LONG-PERSISTENCE BLUE PHOSPHORS

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

$$M_{1-m}Al_2O_3:Eu^{2+},R^{3+}$$

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.

30 Claims, 16 Drawing Sheets


(List continued on next page.)
OTHER PUBLICATIONS


FIG. 1

- after 5sec
- after 20sec
- after 60sec

Intensity (a.u.)

Wavelength (nm)
FIG. 2
FIG. 3
FIG. 5
FIG. 6
FIG. 7
FIG. 8
FIG. 10
FIG. 12
FIG. 13
FIG. 14

Intensity (a.u.)

Delay Time (minute)

10^6

10^5

10^4

10^3

10^2

1

10

100

1000

a

b

c

FIG. 14
FIG. 15
FIG. 16

- after 5 sec
- after 20 sec
- after 60 sec
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 MURC-NCCW-0088 and NCCS-252, ARO DAAHO4-96-10416 and DOE DE-FG02-94ER75764. The United States government has certain rights in this invention.

FIELD OF THE INVENTION

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

BACKGROUND OF THE INVENTION

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

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

Long lasting and more efficient phosphorescence has obtained in Eu2+ doped SrAl2O4 synthesized with excess alumina which results in formation of trapping centers associated with the Sr2+ vacancy (Abbruscato et al. (1971) J. Electrochem. Soc. 118:930). Reports Eu2+-activated strontium aluminate 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.

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

$\text{Na}_{x}\text{Al}_{y}\text{O}_{z}:\text{Eu}^{2+}, \text{R}^{3+}$

where the phosphors are blue with a phosphorescent band at about 488 nm. Phosphors of this invention indicating the presence of B2O3 flux is:

$\text{Ba}_{0.3}\text{Al}_{1.7}\text{O}_{4}:\text{Eu}^{2+}, \text{R}^{3+}$

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 Pb3+, 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 $\text{M}_{x}\text{Al}_{y}\text{O}_{z}$. 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-persistent phosphors of the general formula:

$\text{MO}_{x}\text{Al}_{y}\text{O}_{z}:\text{Eu}^{2+}, \text{R}^{3+}$

where M is Sr or a combination of Sr with Ca and/or Ba; $\text{R}^{3+}$ 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:

$\text{MO}_{x}\text{Al}_{y}\text{O}_{z}:(\text{Bi}, \text{Sr}, \text{Ca})_{2}\text{O}_{3}:\text{Eu}^{2+}, \text{R}^{3+}$

where M, m and R3+ are as defined in formula 1 and z is a number ranging from about 0.02 to about 0.2.

The phosphors of this invention comprise an alkaline earth aluminate matrix activated with Eu2+ and doped with certain trivalent metal ions $\text{R}^{3+}$. The phosphors are activated with about 0.02 mol % to about 10 mol % of $\text{Eu}^{2+}$ activator and co-doped with about 0.02 mol % to about 20 mol % of trivalent metal ions $\text{R}^{3+}$ (preferably about 0.2 mol % to about 2 mol %) to 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.

The phosphors of this invention are chemically stable, resistant to moisture and UV radiation and are believed to be relatively harmless to the environment.

JP Patent 76031037 (1976, Tokyo Shibaura Electric Co.) reports blue-emitting phosphors containing barium (or calcium or strontium)-potassium (or sodium) aluminites activated with europium and manganese.


JP Patent 94029416 (1994, Matsushita Electronics) reports a europium activated barium aluminate phosphor containing yttrium oxide to enhance phosphorescence.


Phosphors of this invention are those in which M is Sr.

Phosphors of this invention are activated with Eu and codoped with a trivalent rare earth metal ion or Bi. 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+, La3+, Lu3+, Ce3+, Y3+, Sm3+, Gd3+, Tb3+, Yb3+ and the Group VA metal ion Bi3+. Preferred trivalent dopants are Pr3+, Ho3+, Dy3+, Nd3+. Co-doping of Dy3+ or Y3+ with another trivalent metal ion results in phosphor of improved brightness, e.g. MAi04:Eu2+, Pr3+ Dy3+; MAi04:Eu2+, Ho3+, Dy3+. Preferred phosphors are those with m ranging from about 1.70 to about 2.05 and more, are those where m=1.75, the host material being MAi04, and m=2, the host material being MA1407. More preferred are phosphors where M=Sr and m=1.75 or m=2. Sm3+, Gd3+, Eu3+, La3+, Lu3+, Ce3+, Y3+, Sm3+, Gd3+, Tb3+, Yb3+ and the Group VA metal ion Bi3+. Preferred trivalent dopants are Pr3+, Ho3+, Dy3+, Nd3+. Co-doping of Dy3+ or Y3+ with another trivalent metal ion results in phosphor of improved brightness, e.g. MAi04:Eu2+, Pr3+ Dy3+; MAi04:Eu2+, Ho3+, Dy3+.

Preferred 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+, La3+, Lu3+, Ce3+, Y3+, Sm3+, Gd3+, Tb3+, Yb3+ and the Group VA metal ion Bi3+. Preferred trivalent dopants are Pr3+, Ho3+, Dy3+, Nd3+. Co-doping of Dy3+ or Y3+ with another trivalent metal ion results in phosphor of improved brightness, e.g. MAi04:Eu2+, Pr3+ Dy3+; MAi04:Eu2+, Ho3+, Dy3+.

