(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
5 October 2006 (05.10.2006)

PCT

(10) International Publication Number
WO 2006/104860 A2

(51) International Patent Classification:
H01L 33/00 (2006.01) *C09K 11/08* (2006.01)

(21) International Application Number:
PCT/US2006/010659

(22) International Filing Date: 23 March 2006 (23.03.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/665,458	25 March 2005 (25.03.2005)	US
60/665,636	25 March 2005 (25.03.2005)	US
60/665,456	25 March 2005 (25.03.2005)	US
60/665,457	25 March 2005 (25.03.2005)	US
60/684,373	24 May 2005 (24.05.2005)	US
11/149,648	10 June 2005 (10.06.2005)	US

(71) Applicant *(for all designated States except US)*: **SARNOFF CORPORATION** [US/US]; 201 Washington Road, Princeton, New Jersey 08540 (US).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **TIAN, Yongchi** [US/US]; 1 Roseland Court, Priceton Junction, New Jersey 08550 (US).

(74) Agents: **DI NUNZIO, Mary, Catherine** et al.; LOWENSTEIN SANDLER PC, 65 Livingston Avenue, Roseland, New Jersey 07068 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2006/104860 A2

(54) Title: METAL SILICATE-SILICA-BASED POLYMORPHOUS PHOSPHORS AND LIGHTING DEVICES

(57) Abstract: Provided, among other things, is a phosphor according to the formula: $[(Bv\text{-}SiO_3)_x(Mv_2SiO_3)_y(Tv_2(SiO_3)_3)_z]_m.(SiO_2)_n$: Rε, X (I) wherein x, y and z are any value, where x + y + z = l, Bv is one or more divalent alkaline earth metal ions, Mv is one or more monovalent alkaline metal ions, Tv is one or more trivalent metal ions, Rε is one or more activators selected from Eu^{2+} or Mn^{2+} ions, X is one or more halides, m is 1 or O provided that if m is 1 and provides an amount of silica effective to host useful luminescence, then n is greater than 3 or if m is O, then n isl .

Metal Silicate-Silica-Based Polymorphous Phosphors and Lighting Devices

[0001] The present invention relates to metal silicate-silica-based, polymorphous phosphors, methods of making the phosphors, and semiconductor lighting devices modified with the phosphors.

[0002] In lighting applications, phosphors can be used to modify or manage the wavelength of light output. For example, UV or blue light emitting diodes (LEDs) can be enhanced to produce visible light or less blue light by positioning phosphors along the emission pathway to convert light to longer wavelengths. Blue, green and red emitting phosphors can be used to modify UV light to white light. Green and red emitting phosphors can be used to modify a blue output to white light. Yellow emitting phosphors can be mixed with light from a blue emitting diode or a blue emitting phosphor to create light of white chromaticity. The phosphors described here, when matched with appropriate light sources, can be used in such applications.

[0003] Near UV emitting solid state lighting devices incorporating semiconductor light sources (such as LEDs) hold the promise of producing light with sufficient efficiency that, with the light emission modified to the visible range with appropriate phosphors, they may be cost-effectively employed to provide a wide range of lighting devices for use in electronics as well as general illumination. The lattices of these semiconductor light emitting diodes are typically InGaN-based doped by minor portions of magnesium to generate enough defects for radiation recombination of electrons and holes. For example, Nichia Corp. (Anan-shi, Japan) has made a 100 mW InGaN-based semiconductor light source designated NCCU033E, and an 85 mW GaN-based semiconductor light source designated NCCU001E. To utilize these near UV light sources in lighting products, phosphors with the appropriate excitation and emission characteristics are needed.

[0004] For near UV-LED devices, phosphors are used to convert the primary emission wavelength from 360 to 420 nm to visible light, especially to produce white light. These phosphors can be categorized into red-emitting, green-emitting and blue-emitting components. There are some existing phosphors, developed for other applications, which have an excitation profile to enable visible emission. Green-emitting examples include $(Ba_{1-x-y},Ca_xSr_y)_2(Mg_{1-z}Zn_z)Si_2O_7$:Eu, $Ca_8Mg(SiO_4)_4Cl_2$:Eu,Mn, Ba_2SiO_4:Eu, $Ba_2MgSi_2O_7$:Eu,

$Ba_2ZnSi_2O_7$:Eu, $BaAl_2O_4$:Eu, $SrAl_2O_4$:Eu, $BaMg_2Al_{16}O_{27}$:Eu, and $Ca_8Mg(SiO_4)_4Cl_2$:Eu, Mn. Blue-emitting examples include $BaMg_2Al_{16}O_{27}$:Eu, $(Sr,Ba,Ca)_5(PO_4)_3Cl$:Eu and $Sr_4Al_{14}O_{25}$:Eu. These phosphors are fairly efficiently excited by near UV light in the wavelength ranging from 360 to 420 nm. Red-emitting examples include Y_2O_2S:Eu,Bi, Y_2O_3:Eu, Bi and $3.5MgO{\cdot}0.5MgF_2{\cdot}GeO_2$:Mn.

[0005] However, some of these phosphors are not ideally suited for wavelength conversion and in many cases have low efficiency when excited by a typical UV LED wavelength of 400 nm. Phosphors that are engineered to have the desired emission characteristics and which possess an excitation profile ideally suited for UV LEDs, are still needed.

[0006] Certain heterogeneous divalent europium and manganese activated, metal halide-silica phosphors have been described (Lehmann, J. Elect. Soc. 22:748-52, 1975), but with no description of use. The phosphors, which were doped with europium or europium plus manganese, were described as "***luminescent halides*** dispersed in small segregations inside of bigger and nonluminescent SiO_2 particles." (Emphasis added.) According to the author, X-ray diffraction data "normally show only lines corresponding to the α-cristobalite modification of SiO_2. Whatever else is present must be either amorphous or in amounts too small to be detected by routine x-ray analysis (detectability limit: several %)." These phosphors have been described as being produced by firing in the presence of an excess of ammonium halide in a slightly reducing atmosphere. Attempts to reproduce this preparation method yielded explosions. The materials processed by the methods described below yielded product that XRD analysis has repeatedly shown to have a metal inosilicate and crystalline silica composition.

[0007] The metal silicate-silica-based, polymorphous phosphors are effectively used as wavelength converters with near UV or blue-emitting semiconductor or LED light sources. They can provide stable phosphors that are usefully excited with near UV light, including red-emitting phosphors, pink-emitting phosphors, blue-emitting phosphors, and the like. Different phosphors of the present invention, or such phosphor(s) and other phosphoSr, can be mixed to achieve different chromaticities, including white light.

Exemplary Embodiments

[0008] A family of activated metal silicate-silica-based, polymorphous phosphors are believed to be useful for such applications. In one embodiment, the phosphors of the invention are according to the formula:

$$[(BvSiO_3)_x(Mv_2SiO_3)_y(Tv_2(SiO_3)_3)_z]_m \bullet (SiO_2)_n: R\varepsilon, X \qquad (I)$$

wherein Bv is one or more divalent metal ions; Mv is one or more monovalent ions; Tv is one or more trivalent metal ions; x, y and z are any value such that $x + y + z = 1$; Rε is one or more activators selected from Eu^{2+} and Mn^{2+}; X is one or more monovalent halides selected from F^-, Cl^-, Br^- or I^-. Rε is present, for example in an amount effective to provide luminescent emission. The value of m is 1 or 0. The value of n is > 3 if m = 1, and is such as to provide an amount of silica effective to host useful luminescence. The value of n is 1 if m = 0. Bv, Mv and Tv are metal ions that support the formation of the metal silicates. As used herein, the term "halide" or "halides," refers to a crystalline material comprised of metal cations and anions of group VII elements that are ionically bonded.

[0009] It is believed that where a mix of Mv and Bv, or Mv and Tv, or Bv and Tv, or Mv, Bv and Tv, is present, the Mv silicate, Bv silicate and Tv silicates are in separate crystalline phases. The metal silicate is believed to be in a separate phase from the silica $(SiO_2)_n$. The phases are separate in that they can be detected in XRD data.

[0010] The metal silicate is present in an amount that supports formation of other crystals in the host materials. Useful amounts are believed to include, for example, amounts from 1-10% of the phosphor composition. n describes an amount of matrix silica, which can be 100% amorphous, 100% cristobolite, contain quartz, or a mixture anywhere in between. The value of n can be determined from a compositional analysis and XRD estimation of the amount of $MSiO_3$.

[0011] In one embodiment, Bv is an alkaline earth metal ion, such as one or more ions of Be, Mg, Ca, Sr or Ba. In one embodiment, Bv is one or more ions of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Ta, W, Re, Os, Ir, Pt, Au or Hg. In one embodiment, Bv is one or more ions of Be, Mg, Ca, Sr, Ba, Mn, Co, Ni, Cu, Zn, Cd or Hg. In one embodiment, Tv is one or more ions of Al, Ga, In, Sc, Y or La. In one embodiment, Mv is one or more alkaline metal ions, such as Li, Na or K.

[0012] The composition can be very stable, in that it retains 85% or more, 86% or more, 87% or more, 88% or more, 89% or more, 90% or more, 91% or more, or 92% or more of its relative emission intensity after 400 hours at 85°C in the presence of 85% relative humidity.

[0013] In certain embodiments, the mole percentage of Rε in the composition is 0.001% to 10% of silica (SiO_2) (or, in some embodiments, of formula components). In certain embodiments, the range of the mole percentage of Rε is from one of the following lower endpoints (inclusive) or from one of the following upper endpoints (inclusive). The lower endpoints are 0.001%, 0.01%, 0.02%, 0.05%, 0.1%, 0.2%, 0.5%, 1%, 2%, 3%, 4% and 5%. The upper endpoints are 0.01%, 0.02%, 0.05%, 0.1%, 0.2%, 0.5%, 1%, 2%, 3%, 4%, 5% and 10%. For example, the range can be 0.01% to 5%.

[0014] In certain embodiments, the mole percentage of X in the composition is 0.002% to 5% of silica (SiO_2) (or, in some embodiments, of formula components). In certain embodiments, the range of the mole percentage of Rε is from one of the following lower endpoints (inclusive) or from one of the following upper endpoints (inclusive). The lower endpoints are 0.002%, 0.01%, 0.02%, 0.05%, 0.1%, 0.2%, 0.5%, 1%, 2%, 3% and 4%. The upper endpoints are 0.01%, 0.02%, 0.05%, 0.1%, 0.2%, 0.5%, 1%, 2%, 3%, 4% and 5%. For example, the range can be 0.01% to 5%.

[0015] In certain embodiments, the mole percentage of $BvSiO_3$ and/or Mv_2SiO_3 and/or $Tv_2(SiO_3)_3$ is 0.1% to 40% of silica (SiO_2) (or, in some embodiments, of formula components). In certain embodiments, the range of the mole percentage of $BvSiO_3$ and/or $MvSiO_3$ and/or $Tv_2(SiO_3)_3$ is from one of the following lower endpoints (inclusive) or from one of the following upper endpoints (inclusive). The lower endpoints are 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.7%, 1%, 2%, 5%, 10%, 15%, 20%, 30% and 40%. The upper endpoints are 0.2%, 0.3%, 0.4%, 0.5%, 0.7%, 1%, 2%, 5%, 10%, 15%, 20%, 30%, 40% and 50%. For example, the range can be 5% to 10%.

[0016] In certain embodiments, $x = 1$. In certain embodiments, $y = 1$. In certain embodiments, $z = 1$. In certain embodiments, one or two of x, y and z are zero.

[0017] In certain embodiments, X is a halide and is ≥ 99.9% (molar) of a given metal halide, such as ≥ 99.9% (molar) of a metal halide comprising chlorine, or ≥ 99.9% (molar) of a metal

halide comprising iodine, or ≥ 99.9% (molar) of a metal halide comprising bromine. X is generally present in an amount that charge neutralizes Rε.

Brief Description of the Drawings

[0018] Figures 1 (Ex. 1), **4** (Ex. 2), **5** (Ex. 3), **7** (Ex. 4), **8** (Ex. 5), **10** (Ex. 6), **11** (Ex. 7) and **12** (Ex. 8) show excitation and emission spectra of phosphors of the invention.

