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(71) Applicant (for all designated States except US): **GENERAL ELECTRIC COMPANY** [US/US]; 1 River Road, Schenectady, NY 12345 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **HANCU, Dan** [US/US]; General Electric Company Global Research, One Research Circle Bldg. K1-359, Niskayuna, NY 12309

(US). **BHAT, Shyamala, Halady Subraya** [IN/IN]; General Electric Company Global Research, One Research Circle, bldg K1-359, Niskayuna, NY 12309 (US). **NAMMALWAR, Prasanth, Kumar** [IN/IN]; General Electric Company Global Research, One Research Circle, Bldg. K1-3A59, Niskayuna, NY 12309 (US). **MANEPALLI, Satya, Kishore** [IN/IN]; General Electric Company Global Research, One Research Circle, Bldg. K1-3A59, Niskayuna, NY 12309 (US). **SETLUR, Anant, Achyut** [US/US]; General Electric Company Global Research, One Research Circle, Bldg. K1-3A59, Niskayuna, NY 12309 (US). **POROB, Digamber, Gurudas** [IN/IN]; General Electric Company Global Research, One Research Circle, Bldg. K1-3A59, Niskayuna, NY 12309 (US).

(74) Agents: **DIMAURO, Peter, T.** et al.; General Electric Company, Global Patent Operation, 2 Corporate Drive, Suite 648, Shelton, CT 06484 (US).

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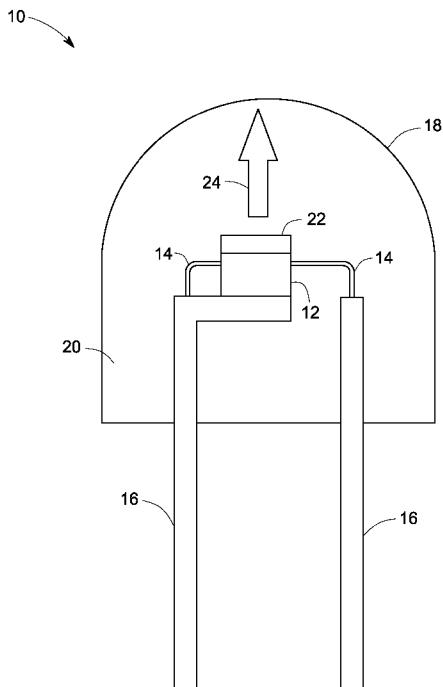


FIG. 1

(57) Abstract: An oxynitride phosphor is presented. The oxynitride phosphor has a formula: $ApBqOrNs$: R such that A is barium or a combination of barium with at least one of Li, Na, K, Y, Sc, Be, Mg, Ca, Sr, Ba, Zn, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu; B is silicon or a combination of silicon with at least one of Al, B, Ga, and Ge; R is europium or a combination of europium with at least one of Ce, Pr, Sm, Nd, Tb, Dy, Yb, Tm, Er, Ho, and Mn. p, q, r, s are numbers such that p is greater than about 2 and less than about 6, q is greater than about 8 and less than about 10, r is greater than about 0.1 and less than about 6, and s is greater than about 10 and less than about 15. The method of preparing the oxynitride phosphors and light emitting apparatus including the oxynitride phosphors are included.



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OXYNITRIDE PHOSPHORS, METHOD OF PREPARATION, AND LIGHT EMITTING INSTRUMENT

BACKGROUND

[0001] The invention generally relates to oxynitride phosphors, their preparation methods and light emitting equipments that include the oxynitride phosphors.

[0002] Over the past ten years, developments and breakthroughs in solid state lighting based on phosphor down conversion of indium gallium nitride (InGaN) light emitting diodes (LED) have shown the potential for replacing traditional fluorescent and incandescent lamps. These colored semiconductor light emitting devices, including light emitting diodes and lasers (both are generally referred to herein as LEDs), have been also produced from Group III-V alloys such as gallium nitride (GaN). To form the LEDs, layers of the alloys are typically deposited epitaxially on a substrate, such as silicon carbide or sapphire, and may be doped with a variety of n and p type dopants to improve properties, such as light emission efficiency. With reference to the InGaN-based LEDs, light is generally emitted in the UV and/or blue range of the electromagnetic spectrum. Until quite recently, LEDs have not been suitable for lighting uses where a bright white light is needed, due to the inherent color of the light produced by the LED.

[0003] Recently, techniques have been developed for converting the light emitted from LEDs to useful light for illumination purposes. In one technique, the LED is coated or covered with a phosphor layer. A phosphor is a luminescent material that absorbs radiation energy in a portion of the electromagnetic spectrum and emits energy in another portion of the electromagnetic spectrum. Phosphors of one important class are crystalline inorganic compounds of very high chemical purity and of controlled composition to which small quantities of other elements (called "activators") have been added to convert them into efficient fluorescent materials. With the right combination of activators and host inorganic compounds, the color of the emission can be controlled. Most useful and well-known phosphors emit radiation

in the visible portion of the electromagnetic spectrum in response to excitation by electromagnetic radiation outside the visible range.

[0004] By interposing a phosphor excited by the radiation generated by the LED, light of a different wavelength, e.g., in the visible range of the spectrum, may be generated. Colored LEDs are often used in toys, indicator lights and other devices. Manufacturers are continuously looking for new colored phosphors for use in such LEDs to produce custom colors and higher luminosity.

[0005] In addition to colored LEDs, a combination of LED generated light and phosphor generated light may be used to produce white light. The most popular white LEDs are based on blue emitting InGaN chips. The blue emitting chips are coated with a phosphor that converts some of the blue radiation to a complementary color, e.g. a yellow-green emission. The total of the light from the phosphor and the LED chip provides a color point with corresponding color coordinates (x and y) and correlated color temperature (CCT), and its spectral distribution provides a color rendering capability, measured by the color rendering index (CRI).

[0006] One known white light emitting device comprises a blue light-emitting LED having a peak emission wavelength in the blue range (from about 440 nm to about 480 nm) combined with a phosphor, such as cerium doped yttrium aluminum garnet $Y_3Al_5O_{12}: Ce^{3+}$ ("YAG:Ce"). The phosphor absorbs a portion of the radiation emitted from the LED and converts the absorbed radiation to a yellow-green light. The remainder of the blue light emitted by the LED is transmitted through the phosphor and is mixed with the yellow light emitted by the phosphor. A viewer perceives the mixture of blue and yellow light as a white light.

[0007] Such systems can be used to make white light sources having correlated color temperatures (CCTs) of >4500 K and color rendering indices (CRIs) of about 70-80. While this range is suitable for many applications, general illumination sources usually require higher CRIs and lower CCTs. Given the high quantum efficiency of YAG:Ce at room and elevated temperatures and the strong blue absorption from the allowed $4f^1 \rightarrow 5d^1 Ce^{3+}$ transition, such a system fulfills many of

the requirements for LED lighting. However, a shortcoming is that they typically cannot fulfill the color requirements for general illumination, low CCTs (<3500K) and higher CRIs. In order to fulfill these requirements, new phosphor compositions are needed.

BRIEF DESCRIPTION

[0008] Briefly, in one embodiment, an oxynitride phosphor is presented. The oxynitride phosphor has a formula: $A_pB_qOrNs:R$ such that A is barium or a combination of barium with at least one of Li, Na, K, Rb, Cs, Y, Sc, Be, Mg, Ca, Sr, Zn, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu; B is silicon or a combination of silicon with at least one of Al, B, Ga, and Ge; R is europium or a combination of europium with at least one of Ce, Pr, Sm, Nd, Tb, Dy, Yb, Tm, Er, Ho, and Mn. p, q, r, s are numbers such that p is greater than about 2 and less than about 6, q is greater than about 8 and less than about 10, r is greater than about 0.1 and less than about 6, and s is greater than about 10 and less than about 15.

[0009] In one embodiment, a method of preparing an oxynitride phosphor of formula $(Ba, Ca, Sr, Mg)_4Si_9OrN_{14.66 - (2/3)r}:Eu$ is presented such that r is greater than about 1 and less than or equal to about 4. The method includes the steps of weighing constituent raw materials and fluxes, transferring the weighed raw materials and fluxes to a crucible, calcining the materials of the crucible at a temperature in a range from about 1250°C to about 1400°C in a reducing atmosphere, and washing the materials of the crucible using a dilute acid.

[0010] In one embodiment, a lighting apparatus capable of emitting white light is presented. The lighting apparatus includes a semiconductor light source and an oxynitride phosphor radiationally coupled to the light source, and having a general formula: $A_pB_qOrNs : R$ such that A is barium or a combination of barium with at least one of Li, Na, K, Rb, Cs, Y, Sc, Be, Mg, Ca, Sr, Zn, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu; B is silicon or a combination of silicon with at least one of Al, B, Ga, and Ge; R is europium or a combination of europium with at least one of Ce, Pr, Sm, Nd, Tb, Dy, Yb, Tm, Er, Ho, and Mn. p, q, r, s are numbers such that p is

greater than about 2 and less than about 6, q is greater than about 8 and less than about 10, r is greater than about 0.1 and less than about 6, and s is greater than about 10 and less than about 15.

DRAWINGS

[0011] These and other features, aspects, and advantages of the present invention will become better understood when the following detailed description is read with reference to the accompanying drawings in which like characters represent like parts throughout the drawings, wherein:

[0012] FIG. 1 is a schematic cross-sectional view of a lighting apparatus according to one embodiment of the present invention.

[0013] FIG. 2 is a comparison of X-Ray diffraction graphs of two phosphor compositions according to one embodiment of the present invention.

[0014] FIG. 3 is an X-Ray diffraction graph of a phosphor composition according to one embodiment of the present invention.

[0015] FIG. 4 is an emission spectrum of a phosphor composition according to one embodiment of the present invention.

[0016] FIG. 5 is a graphical representation of normalized emission data with respect to temperature according to one embodiment of the present invention.

[0017] FIG. 6 is a comparison of X-Ray diffraction graphs of two phosphor compositions according to one embodiment of the present invention.

[0018] FIG. 7 is a comparison of X-Ray diffraction graphs of two phosphor compositions according to one embodiment of the present invention.

[0019] FIG. 8 is a comparison of X-Ray diffraction graphs of two phosphor compositions according to one embodiment of the present invention.

[0020] FIG. 9 is a comparison of emission spectra graphs of four phosphor compositions according to one embodiment of the present invention.

DETAILED DESCRIPTION

[0021] With reference to FIG 1, a lighting apparatus or light emitting assembly or lamp 10 is shown in accordance with one embodiment of the present invention. Lighting apparatus 10 comprises a semiconductor UV radiation source, such as a light emitting diode (LED) chip 12 and leads 14 electrically attached to the LED chip. The leads 14 may comprise thin wires supported by a thicker lead frame(s) 16 or the leads may comprise self-supported electrodes and the lead frame may be omitted. The leads 14 provide current to the LED chip 12 and thus cause the LED chip 12 to emit radiation.

[0022] The lamp may include any semiconductor blue or UV light source that is capable of producing white light when its emitted radiation is directed onto the phosphor. In one embodiment, the semiconductor light source comprises a blue emitting LED doped with various impurities. Thus, the LED may comprise a semiconductor diode based on any suitable III-V, II-VI or IV-IV semiconductor layers and having an emission wavelength of about 250 to 550 nm. In particular, the LED may contain at least one semiconductor layer comprising GaN, ZnSe or SiC. For example, the LED may comprise a nitride compound semiconductor represented by the formula $_{i}N_{j}G_{a}a_{k}N$ (where $0 \leq i; 0 \leq j; 0 \leq k$ and $i + j + k = 1$) having an emission wavelength greater than about 250 nm and less than about 550 nm. Preferably, the chip is a near-uv or blue emitting LED having a peak emission wavelength from about 400 to about 500 nm. Such LED semiconductors are known in the art. The radiation source is described herein as an LED for convenience. However, as used herein, the term is meant to encompass all semiconductor radiation sources including, e.g., semiconductor laser diodes.

