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(54) YTTRIUM SUBSTITUTED BARIUM THIOALUMINATE PHOSPHOR MATERIALS

YTTRIUM-SUBSTITUIERTE BARIUM-THIOALUMINATE-PHOSPHORMATERIALIEN

MATIERES LUMINOPHOREES DE THIOALUMINATE DE BARYUM A YTTRIUM SUBSTITUE

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Description

Field of the Invention

[0001] The present invention relates to phosphor materials which are used as thin films in electroluminescent displays. More specifically, the invention relates to yttrium substitution in such phosphor materials and in particular, yttrium substituted barium thioaluminate phosphor materials.

[0002] The invention also relates to improving the luminance of and optimizing the emission spectra of the phosphor materials when they are used for full color electroluminescent displays, particularly those employing thick film dielectric layers with a high dielectric constant.

Background to the Invention

[0003] Thick film dielectric structures provide for superior resistance to dielectric breakdown, as well as a reduced operating voltage, compared to thin film electroluminescent (TFEL) displays e.g. as exemplified by U.S. patent 5,432,015. The thick film dielectric structure when it is deposited on a ceramic substrate will withstand higher processing temperatures than TFEL devices, which are typically fabricated on glass substrates. This increased high temperature tolerance facilitates annealing of phosphor films at higher temperatures to improve their luminosity. With these advantages and with recent advances in blue-emitting phosphor materials, displays have approached the luminosity and color coordinates required to achieve the technical performance of traditional cathode ray tube (CRT) displays. Nevertheless, further improvement in blue phosphor performance is required to simplify display design, to improve display reliability by lowering operating voltages and to keep pace with a trend towards higher color temperature specifications for displays.

[0004] Cerium-activated strontium sulphide phosphor materials have traditionally been used in electroluminescent displays for blue colors while manganese-activated zinc sulphide have been employed for red and green colors. The optical emission from these phosphor materials must be passed through an appropriate chromatic filter to achieve the necessary color coordinates for red, green and blue sub-pixels, resulting in a loss of luminance and energy efficiency. The manganese-activated zinc sulphide phosphor has a relatively high electrical to optical energy conversion efficiency of up to about 10-lumens per Watt of input power. Cerium-activated strontium sulphide phosphor has an energy conversion efficiency of 1 lumen per Watt, which is relatively high for blue emission. However, the spectral emission for these phosphors is quite wide, with spectral emission for the zinc sulphide-based phosphor material spanning the color spectrum from green to red and that for the strontium sulphide-based material spanning the range from blue to green. This necessitates the use of the optical filters. The spectral emission of the cerium-activated strontium sulphide phosphor can be shifted to some degree towards.the blue by controlling the deposition conditions and activator concentration, but not to the extent required to eliminate the need for an optical filter.

[0005] Alternative blue phosphor materials having narrower emission spectra to provide the color coordinates required for a blue sub-pixel have also been developed. These phosphor materials include cerium-activated alkaline earth thiogallate compounds which provide good blue color coordinates, but exhibit relatively poor luminosity and stability. Higher luminosity and excellent color coordinates for blue pixels have been achieved with europium-activated barium thioaluminate phosphor materials.

[0006] More recently europium activated lanthanum thioaluminate has been shown to have utility as a blue light emitting electroluminescent phosphor. European Patent Application 1,148,111 discloses a thin film phosphor of this composition incorporated into a thick dielectric electroluminescent device for which a luminance of 300 candelas per m^2 was realized when a 1 kHz electric field was applied across the device. While this application suggests the use of yttrium as a possible choice of cation for thioaluminate based phosphor materials, it does not suggest a partial substitution of yttrium for any metallic species in the phosphor.

[0007] Yttrium has been used as a co-activator to enhance the luminosity of rare earth-activated sulphide phosphor materials in thin film electroluminescent devices. U.S. Patents 6,043,602 and 5,939,825 teach the use of yttrium as one of a series of co-activator species that may enhance the luminance of green and blue light-emitting calcium, strontium, barium or magnesium sulfide phosphor materials. These phosphors also include a metal dopant such as copper or lead, and in the case of U.S. 6,043,602, a halogen selected from fluorine, chlorine or iodine. U.S. Patent 5,662,831 teaches a method for the preparation of an europium activated yttrium oxy-sulfide material as a cathodoluminescent phosphor material. The phosphor is provided as a slurry further pulverized to attain small particle sizes. These aforementioned patents simply disclose yttrium as a dopant or co-dopant in a binary alkaline earth sulfide or alternatively, as the sole cation of the host material. These aforementioned patents do not teach or suggest the use of yttrium for controlled partial substitution of the metallic species of the phosphor.

[0008] There remains a need in the art for new phosphors having improved properties that have use as thin films in electroluminescent displays. The present invention fulfills this and other needs.

Summary of the Invention

[0009] In accordance with an aspect of the present invention there is provided a thin film phosphor for an electroluminescent device, said phosphor being selected from the group consisting of thioaluminates, thiogallates and thioindates having at least one cation selected from elements of Groups IIA and IIB of the Periodic Table of Elements, said phosphor being activated by a rare earth metal and containing a Group IIIB element as a partial substitute for a portion of aluminum, gallium or indium of said thiogallate, thioindate and thioaluminate.

[0010] In accordance with another aspect of the present invention there is provided a thin film phosphor for an electroluminescent device, the phosphor being selected from the group consisting of thioaluminates, thiogallates and thioindates having at least one cation selected from elements of Groups IIA and IIB of the Periodic Table of Elements, said phosphor being activated by a rare earth metal and wherein a portion of the aluminum, gallium or indium of the thioaluminate, thiogallate or thioindate is replaced with yttrium.

[0011] According to another aspect of the present invention is a phosphor material having the formula:

$$A_{1-w}\, D_w\, [Y_x Z_{1-x}]_y S_4,$$

wherein

A is a Group IIA or Group IIB cation;
D is a rare earth metal;
Z is selected from Al, Ga and In;
$0<x<0.2$;
$y= 2$; and
$0.005<w<0.1$.

[0012] The invention provides for a partial substitution of yttrium for the metal species selected from aluminum, gallium and indium where such substitution does not substantially alter the crystal lattice structure of the phosphor.

[0013] In a preferred embodiment of the present invention, the phosphor is a thioaluminate.

[0014] In another embodiment, said rare earth metal is selected from europium and/or cerium, most preferably europium.

[0015] In another preferred embodiment, the cation is barium.

[0016] In further embodiments, the phosphor contains europium in an amount in the range of 1-10 atomic percent of the Group IIA or IIB cation present and yttrium in an amount in the range of about 0.1-20 atomic percent of the aluminum, gallium or indium. Preferably, the amount of europium is between about 2-7 atomic percent of the Group IIA or IIB cation present and yttrium replaces between about 1-7 atomic percent of the aluminum, gallium or indium content.

[0017] According to another aspect of the present invention is a phosphor material having the formula:

$$A_{1-w}\, D_w\, [M_x Z_{1-x}]_y S_4,$$

wherein

A is a Group IIA or Group IIB cation;
D is a rare earth metal;
M is a Group IIIB metal selected from Y, Sc, La and Ac;
Z is selected from Al, Ga and In;
$0<x<0.2$;
$y= 2$; and
$0.005<w<0.1$.

[0018] According to a further aspect of the present invention is an electroluminescent device comprising a thin film phosphor as described herein on a substrate structure.

[0019] According to still another aspect of the present invention is a method for making a phosphor material selected from the group consisting of thioaluminates, thiogallates and thioindates having at least one cation selected from elements of Groups IIA and IIB of the Periodic Table of Elements, said phosphor being activated by a rare earth metal and wherein a portion of the aluminum, gallium or indium is replaced with yttrium.

[0020] According to yet a further aspect of the present invention is a method for making a phosphor material having the formula:

$$A_{1-w}\,D_w[Y_xZ_{1-x}]_yS_4,$$

wherein

A is a Group IIA or Group IIB cation;
D is a rare earth metal;
Z is selected from Al, Ga and In;
$0<x<0.2$;
$y= 2$; and
$0.005<w<0.1$.

