LONG-PERSISTENCE BLUE PHOSPHORS

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Appl. No.: 09/187,944
Filed: Nov. 6, 1998

Related U.S. Application Data
Provisional application No. 60/064,690, Nov. 7, 1997, and provisional application No. 60/064,691, Nov. 7, 1997.

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ABSTRACT

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

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

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

30 Claims, 16 Drawing Sheets
OTHER PUBLICATIONS


FIG. 1
FIG. 3
FIG. 4

Intensity (normalized)

D (Å)

Intensity (counts)

2θ (degree)

θ (degree)

4

1.54

1.82

2.25

2.98

4.44

8.84

1416.0

1274.4

1132.8

991.2

849.6

708.0

566.4

424.8

283.2

141.6

0.0
FIG. 5
FIG. 6
FIG. 7
FIG. 8
Excitation

Emission

Wavelength (nm)

Intensity (a.u.)

FIG. 10
FIG. 11
FIG. 12

Graph showing the intensity (a.u.) over time (second) for different elements: Y, Lu, La.
FIG. 13
FIG. 14
FIG. 15
FIG. 16
LONG-PERSISTENCE BLUE PHOSPHORS
CROSS-REFERENCE TO RELATED APPLICATIONS
This application takes priority under 35 U.S.C. §119(e) from U.S. provisional applications Ser. No. 60/064,690, filed Nov. 7, 1997 and Ser. No. 60/064,691, filed Nov. 7, 1997, both of which are incorporated by reference herein to the extent not inconsistent herewith.

This invention was made at least in part with U.S. government funding through NASA grant NCCW-0088 and NCCS-252, ARO DAAH04-96-10416 and DOE DE-FG02-94ER57564. 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 phosphorescent materials, such as ZnS:Cu,Co, ZnCdS:Cu and CaS:Si: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. Pallila, A. K. Levine and M. R. Tomkus (1968) J. Electrochem. Soc. 115:642).

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

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

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

EP published application 710,709 (Murayama et al.) reports phosphors of matrix M₁₋ₓSrₓAl₂O₄₋ₓ, Where M is at least one metal selected from calcium, strontium, barium and, optionally, magnesium, and x is a number not equal to 0. The matrix comprises europium as an activator and a co-activator elected from a rare earth metal, manganese, tin or bismuth.

SUMMARY OF THE INVENTION
This invention relates to long-persistence phosphors of general formula:

MOₙ₋ₓ(M₁₋ₓSrₓ)ₐAlₙ₋ₓ₂O₄₋ₓ:Eu²⁺,R³⁺

where M is Sr or a combination of Sr with Ca and/or Ba; R³⁺ is a trivalent rare earth metal ion; and MO is a mixture of trivalent metal ions; and n is a number ranging from about 1.6 to about 2.2. The phosphors are prepared using a flux, particularly B₂O₅. The preferred phosphor formula of this invention indicating the presence of B₂O₅ flux is:

MOₙ₋ₓ(M₁₋ₓSrₓ)ₐAlₙ₋ₓ₂O₄₋ₓ:Eu²⁺,R³⁺

where M, n 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 %, preferably about 0.2 mol % to about 1.0 mol % of Eu²⁺, activator and co-doped with about 0.02 mol % to about 20 mol % of R³⁺ ions (preferably about 0.2 mol % to about 2 mol %) to of at least one trivalent rare earth metal ion or Bi³⁺. The activator and dopant concentration are measured in terms of mol % relative to the alkaline earth metal element, M.

Preferred phosphors of this invention are blue with a phosphorescent band at about 488 nm. Phosphors of this invention have significantly improved brightness compared to sulfide phosphors, such as CaS:Si:B. 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 Eu$^{2+}$ and are codoped with a trivalent rare earth metal ion or Bi$^{3+}$. The phosphors may be codoped with a single ion or a combination of such ions selected from the group of rare earth metal ions: Pr$^{3+}$, Ho$^{3+}$, Nd$^{3+}$, Dy$^{3+}$, Er$^{3+}$, Eu$^{2+}$, Ce$^{3+}$, Y$^{3+}$, Sm$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, Tm$^{3+}$, and Yb$^{3+}$ and the Group VA metal ion Bi$^{3+}$. Preferred trivalent dopants are Pr$^{3+}$, Ho$^{3+}$, Dy$^{3+}$, and Nd$^{3+}$. Co-doping of Dy$^{3+}$ or Y$^{3+}$ with another trivalent metal ion results in phosphor of improved brightness, e.g. SrAl$_2$O$_3$:Eu$^{2+}$, Pr$^{3+}$, Dy$^{3+}$ or SrAl$_2$O$_3$:Eu$^{2+}$, Ho$^{3+}$, Dy$^{3+}$.

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 SrAl$_2$O$_3$ and m=2, the host material being MA$_2$O$_5$. More preferred are phosphors where M=Sr and m=1.75 or m=2.

Phosphors of this invention also include those in which Mg$^{2+}$ or Zn$^{2+}$, or a mixture of both, is substituted for Sr$^{2+}$ in the matrix material and where M$^{2+}$, particularly Sr$^{2+}$, 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 SrAl$_2$O$_3$:Eu$^{2+}$ after exposure of the sample to a 4 W UV lamp for two minutes.

**FIG. 2** is a graph of the decay of the after-glow of (a) SrAl$_2$O$_3$:Eu$^{2+}$, (b) SrAl$_2$O$_3$:Eu$^{2+}$, and (c) SrAl$_2$O$_3$:Eu$^{2+}$ after exposure to a 13 W fluorescent lamp for 10 minutes. The threshold of eye sensitivity is indicated by a horizontal dashed line.

**FIG. 3** illustrates the excitation and emission spectra of SrAl$_2$O$_3$:Eu$^{2+}$ after 5 sec. and after 60 sec., and (c) of commercial blue phosphor CaS:S:Bi after exposure of the phosphor to a 13 W fluorescent lamp for 10 minutes. The threshold of eye sensitivity is indicated by a horizontal dashed line.

**FIG. 4** is a graph of decay of the after-glow of (a) SrAl$_2$O$_3$:Eu$^{2+}$, (b) SrAl$_2$O$_3$:Eu$^{2+}$, and (c) SrAl$_2$O$_3$:Eu$^{2+}$ after exposure to a 13 W fluorescent lamp for 10 minutes. The threshold of eye sensitivity is indicated by a horizontal dashed line.

