LONG-PERSISTENCE BLUE PHOSPHORS

Inventors: William M. Yen, Athens, Ga.; Weiyi Jia, Mayaguez, Puerto Rico; Lizhu Lu; Huabiao Yuan, both of Athens, Ga.

Assignees: University of Georgia Research Foundation, Inc., Atlanta, Ga.; University of Puerto Rico, San Juan, Puerto Rico

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Related U.S. Application Data

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References Cited

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ABSTRACT

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

\[ MO \cdot mAl_2O_3:Eu^{2+},R^{3+} \]

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

30 Claims, 16 Drawing Sheets
OTHER PUBLICATIONS


FIG. 1
FIG. 2
FIG. 3
FIG. 5
FIG. 7
FIG. 8
FIG. 9
FIG. 10
FIG. 11
FIG. 12
FIG. 13
FIG. 14

Intensity (a.u.) vs. Delay Time (minute)

- Line a
- Line b
- Line c

Log-log scale
FIG. 15
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 DAAH04-96-10416 and DOE DE-FG02-94ER75764. The United States government has certain rights in this invention.

FIELD OF THE INVENTION

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

BACKGROUND OF THE INVENTION

Persistent phosphorescing materials, such as ZnS:Cu,Cr, ZnCdS:Cu and CaSrS: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).

Enhanced brightness and persistence compared to alkaline earth aluminate matrix activated with Eu$^{2+}$ and doped with one trivalent rare earth metal ion or Bi$^{3+}$, or mixtures of these trivalent metal ions; and m is a number ranging from about 0.02 to about 0.2, preferably about 0.2 mol %.

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 Eu$^{2+}$-activated SrAl$_2$O$_4$ was improved by co-doping with rare earth ions to produce appropriate trapping centers associated with the Sr$^{2+}$ vacancy (Abbruscato et al. (1971) J. Electrochem. Soc. 118:930).

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.

SUMMARY OF THE INVENTION

This invention relates to long-persistent phosphors of general formula: MO$_1$-xAI$_2$O$_3$:Eu$^{2+}$,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: MO$_1$-xAI$_2$O$_3$:Eu$^{2+}$,Bi$^{3+}$, 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 rare earth metals or Bi$^{3+}$. The preferred phosphors are activated with about 0.02 mol % to about 10 mol % Eu$^{2+}$, preferably about 0.2 mol % to about 1.0 mol % Eu$^{2+}$ activator and co-doped with about 0.02 mol % to about 20 mol % of at least one trivalent rare earth metal ion or Bi$^{3+}$. 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 persistence time of about 18 hr. The phosphors of this invention have significantly improved brightness compared to sulfide phosphors, such as CaSrS:Bi. Phosphors of this invention can have persistence times up to about 18 hr.

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

REFERENCES


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


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


T. R. Kutty et al. (1990) Mater. Res. Bull. 25:1355-1362 reports luminescence of Eu$^{2+}$, in strontium aluminates prepared by the hydrothermal method. Blue to green luminescence of general formula SrAl$_2$O$_4$--Eu$^{2+}$ is reported. The reference also reports the preparation of certain aluminoborates.

B. Smets et al. (1989) J. Electrochem. Soc. 136(7):2119-2123 reports blue-emitting phosphors: 2SrO . 3Al$_2$O$_3$:Eu$^{2+}$ and 1.29 (Ba, Ca)O, 6 Al$_2$O$_3$:Eu$^{2+}$. In the background section of the reference the authors refer to earlier report of blue-green emitting phosphors 4SrO . 7Al$_2$O$_3$:Eu$^{2+}$ and BaO : 4Al$_2$O$_3$:Eu$^{2+}$, which could be synthesized only in the presence of small amounts of B$_2$O$_3$.

EP published application 710,709 (1976, Tokyo Shibaura Electric Co.) reports blue-emitting phosphors containing barium (or calcium or strontium)-potassium (or sodium) aluminates activated with europium and manganese.

EP published application 745,006 (1976, Tokyo Shibaura Electric Co.) reports blue-emitting phosphors containing calcium, strontium, barium and, optionally, magnesium, and x is a number not equal to 0. The phosphor comprises europium as an activator and a co-activator electing from a rare earth metal, manganese, tin or bismuth.

EP published application 765,925 (1976, Tokyo Shibaura Electric Co.) reports blue-emitting phosphors containing barium (or calcium or strontium)-potassium (or sodium) aluminates activated with europium and manganese.


JP Patent 94029416 (1994, Matsushita Electronics) reports a europium activated barium aluminate phosphor containing yttrium oxide to enhance phosphorescence.
Preferred phosphors of this invention are those in which M is Sr.

Phosphors of this invention are activated with Eu$^{2+}$ and are co-doped with a trivalent rare earth metal ion or Bi$^{3+}$. The phosphors may be co-doped 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$^{3+}$, Lu$^{3+}$, Ce$^{3+}$, Y$^{3+}$, Sm$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, Tm$^{3+}$, and Yb$^{3+}$ and the Group VA metal ion Bi$^{3+}$. Preferred trivalent dopants are Pr$^{3+}$, Ho$^{3+}$, Dy$^{3+}$, and Nd$^{3+}$. Co-doping of Dy$^{3+}$ or Y$^{3+}$ with another trivalent metal ion results in phosphor of improved brightness, e.g., SrAl$_2$O$_{4}$:Eu$^{2+}$, Pr$^{3+}$, Dy$^{3+}$ or SrAl$_2$O$_{4}$:Eu$^{2+}$, Ho$^{3+}$, Dy$^{3+}$.

Preferred phosphors are those with m ranging from about 1.70 to about 2.05 and, more preferred, are those where m=1.75, the host material being SrAl$_2$O$_{4}$ 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$^{3+}$, Y$_2$O$_3$, Dy$^{3+}$, Er$^{3+}$, La$^{3+}$, Lu$^{3+}$, Ce$^{3+}$, Y$^{3+}$, and Tb$^{3+}$ are the Group VA metal ion Bi$^{3+}$. Preferred trivalent dopants are Pr$^{3+}$, Ho$^{3+}$, Dy$^{3+}$, and Nd$^{3+}$. Co-doping of Dy$^{3+}$ or Y$^{3+}$ with another trivalent metal ion results in phosphor of improved brightness, e.g., SrAl$_2$O$_{4}$:Eu$^{2+}$, Pr$^{3+}$, Dy$^{3+}$ or SrAl$_2$O$_{4}$:Eu$^{2+}$, Ho$^{3+}$, Dy$^{3+}$.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 is a spectrum of the after-glow of a pellet of SrAl$_2$O$_{4}$: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. 2 is a graph of decay of the after-glow of (a) SrAl$_2$O$_{4}$:0.01Eu$^{2+}$,0.02Pr$^{3+}$; (b) SrAl$_2$O$_{4}$:0.01Eu$^{2+}$,0.02Pr$^{3+}$; (c) SrAl$_2$O$_{4}$:0.01Eu$^{2+}$,0.02Pr$^{3+}$ and (d) of commercial blue phosphor CaS:Si 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$_{4}$:0.01Eu$^{2+}$,0.02Nd$^{3+}$ measured after excitation at 488 nm.

