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

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

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

30 Claims, 16 Drawing Sheets
OTHER PUBLICATIONS

FIG. 1
FIG. 3
FIG. 5
FIG. 8

- ○ after 5 sec
- ○ after 20 sec
- △ after 60 sec

Intensity (a.u.)

Wavelength (nm)
Figure 9

A log-log plot showing the relationship between intensity (a.u.) and delay time (minutes). The graph includes three lines labeled 'a', 'b', and 'c', each representing different conditions or data sets. The x-axis represents delay time in minutes, while the y-axis represents intensity in a.u. with a logarithmic scale.
FIG. 10
FIG. 11
FIG. 12
FIG. 13
FIG. 14

Graph showing the relationship between intensity (a.u.) and delay time (minutes). The graph is a log-log plot with intensity on the y-axis and delay time on the x-axis. Three curves are plotted: a, b, and c, each representing a different decay process.

- Curve a: A steep decline indicating a faster decay rate.
- Curve b: A moderate decline indicating a medium decay rate.
- Curve c: A gentle decline indicating a slower decay rate.

The intensity values range from $10^2$ to $10^6$, and the delay times range from 1 to 1000 minutes.
FIG. 15
FIG. 16

- ○ after 5 sec
- ○ after 20 sec
- ▲ after 60 sec

Intensity (a.u.)

Wavelength (nm)
1 LONG-PERSISTENCE BLUE PHOSPHORS
CROSS-REFERENCE TO RELATED APPLICATIONS

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

This invention was made at least in part with U.S. government funding through NASA grant MURC-NCCW-0088 and NCC5–252, ARO DAAH04-96–10416 and DOE DE-FG02–94ER57564. The United States government has certain rights in this invention.

FIELD OF THE INVENTION

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

BACKGROUND OF THE INVENTION

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

Strong green luminescence from Eu$^{2+}$-doped SrAlO$_2$ was reported by H. Lange in Belgian patent 1,347,475 and U.S. Pat. No. 3,294,696. Efficient luminescence in the spectral range 450–520 nm was also reported from Eu$^{2+}$-doped CaAl$_2$O$_4$, MgAl$_2$O$_4$, BaAl$_2$O$_4$, and SrAlO$_2$ and their counterparts using alkaline earth cationic combinations. (C. Palilla, A. K. Levine and M. R. Tomkis (1968) J. Electrochem. Soc. 115:642).

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 SrAlO$_2$ 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 SrAlO$_2$ and Nd$^{3+}$ with Eu$^{2+}$ into CaAlO$_2$ 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 SrAlO$_2$: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 SrAlO$_2$:Eu$^{2+}$, Dy$^{3+}$.

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

SUMMARY OF THE INVENTION

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

$$\text{MO}_{1-m} \text{Al}_m \text{O}_2: \text{Eu}^{2+}, \text{R}^{3+}$$

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; 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:

$$\text{MO}_{1-m} \text{Al}_m \text{O}_2(2\text{B}_2\text{O}_3): \text{Eu}^{2+}, \text{R}^{3+}$$

where M, m and R$^{3+}$ are as defined in formula 1 and x 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 % of R$^{3+}$, 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 % of R$^{3+}$ (preferably about 0.2 mol % to about 2 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 phosphorescent band at about 488 nm. 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.
Phosphors in ceramic form can be used for manufacture of powder form or as a ceramic. Phosphor materials of this kind include SrAl₄O₉:Eu₃⁺ after exposure to a 13 W fluorescent lamp for 10 minutes. The threshold of eye sensitivity is indicated by a horizontal dashed line.

FIG. 1 illustrates the excitation and emission spectra of SrAl₄O₉:Eu³⁺, Pr³⁺, and Ho³⁺ after exposure to a 4 W UV lamp for 2 minutes as a function of time after illumination (C), after 20 sec., and after 60 sec.

Partial 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 quantum efficiency of the activated material) 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 luminescence to occur.

Phosphors exhibit persistence times greater than about 10-12 hrs. The exact role of the flux in the phosphor properties has been difficult to grow crystals from the melt.  

Phosphors facilitate studies of phosphorescence dynamics. Phosphorescence intensity and/or long persistence of phosphorescence can be used to refer to ZnS:Cu, CaS:Eu, Tm, and similar materials.  

Phosphors exhibit persistence times greater than about 3-5 hrs. More preferred phosphors exhibit persistence times greater than about 10-12 hrs.  

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.

This invention specifically exemplifies phosphors in powder or ceramic form prepared by combining the host, activator and trivalent metal ion dopants with a flux material. The flux material of most interest is B₂O₃. The properties of the powder and ceramic phosphors of this invention are significantly affected by the use of the flux material during preparation. Both the presence or absence of the flux and the amount of flux employed can affect phosphor properties. It has been demonstrated with the hosts of this invention that varying the molar amount of B₂O₃ relative to other components (where the molar proportion of M is 1) from 0.02 to 0.2 (z in formulas herein) results in blue-emitting phosphors with acceptable persistence and brightness. Inclusion of the flux in a molar proportion z=about 0.08 to about 0.15 is preferred and inclusion of flux in a molar proportion z=about 0.1 to about 0.15 is more preferred. B₂O₃ can be replaced in all formulations of this invention by an amount of H₂BO₃ sufficient to provide an equivalent molar amount of B (i.e., 2H₂BO₃ replaces each B₂O₃).

The exact role of the flux B₂O₃ in the phosphor properties is not clear. However, the phosphorescent phase in the compounds of this invention cannot be obtained without the use of flux. It is believed that the presence of flux is importan 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 Sr₅Al₂O₇ 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 Sr₅Al₂O₇ formed in the presence of flux is similar in structure to orthorhombic Sr₅Al₂O₇ (see FIG. 4). This material is monoclinic with space group C₂h.₅,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 combined 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.