**FIG. 5** illustrates the excitation and emission spectra of SrAl$_2$O$_3$:Eu$^{2+}$ after 60 sec. and after 150 sec., and (c) of commercial blue phosphor CaS:S:Bi after exposure of the phosphor to a 13 W fluorescent lamp for 10 minutes. The threshold of eye sensitivity is indicated by a horizontal dashed line.

**FIG. 6** illustrates the excitation and emission spectra of SrAl$_2$O$_3$:Eu$^{2+}$ after 60 sec. and after 150 sec., and (c) of commercial blue phosphor CaS:S:Bi after exposure of the phosphor to a 13 W fluorescent lamp for 10 minutes. The threshold of eye sensitivity is indicated by a horizontal dashed line.

**FIG. 7** illustrates the excitation and emission spectra of SrAl$_2$O$_3$:Eu$^{2+}$ after 60 sec. and after 150 sec., and (c) of commercial blue phosphor CaS:S:Bi after exposure of the phosphor to a 13 W fluorescent lamp for 10 minutes. The threshold of eye sensitivity is indicated by a horizontal dashed line.

**FIG. 8** is a graph of decay of the after-glow of a sample of SrAl$_2$O$_3$:Eu$^{2+}$ after exposure of the sample to a 4 W UV lamp for two minutes.

**FIG. 9** is a graph of decay of the after-glow of (a) SrAl$_2$O$_3$:Eu$^{2+}$, (b) SrAl$_2$O$_3$:Eu$^{2+}$, and (c) of commercial blue phosphor CaS:S:Bi after exposure of the phosphor 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 SrAl$_2$O$_3$:Eu$^{2+}$, and (c) of commercial blue phosphor CaS:S:Bi after exposure of the phosphor 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 SrAl$_2$O$_3$:Eu$^{2+}$, and (c) of commercial blue phosphor CaS:S:Bi after exposure of the phosphor to a 13 W fluorescent lamp for 10 minutes. The threshold of eye sensitivity is indicated by a horizontal dashed line.

**FIG. 12** is a graph comparing after-glow decay curves for samples of SrAl$_2$O$_3$:Eu$^{2+}$, and (c) of commercial blue phosphor CaS:S:Bi after exposure of the sample to a 4 W UV lamp for 2 minutes as a function of time after illumination (C), after 5 sec.; (C), after 20 sec. and (C), after 60 sec.

**FIG. 13** illustrates the excitation and emission spectra of SrAl$_2$O$_3$:Eu$^{2+}$, and (c) of commercial blue phosphor CaS:S:Bi after exposure of the phosphor to a 13 W fluorescent lamp for 10 minutes. The threshold of eye sensitivity is indicated by a horizontal dashed line.

**FIG. 14** is a graph comparing after-glow decay curves of SrAl$_2$O$_3$:Eu$^{2+}$, and (c) of commercial blue phosphor CaS:S:Bi after exposure of the sample to a 4 W UV lamp for 2 minutes as a function of time after illumination (C), after 5 sec.; (C), after 20 sec. and (C), 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, CuS, 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 which have a persistence time of 20 to 40 minutes. Materials herein can exhibit persistence time up to about 16–18 hrs or more. It is generally the case that phosphors having longer persistence times are more preferred. Preferred phosphor materials, including single crystals and single crystal fibers, of this invention can exhibit phosphorescence persistence times of greater than about 3–5 hrs. More preferred phosphors exhibit persistence times greater than about 10–12 hrs. Most preferred phosphors exhibit persistence times of greater than about 15–18 hrs.

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

The hosts of this invention are alkaline earth aluminates Mo4+ 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 1.70 to about 2.05 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 (SrAl11O19) or m is 2 (SrAl5O12) 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+, Yb3+, Sm3+, Gd3+, Tb3+, Tm3+, and Yb3+ and trivalent Bi3+. Preferred for the hosts of this invention is doping with trivalent Pr, Ho, Nd or Dy, with trivalent Pr and Ho being generally more preferred dopants.

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

Phosphors of this invention also include those in which a portion of Al2O3 in the host is replaced with a divalent ion, such as Mg2+ or Zn2+ (alone or in combination) and those in which a portion of the alkaline earth metal ion (M2+) is replaced with a monovalent alkali metal ion, such as Na+ or K+ (alone or in combination). The doping level is designed to compensate the charge defects which are induced due to substitution of Sr2+ by 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 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 about 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., 2H3B03 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 aluminates can affect the ultimate structure of the aluminate. For example, when m=1.75 and M=Sr, the host material becomes Sr4Al14O35 with an orthorhombic structure with space group Pmma 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 Sr3Al5O12, formed in the presence of flux is similar in structure to orthorhombic Sr3Al5O12 (see FIG. 4). This material is monoclinic with space group C2h,5,2/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-
ted 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 prefired at temperatures between about 600 to 800°C 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 prefired before sintering. The powder or pellets are the sintered at about 1300°C under a reducing atmosphere, e.g., H₂/N₂, having 2–5% by volume H₂.

Sintered phosphor material can be used to grow single crystals or single crystal fibers. Any crystallization technique can be employed. The laser heated pedestal method is preferred. Sintered pellets are cut into bars to introduction into the crystal growth chamber (1×1 mm ×1.5×1.5 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 crystal bar can be used as a "seed" to stimulate spontaneous nucleation in the LHGP process. It was observed that the initial part of the fiber prepared by the LHGP process was a twinned crystal. The fiber eventually becomes one single crystal after a transition stage, but the crystal is not oriented. Fiber lengths of single crystals grown vary, but can be as long as several centimeters in length. Single crystals with an average diameter of about 0.8 mm can be grown. The basic phosphors of this invention are most generally prepared by admixing the components in the following molar proportions:

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

and will have the general formula:

