Long-persistence blue phosphors

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Phosphors of the invention are represented by the general formula:

$$MO_nAl_2O_3:Eu^{2+},R^{3+}$$

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

30 Claims, 16 Drawing Sheets
OTHER PUBLICATIONS


FIG. 1
FIG. 2

Graph showing the relationship between intensity (a.u.) and delay time (minute). Two lines, labeled 'a' and 'b', are plotted on a logarithmic scale.
FIG. 3
FIG. 5
FIG. 6
FIG. 8
FIG. 9

Delay Time (minute)

Intensity (a.u.)

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

1 10 100 1000
FIG. 10
FIG. 11
FIG. 12
FIG. 13
FIG. 14

![Graph showing intensity vs. delay time with three lines labeled a, b, and c. The x-axis represents delay time in minutes, ranging from 1 to 1000, and the y-axis represents intensity in arbitrary units (a.u.), with logarithmic scaling from $10^2$ to $10^6$. Each line represents a different intensity level, with line c being the lowest and line a being the highest.]
FIG. 15

The diagram shows the intensity (a.u.) as a function of wavelength (nm) for different time intervals: after 5 seconds, after 20 seconds, and after 60 seconds.
LONG-PERSISTENCE BLUE PHOSPHORS

FIELD OF THE INVENTION

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

BACKGROUND OF THE INVENTION

Persistent phosphorescing materials, such as ZnS:Cu,Zn, ZnCdS:Cu and CaS:Sb:Bi, have been used for many years. Recently a much brighter and longer lasting green phosphor, SrAl$_2$O$_4$:Eu$^{2+}$:Dy$^{3+}$, has been produced.

Strong green luminescence from Eu$^{2+}$-doped SrAl$_2$O$_4$ was reported by H. Lange in Belgian patent 1,347,45 and U.S. Pat. No. 3,294,696. Efficient luminescence in the spectral range 450–520 nm was also reported from Eu$^{2+}$-doped CaAl$_2$O$_4$, MgAl$_2$O$_4$, BaAl$_2$O$_4$, and SrAl$_2$O$_4$ and their counterparts using alkaline earth cationic combinations. (C. Palilla, A. K. Levine and M. R. Tomkus (1968) J. Electrochem. Soc. 115:642).

Long lasting and more efficient phosphorescence has obtained in Eu$^{2+}$ doped SrAl$_2$O$_4$ synthesized with excess alumina which results in formation of trapping centers associated with the Sr$^{2+}$ 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 SrAl$_2$O$_4$:Eu$^{2+}$-Dy$^{3+}$ was improved by co-doping various trivalent rare earth ions to produce appropriate trapping centers. The best result was obtained by co-doping Dy$^{3+}$ with Eu$^{2+}$ into SrAl$_2$O$_4$ and Nd$^{3+}$ with Eu$^{2+}$ into CaAl$_2$O$_4$ to get long persistent green and purple emission, respectively. U.S. Pat. No. 5,424,006 also reports phosphors in which Mg$^{2+}$ is substituted for Sr$^{2+}$ in SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$.

EP published application 765,925 (Moriyama et al.) reports Eu$^{2+}$-activated strontium aluminate phosphors in which part of the Sr$^{2+}$ of the host is replaced with Pb$^{2+}$, Dy$^{3+}$ or Zn$^{2+}$. The zinc-doped materials are reported to display enhanced brightness and persistence compared to SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$.

EP published application 710,709 (Murayama et al.) reports phosphors of matrix M$_1$-xSrAl$_2$O$_4$, Where M is at least one metal selected from calcium, strontium, barium and, optionally, magnesium, and x is a number not equal to 0. The matrix comprises europium as an activator and a co-activator elected from a rare earth metal, manganese, tin or bismuth.

SUMMARY OF THE INVENTION

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

\[ \text{MO} \cdot m\text{Al}_x\text{O}_{y},\text{Eu}^{2+},\text{R}^{3+} \]

where M is Sr or a combination of Sr with Ca and/or Ba; R$^{3+}$ is a trivalent rare earth metal ion or Bi$^{3+}$, or mixtures of these trivalent metal ions; and m is a number ranging from about 1.6 to about 2.2. The phosphors are prepared using a flux, particularly B$_2$O$_3$. The preferred phosphor formula of this invention indicating the presence of B$_2$O$_3$ flux is:

\[ \text{MO} \cdot m\text{Al}_x\text{O}_{y}(2\text{B}_2\text{O}_3):\text{Eu}^{2+},\text{R}^{3+} \]

where M, m and R$^{3+}$ 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 Eu$^{2+}$ and doped with certain trivalent metal ions R$^{3+}$. The phosphors are activated with about 0.02 mol % to about 10 mol % preferably about 0.2 mol % to about 1.0 mol % of Eu$^{2+}$ 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 Bi$^{3+}$.

Preferred phosphors of this invention are blue with a phosphorescent band at about 488 nm. The phosphors of this invention have significantly improved brightness compared to sulfdide phosphors, such as CaSrS:Bi. Phosphors of this invention can have persistence times up to about 18 hr.

The phosphors of this invention are chemically stable, resistant to moisture and UV radiation and are believed to be relatively harmless to the environment.
Phosphors in ceramic form can be used for manufacture of 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\(^{3+}\), Ce\(^{3+}\), Y\(^{3+}\), Sm\(^{3+}\), Gd\(^{3+}\), Tb\(^{3+}\), Tm\(^{3+}\), and Yb\(^{3+}\) and the Group VA metal ions 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. MAI\(_4\)O\(_7\)Eu\(^{2+}\), Pr\(^{3+}\), Dy\(^{3+}\) or MAI\(_4\)O\(_7\)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 MAI\(_4\)O\(_7\) and m=2, the host material being MAI\(_4\)O\(_7\). More preferred are phosphors where M=Sr and m=1.75 or m=2. Sm\(^{3+}\), Gd\(^{3+}\), N\(^{3+}\), Tm\(^{3+}\), and the Group VA metal sensitivity is indicated by a horizontal dashed line. Chen, R and McKeever, W. M. (eds.), CRC Press, Inc., Boca Raton, N.Y., 1998.

Phosphors of this invention can also include those in which Mg\(^{2+}\) or Zn\(^{2+}\), or a mixture of both, is substituted for MAI\(_4\)O\(_7\). The threshold of eye sensitivity is indicated by a horizontal dashed line. 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 compared with 0.01 Y, Lu(V) or Lu(A).

FIG. 1 is a spectrum of the after-glow of SrAl\(_2\)O\(_4\):(0.1B\(_2\)O\(_3\)):0.01Eu\(^{2+}\),0.02Pr\(^{3+}\) measured in 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.