[0019] Figures 2 (Ex. 1) and **6** (Ex. 3) show stability data for phosphors of the invention.

[0020] Figures 3 (Ex. 1) and **9** (Ex. 5) show X-ray diffraction data for phosphors of the invention.

[0021] Figures 13 and **14** show light emitting devices.

[0022] Figure 15 illustrates an exemplary layered structure for a near UV emitting semiconductor light source.

Detailed Description of the Invention

[0023] The host material of the phosphors is believed to be polymorphous metal silicates and silica. The silica, SiO_2, constitutes the greater part of the host materials. The silica can be crystallized in cristobalite, which is made from SiO_4 tetrahedral units fused together by sharing oxygen atoms. The crystal can have the space group of $P4_32_12$ of a tetragonal system. The silica can also be present in quartz or amorphous forms. The metal silicates, $BvSiO_3$ and Mv_2SiO_3, are believed to be in the form of inosilicates in which tetrahedral polymerization is based upon (SiO_3), as in the pyroxene jadeite, $NaAl[Si_2O_6]$, and double chain silicates with tetrahedral polymerization, as found in the amphilbole glaucophane. Typically, the (SiO_3) units form single chains by sharing an oxygen atom of the SiO_4 tetrahedra, and the single chains repeat their tetrahedral growth or translation pattern in multiples of three forming Wollastonite, calcite or enstalite.

[0024] A reaction in forming the phosphor at high temperature is considered to be, in a number of embodiments of the invention, the crystallization of silica into cristobalite, while incorporating activators Eu^{2+} and/or Mn^{2+} in the crystals. This reaction is supported by a medium that at the firing temperature is liquid. In other words, by a "flux". There are other types of metal silicates that can be molten in the temperature range for the crystallization.

These silicates can function as flux providing the fluid medium at the temperatures of, for example, ~900 to ~1300 °C.

[0025] Synthesis can, for example, include: (1) providing an appropriate mixture of precursors (e.g., the metal carbonates, and/or metal nitrates, and/or metal oxides, and/or metal halides -- such as metal halides comprising fluorine, iodine, bromine and/or chlorine, such as $CaCl_2$, and/or optionally, a source of halide X), where at some point in the mixing a slurry can be used to ensure the intimate contact of the reactant ingredients ready for the solid-state chemical reactions; (2) optionally milling the mixture to achieve further contact at a fine particle level of the inorganic solids; (3) optionally drying the mixed material; (4) optionally heating under a reducing gas, such as, for example, hydrogen, at a given first temperature; (5) optionally mixing in further precursor of X; (6) firing at a temperature higher than the given first temperature, under a reducing gas; (7) optionally washing the phosphor with a solvent effective to wash out unreacted ingredients; and (8) optionally applying a post formation treatment such as sieving or size separation.

[0026] It will be recognized that the materials provided in the forming reaction may not altogether convert to the forms of formula I, and that all unreacted materials may not wash out (if a washing step is used). However, it is believed that formula I describes the significant hosting and flux providing phases of the phosphor.

[0027] The first temperature can be at, for example, 700 to 1100 °C. For example, it can be a range from 700°C, 710°C, 720°C, 730°C, 740°C, 750°C, 760°C, 770°C, 780°C, 790°C, 800°C, 810°C, 820°C, 830°C, 840°C, 850°C, 860°C, 870°C, 880°C, 890°C, 900°C, 910°C, 920°C, 930°C, 940°C, 950°C, 960°C, 970°C, 980°C, 990°C or 1000°C upwards. Or a range from 1100°C, 1090°C, 1080°C, 1070°C, 1060°C, 1050°C, 1040°C, 1030°C, 1020°C, 1010°C, 1000°C, 990°C, 980°C, 970°C, 960°C, 950°C, 940°C, 930°C, 920°C, 910°C, 900°C, 890°C, 880°C, 870°C, 860°C, 850°C, 840°C, 830°C, 820°C, 810°C, 800°C downwards.

[0028] The firing can be at, for example, 900 to 1300 °C. For example, it can be a range from 900°C, 910°C, 920°C, 930°C, 940°C, 950°C, 960°C, 970°C, 980°C, 990°C, 1000°C, 1010°C, 1020°C, 1030°C, 1040°C, 1050°C, 1060°C, 1070°C, 1080°C, 1090°C, 1100°C, 1110°C, 1120°C, 1130°C, 1140°C, 1150°C, 1160°C, 1170°C, 1180°C, 1190°C or 1200°C, upwards. Or a range from 1300°C, 1290°C, 1280°C, 1270°C, 1260°C, 1250°C, 1240°C,

1230°C, 1220°C, 1210°C, 1200°C, 1190°C, 1180°C, 1170°C, 1160°C, 1150°C, 1140°C, 1130°C, 1120°C, 1110°C, 1100°C, 1090°C, 1080°C, 1070°C, 1060°C, 1050°C, 1040°C, 1030°C, 1020°C, 1010°C or 1000°C downwards. The firing can be, for example, at a temperature 40°C or more, 50°C or more, 60°C or more, 70°C or more, 48°C or more, 90°C or more, or 100°C or more higher than the flux temperature.

[0029] In certain embodiments, the SiO_2 component is substantially 0% cristobolite, and the rest amorphous or quartz, or a given molar percent or more cristobolite, and the rest amorphous or quartz. The given percent can be, for example, 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 or 100%. Or, SiO_2 component can be a given percentage or less cristobolite. The second given percent can be, for example, 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90 or 95%.

[0030] In certain embodiments x is substantially 1. In other embodiments, x is substantially 0. In certain embodiments z is substantially 0. In certain embodiments, z = 0, and x or y is 0.50 or less, 0.49 or less, 0.48 or less, 0.47 or less, 0.46 or less, and so on by 0.01 increments to 0.01 or less. In certain embodiments x or y or z is 0.50 or less, 0.49 or less, 0.48 or less, 0.47 or less, 0.46 or less, and so on by 0.01 increments to 0.01 or less.

[0031] In certain embodiments, the quantum efficiency of phosphors of the invention is 40% or more.

[0032] The emission peak of metal silicate-silica-based, polymorphous phosphors of the invention is measured with the excitation source being light at 300-500 nm ± 10 nm. In certain embodiments, the emission peak range is from one of the following lower endpoints (inclusive) or from one of the following upper endpoints (inclusive). The lower endpoints are 360, 361, 362, 363, and each one nm increment up to 799 nm. The upper endpoints are 800, 799, 798, 797, and each one nm down to 361.

[0033] In some embodiments, the lower endpoints are 430, 431, 432, and each one nm increment up to 489 nm. In some embodiments, the upper endpoints are 490, 489, 488, and each one nm increment down to 431 nm.

[0034] In some embodiments, the lower endpoints are 500, 501, 502, and each one nm increment up to 559 nm. In some embodiments, the upper endpoints are 560, 559, 558, and each one nm increment down to 501 nm.

[0035] In some embodiments, the lower endpoints are 590, 591, 592, and each one nm increment up to 659 nm. In some embodiments, the upper endpoints are 660, 659, 658, and each one nm increment down to 591 nm.

[0036] In certain embodiments, the phosphor is effectively excited (sufficiently for use with a corresponding semiconductor light emitting device) with light of wavelength from 400 to 420 nm.

[0037] Rε is substantially composed of all Eu or Mn or both, but minor amounts, such as 4% or less, 2% or less, 1% or less, 0.5% or less, 0.4% or less, 0.3% or less, 0.2% or less, or 0.1% or less of activators, may be other activator(s).

[0038] Among candidate metal ions M, ions of Mg and Ba are less preferred. In certain embodiments, M is 99% (molar) or more, 99.1% or more, 99.5% or more, 99.7% or more, 99.8% or more, 99.8% or more, or 99.9% or more of one metal (such as, for example, Ca).

[0039] In certain embodiments, the phosphor is according to $[(CaSiO_3)]_m \bullet (SiO_2)_n:Eu^{2+}$, Mn^{2+}, I^-, with the concentration and ratio of Eu^{2+} and Mn^{2+} selected to provide a peak emission between 600 nm and 640 nm, or 620 nm and 660 nm (or an included range to one of the foregoing ranges), and a chromaticity of x = 0.62 ±0.06, y = 0.30 ±0.06.

[0040] In certain embodiments, the phosphor is according to $[(CaSiO_3)]_m \bullet (SiO_2)_n:Eu^{2+}$, I^-, with the concentration of Eu^{2+} selected to provide a peak emission between 445 nm and 480 nm, or 455 nm and 475 nm, or 445 nm and 475 nm (or an included range to one of the foregoing ranges), and a chromaticity of x = 0.20 ±0.06, y = 0.10 ±0.06.

[0041] In certain embodiments, the phosphor is according to $[(CaSiO_3)]_m \bullet (SiO_2)_n:Eu^{2+}$, Mn^{2+}, Cl^-, with the concentration and ratio of Eu^{2+} and Mn^{2+} selected to provide a chromaticity of x = 0.40 ±0.06, y = 0.20 ±0.06.

[0042] When used in a lighting device, it will be recognized that the phosphors can be excited by light from a primary source, such as an semiconductor light source emitting in the wavelength of 300-420 nm, or from secondary light such as emissions from other phosphor(s) emitting in the same wavelength range. Where the excitation light is secondary, in relation to the phosphors of the invention, the excitation-induced light is the relevant source light. Devices that use the phosphor of the invention can include mirrors, such as dielectric mirrors,

to direct light produced by the phosphors to the light output rather than the interior of the device (such as the primary light source).

[0043] The semiconductor light source can, in certain embodiments, emit light of 300 nm or more, or 305 nm or more, or 310 nm or more, and so on in increments of 5 nm to 400 nm or more. The semiconductor light source can, in certain embodiments, emit light of 420 nm or less, or 415 nm or less, or 410 nm or less, and so on in increments of 5 nm to 350 nm or less.

[0044] Phosphor particles may be dispersed in the lighting device with a binder or solidifier, dispersant (i.e., light scattering material), filler or the like, The binder can be, for example, a light curable polymer such as an acrylic resin, an epoxy resin, polycarbonate resin, a silicone resin, glass, quartz and the like. The phosphor can be dispersed in the binder by methods known in the art. For example, in some cases the phosphor can be suspended in a solvent, and the polymer suspended, dissolved or partially dissolved in the solvent, the slurry dispersed on the lighting device, and the solvent evaporated. In some cases, the phosphor can be suspended in a liquid, pre-cured precursor to the resin, the slurry dispersed, and the polymer cured. Curing can be, for example, by heat, UV, or a curing agent (such as a free radical initiator) mixed in the precursor. Or, in another example, the binder may be liquefied with heat, a slurry formed, and the slurry dispersed and allowed to solidify in situ. Dispersants include, for example, titanium oxide, aluminum oxide, barium titanate, silicon dioxide, and the like.

[0045] It is anticipated that lighting devices of the invention will use semiconductor light sources such as LEDs to either create excitation energy, or excite another system to provide the excitation energy for the phosphors. Devices using the invention can include, for example, white light producing lighting devices, indigo light producing lighting devices, blue light producing lighting devices, green light producing lighting devices, yellow light producing lighting devices, orange light producing lighting devices, pink light producing lighting devices, red light producing lighting devices, or lighting devices with an output chromaticity defined by the line between the chromaticity of a phosphor of the invention and that of one or more second light sources. Headlights or other navigation lights for vehicles can be made with the devices of the invention. The devices can be output indicators for small electronic devices such as cell phones and PDAs. The lighting devices can also be the backlights of the liquid crystal displays for cell phones, PDAs and laptop computers. Given

appropriate power supplies, room lighting can be based on devices of the invention. The warmth (i.e., amount of yellow/red chromaticity) of lighting devices can be tuned by selection of the ratio of light from a phosphor of the invention to light from a second source.

[0046] Suitable semiconductor light sources are any that create light that excites the phosphors, or that excites a phosphor that in turn excites the phosphors of the invention. Such semiconductor light sources can be, for example, Ga-N type semiconductor light sources, In-Al-Ga-N type semiconductor light sources, and the like. In some embodiments, blue or near UV emitting semiconductor light sources are used.