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

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 0.0001 to about 0.05 and is preferably about 0.001 to about 0.005. The amount of divalent ion \( 9 \) from 0.0001 to about 0.20. The amount of monovalent ion \( x \) to the amount of \( 9 \) preferably the value of \( y \). A slight excess over the desired or preferred amount of \( 9 \) 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 used to prepare single crystal powders and 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 appurtenances. The phosphors have application in low 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: \( \text{M}_2\text{O}_3 \cdot m\text{Al}_2\text{O}_3 \), where \( M \) is an alkaline earth metal, and \( m \) is a number ranging from about 1.6 to about 2.2, 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 \( \text{Pr}^{3+}, \text{Ho}^{3+}, \text{Nd}^{3+}, \text{Dy}^{3+}, \text{Er}^{3+}, \text{La}^{3+}, \text{Lu}^{3+}, \text{Ce}^{3+}, \text{Y}^{3+}, \text{Sm}^{3+}, \text{Gd}^{3+}, \text{Th}^{3+}, \text{TM}^{3+}, \text{and} \text{Yb}^{3+} \).
Phosphorescent material as in paragraph A further comprising from about 2 mol % to about 20 mol %, relative to M, of B₂O₃ in said host and/or wherein B₂O₃ is present in the host in an amount ranging from about 8 mol % to about 15 mol %, relative to M.

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

B. A phosphorescent material having the formula:

\[ M₂O \cdot mAl₂O₃ (xB₂O₃):2xEu³⁺,2yR³⁺, \]

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 0.05; y is a number ranging from about 0.0001 to about 0.005; k is greater than 0; 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⁺, Tb³⁺, Eu³⁺, Yb³⁺ and Bi³⁺.

A phosphorescent material as defined in paragraph B wherein M is Sr²⁺ or a mixture of Sr²⁺ with Ca²⁺, Ba²⁺ or both; x 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; y is a number ranging from about 0.0001 to about 0.005; x is a number ranging from about 0.0001 to about 0.005; y is a number ranging from about 0.0001 to about 0.005; and 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⁺, Tb³⁺, Eu³⁺, Yb³⁺ and Bi³⁺.

C. A phosphorescent material of having the formula:

\[ M₂O \cdot mAl₂O₃ (xB₂O₃):2xEu³⁺,2yR³⁺, \]

where k is 1–2x–2y, with y=y₁+y₂; 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⁺, Tb³⁺, Eu³⁺, Yb³⁺ and Bi³⁺.

D. A phosphorescent material having the formula:

\[ M₂O \cdot mAl₂O₃ (xB₂O₃):2xEu³⁺,2yR³⁺, \]

where k is 1–2x–2y, with y=y₁+y₂; 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⁺, Tb³⁺, Eu³⁺, Yb³⁺ and Bi³⁺.

E. A phosphorescent material having the formula:

\[ M₂O \cdot mAl₂O₃ (xB₂O₃):2xEu³⁺,2yR³⁺, \]

where k=1–2x–2y–2z; x ranges from about 0.0001 to about 0.05; y is a number ranging from about 0.0001 to about 0.10; z ranges from about 0.02 to about 0.2; Z is an alkali metal ion, particularly Na⁺ or K⁺ and r is the value of y.

F. A phosphorescent material having the formula:

\[ M₂O \cdot mAl₂O₃ (xB₂O₃):2xEu³⁺,2yR³⁺, \]

where k=1–n–p–2x–2y, where k is greater than 0; n and p are numbers greater than or equal to 0 and less than 1; m is a number ranging from about 1.6 to about 2.2; z ranges from about 0.02 to about 0.2; y ranges from about 0.0001 to about 0.005; x ranges from about 0.0001 to about 0.005; and 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⁺, Tb³⁺, Eu³⁺, Yb³⁺ and Bi³⁺.

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

THE EXAMPLES

Example 1

Methods of Preparation of Blue Phosphors with Host Material MA₁₀₃ (where M is Sr or a mixture of Sr with Ba and/or Ca)

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

\[ (1–2x–2y)MCO₃+2xAl₂O₃+yR₂O₃+zB₂O₃; \]

where:

- 2x+y is less than 1, preferably x=about 0.0001 to about 0.05 and more preferably x=about 0.0001 to about 0.005; y is a number ranging from about 0.0001 to about 0.010 and preferably the value of y=the value of x;
- z ranges from about 0.02 to about 0.2; M is Sr or a combination of Sr with Ca and/or Ba; and R is a trivalent rare earth metal or Bi³⁺.
- B₂O₃ is used as a flux in the composition and is important for ensuring the formation of the phosphorescent phase. B₂O₃ can be replaced by two molar equivalents of H₂BO₃.
- The mixture of components is milled or ground to form a homogeneous fine powder for prefiring. The powder is preferably pressed into pellets under about 1.3 ton/cm² pressure prior to prefiring. The mixed powder or the pressed pellets are then prefired at about 600°C. in air for about one hour. The prefired material is then pulverized and milled again into a fine powder suitable for sintering. The prefired powder is preferably again pressed into ceramic pellets under 1.3 ton/cm² pressure before sintering. The powder or pellets are then sintered at about 1,300°C. for one hour in H₂–N₂ gas flow containing about 2–5% H₂ (by volume) at a flow rate of about 0.1 liter per minute. The resulting material exhibits phosphor properties as described herein.

Example 2

Preparation and Characterization of SrAl₂O₄(B₂O₃):Eu³⁺,Pr³⁺ Phosphors

The methods and phosphors of this invention are specifically exemplified by preparation of SrAl₂O₄(0.1B₂O₃):Eu³⁺,
R³⁺ (Eu²⁺ and R³⁺ co-doped strontium aluminate) phosphors. These methods of preparation also specifically apply to Sr₃Al₂O₅:Eu²⁺-R³⁺ phosphors and the properties exhibited by SrAl₂O₃:Eu²⁺-R³⁺ phosphors generally exemplify those of Sr₃Al₂O₅:Eu²⁺-R³⁺ phosphors.