[0023] Although the general discussion of the exemplary structures of the invention discussed herein are directed toward inorganic LED based light sources, it should be understood that the LED chip may be replaced by another radiation source

unless otherwise noted and that any reference to LED chip or semiconductor is merely representative of any appropriate radiation source.

[0024] The LED chip 12 may be encapsulated within a shell 18, which encloses the LED chip and an encapsulant material 20. The shell 18 may be, for example, glass or plastic. Preferably, the LED 12 is substantially centered in the encapsulant 20. The encapsulant 20 is preferably an epoxy, plastic, low temperature glass, polymer, thermoplastic, thermoset material, resin, silicone or other type of LED encapsulating material as is known in the art. Optionally, the encapsulant 20 is a spin-on glass or some other high index of refraction material. Preferably, the encapsulant material 20 is an epoxy or a polymer material, such as silicone. Both the shell 18 and the encapsulant 20 are preferably transparent or substantially optically transmissive with respect to the wavelength of light produced by the LED chip 12 and a phosphor composition 22 (described below). Alternately, the lamp 10 may only comprise an encapsulant material without an outer shell 18. The LED chip 12 may be supported, for example, by the lead frame 16, by the self supporting electrodes, the bottom of the shell 18, or by a pedestal (not shown) mounted to the shell or to the lead frame. In some embodiments, the LED chip 12 is mounted in a reflective cup (not shown). The cup may be made from or coated with a reflective material, such as alumina, titania, or other dielectric powder known in the art. An example of a reflective material is Al_2O_3 .

[0025] Lighting apparatus 10 includes phosphor composition 22, described below, radiationally coupled to the LED chip 12. Radiationally coupled means that the elements are associated with each other so radiation from one is transmitted to the other. Phosphor composition 22 is deposited on the LED 12 by any appropriate method. For example, a water-based suspension of the phosphor(s) can be formed, and applied as a phosphor layer to the LED surface. In one such method, a silicone slurry in which the phosphor particles are randomly suspended is placed around the LED. This method is merely exemplary of possible positions of the phosphor composition 22 and LED 12. Thus, the phosphor composition 22 may be coated over or directly on the light emitting surface of the LED chip 12 by coating and drying the phosphor suspension over the LED chip 12. Both the shell 18 and the encapsulant 20

should be transparent to allow white light 24 to be transmitted through those elements. Although not intended to be limiting, in one embodiment, the median particle size of the phosphor composition as measured by light scattering may be from about 1 to about 15 microns.

[0026] In other embodiments, the phosphor composition 22 is interspersed within the encapsulant material 20, instead of being formed directly on the LED chip 12. The phosphor (in the form of a powder) may be interspersed within a single region of the encapsulant material 20 or, more preferably, throughout the entire volume of the encapsulant material. Blue light emitted by the LED chip 12 mixes with the light emitted by the phosphor composition 22, and the mixed light appears as white light. If the phosphor is to be interspersed within the material of encapsulant 20, then a phosphor powder may be added to a polymer precursor, loaded around the LED chip 12, and then the polymer precursor may be cured to solidify the polymer material. Other known phosphor interspersion methods may also be used, such as transfer loading.

[0027] In yet another embodiment, phosphor composition 22 is coated onto a surface of the shell 18, instead of being formed over the LED chip 12. The phosphor composition is preferably coated on the inside surface of the shell 18, although the phosphor may be coated on the outside surface of the shell, if desired. The phosphor composition 22 may be coated on the entire surface of the shell or only a top portion of the surface of the shell. The UV light emitted by the LED chip 12 mixes with the light emitted by the phosphor composition 22, and the mixed light appears as white light. Of course, the phosphor may be located in any two or all three locations or in any other suitable location, such as separately from the shell or integrated into the LED.

[0028] Phosphor composition 22 includes an oxynitride phosphor material, optionally blended with one or more other phosphors. In particular embodiments, the oxynitride phosphor is of the formula $ApBqOrNs: R$. In this embodiment, A is barium or a combination of barium with at least one of the elements Li, Na, K, Rb, Cs, Y, Sc, Be, Mg, Ca, Sr, Zn, and lanthanides; B is silicon or a combination of

silicon with at least one of the elements Al, B, Ga, and Ge; R is europium or a combination of europium with at least one of the elements Ce, Pr, Sm, Nd, Tb, Dy, Yb, Tm, Er, Ho, and Mn; and p, q, r, and s are greater than zero and are in a range such that $2 < p < 6$, $8 < q < 10$, $0.1 < r < 6$, $10 < s \leq 15$.

[0029] As used herein, the term ‘greater than zero’ denotes that the intended component is intentionally added, rather than an incidental amount that may be present as an impurity. As used herein, end points of the ranges include incidental variations above and below the stated number, as appropriate for normal measurement and process variations.

[0030] In one embodiment, A is Ba. In another embodiment, A is a combination of barium with strontium or calcium or a combination of barium with strontium and calcium. In a further embodiment, the amount of strontium or calcium or a combination of strontium and calcium put together in the A site along with barium is in the range of about 0.001 to about 0.5 mole fraction of barium.

[0031] In one embodiment, B is silicon. In another embodiment, B is a combination of silicon with aluminum. In one embodiment R is europium. In another embodiment, R is a combination of europium and cerium. In one embodiment, R is present in the oxynitride material at a level of about 0.001 to about 0.5 mole fraction of the oxynitride material.

[0032] In one embodiment, a particularly useful oxynitride material is of formula $(\text{Ba, Ca, Sr, Mg})_4\text{Si}_9\text{O}_r\text{N}_{14.66 - (2/3)r} : \text{Eu}$ such that r is greater than about 1 and less than or equal to about 4. In another embodiment, the oxynitride material includes $(\text{Ba, Ca, Sr, Mg})_4\text{Si}_{9-a}\text{Al}_a\text{O}_{r+a}\text{N}_{14.66 - a - (2/3)r} : \text{Eu}$, such that r is greater than about 1 and less than or equal to about 4, and a is greater than 0 and less than or equal to about 4. In yet another embodiment, the oxynitride material includes $(\text{Ba, Ca, Sr, Mg})_4\text{Si}_9\text{O}_r\text{N}_{14.66 - (2/3)r} : (\text{Eu, Ce})$, such that r is greater than about 1 and less than or equal to about 4. In yet another embodiment, an example of an useful oxynitride material includes $(\text{Ba, Ca, Sr, Mg})_4\text{Si}_{9-a}\text{Al}_a\text{O}_{r+a}\text{N}_{14.66 - a - (2/3)r} : (\text{Eu, Ce})$, such that r is greater

than about 1 and less than or equal to about 4, and a is greater than 0 and less than or equal to about 4.

[0033] When used with an LED emitting at from 350 to 550 nm and one or more other appropriate phosphors, the resulting lighting system will produce a light having a white color, the characteristics of which will be discussed in more detail below. Lamp 10 may also include scattering particles (not shown), which are embedded in the encapsulant material. The scattering particles may comprise, for example, Al_2O_3 particles such as alumina powder or TiO_2 particles. The scattering particles effectively scatter the coherent light emitted from the LED chip, preferably with a negligible amount of absorption.

[0034] The phosphors with the oxynitride materials described above may contain optically inert trace impurities. The presence of such impurities in an amount up to 10% by weight of the phosphor composition will not significantly affect the quantum efficiency or color of the phosphor.

[0035] It may be desirable to add pigments or filters to the phosphor material. The phosphor layer 22 may also comprise from 0 up to about 5 % by weight (based on the total weight of the phosphors) of a pigment or other UV absorbent material capable of absorbing UV radiation having a wavelength between 250 nm and 450 nm.

[0036] Suitable pigments or filters include any of those known in the art that are capable of absorbing radiation generated between 250 nm and 450 nm. Such pigments include, for example, nickel titanate or praseodymium zirconate. The pigment is used in an amount effective to filter 10% to 100% of the radiation generated in the 250 nm to 450 nm range.

[0037] Phosphors of oxynitride materials described above may be produced using known solid-state reaction methods by combining, for example, elemental oxides, carbonates, nitrides, and/or hydroxides as starting materials. Other starting materials may include nitrates, sulfates, acetates, citrates, or oxalates. Alternately, coprecipitates of the rare earth oxides could be used as the starting materials for the rare earth elements. In a typical process, the starting materials are combined via a dry

blending process and fired in air or under a slightly reducing atmosphere at from, e.g., 1000 to 1600°C.

[0038] In one embodiment, the oxynitride phosphor material is obtained by mixing w amount of Ba_3N_2 , x amount of BaCO_3 , y amount of Si_3N_4 , z amount of Eu_2O_3 , u amount of BaCl_2 , and v amount of LiOH , where w varies in a range such that $0.2 < w < 1$, x varies in a range such that $0.2 < x < 1.5$, y varies in a range such that $2.5 < y < 3.3$, z varies in a range such that $0.001 < z < 0.2$, u varies in a range such that $0.1 < u < 1$, and v varies in a range such that $0.1 < v < 1$. The resultant material from this combination, after following the mixing, drying, calcining and firing steps of the preparation yields to an oxynitride phosphor material having an excitation spectrum in the range of about 200 nm to about 500 nm and the emission spectrum in the range of about 500 nm to about 750 nm.

[0039] In another typical process, the starting materials are combined via a dry or wet blending process and fired in air or under a reducing atmosphere at from, e.g., 800 to 1600°C. A flux may be added to the mixture before or during the step of mixing. This flux may be any conventional fluxes, such as a chloride or a fluoride of an alkali/alkaline earth metal. In one embodiment, the flux includes barium chloride, barium fluoride, lithium chloride, lithium fluoride, lithium hydroxide, lithium nitride, lithium tetra borate, aluminum chloride, aluminum fluoride, ammonium chloride, boric acid, magnesium chloride, magnesium fluoride, or any combination of these materials. A quantity of a fluxing agent of less than about 20 percent by weight of the total weight of the mixture is adequate for fluxing purposes. In one embodiment, the fluxing agent less than about 10 percent by weight of the total weight of the mixture is used as flux.

[0040] The starting materials may be mixed together by any mechanical method including, but not limited to, stirring or blending in a high-speed blender or a ribbon blender. The starting materials may be combined and pulverized together in a ball mill, a hammer mill, or a jet mill. The mixing may be carried out by wet milling in alcohol or organic solvents especially when the mixture of the starting materials is to be made into a solution for subsequent precipitation. If the mixture is wet, in one

embodiment, the mixture is dried first before being fired under a reducing atmosphere at a temperature from about 900°C to about 1700°C, preferably from about 1000°C to about 1600°C, for a time sufficient to convert all of the mixture to the final composition.

[0041] The firing may be conducted in a batch wise or continuous process, some times with a stirring or mixing action to promote good gas-solid contact. The firing time depends on the quantity of the mixture to be fired, the rate of gas conducted through the firing equipment, and the quality of the gas-solid contact in the firing equipment. Typically, a firing time up to about 10 hours is adequate. The reducing atmosphere typically comprises a reducing gas such as hydrogen, carbon monoxide, or a combination thereof, optionally diluted with an inert gas, such as nitrogen or helium, or a combination thereof. Alternatively, the crucible containing the mixture may be packed in a second closed crucible containing high-purity carbon particles and fired in air so that the carbon particles react with the oxygen present in air, thereby, generating carbon monoxide for providing a reducing atmosphere.