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 Al 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 material 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.
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. The preferred 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., \( H_2/N_2 \) having 2-5% by volume \( H_2 \).

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 (1x1 mm x1.5x1.5 mm pieces). The bars are carefully cleaned prior to introduction into the chamber which is filled with a non-reactive or inert gas (e.g., \( N_2 \)) or a somewhat reducing gas (about 1% by volume \( H_2 \) in \( N_2 \)). Care should be taken to minimize or avoid reoxidation of Eu\(^{2+}\) 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:

\[
1-2x-2y M,O_{3-x} Al_{2}O_{3-x} Fe_{2}O_{3-y} R_{2}O_{3-y} B_{2}O_{3}
\]

and will have the general formula:

\[
M_{1-x} \cdot \text{Al}_{x} \cdot \text{O}_{3-x} \cdot \text{B}_{2} \cdot \text{O}_{3-z} \cdot \text{Fe}_{2} \cdot \text{O}_{3-y} \cdot \text{R}_{2} \cdot \text{O}_{3-y} \cdot \text{Eu}_{2} \cdot \text{O}_{3-y} \cdot \text{R}_{3}^{+} \cdot \text{B}_{2} \cdot \text{O}_{3-z}
\]

where \( k = 1-2x-2y \), \( m \) is a number ranging from about 1.6 to about 1.2, \( x \) can range from about 0.0001 to about 0.05 and is preferably about 0.005 to about 0.0005, \( y \) 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. \( R^{3+} \) is generally one or more trivalent metal ions, but is preferably a trivalent metal ion selected from the group: \( \text{Pr}^{3+}, \text{Ho}^{3+}, \text{Nd}^{3+}, \text{Dy}^{3+}, \text{Er}^{3+}, \text{Lu}^{3+}, \text{Ce}^{3+}, \text{Y}^{3+}, \text{Sm}^{3+}, \text{Gd}^{3+}, \text{Th}^{3+}, \text{Yb}^{3+} \) and \( \text{Bi}^{3+} \). Preferred trivalent codopants are \( \text{Pr}^{3+}, \text{Ho}^{3+}, \text{Dy}^{3+}, \text{Nd}^{3+} \) and \( \text{Nd}^{3+} \). Co-doping of \( \text{Dy}^{3+} \) or \( \text{Y}^{3+} \) along with other trivalent metal ions improves brightness of other phosphors of this invention.

The combined phosphor components are milled or ground into a homogeneous fine powder, optionally pressed into pellets and prefired in air for about 1 hr at about 600°C. The prefired material is milled or ground into a fine powder for sintering. The powder is optionally pressed before sintering. The material is sintered at about 1300°C for one hour in a reducing atmosphere, such as a mixture of \( N_2 \) and \( H_2 \) (about 1-5% by volume).

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

\[
M_{x} \cdot \text{Al}_{y} \cdot \text{O}_{3-x} \cdot \text{B}_{2} \cdot \text{O}_{3-z} \cdot \text{Fe}_{2} \cdot \text{O}_{3-y} \cdot \text{R}_{2} \cdot \text{O}_{3-y} \cdot \text{Eu}_{2} \cdot \text{O}_{3-y} \cdot \text{R}_{3}^{+} \cdot \text{B}_{2} \cdot \text{O}_{3-z}
\]

where \( k = 1-2x-2y \), \( m \) is as defined above, \( y_{+} + y_{-} = y \), and \( R_{1} \) and \( R_{2} \) are two different trivalent metal ions. The number \( x \) can range from about 0.0001 to about 0.05 and is preferably about 0.01 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 equal amounts of \( R_{1} \) and \( R_{2} \).

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

\[
M_{1-x} \cdot \text{Al}_{x} \cdot \text{O}_{3-x} \cdot \text{Zn}_{2} \cdot \text{O}_{3-z} \cdot \text{Fe}_{2} \cdot \text{O}_{3-y} \cdot \text{Eu}_{2} \cdot \text{O}_{3-y} \cdot \text{R}_{3}^{+} \cdot \text{B}_{2} \cdot \text{O}_{3-z}
\]

where \( k = 1-2x-2y-2z \), \( m \) is 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. These phosphors have the general formula:

\[
M_{1-x} \cdot \text{Al}_{x} \cdot \text{O}_{3-x} \cdot \text{Sr}_{2} \cdot \text{O}_{3-z} \cdot \text{Fe}_{2} \cdot \text{O}_{3-y} \cdot \text{Eu}_{2} \cdot \text{O}_{3-y} \cdot \text{R}_{3}^{+} \cdot \text{B}_{2} \cdot \text{O}_{3-z}
\]

where \( k = 1-2x-2y-2z \), \( m \) is 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. These phosphors have the general formula:

\[
M_{1-x} \cdot \text{Al}_{x} \cdot \text{O}_{3-x} \cdot \text{Fe}_{2} \cdot \text{O}_{3-y} \cdot \text{Eu}_{2} \cdot \text{O}_{3-y} \cdot \text{R}_{3}^{+} \cdot \text{B}_{2} \cdot \text{O}_{3-z}
\]

where \( k = 1-2x-2y-2z \), \( m \) is 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. These phosphors have the general formula:

\[
M_{1-x} \cdot \text{Al}_{x} \cdot \text{O}_{3-x} \cdot \text{Fe}_{2} \cdot \text{O}_{3-y} \cdot \text{Eu}_{2} \cdot \text{O}_{3-y} \cdot \text{R}_{3}^{+} \cdot \text{B}_{2} \cdot \text{O}_{3-z}
\]

where \( k = 1-2x-2y-2z \), \( m \) is 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. These phosphors have the general formula:

\[
M_{1-x} \cdot \text{Al}_{x} \cdot \text{O}_{3-x} \cdot \text{Fe}_{2} \cdot \text{O}_{3-y} \cdot \text{Eu}_{2} \cdot \text{O}_{3-y} \cdot \text{R}_{3}^{+} \cdot \text{B}_{2} \cdot \text{O}_{3-z}
\]
A phosphorescent material as in paragraph A further comprising from about 2 mol % to about 20 mol %, relative to M, of B₂O₃ in said host and/or wherein B₂O₃ is present in the host in an amount ranging from about 8 mol % to about 15 mol %, relative to M.