SrAl₂O₃:0.01Eu²⁺-0.02Pr³⁺ is prepared by the general method of Example 1 mixing the components in the following molar proportions:

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

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

FIG. 1 shows the spectrum of the after-glow of a sample of SrAl₂O₃:0.01Eu²⁺-0.02Pr³⁺ exposed to a 4 W UV lamp for two minutes. The phosphorescence exhibits a broad band peaking at about 488 nm with a bandwidth of about 65 nm (2640 cm⁻¹). The figure illustrates phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

FIG. 2 is a graph of decay of the after-glow of a sample of SrAl₂O₃:0.01Eu²⁺-0.02Pr³⁺ exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of the after-glow of a commercial blue phosphor CaSr₅S₂Bi after similar exposure is also shown (line b). The SrAl₂O₃(0.1B₂O₃)0.01Eu²⁺-0.02Pr³⁺ phosphor is about 10x brighter than the commercial blue phosphor and has a persistence time about 20 times longer. After 18 hours SrAl₂O₃(0.1B₂O₃)0.01 Eu²⁺-0.02Pr³⁺ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

FIG. 3 presents the excitation and emission spectra of SrAl₂O₃(0.1B₂O₃)0.01Eu²⁺-0.02Pr³⁺ where the excitation spectrum was monitored at 488 nm.

FIG. 4 is the x-ray diffraction pattern of the SrAl₂O₃(0.1B₂O₃)0.01Eu²⁺-0.02Pr³⁺ sample. This x-ray pattern indicated that the structure of SrAl₂O₃(0.1B₂O₃) is similar to Sr₃Al₂O₅(0.3B₂O₃).

Example 3
Preparation and Characterization of SrAl₃O₇(0.1B₂O₃):Eu²⁺-Pr³⁺, Phosphors with Varying Amounts of Eu²⁺

Eu-concentration dependence of SrAl₃O₇(0.1B₂O₃):Eu²⁺-Pr³⁺ phosphor after-glow was examined by preparing phosphor samples in which x (Eu₂O₃ molar concentration) was varied from 0.005 to 0.02.

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

\[(1-6x) \text{SrCO}_3 + 2.00 \text{Al}_2 \text{O}_3 + x \text{Eu}_2 \text{O}_3 + 2x \text{Pr}_2 \text{O}_3 + 0.1 \text{B}_2 \text{O}_3\]

where x was varied from 0.01 to 0.15 as indicated in Table 1. In each case samples were pressed into pellets before prefiring and before sintering.

Table 1 shows time persistence of after-glow of the phosphor as a function of Eu²⁺ content (x) with Pr³⁺ content held at 2x. Data in Table 1 indicate that the longest persistence is obtained with samples where x is 0.001-0.005, with y (Pr₂O₃ molar proportion) = 2x.

Example 4
Preparation and Characterization of SrAl₃O₇(0.1B₂O₃):Eu²⁺-Pr³⁺ Phosphors with Varying Amounts of Pr³⁺

Pr-concentration dependence of SrAl₃O₇(0.1B₂O₃):Eu²⁺-Pr³⁺ phosphor after-glow was examined by preparing phosphor samples in which y (Pr₂O₃ molar concentration) was varied from 0.005 to 0.02.

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

\[(0.99-2y) \text{SrCO}_3 + 2.00 \text{Al}_2 \text{O}_3 + 0.005 \text{Eu}_2 \text{O}_3 + 4x \text{Pr}_2 \text{O}_3 + 0.1 \text{B}_2 \text{O}_3\]

where y was varied from 0.005 to 0.02 with Eu²⁺ molar concentration held at 0.01 (2x) as indicated in Table 2.

Table 2 shows time persistence of after-glow of the phosphor as a function of Pr³⁺ content (y) with Eu²⁺ content held at 0.01. Data in Table 2 indicate that the intensity of the after glow is not sensitive to variations in Pr³⁺ in the range examined. However, it is generally preferred to employ lower concentration of Pr (y=x to 2x) because Pr³⁺ absorbs in the range of 450-480 nm due to transitions from the ground state 3H₄ to excited states 3P₅, 3P₄, 3P₃.

Table 1
<table>
<thead>
<tr>
<th>Samples</th>
<th>x = 0.001</th>
<th>10 min after-glow</th>
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<th>60 min after-glow</th>
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<tr>
<td>B-1</td>
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<td>B-2</td>
<td>98</td>
<td>33</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>B-3</td>
<td>98</td>
<td>31</td>
<td>15</td>
<td></td>
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Table 2
<table>
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<tr>
<th>Samples</th>
<th>y = 0.005</th>
<th>10 min after-glow</th>
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</thead>
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<tr>
<td>C-1</td>
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<td>C-4</td>
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<tr>
<td>C-5</td>
<td>92</td>
<td>29</td>
<td>16</td>
<td></td>
</tr>
</tbody>
</table>

Example 5
Preparation and Characterization of SrAl₃O₇(B₂O₃):Eu²⁺-Ho³⁺, Blue Phosphors

SrAl₃O₇(0.1B₂O₃):0.01Eu²⁺-0.02Ho³⁺ was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

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

where B₂O₃ serves as flux.

FIG. 5 shows the spectrum of the after-glow of a sample of SrAl₃O₇(0.1B₂O₃):0.01 Eu²⁺-0.02 Ho³⁺, exposed to a 4 W UV lamp for two minutes. The phosphorescence exhibits...
a broad band peaking at about 488 nm with a bandwidth of about 60 nm (2640 cm⁻¹). The figure illustrates phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

**FIG. 6** is a graph of decay of the after-glow of a sample of SrAl₂O₃·(1.1B₂O₃):0.01Eu²⁺:0.02Nd³⁺ exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of the after-glow of SrAl₂O₃·(1.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺ (line b) and a commercial blue phosphor CaSr₅S:Bi (c) after similar exposure are also shown. The SrAl₂O₃·(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺ phosphor shows similar brightness and persistence to that of SrAl₂O₃·(1.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺. After 20 hours SrAl₂O₃·(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 SrAl₂O₃·(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺ where the excitation spectrum was monitored at 488 nm.

**Example 6**

Preparation and Characterization of SrAl₂O₃·(B₂O₃) :Eu²⁺:Nd³⁺ Blue Phosphors

SrAl₂O₃·(0.1B₂O₃):0.01Eu²⁺:0.02Nd³⁺ was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

0.97 SrCO₃+2.00 Al₂O₃+0.005 Eu₂O₃+0.01 Nd₂O₃+0.1 B₂O₃

where B₂O₃ serves as flux.