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 sample of SrAl2O4:0.1B2O3:0.01Eu2+,0.02Pr2+ 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+,0.02Pr2+; (b) SrAl2O4:0.01Eu2+,0.02Pr2+ and (c) of commercial blue phosphor CaSrS:Bi after exposure of the phosphors to a 13 W fluorescent lamp for 10 minutes. The threshold of eye sensitivity is indicated by a horizontal dashed line.

**FIG. 11** is a graph of decay curves of the after-glow of SrAl2O4:0.1B2O3:0.01Eu2+,0.02Pr2+ measured in the first 15 sec. after exposure to a 13 W fluorescent lamp (measured at 488 nm). Decay curves for R=La (○), Ce (□), Sm (●), Gd (□), Tb (□), Dy (□), Er (△), Tm (□), Yb (○), and Lu (+) are shown. The decay curve of the sample SrAl2O4:Eu,Nd (●) is also shown for comparison.

**FIG. 12** is a graph comparing after-glow decay curves for samples of SrAl2O4:0.1B2O3:0.01Eu, 0.01Pr co-doped with 0.01 Y (x),Lu (△) or La (△). **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 Sr0.6Ba0.4Al2O4:0.01Eu, 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 60 sec. **FIG. 16** illustrates the spectra of the after-glow of Sr0.4Ca0.6Al2O4:0.01Eu, 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 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 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 measurement comparisons of persistence times must be performed under identical conditions using the same detection systems. The term “persistent phosphors” has been applied to materials exhibiting phosphorescence lasting form minutes to hours. The term “long-persistent phosphor” historically has been used to refer to ZnS:Cu, CaS:Eu, Tm and similar materials that have a persistence time of 20 to 40 minutes. Materials phosphors with acceptable persistence and brightness. Inclusion of ratios of activators and 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 Al³⁺ in the host is replaced with a divalent ion, such as Mg²⁺ or Zn²⁺ (alone or in combination) and those in which a portion of the alkaline earth metal ion (M²⁺) is replaced with a monovalent alkali metal ion, such as Na⁺ or K⁺ (alone or in combination). The doping level is designed to compensate the charge defects which are induced due to substitution of Se²⁻ by R²⁺.

This invention specifically exemplifies phosphors in powder or ceramic form prepared by combining the host, activator and trivalent metal ion dopants with a flux material. The flux material of most interest is B₂O₃. The properties of the powder and ceramic phosphors of this invention are significantly affected by the use of the flux material during preparation. Both the presence or absence of the flux and the amount of flux employed can affect phosphor properties. It has been demonstrated with the hosts of this invention that varying the molar amount of B₂O₃ relative to other components (where the molar proportion of M is 1) from 0.02 to 0.2 (z in formulas herein) results in blue-emitting phosphors with acceptable persistence and brightness. Inclusion of the flux in a molar proportion z 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.

B₂O₃ can be replaced in all formulations of this invention by an amount of H₂BO₃ sufficient to provide an equivalent molar amount of B (i.e., 2H₂BO₃ replaces each B₂O₃). The exact role of the flux B₂O₃ in the phosphor properties is not clear. However, the phosphorescent phase in the compounds of this invention cannot be obtained without the use of flux. It is believed that the presence of flux is important to obtaining a particular phosphorescent phase with improved properties. The presence or absence of flux in the preparation of strontium aluminate can affect the ultimate structure of the aluminate. For example, when m=1.75 and M=Sr, the host material becomes Sr₅Al₃O₁₅ with an orthorhombic structure with space group Pnma in the presence of flux (e.g., B₂O₃). This structure of strontium aluminate can be made only in the presence of flux. In the case where m=2 and M=Sr, the host material Sr₅Al₃O₁₅ formed in the presence of flux is similar in structure to orthorhombic Sr₅Al₃O₁₅ (see FIG. 4). This material is monoclinic with space group C₂h, 6,2/c when synthesized without flux (e.g., B₂O₃).

The phosphors of this invention can be made by the following general method. Phosphor components are com-
bined as indicated in stoichiometric formulas (with or without a flux). The mixture is treated to form a homogeneous fine powder, for example by milling or grinding. The powder is preferably pressed into pellets. The powder or pellets are prefired at temperatures between about 600 to 800° C. (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 pelletted 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 liquid heat pedestal method is preferred. Sintered pellets are cut into bars to introduce into the crystal growth chamber (1x1 mm/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 somwhat 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:

\[(1-2x-2y)\text{MCO}_3 + \text{mA1}_2\text{O}_3 \times \text{xB}_2\text{O}_3 \times \text{yEu}_2\text{O}_3 \times \text{zR}_3\text{O}_3 \quad 3\]

and will have the general formula:

\[\text{M}_2\text{O}_3 \cdot \text{mAl}_2\text{O}_3 \times (\text{xB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\]

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 0.02 to about 0.2. \(M\) is generally 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: \(\text{Pr}^{3+}\), \(\text{Ho}^{3+}\), \(\text{Nd}^{3+}\), \(\text{Dy}^{3+}\), \(\text{Er}^{3+}\), \(\text{Lu}^{3+}\), \(\text{Ce}^{3+}\), \(\text{Y}^{3+}\), \(\text{Sm}^{3+}\), \(\text{Gd}^{3+}\), \(\text{Tb}^{3+}\), \(\text{Th}^{3+}\), \(\text{Yb}^{3+}\) and \(\text{Bi}^{3+}\). Preferred trivalent cophants are \(\text{Pr}^{3+}\), \(\text{Ho}^{3+}\), \(\text{Dy}^{3+}\), and \(\text{Nd}^{3+}\). Co-doping of \(\text{Dy}^{3+}\) or \(\text{Y}^{3+}\) 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 about 1 hr at about 600° C. The prefired material is remilled 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:

\[\text{M}_2\text{O}_3 \cdot \text{mA1}_2\text{O}_3 \times (\text{xB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}_1^{3+},2\text{yR}_2^{3+}\]

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 from about 0.001 to about 0.005, \(y\) can range from about 0.0001 to about 0.10 and the value of \(y\) is preferably equal to the value of \(x\) and \(z\) can range from about 0.02 to about 0.2. Preferred phosphors contain about equal amounts of \(R_1\) and \(R_2\).