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

B. A phosphorescent material having the formula:

\[ M₂O \cdot mAl₂O₃ \cdot (B₂O₃):2xEu²⁺,2yR³⁺, \]

where: k is 1-2x-2y,

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

z is a number ranging from about 0.02 to about 0.2

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

y is a number ranging from about 0.0001 to about 0.010;

M is Sr²⁺ or a mixture of Sr²⁺ with Ca²⁺, Ba²⁺ or both;

R³⁺ is one or more of Pr³⁺, Ho³⁺, Dy³⁺, Er³⁺, La³⁺, Lu³⁺, Ce³⁺, Y³⁺, Sm³⁺, Gd³⁺, Tb³⁺, Tm³⁺, Yb³⁺ and Bi³⁺.

A phosphorescent material as defined in paragraph B wherein R³⁺ is Pr³⁺, Ho³⁺, Dy³⁺, or Nd³⁺ 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:

\[ M₂O \cdot mAl₂O₃ \cdot (B₂O₃):2xEu²⁺,2yR³⁺, \]

where k=1-2x-2y-2r;

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

y is a number ranging from about 0.0001 to about 0.010;

M is Sr²⁺ or a combination of Sr²⁺ with Ca²⁺ and/or Ba²⁺; under 1.3 ton/cm² pressure before sintering. The powder or the pressed pellets are then sintered at about 1,300°C for one hour in a reducing atmosphere or in a flow of reducing gas containing 0,20 to 0.20 mol % of H₂ and 0,20 to 0.20 mol % of N₂. The resulting material exhibits phosphor properties as described herein.

D. A phosphorescent material having the formula:

\[ M₂O \cdot mAl₂O₃ \cdot (B₂O₃):2xEu²⁺,2yR³⁺, \]

where k=1-2x-2y-2r;

x ranges from about 0.0001 to about 0.05;

y is a number ranging from about 0.0001 to about 0.10;

z ranges from about 0.02 to about 0.2;

Z is an alkali metal ion, particularly Na⁺ or K⁺ and r ranges from 0 to 0.20.

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

E. A phosphorescent material having the formula:

\[ M₂O \cdot mAl₂O₃ \cdot (B₂O₃):2xEu²⁺,2yR³⁺, \]

where n and p are numbers greater than 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 0.02 to about 0.2

x is a number ranging from about 0.0001 to about 0.02

y is a number ranging from about 0.0001 to about 0.010;

M is Sr²⁺ or a mixture of Sr²⁺ with Ca²⁺, Ba²⁺ or both; (1-2x-2y)MC0₃+2.00 Al₂O₃+xEu₂O₃+yR₂O₃+(zB₂O₃); where:

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 0.05;

y is a number ranging from about 0.0001 to about 0.010;

M is Sr²⁺ or a combination of Sr²⁺ with Ca²⁺ and/or Ba²⁺; under 1.3 ton/cm² pressure before sintering. The powder or the pressed pellets are then sintered at about 1,300°C for one hour in an air atmosphere containing 0.20 to 0.20 mol % of H₂ and 0,20 to 0.20 mol % of N₂. The resulting material exhibits phosphor properties as described herein.

F. A phosphorescent material having the formula:

\[ M₂O \cdot mAl₂O₃ \cdot (B₂O₃):2xEu²⁺,2yR³⁺, \]

where n and p are numbers greater than 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 0.02 to about 0.2

x is a number ranging from about 0.0001 to about 0.02

y is a number ranging from about 0.0001 to about 0.010;

M is Sr²⁺ or a mixture of Sr²⁺ with Ca²⁺, Ba²⁺ or both; (1-2x-2y)MC0₃+2.00 Al₂O₃+xEu₂O₃+yR₂O₃+(zB₂O₃); where:

x is a number ranging from about 0.0001 to about 0.05;

y is a number ranging from about 0.0001 to about 0.010;

M is Sr²⁺ or a combination of Sr²⁺ with Ca²⁺ and/or Ba²⁺; under 1.3 ton/cm² pressure before sintering. The powder or the pressed pellets are then sintered at about 1,300°C for one hour in an air atmosphere containing 0.20 to 0.20 mol % of H₂ and 0,20 to 0.20 mol % of N₂. The resulting material exhibits phosphor properties as described herein.

THE EXAMPLES

Example 1

Methods of Preparation of Blue Phosphors with Host Material M₅Al₃O₁₂, (where M is Sr or a mixture of Sr with Ba and/or Ca)

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

\[(1-2x-2y)MCO₃+2.00 Al₂O₃+xEu₂O₃+yR₂O₃+(zB₂O₃); \]

where:

x=2+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 0.010 and preferably the value of y is 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⁺.

B₂O₃ is used as a flux in the composition and is important for ensuring the formation of the phosphorescent phase. B₂O₃ can be replaced by two molar equivalents of H₂BO₃.

The mixture of components is milled or ground to form a homogeneous fine powder for sintering. The powder is preferably pressed into pellets under about 1.3 ton/cm² pressure prior to sintering. The mixed powder or the pressed pellets are then sintered 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 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⁺,Pr³⁺.
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{1-x}Al\textsubscript{x}O\textsubscript{1.97}Eu\textsuperscript{2+}:R\textsuperscript{3+} phosphors and the properties exhibited by SrAl\textsubscript{0.97}O\textsubscript{1.97}Eu\textsuperscript{2+}:R\textsuperscript{3+} phosphors generally exemplify those of Sr\textsubscript{1-x}Al\textsubscript{x}O\textsubscript{1.97}Eu\textsuperscript{2+}:R\textsuperscript{3+} phosphors.

