LONG-PERSISTENCE BLUE PHOSPHORS

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 Provisional application No. 60/064,690, Nov. 7, 1997, and provisional application No. 60/064,691, Nov. 7, 1997.

Field of Search
 252/301.4 R; 117/946

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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:

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

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
FIG. 3
FIG. 6
FIG. 7
FIG. 8
FIG. 9
FIG. 10
FIG. 11
FIG. 12

Graph showing the intensity (a.u.) vs. time (seconds) for different materials:
- Y
- Lu
- La

The graph is a log-log plot with intensity on a logarithmic scale ranging from $10^3$ to $10^6$ and time on a linear scale ranging from 0 to 3000 seconds.
FIG. 13
FIG. 14

Delay Time (minute)

Intensity (a.u.)

10^6

10^5

10^4

10^3

10^2

10^1

FIG. 14
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 NURC-NCCW-0088 and NCCS-252, ARO DAAHH-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,Cl, 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, Mg₃Al₂O₄, BaAl₂O₄, and SrAl₂O₄ and their counterparts using alkaline earth cationic combinations. (F. 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 (Abrussacato et al. (1971) J. Electrochem. Soc. 118:930).

Improved long persisting phosphors of certain alkaline earth phosphates were reported by T. Matsuzawa, Y. Aoki, N. Takeuchi and T. Murayama (1996) J. Electrochem. Soc. 143(8):2670, and in U.S. Pat. No. 5,424,006. The brightness and persistence time of Eu²⁺-activated SrAl₂O₄ 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 electo from a rare earth metal, manganese, tin or bismuth.

SUMMARY OF THE INVENTION

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

\[ \text{MO.}_x\text{M}_y\text{Al}_z\text{O}_{2x+y} \text{Eu}^{2+}, \text{R}^{3+} \]

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; and 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 indicating the presence of B₂O₃ flux is:

\[ \text{MO.}_x\text{M}_y\text{Al}_z\text{O}_{2x+y} \text{Eu}^{2+}, \text{R}^{3+} \]

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 0.02 mol % to about 10 mol % of at least one trivalent rare earth metal ion or Bi³⁺, and co-doped with about 0.02 mol % to about 2 mol % of preferably about 0.2 mol % to about 1.0 mol % of Eu²⁺, 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⁺, 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. MAI₆O₈:Eu²⁺, Pr³⁺, Dy³⁺ or MAI₆O₈: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 MAI₆O₈ and m=2, the host material being MAI₆O₇. 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 Al³⁺ in the matrix material and where 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 powdered sample of SrA₁₄O₇(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) SrA₁₄O₇(0.1B₂O₃):0.01 Eu²⁺,0.02Nd²⁺; (b) SrA₁₄O₇(0.1B₂O₃):0.01Eu²⁺,0.02Pr³⁺ and (c) of commercial blue phosphor Ca₆Sr₅S₄Bi 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 SrA₁₄O₇(0.1B₂O₃):0.01Eu²⁺,0.02Nd²⁺ where excitation was monitored at 488 nm.

**FIG. 11** is a graph of decay curves of the after-glow of SrA₁₄O₇(0.1B₂O₃):0.01Eu²⁺,0.02R³⁺ measured in the first 15 sec. after exposure to a 13 W fluorescence lamp (measured at 488 nm). Decay curves for R=La (γ), Ce (δ), Sm (β), Gd (f), Tb (γ), Dy (ζ), Er (λ), Tm (φ), Ye (x), and Lu (ϕ) are shown. The decay curve of the sample SrA₁₄O₇:Eu,Nd (●) is also shown for comparison.

**FIG. 12** is a graph comparing after-glow decay curves for samples of SrA₁₄O₇(0.1B₂O₃):0.01Eu, 0.01Pr co-doped with 0.01 Y (z), Lu(ϕ) or La(λ).

**FIG. 13** illustrates the excitation and emission spectra monitored at 488 nm of SrA₁₄O₇(0.1B₂O₃) activated with Eu and codoped with Pr and Y.

**FIG. 14** is a graph comparing after-glow decay curves of SrA₁₄O₇(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 Sr₀.₆Ba₃Al₃O₁₂:0.01Eu, 0.02Pr after exposure to a 4 W UV lamp for 2 minutes as a function of time after illumination (C), after 5 sec.; (¢), after 20 sec. and Δ, after 60 sec.