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-

**BRIEF DESCRIPTION OF THE FIGURES**

FIG. 1 is a spectrum of the after-glow of a pellet sample of SrAl\(_2\)O\(_4\):(0.1B\(_2\)O\(_3\)):0.01Eu\(^{2+}\),0.02Pr\(^{3+}\) 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) SrAl\(_2\)O\(_4\):(0.1B\(_2\)O\(_3\)):0.01 Eu\(^{2+}\),0.02Nd\(^{3+}\); (b) SrAl\(_2\)O\(_4\):(0.1B\(_2\)O\(_3\)):0.01Eu\(^{2+}\),0.02Pr\(^{3+}\) and (c) of commercial blue phosphor CaS:S: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 SrAl\(_2\)O\(_4\):(0.1B\(_2\)O\(_3\)):0.01Eu\(^{2+}\),0.02Nd\(^{3+}\) where excitation was monitored at 488 nm.

FIG. 11 is a graph of decay curves of the after-glow of SrAl\(_2\)O\(_4\):(0.1B\(_2\)O\(_3\)):0.01Eu\(^{2+}\),0.02R\(^{3+}\) measured in the first 15 sec. after exposure to a 13 W fluorescent lamp (measured at 488 nm). Decay curves for R=La (\(\bigcirc\)), Ce (\(\bigcirc\)), Sm (\(\bigcirc\)), Gd (\(\bigcirc\)), Tb (\(\bigcirc\)), Dy (\(\bigcirc\)), Er (\(\bigcirc\)), Tm (\(\bigcirc\)), Yb (\(\bigcirc\)), and Lu (\(\bigcirc\)) are shown. The decay curve of the sample SrAl\(_2\)O\(_4\):Eu,Nd (\(\bigcirc\)) is also shown for comparison.

FIG. 12 is a graph comparing after-glow decay curves for samples of SrAl\(_2\)O\(_4\):(0.1B\(_2\)O\(_3\)):0.01Eu, 0.01Pr co-doped with 0.01 Y (\(\bigcirc\)), Lu(\(\bigcirc\)) or Lu(\(\bigcirc\)).

FIG. 13 illustrates the excitation and emission spectra monitored at 488 nm of SrAl\(_2\)O\(_4\):(0.1B\(_2\)O\(_3\)) activated with Eu and codoped with Pr and Y.

FIG. 14 is a graph comparing after-glow decay curves of SrAl\(_2\)O\(_4\):(0.1B\(_2\)O\(_3\)) activated with Eu and codoped with either (a) Pr and Dy, (b) Ho and Dy or (c) doped only with Pr. The threshold of eye sensitivity is indicated by a horizontal dashed line.

FIG. 15 illustrates the spectra of the after-glow of Sr\(_{0.65}\)Ba\(_{0.35}\)Al\(_2\)O\(_4\):0.01Eu, 0.02Pr after exposure to a 4 W UV lamp for 2 minutes as a function of time after illumination (\(\bigcirc\)), after 5 sec.; \(\ast\), after 20 sec. and \(\Delta\), after 60 sec.).

FIG. 16 illustrates the spectra of the after-glow of Sr\(_{0.45}\)Ca\(_{0.46}\)Al\(_2\)O\(_4\):0.01Eu, 0.02Pr after exposure to a 4 W UV lamp for 2 minutes as a function of time after illumination (\(\bigcirc\)), after 5 sec.; \(\ast\), after 20 sec. and \(\Delta\), 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.
activated at room temperature, it will show persistent phosphorescence. Deeper trapping centers can be activated by heating or photostimulation. Therefore, a study of phosphorescence dynamics allows the characterization of these three important luminescence processes. Single crystal phosphors facilitate studies of phosphorescence dynamics.

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

Methods described herein allow the preparation of phosphorescent single crystals. Single crystals are readily distinguishable by appearance from polycrystalline materials and from grained crystals. Polycrystals or grained crystals are opaque and exhibit grain boundaries, because the grains are small (one the order of tens of micrometers). Large grained crystals have the appearance of broken glass, the grains are not crystallographically oriented and as a result light traversing grained crystals will be scattered and refracted limiting transparency. In contrast, single crystals are clear and transparent without grain boundaries.

Phosphor materials of this invention can exhibit enhanced phosphorescence intensity and/or long persistence of phosphorescence. Preferred phosphors of this invention have intensity enhanced (as measured in a similar measurement system) compared to a standard commercial sample of ZnS phosphor. Persistence of phosphorescence is measured herein as persistence time, which is the time after discontinuing irradiation that it takes for phosphorescence of a sample to decrease to the threshold of eye sensitivity. This threshold is the signal level of emission intensity that a naked (i.e., unaided) eye can clearly see in the dark. Persistence times are assessed by following phosphorescence intensity as a function of time. Clearly measurement comparisons of persistence times must be performed under identical conditions using the same detection systems. The term “persistent phosphors” has been applied to materials exhibiting phosphorescence lasting form minutes to hours. The term “long-persistent phosphor” historically has been used to refer to ZnS-Cu, CaS-Eu, Tm and similar materials 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 MO₄mAl₉O₁₈ (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 (SrAl₉O₁₈) or m is 2 (Sr₂Al₅O₁₄) 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 (M⁺⁰) 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 H₂B₂O₃ sufficient to provide an equivalent molar amount of B (i.e., 2H₂B₂O₃ 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 Sr₃Al₉O₁₈ with an orthorhombic structure with space group Pmmm 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 Sr₃Al₉O₁₈ formed in the presence of flux is similar in structure to orthorhombic Sr₃Al₉O₁₈ (see FIG. 4). This material is monoclinic with space group C₂h₅ and c when synthesized without flux (e.g., B₂O₃).

The phosphors of this invention can be made by the following general method. Phosphor components are com-
bined as indicated in stoichiometric formulas (with or without a flux). The mixture is treated to form a homogeneous fine powder, for example by milling or grinding. The powder is preferably pressed into pellets. The powder or pellets are prefired at temperatures between about 600 to 800°C. (dependent upon the phase transitions of the material) in air for about 1–2 hrs. The prefired material is again treated to form a fine homogeneous powder (e.g., milling, grinding, pulverizing) suitable for sintering. Preferably, the powder is pelleted 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 ceramic bar can be used as a “seed” to stimulate spontaneous nucleation in the LHPG process. It was observed that the initial part of the fiber prepared by the LHPG process was a twinned crystal. The fiber eventually becomes one single crystal after a transition stage, but the crystal is not oriented. Fiber lengths of single crystals grown are variable, but can be as long as several centimeters in length. Single crystals with an average diameter of about 0.8 mm can be grown.

The basic phosphors of this invention are most generally prepared by admixing the components in the following molar proportions:

\[(1-2x-2y)M₂O₃+nxAl₂O₃×Eu⁺2+yR₃⁺2yR₃⁺\]

and will have the general formula:

\[M₅O₆·mAl₂O₃·(xB₂O₃)·2xEu⁺2+yR₃⁺·2yR₃⁺\]

where \(k=1-2x-2y\), \(m\) is a number ranging from about 1.6 to about 2.2, \(x\) can range from about 0.0001 to about 0.05 and is preferably about 0.001 to about 0.005, \(y\) can range from about 0.00001 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.