\text{SrAl\textsubscript{2}O\textsubscript{2}Eu\textsuperscript{3+}:Bi} after similar exposure is also shown. These methods of preparation also specifically apply to SrAl\textsubscript{2}O\textsubscript{2}Eu\textsuperscript{3+}:Bi phosphors and the properties exhibited by SrAl\textsubscript{2}O\textsubscript{2}Eu\textsuperscript{3+}:Bi phosphors generally exemplify those of SrAl\textsubscript{2}O\textsubscript{2}Eu\textsuperscript{3+}:R\textsuperscript{3+} phosphors.

Preparation and Characterization of \text{SrAl\textsubscript{4}O\textsubscript{7}:Eu\textsuperscript{2+}:Pr\textsuperscript{3+}, Phosphors with Varying Amounts of Pr\textsuperscript{3+}}

Preparation of \text{SrAl\textsubscript{4}O\textsubscript{7}(1-6x)SrC\textsubscript{0.97},Al\textsubscript{2}O\textsubscript{3+2x}Eu\textsuperscript{2+}Pr\textsuperscript{3+}+0.1 B\textsubscript{2}O\textsubscript{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 Sr\textsubscript{1-x}Al\textsubscript{x}O\textsubscript{1.97}Eu\textsuperscript{2+}:R\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 decay of the after-glow of a sample of Sr\textsubscript{1-x}Al\textsubscript{x}O\textsubscript{1.97}Eu\textsuperscript{2+}:R\textsuperscript{3+} exposed to a 13 W fluorescent lamp for 10 minutes (line a). For comparison, the decay characteristics of a fluorescent light after a commercial blue phosphor CaSr\textsubscript{3}Si\textsubscript{2}Bi\textsubscript{4} after similar exposure is also shown (line b). The Sr\textsubscript{1-x}Al\textsubscript{x}O\textsubscript{1.97}Eu\textsuperscript{2+}:R\textsuperscript{3+} phosphor is about 10 times brighter than the commercial blue phosphor and has a persistence time of about 20 times longer. After 18 hours Sr\textsubscript{1-x}Al\textsubscript{x}O\textsubscript{1.97}Eu\textsuperscript{2+}:R\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 Sr\textsubscript{1-x}Al\textsubscript{x}O\textsubscript{1.97}Eu\textsuperscript{2+}:R\textsuperscript{3+} where the excitation spectrum was monitored at 488 nm. FIG. 4 is the x-ray diffraction pattern of the Sr\textsubscript{1-x}Al\textsubscript{x}O\textsubscript{1.97}Eu\textsuperscript{2+}:R\textsuperscript{3+} sample. This x-ray pattern indicated that the structure of Sr\textsubscript{1-x}Al\textsubscript{x}O\textsubscript{1.97}Eu\textsuperscript{2+} is similar to a Sr\textsubscript{4}Al\textsubscript{0.5}(0.3B\textsubscript{2}O\textsubscript{3}).

Example 3

Preparation and Characterization of Sr\textsubscript{4}Al\textsubscript{0.5}(0.3B\textsubscript{2}O\textsubscript{3}):Eu\textsuperscript{2+}:Pr\textsuperscript{3+}, Phosphors with Varying Amounts of Eu\textsuperscript{2+}

Eu-concentration dependence of Sr\textsubscript{1-x}Al\textsubscript{x}O\textsubscript{1.97}Eu\textsuperscript{2+}:Pr\textsuperscript{3+} phosphor after-glow was examined by preparing phosphor samples in which x (Pr\textsubscript{2}O\textsubscript{3} molar concentration) was varied from 0.001 to 0.02.

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

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

where x was varied from 0.01 to 0.15 as indicated in Table 1. In each case samples were pressed into pellets before prefiring and after 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 2x. Data in Table 1 indicate that the longest persistence is obtained with samples where x is 0.001–0.005, with y (Pr\textsubscript{2}O\textsubscript{3} molar proportion)=2x.

<table>
<thead>
<tr>
<th>Sample</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>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>60</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 5

Preparation and Characterization of Sr\textsubscript{4}Al\textsubscript{0.5}O\textsubscript{3}:Eu\textsuperscript{2+}:Ho\textsuperscript{3+}, Blue Phosphors

Sr\textsubscript{4}Al\textsubscript{0.5}O\textsubscript{3}:Eu\textsuperscript{2+}:Ho\textsuperscript{3+} was prepared following the general procedure of Example 1 with components mixed in the following molar proportions:

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

TABLE 2

<table>
<thead>
<tr>
<th>Sample</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>0.0075</td>
<td>95</td>
<td>28</td>
<td>15</td>
</tr>
<tr>
<td>C-3</td>
<td>0.010</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>

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):0.01Eu⁺:0.02Nd³⁺ 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):0.01Eu⁺:0.02Pr³⁺ (line b) and a commercial blue phosphor CaSrS:Bi (c) after similar exposure are also shown. The SrAl₂O₄(0.1B₂O₃):0.01Eu⁺:0.02Ho³⁺ phosphor shows similar brightness and persistence to that of SrAl₂O₄(0.1B₂O₃):0.01Eu⁺:0.02Pr³⁺. After 20 hours SrAl₂O₄(0.1B₂O₃):0.01Eu⁺:0.02Nd³⁺ 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):0.01Eu⁺:0.02Nd³⁺ where the excitation spectrum was monitored at 488 nm.

Example 6

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

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

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

where B₂O₃ serves as flux.