[0042] In one embodiment, an oxynitride phosphor of the formula $A_pB_qO_rN_s:R$ with any of the previously defined A, B, R, p, q, r, and s values were prepared by dry mixing the raw materials along with any fluxes that aid in the phase formation of the intended oxynitride phosphor in a ball mill in the presence of suitable grinding media. The mixing and grinding was some times carried out in a controlled atmosphere so that the contents are not exposed <5 ppm oxygen and <0.1 ppm water. The mixed and ground contents were transferred to a container maintaining suitable minimum exposure to oxygen and water. One suitable container that is often used is a Molybdenum (Mo) crucible. The container, along with the constituents were placed inside a furnace and subjected to calcining to a required temperature for phase formation. Typically the temperature of the calcination is in the range of about 1250°C to about 1500°C. The atmosphere surrounding the Mo crucible and the contents are often adjusted to be a slight reducing atmosphere. In one example, an atmosphere of about 3% hydrogen in nitrogen is used for the calcination. After calcination, the products were cooled and washed to remove any extra materials. Typically, a dilute nitric acid solution was used to wash out many of the impurities.

One particular phosphor that is prepared using this method is (Ba, Ca, Sr, Mg)₄Si₉O_rN_{14.66-(2/3)r}:Eu, wherein 1 < r ≤ 4.

[0043] The oxynitride phosphors of claim 1 may be blended with one or more additional phosphors for use in LED light sources. Thus, in another embodiment, an LED lighting apparatus is provided including a phosphor composition 22 comprising a blend of any of the oxynitride phosphor described above with one or more additional phosphors.

[0044] The relative amounts of each phosphor in a phosphor blend can be described in terms of spectral weight. Spectral weight is the relative amount that each phosphor contributes to the overall emission spectrum of the device. The spectral weight amounts of all the individual phosphors and any residual bleed from the LED source should add up to 1.0 (i.e. 100%). In one embodiment, the above-described oxynitride phosphor has a spectral weight ranging from about 0.001 to 0.75. Any known blue, blue-green, green, yellow, orange or red phosphor suitable for use in UV or blue LED systems may be used in blends with this phosphor to customize the white color of the resulting light and produce higher CRI sources.. While not intended to be limiting, suitable phosphors that can be used in the blend with the present oxynitride phosphors include phosphors such as

BLUE/BLUE-GREEN

(Ba,Sr,Ca)₅(PO₄)₃(Cl,F,Br,OH):Eu²⁺,Mn²⁺ (SECA)

(Ba,Sr,Ca)BPO₅:Eu²⁺,Mn²⁺

(Sr,Ca)₁₀(PO₄)₆ • vB₂O₃:Eu²⁺ (wherein 0 < v ≤ 1)

Sr₂Si₃O₈ • 2SrCl₂:Eu²⁺

(Ca,Sr,Ba)₃MgSi₂O₈:Eu²⁺,Mn²⁺

BaAl₈O₁₃:Eu²⁺

2SrO • 0.84P₂O₅ • 0.16B₂O₃:Eu²⁺

(Sr,Ca,Ba)₄Al₁₄O₂₅:Eu²⁺ (SAE)

(Ba,Sr,Ca)MgAl₁₀O₁₇:Eu²⁺,Mn²⁺

GREEN/YELLOW-GREEN

(Ba,Sr,Ca)Al₂O₄:Eu²⁺

(Y,Gd,Lu,Sc,La)BO₃:Ce³⁺,Tb³⁺

(Ba,Sr,Ca)₂Si_{1- ξ} O_{4+2 ξ} :Eu²⁺ (wherein 0≤ ξ ≤0.2) (SASI)

(Ba,Sr,Ca)₂(Mg,Zn)Si₂O₇:Eu²⁺

(Sr,Ca,Ba)(Al,Ga,In)₂S₄:Eu²⁺

(Sr,Ca,Ba)₃Al_{1-x}Si_xO_{4+x}F_{1-x}:Ce³⁺ (SASOF)

(Y,Gd,Tb,La,Sm,Pr, Lu)₃(Sc,Al,Ga)_{5- α} O_{12-3/2 α} :Ce³⁺ (wherein 0≤ α ≤0.5) (YAG)

(Lu,Sc,Y,Tb)_{2-u-v}Ce_vCa_{1+u}Li_wMg_{2-w}P_w(Si,Ge)_{3-w}O_{12-u/2} where -0.5≤u≤1; 0<v≤0.1; and 0≤w≤0.2 (LuSi)

(Ca,Ba,Sr)Si₂O₂N₂:Eu²⁺,Ce³⁺

(Ca,Sr)₈(Mg,Zn)(SiO₄)₄Cl₂:Eu²⁺,Mn²⁺

Na₂Gd₂B₂O₇:Ce³⁺,Tb³⁺

(Sr,Ca,Ba,Mg,Zn)₂P₂O₇:Eu²⁺,Mn²⁺

ORANGE/RED

(Gd,Y,Lu,La)₂O₃:Eu³⁺,Bi³⁺

(Gd,Y,Lu,La)₂O₂S:Eu³⁺,Bi³⁺

(Gd,Y,Lu,La)VO₄:Eu³⁺,Bi³⁺

(Ca,Sr)S:Eu²⁺,Ce³⁺

SrY₂S₄:Eu²⁺

CaLa₂S₄:Ce³⁺

(Ba,Sr,Ca)MgP₂O₇:Eu²⁺,Mn²⁺

(Y,Lu)₂WO₆:Eu³⁺,Mo⁶⁺

(Ba,Sr,Ca)_βSi_γN_μ:Eu²⁺,Ce³⁺ (wherein 2β+4γ=3μ)

Ca₃(SiO₄)Cl₂:Eu²⁺

(Y,Lu,Gd)_{2-φ}Ca_φSi₄N_{6+φ}C_{1-φ}:Ce³⁺, (wherein 0≤φ≤0.5)

(Lu,Ca,Li,Mg,Y)alpha-SiAlON:Eu²⁺,Ce³⁺

3.5MgO • 0.5MgF₂ • GeO₂:Mn⁴⁺ (MFG)

Ca_{1-c-f}Ce_cEu_fAl_{1+c}Si_{1-c}N₃, (where 0<c≤0.2, 0≤f≤0.2)

Ca_{1-h-r}Ce_hEu_rAl_{1-h}(Mg,Zn)_hSiN₃, (where 0<h≤0.2, 0≤r≤0.2)

Ca_{1-2s-t}Ce_s(Li,Na)_sEu_tAlSiN₃, (where 0≤s≤0.2, 0≤f≤0.2, s+t>0)

Ca_{1-σ-χ-φ}Ce_σ(Li,Na)_χEu_φAl_{1+σ-χ}Si_{1-σ+χ}N₃, (where 0≤σ≤0.2, 0<χ≤0.4, 0≤φ≤0.2)

Complex fluorides doped with Mn^{4+} , such as $(Na,K,Rb,Cs,NH_4)_2(Ti,Ge,Sn,Si,Zr,Hf)F_6:Mn^{4+}$.

[0045] The ratio of each of the individual phosphors in the phosphor blend may vary depending on the characteristics of the desired light output. The relative proportions of the individual phosphors in the various embodiment phosphor blends may be adjusted such that when their emissions are blended and employed in an LED lighting device, there is produced visible light of predetermined x and y values on the CIE chromaticity diagram. As stated, a white light is preferably produced. This white light may, for instance, possess an x value in the range of about 0.30 to about 0.55, and a y value in the range of about 0.30 to about 0.55. As stated, however, the exact identity and amounts of each phosphor in the phosphor composition can be varied according to the needs of the end user. When combined with a LED emitting at from 350-550 nm and, optionally, one or more additional phosphors, the use of the oxynitride phosphor material described above allows for a white LED device having a higher CRI value and lower CCT as compared to a YAG based lighting device. LED devices having CCT values from about 2500 to about 10000, preferably from 2500 to 4500, and high CRI values from about 70 to 99 can be made.

[0046] For example, when using 405 nm LEDs these oxynitride phosphors described above can be combined with a combination of phosphors that can include blue, blue-green, and red phosphors to make white light with CCT values ranging from 2500-10000 K and CRIs ranging from 70-99. One example of such a blend would be the oxynitride phosphor described above in combination with the SECA blue phosphor, the SAE blue-green phosphor, and the MFG red phosphor. Alternatively, the phosphor composition described above can also be used in combination with 430-450 nm LEDs and appropriate phosphor blends using a combination of phosphors that can include green, yellow-green and red phosphors. One example of such a blend would be the oxynitride phosphor described above in combination with a green/yellow-green phosphor such as SASOF, YAG, or LuSi and a complex fluoride doped with Mn^{4+} , such as $(Na,K,Rb,Cs,NH_4)_2(Ti,Ge,Sn,Si,Zr,Hf)F_6:Mn^{4+}$.

[0047] The phosphor composition described above may be used in additional applications besides LEDs. For example, the material may be used as a phosphor in a fluorescent lamp, in a cathode ray tube, in a plasma display device or in a liquid crystal display (LCD). The material may also be used as a scintillator in an electromagnetic calorimeter, in a gamma ray camera, in a computed tomography scanner or in a laser. These uses are meant to be merely exemplary and not exhaustive.

[0048] In one embodiment, the oxynitride phosphor material defined by claim 1 is having a monoclinic crystal structure. In one embodiment, an oxynitride phosphor material is provided, which is believed to have a novel crystal structure as determined by X-ray diffraction. This phosphor composition (also denoted as YON) can accommodate a wide range of oxygen and nitrogen. Experiments that have led to the invention described here have shown that phases hitherto unknown are present. An example of an X-ray diffraction analyses carried out on this novel powder within the BaO—Si₃N₄ system yielded a characteristic X-ray powder diagram 30 shown in FIG. 2. Here the X-Ray diffraction diagram 30 of the new phosphor is compared with X-ray powder diagram 32 of a known composition in the Ba₃N₂—Si₃N₄ system corresponding to Ba₂Si₅N₈. The X-ray powder diagram was taken using Cu-K α radiation of wavelength 1.5418 Å. Table 1 gives a list of reflections with d values for lattice spacings (in Angstroms) and the intensity (normalized to the maximum intensity which is set at 100). An X-ray powder diagram, as is known, characteristic of and reproducible for the crystalline phase of the substance concerned.

Table 1.

No	d(Å)	Intensity	No	d(Å)	Intensity	No	d(Å)	Intensity
1	9.240	99	16	2.705	620	30	1.824	121
2	7.071	650	17	2.671	402	31	1.806	270
3	5.615	57	18	2.565	800	32	1.766	128
4	5.506	21	19	2.444	652	33	1.743	76
5	4.608	268	20	2.316	295	34	1.705	57
6	4.345	282	21	2.189	128	35	1.682	119
7	4.204	32	22	2.171	194	36	1.657	97

8	3.859	121	23	2.095	98	37	1.646	90
9	3.614	320	24	2.054	99	38	1.628	147
10	3.299	785	25	2.014	177	39	1.603	132
11	3.106	418	26	1.928	143	40	1.568	115
12	2.972	676	27	1.876	80	41	1.535	139
13	2.885	708	28	1.868	104	42	1.516	106
14	2.843	657	29	1.862	93	43	1.442	153
15	2.817	1000						

[0049] There is an understanding that due to differences in the treatment of specific samples, small variations can occur, in particular for the intensity ratios. In addition, there can be shifts in the d values within this type of material due to the presence of additional ions and/or changes in the stoichiometry, which modify the crystal lattice parameters. It is possible to substitute other cations or anions and/or alter the stoichiometry in this material while retaining the same crystal structure. The X-ray powder diagram will be substantially the same as the materials within the BaO—Si₃N₄ system with shifts in the d values (e.g. to within +/-5%) depending upon the size of the cations/anions and the extent of substitution and/or non-stoichiometry. There may also be changes in the intensity ratios, which can also be dependent upon the exact treatment of specific samples, as is known. One such example is the texturing of powder samples, known in the prior art that can enhance specific diffraction peaks relative to others. Impurity peaks (e.g. from unreacted raw materials) in experimental data sets are marked with asterisks, as also customary in the art. The latter peaks are easily identified e.g. by comparison against the known patterns of the raw materials in the existing XRD databases such as the Powder Diffraction File (PDF) of the International Centre for Diffraction Data (ICDD).