The preferred phosphors contain about equal amounts of \(R₁\) and \(R₂\), where \(R₁\) is as defined above, \(y₁+y₂=y\), and \(R₁\) and \(R₂\) are two different trivalent metal ions. The number \(x\) can range from about 0.0001 to about 0.05 and is preferably about 0.001 to about 0.005, \(y\) can range from about 0.00001 to about 0.10 and the value of \(y\) is preferably equal to the value of \(x\) and \(z\) can range from about 0.02 to about 0.2. Preferred phosphors contain about equal amounts of \(R₁\) and \(R₂\).

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

\[M₅O₆·mAl₂O₃·qXO(zB₂O₃)·2xEu⁺2+yR₃⁺\]

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 0.00001 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. These phosphors contain about equal amounts of \(R₁\) and \(R₂\).

The phosphors of this invention include those in which \(M²⁺\) in the host is substituted by a monovalent alkali metal ion, particularly Na⁺ or K⁺. These phosphors have the general formula:

\[M₅O₆·(m-q)Al₂O₃·qXO(zB₂O₃)·2xEu⁺2+yR₃⁺\]

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 0.00001 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. These phosphors contain about equal amounts of \(R₁\) and \(R₂\).

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 remilled or ground into a fine powder for sintering. The powder is optionally pressed before sintering. The material is sintered at about 1300°C for one hour in a reducing atmosphere, e.g., H₂/N₂ containing from about 0.01 mol % to about 5 mol %, relative to M, of an activator, and containing from about 0.01 mol % to about 5 mol %, relative to M, of a trivalent metal ion dopant selected from the group of trivalent ions Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tm³⁺, and Yb³⁺ and Bi³⁺.
A phosphorescent material as in paragraph A further comprising from about 2 mol % to about 20 mol %, relative to \(M\), of \(B_2O_3\) in said host and/or wherein \(B_2O_3\) is present in the host in an amount ranging from about 8 mol % to about 15 mol %, relative to \(M\).

A phosphorescent material as in paragraph A wherein \(M\) is 2 or 1.75 and/or wherein \(M\) is Sr\(^{2+}\).

B. A phosphorescent material having the formula:

\[
M_2O \cdot mAl_2O_3 \cdot (nB_2O_3) \cdot (xEu^{2+},yR^{3+}),
\]

where: \(k\) is 1–2\(x\)–2\(y\); \(m\) is a number ranging from about 1.6 to about 2.2; \(z\) is a number ranging from about 0.0001 to about 0.010; \(x\) is a number ranging from about 0.0001 to about 0.0005; \(y\) is a number ranging from about 0.0001 to about 0.0010; \(M\) is Sr\(^{2+}\) or a mixture of Sr\(^{2+}\) with Ca\(^{2+}\), Ba\(^{2+}\) or both; \(R^{3+}\) is one or more of Pr\(^{3+}\), Ho\(^{3+}\), Dy\(^{3+}\), Er\(^{3+}\), La\(^{3+}\), Lu\(^{3+}\), Ce\(^{3+}\), Y\(^{3+}\), Sm\(^{3+}\), Gd\(^{3+}\), Tb\(^{3+}\), Tm\(^{3+}\), Yb\(^{3+}\) and Bi\(^{3+}\).

A phosphorescent material as defined in paragraph B wherein \(R^{3+}\) is Pr\(^{3+}\), Ho\(^{3+}\), Dy\(^{3+}\), or Nd\(^{3+}\) and/or wherein \(x\) ranges from about 0.001 to about 0.005 and \(y=x\). Preferred phosphorescent material of paragraph B are those in which \(m\) is equal to 1.75 or 2.

C. A phosphorescent material of having the formula:

\[
M_2O \cdot mAl_2O_3 \cdot (nB_2O_3) \cdot (xEu^{2+},yR^{3+}),
\]

where \(k\) is 1–2\(x\)–2\(y\), with \(y=y_1+y_2\); \(m\) is a number ranging from about 1.6 to about 2.2; \(z\) is a number ranging from about 0.0001 to about 0.010; \(x\) is a number ranging from about 0.0001 to about 0.0005; \(y\) is a number ranging from about 0.0001 to about 0.0010; \(M\) is Sr\(^{2+}\) or a mixture of Sr\(^{2+}\) with Ca\(^{2+}\), Ba\(^{2+}\) or both; \(R\) is a trivalent rare earth metal ion or Bi\(^{3+}\).

A phosphorescent material of paragraph C wherein \(R\) is Pr\(^{3+}\), Ho\(^{3+}\), Dy\(^{3+}\), or Nd\(^{3+}\) and/or wherein \(x\) ranges from about 0.001 to about 0.005 and \(y=x\). Preferred phosphorescent material of paragraph C are those wherein \(m\) is Sr\(^{2+}\) and/or wherein \(m=1.75\) or 2.

D. A phosphorescent material having the formula:

\[
M_2O \cdot (m-q)Al_2O_3 \cdot qXO \cdot (pB_2O_3) \cdot (xEu^{2+},yR^{3+}),
\]

where \(k\) is 1–2\(x\)–2\(y\), with \(y=y_3+y_4\); \(m\) is a number ranging from about 1.6 to about 2.2; \(z\) is a number ranging from about 0.0001 to about 0.010; \(x\) is a number ranging from about 0.0001 to about 0.0005; \(y\) is a number ranging from about 0.0001 to about 0.0010; \(M\) is Sr\(^{2+}\) or a combination of Sr\(^{2+}\) with Ca\(^{2+}\) and/or Ba; \(R\) is a trivalent rare earth metal ion or Bi\(^{3+}\).

A phosphorescent material of paragraph C wherein \(R\) is Pr\(^{3+}\), Ho\(^{3+}\), Dy\(^{3+}\), or Nd\(^{3+}\) and/or wherein \(x\) ranges from about 0.001 to about 0.005 and \(y=x\). Preferred phosphorescent material of paragraph C are those wherein \(m=1.75\) or 2.

E. A phosphorescent material having the formula:

\[
M_2O \cdot mAl_2O_3 \cdot zO(xB_2O_3) \cdot (xEu^{2+},yR^{3+}),
\]

where \(k=1-2x-2y\); \(x\) 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; \(M\) 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:

\[
S_bB_aC_aO_{10} \cdot mAl_2O_3 \cdot (nB_2O_3) \cdot (xEu^{2+},yR^{3+}),
\]

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 \(R^{3+}\) is one or more of Pr\(^{3+}\), Ho\(^{3+}\), Nd\(^{3+}\), Dy\(^{3+}\), Er\(^{3+}\), La\(^{3+}\), Lu\(^{3+}\), Ce\(^{3+}\), Y\(^{3+}\), Sm\(^{3+}\), Gd\(^{3+}\), Tb\(^{3+}\), Tm\(^{3+}\), Yb\(^{3+}\) and Bi\(^{3+}\).

