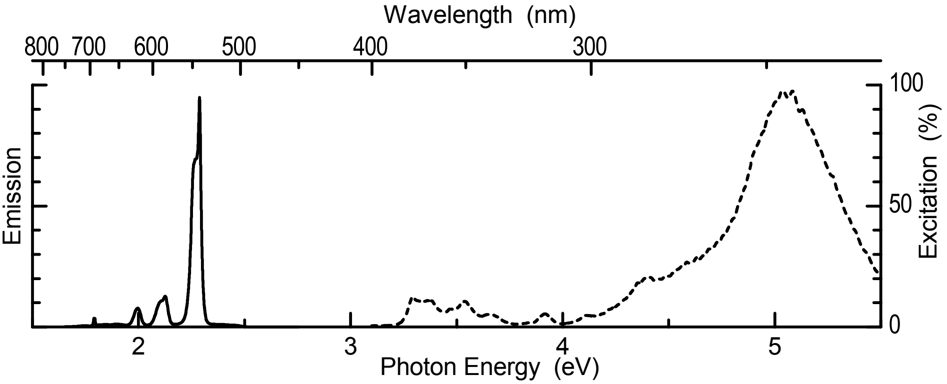
Preparation

Mix by dry grinding in a mortar for 30 minutes.
Press into pellets with a hydraulic press machine at 40,000 psi.
1. Fire in N_2, 900°C, 2 hours.
Powderize.
Grind and press into pellets again.
2. Fire in N_2, 1400°C, 3 hours.

Optical Properties

Emission color: Green
Emission peak: 543 nm, with smaller peaks at 590 and 620 nm
Emission width (FWHM): 0.48 eV
Excitation efficiency by UV: ++ (3.40 eV), + (4.88 eV)

Spectra



Remarks

1. This contribution is from Weiyi Jia.
2. This compound is known as calcium aluminate.

References

1. Jia, D., Meltzer, R.S., Yen, W.M. et al., Green phosphorescence of $CaAl_2O_4:Tb^{3+},Ce^{3+}$ through persistence energy transfer, *Appl. Phys. Lett.,* 80, 1535 (2002).
2. Jia, D., Wang, X.J., Jia, W., et al., Persistent energy transfer in $CaAl_2O_4:Tb^{3+},Ce^{3+}$, *J. Appl. Phys.*, 93, 148 (2003).

$CaAl_4O_7:Ce^{3+}$

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	10
Al_2O_3	200	20.4
$Ce(NO_3)_3{\cdot}4H_2O$	2	0.366
B_2O_3	2	0.139

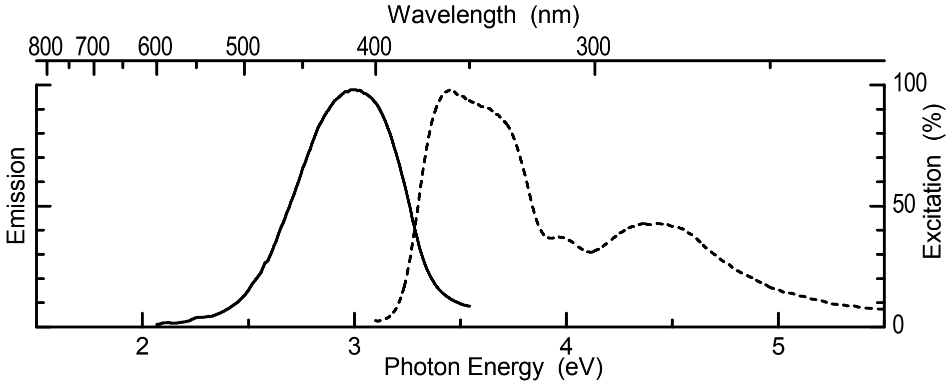
Preparation

Mix by dry grinding in a mortar for 30 minutes.
Press into pellets with a hydraulic press machine at 40,000 psi
1. Fire in N_2, 900°C, 2 hours.
Powderize.
Grind and press into pellets again.
2. Fire in 95% N_2 + 5% H_2, 1400°C, 3 hours.

Optical Properties

Emission color: Violet
Emission peak: 407 nm
Emission width (FWHM): 4580 cm^{-1}
Excitation efficiency by UV: ++ (3.40 eV), ++ (4.88 eV)

Spectra



Remarks

1. This contribution is from Weiyi Jia.
2. This compound is known as calcium tetra-aluminate.

Reference

1. Jia, W., Unpublished data.

$CaTi_{0.9}Al_{0.1}O_3:Bi^{3+}$

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	90	9.01
TiO_2	90	7.18
Bi_2O_3	10	4.66
Al_2O_3	10	1.02

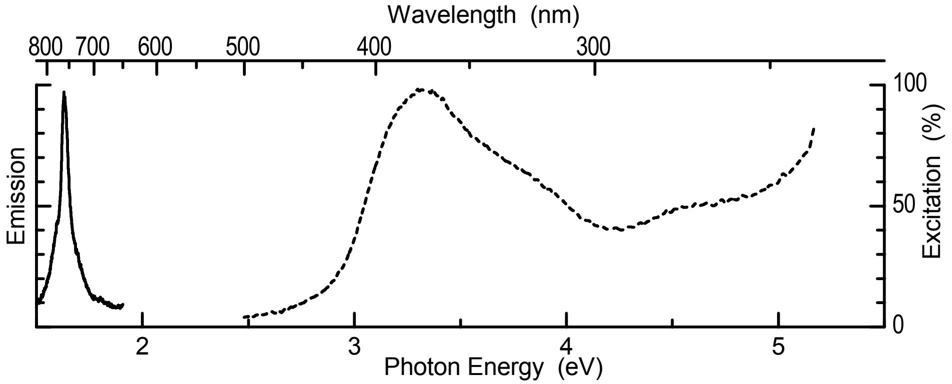
Preparation

Mix by dry grinding or milling.
Press into pellets.
1. Fire in air, 1000°C, 1 hour.
Powderize.
Grind and press into pellets again.
2. Fire in open quartz boats, air, 1300°C, 3 hours.

Optical Properties

Emission color: Deep red
Emission peak: 760 nm
Emission width (FWHM): 440 cm^{-1}
Excitation efficiency by UV: + (3.40 eV), + (4.88 eV)

Spectra



Remarks

1. This contribution is from Weiyi Jia.
2. This compound is known as calcium titanate.

Reference

1. Jia, W., Perez-Andujar, A., and Rivera, I., Energy transfer between Bi^{3+} and Pr^{3+} in doped $CaTiO_3$, *J. Electrochem. Soc.*, 150, 161 (2003).

$CaYAlO_4:Eu^{3+}$

Structure: Tetrahedral

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	100	10.01
Y_2O_3	100	22.56
Al_2O_3	100	10.19
Eu_2O_3	1	0.352
B_2O_3	3	0.209

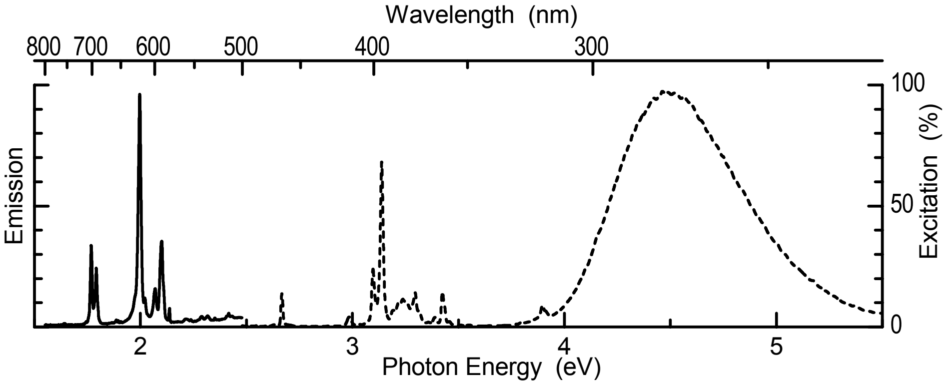
Preparation

Mix by dry grinding in a mortar for 30 minutes.
Press into pellets with a hydraulic press machine at 40,000 psi.
1. Fire in air, 1000°C, 2 hours.
Powderize.
Grind and press into pellets again.
2. Fire in air, 1400°C, 3 hours.

Optical Properties

Emission color: Red
Emission peak: 621 nm, with weaker peaks at 588 and 702 nm
Excitation efficiency by UV: + (3.40 eV), + (4.88 eV)

Spectra



Remarks

1. This contribution is from Weiyi Jia.
2. This compound is also known as calcium-yttrium aluminate.

Reference

1. Jia, W., Unpublished data.

$MgCeAl_{11}O_{19}:Tb^{3+}$

Structure: Hexagonal

Composition

Ingredient	**Mole %**	**By weight (g)**
$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 3H_2O \cdot 2$	9.0	
CeO_2	6	10.3
Al_2O_3	55	56.1
Tb_4O_7	1	7.5

* Desirable ingredient: $(Ce,Tb)O_x$ (Oxide of coprecipitate as a Ce-Tb ingredient).

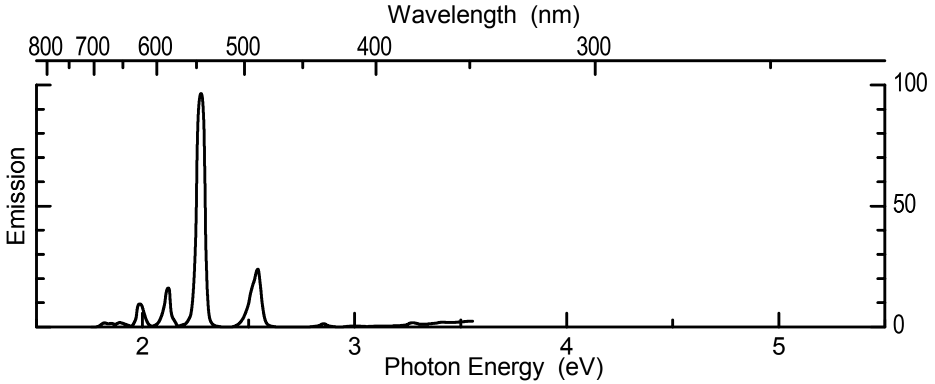
Preparation

Mix by automatic mill.
Fire in alumina crucibles, stagnant air, 1650°C, 2 hours.
Powderize by automatic mill.
Re-fire, in alumina boats, reducing atmosphere (95% N_2/5% H_2), 1600°C, 2 hours.
Powderize.
Store in a well-sealed container.

Optical Properties

Emission peak: 2.28 eV (543 nm)
Emission width (FWHM): 0.048 eV (9.76 nm)
Excitation efficiency by UV: −(3.40eV), +++(4.88eV)

Spectra



Remark

This contribution is from Shozo Oshio.

Reference

1. Oshio, S., Shigeta, T., and Matsuoka, T., U.S. Pat., 6 290 875 (2001).

$SrAl_4O_7:Eu^{3+}$

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
$SrCO_3$	100	10.01
Al_2O_3	200	7.98
Eu_2O_3	1	0.352
B_2O_3	3	0.209

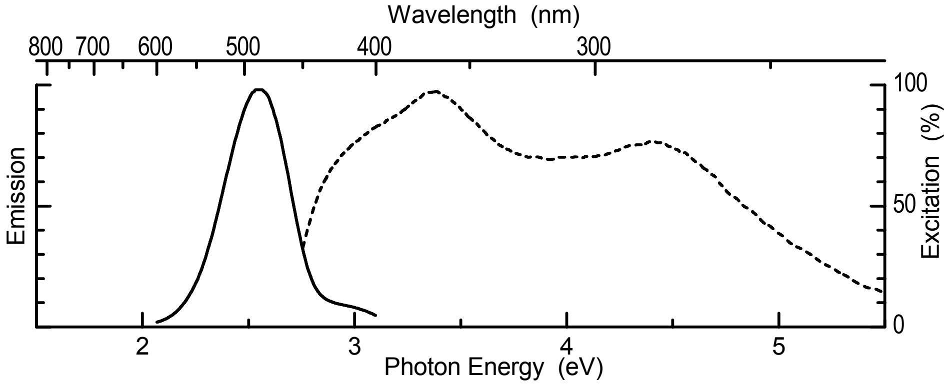
Preparation

Mix by dry grinding in a mortar for 30 minutes.
Press into pellets with a hydraulic press machine at 40,000 psi.
1. Fire in air, 1000°C, 2 hours.
Powderize.
Grind and press into pellets again.
2. Fire in air, 1350°C, 3 hours.

Optical Properties

Emission color: Red
Emission peak: 612 nm
Excitation efficiency by UV: + (3.40 eV), + (4.88 eV)

Spectra



Remarks

1. This contribution is from Weiyi Jia.
2. This compound is also known as strontium tetra-aluminate.

Reference

1. Jia, W., Unpublished data.

$Sr_xBa_yCl_zAl_2O_{4-z/2}$:$Mn^{2+}$,$Ce^{3+}$

Composition

Ingredient	Mole %	By weight (g)
$Sr(OH)_2{\cdot}8H_2O$	7.80	60.86
$Ba(OH)_2{\cdot}8H_2O$	4.26	39.43
$BaCl_2$	19.17	117.24
$Al(OH)_3$	68.10	156.02
$Mn(NO_3)_2$ (52% solution)	0.34	1.79
$Ce(NO_3)_3$ (47.5% solution)	0.34	2.64

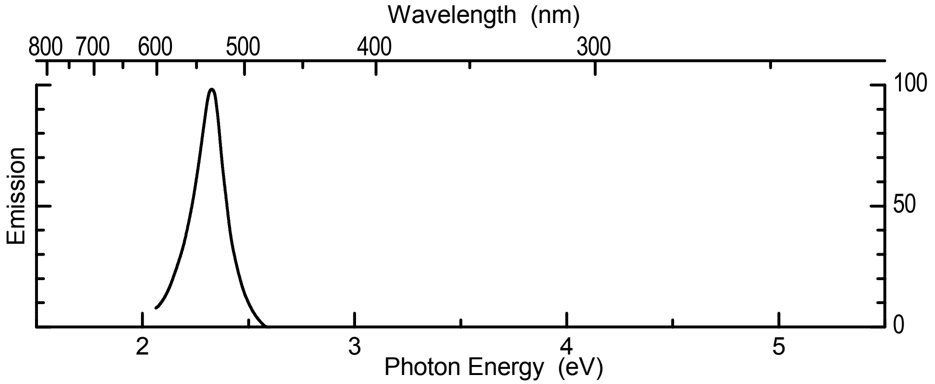
Preparation

Wet blend all components, powders, and standard solutions in acetone for 15 minutes. Dry the admixture in air at 160°C for 5 hours. Re-blend and place in an open container. Fire at a temperature below 400°C for an additional 5 hours. Increase the temperature to 1100–1200°C and fire for 4 hours in a flow of 0.4% H_2 in N_2 gas. Cool to ambient temperature and sieve admixture through 100-mesh stainless screen. Re-fire at 1100–1200°C for about 4 hrs, in a nitrogen atmosphere containing 4% H_2.

Optical Properties

Emission color: Green
Emission peak: 512 nm
Emission width (FWHM): 32 nm
Excitation by UV: In a broad range suitable for mercury discharge
Excitation by e-beam and x-rays: Specified as a phosphor for x-ray intensifiers

Spectra



Remarks

1. This contribution is from Madis Raukas.
2. This is a cerium-sensitized xerographic lamp phosphor.
3. The approximate formula is $Sr_{0.229}Ba_{0.688}Cl_{1.126}Al_2O_{0.3.437}$:$Mn_{0.005}$,$Ce_{0.005}$.

References

1. Chenot, C.F., U.S. Pat., 3 649 550 (1972).
2. Chenot, C.F., U.S. Pat., 3 693 006 (1972).
3. Chenot, C.F., U.S. Pat., 3 448 056 (1969).

$Y_3Al_5O_{12}$:Ce

Structure: Cubic (garnet)

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	35.5 (Y)	40
Al_2O_3	62.5 (Al)	32
CeO_2	2	3.44
NH_4Cl	5	2.7

Preparation

Mix by ball-milling or magnetic stirring in water and dry in air.
Powderize.
Firing should occur in reducing atmosphere, (e.g. forming gas or CO, at a temperature of about 1300–1500°C for at least 1 hour).

The emission spectrum consists of two bands, due to the spin-orbit split ground state of Ce^{3+}. The material has a pronounced daylight color, as Ce^{3+} absorbs in the blue part of the spectral region and emits yellow light. The spectral position of the emission band of Ce^{3+} can be varied by replacing part of the Al by (e.g., Ga).

This phosphor is used in white LED lamps and also in high-pressure Hg lamps. In LEDs it partially converts blue light into yellow light, resulting in white light. In high-pressure Hg lamps it reduces the color temperature of the light.

Remark

This contribution is from Cees Ronda.

$Y_3Al_5O_{12}:Ce^{3+}$

Structure: Cubic (garnet)

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	100	10
Al_2O_3	200	9.03
$Ce(NO_3)_3{\cdot}4H_2O$	2	0.555
B_2O_3	2	0.062

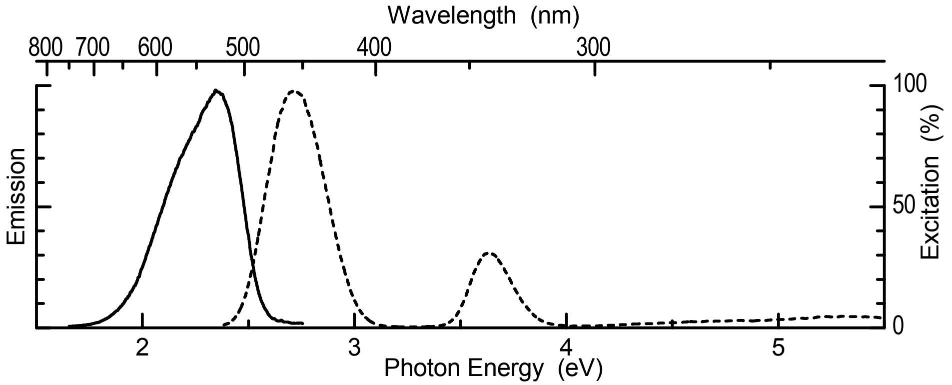
Preparation

Mix by dry grinding in a mortar for 30 minutes.
Press into pellets with a hydraulic press machine at 40,000 psi
Dry in air. Powderize when dry.
1. Fire in N_2, 1000°C, 2 hours.
Powderize.
Press into pellets again.
2. Fire in 95% N_2 + 5% H_2, 1400°C, 3 hours.

Optical Properties

Emission color: Violet
Emission peak: 528 nm
Emission width (FWHM): 4580 cm^{-1}
Excitation efficiency by UV: ++ (3.40 eV), ++ (4.88 eV)

Spectra



Remark

This contribution is from Weiyi Jia.

Reference

1. Jia, W., and Rivera, E., Unpublished data.

$Y_3Al_5O_{12}$:Mn^{4+}

Structure: Cubic (garnet)

Composition

Ingredient	Mole %	By weight (g)
Y_2O_3	33	10
Al_2O_3	66	9.03
$MnCO_3$	19	0.051
B_2O_3	2	0.062

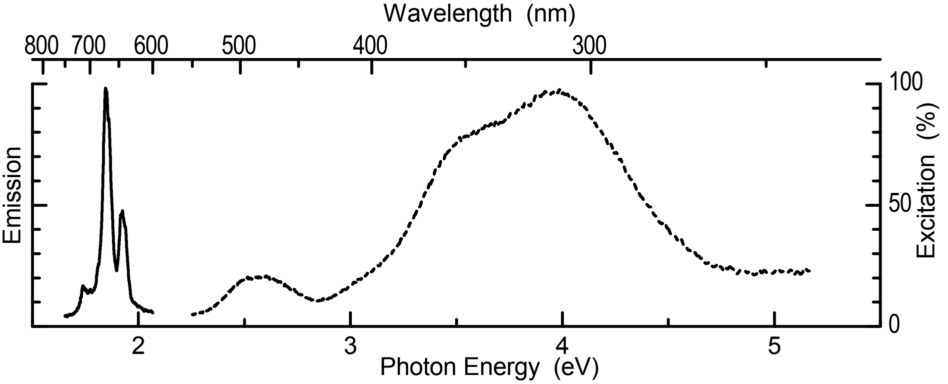
Preparation

Mix by dry grinding in a mortar for 30 minutes.
1. Fire in N_2, 900°C, 2 hours.
   Grind.
2. Fire in 95% N_2 + 5% H_2, 1400°C, 3 hours.

Optical Properties

Emission color: Deep red
Emission peak: 640 and 667 nm
Emission width (FWHM): 4580 cm^{-1}
Excitation efficiency by UV: ++ (3.40 eV), ++ (4.88 eV)

Spectra



Remark

This contribution is from Weiyi Jia.

Reference

1. Jia, W., and Rivera, E., Unpublished data.

$Y_3Al_5O_{12}$:Cr^{3+}

Structure: Cubic (garnet)

Composition

Ingredient	Mole %	By weight (g)
For precursor:		
$Y(NO_3)_3 \cdot 6H_2O$	4.04	—
$Al(NO_3)_3$	6.72	—
$Cr(NO_3)_3 \cdot 9H_2O$	0.0067	—

Fuels:

CH_6N_4O (carbohydrazide)	1.5 (fuel/oxidizer ratio)
$C_2H_5NO_2$ (glycine)	1.7
CH_4N_2O (urea)	2.5

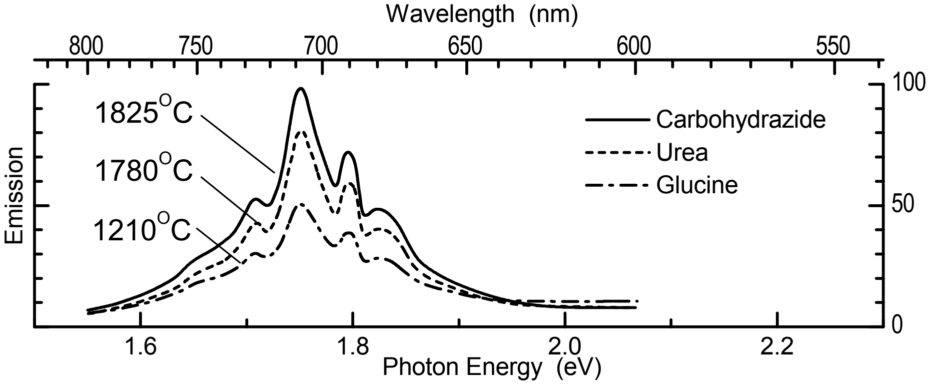
Preparation

Mix the precursor and the fuel thoroughly in a glass mortar. Place the mixture in an appropriate flameproof dish and dissolve using de-ionized water (~50 ml). Place the dish into a muffle furnace, preheated to 500°C. The solution boils, dehydrates, and ruptures into a flame in 5–10 minutes; the flame lasts for about 15 sec. For carbohydrazide and urea fuels, the result is a foamy powder which can be powderized. When glycine is used, an amorphous ash is produced that needs to be annealed in air at 1000°C for 1 hour. Powders should be placed in well-sealed containers.