[0021] Other features and advantages of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples while indicating embodiments of the invention are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from said detailed description.

Brief Description of the Drawings

[0022] The present invention will be described with reference to the embodiments shown in the drawings, in which:

Figure 1 is a schematic representation of a section of an electroluminescent element comprising a thick film dielectric layer and a phosphor composition typical of the present invention;

Figure 2 is a schematic representation of a plan view of a full color electroluminescent pixel and its constituent sub-pixels;

Figure 3 is a graphical representation of photoexcitation and photoluminescence spectra for several barium yttrium thioaluminate powders doped with europium;

Figure 4 is a graphical representation of x-ray diffraction patterns for several yttrium substituted barium thioaluminate phosphor materials;

Figure 5 is a graphical representation of luminosity as a function of applied voltage for similar electroluminescent devices having phosphor films with and without added yttrium;

Figure 6 is a graphical representation of the luminance and the phosphor efficiency of a electroluminescent device with a europium activated barium thioaluminate phosphor containing yttrium;

Figure 7 is a graphical representation of luminosity as a function of applied voltage for several electroluminescent devices with a barium yttrium thioaluminate phosphor; and

Figure 8 is a graphical representation of the luminosity of electroluminesacent devices as a function of the yttrium concentration in the phosphor material.

Detailed Description of the Invention

[0023] The present invention relates to the partial replacement of aluminum, gallium or indium in a rare earth metal activated thioaluminate, thiogallate or thioindate phosphor with a group IIIB element wherein such partial replacement does not substantially distort or affect the crystal lattice structure of the phosphor material.

[0024] In one embodiment, the present invention relates to yttrium as a partial replacement for aluminum in europium activated alkaline earth thioaluminate phosphors, and especially to the incorporation of yttrium in such phosphors when they are deposited as thin films in electroluminescent displays. Such partial replacement provides several advantages with respect to the phosphor material and the electroluminescent display incorporating such phosphor material. In one aspect, the yttrium functions to lower the maximum temperature required in a heat treatment process (annealing) to form a preferred crystal phase. Furthermore, the luminescence of the phosphor composition is enhanced with the partial replacement or substitution of aluminum.

[0025] While it is desirable to partially replace aluminum with yttrium, it is within the scope of the present invention to partially replace aluminum, gallium or indium with yttrium or its related Group IIIB species which includes scandium, lanthanum and actinium so long as such substitution does not substantially distort or affect the crystal lattice structure of the phosphor in a manner that affects the function and properties of the phosphor.

[0026] In embodiments, and as exemplified herein, the electroluminance of europium-activated barium thioaluminate, a blue emitting phosphor, is increased by a factor of more than two when about three atomic percent of the aluminum is replaced with yttrium. There is a corresponding increase in the electrical to optical energy conversion efficiency of the device from less than 1 lumen per Watt without yttrium to 2 lumens per Watt with three atomic percent yttrium, a very high value for a blue emitting pixel. The optical emission spectrum is also shifted towards the blue with yttrium addition.

[0027] The present invention is particularly directed to use of a partially yttrium substituted and europium activated alkaline earth thioaluminate host material to form a phosphor. The invention is applicable to ternary, quaternary and higher thioaluminate, thiogallate and thioindate phosphors, and composites thereof synthesized with cation(s) for these compounds. Suitable cations are selected from Groups IIA and IIB of the Periodic Table of Elements which are known to those of skill in the art. Examples of such cations include barium, calcium, strontium, magnesium and zinc.

[0028] A variety of rare earth activators known to those of skill in the art may be used in the phosphor material in conjunction with substitute species, for example cerium and europium. The preferred activator used in conjunction with yttrium is europium. In preferred embodiments of the invention, are partially yttrium substituted barium thioaluminate ($BaAl_2S_4$) phosphors, which emit blue light.

[0029] The present invention is suited for use in an electroluminescent display or device shown in Figures 1 and 2. Figure 1 shows a cross-section of an electroluminescent device utilizing a phosphor of the present invention. Figure 2 shows a plan view of the electroluminescent device. The electroluminescent device, generally indicated by 10, has a base substrate 12 on which is located row electrode 14. Thick film dielectric 16 has thin film dielectric 18 thereon. Thin film dielectric 18 is shown with three pixel columns, referred to as 20, 22 and 24, located thereon. The , pixel columns contain phosphors to provide the three basic colors viz. red, green and blue. Pixel column 20 has red phosphor 26 located in contact with thin film dielectric 18. Another thin film dielectric 28 is located on red phosphor 26, and column electrode 30 is located on thin film dielectric 28. Similarly, pixel column 22 has green phosphor 32 on thin film dielectric 18, with thin film dielectric 34 and column electrode 36 thereon. Pixel column 24 has blue phosphor 38 on thin film dielectric 18, with thin film dielectric 40 and column electrode 42 thereon.

[0030] The electroluminescent device of the present invention may incorporate a variety of substrate structures as will be understood by persons skilled in the art. In particular, the substrate structure comprises a thick film ceramic material having a base substrate which is a ceramic sheet having an electrically conductive film deposited thereon with a thick film layer deposited on the film. Examples of suitable base substrates are ceramic sheet materials that include but are not limited to alumina, metal ceramic composites, glass ceramic materials and high temperature glass materials. Suitable electrically conductive films are known to those of skill in the art such as, but not limited to, gold and silver alloy. The thick film layer comprises ferroelectric material. Suitable ferroelectric materials may be selected from lead magnesium niobate titanate, lead zirconate titanate, barium titanate and mixtures thereof. The thick film layer may also comprise one or more thin film layers thereon.

[0031] The deposition of the composition may be carried out in an atmosphere of H_2S, sulphur or other volatile sulphur bearing compounds that will not contaminate the phosphor film as it is deposited if there is a tendency for the deposited compound to be deficient in sulphur. In one embodiment, the deposition is done in a hydrogen sulphide atmosphere so that deposited species in the film can react with sulphide derived from the hydrogen sulphide to adequately saturate the deposited film with sulphide and achieve the desired film composition. However, in some instances, it may be possible to operate the method in a low pressure inert gas atmosphere without H_2S Thus, a strict oxygen-free environment may not be necessary.

[0032] The deposition of the phosphor may be done using a variety of methods. For example, phosphor deposition can be done by electron beam evaporation, particularly dual source electron beam evaporation. Deposition may also be carried out by dual source rf magnetron sputtering wherein there is a facility for injecting and exhausting gases including hydrogen sulphide. In this sputtering process the deposition substrate has a heating means and aluminum sulphide or metallic aluminum is present in one of the sputtering targets. Alternatively deposition can be conducted using thermal evaporation. One of skill in the art would readily comprehend how to deposit the phosphor of the present invention using different methods.

[0033] Alkaline earth thioaluminates have been reported to have utility as electroluminescent phosphors, but with low luminosity. It has now been demonstrated that improved control of the stoichiometry of the host material facilitates an electroluminescent element with higher luminance. It is presently demonstrated that the use of yttrium as a partial substitute for aluminum facilitates an electroluminescent element with still higher luminance than previously known phosphors.

[0034] The above disclosure generally describes the present invention. A more complete understanding can be obtained by reference to the following specific Examples. These Examples are described solely for purposes of illustration and are not intended to limit the scope of the invention. Changes in form and substitution of equivalents are contemplated as circumstances may suggest or render expedient. Although specific terms have been employed herein, such terms are intended in a descriptive sense and not for purposes of limitation.

Examples

[0035] The examples are described for the purposes of illustration and are not intended to limit the scope of the invention.

[0036] Methods of chemistry, photochemistry and spectrometry referred to but not explicitly described in this disclosure and examples are reported in the scientific literature and are well known to those skilled in the art.