FIG. 11 is an after-glow decay curve of (a) SrAl$_2$O$_{4}$:0.01Eu$^{2+}$,0.02Pr$^{3+}$; (b) SrAl$_2$O$_{4}$:0.01Eu$^{2+}$,0.02Pr$^{3+}$ and (c) of commercial blue phosphor CaS:Si 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.

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 18th 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 given by Chen, R. and McKeever, S. W. S. (1997), Theory of Thermoluminescence and Related Phenomena, World Scientific, Singapore; Sonoda, M. et al. (1983) Radiology 148:833). The main difference between these three phenomena appears to be the depth of traps. When a phosphor possesses centers with certain trapping depth which can be effectively acti-
activated at room temperature, it will show persistent phosphorescence. Deeper trapping centers can be activated by heating or photostimulation. Therefore, a study of phosphorescence dynamics allows the characterization of these three important luminescence processes. Single crystal phosphors facilitate studies of phosphorescence dynamics.

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

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

Phosphor materials of this invention can exhibit enhanced phosphorescence intensity and/or long persistence of phosphorescence. Preferred phosphors of this invention have intensity enhanced (as measured in a similar measurement system) compared to a standard commercial sample of ZnS phosphor. Persistence of phosphorescence is measured herein as persistence time, which is the time after discontinuing irradiation that it takes for phosphorescence of a sample to decrease to the threshold of eye sensitivity. This threshold is the signal level of emission intensity that a naked (i.e., unaided) eye can clearly see in the dark. Persistence times are assessed by following phosphorescence intensity as a function of time. Clearly measurement comparisons of persistence times must be performed under identical conditions using the same detection systems. The term “persistent phosphors” has been applied to materials exhibiting phosphorescence lasting form minutes to hours.

The term “long-persistent phosphor” historically has been used to refer to ZnS-Cu, CaS-Eu, Tm and similar materials, 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 preferred phosphors exhibit persistence times of greater than about 15–18 hrs.

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

The hosts of this invention are alkaline earth aluminates MO₄: mAl₂O₄ (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 Eu²⁺. Hosts in which m=about 1.6 to about 2.2 provide the desired blue color and good phosphorescence brightness in combination with the Eu activator. Hosts where m=about 1.7 to about 2.0 are preferred, with those where m=1.75 or m=2.0 being more preferred. Hosts where M is Sr and m is either 1.75 (SrAl₄O₇) or m is 2 (SrAl₂O₄) are preferred for use in blue phosphors of this invention.

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

This invention demonstrates that doping of trivalent metal ions, particularly trivalent rare earth metal ions, into the host matrix of this invention results in phosphors having improved phosphorescence brightness and persistence time. Dopants for creating trapping centers include trivalent rare earth metal ions: Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Yb³⁺, 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 or Pr or Ho and Y with Pr or Ho.

Phosphors of this invention also include those in which a portion of Al₂O₃ in the host is replaced with a divalent ion, such as Mg²⁺ or Zn²⁺ (alone or in combination) and those in which a portion of the alkaline earth metal ion (M²⁺) is replaced with a monovalent alkali metal ion, such as Na⁺ or K⁺ (alone or in combination). The doping level is designed to compensate the charge defects which are induced due to substitution of Sr²⁺ by R⁺.

This invention specifically exemplifies phosphors in powder or ceramic form prepared by combining the host, activator and trivalent metal ion dopants with a flux material. The flux material of most interest is B₂O₃. The properties of the powder and ceramic phosphors of this invention are significantly affected by the use of the flux material during preparation. Both the presence or absence of the flux and the amount of flux employed can affect phosphor properties. It has been demonstrated with the hosts of this invention that varying the molar amount of B₂O₃ relative to other components (where the molar proportion of M is 1) from about 0.02 to 0.2 (z in formulas herein) results in blue-emitting phosphors with acceptable persistence and brightness. Inclusion of the flux in a molar proportion z=about 0.08 to about 0.15 is preferred and inclusion of flux in a molar proportion z=about 0.1 to about 0.15 is more preferred.

B₂O₃ can be replaced in all formulations of this invention by an amount of H₂BO₃ sufficient to provide an equivalent molar amount of B (i.e., 2H₂BO₃ replaces each B₂O₃).

The exact role of the flux B₂O₃ in the phosphor properties is not clear. However, the phosphorescent phase in the compounds of this invention cannot be obtained without the use of flux. It is believed that the presence of flux is important to obtaining a particular phosphorescent phase with improved properties. The presence or absence of flux in the preparation of strontium aluminates can affect the ultimate structure of the aluminates. For example, when m=1.75 and M=Sr, the host material becomes Sr₄Al₄O₁₉ 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 Sr₄Al₂O₇ forms in the presence of flux is similar in structure to orthorhombic Sr₄Al₂O₇ (see FIG. 4). This material is monoclinic with space group C₁₆, C2/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 to 2 hours. 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 to 5% by volume H₂.

Sintered phosphor material can be used to grow single crystals or single crystal fibers. Any crystallization technique may 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 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:

\[(1-2x-2y)MCO₃+(nAl₂O₃)ₓ(EuₓZ̅₂y)₂(x+y)R₂O₃+zB₂O₃\]

and will have the general formula:

\[MₓO₁₋₂ₓ₋₂ᵧ(M₂₋ₓ₋₂ᵧAlₓ₂₋₂ᵧO₃₋ₓ₋₂ᵧ)(y₁R₁₂ₓ₋₂ᵧR₂₂ₓ₋₂ᵧB₂O₃)\]

where \(k=1-2x-2y\), \(m\) is a number ranging from about 1.6 to about 2.2, \(x\) can range from about 0.0001 to about 0.05 and is preferably about 0.001 to about 0.005, \(y\) can range from about 0.0001 to about 0.10 and the value of \(y\) is preferably equal to the value of \(x\) and \(z\) can range from about 0.02 to about 0.2. \(M\) is most generally an alkaline earth metal, but is preferably Sr or a mixture of Sr with Ca, Ba or both. \(R³⁺\) is generally one or more trivalent metal ions, but is preferably a trivalent metal ion selected from the group: Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, Tm³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tm³⁺, and Yb³⁺ and Bi³⁺. Preferred trivalent co-dopants are Pr³⁺, Ho³⁺, Dy³⁺, and Nd³⁺. Co-doping of Dy³⁺ or Y³⁺ along with other trivalent metal ions improves brightness of other phosphors of this invention.

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

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

\[MₓO₁₋₂ₓ₋₂ᵧ(M₂₋ₓ₋₂ᵧAlₓ₂₋₂ᵧO₃₋ₓ₋₂ᵧ)(y₁R₁₂ₓ₋₂ᵧR₂₂ₓ₋₂ᵧB₂O₃)\]

where \(k=1-2x-2y\), \(m\) 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 0.0001 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 \(R₁\) and \(R₂\).