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

\[\text{M}_2\text{O}_3 \cdot (\text{mA1}_2\text{O}_3 \times \text{zXO}(\text{xB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\]

where \(k=1-2x-2y\), \(m\) is as defined above, \(x\) can range from about 0.0001 to about 0.05 and is preferably about 0.001 to about 0.05, \(y\) 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. \(X\) is a metal oxide, preferably \(\text{MgO}\) or \(\text{ZnO}\) 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 \(R^{3+}\) doped into the matrix (i.e., the value of \(q\) preferably-equal to 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:

\[\text{M}_2\text{O}_3 \cdot (\text{mA1}_2\text{O}_3 \times \text{zXO}(\text{xB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\]

where \(k=1-2x-2y\), \(m\) is as defined above, \(x\) can range from about 0.0001 to about 0.05 and is preferably about 0.001 to about 0.005, \(y\) can range from about 0.0001 to about 0.10 and the value of \(y\) is preferably equal to the value of \(x\) and \(z\) can range from about 0.02 to about 0.2. \(Z\) is an alkali metal oxide, preferably \(\text{Na}_2\text{O}\) or \(\text{K}_2\text{O}\) 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 \(R^{3+}\) doped into the matrix (i.e., the value of \(r\) preferably-equal to value of \(2y\)). A slight excess over the desired or preferred amount of \(Z\) 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: 
\[\text{M}_2\text{O}_3 \cdot \text{mA1}_2\text{O}_3\]
where \(M\) is an alkaline earth metal, and \(m\) is a number ranging from about 1.6 to about 2.2, 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 \(\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{Yb}^{3+}, \text{and Bi}^{3+}.\]
A phosphorescent material as in paragraph A further comprising from about 2 mol % to about 20 mol %, relative to M, of B$_2$O$_3$, in said host and/or wherein B$_2$O$_3$ 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 Sr$^{2+}$.

A phosphorescent material having the formula:

$$M_2O \cdot mAl_2O_3\cdot (zB_2O_3):2xEu^{3+},2yR^{3+},$$

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 0.02 to about 0.2
- x is a number ranging from about 0.0001 to about 0.005;
- y is a number ranging from about 0.0001 to about 0.010;

A phosphorescent material as defined in paragraph B wherein R$_3^+$ is Pr$^{3+}$, Ho$^{3+}$, Dy$^{3+}$, or Nd$^{3+}$; and preferably the value of y=the value of x;

- z ranges from about 0.02 to about 0.2;
- m is a number ranging from about 1.6 to about 2.2;
- x is a number ranging from about 0.02 to about 0.2;

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

Methods of Preparation of Blue Phosphors with Host Material Mal$_2$O$_4$ (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:

$$1-2x-2y)MC0_{3+z-2x-2y}Al_2O_3+xEu_2O_3+yR_2O_3+zB_2O_3;$$

where:

- x=0.0001 to about 0.05;
- y=0.0001 to about 0.10;
- z=0.0001 to about 0.030.

Example 1

Preparation and Characterization of SrAl$_2$O$_4$(B$_2$O$_3$):Eu$^{2+}$,Pr$^{3+}$ Phosphors

The methods and phosphors of this invention are specifically exemplified by preparation of SrAl$_2$O$_4$(0.1B$_2$O$_3$):Eu$^{2+}$,
Preparation and Characterization of SrAl$_2$O$_3$ 

Preparation and Characterization of SrAl$_2$O$_3$:Eu$^{2+}$, Pr$^{3+}$ Phosphors with Varying Amounts of Pr$^{3+}$

Table 1 shows time persistence of after-glow of the samples SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:Ho$^{3+}$, 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$^{-1}$). The figure illustrates phosphorescence intensity as a function of wavelength in 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

Table 2 shows time persistence of after-glow of the samples SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:2xPr$^{3+}$ after-glow after-exposure (triangles). The phosphor samples in which y (Pr$_{2}O_3$ molar concentration) was varied from 0.005 to 0.02. Data in Table 2 indicate that the intensity of the after-glow is not sensitive to variations in Pr$_{3+}$ in the range examined. However, it is generally preferred to employ lower concentration of Pr (y=0.01 to 2x) because Pr$_{3+}$ absorbs in the range of 450-480 nm due to transitions from the ground state $^3$P$_0$ to excited states $^3$P$_1$, $^3$P$_2$, $^3$P$_3$.

Table 2 presents the excitation and emission spectra of SrAl$_2$O$_3$:(0.01B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$ where the excitation spectrum was monitored at 488 nm.