Example 1

[0037] A series of europium-doped magnesium barium yttrium thioaluminate powders were prepared by blending powders of barium sulphide, yttrium trisulphide, aluminum sulphide and europium sulphide in various ratios. The barium yttrium thioaluminate phosphor powders had the nominal composition $Ba_{0.97}Eu_{0.03}(Y_xAl_{1-x})_2S_4$. Samples were prepared with (i) x = 0.0, (ii) x = 0.05 and (iii) x = 0.10

[0038] The blended powders were pressed to form pellets with a diameter of 1.3 cm and a height of 0.75 cm. The pellets were heat treated by placing them in an alumina boat and passing them through a belt furnace in a nitrogen environment with a peak temperature of about 950°C for 10 minutes. The actual temperatures of the pellet may have been moderately lower due to the large thermal loading introduced by the alumina boat.

[0039] The photoluminescence and excitation spectra of the resultant phosphors were measured using a Model 814 photomultiplier detection system and an A-1010B Arc Lamp xenon flash lamp from Photon Technology International of London, Ontario, Canada. A monochromator was used to select the excitation wavelength.

[0040] The photoluminescence and excitation spectra are shown in Figure 3. The emission spectra have peaks near 480 nm, with a tendency for a shift to shorter wavelength at higher yttrium content. These spectra, especially the shorter wavelength ones, are capable of providing CIE coordinates suitable for full color displays with minimal filtering. The excitation spectra for the sample with no yttrium has two peaks, one near 300 nm and the other near 350 nm. The samples containing yttrium had excitation spectra with the 300 nm peak reduced in magnitude, but with the 350 nm peak essentially unchanged as compared to that of the sample containing no yttrium.

Example II

[0041] A series of europium-doped magnesium barium yttrium thioaluminate powders were prepared by blending powders of barium sulphide, yttrium trisulphide, aluminum sulphide and europium sulphide in various ratios. The barium yttrium thioaluminate phosphor powders had the nominal composition $Ba_{0.97}Eu_{0.03}(Y_xAl_{1-x})_2S_4$. Samples were prepared with (i) x = 0.0, (ii) x = 0.02 (iii) x = 0.05, (iv) x = 0.10 and (v) x = 0.20. The samples were fired in a belt furnace as in Example 1, except that the maximum temperature was about 1000°C rather than about 950°C. Powder x-ray diffraction (XRD) patterns of the samples were obtained that could be indexed to the XRD pattern for cubic $BaAl_2S_4$. These patterns are shown in Figure 4, The addition of yttrium caused the widths of the XRD peaks to become sharper, indicating a higher degree of crystallinity, a lower crystal defect density or a larger grain size for these materials. The angles for the peaks were unchanged, however, for the yttrium substituted materials, no substantial change in the crystal unit cell dimensions with yttrium substitution was indicated. For a yttrium content of x = 0.1 or higher, however, additional XRD peaks appeared that may be barium sulfide, yttrium trisulfide or aluminum yttrium sulfide phases.

Example III

[0042] Two thick dielectric electroluminescent devices incorporating thin film phosphor layers comprising yttrium substituted barium thioaluminate activated with europium were constructed. The thick film substrate was comprised of a 5 cm by 5 cm alumina substrate having a thickness of 0.1 cm. A gold electrode was deposited on the substrate, followed with a thick film high dielectric constant dielectric layer in accordance with the methods exemplified in Applicant's co-pending international application WO-A-0070917 filed May 12, 2000. A thin film dielectric layer consisting of barium titanate, with a thickness of about 100-200 nanometers, was deposited on top of the thick film dielectric layer using the sol gel technique described in Applicant's co-pending U.S. Patent Application 09/761,971 filed January 17, 2001 (the entirety of which is incorporated herein by reference).

[0043] The phosphor film was electron beam evaporated on top of the barium titanate layer using du source electron beam evaporation as described in Applicant's US-A-2002094451. The two evaporation sources were aluminum sulphide and a fused mixture of barium sulphide and europium sulphide. For one of the devices, yttrium trisulphide was also added to the fused mixture in a quantity corresponding to x = 0.05 in the formula $Ba_{0.97}Eu_{0.03}(Y_xAl_{1-x})_2S_4$. For both samples, each evaporation source was in the form of a pellet, which was prepared using the method outlined in Example I.

[0044] The phosphor deposition was carried out in a low pressure atmosphere of hydrogen sulphide at a pressure of about 8 x 10^{-5} to about 2 x 10^{-4} torr and with the substrate at a temperature in the range of about 350°C to 500°C. The deposition was carried out by electron beam evaporation using the dual sources. The deposition rate of the aluminum sulphide, as measured in the absence of the remaining constituents using a quartz crystal monitor, was in the range of 5 to 7 Angstroms per second and the deposition rate of the remaining constituents in the absence of aluminum sulphide, also as measured using a quartz crystal monitor, was in the range of 3.5 to 5.5 Angstroms per second. The deposited phosphor film thickness was in the range 3000 to 4500 Angstroms.

[0045] Following deposition, the phosphor-coated substrates were annealed under a nitrogen atmosphere in a temperature of about 650°C to 700°C for about 2 minutes. A 50 nanometer thick alumina thin film and an indium tin oxide transparent conductor were deposited over the phosphor to provide a second electrode.

[0046] The resultant devices were tested using alternating polarity 32 microsecond wide square-wave pulses and a frequency of 120 Hz giving 240 light pulses per second. The pulse amplitude was varied in increments of 10 volts up to 260 volts and comparative data is shown in Figure 5 for the two devices. As can be seen from Figure 5, the luminance for the device with the phosphor containing yttrium is about twice that for the device not containing yttrium. The luminance increases linearly with the incremental voltage above the threshold voltage for the onset of luminance, and so the increased luminance with the yttrium additive can be realized without increasing the applied voltage. Figure 6 also shows the phosphor efficiency for the device having a phosphor containing yttrium. A peak efficiency of 2.4 lumens per Watt is realized, a new record for blue phosphor luminance in this wavelength range.

Example IV

[0047] Several thick dielectric devices with phosphors containing containing yttrium at a concentration corresponding to x = 0.05 were constructed and tested. Figure 7 shows the dependence of the realized luminance as a function of the applied voltage. As can be seen from Figure 7, the luminance performance of these devices were quite similar to one another, illustrating the repeatability of the device performance.

Example V

[0048] Five more thick dielectric electroluminescent devices were constructed according to the methods of Example III, except that the yttrium concentration in the phosphor was varied. The first of the devices had a phosphor film with a europium concentration of about 3 atomic percent with respect to barium and a yttrium concentration of zero atomic percent with respect to aluminum. The second device had a phosphor film with a europium concentration of about 3 atomic percent with respect to barium and a yttrium concentration of about one atomic percent with respect to aluminum. The third device had a phosphor film with a europium concentration of about 3 atomic percent with respect to barium and a yttrium concentration of about 3 atomic percent with respect to aluminum. The fourth device had a phosphor film with europium concentration of about 3 atomic percent with respect to barium and a yttrium concentration of about 5 atomic percent with respect to aluminum. The fifth device had a phosphor film with a europium concentration of about 3 atomic percent with respect to barium and a yttrium concentration of about 10 atomic percent with respect to aluminum. The measured luminance for these devices is shown in Figure 8 as a function of the yttrium concentration in the phosphor. The luminance is seen to increase as the value of x is increased.

Claims

1. A thin film phosphor for an electroluminescent device, said phosphor being selected from the group consisting of thioaluminates, thiogallates and thioindates having at least one cation selected from elements of Groups IIA and IIB of the Periodic Table of Elements, said phosphor being activated by a rare earth metal and containing a Group IIIB element as a partial substitute for a portion of aluminum, gallium or indium of said thiogallate, thioindate and thioaluminate.

2. The thin film phosphor of Claim 1, wherein said Group IIIB element is selected such that it does not substantially distort or affect the crystal lattice structure of said phosphor.

3. The thin film phosphor of Claim 2, wherein said Group IIIB element is selected from the group consisting of scandium, yttrium, lanthanum and actinium.