The phosphors of this invention include those in which \(Al³⁺\) in the host is substituted by a divalent metal ion, particularly Mg²⁺ or Zn²⁺. These phosphors have the general formula:

\[MₓO₁₋₂ₓ₋₂ᵧ(M₂₋ₓ₋₂ᵧAlₓ₂₋₂ᵧO₃₋ₓ₋₂ᵧ)(y₁R₁₂ₓ₋₂ᵧR₂₂ₓ₋₂ᵧB₂O₃)\]

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. \(XO\) is a metal oxide, preferably MgO or ZnO and \(q\) can range from about 0.0001 to about 0.20. The amount of divalent ion \((q)\) from \(XO\) added to the matrix to replace \(Al³⁺\) is preferably equal to the amount of \(R₂\) divided into the matrix (i.e., the value of \(q\) preferably is the value of \(2y\)).

The phosphors of this invention include those in which \(M⁺²\) in the host is substituted by a monovalent alkali metal ion, particularly Na⁺ or K⁺. These phosphors have the general formula:

\[MₓO₁₋₂ₓ₋₂ᵧ(M₂₋ₓ₋₂ᵧAlₓ₂₋₂ᵧO₃₋ₓ₋₂ᵧ)(y₁R₁₂ₓ₋₂ᵧR₂₂ₓ₋₂ᵧB₂O₃)\]

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. \(Z₂O\) is an alkali metal oxide, preferably Na₂O or K₂O 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 \(Z₂O\) doped into the matrix (i.e., the value of \(r\) preferably is the value of \(2y\)). A slight excess over the desired or preferred amount of \(Z₂O\) 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: MO·\(m\)Al₂O₃, where \(M\) is an alkaline earth metal, and \(m\) is a number ranging from about 1.6 to about 2.2, the host containing from about 0.01 mol % to about 5 mol %, relative to \(M\), of an activator, and containing from about 0.01 mol % to about 5 mol %, relative to \(M\), of a trivalent metal ion dopant selected from the group of trivalent ions Pr³⁺, Ho³⁺, Nd³⁺, Dy³⁺, Er³⁺, 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 Bi₂O₃ in said host and/or wherein Bi₂O₃ is present in the host in an amount ranging from about 8 mol % to about 15 mol %, relative to M.

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

B. A phosphorescent material having the formula:

\[ M₂O \cdot mAl₂O₃ (dB₂O₃)_{2x}Eu^{3+},2yR^{3+}, \]

where: k=1-2x-2y, with y=y₁+y₂;

\[ mAl₂O₃ (dB₂O₃)_{2x}Eu^{3+},2yR^{3+}, \]

m is a number ranging from about 1.6 to about 2.2;

z is a number ranging from about 0.02 to about 0.2;

x is a number ranging from about 0.0001 to about 0.005;

y is a number ranging from about 0.0001 to about 0.005;

M is Sr²⁺ or a mixture of Sr²⁺ with Ca²⁺, Ba²⁺ or both; under 1.3 ton/cm² pressure before sintering. The powder or ceramic or single crystal form.

THE EXAMPLES

Example 1

Methods of Preparation of Blue Phosphors with Host Material MAI₂O₄ (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:

\[(1-x)Al₂O₃+yR₂O₃+yE₂O₃ \]

where:

x=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 0.10 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 Bi³⁺.

Bi₂O₃ is used as a flux in the composition and is important for ensuring the formation of the phosphorescent phase. Bi₂O₃ can be replaced by two molar equivalents of H₂BO₃.

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 into a fine powder suitable for sintering. The prefired powder is preferably again pressed into ceramic or single crystal form.

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⁺,
R\textsuperscript{3+} (Eu\textsuperscript{2+} and R\textsuperscript{3+} co-doped strontium aluminate) phosphors. These methods of preparation also specifically apply to Sr\textsubscript{x}Al\textsubscript{y}O\textsubscript{z},:Eu\textsuperscript{2+}-R\textsuperscript{3+} phosphors and the properties exhibited by SrAl\textsubscript{x}O\textsubscript{y},:Eu\textsuperscript{2+}-R\textsuperscript{3+} phosphors generally exemplify those of SrAl\textsubscript{x}O\textsubscript{y},:Eu\textsuperscript{2+}-R\textsuperscript{3+} phosphors.

SrAl\textsubscript{x}O\textsubscript{y},:Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} is prepared by the general method of Example 1 mixing the components in the following molar proportions:

$$0.97 \text{SrCO}_{3}+2.00 \text{Al}_{2}O_{3}+0.005 \text{Eu}_{2}O_{3}+0.01 \text{Pr}_{2}O_{3}+0.1 \text{B}_{2}O_{3}$$

where B\textsubscript{2}O\textsubscript{3} serves as a flux. The milled mixed powders are pelletized prior to prefiring and pelletized prior to sintering.

FIG. 1 shows the spectrum of the after-glow of a sample of SrAl\textsubscript{x}O\textsubscript{y},:0.01Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} exposed to a 4 W UV lamp for two minutes. The phosphorescence exhibits a broad band peaking at about 488 nm with a bandwidth of about 65 nm (2640 cm\textsuperscript{-1}). The figure illustrates phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

FIG. 2 is a graph of the decay of the after-glow of a sample of SrAl\textsubscript{x}O\textsubscript{y},:0.01Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of the after-glow of a commercial blue phosphor CaSrS:Bi after similar exposure is also shown (line b). The SrAl\textsubscript{x}O\textsubscript{y},:0.01Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} phosphor is about 10 times brighter than the commercial blue phosphor and has a persistence time about 20 times longer. After 18 hours SrAl\textsubscript{x}O\textsubscript{y},:0.01Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} intensity is still well above the threshold of eye-sensitivity (the horizontal dashed line).

FIG. 3 presents the excitation and emission spectra of SrAl\textsubscript{x}O\textsubscript{y},:0.01Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} where the excitation spectrum was monitored at 488 nm.

FIG. 4 is the x-ray diffraction pattern of the SrAl\textsubscript{x}O\textsubscript{y},:0.01Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} sample. This x-ray pattern indicated that the structure of SrAl\textsubscript{x}O\textsubscript{y},:0.01Eu\textsuperscript{2+}-0.02Pr\textsuperscript{3+} is similar to SrAl\textsubscript{x}O\textsubscript{y},:0.3B\textsubscript{2}O\textsubscript{3}.

Example 3

Preparation and Characterization of SrAl\textsubscript{x}O\textsubscript{y},(B\textsubscript{2}O\textsubscript{3})

:Eu\textsuperscript{2+}:Pr\textsuperscript{3+}, Phosphors with Varying Amounts of Eu\textsuperscript{2+}

Eu-concentration dependence of SrAl\textsubscript{x}O\textsubscript{y},:0.1B\textsubscript{2}O\textsubscript{3},:Eu\textsuperscript{2+}:Pr\textsuperscript{3+} phosphors after-glow was examined by preparing phosphor samples in which x (Eu\textsuperscript{2+} molar concentration) was varied from 0.001 to 0.015 as indicated in Table 1. In each case samples were pressed into pellets before prefiring and before sintering.