EXAMPLES

[0050] In some of the examples, excess amount of one or more constituent is taken in order to get better phase purity or as a fluxing agent. Further, the CO₂ and moisture evolved during the reaction has tendency to oxidize and remove some

nitrogen from the starting materials, hence there may be some variation in actual nitrogen and oxygen content of final product with respect to starting composition.

Example 1.

[0051] About 3.156g of Si_3N_4 , about 0.158g of Eu_2O_3 , about 1.805g of BaCO_3 and about 2.926g of Ba_3N_2 were dry mixed along with about 1.01g of BaCl_2 and 0.107g of LiOH for about 5 to 15 min along with zirconia media in a nalgene bottle inside a glove box that was maintained at about 0.1ppm of oxygen and about 0.1ppm of H_2O . After mixing, the mixture was transferred to a Mo crucible and sealed in a zip lock bag inside the glove box. The sample was then transferred outside the glove box, taken to a furnace and fired in the Mo crucible at about 1350°C in a 1% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and sieved using 350 mesh and again fired at about 1350°C for 5 hours under 1% hydrogen in nitrogen atmosphere. The sample was then ground again and repeatedly washed with water and dilute nitric acid until the pH of the solution turns to neutral. The dilute nitric acid was prepared using about 2 volume percentage of nitric acid in water.

[0052] The X-ray diffraction pattern 34 taken using $\text{Cu-K}\alpha$ radiation of 1.5418\AA of the resultant phosphor indicated an unique phosphor of formula $\text{Ba}_{3.88}\text{Eu}_{0.12}\text{Si}_9\text{O}_{1.4}\text{N}_{13.76}$, as shown in FIG. 3. The small amount of $\text{BaSi}_7\text{N}_{10}$ phase present in this X-Ray diffraction pattern is denoted as impurity. The excitation 36 and emission 38 spectra of this phosphor was measured and given in FIG 4. The quantum efficiency (QE) and absorbance (Abs) were determined using phosphor powders pressed into plaques. The QE measured was a relative measurement versus a standard LED phosphor $\text{Sr}_{1.64}\text{Ca}_{0.3}\text{Eu}_{0.06}\text{Si}_{0.96}\text{O}_{3.92}$ (SASI) set at 100%. The absorbance was calculated from reflectance measurements calibrated with pressed powder plaque of BaSO_4 as customary in the art. The relative QE/Abs of the sample under 405nm excitation was 90%/80%. The luminescent intensity as a function of temperature for this phosphor 40 versus the standard SASI yellow oxide phosphor $(\text{Sr,Ca})_2\text{SiO}_4:\text{Eu}^{2+}$ (SASI) 42 is shown in FIG. 5. It can be seen that the present phosphor exhibits much less thermal quenching than the yellow oxide phosphor.

[0053] FIG. 6 compares the X-Ray diffraction pattern 50 of the unique phosphor YON of $\text{BaO}-\text{Si}_3\text{N}_4$ system with the X-Ray pattern 52 of the strontium substituted YON phosphor. Similarly FIG. 7 and 8 compare X-Ray diffraction pattern 50 of YON with the X-Ray diffraction patterns 54 of Aluminum substituted YON and 56 of calcium substituted YON, respectively. FIG. 9 compares the emission spectra 60 of YON with the emission spectra 62 of strontium substituted YON, 64 of aluminum substituted YON, and 66 of calcium substituted YON. Emission spectra 60 of YON has an emission maximum at 585 nm, while the emission maximum of strontium 62, aluminum 64, and calcium 66 substituted YON are at 625, 575, and 620, respectively. Hence, it can be seen from FIG. 9 that the emission maximum of the YON spectra can be shifted to lower or higher wavelengths by cation substitutions.

Example 2.

[0054] About 3.156g of Si_3N_4 , about 0.158g of Eu_2O_3 , about 1.657g of BaCO_3 , about 0.03g of MgO and about 2.926g of Ba_3N_2 were dry mixed along with about 1.01g of BaCl_2 and about 0.107g of LiOH for about 5 to 15 min along with zirconia media in a nalgene bottle inside a glove box that was maintained at about 0.1ppm of oxygen and about 0.1ppm of H_2O . After mixing, the mixture was transferred to a Mo crucible and sealed in a zip lock bag inside the glove box. The sample was then transferred outside the glove box, taken to a furnace and fired in the Mo crucible at about 1350°C in a 1% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and sieved using 350mesh and again fired at about 1350°C for 5 hours under 1% hydrogen in nitrogen atmosphere. The sample was then ground again and repeatedly washed with water and dilute nitric acid until the pH of the solution turns to neutral. The relative QE/Abs of the sample under 405nm excitation was 100%/80%. The X-ray diffraction pattern taken using $\text{Cu-K}\alpha$ radiation indicated a unique phosphor of formula $\text{Ba}_{3.78}\text{Mg}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$ where r and s can vary such that $1.2 \leq r \leq 4$ and $12 \leq s \leq 13.866$.

Example 3.

[0055] About 3.156g of Si_3N_4 , about 0.158g Eu_2O_3 , about 0.621g BaCO_3 , about 0.6g CaCO_3 and about 2.926g Ba_3N_2 were dry mixed along with about 1.01g of BaCl_2 and about 0.107g of LiOH for about 5 to 15 min along with zirconia media in a nalgene bottle inside a glove box that was maintained at about 0.1ppm of oxygen and about 0.1ppm of H_2O . After mixing, the mixture was transferred to a Mo crucible and sealed in a zip lock bag inside the glove box. The sample was then transferred outside the glove box, taken to a furnace and fired in the Mo crucible at about 1350°C in 1% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and sieved using 350mesh and again fired at about 1350°C for 5 hours under 1% hydrogen in nitrogen atmosphere. The sample was then ground again and repeatedly washed with water and dilute nitric acid until the pH of the solution turns to neutral. The relative QE/Abs of the sample under 405nm excitation was 80%/80%. The X-ray diffraction pattern taken using $\text{Cu-K}\alpha$ radiation indicated a unique phosphor of formula $\text{Ba}_{3.08}\text{Ca}_{0.8}\text{Eu}_{0.12}\text{Si}_9\text{O}_{14}\text{N}_{13.76}$.

Example 4.

[0056] About 3.156g of Si_3N_4 , about 0.158g of Eu_2O_3 , about 0.917g of BaCO_3 , about 0.664g of SrCO_3 and about 2.926g of Ba_3N_2 were dry mixed along with about 1.01g of BaCl_2 and about 0.107g of LiOH for about 5 to 15 min along with zirconia media in a nalgene bottle inside a glove box that was maintained at about 0.1ppm of oxygen and about 0.1ppm of H_2O . After mixing, the mixture was transferred to a Mo crucible and sealed in a zip lock bag inside the glove box. The sample was then transferred outside the glove box, taken to a furnace and fired in the Mo crucible at about 1350°C in 1% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and sieved using 350mesh and again fired at about 1350°C for 5 hours under 1% hydrogen in nitrogen atmosphere. The sample was then ground again and repeatedly washed with water and dilute nitric acid until the pH of the solution turns to neutral. The X-ray diffraction pattern taken using $\text{Cu-K}\alpha$ radiation indicated a unique phosphor of formula $\text{Ba}_{3.28}\text{Sr}_{0.6}\text{Eu}_{0.12}\text{Si}_9\text{O}_{14}\text{N}_{13.76}$. Different levels of strontium substitution for

barium was tried by changing the SrCO_3 and Ba_3N_2 raw material weights to get the oxynitrides of the formula $\text{Ba}_{4-b}\text{Sr}_b\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$ wherein $0 \leq b \leq 0.6$, $1.2 \leq r \leq 4$ and $12 \leq s \leq 13.866$. The relative QE/Abs of some of the samples under 405nm excitation was as given below in the table 2. The oxygen and nitrogen levels of the compositions in the table 2 can vary such that $1.2 \leq r \leq 4$ and $12 \leq s \leq 13.866$.

Table 2.

Compound	λ_{max} (nm)	QE	Absorbance
$\text{Ba}_{3.88}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$	585	94	72
$\text{Ba}_{3.68}\text{Sr}_{0.2}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$	587	93	75
$\text{Ba}_{3.48}\text{Sr}_{0.4}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$	600	77	72
$\text{Ba}_{2.88}\text{Sr}_{1.0}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$	610	73	75

Example 5.

[0057] 10g batches of various phosphor formulations were produced as explained below. Sc_2O_3 , Y_2O_3 , La_2O_3 , Gd_2O_3 , Yb_2O_3 , Lu_2O_3 , Eu_2O_3 , MgO , and Si_3N_4 were used as the raw materials for elements Sc, Y, La, Gd, Yb, Lu, Eu, Mg, and Si, respectively. BaCO_3 and Ba_3N_2 were added as the sources for Ba. These raw materials were dry mixed along with about 1.01g of BaCl_2 and about 0.107g of LiOH for about 5 to 15 min along with zirconia media in a nalgene bottle inside a glove box that was maintained at about 0.1ppm of oxygen and about 0.1ppm of H_2O . After mixing, the mixture was transferred to a Mo crucible and sealed in a zip lock bag inside the glove box. The sample was then transferred outside the glove box, taken to a furnace and fired in the Mo crucible at about 1350°C in 1% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and sieved using 350mesh and again fired at about 1350°C for 5 hours under 1% hydrogen in nitrogen atmosphere. The sample was then ground again and repeatedly washed with water and dilute nitric acid until the pH of the solution turns to neutral. The QE/Abs values versus composition are as given in the table 3 below. The oxygen and nitrogen

levels of the compositions in the table 3 can vary such that $1.2 \leq r \leq 4$ and $12 \leq s \leq 13.866$.

Table 3.

Compound	QE	Absorbance
$\text{Ba}_{3.68}\text{Mg}_{0.1}\text{Sc}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$	82	81
$\text{Ba}_{3.68}\text{Mg}_{0.1}\text{Y}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$	110	72
$\text{Ba}_{3.68}\text{Mg}_{0.1}\text{La}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$	91	72
$\text{Ba}_{3.68}\text{Mg}_{0.1}\text{Gd}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$	84	79
$\text{Ba}_{3.68}\text{Mg}_{0.1}\text{Yb}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$	114	65
$\text{Ba}_{3.68}\text{Mg}_{0.1}\text{Lu}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$	105	68

Example 6.

[0058] 10g batches of various aluminum, boron, gallium and germanium doped phosphor formulations were produced as explained below. Al_2O_3 , B_2O_3 , Ga_2O_3 , GeO_2 , AlN , BN , BaCO_3 , MgO , Eu_2O_3 , Ba_3N_2 and Si_3N_4 were used as raw materials. These raw materials were dry mixed along with about 1.01g of BaCl_2 and about 0.107g of LiOH for about 5 to 15 min along with zirconia media in a nalgene bottle inside a glove box that was maintained at about 0.1ppm of oxygen and about 0.1ppm of H_2O . After mixing, the mixture was transferred to a Mo crucible and sealed in a zip lock bag inside the glove box. The sample was then transferred outside the glove box, taken to a furnace and fired in the Mo crucible at about 1350°C in 1% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and sieved using 350mesh and again fired at about 1350°C for 5 hours under 1% hydrogen in nitrogen atmosphere. The sample was then ground again and repeatedly washed with water and dilute nitric acid until the pH of the solution turns to neutral. The QE/Abs values versus composition are as given in the table 4 below. The X-ray diffraction pattern taken using $\text{Cu-K}\alpha$ radiation for the Al doped phosphor is given in Fig 5. The oxygen and nitrogen levels of the compositions in the table 5 can vary such that $1.2 \leq r \leq 4$ and $12 \leq s \leq 13.866$.