Optical Properties

Emission color: Deep red
Emission peaks: 1.8, 1.75, and 1.71 eV; (688, 707, and 725 nm)
Emission width: 0.05 eV at 707 nm
Excitation efficiency by UV: 2.85 eV (435 nm)

Spectra



Remark

1. This contribution is from Lauren E. Shea-Rohwer.
2. The combustion flame temperature is dependent on the fuel used; carbohydrazide produces the highest temperature (1825°C) while glycine produces the lowest (1210°C). The spectra obtained have the same structure but the materials produced by higher temperatures show higher intensities.

References

1. Sluzky, E. Lemoine, M., and Hesse, K., Phosphor development for alpha-silicon liquid-crystal light valve projection display, *J. Electrochem. Soc.*, 141, 3172 (1994).
2. Hess, N.J. et al., Synthesis and crystallization of yttrium-aluminum-garnet and related-compounds, *J. Mater. Sci.*, 29, 1873 (1994).
3. Shea, L.E. et al., *J. Am. Ceram. Soc.*, 79, 3257 (1996).
   Shea Rohwer, L.E., and Walko, R.J., Synthesis and Characterization of Phosphors for Flat Panel Displays, *Handbook of Luminescence, Display Materials, and Devices*, H.S. Nalwa and L.S. Rohwer, Eds., American Scientific Publishers, Stevenson Ranch, CA, (2003).

7.5 Halides and Oxyhalides

The following host compounds and activators are included in this subsection:

$(ErCl_3)_{0.25}(BaCl_2)_{0.75}$
$Ba_2Mg_3F_{10}:Eu^{2+}$
$BaFBr:Eu^{2+}$
$BaFCl:Eu^{2+},Pb^{2+}$
$BaFCl:Eu^{2+}$
$BaMg_3F_8:Eu^{2+},Mn^{2+}$
$BaY_2F_8:Er^{3+},Yb^{3+}$
CsI:Tl
$LaOBr:Tb^{3+}$
$LaOBr:Tm^{3+}$
$NaYF_4:Er^{3+},Yb^{3+}$
$YF_3:Er^{3+},Yb^{3+}$
$YF_3:Tm^{3+},Yb^{3+}$

$(ErCl_3)_{0.25}(BaCl_2)_{0.75}$

Composition

Ingredient	Mole %	By weight (g)
$ErCl_3$	25	—
$BaCl_2$	75	—

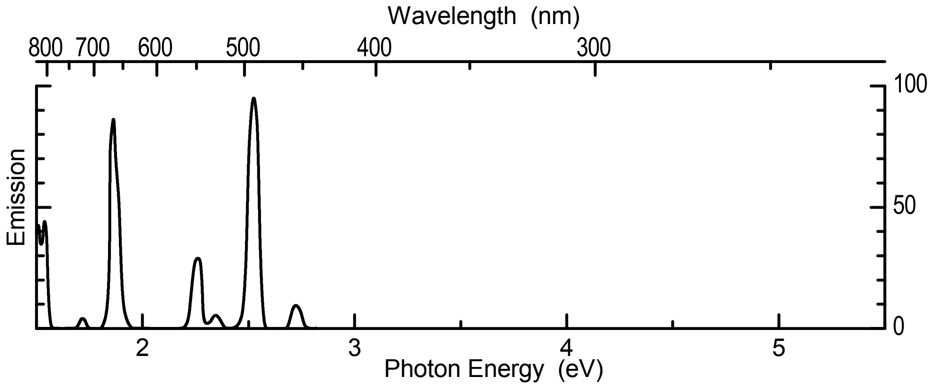
Preparation

Mix thoroughly in dry, inert box.
Heat at 1000°C after eliminating water and O_2 in stream of N_2, Ar, and Cl_2.
Crush after cooling and seal in glass capsule.

Optical Properties

Emission color: Mostly green
Emission peak: 550 nm
Excitation efficiency by IR: Can be excited with 800, 1000, and 1500 nm light

Spectra



Remarks

1. This contribution is from Hajime Yamamoto.
2. The phosphor is hygroscopic.

Reference

1. Wang, Y., and Ohwaki, J., High-efficiency infrared-to-visible up-conversion of Er^{3+} in $BaCl_2$, *J. Appl. Phys.*, 74, 1272 (1993).

$Ba_2Mg_3F_{10}$:Eu^{2+}

Composition

Ingredient	Mole %	By weight (g)
BaF_2	38.80	68.04
MgF_2	60.00	37.39
EuF_2	1.20	2.28

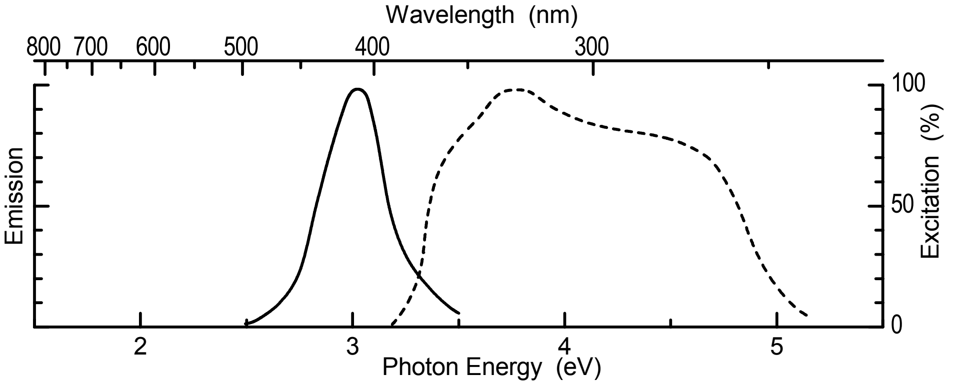
Preparation

Dry mix.
Fire in 5% volume of H_2 in N_2, 830°C, 2 hours.
Powderize.

Optical Properties

Emission color: Deep blue
Emission peak: 415 nm
Excitation efficiency by UV: In a broad range, peaking at around 330 nm
Excitation efficiency by e-beam: Good for x-ray intensifier screens

Spectra



Remarks

1. This contribution is from Madis Raukas.
2. The firing temperature can be lower (down to 700–750°C) for undoped barium magnesium fluoride; higher temperature is required for activator diffusion. Although not producing as efficiently luminescent material, an inert or even air atmosphere can be used for the reaction.

Reference

1. Wolfe, R.W., and Messier, R.F., U.S. Pat., 4 112 328 (1978).

$BaFBr:Eu^{2+}$

Structure: Tetragonal

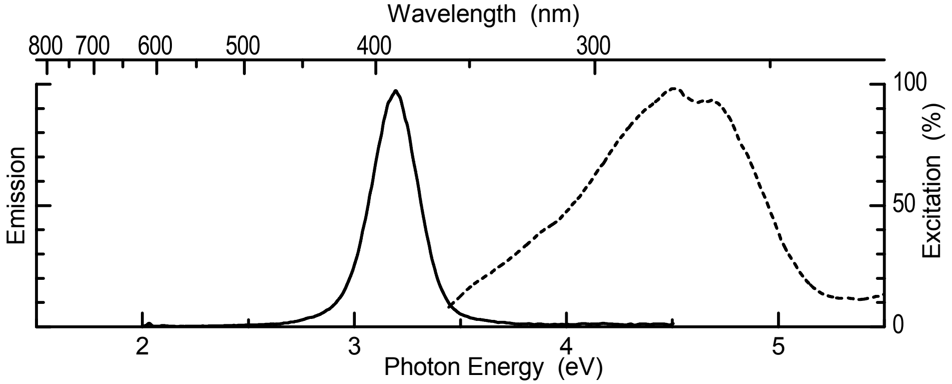
Preparation

Intimate mixtures of raw materials (BaF_2, $BaBr_2$, EuF_3) are fired in a H_2/N_2 atmosphere at 600–1000°C (desirably at 700°C). Excess ammonium halide may be used as flux. The phosphors are ground and re-fired. The fired material is ground, washed with cold water or organic liquids, dried, and sieved. Before firing, the materials are dried at 200–300°C. Care is taken to avoid oxygen during firing, and to protect from dissolving in water during washing.

Optical Properties

Emission color: UV/blue
Excitation efficiency by UV: – (3.40 eV), + (4.88 eV)
Excitation efficiency by e-beam: +

Spectra



Remarks

1. This contribution is from Masaaki Tamatani.
2. This compound is photostimulable and, therefore, useful for radiography.

References

1. Takahashi, K., Phosphors for X-ray and ionizing radiation, *The Phosphor Handbook*, Eds. Shionoya, S., and Yen, W.M., CRC Press, New York (1998).
2. Radzhabov, E., and Kurobori, T., Photoionization processes in barium fluorohalide crystals doped with Eu^{2+}, *J. Phys., Condens. Matter,* 13, 1159 (2001).
3. Kotera et al., Japanese Patent Kokai, 55 12143, 55 12144, 55 12145.
4. Kotera et al., U.S. Pat., 439 458 1.

$BaFCl:Eu^{2+},Pb^{2+}$

Composition

Ingredient	Mole %	By weight (g)
BaF_2	49.52	14.70
$BaCl_2$	49.25	17.36
$EuCl_2$	1.13	0.428
PbF_2	0.0096	0.040

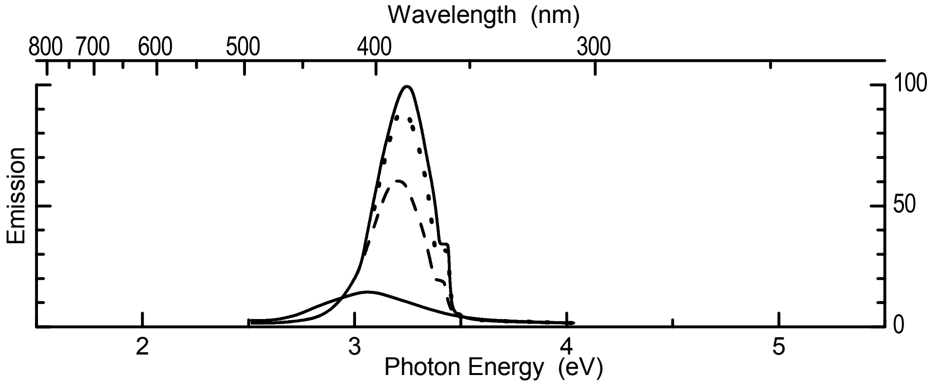
Preparation

Dry blend together.
Fire in N_2, ~ 830°C, 2 hours.
Sieve to –200 +355-mesh size.

Optical Properties

Emission peak: Around 385 nm
Emission width (FWHM): About 35 nm
Excitation by e-beam: Specified as a phosphor for x-ray intensifiers

Spectra



Remarks

1. This contribution is from Madis Raukas.
2. This x-ray phosphor is represented by the formula $Ba_{0.9989}Eu_{0.01}Pb_{0.0001}FCl$.
3. Lead is an important additive for brightness enhancement and its amount can be varied from about 10 to 1000 molar ppm parts of host, the optimum being at around 100 ppm. For the same purpose, lead can be replaced by aluminum or thallium in slightly different proportions (10–50 ppm Tl, 8,000–15,000 ppm Al).
4. As a further improvement, yttrium or lithium can be used for reducing the persistence (see the second reference).

References

1. Wolfe, R.W., and Messier, R.F., U.S. Pat., 3 951 848 (1976).
2. Wolfe, R.W., and Messier, R.F., U.S. Pat., 4 057 508 (1977).
3. Dietz, H.J., U.S. Pat., 2 303 917 (1942).
4. Uhle, O., U.S. Pat., 2 303 963 (1942).

BaFCl:Eu^{2+}

Structure: Tetragonal

Preparation

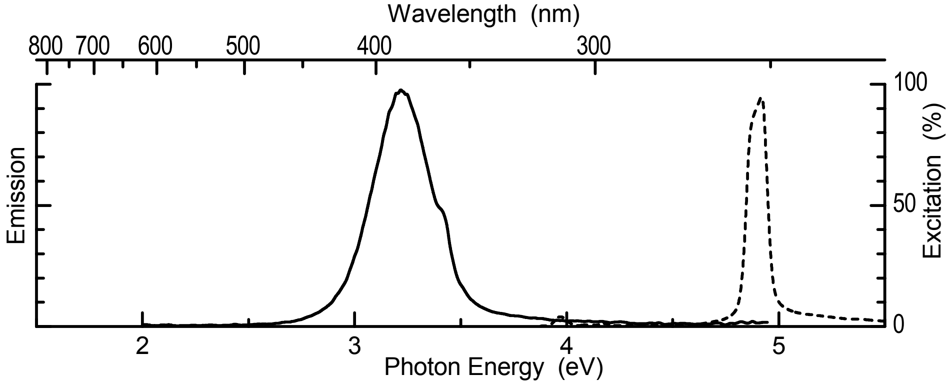
Stir the following overnight:
$(1\text{-}2x)BaF_2(s) + BaCl_2(aq) + 2x\ EuF_2(s) \rightarrow 2\ Ba_{1\text{-}x}Eu_xFCl(s)$
A stoichiometric excess of aqueous $BaCl_2$ solution is used.
Separate the precipitate.
Blend with with $BaCl_2$ to serve as a flux.
Fire in a 5% H_2-N_2 mixture at 600–1000°C for 1 hour.
Spray dry the slurry of BaFCl:Eu and aqueous $BaCl_2$.

Heat the resultant phosphor/flux intermediate at 1000°C.
Wash.
Store in a well-sealed container.

Optical Properties

Emission color: UV/blue
Emission peak: 380 nm
Excitation efficiency by UV: – (3.40 eV), + (4.88 eV)
Excitation efficiency by e-beam: +
Decay to 1/e: 5.7×10^{-6} sec (UV exc.)

Spectra



Remarks

1. This contribution is from Masaaki Tamatani.
2. This compound is photostimulable.

References

1. Issler, S.L., and Torardi, C.C., Solid state chemistry and luminescence of X-ray phosphors, *J. Alloys Ingredients*, 229, 54 (1995).
2. Ferretti, A., U.S. Pat., 4 524 016 (1985).
3. Radzhabov, E., and Kurobori, T., Photoionization processes in barium fluorohalide crystals doped with Eu^{2+}, *J. Phys. Condens. Matter,* 13, 1159 (2001).

$BaMg_3F_8:Eu^{2+},Mn^{2+}$

Composition

Ingredient	Mole %	By weight (g)
BaF_2	23.53	41.26
MgF_2	70.59	43.99
EuF_2	1.18	2.23
MnF_2	4.70	6.07

Preparation

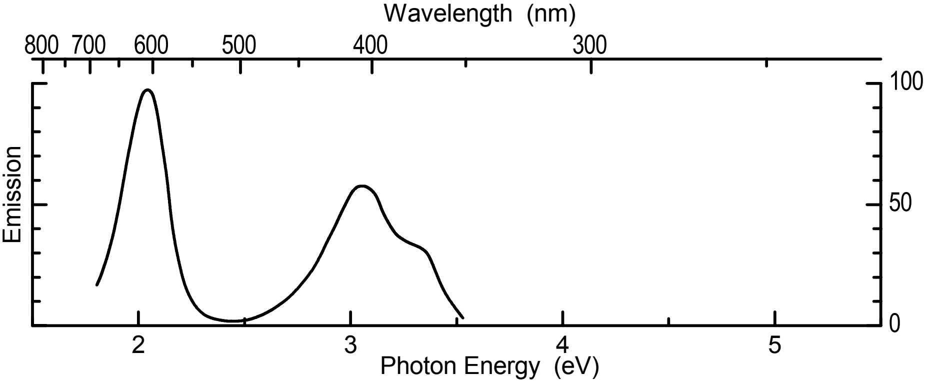
Dry blend together.
Fire in a flow of 5% H_2 in N_2 at 830°C for 2 hours.

Optical Properties

Emission color: Deep blue (Eu^{2+})

Emission peaks: Two bands. 410 nm (Eu^{2+}) and 610 nm (Mn^{2+})
Emission width (FWHM): 80 nm (Mn^{2+})
Excitation efficiency by UV: In a broad range, peaking at around 330 nm
Excitation by e-beam: Good

Spectra



Remarks

1. This contribution is from Madis Raukas.
2. The ingredients in the ratio shown above yields the composition of $Ba_{1.95}Eu_{0.05}Mg_{2.80}Mn_{0.20}F_{10}$.
3. Forming undoped barium magnesium fluoride requires lower firing temperature (700–750°C), higher temperature is required for activator diffusion.

Reference

1. Wolfe, R.W., and Messier, R.F., U.S. Pat., 4 112 328 (1978).

BaY_2F_8:Er^{3+},Yb^{3+}

Structure: Monoclinic

Composition

Ingredient	Mole %	By weight (g)
YF_3	78	
YbF_3	20	
Er F_3	2	
BaF_2	100	
ZnF_2	10	

Preparation

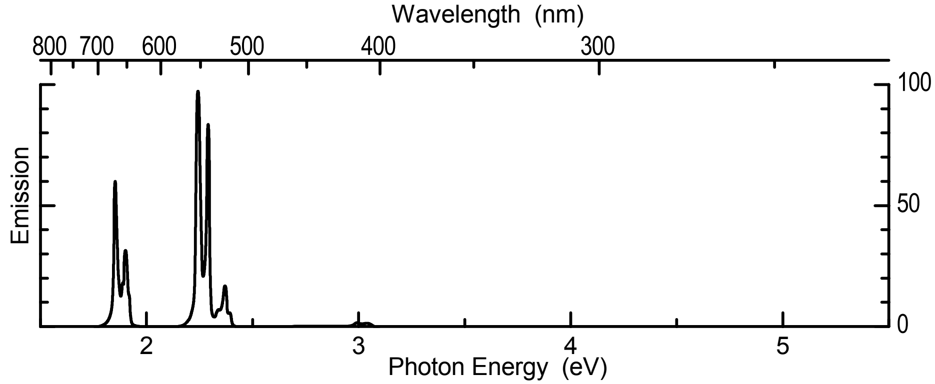
Mix thoroughly in ethanol.
Fire in a capped alumina crucible in inert or fluorizing atmosphere above 1100°C.
Wash with water after cooling to remove flux.

Optical Properties

Emission color: Green
Emission peak: 550 nm

Excitation efficiency by UV: Weak red emission
Excitation efficiency by e-beam: Weak red emission
Excitation efficiency by infrared light: Efficient under 970 nm

Spectra



Remarks

1. This contribution is from Hajime Yamamoto.
2. Luminescence characteristics are similar to those of YF_3.

References

1. Mita, Y., Detection of 1.5-µm wavelength laser-light emission by infrared-excitable phosphors, *Appl. Phys. Lett.*, 39, 587 (1981).
2. Kaminskii, A.A. et al., Spectroscopic and laser properties of Er^{3+}-doped monoclinic BaY_2F_8 single-crystals, *Opt. Quant. Electron.*, 22, S95 (1990).

CsI:Tl

Structure: Cubic

Preparation

Single crystals can be grown by several conventional methods:

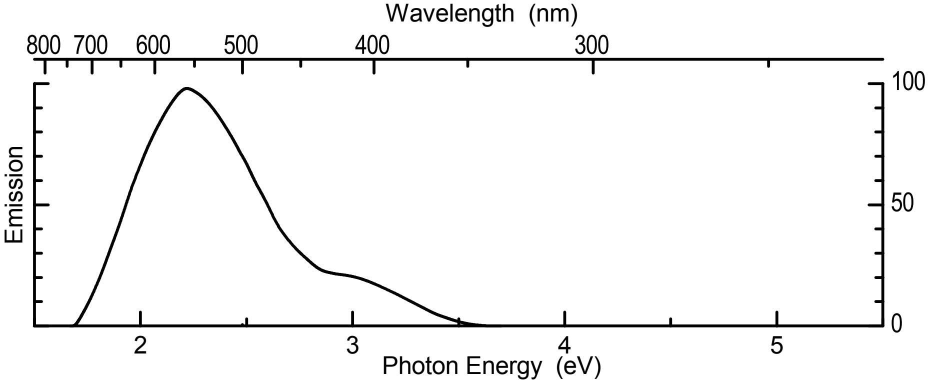
1. zone melting in a closed vertical crucible after Bridgman–Stockbarger
2. grown from the melt after Czochralski.

Thallium iodide is mixed with CsI before heating, and dissolved in the melt (melting point 623°C).

Optical Properties

Emission color: Green
Emission peak: 550 nm
Absorption edge: 4.13 eV (299 nm), 4.61 eV (269 nm), 5.14 eV (241 nm)
Excitation efficiency by UV: + (4.88 eV)
Excitation efficiency by e-beam: ++
Decay to 1/e: 0.98×10^{-6}

Spectra



Spectrum of the emission under x-ray excitation.

Remarks

1. This contribution is from Masaaki Tamatani.
2. The luminescence intensity is nearly constant for Tl^+ concentrations between 0.06 and 0.3 mol%.
3. During crystal growth, some of the thallium may be lost by evaporation.

References

1. Grabmaier, B.C., Crystal scintillators, *IEEE Trans. Nucl. Sci.* NS-31, 372 (1984).
2. Blasse, G., and Grabmaier, B.C., *Luminescent Materials*, Springer-Verlag, Heidelberg (1994).
3. Birks, J.B., The theory and practice of scintillation counting, Pergamon Press, London (1964).

LaOBr:Tb^{3+}

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
La_2O_3	19.6	100
Tb_4O_7	0.2	2.3
HNO_3	39.1	38.7
Na_2CO_3	2.0	3.3
NH_4Br	39.1	60.1

Preparation

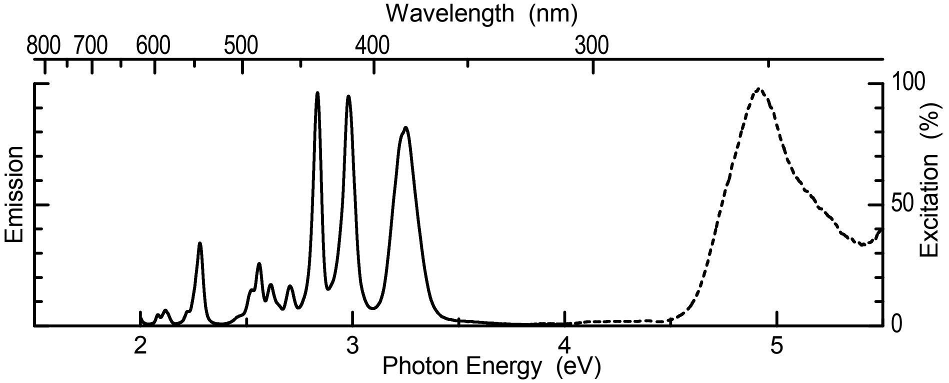
Combine the La_2O_3, Tb_4O_7, and HNO_3. Blend with the Na_2CO_3, and NH_4Br.
Ball-mill the powder with a grinding media and a liquid vehicle, such as water.