4. The thin film phosphor of Claim 3, wherein said element is yttrium.

5. The thin film phosphor of Claim 4, wherein said phosphor is a thioaluminate.

6. The thin film phosphor of Claim 4, wherein said phosphor is a thiogallate.

7. The thin film phosphor of Claim 4, wherein said phosphor is a thioindate.

8. The thin film phosphor of any one of Claims 1 to 7, wherein said rare earth metal is selected from the group consisting of europium and cerium.

9. The thin film phosphor of Claim 8, wherein said rare earth metal is europium.

10. The thin film phosphor of Claim 9, wherein said cation is barium.

11. The thin film phosphor of Claim 10, wherein said phosphor contains europium in an amount in the range of about 1-10 atomic percent of barium and yttrium is present in an amount in the range of about 0.1 - 20 atomic percent of aluminum.

12. The thin film phosphor of Claim 10, wherein said phosphor contains europium in an amount in the range of about 2 -7 atomic percent of barium and yttrium is present in an amount in the range of about 1-7 atomic percent of aluminum.

13. The thin film phosphor of claim 11 or 12, wherein said phosphor is $Ba_{0.97}Eu_{0.03}(Y_xAl_{1-x})_2S_4$, wherein $0<x<1.0$.

14. An electroluminescent device comprising a thin film phosphor of claim 1 or 12 on a substrate structure.

15. The device of claim 14, wherein said substrate structure comprises a thick film ceramic material.

16. The device of claim 15, wherein said thick film ceramic material comprises a base substrate having an electrically conductive film deposited thereon and a thick film layer deposited on said electrically conductive film.

17. The device of claim 16, wherein said base substrate comprises a ceramic material selected from the group consisting of a ceramic sheet, a metal ceramic composite, a glass ceramic and a high temperature glass.

18. The device of claim 17, wherein said ceramic sheet is alumina.

19. The device of claim 18, wherein said electrically conductive thin film is selected from the group consisting of gold and silver alloy.

20. The device of claim 19, wherein said thick film layer comprises ferroelectric material.

21. The device of claim 20, wherein said ferroelectric material is selected from the group consisting of lead magnesium niobate titanate, lead zirconate titanate, barium titanate and mixtures thereof.

22. The device of claim 20, wherein said substrate structure additionally comprises one or more thin film dielectric layers on the thick film layer.

23. The device of claim 22, wherein device additionally comprises a thin film dielectric layer on top of said thin-film phosphor.

24. A phosphor material having the formula:

$$A_{1-w} D_w [Y_xZ_{1-x}]_yS_4,$$

wherein

A is a Group IIA or Group IIB cation;
D is a rare earth metal;
Z is selected from Al, Ga and In;
$0<x<0.2$;
$y= 2$; and
$0.005<w<0.1$

25. The phosphor of Claim 24, wherein Z is aluminum.

26. The phosphor of Claim 24 or 25, wherein D is selected from the group consisting of europium and cerium.

27. The phosphor of Claim 26, wherein said rare earth metal is europium.

28. The phosphor of Claim 27, wherein said cation is barium.

29. The phosphor of claim 28, wherein said phosphor is $Ba_{0.97}Eu_{0.03}(Y_xAl_{1-x})_2S_4$, wherein $0<x<0.1$

30. An electroluminescent device comprising a phosphor of claim 24 on a substrate structure.

31. The device of claim 30, wherein said substrate structure comprises a thick film ceramic material.

32. The device of claim 31, wherein said thick film ceramic material comprises a base substrate having an electrically conductive film deposited thereon and a thick film layer deposited on said electrically conductive film.

33. The device of claim 32, wherein said base substrate comprises a ceramic material selected from the group consisting of a ceramic sheet, a metal ceramic composite, a glass ceramic and a high temperature glass.

34. The device of claim 33, wherein said ceramic sheet is alumina.

35. The device of claim 34, wherein said electrically conductive thin film is selected from the group consisting of gold and silver alloy.

36. The device of claim 35, wherein said thick film layer comprises ferroelectric material.

37. The device of claim 36, wherein said ferroelectric material is selected from the group consisting of lead magnesium niobate titanate, lead zirconate titanate, barium titanate and mixtures thereof.

38. The device of claim 36, wherein said substrate structure additionally comprises one or more thin film dielectric layers on the thick film layer.

39. The device of claim 38, wherein device additionally comprises a thin film dielectric layer on top of said thin-film phosphor.

40. A phosphor material having the formula:

$$A_{1-w}\,D_w\,[M_xZ_{1-x}]_yS_4,$$

wherein

A is a Group IIA or Group IIB cation;
D is a rare earth metal;
M is a Group IIIB metal selected from Y, Sc, La and Ac;
Z is selected from Al, Ga and In;
$0<x<0.2$;
$y= 2$; and
$0.005<w<0.1$

41. The phosphor of claim 40, wherein M is yttrium, A is barium, D is europium and Z is aluminum.

Patentansprüche

1. Dünnfilm-Phosphor für eine Elektrolumineszenzvorrichtung, wobei der Phosphor ausgewählt ist aus der Gruppe bestehend aus Thioaluminaten, Thiogallaten und Thioindaten mit mindestens einem Kation, das aus Elementen der Gruppen IIA und IIB des Periodensystems der Elemente ausgewählt ist, wobei der Phosphor durch ein Seltenerdmetall aktiviert ist und ein Element der Gruppe IIIB als partiellen Ersatz für einen Teil des Aluminiums, Galliums oder Indiums des Thiogallats, Thioindats und Thioaluminats enthält.

2. Dünnfilm-Phosphor nach Anspruch 1, in dem das Element der Gruppe IIIB so ausgewählt ist, dass es nicht wesentlich die Kristallgitterstruktur des Phosphors verzerrt oder beeinflusst.

3. Dünnfilm-Phosphor nach Anspruch 2, in dem das Element der Gruppe IIIB ausgewählt ist aus der Gruppe bestehend aus Scandium, Yttrium, Lanthan und Actinium.

4. Dünnfilm-Phosphor nach Anspruch 3, in dem das Element Yttrium ist.

5. Dünnfilm-Phosphor nach Anspruch 4, in dem der Phosphor ein Thioaluminat ist.

6. Dünnfilm-Phosphor nach Anspruch 4, in dem der Phosphor ein Thiogallat ist.

7. Dünnfilm-Phosphor nach Anspruch 4, in dem der Phosphor ein Thioindat ist.

8. Dünnfilm-Phosphor nach irgendeinem der Ansprüche 1 bis 7, in dem das Seltenerdmetall ausgewählt ist aus der Gruppe bestehend aus Europium und Cer.

9. Dünnfilm-Phosphor nach Anspruch 8, in dem das Seltenerdmetall Europium ist.

10. Dünnfilm-Phosphor nach Anspruch 9, in dem das Kation Barium ist.

11. Dünnfilm-Phosphor nach Anspruch 10, in dem der Phosphor Europium in einer Menge im Bereich von etwa 1-10 Atomprozent des Bariums enthält und Yttrium in einer Menge im Bereich von etwa 0,1-20 Atomprozent von Aluminium vorliegt.

12. Dünnfilm-Phosphor nach Anspruch 10, in dem der Phosphor Europium in einer Menge im Bereich von etwa 2-7 Atomprozent des Bariums enthält und Yttrium in einer Menge im Bereich von etwa 1-7 Atomprozent von Aluminium vorliegt.

13. Dünnfilm-Phosphor nach Anspruch 11 oder 12, in dem der Phosphor $Ba_{0,97}Eu_{0,03}(Y_xAl_{1-x})_2S_4$ ist, worin $0<x<1,0$.

14. Elektrolumineszenzvorrichtung, umfassend einen Dünnfilm-Phosphor nach Anspruch 1 oder 12 auf einer Substratstruktur.

15. Vorrichtung nach Anspruch 14, in der die Substratstruktur ein Dickfolien-Keramikmaterial umfasst.

16. Vorrichtung nach Anspruch 15, in der das Dickfolien-Keramikmaterial ein Grundsubstrat, auf dem ein elektrisch leitender Film abgeschieden ist, und eine Dickfolien-Schicht umfasst, die auf dem elektrisch leitenden Film abgeschieden ist.

