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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 April 2007 (12.04.2007)

PCT

(10) International Publication Number
WO 2007/041563 A2

(51) International Patent Classification:
H01J 1/62 (2006.01)

(21) International Application Number:
PCT/US2006/038582

(22) International Filing Date: 2 October 2006 (02.10.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/722,900 30 September 2005 (30.09.2005) US
60/722,682 30 September 2005 (30.09.2005) US

(71) Applicant (*for all designated States except US*): THE REGENTS OF THE UNIVERSITY OF CALIFORNIA [US/US]; 1111 Franklin Avenue, 12th Floor, Oakland, CA 94607 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **CHEETHAM, Anthony, K.** [US/US]; 1695 East Valley Road, Santa Barbara, CA 93108 (US). **LE TOQUIN, Ronan, P.** [FR/US]; 1430 De La Vina Street, #b, Santa Barbara, CA 93108 (US).

(74) Agent: **GATES, George, H.**; GATES & COOPER LLP, 6701 Center Drive West, Suite 1050, Los Angeles, CA 90045 (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, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

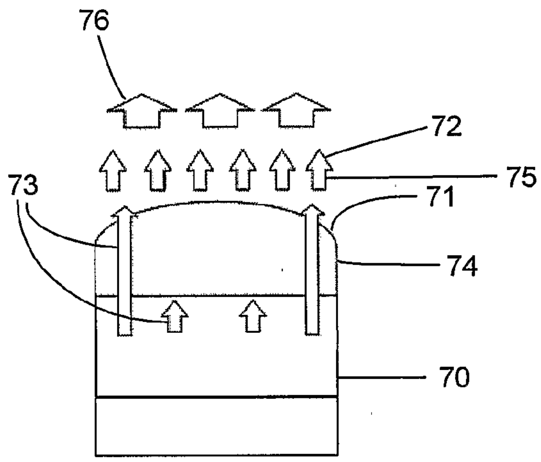
(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, 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).

Declaration under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

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

[Continued on next page]

(54) Title: CERIUM BASED PHOSPHOR MATERIALS FOR SOLID-STATE LIGHTING APPLICATIONS



(57) Abstract: A luminescent cerium (Ce) doped compound emitting bright red light, comprising a calcium silicate nitride ternary system, such as $CaSiN_{2-\delta}O_{\delta}:Ce^{3+}$, that crystallizes in a face-centered cubic unit cell with a lattice parameter of ~a = 14.88 A. The Ce doped compound can be used for white light applications either: (i) to enhance the light quality of the system based on a blue LED with a yellow or green phosphor, (ii) as an orange phosphor in combination with a blue LED and a green phosphor, or (iii) as a red phosphor in a setup comprising a ultraviolet (UV) LED and red, green and blue (RGB) phosphors. Substitution of smaller elements on the Ca site or larger elements on the Si site leads to a decrease of the emission wavelength towards the yellow or orange region.

WO 2007/041563 A2

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.

CERIUM BASED PHOSPHOR MATERIALS FOR SOLID-STATE LIGHTING APPLICATIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit under 35 U.S.C. Section 119(e) of the following co-pending and commonly-assigned U.S. patent applications:

U.S. Provisional Application Serial No. 60/722,900, filed on September 30, 2005, by Anthony K. Cheetham and Ronan P. Le Toquin, entitled "CERIUM BASED PHOSPHOR MATERIALS FOR SOLID-STATE LIGHTING APPLICATIONS," attorneys' docket number 30794.138-US-P1 (2005-618-1); and

U.S. Provisional Patent Application Serial No. 60/722,682, filed on September 30, 2005, by Ronan P. Le Toquin and Anthony K. Cheetham, entitled "NITRIDE AND OXY-NITRIDE CERIUM BASED PHOSPHOR MATERIALS FOR SOLID-STATE LIGHTING APPLICATIONS," attorneys' docket number 30794.145-US-P1 (2005-753-1);

which applications are incorporated by reference herein.

