LONG-PERSISTENCE BLUE PHOSPHORS

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ABSTRACT

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

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

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

30 Claims, 16 Drawing Sheets
OTHER PUBLICATIONS


FIG. 1
FIG. 2

[Graph showing a and b lines on a log-log plot of intensity (a.u.) vs. delay time (minute)].
FIG. 3
FIG. 5
FIG. 6

Delay Time (minute)

Intensity (a.u.)

10^6

10^5

10^4

10^3

10^2

1

10

100

1000

a

b

c

FIG. 8
FIG. 9

Graph showing the relationship between delay time (in minutes) and intensity (in arbitrary units). Three lines are plotted: a, b, and c, each representing different scenarios or conditions. The y-axis is a logarithmic scale ranging from $10^2$ to $10^6$, and the x-axis is a logarithmic scale ranging from 1 to 1000 minutes. The figure illustrates how intensity decreases with increasing delay time.
FIG. 10
FIG. 11
FIG. 12
FIG. 13
FIG. 15

The diagram shows the intensity (a.u.) as a function of wavelength (nm) for different time periods: after 5 sec, after 20 sec, and after 60 sec. The peaks in the intensity are observed at specific wavelengths, indicating a change in the properties of the material over time.
FIG. 16
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LONG-PERSISTENCE BLUE PHOSPHORS
CROSS-REFERENCE TO RELATED APPLICATIONS

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

This invention was made at least in part with U.S. government funding through NASA grant NCCW-0088 and NCC5-252, ARO DAADH4-96-10416 and DOE DE-FG02-94ER57764. 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:S:Bi, have been used for many years. Recently a much brighter and longer existing 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. (F. C. Palilla, A. K. Levine and M. R. Tomkus (1968) J. Electrochem. Soc. 115:642)

Long lasting and more efficient phosphorescence has obtained in Eu2+ doped SrAl2O4 synthesized with excess alumina which results in formation of trapping centers associated with the Sr2+ vacancy (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 phosphor 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-xSrAl2O4, Where M is at least one metal selected from calcium, strontium, barium and, optionally, magnesium, and x is a number not equal to 0. The matrix comprises europian as an activator and a co-activator elicited from a rare earth metal, manganese, tin or bismuth.

SUMMARY OF THE INVENTION

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

\[ \text{M}_x \text{Sr}_1-x \text{Al}_{2-n} \text{O}_{4+n} : \text{Eu}^{2+}, \text{R}^{3+} \]

where M is Sr or a combination of Sr with Ca and/or Ba; R3+ is a trivalent rare earth metal ion or Bi3+, or mixtures of these trivalent metal ions; and m is a number ranging from about 1.6 to about 2.2

The phosphors of this invention indicating the presence of B2O3. The preferred phosphor formula of this invention according to the presence of B2O3 is:

\[ \text{MO}_x \text{Sr}_{1-x} \text{Al}_{2-n} \text{O}_{4+n} : \text{Eu}^{2+}, \text{R}^{3+} \]

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

The phosphors of this invention comprise an alkaline earth aluminate matrix activated with Eu2+ and doped with certain trivalent metal ions R3+. The phosphors are activated with about 0.02 mol % to about 10 mol % of Eu2+, activator and co-doped with about 0.02 mol % to about 20 mol % (preferably about 0.2 mol % to about 2 mol %) of at least one trivalent rare earth metal ion or Bi3+. The activator and dopant concentration are measured in terms of mol % relative to the alkaline earth metal element M.

Preferred phosphors of this invention are blue with a 450-520 nm phosphorescent band at about 488 nm. Phosphors of this invention have significantly improved brightness compared to sulfide phosphors, such as CaS:S:Bi. Phosphors of this invention can have persistence times up to about 18 hr.

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

Phosphors of this invention are activated with $\text{Eu}^{2+}$ and are codoped with a trivalent rare earth metal ion or $\text{Bi}^{3+}$. The phosphors may be codoped with a single ion or a combination of such ions selected from the group of rare earth metal ions: $\text{Pr}^{3+}, \text{Ho}^{3+}, \text{Nd}^{3+}, \text{Dy}^{3+}, \text{Er}^{3+}, \text{Lu}^{3+}, \text{Ce}^{3+}, \text{Y}^{3+}, \text{Sm}^{3+}, \text{Gd}^{3+}, \text{ Tb}^{3+}, \text{Tm}^{3+}$, and $\text{Yb}^{3+}$ and the Group VA metal ion $\text{Bi}^{3+}$. Preferred trivalent dopants are $\text{Pr}^{3+}, \text{Ho}^{3+}, \text{Dy}^{3+}$, and $\text{Nd}^{3+}$. Co-doping of $\text{Dy}^{3+}$ or $\text{Y}^{3+}$ with another trivalent metal ion results in phosphor of improved brightness, e.g. $\text{MAl}_{4}\text{O}_{7}:\text{Eu}^{2+}, \text{Pr}^{3+}$. 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 $\text{M}_{4}\text{Al}_{4}\text{O}_{12}$ and $m$=2, the host material being $\text{MAI}_{4}\text{O}_{7}$. More preferred are phosphors where $\text{M}=$Sr and $m=1.75$ or $m=2$.

Phosphors of this invention also include those in which $\text{Mg}^{2+}$ or $\text{Zn}^{2+}$, or a mixture of both, is substituted for $\text{Al}^{3+}$ in the matrix material and where $\text{M}^{2+}$, particularly $\text{Sr}^{2+}$, are replaced with an alkali metal (e.g., $\text{Na}^{+}$ or $\text{K}^{+}$) 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 pellet of $\text{SrAlO}_{2}(0.1\text{B}203):0.01\text{Eu}^{2+},0.02\text{Pr}^{3+}$ 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) $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3}):0.01\text{Eu}^{2+},0.02\text{Pr}^{3+}$ and (b) of commercial blue phosphor $\text{CaS}:\text{Bi}$ 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. 3** illustrates the excitation and emission spectra of $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3}):0.01\text{Eu}^{2+},0.02\text{Pr}^{3+}$ where excitation was measured at 488 nm.

**FIG. 4** is the X-ray diffraction pattern of a sample of $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3}):0.01\text{Eu}^{2+},0.02\text{Pr}^{3+}$ measured at varying time (5-60 sec) after exposure of the sample to a 4 W UV lamp for two minutes.

**FIG. 5** is a spectrum of the after-glow of a sample of $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3}):0.01\text{Eu}^{2+},0.02\text{Ho}^{3+}$ measured at varying times (5-60 sec) after exposure of the sample to a 4 W UV lamp for two minutes.