Table 1 shows time persistence of after-glow of the phosphor as a function of Eu\textsuperscript{2+} content (x) with Pr\textsuperscript{3+} content held at 0.01 (2x) as indicated in Table 2. 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 a 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>
<thead>
<tr>
<th>Samples</th>
<th>x</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>100</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>97</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\textsubscript{x}O\textsubscript{y},(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{x}O\textsubscript{y},(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:

$$0.99-2y \text{SrCO}_{3}+2.00 \text{Al}_{2}O_{3}+0.005 \text{Eu}_{2}O_{3}+y \text{Pr}_{2}O_{3}+0.1 \text{B}_{2}O_{3}$$

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 a 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>
<thead>
<tr>
<th>Samples</th>
<th>y</th>
<th>10 min after-glow</th>
<th>30 min after-glow</th>
<th>60 min after-glow</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>0.005</td>
<td>100</td>
<td>31</td>
<td>15</td>
</tr>
<tr>
<td>C-2</td>
<td>0.007</td>
<td>95</td>
<td>28</td>
<td>15</td>
</tr>
<tr>
<td>C-3</td>
<td>0.003</td>
<td>105</td>
<td>24</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\textsubscript{x}O\textsubscript{y},(B\textsubscript{2}O\textsubscript{3})

:Eu\textsuperscript{2+}:Ho\textsuperscript{3+}, Blue Phosphors

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

$$0.97 \text{SrCO}_{3}+2.00 \text{Al}_{2}O_{3}+0.005 \text{Eu}_{2}O_{3}+0.01 \text{Ho}_{2}O_{3}+0.1 \text{B}_{2}O_{3}$$

where B\textsubscript{2}O\textsubscript{3} serves as flux.

FIG. 5 shows the spectrum of the after-glow of a sample of SrAl\textsubscript{x}O\textsubscript{y},(0.1B\textsubscript{2}O\textsubscript{3}):0.01 Eu\textsuperscript{2+}:0.02 Ho\textsuperscript{3+} exposed to a 4 W UV lamp for two minutes. The phosphorescence exhibits...
a broad band peaking at about 488 nm with a bandwidth of about 60 nm (2640 cm⁻¹). The figure illustrates phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

FIG. 6 is a graph of decay of the after-glow of a sample of SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺ exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of the after-glow of 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).

FIG. 7 is the excitation and emission spectra of a sample of SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.02Ho³⁺ where the excitation spectrum was monitored at 488 nm.

Example 6

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

SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.02 Nd³⁺ was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

0.97 ScO₀₂+2.00 AlO₀₂+0.005 Eu₂O₃+0.01 Nd₂O₃+0.1 B₂O₃

where B₂O₃ serves as flux.

FIG. 8 shows the spectrum of the after-glow of a sample of SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.02 Nd³⁺ exposed to a 4 W UV lamp for two minutes. The phosphorescence exhibits a broad band peaking at about 488 nm with a bandwidth of about 60 nm (2640 cm⁻¹). The figure illustrates phosphorescence intensity as a function of wavelength 5 sec after exposure (squares), 20 sec after exposure (circles) and 60 sec after exposure (triangles).

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

FIG. 10 is the excitation and emission spectra of a sample of SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.02 Nd³⁺ where the excitation spectrum was monitored at 488 nm.

Example 7

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

SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.02 R³⁺ were prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

0.97 ScO₀₂+2.00 AlO₀₂+0.005 Eu₂O₃+0.01 R₂O₃+0.1 B₂O₃

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

FIG. 11 shows the decay curves of the after-glow of the 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 (W), Ce (●), Sm (□), Gd (○), Tb (∗), Dy (□), Er (△), Tm (○), Yb (×), and Lu (⊥). The decay curve of the sample SrAl₂O₄(0.1B₂O₃):Eu₂⁺Nd (closed circles) is also shown for comparison. It can be seen that the after-glow of these samples are generally less intense than analogous phosphor samples codoped with Nd. The sample codoped with Dy exhibits much longer decay time (shallower slope) than the Nd codoped phosphor. This indicates that Dy forms a much deeper trapping center than Nb, Ho, or Pr.

The luminescence spectra from SrAl₂O₄(0.1B₂O₃):0.01Eu₂⁺:0.02R³⁺ where R is La, Er, Nd, and Tm have similar wavelength dependence to that of the phosphor where R is Pr. There is no notable spectral shift with R.

Example 8

Preparation and Characterization of SrAl₂O₄(B₂O₃)
:0.01 Eu²⁺:0.01Pr²⁺:0.01R³⁺ where R is La, Lu, Er, Y, and Bi.

This example is intended to determine if co-doping of metal ions into a SrAl₂O₄(B₂O₃):Eu²⁺:Pr²⁺ phosphor increases UV excitation efficiency and improves phosphor brightness.

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

(1−2x−2y−3z+2B₂O₃)MCO₃+xAl₂O₃+yEu₂O₃+y₁Pr₂O₃+y₁R₂O₃+zB₂O₃

where y₁+y₂+y₃=1−2x−2y−3z and the ranges of in, x, y and z are as in formula 1 above.

More specifically where M=Sr and m=2 the components are combined in the following proportions:

0.97 ScO₀₂+2.00 AlO₀₂+0.005 Eu₂O₃+0.005 Pr₂O₃+0.05 R₂O₃+0.1 B₂O₃

where R=Y, La, Lu, Er, and Bi. The intensity of the after-glow of SrAl₂O₄(0.1B₂O₃):0.01Eu₂⁺:0.01Pr²⁺: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.

FIG. 12 shows decay curves of the after-glow of SrAl₂O₄(0.1B₂O₃):0.01Eu₂⁺:0.01Pr²⁺:0.01R³⁺ (R=Y³⁺, Lu³⁺, and La³⁺) samples in the first 60 minutes. The samples were exposed to a 4 W UV lamp for two minutes.

FIG. 13 is the excitation and emission spectra of the sample SrAl₂O₄(0.1B₂O₃):0.01Eu²⁺:0.01Pr²⁺:0.01Y³⁺ where the excitation spectrum was monitored at 488 nm. Codoping with Y³⁺ and Pr²⁺ increases the UV excitation...
efficiency and improve the brightness by 50% compared to the analogous Pr\(^{3+}\)-doped phosphor.