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 \(MAl_2O_3\) (where \(M\) is Sr or a mixture of Sr with Ba and/or Ca)

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

\(1-(2-x-y)MCO_3+xAl_2O_3+yEu_2O_3+2yR_2O_3+2zB_2O_3;\)

where:

\(2x+y\) is less than 1, preferably \(x=\)about 0.0001 to about 0.05 and more preferably \(x=\)about 0.001 to about 0.005; \(y\) is a number ranging from about 0.0001 to about 0.10 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\(^{3+}\).

\(B_2O_3\) is used as a flux in the composition and is important for ensuring the formation of the phosphorescent phase. \(B_2O_3\) can be replaced by two molar equivalents of \(H_2BO_3\).

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/cm\(^2\) 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/cm\(^2\) pressure before sintering. The powder or pellets are then sintered at about 1,300°C for one hour in \(H_2\)--N\(_2\) gas flow containing about 2–5% \(H_2\) (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 \(SrAl_2O_3(B_2O_3)\) :\(Eu^{2+},Pr^{3+}\) Phosphors

The methods and phosphors of this invention are specifically exemplified by preparation of \(SrAl_2O_3(0.1B_2O_3)\) :Eu\(^{2+}\),
Preparation and Characterization of SrAl$_2$O$_3$ 

- Eu$^{2+}$: Pr$^{3+}$ Phosphors with Varying Amounts of Eu$^{2+}$

**Eu-Concentration dependence of the after-glow of the samples SrAl$_2$O$_3$:0.1B$_2$O$_3$:Eu$^{2+}$Pr$^{3+}$**

<table>
<thead>
<tr>
<th>Samples</th>
<th>x = 0.001</th>
<th>10 min after-glow</th>
<th>30 min after-glow</th>
<th>60 min after-glow</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1</td>
<td>0.001</td>
<td>100</td>
<td>31</td>
<td>14</td>
</tr>
<tr>
<td>B-2</td>
<td>0.003</td>
<td>106</td>
<td>33</td>
<td>15</td>
</tr>
<tr>
<td>B-3</td>
<td>0.005</td>
<td>98</td>
<td>31</td>
<td>15</td>
</tr>
<tr>
<td>B-4</td>
<td>0.007</td>
<td>90</td>
<td>17</td>
<td>8</td>
</tr>
<tr>
<td>B-5</td>
<td>0.010</td>
<td>50</td>
<td>14</td>
<td>6</td>
</tr>
<tr>
<td>B-6</td>
<td>0.015</td>
<td>30</td>
<td>9</td>
<td>4</td>
</tr>
</tbody>
</table>

**Example 4**

Preparation and Characterization of SrAl$_2$O$_3$ 

- (0.1B$_2$O$_3$):Eu$^{2+}$Pr$^{3+}$ Phosphors with Varying Amounts of Pr$^{3+}$

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

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

$$(0.99-2y)\text{SrCO}_3+2\text{Al}_2\text{O}_3+0.005\text{Eu}_2\text{O}_3+0.01\text{Pr}_2\text{O}_3+0.1\text{B}_2\text{O}_3$$

where y was varied from 0.005 to 0.02 with Eu$^{2+}$ 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$^{3+}$ content (y) with Eu$^{2+}$ content held at 0.01. Data in Table 2 indicate that the intensity of the after-glow is not sensitive to variations in Pr$^{3+}$ in the range examined. However, it is generally preferred to employ lower concentration of Pr (y=x to 2x) because Pr$^{3+}$ absorbs in the range of 450-480 nm due to transitions from the ground state $^3H_4$ to excited states $^3P_2, ^3P_1, ^3P_0$.

**Example 5**

Preparation and Characterization of SrAl$_2$O$_3$(B$_2$O$_3$) 

- Eu$^{2+}$: Ho$^{3+}$ Blue Phosphors

SrAl$_2$O$_3$(0.1B$_2$O$_3$):0.01Eu$^{2+}$0.02Ho$^{3+}$ was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

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

where B$_2$O$_3$ serves as flux.

**TABLE 2**

<table>
<thead>
<tr>
<th>Samples</th>
<th>y = 0.005</th>
<th>10 min after-glow</th>
<th>30 min after-glow</th>
<th>60 min after-glow</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>0.005</td>
<td>100</td>
<td>31</td>
<td>15</td>
</tr>
<tr>
<td>C-2</td>
<td>0.0075</td>
<td>95</td>
<td>28</td>
<td>15</td>
</tr>
<tr>
<td>C-3</td>
<td>0.0100</td>
<td>105</td>
<td>34</td>
<td>16</td>
</tr>
<tr>
<td>C-4</td>
<td>0.015</td>
<td>91</td>
<td>28</td>
<td>14</td>
</tr>
<tr>
<td>C-5</td>
<td>0.02</td>
<td>92</td>
<td>29</td>
<td>16</td>
</tr>
</tbody>
</table>

**Example 5**

Preparation and Characterization of SrAl$_2$O$_3$(B$_2$O$_3$) 

- Eu$^{2+}$: Ho$^{3+}$ Blue Phosphors

SrAl$_2$O$_3$(0.1B$_2$O$_3$):0.01Eu$^{2+}$0.02Ho$^{3+}$ was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

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

where B$_2$O$_3$ serves as flux.

**TABLE 2**

<table>
<thead>
<tr>
<th>Samples</th>
<th>y = 0.005</th>
<th>10 min after-glow</th>
<th>30 min after-glow</th>
<th>60 min after-glow</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>0.005</td>
<td>100</td>
<td>31</td>
<td>15</td>
</tr>
<tr>
<td>C-2</td>
<td>0.0075</td>
<td>95</td>
<td>28</td>
<td>15</td>
</tr>
<tr>
<td>C-3</td>
<td>0.0100</td>
<td>105</td>
<td>34</td>
<td>16</td>
</tr>
<tr>
<td>C-4</td>
<td>0.015</td>
<td>91</td>
<td>28</td>
<td>14</td>
</tr>
<tr>
<td>C-5</td>
<td>0.02</td>
<td>92</td>
<td>29</td>
<td>16</td>
</tr>
</tbody>
</table>
a broad band peaking at about 488 nm with a bandwidth of about 60 nm (2640 cm\(^{-1}\)). The figure illustrates phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

**Example 6**

Preparation and Characterization of \(\text{SrAl}_{2}O_{4}(B_{2}O_{3})\) \(:\text{Eu}^{2+}::\text{Nd}^{3+}\) Blue Phosphors

\(\text{SrAl}_{2}O_{4}(0.1B,03):0.01\text{Eu}^{2+}:0.02\text{Nd}^{3+}\) was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

\[
0.97 \text{ScCO}_{3}+2.00 \text{Al}_{2}O_{3}+0.005 \text{Eu}_{2}O_{3}+0.01 \text{Nd}_{2}O_{3}+0.1 B_{2}O_{3}
\]

where \(B_{2}O_{3}\) serves as flux.