**FIG. 8** shows the spectrum of the after-glow of a sample of SrAl₂O₃·(0.1B₂O₃):0.01Eu²⁺:0.02Nd³⁺ exposed to a 4 W UV lamp for two minutes. The phosphorescence exhibits a broad band peaking at about 488 nm with a bandwidth of about 60 nm (2640 cm⁻¹). The figure illustrates phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

**FIG. 9** is a graph of decay of the after-glow of a sample of SrAl₂O₃·(0.1B₂O₃):0.01 Eu²⁺:0.02 Nd³⁺ exposed to a 13 W fluorescent lamp for 10 minutes (a). For comparison, the decay characteristics of the after-glow of SrAl₂O₃·(0.1B₂O₃):0.01 Eu²⁺:0.02Pr³⁺ (b) and a commercial blue phosphor CaSr₅S:Bi (c) after similar exposure are also shown. The SrAl₂O₃·(0.1B₂O₃):0.01Eu²⁺:0.02Nd³⁺ phosphor shows similar brightness and persistence to that of SrAl₂O₃·(0.1B₂O₃):0.01 Eu²⁺:0.02Pr³⁺. After 20 hours SrAl₂O₃·(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 SrAl₂O₃·(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 SrAl₂O₃·(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.

SrAl₂O₃·(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 SrCO₃+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 SrAl₂O₃·(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 fluorescence lamp. Decay curves for R=La ( ), Ce ( ), Sm ( ), Gd ( ), Tb ( ), Dy ( ), Er ( ), Tm ( ), Yb ( ), and Lu ( ). The decay curve of the sample SrAl₂O₃·(0.1B₂O₃):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 co-doped with Nd. The sample co-doped with Dy exhibits much longer decay time (shallower slope) than the Nd co-doped phosphor. This indicates that Dy forms a much deeper trapping center than Nb, Ho or Pr.

The luminescence spectra from SrAl₂O₃·(0.1B₂O₃):0.01Eu₂⁺:0.02Nd³⁺ 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 SrAl₂O₃·(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 SrAl₂O₃·(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-2(y₁+y₂))MCO₃+mAl₂O₃+y₁Eu₂O₃+y₂Pr₂O₃+y₃R₂O₃+zB₂O₃

where y₁+y₂+y₃=1-2x-2y 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 SrCO₃+2.00 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 SrAl₂O₃·(0.1B₂O₃):0.01Eu₂⁺:0.01Pr₂⁺:0.01R⁺ samples measured at 488 nm relative to that of SrAl₂O₃·(0.1B₂O₃):0.01Eu₂⁺:0.02Pr³⁺ is given in Table 3. Some results are also shown in FIG. 12.

**FIG. 12** shows decay curves of the after-glow of SrAl₂O₃·(0.1B₂O₃):0.01Eu₂⁺:0.01Pr₂⁺: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 SrAl₂O₃·(0.1B₂O₃):0.01Eu²⁺:0.01Pr²⁺:0.01Y³⁺ where the excitation spectrum was monitored at 488 nm. Co-doping with Y³⁺ and Pr²⁺ increases the UV excitation
efficiency and improve the brightness by 50% compared to the analogous Pr\textsuperscript{3+}-doped phosphor.

### TABLE 3

<table>
<thead>
<tr>
<th>after (min)</th>
<th>Pr\textsuperscript{3+}</th>
<th>Y</th>
<th>La</th>
<th>Lu</th>
<th>Er</th>
<th>Bi</th>
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<td>32</td>
<td>16</td>
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<td>15</td>
<td>18</td>
</tr>
</tbody>
</table>

\textsuperscript{1}Data is referenced to that of the SrAl\textsubscript{2}O\textsubscript{4} (B,O\textsubscript{3}) : Eu\textsubscript{2}Pr phosphor.

### Example 9

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

This example demonstrates the influence of deep trapping centers formed by Dy\textsuperscript{3+} on the decay characteristics of MAl\textsubscript{2}O\textsubscript{4} (0.1B,O\textsubscript{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 general molar proportions:

\[ (1-2x-2y)MCO\textsubscript{3}+(n+2x+2y)BaCO\textsubscript{3}+mAl\textsubscript{2}O\textsubscript{3}+xEu\textsubscript{2}O\textsubscript{3}+yR\textsubscript{2}O\textsubscript{3}+zB\textsubscript{2}O\textsubscript{3} \]

where:
- \( n+2x+2y < 1 \) (there is some Sr present)
- \( y \) ranges from about 0.0001 to about 0.010 and preferably the value of \( y \) is within the range of 0.010 to 0.011
- \( z \) ranges from about 0.02 to about 0.1
- \( R^\text{3+} \) is a trivalent rare earth metal ion or Bi\textsuperscript{3+}.

### TABLE 4

<table>
<thead>
<tr>
<th>after (min)</th>
<th>SAO-EuPr\textsuperscript{3+}</th>
<th>SAO-EuPrDy</th>
<th>SAO-EuHoDy</th>
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</thead>
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<tr>
<td>10</td>
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<td>301</td>
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<td>60</td>
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<td>35</td>
</tr>
</tbody>
</table>

\textsuperscript{4}Data is referenced to that of SAO-EuPr.

### Example 10

Preparation and Characterization of mixed alkaline earth aluminate phosphors

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

\[ (1-n-2x-2y)SrCO\textsubscript{3}+nBaCO\textsubscript{3}+mAl\textsubscript{2}O\textsubscript{3}+xEu\textsubscript{2}O\textsubscript{3}+yR\textsubscript{2}O\textsubscript{3}+zB\textsubscript{2}O\textsubscript{3} \]

where:
- \( n+2x+2y < 1 \) (there is some Sr present)
- \( y \) ranges from about 0.0001 to about 0.010 and preferably the value of \( y \) is within the range of 0.010 to 0.011
- \( z \) ranges from about 0.02 to about 0.1
- \( R^\text{3+} \) is a trivalent rare earth metal ion or Bi\textsuperscript{3+}.