Table 3 shows the excitation spectra of SrAl$_2$O$_3$:(0.01B$_2$O$_3$):0.01Eu$^{2+}$:2xPr$^{3+}$ where the excitation spectrum is monitored at 488 nm (line a). For comparison, the decay characteristics of a commercial blue phosphor CaS:Bi after similar exposure is also shown (line b). The SrAl$_2$O$_3$:(0.01B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$ phosphor is about 10 times brighter than the commercial blue phosphor and has a persistence time about 20 times longer. After 18 hours SrAl$_2$O$_3$:(0.01B$_2$O$_3$):0.01 Eu$^{2+}$:0.02Pr$^{3+}$ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

Table 4 presents the excitation and emission spectra of SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$ where the excitation spectrum was monitored at 488 nm.

Table 5 shows the excitation spectra of SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:2xPr$^{3+}$ where the excitation spectrum is monitored at 488 nm (line a). For comparison, the decay characteristics of a commercial blue phosphor CaS:Bi after similar exposure is also shown (line b). The SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$ phosphor is about 10 times brighter than the commercial blue phosphor and has a persistence time about 20 times longer. After 18 hours SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01 Eu$^{2+}$:0.02Pr$^{3+}$ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

Table 6 presents the excitation and emission spectra of SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:2xPr$^{3+}$ where the excitation spectrum is monitored at 488 nm (line a). For comparison, the decay characteristics of a commercial blue phosphor CaS:Bi after similar exposure is also shown (line b). The SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$ phosphor is about 10 times brighter than the commercial blue phosphor and has a persistence time about 20 times longer. After 18 hours SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01 Eu$^{2+}$:0.02Pr$^{3+}$ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

Table 7 shows the excitation spectra of SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:2xPr$^{3+}$ where the excitation spectrum is monitored at 488 nm (line a). For comparison, the decay characteristics of a commercial blue phosphor CaS:Bi after similar exposure is also shown (line b). The SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$ phosphor is about 10 times brighter than the commercial blue phosphor and has a persistence time about 20 times longer. After 18 hours SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01 Eu$^{2+}$:0.02Pr$^{3+}$ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

Table 8 presents the excitation and emission spectra of SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:2xPr$^{3+}$ where the excitation spectrum is monitored at 488 nm (line a). For comparison, the decay characteristics of a commercial blue phosphor CaS:Bi after similar exposure is also shown (line b). The SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$ phosphor is about 10 times brighter than the commercial blue phosphor and has a persistence time about 20 times longer. After 18 hours SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01 Eu$^{2+}$:0.02Pr$^{3+}$ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

Table 9 shows the excitation spectra of SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:2xPr$^{3+}$ where the excitation spectrum is monitored at 488 nm (line a). For comparison, the decay characteristics of a commercial blue phosphor CaS:Bi after similar exposure is also shown (line b). The SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$ phosphor is about 10 times brighter than the commercial blue phosphor and has a persistence time about 20 times longer. After 18 hours SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01 Eu$^{2+}$:0.02Pr$^{3+}$ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

Table 10 presents the excitation and emission spectra of SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:2xPr$^{3+}$ where the excitation spectrum is monitored at 488 nm (line a). For comparison, the decay characteristics of a commercial blue phosphor CaS:Bi after similar exposure is also shown (line b). The SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$ phosphor is about 10 times brighter than the commercial blue phosphor and has a persistence time about 20 times longer. After 18 hours SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01 Eu$^{2+}$:0.02Pr$^{3+}$ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

Table 11 shows the excitation spectra of SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:2xPr$^{3+}$ where the excitation spectrum is monitored at 488 nm (line a). For comparison, the decay characteristics of a commercial blue phosphor CaS:Bi after similar exposure is also shown (line b). The SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$ phosphor is about 10 times brighter than the commercial blue phosphor and has a persistence time about 20 times longer. After 18 hours SrAl$_2$O$_3$:(0.1B$_2$O$_3$):0.01 Eu$^{2+}$:0.02Pr$^{3+}$ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).
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 SrAl₂O₄(O.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 SrAl₂O₄(O.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺ (line b) and a commercial blue phosphor CaSr₂S::Bi (c) after similar exposure are also shown. The SrAl₂O₄(O.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺ phosphor shows similar brightness and persistence to that of SrAl₂O₄(O.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺. After 20 hours SrAl₂O₄(O.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 SrAl₂O₄(O.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺ where the excitation spectrum was monitored at 488 nm.

Preparation and Characterization of SrAl₂O₄(B₂O₃)
:Eu²⁺:Nd³⁺ Blue Phosphors

SrAl₂O₄(O.1B₂O₃):0.01Eu²⁺:0.02Nd³⁺ was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

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

where B₂O₃ serves as flux.

FIG. 8 shows the spectrum of the after-glow of a sample of SrAl₂O₄(O.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 SrAl₂O₄(O.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 SrAl₂O₄(O.1B₂O₃):0.01 Eu²⁺:0.02Pr³⁺ (b) and a commercial blue phosphor CaSr₂S::Bi (c) after similar exposure are also shown. The SrAl₂O₄(O.1B₂O₃):0.01 Eu²⁺:0.02 Nd³⁺ phosphor shows similar brightness and persistence to that of SrAl₂O₄(O.1B₂O₃):0.01 Eu²⁺:0.02Pr³⁺. After 20 hours SrAl₂O₄(O.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 SrAl₂O₄(O.1B₂O₃):0.01 Eu²⁺:0.02 Nd³⁺ where the excitation spectrum was monitored at 488 nm.

Preparation and Characterization of Phosphors of Formulas SrAl₂O₄(B₂O₃):0.01 Eu²⁺:0.02 R³⁺, where R are trivalent metal ions of La, Ce, Sm, Gd, Tb, Dy, Er, Tm, Yb, and Lu.

