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


FIG. 1
FIG. 2

[Graph showing a log-log plot with two straight lines labeled 'a' and 'b', representing the relationship between intensity (a.u.) and delay time (minute).]
FIG. 3
FIG. 5
FIG. 6

Delay Time (minute)

Intensity (a.u.)
FIG. 7
FIG. 8

Wavelength (nm)

Intensity (a.u.)

- after 5 sec
- after 20 sec
- after 60 sec
FIG. 9

Delay Time (minute)

Intensity (a.u.)

10^6
10^5
10^4
10^3
10^2

1 10 100 1000

Lines a, b, and c are plotted on a log-log scale, showing the relationship between intensity and delay time.
FIG. 10
FIG. 11
FIG. 12
FIG. 13
FIG. 14

Graph showing the relationship between intensity (a.u.) and delay time (minute). Lines labeled a, b, and c.
FIG. 15

Graph showing the intensity (a.u.) as a function of wavelength (nm) for different time periods: after 5 sec, after 20 sec, and after 60 sec.
FIG. 16

The graph shows the intensity (a.u.) vs. wavelength (nm) with data points labeled as follows:
- ○ after 5 sec
- ○ after 20 sec
- ▲ after 60 sec

The intensity peaks at around 500 nm with a peak intensity of approximately 5,500 a.u. after 20 seconds.
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 NCCS-252, ARO DAHH4-96-10416 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,Zn, 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 been 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).

Improved long persistence phosphors of certain alkaline earth aluminates were reported by T. Matsuzawa, Y. Aoki, N. Takeuchi and Y. Murayama (1996) J. Electrochem. Soc. 143(8):2670, and in U.S. Pat. No. 5,424,006. The brightness and persistence time of SrAl₂O₄:Eu²⁺ was improved by co-doping various trivalent rare earth ions to produce appropriate trapping centers. The best result was obtained by co-doping Dy³⁺ with Eu²⁺ into SrAl₂O₄ and Nd³⁺ with Eu²⁺ into CaAl₂O₄ to get long persistent green and purple emission, respectively. U.S. Pat. No. 5,424,006 also reports phosphors in which Mg²⁺ is substituted for Sr²⁺ in SrAl₂O₄:Eu²⁺, Dy³⁺.

EP published application 765,925 (Moriyama et al.) reports Eu²⁺-activated strontium aluminate phosphors in which part of the Sr²⁺ of the host is replaced with Pb²⁺, Dy³⁺ or Zn²⁺. The zinc-doped materials are reported to display enhanced brightness and persistence compared to SrAl₂O₄:Eu²⁺, Dy³⁺.

EP published application 710,709 (Murayama et al.) reports phosphors of matrix Mₓ-xSrAl₂O₄. Where M is at least one metal selected from calcium, strontium, barium and, optionally, magnesium, and x is a number not equal to 0. The matrix comprises europium as an activator and a co-activator elected from a rare earth metal, manganese, tin or bismuth.

SUMMARY OF THE INVENTION

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

MO.ₙMₓ-xAl₂O₄:Eu²⁺,R³⁺

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; and n is a number ranging from about 0.6 to about 2.2. The phosphors are prepared using a flux, particularly B₂O₃. The preferred phosphor formula of this invention indicating the presence of B₂O₃ flux is:

MO.ₙMₓ-xAl₂O₄:Eu²⁺,R³⁺

where M, n and R³⁺ are as defined in formula 1 and x 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 0.02 mol % to about 10 mol % of 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 2.0 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 in ceramic form can be used for manufacture of persistence. Phosphor materials of this invention are those in which M is Sr.

Preferred phosphors of this invention are activated with Eu²⁺ and are co-doped with a trivalent rare earth metal ion or Bi³⁺. The phosphors may be co-doped with a single ion or a combination of such ions selected from the group of rare earth metal ions: Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, 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. Sr₂Al₄O₉:Eu²⁺, Pr³⁺, Dy³⁺ or Sr₂Al₄O₉:Eu²⁺, Ho³⁺, Dy³⁺.

Preferred phosphors are those with m ranging from about 1.70 to about 2.05 and, more preferred, are those where m=1.75, the host material being Sr₂Al₄O₉ and m=2, the host material being MAI₄O₇. More preferred are phosphors where M=Sr and m=1.75 or m=2.

Phosphors of this invention also include those in which Mg²⁺ or Zn²⁺, or a mixture of both, is substituted for M²⁺, particularly Sr²⁺, 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 phosphors 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 pelletled 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)0.01Eu²⁺,0.02Pr³⁺, and (b) of commercial blue phosphor CaS:Si: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. 10** illustrates the excitation and emission spectra of SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺,0.02Nd³⁺ where excitation was monitored at 488 nm. **FIG. 11** is a graph of decay curves of the after-glow of SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺,0.02Nd³⁺ measured in the first 15 sec. after exposure to a 13 W fluorescent lamp (measured at 488 nm). Decay curves for R=La ( VII), Ce ( V), Sm ( V), Gd (IV), Tb (VII), Dy (VI), Er (VI), Tm (V), Yb (V), and Lu (V) are shown. The decay curve of the sample Sr₂Al₄O₉:Eu:Nd is also shown for comparison.