Table 4.

Compound	QE	Absorbance
$\text{Ba}_{3.78}\text{Mg}_{0.1}\text{Eu}_{0.12}\text{Si}_{8.9}\text{Al}_{0.1}\text{O}_r\text{N}_s$	122	64
$\text{Ba}_{3.78}\text{Mg}_{0.1}\text{Eu}_{0.12}\text{Si}_{8.9}\text{Al}_{0.1}\text{O}_r\text{N}_s$	109	75
$\text{Ba}_{3.78}\text{Mg}_{0.1}\text{Eu}_{0.12}\text{Si}_{8.9}\text{B}_{0.1}\text{O}_r\text{N}_s$	94	72
$\text{Ba}_{3.78}\text{Mg}_{0.1}\text{Eu}_{0.12}\text{Si}_{8.9}\text{B}_{0.1}\text{O}_r\text{N}_s$	91	75
$\text{Ba}_{3.78}\text{Mg}_{0.1}\text{Eu}_{0.12}\text{Si}_{8.9}\text{Ga}_{0.1}\text{O}_r\text{N}_s$	103	73
$\text{Ba}_{3.78}\text{Mg}_{0.1}\text{Eu}_{0.12}\text{Si}_{8.9}\text{Ge}_{0.1}\text{O}_r\text{N}_s$	112	62

Example 7.

[0059] About 2.629g of Si_3N_4 , about 0.198g of Eu_2O_3 and about 7.174g of BaCO_3 were dry milled for about 5 hours along with zirconia media in a nalgene bottle. After mixing, the mixture was separated from zirconia media and transferred to a Mo crucible. This sample was transferred to a furnace and fired at about 1300°C in 4% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and washed with dilute nitric acid followed by water until the pH of the solution turns to neutral. The composition of the sample prepared as determined by X-Ray diffraction was $\text{Ba}_{3.88}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$ where $1.2 \leq r \leq 4$ and $12 \leq s \leq 13.866$. The relative QE/Abs of the sample under 405nm excitation was 72%/74%.

Example 8.

[0060] About 2.386g of Si_3N_4 , about 0.179g of Eu_2O_3 and about 7.583g of $\text{BaC}_2\text{O}_4\cdot0.5\text{H}_2\text{O}$ were dry milled for about 5 hours along with zirconia media in a nalgene bottle. After mixing, the mixture was separated from zirconia media and transferred to a Mo crucible. This sample was transferred to a furnace and fired at about 1350°C in 4% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and washed with dilute nitric acid followed by water until the pH of the solution turns to neutral. The composition of the sample prepared as determined by X-Ray diffraction was $\text{Ba}_{3.88}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$ where $1.2 \leq r \leq 4$ and $12 \leq s \leq 13.866$. The cell parameters for this material are $a = 5.7685\text{\AA}$, $b =$

7.0611 \AA , c = 9.6493 \AA , beta = 107.42 $^{\circ}$. The relative QE/Abs of the sample under 405nm excitation was 92%/67%.

Example 9.

[0061] About 1.519g of Si_3N_4 , about 0.114g of Eu_2O_3 and about 5.366g of Ba-acetate were dry milled for about 5 hours along with zirconia media in a nalgene bottle. After mixing, the mixture was separated from zirconia media and transferred to a Mo crucible. This sample was transferred to a furnace and fired at about 1300 $^{\circ}\text{C}$ in 4% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and washed with dilute nitric acid followed by water until the pH of the solution turns to neutral. The composition of the sample prepared as determined by X-Ray diffraction was $\text{Ba}_{3.88}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$ where $1.2 \leq r \leq 4$ and $12 \leq s \leq 13.866$. The relative QE/Abs of the sample under 405nm excitation was 75%/64%.

Example 10.

[0062] About 1.367g of Si_3N_4 , about 0.344g AlN, about 0.059g of Eu_2O_3 and about 3.231g of BaCO_3 were dry milled for about 5 hours along with zirconia media in a nalgene bottle. After mixing, the mixture was separated from zirconia media and transferred to a Mo crucible. This sample was transferred to a furnace and fired at about 1400 $^{\circ}\text{C}$ in 2% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and washed with dilute nitric acid followed by water until the pH of the solution turns to neutral. The composition of the sample prepared as determined by X-Ray diffraction was $\text{Ba}_{3.88}\text{Eu}_{0.12}\text{Si}_7\text{Al}_2\text{O}_r\text{N}_s$ where $3.2 \leq r \leq 6$ and $10 \leq s \leq 11.866$. The cell parameters for this material are a = 5.8339 \AA , b = 7.0393 \AA , c = 9.7450 \AA , beta = 107.07 $^{\circ}$. The relative QE/Abs of the sample under 405nm excitation was 52%/62%.

Example 11.

[0063] About 1.471g of Si_3N_4 , about 0.143g of AlN, about 0.074g of Eu_2O_3 about 1.256g of BaCO_3 and about 1.109g of Ba_3N_2 were dry mixed for about 5 to 15 min along with zirconia media in a nalgene bottle inside a glove box that was

maintained at about 0.1ppm of oxygen and about 0.1ppm of H₂O. After mixing, the mixture was transferred to a Mo crucible and sealed in a zip lock bag inside the glove box. This sample was transferred to a furnace and fired at about 1350°C in 2% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and washed with dilute nitric acid followed by water until the pH of the solution turns to neutral. The composition of the sample prepared as determined by X-Ray diffraction was Ba_{3.88}Eu_{0.12}Si₇Al₂O_rN_s where 3.2 ≤ r ≤ 6 and 10 ≤ s ≤ 11.866. The relative QE/Abs of the sample under 405nm excitation was 79%/65%.

Example 12.

[0064] About 1.445g of Si₃N₄, about 0.073g of Eu₂O₃, about 0.827g of BaCO₃, about 1.064g of Ba₃N₂, about 0.104g of Ca₃N₂, about 0.465g of BaCl and about 0.051g of LiCl were dry mixed for about 5 to 15 min along with zirconia media in a nalgene bottle inside a glove box that was maintained at about 0.1ppm of oxygen and about 0.1ppm of H₂O. After mixing, the mixture was transferred to a Mo crucible and sealed in a zip lock bag inside the glove box. This sample was transferred to a furnace and fired at about 1350°C in 1% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and again fired at about 1350°C for 5 hours in 1% hydrogen (balance nitrogen) atmosphere. The sample was then ground using a mortar and pestle and washed with dilute nitric acid followed by water until the pH of the solution turns to neutral. The composition of the sample prepared as determined by X-Ray diffraction was Ba_{3.28}Ca_{0.6}Eu_{0.12}Si₉O_rN_s where 1.2 ≤ r ≤ 4 and 12 ≤ s ≤ 13.866. The relative QE/Abs of the sample under 405nm excitation was 82%/78%. Different compositions of the formula Ba_{4-b}Ca_bEu_{0.12}Si₉O_rN_s wherein 0 ≤ b ≤ 0.6, 1.2 ≤ r ≤ 4 and 12 ≤ s ≤ 13.866 were prepared and studied.

Example 13.

[0065] About 3.156g of Si₃N₄, about 0.013g of Eu₂O₃, about 1.901g of BaCO₃, about 0.03g of MgO and about 2.938g of Ba₃N₂ were dry mixed along with about 1.01g of BaCl₂ and about 0.107g of LiOH for about 5 to 15 min along with

zirconia media in a nalgene bottle inside a glove box that was maintained at about 0.1ppm of oxygen and about 0.1ppm of H₂O. After mixing, the mixture was transferred to a Mo crucible and sealed in a zip lock bag inside the glove box. The sample was then transferred outside the glove box, taken to a furnace and fired in the Mo crucible at about 1350°C in a 2% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and sieved using 350mesh and again fired at about 1350°C for 5 hours under 1% hydrogen in nitrogen atmosphere. The sample was then ground again and repeatedly washed with water and dilute nitric acid until the pH of the solution turns to neutral. The relative QE/Abs of the sample under 405nm excitation was 95%/45%. The X-ray diffraction pattern taken using Cu-K α radiation indicated a unique phosphor of formula Ba_{3.89}Mg_{0.1}Eu_{0.01}Si₉O_rN_s where r and s can vary such that 1.2 ≤ r ≤ 4 and 12 ≤ s ≤ 13.866.

Example 14.

[0066] About 3.156g of Si₃N₄, about 0.527g of Eu₂O₃, about 1.036g of BaCO₃, about 0.03g of MgO and about 3.158g of Ba₃N₂ were dry mixed along with about 1.01g of BaCl₂ and about 0.107g of LiOH for about 5 to 15 min along with zirconia media in a nalgene bottle inside a glove box that was maintained at about 0.1ppm of oxygen and about 0.1ppm of H₂O. After mixing, the mixture was transferred to a Mo crucible and sealed in a zip lock bag inside the glove box. The sample was then transferred outside the glove box, taken to a furnace and fired in the Mo crucible at about 1350°C in a 2% hydrogen in nitrogen atmosphere for about 5 hours. The sample was then ground using a mortar and pestle and sieved using 350mesh and again fired at about 1350°C for 5 hours under 1% hydrogen in nitrogen atmosphere. The sample was then ground again and repeatedly washed with water and dilute nitric acid until the pH of the solution turns to neutral. The relative QE/Abs of the sample under 405nm excitation was 80%/82%. The X-ray diffraction pattern taken using Cu-K α radiation indicated a unique phosphor of formula Ba_{3.5}Mg_{0.1}Eu_{0.4}Si₉O_rN_s where r and s can vary such that 1.2 ≤ r ≤ 4 and 12 ≤ s ≤ 13.866.

[0067] While only certain features of the invention have been illustrated and described herein, many modifications and changes will occur to those skilled in the art. It is, therefore, to be understood that the appended claims are intended to cover all such modifications and changes as fall within the true spirit of the invention.

CLAIMS:

1. An oxynitride phosphor of formula $A_pB_qO_rN_s$; R wherein

A is barium or a combination of barium with at least one of Li, Na, K, Rb, Cs, Y, Sc, Be, Mg, Ca, Sr, Zn, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu;

B is silicon or a combination of silicon with at least one of Al, B, Ga, and Ge;

R is europium or a combination of europium with at least one of Ce, Pr, Sm, Nd, Tb, Dy, Yb, Tm, Er, Ho, and Mn;

p is greater than about 2 and less than about 6; q is greater than about 8 and less than about 10;

r is greater than about 0.1 and less than about 6; and

s is greater than about 10 and less than about 15.

2. The oxynitride phosphor of claim 1, wherein A is a combination of Ba with at least one of Sr and Ca.

3. The oxynitride phosphor of claim 2, wherein Sr, Ca, or a combination of Sr and Ca is present at a level ranging from about 0.001 to about 0.5 mole fraction based on total moles of Ba.

4. The oxynitride phosphor of claim 1, wherein R is present at a level ranging from about 0.001 to about 0.5 mole fraction of the oxynitride material.

5. The oxynitride phosphor of claim 1, wherein A is Ba.

6. The oxynitride phosphor of claim 1, wherein R is Eu.

7. The oxynitride phosphor of claim 1, wherein the oxynitride material is $(\text{Ba, Ca, Sr, Mg})_4\text{Si}_9\text{O}_{14.66 - (2/3)r}\text{:Eu}$, wherein r is greater than about 1 and less than or equal to about 4.

