LONG-PERSISTENCE BLUE PHOSPHORS

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ABSTRACT

This invention relates to phosphors including long-persistence blue phosphors. Phosphors of the invention are represented by the general formula:

$$\text{MO}_{m}\text{Al}_3\text{O}_3: \text{Eu}^{2+}, \text{R}^{3+}$$

wherein m is a number ranging from about 1.6 to about 2.2, M is Sr or a combination of Sr with Ca and Ba or both, R$^{3+}$ is a trivalent metal ion or trivalent Bi or a mixture of these trivalent ions, Eu$^{2+}$ is present at a level up to about 5 mol % of M, and R$^{3+}$ is present at a level up to about 5 mol % of M. Phosphors of this invention include powders, ceramics, single crystals and single crystal fibers. A method of manufacturing improved phosphors and a method of manufacturing single crystal phosphors are also provided.

30 Claims, 16 Drawing Sheets

OTHER PUBLICATIONS


OTHER PUBLICATIONS


FIG. 1
FIG. 2
FIG. 3
FIG. 4

Intensity (normalized)

D (Å)

2.25

1.82

1.54

1.00

5

4

3

2

1

0

30

20

10

0

THETA (degree)

Intensity (counts/second)

1416.0

1274.4

1132.8

991.2

849.6

708.0

566.4

424.8

283.2

141.6
FIG. 5
FIG. 6
FIG. 7
FIG. 8
FIG. 9
FIG. 10

Excitation

Emission

Intensity (a.u.)

Wavelength (nm)
FIG. 11
FIG. 12

Intensity (a.u.) vs. Time (second)
FIG. 13
FIG. 14

- Intensity (a.u.)
  - 10^6
  - 10^5
  - 10^4
  - 10^3
  - 10^2

- Delay Time (minute)
  - 1
  - 10
  - 100
  - 1000

Lines a, b, and c are plotted on the graph.
FIG. 15
FIG. 16
1

LONG-PERSISTENCE BLUE PHOSPHORS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application takes priority under 35 U.S.C. §119(e) from U.S. provisional applications Ser. No. 60/064,690, filed Nov. 7, 1997 and Ser. No. 60/064,691, filed Nov. 7, 1997, both of which are incorporated by reference herein to the extent not inconsistent herewith.

This invention was made at least in part with U.S. government funding through NASA grant NCCW-0088 and NCC5-252, ARO DAAH04-96-10416 and DOE DE-FG02-94ER75764. The United States government has certain rights in this invention.

FIELD OF THE INVENTION

This invention is generally related to phosphors and more particularly is related to long-persistence blue phosphors. The invention is also directed to methods for making phosphors in powder and ceramic form as well as single crystal phosphors. The invention is further directed to articles of manufacture comprising the phosphors of this invention.

BACKGROUND OF THE INVENTION

Persistent phosphorescing materials, such as ZnS:Cu,Co, ZnCdS:Cu and CaSrS:Bi, have been used for many years. Recently a much brighter and longer lasting green phosphor, SrAl₂O₄:Eu²⁺:Dy³⁺ has been produced.

Strong green luminescence from Eu²⁺-doped SrAl₂O₄ was reported by H. Lange in Belgian patent 1,347,475 and U.S. Pat. No. 3,294,696. Efficient luminescence in the spectral range 450-520 nm was also reported from Eu²⁺-doped CaAl₂O₄, MgAl₂O₄, BaAl₂O₄, and SrAl₂O₄ and their counterparts using alkaline earth cationic combinations. (C. Palilla, A. K. Levine and M. R. Tomkus (1968) J. Electrochem. Soc. 115:642).

Long lasting and more efficient phosphorescence has obtained in Eu²⁺ doped SrAl₂O₄ synthesized with excess alumina which results in formation of trapping centers associated with the Sr²⁺ vacancy (Abbruscato et al. (1971) J. Electrochem. Soc. 118:930). The matrix comprises europium as an activator and a 60% Sr₂O₃, 40% Al₂O₃ composition. Blue to green luminescence of Eu²⁺ in strontium aluminates prepared by the hydrothermal method. Blue to green luminescence of Eu²⁺ doped SrAl₂O₄, (Eu²⁺:SrAl₂O₄) is reported. The reference also reports the preparation of certain aluminoborates.

B. Smets et al. (1989) J. Electrochem. Soc. 136(7) :2119-2123 reports blue-emitting phosphors: 2SrO . 3Al₂O₃ :Eu²⁺ and 1.29 (Ba, Ca)O, 6 Al₂O₃ :Eu²⁺. In the background section of the reference the authors refer to an earlier report of blue-green emitting phosphors 4SrO . 7Al₂O₃ :Eu²⁺ and BaO : 4Al₂O₃ :Eu²⁺, which could be synthesized only in the presence of small amounts of B₂O₃.


SUMMARY OF THE INVENTION

This invention relates to long-persistent phosphors of general formula:

$$\text{MO} . \text{mAl}_2\text{O}_3 : \text{Eu}^{2+} , \text{R}^{3+}$$

where M is Sr or a combination of Sr with Ca and/or Ba; R³⁺ is a trivalent rare earth metal ion or Bi³⁺, or mixtures of these trivalent metal ions; m is a number ranging from about 1.6 to about 2.2. The phosphors are prepared using a flux, particularly B₂O₃. The preferred phosphor formula of this invention indicates the presence of B₂O₃ flux is:

$$\text{MO} . \text{mAl}_2\text{O}_3(bz\text{Al}_2\text{O}_3) : \text{Eu}^{2+} , \text{R}^{3+}$$

where M, m and R³⁺ are as defined in formula 1 and z is a number ranging from about 0.02 to about 0.2. The phosphors of this invention comprise an alkaline earth aluminate matrix activated with Eu²⁺ and doped with certain trivalent metal ions R³⁺. The phosphors are activated with about 0.00 mol % to about 0.1 mol % of Eu²⁺, preferably about 0.2 mol % to about 1.0 mol % of Eu²⁺, activator and co-doped with about 0.02 mol % to about 20 mol % (preferably about 0.2 mol % to about 2 mol %) of at least one trivalent rare earth metal ion or Bi³⁺. The activator and dopant concentration are measured in terms of mol % relative to the alkaline earth metal element M.

Preferred phosphors of this invention are blue with a phosphorescent band at about 488 nm. Phosphors of this invention have significantly improved brightness compared to sulfide phosphors, such as CaSrS:Bi. Phosphors of this invention can have persistence times up to about 18 hr.

The phosphors of this invention are chemically stable, resistant to moisture and UV radiation and are believed to be relatively harmless to the environment.
Phosphors of this invention are those in which M is Sr.

Phosphors of this invention are activated with Eu²⁺ and are codoped with a trivalent rare earth metal ion or Bi³⁺. The phosphors may be codoped with a single ion or a combination of such ions selected from the group of rare earth metal ions: Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm²⁺, Gd²⁺, Tb³⁺, Tm³⁺, and Yb³⁺ and the Group VA metal ion Bi³⁺. Preferred trivalent dopants are Pr³⁺, Ho³⁺, Dy³⁺, and Nd³⁺. Co-doping of Dy³⁺ or Y³⁺ with another trivalent metal ion results in phosphor of improved brightness, e.g. MA1₄O₇:Eu²⁺, Pr³⁺, Dy³⁺ or MA1₄O₇:Eu²⁺, Ho³⁺, Dy³⁺.

Preferred phosphors are those with m ranging from about 1.70 to about 2.05 and, more preferably, are those where m=1.75, the host material being MA1₄O₇ and m=2, the host material being MA1₂O₁₇. More preferred are phosphors where M=Sr and m=1.75 or m=2. Sm³⁺, Gd³⁺, Eu²⁺, Sr⁺⁺, or a mixture of both, is substituted for the host material being MA1₂O₁₇. More preferred are phosphors of this invention also include those in which Mg²⁺ or Zn²⁺, or a mixture of both, is substituted for Al³⁺ in the matrix material and where M⁺⁺, particularly Sr⁺⁺, are replaced with an alkali metal (e.g., Na⁺ or K⁺) ion in the matrix. These substitutions are believed to effect charge compensation.

The phosphors of this invention can be prepared in powder form or as a ceramic. Phosphor materials of this invention can also be grown as single crystals which display desirable phosphorescence properties, including long-persistence.

The phosphors of this invention can be used in a variety of applications, e.g., in luminous paints, luminous plastics and for night vision devices and manufactures. The phosphor in ceramic form can be used for manufacture of phosphorescent jewelry and other ornaments or apparel. The phosphors may also be used in manufacture of infrared laser beam sensors.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 is a spectrum of the after-glow of a sample of SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺,0.02Pr³⁺ measured at varying time (5-60 sec) after exposure of the sample to a 4 W UV lamp for two minutes.

FIG. 2 is a graph of decay of the after-glow of (a) SrAl₂O₄(0.1B₂O₃):0.01 Eu²⁺,0.02Pr³⁺, and (b) of commercial blue phosphor Ca₃S₂S:Bi after exposure of the phosphors to a 13 W fluorescent lamp for 10 minutes. The threshold of eye sensitivity is indicated by a horizontal dashed line.

FIG. 11 is a graph of decay curves of the after-glow of SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺,0.02Pr³⁺ measured in the first 15 sec. after exposure to a 13 W fluorescent lamp (measured at 488 nm). Decay curves for R=La (○), Ce (△), Sm (●), Gd (□), Tb (♦), Dy (□), Er (▲), Tm (□), and Yb (×), and Lu (+) are shown. The decay curve of the sample SrAl₂O₄:Eu,Nd (●) is also shown for comparison.

FIG. 12 is a graph comparing after-glow decay curves for samples of SrAl₂O₄(0.1B₂O₃):0.01Eu, 0.01Pr co-doped with 0.01Y (x), Lu(▼) or Lu(▲).

FIG. 13 illustrates the excitation and emission spectra monitored at 488 nm of SrAl₂O₄(0.1B₂O₃) activated with Eu and codoped with Pr and Y.

FIG. 14 is a graph comparing after-glow decay curves of SrAl₂O₄(0.1B₂O₃) activated with Eu and codoped with either (a) Pr and Dy, (b) Ho and Dy or (c) doped only with Pr. The threshold of eye sensitivity is indicated by a horizontal dashed line.