**FIG. 6** is a graph of decay of the after-glow of (a) $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3}):0.01\text{Eu}^{2+},0.02\text{Ho}^{3+}$; (b) $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3}):0.01\text{Eu}^{2+},0.02\text{Pr}^{3+}$ and (c) of commercial blue phosphor $\text{CaS}:\text{Bi}$ 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. 7** illustrates the excitation and emission spectra of $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3}):0.1\text{Eu}^{2+},0.02\text{Ho}^{3+}$ where excitation was measured at 488 nm.

**FIG. 8** is a spectrum of the after-glow of a sample of $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3}):0.01\text{Eu}^{2+},0.02\text{Nd}^{3+}$ measured at varying time (5-60 sec) 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) $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3}):0.01\text{Eu}^{2+},0.02\text{Nd}^{3+}$; (b) $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3}):0.01\text{Eu}^{2+},0.02\text{Pr}^{3+}$ and (c) of commercial blue phosphor $\text{CaS}:\text{Bi}$ after exposure of the phosphors to a 13 W fluorescent lamp for 10 minutes. The threshold of eye sensitivity is indicated by a horizontal dashed line.

**FIG. 10** illustrates the excitation and emission spectra of $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3}):0.01\text{Eu}^{2+},0.02\text{Nd}^{3+}$ where excitation was monitored at 488 nm.

**FIG. 11** is a graph of decay curves of the after-glow of $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3}):0.01\text{Eu}^{2+},0.02\text{R}^{3+}$ measured in the first 15 sec. after exposure to a 13 W fluorescence lamp (measured at 488 nm). Decay curves for $\text{R}=$La ( ), $\text{Ce} (\bullet)$, $\text{Sm} (\circ)$, $\text{Gd} (I)$, $\text{Tb} (\ast)$, $\text{Dy} (\bigtriangleup)$, $\text{Er} (\blacktriangle)$, $\text{Tm} (\bigtriangledown)$, $\text{Yb} (\times)$, and $\text{Lu} (\ast\ast)$ are shown. The decay curve of the sample $\text{SrAlO}_{2}:\text{Eu}$.Nd ( ) is also shown for comparison.

**FIG. 12** is a graph comparing after-glow decay curves for samples of $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3}):0.01\text{Eu}$, 0.01Pr co-doped with 0.01 Y ( ), Lu ( ) or $\text{Li} (\Delta)$.

**FIG. 13** illustrates the excitation and emission spectra monitored at 488 nm of $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3})$ activated with $\text{Eu}$ and codoped with $\text{Pr}$ and $\text{Y}$.

**FIG. 14** is a graph comparing after-glow decay curves of $\text{SrAlO}_{2}(0.1\text{B}_{2}0_{3})$ activated with $\text{Eu}$ and codoped with either (a) $\text{Pr}$ 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 $\text{Sr}_{0.6}\text{Ba}_{0.3}\text{AlO}_{2}:0.01\text{Eu}$, 0.02Pr after exposure to a 4 W UV lamp for 2 minutes as a function of time after illumination ( ), after 5 sec.; ( ), after 60 sec. (

**FIG. 16** illustrates the spectra of the after-glow of $\text{Sr}_{0.4}\text{Ca}_{0.6}\text{AlO}_{2}:0.01\text{Eu}$, 0.02Pr after exposure to a 4 W UV lamp for 2 minutes as a function of time after illumination ( ), after 5 sec.; ( ), after 20 sec. and ( , after 60 sec.).

**DETAILED DESCRIPTION OF THE INVENTION**

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

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. 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-
vated at room temperature, it will show persistent phosphorescence. Deeper trapping centers can be activated by heating or photostimulation. Therefore, a study of phosphorescence dynamics allows the characterization of these three important luminescence processes. Single crystal phosphors facilitate studies of phosphorescence dynamics.

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

Methods described herein allow the preparation of phosphorescent single crystals. Single crystals are readily distinguishable by appearance from polycrystalline materials and from grainy crystals. Polycrystals or grainy crystals are opaque and exhibit grain boundaries, because the grains are small (one the order of tens of micrometers). Large grainy crystals have the appearance of broken glass, the grains are not crystallographically oriented and as a result light traversing grainy crystals will be scattered and refracted limiting transparence. 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 MO₃mAlO₃ (where M is an alkaline earth or mixture of alkaline earths, e.g., Sr, Ca and/or Ba) with a certain range of ratios of Al/M defined by m. The activator employed in the phosphors of this invention is Eu³⁺. Hosts in which m=about 1.6 to about 2.2 provide the desired blue color and good phosphorescence brightness in combination with the Eu activator. Hosts where m=about 1.7 to about 2.0 are preferred, with those where m=1.75 or m=2.0 being more preferred. Hosts where M=Ca and m is either 1.75 (Sr₃Al₄O₁₂) or m is 2 (SrAl₄O₁₁) are preferred for use in blue phosphors of this invention.

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

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

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

Phosphors of this invention also include those in which a portion of 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 (M⁰⁺) 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 Se⁰⁺ by R⁰⁺.

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 H₂B₂O₄ sufficient to provide an equivalent molar amount of B (i.e., 2H₂B₂O₄ 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 aluminates. For example, when m=1.75 and M=Sr, the host material becomes Sr₃Al₄O₁₂, 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 Sr₃Al₂O₆, formed in the presence of flux is similar in structure to orthorhombic Sr₃Al₂O₆ (see FIG. 4). This material is monoclinic with space group C₂h. 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 to 2 h. The prefired material is again treated to form a fine homogeneous powder (e.g., milling, grinding, pulverizing) suitable for sintering. Preferably, the powder is pelleted before sintering. The powder or pellets are sintered at about 1300°C under a reducing atmosphere, e.g., H2/N2 having 2–5% by volume H2.

Sintered phosphor material can be used to grow single crystals or single crystal fibers. Any crystallization technique can be employed. The laser heated pedestal method is preferred. Sintered pellets are cut into bars to introduce 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 oxidation 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 only 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:

\[(1-2x-2y)MCO_{2n+1}Al_{2}O_{3}:2xEu^{2+},2yR^{3+}\]

and will have the general formula:

\[M_{2-x}O_{2n+1}Al_{2}O_{3}:2xEu^{2+},2yR^{3+}\]

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. \(R^{3+}\) is generally one or more trivalent metal ions, and is preferably a trivalent metal ion selected from the group: Pr3+, Nd3+, Tb3+, Eu3+, Gd3+, Tm3+, Yb3+, and Bi3+. Preferred trivalent co-dopants are Pr3+, Ho3+, Dy3+, Er3+, Lu3+, Ce3+, Y3+, Sm3+, Gd3+, Tb3+, Tm3+, and Yb3+.