8. The oxynitride phosphor of claim 1, wherein the oxynitride material is $(\text{Ba, Ca, Sr, Mg})_4\text{Si}_{9-a}\text{Al}_a\text{O}_{r+a}\text{N}_{14.66 - a - (2/3)r}\text{:Eu}$, wherein r is greater than about 1 and less than or equal to about 4, and a is greater than 0 and less than or equal to about 4.

9. The oxynitride phosphor of claim 1, wherein the oxynitride material is $(\text{Ba, Ca, Sr, Mg})_4\text{Si}_{9}\text{O}_{r}\text{N}_{14.66 - (2/3)r}\text{: (Eu, Ce)}$, wherein r is greater than about 1 and less than or equal to about 4.

10. The oxynitride phosphor of claim 1, wherein the oxynitride material is $(\text{Ba, Sr, Ca, Mg})_4\text{Si}_{9-a}\text{Al}_a\text{O}_{r+a}\text{N}_{14.66 - a - (2/3)r}\text{: (Eu, Ce)}$, wherein r is greater than about 1 and less than or equal to about 4, and a is greater than 0 and less than or equal to about 4.

11. The oxynitride phosphor of claim 1, of formula $\text{Ba}_{4-x}\text{Ca}_x\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$ wherein x is greater than or equal to zero and less than or equal to about 0.6, r is greater than or equal to about 1.2 and less than or equal to about 4, and s is greater than or equal to about 12 and less than or equal to about 13.866.

12. The oxynitride phosphor of claim 1, of formula $\text{Ba}_{4-x}\text{Sr}_x\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$ wherein x is greater than or equal to zero and less than or equal to about 0.6, r is greater than or equal to about 1.2 and less than or equal to about 4, and s is greater than or equal to about 12 and less than or equal to about 13.866.

13. The oxynitride phosphor of claim 1, of formula $\text{Ba}_{3.88}\text{Eu}_{0.12}\text{Si}_9\text{-}_a\text{Al}_a\text{O}_r\text{N}_s$ wherein a is greater than or equal to zero and less than or equal to about 4, r is greater than or equal to about 3 and less than or equal to about 8, and s is greater than or equal to about 8 and less than or equal to about 13.866.

14. The oxynitride phosphor of claim 1, selected from the group consisting of $\text{Ba}_{3.88}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$, $\text{Ba}_{3.78}\text{Mg}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$, $\text{Ba}_{3.58}\text{Ca}_{0.4}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$, $\text{Ba}_{3.28}\text{Sr}_{0.6}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$, $\text{Ba}_{3.68}\text{Sr}_{0.2}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$, $\text{Ba}_{3.48}\text{Sr}_{0.4}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$,

$\text{Ba}_{2.88}\text{Sr}_{1.0}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$, $\text{Ba}_{3.68}\text{Mg}_{0.1}\text{Sc}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$, $\text{Ba}_{3.68}\text{Mg}_{0.1}\text{Y}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$,
 $\text{Ba}_{3.68}\text{Mg}_{0.1}\text{La}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$, $\text{Ba}_{3.68}\text{Mg}_{0.1}\text{Gd}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$,
 $\text{Ba}_{3.68}\text{Mg}_{0.1}\text{Yb}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$, $\text{Ba}_{3.68}\text{Mg}_{0.1}\text{Lu}_{0.1}\text{Eu}_{0.12}\text{Si}_9\text{O}_r\text{N}_s$,
 $\text{Ba}_{3.78}\text{Mg}_{0.1}\text{Eu}_{0.12}\text{Si}_{8.9}\text{Al}_{0.1}\text{O}_r\text{N}_s$, $\text{Ba}_{3.88}\text{Eu}_{0.12}\text{Si}_8\text{Al}_1\text{O}_r\text{N}_s$, $\text{Ba}_{3.88}\text{Eu}_{0.12}\text{Si}_7\text{Al}_2\text{O}_r\text{N}_s$,
 $\text{Ba}_{3.86}\text{Mg}_{0.1}\text{Eu}_{0.04}\text{Si}_9\text{O}_r\text{N}_s$, $\text{Ba}_{3.78}\text{Mg}_{0.1}\text{Eu}_{0.12}\text{Si}_{8.9}\text{B}_{0.1}\text{O}_r\text{N}_s$,
 $\text{Ba}_{3.78}\text{Mg}_{0.1}\text{Eu}_{0.12}\text{Si}_{8.9}\text{B}_{0.1}\text{O}_r\text{N}_s$, $\text{Ba}_{3.78}\text{Mg}_{0.1}\text{Eu}_{0.12}\text{Si}_{8.9}\text{Ga}_{0.1}\text{O}_r\text{N}_s$,
 $\text{Ba}_{3.78}\text{Mg}_{0.1}\text{Eu}_{0.12}\text{Si}_{8.9}\text{Ge}_{0.1}\text{O}_r\text{N}_s$, $\text{Ba}_{3.89}\text{Mg}_{0.1}\text{Eu}_{0.01}\text{Si}_9\text{O}_r\text{N}_s$, and $\text{Ba}_{3.5}\text{Mg}_{0.1}\text{Eu}_{0.4}\text{Si}_9\text{O}_r\text{N}_s$
wherein r is greater than or equal to about 1.2 and less than or equal to about 8, and s is greater than or equal to about 8 and less than or equal to about 13.866.

15. The oxynitride phosphor of claim 1, wherein an unit cell has a monoclinic crystal structure as determined by X-ray diffraction.

16. The oxynitride phosphor of claim 1, having an excitation spectrum in the range of about 200nm to about 500nm.

17. The oxynitride phosphor of claim 1, having an emission spectrum in the range of about 500nm to about 750nm.

18. The oxynitride phosphor of claim 1, synthesized using a starting mixture of $w\text{Ba}_3\text{N}_2$, $x\text{BaCO}_3$, $y\text{Si}_3\text{N}_4$, $z\text{Eu}_2\text{O}_3$, $u\text{BaCl}_2$, $v\text{LiOH}$ wherein

w is greater than about 0.2 and less than about 1;

x is greater than about 0.2 and less than about 1.5;

y is greater than about 2.5 and less than about 3.3;

z is greater than about 0.001 and less than about 0.2;

u is greater than about 0.1 and less than about 1; and

v is greater than about 0.1 and less than about 1.

19. A method of preparing an oxynitride phosphor of formula (Ba, Ca, Sr, Mg)₄Si₉O_rN_{14.66 - (2/3)r}:Eu, wherein r is greater than about 1 and less than or equal to about 4, comprising the steps of:

weighing constituent raw materials and fluxes;

transferring the weighed raw materials and fluxes to a crucible;

calcining materials of the crucible at a temperature in a range from about 1200°C to about 1500°C in a reducing atmosphere; and

washing the materials of the crucible using a dilute acid.

20. The method of claim 19, wherein the flux comprises barium chloride, barium fluoride, lithium chloride, lithium fluoride, lithium hydroxide, lithium nitride, lithium tetra borate, aluminum chloride, aluminum fluoride, ammonium chloride, boric acid, magnesium chloride, magnesium fluoride, or any combination thereof.

21. A lighting apparatus capable of emitting white light, said lighting apparatus comprising:

a semiconductor light source; and

an oxynitride phosphor radiationally coupled to the light source, and having a general formula: A_pB_qO_rN_s : R wherein

A is barium or a combination of barium with at least one of Li, Na, K, Rb, Cs, Y, Sc, Be, Mg, Ca, Sr, Zn, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu;

B is silicon or a combination of silicon with at least one of Al, B, Ga, and Ge;

R is europium or a combination of europium with at least one of Ce, Pr, Sm, Nd, Tb, Dy, Yb, Tm, Er, Ho, and Mn;

p is greater than about 2 and less than about 6;

q is greater than about 8 and less than about 10;

r is greater than about 0.1 and less than about 6; and

s is greater than about 10 and less than about 15.

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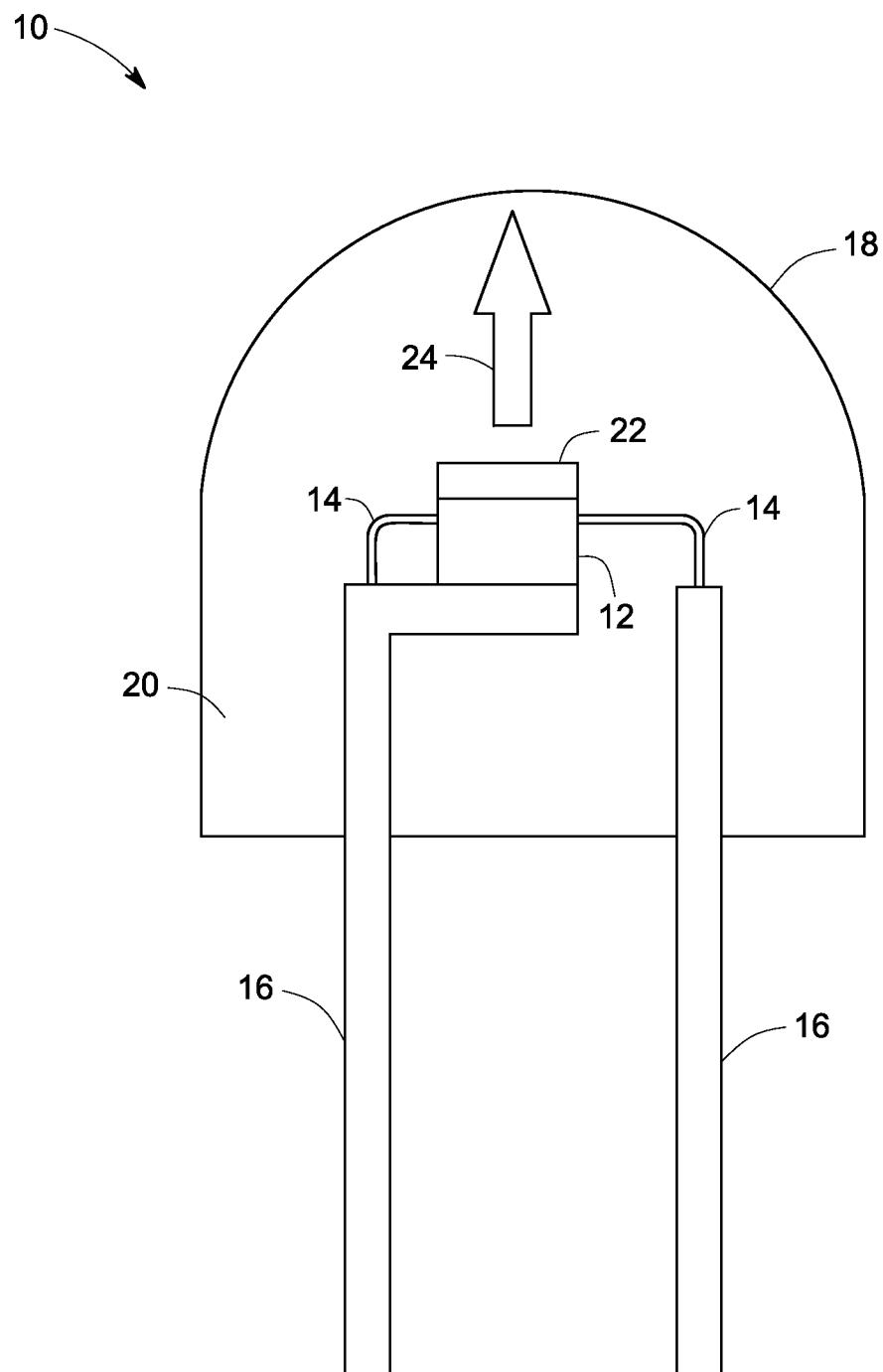