FIG. 8 shows the spectrum of the after-glow of a sample of SrAl₂O₄(0.1B₂O₃):0.01Eu⁺: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):0.01 Eu⁺: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):0.01 Eu⁺:0.02Pr³⁺ (b) and a commercial blue phosphor CaSrS:Bi (c) after similar exposure are also shown. The SrAl₂O₄(0.1B₂O₃):0.01Eu⁺:0.02Nd³⁺ phosphor shows similar brightness and persistence to that of SrAl₂O₄(0.1B₂O₃):0.01Eu⁺:0.02Pr³⁺. After 20 hours SrAl₂O₄(0.1B₂O₃):0.01Eu⁺:0.02Nd³⁺ 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):0.01 Eu⁺:0.02 Nd³⁺ where the excitation spectrum was monitored at 488 nm.

Example 7

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

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

0.97 SrCO₃+2.00 Al₂O₃+0.005 Eu₂O₃+0.01 R₂O₃+0.1 B₂O₃

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

FIG. 11 shows the decay curves of the after-glow of the SrAl₂O₄(0.1B₂O₃):0.01Eu⁺:0.02 R³⁺ samples measured at 488 nm prepared in the first 15 seconds after exposure to the light of a 13 W fluorescent lamp. Decay curves for R=La (V), Ce (○), Sm (●), Gd (□), Tb (*), Dy (□), Er (▲), Tm (●), Yb (●), and Lu (×). The decay curve of the sample SrAl₂O₄(0.1B₂O₃):Eu,Nd (closed circles) is also shown for comparison. It can be seen that the after-glow of these samples are generally less intense than analogous phosphor samples 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):0.01Eu⁺:0.02R³⁺ where R is La, Er, Nd, and Tm have similar wavelength dependence to that of the phosphor where R is Pr. There is no notable spectral shift with R.

Example 8

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

This example is intended to determine if co-doping of metal ions into a SrAl₂O₄(B₂O₃):Eu²⁺:Pr²⁺ phosphor increases UV excitation efficiency and improves phosphor brightness. Phosphors are prepared by the method of Example 1 with components combined in the following general molar proportions:

(1-2x-2y)ySr⁺+(2y+2x)Al₂O₃+2yEu₂O₃+2xPr₂O₃+yR₂O₃+2yB₂O₃

where y₁+y₂=y₁+2x+2y=0 and the ranges of in, x, y and z are as in formula 1 above.

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

0.97 SrCO₃+2.0 Al₂O₃+0.005 Eu₂O₃+0.005 Pr₂O₃+0.005 R₂O₃+0.1 B₂O₃

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

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

FIG. 13 is the excitation and emission spectra of the sample SrAl₂O₄(0.1B₂O₃):0.01Eu⁺:0.01Pr⁺:0.01Y⁺ 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

The influence of codoping Y, Lu, Lu, or Bi into SrAl$_2$O$_3$:Eu,Pr on the phosphorescence at 488 nm

<table>
<thead>
<tr>
<th>after (min)</th>
<th>Pr$^1$</th>
<th>Y</th>
<th>Lu</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>

$^1$Data is referenced to that of the SrAl$_2$O$_3$:Eu,Pr phosphor.

### Example 9

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

This example demonstrates the influence of deep trapping centers formed by Dy$^{3+}$ on the decay characteristics of MAl$_2$O$_7$ (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:

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

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 $y$=the value of $x$ if $R$ is a trivalent rare earth metal ion or Bi$^{3+}$.
- $z$ ranges from about 0.02 to about 0.2; and $R$ is a trivalent rare earth metal ion or Bi$^{3+}$.

The mixed alkaline earth aluminate compound, $(\text{Sr}_{0.33}\text{Ca}_{0.41}\text{Al}_{0.29})(\text{B}_2\text{O}_3)\text{Al}_{1.61}\text{Eu}_{0.01}\text{Pr}_{0.01}$ 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 phosphors have the general formula:

$$(\text{Sr}_{1-p}\text{Ba}_p\text{Ca}_2)_x\text{Al}_{2+y}\text{O}_{7+z}$$

FIG. 15 shows the luminescence spectra of this phosphor. No obvious spectral shift compared to the analogous Sr phosphor was observed.

### Example 11

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:

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

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 $y$=the value of $x$ if $R$ is a trivalent rare earth ion or Bi$^{3+}$.

The phosphors have the generic formula:

$$\text{Sr}_{1-p}\text{Ca}_p\text{O}_{2+y}\text{Al}_2\text{O}_{7+z}$$

where $p+2x+2y$ 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:

\[ \text{Sr}_{x-y} \text{Ba}_y \text{Ca}_z \text{Al}_2 \text{O}_6 + y \text{Eu}_2^+ + (2x+y) \text{R}_{3+} \]

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

Example 12
Codoping of Mg
2+
 or Zn
2+
 into MO
m
\text{Al}_2 \text{O}_3: \text{Eu}^2+, \text{R}_{3+}
 phosphors

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

\[ (1-2x-2y) \text{MC}_2 \text{O}_4 + (n-2x-2y) \text{Al}_2 \text{O}_3 + y \text{R}_2 \text{O}_3 + q \text{ZO}_2 \]

where: 2x+2y is less than 1;
q is less than m and preferably ranges from 0.002 to 0.2;
the ranges for x, y, m and z are as given in formula 1.
XO, in particular, can be MgO and/or ZnO. These phosphors will have the generic formula:

\[ \text{MO} \cdot \text{mAl}_2 \text{O}_3 \cdot q \text{XO}_2: (2x+y) \text{Eu}^2+, 2y \text{R}_{3+} \]

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

\[ 0.98 \text{SrCO}_3 + 1.99 \text{Al}_2 \text{O}_3 + 0.005 \text{Eu}_2 \text{O}_3 + 0.01 \text{Pr}_2 \text{O}_3 + 0.1 \text{B}_2 \text{O}_3 \]

where XO can be MgO or ZnO.