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

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

\[M_{2-x}O_{2n+1}Al_{2}O_{3}:2xEu^{2+},2yR_{1}^{3+},2zR_{2}^{3+}\]

where \(k=1-2x-2y\), \(m\) is as defined above, \(y_{1}+y_{2}=y\), and \(R_{1}\) and \(R_{2}\) are two different trivalent metal ions. The number \(x\) can range from about 0.0001 to about 0.05 and is preferably about 0.001 to about 0.005, \(y\) can range from about 0.0001 to about 0.10 and the value of \(y\) is preferably equal to the value of \(x\) and \(z\) can range from about 0.02 to about 0.2.

Preferred phosphors contain about equal amounts of \(R_{1}\) and \(R_{2}\).

The phosphors of this invention 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:

\[M_{2-x}O_{2n+1}Al_{2}O_{3}:2xEu^{2+},2yR^{3+}\]

where \(k=1-2x-2y\), \(m\) is as defined above, \(x\) can range from about 0.0001 to about 0.05 and is preferably about 0.001 to about 0.005, \(y\) can range from about 0.0001 to about 0.10 and the value of \(y\) is preferably equal to the value of \(x\) and \(z\) can range from about 0.02 to about 0.2. \(Z_{2}O\) is an alkali metal oxide, preferably \(Na_{2}O\) or \(ZnO\) and \(q\) can range from about 0.0001 to about 0.20. The amount of divalent ion \((q)\) from \(Z_{2}O\) added to the matrix to replace \(Al^{3+}\) is preferably equal to the amount of \(M^{2+}\) doped into the matrix (i.e., the value of \(r\) preferably the value of \(x\)).

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:

\[M_{2-x}O_{2n+1}Al_{2}O_{3}:2xEu^{2+},2yR^{3+}\]

where \(k=1-2x-2y\), \(m\) is as defined above, \(x\) can range from about 0.0001 to about 0.05 and is preferably about 0.001 to about 0.005, \(y\) can range from about 0.0001 to about 0.10 and the value of \(y\) is preferably equal to the value of \(x\) and \(z\) can range from about 0.02 to about 0.2. \(Z_{2}O\) is an alkali metal oxide, preferably \(Na_{2}O\) or \(K_{2}O\) 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 the value of \(y\)). A slight excess over the desired or preferred amount of \(Z_{2}O\) 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: \(M_{2}O_{2n+1}Al_{2}O_{3}\), where \(M\) is an alkaline earth metal, and \(n\) 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 \(M_{2}O_{2n+1}Al_{2}O_{3}\), 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 \(Pr^{3+}\), \(Ho^{3+}\), \(Nd^{3+}\), \(Dy^{3+}\), \(Er^{3+}\), \(La^{3+}\), \(Lu^{3+}\), \(Ce^{3+}\), \(Y^{3+}\), \(Sm^{3+}\), \(Gd^{3+}\), \(Tb^{3+}\), \(Tm^{3+}\), and \(Yb^{3+}\).
A phosphorescent material as in paragraph A further comprising from about 2 mol % to about 20 mol %, relative to M, of B₂O₃ in said host and/or wherein B₂O₃ is present in the host in an amount ranging from about 8 mol % to about 15 mol %, relative to M.

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

B. A phosphorescent material having the formula:

\[ M₂O₃ \cdot mAl₂O₃ \cdot (B₂O₃) \cdot 2xEu²⁺ \cdot 2yR³⁺, \]

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 0.0001 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 0.005; M is Sr⁺⁺ or a mixture of Sr⁺⁺ with Ca⁺⁺, Ba⁺⁺ or both; R³⁺ is one or more of Pr⁺⁺, Ho⁺⁺, Dy⁺⁺, Er⁺⁺, La⁺⁺, Lu⁺⁺, Ce⁺⁺, Y⁺⁺, Sm⁺⁺, Gd⁺⁺, Tb⁺⁺, Tm⁺⁺, Yb⁺⁺, and Bi⁺⁺.

A phosphorescent material as defined in paragraph B wherein R³⁺ is Pr⁺⁺, Ho⁺⁺, Dy⁺⁺, or Nd⁺⁺ and/or wherein x ranges from about 0.0001 to about 0.005 and y=x. Preferred phosphorescent material of paragraph B are those in which m is equal to 1.75 or 2.

C. A phosphorescent material of having the formula:

\[ M₂O₃ \cdot mAl₂O₃ \cdot (B₂O₃) \cdot 2xEu²⁺ \cdot 2yR³⁺, \]

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 0.0001 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 0.005; M is Sr⁺⁺ or a mixture of Sr⁺⁺ with Ca⁺⁺, Ba⁺⁺ or both; R³⁺ and R₂⁺³ are different trivalent metal ions that are one or more of Pr⁺⁺, Ho⁺⁺, Nd⁺⁺, Dy⁺⁺, Er⁺⁺, La⁺⁺, Lu⁺⁺, Ce⁺⁺, Y⁺⁺, Sm⁺⁺, Gd⁺⁺, Tb⁺⁺, Tm⁺⁺, Yb⁺⁺, and Bi⁺⁺.

A phosphorescent material of paragraph C wherein R³⁺ and R₂⁺³ are one or more of Pr⁺⁺, Ho⁺⁺, Nd⁺⁺, Dy⁺⁺, Er⁺⁺, and Y⁺⁺. Preferred phosphorescent materials of paragraph C are those wherein R₁⁺³ is Pr⁺⁺, Ho⁺⁺, Dy⁺⁺, or Nd⁺⁺ and R₂⁺³ is Y⁺⁺.

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

D. A phosphorescent material having the formula:

\[ M₂O₃ \cdot (m-q)Al₂O₃ \cdot qXO₃(B₂O₃) \cdot 2xEu²⁺ \cdot 2yR³⁺, \]

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 0.0001 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 0.005; M is Sr⁺⁺ or a mixture of Sr⁺⁺ with Ca⁺⁺, Ba⁺⁺ or both; R³⁺ is one or more of Pr⁺⁺, Ho⁺⁺, Nd⁺⁺, Dy⁺⁺, Er⁺⁺, La⁺⁺, Lu⁺⁺, Ce⁺⁺, Y⁺⁺, Sm⁺⁺, Gd⁺⁺, Tb⁺⁺, Tm⁺⁺, Yb⁺⁺, and Bi⁺⁺; X is a divalent metal ion selected from Mg⁺⁺ or Zn⁺⁺; and q can range from about 0.0001 to about 0.030. A preferred phosphorescent material of paragraph D has q equal to 2y.