FIG. 1

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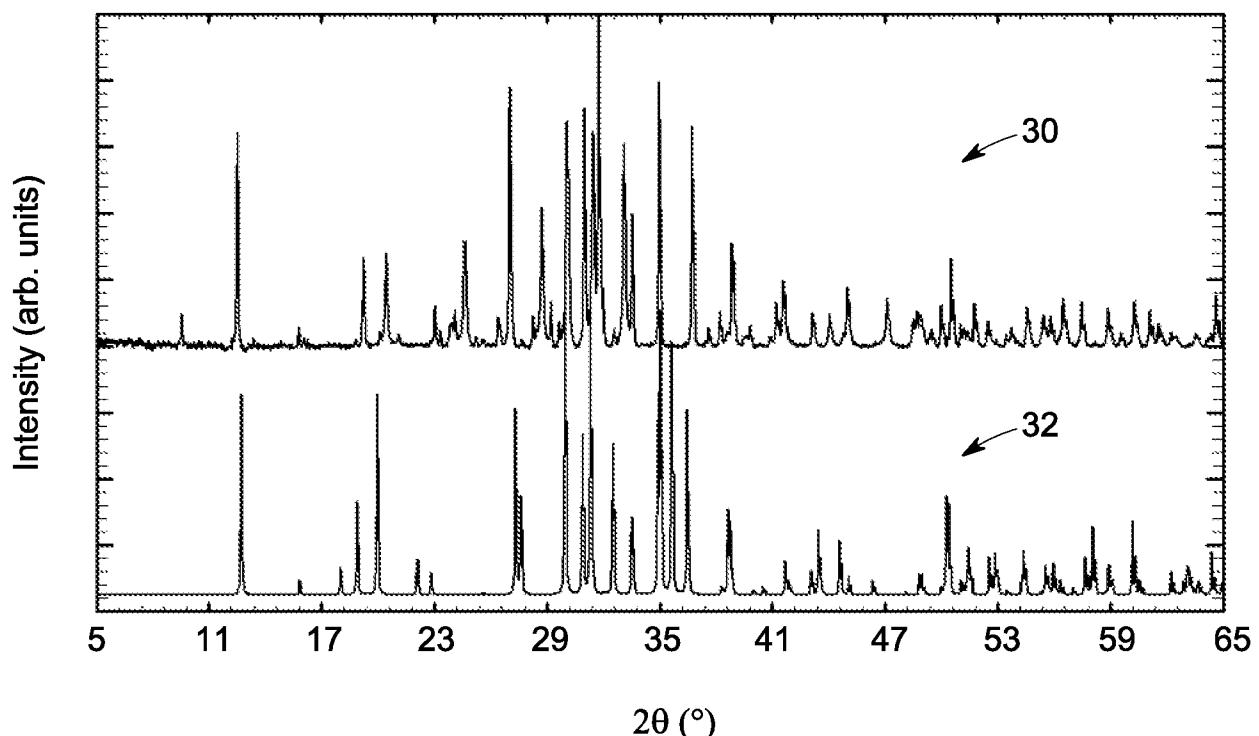


FIG. 2

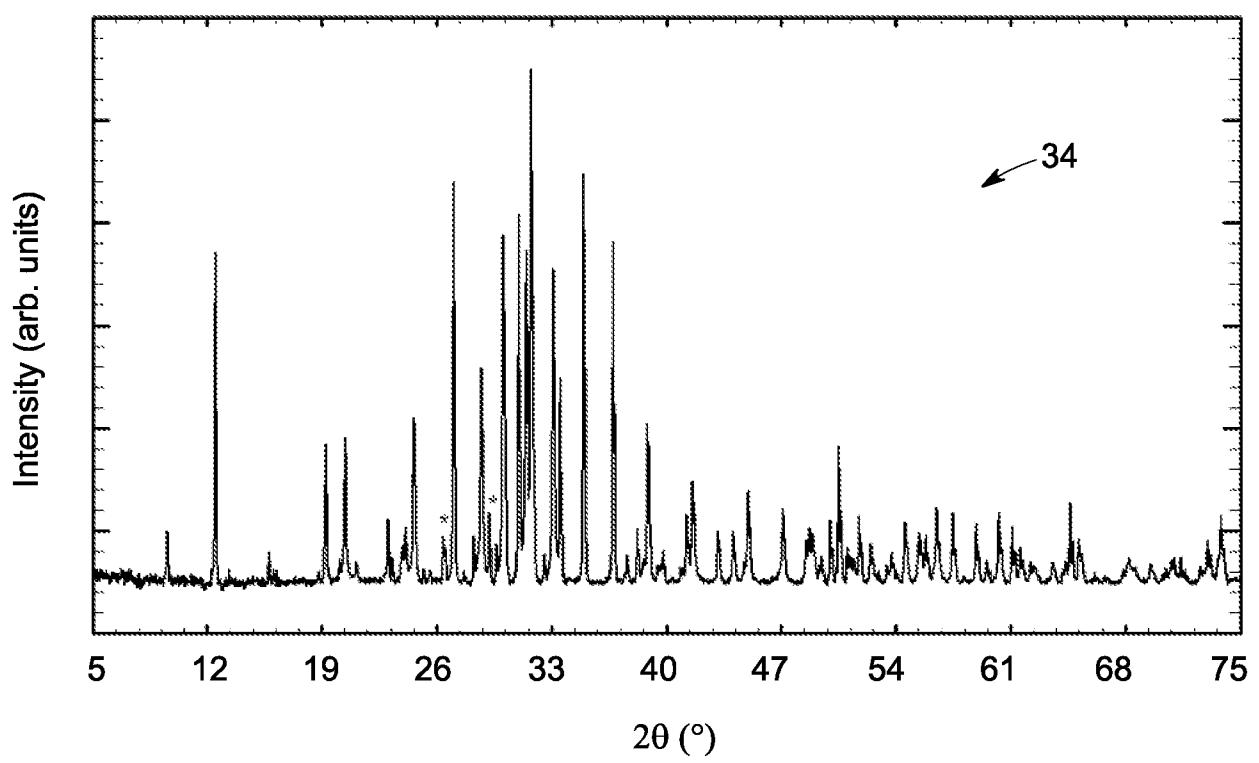


FIG. 3

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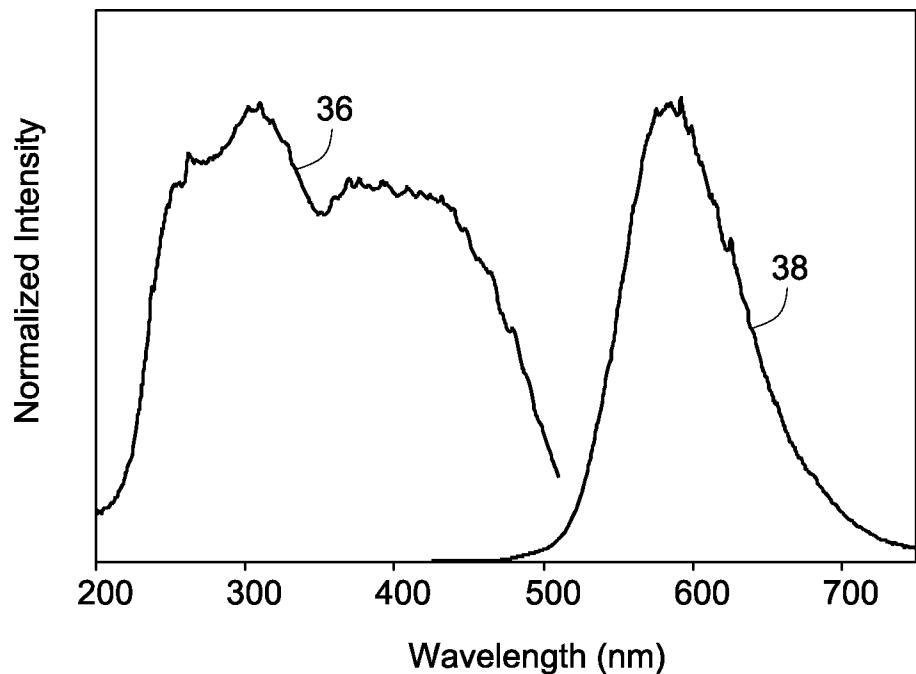


FIG. 4

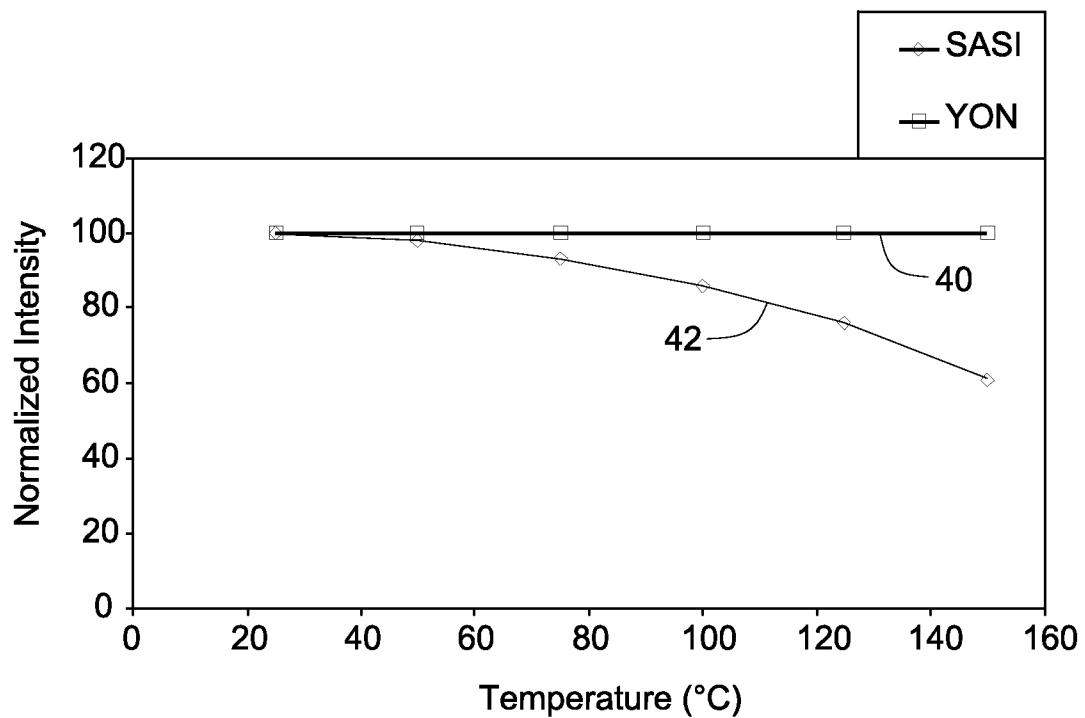


FIG. 5

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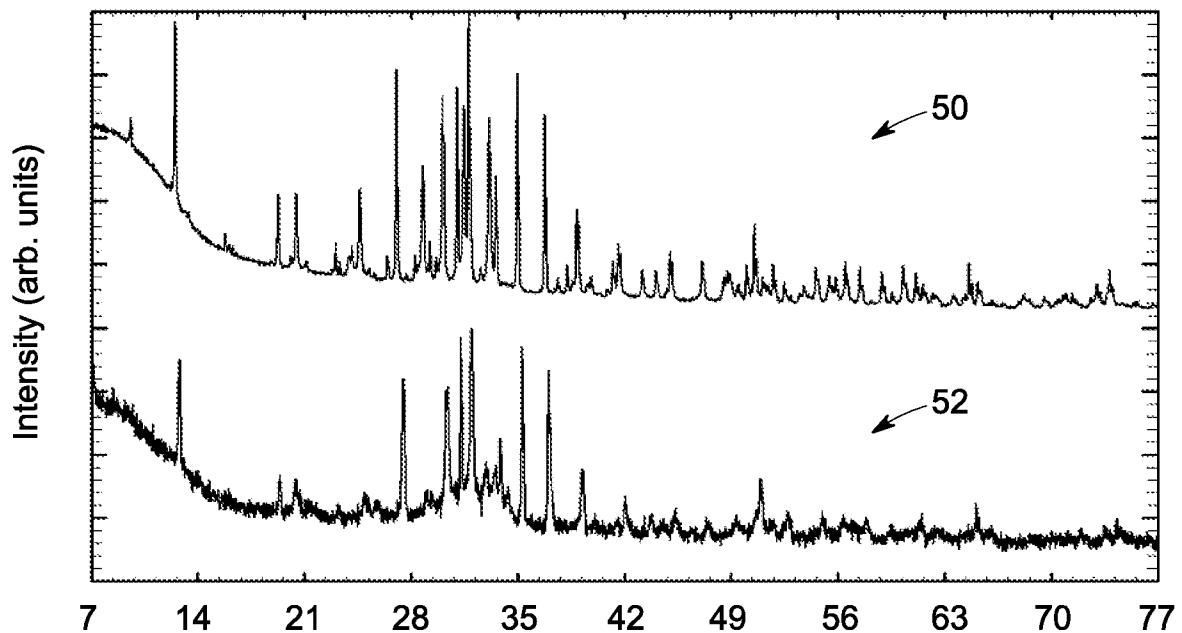