**FIG. 16** illustrates the spectra of the after-glow of Sr₀.₄Ca₀.₆Al₂O₁₂:0.01Eu, 0.02Pr after exposure to a 4 W UV lamp for 2 minutes as a function of time after illumination (C), after 5 sec.; (¢), after 20 sec. and Δ, 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 You, W. M. (eds.), CRC Press, Inc., Boca Ratón, 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 photo-stimulable phosphorescence are physically governed by mechanisms similar to persistent phosphorescence.
vated 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). 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 measurements comparisons of persistence times must be performed under identical conditions using the same detection systems. The term “persistent phosphor” 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 greater than about 3-5 hrs. More preferred phosphors exhibit persistence times greater than about 10-12 hrs. Most preferred phosphors exhibit persistence times 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 phosphors of this invention are alkaline earth aluminates MO · 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 Eu³⁺. Hosts in which m=about 1.6 to about 2.2 provide the desired blue color and good phosphorescence brightness in combination with the Eu activator. Hosts where m=about 1.7 to about 2.0 are preferred, with those where m=1.75 or m=2.0 being more preferred. Hosts where M is Sr and m is either 1.75 (Sr₅Al₇O₁₆ martyr) or m is 2 (Sr₂Al₄O₁₁) 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 $\text{Al}^{3+}$ in the host is replaced with a divalent ion, such as $\text{Mg}^{2+}$ or $\text{Zn}^{2+}$ (alone or in combination) and those in which a portion of the alkaline earth metal ion ($M^{2+}$) 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 $Se^{2-}$ by $R^+$. 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 $\text{B}_2\text{O}_3$. 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 $\text{B}_2\text{O}_3$ 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 $z$ about 0.08 to about 0.15 is preferred and inclusion of flux in a molar proportion $z$ about 0.1 to about 0.15 is more preferred. $\text{B}_2\text{O}_3$ can be replaced in all formulations of this invention by an amount of $\text{H}_2\text{B}_2\text{O}_5$, sufficient to provide an equivalent molar amount of B (i.e., $2\text{H}_2\text{B}_2\text{O}_5$ replaces each $\text{B}_2\text{O}_3$).

The exact role of the flux $\text{B}_2\text{O}_3$ 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 Sr₅Al₇O₁₆ with an orthorhombic structure with space group $Pmn2_1$ in the presence of flux (i.e., $\text{Sr}_5\text{Al}_7\text{O}_{16}$). This structure of strontium aluminates can be made only in the presence of flux. In the case where $m=2$ and $M=$Sr, the host material $\text{Sr}_2\text{Al}_{10}\text{O}_{23}$ formed in the presence of flux is similar in structure to orthorhombic $\text{Sr}_2\text{Al}_{10}\text{O}_{23}$ (see FIG. 4). This material is monoclinic with space group $C_{2h}^5$ when synthesized without flux (i.e., $\text{Sr}_2\text{Al}_{10}\text{O}_{23}$). The phosphors of this invention can be made by the following general method. Phosphor components are com-
The phosphor material is sintered at about 1300 °C. for one hour in 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 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:

\[
(1-2x-2y)MC_{0.5}(3yZ_{0.5})_{0.5}Al_{2}O_{3}:2xEu^{2+},2yR^{3+}
\]

and will have the general formula:

\[
M_{x}O_{y-z} (2B_{0}O_{3})_{2}zEu^{2+},zR_{2}^{3+}
\]

where \(k=1-2x-2y\) 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. \(XO\) is a metal oxide, preferably MgO or ZnO and \(q\) can range from about 0.0001 to about 0.2. \(ZO\) is an alkali metal oxide, preferably Na₂O or K₂O and \(r\) can range from about 0.0001 to about 0.2. \(Z_{0}O\) is an alkaline earth metal, but is preferably Sr or a mixture of Sr with Ca, Ba or both. \(R_{3}^{+}\) is generally one or more trivalent metal ions, but is preferably a trivalent metal ion selected from the group: \(Pr^{3+}, Ho^{3+}, Nd^{3+}, Dy^{3+}, Er^{3+}, La^{3+}, Lu^{3+}, Ce^{3+}, Y^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+}, Tm^{3+}, \mathrm{and} \ Yb^{3+} \) and \(B^{3+}\). Preferred trivalent co-dopants are \(Pr^{3+}, Ho^{3+}, Dy^{3+}, \) and \(Nd^{3+}\). Co-doping of \(Dy^{3+}\) or \(Y^{3+}\) 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 \(N_{2}\) and \(H_{2}\) (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:

\[
M_{x}O_{y-z} (2B_{0}O_{3})_{2}zEu^{2+},zR_{2}^{3+}
\]

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 are particularly useful as a “seed” to stimulate spontaneous nucleation in the LHPG process. It was observed that the initial part of a single crystal that is being grown may have a small number of interstitial microcrystals. These microcrystals are not oriented and are generally surrounded by a larger single crystal. The phosphors of this invention can be used as a “seed” to stimulate spontaneous nucleation in the LHPG process.
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:

\[ M₂O₃·mAl₂O₃·n(M₂O₃)·(zB₂O₃)·2xEu⁺₂⁺·2yR³⁺, \]

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 0.0 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:

\[ M₂O₃·mAl₂O₃·(zB₂O₃)·2xEu⁺₂⁺·2yR³⁺, \]

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 0.0 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 Sr or a combination of Sr with Ca and/or Ba; and

R³⁺ is one or more of 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 a number ranging from about 1.6 to about 2.2; z is a number ranging from about 0.0 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 z ranges from about 0.02 to about 0.2.