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

TABLE 5

<table>
<thead>
<tr>
<th>after (min)</th>
<th>SAO-EuPr(^1)</th>
<th>SAO-EuPrMg</th>
<th>SAO-EuPrZn</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>104</td>
<td>104</td>
</tr>
<tr>
<td>30</td>
<td>33</td>
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<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-EuPr.

Example 13
Co-doping of Na
+ + or K
+ + into MO
m
\text{Al}_2 \text{O}_3: \text{Eu}^{2+}, \text{R}^{3+}
 phosphors

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

\[ (1-2x-2y-2r) \text{MC}_2 \text{O}_4 + (n-2x-2y) \text{Al}_2 \text{O}_3 + y \text{R}_2 \text{O}_3 + q \text{ZO}_2 \]

where: 2x+2y+2r is less than 1;
r preferably ranges from 0.002 to 0.2; and the ranges for x, y, m and z are as given in formula 1.
Z
2+CO₃, in particular, can be Na₂CO₃ and/or K₂CO₃.
These phosphors will have the generic formula:

\[ \text{MO} \cdot \text{mAl}_2 \text{O}_3 \cdot q \text{Na}_2 \text{CO}_3: (2x+y) \text{Eu}^{2+}, 2y \text{R}_{3+} \]

where: \( k = 1 - 2x - 2y \) and where the ranges for r, m, x and y are as above.
Exemplary Na and K doped phosphors are prepared by combining the components according to the following molar proportions:

\[ 0.97 \text{SrCO}_3 + 2 \text{Al}_2 \text{O}_3 + 0.005 \text{Eu}_2 \text{O}_3 + 0.005 \text{Dy}_2 \text{O}_3 + 0.005 \text{X}_2 \text{CO}_3 + 0.1 \text{B}_2 \text{O}_3 \]

where Z
2+CO₃ can be Na₂CO₃ or K₂CO₃.
Table 6 provides measurements of relative after-glow intensity at 488 nm of strontium aluminate (SrAl,O,) phosphors in which Na
+ + or K
+ + replaces Sr
3+
.

TABLE 6

<table>
<thead>
<tr>
<th>after (min)</th>
<th>SAO-EuPr(^1)</th>
<th>SAO-EuPrNa</th>
<th>SAO-EuPrK</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>112</td>
<td>135</td>
</tr>
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<td>30</td>
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<tr>
<td>60</td>
<td>15</td>
<td>17</td>
<td>20</td>
</tr>
</tbody>
</table>

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

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

\[ 0.98 \text{SrCO}_3 + 1.99 \text{Al}_2 \text{O}_3 + 0.01 \text{Eu}_2 \text{O}_3 + 0.05 \text{Pr}_2 \text{O}_3 + 0.1 \text{B}_2 \text{O}_3 \]

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 Sr₇Al₁₄O₃₅ exhibits somewhat brighter phosphorescence.

TABLE 7

<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 (^1)</th>
<th>2.15</th>
</tr>
</thead>
<tbody>
<tr>
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<td>113</td>
<td>121</td>
<td>106</td>
<td>100</td>
<td>100</td>
<td>88</td>
</tr>
<tr>
<td>30</td>
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<td>32</td>
<td>31</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>60</td>
<td>17</td>
<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,O₃) activated with Eu
2+ and doped with Pr
3+ were prepared...
using varying amounts of flux (2B₂O₃). Phosphor components were mixed according to the molar proportions:

\[ 0.08 \text{SrCO}_3 + 4 \text{Al}_2 \text{O}_3 + 0.005 \text{Eu}_2 \text{O}_3 + 0.005 \text{Pr}_2 \text{O}_3 + 2 \text{B}_2 \text{O}_3 \]

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

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

Example 16

General Methods of Preparation of Blue Phosphors with Host Material \( \text{M}_x \text{Al}_{y} \text{O}_{z} \) (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:

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

where:

- \( 8x + 8y < 4 \), \( x \) is preferably about 0.0001 to about 0.05 and more preferably \( x = 0.001 \) to about 0.005; \n- \( y \) 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 \( \text{Sr} \) or a combination of \( \text{Sr} \) with \( \text{Ca} \) and/or \( \text{Ba} \); 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: The influence of varying B₂O₃ in preparation of phosphor. |
|------------------|----------|----------|----------|----------|----------|----------|----------|
|                  | After/min | 0.03     | 0.05     | 0.08     | 0.10     | 0.12     | 0.15     |
|                  |          | 131      | 121      | 106      | 100      | 132      | 100      |
|                  |          | 37       | 37       | 32       | 31       | 41       | 32       |
|                  |          | 17       | 16       | 15       | 14       | 17       | 15       |

*Data is referenced to that at \( x = 0.10 \).*

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.

Trans. AIME 194:747) or the laser heated pedestal method:

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

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

The phosphor of claim 1 which is a single crystal.

The phosphor of claim 1 which has the formula:

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

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

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

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

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

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

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, \( M = \text{Sr} \) 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 \( M \).

1. A phosphor represented by the formula:

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

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

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

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

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

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

10. A phosphor represented by the formula:

\[ \text{MO} \cdot (m \text{Al}_2 \text{O}_3 : \text{Eu}^{2+}, \text{R}^{3+}) \]
21 a mixture of Y\textsuperscript{3+} with another trivalent metal ion, Eu\textsuperscript{2+} is present at a level from about 0.02 mol % to about 10 mol % of M, and R\textsuperscript{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\textsuperscript{3+} is a mixture of Y\textsuperscript{3+} with another trivalent metal ion, Eu\textsuperscript{2+} is mol % of M, and R\textsuperscript{3+} is present at a level from about 0.02 mol % to about 10 mol % of M.

16. A phosphor of claim 15 wherein a portion of the Al\textsuperscript{3+} in the host is substituted by a divalent metal ion or in which a portion of the M\textsuperscript{2+} in the phosphor is substituted by a monovalent metal ion.