[0047] For a semiconductor light source using at least two different phosphors, it can be useful to disperse the phosphors separately, and superimpose the phosphor layers instead of dispersing the phosphors together in one matrix. Such layering can be used to obtain a final light emission color by way of a plurality of color conversion processes. For example, the light emission process is: absorption of the semiconductor light source light emission by a first phosphor, light emission by the first phosphor, absorption of the light emission of the first phosphor by a second phosphor, and the light emission by the second phosphor.

[0048] **Figure 15** shows an exemplary layered structure of a semiconductor light source. The blue semiconductor light comprises a substrate Sb, for example, a sapphire substrate. For example, a buffer layer B, an n-type contact layer NCt, an n-type cladding layer NCd, a multi-quantum well active layer MQW, a p-type cladding layer PCd, and a p-type contact layer PCt are formed in that order as nitride semiconductor layers. The layers can be formed, for example, by organometallic chemical vapor deposition (MOCVD), on the substrate Sb. Thereafter, a light-transparent electrode LtE is formed on the whole surface of the p-type contact layer PCt, a p electrode PEl is formed on a part of the light-transparent electrode LtE, and an n electrode NEl is formed on a part of the n-type contact layer NCt. These layers can be formed, for example, by sputtering or vacuum deposition.

[0049] A multi-quantum well structure is a multi-layered structure having more than one quantum well structures that are vertically integrated, and includes e.g., double hetero structures having a light emitting layer sandwiched between the p-type clad layer and the n-type clad layer. A single quantum well structure is a three layered structure that is composed of two barrier layers cladding a quantum well layer in between. Each layer in the quantum

well structure is formed by a semiconductor material, and the band-gap of the quantum well layer is larger than that of the two barrier layers.

[0050] The buffer layer B can be formed of, for example, AlN, and the n-type contact layer **NCt** can be formed of, for example, GaN.

[0051] The n-type cladding layer NCd can be formed, for example, of $Al_rGa_{1-r}N$ wherein $0 \leq r < 1$, the p-type cladding layer PCd can be formed, for example, of $Al_qGa_{1-q}N$ wherein $0 < q < 1$, and the p-type contact layer PCt can be formed, for example, of $Al_sGa_{1-s}N$ wherein $0 \leq s < 1$ and $s < q$. The band gap of the p-type cladding layer PCd is made larger than the band gap of the n-type cladding layer NCd. The n-type cladding layer NCd and the p-type cladding layer PCd each can have a single-composition construction, or can have a construction such that the above-described nitride semiconductor layers having a thickness of not more than 100 angstroms and different from each other in composition are stacked on top of each other so as to provide a superlattice structure. When the layer thickness is not more than 100 angstroms, the occurrence of cracks or crystal defects in the layer can be prevented.

[0052] The multi-quantum well active layer MQW, can be composed of a plurality of InGaN well layers and a plurality of GaN barrier layers. The well layer and the barrier layer can have a thickness of not more than 100 angstroms, preferably 60 to 70 angstroms, so as to constitute a superlattice structure. Since the crystal of InGaN is softer than other aluminum-containing nitride semiconductors, such as AlGaN, the use of InGaN in the layer constituting the active layer MQW can offer an advantage that all the stacked nitride semiconductor layers are less likely to crack. The multi-quantum well active layer MQW can also be composed of a plurality of InGaN well layers and a plurality of AlGaN barrier layers. Or, the multi-quantum well active layer MQW can be composed of a plurality of AlInGaN well layers and a plurality of AlInGaN barrier layers. In this case, the band gap energy of the barrier layer can be made larger than the band gap energy of the well layer.

[0053] A reflecting layer can be provided on the substrate Sb side from the multi-quantum well active layer MQW, for example, on the buffer layer B side of the n-type contact layer NCt. The reflecting layer can also be provided on the surface of the substrate Sb remote from the multi-quantum well active layer MQW stacked on the substrate Sb. The reflecting layer can have a maximum reflectance with respect to light emitted from the active layer MQW

and can be formed of, for example, aluminum, or can have a multi-layer structure of thin GaN layers. The provision of the reflecting layer permits light emitted from the active layer MQW to be reflected from the reflecting layer, can reduce the internal absorption of light emitted from the active layer MQW, can increase the quantity of light output toward above, and can reduce the incidence of light on the mount for the light source to prevent a deterioration.

[0054] Shown in Figures 13-14 are some exemplary semiconductor light source-phosphor structures. Figure 13 shows a light emitting device 10 with an semiconductor light source chip 1 powered by leads 2, and having phosphor-containing material 4 secured between the semiconductor light source chip and the light output 6. A reflector 3 can serve to concentrate light output. A transparent envelope 5 can isolate the semiconductor light source and phosphor from the environment and/or provide a lens. The lighting device 20 of Figure 14 is a panel device having multiple semiconductor light source chips 11, leads 12, phosphor-containing material 14, and transparent envelope 15.

[0055] It will be understood by those of ordinary skill in the art that there are any number of ways to associate phosphors with an semiconductor light source such that light from the semiconductor light source is managed by its interaction with the phosphors. U.S. Published Patent Application Nos. 2004/0145289 and 2004/0145288 illustrate lighting devices where phosphor is positioned away from the light output of the semiconductor light sources. U.S. Published Patent Application Nos. 2004/01450307 and 2004/0159846 further illustrate, without limitation, lighting devices that can be used in the invention.

[0056] Semiconductor light source-based white light devices can be used, for example, in a self-emission type display for displaying a predetermined pattern or graphic design on a display portion of an audio system, a household appliance, a measuring instrument, a medical appliance, and the like. Such semiconductor light source-based light devices can also be used, for example, as light sources of a back-light for LCD displays, a printer head, a facsimile, a copying apparatus, and the like.

[0057] Among the additional phosphors that can be mixed with phosphors of the invention, some of those believed to be useful include those identified above in the initial paragraphs of this specification.

[0058] Among the additional phosphors that can be mixed with phosphors of the invention, some of those believed to be useful include: $Y_3Al_5O_{12}:Ce^{3+}$ (YAG), $Lu_3Ga_2(AlO_4)_3:Ce^{3+}$, $La_3In_2(AlO_4)_3:Ce^{3+}$; $Ca_3Ga_5O_{12}:Ce^{3+}$, $Sr_3Al_5O_{12}:Tb^{3+}$, $BaYSiAlO_{12}:Ce^{3+}$, $CaGa_2S_4:Eu^{2+}$, $SrCaSiO_4:Eu^{2+}$, ZnS:Cu, $CaSi_2O_2N:Eu^{2+}$, $SrSi_2O_2N:Eu^{2+}$, $SrSiAl_2O_3N_2:Eu^{2+}$, $Ba_2MgSi_2O_7:Eu^{2+}$, $Ba_2SiO_4:Eu^{2+}$, $La_2O_3.11Al_2O_3:Mn^{2+}$, $Ca_8Mg(SiO_4)_4Cl_4:Eu^{2+},Mn^{2+}$, $(CaM)(Si,Al)_{12}(O,N)_{16}:Eu^{2+},Tb^{3+},Yb^{3+}$, $YBO_3:Ce^{3+},Tb^{3+}$, $BaMgAl_{10}O_{17}:Eu^{2+}, Mn^{2+}$, $(Sr,Ca,Ba)(Al,Ga)_2S_4:Eu^{2+}$, $BaCaSi_7N_{10}:Eu^{2+}$, $(SrBa)_3MgSi_2O_8:Eu^{2+}$, $(SrBa)_2P_2O_7:Eu^{2+}$, $(SrBa)_2Al_{14}O_{25}:Eu^{2+}$, $LaSi_3N_5:Ce^{3+}$, $(BaSr)MgAl_{10}O_{17}:Eu^{2+}$, and $CaMgSi_2O_7:Eu^{2+}$.

[0059] Temperatures described herein for synthetic processes involving a substantial gas phase are of the oven or other reaction vessel in question, not of the reactants per se.

[0060] "White light" is light of certain chromaticity values, which is known and well published in the art.

[0061] The following examples further illustrate the present invention, but of course, should not be construed as in any way limiting its scope.

Example 1a: Preparation of $CaSiO_3•(SiO_2)_n$: Eu^{2+}, Mn^{2+}, I

[0062] Europium oxide, Eu_2O_3 (1.14 g, 0.65 mole %), 3.9 g of CaO (7 mole %), 0.78 g of CaF_2 (1 mole %), 0.115 g of $MnCO_3$ (0.1 mole %), 60.08 g of silicic acid (100 mole%) and 21 g of NH_4I (14.4 mole%) were mixed in dry powder form. The mixed powder was further dried in dry nitrogen at 140 °C for 4 hours. The powder was then fired at 900 °C in forming gas (5% v/v H_2 in N_2) for 1 hour. After the material cooled down, 14 g of NH_4I was added and the powder mixed again. The mixed powder was fired at 1000 °C in forming gas for 1 hour. The phosphor obtained was $(CaSiO_3)·(SiO_2):Eu^{2+}$, Mn^{2+}, I. The silica, SiO_2, was in cristobalite form and the calcium inosilicate was in the Wollastonite form, as evidenced by X-ray diffraction pattern shown in Figure 3 (shown relative to Wollastonite inosiliate, to quartz, and to cristobalite silica). The phosphor emitted bright red light peaking at 635 nm upon 410 nm light excitation, as shown in Figure 1. The long term stability (longevity) of the phosphor when subjected to 85 °C and 85% relative humidity is shown in Figure 2.

Example 1b-f: Preparation of CaSiO3•(SiO2)n: Eu2+, Mn2+, I

[0063] The method of Example 1a was used, except that the ratio of Eu^{2+} and Mn^{2+} were varied to obtain the following phosphors:

	Phosphor Formula	$[Eu^{2+}]$, mol%	$[Mn^{2+}]$, mol%	Emitting Color
b	$(CaSiO_3)\cdot(SiO_2):Eu^{2+}, Mn^{2+}, I^-$	0.65	0.05	Pink
c	$(CaSiO_3)\cdot(SiO_2):Eu^{2+}, Mn^{2+}, I^-$	0.65	0.1	Pink
d	$(CaSiO_3)\cdot(SiO_2):Eu^{2+}, Mn^{2+}, I^-$	0.65	0.15	Pink
e	$(CaSiO_3)\cdot(SiO_2):Eu^{2+}, Mn^{2+}, I^-$	0.65	0.2	Red
f	$(CaSiO_3)\cdot(SiO_2):Eu^{2+}, Mn^{2+}, I^-$	0.65	0.5	Red

Example 2: Preparation of CaSiO3•(SiO2)n: Eu2+, Mn2+, Cl

[0064] By dry grinding, mixed were europium oxide, Eu_2O_3 (1.14 g, 0.65 mole %), 3.9 g of CaO (7 mole %), 0.78 g of CaF_2 (1 mole %), 0.115 g of $MnCO_3$ (0.1 mole %), 60.08 g of silicic acid (100 mole%) and 14 g of NH_4Cl (26 mol%). The mixed powder was further dried in dry nitrogen at 140 °C for 4 hours. The powder was then fired at 900 °C in dry nitrogen for 1 hour. After the material cooled down to room temperature, 14 g of NH_4Cl were added and the material mixed once again. The mixed powder was then fired at 1000 °C in forming gas for 1 hour. The phosphor obtained was $CaSiO_3 \cdot (SiO_2)_n$: Eu^{2+}, Mn^{2+}, Cl^-. The phosphor emitted bright orange-red light peaking at 422 nm and 585 nm upon 410 nm light excitation, as shown in Figure 4.

Example 3a: Preparation of CaSiO3•(SiO2)n: Eu2+, I

[0065] Europium oxide, Eu_2O_3 (1.14 g, 0.65 mole %), 3.9 g of CaO (7 mole %), 0.78 g of CaF_2 (1 mole %), 60.08 g of silicic acid (100 mole%) and 14 g of NH_4I (9.6 mole%) was mixed in dry powder form. The mixed powder was further dried in nitrogen at 140 °C for 4 hours. The powder was then fired at 900 °C in dry nitrogen for 1 hour. After the material cooled down, 14 g of NH_4I was added and mixed again. The mixed powder was fired at 1000°C in forming gas for 1 hour. The phosphor obtained was $CaSiO_3 \cdot (SiO_2)_n$: Eu^{2+}, I^-, and emitted bright blue light peaking at 465 nm upon 410 nm light excitation, as shown in Figure 5. The phosphor showed polymorphous crystalline composition with Wollastonite of $CaSiO_3$ and cristobalite SiO_2. Longevity is shown in Figure 6.