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

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

A preferred phosphorescent material of paragraph D has x=about 0.001 to about 0.005; y=about 0.001 to about 0.005; and z ranges from about 0.02 to about 0.2. Preferred phosphorescent material of paragraph C wherein M is Sr²⁺ and/or wherein m=1.75 or 2.

E. A phosphorescent material having the formula:

\[ M₂O₃·mAl₂O₃·(zB₂O₃)·2xEu⁺₂⁺·2yR³⁺, \]
Preparation and Characterization of SrAl$_2$O$_3$ ($0.1B_2O_3$):Eu$^{2+}$:Pr$^{3+}$ Phosphors with Varying Amounts of Pr$^{3+}$

**Example 4**

Pr-concentration dependence of SrAl$_2$O$_3$($0.1B_2O_3$):Eu$^{2+}$:Pr$^{3+}$ phosphor after-glow was examined by preparing phosphor samples in which y (Pr$_2$O$_3$ molar concentration) was varied from 0.005 to 0.02.

**TABLE 2**

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<tr>
<th>Samples</th>
<th>y</th>
<th>10 min after-glow</th>
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<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>19</td>
</tr>
</tbody>
</table>

**Example 5**

Preparation and Characterization of SrAl$_2$O$_3$($B_2O_3$) : Eu$^{2+}$:Ho$^{3+}$ Blue Phosphors

**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>19</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 decay of the after-glow of a sample of SrAlO₄(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺ exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of the after-glow of SrAlO₄(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺ (line b) and a commercial blue phosphor CaSrS:Bi (c) after similar exposure are also shown. The SrAlO₄(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺ phosphor shows similar brightness and persistence to that of SrAlO₄(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺. After 20 hours SrAlO₄(0.1B₂O₃):0.01Eu²⁺: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 SrAlO₄(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺ where the excitation spectrum was monitored at 488 nm.

Example 6

Preparation and Characterization of SrAlO₄(B₂O₃) :Eu²⁺:Nd³⁺ Blue Phosphors

SrAlO₄(0.1B₂O₃):0.01Eu²⁺: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 SrAlO₄(0.1B₂O₃):0.01Eu²⁺:0.02 Nd³⁺ 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 SrAlO₄(0.1B₂O₃):0.01 Eu²⁺: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 SrAlO₄(0.1B₂O₃):0.01 Eu²⁺:0.02 Pr³⁺ (b) and a commercial blue phosphor CaSrS:Bi (c) after similar exposure are also shown. The SrAlO₄(0.1B₂O₃):0.01 Eu²⁺:0.02 Nd³⁺ phosphor shows similar brightness and persistence to that of SrAlO₄(0.1B₂O₃):0.01 Eu²⁺:0.02 Pr³⁺. After 20 hours SrAlO₄(0.1B₂O₃):0.01 Eu²⁺: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 SrAlO₄(0.1B₂O₃):0.01 Eu²⁺:0.02 Nd³⁺ where the excitation spectrum was monitored at 488 nm.

Example 7

Preparation and Characterization of Phosphors of Formula SrAlO₄(BO₃) :0.01 Eu²⁺:0.02 R³⁺, where R are trivalent metal ions of La, Ce, Sm, Gd, Tb, Dy, Er, Tm, Yb, and Lu.

SrAlO₄(0.1B₂O₃):0.01Eu²⁺:0.02 R³⁺ were 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 R₂O₃ + 0.1 B₂O₃

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 SrAlO₄(0.1B₂O₃):0.01Eu²⁺:0.02 R³⁺ 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 (\(\mathbb{V}\)), Ce (\(\mathbb{O}\)), Sm (\(\mathbb{C}\)), Gd (\(\mathbb{J}\)), Tb (\(\mathbb{+}\)), Dy (\(\mathbb{C}\)), Er (\(\mathbb{A}\)), Tm (\(\mathbb{C}\)), Yb (\(\mathbb{A}\)) and Lu (\(\mathbb{C}\)). The decay curve of the sample SrAlO₄(0.1B₂O₃):EuNd (closed circles) is also shown for comparison. It can be seen that the after-glow of these samples are generally 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 SrAlO₄(0.1B₂O₃):0.01Eu₂⁺:0.02Pr³⁺ 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 SrAlO₄(B₂O₃) :0.01 Eu²⁺:0.01 Pr²⁺:0.01R³⁺ where R is La, Lu, Er, Y, and Bi.