**FIG. 12** is a graph comparing after-glow decay curves for samples of SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺,0.01Pr²⁺ co-doped with 0.01 Y (IV), Lu(IV), or La(IV). **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 Sr₀·₆B₂O₃·Al₂O₃:0.01Eu²⁺,0.02Pr²⁺ after exposure to a 4 W UV lamp for 2 minutes as a function of time after illumination (C₁, after 5 sec.; C₂, after 20 sec. and C₃, after 60 sec.). **FIG. 16** illustrates the spectra of the after-glow of Sr₀·₄Ca₀·₆Al₂O₄:0.01Eu²⁺,0.02Pr²⁺ after exposure to a 4 W UV lamp for 2 minutes as a function of time after illumination (C₁, after 5 sec.; C₂, after 20 sec. and C₃, 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.

Persistent phosphorescence was discovered in the 11th century in China and Japan and in the 16th century in Europe (Shionoya, S. (1998) in Phosphor Handbook, Shionoya, S. and Yen, W. M. (eds.), CRC Press, Inc., Boca Raton, N.Y., p. 3). The phenomenon involves two kinds of active centers: emitters and traps. The phosphorescent dynamics are complex and many aspects remain unclear. Thermoluminescence and photostimulable phosphorescence are physically governed by mechanisms similar to persistent phosphorescence. Chen, R and McKeever, S. W. S. (1997), Theory of Thermoluminescence and Related Phenomena, World Scientific, Singapore; Sonoda, M. et al. (1983) Radiology 148:833). 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 photo-stimulation. 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). Large 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. Variations in the term “long-persistent phosphor” historically has been used to refer to ZnS:Cu, CaS:Eu, Tm and similar materials. 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 aluminates with improved properties. The presence or absence of flux in the preparation of strontium aluminates can affect the ultimate structure of the aluminate. For example, when m=1.75 and M=Sr, the host material becomes Sr,Al, O, with an orthorhombic structure with space group Pnma in the monoclinic with space group C2/c when synthesized without flux (e.g., B, O,).

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

The exact role of the flux B, O, 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 aluminates can affect the ultimate structure of the aluminate. For example, when m=1.75 and M=Sr, the host material becomes Sr,Al, O, with an orthorhombic structure with space group Pnma in the presence of flux (e.g., B, O,). This structure of strontium aluminate can be made only in the presence of flux. In the case where m=2 and M=Sr, the host material Sr,Al, O, formed in the presence of flux is similar in structure to orthorhombic Sr,Al, O, (see FIG. 4). This material is monoclinic with space group C, 2/c when synthesized without flux (e.g., B, O,).

The phosphors of this invention can be made by the following general method. Phosphor components are com-
bined 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. (dependent 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 Eu²⁺ ions and to minimize or avoid oxidation 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 LHGP process. It was observed that the initial part of the fiber prepared by the LHGP 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:

\[(1-2x-2y)MCO₃ + 3Al₂O₃ + 2Eu²⁺ + 2yR³⁺ \]

and will have the general formula:

\[M₃O₆ \cdot mAl₂O₃ (zB₂O₅):2xEu²⁺,2yR³⁺\]

where \(k=1-2x-2y\), \(m\) 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 0.0 to about 0.2. \(M\) is most generally an alkaline earth metal, but is preferably Sr or a mixture of Sr with Ca, Ba or both. \(R³⁺\) is generally one or more trivalent metal ions, but is preferably a trivalent metal ion selected from the group: Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tm³⁺, and Yb³⁺ and Bi³⁺. Preferred trivalent codopants are Pr³⁺, Ho³⁺, Dy³⁺, and Nd³⁺. Co-doping of Dy³⁺ or Y³⁺ along with other trivalent metal ions improves brightness of other phosphors of this invention.

The combined phosphor components are milled or ground into a homogeneous fine powder, optionally pressed into pellets and prefired in air for about 1 hr at about 600°C. The prefired material is milled or ground into a fine powder for sintering. The powder is optionally pressed before sintering. The material is sintered at about 1300°C for one hour in a reducing atmosphere, such as a mixture of N₂ and H₂ (about 1–5% by volume).

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

\[M₃O₆ \cdot mAl₂O₃ (zB₂O₅):2xEu²⁺,2yR²⁺,2yR³⁺\]

where \(k=1-2x-2y\), \(m\) is as defined above, \(y₁+y₂=2y\), and \(R₁\) and \(R₂\) 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 \(R₁\) and \(R₂\).

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

\[M₃O₆ \cdot (m-q)Al₂O₃ \cdot qXO₂ZB₂O₅:2xEu²⁺,2yR²⁺\]

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. \(XO\) is a metal oxide preferably MgO or ZnO and \(q\) can range from about 0.0001 to about 0.20. The amount of divalent ion (q) from \(XO\) added to the matrix to replace \(Al^{3+}\) is preferably equal to the amount of \(R²⁺\) doped into the matrix (i.e., the value of \(r\) preferably-the value of \(2y\)).

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

\[M₃O₆ \cdot mAl₂O₃ \cdot (zB₂O₅):2xEu²⁺,2yR²⁺\]

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. \(ZO\) is an alkali metal oxide preferably \(Na₂O\) or \(K₂O\) and \(r\) can range from about 0.0001 to about 0.20. The amount of monovalent ion (2r) added to the matrix to replace \(M^{2+}\) is preferably equal to the amount of \(R²⁺\) doped into the matrix (i.e., the value of \(r\) preferably-the value of \(y\)). A slight excess over the desired or preferred amount of \(ZO\) may be added to compensate for any \(Z⁺\) that may be vaporized during sintering.