Example 3b-i: Preparation of CaSiO3•(SiO2)n: Eu2+, I

[0066] The method of Example 3a was used, except that the ratio of Eu^{2+} and Mn^{2+} were varied to obtain the following phosphors:

	Phosphor Formula	$[Eu^{2+}]$, mol%	Emitting Peak, nm
b	$(CaSiO_3) \cdot (SiO_2):Eu^{2+}, I^-$	0.25	466
c	$(CaSiO_3) \cdot (SiO_2):Eu^{2+}, I^-$	0.45	465

d	$(CaSiO_3)\cdot(SiO_2):Eu^{2+}, I^-$	0.65	465
e	$(CaSiO_3)\cdot(SiO_2):Eu^{2+}, I^-$	0.85	466
f	$(CaSiO_3)\cdot(SiO_2):Eu^{2+}, I^-$	1.2	466
g	$(CaSiO_3)\cdot(SiO_2):Eu^{2+}, I$	1.5	466
h	$(CaSiO_3)\cdot(SiO_2):Eu^{2+},I$	2.0	465
i	$(CaSiO_3)\cdot(SiO_2):Eu^{2+}, I$	3.0	465

Example 4: Preparation of CaSiO3•(SiO2)n: Eu2+, Mn2+, Br

[0067] Europium oxide, Eu_2O_3 (1.14 g, 0.65 mole %), 3.9 g of CaO (9.7 mole %), 0.78 g of CaF_2 (1 mole %), 0.115 g of $MnCO_3$ (0.1 mole %), 60.08 g of silicic acid (100 mole%) and 16 g of NH_4Br (16 mole%) was mixed by dry grinding. The mixed powder was further dried in dry nitrogen at 140 °C for 4 hours. The powder was then fired at 900 °C in forming gas for 1 hour. After the material cooled down, 14 g of NH_4Br was added and mixed again. The mixed powder was fired at 1000 °C in forming gas for 1 hour. The phosphor obtained was $CaSiO_3\cdot(SiO_2)_n$: Eu^{2+}, Mn^{2+}, Br^-, and emitted bright blue light (430 nm) and orange light (584 nm) upon 400 nm light excitation, as shown in Figure 7.

Example 5: Preparation of MgSiO3•(SiO2)n: Eu2+, Mn2+, I-

[0068] Europium oxide, Eu_2O_3 (1.14 g, 0.65 mole %), 3.9 g of MgO (7 mole %), 0.115 g of $MnCO_3$ (0.1 mole %), 60.08 g of silicic acid (100 mole%) and 14 g of NH_4I (15 mole%) were mixed in dry powder form. The mixed powder was further dried in dry nitrogen at 140 °C for 4 hours. The powder was then fired at 900°C in forming gas for 1 hour. After the material cooled down, 14 g of NH_4I was added and mixed again. The mixed powder was fired at 1000 °C in dry forming for 1 hour. The phosphor obtained was $([Mg]SiO_3)\cdot(SiO_2)_n$:$Eu^{2+}$, Mn^{2+}, I^-. The silica, SiO_2, was crystallized in cristobalite form and the magnesium inosilicate was in the enstalite form, as evidenced by X-ray diffraction pattern shown in Figure 9 (shown relative to Enstalite Mg and to quartz). This diffraction pattern shows the silica is largely

amorphous. This phosphor emitted upon 410 nm light excitation as shown in Figure 8 (blue at 430 nm and red at 644 nm).

Example 6: Preparation of MgSiO3•(SiO2)n: Eu2+, Mn2+, Br-

[0069] Europium oxide, Eu_2O_3 (1.14 g, 0.65 mole %), 3.9 g of MgO (7 mole %), 0.115 g of $MnCO_3$ (0.1 mole %), 60.08 g of silicic acid (100 mole%) and 16 g of NH_4Br (16.3 mole%) was mixed by dry grinding. The mixed powder was further dried in dry nitrogen at 140 °C for 4 hours. The powder was then fired at 900 °C in forming gas for 1 hour. After the material cooled down, 14 g of NH_4Br was added and mixed again. The mixed powder was fired at 1000 °C in forming gas for 1 hour. The phosphor obtained was $MgSiO_3 \cdot (SiO_2)n:Eu^{2+}$, Mn^{2+} Br^-, and emitted upon 400 nm light excitation as shown in **Figure 10** (blue at 410 nm, blue at 475 nm and red at 620 nm).

Example 7: Preparation of $CaSiO_3:Eu^{2+},Mn^{2+}, I^-$

[0070] Europium oxide, Eu_2O_3 (1.14 g, 0.65 mole %), 3.9 g of CaO (7 mole %), 0.78 g of CaF_2 (1 mole %), 0.115 g of $MnCO_3$ (0.1 mole %), 60.08 g of silicic acid (100 mole%) and 16 g of NH_4I (11 mole%) was mixed by dry grinding. The mixed powder was further dried in dry nitrogen at 140 °C for 4 hours. The powder was then fired at 900 °C in forming gas for 1 hour. After the material cooled down, 14 g of NH_4I was added and mixed again. The mixed powder was fired at 1000 °C in forming gas for 1 hour. The phosphor obtained was $CaSiO_3:Eu^{2+}$, Mn^{2+}, I^-, and emitted upon 400 nm light excitation, as shown in Figure 11 (blue at 460 nm and red at 610 nm).

Example 8: Preparation of (SiO2)n:Eu2+,Mn2+, I-

[0071] Europium oxide, Eu_2O_3 (1.14 g, 0.65 mole %), 0.78 g of CaF_2 (1 mole %), 0.115 g of $MnCO_3$ (0.1 mole %), 60.08 g of silicic acid (100 mole%) and 16 g of NH_4I (11 mole%) was mixed by dry grinding. The mixed powder was further dried in dry nitrogen at 140 °C for 4 hours. The powder was then fired at 900 °C in forming gas for 1 hour. After the material cooled down, 14 g of NH_4Br was added and mixed again. The mixed powder was fired at 1000 °C in forming gas for 1 hour. The phosphor obtained was $(SiO_2)_n:Eu^{2+}$, Mn^{2+}, I^-, and emitted upon 400 nm light excitation as shown in **Figure 12** (blue at 430 nm and red at 640 nm).

Example 9: Making a White Light Device with 410 nm-emitting LED Chip and a First Phosphor Blend

[0072] The phosphor blend is made of a red emitting metal silicate-silica-based, polymorphous phosphor $CaSiO_3 \cdot (SiO_2)_n$: Eu^{2+}, Mn^{2+}, I^- as made in the **Example 1**, a green-emitting phosphor, $BaMgAl_{10}O_{17}:Eu^{2+}$, Mn^{2+} (BAM:Eu, Mn) (G) and a blue-emitting phosphor $CaSiO_3 \cdot (SiO_2)_n$: Eu^{2+}, I^- (B) as made in the Example 3. Mix the three phosphors with appropriate weight ratios and further mix the phosphor blend with epoxy resin to form a slurry. Apply the slurry onto an InGaN-based LED chip that emits at 410 nm. The device generates light with white color whose color coordinates can be varied by changing the ratio of the three phosphors.

Example 10: Making a White Light Device with 410 nm-emitting LED Chip and a Second Phosphor Blend

[0073] The phosphor blend is made of a red emitting metal silicate-silica-based, polymorphous phosphor $CaSiO_3 \cdot (SiO_2)_n$: Eu^{2+}, Mn^{2+}, I^- as made in the Example 1, a green-emitting phosphor, $SrGa_2S_4:Eu^{2+}$ (STG:Eu) (G) and a blue-emitting phosphor $CaSiO_3 \cdot (SiO_2)_n$: Eu^{2+}, I^- (B) as made in the Example 3. Mix the three phosphors with appropriate weight ratios and further mix the phosphor blend with epoxy resin to form a slurry. Apply the slurry onto an InGaN-based LED chip that emits at 410 nm. The device generates light with white color whose color coordinates can be varied by changing the ratio of the three phosphors. The device architecture can be as in Figure 13.

Example 11: Making a Purple Light Device with 410 nm-emitting LED Chip and a Purple-Emitting Phosphor

[0074] A single phosphor, the purple-emitting $CaSiO_3 \cdot (SiO_2)_n$: Eu^{2+}, Mn^{2+}, Cl^- as made in the Example 2 is mixed with epoxy resin to form a slurry. The slurry is applied onto an InGaN-based LED chip that emits at 410 nm. The device generates light with purple color. This light color is suitable for certain lighting in entertainment environments.

[0075] Publications and references, including but not limited to patents and patent applications, cited in this specification are herein incorporated by reference in their entirety in the entire portion cited as if each individual publication or reference were specifically and individually indicated to be incorporated by reference herein as being fully set forth. Any

patent application to which this application claims priority is also incorporated by reference herein in the manner described above for publications and references.

[0076] While this invention has been described with an emphasis upon preferred embodiments, it will be obvious to those of ordinary skill in the art that variations in the preferred devices and methods may be used and that it is intended that the invention may be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications encompassed within the spirit and scope of the invention as defined by the claims that follow.

[0077] This application claims benefit of priority from the following cases filed March 25, 2005: U.S. Patent Application Serial Nos. 60/665,458; 60/665,636; 60/665,456; and 60/665,457; U.S. Patent Application Serial No. 60/684,373, filed May 24, 2005, and U.S. Patent Application Serial No. 11/149,648, filed June 10, 2005

CLAIMS

What is claimed:

1. A light emitting device comprising:

a semiconductor light source producing light output including wavelengths of 300 nm or more; and

a wavelength manager located between 28

the light source and the light output for the device, comprising a phosphor according to the formula:

$$[(BvSiO_3)_x(Mv_2SiO_3)_y(Tv_2(SiO_3)_3)_z]_m \bullet (SiO_2)_n: R\varepsilon, X \qquad (I)$$

wherein:

x, y and z are any value, wherein $x + y + z = 1$;

Bv is one or more divalent alkaline earth metal ions;

Mv is one or more monovalent alkaline metal ions;

Tv is one or more trivalent metal ions;

Rε is one or more activators selected from Eu^{2+} or Mn^{2+};

X is one or more halides; and

m is 1 or 0; provided that:

if m is1 and provides an amount of silica effective to host useful luminescence, then n is greater than3; or

if m = 0, then n is 1.

2. The light emitting device of claim 1, wherein Mv comprises one or more ions selected from Li, Na or K.

3. The light emitting device of claim 1, wherein Bv comprises one or more divalent alkaline earth metal ions.

4. The light emitting device of claim 2, wherein Bv comprises one or more Ca or Sr ions.

5. The light emitting device of claim 1, wherein Bv comprises one or more Be, Mg, Ca, Sr, Ba, Mn, Co, Ni, Cu, Zn, Cd or Hg ions.

6. The light emitting device of claim 1, wherein Tv comprises one or more Al, Ga, In, Sc, Y or La ions.

7. The light emitting device of claim 1, wherein Rε comprises Eu^{2+} ions.

8. The light emitting device of claim 1, wherein Rε comprises Mn^{2+} ions.

9. The light emitting device of claim 1, wherein Rε comprises Eu^{2+} and Mn^{2+} ions.

10. The light emitting device of claim 1, wherein the wavelength manager comprises one or more additional phosphors, wherein the one or more additional phosphors adjusts light produced by the device.

11. The light emitting device of claim 10, wherein the wavelength manager changes the light output to white light.

12. A light emitting device according to claim 1, wherein the semiconductor light source comprises a quantum well structure comprising a light emitting layer sandwiched between a p-type clad layer and an n-type clad layer.

13. The light emitting device according to claim 12, wherein:

the p-type clad layer is formed of $Al_qGa_{1-q}N$, wherein $0 < q < 1$;

the n-type clad layer is formed of $Al_rGa_{1-r}N$, wherein $0 \leq r < 1$; and

optionally, the p-type clad layer has a band gap that is larger than the band gap of the n-type clad layer.