This example is intended to determine if co-doping of metal ions into a SrAlO₄(B₂O₃):Eu²⁺:Pr³⁺ 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:

\[(1-2x-2y-zM)CO₃ + xAl₂O₃ + yEu₂O₃ + zR₂O₃ + MCO₃ + mAl₂O₃ + nEu₂O₃ + pPr₂O₃ + qY₂O₃ + zNd₂O₃\]

where \(y₁+y₂+y₃ = y\), \(1-2x-2y = 0\) and the ranges of \(n, x, y\) and \(z\) are as in formula 1 above.

More specifically where \(M=\text{Sr}\) and \(m=2\) the components are combined in the following proportions:

0.97 Sc₂O₃ + 2.0 Al₂O₃ + 0.005 Eu₂O₃ + 0.005 Pr₂O₃ + 0.005 R₂O₃ + 0.1 B₂O₃

where R=La, Lu, Er, and Bi. The intensity of the after-glow of SrAlO₄(0.1B₂O₃):0.01Eu₂⁺:0.01Pr₂⁺:0.01R is given in Table 3. Some results are also shown in FIG. 12.

FIG. 12 shows decay curves of the after-glow of SrAlO₄(0.1B₂O₃):0.01Eu₂⁺:0.01Pr₂⁺:0.01R (\(\mathbb{R} = Y\), Lu\(^{3+}\), and La\(^{3+}\)) 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 SrAlO₄(0.1B₂O₃):0.01Eu²⁺:0.01Pr²⁺:0.01Y³⁺ where the excitation spectrum was monitored at 488 nm. Codoping with Y\(^{3+}\) and Pr\(^{3+}\) increases the UV excitation...
efficiency and improve the brightness by 50% compared to the analogous Pr3+-doped phosphor.

**TABLE 3**

The influence of codoping Y, La, Lu, Er, or Bi into SrAl2O4(B2O3):Eu,Pr on the phosphorescence at 488 nm after

<table>
<thead>
<tr>
<th>after (min)</th>
<th>Pr3+</th>
<th>Y3+</th>
<th>La3+</th>
<th>Lu3+</th>
<th>Er3+</th>
<th>Bi3+</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>
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<td>30</td>
<td>31</td>
<td>55</td>
<td>30</td>
<td>32</td>
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<td>33</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
<td>32</td>
<td>16</td>
<td>17</td>
<td>15</td>
<td>18</td>
</tr>
</tbody>
</table>

1Data is referenced to that of the SrAl2O4(B2O3):Eu,Pr phosphor.

**Example 9**

Preparation and Characterization of SrAl2O4
(0.1B2O3)0.01Eu0.01Dy0.01Ho and SrAl2O4
(0.1B2O3)0.01Eu0.01Pr

This example demonstrates the influence of deep trapping centers formed by Dy3+ on the decay characteristics of MAl2O4(0.1B2O3):0.01Eu doped with 0.01Pr or 0.01Ho. Samples are generally prepared by the method of Example 1 combining the components in the following molar proportions:

(1-2x-y)MCO3+nBaCO3+mAl2O3+xEu2O3+y2yR2O3+zB2O3

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=the value of x z ranges from about 0.02 to about 0.2; and

R3+ is a trivalent rare earth metal ion or Bi3+.

**TABLE 4**

The influence of deep centers of Dy on the after-glow of SrAl2O4(0.1B2O3):0.01Eu:0.01Pr or SrAl2O4(0.1B2O3):0.01Eu:0.01Ho after (min)

<table>
<thead>
<tr>
<th>after (min)</th>
<th>SAO-En-Pr</th>
<th>SAO-En-Pr/Dy</th>
<th>SAO-En-Ho-Dy</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>15</td>
<td>47</td>
<td>35</td>
</tr>
</tbody>
</table>

4Data is referenced to that of SAO-En-Pr.

**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)SrCO3+pBaCO3+mAl2O3+xEu2O3+yR2O3+zB2O3

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=the value of x z ranges from about 0.02 to about 0.2; and

R3+ is a trivalent rare earth metal ion or Bi3+.

**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)SrCO3+nCaCO3+mAl2O3+xEu2O3+yR2O3+zB2O3

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=the value of x z ranges from about 0.02 to about 0.1; and

R3+ is a trivalent rare earth ion or Bi3+.

These phosphors have the generic formula:

Sr,Ca,O
mAl,O, (zB,03):2xEu,2yR, 8

where k=1-n-2x-2y.

**Example 12**

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)SrCO3+pBaCO3+mAl2O3+xEu2O3+yR2O3+zB2O3

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=the value of x z ranges from about 0.02 to about 0.2; and

R3+ is a trivalent rare earth metal ion or Bi3+.