The mixed alkaline earth aluminate compound, (Sr\textsubscript{0.33}Ba\textsubscript{0.67})Al\textsubscript{2}O\textsubscript{4} : 0.01Eu : 0.02Pr was prepared following the general procedure of Example 1 combining the components in the following molar proportions:

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

These mixed alkaline earth aluminate phosphors have the general formula:

\[ \text{Sr}_{0.33}\text{Ba}_{0.67} \text{Al}_2\text{O}_4 : 0.01\text{Eu}, 0.02\text{Pr} \]

### 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:

\[ (1-n-2x-2y)SrCO\textsubscript{3}+nCaCO\textsubscript{3}+mAl\textsubscript{2}O\textsubscript{3}+xEu\textsubscript{2}O\textsubscript{3}+yR\textsubscript{2}O\textsubscript{3}+zB\textsubscript{2}O\textsubscript{3} \]

where:
- \( n+2x+2y < 1 \) (there is at least some Sr present)
- \( y \) ranges from about 0.0001 to about 0.010 and preferably the value of \( y \) is within the range of 0.010 to 0.011
- \( z \) ranges from about 0.02 to about 0.1
- \( R^\text{3+} \) is a trivalent rare earth metal ion or Bi\textsuperscript{3+}.

These phosphors have the generic formula:

\[ \text{Sr}_{0.485}\text{Ca}_{0.485}\text{Al}_2\text{O}_4 : 0.01\text{Eu}, 0.02\text{Pr} \]

where \( k=1-n=2x-2y \).
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\textsuperscript{3+} is a trivalent rare earth ion or Bi\textsuperscript{3+}.

These mixed alkaline earth aluminates have the formula:

\[ \text{Sr}, \text{Ba,Ca}, \text{O} \cdot \text{mA1,O} \cdot (z \text{B,O},) : 2 \text{xEu}, 2y \text{R}, 9 \]

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

Example 12

Codoping of Mg\textsuperscript{2+} or Zn\textsuperscript{2+} into MO \text{mAl,O} : Eu\textsuperscript{2+}, R\textsuperscript{3+} phosphors

In phosphor materials of this invention, Al\textsuperscript{3+}, in the alkaline earth aluminate can be replaced with divalent ions, such as Mg\textsuperscript{2+} or Zn\textsuperscript{2+}. Phosphor components are combined according to the molar proportions in the following general recipe:

\[ (1 - 2x - 2y)\text{MCO} + (n)\text{Al,O} + x\text{Eu,O} + y\text{R,O} + q\text{XO} + z\text{B,O} \]

where: \( 2x + 2y \) is less than 1;

q is less than m and preferably ranges from 0.002 to 0.2;

the ranges for x, y, m and z are as given in formula 1.

XO, in particular, can be MgO and/or ZnO. These phosphors will have the generic formula:

\[ \text{M,O} \cdot \text{mAl,O} \cdot r\text{NaZO} : 2x\text{Eu}, 2y\text{R}, 10 \]

where \( k = 1 - 2x - 2y \) and where the ranges for r, 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 \text{SrCO}, + 1.99 \text{Al,O} + 0.005 \text{Eu,O} + 0.005 \text{Dy,O} + 0.1 \text{B,O}.

Table 5 provides measurements of relative after-glow intensity at 488 nm of strontium aluminate (SrAl,O,) phosphors in which Mg\textsuperscript{2+} or Zn\textsuperscript{2+} replaces Sr\textsuperscript{3+}.

Example 13

Co-doping of Na\textsuperscript{+} or K\textsuperscript{+} into MO \text{mAl,O} : Eu\textsuperscript{2+}, R\textsuperscript{3+} phosphors

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

\[ (1 - 2x - 2y - 2z)\text{MCO} + (n)\text{Al,O} + x\text{Eu,O} + y\text{R,O} + r\text{CO}, + z\text{B,O} \]

where: \( 2x + 2y + 2z \) 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\text{CO}, in particular, can be Na\text{2CO}, and/or K\text{2CO},. These phosphors will have the generic formula:

\[ \text{M,O} \cdot \text{mAl,O} \cdot (n)\text{Na,O} : 2x\text{Eu}, 2y\text{R}, 11 \]

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

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

0.97 \text{SrCO}, + 2 \text{Al,O} + 0.005 \text{Eu,O} + 0.005 \text{Dy,O} + 0.005 \text{X,O} + 0.1 \text{B,O}.

where \( Z\text{CO}, \) can be Na\text{2CO}, or K\text{2CO},.

Table 6 provides measurements of relative after-glow intensity at 488 nm of strontium aluminate (SrAl,O,) phosphors in which Na\textsuperscript{+} or K\textsuperscript{+} replaces Sr\textsuperscript{3+}.

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\textsuperscript{2+} and doped with Pr\textsuperscript{3+} were prepared having different ratios of Al/Sr. Phosphor components were mixed according to the molar proportions:

\[ 0.98 \text{SrCO}, + 1.99 \text{Al,O} + 0.01 \text{ZO} + 0.005 \text{Eu,O} + 0.005 \text{Dy,O} + 0.1 \text{B,O} \]

where XO can be MgO or ZnO.

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 \text{Sr,Al,}O, exhibits somewhat brighter phosphorescence.

Example 15

Effect of variation of the amount of flux on phosphor properties

A series of strontium aluminate phosphors (SrAl,O,) activated with Eu\textsuperscript{2+} and doped with Pr\textsuperscript{3+} were prepared

\[ \text{Sr,Cr}, \text{Al,...} \]
using varying amounts of flux \((zB_2O_3)\). Phosphor components were mixed according to the molar proportions:

\[
0.98 \text{SrCO}_3+4\text{Al}_2\text{O}_3+0.005 \text{Eu}_2\text{O}_3+0.005 \text{Pr}_2\text{O}_3+2z\text{B}_2\text{O}_3
\]

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 \(\text{M}_x\text{Al}_y\text{O}_{z+1}\) (where \(\text{M}\) is \(\text{Sr}\) or a mixture of \(\text{Sr}\) with \(\text{Ba}\) and/or \(\text{Ca}\))

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:

- \(8x+8y\) is less than 4, \(x\) is preferably about 0.0001 to about 0.05 and more preferably is 0.001 to about 0.005;
- \(y\) ranges from about 0.0001 to about 0.01 and preferably the value of \(y\) the value of \(x\);
- \(z\) ranges from about 0.02 to about 0.1;
- \(\text{M}\) is \(\text{Sr}\) or a combination of \(\text{Sr}\) with \(\text{Ca}\) and/or \(\text{Ba}\); and
- \(\text{R}\) is a trivalent rare earth ion or \(\text{Bi}^{3+}\).