14. The light emitting device according to claim 1, wherein the semiconductor light source further comprises a light emitting layer containing indium and one or more quantum well structure.

15. The light emitting device according to claim 14, wherein:

optionally, the quantum well structure comprises one or more well layers of InGaN and one or more barrier layers of GaN;

optionally, the quantum well structure comprises one or more well layers of InGaN and one or more barrier layers of AlGaN;

optionally, the quantum well structure comprises one or more well layers of AlInGaN and one or more barrier layers of AlInGaN;

the barrier layer has a band gap energy that is larger than the band gap energy of the well layer; and

wherein optionally, the well layer has a thickness of not more than 100 angstroms.

16. The light emitting device according to claim 1, wherein the semiconductor light source comprises one or more quantum well structures.

17. The light emitting device according to claim 16, wherein the quantum well structure is a single quantum well structure.

18. The light emitting device according to claim 16, wherein the quantum well structure is a multi-quantum well structure.

19. The light emitting device according to claim 1, wherein the semiconductor light source comprises more than one light emitting diodes (LED) on a substrate.

20. The light emitting device according to claim 1, wherein the phosphor has a formula of:

$[(CaSiO_3)]_m \bullet (SiO_2)_n:Eu^{2+}, Mn^{2+}, I^-$

wherein the Eu^{2+} and Mn^{2+} ions have a concentration and ratio that provides a peak emission between about 620 nm and about 660 nm and a chromaticity of x = 0.62 ±0.06, y = 0.30 ±0.06.

21. The light emitting device according to claim 1, wherein the phosphor has a formula of:

$[(CaSiO_3)]_m \bullet (SiO_2)_n:Eu^{2+}, I^-$

wherein the Eu^{2+} and Mn^{2+} ions have a concentration and ratio that provides a peak emission between about 445 nm and about 480 nm and a chromaticity of x = 0.20 ±0.06, y = 0.10 ±0.06.

22. The light emitting device according to claim 1, wherein the phosphor has a formula of:

$[(CaSiO_3)]_m \bullet (SiO_2)_n:Eu^{2+}, Mn^{2+}, Cl^-$

wherein the Eu^{2+} and Mn^{2+} ions has a concentration and ratio that provides a chromaticity of $x = 0.40 \pm 0.06$, $y = 0.20 \pm 0.06$.

23. The light emitting device according to claim 1, wherein Bv, Mv, Tv or a mixture thereof comprises metal silicate in Wollastonite form.

24. The light emitting device according to claim 23, wherein the silica comprises a cristobalite form.

25. The light emitting device according to claim 1, wherein Bv, Mv, Tv or a mixture thereof comprises metal silicate in calcite form.

26. The light emitting device according to claim 25, wherein the silica comprises a cristobalite form.

27. The light emitting device according to claim 1, wherein Bv, Mv, Tv or a mixture thereof comprises metal silicate in enstalite form.

28. The light emitting device according to claim 27, wherein the silica comprises a cristobalite form.

29. A phosphor according to the formula:

$$[(BvSiO_3)_x(Mv_2SiO_3)_y(Tv_2(SiO_3)_3)_z]_m \bullet (SiO_2)_n: R\varepsilon, X \qquad (I)$$

wherein:

x, y and z are any value, wherein $x + y + z = 1$;

Bv is one or more divalent alkaline earth metal ions;

Mv is one or more monovalent alkaline metal ions;

Tv is one or more trivalent metal ions;

Rε is one or more activators selected from Eu^{2+} or Mn^{2+} ions;

X is one or more halides; and

m is 1 or 0; and

provided that if m is 1 and provides an amount of silica effective to host useful luminescence, then n is greater than 3; or if m is 0, then n is1.

30. The phosphor of claim 29, wherein Mv comprises one or more ions selected from Li, Na or K.

31. The phosphor of claim 29, wherein Bv comprises one or more Ca or Sr ions.

32. The phosphor of claim 29, wherein Bv comprises one or more Be, Mg, Ca, Sr, Ba, Mn, Co, Ni, Cu, Zn, Cd or Hg ions.

33. The phosphor of claim 29, wherein Tv comprises one or more Al, Ga, In, Sc, Y or La ions.

34. The phosphor of claim 29, wherein Rε comprises Eu^{2+} ions.

35. The phosphor of claim 29, wherein Rε comprises Mn^{2+} ions.

36. The phosphor of claim 29, wherein Rε comprises Eu^{2+} and Mn^{2+} ions.

37. The phosphor of claim 29, wherein the phosphor has a formula of:

$$[(CaSiO_3)]_m \bullet (SiO_2)_n : Eu^{2+}, Mn^{2+}, I^-,$$

wherein the Eu^{2+} and Mn^{2+} ions have a concentration and ratio that provides a peak emission between about 620 nm and about 660 nm and a chromaticity of x = 0.62 ±0.06, y = 0.30 ±0.06.

38. The phosphor of claim 29, wherein the phosphor has a formula of:

$$[(CaSiO_3)]_m \bullet (SiO_2)_n : Eu^{2+}, I^-,$$

wherein the Eu^{2+} ions have a concentration that provides a peak emission between about 445 nm and about 480 nm and a chromaticity of x = 0.20 ±0.06, y = 0.10 ±0.06.

39. The phosphor of claim 29, wherein the phosphor has a formula of:

$$[(CaSiO_3)]_m \bullet (SiO_2)_n : Eu^{2+}, Mn^{2+}, Cl^-,$$

wherein the Eu^{2+} and Mn^{2+} ions have a concentration and ratio that provides a chromaticity of x = 0.40 ±0.06, y = 0.20 ±0.06.

40. The phosphor of claim 29, wherein Bv, Mv, Tv or a mixture thereof comprises metal silicate in Wollastonite form and the silica comprises a cristobalite form.

41. The phosphor of claim 29, wherein Bv, Mv, Tv or a mixture thereof comprises metal silicate in calcite form and the silica comprises a cristobalite form.

42. The phosphor of claim 29, wherein Bv, Mv, Tv or a mixture thereof comprises metal silicate in enstalite form and the silica comprises a cristobalite form.

43. The phosphor of claim 29, wherein X has a mole percentage of SiO_2 of about 5% or less.

44. A method of making a phosphor according to the formula:

$$[(BvSiO_3)_x(Mv_2SiO_3)_y(Tv_2(SiO_3)_3)_z]_m \bullet (SiO_2)_n: R\varepsilon, X \qquad (I)$$

wherein:

x, y and z are any value, wherein $x + y + z = 1$;

Bv is one or more divalent alkaline earth metal ions;

Mv is one or more monovalent alkaline metal ions;

Tv is one or more trivalent metal ions;

Rε is one or more activators selected from Eu^{2+} or Mn^{2+};

X is one or more halides;

m is 1 or 0; and

provided that if m is 1 and provides an amount of silica effective to host useful luminescence, then n is greater than 3; or if m is 0, then n is1;

comprising:

a) providing an appropriate mixture of precursors, which optionally include a halide source; and

b) firing the product of the first heating at a temperature from 900 °C to 1300 °C under a reducing atmosphere and in the presence of a halide source,

wherein the process further comprises one or more of the following:

c) heating the appropriate mixture prior to the firing, wherein the heating is at a temperature lower than that of the firing;

d) including a halide source at a temperature from 700°C to 1100°C under a reducing atmosphere; or

e) maintaining X in the phosphor at a mole percentage of about 5% or less of SiO_2.

45. A method of making a phosphor according to the formula:

$$[(BvSiO_3)_x(Mv_2SiO_3)_y(Tv_2(SiO_3)_3)_z]_m \bullet (SiO_2)_n: R\varepsilon, X \qquad (I)$$

wherein:

x, y and z are any value, wherein $x + y + z = 1$;

Bv is one or more divalent alkaline earth metal ions;

Mv is one or more monovalent alkaline metal ions;

Tv is one or more trivalent metal ions;

Rε is one or more activators selected from Eu^{2+} or Mn^{2+} ions;

X is one or more halides; and

m is 1 or 0; provided that

if m is 1 and provides an amount of silica effective to host useful luminescence, then n is greater than 3; or

if m = 0, then n =1;

comprising:

a) mixing appropriate precursors;

b) forming a slurry;

c) optionally, milling the slurry;

d) optionally, drying the slurry

e) optionally, heating the slurry under a reducing gas at a first temperature;

f) optionally, further mixing in a precursor of X;

g) firing any of b) through f) at a second temperature under reducing gas, wherein the second temperature is higher than the first temperature, if e) is done;

h) optionally, washing g) with a solvent that is effective in removing unreactive ingredients; and

i) optionally, applying a post formation treatment.

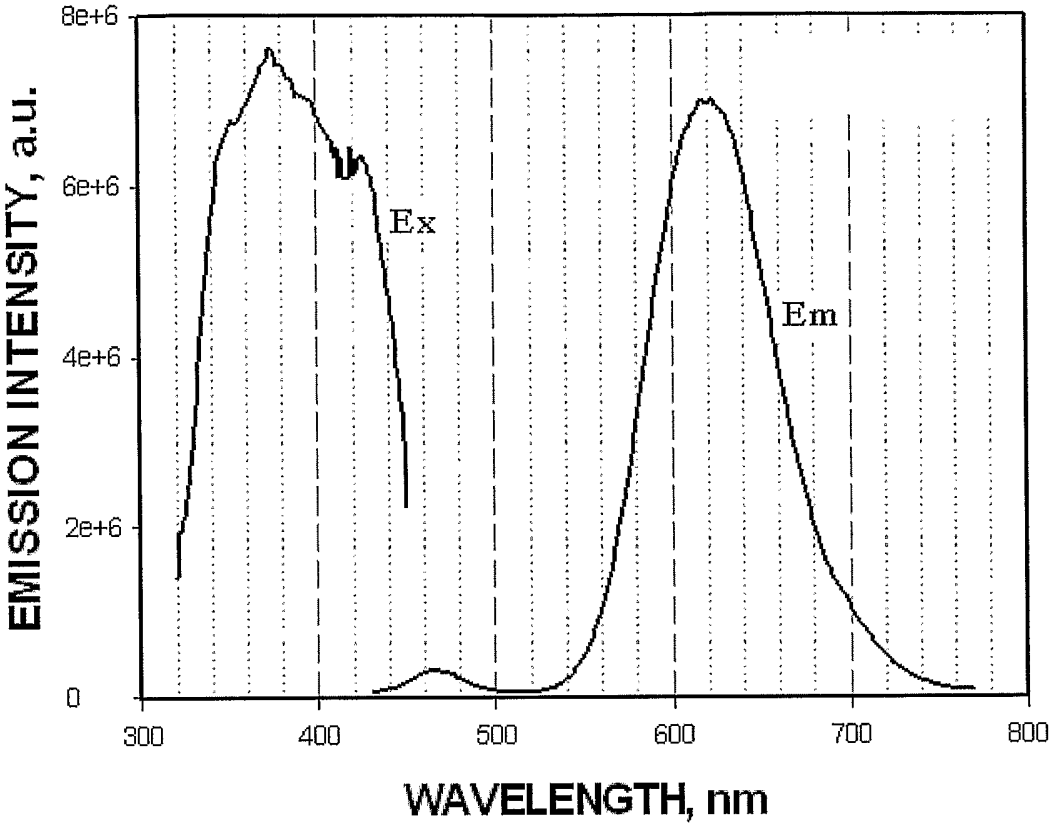
EMISSION INTENSITY, a.u.
8e+6
6e+6
4e+6
2e+6
0
Ex
Em
300
400
500
600
700
800
WAVELENGTH, nm