The mixed alkaline earth aluminate compound, (Sr0.33, Ba0.67)Al1.2O4:0.01Eu0.01Pr was prepared following the general procedure of Example 1 combining the components in the following molar proportions:

0.33 SrCO3+1.64 BaCO3+2.00 Al2O3+0.005 Eu2O3+0.01 Pr2O3+0.1 B2O3

These mixed alkaline earth aluminate phosphors have the general formula:

Sr,Ba-O . mAl2O3 . (zB2O3):2Eu2O3, 2yR, 7

**Example 13**

Preparation and Characterization of mixed alkaline earth aluminate phosphors

These phosphors have the generic formula:

Sr,Ca,O
mAl,O, (zB,03):2xEu,2yR, 8

where k=1-n-2x-2y.

**Example 14**

Preparation and Characterization of mixed alkaline earth aluminate phosphors

These phosphors have the generic formula:

Sr,Ca,O
mAl,O, (zB,03):2xEu,2yR, 8

where k=1-n-2x-2y.
y ranges from about 0.0001 to about 0.010 and preferably the value of y is about 0.001. 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:

\[ Sr_xBa_{1-x},Ca_0.1+.1Al_2O_3(zB_2O_3):2xEu,2yR, \]

where k = 1 - n - p - 2x - 2y.

Example 12
Codoping of Mg^{2+} or Zn^{2+} into MO . mAl_2O_3: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:

\[ (1-2x-2y)MCO_x+(m-q)Al_2O_3+xEu_0+yR_0+zXO+zB_2O_3 \]

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 or ZnO. These phosphors will have the generic formula:

\[ M_2O_{(m-q)}Al_2O_3.qXO:2xEu,2yR, \]

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

Exemplary Mg or Zn doped phosphors are prepared by combining the components according to the following molar proportions:

\[ 0.98 SrCO_3+1.99 Al_2O_3+0.005 Eu_0+0.005 Dy_0+0.1 B_2O_3 \]

where XO can be MgO or ZnO.

Table 5 provides measurements of relative after-glow intensity at 488 nm of strontium aluminate (SrAl_2O_4) phosphors in which Mg^{2+} or Zn^{2+} replaces Sr^{2+}.

<table>
<thead>
<tr>
<th>Table 5</th>
<th>The influence of substituting Mg or Zn for Sr^{2+} on the after-glow of SrAl_2O_4:Eu^{2+},Pr^{3+}</th>
<th>after (min)</th>
<th>SAO:EuPr/Mg</th>
<th>SAO:EuPr/PZn</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>104</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>15</td>
<td>16</td>
<td>16</td>
<td></td>
</tr>
</tbody>
</table>

\[ \text{Data is referenced to that of SAO:EuPr.} \]

Example 13
Co-doping of Na^{+} or K^{+} into MO . mAl_2O_3: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:

\[ (1-2x-2y-2r)MCO_x+(m-q)Al_2O_3+xEu_0+yR_0+rZ_2CO_3+zB_2O_3 \]

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

r preferably ranges from 0.002 to 0.2; and the ranges for x, y, m and z are as given in formula 1. Z_2CO_3, in particular, can be Na_2CO_3 and/or K_2CO_3. These phosphors will have the generic formula:

\[ M_2O_{(m-q)}Al_2O_3.qXO:2xEu,2yR, \]

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

Table 6 provides measurements of relative after-glow intensity at 488 nm of strontium aluminate (SrAl_2O_4) phosphors in which Na^{+} or K^{+} replaces Sr^{2+}.

<table>
<thead>
<tr>
<th>Table 6</th>
<th>The influence of substituting Na or K for Sr^{2+} on the after-glow of SrAl_2O_4:Eu^{2+},Pr^{3+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>after (min)</td>
<td>SAO:EuPr/Mg</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>30</td>
<td>31</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
</tr>
</tbody>
</table>

\[ \text{Data is referenced to that of SAO:EuPr.} \]

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:

\[ 0.98 SrCO_3+1.99 Al_2O_3+0.005 Eu_0+0.005 Dy_0+0.1 B_2O_3 \]

with m = 1.6, 1.75, 1.85, 1.95, 2.0, and 2.15 and phosphors prepared according to the general procedure of Example 1. Table 7 provides measurements of relative after-glow intensity at 488 nm of strontium aluminates as indicated. All of the samples tested have acceptable brightness and persistence. The sample where m = 1.75 corresponding to Sr_0.95Al_1.05O_2 exhibits somewhat brighter phosphorescence.