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: \(MO \cdot mAl₂O₃\), where \(M\) is an alkaline earth metal, and \(m\) is a number ranging from about 1.6 to about 2.2, the host containing from about 0.01 mol % to about 5 mol %, relative to \(M\), of an activator, and containing from about 0.01 mol % to about 5 mol %, relative to \(M\), of a trivalent metal ion dopant selected from the group of trivalent ions Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tm³⁺, and Yb³⁺ and Bi³⁺.
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⁺.

A phosphorescent material having the formula:

\[ M₉O \cdot mAl₂(O₃)₂xB₃O₃ : 2xEu³⁺ , 2yR³⁺ , \]

where: k = 1 - 2x - 2y, m is a number ranging from about 1.6 to about 2.2; z is a number ranging from about 0.01 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.

A phosphorescent material of having the formula:

\[ M₉O \cdot mAl₂(O₃)₂xB₃O₃ : 2xEu³⁺ , 2yR³⁺ , \]

where: k = 1 - 2x - 2y, m is a number ranging from about 1.6 to about 2.2; z is a number ranging from about 0.01 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 R²⁺ 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 R₂³⁺ is Y³⁺.

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

A phosphorescent material having the formula:

\[ M₉O \cdot (m-q)Al₂(O₃)₂xB₃O₃ : 2xEu³⁺ , 2yR³⁺ , \]

where: k = 1 - 2x - 2y, m is a number ranging from about 1.6 to about 2.2; z is a number ranging from about 0.01 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⁺, Nd³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tm³⁺, Yb³⁺ and Bi³⁺.

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

A phosphorescent material having the formula:

\[ M₉O \cdot mAl₂(O₃)₂xB₃O₃ : 2xEu³⁺ , 2yR³⁺ , \]

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; Z is an alkali metal ion, particularly Na⁺ or K⁺ and r ranges from 0 to 0.2.

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

A phosphorescent material having the formula:

\[ Sr₉Ba₂Ce₅O₁₉ : Eu³⁺, Pr³⁺ \]

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 0.01 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 M₉O₃ (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:

\[(1~2x~2y)M(CO)₃+2.00 Al₂O₃+xEu₂O₃+yR₂O₃+zB₂O₃; \]

where:

2x+2y is less than 1, preferably x=about 0.001 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 homogeneous 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) : Eu³⁺,Pr³⁺ Phosphors

The methods and phosphors of this invention are specifically exemplified by preparation of SrAl₂O₄(0.1B₂O₃):Eu³⁺,
R\textsuperscript{3+} (Eu\textsuperscript{2+} and R\textsuperscript{3+} co-doped strontium aluminate) phosphors. These methods of preparation also specifically apply to Sr\textsubscript{4}Al\textsubscript{5}O\textsubscript{12}:Eu\textsuperscript{2+}-R\textsuperscript{3+} phosphors and the properties exhibited by SrAl\textsubscript{2}O\textsubscript{4}:Eu\textsuperscript{2+}-R\textsuperscript{3+} phosphors generally exemplify those of SrAl\textsubscript{4}O\textsubscript{25}:Eu\textsuperscript{2+}-R\textsuperscript{3+} phosphors.

SrAl\textsubscript{2}O\textsubscript{4}:0.01Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} is prepared by the general method of Example 1 mixing the components in the following molar proportions:

\[
0.97 \text{SrCO}_3+2.00 \text{Al}_2\text{O}_3+0.005 \text{Eu}_2\text{O}_3+0.01 \text{Pr}_2\text{O}_3+0.1 \text{B}_2\text{O}_3
\]

where B\textsubscript{2}O\textsubscript{3} serves as a flux. The milled mixed powders are pelletized prior to pre firing and pelletized prior to sintering.

FIG. 1 shows the spectrum of the after-glow of a sample of SrAl\textsubscript{2}O\textsubscript{4}:0.01Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} 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\textsuperscript{-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 SrAl\textsubscript{2}O\textsubscript{4}:0.01Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of a commercial blue phosphor CaSrS:Bi after similar exposure is also shown (line b). The SrAl\textsubscript{2}O\textsubscript{4}:0.01Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} phosphor is about 10x brighter than the commercial blue phosphor and has a persistence time about 20 times longer. After 18 hours SrAl\textsubscript{2}O\textsubscript{4}:0.01Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

FIG. 3 presents the excitation and emission spectra of SrAl\textsubscript{2}O\textsubscript{4}:0.01Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} where the excitation spectrum was monitored at 488nm.

FIG. 4 is the x-ray diffraction pattern of the SrAl\textsubscript{2}O\textsubscript{4} (0.1B\textsubscript{2}O\textsubscript{3})sample. This x-ray pattern indicated that the structure of SrAl\textsubscript{2}O\textsubscript{4} (0.1B\textsubscript{2}O\textsubscript{3}) is similar to Sr\textsubscript{4}Al\textsubscript{5}O\textsubscript{12} (0.3B\textsubscript{2}O\textsubscript{3}).

Example 3

Preparation and Characterization of SrAl\textsubscript{2}O\textsubscript{4}(B\textsubscript{2}O\textsubscript{3}) :Eu\textsuperscript{2+},Pr\textsuperscript{3+}, Phosphors with Varying Amounts of Eu\textsuperscript{2+}

Table 1 shows time persistence of after-glow of the phosphor as a function of Eu\textsuperscript{2+} content (x) with Pr\textsuperscript{3+} content held at 0.01 (2x).