**Example 7**

Preparation and Characterization of Phosphors of Formula \(\text{SrAl}_{2}O_{4}(B_{2}O_{3}):0.01\text{Eu}^{2+}0.02\text{R}^{3+}\), where \(R\) are trivalent metal ions of La, Ce, Sm, Gd, Tb, Dy, Er, Tm, Yb, and Lu.

\(\text{SrAl}_{2}O_{4}(0.1B,03):0.01\text{Eu}^{2+}0.02\text{R}^{3+}\) were prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

\[
0.97 \text{ScCO}_{3}+2.00 \text{Al}_{2}O_{3}+0.005 \text{Eu}_{2}O_{3}+0.01 R_{2}O_{3}+0.1 B_{2}O_{3}
\]

with \(R=\text{La}, \text{Ce}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}, \text{Tm}, \text{Yb}, \text{and Lu}\).

**Example 8**

Preparation and Characterization of \(\text{SrAl}_{2}O_{4}(B_{2}O_{3})\) \(:0.01\text{Eu}^{2+}0.01\text{Pr}^{3+}0.01R^{3+}\) where \(R\) is \(\text{La}, \text{Lu}, \text{Er}, \text{Y}, \text{and Bi}\).

This example is intended to determine if co-doping of metal ions into a \(\text{SrAl}_{2}O_{4}(B_{2}O_{3}):\text{Eu}^{2+}:\text{Pr}^{3+}\) phosphor increases UV excitation efficiency and improves phosphor brightness.

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

\[
(1-2x-2y-z)\text{MCO}_{3}+m\text{Al}_{2}O_{3}+xy\text{Eu}_{2}O_{3}+y\text{Pr}_{2}O_{3}+z\text{R}_{2}O_{3}+z\text{B}_{2}O_{3}
\]

where \(y_{1}+y_{2}=y, 1-2x-2y=0\) and the ranges of \(m, x, y\) 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:

\[
0.97 \text{ScCO}_{3}+2.0 \text{Al}_{2}O_{3}+0.005 \text{Eu}_{2}O_{3}+0.005 \text{Pr}_{2}O_{3}+0.01 \text{R}_{2}O_{3}+0.1 \text{B}_{2}O_{3}
\]

where \(R=\text{Y}, \text{La}, \text{Lu}, \text{Er}, \text{and Bi}\). The intensity of the afterglow of \(\text{SrAl}_{2}O_{4}(0.1B,03):0.01\text{Eu}^{2+}0.01\text{Pr}^{3+}0.01R^{3+}\) samples measured at 488 nm relative to that of \(\text{SrAl}_{2}O_{4}(0.1B,03):0.01\text{Eu}^{2+}0.02\text{Pr}^{3+}\) is given in Table 3. Some results are also shown in FIG. 12.

**FIG. 12** shows decay curves of the afterglow of \(\text{SrAl}_{2}O_{4}(0.1B,03):0.01\text{Eu}^{2+}0.01\text{Pr}^{3+}0.01R^{3+}\) samples in the first 60 minutes. The samples were exposed to a 4 W UV lamp for two minutes.

**FIG. 13** shows decay curves of the afterglow of \(\text{SrAl}_{2}O_{4}(0.1B,03):0.01\text{Eu}^{2+}0.01\text{Pr}^{3+}0.01Y^{3+}\) samples in the first 60 minutes. The samples were exposed to a 4 W UV lamp for two minutes.

Codoping with \(Y^{3+}\) and \(R^{3+}\) increases the UV excitation efficiency.
efficiency and improve the brightness by 50% compared to the analogous Pr-doped phosphor.

<table>
<thead>
<tr>
<th>TABLE 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>The influence of codoping Y, Lu, Er, or Bi into SrAlO$_2$(B$_2$O$_3$):Eu,Pr on the phosphorescence at 488 nm.</td>
</tr>
<tr>
<td>after (min)</td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>60</td>
</tr>
</tbody>
</table>

*Data is referenced to that of the SrAlO$_2$(B$_2$O$_3$):Eu,Pr phosphor.*

**Example 9**

Preparation and Characterization of SrAlO$_2$(0.1B$_2$O$_3$):0.01Eu,0.01Dy,0.01Ge

This example demonstrates the influence of deep trapping centers formed by Dy$^{3+}$ on the decay characteristics of MAl$_2$O$_4$(0.1B$_2$O$_3$):0.01Eu doped with 0.01Pr or 0.01Ho. Samples are generally prepared by the method of Example 1 combining the components in the following general molar proportions:

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

where $y_1+y_2=y$, and $m$, $x$, $y$ and $z$ ranges are as described above for formula 1.

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

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

where R=Pr and Ho.

Table 4 provides measurements of relative after-glow intensity at 488 nm of SrAlO$_2$(0.1B$_2$O$_3$):0.01Eu,0.01Dy,0.01Ho relative to that of SrAlO$_2$(0.1B$_2$O$_3$):0.01Eu,0.01Pr. The materials doped with Dy$^{3+}$ and Pr$^{3+}$ or Ho$^{3+}$ exhibit enhanced brightness and persistence compared to the Pr$^{3+}$ doped or Ho$^{3+}$, doped phosphors.

<table>
<thead>
<tr>
<th>TABLE 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>The influence of deep centers of Dy on the after-glow of SrAlO$_2$(0.1B$_2$O$_3$):0.01Eu:0.02Pr and SrAlO$_2$(0.1B$_2$O$_3$):0.01Eu:0.02Ho after (min) SAO-EuPr $^1$ SAO-EuPrDy SAO-EuHoDy</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>60</td>
</tr>
</tbody>
</table>

*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:

$\text{(1}-n\text{-}2x\text{-}2y)\text{SrCO}_3$$+n\text{BaCO}_3$$+x\text{Al}_2\text{O}_3$$+y\text{Eu}_2\text{O}_3$$+y\text{R}_2\text{O}_3$$+z\text{B}_2\text{O}_3$

where:

$n+2x+2y$ is less than 1 (there is some Sr present) $y$ ranges from about 0.0001 to about 0.010 and preferably the value of $y$; the value of $x$ $z$ ranges from about 0.02 to about 0.2; and $R^{3+}$ is a trivalent rare earth metal ion or Bi$^{3+}$.

The mixed alkaline earth aluminate compound, SrAlO$_2$(0.1B$_2$O$_3$):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}_3\text{Ba}_2\text{O}_7$$+\text{mAl}_2\text{O}_3$$+2\text{EuO}_2$$+2\text{R}_2\text{O}_3$ $\text{R}^{3+}$

**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:

$\text{(1}-n\text{-}2x\text{-}2y)\text{SrCO}_3$$+n\text{CaCO}_3$$+x\text{Al}_2\text{O}_3$$+y\text{Eu}_2\text{O}_3$$+y\text{R}_2\text{O}_3$$+z\text{B}_2\text{O}_3$

where:

$n+2x+2y$ is less than 1 (there is at least some Sr present) $y$ ranges from about 0.0001 to about 0.010 and preferably the value of $y$; the value of $x$ $z$ ranges from about 0.02 to about 0.1; and $R^{3+}$ is a trivalent rare earth ion or Bi$^{3+}$.