1. Fire in air, 400–500°C, 1 hour. Powderize and reblend powder.
2. Fire in air, 800–1100°C, 1 hour. Powderize, wash, filter, and dry.

Optical Properties

Emission color: Whitish blue
Excitation efficiency by UV: – (3.40 eV), ++ (4.88 eV)
Excitation efficiency by e-beam: +

Spectra



Remarks

1. This contribution is from Masaaki Tamatani.
2. Alkali bromide formed by the interaction of alkali carbonate and ammonium bromide serves as a re-crystallizing agent.

References

1. Rabatin, J.G., U.S. Pat., 3 617 743 (1971).
2. Rabatin, J.G., Tb activated rare earth oxyhalides for x-ray intensifying screen, *Electrochem. Soc. Spring Meeting,* Abstr. 102 (1974).
3. Blasse, G., and Bril, A., Investigations of Tb^{3+}-activated phosphors, *Philips Res. Rep.*, 22, 481 (1967).
4. Holsa, J. et al, Concentration quenching of Tb^{3+} luminescence in LaOBr and Gd_2O_2S phosphors, *Mater. Res. Bull.*, 14, 1403 (1979).

LaOBr:Tm^{3+}

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
NH_4Br	—	—
Tm_2O_3	—	—
La_2O_3	—	—

Preparation

$(1\text{-}x)La_2O_3 + xTm_2O_3 + 2NH_4Br$.

Fire in air, 800°C.

Ammonium bromide serves as the brominating agent, while potassium bromide acts as the flux.

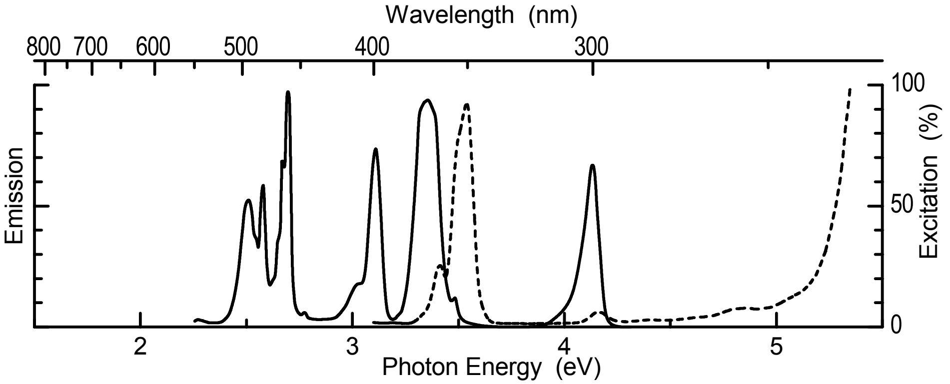
Optical Properties

Emission color: UV/blue

Excitation efficiency by UV: – (3.40 eV), – (4.88 eV)

Excitation efficiency by e-beam: +

Spectra



Remarks

1. This contribution is from Masaaki Tamatani.
2. If water vapor sensitivity is a problem, add some potassium antimony tartrate to the final product.

References

1. Issler, S.L., and Torardi, C.C., Solid state chemistry and luminescence of X-ray phosphors, *J. Alloys Ingredients*, 229, 54 (1995).
2. Rabatin, J.G., U.S. Pat., 3 591 516 (1971).
3. Rabatin, J.G., U.S. Pat., 4 208 470 (1978).

$NaYF_4$:Er^{3+},Yb^{3+}

Structure: Trigonal

Composition

Ingredient	Mole %	By weight (g)
YF_3	57	100
YbF_3	39	107.9
Er F_3	4	10.8
Na_2SiF_6	100	226.2

Preparation

Mix Na_2SiF_6 with the proper amount of (Y,Yb,Er)F_3, which has been precipitated from aqueous nitrate solution with HF solution.

Dry.

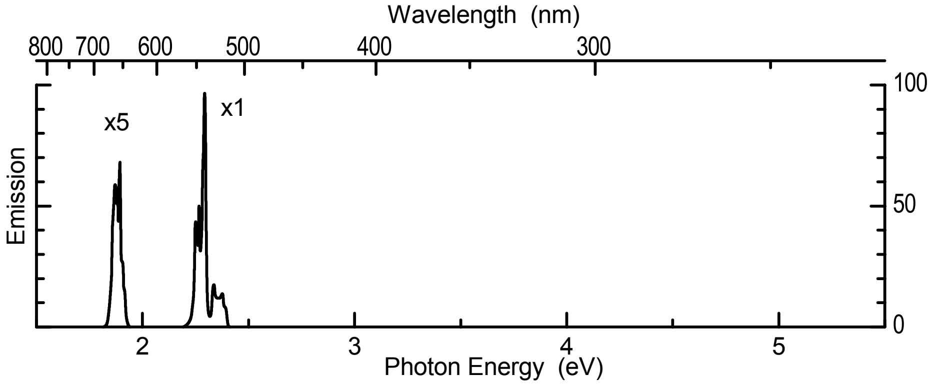
Fire in capped Pt crucibles, in Ar atmosphere, 630°C, for 2 hours.

NaF produced during decomposition of Na_2SiF_6 acts as flux and forms $NaYF_4$ lattice.

Optical Properties

Emission color: Green
Emission peak: 550 nm
Excitation efficiency by IR: Efficient at 970-nm wavelength
Excitation efficiency by UV: Weak red emission
Excitation efficiency by e-beam: Weak red emission
Excitation by infrared light: Efficient under 970nm

Spectra



Remarks

1. This contribution is from Yoh Mita.
2. Luminescence characteristics are similar to those of YF_3 but more intense emission is reported.

Reference

1. Kano, T., Yamamoto, H., and Otomo, Y., $NaLnF_4$-Yb^{3+},Er^{3+} (Ln-Y,Gd,La) — efficient green-emitting infrared-excited phosphors, *J. Electrochem. Soc.*, 119, 1561 (1972).

YF_3:Er^{3+},Yb^{3+}

Structure: Orthorhombic

Composition

Ingredient	Mole %	By weight (g)
YF_3	78	—
YbF_3	20	—
ErF_3	2	—
ZnF_2	10	—

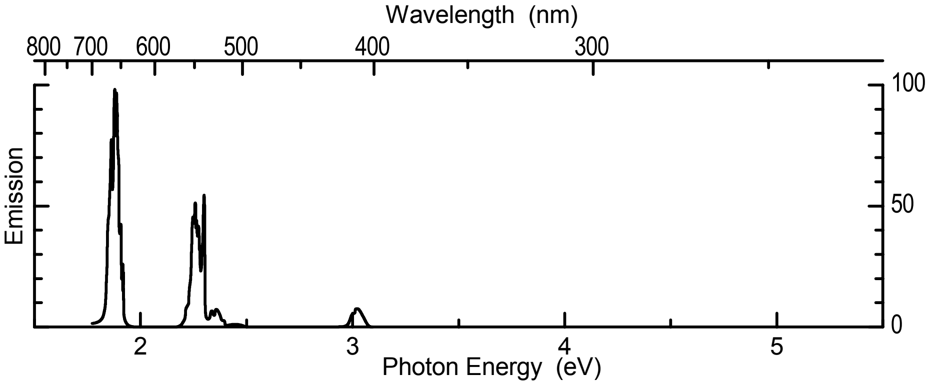
Preparation

Mix thoroughly in ethanol.
Fire in a capped alumina crucible in inert or fluorizing atmosphere above 1100°C.
Wash with water after cooling to remove flux.

Optical Properties

Emission color: Green
Emission peak: 550 nm
Excitation efficiency by UV: Weak
Excitation efficiency by e-beam: Weak
Excitation efficiency by infrared light: Efficient under 970-nm excitation

Spectra



Remarks

1. This contribution is from Hajime Yamamoto.
2. The green emission is accompanied with red emission, which may be predominant upon higher incorporation of Er^{3+} and Yb^{3+} or partial oxidization. The green emission is observed also under 800 or 1500 nm wavelength light, but higher content of Er dopant is required for obtaining efficient emission.

Reference

1. Johnson, L.F. et al., Comments on materials for efficient infrared conversion, *Appl. Phys. Lett.*, 15, 48 (1969).

YF_3:Tm^{3+},Yb^{3+}

Structure: Orthorombic

Composition

Ingredient	Mole %	By weight (g)
YF_3	74	—
YbF_3	35	—
TmF_3	0.2	—
ZnF_2	10	—

Preparation

Mix thoroughly in ethanol.

Fire in a capped alumina crucible in inert or fluorizing atmosphere above 1100°C.

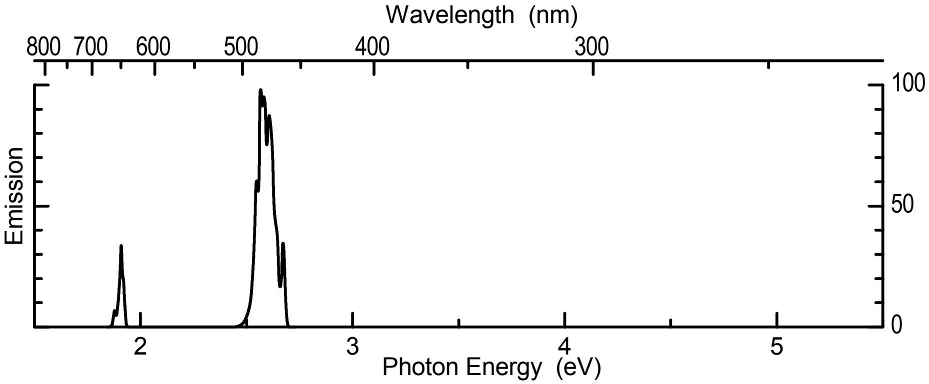
Wash with water after cooling to remove flux.

Optical Properties

Emission color: Pinkish-blue

Excitation efficiency by IR: Excitable with 970-nm light

Spectra



Remarks

1. This contribution is from Yoh Mita.
2. Blue emission is accompanied by red emission.

Reference

1. Johnson, L.F. et al., Comments on materials for efficient infrared conversion, *Appl. Phys. Lett.*, 15, 48 (1969).

7.6 CaS and ZnS-Type Sulfides

The following host compounds and activators are included in this subsection:

CaS:Bi^{3+}
CaS:Eu^{2+}
CdS:In
CdS:In, Ultrafast
CdS:Te
CdS:In,Te
ZnS:Ag,Cl
ZnS:Cu,Al
ZnS:Te,Mn

CaS:Bi^{3+}

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
CaS	100	10
Bi_2O_3	0.5	0.323
S		0.2

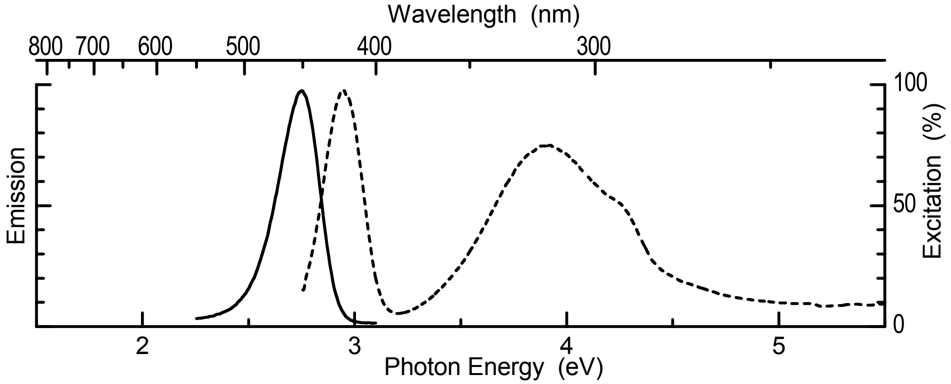
Preparation

Mix by dry grinding or milling.
Fire in N_2, 1200°C, 1 hour.
Powderize.
Store in a well-sealed container.

Optical Properties

Emission color: Deep blue, long blue afterglow
Emission peak: 450 nm
Emission width (FWHM): 1950 cm^{-1}
Excitation efficiency by UV: ++ (3.40 eV), ++ (4.88 eV)

Spectra



Remark

This contribution is from Weiyi Jia.

References

1. Jia, W., Unpublished data.
2. Lehmann, W., Activators and co-activators in calcium sulfide phosphors, *J. Lumin.*, 5, 87 (1972).

CaS:Eu^{2+}

Structure: Cubic

Composition

Ingredient	Mole %	By weight (g)
CaS	100	10
Eu_2O_3	1	0.488
S		0.2

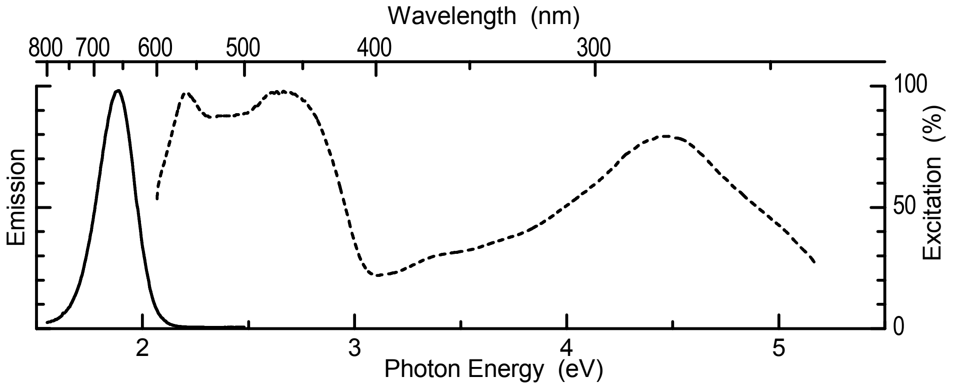
Preparation

Mix by dry grinding or milling.
Fire in 95% N_2 + 5% H_2, 1200°C, 1 hour.
Powderize.
Store in a well-sealed container.

Optical Properties

Emission color: Red, long red afterglow
Emission peak: 655 nm
Emission width (FWHM): 1660 cm^{-1}

Spectra.



Remark

This contribution is from Weiyi Jia.

References

1. Jia, D.D., Jia, W.Y., Evans, D.R. et al., Trapping processes in CaS:Eu^{2+},Tm^{3+}, *J. Appl. Phys.,* 88, 3402 (2000).
2. Lehmann, W., Ryan, F.M., Cathodoluminescence of CaS:Ce^{3+} and Cas:Eu^{2+} Phosphors, *J. Electrochem. Soc.*, 118, 477 (1971).

CdS:In

Structure: hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight
CdS	99 %	1 g
In_2O_3	1 %	7.95 mg

Preparation

Place the dry CdS and In powders in a quartz ampoule.
Mix vigorously using a Vortex mixer.
Seal the quartz ampoule under vacuum, about 1 × 10 torr.
Anneal in the sealed quartz ampoule at 900ºC for 10 hours.
Break the ampoule open and grind the compound mixture to a fine powder using a mortar and pestle.
Place the compound in a quartz ampoule.
Seal the quartz ampoule under vacuum, about 1 × 10 torr.
Anneal in the sealed quartz ampoule at 900ºC for 10 hours.
Break the ampoule open and grind the compound.
The compound should be a uniform light green color. If it is not uniform it can be treated a third time at 900ºC for 10 hours in a vacuum-sealed ampoule.

Optical Properties

Body color: Greenish-yellow
Emission: Peak about 519 nm. Color: green
Excitation by UV: By all UV and by visible blue light
Decay time: <1 nsec; exponential

Remarks

1. This contribution is from Edith Bourret-Courchesne.

References

1. Derenzo, S.E., Weber, M.J., and Klintenberg, M.K., Temperature dependence of the fast, near-band-edge scintillation from CuI, HgI_2, PbI_2, ZnO:Ga and CdS:In, *Nucl. Instr. Meth.* A 486, 214 (2002).
2. Derenzo, S.E., Weber, M.J., Bourret-Courchesne, E., and Klintenberg, M.K., The quest for the ideal scintillator, *Nucl. Instr. Meth.* A 505, 111 (2003).

CdS:In, Ultrafast

Composition

Ingredient	Mole %	By weight
CdS	100 %	145 g
In_2O_3	0.1 %	0.139 g
NH_4Cl	about 2 (not critical)	1 g
pure sulfur		about 2 g

Preparation

Make a slurry of the CdS in alcohol. Dissolve the In_2O_3 in a little HNO_3. Boil till development of brown N_2O_3 vapor ceases (but not to dry). Dissolve the NH_4Cl in a little water. Add both solutions to the CdS slurry, stir to uniformity, and dry at room temperature or at moderate heat (e.g., over night). Then add the sulfur to the dry raw mix.

1. Fire in loosely capped quartz tubes (about half full, not more) slowly flowing H_2S, 900°C, 1 hour. When cool, inspect under UV lamp. Material should be uniformly deep red luminescent. Remove any suspicious parts and powderize the rest.
2. Fire in open quartz boats, slowly flowing H_2, 600°C, one-quarter hour. Cool while still in H_2 (Important!)
   Inspect again under a UV lamp. The material should now be uniformly green luminescent (if it does not, repeat the last firing step at about 100°C higher temperature). Remove any parts (if present) that look different.

Optical Properties

Body color: Grayish-yellow
Particles: About in the 5–10 μm size range
Emission: Narrow band. Peak about 510 nm. Color: green
Excitation by UV: By all UV and by visible blue light
Excitation by e-beam: Energy—$\eta \approx$ 1–1.2%, decay < 1 nsec

Remarks

1. The NH_4Cl in the above recipe can be replaced by about 3.6 g $CdCl_2$.
2. The H_2S in the above recipe can be diluted with N_2 (about to 25% H_2S, 75% N_2).
3. This phosphor is in a frozen-in semistable state. Do not heat higher than about 250°C except in pure hydrogen.

References

3. Lehmann, W., Edge emission of n-type conducting ZnO and CdS, *Solid State Electron.,* 9, 1107 (1966).
4. Lehmann, W., U.S. Patent 3 583 929 (issued June 1971).
5. Derenzo, S.E., Weber, M.J., Klintenberg, M.K., Temperature dependence of the fast, near-band-edge scintillation from CuI, HgI_2, PbI_2, ZnO:Ga and CdS:In, *Nucl. Instr. Meth.* A 486, 214 (2002).
6. Derenzo, S.E., Weber, M.J., Bourret-Courchesne, E., and Klintenberg, M.K., The quest for the ideal scintillator, *Nucl. Instr. Meth.* A 505, 111 (2003).

The above recipe was provided by W. Lehmann during a visit to the Lawrence Livermore National Laboratory in 1987.

CdS:Te

Structure: hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight
CdS	99.99 %	10 g
CdTe	0.01 %	1.66mg

Preparation

Place the dry CdS and CdTe powders in a quartz ampoule.
Mix vigorously using a Vortex mixer.
Seal the quartz ampoule under vacuum, about 5 × 10^{-5} torr.
Anneal in the sealed quartz ampoule at 900ºC for 10 hours.
Break the ampoule open and grind the compound mixture to a fine powder using a mortar and pestle.
Place the compound in a quartz ampoule.
Seal the quartz ampoule under vacuum, about 5 × 10^{-5} torr.
Anneal in the sealed quartz ampoule at 900ºC for 10 hours.
Break the ampoule open and grind the compound.
The compound should be a uniform yellow color.

Optical Properties

Body color: yellow
Emission: Peak about ~640 nm. Color: red
Excitation by UV: By all UV and by visible blue light
Decay time: ≈ 270 nsec; nonexponential

Remarks

1. This contribution is from Edith Bourret-Courchesne.

References

1. Cuthbert, J.D. and Thomas, D.G., Optical properties of tellurium as an isoelectronic trap in cadmium sulfide, *J. Appl. Phys*. 39, 1573 (1968).
2. Schotanus, P., Dorenbos, P., and Ryzhikov, V.D., Detection of CdS(Te) and ZnSe(Te) scintillation light with silicon photodiodes, *IEEE Trans. Nucl. Sci.* 39, 546 (1992).
3. Derenzo, S.E., Weber, M.J., and Klintenberg, M.K., Temperature dependence of the fast, near-band-edge scintillation from CuI, HgI_2, PbI_2, ZnO:Ga and CdS:In, *Nucl. Instr. Meth.* A 486, 214 (2002).
4. Derenzo, S.E., Weber, M.J., Bourret-Courchesne, E., and Klintenberg, M.K., The quest for the ideal scintillator, *Nucl. Instr. Meth.* A 505, 111 (2003).

CdS:In,Te

Structure: hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight
CdS:In*	1% (In) 99%(CdS)	1g
CdS:CdTe*	0.01% (CdTe) 99.99%(CdS)	1g

*see previous pages

Preparation

Place the dry CdS:In and CdS:CdTe powders in a quartz ampoule.
Mix vigorously using a Vortex mixer.
Seal the quartz ampoule under vacuum, about 5×10^{-5} torr.
Anneal in the sealed quartz ampoule at 900ºC for 10 hours.
Break the ampoule open and grind the compound mixture to a fine powder using a mortar and pestle.
The compound should be a uniform dark yellow color.

Optical Properties

Body color: dark yellow
Emission: Peak about 618 nm. Color: red.
Excitation by UV: By all UV and by visible blue light.
Decay time:3.5 nsec; exponential.

Remarks

2. This contribution is from Edith Bourret-Courchesne.

References

7. Derenzo, S.E., Weber, M.J., and Klintenberg, M.K., Temperature dependence of the fast, near-band-edge scintillation from CuI, HgI_2, PbI_2, ZnO:Ga and CdS:In, *Nucl. Instr. Meth.* A 486, 214 (2002).
8. Derenzo, S.E., Weber, M.J., Bourret-Courchesne, E., and Klintenberg, M.K., The quest for the ideal scintillator, *Nucl. Instr. Meth.* A 505, 111 (2003).

ZnS:Ag,Cl

Composition

Ingredient	Mole %	By weight (g)
ZnS	100	98
$AgNO_3$	0.03	0.050
NH_4Cl	5	2.5
S	—	2–3 g

Preparation

$AgNO_3$ and NH_4Cl are dissolved separately in water. A ZnS slurry is made with water or an alcohol. During stirring, first the $AgNO_3$ solution is added, followed by adding the NH4Cl solution.

The mixture is dried in air and powdered. Then sulfur is added. Heating takes place at bout 1100°C in a CO atmosphere. The material can be washed with water to remove any flux residue.

This material is used as blue primary in cathode-ray tubes. It can also be co-doped with Al, instead of Cl. In addition, two modifications can be made (cubic sphalerite and hexagonal wurtzite) with slightly difference spectra. Wurtzite is obtained by heating above about 1020°C and fast cooling.

Remark

This contribution is from Cees Ronda.

ZnS:Cu,Al

Composition

Ingredient	Mole %	By weight (g)
ZnS	100	98
$Cu(C_2H_3O_2)2H_2O$	0.03	0.06
$AlCl_3$	0.3	0.4
S	—	2–3 g

Preparation

Copper acetate and aluminum chloride are dissolved in water and added to ZnS. Afterwards methanol or water is added to make a uniform slurry which is stirred.