<table>
<thead>
<tr>
<th>Table 7</th>
<th>The influence of varying Al/Sr ratio on after-glow of SrO</th>
</tr>
</thead>
<tbody>
<tr>
<td>m =</td>
<td>1.6</td>
</tr>
<tr>
<td>10</td>
<td>113</td>
</tr>
<tr>
<td>30</td>
<td>37</td>
</tr>
<tr>
<td>60</td>
<td>17</td>
</tr>
</tbody>
</table>

\[ \text{Data is referenced to that at m = 2.} \]

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

A series of strontium aluminate phosphors (SrAl_2O_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:

$$0.08 \text{SrCO}_3 + 4\text{Al}_{2}O_3 + 0.005 \text{Eu}_{2}O_3 + 0.005 \text{Pr}_{2}O_3 + zB_2O_3$$

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 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 $M_xA_{1-y}O_y$ (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:

$$(4-8x-8y) \text{MCO}_3 + 7.00 \text{Al}_{2}O_3 + 4x\text{Eu}_{2}O_3 + 4yR_2O_3 + 4zB_2O_3$$

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**

<table>
<thead>
<tr>
<th>$z$</th>
<th>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>After/min</td>
<td>10</td>
<td>113</td>
<td>121</td>
<td>106</td>
<td>100</td>
<td>132</td>
<td>100</td>
</tr>
<tr>
<td>20</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>60</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>

where $x$ ranges from about 0.0001 to about 0.10; $M$ is Sr or a combination of Sr with Ca and/or Ba; and $R$ is a trivalent rare earth ion or $\text{Bi}^{3+}$.

**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 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 pellets are 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 $H_2-\text{N}_2$ 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% $N_2$) Care must be taken to prevent re-oxidation of the europium ions from the $2+\text{state}$ to the $3+\text{state}$ 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:

$$\text{MO}._m\text{A}_{x}\text{O}_{y} \cdot \text{Eu}^{2+}, \text{R}^{3+}$$

wherein $m$ is a number ranging from about 1.6 to about 2.2, $M$ is Sr or a combination of Sr with Ca, Ba or both, $R^{3+}$ is a trivalent metal ion or a mixture thereof, $\text{Eu}^{2+}$ is present at a level from about 0.02 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 $M$.

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

$$\text{SrA}l_{2}O_{3} \cdot 2x\text{Eu}^{2+}, 2yR^{3+}$$

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:

$$\text{MO} . m\text{Al}_{x}\text{O}_{y} \cdot \text{Eu}^{2+}, R^{3+}$$

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\textsuperscript{3+} with another trivalent metal ion, Eu\textsuperscript{2+} is present at a level from about 0.02 mol % to about 10 mol % of M, and R\textsuperscript{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\textsuperscript{3+} is a mixture of Y\textsuperscript{3+} with a trivalent metal ion selected from the group Pr\textsuperscript{3+}, Ho\textsuperscript{3+}, Nd\textsuperscript{3+}, Dy\textsuperscript{3+}, Er\textsuperscript{3+}, Tm\textsuperscript{3+}, Eu\textsuperscript{3+}, Tb\textsuperscript{3+}, Tm\textsuperscript{3+}, Yb\textsuperscript{3+} and Bi\textsuperscript{3+}.

12. A phosphor having the formula:

\[
S_{2}Ba,Ca,O_{m}Al_{2}O_{3}:2xEu^{2+},2yR^{3+}
\]

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:

\[
MO_{m}Al_{2}O_{3}:Eu^{2+},R^{3+}
\]

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\textsuperscript{3+} is a trivalent rare earth metal ion or a mixture thereof, Eu\textsuperscript{2+} is present at a level from about 0.02 mol % to about 10 mol % of M, and R\textsuperscript{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:

\[
MO_{m}Al_{2}O_{3}:Eu^{2+},R^{3+}
\]

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\textsuperscript{3+} is a trivalent rare earth metal ion, Bi\textsuperscript{3+} or mixtures thereof, Eu\textsuperscript{2+} is present at a level from about 0.02 mol % to about 10 mol % of M, and R\textsuperscript{3+} is present at a level from about 0.02 mol % to about 20 mol % of M in which a portion of the Al\textsuperscript{3+} in the host is substituted by a divalent metal ion or in which a portion of the M\textsuperscript{2+} in the phosphor is substituted by a monovalent metal ion.

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

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

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

19. The phosphor of claim 16 wherein a portion of the M\textsuperscript{2+} in the phosphor is substituted by a divalent metal ion or in which a portion of the M\textsuperscript{2+} in the phosphor is substituted by a monovalent metal ion.

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\textsuperscript{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\textsuperscript{+} or K\textsuperscript{+}.

23. The phosphor of claim 22 wherein R\textsuperscript{3+} is Pr\textsuperscript{3+}, Ho\textsuperscript{3+}, Dy\textsuperscript{3+}, or Nd\textsuperscript{3+} or mixtures thereof.

24. The phosphor of claim 22 wherein 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\textsuperscript{3+} is selected from the group Pr\textsuperscript{3+}, Ho\textsuperscript{3+}, Nd\textsuperscript{3+}, Dy\textsuperscript{3+}, Er\textsuperscript{3+}, Tm\textsuperscript{3+}, Lu\textsuperscript{3+}, Ce\textsuperscript{3+}, Y\textsuperscript{3+}, Sm\textsuperscript{3+}, Gd\textsuperscript{3+}, Tb\textsuperscript{3+}, Tb\textsuperscript{3+}, Eu\textsuperscript{3+} and Bi\textsuperscript{3+}.