These phosphors have the generic formula:

$\text{Sr}_3\text{Ca}_2\text{O}_7$$+\text{mAl}_2\text{O}_3$$+2\text{EuO}_2$$+2\text{R}_2\text{O}_3$ $\text{R}^{3+}$

**Example 12**

Preparation and Characterization of mixed alkaline earth aluminate phosphors

Mixed alkaline earth aluminate phosphors in which the host contains Sr, Ca and Ba can also be prepared by combining the components in the following molar proportions:

$\text{(1}-n\text{-}2x\text{-}2y)\text{SrCO}_3$$+\text{pBaCO}_3$$+x\text{CaCO}_3$$+y\text{Eu}_2\text{O}_3$$+y\text{R}_2\text{O}_3$$+z\text{B}_2\text{O}_3$

where:

$p+n+2x+2y$ is less than 1,
y ranges from about 0.0001 to about 0.010 and preferably the value of y=the value of x
z ranges from about 0.02 to about 0.2; and
$R^{3+}$ is a trivalent rare earth ion or Bi$^{3+}$.
These mixed alkaline earth aluminates have the formula:
$$Sr_{x}Ba_{y}Ca_{z}O_{mAl_{n}O_{a}(zB,O_{b}):2xEu_{n}2yR_{b}}$$
where $k=1-n-p-2x-2y$.

**Example 12**

**Codoping of Mg$^{2+}$ or Zn$^{2+}$ into MO . mAl$_2$O$_3$:Eu$^{3+}$ 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:

$$(1-2x-2y)MC_{0.5}+(m-q)Al_{2}O_{3}+(q)XO+2yR_{b}$$

where: 2x+2y is less than 1;
q is less than m and preferably ranges from 0.002 to 0.2;
the ranges for x, y, m and z are as given in formula 1.
XO, in particular, can be MgO and/or ZnO. These phosphors will have the generic formula:
$$M_{0.5}O_{mAl_{2}O_{3}.qXO.2yR_{b}}$$

where $k=1-2x-2y$ where the ranges for m, x and y are as above.
Exemplary Mg or Zn doped phosphors are prepared by combining the components according to the following molar proportions:

$$(0.98 SrCO_{3},0.02 Al_{2}O_{3},0.005 Eu_{2}O_{3},0.005 Dy_{2}O_{3},0.1 B_{2}O_{3})$$

where XO can be MgO or ZnO.

**Example 13**

**Co-doping of Na$^{+}$ or K$^{+}$ into MO. mAl$_2$O$_3$:Eu$^{3+}$, 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:

$$(1-2x-2y)MC_{0.5}+(m-q)Al_{2}O_{3}+(q)XO+2yR_{b}$$

where: 2x+2y+2r is less than 1;
q is less than m and preferably ranges from 0.002 to 0.2; and the ranges for x, y, m and z are as given in formula 1.

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

$$(0.98 SrCO_{3},1.99 Al_{2}O_{3},0.005 Eu_{2}O_{3},0.005 Dy_{2}O_{3},0.1 B_{2}O_{3})$$

where XO can be Na$_2$CO$_3$ or K$_2$CO$_3$.

**Example 15**

Effect of variation of the amount of flux on phosphor properties

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

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

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.

Table 8 provides measurements of relative after-glow intensity at 488 nm of strontium aluminate 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 \( \text{M} = \text{Sr} \) 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:

\[ (4-8x-8y) \text{MC}_x+(7.00-x)\text{Al}_2\text{O}_3+4y\text{Eu}_2\text{O}_3+2y\text{R}_2\text{O}_3+4z\text{B}_2\text{O}_3 \]

where:

- \( 8x+8y < 4, \) \( x \) is preferably about 0.0001 to about 0.05 and more preferably \( x \) is 0.001 to about 0.005;
- \( y \) ranges from about 0.0001 to about 0.010 and preferably the value of \( y \) is the value of \( x \);
- \( z \) ranges from about 0.02 to about 0.1;
- \( M \) is \( \text{Sr} \) or a combination of \( \text{Sr} \) with \( \text{Ba} \) and/or \( \text{Ca} \); and
- \( R \) 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.

<p>| TABLE 8 |<br />
| --- | --- | --- | --- | --- | --- | --- | --- |
| The influence of varying ( \text{B}_2\text{O}_3 ) in preparation of phosphors |</p>
<table>
<thead>
<tr>
<th>( z )</th>
<th>After/min.</th>
<th>0.03</th>
<th>0.08</th>
<th>0.08</th>
<th>0.10</th>
<th>0.12</th>
<th>0.15</th>
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<td>14</td>
<td>17</td>
<td>15</td>
<td>14</td>
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</tbody>
</table>

\(^{1}\)Data is referenced to that at \( n=0.10 \).

Example 17

Single Crystal Blue Phosphors

Single crystals of the alkaline earth aluminate phosphors of this invention can be grown directly from a melt by well-known techniques. For example, the conventional Czochralski method (J. Czochralski (1918) Z. Phys. Chem. 92:219), the floating zone method (W. G. Pfann (1952) Trans. AIME 194:747) or the laser heated pedestal method (B. M. Tissue et al. (1991) J. Crystal Growth 109:323) can be used. The following procedure employs the laser heated pedestal method:

The phosphor components are mixed in the appropriate molar proportions according to the preparative examples hereinabove and the mixtures are milled or ground to give a homogeneous fine powder. The powder is pressed into pellets under about 1.3 ton/cm\(^2\) pressure. The pressed pellets are then prefired in air at about 600° C. for about one hour. The prefired powder is pulverized and milled again into a fine powder. The prefired powder is pressed again into ceramic pellets at the same pressure. The pellets are then sintered at about 1,300° C. for one hour in a flowing \( \text{H}_2-\text{N}_2 \) 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 \( \text{H}_2 \), 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:

\[ \text{M}_x\text{Al}_y\text{O}_{z+1}:\text{Eu}^{2+},\text{R}^{3+} \]

wherein \( m \) is a number ranging from about 1.6 to about 2.2, \( M \) is \( \text{Sr} \) or a combination of \( \text{Sr} \) with \( \text{Ca}, \text{Ba} \) or both, \( R^{3+} \) is a trivalent metal ion or a mixture thereof, \( \text{Eu}^{2+} \) is present at a level from about 0.02 mol% to about 10 mol% of \( M \), and \( R^{3+} \) is present at a level from about 0.02 mol% to about 20 mol% of \( M \).

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

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

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

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

\[ \text{Sr}_x\text{Al}_y\text{O}_{z+1}:2\text{Eu}^{2+},2y\text{R}^{3+} \]

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

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

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

8. The phosphor of claim 1 wherein \( m \) is 2 or 1.75.

9. The phosphor of claim 8 wherein \( M \) is \( \text{Sr} \).

10. A phosphor represented by the formula:

\[ \text{M}_x\text{Al}_y\text{O}_{z+1}:\text{Eu}^{2+},\text{R}^{3+} \]

wherein \( m \) is a number ranging from about 1.6 to about 2.2, \( M \) is \( \text{Sr} \) or a combination of \( \text{Sr} \) with \( \text{Ca}, \text{Ba} \) or both, \( R^{3+} \) is
a mixture of $\text{Y}^{3+}$ with another trivalent metal ion, $\text{Eu}^{2+}$ 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 0.02 mol% to about 20 mol% of M.