Table 2 presents the excitation and emission spectra of SrAl\textsubscript{2}O\textsubscript{4}(B\textsubscript{2}O\textsubscript{3}) :Eu\textsuperscript{2+},Pr\textsuperscript{3+} phosphors with varying amounts of Pr\textsuperscript{3+}.

Example 4

Preparation and Characterization of SrAl\textsubscript{2}O\textsubscript{4} (0.1B\textsubscript{2}O\textsubscript{3}):Eu\textsuperscript{2+},Pr\textsuperscript{3+} Phosphors with Varying Amounts of Pr\textsuperscript{3+}

Table 2 shows time persistence of after-glow of the phosphor as a function of Pr\textsuperscript{3+} content (y) with Eu\textsuperscript{2+} content held at 0.01 (2x). In Table 2, the phosphor samples in which y (Pr\textsubscript{2}O\textsubscript{3} 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:

\[
(0.99-2y) \text{SrCO}_3+2.00 \text{Al}_2\text{O}_3+0.005 \text{Eu}_2\text{O}_3+y\text{Pr}_2\text{O}_3+0.1 \text{B}_2\text{O}_3
\]

where y was varied from 0.005 to 0.02 with Eu\textsuperscript{2+} molar concentration held at 0.01 (2x) as indicated in Table 2.

Pre-concentration dependence of SrAl\textsubscript{2}O\textsubscript{4}(0.1B\textsubscript{2}O\textsubscript{3}):Eu\textsuperscript{2+},Pr\textsuperscript{3+} phosphor after-glow was examined by preparing phosphor samples in which y (Pr\textsubscript{2}O\textsubscript{3} molar concentration) was varied from 0.005 to 0.02.

Example 5

Preparation and Characterization of SrAl\textsubscript{2}O\textsubscript{4}(B\textsubscript{2}O\textsubscript{3}) :Eu\textsuperscript{2+},Ho\textsuperscript{3+} Blue Phosphors

SrAl\textsubscript{2}O\textsubscript{4}(0.1B\textsubscript{2}O\textsubscript{3}) :0.01Eu\textsuperscript{2+}-0.02Ho\textsuperscript{3+} was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

\[
0.97 \text{SrCO}_3+2.00 \text{Al}_2\text{O}_3+0.005 \text{Eu}_2\text{O}_3+y\text{Ho}_2\text{O}_3+0.1 \text{B}_2\text{O}_3
\]

where B\textsubscript{2}O\textsubscript{3} serves as flux.

FIG. 5 shows the spectrum of the after-glow of a sample of SrAl\textsubscript{2}O\textsubscript{4}(0.1B\textsubscript{2}O\textsubscript{3}) :Eu\textsuperscript{2+},Ho\textsuperscript{3+} 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 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 decay of the after-glow of a sample of SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Nd³⁺ exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of the after-glow of SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Pr³⁺ (line b) and a commercial blue phosphor CaSrS:Bi (c) after similar exposure are also shown. The SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Pr³⁺ phosphor shows similar brightness and persistence to that of SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Nd³⁺. After 20 hours SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Nd³⁺ 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 SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Nd³⁺ where the excitation spectrum was monitored at 488 nm.

Example 6

Preparation and Characterization of SrAlO₃(B₂O₃)
:Eu²⁺:Nd³⁺ Blue Phosphors

SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Nd³⁺ was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

\[ 0.97 \text{SrCO}_₃ + 2.00 \text{Al}_₂\text{O}_₃ + 0.005 \text{Eu}_₂\text{O}_₃ + 0.01 \text{Nd}_₂\text{O}_₃ + 0.1 \text{B}_₂\text{O}_₃ \]

where B₂O₃ serves as flux.

FIG. 8 shows the spectrum of the after-glow of a sample of SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Nd³⁺ 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 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 SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Nd³⁺ exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of the after-glow of SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Pr³⁺ (b) and a commercial blue phosphor CaSrS:Bi (c) after similar exposure are also shown. The SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Pr³⁺ phosphor shows similar brightness and persistence to that of SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Nd³⁺. After 20 hours SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Pr³⁺ 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 SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂Nd³⁺ where the excitation spectrum was monitored at 488 nm.

Example 7

Preparation and Characterization of Phosphors of Formula SrAlO₃(B₂O₃)₀.₀₁Eu²⁺:₀.₀₂R³⁺, where R are trivalent metal ions of La, Ce, Sm, Gd, Tb, Dy, Er, Tm, Yb, and Lu.

SrAlO₃(0.1B₂O₃)₀.₀₁Eu²⁺:₀.₀₂R³⁺ were prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

\[ 0.97 \text{SrCO}_₃ + 2.00 \text{Al}_₂\text{O}_₃ + 0.005 \text{Eu}_₂\text{O}_₃ + 0.01 \text{R}_₂\text{O}_₃ + 0.1 \text{B}_₂\text{O}_₃ \]

with R=La, Ce, Sm, Gd, Tb, Dy, Er, Tm, Yb, and Lu.

FIG. 11 shows the decay curves of the after-glow of the SrAlO₃(B₂O₃)₀.₀₁Eu²⁺:₀.₀₂R³⁺ samples measured at 488 nm prepared in the first 15 seconds after exposure to the light of a 13 W fluorescent lamp. Decay curves for R=La (W), Ce (o), Sm (u), Gd (d), Tb (s), Dy (e), Er (A), Tm (o), Yb (x), and Lu (u). The decay curve of the sample SrAlO₃(0.1B₂O₃):Eu:Nd (closed circles) is also shown for comparison. It can be seen that the after-glow of these samples are generally much less intense than analogous phosphor samples codoped with Nd. The sample codoped with Dy exhibits much longer decay time (shallower slope) than the Nd codoped phosphor. This indicates that Dy forms a much deeper trapping center than Nb, Ho or Pr.