The mixture is dried in air and powdered. Then sulfur is added. Heating takes place at about 1100°C in a CO atmosphere. The material can be washed with water to remove any flux residue.

This material is used as green primary in cathode-ray tubes. It can also be co-doped with Au and Cu, to obtain more green emission.

Remark

This contribution is from Cees Ronda.

ZnS:Te,Mn

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	94	10.00
ZnTe	3	0.632
MnO	3	0.232
S	10	1.08

Preparation

Mix and grind. Pre-sinter at 800°C in N_2 for 2 hours. Powderize and grind. Sinter at 1200°C in N_2 gas flow for 3 hours.

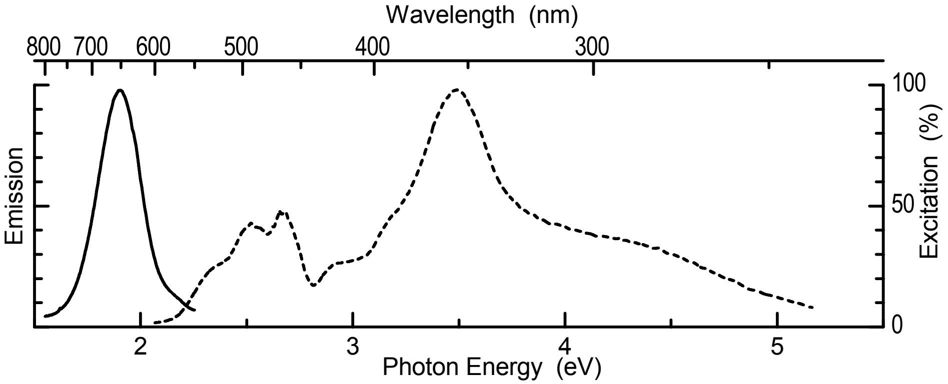
Optical Properties

Emission color: Red

Emission peak: 650 nm

Excitation efficiency by UV: Excited by 280–380 nm and blue green 450–540 nm

Spectra



Remarks

1. This contribution comes from Dongdong Jia.
2. This compound exhibits strong tribo-luminescence.

Reference

1. Smirnova, R.I., and Pron, G.F., Effect of tellurium on luminescence properties of zinc sulfide luminors, *Opt. Spectrosc.—USSR*, 23, 67 (1967).

7.7 Other Compounds

The following host compounds and activators are included in this subsection:

$CaWO_4:Pb^{2+}$
GaN:Zn
$Gd_2O_2S:Pr^{3+}$
$Gd_2O_2S:Tb$
$Na(Mg_{2-x}Mn_x)LiSi_4O_{10}F_2:Mn$
$Na_{1.23}K_{0.42}Eu_{0.12}TiSi_5O_{13}\cdot xH_2O:Eu^{3+}$
$Na_{1.23}K_{0.42}Eu_{0.12}TiSi_4O_{11}:Eu^{3+}$
$Na_{1.29}K_{0.46}Er_{0.08}TiSi_4O_{11}:Eu^{3+}$
$Na_2Mg_3Al_2Si_2O_{10}F_2:Tb$

$CaWO_4:Pb^{2+}$

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
$CaCO_3$	48.5	231.7
WO_3	49.5	100
PbO	1	4.5

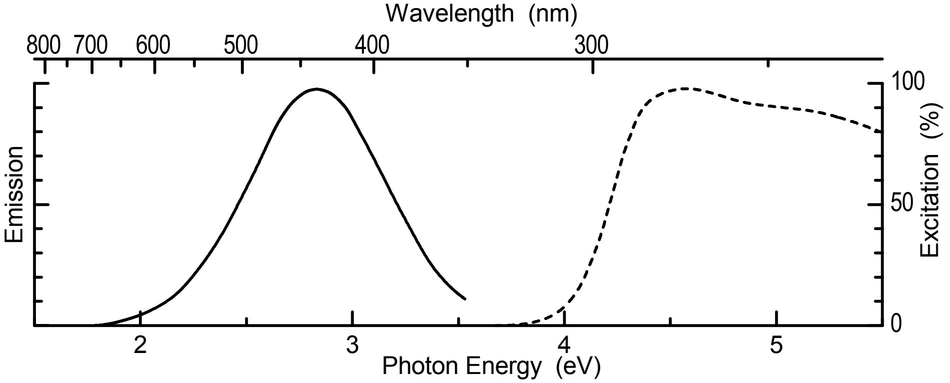
Preparation

Mix ingredients.
Fire in air, 1100°C, several hours.
Powderize, and then wash with 3% HCl (to remove the excess CaO).

Optical Properties

Emission color: Blue
Emission peak: 435 nm
Excitation efficiency by UV: − (3.40 eV), ++ (4.88 eV)
Excitation efficiency by e-beam: +
Decay to 1/e: 10^{-5}sec

Spectra



Remarks

1. This contribution is from Masaaki Tamatani.
2. Excess Ca in the material blend gives favorable results.
3. NBS1026 is used for lamps, CRTs.

References

1. Kamiya, S., and Mizuno, H., Phosphors for lamps, in *Phosphor Handbook*, Ed. Shionoya, S., and Yen, W.M., CRC Press, New York, pp. 422–423 (1998).
2. Kojima, T., Phosphors for plasma display, in *Phosphor Handbook*, Ed. Shionoya, S., and Yen, W. M., CRC Press, New York, pp. 629–630 (1998).
3. Bril, A., and Hoekstra, W., Efficiencies of phosphors for short-wave ultra-violet excitation, *Philips Res. Rep*. 16, 356–370 (1961).
4. Bril, A., and Hoekstra, W., Properties of the fluorescence of some N.B.S. standard phosphors, *Philips Res. Rep*. 19, 296–306 (1964).

GaN:Zn

Structure: Hexagonal (wurtzite)

Composition

Ingredient	Mole %	By weight (g)
ZnS	—	—
Ga_2S_3	—	—

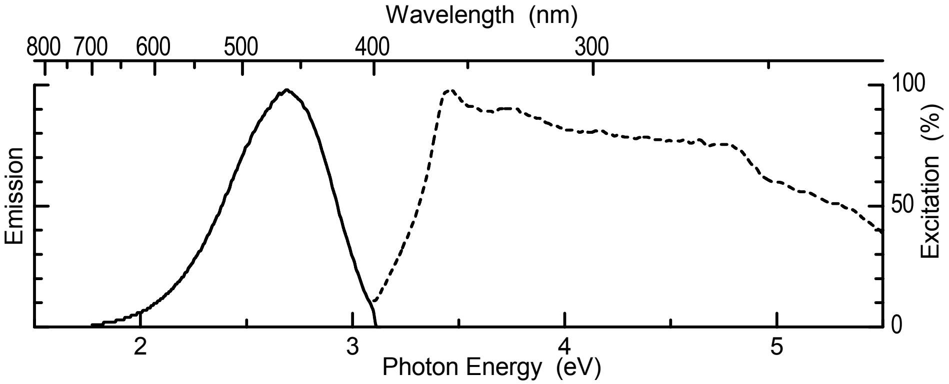
Preparation

Mix by slurrying in water or methanol.
Dry in air. Powderize when dry.
Fire in quartz tubes, NH_3, 1100°C, 2 hours.
Powderize. Wash with de-ionized water.
Add solution of Mn^{2+} and vaporize water by warming.
Re-fire in H_2+N_2 atmosphere, 1100°C, 1 hour.
Powderize.

Optical Properties

Emission color: Blue
Emission peak: 460 nm
Emission width (FWHM): 100 nm
Absorption edge: 354 nm (3.5 eV)
Luminance by cr: 650 cd/m^2 at 50 V DC

Spectra



Remark

This contribution is from Yoshitaka Sato.

References

1. Sato, Y. et al., *Proceeding of IDW'02* (2002).
2. Sato, Y., Takahashi, H., Tamaki, H., and Kameshima, M., Luminescence Properties of a Blue Phosphor, GaN:Zn for VFDs, Proceedings of the 9th International Display Workshops, Dec. 4–6 (2002).

$Gd_2O_2S:Pr^{3+}$

Structure: Hexagonal

Composition

Ingredient	Mole %	By weight (g)
Gd_2O_3	100	100
Pr_6O_{11}	0.2	0.56
HNO_3	some	some
S_2	some	3
Na_2CO_3	10	2.92

Preparation

Combine Gd_2O_3 and Pr_6O_{11} powders with some nitric acid to form a precipitate.

1. Fire in air, 1000°C.

Take the oxide, and combine with sulfur and $NaCO_3$.

2. Fire in air, 1100°C.

Rinse well in water.

Co-doping with a small amount of Ce reduces the afterglow.

Optical Properties

Emission color: Green
Emission peak: 510 nm
Excitation efficiency by UV: − (3.40 eV), ++ (4.88 eV)
Excitation efficiency by e-beam: +
Decay to 1/e: 3×10^{-6}s

Remarks

1. This contribution is from Masaaki Tamatani.
2. Three groups have proposed different processes for fabricating the oxysulfide ceramics. Toshiba proposed a high-temperature, hot-isostatic-pressing process using a phosphor powder prepared by the conventional method for CRT phosphors. Hitachi is able to lower the sintering temperature during HIP by adding a sintering aid using a powder having large particle size. Siemens proposed to apply a uni-axial hot pressing process instead of HIP, using powders with very small particle size.

References

1. Matsuda, N., Yokota, K., and Tamatani, M., Praseodimium-doped gadolinium oxysulfide ceramics prepared by the hot isostatic pressing process, *Electrochem. Soc. Fall Meeting*, Honolulu, Abstr. No. 1870RNP (1987).
2. Yamada, H., Suzuki, A., Uchida, Y., Yoshida, M., and Yamamoto, H., A scintillator Gd_2O_2S:Pr,Ce,F for X-ray computed tomography*, J. Electrochem. Soc.*, 136, 2713 (1989).
3. Rossner, W., and Ostertag, M., Properties and application of gadolinium oxysulfide based ceramic scintillators, *Electrochem. Soc. Fall Meeting*, Boston, Abstr. No. 879 (1998).

Gd_2O_2S:Tb

Composition

Ingredient	Mole %	By weight (g)
Gd_2O_3	94 (Y)	170.4
Tb_4O_7	6 (Tb)	11.3
Na_2CO_3	100	53
S	300	96

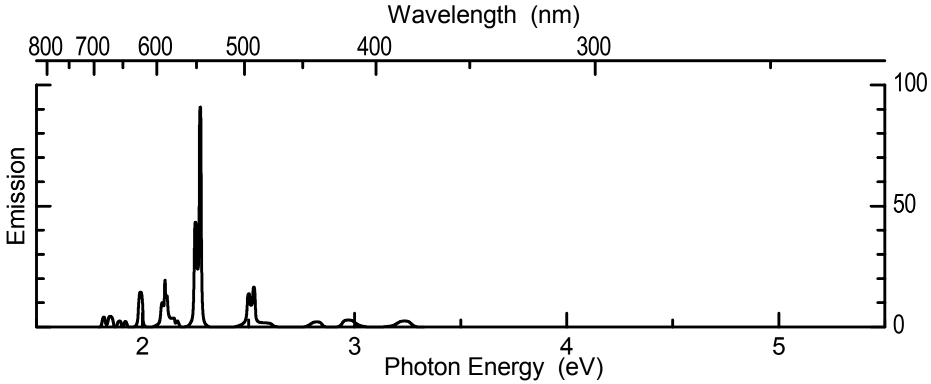
Preparation

Mix the rare-earth oxides by slurrying in water or methanol and dry in air. After drying, mixture should be powdered in mortar. Subsequently, mix the rare-earth mixture with Na_2CO_3 and S by dry mixing.

Firing should occur in air in a vessel with a well-closing lid, at a temperature of about 1100°C for a few hours.

After cooling, the reaction product has to be washed a few times with water to remove residual flux.

Spectra



Remarks

1. This contribution is from Cees Ronda.
2. This material is used in X-ray intensifying screens and in oscilloscope CRTs.

$Na(Mg_{2-x}Mn_x)LiSi_4O_{10}F_2$:Mn

Structure: Lamellar intercalation

Composition

Ingredient	Mole %	By weight (g)
Na_2CO_3	2.50	1.82
MgO	28.80	7.96
Li_2CO_3	7.50	3.80
Na_2SiF_6	5.00	6.45
SiO_2	55.00	22.66
$MnCO_3$	1.20	0.946

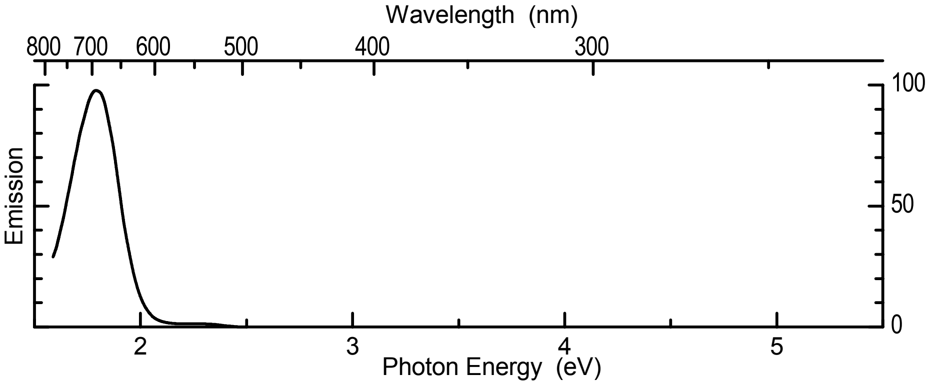
Preparation

Mix stoichiometric amounts in a paint shaker for 30 minutes with about 20 mol% of excess potassium carbonate to compensate for losses due to volatilization.
Fire in covered alumina crucibles, air, 915°C, 36 hours.
Grind.
Fire in covered alumina crucibles, 4% H_2 /N_2, 850°C.
Cool to room temperature.
Powderize.
Screen through a 325-mesh stainless steel sieve.

Optical Properties

Emission color: Redish-pink
Emission peak: 695 nm
Excitation efficiency by UV: + (3.40 eV), + (4.88 eV)
Excitation efficiency by e-beam: Characteristic emission at about 1.4 fL level under focused 15 kV/8 μA excitation

Spectra



Remarks

1. This contribution is from Madis Raukas.
2. This phosphor in formulation of $Na(Mg_{2-x}Mn_x)LiSi_4O_{10}F_2$ is an example of a broad family of intercalation ingredient that, besides micas and fluoromicas, includes vermiculites and zeolites.
3. Described composition yields a concentration of 0.08 mol Mn per mole of phosphor.
4. Good electroluminescent properties when intercalated with conductive polymers or metals.

References

1. Qi, R.Y., Karam, R.E., Reddy, V.B., and Cox, J.R., U.S. Pat., 5 567 351 (1996).
2. Qi, R.Y., and Karam, R.E., U.S. Pat., 5 658 495 (1997).
3. Reddy, V.B., Karam, R.E., and Northrop, S.K., U.S. Pat., 5 489 398 (1996).
4. Qi, R.Y., and Karam, R.E., U.S. Pat., 5 531 926 (1996).
5. Reddy, V.B., and Karam, R.E., Northrop, S.K., and Zhang, Y., U.S. Pat., 5 531 928 (1996).

$Na_{1.23}K_{0.42}Eu_{0.12}TiSi_5O_{13}{\cdot}xH_2O{:}Eu^{3+}$

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
Sodium silicate solution (8% Na_2O; 27% SiO_2; 65% H_2O)	30.7 (of Si)	20.0
TiO_2 (anatase)	5.6 (of Ti)	1.30
NaCl	58.1 (of Na)	6.90
KCl	5.6 (of K)	1.30
$Eu(NO_3)_3{\cdot}5H_2O$	0.12 (of Eu)	0.15

Preparation

1. To prepare ETS-10:
   Mix 20 g of water to the sodium silicate solution and add the NaCl and KCl.
   Stir and add anatase.
   Autoclave the gel under autogeneous pressure for 24 hours at 230°C.
   The resulting powder is filtered and washed with distilled water at room temperature and then allowed to dry at 110°C.

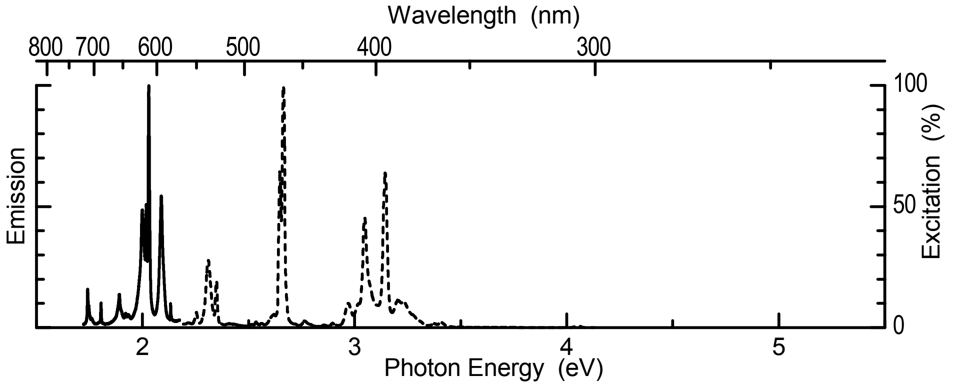
2. To prepare Eu^{3+}-doped ETS-10:
   Dissolve 0.07 g of $Eu(NO_3)_3{\cdot}5H_2O$ in 250 ml of water and add 3.94 g of the already prepared ETS-10.
   The solution is stirred for 24 hours at 60°C.
   The precipitate is filtered and dried in air at 110°C.

   *The next two materials also use this as their basic recipe.

Optical Properties

Emission color: Red
Emission peak: 2.00 eV
Emission width (FWHM): 0.044 eV
Excitation efficiency by UV: The maximum excitation efficiency at 394 nm ($^7F_0 \rightarrow {}^5L_6$) and 465 nm ($^7F_0 \rightarrow {}^5D_2$)
Decay to 10% (or 1/e, as given): To 1/e ≈ 3.63 ± 0.04 and 1.11 ± 0.02 msec

Spectra



Remarks

1. This contribution is from Luis Carlos.
2. ETS-10 is also known as microporous sodium potassium titanosilicate.
3. ETS-10 is doped through an ion exchange between Na^+ and K^+ with Eu^{3+}.

Reference

1. Rainho, J.P., Carlos, L.D., and Rocha, J., New phosphors based on Eu^{3+}-doped microporous titanosilicates, *J. Lumin.*, 87, 1083 (2000).

$Na_{1.23}K_{0.42}Eu_{0.12}TiSi_4O_{11}$:$Eu^{3+}$

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
Sodium silicate solution (8% Na_2O; 27% SiO_2; 65% H_2O)	30.7 (of Si)	20.0
TiO_2 (anatase)	5.6 (of Ti)	1.30
NaCl	58.1 (of Na)	6.90
KCl	5.6 (of K)	1.30
$Eu(NO_3)_3{\cdot}5H_2O$	0.12 (of Eu)	0.15

Preparation

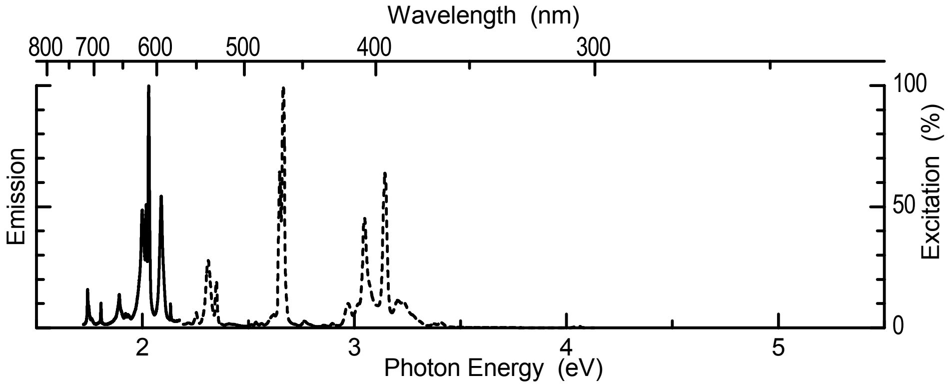
1. ETS-10 and ETS-10 doped with Eu^{3+} are prepared as in the case of the microporous titanosilicate compound described on the previous page.

2. To obtain Eu^{3+} doped narsarsukite:
   Eu^{3+}-doped ETS-10 is calcined in air from room temperature to 800°C at a heating rate of 5°C per minute.
   The material is maintained at 800°C for 3 hours.
   Cool in air.

Optical Properties

Emission color: Red
Emission peak: 2.03 eV
Emission width (FWHM): 0.003 eV
Excitation efficiency by UV: The maximum excitation efficiency at 394 nm $({}^7F_0 \rightarrow {}^5L_6)$ and 465 nm $({}^7F_0 \rightarrow {}^5D_2)$
Decay to 10%: To 1/e ≈ 3.63 ± 0.04 and 1.11 ± 0.02 msec

Spectra



Remarks

1. This contribution is from Luis Carlos.
2. This material is known as synthetic narsarsukite doped with Eu^{3+}.
3. The end product is contaminated with quartz and cristobalite impurities.

References

1. Rainho, J.P., Carlos, L.D., and Rocha, J., New phosphors based on Eu^{3+}-doped microporous titanosilicates, *J. Lumin.*, 87, 1083 (2000).
2. Rainho, J.P. et al., Synthesis and luminescence of Eu^{3+}-doped narsarsukite prepared by the sol-gel process, *J. Sol-Gel Sci. Tecnol.,* 26, 1005 (2003).

$Na_{1.29}K_{0.46}Er_{0.08}TiSi_4O_{11}:Eu^{3+}$

Structure: Tetragonal

Composition

Ingredient	Mole %	By weight (g)
sodium silicate solution (8% Na_2O; 27% SiO_2; 65% H_2O)	30.7 (of Si)	20.0
TiO_2 (anatase)	5.6 (of Ti)	1.30

NaCl	58.1 (of Na)	6.90
KCl	5.6 (of K)	1.30
$Eu(NO_3)_3 \cdot 5H_2O$	0.12 (of Eu)	0.15

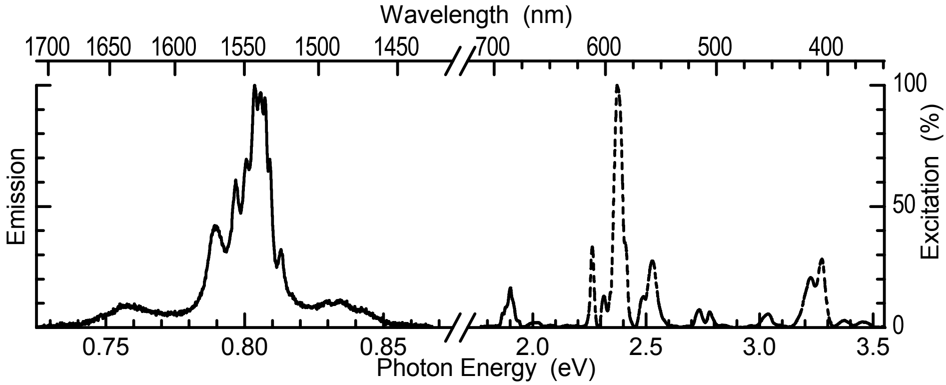
Preparation

1. ETS-10 is prepared as in the case of the microporous titanosilicate compound described in the previous pages.
2. To prepare Eu^{3+}-doped ETS-10:
   Dissolve 0.07 g of $Eu(NO_3)_3 \cdot 5H_2O$ in 250 ml of water and add 3.94 g of the already prepared ETS-10.
   The suspension is stirred for 24 hours at 60°C.
   The precipitate is filtered and dried in air at 110°C.
3. To obtain Er^{3+} doped narsarsukite:
   Eu^{3+} doped ETS-10 is calcined in air from room temperature to 800°C at a heating rate of 5°C per minute.
   The material is maintained at 800°C for 3 hours.