Fig. 1

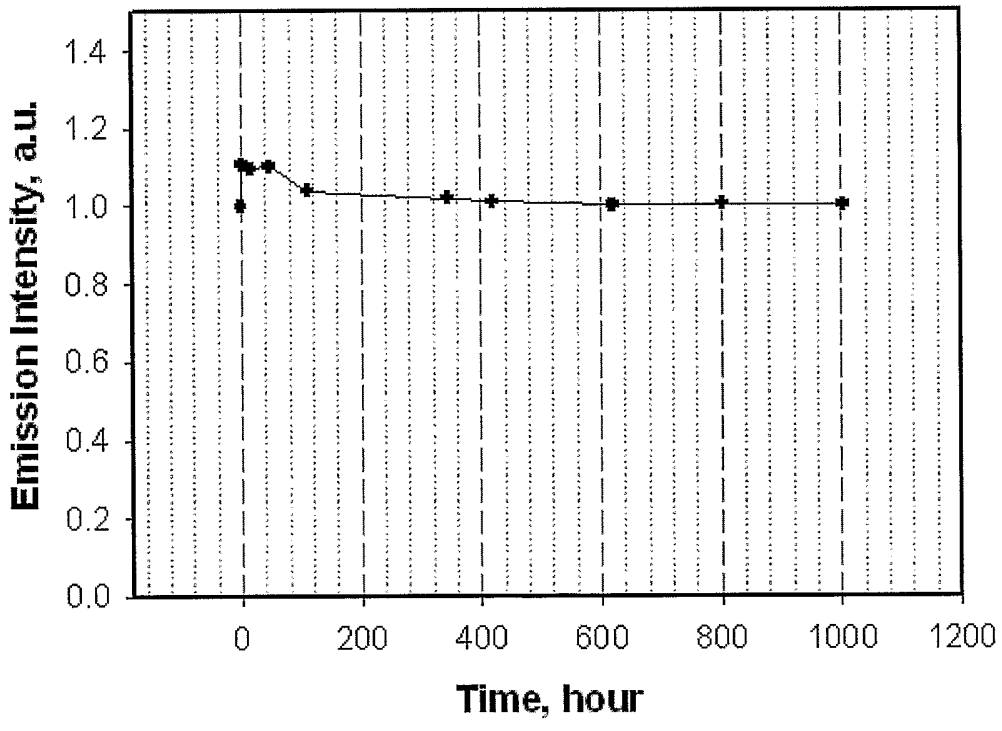
Emission Intensity, a.u.
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
Time, hour

Fig. 2

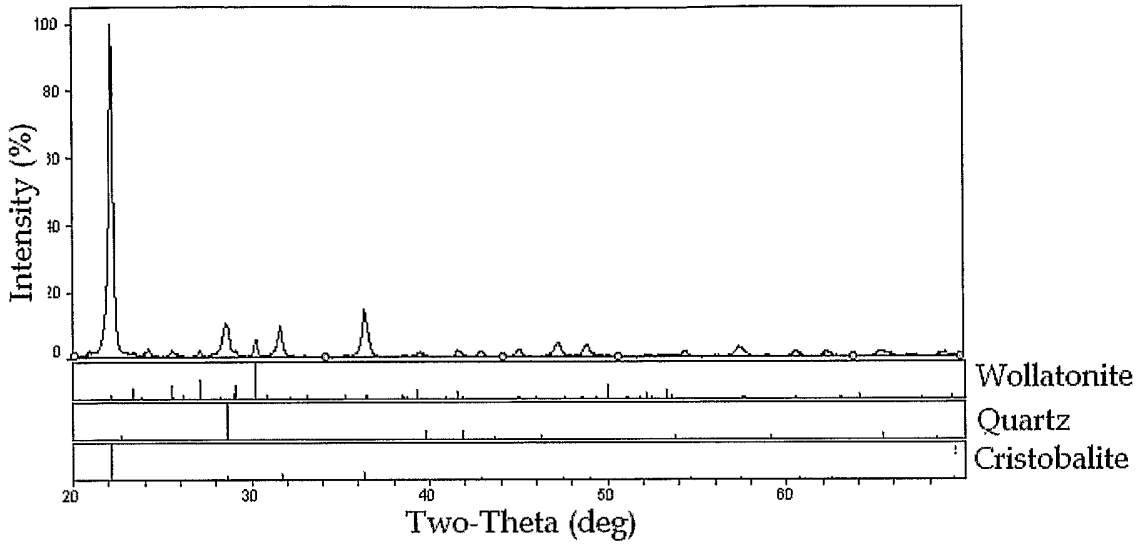
Intensity (%)
Two-Theta (deg)
Wollatonite
Quartz
Cristobalite

Fig. 3

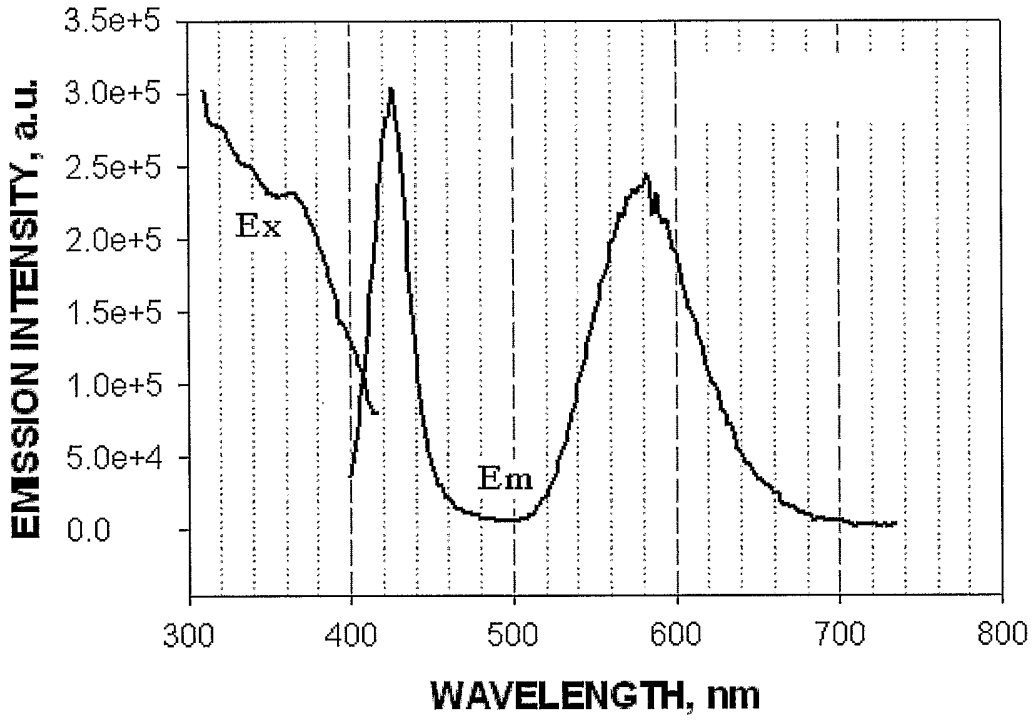
EMISSION INTENSITY, a.u.
WAVELENGTH, nm
Ex
Em

Fig. 4

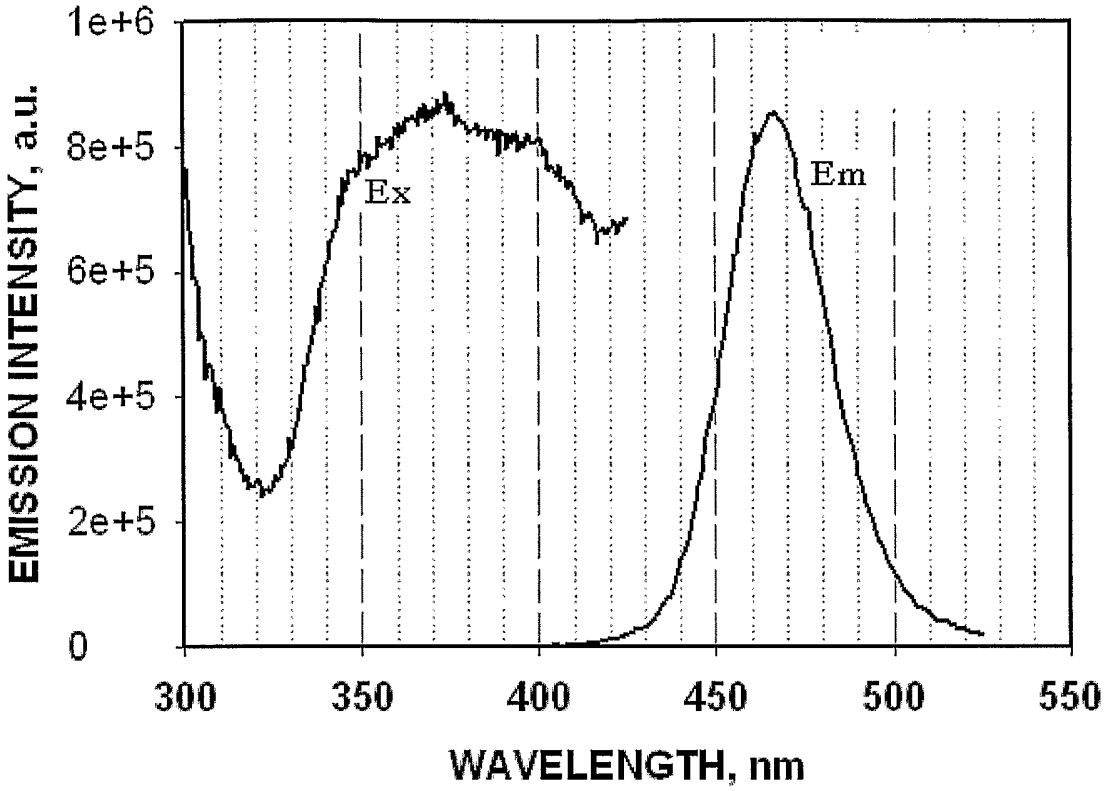
1e+6
8e+5
6e+5
4e+5
2e+5
0
EMISSION INTENSITY, a.u.
Ex
Em
300
350
400
450
500
550
WAVELENGTH, nm

Fig. 5

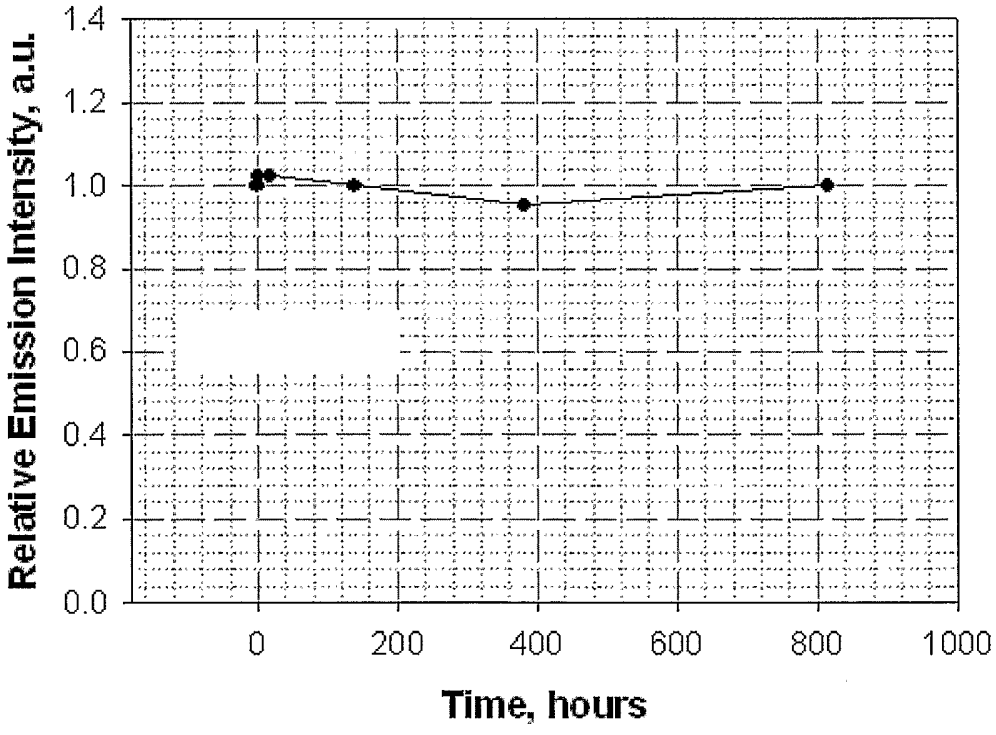
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Relative Emission Intensity, a.u.
0
200
400
600
800
1000
Time, hours