The luminescence spectra from SrAlO₃(0.1B₂O₃)₀.₀₁Eu₂⁺:₀.₀₂Pr where R is La, Er, Nd, and Tm have similar wavelength dependence to that of the phosphor where R is Pr. There is no notable spectral shift with R.

Example 8

Preparation and Characterization of SrAlO₃(B₂O₃)
:₀.₀₁Eu²⁺:₀.₀₁Pr²⁺:₀.₀₁R³⁺ where R is La, Eu, Nd, and Bi.

This example is intended to determine if co-doping of metal ions into a SrAlO₃(B₂O₃):Eu²⁺:Pr²⁺ phosphor increases UV excitation efficiency and improves phosphor brightness.

Phosphors are prepared by the method of Example 1 with components combined in the following general molar proportions:

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

where y₁+y₂=y₂, 1-2x-2y=0 and the ranges of in, x, y and z are as in formula 1 above.

More specifically where M=Sr and m=2 the components are combined in the following proportions:

\[ 0.97 \text{SrCO}_₃ + 2.00 \text{Al}_₂\text{O}_₃ + 0.005 \text{Eu}_₂\text{O}_₃ + 0.005 \text{Pr}_₂\text{O}_₃ + 0.005 \text{R}_₂\text{O}_₃ + 0.1 \text{B}_₂\text{O}_₃ \]

where R= Y, La, Lu, Eu, and Bi. The intensity of the afterglow of SrAlO₃(0.1B₂O₃):₀.₀₁Eu₂⁺:₀.₀₁Pr₂⁺:₀.₀₁R₃⁺ samples measured at 488 nm relative to that of SrAlO₃(0.1B₂O₃):₀.₀₁Eu₂⁺:₀.₀₂Pr₂⁺ is given in Table 3. Some results are also shown in FIG. 12.

FIG. 12 shows decay curves of the after-glow of SrAlO₃(0.1B₂O₃):₀.₀₁Eu₂⁺:₀.₀₁Pr₂⁺:₀.₀₁R₃⁺ (R= Y³⁺, La³⁺, and Lu³⁺) samples in the first 60 minutes. The samples were exposed to a 4 W UV lamp for two minutes.

FIG. 13 is the excitation and emission spectra of the sample SrAlO₃(0.1B₂O₃):₀.₀₁Eu²⁺:₀.₀₁Pr²⁺:₀.₀₁Y³⁺ where the excitation spectrum was monitored at 488 nm. Codoping with Y³⁺ and Pr²⁺ increases the UV excitation.
efficiency and improve the brightness by 50\% compared to the analogous Pr\(^3\+\)-doped phosphor.

### TABLE 3

<table>
<thead>
<tr>
<th>after (min)</th>
<th>Pr(^3+)</th>
<th>Y</th>
<th>La</th>
<th>Lu</th>
<th>Er</th>
<th>Bi</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>105</td>
<td>105</td>
<td>105</td>
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<td>32</td>
<td>16</td>
<td>17</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\)Data is referenced to that of the SrAl\(_2\)O\(_4\):(B\(_2\)O\(_3\)):Eu,Pr phosphor.

### Example 9

Preparation and Characterization of SrAl\(_2\)O\(_4\):(0.1B\(_2\)O\(_3\)):0.01Eu,0.01Dy,0.01Ho

This example demonstrates the influence of deep trapping centers formed by Dy\(^3\+) on the decay characteristics of SrAl\(_2\)O\(_4\):(B\(_2\)O\(_3\)):Eu,Pr doped with 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\(_2\)O\(_3\)+xEu\(_2\)O\(_3\)+yR\(_2\)O\(_3\)+zB\(_2\)O\(_3\)\]

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 0.2; and \(R\)\(^{3+}\) is a trivalent rare earth metal ion or Bi\(^{3+}\).

These mixed alkaline earth aluminate phosphors have the general formula:

\[Sr\(_{0.33}\)Ba\(_{0.4}\)Al\(_{2}\)O\(_7\):0.01Eu:0.02Pr\]

where \(k=1-\frac{p-2x}{2y}\).

### TABLE 4

The influence of deep centers of Dy on the after-glow of SrAl\(_2\)O\(_4\):(B\(_2\)O\(_3\)):Eu,Pr after (min)

<table>
<thead>
<tr>
<th>after (min)</th>
<th>SAO-EuPr(^3+)</th>
<th>SAO-EuPrDy</th>
<th>SAO-EuHoDy</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>301</td>
<td>252</td>
</tr>
<tr>
<td>30</td>
<td>31</td>
<td>99</td>
<td>75</td>
</tr>
<tr>
<td>60</td>
<td>60</td>
<td>47</td>
<td>35</td>
</tr>
</tbody>
</table>

\(^1\)Data is referenced to that of SAO-EuPr.

### Example 10

Preparation and Characterization of mixed alkaline earth aluminate phosphors

Mixed 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\(_2\)O\(_3\)+xEu\(_2\)O\(_3\)+yR\(_2\)O\(_3\)+zB\(_2\)O\(_3\)\]

where: \(n+2x+2y\) is less than 1 (there is some Sr present).