Optical Properties

Emission color: IR
Emission peak: 0.80 eV
Emission width (FWHM): 0.014 eV
Excitation efficiency by UV: Maximum excitation efficiency at 520 nm ($^4I_{15/2} \rightarrow {}^2H_{11/2}$) and 488 nm ($^4I_{15/2} \rightarrow {}^4F_{7/2}$)
Decay to 10%: To $1/e \approx 7.8 \pm 0.2$ msec

Spectra



Remarks

1. This contribution is from Luis Carlos.
2. ETS-10 is doped through an ion exchange between Na^+ and K^+ with Eu^{3+}.
3. This material is known as synthetic narsarsukite.
4. The end product is contaminated with quartz and cristobalite impurities.

References

1. Rocha, J. et al., New phosphors based on Eu^{3+}-doped microporous titanosilicates, *J. Mater. Chem.*, 10, 1371 (2000).
2. Rainho, J.P. et al., Er(III) environment in luminescent titanosilicates prepared from microporous precursors, *J. Mater. Chem.,* 12, 1162 (2002).

$Na_2Mg_3Al_2Si_2O_{10}F_2$:Tb

Structure: Lamellar intercalation

Composition

Ingredient	Mole %	By weight (g)
Na_2CO_3	14.23	12.26
MgO	42.66	13.98
Al_2O_3	13.94	11.56
$(NH_4)_2SiF_6$	4.74	6.87
SiO_2	23.74	11.60
TbF_3	0.69	1.21

Preparation

Mix all the ingredients thoroughly for 20–30 minutes, preferably in a paint shaker or similar device.

Fire in a covered alumina crucible, with graphite pellets added, 1100°C, 12–24 hours.

Cool to ambient temperature, powderize, and wash in de-ionized water.

Optical Properties

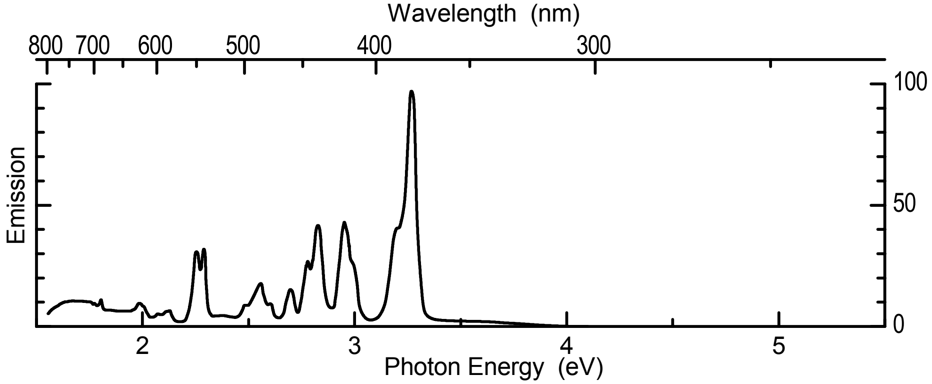
Emission Color: Bluish-green

Emission peaks: 380, 415, 440, and 540 nm

Excitation efficiency by UV: + (3.40 eV), + (4.88 eV)

Excitation efficiency by e-beam: About 1 fL level under focused 15 kV/8 μA excitation

Spectra



Remarks

1. This contribution is from Madis Raukas.
2. The described procedure yields a concentration of 0.04 mol% Tb. The formula of the compound is $Na_2(Mg_{3-x}Tb_x)Al_2Si_2O_{10}F_2$.
3. This phosphor is an example of a broad family of intercalation compounds that includes mica, fluoromica, vermiculite, and zeolite.
4. Phosphor has good electroluminescent properties if intercalated with polymers or metals.

References

1. Cox, J.R., and Karam, R.E., U.S. Pat., 5 656 199 (1997).
2. Reddy, V.B., Karam, R.E., and Northrup, S.K., U.S. Pat., 5 489 398 (1996).
3. Oi, R.Y., and Karam, R.E., U.S. Pat., 5 531 926 (1996).
4. Karam, R.E., Reddy, V.B., Northrup, S.K., and Zhang, Y., U.S. Pat., 5 531 928 (1996).
5. Oi, R.Y., and Karam, R.E., and Cox, J.R., U.S. Pat., 5 567 351 (1996).

Section 8:
Commercial Phosphors and Scintillators

Section 8

COMMERCIAL PHOSPHORS AND SCINTILLATORS

Commercial phosphors and scintillators are arranged in order of increasing wavelength in Table 1. The data were compiled for recent producers' data sheets and literature. Note that these may not be the only phosphors and scintillators available commercially or the materials still may not be manufactured.

Many phosphors are specified by P numbers assigned by the Electronics Industries Association of the United States; these have been used since 1945 and are included in Table 1. The World Phosphor Type Designation System (WPTDS), established in 1982, is a more detailed, unified phosphor system designation system. It usually consisting of two letters: the first letter indicating the criterion for the phosphor screen emission color, the second letter indicating differences from the criterion. These symbols, together with other numbers and symbols used in Japan and Europe, are included in an extensive tabulation by Inaho and Hase in chapter 6—Section 6 of the *Phosphor Handbook*.

Table 1 Commercial phosphors and scintillators

Wavelength of maximum emission (nm)	Chemical formula	Designation or acronym
220, 310(1)	BaF_2(1,2)	
305	CeF_3(2)	
307	$MgSrAl_{10}O_{17}$:Ce	
315	CsI(2)	
330–352	$LaCl_3:Ce^{3+}$(2)	
338	$(CeMg)SrAl_{11}O_{18}$:Ce	
342–347	$(CeMg)BaAl_{11}O_{18}$:Ce	
350	$YAlO_3:Ce^{3+}$(2)	YAP, YALO
351	$BaSi_2O_5$:Pb	
358–385	$LaBr_3:Ce^{3+}$(2)	
365	$LuAlO_3:Ce^{3+}$(2)	LuAP
371	SrB_4O_7:Eu	
380	$Lu_2Si_2O_7:Ce^{3+}$(2)	LPS
385	$Ca_2MgSi_2O_7:Ce^{3+}$	P16
390	CsF(1,2)	
390	ZnO:Ga	
400	$Y_2SiO_5:Ce^{3+}$	P47
400	Zn_2SiO_4:Ti	P52
400, 525	P46 (70%) + P47 (30%)	P48
410	$Y_2SiO_5:Ce^{3+}$(2)	YSO:Ce

Table 1 Commerical phosphors and scintillators—*continued*

Wavelength of maximum emission (nm)	**Chemical formula**	**Designation or acronym**
410	$YTaO_4$:Nb	
415	$Lu_{1\text{-}x}Y_xAlO_3$:$Ce^{3+(2)}$	LuYAP
415	NaI:$Tl^{(2)}$	
418–420	—	MSL
420	CsI:$Na^{+(2)}$	
420	$CaWO_4^{(2)}$	CWO
420	$CaWO_4$:W	P5
420	Lu_2SiO_5:Ce^{3+}	LSO
420	$Sr_2P_2O_7$:Eu	
425–430	$(Lu,Gd)_2SiO_5$:Ce^{3+}	LGSO
433	$CaWO_4$:Pb	
435	CaF_2:$Eu^{2+(2)}$	
440	Gd_2SiO_5: $Ce^{3+(2)}$	GSO
447	$Sr_5Cl(PO_4)_3$:Eu	
450	$BaMgAl_{10}O_{17}$:Eu	BAM
455–504	ZnS:Cu	
456, 514	$BaMgAl_{10}O_{17}$:Eu:Mn	BAM:Eu,Mn
460	$Sr_2P_2O_7$:Sn	
460	ZnS:Ag,Cl	P11*
465	ZnS:Ag,Ni	P37
470/540	$CdWO_4^{(2)}$	CWO
473	$MgWO_4$	
480	$ZnWO_4^{(2)}$	
480	$Bi_4Ge_3O_{12}^{(2)}$	BGO
480	$Sr_6P_5BO_{20}$:Eu	
482	$Ca_5(PO_4)_3F$:Sb	
494	$(Ba,Ti)_2P_2O_7$:Ti	
504	ZnO:Zn	P15
509	$Sr_5(PO_4)_3F$:Sb,Mn	
510	Gd_2O_2S:$Pr^{(3)}$	UFC
510	Gd_2O_2S:Pr,Ce,$F^{(3)}$	
510	ZnO:Zn	P24
513	Y_2O_2S:Pr^{3+}	
520	ZnS:Cu,Cl	P31
525	CdS:In	
525	Zn_2SiO_4:Mn,As	P39

Table 1 Commercial phosphors and scintillators—*continued*

Wavelength of maximum emission (nm)	Chemical formula	Designation or acronym
525	$Zn_2SiO_4:Mn^{2+}$	P1
526	$Zn_2SiO_4:Mn^{2+}$	ZSM
528	$Zn_2SiO_4:Mn;Sb_2O_3$	
530	$Y_3Al_5O_{12}:Ce^{3+(2)}$	P46
540	ZnS:Pb,Cu	P34
543	ZnS:Ag,Cu,Cl	P2
544	$Gd_2O_2S:Tb^{3+}$	P43, GOS
544	$La_2O_2S:Tb^{3+}$	P44
544	$Y_2O_2S:Tb^{3+}$	P45
544	$Y_3Al_5O_{12}:Tb^{3+}$	P53
546	$(Ce,Tb)MgAl_{11}O_{19}:Ce:Tb$	
546	$(La,Ce,Tb)PO_4:Ce:Tb$	
550	(Zn,Cd)S:Cu	P28
550	$Y_3Al_5O_{12}:Ce^{3+(2)}$	YAG:Ce
559	$MgF_2:Mn^{2+}$	P33
560	(Zn,Cd)S:Ag,Cl	P20
560	$CsI:Tl^{(2)}$	
560	$Zn_{0.6}Cd_{0.4}S:Ag$	
584	ZnS:Mn,Cu	
585	$KMgF_3:Mn^{2+}$	P26
590	$(Zn,Mg)F_2:Mn^{2+}$	P12
590	$KMgF_3:Mn^{2+}$	P19
593, 611	$(Y,Gd)BO_3:Eu^{3+}$	
593, 619, 696	$Y(P,V)O_4:Eu^{3+}$	
600	$(Zn,Mg)F_2:Mn^{2+}$	P38
605	$MgF_2:Mn^{2+}$	P21
610	$(Ca,Zn,Mg)_3(PO_4)_2:Sn$	
610	$(Y,Gd)_2O_3:Eu^{3+(2,3)}$	
610	$CaSiO_3:Mn^{2+},Pb$	P25
610	$Y_{1.34}Gd_{0.60}O_3(Eu,Pr)_{0.06}{}^{(3)}$	Hilight™
610	$Y_{1.34}Gd_{0.60}O_3(Eu,Pr)_{0.06}$	YGO
611	$Y_2O_3:Eu^{3+}$	P56, YOE
619	$YVO_4:Eu^{3+}$	P49*, YVE
626	$(Sr,Mg)_3(PO_4)_2:Sn$	
626	$Y_2O_2S:Eu^{3+}$	P54*
627	$(Sr,Mg)_3(PO_4)_2:Sn$	

Table 1 Commercial phosphors and scintillators—*continued*

Wavelength of maximum emission (nm)	**Chemical formula**	**Designation or acronym**
627	$Gd_2O_2S:Eu^{3+}$	
630	$Zn_{0.4}Cd_{0.6}S:Ag$	
635	$Zn_3(PO_4)_2:Mn^{2+}$	P27
640	$MgSiO_3:Mn^{2+}$	P13
658	$Mg_4(F)(Ge,Sn)O_6:Mn^{2+}$	
658	$Mg_4(F)GeO_6:Mn^{2+}$	
730	$Gd_3Ga_5O_{12}:Cr,Ce^{(2)}$	GGG:Cr

* These compositions are also sometimes designated as P22. P22 can be any of several compounds.

(1) Core-valence luminescence
(2) Single crystal scintillator
(3) Transparent ceramic

Appendices

APPENDIX I

Historical Note on Phosphor Recipes

The word phosphorus derives from the Greek ϕϖσϕορος*[fosforos],* combining φϖσ (light) and φερϖ (to carry), and meaning light carrying or luminous. Initially, the assignation of this word was given to any substance that evinced the property of phosphorescence. The term phosphorescence was, for a time, used to describe the emission of diffuse light from causes other than combustion; this word was used more specifically to describe substances which became luminous following exposure to light excitation. These developments and observations had their origin in alchemical attempts to manufacture noble metals through use of the evasive Philosopher’s Stone. The element phosphorus (P) was discovered in such a search by Henning Brand (1669) while experimenting with concentrated urine; distillation resulted in a white substance that gave out enough light to allow Brand to read in the dark. This phosphorescence property lent its name to the element (Figure 1).[1]

Figure 1 Depiction of the discovery of phosphorus by Brand as perceived by Joseph Wright of Derby some years later (Copyright by Derby City Council Art Galleries, permission pending).

Historically, there is documented evidence that phosphors have been produced and put to use as early as 2000 years ago as is recorded in a Chinese text (Figure 2). The phosphors described were of the persistent type and were used in a painting which glowed in the dark and was considered to some to have inexplicable magic. The methods for preparing the phosphors or the phosphors used in these paintings apparently were obtained from Japan where raw materials, such as calcium from seashells and sulfur from volcanic activity, used for the synthesis of sulfide phosphors occur naturally. The page describing the phosphorescent painting is shown in Figure 2, courtesy of Dr. M. Tamatani.[2] (A translation of the Chinese text, kindly provided by Professor Y. Zhao, is given in the caption.)

欽定四庫全書

湘山野錄 卷下

主

江南徐知諤爲潤州節度使温之少子也美姿度喜畜奇玩蠻商得一鳳頭乃飛禽之枯骨也彩翠奪目朱冠紺毛金嘴如生正類大雄雞廣五寸其腦平正可爲枕諤償錢五十萬又得畫牛一軸晝則嚙草欄外夜則歸卧欄中諤獻後主煜煜持貢闕下太宗張後苑以示羣臣俱無知者惟僧錄贊寧曰南倭（烏和反）海水或減則灘磧微露倭人拾方諸蚌胎中有餘淚數滴者得之和色著物則晝隱而夜顯沃焦山時或風撓飄擊忽有石落海岸得之滴水磨色染物則晝顯而夜晦諸學士皆以爲無稽寧曰見張騫海外異記後杜鎬檢三館書目果見於六朝舊本書中載之

眞宗深念稼穡聞占城稻耐旱西天菉豆子多而粒大各遣使以珍貨求其種占城得種二十石至今在處播之西天中印土得菉豆種二石不知今之菉豆是否始植於後苑秋成日宣近臣嘗之仍賜占稻及西天菉豆御詩

Figure 2 Copy of the Chinese text describing the acquisition of a luminescent painting by *Xu Zhi-e* written for a compilation of historical and folk tales published in the Song dynasty (960–1279 A.D.) by *Wen Ying*. In the text, reference is made to a book published in the reign of *Han Wu Di* (140–88 B.C.) which would indicate that man-made phosphors have been available for more than 2000 years. Some questions have been raised as to the accuracy of the compilations, *Xiang-shan Ye Lu,* from which this passage is taken; regardless, it is apparent that phosphorescent materials have been around for some time. The Chinese written text reads as follows (right to left):

> *Xu Zhi-e*, born South of the Yangtze River, was the yongest son of the governor of *Xu Wen*, of Run Zhou. He was fond of collecting rare antiques and other curios. On one occasion, he spent five hundred thousand in cash to acquire the head of a phoenix complete with a shining and colorful skeleton. The head possessed a red crest and a golden beak which vividly resembled those of a real rooster; it was five inches wide and the back of the head was flat, like a pillar. He acquired at the same time a painting of a cow; the painting when viewed in daylight showed the cow grazing outside an open pen; however, when viewed in the dark, the picture showed the cow resting inside the barn. *Xu* presented the painting to his sovereign, *Li Yu*, the last emperor of the Southern Tang Dynasty. Following the fall of the Tang Dynasty, the painting eventually passed to *Tai Zong*, the second emperor of the Song Dynasty. *Tai Zong* showed this painting to all his Ministers; none of them could explain the secret of the phenomena except for an officer in charge of religious matters named *Zhan Nin*. He explained that at low tide in the China Sea, southern people (Japanese) frequented the beaches to harvest nacre. Often they found that these shells contained a special liquid which when collected and mixed with paint formed a special type of ink. Writings or paintings using this ink had the properties of vanishing in daylight and becoming visible in the dark. He added that in the sea shores of the land of southern people (Japan) sometimes strong winds would grind these rocks with water to form a similar paint. All the court officials thought the Ning's explanation was nonsense; he claimed that he had obtained his information from a book, *Hai Wai Yi Ji* written by *Zhang Qian*, the famous envoy sent to the Western regions by *Han Wu Di*. Later, a scholar named *Du Gao*, who consulted some imperial collections, found the reference in a work dating back to the Six Dynasties (220–586 A.D.).

The denomination of phosphor (*phosphori*) first appeared in the seventeenth century in connection with the discovery of the Bolognian Stone (BaS) by Vincenzo Casciarolo in 1602.[3] The base material ($BaSO_4$, barite) is found near Monte Paderno as scattered stones; when properly treated it gave rise to a reddish glow which led to the scientific study of luminescent objects. There was considerable interest throughout Italy in these materials and attempts were made to use it as the Philosopher's Stone (i.e., as the catalyst for the conversion of ignoble to noble metals). Cesare La Galla described the properties of the stone in *De Phenomenis in Orbe Lunae* published in 1612; he was the first to point out that phosphorescence only occurred after calcinations and he tried to explain the phenomena as due to the slow release of fire and/or light trapped in the material during exposure. The method for preparation of the Bolognian Stone was described in detail by Pierre Potier in *Pharmacopea Spagirica* in 1625; the stone was of interest to pharmacologists because it reputedly also possessed depilatory properties. Potier's recipe is likely the first phosphor recipe on record, though published in Latin. As quoted by E.N. Harvey,[4] it reads:

> According to the light-bearing quality sought for, it ($BaSO_4$) is calcinated in two ways. The first is to reduce the stone to very fine meal, then to calcinate it in a crucible with very strong fire. The second is to reduce it to a meal and, in the place of thalerum (?), work it into cake either with water or the white of an egg. After they have dried out they are put in layers with coal in a blast furnace and, after a very hot fire has been made, they are calcinated for four or five hours. When the oven has cooled off the cakes are taken out. If not cooked sufficiently the procedure is repeated as before. Sometimes this is done three times. The best calcinations results when stones, shining, pure and diaphanous are used. From this powder various animals are formed in little boxes (pyxidiculum) which shine wonderfully in the dark.

Preliminary scientific investigations of the properties of this stone were discussed in *De Illuminabili Lapide Bononiensi Epistola* by Ovido Montalbani and in *Litheosphorus Sive De Lapide Boboniensi* by Fortinius Licetus in 1634 and 1640, respectively; both authors were professors at the famed University of Bologna. In his book, Montalbani described the various colors of light that could be obtained from the stone as a function of preparation and first suggested an analogy between the phosphorescence and burning. Licetus, on the other hand, related in some detail the history of the stone and various attempts by the learned community in Bologna to explain the origin of the emitted light. Licetus postulated, for example, that the faint light of a new moon was produced by lunar material similar to the Bolognian Stone; this suggestion lead to controversy on the source of this radiation with no lesser a luminary than Galileo Galilei. Of course, Galileo was right and the diffuse light observed in that lunar phase is due to sunlight reflected from Earth.[5]

The properties of the phosphorescent stone attracted attention throughout the Italian peninsula and the European continent and led to much speculation as to the origin of the emission. One popular belief advanced by Athanasius Kircher of Fulda (Hesse) was that the phosphorus attracted light much as a magnet attracted iron filings. Calcination was thought to produce pores in the stone; these pores then held air suffused with light whose gradual release led to the observed phosphorescence. The experiments leading to this conclusion are detailed in *Ars Magna Lucis Et Umbra*, published in 1646. News regarding the unusual properties of the *lapide Bononiensi* was carried to the British Isles by John Evelyn (1620–1706) following a visit to Bologna in 1645;[6] he reported that the recipe for the preparation of the stone had been lost by then and he apparently had not been aware of Potier's pharmacological work.

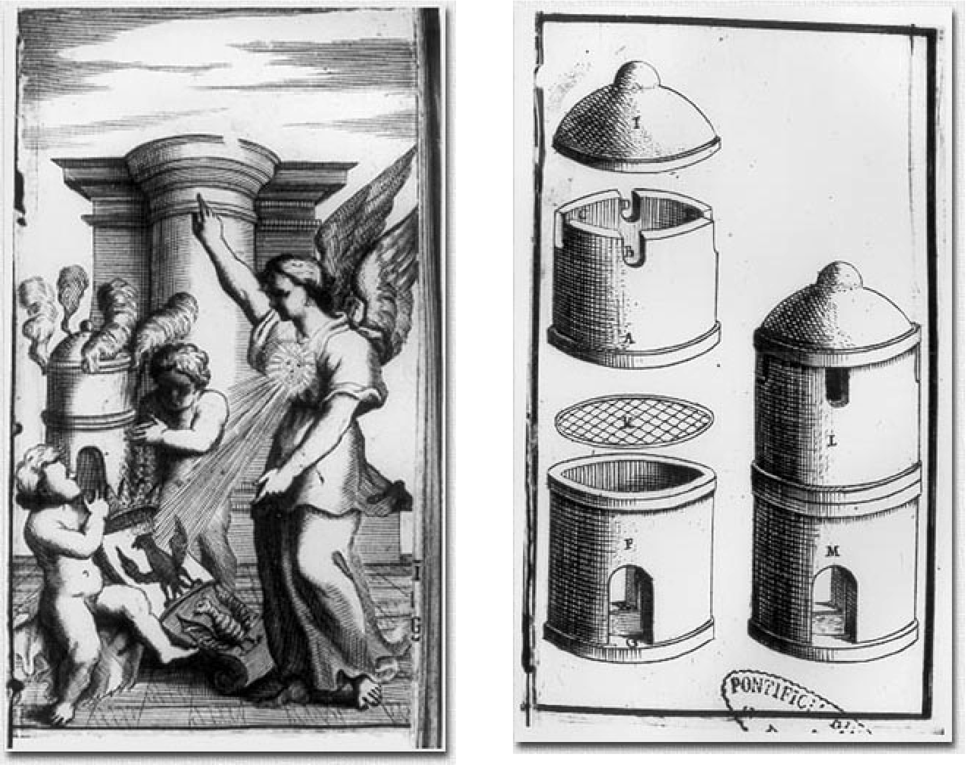


Figure 3 (left). An illustration by Marc'Antonio Cellio allegorizing the magical phosphorescent qualities of the Bolognia Stone produced in the course of calcinations. (right). Drawing of the furnace used by Casciarolo for calcinations of $BaSO_4$ (barite) to produce his magical stone. Note that the structure of this furnace is not much different than modern ovens used for similar purposes. These drawings appeared in *Il Fosforo o vero la Pietra Bolognese*, published in 1680 by Cellio and are reproduced from Ref. 3; this volume is in the University Library of Bologna.