**TABLE 3**

<table>
<thead>
<tr>
<th>after (min)</th>
<th>Pr(^{3+})</th>
<th>Y</th>
<th>La</th>
<th>Lu</th>
<th>Er</th>
<th>Bi</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>

*Data is referenced to that of the SrAl\(_2\)O\(_4\):(B\(_2\)O\(_3\))Eu:Pr phosphor.*

**Example 9**

Preparation and Characterization of SrAl\(_2\)O\(_4\):(0.1B\(_2\)O\(_3\)):0.01Eu,0.01Dy,0.01Pr

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

\[
(1-2x-2y)MCO\(_3\)+nxCaCO\(_3\)+mAl\(_2\)O\(_3\)+xEu\(_2\)O\(_3\)+xR\(_2\)O\(_3\)+zB\(_2\)O\(_3\)
\]

where:

\[
y_1+y_2+y_m+n+x+y+z<1\]  

\[
is equal to x\]  

**TABLE 4**

The influence of deep centers of Dy on the after-glow of SrAl\(_2\)O\(_4\):(0.1B\(_2\)O\(_3\)):0.01Eu,0.01Pr

<table>
<thead>
<tr>
<th>after (min)</th>
<th>SAO-EuPr(^{3+})</th>
<th>SAO-EuPrDy</th>
<th>SAO-EuHoDy</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>301</td>
<td>252</td>
</tr>
<tr>
<td>30</td>
<td>31</td>
<td>99</td>
<td>75</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
<td>47</td>
<td>35</td>
</tr>
</tbody>
</table>

*Data is referenced to that of SAO-EuPr.*

**Example 10**

Preparation and Characterization of mixed alkaline earth aluminate phosphors

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

\[
(1-n-2x-2y)SrCO\(_3\)+nBaCO\(_3\)+mAl\(_2\)O\(_3\)+xEu\(_2\)O\(_3\)+yR\(_2\)O\(_3\)+zB\(_2\)O\(_3\)
\]

where:

\[
y_1+y_2+y_m+n+x+y+z<1\]  

\[
is equal to x\]  

**Example 11**

Preparation and Characterization of mixed alkaline earth aluminate phosphors

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

\[
(1-n-2x-2y)SrCO\(_3\)+nCaCO\(_3\)+mAl\(_2\)O\(_3\)+xEu\(_2\)O\(_3\)+yR\(_2\)O\(_3\)+zB\(_2\)O\(_3\)
\]

where:

\[
y_1+y_2+y_m+n+x+y+z<1\]  

\[
is equal to x\]  

The mixed alkaline earth aluminate compound, (Sr\(_{0.33}\),Ca\(_{0.41}\),Ba\(_{0.26}\))Al\(_2\)O\(_4\):(0.01Eu,0.02Pr) was prepared following the general procedure of Example 1 combining the components in the following molar proportions:

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

These mixed alkaline earth phosphor have the general formula:

\[
\text{Sr}_k\text{Ba}_y\text{O} \cdot \text{mAl}_2\text{O}_3 \cdot \text{zB}_2\text{O}_3 ; \text{2xEu} \cdot \text{2yR} \cdot \text{2zB}_2\text{O}_3
\]

Figure 16 shows the luminescence spectra of this phosphor. A small red shift of 27 nm was observed compared to the analogous Sr phosphor.

**Example 12**

Preparation and Characterization of mixed alkaline earth aluminate phosphors

Phosphors containing Sr, Ca and Ba can also be prepared by combining the components in the following molar proportions:

\[
(1-n-2x-2y)\text{SrCO}_3+\text{pBaCO}_3+\text{nCaCO}_3+\text{mAl}_2\text{O}_3+\text{xEu}_2\text{O}_3+\text{yR}_2\text{O}_3+\text{zB}_2\text{O}_3
\]

where:

\[n+p+x+y+z<1\]

\[R\] is a trivalent rare earth ion or Bi\(^{3+}\).

The mixed alkaline earth aluminate compound, (Sr\(_{0.33}\),Ca\(_{0.41}\),Ba\(_{0.26}\))Al\(_2\)O\(_4\):(0.01Eu,0.02Pr) were prepared as in Example 1 combining the components in the following molar proportions:

\[
0.485 \text{SrCO}_3+0.485 \text{CaCO}_3+2.00 \text{Al}_2\text{O}_3+0.005 \text{Eu}_2\text{O}_3+0.01 \text{Pr}_2\text{O}_3+0.1 \text{B}_2\text{O}_3
\]

where:

\[n+p+x+y+z<1\]

\[R\] is a trivalent rare earth ion or Bi\(^{3+}\).

**FIG. 15** shows the luminescence spectra of the (Sr\(_{0.33}\),Ca\(_{0.41}\),Ba\(_{0.26}\))Al\(_2\)O\(_4\):(0.01Eu,0.02Pr) sample. No obvious spectral shift compared to the Sr phosphor was observed.
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:

\[ \text{Sr, Ba, Ca, O} \cdot m Al_2 O_3 \cdot z B_2 O_3 \cdot 2x Eu_2 y R_2 y \]

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

Example 12
Codoping of Mg
2+
+ or Zn
2+
+ into MO .

mAl_2 O_3:Eu
2+, R
3+
+ phosphors

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

\[ (1-2x-2y)MC_0_2 + (m-q)Al_2 O_3 + xEu_2 y R_2 y + qXO + zB_2 O_3 \]

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

\[ M_2 O \cdot m Al_2 O_3 \cdot rNaZO:2xEu,2yR, \]

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

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

\[ 0.98 \text{Sc}_2 O_3 + 1.99 Al_2 O_3 + 0.01 SO_4 + 0.005 Eu_2 O_3 + 0.005 \text{ Dy}_2 O_3 + 0.1 B_2 O_3 \]

where XO can be MgO or ZnO.

Table 5 provides measurements of relative after-glow intensity at 488 nm of strontium aluminate (SrAl_2 O_3) phosphors in which Na
+ or K
+ replaces Sr
3+
+.

<table>
<thead>
<tr>
<th>After (min)</th>
<th>SAO-EnPr (^1)</th>
<th>SAO-EnPr/Mg</th>
<th>SAO-EnPr/Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>104</td>
<td>104</td>
<td>104</td>
</tr>
<tr>
<td>30</td>
<td>33</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>60</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
</tbody>
</table>

\(^1\)Data is referenced to that of SAO-EnPr.

Example 13
Co-doping of Na
+ or K
+ into MO .
mAl_2 O_3:Eu
2+, R
3+
+ phosphors

In phosphor materials of this invention, M
3+
+, 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:

\[ (1-2x-2y)MC_0_2 + (m-q)Al_2 O_3 + xR_2 y + qSO_4 + zB_2 O_3 \]

where: 2x+2y+2r is less than 1;
where \( r \) preferably ranges from 0.002 to 0.2; and the ranges for x, y, m and z are as given in formula 1.
Z
2+CO_3, in particular, can be Na_2 CO_3 and/or K_2 CO_3.

These phosphors will have the generic formula:

\[ M_2 O \cdot m Al_2 O_3 \cdot (Na_2 O.02eEu.2yR, \]

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

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

\[ 0.97 \text{Sc}_2 O_3 + 2 Al_2 O_3 + 0.005 Eu_2 O_3 + 0.005 \text{ Dy}_2 O_3 + 0.005 X_2 O_3 + 0.1 B_2 O_3 \]

where Z
2+CO_3 can be Na_2 CO_3 or K_2 CO_3.

Table 6 provides measurements of relative after-glow intensity at 488 nm of strontium aluminate (SrAl_2 O_3) phosphors in which Na
+ or K
+ replaces Sr
3+
+.