FIG. 15 illustrates the spectra of the after-glow of Sr₀.₆Ba₃Al₁₅O₄:0.01Eu, 0.02Pr after exposure to a 4 W UV lamp for 2 minutes as a function of time after illumination (□, after 5 sec.; △, after 20 sec. and ▲, after 60 sec.).

FIG. 16 illustrates the spectra of the after-glow of Sr₀.₄Ca₀.₆Al₁₅O₄:0.01Eu, 0.02Pr after exposure to a 4 W UV lamp for 2 minutes as a function of time after illumination (□, after 5 sec.; △, after 20 sec. and ▲, after 60 sec.).

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to long-persistence blue phosphors. Phosphors of this invention are based on doping of an activator (an emitter) into a host matrix. Several basic physical factors should be considered in developing such phosphors. The host (or matrix) and activator are selected to provide the desired emission color (dependent upon the wavelength of emission) and high quantum efficiency. The energy of the localized ground state of the activator should be well above the valence band of the host to allow persistent phosphorescence to occur.


The main difference between these three phenomena appears to be the depth of traps. When a phosphor possesses centers with certain trapping depth which can be effectively acti-
activated at room temperature, it will show persistent phosphorescence. Deeper trapping centers can be activated by heating or photostimulation. Therefore, a study of phosphorescence dynamics allows the characterization of these three important luminescence processes. Single crystal phosphors facilitate studies of phosphorescence dynamics.

The traditional persistent phosphors are sulfides, ZnS, CdS, CaS and SrS, and their mixed crystals. All of these compounds have high vapor pressure, and it has generally been difficult to grow crystals from the melt.

Methods described herein allow the preparation of phosphorescent single crystals. Single crystals are readily distinguishable by appearance from polycrystalline materials and from grained crystals. Polycrystals or grained crystals are opaque and exhibit grain boundaries, because the grains are small (one the order of tens of micrometers). Larger grained crystals have the appearance of broken glass, the grains are not crystallographically oriented and as a result light traversing grained crystals will be scattered and refracted limiting transparency. In contrast, single crystals are clear and transparent without grain boundaries.

Phosphor materials of this invention can exhibit enhanced phosphorescence intensity and/or long persistence of phosphorescence. Preferred phosphors of this invention have intensity enhanced (as measured in a similar measurement system) compared to a standard commercial sample of ZnS phosphor. Persistence of phosphorescence is measured herein as persistence time, which is the time after discontinuing irradiation that it takes for phosphorescence of a sample to decrease to the threshold of eye sensitivity. This threshold is the signal level of emission intensity that a naked (i.e., unaided) eye can clearly see in the dark. Persistence times are assessed by following phosphorescence intensity as a function of time. Clearly measurement comparisons of persistence times must be performed under identical conditions using the same detection systems. The term “persistent phosphors” has been applied to materials exhibiting phosphorescence lasting form minutes to hours. The term “long-persistent phosphor” historically has been used to refer to ZnS-Cu, CaS-Eu, Tm and similar materials which have a persistence time of 20 to 40 minutes. Materials herein can exhibit persistence time up to about 16–18 hrs or more. It is generally the case that phosphors having longer persistence times are more preferred. Preferred phosphor materials, including single crystals and single crystal fibers, of this invention can exhibit phosphorescence persistence times of greater than about 3–5 hrs. More preferred phosphors exhibit persistence times greater than about 10–12 hrs. Most preferred phosphors exhibit persistence times of greater than about 15–18 hrs.

Persistence times of ceramics can be longer or shorter than those of single crystals of the same materials.

The hosts of this invention are alkaline earth alumina by M-O-mAl2O3 (where M is an alkaline earth or mixture of alkaline earths, e.g., Sr, Ca and/or Ba) with a certain range of ratios of Al/M defined by m. The activator employed in the phosphors of this invention is Eu2+. Hosts in which m is about 1.6 to about 2.2 prefer the desired blue color and good phosphorescence brightness in combination with the Eu activator. Hosts where m is about 1.7 to about 2.05 are preferred, with those where m is about 1.75 or m is 2 being more preferred. Hosts where M is Sr and m is either 1.75 (SrAl2O4) or m is 2 (SrAl2O4) are preferred for use in blue phosphors of this invention.

Although not wishing to be bound by any particular theory, it is believed that long persistence time in the activated matrix phosphors of this invention is obtained by creating proper trapping centers in the matrix. Such trapping centers can store excitation energy and release it gradually to the emitter.

This invention demonstrates that doping of trivalent metal ions, particularly trivalent rare earth metal ions, into the host matrix of this invention results in phosphors having improved phosphorescence brightness and persistence time. Dopants for creating trapping centers include trivalent rare earth metal ions: Pr3+, Ho3+, Nd3+, Dy3+, Er3+, La3+, Lu3+, Ce3+, Y3+, Sm3+, Gd3+, Tb3+, Tm3+, and Yb3+ and trivalent Bi3+. Preferred for the hosts of this invention is doping with trivalent Pr, Ho, Nd or Dy, with trivalent Pr and Ho being generally more preferred dopants.

This invention demonstrates for the host matrices of this invention that co-doping of trivalent Dy or Y along with another trivalent rare earth metal ion results in phosphors improved over those doped with a single trivalent rare earth metal ion. Preferred combinations of trivalent rare earth metal ions are Dy with Pr or Ho and Y with Pr or Ho.

Phosphors of this invention also include those in which a portion of Al2O3 in the host is replaced with a divalent ion, such as Mg2+ or Zn2+ (alone or in combination) and those in which a portion of the alkaline earth metal ion (M2+) is replaced with a monovalent alkali metal ion, such as Na+ or K+ (alone or in combination). The doping level is designed to compensate the charge defects which are induced due to substitution of Sr2+ by R2+. This invention specifically exemplifies phosphors in powder or ceramic form prepared by combining the host, activator and trivalent metal ion dopants with a flux material. The flux material of most interest is B2O3. The properties of the powder and ceramic phosphors of this invention are significantly affected by the use of the flux material during preparation. Both the presence or absence of the flux and the amount of flux employed can affect phosphor properties. It has been demonstrated with the hosts of this invention that varying the molar amount of B2O3 relative to other components (where the molar proportion of M is 1) from 0.02 to 0.2 (z in formulas herein) results in blue-emitting phosphors with acceptable persistence and brightness. Inclusion of the flux in a molar proportion z of about 0.08 to about 0.15 is preferred and inclusion of flux z of about 0.1 to about 0.15 is more preferred.

B2O3 can be replaced in all formulations of this invention by an amount of H2BO3 sufficient to provide an equivalent molar amount of B (i.e., 2H3BO3 replaces each B2O3).

The exact role of the flux B2O3 in the phosphor properties is not clear. However, the phosphorescent phase in the compounds of this invention cannot be obtained without the use of flux. It is believed that the presence of flux is important to obtaining a particular phosphorescent phase with improved properties. The presence or absence of flux in the preparation of strontium alumina can affect the ultimate structure of the aluminate. For example, when m is 1.75 and M=Sr, the host material becomes Sr3Al2O5 with an orthorhombic structure with space group Pmna in the presence of flux (e.g., B2O3). This structure of strontium aluminate can be made only in the presence of flux. In the case where m is 2 and M=Sr, the host material Sr3Al2O5 formed in the presence of flux is similar in structure to orthorhombic Sr3Al2O5 (see FIG. 4). This material is monoclinic with space group C2h. The phosphors of this invention can be made by the following general method. Phosphor components are com-
bined as indicated in stoichiometric formulas (with or without a flux). The mixture is treated to form a homogeneous fine powder, for example by milling or grinding. The powder is preferably pressed into pellets. The powder or pellets are prefired at temperatures between about 600 to 800°C (depending upon the phase transitions of the material) in air for about 1-2 hrs. The prefired material is again treated to form a fine homogeneous powder (e.g., milling, grinding, pulverizing) suitable for sintering. Preferably, the powder is pelleted before sintering. The powder or pellets are sintered at about 1300°C under a reducing atmosphere, e.g., H₂/N₂ having 2-5% by volume H₂.

Sintered phosphor material can be used to grow single crystals or single crystal fibers. Any crystallization technique can be employed. The laser heated pedestal method is preferred. Sintered pellets are cut into bars to introduction into the crystal growth chamber (1x1 mm x 1.5x1.5 mm pieces). The bars are carefully cleaned prior to introduction into the chamber which is filled with a non-reactive or inert gas (e.g., N₂) or a somewhat reducing gas (about 1% by volume H₂ in N₂). Care should be taken to minimize or avoid reoxidation of Eu⁺ ions and to minimize or avoid reduction to the monovalent or zero valent (i.e., metal) state. Other metals in the materials preferably remain in the same oxidation state during crystallization. A pointed ceramic bar can be used as a "seed" to stimulate spontaneous nucleation in the LHPG process. It was observed that the initial part of the fiber prepared by the LHPG process was a twinned crystal. The fiber eventually becomes one single crystal after a transition stage, but the crystal is not oriented. Fiber lengths of single crystals grown are variable, but can be as long as several centimeters in length. Single crystals with an average diameter of about 0.8 mm can be grown.

The basic phosphors of this invention are most generally prepared by admixing the components in the following molar proportions:

\[(1-2x-2y)\text{MCO}_3 + m\text{Al}_2\text{O}_3 + x\text{EuO}_2 + yR_2\text{O}_3 + z\text{B}_2\text{O}_3\]

and will have the general formula:

\[M\text{O}_3 \cdot m\text{Al}_2\text{O}_3 \cdot (zB_2O_3) \cdot 2x\text{Eu}^{2+} \cdot 2yr^{3+}\]

where \(k=1-2x-2y\), \(m\) is as defined above, \(y_1+y_2=y\), and \(R_1\) and \(R_2\) are two different trivalent metal ions. The number \(x\) can range from about 0.0001 to about 0.05 and is preferably about 0.001 to about 0.005, \(y\) can range from about 0.0001 to about 0.10 and the value of \(y\) is preferably equal to the value of \(x\) and \(z\) can range from about 0.02 to about 0.2. Preferred phosphors contain about equal amounts of \(R_1\) and \(R_2\).