\(\text{B}_2\text{O}_3\) is used as a flux in the composition and is important for ensuring the formation of the phosphorescent phase.

**TABLE 8**

<table>
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<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>
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<td>15</td>
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<td>17</td>
<td>15</td>
<td>14</td>
</tr>
</tbody>
</table>

\(^1\) Data is referenced to that at \(z=0.10\).

Example 17

Single Crystal Blue Phosphors

Single crystals of the alkaline earth aluminate phosphors of this invention can be grown directly from a melt by well-known techniques. For example, the conventional Czochralski method (J. Czochralski (1918) Z. Phys. Chem. 92:219), the floating zone method (W. G. Pfann (1952) Trans. AIME 194:747) or the laser heated pedestal method (J. Czochralski (1918) Z. Phys. Chem. 55)

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 \(\text{H}_2\) N\(_2\) gas mixture (2%-5% by volume \(\text{H}_2\)) 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 \(<1\%\) \(\text{H}_2\), e.g., 99.99% \(\text{N}_2\)). Care must be taken to prevent re-oxidation of the europium ions from the 2+ state to the 3+ state and to prevent reduction to the monovalent state or metal at the melting temperature. Other metals present in the material should remain in their original valence state.


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

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

We claim:

1. A phosphor represented by the formula:

\[
\text{MO.} m\text{Al}_2\text{O}_3\text{Eu}^{2+},\text{Pr}^{3+}
\]

wherein \(m\) is a number ranging from about 1.6 to about 2.2, \(\text{M}\) is \(\text{Sr}\) or a combination of \(\text{Sr}\) with \(\text{Ba}\) or both, \(\text{R}^{3+}\) 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 \(\text{M}\), and \(\text{R}^{3+}\) is present at a level from about 0.02mol % to about 20 mol % of \(\text{M}\).

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

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

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

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

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

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 \(\text{R}^{3+}\) 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 \(\text{M}\) is \(\text{Sr}\).

10. A phosphor represented by the formula:

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

wherein \(m\) is a number ranging from about 1.6 to about 2.2, \(\text{M}\) is \(\text{Sr}\) or a combination of \(\text{Sr}\) with \(\text{Ca}, \text{Ba}\) or both, \(\text{R}^{3+}\) is...
a mixture of Y³⁺ with another trivalent metal ion, Eu²⁺ is present at a level from about 0.02 mol % to about 10 mol % of M, and R³⁺, is present at a level from about 0.02 mol % to about 20 mol % of M.

11. The phosphor of claim 10 wherein R³⁺ is a mixture of Y³⁺ with a trivalent metal ion selected from the group Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tm³⁺, Yb³⁺ and Bi³⁺.

12. A phosphor having the formula:

$$\text{Sr}, \text{Ba}, \text{Ca}, \text{O} \cdot \text{mA}_1 \text{O}_3: \text{Eu}^2+, \text{R}^3+$$

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

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

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

$$\text{MO} \cdot \text{mA}_1 \text{O}_3: \text{Eu}^2+, \text{R}^3+$$

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 a trivalent rare earth metal ion or a mixture thereof, Eu²⁺ is present at a level from about 0.02 mol % to about 10 mol % of M, and R³⁺ 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:

$$\text{MO} \cdot \text{mA}_1 \text{O}_3: \text{Eu}^2+, \text{R}^3+$$

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 a trivalent rare earth metal ion, Bi³⁺ or mixtures thereof, Eu²⁺ is present at a level from about 0.02 mol % to about 10 mol % of M, and R³⁺ is present at a level from about 0.02 mol % to about 20 mol % of M in which a portion of the Al³⁺ in the host is substituted by a divalent metal ion or in which a portion of the M²⁺ in the phosphor is substituted by a monovalent metal ion.

16. A phosphor of claim 15 wherein a portion of the Al³⁺ in the host is substituted by a divalent metal ion.

17. The phosphor of claim 16 wherein the divalent ion is Mg²⁺ or Zn²⁺ or a mixture thereof.

18. The phosphor of claim 16 in which M²⁺ in the phosphor is substituted by a monovalent metal ion.

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

20. The phosphor of claim 15 in which the amount of divalent metal ion substituted into the phosphor is equal to the amount of R³⁺ in the phosphor.

21. The phosphor of claim 15 in which the amount of divalent metal ion substituted into the phosphor ranges from about 0.02 mol % to about 20 mol %.

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

23. The phosphor of claim 22 wherein M is Sr, under an inert atmosphere.

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 R³⁺ is selected from the group Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tm³⁺, Yb³⁺ and Bi³⁺.

26. The phosphor of claim 15 wherein R³⁺ is a mixture of Pr³⁺, Ho³⁺, Dy³⁺, or Nd³⁺ or mixtures thereof.

27. The phosphor of claim 15 wherein R³⁺ is a mixture of Y³⁺ 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 B₂O₃.

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(2B2O3):Eu2+,R3+" and replace with -- MO.mAl2O3(2B2O3):Eu2+,R3+ --.

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

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 "M₀.mA₁₂O₃(zB₂O₅):2xEu²⁺,2yR³⁺" and replace with -- M₀.mA₁₂O₃(zB₂O₅):2xEu²⁺,2yR³⁺ --.

Column 8,
Line 1, delete "M₀.mA₁₂O₃(zB₂O₅):2xEu²⁺,2yR³⁺" and replace with -- M₀.mA₁₂O₃(zB₂O₅):2xEu²⁺,2yR³⁺ --.
Line 15, delete "M₀.(m-q)A₁₂O₃.qXO(zB₂O₅):2xEu²⁺,2yR³⁺" and replace with -- M₀.(m-q)A₁₂O₃.qXO(zB₂O₅):2xEu²⁺,2yR³⁺ --.
Line 31, delete "M₀.mA₁₂O₃.rZ₂(zB₂O₅):2xEu²⁺,2yR³⁺" and replace with -- M₀.mA₁₂O₃.rZ₂(zB₂O₅):2xEu²⁺,2yR³⁺ --.
Line 60, delete "M₀.mA₁₂O₃" and replace with -- M₀.mA₁₂O₃ --.