<table>
<thead>
<tr>
<th>After (min)</th>
<th>SAO-EnPr (m)</th>
<th>SAO-EnPr/Na</th>
<th>SAO-EnPr/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>112</td>
<td>135</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>34</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>17</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\)Data is referenced to that of SAO-EnPr.

Example 14
Preparation and Characterization of Alkaline earth aluminate phosphors of varying ratio of Al/M
A series of strontium aluminate phosphors activated with Eu
2+
+ and doped with Pr
3+
+ were prepared having different ratios of Al/Sr. Phosphor components were mixed according to the molar proportions:

\[ 0.98 \text{Sc}_2 O_3 + m Al_2 O_3 + 0.005 Eu_2 O_3 + 0.005 \text{ Pr}_2 O_3 + 0.1 B_2 O_3 \]

with m=1.6, 1.75, 1.85, 1.95, 2.0, and 2.15 and phosphors prepared according to the general procedure of Example 1.

Table 7 provides measurements of relative after-glow intensity at 488 nm of strontium aluminates as indicated. All of the samples tested have acceptable brightness and persistence. The sample where m=1.75 corresponding to Sr_2 Al_1 O_2.5 exhibits somewhat brighter phosphorescence.

<table>
<thead>
<tr>
<th>After (min)</th>
<th>1.6</th>
<th>1.75</th>
<th>1.85</th>
<th>1.95</th>
<th>2.0</th>
<th>2.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>113</td>
<td>121</td>
<td>106</td>
<td>100</td>
<td>100</td>
<td>88</td>
</tr>
<tr>
<td>30</td>
<td>37</td>
<td>37</td>
<td>32</td>
<td>31</td>
<td>30</td>
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<tr>
<td>60</td>
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<td>16</td>
<td>15</td>
<td>14</td>
<td>14</td>
<td>12</td>
</tr>
</tbody>
</table>

\(^1\)Data is referenced to that at m = 2.

Example 15
Effect of variation of the amount of flux on phosphor properties
A series of strontium aluminate phosphors (SrAl_2 O_3) activated with Eu
2+
+ and doped with Pr
3+
+ were prepared
using varying amounts of flux (zB₂O₃). Phosphor components were mixed according to the molar proportions:

\[ 0.08 \text{ SrCO}_3 + \text{mAl}_{2}O_3 + 0.005 \text{ Eu}_2O_3 + 0.005 \text{ Pr}_2O_3 + zB₂O₃ \]

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

Table 8 provides measurements of relative after-glow intensity at 488 nm of strontium aluminates as indicated. The samples where \( z = 0.03 \) to 0.20 have acceptable brightness and persistence. The sample where \( z = 0.12 \) was brighter than other samples tested.

**Example 16**

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

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

\[ (4-8x-8y) \text{MC}_0 + 7.00 \text{Al}_x\text{O}_y + 4x\text{Eu}_2O_3 + 4y\text{R}_2O_3 + 4zB₂O₃ \]

where:

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

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

**TABLE 8**

<table>
<thead>
<tr>
<th>After/min.</th>
<th>0.03</th>
<th>0.05</th>
<th>0.08</th>
<th>0.10</th>
<th>0.12</th>
<th>0.15</th>
<th>0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>113</td>
<td>121</td>
<td>106</td>
<td>100</td>
<td>125</td>
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<td>37</td>
<td>37</td>
<td>32</td>
<td>31</td>
<td>41</td>
<td>32</td>
<td>30</td>
</tr>
<tr>
<td>60</td>
<td>17</td>
<td>16</td>
<td>15</td>
<td>14</td>
<td>17</td>
<td>15</td>
<td>14</td>
</tr>
</tbody>
</table>

\(^4\)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 hereinafter and the mixtures are milled or ground to give a homogeneous fine powder. The powder is pressed into pellets under about 1.3 ton/cm² pressure. The pressed pellets are then prefired in air at about 600°C for about one hour. The prefired pellets are pulverized and milled again into a fine powder. The prefired powder is pressed again into ceramic pellets at the same pressure. The pellets are then sintered at about 1,300°C for one hour in a flowing \( \text{H}_2-\text{N}_2 \) gas mixture (2%–5% by volume \( \text{H}_2 \)) with a flow rate of about 0.1 liter/min. \( \text{Eu} \) in the material is reduced to the divalent state, while the other metallic ions remain in the original valence state. The sintered pellets are cut into bars with cross-sections of about 1x1 mm. The bars are carefully cleaned with solvents (such as alcohol or acetone) before introduction into the growth chamber. The growth chamber is filled with inert gas (or a mixture of inert gas and <1% \( \text{H}_2 \), e.g., 99.99% \( \text{N}_2 \)). Care must be taken to prevent re-oxidation of the europium ions from the 2+ state to the 3+ state and to prevent reduction to the monovalent state or metal at the melting temperature. Other metals present in the material should remain in their original valence state.


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

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

We claim:

1. A phosphor represented by the formula:

\[ \text{M}_o\text{Al}_x\text{O}_y\text{Eu}^{2+},\text{R}^{3+} \]

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

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

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

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

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

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

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

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

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

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...
21. 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\(^{3+}\), Tm\(^{3+}\), Yb\(^{3+}\), Sm\(^{3+}\), Gd\(^{3+}\), Tb\(^{3+}\), and Bi\(^{3+}\).

12. A phosphor having the formula:

\[ \text{Sr}_{\text{k}}\text{Ba}_{\text{n}}\text{Ca}_{\text{p}}\text{O}_{\text{m}} \cdot \text{mAl}_{\text{z}}\text{O}_{\text{3}}\cdot \text{Eu}_{\text{x}}\text{R}_{\text{y}} \]

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

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

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

\[ \text{MO} \cdot \text{mAl}_{\text{z}}\text{O}_{\text{3}}\cdot \text{Eu}_{\text{x}}\text{R}_{\text{y}} \]

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 10 mol % of M. A phosphor represented by the formula:

\[ \text{MO} \cdot \text{mAl}_{\text{z}}\text{O}_{\text{3}}\cdot \text{Eu}_{\text{x}}\text{R}_{\text{y}} \]

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 wherein a portion of the M\(^{2+}\) in the phosphor is substituted by a divalent metal ion.

20. 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.

21. 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 %.

22. The phosphor of claim 21 in which the divalent ion is Mg\(^{2+}\) or Zn\(^{2+}\) or a mixture thereof.

23. The phosphor of claim 22 in which the amount of divalent metal ion substituted into the phosphor ranges from about 0.02 mol % to about 20 mol %.

24. The phosphor of claim 21 in which the amount of divalent metal ion substituted into the phosphor is equal to the amount of R\(^{3+}\) the phosphor.

25. The phosphor of claim 21 wherein R\(^{3+}\) is Pr\(^{3+}\), Ho\(^{3+}\), Nd\(^{3+}\), Dy\(^{3+}\), Er\(^{3+}\), Tm\(^{3+}\), Yb\(^{3+}\), or Bi\(^{3+}\).