The phosphors of this invention include those in which \(\text{Al}^{3+}\) in the host is substituted by a divalent metal ion, particularly \(\text{Mg}^{2+}\) or \(\text{Zn}^{2+}\). These phosphors have the general formula:

\[M\text{O}_3 \cdot (m-q)\text{Al}_2\text{O}_3 \cdot q\text{XO} \cdot z\text{B}_2\text{O}_3 \cdot 2x\text{Eu}^{2+} \cdot 2yr^{3+}\]

where \(k=1-2x-2y\), \(m\) is as defined above, \(x\) can range from about 0.0001 to about 0.05 and is preferably about 0.001 to about 0.005, \(y\) can range from about 0.0001 to about 0.10 and the value of \(y\) is preferably equal to the value of \(x\) and \(z\) can range from about 0.02 to about 0.2. Preferred phosphors contain about equal amounts of \(R_1\) and \(R_2\).

The phosphors of this invention include those in which \(\text{M}^{2+}\) in the host is substituted by a monovalent alkali metal ion, particularly \(\text{Na}^+\) or \(\text{K}^+\). These phosphors have the general formula:

\[M\text{O}_3 \cdot m\text{Al}_2\text{O}_3 \cdot (z\text{O}_2\text{B}_2\text{O}_5) \cdot 2x\text{Eu}^{2+} \cdot 2yr^{3+}\]

where \(k=1-2x-2y\), \(m\) is as defined above, \(x\) can range from about 0.0001 to about 0.05 and is preferably about 0.001 to about 0.005, \(y\) can range from about 0.0001 to about 0.10 and the value of \(y\) is preferably equal to the value of \(x\) and \(z\) can range from about 0.02 to about 0.2. Preferred phosphors contain about equal amounts of \(Z\) and \(Z^+\). The formulas 1-6 are intended to represent the chemical composition of the phosphor and do not indicate structure.

The phosphors of this invention can be prepared as powders or ceramics as indicated in the examples. Materials of this invention can be used to prepare single crystal phosphors as described, for example, in Example 17.

The phosphors of this invention have a variety of applications for the manufacture of luminous materials, including paints, inks, plastic articles, toys, jewelry, ornaments and apparel. The phosphors have application in night vision apparatus and in optoelectronic devices. The phosphors of this invention can for example be employed in detection of UV radiation.

More specifically this invention provides:

A. A phosphorescent material comprising:

a host with chemical formula: \(\text{MO} \cdot m\text{Al}_2\text{O}_3\), where \(M\) is an alkaline earth metal, and \(m\) is a number ranging from about 1.6 to about 2.2, \(x\) can range from about 0.0001 to about 0.05 and is preferably about 0.001 to about 0.005, \(y\) can range from about 0.0001 to about 0.10 and the value of \(y\) is preferably equal to the value of \(x\) and \(z\) can range from about 0.02 to about 0.2. Preferred phosphors contain about equal amounts of \(R_1\) and \(R_2\).

Phosphors of this invention include those in which two trivalent metal ions are doped into the matrix having the general formula:

\[M\text{O}_3 \cdot m\text{Al}_2\text{O}_3 \cdot (z\text{B}_2\text{O}_3) \cdot 2x\text{Eu}^{2+} \cdot 2yr^{3+}\]
A phosphorescent material as in paragraph A further comprising from about 2 mol % to about 20 mol %, relative to M, of B₂O₃ in said host and/or wherein B₂O₃ is present in the host in an amount ranging from about 8 mol % to about 15 mol %, relative to M.

A phosphorescent material as in paragraph A where m is 2 or 1.75 and/or wherein M is Sr²⁺.

B. A phosphorescent material having the formula:

\[ M₂O \cdot mAl₂O₃ \cdot (xB₂O₃):(2xEu⁴⁺,yR³⁺), \]

where: k is 1-2x-2y, with y=y₁+y₂;

- m is a number ranging from about 1.6 to about 2.2;
- z is a number ranging from about 0.00 to about 0.2
- x is a number ranging from about 0.0001 to about 0.005;
- y is a number ranging from about 0.0001 to about 0.010; M is Sr²⁺ or a mixture of Sr²⁺ with Ca²⁺, Ba²⁺ or both;
- R³⁺ is one or more of Pr³⁺, Ho³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tm³⁺, Yb³⁺ and Bi³⁺;

A phosphorescent material as defined in paragraph B wherein R³⁺ is Pr³⁺, Ho³⁺, Dy³⁺, or Nd³⁺ and/or wherein x ranges from about 0.001 to about 0.005 and y=x. Preferred phosphorescent material of paragraph B are those in which m is equal to 1.75 or 2.

C. A phosphorescent material of having the formula:

\[ M₂O \cdot mAl₂O₃ \cdot (xB₂O₃):(2xEu⁴⁺,yR³⁺), \]

where k is 1-2x-2y,

- m is a number ranging from about 1.6 to about 2.2;
- z is a number ranging from about 0.00 to about 0.2
- x is a number ranging from about 0.0001 to about 0.005;
- y is a number ranging from about 0.0001 to about 0.010; M is Sr²⁺ or a mixture of Sr²⁺ with Ca²⁺, Ba²⁺ or both;
- R³⁺ and R₂⁻ are different trivalent metal ions that are one or more of Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tm³⁺, Yb³⁺, and Bi³⁺;

A phosphorescent material of paragraph C wherein R³⁺ and R⁺ are one or more of Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, and Y³⁺. Preferred phosphorescent materials of paragraph C are those wherein R₁³⁺ is Pr³⁺, Ho³⁺, Dy³⁺, or Nd³⁺ and R₂⁻ is Y³⁺.

A phosphorescent material of paragraph C wherein M is Sr²⁺ and/or wherein m=1.75 or 2.

D. A phosphorescent material having the formula:

\[ M₂O \cdot (m-q)Al₂O₃ \cdot qXO(xB₂O₃):(2xEu⁴⁺,yR³⁺), \]

where k is 1-2x-2y,

- m is a number ranging from about 1.6 to about 2.2;
- z is a number ranging from about 0.00 to about 0.2
- x is a number ranging from about 0.0001 to about 0.005;
- y is a number ranging from about 0.0001 to about 0.010; M is Sr²⁺ or a mixture of Sr²⁺ with Ca²⁺ and/or Ba; and
- R is a trivalent rare earth metal ion or Bi³⁺.

A preferred phosphorescent material of paragraph D has q equal to 2y.

E. A phosphorescent material having the formula:

\[ M₂O \cdot mAl₂O₃ \cdot (xB₂O₃):(2xEu⁴⁺,yR³⁺), \]

where k=1-2x-2y-2r;

- x ranges from about 0.0001 to about 0.05;
- y is a number ranging from about 0.0001 to about 0.10; z ranges from about 0.02 to about 0.2;
- R is an alkali metal ion, particularly Na⁺ or K⁺ and r ranges from 0 to 0.20.

A preferred phosphorescent material of paragraph E has r=the value of y.

F. A phosphorescent material having the formula:

\[ Sr_xBa_yO \cdot m(Al₂O₃):(2xEu⁴⁺,yR³⁺), \]

where k=1-n-p-2x-2y, where k is greater than 0;

- n and p are numbers greater than or equal to 0 and less than 1;
- m is a number ranging from about 1.6 to about 2.2;
- z is a number ranging from about 0.02 to about 0.2
- x is a number ranging from about 0.0001 to about 0.005;
- y is a number ranging from about 0.0001 to about 0.010; and

R³⁺ is one or more of Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tm³⁺, Yb³⁺ and Bi³⁺.

Phosphorescent materials of paragraphs A-E can be in ceramic or single crystal form.

THE EXAMPLES

Example 1

Methods of Preparation of Blue Phosphors with Host Material MAI₂O₃ (where M is Sr or a mixture of Sr with Ba and/or Ca)

Phosphor components are mixed according to the molar proportions in the following general recipes:

\[ (1-2x-2y)MCO₃+2xEu₂O₃+yR₂O₃+2xB₂O₃; \]

where:

- 2x+2y is less than 1, preferably x=about 0.0001 to about 0.05 and more preferably x=about 0.001 to about 0.005;
- y is a number ranging from about 0.0001 to about 0.010 and preferably the value of y=the value of x;
- z ranges from about 0.02 to about 0.2;
- M is Sr or a combination of Sr with Ca and/or Ba; and
- R is a trivalent rare earth metal ion or Bi³⁺.

B₂O₃ is used as a flux in the composition and is important for ensuring the formation of the phosphorescent phase. B₂O₃ can be replaced by two molar equivalents of H₂BO₃.

The mixture of components is milled or ground to form a homogenous fine powder for prefireing. The powder is preferably pressed into pellets under about 1.3 ton/cm² pressure prior to prefireing. The mixed powder or the pressed pellets are then prefired at about 600°C in air for about one hour. The prefired material is then pulverized and milled again into a fine powder suitable for sintering. The prefired powder is preferably again pressed into ceramic pellets under 1.3 ton/cm² pressure before sintering. The powder or pellets are then sintered at about 1,300°C. For one hour in H₂—N₂ gas flow containing about 2%–5% H₂ (by volume) at a flow rate of about 0.1 liter per minute. The resulting material exhibits phosphor properties as described herein.

Example 2

Preparation and Characterization of SrAl₂O₄(B₂O₃) :Eu²⁺,Pr⁵⁺ Phosphors

The methods and phosphors of this invention are specifically exemplified by preparation of SrAl₂O₄(0.1B₂O₃):Eu²⁺,
R3+ (Eu2+ and R3+ co-doped strontium aluminate) phosphors. These are often used as a flux. The properties of these phosphors have been studied extensively, and they generally exemplify those of SrAl12O19:Eu2+.-R3+. Phosphor samples in which x (Eu2+) was varied from 0.001 to 0.015.

The milled mixed powders are pelletized prior to prefiring and pelletized prior to sintering.

where B2O3 serves as a flux. The milled mixed powders are pelletized prior to prefiring and pelletized prior to sintering.