17. Vorrichtung nach Anspruch 16, in der das Grundsubstrat ein Keramikmaterial umfasst, das ausgewählt ist aus der Gruppe bestehend aus einer dicken Keramikfolie, einem Metall-Keramik-Verbundstoff, einer Glaskeramik und einem Hochtemperaturglas.

18. Vorrichtung nach Anspruch 17, in der die dicke Keramikfolie Aluminiumoxid ist.

19. Vorrichtung nach Anspruch 18, in der der elektrisch leitende Dünnfilm ausgewählt ist aus der Gruppe bestehend aus Gold- und Silberlegierung.

20. Vorrichtung nach Anspruch 19, in der die Dickfolien-Schicht ein ferroelektrisches Material umfasst.

21. Vorrichtung nach Anspruch 20, in der das ferroelektrische Material ausgewählt ist aus der Gruppe bestehend aus Bleimagnesiumniobattitanat, Bleizirconattitanat, Bariumtitanat und deren Mischungen.

22. Vorrichtung nach Anspruch 20, in der die Substratstruktur zusätzlich eine oder mehrere dielektrische Dünnfilm-

Schichten auf der Dickfolien-Schicht umfasst.

23. Vorrichtung nach Anspruch 22, in der die Vorrichtung zusätzlich eine dielektrische Dünnfilm-Schicht oben auf dem Dünnfilm-Phosphor umfasst.

24. Phosphormaterial mit der Formel:

$$A_{1-w}D_w[Y_xZ_{1-x}]_yS_4,$$

worin

A ein Kation der Gruppe IIA oder Gruppe IIB ist;
D ein Seltenerdmetall ist;
Z aus Al, Ga und In ausgewählt ist;
$0<x<0.2$;
$y=2$; und
$0,005<w<0.1$

25. Phosphor nach Anspruch 24, in dem Z Aluminium ist.

26. Phosphor nach Anspruch 24 oder 25, in dem D ausgewählt ist aus der Gruppe bestehend aus Europium und Cer.

27. Phosphor nach Anspruch 26, in dem das Seltenerdmetall Europium ist.

28. Phosphor nach Anspruch 27, in dem das Kation Barium ist.

29. Phosphor nach Anspruch 28, in dem der Phosphor $Ba_{0,97}Eu_{0,03}(Y_xAl_{1-x})_2S_4$ ist, worin $0<x<0,1$.

30. Elektrolumineszenzvorrichtung, umfassend einen Phosphor nach Anspruch 24 auf einer Substratstruktur.

31. Vorrichtung nach Anspruch 30, in der die Substratstruktur ein Dickfolien-Keramikmaterial umfasst.

32. Vorrichtung nach Anspruch 31, in der das Dickfolien-Keramikmaterial ein Grundsubstrat, auf dem ein elektrisch leitender Film abgeschieden ist, und eine Dickfolien-Schicht umfasst, die auf dem elektrisch leitenden Film abgeschieden ist.

33. Vorrichtung nach Anspruch 32, in der das Grundsubstrat ein Keramikmaterial umfasst, das ausgewählt ist aus der Gruppe bestehend aus einer dicken Keramikfolie, einem Metall-Keramik-Verbundstoff, einer Glaskeramik und einem Hochtemperaturglas.

34. Vorrichtung nach Anspruch 33, in der die dicke Keramikfolie Aluminiumoxid ist.

35. Vorrichtung nach Anspruch 34, in der der elektrisch leitende Dünnfilm ausgewählt ist aus der Gruppe bestehend aus Gold- und Silberlegierung.

36. Vorrichtung nach Anspruch 35, in der die Dickfolien-Schicht ein ferroelektrisches Material umfasst.

37. Vorrichtung nach Anspruch 36, in der das ferroelektrische Material ausgewählt ist aus der Gruppe bestehend aus Bleimagnesiumniobattitanat, Bleizirconattitanat, Bariumtitanat und deren Mischungen.

38. Vorrichtung nach Anspruch 36, in der die Substratstruktur zusätzlich eine oder mehrere dielektrische Dünnfilm-Schichten auf der Dickfolien-Schicht umfasst.

39. Vorrichtung nach Anspruch 38, in der die Vorrichtung zusätzlich eine dielektrische Dünnfilm-Schicht oben auf dem Dünnfilm-Phosphor umfasst.

40. Phosphormaterial mit der Formel:

$A_{1-w}D_w[M_xZ_{1-x}]_yS_4$,

worin

A ein Kation der Gruppe IIA oder Gruppe IIB ist;
D ein Seltenerdmetall ist;
M ein Metall der Gruppe IIIB ist, das aus Y, Sc, La und Ac ausgewählt ist;
Z aus Al, Ga und In ausgewählt ist;
$0<x<0.2$;
$y=2$; und
$0{,}005<w<0.1$

41. Phosphor nach Anspruch 40, in dem M Yttrium ist, A Barium ist, D Europium ist und Z Aluminium ist.

Revendications

1. Luminophore en couche mince destiné à un dispositif électroluminescent, ledit luminophore étant choisi dans le groupe comprenant des thioaluminates, des thiogallates et des thioindates dont au moins un cation est choisi parmi des éléments des groupes IIA et IIB du tableau périodique des éléments, ledit luminophore étant activé par un lanthanide et contenant un élément du groupe IIIB en tant que produit de remplacement partiel d'une partie de l'aluminium, du gallium ou de l'indium desdits thiogallates, thioindates et thioaluminates.

2. Luminophore en couche mince selon la revendication 1, dans lequel ledit élément du groupe IIIB est choisi de telle sorte qu'il ne déforme ou qu'il n'affecte pratiquement pas la structure réticulaire des cristaux dudit luminophore.

3. Luminophore en couche mince selon la revendication 2, dans lequel ledit élément du groupe IIIB est choisi dans le groupe comprenant du scandium, de l'yttrium, du lanthane et de l'actinium.

4. Luminophore en couche mince selon la revendication 3, dans lequel ledit élément représente de l'yttrium.

5. Luminophore en couche mince selon la revendication 4, dans lequel ledit luminophore représente un thioaluminate.

6. Luminophore en couche mince selon la revendication 4, dans lequel ledit luminophore est un thiogallate.

7. Luminophore en couche mince selon la revendication 4, dans lequel ledit luminophore représente un thioindate.

8. Luminophore en couche mince selon l'une quelconque des revendications 1 à 7, dans lequel ledit lanthanide est choisi dans le groupe comprenant l'europium et le cérium.

9. Luminophore en couche mince selon la revendication 8, dans lequel ledit lanthanide représente de l'europium.

10. Luminophore en couche mince selon la revendication 9, dans lequel ledit cation représente du baryum.

11. Luminophore en couche mince selon la revendication 10, dans lequel ledit luminophore contient de l'europium en une quantité variant d'environ 1 à 10 pourcent atomique de baryum et l'yttrium est présent en une quantité variant d'environ 0,1 à 20 pourcent atomique d'aluminium.

12. Luminophore en couche mince selon la revendication 10, dans lequel ledit luminophore contient de l'europium en une quantité variant d'environ 2 à 7 pourcent atomique de baryum et l'yttrium est présent en une quantité variant d'environ 1 à 7 pourcent atomique d'aluminium.

13. Luminophore en couche mince selon la revendication 11 ou 12, dans lequel ledit luminophore représente $Ba_{0,97}Eu_{0,03}(Y_xAl_{1-x})_2S_4$, dans laquelle formule $0<x<1{,}0$.

14. Dispositif électroluminescent comprenant un luminophore en couche mince selon la revendication 1 ou 12 sur une structure substrat.

15. Dispositif selon la revendication 14, dans lequel ladite structure substrat comprend une céramique en couche épaisse.