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

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

19. The phosphor of claim 16 in which a portion of the M\textsuperscript{2+} in the phosphor is substituted by a divalent metal ion.

15. A phosphor represented by the formula:

\[
\text{Sr}_\text{m} \text{Ba}_\text{n} \text{Ca}_\text{p} \text{Al}_\text{2x} \text{Eu}_\text{2y} \text{R}_\text{3z} \text{O}_\text{3m+2x+2y+2z}
\]

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 v 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:

\[
\text{MO}_\text{m} \text{Al}_\text{2x} \text{Eu}_\text{2y} \text{R}_\text{3z} \text{O}_\text{3m+2x+2y+2z}
\]

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\textsuperscript{3+} is a trivalent metal ion or a mixture thereof, Eu\textsuperscript{2+} is present at a level from about 0.02 mol % to about 10 mol % of M, and R\textsuperscript{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:

\[
\text{MO}_\text{m} \text{Al}_\text{2x} \text{Eu}_\text{2y} \text{R}_\text{3z} \text{O}_\text{3m+2x+2y+2z}
\]

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

25. The phosphor of claim 15 wherein R\textsuperscript{3+} is Pr\textsuperscript{3+}, Ho\textsuperscript{3+}, Dy\textsuperscript{3+}, Tb\textsuperscript{3+}, Y\textsuperscript{3+}, Yb\textsuperscript{3+} and Bi\textsuperscript{3+}.

26. The phosphor of claim 15 wherein R\textsuperscript{3+} is a mixture of Y\textsuperscript{3+} with another trivalent metal ion.

27. The phosphor of claim 15 wherein R\textsuperscript{3+} is a mixture of Y\textsuperscript{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\textsubscript{2}O\textsubscript{3}.

30. The phosphor of claim 15 wherein M is Sr.
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:

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+n" and replace with -- Dy3+ --.
Line 50, delete "Eu2+n" and replace with -- Eu2+ --.
Line 62, delete "M1-xAl2O4-x Where" and replace with -- M1-xAl2O4-x, where --.

Column 2.
Line 21, delete the comma after "Eu2+n".
Lines 22-23, delete "2SrO.3Al2O3:Eu2+n" and replace with -- 2SrO.3Al2O3:Eu2+n --.
Lines 25-26, delete "4SrO.7Al2O3:Eu2+n" and replace with -- 4SrO.7Al2O3:Eu2+n --.
Line 29, delete "BaO.4Al2O3:Eu2+n" and replace with -- BaO.4Al2O3:Eu2+n --.
Line 38, delete "MO.mA12O3:Eu2+n,R3+" and replace with -- MO.mA12O3:Eu2+n,R3+ --.
Line 47, delete "MO.mA12O3(xB2O3):Eu2+n,R3+" and replace with -- MO.mA12O3(xB2O3):Eu2+n,R3+ --.

Column 4.
Line 32, delete "Sr0.64Ba0.33Al2O7" and replace with -- Sr0.33Ba0.64Al2O7 --.
Line 36, delete "Sr0.49Ca0.49Al2O7" and replace with -- Sr0.48Ca0.485Al2O7 --.

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

**Column 7.**
Line 10, delete "pellets are the" and replace with -- pellets are then --.
Line 15, delete "laser heated pedestal method" and replace with -- laser heated pedestal growth (LHPG) method --.
Line 16, delete "bars to" and replace with -- bars for --.
Line 20, delete "somewhat" and replace with -- somewhat --.
Line 28, delete "LHPG" and replace with -- LHGP --.
Line 42, delete "M_{0.2}m_{0.2}Al_{0.2}(zB_{0.2}):2xEu^{2+},2yR^{3+}n" and replace with -- M_{0.2}m_{0.2}Al_{0.2} (zB_{0.2}):2xEu^{2+},2yR^{3+} --.

**Column 8.**
Line 1, delete "M_{0.2}m_{0.2}Al_{0.2}(zB_{0.2}):2xEu^{2+},2yR^{3+}n" and replace with -- M_{0.2}m_{0.2}Al_{0.2}(zB_{0.2}):2xEu^{2+},2yR^{3+} --.
Line 15, delete "M_{0.2}(m-q)Al_{0.2}qXO(zB_{0.2}):2xEu^{2+},2yR^{3+}n" and replace with -- M_{0.2}(m-q)Al_{0.2}qXO(zB_{0.2}):2xEu^{2+},2yR^{3+} --.
Line 31, delete "M_{0.2}m_{0.2}Al_{0.2}rZ_{2}(zB_{0.2}):2xEu^{2+},2yR^{3+}n" and replace with -- M_{0.2}m_{0.2}Al_{0.2}rZ_{2}(zB_{0.2}):2xEu^{2+},2yR^{3+} --.
Line 60, delete "MO.m_{0.2}Al_{0.2}3" and replace with -- MO.m_{0.2}Al_{0.2}3 --.

**Column 9.**
Line 10, delete "M_{0.2}m_{0.2}Al_{0.2}(zB_{0.2}):2xEu^{2+},2yR^{3+}n" and replace with -- M_{0.2}m_{0.2}Al_{0.2} (zB_{0.2}):2xEu^{2+},2yR^{3+} --.
Line 28, delete "M_{0.2}m_{0.2}Al_{0.2}(zB_{0.2}):2xEu^{2+},2yR^{3+}n" and replace with -- M_{0.2}m_{0.2}Al_{0.2}(zB_{0.2}):2xEu^{2+},2yR^{3+}n --.
Line 50, delete "M_{0.2}(m-q)Al_{0.2}qXO(zB_{0.2}):2xEu^{2+},2yR^{3+}n" and replace with -- M_{0.2}(m-q)Al_{0.2}qXO(zB_{0.2}):2xEu^{2+},2yR^{3+}n --.
Line 67, delete "M_{0.2}m_{0.2}Al_{0.2}rZ_{2}(zB_{0.2}):2xEu^{2+},2yR^{3+}n" and replace with -- M_{0.2}m_{0.2}Al_{0.2}rZ_{2}(zB_{0.2}):2xEu^{2+},2yR^{3+}n --.