FIG. 1 shows the spectrum of the after-glow of a sample of SrAl12O19:0.01Eu2+:0.02Pr3+ exposed to a 4 W UV lamp for two minutes. The phosphorescence exhibits a broad band peaking at about 488 nm with a bandwidth of about 65 nm (2640 cm−1). The figure illustrates phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

FIG. 2 is a graph of decay of the after-glow of a sample of SrAl12O19:0.1B2O3:0.01Eu2+:0.02Pr3+ exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of a commercial blue phosphor CaS:S:B:Bi after similar exposure is also shown (line b). The SrAl12O19:0.1B2O3:0.01Eu2+:0.02Pr3+ phosphor is about 10x brighter than the commercial blue phosphor and has a persistence time about 20 times longer. After 18 hours SrAl12O19:0.1B2O3:0.01 Eu2+:0.02Pr3+ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

FIG. 3 presents the excitation and emission spectra of SrAl12O19:0.1B2O3:0.01Eu2+:0.02Pr3+ where the excitation spectrum was monitored at 488 nm.

FIG. 4 is the x-ray diffraction pattern of the SrAl12O19:0.1B2O3:0.01Eu2+:0.02Pr3+ sample. This x-ray pattern indicated that the structure of SrAl12O19:0.1B2O3 is similar to SrAl12O19:0.3B2O3.

Example 3
Preparation and Characterization of SrAl12O19(B2O3) :Eu2+:Pr3+, Phosphors with Varying Amounts of Eu2+

Eu-concentration dependence of SrAl12O19:0.1B2O3:Eu2+:Pr3+ phosphor after-glow was examined by preparing phosphor samples in which x (Eu2+ molar concentration) was varied from 0.001 to 0.015.

Phosphors were prepared by the method of Example 1 with components mixed in the following molar proportions:

Table 1 shows time persistence of after-glow of the samples SrAl12O19:0.1B2O3:Eu2+:Pr3+.

TABLE 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>x</th>
<th>10 min after-glow</th>
<th>30 min after-glow</th>
<th>60 min after-glow</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1</td>
<td>0.001</td>
<td>100</td>
<td>31</td>
<td>14</td>
</tr>
<tr>
<td>B-2</td>
<td>0.003</td>
<td>106</td>
<td>33</td>
<td>15</td>
</tr>
<tr>
<td>B-3</td>
<td>0.005</td>
<td>98</td>
<td>31</td>
<td>15</td>
</tr>
<tr>
<td>B-4</td>
<td>0.007</td>
<td>90</td>
<td>17</td>
<td>8</td>
</tr>
<tr>
<td>B-5</td>
<td>0.010</td>
<td>50</td>
<td>14</td>
<td>6</td>
</tr>
<tr>
<td>B-6</td>
<td>0.015</td>
<td>30</td>
<td>9</td>
<td>4</td>
</tr>
</tbody>
</table>

Example 4
Preparation and Characterization of SrAl12O19:0.1B2O3:Eu2+:Pr3+ Phosphors with Varying Amounts of Pr3+

Pr-concentration dependence of SrAl12O19:0.1B2O3:Eu2+:Pr3+ phosphor after-glow was examined by preparing phosphor samples in which y (Pr3+ molar concentration) was varied from 0.005 to 0.02.

Phosphors were prepared by the method of Example 1 with components mixed in the following molar proportions:

Table 2 shows time persistence of after-glow of the samples SrAl12O19:(0.1B2O3):Eu2+:Pr3+.

TABLE 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>y</th>
<th>10 min after-glow</th>
<th>30 min after-glow</th>
<th>60 min after-glow</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>0.005</td>
<td>100</td>
<td>31</td>
<td>15</td>
</tr>
<tr>
<td>C-2</td>
<td>0.0075</td>
<td>95</td>
<td>28</td>
<td>15</td>
</tr>
<tr>
<td>C-3</td>
<td>0.010</td>
<td>105</td>
<td>34</td>
<td>16</td>
</tr>
<tr>
<td>C-4</td>
<td>0.015</td>
<td>91</td>
<td>28</td>
<td>14</td>
</tr>
<tr>
<td>C-5</td>
<td>0.02</td>
<td>92</td>
<td>29</td>
<td>16</td>
</tr>
</tbody>
</table>

Example 5
Preparation and Characterization of SrAl12O19(B2O3):Eu2+:Ho3+ Blue Phosphors

SrAl12O19:0.1B2O3:0.01Eu2+:0.02Ho3+ was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

Table 3 shows time persistence of after-glow of the samples.

TABLE 3

<table>
<thead>
<tr>
<th>Samples</th>
<th>y</th>
<th>10 min after-glow</th>
<th>30 min after-glow</th>
<th>60 min after-glow</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-1</td>
<td>0.005</td>
<td>100</td>
<td>31</td>
<td>15</td>
</tr>
<tr>
<td>D-2</td>
<td>0.0075</td>
<td>95</td>
<td>28</td>
<td>15</td>
</tr>
<tr>
<td>D-3</td>
<td>0.010</td>
<td>105</td>
<td>34</td>
<td>16</td>
</tr>
<tr>
<td>D-4</td>
<td>0.015</td>
<td>91</td>
<td>28</td>
<td>14</td>
</tr>
<tr>
<td>D-5</td>
<td>0.02</td>
<td>92</td>
<td>29</td>
<td>16</td>
</tr>
</tbody>
</table>
a broad band peaking at about 488 nm with a bandwidth of about 60 nm (2640 cm⁻¹). The figure illustrates phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

FIG. 6 is a graph of the after-glow of the sample of SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02Nd³⁺ exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of the after-glow of SrAl₂O₃ (0.1B₂O₃):0.01Eu⁺⁺:0.02Pr³⁺ (line b) and a commercial blue phosphor CaSrS:Bi (c) after similar exposure are also shown. The SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02Ho³⁺ phosphor shows similar brightness and persistence to that of SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02Pr³⁺. After 20 hours SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02Ho³⁺ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

FIG. 7 is the excitation and emission spectra of a sample of SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02Ho³⁺ where the excitation spectrum was monitored at 488 nm.

Preparation and Characterization of SrAl₂O₃(B₂O₃)

SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02Nd³⁺ was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

0.97 Sc₂O₃+2.00 Al₂O₃+0.005 Eu₂O₃+0.01 Nd₂O₃+0.1 B₂O₃

where B₂O₃ serves as flux.

FIG. 8 shows the spectrum of the after-glow of a sample of SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02 Nd³⁺ excited by a 4 W UV lamp for two minutes. The phosphorescence exhibits a broad band peaking at about 488 nm with a bandwidth of about 60 nm (2640 cm⁻¹). The figure illustrates phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

FIG. 9 is a graph of decay of the after-glow of a sample of SrAl₂O₃(0.1B₂O₃):0.01 Eu⁺⁺:0.02 Nd³⁺ exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of the after-glow of SrAl₂O₃ (0.1B₂O₃):0.01Eu⁺⁺:0.02Pr³⁺ (b) and a commercial blue phosphor CaSrS:Bi (c) after similar exposure are also shown. The SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02 Nd³⁺ phosphor shows similar brightness and persistence to that of SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02Pr³⁺. After 20 hours SrAl₂O₃(0.1B₂O₃):0.01 Eu⁺⁺:0.02 Nd³⁺ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

FIG. 10 is the excitation and emission spectra of a sample of SrAl₂O₃(0.1B₂O₃):0.01 Eu⁺⁺:0.02 Nd³⁺ where the excitation spectrum was monitored at 488 nm.

Example 6

Preparation and Characterization of Phosphors of SrAl₂O₃(B₂O₃):Eu⁺⁺-Nd³⁺ Blue Phosphors

SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02 Nd³⁺ was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

0.97 Sc₂O₃+2.00 Al₂O₃+0.005 Eu₂O₃+0.01 Nd₂O₃+0.1 B₂O₃

where B₂O₃ serves as flux.

FIG. 8 shows the spectrum of the after-glow of a sample of SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02 Nd³⁺ excited by a 4 W UV lamp for two minutes. The phosphorescence exhibits a broad band peaking at about 488 nm with a bandwidth of about 60 nm (2640 cm⁻¹). The figure illustrates phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

FIG. 9 is a graph of decay of the after-glow of a sample of SrAl₂O₃(0.1B₂O₃):0.01 Eu⁺⁺:0.02 Nd³⁺ exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of the after-glow of SrAl₂O₃ (0.1B₂O₃):0.01Eu⁺⁺:0.02Pr³⁺ (b) and a commercial blue phosphor CaSrS:Bi (c) after similar exposure are also shown. The SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02 Nd³⁺ phosphor shows similar brightness and persistence to that of SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02Pr³⁺. After 20 hours SrAl₂O₃(0.1B₂O₃):0.01 Eu⁺⁺:0.02 Nd³⁺ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

FIG. 10 is the excitation and emission spectra of a sample of SrAl₂O₃(0.1B₂O₃):0.01 Eu⁺⁺:0.02 Nd³⁺ where the excitation spectrum was monitored at 488 nm.

Example 7

Preparation and Characterization of Phosphors of SrAl₂O₃(B₂O₃):Eu⁺⁺-Nd³⁺ Blue Phosphors

SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02 Nd³⁺ was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

0.97 Sc₂O₃+2.00 Al₂O₃+0.005 Eu₂O₃+0.01 Nd₂O₃+0.1 B₂O₃

where B₂O₃ serves as flux.

FIG. 8 shows the spectrum of the after-glow of a sample of SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02 Nd³⁺ excited by a 4 W UV lamp for two minutes. The phosphorescence exhibits a broad band peaking at about 488 nm with a bandwidth of about 60 nm (2640 cm⁻¹). The figure illustrates phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

FIG. 9 is a graph of decay of the after-glow of a sample of SrAl₂O₃(0.1B₂O₃):0.01 Eu⁺⁺:0.02 Nd³⁺ exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of the after-glow of SrAl₂O₃ (0.1B₂O₃):0.01Eu⁺⁺:0.02Pr³⁺ (b) and a commercial blue phosphor CaSrS:Bi (c) after similar exposure are also shown. The SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02 Nd³⁺ phosphor shows similar brightness and persistence to that of SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02Pr³⁺. After 20 hours SrAl₂O₃(0.1B₂O₃):0.01 Eu⁺⁺:0.02 Nd³⁺ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

FIG. 10 is the excitation and emission spectra of a sample of SrAl₂O₃(0.1B₂O₃):0.01 Eu⁺⁺:0.02 Nd³⁺ where the excitation spectrum was monitored at 488 nm.