E. A phosphorescent material having the formula:

\[ M₂O₃ \cdot mAl₂O₃ \cdot (Z₇O₃(B₂O₃)) \cdot 2xEu²⁺ \cdot 2yR³⁺, \]

where k=1-2x-2y=2r; x ranges from about 0.0001 to about 0.05; y is a number ranging from about 0.0001 to about 0.10; z ranges from about 0.02 to about 0.2; Z is an alkali metal ion, particularly Na⁺ or K⁺ and r ranges from 0 to 0.20.

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

F. A phosphorescent material having the formula:

\[ S₂Ba₁₂Cu₆O₆ \cdot mAl₂O₃ \cdot (B₂O₃) \cdot 2xEu²⁺ \cdot 2yR³⁺, \]

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 is a number ranging from about 0.0001 to about 0.005; y is a number ranging from about 0.0001 to about 0.010; and R³⁺ is one or more of Pr⁺⁺, Ho⁺⁺, Nd⁺⁺, Dy⁺⁺, Er⁺⁺, La⁺⁺, Lu⁺⁺, Ce⁺⁺, Y⁺⁺, Sm⁺⁺, Gd⁺⁺, Tb⁺⁺, Tm⁺⁺, Yb⁺⁺, and Bi⁺⁺.

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 MAI₃O₃ (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:

\[(1-2x-2y)MCO₃+2.00 Al₂O₃+xEu₂+ₚ₊yRₚ₊zB₂O₃,\]

where:
2x+2y 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 ion or Bi⁺⁺.

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 H₃BO₃.

The mixture of components is milled or ground to form a homogenous 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 H₃N₂ gas flow containing about 2–5% H₂ (by volume) at a flow rate of about 0.1 liter per minute. The resulting material exhibits phosphor properties as described herein.

Example 2

Preparation and Characterization of SrAl₂O₄(B₂O₃) :Eu²⁺,Pr³⁺ Phosphors

The methods and phosphors of this invention are specifically exemplified by preparation of SrAl₂O₄(0.1B₂O₃):Eu²⁺,
Preparation and Characterization of SrAl\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{2+}:Pr\textsuperscript{3+} Phosphors with Varying Amounts of Pr\textsuperscript{3+}

**TABLE 1**

<table>
<thead>
<tr>
<th>Eu-Concentration dependence of the after-glow of the samples SrAl\textsubscript{2}O\textsubscript{3}:0.1B\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{2+}Eu\textsuperscript{2+}Pr\textsuperscript{3+}</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>x</td>
<td>10 min after-glow</td>
<td>30 min after-glow</td>
</tr>
<tr>
<td>B-1</td>
<td>0.001</td>
<td>100</td>
<td>31</td>
</tr>
<tr>
<td>B-2</td>
<td>0.003</td>
<td>106</td>
<td>33</td>
</tr>
<tr>
<td>B-3</td>
<td>0.005</td>
<td>98</td>
<td>31</td>
</tr>
<tr>
<td>B-4</td>
<td>0.007</td>
<td>90</td>
<td>17</td>
</tr>
<tr>
<td>B-5</td>
<td>0.010</td>
<td>50</td>
<td>14</td>
</tr>
<tr>
<td>B-6</td>
<td>0.015</td>
<td>30</td>
<td>9</td>
</tr>
</tbody>
</table>

**Example 4**

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

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

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

\((0.09-2y)\text{SrCO}_{3}+2\text{Al}_{2}O_{3}+0.005\text{Eu}_{2}O_{3}+y\text{Pr}_{2}O_{3}+0.1\text{B}_{2}O_{3}\)

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

Table 2 shows time persistence of after-glow of the phosphor as a function of Pr\textsuperscript{3+} content (y) with Eu\textsuperscript{2+} content held at 0.01. Data in Table 2 indicate that the intensity of the after-glow is not sensitive to variations in Pr\textsuperscript{3+} in the range examined. However, it is generally preferred to employ lower concentration of Pr (y=x to 2x) because Pr\textsuperscript{3+} absorbs in the range of 450–480 nm due to transitions from the ground state \(^{3}\text{H}_{4}\) to excited states \(^{3}\text{P}_{0}, ^{3}\text{P}_{1}, ^{3}\text{P}_{2}\).

**TABLE 2**

<table>
<thead>
<tr>
<th>Pr-concentration dependence of the after-glow of the samples SrAl\textsubscript{2}O\textsubscript{3} (0.1B\textsubscript{2}O\textsubscript{3})</th>
<th>10 min after-glow</th>
<th>30 min after-glow</th>
<th>60 min after-glow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-1</td>
<td>0.005</td>
<td>100</td>
<td>31</td>
</tr>
<tr>
<td>C-2</td>
<td>0.0075</td>
<td>95</td>
<td>28</td>
</tr>
<tr>
<td>C-3</td>
<td>0.010</td>
<td>105</td>
<td>34</td>
</tr>
<tr>
<td>C-4</td>
<td>0.015</td>
<td>91</td>
<td>28</td>
</tr>
<tr>
<td>C-5</td>
<td>0.02</td>
<td>92</td>
<td>29</td>
</tr>
</tbody>
</table>

**Example 5**

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

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

\((1-6x)\text{SrCO}_{3}+2.00\text{Al}_{2}O_{3}+x\text{Eu}_{2}O_{3}+2x\text{Pr}_{2}O_{3}+0.1\text{B}_{2}O_{3}\)

where x was varied from 0.01 to 0.15 as indicated in Table 2. In each case samples were pressed into pellets before prefiring and before sintering.

Table 2 shows time persistence of after-glow of the phosphor as a function of Eu\textsuperscript{2+} content (x) with Pr\textsuperscript{3+} content held at 2x. Data in Table 2 indicate that the longest persistence is obtained with samples where x is 0.001-0.005, with y (Pr\textsubscript{3+} molar proportion)=2x.