16. Dispositif selon la revendication 15, dans lequel ladite céramique en couche épaisse comprend un substrat de base sur lequel une couche conductrice est déposée, une pellicule en couche épaisse étant déposée sur la couche conductrice.

17. Dispositif selon la revendication 16, dans lequel ledit substrat de base comprend une céramique choisi dans le groupe comprenant une feuille céramique, un composite métal/céramique, un vitrocéramique et du verre haute température.

18. Dispositif selon la revendication 17, dans lequel ladite feuille céramique est de l'alumine.

19. Dispositif selon la revendication 18, dans lequel la couche mince conductrice est choisie dans le groupe comprenant un alliage d'or et d'argent.

20. Dispositif selon la revendication 19, dans lequel ladite pellicule en couche épaisse comprend un matériau ferroélectrique.

21. Dispositif selon la revendication 20, dans lequel ledit matériau ferroélectrique est choisi dans le groupe comprenant le niobate de plomb-magnésium et titane, le titanate-zirconate de plomb, le titanate de baryum et leurs mélanges.

22. Dispositif selon la revendication 20, dans lequel ladite structure substrat comprend en plus une ou plusieurs fines couches diélectriques sur la pellicule en couche épaisse.

23. Dispositif selon la revendication 22, dans lequel le dispositif comprend en plus une fine couche diélectrique sur ledit luminophore en couche mince.

24. Matériau luminophore répondant à la formule :

$$A_{1-w}D_w[Y_xZ_{1-x}]_yS_4,$$

dans laquelle,

A représente un cation du groupe IIA ou du groupe IIB ;
D représente un lanthanide ;
Z est choisi parmi Al, Ga et In ;
$0 < x < 0,2$;
y vaut 2 ; et
$0,005 < w < 0.1$.

25. Luminophore selon la revendication 24, dans lequel Z représente de l'aluminium.

26. Luminophore selon la revendication 24 ou 25, dans lequel D est choisi dans le groupe comprenant l'europium et le cérium.

27. Luminophore selon la revendication 26, dans lequel ledit lanthanide représente de l'europium.

28. Luminophore selon la revendication 27, dans lequel ledit cation représente du baryum.

29. Luminophore selon la revendication 28, dans lequel ledit luminophore représente $Ba_{0,97}Eu_{0,03}(Y_xAl_{1-x})_2S_4$, dans laquelle formule $0 < x < 0,1$.

30. Dispositif électroluminescent comprenant un luminophore selon la revendication 24 sur une structure substrat.

31. Dispositif selon la revendication 30, dans lequel ladite structure substrat comprend une céramique en couche épaisse.

32. Dispositif selon la revendication 31, dans lequel ladite céramique en couche épaisse comprend un substrat de base sur lequel une couche conductrice est déposée, une pellicule en couche épaisse étant déposée sur la couche conductrice.

33. Dispositif selon la revendication 32, dans lequel ledit substrat de base comprend une céramique choisie dans le groupe comprenant une feuille céramique, un composite métal/céramique, un vitrocéramique et du verre haute température.

34. Dispositif selon la revendication 33, dans lequel ladite feuille céramique représente de l'alumine.

35. Dispositif selon la revendication 34, dans lequel la couche mince conductrice est choisie dans le groupe comprenant un alliage d'or et d'argent.

36. Dispositif selon la revendication 35, dans lequel ladite pellicule en couche épaisse comprend un matériau ferroélectrique.

37. Dispositif selon la revendication 36, dans lequel ledit matériau ferroélectrique est choisi dans le groupe comprenant le nobiate de plomb-magnésium et titane, le titanate-zirconate de plomb, le titanate de baryum et leurs mélanges.

38. Dispositif selon la revendication 36, dans lequel ladite structure substrat comprend en plus une ou plusieurs fines couches diélectriques sur la pellicule en couche épaisse.

39. Dispositif selon la revendication 38, dans lequel le dispositif comprend en plus une fine couche diélectrique sur la partie supérieure dudit luminophore en couche mince.

40. Matériau luminophore répondant à la formule :

$$A_{1-w}D_w[Y_xZ_{1-x}]_yS_4,$$

dans laquelle,

A représente un cation du groupe IIA ou du groupe IIB ;
D représente un lanthanide ;
M représente un métal du groupe IIIB choisi parmi Y, Sc, La et Ac ;
Z est choisi parmi Al, Ga et In ;
$0 < x < 0,2$;
y vaut 2 ; et
$0,005 < w < 0.1$.

41. Luminophore selon la revendication 40, dans lequel M représente de l'yttrium, A représente du baryum, D représente de l'europium et Z représente de l'aluminium.