SrAl₂O₄(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 Sc₂O₃+2.00 Al₂O₃+0.005 Eu₂O₃+0.01 R₂O₃+0.1 B₂O₃

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

FIG. 11 shows the decay curves of the after-glow of the SrAl₂O₄(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 (V), Ce (Ο), Sm (●), Gd (Δ), Tb (□), Dy (□), Er (△), Tm (●), Yb (⊙), and Lu (♦). The decay curve of the sample SrAl₂O₄(O.1B₂O₃):Eu,Nd (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 SrAl₂O₄(O.1B₂O₃):0.01Eu⁺:0.02R³⁺ 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 SrAl₂O₄(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 SrAl₂O₄(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:

(1-2x-2y)MCO₃+2xAl₂O₃+2yEu₂O₃+4xPr₂O₃+4yalR₂O₃+ιZBO₃

where y₁+y₂=y, 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 Sc₂O₃+2.00 Al₂O₃+0.005 Eu₂O₃+0.005 Pr₂O₃+0.005 R₂O₃+0.1 B₂O₃

where R=Y, La, Lu, Er, and Bi. The intensity of the after-glow of SrAl₂O₄(O.1B₂O₃):0.01Eu⁺:0.01Pr⁺:0.01R⁺ measured at 488 nm relative to that of SrAl₂O₄(O.1B₂O₃):0.01Eu⁺:0.02Pr⁺ is given in Table 3. Some results are also shown in FIG. 12.

FIG. 12 shows decay curves of the after-glow of SrAl₂O₄(O.1B₂O₃):0.01Eu⁺:0.01Pr⁺:0.01R⁺ (R=Y³⁺, Lu³⁺, and La³⁺) 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 SrAl₂O₄(O.1B₂O₃):0.01Eu⁺:0.01Pr⁺:0.01Y⁺ where the excitation spectrum was monitored at 488 nm. Codoping with Y³⁺ and Pr⁺ increases the UV excitation
efficiency and improve the brightness by 50% compared to the analogous Pr$^{3+}$-doped phosphor.

**TABLE 3**

<table>
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<tr>
<th>after (min)</th>
<th>Pr$^3+$</th>
<th>Y</th>
<th>La</th>
<th>Lu</th>
<th>Er</th>
<th>Bi</th>
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<td>18</td>
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</tr>
</tbody>
</table>

1Data 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 and SrAl$_2$O$_4$
(0.1B$_2$O$_3$):0.01Eu,0.01Dy,0.01Pr

This example demonstrates the influence of deep trapping centers formed by Dy$^{3+}$ on the decay characteristics of MAl$_2$O$_4$(0.1B$_2$O$_3$):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:

\[
(1-2x-2y)MC0,+nBaCO_3+mAl_2O_3+xEu,O,+yRzO_3+zB_2O_3 \]

where y$_1$, y$_2$, y, m, x, y and z ranges are as described above for formula 1.

For preparation of specific phosphors where M is Sr, the components were combined in the following molar proportions:

\[
0.97 SrC0,+0.64 BaC0,+2.00 A1,0,+0.005 Eu,O,+0.001 Pr,O,+0.1 B,O, \]

These mixed alkaline earth aluminate compounds, (Sr$_{0.33}$Ba$_{0.45}$)(0.1B$_2$O$_3$)Al$_{1.0}$:0.01Eu,0.01Pr were prepared following the general procedure of Example 1 combining the components in the following molar proportions:

\[
0.33 SrCO,+0.64 BaCO,+2.00 Al,O,+0.005 Eu,O,+0.01 Pr,O,+0.1 B,O, \]

**TABLE 4**

<table>
<thead>
<tr>
<th>after (min)</th>
<th>SAO-EuPr$^1$</th>
<th>SAO-EuPrDy</th>
<th>SAO-EuHoDy</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>60</td>
<td>15</td>
<td>47</td>
<td>35</td>
</tr>
</tbody>
</table>

4Data 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:

\[
(1-n-2x-2y)SrCO,+nBaCO,+mAl_2O,+xEu,O,+yRzO,+zB_2O, \]

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 0.1; and
- R$^{3+}$ is a trivalent rare earth ion or Bi$^{3+}$.

The mixed alkaline earth aluminate compound, (Sr$_{0.33}$Ba$_{0.45}$)(0.1B$_2$O$_3$)Al$_{1.0}$:0.01Eu,0.01Pr was prepared following the general procedure of Example 1 combining the components in the following molar proportions:

\[
0.33 SrCO,+0.64 BaCO,+2.00 Al,O,+0.005 Eu,O,+0.01 Pr,O,+0.1 B,O, \]

These mixed alkaline earth phosphors have the general formula:

\[
Sr_xB_yO - mAl_2O_3(zB_2O_3):2xEu_2zR_2 \]

For preparation of specific phosphors where M is Sr, the components were combined in the following molar proportions:

\[
0.97 SrC0,+0.64 BaC0,+2.00 A1,0,+0.005 Eu,O,+0.001 Pr,O,+0.1 B,O, \]

These mixed alkaline earth phosphors have the general formula:

\[
Sr_xC_yO - mAl_2O_3(zB_2O_3):2xEu_2zR_2 \]

**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:

\[
(1-n-2x-2y)SrCO,+nCaCO,+mAl_2O,+xEu,O,+yRzO,+zB_2O, \]

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
- R$^{3+}$ is a trivalent rare earth ion or Bi$^{3+}$.