The mixed alkaline earth aluminate compound, (Sr\(_{0.33}\)Ba\(_{0.4}\)Al\(_{2}\)O\(_7\)):0.01Eu:0.02Pr was prepared following the general procedure of Example 1 combining the components in the following molar proportions:

\[0.33 \text{ ScCO}_3+0.64 \text{ BaCO}_3+2.00 \text{ Al}_2\text{O}_3+0.005 \text{ Eu}_2\text{O}_3+0.01 \text{ Pr}_2\text{O}_3+0.1 \text{ B}_2\text{O}_3\]

These mixed alkaline earth aluminate phosphors have the general formula:

\[Sr\(_{0.33}\)Ba\(_{0.4}\)Al\(_{2}\)O\(_7\):0.01Eu:0.02Pr\]

where \(k=1-\frac{p-2x}{2y}\).

### Example 11

Preparation and Characterization of mixed alkaline earth aluminate phosphors

Mixed 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\(_2\)O\(_3\)+xEu\(_2\)O\(_3\)+yR\(_2\)O\(_3\)+zB\(_2\)O\(_3\)\]

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 0.2; and
\( R^{3+} \) is a trivalent rare earth ion or \( Bi^{3+} \).
These mixed alkaline earth aluminates have the formula:
\[
6,117,362
\]
where \( k=1-n-p-2x-2y \).

Example 12
Codoping of \( Mg^{2+} \) or \( Zn^{2+} \) into \( MO_{m}Al_{3}O_{6}:Eu^{2+},R^{3+} \) phosphors

In phosphor materials of this invention, \( Al^{3+} \), in the alkaline earth aluminate can be replaced with divalent ions, such as \( Mg^{2+} \) or \( Zn^{2+} \). Phosphor components are combined according to the molar proportions in the following general recipe:
\[
(1-2x-2y)MCO_{3}+(m-q)Al_{2}O_{3}+xEu_{2}O_{3}+yR_{2}O_{3}+qXO+zB_{2}O_{3}
\]
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:
\[
M_{2}O_{m}(m-q)Al_{2}O_{3}qXO:zB_{2}O_{3}
\]
where \( k=1-2x-2y \) and where the ranges for \( m, x \) and \( y \) are as above.

Example 13
Co-doping of \( Na^{+} \) or \( K^{+} \) into \( MO_{m}Al_{3}O_{6}:Eu^{2+},R^{3+} \) 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:
\[
(1-2x-2y)MCO_{3}+(m-q)Al_{2}O_{3}+xEu_{2}O_{3}+yR_{2}O_{3}+qXO+zB_{2}O_{3}
\]
where:
\( 2x+2y+2r \) is less than 1;
\( r \) preferably ranges from 0.002 to 0.2;
and the ranges for \( x, y, m, n, p, q, r, s, t, \) and \( z \) are as given in formula 1.
\( Z_{2}CO_{3} \), in particular, can be \( Na_{2}CO_{3} \) and/or \( K_{2}CO_{3} \).
These phosphors will have the generic formula:
\[
M_{2}O_{m}Al_{3}O_{6}(nNa_{2}O_{3}pK_{2}O):qEu_{2}O_{3}rR_{2}O_{3}
\]
where \( k=1-2r-2x-2y \) and where the ranges for \( r, m, n, p, q, \) and \( y \) are as above.

Example 14
Preparation and Characterization of Alkaline earth aluminate phosphors of varying ratio of \( Al/M \)

A series of strontium aluminate phosphors activated with \( Eu^{2+} \) and doped with \( Pr^{3+} \) were prepared having different ratios of \( Al/ Sr \). Phosphor components were mixed according to the molar proportions:
\[
0.98 SrCO_{3}+0.99 Al_{2}O_{3}+0.01 XO+0.005 Eu_{2}O_{3}+0.005 Dy_{2}O_{3}+0.1 B_{2}O_{3}
\]
where \( XO \) can be \( MgO \) or \( ZnO \). Table 5 provides measurements of relative after-glow intensity at 488 nm of strontium aluminate (\( SrAl_{2}O_{4} \)) phosphors in which \( Na^{+} \) or \( K^{+} \) replaces \( Sr^{2+} \).

Table 6 provides measurements of relative after-glow intensity at 488 nm of strontium aluminate (\( SrAl_{2}O_{4} \)) phosphors in which \( Na^{+} \) or \( K^{+} \) replaces \( Sr^{2+} \).

Example 15
Effect of variation of the amount of flux on phosphor properties

A series of strontium aluminate phosphors (\( SrAl_{2}O_{4} \)) activated with \( Eu^{2+} \) and doped with \( Pr^{3+} \) were prepared.
using varying amounts of flux ($zB_2O_3$). Phosphor components were mixed according to the molar proportions:

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

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 Table 8 provides measurements of relative after-glow intensity at 488 nm of strontium aluminates as indicated. The samples where $z=0.03$ to 0.20 have acceptable brightness and persistence. The sample where $z=0.12$ was brighter than other samples tested.

Example 16

General Methods of Preparation of Blue Phosphors with Host Material $M_xA_1_{2-x}O_3$ (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 recipe:

$$(4-8x-8y) \text{MCO}_3 + 7.00 \text{Al}_2\text{O}_3 + 4xy\text{Eu}_2\text{O}_3 + 4y\text{R}_2\text{O}_3 + 4z\text{B}_2\text{O}_3$$

where:

- $8x+8y$ is less than 4, $x$ is preferably about 0.0001 to about 0.05 and more preferably $x$ is 0.001 to about 0.005;
- $y$ 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;
- $M$ is Sr or a combination of Sr with Ca and/or Ba; and
- $R$ is a trivalent rare earth ion or $\text{Bi}^{3+}$.