Example 8

Preparation and Characterization of Phosphors of SrAl₂O₃(B₂O₃):Eu⁺⁺-Nd³⁺ Blue Phosphors

SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02 Nd³⁺ was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

0.97 Sc₂O₃+2.00 Al₂O₃+0.005 Eu₂O₃+0.01 Nd₂O₃+0.1 B₂O₃

where B₂O₃ serves as flux.

FIG. 8 shows the spectrum of the after-glow of a sample of SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02 Nd³⁺ excited by a 4 W UV lamp for two minutes. The phosphorescence exhibits a broad band peaking at about 488 nm with a bandwidth of about 60 nm (2640 cm⁻¹). The figure illustrates phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

FIG. 9 is a graph of decay of the after-glow of a sample of SrAl₂O₃(0.1B₂O₃):0.01 Eu⁺⁺:0.02 Nd³⁺ exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of the after-glow of SrAl₂O₃ (0.1B₂O₃):0.01Eu⁺⁺:0.02Pr³⁺ (b) and a commercial blue phosphor CaSrS:Bi (c) after similar exposure are also shown. The SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02 Nd³⁺ phosphor shows similar brightness and persistence to that of SrAl₂O₃(0.1B₂O₃):0.01Eu⁺⁺:0.02Pr³⁺. After 20 hours SrAl₂O₃(0.1B₂O₃):0.01 Eu⁺⁺:0.02 Nd³⁺ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

FIG. 10 is the excitation and emission spectra of a sample of SrAl₂O₃(0.1B₂O₃):0.01 Eu⁺⁺:0.02 Nd³⁺ where the excitation spectrum was monitored at 488 nm.
efficiency and improve the brightness by 50% compared to the analogous Pr\textsuperscript{3+}-doped phosphor.

### TABLE 3

The influence of codoping Y, La, Lu, Er, or Bi into SrAl\textsubscript{2}O\textsubscript{4}:Eu,Pr on the phosphorescence at 488 nm after (min)

<table>
<thead>
<tr>
<th>after (min)</th>
<th>Pr</th>
<th>Y</th>
<th>La</th>
<th>Lu</th>
<th>Er</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>178</td>
<td>105</td>
<td>110</td>
<td>105</td>
<td>107</td>
</tr>
<tr>
<td>30</td>
<td>55</td>
<td>30</td>
<td>32</td>
<td>30</td>
<td>32</td>
<td>33</td>
</tr>
<tr>
<td>60</td>
<td>16</td>
<td>17</td>
<td>17</td>
<td>15</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{1}Data is referenced to that of the SrAl\textsubscript{2}O\textsubscript{4}:Eu,Pr phosphor.

### Example 9

**Preparation and Characterization of SrAl\textsubscript{2}O\textsubscript{4} (0.1B\textsubscript{2}O\textsubscript{3}):0.01Eu,0.01Dy,0.01Ho**

This example demonstrates the influence of deep trapping centers formed by Dy\textsuperscript{3+} on the decay characteristics of MAl\textsubscript{2}O\textsubscript{4} doped with 0.01Eu, 0.01Pr or 0.01Ho.

Samples are generally prepared by the method of Example 1 combining the components in the following general molar proportions:

\[(1-2x-2y) MCO_3+nBaCO_3+mAl_2O_3+xEu_2O_3+yR_2O_3+zB_2O_3\]

where: \(n+2x+2y\) is less than 1 (there is some Sr present), \(y\) ranges from about 0.0001 to about 0.010 and preferably the value of \(y\) is the value of \(x\);

\(z\) ranges from about 0.02 to about 0.1; and

R\textsuperscript{3+} is a trivalent rare earth metal ion or Bi\textsuperscript{3+}.

The mixed alkaline earth aluminates have the general formula:

\[Sr_{1-p}Ca_p \cdot mAl_2O_3 \cdot zB_2O_3 : 2xEu_2yR_3\]

where \(k\) is the value of \(x\).

### TABLE 4

The influence of deep centers of Dy on the after-glow of SrAl\textsubscript{2}O\textsubscript{4} (0.1B\textsubscript{2}O\textsubscript{3}):0.01Eu,0.01Pr or SrAl\textsubscript{2}O\textsubscript{4} (0.1B\textsubscript{2}O\textsubscript{3}):0.01Eu,0.01Dy,0.01Ho after (min)

<table>
<thead>
<tr>
<th>after (min)</th>
<th>SAO-EuPr\textsuperscript{1}</th>
<th>SAO-EuPrDy</th>
<th>SAO-EuHo-Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>301</td>
<td>252</td>
</tr>
<tr>
<td>30</td>
<td>39</td>
<td>99</td>
<td>75</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
<td>47</td>
<td>35</td>
</tr>
</tbody>
</table>

\textsuperscript{1}Data is referenced to that of SAO-EuPr.

FIG. 14 provides decay curves of the after-glow measured at 488 nm of the samples SrAl\textsubscript{2}O\textsubscript{4} (0.1B\textsubscript{2}O\textsubscript{3}):0.01Eu,0.01Pr (c); SrAl\textsubscript{2}O\textsubscript{4} (0.1B\textsubscript{2}O\textsubscript{3}):0.01Eu,0.01Pr,0.01Dy (a); and SrAl\textsubscript{2}O\textsubscript{4} (0.1B\textsubscript{2}O\textsubscript{3}):0.01Eu,0.01Ho,0.01Dy (b). The samples were exposed to a 4 W UV lamp for two minutes prior to measurement. Codoping the phosphor with Dy improves phosphor persistence and the brightness.

### Example 10

**Preparation and Characterization of mixed alkaline earth aluminate phosphors**

Mixes of alkaline earth aluminate phosphors in which the host contains Sr and Ba are prepared using the general method of Example 1 combining the components in the following general molar proportions:

\[(1-n-2x-2y) SrCO_3+nBaCO_3+mAl_2O_3+xEu_2O_3+yR_2O_3+zB_2O_3\]

where: \(n+2x+2y\) is less than 1 (there is some Sr present), \(y\) ranges from about 0.0001 to about 0.010 and preferably the value of \(y\) is the value of \(x\);

\(z\) ranges from about 0.02 to about 0.1; and

R\textsuperscript{3+} is a trivalent rare earth metal ion or Bi\textsuperscript{3+}.

The mixed alkaline earth aluminates have the general formula:

\[Sr_{1-p}Ca_p \cdot mAl_2O_3 \cdot zB_2O_3 : 2xEu_2yR_3\]

where \(k\) is the value of \(x\).

FIG. 15 shows the luminescence spectra of this phosphor. A small red shift of 27 nm was observed compared to the analogous Sr phosphor.

### Example 11

**Preparation and Characterization of mixed alkaline earth aluminate phosphors**

Mixes of alkaline earth aluminate phosphors in which the host contains Sr and Ca are prepared using the general method of Example 1 combining the components in the following general molar proportions:

\[(1-n-2x-2y) SrCO_3+nCaCO_3+mAl_2O_3+xEu_2O_3+yR_2O_3+zB_2O_3\]

where: \(n+2x+2y\) is less than 1 (there is at least some Sr present), \(y\) ranges from about 0.0001 to about 0.010 and preferably the value of \(y\) is the value of \(x\);

\(z\) ranges from about 0.02 to about 0.1; and

R\textsuperscript{3+} is a trivalent rare earth ion or Bi\textsuperscript{3+}.

The phosphors have the generic formula:

\[Sr_{1-p}Ca_p \cdot mAl_2O_3 \cdot zB_2O_3 : 2xEu_2yR_3\]

where \(k\) is the value of \(x\).

The mixed alkaline earth aluminates have the general formula:

\[Sr_{1-p}Ca_p \cdot mAl_2O_3 \cdot zB_2O_3 : 2xEu_2yR_3\]

where \(k\) is the value of \(x\).

FIG. 16 is the luminescence spectra of the [(Sr\textsubscript{0.48S}Ca\textsubscript{0.48S})\textsubscript{0.001}Al\textsubscript{2}O\textsubscript{3}] (0.1B\textsubscript{2}O\textsubscript{3}):0.01Eu,0.02Pr sample. No obvious spectral shift compared to the Sr phosphor was observed. Phosphors containing Sr, Ca and Ba can also be prepared using the general method of Example 1 combining the components in the following general molar proportions:

\[(1-n-2x-2y) SrCO_3+nCaCO_3+mAl_2O_3+xEu_2O_3+yR_2O_3+zB_2O_3\]

where \(n+2x+2y\) is less than 1 (there is some Sr present), \(y\) ranges from about 0.0001 to about 0.010 and preferably the value of \(y\) is the value of \(x\);

\(z\) ranges from about 0.02 to about 0.1; and

R\textsuperscript{3+} is a trivalent rare earth ion or Bi\textsuperscript{3+}.

These phosphors have the generic formula:

\[Sr_{1-p}Ca_p \cdot mAl_2O_3 \cdot zB_2O_3 : 2xEu_2yR_3\]

where \(k\) is the value of \(x\).

The mixed alkaline earth aluminates have the general formula:

\[Sr_{1-p}Ca_p \cdot mAl_2O_3 \cdot zB_2O_3 : 2xEu_2yR_3\]

where \(k\) is the value of \(x\).
y ranges from about 0.0001 to about 0.010 and preferably the value of y is the value of x.

z ranges from about 0.0001 to about 0.010 and preferably z ranges from about 0.02 to about 0.2; and R³⁺ is a trivalent rare earth ion or Bi³⁺.

These mixed alkaline earth aluminates have the formula:

\[ \text{Sr}_x \text{Ba}_y \text{Ca}_z \text{O} : \text{mA}_1 \text{O}_3(z \text{B}_2 \text{O}_3) : 2 \text{xEu} : 2y \text{R} \]

where \( k = 1 - n - p - 2x - 2y \).

**Example 12**

**Codoping of Mg²⁺ or Zn²⁺ into MO. mAl₂O₃:Eu³⁺, R³⁺ phosphors**

In phosphor materials of this invention, Al³⁺, in the alkaline earth aluminate can be replaced with divalent ions, such as Mg²⁺ or Zn²⁺. Phosphor components are combined according to the molar proportions in the following general recipe:

\[ (1-2x-2y) \text{MC}_0,+(m-q)\text{Al}_2\text{O}_3+x\text{Eu}_2+y\text{R}_2+q\text{XO}+z\text{B}_2\text{O}_3 \]

where: 2x+2y is less than 1;

q is less than m and preferably ranges from 0.002 to 0.2; the ranges for x, y, m, and z are as given in formula 1. XO, in particular, can be MgO and/or ZnO. These phosphors will have the generic formula:

\[ \text{M}_2 \text{O} : \text{mAl}_2 \text{O}_3 : \text{qXO} : 2\text{xEu} : 2y \text{R} \]

where \( k = 1 - 2x - 2y \) and where the ranges for m, x and y are as above.