These phosphors have the generic formula:

\[
Sr_xCa_yO - mAl_2O_3(zB_2O_3):2xEu_2zR_2 \]

**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:

\[
(1-n-2x-2y)SrCO,+nBaCO,+mAl_2O,+xEu,O,+yRzO,+zB_2O, \]

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 0.1; and
- R$^{3+}$ is a trivalent rare earth ion or Bi$^{3+}$.

These phosphors have the generic formula:

\[
Sr_xBa_yO - mAl_2O_3(zB_2O_3):2xEu_2zR_2 \]
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:

$$Sr_Ba,Ca,O_{mAl,O_3(eB,O_3)2Eu,O2yR_3}$$

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

**Example 12**

Codoping of Mg$^{2+}$ or Zn$^{2+}$ into MO .

$mAl,O_3Eu^{2+},R^{3+}$ 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:

$$(1-2x-2y)MCO_{mAl,O_3+xEuO_2+yR_3O_3+qXO+zB_2O_3}$$

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 and/or ZnO. These phosphors will have the generic formula:

$$M,O_{mAl,O_3},qXO:2xEu,2yR,10$$

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

Example 13

Co-doping of Na$^{+}$ or K$^{+}$ into MO .

$mAl,O_3Eu^{2+},R^{3+}$ 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:

$$(1-2x-2y)MCO_{mAl,O_3+xEuO_2+yR_3O_3+qXO+zB_2O_3}$$

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$_2$CO$_3$, in particular, can be Na$_2$CO$_3$ and/or K$_2$CO$_3$. These phosphors will have the generic formula:

$$M,O_{mAl,O_3},rNa_2CO_3+o.01Eu,0.01Pr,10$$

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

Exemplary Na and K doped phosphors are prepared by combining the components according to the following molar proportions:

$$0.98 ScCO_{3+1.99 Al_2O_3+0.01 XO+0.005 Eu_2O_3+0.005 Dy_2O_3+0.01 CO_2}$$

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 5**
The influence of substituting Na$^+$ or K$^+$ for Sr$^{2+}$ on the after-glow of SrAl$_2$O$_4(0.1B_2O_3):0.01Eu,0.01Pr$

after (min) SAO-EuPr$^1$ SAO-EuPrMg SAO-EuPrK

<table>
<thead>
<tr>
<th>min</th>
<th>10</th>
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$^1$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:

$$0.98 ScCO_{3+1.99 Al_2O_3+0.01 XO+0.005 Eu_2O_3+0.005 Pr_2O_3+0.1 B_2O_3}$$

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$2$Al$_{1.25}$O$_3$ exhibits somewhat brighter phosphorescence.

**TABLE 7**
The influence of varying Al/Sr ratio on after-glow of SrAl$_2$O$_4(0.1B_2O_3):0.01Eu,0.01Pr$

<table>
<thead>
<tr>
<th>m</th>
<th>1.6</th>
<th>1.75</th>
<th>1.85</th>
<th>1.95</th>
<th>2.0$^1$</th>
<th>2.15</th>
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</table>

$^1$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$_2$O$_4$) activated with Eu$^{2+}$ and doped with Pr$^{3+}$ were prepared...
using varying amounts of flux (zB₂O₃). Phosphor components were mixed according to the molar proportions:

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

with z=0.03, 0.05, 0.08, 0.10, 0.12, 0.15, and 0.20 and phosphors were prepared according to the general procedure of Example 1.

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 M₂₃Al₉O₁₉ (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:

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

where:

\[ 8x+8y < 4, x \text{ is preferably about 0.0001 to about 0.05 and more preferably } x \text{ is 0.001 to about 0.005}; \]

\[ y \text{ ranges from about 0.0001 to about 0.10 and preferably the value of } y \text{ is the value of } x \]

where 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 Bi³⁺.

B₂O₃ 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>After/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>113</td>
</tr>
<tr>
<td>0.05</td>
<td>121</td>
</tr>
<tr>
<td>0.08</td>
<td>106</td>
</tr>
<tr>
<td>0.10</td>
<td>100</td>
</tr>
<tr>
<td>0.12</td>
<td>132</td>
</tr>
<tr>
<td>0.15</td>
<td>100</td>
</tr>
<tr>
<td>0.20</td>
<td>99</td>
</tr>
</tbody>
</table>

TABLE 8

The influence of varying B₂O₃ in preparation of phosphors.

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:

1. The pedestal method:

   General Methods of Preparation of Blue Phosphors with Host Material M₃₃Al₉O₁₉ (where M is Sr or a combination of Sr with Ca, Ba or both, R³⁺ is Sr or a combination of Sr with Ba and/or Ca)  

2. The laser heated pedestal method:

   Trans. AIME 194:747) or the laser heated pedestal method (B. M. Tissue et al. (1991) J. Crystal Growth 109:323) can provide measurements of the phosphorescent phase. 35

3. The prefired pellets are pulverized and milled again into a homogeneous fine powder. The powder is pressed into MO bars from 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 N₂, 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:

   \[ \text{MO.mAl}_2\text{O}_3\text{Eu}^{2+}\text{R}^{3+} \]

   wherein m is a number ranging from about 1.6 to about 2.2, M is Sr or a combination of Sr with Ca, Ba or both, R³⁺ is Sr or a combination of Sr with Ca, Ba or both, and x ranges from about 0.0001 to about 0.05 and preferably is about 0.001 to about 0.005; and y ranges from about 0.0001 to about 0.10 and preferably is about 0.001 to about 0.005; and z ranges from about 0.02 to about 0.1;

2. The phosphor of claim 1 wherein R³⁺ is selected from the group Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, Tm³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tb³⁺, Tm³⁺, Yb³⁺, and Bi³⁺.