This application is related to the following co-pending and commonly-assigned applications:

U.S. Utility Patent Application Serial No. xx/xxx,xxx, filed on same date herewith, by Ronan P. Le Toquin and Anthony K. Cheetham, entitled "NITRIDE AND OXY-NITRIDE CERIUM BASED PHOSPHOR MATERIALS FOR SOLID-STATE LIGHTING APPLICATIONS," attorneys' docket number 30794.145-US-U1 (2005-753-2), which application claims priority to U.S. Provisional Patent Application Serial No. 60/722,682, filed on September 30, 2005, by Ronan P. Le Toquin and Anthony K. Cheetham, entitled "NITRIDE AND OXY-NITRIDE CERIUM BASED PHOSPHOR MATERIALS FOR SOLID-STATE LIGHTING APPLICATIONS," attorneys' docket number 30794.145-US-P1 (2005-753-1);

which applications are incorporated by reference herein.

BACKGROUND OF THE INVENTION

1. Field of the Invention.

The present invention relates to cerium (Ce) based phosphor materials for solid-state lighting applications.

2. Description of the Related Art.

(Note: This application references a number of different publications as indicated throughout the specification by one or more reference numbers within brackets, e.g., [x] A list of these different publications ordered according to these reference numbers can be found below in the section entitled "References." Each of these publications is incorporated by reference herein.)

Light emitting diodes (LEDs) based on wide band gap semiconductor materials such as GaN/InGaN produce ultraviolet (UV) and/or blue light (300 nm to 460 nm) with high efficiency and long lifetimes [1,15]. The emission from such LEDs can be converted into lower energy radiation using the luminescence properties of phosphor materials. A high intensity blue light (10) can be used to make white LED devices by combining a blue LED (11) and a yellow phosphor (12), so that blue and yellow light (13) is emitted, which appears as white light (14), as shown in FIG. 1(a). Alternatively, a mix of green and orange phosphor (15), as shown in FIG. 1(b), will emit blue, green and orange light (16) which appears as white light (14). Alternatively, a high intensity UV light (20) can be used to make white LED devices by combining a UV LED (21) and a blend of three red, green and blue (RGB) phosphors (22) which emit red, green and blue light (23) that appears as white light (24), as shown in FIG. 2. The LEDs (11) and (21), may be formed on substrates (17) and (25), respectively.

The first commercially available white LED was based on an InGaN chip emitting blue photons at around 460 nm combined with a $Y_3Al_5O_{12}:Ce^{3+}$ (YAG) phosphor layer that converts blue photons into yellow photons [2,3]. As a result, a slightly bluish white light is produced that may, in principle, be improved by adding red photons from a second phosphor. In fact, red phosphors are necessary for the development of white LEDs regardless of the setup used and should be very bright in order to compensate the low red sensitivity of the human eye [4]. Bright red phosphors are, however, very difficult to achieve due to the quantum yield drop with increasing Stokes shift.

For Ce^{3+} doped materials, UV emission is normally observed [5]. However, high crystal field symmetries (Ce-YAG [2]) or a strongly covalent Ce environment (sulfides or oxynitrides [6]) can decrease the energy of the emission wavelength. Yttrium aluminium garnet (YAG) doped with Ce^{3+} is the most important example, exhibiting a strong yellow emission (at 540 nm) upon blue excitation (at 460 nm). The cubic crystal field at the Ce site associated with a small tetragonal distortion is responsible for this unusual yellow emission [2]. As demonstrated previously by Van Krevel et al. [6], it is also possible to observe green-yellow Ce^{3+} emission in oxynitride compounds, by replacing oxygen by a more covalent anion such as nitrogen. Further increases of the covalent character has led to new Eu^{2+} doped sialon [7,8] or silicon (oxy)nitride [9-11] based materials that have been reported to show very efficient orange luminescence. Eu^{2+} doped $M_2Si_5N_8$ (where M = calcium, strontium, barium) is one of the most interesting so far [10]. The longer emission wavelength observed for nitride compounds is associated with a broader excitation band that covers part of the UV and visible spectral range.