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

**Column 11.**
Lines 6 and 16, delete "SrAlO₂:0.01Eu²⁺:0.02Pr³⁺" and replace with
-- SrAlO₂(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺ --.
Line 25, delete "SrAl₂O₇(1.0B₂O₃):0.01Eu²⁺:0.02Pr³⁺" and replace with
-- SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺ --.
Lines 29, 32, 37 and 39-40, delete "SrAl₂O₇(1.0B₂O₃):0.01Eu²⁺:0.02Pr³⁺" and replace with
-- SrAl₂O₇(0.1B₂O₃):0.01Eu²⁺:0.02Pr³⁺ --.
Line 46, delete "SrAl₂O₇(0.1B₂O₃):Eu²⁺:Pr³⁺" and replace with -- SrAl₂O₇(0.1B₂O₃):Eu²⁺:Pr³⁺ --.
Lines 50-51, delete "SrAl₂O₇(0.1B₂O₃):Eu²⁺:Pr³⁺" and replace with -- SrAl₂O₇(0.1B₂O₃):Eu²⁺:Pr³⁺ --.
Line 60, delete "0.01 to 0.15" and replace with -- 0.001 to 0.015 --.

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

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

Column 14.
Lines 7 and 15, delete "SrAlO₄(0.1B₂O₃):0.01Eu²⁺:0.02R³⁺" and replace with -- SrAlO₄(0.1B₂O₃):0.01Eu²⁺:0.02R³⁺ --.
Line 19, after "(+)" please insert -- are shown --.
Lines 34-35, delete "SrAlO₄(B₂O₃):0.01Eu²⁺:0.01Pr³⁺:0.01R³⁺" and replace with -- SrAlO₄(B₂O₃):0.01Eu²⁺:0.01Pr³⁺:0.01R³⁺ --.
Line 38, delete "SrAlO₄(B₂O₃):Eu²⁺:Pr³⁺" and replace with -- SrAlO₄(B₂O₃):Eu²⁺,Pr³⁺ --.
Line 48, delete "ranges of in" and replace with "ranges of m" --.
Lines 56 and 60-61, delete "SrAlO₄(0.1B₂O₃):0.01Eu:0.01Pr:0.01R" and replace with -- SrAlO₄(0.1B₂O₃):0.01Eu,0.01Pr,0.01R --.

Column 16.
Line 13, delete "([Sr₀.₃₃ Ba₀.₆₄]₀.₁B₂O₃)₄Al₂O₇:0.01Eu:0.02Pr" and replace with -- ([Sr₀.₃₃ Ba₀.₆₄]₀.₁B₂O₃)₄Al₂O₇:0.01Eu,0.02Pr --.
Line 22, delete "SrₓBaₓO·mAl₂O₃(zB₂O₃):2xEu₂⁺yR" and replace with -- SrₓBaₓO·mAl₂O₃(zB₂O₃):2xEu₂⁺yR --.
Line 48, delete "SrₓCaₓO·mAl₂O₃(zB₂O₃):2xEu₂⁺yR" and replace with -- SrₓCaₓO·mAl₂O₃(zB₂O₃):2xEu₂⁺yR --.
Line 52, delete "([Sr₀.₄₈₅ Ca₀.₄₈₅]₀.₁B₂O₃)₄Al₂O₇:0.01Eu:0.02Pr" and replace with -- ([Sr₀.₄₈₅ Ca₀.₄₈₅]₀.₁B₂O₃)₄Al₂O₇:0.01Eu,0.02Pr --.
Lines 58-59, delete "([Sr₀.₄₈₅ Ca₀.₄₈₅]₀.₁B₂O₃)₄Al₂O₇:0.01Eu:0.02Pr" and replace with -- ([Sr₀.₄₈₅ Ca₀.₄₈₅]₀.₁B₂O₃)₄Al₂O₇:0.01Eu,0.02Pr --.

Column 17.
Line 7, delete "SrₓBaₓCaₓO·mAl₂O₃(zB₂O₃):2xEu₂⁺yR" and replace with -- SrₓBaₓCaₓO·mAl₂O₃(zB₂O₃):2xEu₂⁺yR --.
Lines 13-14 and 57-58, delete "MO·mAl₂O₃:Eu²⁺,R³⁺" and replace with -- MO·mAl₂O₃:Eu²⁺,R³⁺ --.
Line 29, delete "MₓO,(m-q)Al₂O₃,qXO:2xEu₂⁺yR" and replace with -- MₓO,(m-q)Al₂O₃,qXO:2xEu₂⁺yR --.

Column 18.
Line 6, delete "MₓO·mAl₂O₃,rNa₄O:2xEu₂⁺yR" and replace with -- MₓO·mAl₂O₃,rNa₄O:2xEu₂⁺yR --.
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+,2yR3+" and replace with -- MO,mAl2O3:Eu2+,R3+ --.

Column 21,
Line 3, delete "R3+, is present" and replace with -- R3+ is present --.
Line 11, delete "Sr,Ba,Ca,O,mAl2O3;2xEu2+,2yR3+ " and replace with -- Sr,Ba,Ca,O,mAl2O3;2xEu2+,2yR3+ --.
Line 15, delete "v" and replace with -- y --.
Lines 22 and 37, delete "MO,mAl2O3:Eu2+,2yR3+" and replace with -- MO,mAl2O3:Eu2+, R3+ --.

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

Signed and Sealed this

Fifteenth Day of April, 2003

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