$B_2O_3$ is used as a flux in the composition and is important for ensuring the formation of the phosphorescent phase.

### Table 8

The influence of varying $B_2O_3$ in preparation of phosphor

<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>
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<td>41</td>
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<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 $z=0.10$.

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 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 pellets under about 1.3 ton/cm² pressure. The pressed pellets are then prefired in air at about 600°C for about one hour. The prefired powder is pulverized and milled again into a fine powder. The prefired powder is pressed again into ceramic pellets at the same pressure. The pellets are then sintered at about 1,300°C for one hour in a flowing $H_2$- inert gas mixture (2%-5% by volume $H_2$) 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 original 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% $H_2$, e.g., 99.99% 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.


Those of ordinary skill in the art will appreciate that the phosphors of this invention can be prepared using starting materials other than those specifically disclosed herein and that procedures and techniques functionally equivalent to those described herein can be employed to make and assess the phosphors herein. Those of ordinary skill in the art will also appreciate that the host matrix of this invention may accommodate metal ions other than those specifically mentioned herein without significant effect upon phosphor properties.

All references cited herein are incorporated by reference herein to the extent that they are not inconsistent herewith.

We claim:

1. A phosphor represented by the formula:

$$\text{MO}_m\text{Al}_2\text{O}_3:z\text{Eu}^{2+},R^{3+}$$

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 metal ion or a mixture thereof, $\text{Eu}^{2+}$ is present at a level from about 0.002 mol % to about 10 mol % of $M$, and $R^{3+}$ is present at a level from about 0.02mol % to about 20 mol % of $M$.

2. The phosphor of claim 1 wherein $R^{3+}$ is selected from the group $\text{Pr}^{3+}, \text{Ho}^{3+}, \text{Nd}^{3+}, \text{Dy}^{3+}, \text{Er}^{3+}, \text{La}^{3+}, \text{Lu}^{3+}, \text{Ce}^{3+}, \text{Y}^{3+}, \text{Sm}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Tm}^{3+}, \text{Yb}^{3+}$ and $\text{Bi}^{3+}$.

3. The phosphor of claim 1 wherein $R^{3+}$ is $\text{Pr}^{3+}, \text{Ho}^{3+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ or mixtures thereof.

4. The phosphor of claim 1 which is a single crystal.

5. The phosphor of claim 1 which has the formula:

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

wherein $x$ can range from about 0.0001 to about 0.05, and $y$ can range from about 0.0001 to about 0.10.

6. The phosphor of claim 5 wherein $R^{3+}$ is $\text{Pr}^{3+}, \text{Ho}^{3+}$, a combination of $\text{Pr}^{3+}$ with $\text{Dy}^{3+}$, or a combination of $\text{Ho}^{3+}$ with $\text{Dy}^{3+}$.

7. The phosphor of claim 5 wherein $x$ is a number ranging from about 0.0001 to about 0.005.

8. The phosphor of claim 1 wherein $m$ is 2 or 1.75.

9. The phosphor of claim 8 wherein $M$ is Sr.

10. A phosphor represented by the formula:

$$\text{MO}_m\text{Al}_2\text{O}_3:z\text{Eu}^{2+},R^{3+}$$

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 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$^{3+}$, Lu$^{3+}$, Ce$^{3+}$, Sm$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, Tm$^{3+}$, Yb$^{3+}$ and Bi$^{3+}$.

12. A phosphor having the formula:

$$Sr_{x}Ba_{y}Ca_{z}O \cdot mAl_{2}O_{3}Eu^{2+},R^{3+}$$

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 $y$ 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:

$$MO \cdot mAl_{2}O_{3}Eu^{2+},R^{3+}$$

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 or a mixture 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 to form a powder;

(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:

$$MO \cdot mAl_{2}O_{3}Eu^{2+},R^{3+}$$

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 trivalent 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 the amount of divalent metal ion substituted into the phosphor is equal to the amount of $R^{3+}$ in the phosphor.

19. 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 %.

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

21. The phosphor of claim 15 in which the amount of divalent metal ion substituted into the phosphor is equal to the amount of $R^{3+}$ in the phosphor.

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 16 wherein $R^{3+}$ is selected from the group Pr$^{3+}$, Ho$^{3+}$, Nd$^{3+}$, Dy$^{3+}$, Er$^{3+}$, 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 $B_{2}O_{3}$.

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.mAl2O3:Eu"+",R"3+" and replace with -- MO.mAl2O3:Eu2+,R3+ --.

**Column 1.**
Line 28, delete "SrAl2O3:Eu2+,Dy"3+" and replace with -- SrAl2O3:Eu2+,Dy3+ --.
Lines 37-38, delete "has obtained" and replace with -- has been obtained --.
Line 41, delete "Sr"2+" and replace with -- Sr"2+ --.
Line 50, delete "Dy"3n+ and replace with -- Dy"3+ --.
Line 50, delete "Eu"2+" and replace with -- Eu"2+ --.
Line 62, delete "M1.3Al2O3-x Where" and replace with -- M1.3Al2O3-x, where --.