Fig. 6

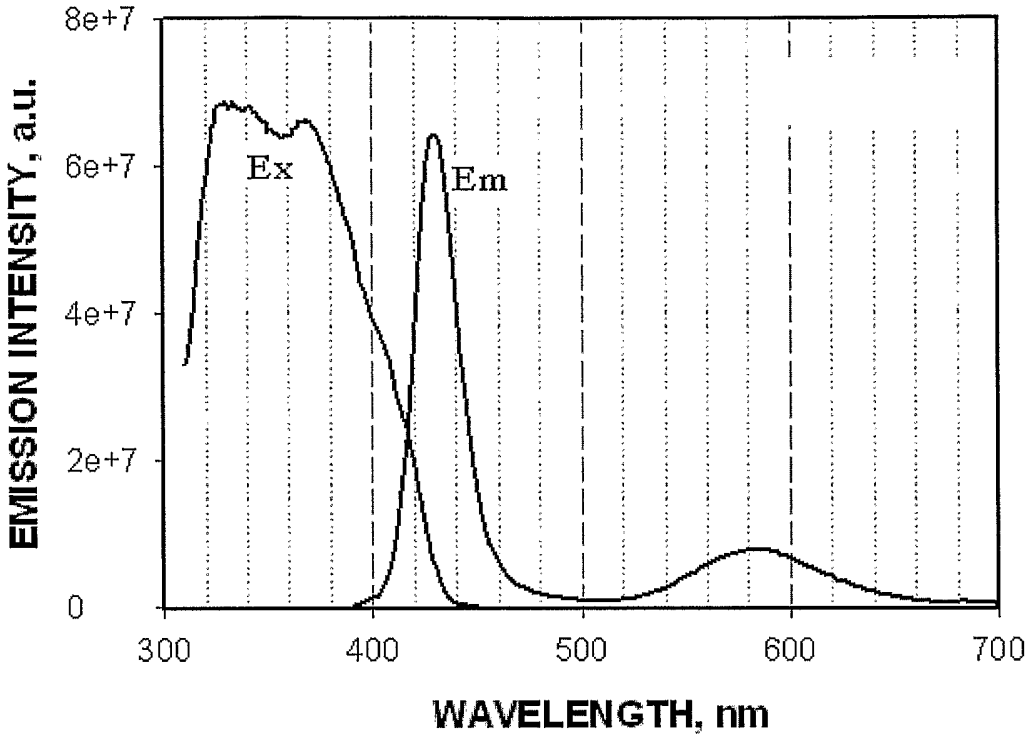
8e+7
6e+7
4e+7
2e+7
0
EMISSION INTENSITY, a.u.
Ex
Em
300
400
500
600
700
WAVELENGTH, nm

Fig. 7

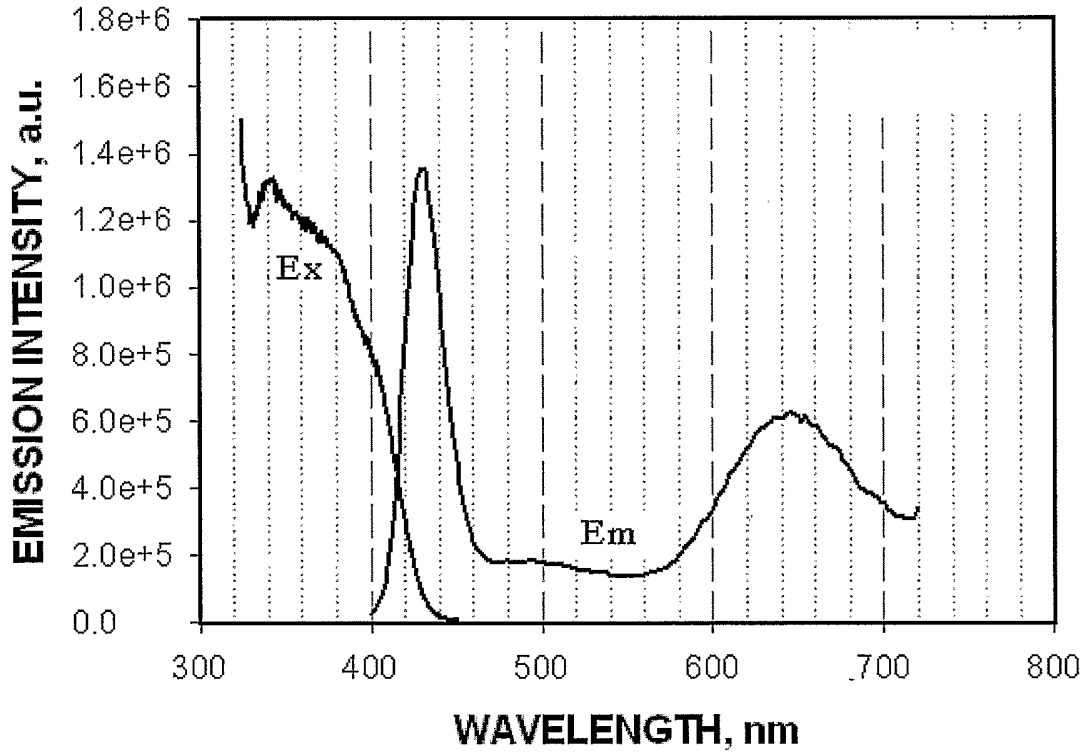
1.8e+6
1.6e+6
1.4e+6
1.2e+6
1.0e+6
8.0e+5
6.0e+5
4.0e+5
2.0e+5
0.0
EMISSION INTENSITY, a.u.
Ex
Em
300
400
500
600
700
800
WAVELENGTH, nm

Fig. 8

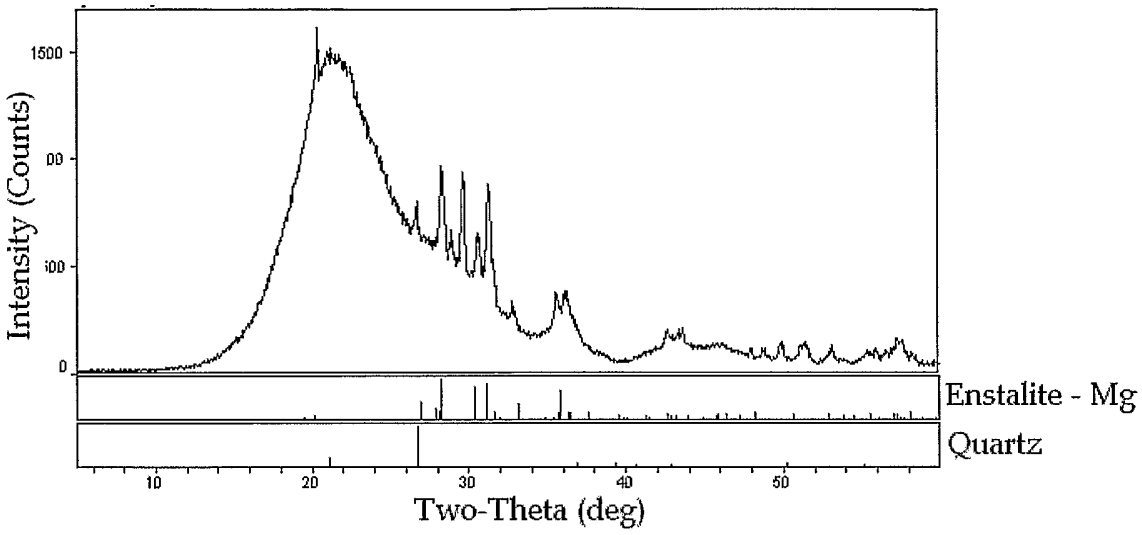
Intensity (Counts)
1500
00
100
0
Enstalite - Mg
Quartz
10
20
30
40
50
Two-Theta (deg)

Fig. 9

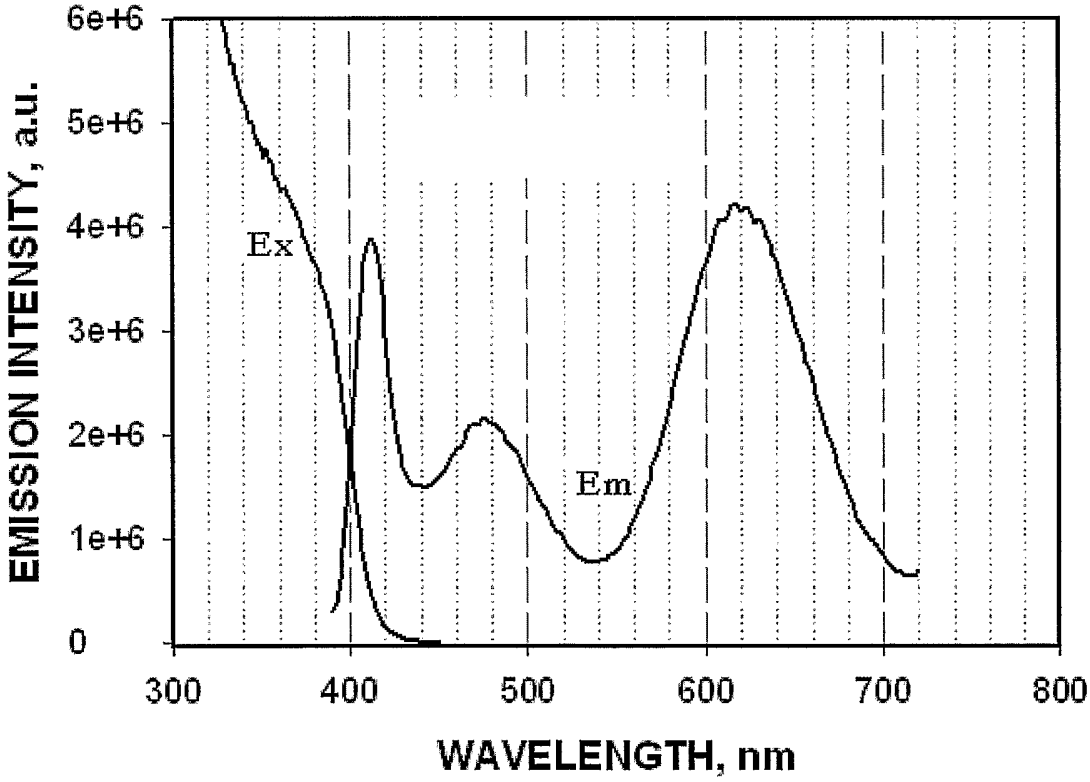
EMISSION INTENSITY, a.u.
6e+6
5e+6
4e+6
3e+6
2e+6
1e+6
0
Ex
Em
300
400
500
600
700
800
WAVELENGTH, nm

Fig. 10

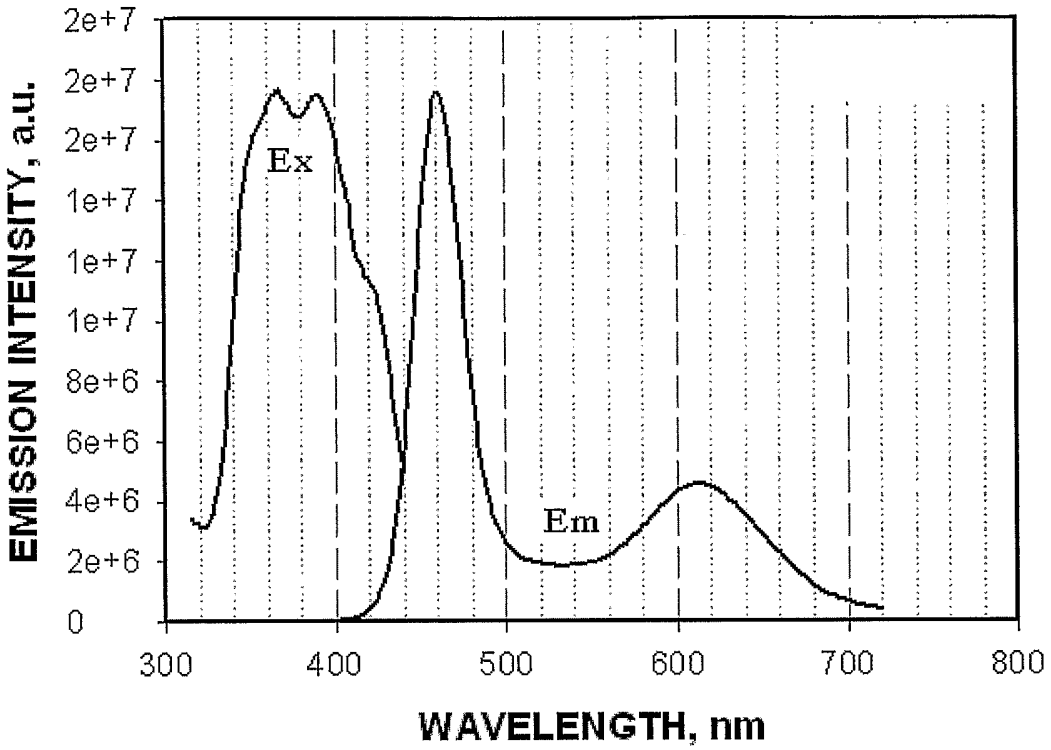
EMISSION INTENSITY, a.u.
2e+7
2e+7
2e+7
1e+7
1e+7
1e+7
8e+6
6e+6
4e+6
2e+6
0
Ex
Em
300
400
500
600
700
800
WAVELENGTH, nm