11. The phosphor of claim 10 wherein $\text{R}^{3+}$ is a mixture of $\text{Y}^{3+}$ 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:

$$\text{Sr}_{x}\text{Ba}_{y}\text{Ca}_{z}\text{O}_{m}\cdot m\text{Al}_{2}\text{O}_{3}:\text{Eu}^{2+},\text{R}^{3+}$$

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:

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

wherein $m$ is a number ranging from about 1.6 to about 2.2, 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 0.02 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:

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

wherein $m$ is a number ranging from about 1.6 to about 2.2, M is Sr or a combination of Sr with Ca, Ba or both, $\text{R}^{3+}$ is a trivalent rare earth metal ion, Bi$^{3+}$ or mixtures 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 0.02 mol% to about 20 mol% of M in which a portion of the $\text{Al}^{3+}$ in the host is substituted by a divalent metal ion or in which a portion of the $\text{M}^{2+}$ in the phosphor is substituted by a monovalent metal ion.

16. A phosphor of claim 15 wherein a portion of the $\text{Al}^{3+}$ 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 $\text{M}^{2+}$ in the phosphor is substituted by a monovalent metal ion.

19. A phosphor having the formula:

$$\text{Sr},\text{Ba},\text{Ca},\text{O}_{m}\cdot m\text{Al}_{2}\text{O}_{3}:\text{Eu}^{2+},\text{R}^{3+}$$

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.

12. The phosphor of claim 21 in which the amount of divalent metal ion substituted into the phosphor is equal to the amount of $\text{R}^{3+}$ 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 $\text{M}^{2+}$ in the phosphor is substituted by a monovalent metal ion.

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

23. The phosphor of claim 22 in which the monovalent metal ion is present in the phosphor in an amount about equal to the amount of $\text{R}^{3+}$ 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 $\text{R}^{3+}$ 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 $\text{R}^{3+}$ is Pr$^{3+}$, Ho$^{3+}$, Dy$^{3+}$, or Nd$^{3+}$ or mixtures thereof.

27. The phosphor of claim 15 wherein $\text{R}^{3+}$ is a mixture of $\text{Y}^{3+}$ 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 $\text{B}_{2}\text{O}_{3}$.

30. The phosphor of claim 15 wherein M is Sr.
Title page.
Item [57], ABSTRACT
Delete "MO.mAl_2O_3:Eu^{2+},R^{3+}" and replace with -- MO.mAl_2O_3:Eu^{2+},R^{3+} --.

Column 1.
Line 28, delete "SrAl_2O_5:Eu^{2+}:Dy^{3+}" and replace with -- SrAl_2O_5:Eu^{2+},Dy^{3+} --.
Lines 37-38, delete "has obtained" and replace with -- has been obtained --.
Line 41, delete "Sr^{2+}" and replace with -- Sr^{2+} --.
Line 50, delete "Dy^{3+}" and replace with -- Dy^{3+} --.
Line 50, delete "Eu^{2+}" and replace with -- Eu^{2+} --.
Line 62, delete "M_{1-x}Al_2O_5.x Where" and replace with -- M_{1-x}Al_2O_{5-x}, where --.

Column 2.
Line 16, delete the comma after "Eu^{2+}".
Lines 22-23, delete "2SrO.3Al_2O_3:Eu^{2+}" and replace with -- 2SrO.3Al_2O_3:Eu^{2+} --.
Lines 25-26, delete "4SrO.7Al_2O_3:Eu^{2+}" and replace with -- 4SrO.7Al_2O_3:Eu^{2+} --.
Line 26, delete "BaO.4Al_2O_3:Eu^{2+}" and replace with -- BaO.4Al_2O_3:Eu^{2+} --.
Line 38, delete "MO.mAl_2O_3:Eu^{2+},R^{3+}" and replace with -- MO.mAl_2O_3:Eu^{2+},R^{3+} --.
Line 47, delete "MO.mAl_2O_3(zB_2O_3):Eu^{2+},R^{3+}" and replace with -- MO.mAl_2O_3(zB_2O_3):Eu^{2+},R^{3+} --.

Column 4.
Line 32, delete "Sr_{0.64}Ba_{0.33}Al_2O_7" and replace with -- Sr_{0.33}Ba_{0.64}Al_2O_7 --.
Line 36, delete "Sr_{0.49}Ca_{0.49}Al_2O_7" and replace with -- Sr_{0.49}Ca_{0.48}Al_2O_7 --.

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 exhibt" and replace with -- can exhibit --.
Line 49, delete "exhibit" and replace with -- exhibit --.
Line 55, delete "MO.mAl_2O_3" and replace with -- MO.mAl_2O_3 --.
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.mAl₂O₃(zB₂O₃):₂xEu²⁺,₂yR³⁺" and replace with -- M₀.mAl₂O₃ (zB₂O₃):₂xEu²⁺,₂yR³⁺ --.

Column 8,
Line 1, delete "M₀.mAl₂O₃(zB₂O₃):₂xEu²⁺,₂y₁R₁⁺,₂y₂R₂⁺" and replace with -- M₀.mAl₂O₃(zB₂O₃):₂xEu²⁺,₂y₁R₁⁺,₂y₂R₂⁺ --.
Line 15, delete "M₀.(m-q)Al₂O₃.qXO(zB₂O₃):₂xEu²⁺,₂yR³⁺" and replace with -- M₀.(m-q)Al₂O₃.qXO(zB₂O₃):₂xEu²⁺,₂yR³⁺ --.
Line 31, delete "M₀.mAl₂O₃.rZ₂(zB₂O₃):₂xEu²⁺,₂yR³⁺" and replace with -- M₀.mAl₂O₃.rZ₂(zB₂O₃):₂xEu²⁺,₂yR³⁺ --.
Line 60, delete "MO.mAl₂O₃" and replace with -- MO.mAl₂O₃ --.