26. The phosphor of claim 15 wherein R\textsuperscript{3+} is a mixture of Y\textsuperscript{3+} with another trivalent metal ion.

27. The phosphor of claim 15 wherein R\textsuperscript{3+} is a mixture of Y\textsuperscript{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\textsubscript{2}O\textsubscript{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:Eu2+,R3+" and replace with -- MO.mAl2O3:Eu2+,R3+ --.

Column 1.
Line 28, delete "SrAl2O3:Eu2+,Dy3+" and replace with -- SrAl2O3:Eu2+,Dy3+ --.
Lines 37-38, delete "has obtained" and replace with "has been obtained".
Line 41, delete "Sr2+" and replace with "Sr2+".
Line 50, delete "Dy3+" and replace with "Dy3+".
Line 50, delete "Eu2+" and replace with "Eu2+".
Line 62, delete "M1-xAl2O4-x Where" and replace with -- M1-xAl2O4-x, where --.

Column 2.
Line 16, delete the comma after "Eu2+".
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:Eu2+,R3+" and replace with -- MO.mAl2O3:Eu2+,R3+ --.
Line 47, delete "MO.mAl2O3(xB2O3):Eu2+,R3+" and replace with -- MO.mAl2O3(xB2O3): Eu2+,R3+ --.

Column 4.
Line 32, delete "Sr0.6Ba0.33Al2O7" and replace with -- Sr0.33Ba0.66Al2O7 --.
Line 36, delete "Sr0.4Ca0.4Al2O7" and replace with -- Sr0.48Ca0.48Al2O7 --.

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_{0.0}m_{Al_{2}O_{3}}(zB_{2}O_{3}):2xEu^{2+},2yR^{3+}n" and replace with -- \( M_{0.0}m_{Al_{2}O_{3}}(zB_{2}O_{3}):2xEu^{2+},2yR^{3+} \).--.

Column 8,
Line 1, delete "M_{0.0}m_{Al_{2}O_{3}}(zB_{2}O_{3}):2xEu^{2+},2y_{1}R_{1}^{3+},2y_{2}R_{2}^{3+}n" and replace with -- \( M_{0.0}m_{Al_{2}O_{3}}(zB_{2}O_{3}):2xEu^{2+},2y_{1}R_{1}^{3+},2y_{2}R_{2}^{3+} \).--.
Line 15, delete "M_{0}(m-q)Al_{2}O_{3}.qXO(zB_{2}O_{3}):2xEu^{2+},2yR^{3+}n" and replace with -- \( M_{0}(m-q)Al_{2}O_{3}.qXO(zB_{2}O_{3}):2xEu^{2+},2yR^{3+} \).--.
Line 31, delete "M_{0.0}m_{Al_{2}O_{3}.rZ_{2}(zB_{2}O_{3}):2xEu^{2+},2yR^{3+}n} and replace with -- \( M_{0.0}m_{Al_{2}O_{3}.rZ_{2}(zB_{2}O_{3}):2xEu^{2+},2yR^{3+} \).--.
Line 50, delete "M_{0}(m-q)Al_{2}O_{3}.qXO(zB_{2}O_{3}):2xEu^{2+},2yR^{3+}n" and replace with -- \( M_{0}(m-q)Al_{2}O_{3}.qXO(zB_{2}O_{3}):2xEu^{2+},2yR^{3+} \).--.
Line 67, delete "M_{0.0}m_{Al_{2}O_{3}.rZ_{2}(zB_{2}O_{3}):2xEu^{2+},2yR^{3+}n} and replace with -- \( M_{0.0}m_{Al_{2}O_{3}.rZ_{2}(zB_{2}O_{3}):2xEu^{2+},2yR^{3+} \).--.