Fig. 11

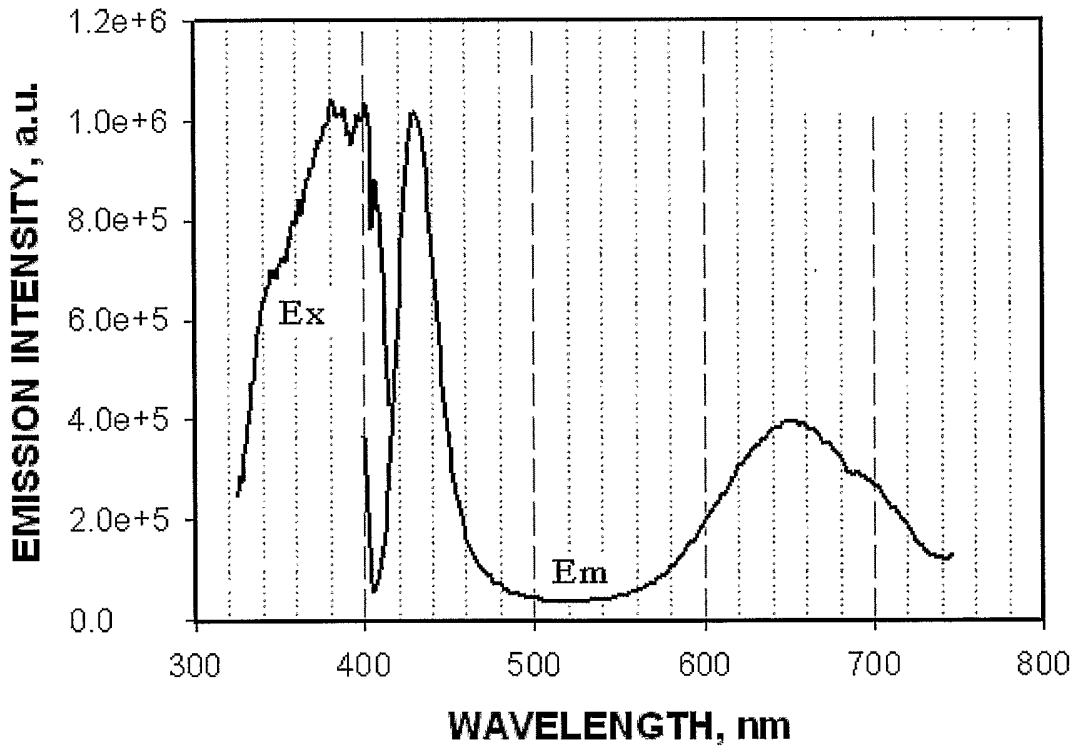
EMISSION INTENSITY, a.u.
1.2e+6
1.0e+6
8.0e+5
6.0e+5
4.0e+5
2.0e+5
0.0
Ex
Em
300
400
500
600
700
800
WAVELENGTH, nm

Fig. 12

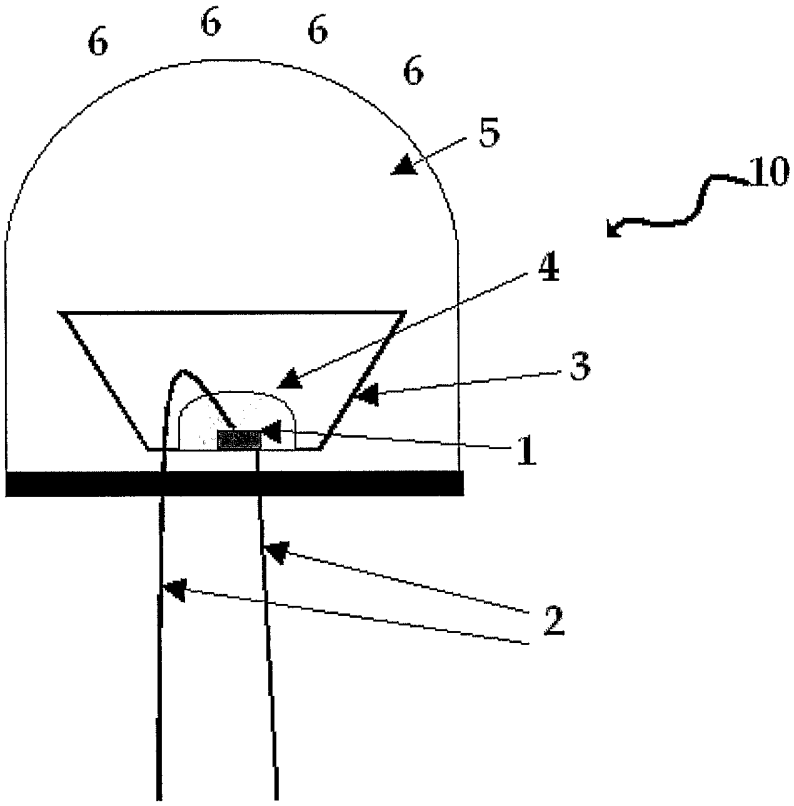

Fig. 13

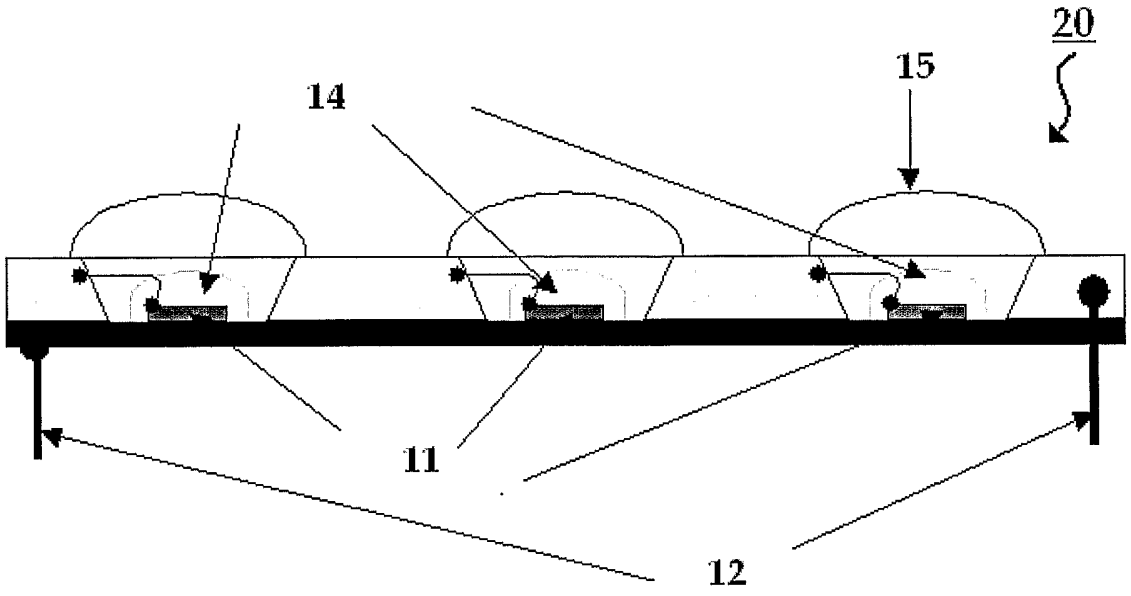

Fig. 14

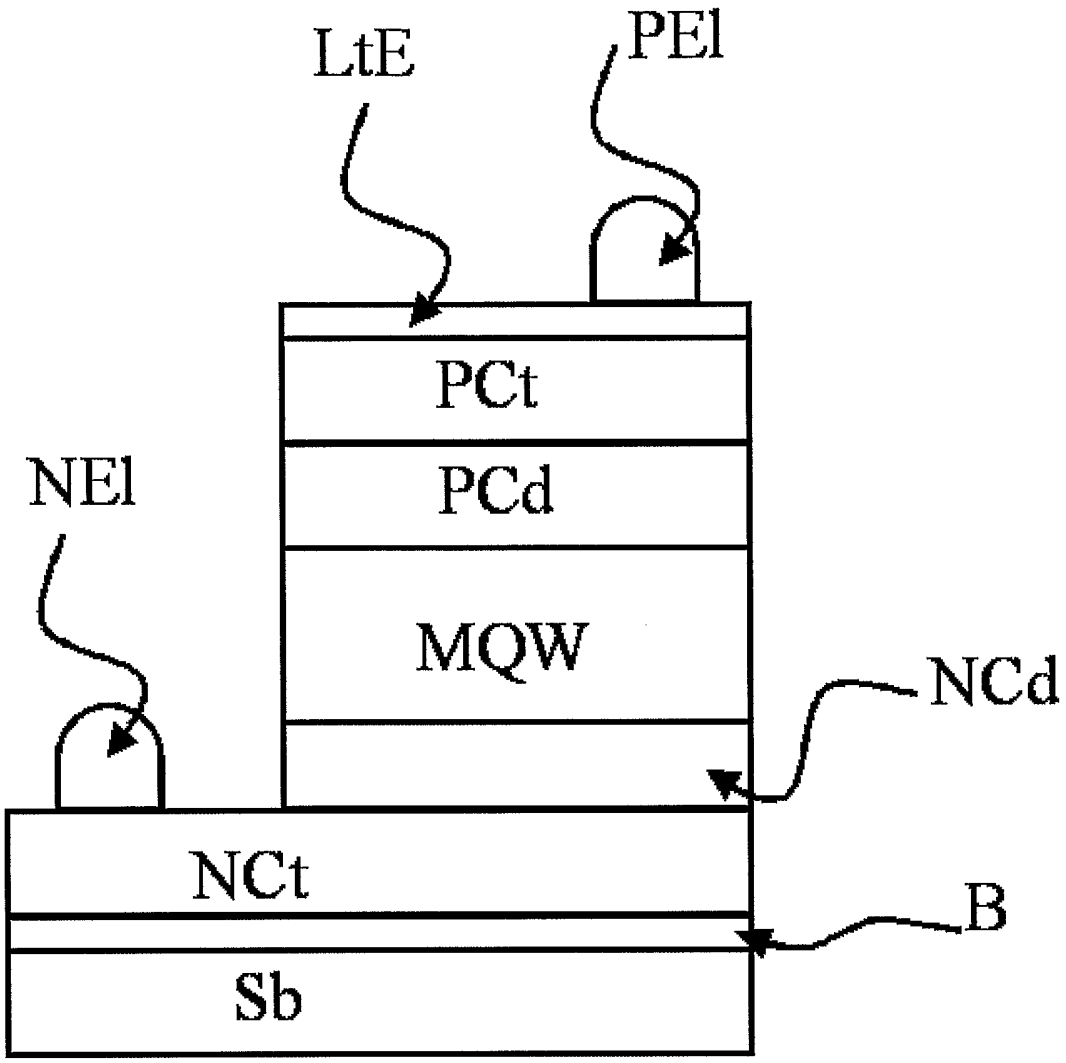

Fig. 15