Column 9,
Line 10, delete "M₀.mAl₂O₃(zB₂O₃):₂xEu²⁺,₂yR³⁺" and replace with -- M₀.mAl₂O₃ (zB₂O₃):₂xEu²⁺,₂yR³⁺ --.
Line 28, delete "M₀.mAl₂O₃(zB₂O₃):₂xEu²⁺,₂y₁R₁⁺,₂y₂R₂⁺" and replace with -- M₀.mAl₂O₃(zB₂O₃):₂xEu²⁺,₂y₁R₁⁺,₂y₂R₂⁺ --.
Line 50, delete "M₀.(m-q)Al₂O₃.qXO(zB₂O₃):₂xEu²⁺,₂yR³⁺" and replace with -- M₀.(m-q)Al₂O₃.qXO(zB₂O₃):₂xEu²⁺,₂yR³⁺ --.
Line 67, delete "M₀.mAl₂O₃.rZ₂(zB₂O₃):₂xEu²⁺,₂yR³⁺" and replace with -- M₀.mAl₂O₃.rZ₂(zB₂O₃):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 "SrBa₂Ca₉O₄.mAl₂O₃(zB₂O₃):₂xEu²⁺,₂yR³⁺" and replace with -- SrBa₂Ca₉O₄.mAl₂O₃(zB₂O₃):₂xEu²⁺,₂yR³⁺ --.
Line 45, delete "Bi⁺⁺" and replace with -- Bi⁺⁺ --.
UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,117,362
DATED : September 12, 2000
INVENTOR(S) : Yen et al.

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 "SrAl$_2$O$_7$:0.01Eu$^{2+}$:0.02Pr$^{3+}$" and replace with -- SrAl$_2$O$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$ --.
Line 25, delete "SrAl$_2$O$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$" and replace with -- SrAl$_2$O$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$ --.
Lines 29, 32, 37 and 39-40, delete "SrAl$_2$O$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$" and replace with -- SrAl$_2$O$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Pr$^{3+}$ --.
Line 46, delete "SrAl$_2$O$_7$(B$_2$O$_3$):Eu$^{2+}$:Pr$^{3+}$" and replace with -- SrAl$_2$O$_7$(B$_2$O$_3$):Eu$^{2+}$:Pr$^{3+}$ --.
Lines 50-51, delete "SrAl$_2$O$_7$(0.1B$_2$O$_3$):Eu$^{2+}$:Pr$^{3+}$" and replace with -- SrAl$_2$O$_7$(0.1B$_2$O$_3$):Eu$^{2+}$:Pr$^{3+}$ --.
Line 60, delete "0.01 to 0.15" and replace with -- 0.001 to 0.015 --.

Column 12.
Lines 17-18 and 21-22, delete "SrAl$_2$O$_7$(0.1B$_2$O$_3$):Eu$^{2+}$:Pr$^{3+}$" and replace with -- SrAl$_2$O$_7$(0.1B$_2$O$_3$):Eu$^{2+}$:Pr$^{3+}$ --.
Line 43, Table 2, delete "SrAl$_2$O$_7$(B$_2$O$_3$):0.01Eu:2yPr" and replace with -- SrAl$_2$O$_7$(B$_2$O$_3$):0.01Eu:2yPr --.
Lines 55-56, delete "SrAl$_2$O$_7$(B$_2$O$_3$):Eu$^{2+}$:Ho$^{3+}$" and replace with -- SrAl$_2$O$_7$(B$_2$O$_3$):Eu$^{2+}$,Ho$^{3+}$ --.
Lines 58 and 66, delete "SrAl$_2$O$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Ho$^{3+}$" and replace with -- SrAl$_2$O$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Ho$^{3+}$ --.

Column 13.
Lines 8, 14, 17 and 22, delete "SrAl$_2$O$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Ho$^{3+}$" and replace with -- SrAl$_2$O$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Ho$^{3+}$ --.
Lines 29-30, delete "SrAl$_2$O$_7$(B$_2$O$_3$):Eu$^{2+}$:Nd$^{3+}$" and replace with -- SrAl$_2$O$_7$(B$_2$O$_3$):Eu$^{2+}$,Nd$^{3+}$ --.
Lines 33, 43, 53, 58, 61 and 66, delete "SrAl$_2$O$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$:0.02Nd$^{3+}$" and replace with -- SrAl$_2$O$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Nd$^{3+}$ --.
Line 54, delete "line (a)" and replace with -- (line a) --.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 14.
Lines 7 and 15, delete "SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺,0.02R³⁺" and replace with -- SrAl₂O₇(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 m" and replace with -- ranges of m --.
Lines 56 and 60-61, delete "SrAl₂O₇(0.1B₂O₃):0.001Eu:0.01Pr:0.01R" and replace with -- SrAl₂O₇(0.1B₂O₃):0.001Eu:0.001Pr:0.001R --.

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 "Sr₅Ba₉O₇·M₅Al₃O₉·2xEu,2yR" and replace with -- Sr₅Ba₉O₇·M₅Al₃O₉·2xEu,2yR --.
Line 48, delete "Sr₅Ca₇O₉·M₅Al₃O₉·2xEu,2yR" and replace with -- Sr₅Ca₇O₉·M₅Al₃O₉·2xEu,2yR --.
Line 52, delete "(Sr₅₄₈Ca₄₈₃)(Al₄O₇):0.01Eu:0.02Pr" and replace with -- (Sr₅₄₈Ca₄₈₃)Al₄O₇:0.01Eu:0.02Pr --.
Lines 58-59, delete "(Sr₅₄₈Ca₄₈₃)(0.1B₂O₃)Al₄O₇:0.01Eu:0.02Pr" and replace with -- (Sr₅₄₈Ca₄₈₃)(0.1B₂O₃)Al₄O₇:0.01Eu:0.02Pr --.

Column 17.
Line 7, delete "Sr₅Ba₅Ca₅O₉·M₅Al₃O₉·(zB₂O₃):2xEu,2yR" and replace with -- Sr₅Ba₅Ca₅O₉·M₅Al₃O₉·(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\_m\_Al\_2\_O\_3\_E\_u\_2\_+,\_R\_3\_+" and replace with -- MO\_m\_Al\_2\_O\_3\_E\_u\_2\_+,\_R\_3\_+ --.
Lines 44-45, delete "selected from the group".
Line 46, delete "and" and replace with -- or --.
Line 64, delete "MO\_m\_Al\_2\_O\_3\_E\_u\_2\_+,\_R\_3\_+" and replace with -- MO\_m\_Al\_2\_O\_3\_E\_u\_2\_+,\_R\_3\_+ --.

Column 21,
Line 3, delete "R\_3\_+ is present" and replace with -- R\_3\_+ is present --.
Line 11, delete "Sr\_x\_Ba\_y\_Ca\_O\_m\_Al\_2\_O\_3\_2\_x\_Eu\_2\_+,\_2\_y\_R\_3\_+" and replace with -- Sr\_x\_Ba\_y\_Ca\_O\_m\_Al\_2\_O\_3\_2\_x\_Eu\_2\_+,\_2\_y\_R\_3\_+ --.
Line 15, delete "v" and replace with -- y --.
Lines 22 and 37, delete "MO\_m\_Al\_2\_O\_3\_E\_u\_2\_+,\_R\_3\_+", and replace with -- MO\_m\_Al\_2\_O\_3\_E\_u\_2\_+,\_R\_3\_+ --.

Column 22,
Line 4, delete "M\_2\_+" and replace with -- M\_2\_+ --.
Line 10, after "in which" insert -- a portion of the --.

Signed and Sealed this
Fifteenth Day of April, 2003

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