26. The phosphor of claim 21 wherein R\(^{3+}\) is a mixture of Pr\(^{3+}\), Ho\(^{3+}\), Nd\(^{3+}\), Dy\(^{3+}\), Er\(^{3+}\), Tm\(^{3+}\), Yb\(^{3+}\), or Bi\(^{3+}\).

27. The phosphor of claim 21 wherein R\(^{3+}\) is a mixture of Y\(^{3+}\) with another trivalent metal ion.

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

29. The phosphor of claim 15 further comprising from about 2 mol % to about 20 mol % of B\(_2\)O\(_3\).

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

**Title page.**
Item [57], **ABSTRACT**
Delete "MO.mA12O3:Eu²⁺,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 "M₁₋₃Al₂O₄₋ₓ Where" and replace with -- M₁₋₃Al₂O₄₋ₓ, where --.

**Column 2.**
Line 16, delete the comma after "Eu²⁺".
Lines 22-23, delete "2SrO.3Al₂O₃:Eu²⁺" and replace with -- 2SrO.3Al₂O₃:Eu²⁺ --.
Lines 25-26, delete "4SrO.7Al₂O₃:Eu²⁺" and replace with -- 4SrO.7Al₂O₃:Eu²⁺ --.
Line 26, delete "BaO.4Al₂O₃:Eu⁺⁺" and replace with -- BaO.4Al₂O₃:Eu⁺⁺ --.
Line 38, delete "MO.mAl₂O₃:Eu²⁺,R³⁺" and replace with -- MO.mAl₂O₃:Eu²⁺,R³⁺ --.
Line 47, delete "MO.mAl₂O₃(zB₂O₃):Eu²⁺,R³⁺" and replace with -- MO.mAl₂O₃(zB₂O₃): Eu²⁺,R³⁺ --.

**Column 4.**
Line 32, delete "Sr₀.₆₀Ba₂.₃₃Al₄O₇" and replace with -- Sr₀.₃₃Ba₂.₆₆Al₄O₇ --.
Line 36, delete "Sr₀.₄₉Ca₀.₄₉Al₄O₇" and replace with -- Sr₀.₄₈₅Ca₀.₄₈₅Al₄O₇ --.

**Column 5.**
Line 9, delete "pressure" and replace with -- pressures --.
Line 13, delete "distinguishable" and replace with -- distinguishable --.
Line 16, delete "one the order" and replace with -- on the order --.
Line 38, delete "lasting form" and replace with -- lasting from --.
Line 46, delete "can exhibit" and replace with -- can exhibit --.
Line 49, delete "exhibit" and replace with -- exhibit --.
Line 55, delete "MO.mAl₂O₃" and replace with -- MO.mAl₂O₃ --.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 7,
Line 10, delete "pellets are the" and replace with -- pellets are then --.
Line 15, delete "laser heated pedestal method" and replace with -- laser heated pedestal growth (LHPG) method --.
Line 16, delete "bars to" and replace with -- bars for --.
Line 20, delete "somehat" and replace with -- somewhat --.
Line 28, delete "LHGP" and replace with -- LHPG --.
Line 42, delete "M₀.mAl₂O₃(z₀B₂O₃):2xEu²⁺,2yR³⁺n" and replace with -- M₀.mAl₂O₃(z₀B₂O₃):2xEu²⁺,2yR³⁺ --.

Column 8,
Line 1, delete "M₀.mAl₂O₃(z₀B₂O₃):2xEu²⁺,2y₁R₁³⁺,2y₂R₂³⁺n" and replace with -- M₀.mAl₂O₃(z₀B₂O₃):2xEu²⁺,2y₁R₁³⁺,2y₂R₂³⁺ --.
Line 15, delete "M₀.(m-q)Al₂O₃.qXO(z₀B₂O₃):2xEu²⁺,2yR³⁺n" and replace with -- M₀.(m-q)Al₂O₃.qXO(z₀B₂O₃):2xEu²⁺,2yR³⁺ --.
Line 31, delete "M₀.mAl₂O₃.rZ₂(z₀B₂O₃):2xEu²⁺,2yR³⁺n" and replace with -- M₀.mAl₂O₃.rZ₂(z₀B₂O₃):2xEu²⁺,2yR³⁺ --.
Line 60, delete "MO.mAl₂O₃" and replace with -- MO.mAl₂O₃ --.

Column 9,
Line 10, delete "M₀.mAl₂O₃(z₀B₂O₃):2xEu²⁺,2yR³⁺n" and replace with -- M₀.mAl₂O₃(z₀B₂O₃):2xEu²⁺,2yR³⁺ --.
Line 28, delete "M₀.mAl₂O₃(z₀B₂O₃):2xEu²⁺,2y₁R₁³⁺,2y₂R₂³⁺n" and replace with -- M₀.mAl₂O₃(z₀B₂O₃):2xEu²⁺,2y₁R₁³⁺,2y₂R₂³⁺ --.
Line 50, delete "M₀.(m-q)Al₂O₃.qXO(z₀B₂O₃):2xEu²⁺,2yR³⁺n" and replace with -- M₀.(m-q)Al₂O₃.qXO(z₀B₂O₃):2xEu²⁺,2yR³⁺ --.
Line 67, delete "M₀.mAl₂O₃.rZ₂(z₀B₂O₃):2xEu²⁺,2yR³⁺n" and replace with -- M₀.mAl₂O₃.rZ₂(z₀B₂O₃):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 "Sr₂Ba₂Ca₄O₉.mAl₂O₃(z₀B₂O₃):2xEu²⁺,2yR³⁺n" and replace with -- Sr₂Ba₂Ca₄O₉.mAl₂O₃(z₀B₂O₃):2xEu²⁺,2yR³⁺ --.
Line 45, delete "Bi²⁺" and replace with -- Bi³⁺ --.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 11,
Lines 6 and 16, delete "SrAlO$_7$:0.01Eu$^{2+}$,0.02Pr$^{3+}$" and replace with
-- SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Pr$^{3+}$ --.
Line 25, delete "SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Pr$^{3+}$" and replace with
-- SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Pr$^{3+}$ --.
Lines 29, 32, 37 and 39-40, delete "SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Pr$^{3+}$" and replace with
-- SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Pr$^{3+}$ --.
Line 46, delete "SrAlO$_7$(B$_2$O$_3$):Eu$^{2+}$,Pr$^{3+}$" and replace with -- SrAlO$_7$(B$_2$O$_3$):Eu$^{2+}$,Pr$^{3+}$ --.
Lines 50-51, delete "SrAlO$_7$(0.1B$_2$O$_3$):Eu$^{2+}$,Pr$^{3+}$" and replace with -- SrAlO$_7$(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 "SrAlO$_7$(0.1B$_2$O$_3$):Eu$^{2+}$,Pr$^{3+}$" and replace with -- SrAlO$_7$
(0.1B$_2$O$_3$):Eu$^{2+}$,Pr$^{3+}$ --.
Line 43, Table 2, delete "SrAlO$_7$(B$_2$O$_3$):0.01Eu:2yPr" and replace with -- SrAlO$_7$
(B$_2$O$_3$):0.01Eu,2yPr --.
Lines 55-56, delete "SrAlO$_7$(B$_2$O$_3$):Eu$^{2+}$,Ho$^{3+}$" and replace with -- SrAlO$_7$(B$_2$O$_3$):Eu$^{2+}$,
Ho$^{3+}$ --.
Lines 58 and 66, delete "SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Ho$^{3+}$" and replace with -- SrAlO$_7$
(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Ho$^{3+}$ --.