**Table 5**

<table>
<thead>
<tr>
<th>after (min)</th>
<th>SAO-EnPr¹</th>
<th>SAO-EnPrMg</th>
<th>SAO-EnPrZn</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>104</td>
<td>104</td>
</tr>
<tr>
<td>30</td>
<td>31</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
<td>16</td>
<td>16</td>
</tr>
</tbody>
</table>

¹Data is referenced to that of SAO-EnPr.

**Example 13**

**Co-doping of Na⁺ or K⁺ into MO. mAl₂O₃:Eu³⁺, R³⁺ phosphors**

In phosphor materials of this invention, M⁺²⁺, in the alkaline earth aluminate can be replaced with monovalent ions, such as Na⁺ or K⁺. Phosphor components are combined according to the molar proportions in the following general recipe:

\[ (1-2x-2y-2r) \text{MC}_0,+(m-q)\text{Al}_2\text{O}_3+x\text{Eu}_2+y\text{R}_2+r\text{Z}_2\text{O}_3+2z\text{B}_2\text{O}_3 \]

where: 2x+2y+2r is less than 1;

r preferably ranges from 0.002 to 0.2; and the ranges for x, y, m, r, z and m are as given in formula 1. Z₂CO₃, in particular, can be Na₂CO₃ and/or K₂CO₃. These phosphors will have the generic formula:

\[ \text{M}_2 \text{O} : \text{mAl}_2 \text{O}_3 : \text{rZ}_2 \text{O}_3 : (0.1 \text{B}_2 \text{O}_3) : 0.01 \text{Eu} : 0.01 \text{Pr} \]

where \( k = 1 - 2r - 2x - 2y \) and where the ranges for r, m, x and y are as above.

**Table 6**

<table>
<thead>
<tr>
<th>after (min)</th>
<th>SAO-EnPr¹</th>
<th>SAO-EnPrNa</th>
<th>SAO-EnPrK</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>112</td>
<td>135</td>
</tr>
<tr>
<td>30</td>
<td>31</td>
<td>34</td>
<td>42</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
<td>17</td>
<td>20</td>
</tr>
</tbody>
</table>

¹Data is referenced to that of SAO-EnPr.

**Example 14**

**Preparation and Characterization of Alkaline earth aluminate phosphors of varying ratio of Al/M**

A series of strontium aluminate phosphors activated with Eu³⁺ and doped with Pr³⁺ were prepared having different ratios of Al/Sr. Phosphor components were mixed according to the molar proportions:

\[ 0.98 \text{Sc}_2\text{O}_3+1.99 \text{Al}_2\text{O}_3+0.01 \text{XO}+0.005 \text{Eu}_2\text{O}_3+0.005 \text{Dy}_2\text{O}_3+0.1 \text{B}_2\text{O}_3 \]

where XO can be MgO or ZnO.

Table 5 provides measurements of relative after-glow intensity at 488 nm of strontium aluminate (SrAl₂O₄) phosphors in which Na⁺ or K⁺ replaces Sr⁺.

**Table 7**

<table>
<thead>
<tr>
<th>m -</th>
<th>1.6</th>
<th>1.75</th>
<th>1.85</th>
<th>1.95</th>
<th>2.0</th>
<th>2.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aftemin.</td>
<td>101</td>
<td>121</td>
<td>106</td>
<td>100</td>
<td>100</td>
<td>88</td>
</tr>
<tr>
<td>30</td>
<td>37</td>
<td>37</td>
<td>32</td>
<td>31</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>60</td>
<td>17</td>
<td>16</td>
<td>15</td>
<td>14</td>
<td>14</td>
<td>12</td>
</tr>
</tbody>
</table>

¹Data is referenced to that at m = 2.

**Example 15**

**Effect of variation of the amount of flux on phosphor properties**

A series of strontium aluminate phosphors (SrAl₂O₄) activated with Eu³⁺ and doped with Pr³⁺ were prepared
using varying amounts of flux (zB₂O₃). Phosphor components were mixed according to the molar proportions:

\[0.08 \text{SrCO}_3+4\text{Al}_2\text{O}_3+0.005 \text{Eu}_2\text{O}_3+0.005 \text{Pr}_2\text{O}_3+z\text{B}_2\text{O}_3\]

with \(z=0.03, 0.05, 0.08, 0.10, 0.12, 0.15\), and 0.20 and phosphors were prepared according to the general procedure of Example 1. The phosphor components are mixed according to the molar proportions:

\[(4-8x-8y) \text{MC}_0_2+7.00 \text{Al}_2\text{O}_3+4x\text{Eu}_2\text{O}_3+4y\text{R}_2\text{O}_3+z\text{B}_2\text{O}_3\]

where:

- \(x\) ranges from about 0.0001 to about 0.05 and preferably \(x\) is 0.001 to about 0.005;
- \(y\) ranges from about 0.0001 to about 0.01 and preferably the value of \(y\) is about 0.1;
- \(z\) ranges from about 0.02 to about 0.1.

The phosphors herein are obtained by mixing the above phosphor components in the appropriate molar proportions according to the preparative examples hereinafter and the mixtures are milled or ground to give a homogeneous fine powder. The powder is pressed into pellets under about 1.3 ton/cm² pressure. The pellets are then sintered at about 1,300°C for one hour in a flowing H₂-N₂ gas mixture (2%–5% by volume H₂) with a flow rate of about 0.1 liter/min. Eu in the material is reduced to the divalent state, while the other metallic ions remain in the virgin valence state. The sintered pellets are cut into bars with cross-sections of about 1x1 mm. The bars are carefully cleaned with solvents (such as alcohol or acetone) before introduction into the growth chamber. The growth chamber is filled with inert gas (or a mixture of inert gas and <1% H₂, e.g., 99.999% N₂). Care must be taken to prevent re-oxidation of the europium ions from the 2+ state to the 3+ state and to prevent reduction to the monovalent state or metal at the melting temperature. Other metals present in the material should remain in their original valence state.

The Phosphor of claim 1 wherein \(x\) ranges from about 1.6 to about 2.2, \(y\) is Sr or a combination of Sr with Ca, Ba, or both, \(z\) is Sr or a combination of Sr with Ba, and/or Ca (Ba; and/or Ca can range from about 0.01 to about 0.05).

**Example 16**

**General Methods of Preparation of Blue Phosphors with Host Material \(M_xA_l_{y-x}O_{3y}(\text{where} \ M = \text{Sr or a mixture of Sr with Ba and/or Ca})\)**

Phosphor components are mixed according to the molar proportions in the following general recipe:

\[30 \text{SrCO}_3+7.00 \text{Al}_2\text{O}_3+4x\text{Eu}_2\text{O}_3+4y\text{R}_2\text{O}_3+z\text{B}_2\text{O}_3\]

where:

- \(x\) is preferably about 0.001 to about 0.05 and more preferably \(x\) is 0.001 to about 0.005;
- \(y\) is preferably about 0.0001 to about 0.01 and preferably the value of \(y\) is about 0.1;
- \(z\) is preferably about 0.02 to about 0.1.

The phosphor components are mixed in the appropriate molar proportions according to the preparative examples hereinabove and the mixtures are milled or ground to give a homogeneous fine powder. The powder is pressed into MO (where \(M = \text{Sr or a combination of Sr with Ba and/or Ca})\) pellets under about 1.3 ton/cm² pressure. The pressed pellets are then sintered in air at about 600°C for about one hour. The sintered pellets are cut into bars with cross-sections of about 1x1 mm. The bars are carefully cleaned with solvents (such as alcohol or acetone) before introduction into the growth chamber. The growth chamber is filled with inert gas (or a mixture of inert gas and less than 1% H₂, e.g., 99.999% N₂). Care must be taken to prevent re-oxidation of the europium ions from the 2+ state to the 3+ state and to prevent reduction to the monovalent state or metal at the melting temperature. Other metals present in the material should remain in their original valence state.

**Example 17**

**Single Crystal Blue Phosphors**

Single crystals of the alkaline earth aluminate phosphors of this invention can be grown directly from a melt by well-known techniques. For example, the conventional Czochralski method (J. Czochralski (1918) Z. Phys. Chem. 92:219), the floating zone method (W. G. Pfann (1952) Trans. AIME 194:747) or the laser heated pedestal method (B. M. Tissue et al. (1991) J. Crystal Growth 109:323) can be used. The following procedure employs the laser heated pedestal method:

The phosphor components are mixed according to the molar proportions given in Table 8 and are then sintered at about 1,300°C for one hour in a flowing H₂-N₂ gas mixture (2%–5% by volume H₂) with a flow rate of about 0.1 liter/min. Eu in the material is reduced to the divalent state, while the other metallic ions remain in the virgin valence state. The sintered pellets are cut into bars with cross-sections of about 1x1 mm. The bars are carefully cleaned with solvents (such as alcohol or acetone) before introduction into the growth chamber. The growth chamber is filled with inert gas (or a mixture of inert gas and less than 1% H₂, e.g., 99.999% N₂). Care must be taken to prevent re-oxidation of the europium ions from the 2+ state to the 3+ state and to prevent reduction to the monovalent state or metal at the melting temperature. Other metals present in the material should remain in their original valence state.