**TABLE 2**

<table>
<thead>
<tr>
<th>Eu-Concentration dependence of the after-glow of the samples SrAl\textsubscript{2}O\textsubscript{3} (B\textsubscript{2}O\textsubscript{3})</th>
<th>10 min after-glow</th>
<th>30 min after-glow</th>
<th>60 min after-glow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-1</td>
<td>0.005</td>
<td>100</td>
<td>31</td>
</tr>
<tr>
<td>C-2</td>
<td>0.0075</td>
<td>95</td>
<td>28</td>
</tr>
<tr>
<td>C-3</td>
<td>0.010</td>
<td>105</td>
<td>34</td>
</tr>
<tr>
<td>C-4</td>
<td>0.015</td>
<td>91</td>
<td>28</td>
</tr>
<tr>
<td>C-5</td>
<td>0.02</td>
<td>92</td>
<td>29</td>
</tr>
</tbody>
</table>
a broad band peaking at about 488 nm with a bandwidth of about 60 nm (2640 cm⁻¹). The figure shows phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

**Example 6**

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

SrAl₂O₄(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. 9 shows a graph of decay of the after-glow of a sample of SrAl₂O₄(0.1B₂O₃):0.01 Eu²⁺:0.02 Nd³⁺ exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of the after-glow of SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺ (line b) and a commercial blue phosphor CaSrS:Bi (c) after similar exposure are also shown. The SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺ phosphor shows similar brightness and persistence to that of SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺. After 20 hours SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺ intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

**Example 8**

Preparation and Characterization of SrAl₂O₄(B₂O₃):

0.01 Eu²⁺:0.01 Pr³⁺:0.01R³⁺ where R is La, Eu, Nd, and Pr. There is no notable spectral shift with R.

This example is intended to determine if co-doping of metal ions into a SrAl₂O₄(B₂O₃):Eu²⁺:Pr³⁺ phosphor increases UV excitation efficiency and improves phosphor brightness.

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

\[1-2x-2(y+z)]MCO₃+mAl₂O₃+xEu₂O₃+yPr₂O₃+Y₃R₂O₇+\]

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

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

0.97 SrCO₃+2.00 Al₂O₃+0.005 Eu₂O₃+0.005 Pr₂O₃+0.005 R₂O₇+0.1 B₂O₃

where R=La, Lu, Er, and Bi. The intensity of the after-glow of SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.01Pr³⁺:0.01R³⁺ samples measured at 488 nm relative to that of SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺ is given in Table 3. Some results are also shown in FIG. 12.

**Example 14**

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

SrAl₂O₄(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 R₂O₇+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 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 fluorescence lamp. Decay curves for R=La ( ), Ce ( ), Sm ( ), Gd ( ), Tb ( ), Dy ( ), Er ( ), Tm ( ), Yb ( ), and Lu ( ). The decay curve of the sample SrAl₂O₄(0.1B₂O₃):EuNd (closed circles) is also shown for comparison. It can be seen that the after-glow of these samples are generally less intense than analogous phosphor samples codoped with Nd. The sample codoped with Dy exhibits much longer decay time (shallower slope) than the Nd codoped phosphor. This indicates that Dy forms a much deeper trapping center than Nb, Ho or Pr.

The luminescence spectra from SrAl₂O₄(0.1B₂O₃):0.01Eu₂⁺:0.02R³⁺ where R is La, Er, Nd, and Pr have similar wavelength dependence to that of the phosphor where R is Pr. There is no notable spectral shift with R.
efficiency and improve the brightness by 50% compared to the analogous Pr<sup>3+</sup>-doped phosphor.

### TABLE 3

<table>
<thead>
<tr>
<th>after (min)</th>
<th>Pr&lt;sup&gt;4+&lt;/sup&gt;</th>
<th>Y&lt;sup&gt;3+&lt;/sup&gt;</th>
<th>Lu&lt;sup&gt;3+&lt;/sup&gt;</th>
<th>Lu&lt;sup&gt;3+&lt;/sup&gt;</th>
<th>Er&lt;sup&gt;3+&lt;/sup&gt;</th>
<th>Bi&lt;sup&gt;3+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>178</td>
<td>105</td>
<td>110</td>
<td>105</td>
<td>107</td>
</tr>
<tr>
<td>30</td>
<td>31</td>
<td>55</td>
<td>30</td>
<td>32</td>
<td>30</td>
<td>33</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
<td>32</td>
<td>16</td>
<td>17</td>
<td>15</td>
<td>18</td>
</tr>
</tbody>
</table>

1 Data is referenced to that of the SrAl<sub>4</sub>0<sub>3</sub>:Eu<sub>2</sub>Pr phosphor.

### Example 9

Preparation and Characterization of SrAl<sub>4</sub>0<sub>3</sub>(0.1B<sub>2</sub>O<sub>3</sub>):0.01Eu,0.01Dy,0.01Pr

This example demonstrates the influence of deep trapping centers formed by Dy<sup>3+</sup> on the decay characteristics of SrAl<sub>4</sub>O<sub>3</sub>(0.1B<sub>2</sub>O<sub>3</sub>):0.01Eu,0.01Dy and SrAl<sub>4</sub>O<sub>3</sub>(0.1B<sub>2</sub>O<sub>3</sub>):0.01Eu,0.01Dy,0.01Pr. Samples are generally prepared by the method of Example 1 combining the components in the following molar proportions:

0.97 SrCO<sub>3</sub> + 2.00 Al<sub>2</sub>O<sub>3</sub> + 0.005 Eu<sub>2</sub>O<sub>3</sub> + 0.01 Pr<sub>2</sub>O<sub>3</sub> + 0.1 B<sub>2</sub>O<sub>3</sub>

where R<sup>3+</sup> is a trivalent rare earth metal ion or Bi<sup>3+</sup>.

Table 4 provides measurements of relative after-glow intensity at 488 nm of SrAl<sub>4</sub>O<sub>3</sub>(0.1B<sub>2</sub>O<sub>3</sub>):0.01Eu,0.01Dy,0.01Pr relative to that of SrAl<sub>4</sub>O<sub>3</sub>(0.1B<sub>2</sub>O<sub>3</sub>):0.01Eu,0.01Pr. The measured samples with Dy<sup>3+</sup> and Pr<sup>3+</sup> exhibit enhanced brightness and persistence compared to the Pr<sup>3+</sup> doped or Ho<sup>3+</sup>, doped phosphors.