Column 9,
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_{2}Ba_{2}Ca_{m}O_{m}Al_{2}O_{3}(zB_{2}O_{3}):2xEu^{2+},2yR^{3+}n" and replace with -- \( Sr_{2}Ba_{2}Ca_{m}O_{m}Al_{2}O_{3}(zB_{2}O_{3}):2xEu^{2+},2yR^{3+} \).--.
Line 45, delete "Bi^{2+}" and replace with -- \( Bi^{3+} \).--.
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 "SrAl₂O₇:0.01Eu²⁺:0.02Pr³⁺" and replace with
-- SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺,0.02Pr³⁺ --.
Line 25, delete "SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺" and replace with
-- SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺,0.02Pr³⁺ --.
Lines 29, 32, 37 and 39-40, delete "SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺" and replace with
-- SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺,0.02Pr³⁺ --.
Line 46, delete "SrAl₂O₇(0.1B₂O₃):Eu²⁺,Pr³⁺" and replace with -- SrAl₂O₇(0.1B₂O₃):Eu²⁺,Pr³⁺ --.
Lines 50-51, delete "SrAl₂O₇(0.1B₂O₃):Eu²⁺,Pr³⁺" and replace with -- SrAl₂O₇(0.1B₂O₃):
Eu²⁺,Pr³⁺ --.
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 "SrAl₂O₇(0.1B₂O₃):Eu²⁺,Pr³⁺" and replace with -- SrAl₂O₇
(0.1B₂O₃):Eu²⁺,Pr³⁺ --.
Line 43, Table 2, delete "SrAl₂O₇(B₂O₃):0.01Eu²⁺,2Pr³⁺" and replace with -- SrAl₂O₇
(B₂O₃):0.01Eu²⁺,2yPr --.
Lines 55-56, delete "SrAl₂O₇(B₂O₃):Eu²⁺,Ho³⁺" and replace with -- SrAl₂O₇(B₂O₃):Eu²⁺,
Ho³⁺ --.
Lines 58 and 66, delete "SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺" and replace with -- SrAl₂O₇
(0.1B₂O₃):0.01Eu²⁺,0.02Ho³⁺ --.

Column 13.
Lines 8, 14, 17 and 22, delete "SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺" and replace with
-- SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺,0.02Ho³⁺ --.
Lines 29-30, delete "SrAl₂O₇(B₂O₃):Eu²⁺,Nd³⁺" and replace with -- SrAl₂O₇(B₂O₃):Eu²⁺,
Nd³⁺ --.
Lines 33, 43, 53, 58, 61 and 66, delete "SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺:0.02Nd³⁺" and replace with
-- SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺,0.02Nd³⁺ --.
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 "SrAl₂O₇(B₂O₃):0.01Eu²⁺:0.01Pr³⁺:0.01R³⁺" and replace with -- SrAl₂O₇(B₂O₃):0.01Eu²⁺:0.01Pr³⁺:0.01R³⁺ --.

Line 38, delete "SrAl₂O₇(B₂O₃):Eu²⁺:Pr³⁺" and replace with -- SrAl₂O₇(B₂O₃):Eu²⁺,Pr³⁺ --.

Line 48, delete "ranges of in" and replace with -- ranges of m --.

Lines 56 and 60-61, delete "SrAl₂O₇(0.1B₂O₃):0.01Eu:0.01Pr:0.01R" and replace with -- SrAl₂O₇(0.1B₂O₃):0.01Eu,0.01Pr,0.01R --.

**Column 16.**

Line 13, delete "((Sr₃.₃₃ Baₐ.₆₄)(0.1B₂O₃)Al₄O₇:0.01Eu:0.02Pr" and replace with -- (Sr₃.₃₃ Baₐ.₆₄)(0.1B₂O₃)Al₄O₇:0.01Eu,0.02Pr --.

Line 22, delete "Sr₃Baₐ.O·mAl₂O₃(zB₂O₃):2xEu,2yR" and replace with -- Sr₃Baₐ.O·mAl₂O₃(zB₂O₃):2xEu,2yR --.

Line 48, delete "Sr₃Caₐ.O·mAl₂O₃(zB₂O₃):2xEu,2yR" and replace with -- Sr₃Caₐ.O·mAl₂O₃(zB₂O₃):2xEu,2yR --.

Line 52, delete "((Sr₅.₄₈₅ Caₐ.₄₈₅)Al₄O₇:0.01Eu:0.02Pr" and replace with -- (Sr₅.₄₈₅ Caₐ.₄₈₅)Al₄O₇:0.01Eu,0.02Pr --.

Lines 58-59, delete "((Sr₅.₄₈₅ Caₐ.₄₈₅)(0.1B₂O₃)Al₄O₇:0.01Eu:0.02Pr" and replace with -- (Sr₅.₄₈₅ Caₐ.₄₈₅)(0.1B₂O₃)Al₄O₇:0.01Eu,0.02Pr --.

**Column 17.**

Line 7, delete "Sr₃Baₐ.Caₐ.O·mAl₂O₃(zB₂O₃):2xEu,2yR" and replace with -- Sr₃Baₐ.Caₐ.O·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 "M₄O.(m-q)Al₂O₃.qXO:2xEu,2yR" and replace with -- M₄O.(m-q)Al₂O₃.qXO:2xEu,2yR --.

**Column 18.**

Line 6, delete "M₄O·mAl₂O₃.rNaₐ.O:2xEu,2yR" and replace with -- M₄O·mAl₂O₃·rNaₐ.O: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 "SrₓBa₉Ca₉O·mAl₂O₃:2xEu²⁺,2yR³⁺ " and replace with -- SrₓBa₉Ca₉O·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

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