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

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

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

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

   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 R³⁺ is a combination of Pr³⁺ with Dy³⁺, or a combination of Ho³⁺ with Dy³⁺.

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:

    \[ \text{MO.mAl}_2\text{O}_3\text{Eu}^{2+}\text{R}^{3+} \]

    wherein m is a number ranging from about 1.6 to about 2.2, M is Sr or a combination of Sr with Ca, Ba or both, R³⁺ is Sr or a combination of Sr with Ca, Ba or both, and x ranges from about 0.0001 to about 0.05, and y can range from about 0.0001 to about 0.10.

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:
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 $Pr^{3+}$, $Ho^{3+}$, $Nd^{3+}$, $Dy^{3+}$, $Er^{3+}$, $La^{3+}$, $Lu^{3+}$, $Ce^{3+}$, $Sm^{3+}$, $Gd^{3+}$, $Tb^{3+}$, $Tm^{3+}$, $Yb^{3+}$ and $Bi^{3+}$.

12. A phosphor having the formula:

$$Sr_{x}Ba_{y}Ca_{z}O_{m}Al_{2}O_{3}:Eu^{2+},R^{3+}$$

where $k=l-n-p-2x-2y$ 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:

$$MO_{m}Al_{2}O_{3}:Eu^{2+},R^{3+}$$

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, $R^{3+}$ is a trivalent 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:

$$MO_{m}Al_{2}O_{3}:Eu^{2+},R^{3+}$$

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

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

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

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

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

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

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

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

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

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

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

26. The phosphor of claim 15 wherein $R^{3+}$ is a mixture of $Pr^{3+}$, $Ho^{3+}$, $Dy^{3+}$, $Tb^{3+}$, or a mixture 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:Eu²⁺,R³⁺" and replace with -- MO·mAl₂O₃:Eu²⁺,R³⁺ --.

Column 1,
Line 28, delete "SrAl₂O₄:Eu²⁺,Dy³⁺" and replace with -- SrAl₂O₄: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 "M₁ₓAl₂O₄₋ₓ Where" and replace with -- M₁ₓAl₂O₄₋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(2B₂O₃):Eu²⁺,R³⁺" and replace with -- MO·mAl₂O₃(2B₂O₃):Eu²⁺,R³⁺ --.

Column 4,
Line 32, delete "Sr₀.₆₈Ba₀.₃₂Al₂O₇" and replace with -- Sr₀.₃₃Ba₀.₆₄Al₂O₇ --.
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 19, delete "somehat" and replace with -- somewhat --.
Line 28, delete "LHGP" and replace with -- LHPG --.
Line 42, delete \(\text{M}_2\text{O} \cdot \text{mA}_1\text{O}_3(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) and replace with -- \(\text{M}_2\text{O} \cdot \text{mA}_1\text{O}_3(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) --.

**Column 8**, Line 1, delete \(\text{M}_2\text{O} \cdot \text{mA}_1\text{O}_3(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) and replace with -- \(\text{M}_2\text{O} \cdot \text{mA}_1\text{O}_3(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) --.
Line 15, delete \(\text{M}_2\text{O} \cdot \text{(m-q)A}_1\text{O}_3.qXO(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) and replace with -- \(\text{M}_2\text{O} \cdot \text{(m-q)A}_1\text{O}_3.qXO(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) --.
Line 31, delete \(\text{M}_2\text{O} \cdot \text{mA}_1\text{O}_3.rZ2(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) and replace with -- \(\text{M}_2\text{O} \cdot \text{mA}_1\text{O}_3.rZ2(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) --.
Line 60, delete "MO.mAlO3" and replace with -- MO.mAlO3 --.

**Column 9**, Line 10, delete \(\text{M}_2\text{O} \cdot \text{mA}_1\text{O}_3(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) and replace with -- \(\text{M}_2\text{O} \cdot \text{mA}_1\text{O}_3(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) --.
Line 28, delete \(\text{M}_2\text{O} \cdot \text{mA}_1\text{O}_3(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) and replace with -- \(\text{M}_2\text{O} \cdot \text{mA}_1\text{O}_3(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) --.
Line 50, delete \(\text{M}_2\text{O} \cdot \text{(m-q)A}_1\text{O}_3.qXO(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) and replace with -- \(\text{M}_2\text{O} \cdot \text{(m-q)A}_1\text{O}_3.qXO(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) --.
Line 67, delete \(\text{M}_2\text{O} \cdot \text{mA}_1\text{O}_3.rZ2(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) and replace with -- \(\text{M}_2\text{O} \cdot \text{mA}_1\text{O}_3.rZ2(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) --.