### TABLE 4

<table>
<thead>
<tr>
<th>after (min)</th>
<th>SAO-EuPr&lt;sup&gt;1&lt;/sup&gt;</th>
<th>SAO-EuPrDy</th>
<th>SAO-EuH&lt;sub&gt;2&lt;/sub&gt;PrDy</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>301</td>
<td>252</td>
</tr>
<tr>
<td>30</td>
<td>31</td>
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<td>75</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
<td>47</td>
<td>35</td>
</tr>
</tbody>
</table>

1 Data is referenced to that of SAO-EuPr.

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

### Example 10

Preparation and Characterization of mixed alkaline earth aluminate phosphors

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<sub>3</sub>−nBaCO<sub>3</sub>−2xAl<sub>2</sub>O<sub>3</sub>−2yEu<sub>2</sub>O<sub>3</sub>−yR<sub>2</sub>O<sub>3</sub>−zB<sub>2</sub>O<sub>3</sub>

where:

n+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; and

R<sup>3+</sup> is a trivalent rare earth ion or Bi<sup>3+</sup>.

The mixed alkaline earth aluminate compound, (Sr<sub>0.33</sub>Ba<sub>0.67</sub>Al)O<sub>3</sub>:0.01Eu,0.01Pr was prepared following the general procedure of Example 1 combining the components in the following molar proportions:

0.33 SrCO<sub>3</sub> + 0.67 BaCO<sub>3</sub> + 2.00 Al<sub>2</sub>O<sub>3</sub> + 0.005 Eu<sub>2</sub>O<sub>3</sub> + 0.01 Pr<sub>2</sub>O<sub>3</sub> + 0.1 B<sub>2</sub>O<sub>3</sub>

These mixed alkaline earth phosphors have the general formula:

Sr<sub>k</sub>Ba<sub>1−k</sub>O<sub>3</sub> Al<sub>1−p</sub>O<sub>3</sub>·mAl<sub>2</sub>O<sub>3</sub>−2xEu<sub>2</sub>Y<sub>2</sub>R<sub>2</sub>.

These phosphors have the generic formula:

Sr<sub>k</sub>Ca<sub>1−k</sub>O<sub>3</sub> Al<sub>1−p</sub>O<sub>3</sub>·mAl<sub>2</sub>O<sub>3</sub>−2xEu<sub>2</sub>Y<sub>2</sub>R<sub>2</sub>.

The mixed alkaline earth aluminate compound, (Sr<sub>0.33</sub>Ca<sub>0.67</sub>Al)O<sub>3</sub>:0.01Eu,0.01Pr were prepared as in Example 1 combining the components in the following molar proportions:

(1−n−2x−2y)SrCO<sub>3</sub>−nCaCO<sub>3</sub>−2xAl<sub>2</sub>O<sub>3</sub>−2yEu<sub>2</sub>O<sub>3</sub>−yR<sub>2</sub>O<sub>3</sub>−zB<sub>2</sub>O<sub>3</sub>

where:

n+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; and

R<sup>3+</sup> is a trivalent rare earth ion or Bi<sup>3+</sup>.

These phosphors have the generic formula:

Sr<sub>k</sub>Ca<sub>1−k</sub>O<sub>3</sub> Al<sub>1−p</sub>O<sub>3</sub>·mAl<sub>2</sub>O<sub>3</sub>−2xEu<sub>2</sub>Y<sub>2</sub>R<sub>2</sub>.

where k=1−p−2x−2y.

FIG. 15 shows the luminescence spectra of this phosphor. A small red shift of 27 nm was observed compared to the analogous Sr phosphor.
y ranges from about 0.0001 to about 0.010 and preferably the value of y, the value of x, z.

These mixed alkaline earth aluminates have the formula:

\[ \text{Sr}_x\text{Ba}_y\text{Ca}_z\text{O} \cdot \text{mAl}_2\text{O}_3(2\text{B}_2\text{O}_3)\cdot 2\text{Eu}_2\text{y}_2\text{R}_3 \]

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

Example 12
Codoping of Mg\(^{2+}\) or Zn\(^{2+}\) into \( \text{MO} \cdot \text{mAl}_2\text{O}_3\cdot \text{Eu}^{2+}\cdot \text{R}^{3+} \) 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:

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

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

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

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

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

\[ 0.97 \text{SrCO}_3 + 1.99 \text{Al}_2\text{O}_3 + 0.005 \text{Eu}_2\text{O}_3 + 0.005 \text{Dy}_2\text{O}_3 + 0.1 \text{B}_2\text{O}_3 \]

where \( \text{XO}_2 \) can be Na\(_2\text{O}_3 \) or K\(_2\text{O}_3 \).

Table 6 provides measurements of relative after-glow intensity at 488 nm of strontium aluminate (SrAl\(_2\text{O}_4\)) phosphors in which Na\(^{+}\) or K\(^{+}\) replaces Sr\(^{2+}\).

Example 13
Co-doping of Na\(^{+}\) or K\(^{+}\) into \( \text{MO} \cdot \text{mAl}_2\text{O}_3\cdot \text{Eu}^{2+}\cdot \text{R}^{3+} \) phosphors

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

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

where: \( 2x + 2y + 2r \) is less than 1;
using varying amounts of flux (zB2O3). Phosphor components were mixed according to the molar proportions:

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

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

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

where:

- \( 8x+8y \leq 4 \)
- \( x \) is preferably about 0.0001 to about 0.05
- \( y \) ranges from about 0.0001 to about 0.010 and preferably the value of \( y \) is less than 4
- \( z \) ranges from about 0.02 to about 0.1
- \( M \) is Sr or a combination of Sr with Ba and/or Ca
- \( R \) 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>
<thead>
<tr>
<th>TABLE 8</th>
<th>The influence of varying B2O3 in preparation of phosphors.</th>
</tr>
</thead>
<tbody>
<tr>
<td>After/min.</td>
<td>0.03</td>
</tr>
<tr>
<td>10</td>
<td>113</td>
</tr>
<tr>
<td>20</td>
<td>37</td>
</tr>
<tr>
<td>60</td>
<td>17</td>
</tr>
</tbody>
</table>

\(^{a}\) Data is referenced to that at \( n = 0.10 \).

Example 16

General Methods of Preparation of Blue Phosphors with Host Material \( \text{M}_2\text{Al}_2\text{O}_3 \) (where \( M \) is Sr or a mixture of Sr with Ba and/or Ca)

Phosphor components are mixed according to the molar proportions according to the preparative examples hereinabove and the mixtures are milled or ground to give a homogeneous fine powder. The powder is pressed into ceramic pellets at the same pressure. The pellets are then sintered at about 2,000°C for one hour in a flowing \( \text{He}-\text{N}_2 \) gas mixture (2%-5% by volume \( \text{He} \)) 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 \( \text{H}_2 \), 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:

\[ \text{MO}_m\text{Al}_2\text{O}_3:2x\text{Eu}^{2+},2y\text{R}^{3+} \]

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, \( \text{R}^{3+} \) 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 \( M \), and \( \text{R}^{3+} \) is present at a level from about 0.02mol % to about 20 mol % of \( M \).