The interest in light-emitting materials led to the invention and synthesis of three other phosphori of interest to the scientific and/or the alchemical communities of that period. The first one was due to Christian Adolph Balduin (1632–1682) who in 1675 prepared a phosphorescent form of calcium nitrate by mixing chalk and nitric acid and distilling the solution to dryness. When calcium nitrate is overheated it develops a yellowish tint and emits a reddish phosphorescence in the dark following exposure to sunlight. This compound is hygroscopic and turns to a liquid when exposed to atmosphere; he believed that the solution formed in this way represented a *spiritus mundi* and it is likely that the paint used in the Chinese paintings mentioned above was a solution of this type. Because the material needed to be kept in a sealed vessel, Balduin called his material *phosphorus hermeticus* and disclosed his results in *Aurum Superius et Inferius Aurae Superioris et Inferioris Hermeticum* which appeared simultaneous in Amsterdam and in Frankfurt in 1675. Balduin communicated his results to the Royal Society of London in 1676 and as a consequence was elected to Fellowship of the Society. His phosphor was henceforth named Balduin's phophorus.

The second material is known as Homberg's phosphorus named after Wilhelm Homberg (1652–1715) who made notable contributions to the foundation of modern chemistry and who had an interest in the photochromic properties of silver nitrate. In the course of his experimentations, Homberg synthesized calcium chloride sometime in the 1690's and showed it had phosphorescence properties.[7]

John Canton (1718–1772), a man born under modest circumstances, had a wide ranging set of scientific interests including electricity, magnetism, and optics. He showed, for example, that clouds were electrified both positively and negatively and designed experimental methods that are (even now) used to determine the sign of charges via induction. He was awarded the Copley Medal of the Royal Society twice, in 1751 for making artificial magnets and in 1765 for measuring the compressibility of water. In 1768, he reported in *Philosophical Transactions* the discovery of a strong phosphorescent material which was promptly named Canton's phosphorus (CaS).[8] His report is the earliest recipe of any phosphor written in English; Joseph Priestly cites Canton in *The History and Present State of Discoveries Relating to Vision, Light and Colours*, published in London in 1772. Priestly writes (pages 370–372):[9]

> In the next place I shall present my reader with an account of this composition of Mr. Canton's which makes an artificial phosphorus greatly superior to any single natural substance, and has the advantage of being easily and cheaply prepared; by which means it is now in every person's power to amuse himself and his friends with these curious experiments. His receipt for making it is as follows:
> "Calcinate some common oyster shells, by keeping them in a good coal fire for half an hour, and let the purest part of the calx be pulverized and sifted. Mix with three parts of this powder one part of flowers of sulphur; let this mixture be rammed in a crucible, of about an inch and a half depth, till it be almost full, and let it be placed in the middle of the fire, where it must be kept red hot, for one hour at least, and then be set by to cool. When it is cold, turn it out of the crucible, and cutting, or breaking to pieces, scrape off, upon trial, the brightest pieces; which, if good phosphorus, will be a white powder, and may be preserved by keeping it in a dry phial with a ground stopple."

We note, of course, though the language in the recipe is a bit arcane, the method described is not much different than some of those presented in Section 2 of this work.

Beginning with the discovery of the Bolognian Stone, the phenomena of and the origin of the observed phosphorescence were sources of much interest, fascination, and speculation. In addition to Kircher's conjecture as to the source of the light noted above, others such as Giullio Cesare La Galla (1576–1624) of Rome speculated that the emissions were due to the slow release of fire and light trapped in the stone in the process of calcinations, much as a sponge would absorb water and then release it as it is squeezed. He attributed this explanation to Galileo Galilei (1564–1642) himself. In 1652, another Professor from Rome, Nicola Zucchi (1586–1670), reported that the intensity of the phosphorescence emitted from the stone was proportional to the intensity of the excitation light and that the color of the light emitted was independent of the coloration of the excitation light. These conclusions were reaffirmed in 1728 by Francesco Zanotti who also asserted that the light, rather than being attracted like a sponge or magnet to the stone, emanated the radiation on its own. The idea of the Bolognian Stone attracting light and causing the phosphorescence either by reemitting the light or by reflecting it, however, persisted well into the nineteenth century.[3]

The beginning of modern studies of phosphor synthesis can be attributed to a French chemist, Theodore Sidot, who in 1866 was able to grow small ZnS crystals using sublimation. Although Sidot's original purpose was to study crystal growth, he found that his crystals phosphoresced in the dark; the synthesis methods and experimental results were reported to the French Academy by Edmond Becquerel in a note in 1866 and the material was named Sidot's blende.[10] About this time, Becquerel published his opus on light, *La Lumiere-Ses Causes et Ses Effects* (1867);[11] perhaps due to his involvement in the discovery of Sidot's blende, Becquerel discusses at length the phosphorescence of various compounds including ruby ($Al_2O_3:Cr^{3+}$). He believed that in the latter case the luminescence observed in this gem was an intrinsic property of alumina and that Cr simply played a role as an activator. This led to a long-lasting controversy with Lecoq de Boisbaudran who proved to be correct in proposing that the R-line fluorescence arose due to the presence of chromium.[12] Results of studies by V. Klatt and Philip Leonard also showed that the phosphorescence properties of CaS and other phosphori depended on the presence of metal contaminants; the emission from Sidot's blende, for example, is due to trace amounts of copper.[13]

In the late 1800's, the terminology describing phosphorescent phenomena was revised. The word phosphor began to be applied in a more limited sense (i.e., only to those materials which become self-luminous after exposure to light); as of late, the word phosphor is used to describe principally solid luminescent inorganic materials. The technical differences between fluorescence and phosphorescence were resolved following the introduction in 1888 of the word luminescence by Eilhardt Wiedemann in chemical processes;[14] the word luminescence is used to describe most light emission processes following some form of excitation. Phosphorescence and fluorescence are, however, still in use to categorize long- and short-lived luminescent emissions, respectively.

Philip E.A. Lenard and his co-workers helped to establish phosphor research on a firm scientific footing at the turn of the nineteenth and the beginning of the twentieth century. He was able to synthesize not only Sidot's blende but also a series of alkaline earth chalcogenides (sulfides and selenides) and demonstrated that the light emission of the compounds could be altered by introducing metallic ions into the materials. The latter ions form diverse centers in the material and are said to activate the luminescence; hence they were named activator ions. Because of his extensive work on phosphors detailed in a Handbuch article, alkaline chalcogenide phosphors are called Lenard phosphors.[15]

Because of the necessity for better phosphors for the display industries in the late 1940's and early 1950's, considerable work took place at the Radio Corporation of America (RCA). One of the principals there was Humboldt Leverenz who developed synthesized and investigated the properties of many the luminescent materials that are even now in use. In 1950, he published *An Introduction to Luminescence in Solids* in which he summarized much of his life's work; for many years this work was accepted as the standard text in the phosphor art and material in the book remains useful even today.[16]

Because of the advent of atomic and quantum physics and chemistry and the work of many researchers in this area of inquiry which preceded us, we have now a much better understanding as to the mechanisms which produce luminescence in solids and we are almost to the point where we can begin thinking in terms of designing and tailoring materials to our specific technical needs. The *Phosphor Handbook* contains an updated discussion of modern synthesis methods as well as the description of phosphors suitable for a variety of technical purposes. It is our hope that the present volume serves to complement the information found in that handbook.

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6. John Evelyn is a famed seventeenth century chronicler and diarist who traveled extensively in Europe in the early 1600's; he is also known for his books on flora and gardening. He was one of the principals in establishing the Royal Society, and subsequently the Philosophical Transactions of the Royal Society in 1665. Accounts of his visit to Bologna in 1644–1645 appear in the inaugural volumes of the transactions and are also found in editions of his dairies: for example, Evelyn, John, *Dairy of John Evelyn*, J.M. Dent & Sons, London (1973).
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APPENDIX II

Phosphor Materials Arranged in Order of Emission Wavelength

The phosphors and scintillators in Sections 4, 7, and 8 are listed in order of increasing wavelength of the maximum emission.

Wavelength (nm)	**Chemical formula**	**Wavelength (nm)**	**Chemical formula**
220, 310	$\mathrm{BaF_2}$	337	$\alpha\text{-}\mathrm{Ca_3(PO_4)_2{:}Pb^{2+}}$
233	$\mathrm{CaSO_4{:}Pb^{2+}}$	338	$\mathrm{(CeMg)SrAl_{11}O_{18}{:}Ce}$
254	$\mathrm{BaMgAl_{10}O_{17}{:}Ce^{3+}}$	342–347	$\mathrm{(CeMg)BaAl_{11}O_{18}{:}Ce}$
254	$\mathrm{YAlO_3{:}Ce^{3+}}$	347, 388	$\mathrm{YAl_3B_4O_{12}{:}Ce^{3+}}$
267	$\mathrm{MgSO_4{:}Pb^{2+}}$	348	$\mathrm{LaOCl{:}Bi^{3+}}$
280, 355	$\mathrm{Ca_3Al_2Si_3O_{12}{:}2\%Ce^{3+}}$	348, 370	$\mathrm{LaSiO_3Cl{:}Ce^{3+}}$
288	$\mathrm{Ca_2B_5O_9Cl{:}Pb^{2+}}$	350	$\mathrm{BaSi_2O_5{:}Pb^{2+}}$
295	$\mathrm{YAl_3B_4O_{12}{:}Bi^{3+}}$	350	$\mathrm{YAlO_3{:}Ce^{3+}}$
300, 370,		350, 575	$\beta\text{-}\mathrm{Ca_2P_2O_7{:}Sn,Mn}$
400, 460	$\mathrm{LaOBr{:}Tm^{3+}}$	351	$\mathrm{BaSi_2O_5{:}Pb}$
302, 319	$\mathrm{BaSO_4{:}Ce^{3+}}$	352, 371	$\alpha\text{-}\mathrm{Ca_3(PO_4)_2{:}Ce^{3+}}$
302, 319	$\mathrm{SrSO_4{:}Ce^{3+}}$	358–385	$\mathrm{LaBr_3{:}Ce^{3+}}$
303	$\beta\text{-}\mathrm{SrO{\cdot}3B_2O_3{:}Pb^{2+}}$	359	$\mathrm{MgBa(SO_4)_2{:}Eu^{2+}}$
305	$\mathrm{CeF_3}$	359, 636	$\mathrm{Ca_5(PO_4)_3Cl{:}Sn^{2+}}$
307	$\mathrm{MgSrAl_{10}O_{17}{:}Ce}$	360	$\mathrm{Ca_3SiO_4Cl_2{:}Pb^{2+}}$
309, 327	$\mathrm{CaSO_4{:}Ce^{3+}}$	360, 660	$\beta\text{-}\mathrm{Ca_3(PO_4)_2{:}Ce^{3+}}$
310	$\mathrm{SrB_4O_7{:}Pb^{2+}}$	362	$\mathrm{CaO{:}Pb^{2+}}$
314	$\mathrm{CaO{:}Cd^{2+}}$	363	$\mathrm{KMgF_3{:}Eu^{2+}}$
315	CsI	363, 413	$\mathrm{CaSiO_3{:}Ce^{3+}}$
315	$\mathrm{LuTaO_4{:}Nb^{5+}}$	365	$\mathrm{LuAlO_3{:}Ce^{3+}}$
319	$\mathrm{CaSr_2(PO_4)_2{:}Bi^{3+}}$	366	$\mathrm{CaS{:}Pb^{2+}}$
320	$\alpha\text{-}\mathrm{Ca_3(PO_4)_2{:}Tl^{+}}$	366	$\mathrm{CaS{:}Pb^{2+},Cl}$
320, 337	$\mathrm{CaF_2{:}Ce^{3+}}$	368	$\mathrm{SrO{\cdot}3B_2O_3{:}Eu^{2+},Cl}$
320, 344	$\mathrm{Ca_2P_2O_7{:}Ce^{3+}}$	370	$\mathrm{Sr_wF_xB_4O_{6.5}{:}Eu^{2+}}$
320, 345	$\mathrm{LaPO_4{:}Ce^{3+}}$	370	$\mathrm{SrB_4O_7{:}Eu^{2+}(F,Cl,Br)}$
325	$\mathrm{CaB_2O_4{:}Pb^{2+}}$	370	$\mathrm{YAl_3B_4O_{12}{:}Eu^{3+},Cr^{3+}}$
330	$\mathrm{YTaO_4}$	371	$\mathrm{SrB_4O_7{:}Eu}$
330–352	$\mathrm{LaCl_3{:}Ce^{3+}}$	375	$\mathrm{MgSO_4{:}Eu^{2+}}$
333	$\mathrm{CaO{:}Zn^{2+}}$	375	$\mathrm{Y_2O_3{:}Ce^{3+}}$ in $\mathrm{SiO_2}$
334, 355	$\mathrm{YPO_4{:}Ce^{3+}}$	376	$\mathrm{BaSO_4{:}Eu^{2+}}$
335	$\mathrm{CaSiO_3{:}Pb^{2+}}$	376	$\mathrm{SrSO_4{:}Eu^{2+}}$

continued

Wavelength (nm)	Chemical formula	Wavelength (nm)	Chemical formula
378	β-$\mathrm{Sr_3(PO_4)_2:Sn^{2+}}$	410	$\mathrm{MgBaP_2O_7:Eu^{2+}}$
380	$\mathrm{BaFCl:Eu^{2+}}$	410	$\mathrm{YTaO_4:Nb^{5+}}$
380	$\mathrm{Lu_2Si_2O_7:Ce^{3+}}$	410, 610	$\mathrm{BaMg_3F_8:Eu^{2+},Mn^{2+}}$
380, 415,		411	$\mathrm{YOCl:Ce^{3+}}$
440, 540	$\mathrm{Na_2Mg_3Al_2Si_2O_{10}:Tb^{3+}}$	411	$\mathrm{Zn_2SiO_4:Ti^{4+}}$
385	$\mathrm{BaFBr:Eu^{2+}}$	412	β–$\mathrm{Ca_3(PO_4)_2:Eu^{2+}}$
385	$\mathrm{BaFCl:Eu^{2+},\ Pb^{2+}}$	412, 660	β–$\mathrm{Ca_3(PO_4)_2:Eu^{2+},Mn^{2+}}$
385	$\mathrm{Ca_2MgSi_2O_7:Ce^{3+}}$	413	$\mathrm{Ca_5(PO_4)_3F:Sn^{2+}}$
385, 410,		413	$\mathrm{CaYBO_4:Bi^{3+}}$
440	$\mathrm{LaOBr:Tb^{3+}}$	413, 528	$\mathrm{Y_2O_3:Bi^{3+}}$
385, 413	$\mathrm{YBO_3:Ce^{3+}}$	414–626	$\mathrm{YOF:Tb^{3+}}$
386	$\mathrm{Mg_2Sr(SO_4)_3:Eu^{2+}}$	415	$\mathrm{Ba_2Mg_3F_{10}:Eu^{2+}}$
388	$\mathrm{CaSO_4:Eu^{2+}}$	415	$\mathrm{Ca_3Al_2Si_3O_{12}:Eu^{2+}}$
388	$\mathrm{ZnO:Al^{3+},Ga^{3+}}$	415	$\mathrm{Lu_{1-x}Y_xAlO_3:Ce^{3+}}$
388	$\mathrm{ZnO:Ga^{3+}}$	415	NaI:Tl
388, 512	$\mathrm{CaSO_4:Eu^{2+},Mn^{2+}}$	415	$\mathrm{Y_2SiO_5:Ce^{3+}}$
390	CsF	415	$\mathrm{YPO_4:V^{5+}}$
390	$\mathrm{MgSrP_2O_7:Eu^{2+}}$	416	$\mathrm{Ca_2P_2O_7:Eu^{2+}}$
390	ZnO:Ga	416, 643	$\mathrm{Ca_2P_2O_7:Eu^{2+},Mn^{2+}}$
391	$\mathrm{Ca_2MgSi_2O_7}$	418	$\mathrm{CaCl_2:Eu^{2+}}$ in $\mathrm{SiO_2}$
391	$\mathrm{CaO:Bi^{3+}}$	418–420	MSL
394	$\mathrm{BaF_2:Eu^{2+}}$	420	$\mathrm{CaWO_4}$
395	$\mathrm{KAl_{11}O_{17}:Tl^{+}}$	420	$\mathrm{CaWO_4:W}$
400	$\mathrm{BaB_8O_{13}:Eu^{2+}}$	420	$\mathrm{CsI:Na^{+}}$
400	$\mathrm{BaMg_2Si_2O_7:Eu^{2+}}$	420	$\mathrm{Lu_2SiO_5:Ce^{3+}}$
400	$\mathrm{Zn_2SiO_4:Ti}$	420	$\mathrm{Sr_2P_2O_7:Eu^{2+}}$
400, 525	P46 (70%) + P47 (30%)	420	$\mathrm{SrF_2:Eu^{2+}}$
403	$\mathrm{CaB_2P_2O_9:Eu^{2+}}$	422	β–$\mathrm{Sr_3(PO_4)_2:Eu^{2+}}$
405	$\mathrm{Mg_2Ca(SO_4)_3:Eu^{2+}}$	423	$\mathrm{CaF_2:Eu^{2+}}$
405	$\mathrm{SrCl_2:Eu^{2+}}$ in $\mathrm{SiO_2}$	423	$\mathrm{CaSiO_3:Eu^{2+}}$
405, 617	$\mathrm{Mg_2Ca(SO_4)_3:Eu^{2+},Mn^{2+}}$	423	$\mathrm{CaSiO_3:Ti^{4+}}$
405, 620	$\mathrm{MgBaP_2O_7:Eu^{2+},Mn^{2+}}$	425	β-$\mathrm{Sr_3(PO_4)_2:Eu^{2+}}$
405–432	$\mathrm{Sr(Cl,Br,I)_2:Eu^{2+}}$	425	$\mathrm{Sr_2B_5O_9Cl:Eu^{2+}}$
407	$\mathrm{CaAl_4O_7:Ce^{3+}}$	425–430	$\mathrm{(Lu,Gd)_2SiO_5:Ce^{3+}}$
407	$\mathrm{CaAl_2O_4:Ce^{3+}}$	429	$\mathrm{Ba_2Li_2Si_2O_7:Sn^{2+}}$
410	$\mathrm{Ba_3(PO_4)_2:Eu^{2+}}$	430	$\mathrm{GdNbO_4:Bi^{3+}}$
410	$\mathrm{Ca_3Al_2Si_3O_{12}:Ce^{3+}}$	432	$\mathrm{CaWO_4}$

continued

Wavelength (nm)	Chemical formula	Wavelength (nm)	Chemical formula
433	$CaBr_2:Eu^{2+}$ in SiO_2	460	$Sr_2P_2O_7:Sn^{2+}$
433	$CaWO_4:Pb$	460	$ZnS:Ag,Cl$
435	$CaF_2:Eu^{2+}$	463, 512	$CaGa_2S_4:Ce^{3+}$
435	$Ca_5(VO_4)_3Cl$	464	$La_2O_3:Bi^{3+}$
435	$CaWO_4:Pb^{2+}$	464	$SrB_4O_7:Pb^{2+},Mn^{2+}$
437	$Ba_5(PO_4)_3Cl:Eu^{2+}$	464, 532	$ZnS:Au,In$
438, 486	$CaS:Cu^+,Na^+$	465	$Sr_2P_2O_7:Sn^{2+}$
440	$BaSrMgSi_2O_7:Eu^{2+}$	465	$ZnS:Ag,Ni$
440	$Gd_2SiO_5: Ce^{3+}$	467	$CaI_2:Eu^{2+}$ in SiO_2
440	$MgBa_3Si_2O_8:Eu^{2+}$	467	$Sr_2MgSi_2O_7:Eu^{2+}$
440	$MgSrBa_2Si_2O_7:Eu^{2+}$	470	$SrMgSi_2O_6:Eu$
443	$CaAl_2O_4:Eu^{2+}$	470/540	$CdWO_4$
443	$CaS:Y^{3+}$	473	$MgWO_4$
443	$ZnS:Ag^+,Cl^-$	475	$BaAl_2S_4:Eu^{2+}$
444, 530	$ZnS:Cu^+,Cl^-$	477	$YF_3:Mn^{2+},Th^{4+}$
445	$Ba_5SiO_4Cl_6:Eu^{2+}$	477, 521	$YF_3:Mn^{2+}$
446	$Sr_5(PO_4)_3Cl:Eu^{2+}$	479	$YPO_4:Mn^{2+},Th^{4+}$
447	$Sr_5(PO_4)_3Cl:Eu$	480	$Ca_3MgSi_2O_8:Eu^{2+}$
448	$CaMgSi_2O_6:Eu^{2+}$	480	$Bi_4Ge_3O_{12}$
448	$CaS:Bi^{3+},Na$	480	$Sr_6P_5BO_{20}:Eu$
448, 390	$CaO:Cu^+$	480	$ZnWO_4$
450	$BaMgAl_{10}O_{17}:Eu^{2+}$	480, 570	$YVO_4:Dy^{3+}$
450	$CaS:Bi^{3+}$	485	$Bi_4Ge_3O_{12}$
450	$Mg_3Ca_3(PO_4)_4:Eu^{2+}$	485	$YF_3:Tm^{3+},Yb^{3+}$
451	$Sr_5(PO_4)_3F:Sn^{2+}$	486	$CaS:La^{3+}$
453	$Ca_2B_5O_9Br:Eu^{2+}$	488	$ZnS:Pb^{2+},Cl^-$
453	$Ca_2B_5O_9Cl:Eu^{2+}$	490, 680	$(ErCl_3)_{0.25}(BaCl_2)_{0.75}$
454, 490	$BaGa_2S_4:Ce^{3+}$	490–630	$Y_2O_2S:Eu^{3+}$
454, 490	$SrGa_2S_4:Ce^{3+}$	492	α-$Ca_3(PO_4)_2:Eu^{2+}$
454—800	ZnS-$CdS:Ag^+,Cl$	492	$BaGa_2S_4:Eu^{2+}$
455–504	$ZnS:Cu$	492	$Sr_5Si_4O_{10}Cl_6:Eu^{2+}$
456	$Ca_5(PO_4)_3Cl:Eu^{2+}$	492, 500, 656	$ThO_2:Pr^{3+}$
456	ZnS–$CdS:Cu,I$		
456, 514	$BaMgAl_{10}O_{17}:Eu^{2+},Mn^{2+}$	493	$SrIn_2O_4:Pr^{3+},Al^{3+}$
459	$Sr_3MgSi_2O_8:Eu^{2+}$	494	$(Ba,Ti)_2P_2O_7:Ti$
459	$ZnS:Cl^-$	495	$BaTiP_2O_7$
460	$ZnGa_2O_4$	496	$Ca_5(PO_4)_3F:Sb^{3+}$