Column 9,
Line 10, delete "M₀.mA₁₂O₃(zB₂O₅):2xEu²⁺,2yR³⁺" and replace with -- M₀.mA₁₂O₃(zB₂O₅):2xEu²⁺,2yR³⁺ --.
Line 28, delete "M₀.mA₁₂O₃(zB₂O₅):2xEu²⁺,2yR³⁺" and replace with -- M₀.mA₁₂O₃(zB₂O₅):2xEu²⁺,2yR³⁺ --.
Line 50, delete "M₀.(m-q)A₁₂O₃.qXO(zB₂O₅):2xEu²⁺,2yR³⁺" and replace with -- M₀.(m-q)A₁₂O₃.qXO(zB₂O₅):2xEu²⁺,2yR³⁺ --.
Line 67, delete "M₀.mA₁₂O₃.rZ₂(zB₂O₅):2xEu²⁺,2yR³⁺" and replace with -- M₀.mA₁₂O₃.rZ₂(zB₂O₅):2xEu²⁺,2yR³⁺ --.

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 "SrBa₂C₆O₃.mAl₂O₃(zB₂O₅):2xEu²⁺,2yR³⁺" and replace with -- SrBa₂C₆O₃.mAl₂O₃(zB₂O₅):2xEu²⁺,2yR³⁺ --.
Line 45, delete "Bi²⁺" and replace with -- Bi³⁺ --.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 11,
Lines 6 and 16, delete "SrAl₄O₇·0.01Eu²⁺·0.02Pr³⁺" and replace with  
-- SrAl₄O₁₇·0.01Eu²⁺·0.02Pr³⁺ --.
Line 25, delete "SrAl₄O₇·0.01Eu²⁺·0.02Pr³⁺" and replace with  
-- SrAl₄O₁₇·0.01Eu²⁺·0.02Pr³⁺ --.
Lines 29, 32, 37 and 39-40, delete "SrAl₄O₇·0.01Eu²⁺·0.02Pr³⁺" and replace with  
-- SrAl₄O₁₇·0.01Eu²⁺·0.02Pr³⁺ --.
Line 46, delete "SrAl₄O₇·0.01Eu²⁺·0.02Pr³⁺" and replace with  
-- SrAl₄O₁₇·0.01Eu²⁺·0.02Pr³⁺ --.
Lines 50-51, delete "SrAl₄O₇·0.01Eu²⁺·0.02Pr³⁺" and replace with  
-- SrAl₄O₁₇·0.01Eu²⁺·0.02Pr³⁺ --.
Line 60, delete "0.001 to 0.015" and replace with  
-- 0.001 to 0.015 --.

Column 12,
Lines 17-18 and 21-22, delete "SrAl₄O₇·0.01Eu²⁺·0.02Pr³⁺" and replace with  
-- SrAl₄O₁₇·0.01Eu²⁺·0.02Pr³⁺ --.
Line 43, Table 2, delete "SrAl₄O₇·0.01Eu²⁺·0.02Pr³⁺" and replace with  
-- SrAl₄O₁₇·0.01Eu²⁺·0.02Pr³⁺ --.
Lines 55-56, delete "SrAl₄O₇·0.01Eu²⁺·0.02Pr³⁺" and replace with  
-- SrAl₄O₁₇·0.01Eu²⁺·0.02Pr³⁺ --.
Lines 58 and 66, delete "SrAl₄O₇·0.01Eu²⁺·0.02Pr³⁺" and replace with  
-- SrAl₄O₁₇·0.01Eu²⁺·0.02Pr³⁺ --.

Column 13,
Lines 8, 14, 17 and 22, delete "SrAl₄O₇·0.01Eu²⁺·0.02Ho³⁺" and replace with  
-- SrAl₄O₁₇·0.01Eu²⁺·0.02Ho³⁺ --.
Lines 29-30, delete "SrAl₄O₇·0.01Eu²⁺·0.02Ho³⁺" and replace with  
-- SrAl₄O₁₇·0.01Eu²⁺·0.02Ho³⁺ --.
Lines 33, 43, 53, 58, 61 and 66, delete "SrAl₄O₇·0.01Eu²⁺·0.02Ho³⁺" and replace with  
-- SrAl₄O₁₇·0.01Eu²⁺·0.02Ho³⁺ --.
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(0.1B2O3):0.01Eu2+,0.01Pr3+:0.01R3+" and replace with -- SrAl2O7(0.1B2O3):0.01Eu2+,0.01Pr3+,0.01R3+ --.
Line 38, delete "SrAl2O7(0.1B2O3):Eu2+,Pr3+" and replace with -- SrAl2O7(0.1B2O3):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 "((Sr0.33 Ba0.64)(0.1B2O3)Al2O7:0.01Eu:0.02Pr" and replace with -- (Sr0.33 Ba0.64)(0.1B2O3)Al2O7:0.01Eu,0.02Pr --.
Line 22, delete "Sr5Ba4O:mAl2O3(zB2O3):2xEu,2yR" and replace with -- Sr5Ba4O:mAl2O3(zB2O3):2xEu,2yR --.
Line 48, delete "Sr5Ca0.5O:mAl2O3(zB2O3):2xEu,2yR" and replace with -- Sr5Ca0.5O:mAl2O3(zB2O3):2xEu,2yR --.
Line 52, delete "((Sr0.485 Ca0.485)Al2O7:0.01Eu:0.02Pr" and replace with -- (Sr0.485 Ca0.485)Al2O7:0.01Eu,0.02Pr --.
Lines 58-59, delete "((Sr0.485 Ca0.485)(0.1B2O3)Al2O7:0.01Eu:0.02Pr" and replace with -- (Sr0.485 Ca0.485)(0.1B2O3)Al2O7:0.01Eu,0.02Pr --.

Column 17,
Line 7, delete "Sr5Ba4Ca0.5O:mAl2O3(zB2O3):2xEu,2yR" and replace with -- Sr5Ba4Ca0.5O: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.rNa2O:2xEu,2yR" and replace with -- M4O.mAl2O3.rNa2O:2xEu,2yR --.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

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

Column 21,
Line 3, delete "R³⁺, is present" and replace with -- R³⁺ is present --.
Line 11, delete "SrₓBaₚCaₚO.mAl₂O₃:2xEu²⁺,2yR³⁺ " and replace with
-- SrₓBaₚCaₚO.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