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

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:

\[ \text{Sr}\text{Al}_2\text{O}_3:2x\text{Eu}^{2+},2y\text{R}^{3+} \]

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

6. The phosphor of claim 5 wherein \( \text{R}^{3+} \) 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 \( M \) is Sr.

10. A phosphor represented by the formula:

\[ \text{MO}_m\text{Al}_2\text{O}_3:2x\text{Eu}^{2+},2y\text{R}^{3+} \]

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, \( \text{R}^{3+} \) 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 \( M \), and \( \text{R}^{3+} \) is present at a level from about 0.02mol % to about 20 mol % of \( M \).

11. The phosphor of claim 10 wherein \( M \) is Sr, Ba or Ca.

12. The phosphor of claim 10 wherein \( m \) is 2.

13. The phosphor of claim 12 wherein \( x \) is 0.009.

14. The phosphor of claim 12 wherein \( y \) is 0.009.

15. The phosphor of claim 12 wherein \( x \) is 0.005 and \( y \) is 0.005.

16. A phosphor represented by the formula:

\[ \text{SrAl}_2\text{O}_3:2x\text{Eu}^{2+},2y\text{R}^{3+} \]

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

17. The phosphor of claim 16 wherein \( \text{R}^{3+} \) is present at a level from about 0.02 mol % to about 10 mol % of \( M \), and \( \text{R}^{3+} \) is present at a level from about 0.02mol % to about 20 mol % of \( M \).

18. The phosphor of claim 16 wherein \( \text{R}^{3+} \) is \( \text{Pr}^{3+}, \text{Ho}^{3+}, \text{Dy}^{3+}, \text{Nd}^{3+} \), or mixtures thereof.

19. The phosphor of claim 18 which is a single crystal.

20. The phosphor of claim 18 which has the formula:

\[ \text{SrAl}_2\text{O}_3:2x\text{Eu}^{2+},2y\text{R}^{3+} \]

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

21. The phosphor of claim 20 wherein \( m \) is 2.

22. The phosphor of claim 21 wherein \( m \) is 2.

23. The phosphor of claim 21 wherein \( m \) is 2.

24. The phosphor of claim 21 wherein \( m \) is 2.

25. The phosphor of claim 21 wherein \( m \) is 2.
a mixture of $Y^{3+}$ with another trivalent metal ion, $Eu^{2+}$ is present at a level from about 0.02 mol % to about 10 mol % of M, and $R^{3+}$ is present at a level from about 0.02 mol % to about 20 mol % of M.

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

12. A phosphor having the formula:

$$S_{n}Ba_{x}Ca_{y}O_{m}Al_{2}O_{3}:Eu^{2+},2yR^{3+}$$

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

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

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:

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

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 ion.

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

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

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

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

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

21. The phosphor of claim 15 in which a portion of the $M^{2+}$ in the phosphor is substituted by a divalent 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$^{3+}$, Lu$^{3+}$, Ce$^{3+}$, Y$^{3+}$, Sm$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, Tm$^{3+}$, Yb$^{3+}$ and Bi$^{3+}$.

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

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

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

29. The phosphor of claim 15 further comprising from about 2 mol % to about 20 mol % of $B_{2}O_{3}$.

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

Title page.
Item [57], ABSTRACT
Delete "M0.mA1203:E~2+,R3+" and replace with -- MO·mA12O3: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 "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.3A12O3:Eu2+" and replace with -- 2SrO.3A12O3:Eu2+ --.
Lines 25-26, delete "4SrO.7A12O3:Eu2+" and replace with -- 4SrO.7A12O3:Eu2+ --.
Line 26, delete "BaO.4Al2O3:Eu2+" and replace with -- BaO.4Al2O3:Eu2+ --.
Line 38, delete "MO·mA12O3:Eu2+,R3+" and replace with -- MO·mA12O3:Eu2+,R3+ --.
Line 47, delete "MO·mA12O3(zB2O3):Eu2+,R3+" and replace with -- MO·mA12O3(zB2O3):Eu2+,R3+ --.

Column 4.
Line 32, delete "Sr0.68Ba0.33A12O7" and replace with -- Sr0.33Ba0.68A12O7 --.
Line 36, delete "Sr0.49Ca0.49Al2O7" and replace with -- Sr0.49Ca0.49Al2O7 --.

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·mA12O3" and replace with -- MO·mA12O3 --.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 7,
Line 10, delete "pellets are the" and replace with -- pellets are then --.
Line 15, delete "laser heated pedestal method" and replace with -- laser heated pedestal growth (LHPG) method --.
Line 16, delete "bars to" and replace with -- bars for --.
Line 20, delete "somehat" and replace with -- somewhat --.
Line 28, delete "LHGP" and replace with -- LHPG --.
Line 42, delete "M_{0.3}Al_{2}O_{3}(z_{B_{2}O_{3}}):2xEu^{2+},2yR^{3+}" and replace with -- M_{0.3}Al_{2}O_{3}(z_{B_{2}O_{3}}):2xEu^{2+},2yR^{3+} --.

Column 8,
Line 1, delete "M_{0.3}Al_{2}O_{3}(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n" and replace with -- M_{0.3}Al_{2}O_{3}(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n --.
Line 15, delete "M_{0.3}(m-q)Al_{2}O_{3},qXO(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n" and replace with -- M_{0.3}(m-q)Al_{2}O_{3},qXO(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n --.
Line 31, delete "M_{0.3}Al_{2}O_{3},rZ_{2}(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n" and replace with -- M_{0.3}Al_{2}O_{3},rZ_{2}(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n --.
Line 60, delete "MO.mAl_{2}O_{3}" and replace with -- MO.mAl_{2}O_{3} --.

Column 9,
Line 10, delete "M_{0.3}Al_{2}O_{3}(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n" and replace with -- M_{0.3}Al_{2}O_{3}(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n --.
Line 28, delete "M_{0.3}Al_{2}O_{3}(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n" and replace with -- M_{0.3}Al_{2}O_{3}(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n --.
Line 50, delete "M_{0.3}(m-q)Al_{2}O_{3},qXO(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n" and replace with -- M_{0.3}(m-q)Al_{2}O_{3},qXO(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n --.
Line 67, delete "M_{0.3}Al_{2}O_{3},rZ_{2}(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n" and replace with -- M_{0.3}Al_{2}O_{3},rZ_{2}(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n --.