Figure 1

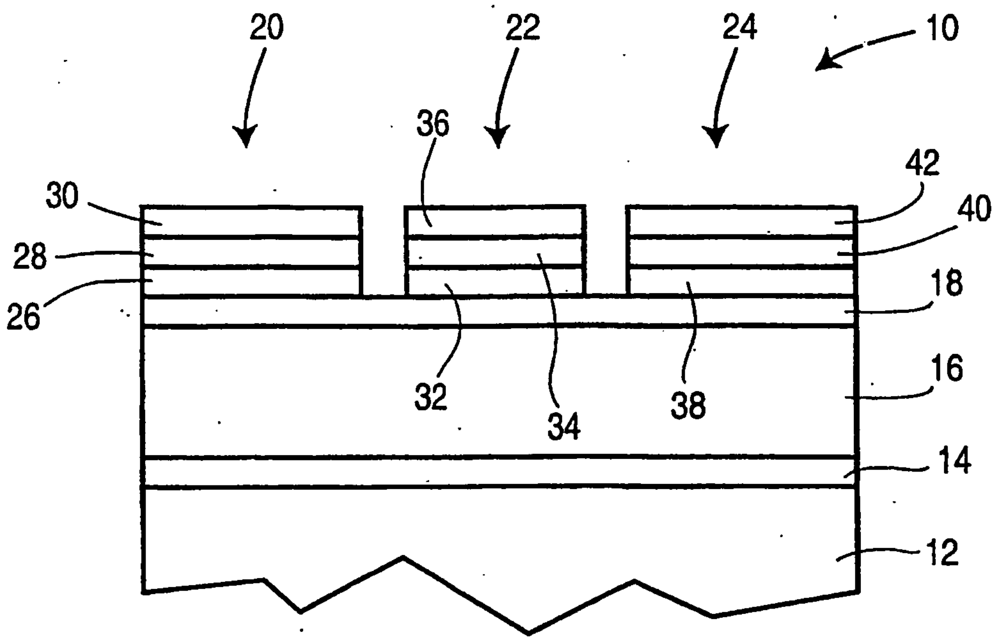


Figure 2

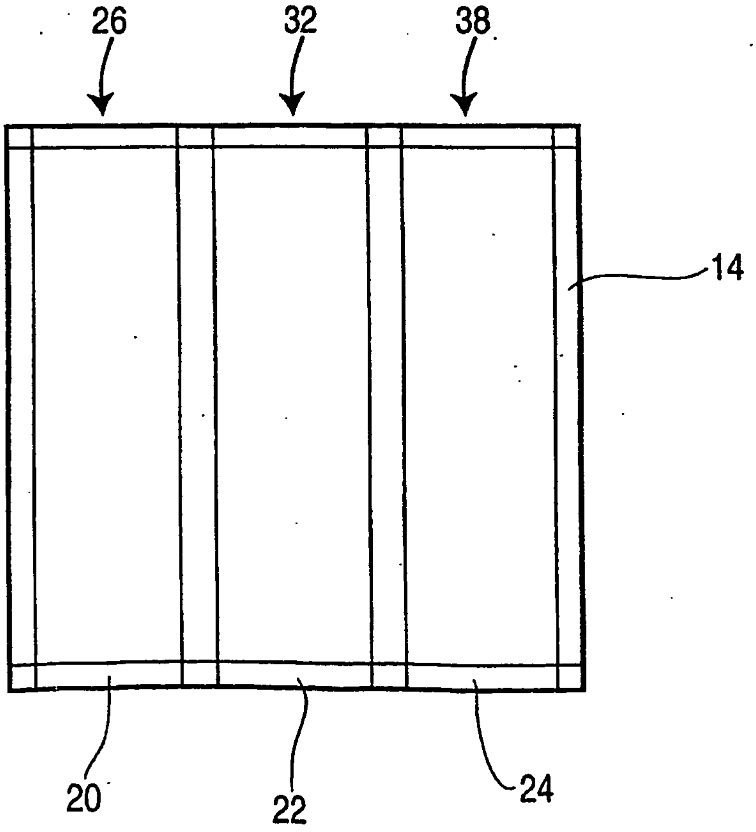


Figure 3

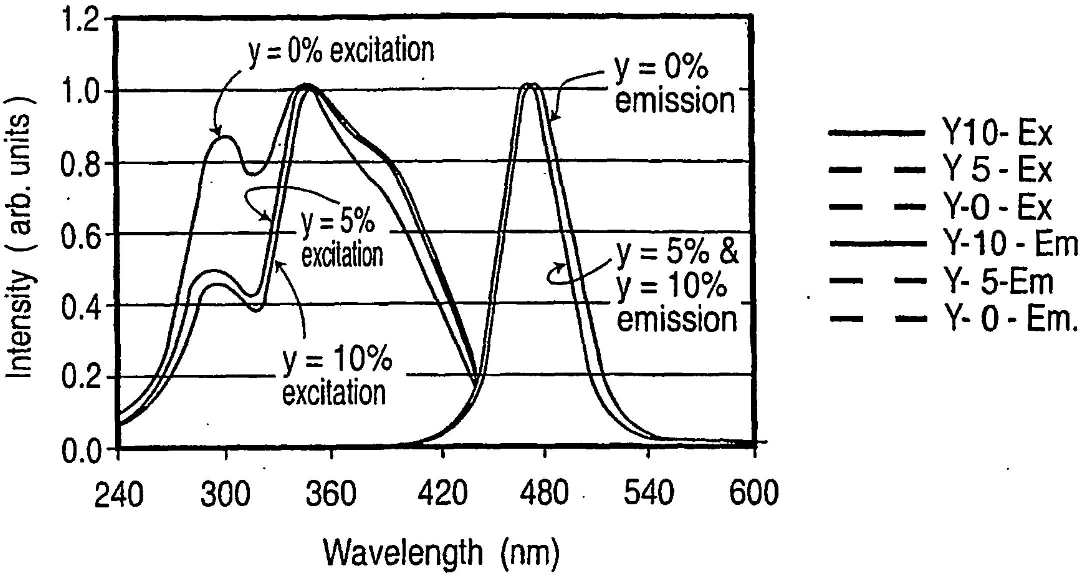


Figure 4

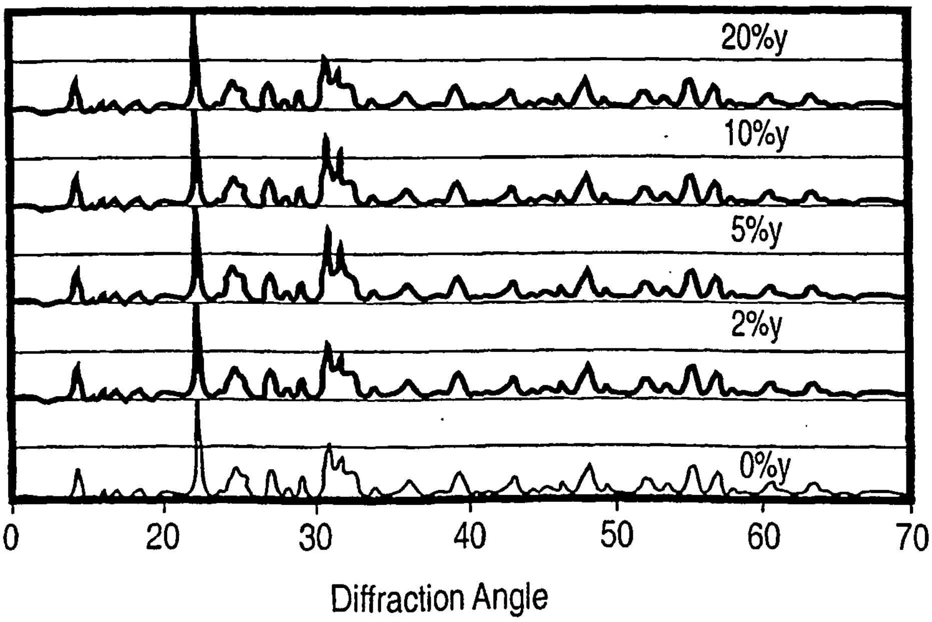


Figure 5

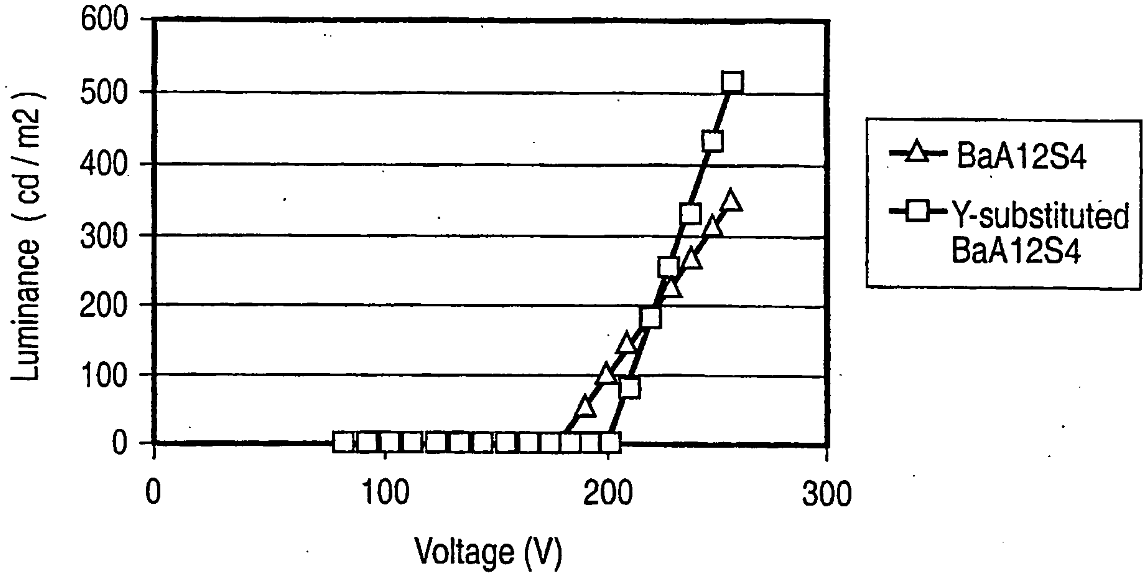


Figure 6

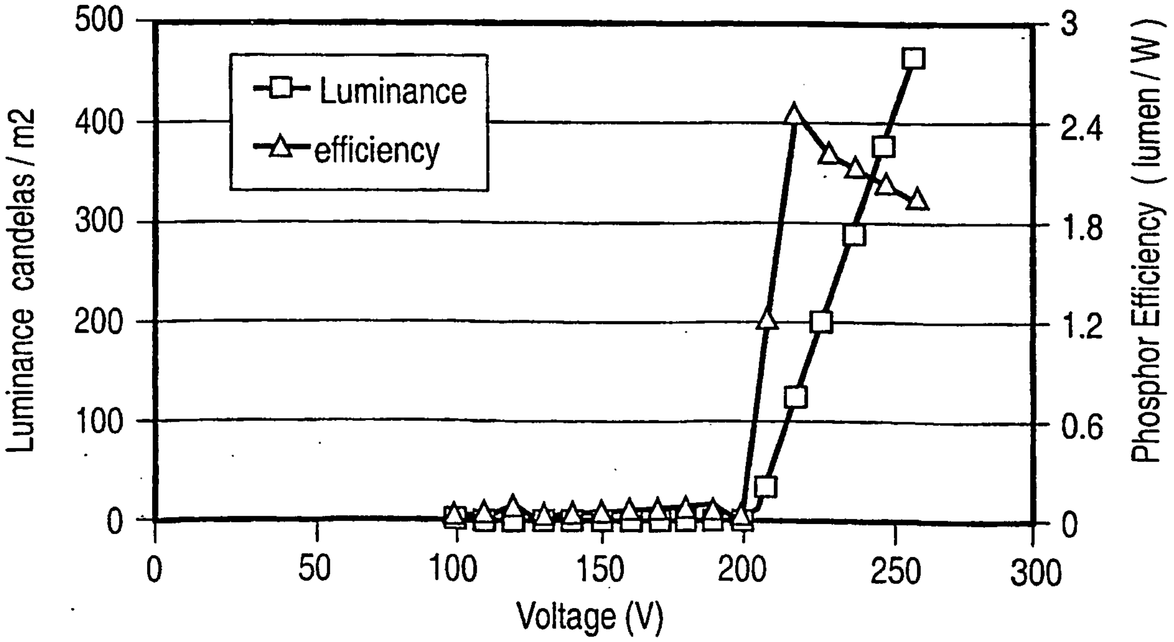


Figure 7

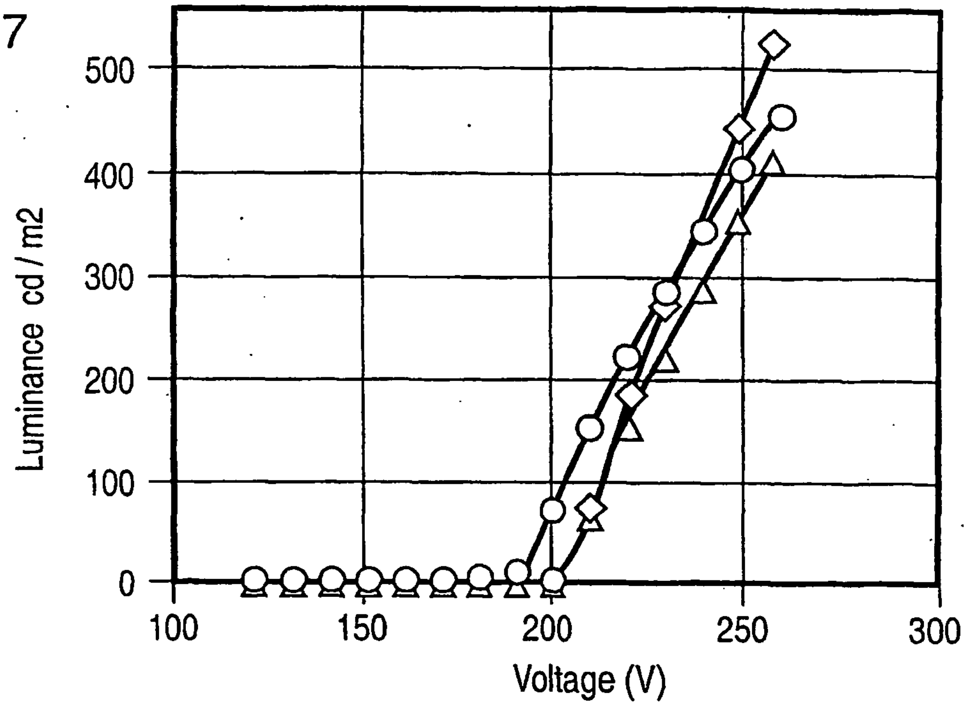
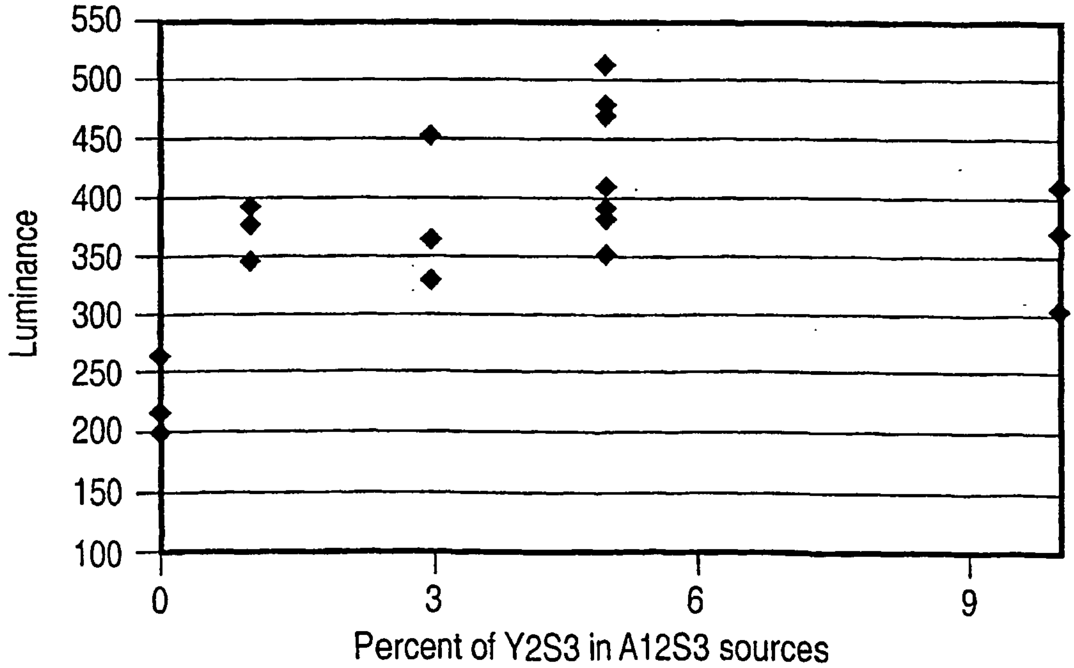


Figure 8



专利名称(译)	钇取代硫铝酸钡磷光体材料		
公开(公告)号	EP1493307B1	公开(公告)日	2007-05-23
申请号	EP2003707980	申请日	2003-03-24
[标]申请(专利权)人(译)	伊菲雷技术公司		
申请(专利权)人(译)	IFIRE TECHNOLOGY INC.		
当前申请(专利权)人(译)	IFIRE科技股份有限公司.		