**TABLE 8**

<table>
<thead>
<tr>
<th>z</th>
<th>After/min. 0.03</th>
<th>0.05</th>
<th>0.08</th>
<th>0.10</th>
<th>0.12</th>
<th>0.15</th>
<th>0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>113</td>
<td>121</td>
<td>106</td>
<td>100</td>
<td>132</td>
<td>100</td>
<td>99</td>
</tr>
<tr>
<td>0.05</td>
<td>37</td>
<td>37</td>
<td>32</td>
<td>31</td>
<td>41</td>
<td>32</td>
<td>30</td>
</tr>
<tr>
<td>0.08</td>
<td>17</td>
<td>16</td>
<td>15</td>
<td>14</td>
<td>17</td>
<td>15</td>
<td>14</td>
</tr>
</tbody>
</table>

*Data is referenced to that at \(n = 0.10\).*

**Example 20**

**The Phosphor of claim 1 wherein \(z\) is Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tm³⁺, Yb³⁺, and Bi³⁺.**

**The Phosphor of claim 1 wherein R³⁺ is Pr³⁺, Ho³⁺, Dy³⁺, Nd³⁺ or mixtures thereof.**

**The Phosphor of claim 1 which is a single crystal.**

**The Phosphor of claim 1 which has the formula:**

\[\text{SrAl}_2\text{O}_4:z\text{Eu}^{2+},2y\text{R}^{3+}\]

wherein \(x\) can range from about 0.0001 to about 0.05, and \(y\) can range from about 0.0001 to about 0.10.

**The phosphor of claim 5 wherein \(x\) is Pr³⁺, Ho³⁺, a combination of Pr³⁺ with Dy³⁺, or a combination of Ho³⁺ with Dy³⁺.**

**The phosphor of claim 5 wherein \(x\) is a number ranging from about 0.0001 to about 0.005.**

**The phosphor of claim 1 wherein \(m\) is 2 or 1.75.**

**The phosphor of claim 8 wherein \(M = \text{Sr.}**

**A phosphor represented by the formula:**

\[\text{MO}_{m}\text{Al}_2\text{O}_3:z\text{Eu}^{2+},z\text{R}^{3+}\]

wherein \(m\) is a number ranging from about 1.6 to about 2.2, \(M = \text{Sr or a combination of Sr with Ca, Ba or both,} R^{3+}\) is Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tm³⁺, Yb³⁺ and Bi³⁺.
21. A mixture of $Y^3+$ with another trivalent metal ion, Eu$^{2+}$ is present at a level from about 0.02 mol % to about 10 mol % of M, and R$^{3+}$ is present at a level from about 0.02 mol % to about 20 mol % of M.

11. The phosphor of claim 10 wherein R$^{3+}$ is a mixture of $Y^3+$ with a trivalent metal ion selected from the group Pr$^{3+}$, Ho$^{3+}$, Nd$^{3+}$, Dy$^{3+}$, Er$^{3+}$, Tm$^{3+}$, Lu$^{3+}$, Ce$^{3+}$, Sm$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, Tm$^{3+}$, Yb$^{3+}$ and Bi$^{3+}$.

12. A phosphor having the formula:

$$S_dBa_CaO \cdot mAl_2O_3:Eu^{2+},R^{3+}$$

where $k=1-n-p-2x-2y$ and $k$ is greater than 0, and $n$ and $p$ are numbers greater than or equal to 0 and less than 1, $x$ is a number that can range from about 0.0001 to about 0.05 and $v$ is a number that can range from 0.0001 to about 0.10.

13. A method for making a single crystal phosphor which comprises the steps of:

(a) combining the phosphor components according to the stoichiometry of the formula:

$$MO \cdot mAl_2O_3:Eu^{2+},R^{3+}$$

wherein $m$ is a number ranging from about 1.6 to about 2.2, $M$ is Sr or a combination of Sr with Ca, Ba or both, $R^{3+}$ is a trivalent rare earth metal ion, Bi$^{3+}$ or mixtures thereof, Eu$^{2+}$ is present at a level from about 0.02 mol % to about 10 mol % of M, and R$^{3+}$ is present at a level from about 0.02 mol % to about 10 mol % of M.

(b) sintering the powder in a reducing atmosphere;

(c) growing single crystals from the sintered powder under an inert atmosphere.

14. The method of claim 13 wherein a flux is combined with phosphor components in step (a).

15. A phosphor represented by the formula:

$$MO \cdot mAl_2O_3:Eu^{2+},R^{3+}$$

wherein $m$ is a number ranging from about 1.6 to about 2.2, $M$ is Sr or a combination of Sr with Ca, Ba or both, $R^{3+}$ is a trivalent rare earth metal ion, Bi$^{3+}$ or mixtures thereof, Eu$^{2+}$ is present at a level from about 0.02 mol % to about 10 mol % of M, and R$^{3+}$ is present at a level from about 0.02 mol % to about 20 mol % of M in which a portion of the Al$^{3+}$ in the host is substituted by a divalent metal ion or in which a portion of the M$^{2+}$ in the phosphor is substituted by a monovalent metal ion.

16. A phosphor of claim 15 wherein a portion of the Al$^{3+}$ in the host is substituted by a divalent metal ion.

17. The phosphor of claim 16 wherein the divalent ion is Mg$^{2+}$ or Zn$^{2+}$ or a mixture thereof.

18. The phosphor of claim 16 in which M$^{2+}$ in the phosphor is substituted by a monovalent metal ion.

19. The phosphor of claim 16 in which the amount of divalent metal ion substituted into the phosphor is equal to the amount of $R^{3+}$ in the phosphor.

20. The phosphor of claim 16 in which the amount of divalent metal ion substituted into the phosphor ranges from about 0.02 mol % to about 20 mol %.

21. The phosphor of claim 15 in which a portion of the M$^{2+}$ in the phosphor is substituted by a monovalent metal ion.

22. The phosphor of claim 21 in which the monovalent metal ion is Na$^+$ or K$^+$.

23. The phosphor of claim 22 in which the monovalent metal ion is present in the phosphor in an amount about equal to the amount of $R^{3+}$ trivalent metal ion doped into the phosphor.

24. The phosphor of claim 21 in which the amount of divalent metal ion substituted into the phosphor ranges from about 0.02 mol % to about 20 mol %.

25. The phosphor of claim 15 wherein $R^{3+}$ is selected from the group Pr$^{3+}$, Ho$^{3+}$, Nd$^{3+}$, Dy$^{3+}$, Er$^{3+}$, Tm$^{3+}$, Lu$^{3+}$, Ce$^{3+}$, Y$^{3+}$, Sm$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, Tm$^{3+}$, Yb$^{3+}$ and Bi$^{3+}$.

26. The phosphor of claim 15 wherein $R^{3+}$ is Pr$^{3+}$, Ho$^{3+}$, Dy$^{3+}$, or Nd$^{3+}$ or mixtures thereof.

27. The phosphor of claim 15 wherein $R^{3+}$ is a mixture of $Y^3+$ with another trivalent metal ion.

28. The phosphor of claim 15 which is a single crystal.

29. The phosphor of claim 15 further comprising from about 2 mol % to about 20 mol % of Bi$_2$O$_3$.

30. The phosphor of claim 15 wherein $M$ is Sr.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page.
Item [57], ABSTRACT
Delete "MO.mA12O3:E\textsuperscript{2+},R\textsuperscript{3+}" and replace with -- MO.mA12O3:Eu\textsuperscript{2+},R\textsuperscript{3+} --.

Column 1.
Line 28, delete "SrAl\textsubscript{2}O\textsubscript{5}:Eu\textsuperscript{2+},Dy\textsuperscript{3+}" and replace with -- SrAl\textsubscript{2}O\textsubscript{5}:Eu\textsuperscript{2+},Dy\textsuperscript{3+} --.
Lines 37-38, delete "has obtained" and replace with -- has been obtained --.
Line 41, delete "Sr\textsuperscript{2+}" and replace with -- Sr\textsuperscript{2+} --.
Line 50, delete "Dy\textsuperscript{3+n}" and replace with -- Dy\textsuperscript{3+n} --.
Line 50, delete "Eu\textsuperscript{2+n}" and replace with -- Eu\textsuperscript{2+n} --.
Line 62, delete "M\textsubscript{1-x}Al\textsubscript{2}O\textsubscript{4-x}: Where" and replace with -- M\textsubscript{1-x}Al\textsubscript{2}O\textsubscript{4-x}, where --.

Column 2.
Line 16, delete the comma after "Eu\textsuperscript{2+}n".
Lines 22-23, delete "2SrO.3Al\textsubscript{2}O\textsubscript{5}:Eu\textsuperscript{2+}n" and replace with -- 2SrO.3Al\textsubscript{2}O\textsubscript{5}:Eu\textsuperscript{2+}n --.
Lines 25-26, delete "4SrO.7Al\textsubscript{2}O\textsubscript{5}:Eu\textsuperscript{2+}n" and replace with -- 4SrO.7Al\textsubscript{2}O\textsubscript{5}:Eu\textsuperscript{2+}n --.
Line 26, delete "BaO.4Al\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{2+}n" and replace with -- BaO.4Al\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{2+}n --.
Line 38, delete "MO.mAl\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{2+},R\textsuperscript{3+n}" and replace with -- MO.mAl\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{2+},R\textsuperscript{3+n} --.
Line 47, delete "MO.mAl\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):Eu\textsuperscript{2+},R\textsuperscript{3+n}" and replace with -- MO.mAl\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):Eu\textsuperscript{2+},R\textsuperscript{3+n} --.

Column 4.
Line 32, delete "Sr\textsubscript{0.64}Ba\textsubscript{0.33}Al\textsubscript{2}O\textsubscript{7}" and replace with -- Sr\textsubscript{0.33}Ba\textsubscript{0.64}Al\textsubscript{2}O\textsubscript{7} --.
Line 36, delete "Sr\textsubscript{0.49}Ca\textsubscript{0.49}Al\textsubscript{2}O\textsubscript{7}" and replace with -- Sr\textsubscript{0.485}Ca\textsubscript{0.485}Al\textsubscript{2}O\textsubscript{7} --.

Column 5.
Line 9, delete "pressure" and replace with -- pressures --.
Line 13, delete "distinguishable" and replace with -- distinguishable --.
Line 16, delete "one the order" and replace with -- on the order --.
Line 38, delete "lasting form" and replace with -- lasting from --.
Line 46, delete "can exhibit" and replace with -- can exhibit --.
Line 49, delete "exhibit" and replace with -- exhibit --.
Line 55, delete "MO.mAl\textsubscript{2}O\textsubscript{3}" and replace with -- MO.mAl\textsubscript{2}O\textsubscript{3} --.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

**Column 7.**
Line 10, delete "pellets are the" and replace with -- pellets are then --.
Line 15, delete "laser heated pedestal method" and replace with -- laser heated pedestal growth (LHPG) method --.
Line 16, delete "bars to" and replace with -- bars for --.
Line 20, delete "somehat" and replace with -- somewhat --.
Line 28, delete "LHGP" and replace with -- LHPG --.
Line 42, delete "M₀_mAl₂O₃(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺" and replace with -- M₀_mAl₂O₃(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺ --.