Column 10,
Line 2, delete "x ranges" and replace with -- x is a number ranging --.
Line 4, delete "z ranges" and replace with -- z is a number ranging --.
Line 4, after "about 0.2;" insert on a new line -- m is a number ranging from about 1.6 to about 2.2; --.
Line 5, start a new line after "K".
Line 7, after "E has" insert -- the value of --.
Line 11, delete "Sr_{2}Ba_{2}Ca_{2}O_{3}(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n" and replace with -- Sr_{2}Ba_{2}Ca_{2}O_{3}(z_{B_{2}O_{3}}):2xEu^{2+},2y_{R_{1}}^{2+},2y_{R_{2}}^{3+}n --.
Line 45, delete "Bi^{2+}" and replace with -- Bi^{3+} --.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 11,
Lines 6 and 16, delete "SrAl₂O₇:0.01Eu²⁺:0.02Pr³⁺" and replace with -- SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺,0.02Pr³⁺ --.
Line 25, delete "SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺" and replace with -- SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺,0.02Pr³⁺ --.
Lines 29, 32, 37 and 39-40, delete "SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺" and replace with -- SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺,0.02Pr³⁺ --.
Line 46, delete "SrAl₂O₇(B₂O₃):Eu²⁺:Pr³⁺" and replace with -- SrAl₂O₇(B₂O₃):Eu²⁺,Pr³⁺ --.
Lines 50-51, delete "SrAl₂O₇(0.1B₂O₃):Eu²⁺:Pr³⁺" and replace with -- SrAl₂O₇(0.1B₂O₃):Eu²⁺,Pr³⁺ --.
Line 60, delete "0.01 to 0.15" and replace with -- 0.001 to 0.015 --.

Column 12,
Lines 17-18 and 21-22, delete "SrAl₂O₇(0.1B₂O₃):Eu²⁺:Pr³⁺" and replace with -- SrAl₂O₇(0.1B₂O₃):Eu²⁺,Pr³⁺ --.
Line 43, Table 2, delete "SrAl₂O₇(B₂O₃):0.01Eu:2yPr" and replace with -- SrAl₂O₇(B₂O₃):0.01Eu,2yPr --.
Lines 55-56, delete "SrAl₂O₇(B₂O₃):Eu²⁺:Ho³⁺" and replace with -- SrAl₂O₇(B₂O₃):Eu²⁺,Ho³⁺ --.
Lines 58 and 66, delete "SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺" and replace with -- SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺,0.02Ho³⁺ --.

Column 13,
Lines 8, 14, 17 and 22, delete "SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺" and replace with -- SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺,0.02Ho³⁺ --.
Lines 29-30, delete "SrAl₂O₇(B₂O₃):Eu²⁺:Nd³⁺" and replace with -- SrAl₂O₇(B₂O₃):Eu²⁺,Nd³⁺ --.
Lines 33, 43, 53, 58, 61 and 66, delete "SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺:0.02Nd³⁺" and replace with -- SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺,0.02Nd³⁺ --.
Line 54, delete "line (a)" and replace with -- (line a) --.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

**Column 14.**
Lines 7 and 15, delete "SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.02R³⁺" and replace with -- SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺,0.02R³⁺ --.
Line 19, after "(++)" please insert -- are shown --.
Lines 34-35, delete "SrAl₂O₇(B₂O₃):0.01Eu²⁺:0.01Pr³⁺:0.01R³⁺" and replace with -- SrAl₂O₇(B₂O₃):0.01Eu²⁺,0.01Pr³⁺,0.01R³⁺ --.
Line 38, delete "SrAl₂O₇(B₂O₃):Eu²⁺:Pr³⁺" and replace with -- SrAl₂O₇(B₂O₃):Eu²⁺,Pr³⁺ --.
Line 48, delete "ranges of in" and replace with -- ranges of m --.
Lines 56 and 60-61, delete "SrAl₂O₇(0.1B₂O₃):0.01Eu:0.01Pr:0.01R" and replace with -- SrAl₂O₇(0.1B₂O₃):0.01Eu,0.01Pr,0.01R --.

**Column 16.**
Line 13, delete "(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 "SrBaₙOₙmA1₂O₃ₙ(zB₂O₃):2xEu,2yR" and replace with -- SrBaₙOₙmA1₂O₃ₙ(zB₂O₃):2xEu,2yR --.
Line 48, delete "SrₙCaₙOₙmA1₂O₃ₙ(zB₂O₃):2xEu,2yR" and replace with -- SrₙCaₙOₙmA1₂O₃ₙ(zB₂O₃):2xEu,2yR --.
Line 52, delete "(Sr₀.₄₈₅Ca₀.₄₇₅)Al₂O₇:0.01Eu:0.02Pr" and replace with -- (Sr₀.₄₈₅Ca₀.₄₇₅)Al₂O₇:0.01Eu,0.02Pr --.
Lines 58-59, delete "(Sr₀.₄₈₅Ca₀.₄₇₅)(0.1B₂O₃)Al₂O₇:0.01Eu:0.02Pr" and replace with -- (Sr₀.₄₈₅Ca₀.₄₇₅)(0.1B₂O₃)Al₂O₇:0.01Eu,0.02Pr --.

**Column 17.**
Line 7, delete "SrₙBaₙCaₙOₙmA1₂O₃ₙ(zB₂O₃):2xEu,2yR" and replace with -- SrₙBaₙCaₙOₙmA1₂O₃ₙ(zB₂O₃):2xEu,2yR --.
Lines 13-14 and 57-58, delete "MO.mAl₂O₃:Eu²⁺,R³⁺" and replace -- MO.mAl₂O₃:Eu²⁺,R³⁺ --.
Line 29, delete "MₙO.(m-q)Al₂O₃,qXO:2xEu,2yR" and replace with -- MₙO.(m-q)Al₂O₃,qXO:2xEu,2yR --.

**Column 18.**
Line 6, delete "MₙO.mAl₂O₃,rNaₙO:2xEu,2yR" and replace with -- MₙO.mAl₂O₃+rNaₙO: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 "SrₓBaᵧCaₜ O.mAl₂O₃:2xEu²⁺,2yR²⁺ " and replace with -- SrₓBaᵧCaₜ O.mAl₂O₃:2xEu²⁺,2yR²⁺ --.
Line 15, delete "v" and replace with -- y --.
Lines 22 and 37, delete "MO.mAl₂O₃:Eu²⁺,R³⁺" and replace with -- MO.mAl₂O₃:Eu²⁺,R³⁺ --.

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

Signed and Sealed this
Fifteenth Day of April, 2003

[Signature]

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