**Column 2.**
Line 16, delete the comma after "Eu"2+".
Lines 22-23, delete "2SrO.3Al2O3:Eu2+" and replace with -- 2SrO.3Al2O3:Eu2+ --.
Lines 25-26, delete "4SrO.7Al2O3:Eu2+" and replace with -- 4SrO.7Al2O3:Eu2+ --.
Line 26, delete "BaO.4Al2O3:Eu2+" and replace with -- BaO.4Al2O3:Eu2+ --.
Line 38, delete "MO.mAl2O3:Eu"2+,R"3+" and replace with -- MO.mAl2O3:Eu2+,R3+ --.
Line 47, delete "MO.mAl2O3(2B2O3):Eu"2+,R"3+" and replace with -- MO.mAl2O3(2B2O3): Eu2+,R3+ --.

**Column 4.**
Line 32, delete "Sr0.68Ba0.33Al2O7" and replace with -- Sr0.33Ba0.68Al2O7 --.
Line 36, delete "Sr0.49Ca0.49Al2O7" and replace with -- Sr0.485Ca0.485Al2O7 --.

**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.mAl2O3" and replace with -- MO.mAl2O3 --.
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 "M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n and replace with -- M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n --.

**Column 8,**
Line 1, delete "M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n and replace with -- M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n --.
Line 15, delete "M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n and replace with -- M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n --.
Line 31, delete "M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3},2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n and replace with -- M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3},2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n --.
Line 60, delete "MO\textsubscript{m}Al\textsubscript{2}O\textsubscript{3}" and replace with -- MO\textsubscript{m}Al\textsubscript{2}O\textsubscript{3} --.

**Column 9,**
Line 10, delete "M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n and replace with -- M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n --.
Line 28, delete "M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n and replace with -- M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n --.
Line 50, delete "M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3},2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n and replace with -- M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3},2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n --.
Line 67, delete "M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3},2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n and replace with -- M\textsubscript{2}O\textsubscript{m}Al\textsubscript{2}O\textsubscript{3},2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n --.

**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 "Sr\textsubscript{2}Ba\textsubscript{m}Ca\textsubscript{m}mol\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n and replace with -- Sr\textsubscript{2}Ba\textsubscript{m}Ca\textsubscript{m}mol\textsubscript{2}O\textsubscript{3}(zB\textsubscript{2}O\textsubscript{3}):2xEu\textsuperscript{2+},2yR\textsuperscript{3+}n --.
Line 45, delete "Bi\textsuperscript{3+}+" and replace with -- Bi\textsuperscript{3+} --.
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 "SrAl2O4(0.1B2O3):0.01Eu2+:0.02R3+" and replace with -- SrAl2O4(0.1B2O3):0.01Eu2+,0.02R3+.--
Line 19, after "+" please insert -- are shown --.
Lines 34-35, delete "SrAl2O4(B2O3):0.01Eu2+:0.01Pr3+:0.01R3+" and replace with -- SrAl2O4(B2O3):0.01Eu2+,0.01Pr3+,0.01R3+.--
Line 38, delete "SrAl2O4(B2O3):Eu2+:Pr3+:R3+" and replace with -- SrAl2O4(B2O3):Eu2+,Pr3+.--
Line 48, delete "ranges of in" and replace with "ranges of m" --.
Lines 56 and 60-61, delete "SrAl2O4(0.1B2O3):0.01Eu:0.01Pr:0.01R" and replace with -- SrAl2O4(0.1B2O3):0.01Eu,0.01Pr,0.01R.--.

Column 16.
Line 13, delete "[(Sr0.33 Ba0.64)(0.1B2O3)Al4O7]:0.01Eu:0.02Pr" and replace with -- (Sr0.33 Ba0.64)(0.1B2O3)Al4O7:0.01Eu,0.02Pr--.
Line 22, delete "SrBaO.mAl2O3(zB2O3):2xEu,2yR" and replace with -- SrBaO.mAl2O3(zB2O3):2xEu,2yR--
Line 48, delete "SrCaO.mAl2O3(zB2O3):2xEu,2yR" and replace with -- SrCaO.mAl2O3(zB2O3):2xEu,2yR--
Line 52, delete "[(Sr0.485 Ca0.485)Al4O7]:0.01Eu:0.02Pr" and replace with -- (Sr0.485 Ca0.485)Al4O7:0.01Eu,0.02Pr--.
Lines 58-59, delete "[(Sr0.485 Ca0.485)(0.1B2O3)Al4O7]:0.01Eu:0.02Pr" and replace with -- (Sr0.485 Ca0.485)(0.1B2O3)Al4O7:0.01Eu,0.02Pr--.

Column 17.
Line 7, delete "SrBa2Ca2O.mAl2O3(zB2O3):2xEu,2yR" and replace with -- SrBa2Ca2O.mAl2O3(zB2O3):2xEu,2yR--.
Lines 13-14 and 57-58, delete "MO.mAl2O3:Eu2+,R3+" and replace with -- MO.mAl2O3:Eu2+,R3+--.
Line 29, delete "M2O,(m-q)Al2O3,qXO:2xEu,2yR" and replace with -- M2O,(m-q)Al2O3,qXO:2xEu,2yR--.

Column 18.
Line 6, delete "M2O.mAl2O3,rNa2O:2xEu,2yR" and replace with -- M2O.mAl2O3,rNa2O:2xEu,2yR--.
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 "SrBa,Ca,0.mAl2O3:2xEu2+,2yR3+" and replace with -- SrBa,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