**Column 8.**
Line 1, delete "M₀_mAl₂O₃(zB₂O₃):2ₓEu²⁺,2ᵧ₁R₁³⁺,2ᵧ₂R₂³⁺" and replace with -- M₀_mAl₂O₃(zB₂O₃):2ₓEu²⁺,2ᵧ₁R₁³⁺,2ᵧ₂R₂³⁺ --.
Line 15, delete "M₀.(m-q)Al₂O₃.qXO(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺" and replace with -- M₀.(m-q)Al₂O₃.qXO(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺ --.
Line 31, delete "M₀_mAl₂O₃.rZ₂(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺" and replace with -- M₀_mAl₂O₃.rZ₂(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺ --.
Line 60, delete "M₀_mAl₂O₃" and replace with -- MO_mAl₂O₃ --.

**Column 9.**
Line 10, delete "M₀_mAl₂O₃(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺" and replace with -- M₀_mAl₂O₃(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺ --.
Line 28, delete "M₀_mAl₂O₃(zB₂O₃):2ₓEu²⁺,2ᵧ₁R₁³⁺,2ᵧ₂R₂³⁺" and replace with -- M₀_mAl₂O₃(zB₂O₃):2ₓEu²⁺,2ᵧ₁R₁³⁺,2ᵧ₂R₂³⁺ --.
Line 50, delete "M₀.(m-q)Al₂O₃.qXO(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺" and replace with -- M₀.(m-q)Al₂O₃.qXO(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺ --.
Line 67, delete "M₀_mAl₂O₃.rZ₂(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺" and replace with -- M₀_mAl₂O₃.rZ₂(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺ --.

**Column 10.**
Line 2, delete "x ranges" and replace with -- x is a number ranging --.
Line 4, delete "z ranges" and replace with -- z is a number ranging --.
Line 4, after "about 0.2;" insert on a new line -- m is a number ranging from about 1.6 to about 2.2; --
Line 5, start a new line after "K".
Line 7, after "E has" insert -- the value of --.
Line 11, delete "SrBa₂Ca₉O₃.mAl₂O₃(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺" and replace with -- SrBa₂Ca₉O₃.mAl₂O₃(zB₂O₃):2ₓEu²⁺,2ᵧR³⁺ --.
Line 45, delete "Bi³⁺" and replace with -- Bi³⁺ --.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

**Column 11.**
Lines 6 and 16, delete "SrAlO$_7$:0.01Eu$^{2+}$:0.02Pr$^{3+}$" and replace with
-- SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Pr$^{3+}$ --.
Line 25, delete "SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$" and replace with
-- SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Pr$^{3+}$ --.
Lines 29, 32, 37 and 39-40, delete "SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$" and replace with
-- SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Pr$^{3+}$ --.
Line 46, delete "SrAlO$_7$(B$_2$O$_3$):Eu$^{2+}$:Pr$^{3+}$" and replace with -- SrAlO$_7$(B$_2$O$_3$):Eu$^{2+}$,Pr$^{3+}$ --.
Lines 50-51, delete "SrAlO$_7$(0.1B$_2$O$_3$):Eu$^{2+}$:Pr$^{3+}$" and replace with -- SrAlO$_7$(0.1B$_2$O$_3$):
Eu$^{2+}$,Pr$^{3+}$ --.
Line 60, delete "0.01 to 0.15" and replace with -- 0.001 to 0.015 --.

**Column 12.**
Lines 17-18 and 21-22, delete "SrAlO$_7$(0.1B$_2$O$_3$):Eu$^{2+}$:Pr$^{3+}$" and replace with -- SrAlO$_7$(0.1B$_2$O$_3$):Eu$^{2+}$,Pr$^{3+}$ --.
Line 43, Table 2, delete "SrAlO$_7$(B$_2$O$_3$):0.01Eu:2yPr" and replace with -- SrAlO$_7$(B$_2$O$_3$):0.01Eu,2yPr --.
Lines 55-56, delete "SrAlO$_7$(B$_2$O$_3$):Eu$^{2+}$:Ho$^{3+}$" and replace with -- SrAlO$_7$(B$_2$O$_3$):Eu$^{2+}$,Ho$^{3+}$ --.
Lines 58 and 66, delete "SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Ho$^{3+}$" and replace with -- SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Ho$^{3+}$ --.

**Column 13.**
Lines 8, 14, 17 and 22, delete "SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Ho$^{3+}$" and replace with -- SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Ho$^{3+}$ --.
Lines 29-30, delete "SrAlO$_7$(B$_2$O$_3$):Eu$^{2+}$:Nd$^{3+}$" and replace with -- SrAlO$_7$(B$_2$O$_3$):Eu$^{2+}$,Nd$^{3+}$ --.
Lines 33, 43, 53, 58, 61 and 66, delete "SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Nd$^{3+}$" and replace with -- SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Nd$^{3+}$ --.
Line 54, delete "line (a)" and replace with -- (line a) --.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

**Column 14,**
Lines 7 and 15, delete "SrAl$_2$O$_4$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02R$^{3+}$" and replace with -- SrAl$_2$O$_4$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02R$^{3+}$ --.
Line 19, after "(+)" please insert -- are shown --.
Lines 34-35, delete "SrAl$_2$O$_4$(B$_2$O$_3$):0.01Eu$^{2+}$:0.01Pr$^{3+}$:0.01R$^{3+}$" and replace with -- SrAl$_2$O$_4$(B$_2$O$_3$):0.01Eu$^{2+}$,0.01Pr$^{3+}$,0.01R$^{3+}$ --.
Line 38, delete "SrAl$_2$O$_4$(B$_2$O$_3$):Eu$^{2+}$:Pr$^{3+}$" and replace with -- SrAl$_2$O$_4$(B$_2$O$_3$):Eu$^{2+}$, Pr$^{3+}$ --.
Line 48, delete "ranges of in" and replace with -- ranges of m --.
Lines 56 and 60-61, delete "SrAl$_2$O$_4$(0.1B$_2$O$_3$):0.01Eu:0.01Pr:0.01R" and replace with -- SrAl$_2$O$_4$(0.1B$_2$O$_3$):0.01Eu,0.01Pr,0.01R --.

**Column 16,**
Line 13, delete "(Sr$_{0.33}$Ba$_{0.64}$)(0.1B$_2$O$_3$)Al$_4$O$_7$:0.01Eu:0.02Pr" and replace with -- (Sr$_{0.33}$Ba$_{0.64}$)(0.1B$_2$O$_3$)Al$_4$O$_7$:0.01Eu,0.02Pr --.
Line 22, delete "Sr$_3$Ba$_2$O$_m$Al$_2$O$_7$(zB$_2$O$_3$):2xEu$_2$yR" and replace with -- Sr$_3$Ba$_2$O$_m$Al$_2$O$_7$(zB$_2$O$_3$):2xEu$_2$yR --.
Line 48, delete "Sr$_3$Ca$_4$O$_m$Al$_4$O$_7$(zB$_2$O$_3$):2xEu$_2$yR" and replace with -- Sr$_3$Ca$_4$O$_m$Al$_4$O$_7$(zB$_2$O$_3$):2xEu$_2$yR --.
Line 52, delete "(Sr$_{0.485}$Ca$_{0.485}$)Al$_4$O$_7$:0.01Eu:0.02Pr" and replace with -- (Sr$_{0.485}$Ca$_{0.485}$)Al$_4$O$_7$:0.01Eu,0.02Pr --.
Lines 58-59, delete "(Sr$_{0.485}$Ca$_{0.485}$)(0.1B$_2$O$_3$)Al$_4$O$_7$:0.01Eu:0.02Pr" and replace with -- (Sr$_{0.485}$Ca$_{0.485}$)(0.1B$_2$O$_3$)Al$_4$O$_7$:0.01Eu,0.02Pr --.

**Column 17,**
Line 7, delete "Sr$_3$Ba$_2$Ca$_4$O$_m$Al$_2$O$_7$(zB$_2$O$_3$):2xEu$_2$yR" and replace with -- Sr$_3$Ba$_2$Ca$_4$O$_m$Al$_2$O$_7$(zB$_2$O$_3$):2xEu$_2$yR --.
Lines 13-14 and 57-58, delete "MO.mAl$_2$O$_3$:Eu$^{2+}$" and replace with -- MO.mAl$_2$O$_3$:Eu$^{2+}$, R$^{3+}$ --.
Line 29, delete "M$_4$O,(m-q)Al$_2$O$_3$,q XO:2xEu$_2$yR" and replace with -- M$_4$O,(m-q)Al$_2$O$_3$,q XO:2xEu$_2$yR --.

**Column 18,**
Line 6, delete "M$_4$O,mAl$_2$O$_3$,rNa$_2$O:2xEu$_2$yR" and replace with -- M$_4$O,mAl$_2$O$_3$,rNa$_2$O:2xEu$_2$yR --.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 20.
Line 7, start a new paragraph after "original valence state."
Line 36, delete "MO.mAl2O3:Eu2+,R3+" and replace with -- MO.mAl2O3:Eu2+,R3+ --.
Lines 44-45, delete "selected from the group".
Line 46, delete "and" and replace with -- or --.
Line 64, delete "MO.mAl2O3:Eu2+,R3+" and replace with -- MO.mAl2O3:Eu2+,R3+ --.

Column 21.
Line 3, delete "R3+, is present" and replace with -- R3+ is present --.
Line 11, delete "Sr2Ba,Ca,0.mAl2O3:2xEu2+,2yR3+ " and replace with -- Sr2Ba,Ca,0.mAl2O3:2xEu2+,2yR3+ --.
Line 15, delete "v" and replace with -- y --.
Lines 22 and 37, delete "MO.mAl2O3:Eu2+,R3+" and replace with -- MO.mAl2O3:Eu2+,R3+ --.

Column 22.
Line 4, delete "M2" and replace with -- M2+ --.
Line 10, after "in which" insert -- a portion of the --.

Signed and Sealed this

Fifteenth Day of April, 2003

[Signature]

JAMES E. ROGAN
Director of the United States Patent and Trademark Office