continued

Wavelength (nm)	**Chemical formula**	**Wavelength (nm)**	**Chemical formula**
496	$CaF_2:Ce^{3+},Mn^{2+}$	521	$Ca_5(PO_4)_3Cl:Sb^{3+}$
496	$CaF_2:Mn^{2+}$	521	$ZnS:Cu^+,Al^{3+}$
496	$MgWO_4$	521, 528	$CaS:Ce^{3+}$
496	$SrAl_2S_4:Eu^{2+}$	522	$LiAl_5O_8:Mn^{2+}$
496, 670	$CaS:Pr^{3+},Pb^{2+},Cl$	522	$LiAlO_2:Mn^{2+}$
498	$KGa_{11}O_{17}:Mn^{2+}$	523	$SrAl_2O_4:Eu^{2+}$
502	$BaAl_2O_4:Eu^{2+}$	525	$CdS:In$
502	$ZnGa_2O_4:Mn^{2+}$	525	$MgAl_2O_4:Mn^{2+}$
502, 564	$SrS:Ce^{3+}$	525	$SrBaSiO_4:Eu^{2+}$
504	$BaSi_2O_5:Eu^{2+}$	525	$Zn_2SiO_4:Mn^{2+},As^{5+}$
504	$Ca_2Ba_3(PO_4)_3Cl:Eu^{2+}$	525	$Zn_2SiO_4:Mn^{2+}$
504	$MgGa_2O_4:Mn^{2+}$	527	$ZnS–CdS:Cu,Br$
504	$ZnO:Zn$	528	$CaSO_4:Ce^{3+},Mn^{2+}$
505	$SrGa_{12}O_{19}:Mn^{2+}$	528	$Zn_2SiO_4:Mn^{2+},As^{5+}$
506	$ZnO:S$	528	$ZnS–CdS:Cu,Br$
508	$\alpha\text{-}Ca_3(PO_4)_2:Sn^{2+}$	528, 608	$Zn_2SiO_4:Mn^{2+},P$
508	$Ba_2Li_2Si_2O_7:Eu^{2+}$	528, 649	$(Zn+Be)_2SiO_4:Mn^{2+}$
508	$Ba_2SiO_4:Eu^{2+}$	529	$CaF_2:U$
509, 575	$Sr_5(PO_4)_3F:Sb^{3+},Mn^{2+}$	530	$CaB_2O_4:Mn^{2+}$
510	$Sr_5(PO_4)_3F:Sb^{3+}$	530	$CaMoO_4$
510	$Gd_2O_2S:Pr^{3+}$	530	$Y_3Al_5O_{12}:Ce^{3+}$
510	$Gd_2O_2S:Pr,Ce,F$	532	$SrS:Cu^+,Na$
510	$Sr_5(PO_4)_3F:Sb^{3+}$	534	$Ba_2Li_2Si_2O_7:Sn^{2+},Mn^{2+}$
512	$Ba_2MgSi_2O_7:Eu^{2+}$	535	$Ca_2B_2O_5:Mn^{2+}$
512	$Sr_xBa_yCl_zAl_2O_{4-z/2}:Mn^{2+},Ce^{3+}$	537	$Sr_5(PO_4)_3Cl:Sb^{3+}$
513	$Y_2O_2S:Pr^{3+}$	537	$SrGa_2S_4:Eu^{2+}$
514	$\beta\text{-}SrO\cdot 3B_2O_3:Pb^{2+},Mn^{2+}$	537	$YAl_3B_4O_{12}:Th^{4+},Ce^{3+},Mn^{2+}$
514	$Ca_{0.5}Ba_{0.5}Al_{12}O_{19}:Ce^{3+},Mn^{2+}$	537	$Zn_2GeO_4:Mn^{2+}$
514	$Ca_3SiO_4Cl_2:Eu^{2+}$	539	$CaO:Sb^{3+}$
514	$Ca_3WO_6:U$	539	$CaP_2O_6:Mn^{2+}$
514	$ZnAl_2O_4:Mn^{2+}$	539	$CaS:Sn^{2+}$
514	$ZnS:Cu,Sn$	539	$CaS:Sn^{2+},F$
517	$CaLaB_3O_7:Ce^{3+},Mn^{2+}$	540	$MgBa_2(PO_4)_2:U$
519	$CdS:In$	540	$ZnS:Pb,Cu$
519	$SrAl_{12}O_{19}:Ce^{3+},Mn^{2+}$	540	$ZnS\text{-}CdS(75–25)$
520	$MgBa_2(PO_4)_2:Sn^{2+}$	542	$Ca_2MgSi_2O_7:Eu^{2+}$
520	$SrAl_{12}O_{19}:Eu^{2+},Mn^{2+}$	542	$LaSiO_3Cl:Ce^{3+},Tb^{3+}$

continued

Wavelength (nm)	Chemical formula	Wavelength (nm)	Chemical formula
542	$YAl_3B_4O_{12}:Ce^{3+},Tb^{3+}$	550, 665	$YF_3:Er^{3+},Yb^{3+}$
542	$ZnB_2O_4:Mn^{2+}$	550, 670	$BaY_2F_8:Er^{3+},Yb^{3+}$
542, 550	$Y_2O_3:Tb^{3+}$	551, 636	$ZnS:Eu^{2+}$
542, 689	$Ca_2MgSi_2O_7:Eu^{2+},Mn^{2+}$	551	$Ba_5(PO_4)_3Cl:U$
542–549	$CaS:Tb^{3+}$	551	$Sr_3WO_6:U$
542–549	$Gd_2O_2S:Tb^{3+}$	551	$ZnS:Eu^{2+}$
542–549	$Y_2O_2S:Tb^{3+}$	556	$Sr_2SiO_4:Eu^{2+}$
543	$CaAl_2O_4:Tb^{3+}$	556–608	$CaS:Sm^{3+}$
543	$MgCeAl_{11}O_{19}:Tb^{3+}$	559	$CaGa_2S_4:Eu^{2+}$
543	$ThO_2:Tb^{3+}$	559	$MgF_2:Mn^{2+}$
543	$Y_2O_3:Ce^{3+},Tb^{3+}$	560	$CsI:Tl$
543	$Y_2O_3:Tb^{3+}$ in SiO_2	560	$Zn_{0.6}Cd_{0.4}S:Ag$
543	$YAlO_3:Tb^{3+}$	562	$Y_2O_3:Er^{3+}$
543	$ZnS:Ag,Cu,Cl$	563	$Ba_3WO_6:U$
544	$(Y,Gd)BO_3:Tb^{3+}$	564	$CaAl_4O_7:Pb^{2+},Mn^{2+}$
544	$Ca_2La_2BO_{6.5}:Pb^{2+}$	564–644	$LaAlO_3:Sm^{3+}$
544	$CaAl_2O_4:Mn^{2+}$	566	$SrSO_4:Eu^{2+},Mn^{2+}$
544	$La_2O_2S:Tb^{3+}$	566–620	$CaO:Sm^{3+}$
544	$SrS:Mn^{2+}$	571	$CaSiO_3:Pb^{2+},Mn^{2+}$
544	$Y_2O_2S:Tb^{3+}$	571	$Sr_5(PO_4)_3F:Mn^{2+}$
544	$Y_2O_3:Ho^{3+}$	573	$Ca_5(PO_4)_3F:Mn^{2+}$
544	$Y_3Al_5O_{12}:Tb^{3+}$	574	$Li_2CaP_2O_7:Ce^{3+},Mn^{2+}$
544–549	$CaO:Tb^{3+}$	574	$Sr_5(PO_4)_3Cl:Mn^{2+}$
545	$YAl_3B_4O_{12}:Ce^{3+},Mn^{2+}$	575	$Mg_3SiO_3F_4:Ti^{4+}$
545	$YPO_4:Ce^{3+},Tb^{3+}$	577–630	$YOBr:Eu^{3+}$
546	$(Ce,Tb)MgAl_{11}O_{19}:Ce:Tb$	577–670	$LiInO_2:Sm^{3+}$
546	$(La,Ce,Tb)PO_4:Ce:Tb$	577–695	$LaAsO_4:Eu^{3+}$
546	$CaF_2:Ce^{3+},Tb^{3+}$	579	$ZnS:P$
546	$CaS:Sb^{3+}$	579	$ZnS:P^{3-},Cl^{-}$
546	$CaS:Sb^{3+},Na$	580	$Y_3Al_5O_{12}:Eu^{3+}$
546	$CaS:Tb^{3+},Cl$	582	$ZnS:Mn^{2+}$
546	$La_2O_3:Pb^{2+}$	582	$ZnS\text{-}CdS:Ag,Br,Ni$
550	$(Zn,Cd)S:Cu$	584	$ZnS:Mn,Cu$
550	$CsI:Tl^{+}$	585	$KMgF_3:Mn^{2+}$
550	$Na_3Ce(PO_4)_2:Tb^{3+}$	585	$MgCaP_2O_7:Mn^{2+}$
550	$NaYF_4:Er^{3+},Yb^{3+}$	585	$ZnF_2:Mn^{2+}$
550	$Y_3Al_5O_{12}:Ce^{3+}$	585, 689	$CaMgSi_2O_6:Eu^{2+},Mn^{2+}$

continued

Wavelength (nm)	Chemical formula	Wavelength (nm)	Chemical formula
586	$LaAlB_2O_6:Eu^{3+}$	608	$CaS:Pb^{2+},Mn^{2+}$
586, 591,		608	$SrGa_2S_4:Pb^{2+}$
683, 695	$LaPO_4:Eu^{3+}$	608	$SrSO_4:Bi$
586–699	$LaVO_4:Eu^{3+}$	608	$YBO_3:Eu^{3+}$
588	$CaS:Mn^{2+}$	609	$CaYBO_4:Eu^{3+}$
588	$MgS:Eu^{2+}$	610	$(Y,Gd)_2O_3:Eu^{3+}$
588, 660	$MgB_2O_4:Mn^{2+}$	610	$(Ca,Zn,Mg)_3(PO_4)_2:Sn$
588, 827	$CaO:Tl^{+}$	610	$CaSiO_3:Mn^{2+},Pb$
589–627	$YOF:Eu^{3+}$	610	$Y_{1.34}Gd_{0.60}O_3(Eu,Pr)_{0.06}$
590	$(Zn,Mg)F_2:Mn^{2+}$	611	$Ca_5B_2SiO_{10}:Eu^{3+}$
590	$Ca_5(PO_4)_3Cl:Mn^{2+}$	611	$CaGa_2S_4:Pb^{2+}$
590	$CaGa_2O_4:Mn^{2+}$	611	$CaLaBO_4:Eu^{3+}$
590	$CaGa_4O_7:Mn^{2+}$	611	$CaYB_{0.8}O_{3.7}:Eu^{3+}$
590	$CaO:Eu^{3+},Na^{+}$	611	$Na_{1.23}K_{0.42}Eu_{0.12}TiSi_4O_{11}:Eu^{3+}$
590	$KMgF_3:Mn^{2+}$	611	$SrY_2O_3:Eu^{3+}$
590	$MgF_2:Mn^{2+}$	611	$Y_2O_3:Eu^{3+}$
590	$Sr_5(PO_4)_3Cl:Eu^{2+},Pr^{3+}$	612	$CaTiO_3:Eu^{3+}$
590	$Y_4Al_2O_9:Eu^{3+}$	612	$CaTiO_3:Pr^{3+}$
592, 608,		612	$NaYO_2:Eu^{3+}$
629	$ThO_2:Eu^{3+}$	612	$SrAl_4O_7:Eu^{3+}$
593	$CaCl_2:Eu^{2+},Mn^{2+}$ in SiO_2	612	$Y_2O_3:Eu^{3+}$ in SiO_2
593, 619		614	$CaMoO_4:Eu^{3+}$
696	$YVO_4:Eu^{3+}$	614	$CaSO_4:Bi$
593, 611,		614	$LaBO_3:Eu^{3+}$
629	$(Y,Gd)BO_3:Eu^{3+}$	614	$LaOCl:Eu^{3+}$
593, 619,		614	$YAl_3B_4O_{12}:Eu^{3+}$
696	$Y(P,V)O_4:Eu^{3+}$	614	$\beta\text{-}Sr_3(PO_4)_2:Sn^{2+},Mn^{2+}(Al)$
594, 617,		614–699	$LiLaO_2:Eu^{3+}$
702	$K_2La_2Ti_3O_{10}:Eu^{3+}$	615	$Ba_2SiO_4:Ce^{3+},Li^{+},Mn^{2+}$
595, 620,		615	$CaO:Eu^{3+}$
710	$YPO_4:Eu^{3+}$	615	$SrTiO_3:Pr^{3+}$
596	$KMgF_3:Mn^{2+}$	615	$YAsO_4:Eu^{3+}$
599	$CaO:Mn^{2+}$	615	$LiCeBa_4Si_4O_{14}:Mn^{2+}$
600	ZnS–CdS (50–50)	615	$LiCeSrBa_3Si_4O_{14}:Mn^{2+}$
602	$YAlO_3:Sm^{3+}$	615–695	$YAlO_3:Eu^{3+}$
605	$LaAlO_3:Eu^{3+}$	617	$CaGeO_3:Mn^{2+}$
605	$LiInO_2:Eu^{3+}$	617	$CaY_2ZrO_6:Eu^{3+}$

continued

Wavelength (nm)	Chemical formula	Wavelength (nm)	Chemical formula
617	$SrTiO_3:Pr^{3+},Al^{3+}$	642	$BaS:Au,K$
618	$CdS:In,Te$	645	$ZnO:Bi^{3+}$
620	$La_2W_3O_{12}:Eu^{3+}$	646	$\beta\text{-}Ca_3(PO_4)_2:Sn^{2+}$
620	$LaAl_3B_4O_{12}:Eu^{3+}$	646	$ZnGa_2S_4:Mn^{2+}$
620	$MgYBO_4:Eu^{3+}$	646	$ZnS:Mn^{2+},Te^{2+}$
620	$Na_{1.23}K_{0.42}Eu_{0.12}TiSi_5O_{13}$	646	$ZnSe:Cu^{+},Cl$
	$\cdot xH_2O:Eu^{3+}$	649	$CaS:Eu^{2+}$
620	$SrS:Eu^{2+}$	646	$ZnS\text{-}ZnTe:Mn^{2+}$ 98-2
620	$YOCl:Eu^{3+}$	650	$ZnS:Te,Mn$
620	$ZnMg_2(PO_4)_2:Mn^{2+}$	658	$Mg_2TiO_4:Mn^{4+}$
621	$CaYAlO_4:Eu^{3+}$	658	$Mg_4(F)(Ge,Sn)O_6:Mn^{2+}$
623	$LiAlF_4:Mn^{2+}$	658	$Mg_4(F)GeO_6:Mn^{2+}$
623	$ZnS:Sn,Ag$	660	$Mg_2SiO_4:Mn^{2+}$
623	$ZnS:Pb,Cu$	660	$Mg_8Ge_2O_{11}F_2:Mn^{4+}$
623	$ZnS:Sn^{2+},Li^{+}$	660	$ZnS–CdS$ (25–75)
625	$Cd_2B_6O_{11}:Mn^{2+}$	661	$SrMoO_4:U$
625	$La_2O_3:Eu^{3+}$	680	$\alpha\text{-}SrO\cdot 3B_2O_3:Sm^{2+}$
626	$(Sr,Mg)_3(PO_4)_2:Sn$	681	$LiAl_5O_8:Fe^{3+}$
626	$LaOF:Eu^{3+}$	681	$MgSr_3Si_2O_8:Eu^{2+},Mn^{2+}$
626	$ZnO:Se$	684–732	$Sr_wF_xB_yO_z:Eu^{2+},Sm^{2+}$
626	$ZnS:Pb^{2+}$	685	$SrB_8O_{13}:Sm^{2+}$
627	$Gd_2O_2S:Eu^{3+}$	688, 707,	
629	$\beta\text{-}(Ca,Sr)_3(PO_4)_2:Sn^{2+},Mn^{2+}$	725	$Y_3Al_5O_{12}:Cr^{3+}$
629	$Be_2SiO_4:Mn^{2+}$	689	$ZnS:Sn$
630	$K_2SiF_6:Mn^{4+}$	695	$Na(Mg_{2-x}Mn_x)LiSi_4O_{10}F_2:Mn$
630	$Zn_{0.4}Cd_{0.6}S:Ag$	713	$CaGa_2S_4:Mn^{2+}$
633	$(Zn,Mg)_3(PO_4)_2:Mn^{2+}$	730	$Gd_3Ga_5O_{12}:Cr,Ce$
635	$Zn_3(PO_4)_2:Mn^{2+}$	730	$Gd_3Ga_5O_{12}:Cr^{3+}$
636	$CaI_2:Eu^{2+},Mn^{2+}$ in SiO_2	742	$LiAlO_2:Fe^{3+}$
639	$Zn_3(PO_4)_2:Mn^{2+}$	747	$CaS:Yb^{2+}$
640	$CdS:Te$	747	$CaS:Yb^{2+},Cl$
640	$MgSiO_3:Mn^{2+}$	760	$CaTi_{0.9}Al_{0.1}O_3:Bi^{3+}$
640	$MgSr_5(PO_4)_4:Sn^{2+}$	800	$CdS:Ag^{+},Cl^{-}$
640, 667	$Y_3Al_5O_{12}:Mn^{4+}$	1540	$Na_{1.29}K_{0.46}Er_{0.08}TiSi_4O_{11}:Eu^{3+}$
641	$ZnBa_2S_3:Mn^{2+}$		

APPENDIX III

Willi Lehmann: A Brief Biography

Information about Willi's early life in Germany has been kindly supplied by one of his sons, Hans, in the form of brief autobiography Willi wrote for his family in 1990. Willi was born born in 1914 in Dinslaken am Niederrhein. He finished elementary school in 1928 and attended a trade school for gardeners until 1931 as preparation for taking responsibilities in the family's plant nursery business. Unavoidably, world events intruded into his pastoral life and set him on a long odyssey, which would eventually bring him into the international phosphor community. Hitler assumed power in Germany in 1933 and of course affected the course of history dramatically and disastrously. Willi had a brief flirtation with the SA but did not become a member; instead, in 1934 he joined the *Deutscher Luftsport Verband,* one of the glider club precursors to the *Luftwaffe.* Participation in the club activities naturally led to his gravitating to the air force when his time came for military service in 1936.

His boot camp was in East Prussia and he did not take well to the training which was according to him "...hot, dirty and plain stupid." He consequently volunteered to become a photographer for the air force when an opportunity arose. He completed a photography course in Tutow and in 1939–1940 was promoted to corporal (*Unteroffizier*) as the head of a small photo group at the *Luftkreigsschule* in Werden, near Berlin. In the Fall of 1941, Willi was assigned to a long range reconnaissance unit on the Eastern front at Luga near Leningrad. With the war situation in flux through 1943, he found himself moving from place to place with his unit…in Cherkov (Ukraine), Kiev, Breslau (Wroclaw), Smolensk, and Minsk. After a short interlude as an engineering student, he was promoted to sergeant (*Feldwebel*) in December 1944 and immediately assigned to an active combat unit defending the home front. He was captured by American forces on February 28, 1945 and interned in Le Mans, France.

While a U.S. prisoner, Willi demonstrated some of his intrinsic versatility for in short order he become the camp's typewriter repairman. Later he moved on to become a truck mechanic in the motor pool which moved to Le Havre in December 1945. With each change of position, his circumstances in the camp improved so much so that in the summer of 1946 he made his first of five escape attempts.

On his first two escape attempts, he was recaptured in France by the French and interned first in Sedan and then near the Belgian border. On his third attempt, he was able to cross into Belgium but was captured and interned by the Belgians. He worked variously as a miner, a camp librarian and as a farmer's aid during his captivity in Belgium. He attempted again to get home in June of 1947 was caught again and confined to solitary for a period. In September of 1947, Willi managed to construct a workable bicycle out of parts from discarded bikes and was able to ride all the way to Germany and a joyful family reunion in Dinslaken.

Willi possessed a keen intellectual sense and a deep natural curiosity. From his teens and in his own words, "Work in father's nursery was pretty dull, and I started to dream about one day becoming an engineer or scientist." With the encouragement of a library clerk, he began reading mathematics books and establishing a technical background which he drew on for the rest of his life. For example, while engaged in the glider *Verband,* he became interested and did some calculations and some nascent experiments in rocket propulsion. He submitted a report on his work to the Air Ministry (*Reichluftfahrtministerium*); though the report went no further, Willi was offered a post as photographer at the rocket facilities in Peenemunde which he declined.

In the middle of his posting to the Eastern Front, Willlie was granted an extended leave so that he could attend an engineering school in Germany. This proved to be a problem since he did not possess the proper credentials (*arbitur*) to matriculate in a university level program having attended a trade rather than a traditional *Gymnasium*. Through a special dispensation, he was allowed to attend the *Techschule* in Duisberg. It was here that he was first encountered physics as a discipline and it immediately piqued his interest. In order to bypass the *arbitur* requirements, Willi attempted and passed a *Begrabtemprufung* (examination for the gifted) in the summer of 1944, just in time to return to the war.

Following his return to Germany, Willi along with a wartime friend, Claus Haake, applied for admission to the Technical University of Braunschweig in October 1947. As their initiation as students, they had to help in the reconstruction of university buildings and other facilities destroyed during the hostilities. Instruction commenced at the University in march 1948. Willi recalled that his first instructor was Erich Krautz who not only taught the Applied Physics course but also nurtured him through to his candidacy in physics (*Cand. Phys.*) in 1950. Professor Krautz also succeeded in getting Willi a scholarship which covered all his school expenses and relieved the financial burden on the Lehmann family now headed by an older brother, Paul, Willi's father having passed on in 1942.

Willi and Claus Haake obtained their *Diplom. Physiker's* (equivalent to American M.S. degree) in 1952. In view of the dearth of jobs for physicists in postwar Germany, Professor Krautz directed them to apply for positions in the lamp division of Westinghouse Electric then located in Bloomfield, New Jersey. Both were offered positions, accepted, and arrived in the States on October 1953 following an extended wait for immigration documents. During the waiting period, Willi met, wooed and wed Renate Bauer. The new Mrs. Lehmann, of course, accompanied Willi to the States and their four children (Caren, George, Hans, and Mary) were all born in the United States.