Column 13,
Lines 8, 14, 17 and 22, delete "SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Ho$^{3+}$" and replace with -- SrAlO$_7$
(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Ho$^{3+}$ --.
Lines 29-30, delete "SrAlO$_7$(B$_2$O$_3$):Eu$^{2+}$,Nd$^{3+}$" and replace with -- SrAlO$_7$(B$_2$O$_3$):Eu$^{2+}$,
Nd$^{3+}$ --.
Lines 33, 43, 53, 58, 61 and 66, delete "SrAlO$_7$(0.1B$_2$O$_3$):0.01Eu$^{2+}$,0.02Nd$^{3+}$" and replace with -- SrAlO$_7$(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 "$\text{SrAl}_2\text{O}_4(0.1\text{B}_2\text{O}_3):0.01\text{Eu}^{2+}:0.02\text{R}^{3+}$" and replace with $\text{SrAl}_2\text{O}_4(0.1\text{B}_2\text{O}_3):0.01\text{Eu}^{2+},0.02\text{R}^{3+}$ --.
Line 19, after "(+)", please insert -- are shown --.
Lines 34-35, delete "$\text{SrAl}_2\text{O}_4(\text{B}_2\text{O}_3):0.01\text{Eu}^{2+}:0.01\text{Pr}^{3+}:0.01\text{R}^{3+}$" and replace with $\text{SrAl}_2\text{O}_4(\text{B}_2\text{O}_3):0.01\text{Eu}^{2+},0.01\text{Pr}^{3+},0.01\text{R}^{3+}$ --.
Line 38, delete "$\text{SrAl}_2\text{O}_4(\text{B}_2\text{O}_3):\text{Eu}^{2+}:\text{Pr}^{3+}$" and replace with $\text{SrAl}_2\text{O}_4(\text{B}_2\text{O}_3):\text{Eu}^{2+},\text{Pr}^{3+}$ --.
Line 48, delete "ranges of in" and replace with -- ranges of m --.
Lines 56 and 60-61, delete "$\text{SrAl}_2\text{O}_4(0.1\text{B}_2\text{O}_3):0.01\text{Eu}:0.01\text{Pr}:0.01\text{R}$" and replace with $\text{SrAl}_2\text{O}_4(0.1\text{B}_2\text{O}_3):0.01\text{Eu},0.01\text{Pr},0.01\text{R}$ --.

**Column 15.**
Line 13, delete "((Sr_{0.33} \text{Ba}_{0.66})(0.1\text{B}_2\text{O}_3)\text{Al}_4\text{O}_7):0.01\text{Eu}:0.02\text{Pr}" and replace with -- (Sr_{0.33} \text{Ba}_{0.64})(0.1\text{B}_2\text{O}_3)\text{Al}_4\text{O}_7:0.01\text{Eu},0.02\text{Pr} --.
Line 22, delete "$\text{Sr}_3\text{Ba}_4\text{O}_3\text{Al}_4\text{O}_7(\text{B}_2\text{O}_3):2x\text{Eu},2y\text{R}$" and replace with $\text{Sr}_3\text{Ba}_4\text{O}_3\text{Al}_4\text{O}_7(\text{B}_2\text{O}_3):2x\text{Eu},2y\text{R}$ --.
Line 48, delete "$\text{Sr}_3\text{Ca}_9\text{O}_3\text{Al}_4\text{O}_7(\text{B}_2\text{O}_3):2x\text{Eu},2y\text{R}$" and replace with $\text{Sr}_3\text{Ca}_9\text{O}_3\text{Al}_4\text{O}_7(\text{B}_2\text{O}_3):2x\text{Eu},2y\text{R}$ --.
Line 52, delete "((Sr_{0.485} \text{Ca}_{0.485})\text{Al}_4\text{O}_7):0.01\text{Eu}:0.02\text{Pr}" and replace with -- (Sr_{0.485} \text{Ca}_{0.485})\text{Al}_4\text{O}_7:0.01\text{Eu},0.02\text{Pr} --.
Lines 58-59, delete "((Sr_{0.485} \text{Ca}_{0.485})(0.1\text{B}_2\text{O}_3)\text{Al}_4\text{O}_7:0.01\text{Eu}:0.02\text{Pr}" and replace with -- (Sr_{0.485} \text{Ca}_{0.485})(0.1\text{B}_2\text{O}_3)\text{Al}_4\text{O}_7:0.01\text{Eu},0.02\text{Pr} --.

**Column 17.**
Line 7, delete "$\text{Sr}_3\text{Ba}_4\text{Ca}_9\text{O}_3\text{Al}_4\text{O}_7(\text{B}_2\text{O}_3):2x\text{Eu},2y\text{R}$" and replace with $\text{Sr}_3\text{Ba}_4\text{Ca}_9\text{O}_3\text{Al}_4\text{O}_7(\text{B}_2\text{O}_3):2x\text{Eu},2y\text{R}$ --.
Lines 13-14 and 57-58, delete "$\text{MO}.m\text{Al}_2\text{O}_3:2x\text{Eu},2y\text{R}$" and replace with -- $\text{MO}.m\text{Al}_2\text{O}_3:2x\text{Eu},2y\text{R}$ --.
Line 29, delete "$\text{M}_4\text{O}.(m-q)\text{Al}_2\text{O}_3.q\text{XO}:2x\text{Eu},2y\text{R}$" and replace with -- $\text{M}_4\text{O}.(m-q)\text{Al}_2\text{O}_3.q\text{XO}:2x\text{Eu},2y\text{R}$ --.

**Column 18.**
Line 6, delete "$\text{M}_6\text{O}.m\text{Al}_2\text{O}_3.r\text{Na}_2\text{O}:2x\text{Eu},2y\text{R}$" and replace with -- $\text{M}_6\text{O}.m\text{Al}_2\text{O}_3.r\text{Na}_2\text{O}:2x\text{Eu},2y\text{R}$ --.
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 "SrKBa,Ca,0.mAl2O3:2xEu2+,2yR3+ " and replace with
-- SrKBa,Ca,0.mAl2O3:2xEu2+,2yR3+ --.
Line 15, delete "v" and replace with -- y --.
Lines 22 and 37, delete "MO.mAl2O3:Eu2+,R3+" and replace with -- MO.mAl2O3:Eu2+,R3+ --.

Column 22,
Line 4, delete "M3+" and replace with -- M3+ --.
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