[标]发明人	NAKUA ABDUL M CHEONG DAN DAEWEON		
发明人	NAKUA, ABDUL, M. CHEONG, DAN, DAEWEON		
IPC分类号	H05B33/14 H05B33/22 H05B33/26 C09K11/84 C09K11/00 C09K11/62 C09K11/64 C09K11/75 C09K11/77 C09K11/89		
CPC分类号	H05B33/14 C09K11/752 C09K11/7768 C09K11/7786 C09K11/892 H05B33/22 H05B33/26 Y10S428/917		
优先权	60/367510 2002-03-27 US		
其他公开文献	EP1493307A1		
外部链接	Espacenet		

摘要(译)

一种用于电致发光器件的薄膜荧光粉，该荧光粉选自硫代铝酸盐，硫代镓酸盐和硫代铟酸盐，其具有至少一种选自元素周期表IIA和IIB族元素的阳离子。磷光体被稀土金属活化并含有IIIB族元素，作为所述硫代镓酸盐，硫代吲哚和硫代铝酸盐的一部分铝，镓或铟的部分替代物。磷光体提供改善的亮度。还描述了在基板上包含薄膜磷光体的电致发光器件。

Figure 1

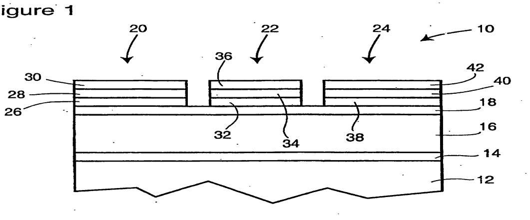


Figure 2