On arrival at Westinghouse, Willi was given the choice of areas to investigate. He chose to study electroluminescence and electroluminescent phosphors. His contributions in this field and his other activities at Bloomfield and later at Westinghouse R&D in Pittsburgh are detailed in the Foreword. It is interesting to note that by 1956, Willi's work on electroluminescence had attracted sufficient interest that he was approached by the University at Braunschweig to explore the possibilities of submitting his work in partial fulfillment of requirements for a doctorate degree. Indeed, his thesis entitled "The Electroluminescence of Zinc Sulfide Phosphors as an Equilibrium Process" was submitted in late 1957 and accepted. He was granted the degree of Doctor of Natural Sciences (Dr.rer.Nat) shortly thereafter.

Also as noted in the Foreword, Willi retired in 1982 at the age of 68 and took up residence in North Carolina. He thought briefly about starting his own phosphor business but rejected the idea on grounds of his lack of acumen in business matters. He acted as a consultant with Rogers Corp. and with Lawrence Livermore Laboratories in the late 1980's. In the early 1980's, he developed an interest in diffraction and the limits that it imposed on resolution and was also attracted by the furor surrounding the announcement of cold fusion.

Willi passed away on January 12, 1993 from brain cancer. Mrs. Lehmann returned to Pittsburgh and currently resides there. The children and several grandchildren appear to be prospering.

William M. Yen
Athens, Georgia

Henry F. Ivey
Coconut Grove, Florida

Materials Index

MATERIALS INDEX

$CaMoO_4:Eu^{3+}$,
$CaO:Bi^{3+}$,
$CaO:Cd^{2+}$,
$CaO:Cu^{+}$,
$CaO:Eu^{3+}$,
$CaO:Eu^{3+},Na^{+}$,
$CaO:Mn^{2+}$,
$CaO:Pb^{2+}$,
$CaO:Sb^{3+}$,
$CaO:Sm^{3+}$,
$CaO:Tb^{3+}$,
$CaO:Tl^{+}$,
$CaO:Zn^{2+}$,
$Ca_2P_2O_7:Ce^{3+}$,
$\alpha\text{-}Ca_3(PO_4)_2:Ce^{3+}$,
$\beta\text{-}Ca_3(PO_4)_2:Ce^{3+}$,
$Ca_5(PO_4)_3Cl:Eu^{2+}$,
$Ca_5(PO_4)_3Cl:Mn^{2+}$,
$Ca_5(PO_4)_3Cl:Sb^{3+}$,
$Ca_5(PO_4)_3Cl:Sn^{2+}$,
$\beta\text{-}Ca_3(PO_4)_2:Eu^{2+},Mn^{2+}$,
$Ca_5(PO_4)_3F:Mn^{2+}$,
$Ca_5(PO_4)_3F:Sb^{3+}$,
$Ca_5(PO_4)_3F:Sn^{2+}$,
$\alpha\text{-}Ca_3(PO_4)_2:Eu^{2+}$,
$\beta\text{-}Ca_3(PO_4)_2:Eu^{2+}$,
$Ca_2P_2O_7:Eu^{2+}$,
$Ca_2P_2O_7:Eu^{2+},Mn^{2+}$,
$CaP_2O_6:Mn^{2+}$,
$\alpha\text{-}Ca_3(PO_4)_2:Pb^{2+}$,
$\alpha\text{-}Ca_3(PO_4)_2:Sn^{2+}$,
$\beta\text{-}Ca_3(PO_4)_2:Sn^{2+}$,
$\beta\text{-}Ca_2P_2O_7:Sn,Mn$,
$\alpha\text{-}Ca_3(PO_4)_2:Tl^{+}$,
$CaS:Bi^{3+}$,
$CaS:Bi^{3+},Na$,
$CaS:Ce^{3+}$,
$CaS:Eu^{2+}$,
$CaS:Cu^{+},Na^{+}$,
$CaS:La^{3+}$,
$CaS:Mn^{2+}$,
$CaSO_4:Bi$,
$CaSO_4:Ce^{3+}$,
$CaSO_4:Ce^{3+},Mn^{2+}$,
$CaSO_4:Eu^{2+}$,
$CaSO_4:Eu^{2+},Mn^{2+}$,
$CaSO_4:Pb^{2+}$,
$CaS:Pb^{2+}$,
$CaS:Pb^{2+},Cl$,
$CaS:Pb^{2+},Mn^{2+}$,
$CaS:Pr^{3+},Pb^{2+},Cl$,
$CaS:Sb^{3+}$,
$CaS:Sb^{3+},Na$,
$CaS:Sm^{3+}$,
$CaS:Sn^{2+}$,
$CaS:Sn^{2+},F$,
$CaS:Tb^{3+}$,
$CaS:Tb^{3+},Cl$,
$CaS:Y^{3+}$,
$CaS:Yb^{2+}$,
$CaS:Yb^{2+},Cl$,
$CaSiO_3:Ce^{3+}$,
$Ca_3SiO_4Cl_2:Eu^{2+}$,
$Ca_3SiO_4Cl_2:Pb^{2+}$,
$CaSiO_3:Eu^{2+}$,
$CaSiO_3:Mn^{2+},Pb$,
$CaSiO_3:Pb^{2+}$,
$CaSiO_3:Pb^{2+},Mn^{2+}$,
$CaSiO_3:Ti^{4+}$,
$CaSr_2(PO_4)_2:Bi^{3+}$,
$\beta\text{-}(Ca,Sr)_3(PO_4)_2:Sn^{2+},Mn^{2+}$,
$CaTi_{0.9}Al_{0.1}O_3:Bi^{3+}$,
$CaTiO_3:Eu^{3+}$,
$CaTiO_3:Pr^{3+}$,
$Ca_5(VO_4)_3Cl$,
$CaWO_4$,
$CaWO_4:Pb^{2+}$,
$CaWO_4:W$,
$Ca_3WO_6:U$,
$CaYAlO_4:Eu^{3+}$,
$CaYBO_4:Bi^{3+}$,
$CaYBO_4:Eu^{3+}$,
$CaYB_{0.8}O_{3.7}:Eu^{3+}$,
$CaY_2ZrO_6:Eu^{3+}$,
$(Ca,Zn,Mg)_3(PO_4)_2:Sn$,
CeF_3,
$(CeMg)BaAl_{11}O_{18}:Ce$,
$(CeMg)SrAl_{11}O_{18}:Ce$,
$(Ce,Tb)MgAl_{11}O_{19}:Ce:Tb$,
$Cd_2B_6O_{11}:Mn^{2+}$,
$CdS:Ag^{+},Cl^{-}$,
$CdS:In$,
$CdS:In$, Ultrafast,
$CdS:In,Te$,

$CdS{:}Te$,
$CdWO_4$,
CsF,
CsI
$CsI{:}Na^+$,
$CsI{:}Tl$,

E

$(ErCl_3)_{0.25}(BaCl_2)_{0.75}$,

G

$GaN{:}Zn$,
$Gd_3Ga_5O_{12}{:}Cr^{3+}$,
$Gd_3Ga_5O_{12}{:}Cr,Ce$,
$GdNbO_4{:}Bi^{3+}$,
$Gd_2O_2S{:}Eu^{3+}$,
$Gd_2O_2S{:}Pr^{3+}$,
$Gd_2O_2S{:}Pr,Ce,F$,
$Gd_2O_2S{:}Tb^{3+}$,
$Gd_2SiO_5{:}Ce^{3+}$,

K

$KAl_{11}O_{17}{:}Tl^+$,
$KGa_{11}O_{17}{:}Mn^{2+}$,
$K_2La_2Ti_3O_{10}{:}Eu$,
$KMgF_3{:}Eu^{2+}$,
$KMgF_3{:}Mn^{2+}$,
$K_2SiF_6{:}Mn^{4+}$,

L

$LaAl_3B_4O_{12}{:}Eu^{3+}$,
$LaAlB_2O_6{:}Eu^{3+}$,
$LaAlO_3{:}Eu^{3+}$,
$LaAlO_3{:}Sm^{3+}$,
$LaAsO_4{:}Eu^{3+}$,
$LaBr_3{:}Ce^{3+}$,
$LaBO_3{:}Eu^{3+}$,
$(La,Ce,Tb)PO_4{:}Ce{:}Tb$,
$LaCl_3{:}Ce^{3+}$,
$La_2O_3{:}Bi^{3+}$,
$LaOBr{:}Tb^{3+}$,
$LaOBr{:}Tm^{3+}$,
$LaOCl{:}Bi^{3+}$,
$LaOCl{:}Eu^{3+}$,
$LaOF{:}Eu^{3+}$,
$La_2O_3{:}Eu^{3+}$,
$La_2O_3{:}Pb^{2+}$,
$La_2O_2S{:}Tb^{3+}$,
$LaPO_4{:}Ce^{3+}$,
$LaPO_4{:}Eu^{3+}$,
$LaSiO_3Cl{:}Ce^{3+}$,
$LaSiO_3Cl{:}Ce^{3+},Tb^{3+}$,
$LaVO_4{:}Eu^{3+}$,
$La_2W_3O_{12}{:}Eu^{3+}$,
$LiAlF_4{:}Mn^{2+}$,
$LiAl_5O_8{:}Fe^{3+}$,
$LiAlO_2{:}Fe^{3+}$,
$LiAlO_2{:}Mn^{2+}$,
$LiAl_5O_8{:}Mn^{2+}$,
$Li_2CaP_2O_7{:}Ce^{3+},Mn^{2+}$,
$LiCeBa_4Si_4O_{14}{:}Mn^{2+}$,
$LiCeSrBa_3Si_4O_{14}{:}Mn^{2+}$,
$LiInO_2{:}Eu^{3+}$,
$LiInO_2{:}Sm^{3+}$,
$LiLaO_2{:}Eu^{3+}$,
$LuAlO_3{:}Ce^{3+}$,
$(Lu,Gd)_2SiO_5{:}Ce^{3+}$,
$Lu_2SiO_5{:}Ce^{3+}$,
$Lu_2Si_2O_7{:}Ce^{3+}$,
$LuTaO_4{:}Nb^{5+}$,
$Lu_{1-x}Y_xAlO_3{:}Ce^{3+}$,

M

$MgAl_2O_4{:}Mn^{2+}$,
$MgSrAl_{10}O_{17}{:}Ce$,
$MgB_2O_4{:}Mn^{2+}$,
$MgBa_2(PO_4)_2{:}Sn^{2+}$,
$MgBa_2(PO_4)_2{:}U$,
$MgBaP_2O_7{:}Eu^{2+}$,
$MgBaP_2O_7{:}Eu^{2+},Mn^{2+}$,
$MgBa_3Si_2O_8{:}Eu^{2+}$,
$MgBa(SO_4)_2{:}Eu^{2+}$,
$Mg_3Ca_3(PO_4)_4{:}Eu^{2+}$,
$MgCaP_2O_7{:}Mn^{2+}$,
$Mg_2Ca(SO_4)_3{:}Eu^{2+}$,
$Mg_2Ca(SO_4)_3{:}Eu^{2+},Mn^{2+}$,
$MgCeAl_{11}O_{19}{:}Tb^{3+}$,
$Mg_4(F)GeO_6{:}Mn^{2+}$,
$Mg_4(F)(Ge,Sn)O_6{:}Mn^{2+}$,
$MgF_2{:}Mn^{2+}$,
$MgGa_2O_4{:}Mn^{2+}$,
$Mg_8Ge_2O_{11}F_2{:}Mn^{4+}$,
$MgS{:}Eu^{2+}$,

$MgSiO_3:Mn^{2+}$,
$Mg_2SiO_4:Mn^{2+}$,
$Mg_3SiO_3F_4:Ti^{4+}$,
$MgSO_4:Eu^{2+}$,
$MgSO_4:Pb^{2+}$,
$MgSrBa_2Si_2O_7:Eu^{2+}$,
$MgSrP_2O_7:Eu^{2+}$,
$MgSr_5(PO_4)_4:Sn^{2+}$,
$MgSr_3Si_2O_8:Eu^{2+},Mn^{2+}$,
$Mg_2Sr(SO_4)_3:Eu^{2+}$,
$Mg_2TiO_4:Mn^{4+}$,
$MgWO_4$,
$MgYBO_4:Eu^{3+}$,
MSL,

N

$Na_3Ce(PO_4)_2:Tb^{3+}$,
NaI:Tl,
$Na_{1.23}K_{0.42}Eu_{0.12}TiSi_4O_{11}:Eu^{3+}$,
$Na_{1.23}K_{0.42}Eu_{0.12}TiSi_5O_{13}\cdot xH_2O:Eu^{3+}$,
$Na_{1.29}K_{0.46}Er_{0.08}TiSi_4O_{11}:Eu^{3+}$,
$Na_2Mg_3Al_2Si_2O_{10}:Tb$,
$Na(Mg_{2-x}Mn_x)LiSi_4O_{10}F_2:Mn$,
$NaYF_4:Er^{3+},Yb^{3+}$,
$NaYO_2:Eu^{3+}$,

P

P46 (70%) + P47 (30%),

S

$SrAl_{12}O_{19}:Ce^{3+},Mn^{2+}$,
$SrAl_2O_4:Eu^{2+}$,
$SrAl_4O_7:Eu^{3+}$,
$SrAl_{12}O_{19}:Eu^{2+},Mn^{2+}$,
$SrAl_2S_4:Eu^{2+}$,
$Sr_2B_5O_9Cl:Eu^{2+}$,
$SrB_4O_7:Eu^{2+}(F,Cl,Br)$,
$SrB_4O_7:Pb^{2+}$,
$SrB_4O_7:Pb^{2+},Mn^{2+}$,
$SrB_8O_{13}:Sm^{2+}$,
$Sr_xBa_yCl_zAl_2O_{4-z/2}:Mn^{2+},Ce^{3+}$,
$SrBaSiO_4:Eu^{2+}$,
$Sr(Cl,Br,I)_2:Eu^{2+}$ in SiO_2,
$SrCl_2:Eu^{2+}$ in SiO_2,
$Sr_5Cl(PO_4)_3:Eu$,
$Sr_wF_xB_4O_{6.5}:Eu^{2+}$,
$Sr_wF_xB_yO_z:Eu^{2+},Sm^{2+}$,
$SrF_2:Eu^{2+}$,
$SrGa_{12}O_{19}:Mn^{2+}$,
$SrGa_2S_4:Ce^{3+}$,
$SrGa_2S_4:Eu^{2+}$,
$SrGa_2S_4:Pb^{2+}$,
$SrIn_2O_4:Pr^{3+},Al^{3+}$,
$(Sr,Mg)_3(PO_4)_2:Sn$,
$SrMgSi_2O_6:Eu^{2+}$,
$Sr_2MgSi_2O_7:Eu^{2+}$,
$Sr_3MgSi_2O_8:Eu^{2+}$,
$SrMoO_4:U$,
$SrO\cdot 3B_2O_3:Eu^{2+},Cl$,
β–$SrO\cdot 3B_2O_3:Pb^{2+}$,
β–$SrO\cdot 3B_2O_3:Pb^{2+},Mn^{2+}$,
α–$SrO\cdot 3B_2O_3:Sm^{2+}$,
$Sr_6P_5BO_{20}:Eu$,
$Sr_5(PO_4)_3Cl:Eu^{2+}$,
$Sr_5(PO_4)_3Cl:Eu^{2+},Pr^{3+}$,
$Sr_5(PO_4)_3Cl:Mn^{2+}$,
$Sr_5(PO_4)_3Cl:Sb^{3+}$,
$Sr_2P_2O_7:Eu^{2+}$,
β–$Sr_3(PO_4)_2:Eu^{2+}$,
$Sr_5(PO_4)_3F:Mn^{2+}$,
$Sr_5(PO_4)_3F:Sb^{3+}$,
$Sr_5(PO_4)_3F:Sb^{3+},Mn^{2+}$,
$Sr_5(PO_4)_3F:Sn^{2+}$,
$Sr_2P_2O_7:Sn^{2+}$,
β–$Sr_3(PO_4)_2:Sn^{2+}$,
β-$Sr_3(PO_4)_2:Sn^{2+},Mn^{2+}(Al)$,
$SrS:Ce^{3+}$,
$SrS:Eu^{2+}$,
$SrS:Mn^{2+}$,
$SrS:Cu^{+},Na$,
$SrSO_4:Bi$,
$SrSO_4:Ce^{3+}$,
$SrSO_4:Eu^{2+}$,
$SrSO_4:Eu^{2+},Mn^{2+}$,
$Sr_5Si_4O_{10}Cl_6:Eu^{2+}$,
$Sr_2SiO_4:Eu^{2+}$,
$SrTiO_3:Pr^{3+}$,
$SrTiO_3:Pr^{3+},Al^{3+}$,
$Sr_3WO_6:U$,
$SrY_2O_3:Eu^{3+}$,

T

$ThO_2:Eu^{3+}$,
$ThO_2:Pr^{3+}$,
$ThO_2:Tb^{3+}$,

Y

$YAl_3B_4O_{12}:Bi^{3+}$,
$YAl_3B_4O_{12}:Ce^{3+}$,
$YAl_3B_4O_{12}:Ce^{3+},Mn^{2+}$,
$YAl_3B_4O_{12}:Ce^{3+},Tb^{3+}$,
$YAl_3B_4O_{12}:Eu^{3+}$,
$YAl_3B_4O_{12}:Eu^{3+},Cr^{3+}$,
$YAl_3B_4O_{12}:Th^{4+},Ce^{3+},Mn^{2+}$,
$YAlO_3:Ce^{3+}$,
$Y_3Al_5O_{12}:Ce^{3+}$,

$Y_3Al_5O_{12}:Cr^{3+}$,
$YAlO_3:Eu^{3+}$,
$Y_3Al_5O_{12}:Eu^{3+}$,
$Y_4Al_2O_9:Eu^{3+}$,
$Y_3Al_5O_{12}:Mn^{4+}$,
$YAlO_3:Sm^{3+}$,
$YAlO_3:Tb^{3+}$,
$Y_3Al_5O_{12}:Tb^{3+}$,
$YAsO_4:Eu^{3+}$,
$YBO_3:Ce^{3+}$,
$YBO_3:Eu^{3+}$,
$YF_3:Er^{3+},Yb^{3+}$,
$YF_3:Mn^{2+}$,
$YF_3:Mn^{2+},Th^{4+}$,
$YF_3:Tm^{3+},Yb^{3+}$,
$(Y,Gd)BO_3:Eu$,
$(Y,Gd)BO_3:Tb$,
$(Y,Gd)_2O_3:Eu^{3+}$,
$Y_{1.34}Gd_{0.60}O_3(Eu,Pr)_{0.06}$,
$Y_2O_3:Bi^{3+}$,
$YOBr:Eu^{3+}$,
$Y_2O_3:Ce$,
$Y_2O_3:Er^{3+}$,
$Y_2O_3:Eu^{3+}$ (YOE),
$Y_2O_3:Ce^{3+},Tb^{3+}$,
$YOCl:Ce^{3+}$,
$YOCl:Eu^{3+}$,
$YOF:Eu^{3+}$,
$YOF:Tb^{3+}$,
$Y_2O_3:Ho^{3+}$,
$Y_2O_2S:Eu^{3+}$,
$Y_2O_2S:Pr^{3+}$,
$Y_2O_2S:Tb^{3+}$,
$Y_2O_3:Tb^{3+}$,
$YPO_4:Ce^{3+}$,
$YPO_4:Ce^{3+},Tb^{3+}$,
$YPO_4:Eu^{3+}$,
$YPO_4:Mn^{2+},Th^{4+}$,
$YPO_4:V^{5+}$,
$Y(P,V)O_4:Eu$,
$Y_2SiO_5:Ce^{3+}$,
$YTaO_4$,
$YTaO_4:Nb^{5+}$,
$YVO_4:Dy^{3+}$,
$YVO_4:Eu^{3+}$,

Z

$ZnAl_2O_4:Mn^{2+}$,
$ZnB_2O_4:Mn^{2+}$,
$ZnBa_2S_3:Mn^{2+}$,
$(Zn+Be)_2SiO_4:Mn^{2+}$,
$Zn_{0.4}Cd_{0.6}S:Ag$,
$Zn_{0.6}Cd_{0.4}S:Ag$,
$(Zn,Cd)S:Ag,Cl$,
$(Zn,Cd)S:Cu$,
$ZnF_2:Mn^{2+}$,
$ZnGa_2O_4$,
$ZnGa_2O_4:Mn^{2+}$,
$ZnGa_2S_4:Mn^{2+}$,
$Zn_2GeO_4:Mn^{2+}$,
$(Zn,Mg)F_2:Mn^{2+}$,
$ZnMg_2(PO_4)_2:Mn^{2+}$,
$(Zn,Mg)_3(PO_4)_2:Mn^{2+}$,
$ZnO:Al^{3+},Ga^{3+}$,
$ZnO:Bi^{3+}$,
$ZnO:Ga^{3+}$,
ZnO:Ga, Ultrafast,
ZnO-CdO:Ga, Ultrafast,
ZnO:S,
ZnO:Se,
ZnO:Zn,
$ZnS:Ag^+,Cl^-$,
ZnS:Ag,Cu,Cl,
ZnS:Ag,Ni,
ZnS:Au,In,
ZnS-CdS (25-75),
ZnS-CdS (50-50),
ZnS-CdS (75-25),
ZnS-CdS:Ag,Br,Ni,
$ZnS\text{-}CdS:Ag^+,Cl$,
ZnS-CdS:Cu,Br high brightness,
ZnS-CdS:Cu,Br long life,
ZnS-CdS:Cu,I,

$ZnS:Cl^-$,
$ZnS:Eu^{2+}$,
$ZnS:Cu$,
$ZnS:Cu^+,Al^{3+}$,
$ZnS:Cu^+,Cl^-$,
$ZnS:Cu,Sn$,
$ZnS:Eu^{2+}$,
$ZnS:Mn^{2+}$,
$ZnS:Mn,Cu$,
$ZnS:Mn^{2+},Te^{2+}$,
$ZnS:P$,
$ZnS:P^{3-},Cl^-$,
$ZnS:Pb^{2+}$,
$ZnS:Pb^{2+},Cl^-$,
$ZnS:Pb,Cu$,
$Zn_3(PO_4)_2:Mn^{2+}$,
$Zn_2SiO_4:Mn^{2+}$,
$Zn_2SiO_4:Mn^{2+},As^{5+}$,
$Zn_2SiO_4:Mn;Sb_2O_3$,
$Zn_2SiO_4:Mn^{2+},P$,
$Zn_2SiO_4:Ti^{4+}$,
$ZnS:Sn^{2+}$,
$ZnS:Sn,Ag$,
$ZnS:Sn^{2+},Li^+$,
$ZnS:Te,Mn$,
$ZnS\text{-}ZnTe:Mn^{2+}$
$ZnSe:Cu^+,Cl$,
$ZnWO_4$,