**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 \(\text{Sr}_2\text{Ba}_2\text{Ca}_4\text{O}_m\text{Al}_2\text{O}_3(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) and replace with -- \(\text{Sr}_2\text{Ba}_2\text{Ca}_4\text{O}_m\text{Al}_2\text{O}_3(\text{zB}_2\text{O}_3):2\text{xEu}^{2+},2\text{yR}^{3+}\) --.
Line 45, delete "Bi" and replace with -- Bi --.
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 "SrAl₃O₇:0.01Eu²⁺:0.02Pr³⁺" and replace with
-- SrAl₃O₇(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺ --.
Line 25, delete "SrAl₃O₇(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺" and replace with
-- SrAl₃O₇(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺ --.
Lines 29, 32, 37 and 39-40, delete "SrAl₃O₇(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺" and replace with
-- SrAl₃O₇(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺ --.
Line 46, delete "SrAl₃O₇(0.1B₂O₃):Eu²⁺:Pr³⁺" and replace with -- SrAl₃O₇(0.1B₂O₃):Eu²⁺,Pr³⁺ --.
Lines 50-51, delete "SrAl₃O₇(0.1B₂O₃):Eu²⁺:Pr³⁺" and replace with -- SrAl₃O₇(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 "SrAl₃O₇(0.1B₂O₃):Eu²⁺:Pr³⁺" and replace with -- SrAl₃O₇(0.1B₂O₃):Eu²⁺:Pr³⁺ --.
Line 43, Table 2, delete "SrAl₃O₇(0.1B₂O₃):0.01Eu²⁺:2yPr" and replace with -- SrAl₃O₇(0.1B₂O₃):0.01Eu²⁺:2yPr --.
Lines 55-56, delete "SrAl₃O₇(0.1B₂O₃):Eu²⁺:Ho³⁺" and replace with -- SrAl₃O₇(0.1B₂O₃):Eu²⁺,Ho³⁺ --.
Lines 58 and 66, delete "SrAl₃O₇(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺" and replace with -- SrAl₃O₇(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺ --.

**Column 13.**
Lines 8, 14, 17 and 22, delete "SrAl₃O₇(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺" and replace with -- SrAl₃O₇(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺ --.
Lines 29-30, delete "SrAl₃O₇(0.1B₂O₃):Eu²⁺:Nd³⁺" and replace with -- SrAl₃O₇(0.1B₂O₃):Eu²⁺,Nd³⁺ --.
Lines 33, 43, 53, 58, 61 and 66, delete "SrAl₃O₇(0.1B₂O₃):0.01Eu²⁺:0.02Nd³⁺" and replace with -- SrAl₃O₇(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 "(Sr₀.₃₃Ba₀.₆₄)(0.1B₂O₃)Al₄O₇:0.01Eu:0.02Pr" and replace with -- (Sr₀.₃₃Ba₀.₆₄)(0.1B₂O₃)Al₄O₇:0.01Eu,0.02Pr --.
Line 22, delete "SrₓBaₐ₋ₓOₐₙAl₆₀₃(zB₂O₃):2xEu,2yR" and replace with -- SrₓBaₐ₋ₓOₐₙAl₆₀₃(zB₂O₃):2xEu,2yR --.
Line 48, delete "SrₓCaₖOₙAl₆₀₃(zB₂O₃):2xEu,2yR" and replace with -- SrₓCaₖOₙAl₆₀₃(zB₂O₃):2xEu,2yR --.
Line 52, delete "(Sr₀.₄₈₅Ca₀.₄₈₅)Al₆₀₃:0.01Eu:0.02Pr" and replace with -- (Sr₀.₄₈₅Ca₀.₄₈₅)Al₆₀₃:0.01Eu,0.02Pr --.
Lines 58-59, delete "(Sr₀.₄₈₅Ca₀.₄₈₅)(0.1B₂O₃)Al₆₀₃:0.01Eu:0.02Pr" and replace with -- (Sr₀.₄₈₅Ca₀.₄₈₅)(0.1B₂O₃)Al₆₀₃:0.01Eu,0.02Pr --.

**Column 17.**
Line 7, delete "SrₓBaₐ₋ₓCaₖCa₇₋ₚAl₆₀₃(zB₂O₃):2xEu,2yR" and replace with -- SrₓBaₐ₋ₓCaₖCa₇₋ₚAl₆₀₃(zB₂O₃):2xEu,2yR --.
Lines 13-14 and 57-58, delete "MO,ₐ₉Al₆₀₃:Eu²⁺,R³⁺" and replace -- MO,ₐ₉Al₆₀₃:Eu²⁺,
R³⁺ --.
Line 29, delete "MₐO,(m-q)Al₆₀₃,qXO:2xEu,2yR" and replace with -- MₐO,(m-q)
Al₆₀₃,qXO:2xEu,2yR --.

**Column 18.**
Line 6, delete "MₐO,mAl₆₀₃,rNa₄O:2xEu,2yR" and replace with -- MₐO,mAl₆₀₃,rNa₄O: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.mAl_2O_3:Eu^{2+},R^{3+}" and replace with -- MO.mAl_2O_3:Eu^{2+},R^{3+} --.
Lines 44-45, delete "selected from the group".
Line 46, delete "and" and replace with -- or --.
Line 64, delete "MO.mAl_2O_3:Eu^{2+},R^{3+}" and replace with -- MO.mAl_2O_3:Eu^{2+},R^{3+} --.

**Column 21.**
Line 3, delete "R^{3+}, is present" and replace with -- R^{3+} is present --.
Line 11, delete "Sr_{x}Ba_{y}Ca_{z}O.mAl_2O_3:2xEu^{2+},2yR^{3+} " and replace with -- Sr_{x}Ba_{y}Ca_{z}O.mAl_2O_3:2xEu^{2+},2yR^{3+} --.
Line 15, delete "v" and replace with -- y --.
Lines 22 and 37, delete "MO.mAl_2O_3:Eu^{2+},R^{3+}" and replace with -- MO.mAl_2O_3:Eu^{2+},R^{3+} --.

**Column 22.**
Line 4, delete "M^{2+}" and replace with -- M^{2+} --.
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