FIG. 6

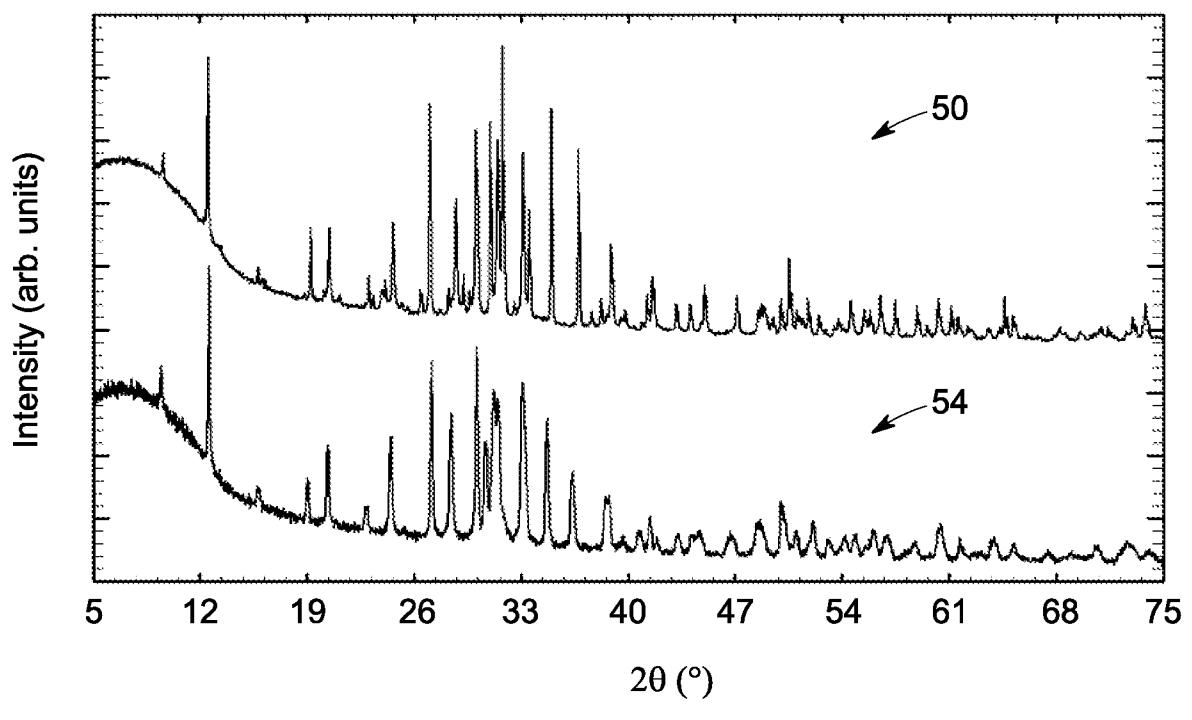


FIG. 7

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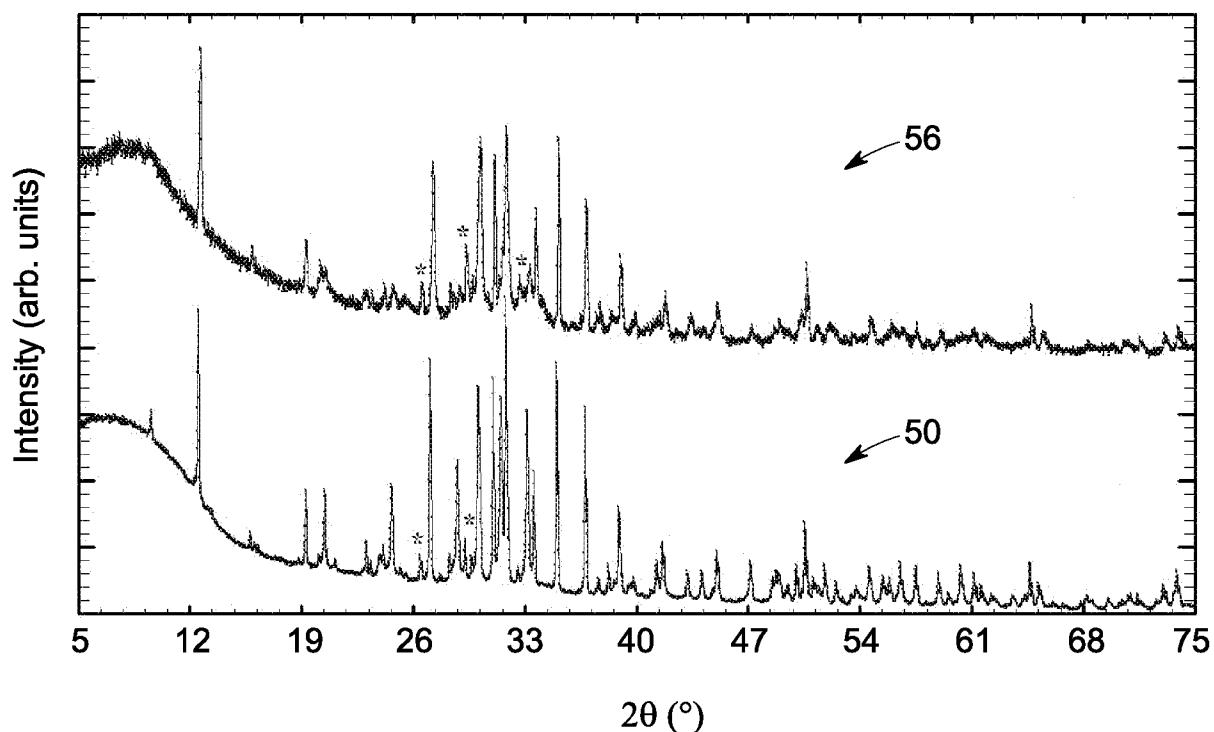


FIG. 8

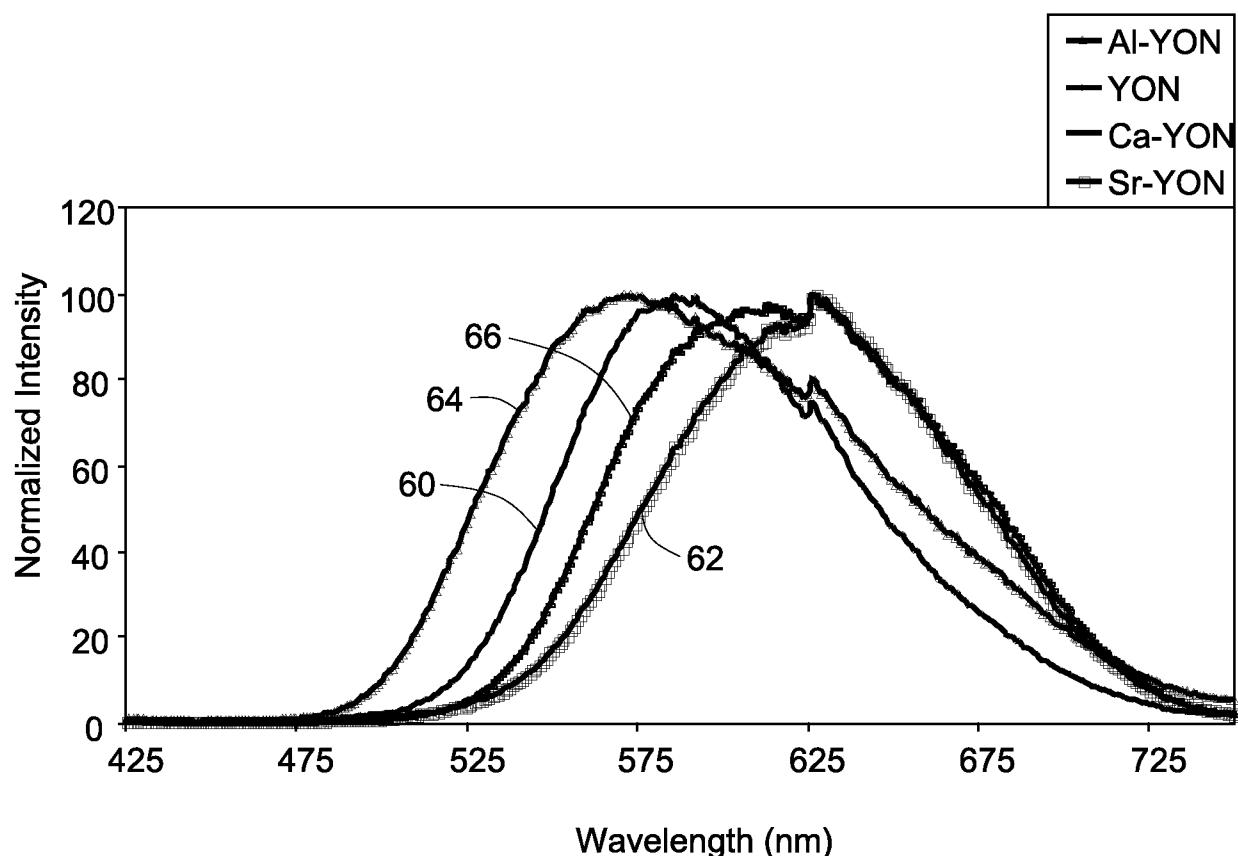


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2011/040434

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C09K11/08 C09K11/77 H05B33/14
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/117148 A2 (NANOGRAM CORP [US]; RAVILISETTY PADMANABHA R [US]; CHIRUVOLU SHIVKUMAR) 24 September 2009 (2009-09-24) claims 8,16 -----	1-13, 15-17, 19-21
A	WO 2006/061778 A1 (PHILIPS INTELLECTUAL PROPERTY [DE]; KONINKL PHILIPS ELECTRONICS NV [NL] 15 June 2006 (2006-06-15) claim 1 -----	1-21



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

5 September 2011

22/09/2011

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European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040,
 Fax: (+31-70) 340-3016

Authorized officer

Saldamli, Saltuk

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2011/040434

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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			EP 2262816 A2 22-12-2010
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			KR 20100128336 A 07-12-2010
			US 2011135928 A1 09-06-2011
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