SUMMARY OF THE INVENTION

The present invention discloses a luminescent Ce compound emitting bright red light, namely, $CaSiN_{2-\delta}O_{\delta}:Ce^{3+}$, which is a new phase in the calcium silicate nitride ternary system that crystallizes in a face-centered cubic unit cell with a lattice parameter of ~a = 14.88 Å. This compound can be used for white light applications either: (i) to enhance the light quality of the system based on a blue LED with a yellow/green phosphor, (ii) as the orange phosphor in a blue LED + orange and green phosphor, or (iii) as the red phosphor in the UV LED plus 3 RGB phosphors setup. Since the substitution of smaller elements on the Ca site or larger elements on the Si site leads to a decrease of the emission wavelength towards the yellow/orange region, this compound may also be used directly as the yellow phosphor with a blue LED. In this regard, the present invention encompasses a number of different embodiments, which are set forth below.

In one embodiment, the present invention is an apparatus for solid state lighting applications, comprising an LED; and a luminescent Ce compound, positioned adjacent the LED, that emits orange to red light when excited by radiation from the LED. The various combinations of the LED and luminescent Ce compound may comprise: (1) a blue LED where the luminescent Ce compound is used in combination with a yellow or green phosphor; (2) a blue LED where the luminescent Ce compound is used as an orange phosphor in combination with a green phosphor; or (3) a UV LED where the luminescent Ce compound is used as a red phosphor in a group of RGB phosphors.

The luminescent Ce compound is described by the formula:

$$M_x(Si,Al)_yN_{z-\delta}O_\delta:Ce^{3+}$$

wherein $x \approx y \approx 1$, $z = 2$, $0 \leq \delta < 2$ and M is calcium (Ca), magnesium (Mg), strontium (Sr) or barium (Ba). In one alternative embodiment, germanium (Ge) may be substituted for silicon (Si). In another alternative embodiment, M is yttrium (Y) or lanthanide (Ln) elements, and Si is replaced by aluminum (Al) or gallium (Ga) for charge compensation.

The luminescent Ce compound may be made using the following steps:

(a) mixing stoichiometric amounts of: (1) Ca_3N_2 or Ca metal, (2) AlN, (3) Si_3N_4 Si_2N_2NH, or $Si(NH)_2$, and (4) Ce, which is a rare earth source, either as a metal, a nitride, or an oxide, in order to form a mixture;

(b) weighting and grinding the mixture in conditions of $[O_2]$ <1 parts per million (ppm) and $[H_2O]$ < 1 ppm in order to prevent oxidation or hydrolysis; and

(c) loading the mixture into Al_2O_3 or BN crucibles for heating under flowing N_2 in conditions of 0.5 to 4 liters per minute to a temperature between 1300°C and 1500°C.

BRIEF DESCRIPTION OF THE DRAWINGS

Referring now to the drawings in which like reference numbers represent corresponding parts throughout:

FIGS. 1(a) and 1(b) are schematic representations of a white LED setup based on a blue LED (~460 nm) with either yellow phosphor, as shown in FIG. 1(a), or a blend of orange and green phosphor, as shown in FIG. 1(b).

FIG. 2 is a schematic representation of the white LED setup based on a UV LED (~380 nm) with three phosphor materials, namely blue, green and red.

FIG. 3 is a flowchart illustrating the method of fabricating a luminescent rare earth doped compound.

FIG. 4 is a graph of a synchrotron X-ray diffraction pattern of the phase $CaSiN_{2-\delta}O_{\delta}$ doped with Ce^{3+}, with Le Bail refinement in the space group F23 with unit cell parameter a=14.8822(5) Å.

FIG. 5(a) is a graph of an emission spectrum of the compound $CaSiN_2$ doped with Ce^{3+}, wherein the excitation wavelength is 535 nm.

FIG. 5(b) is a graph of an excitation spectrum of the compound $CaSiN_2$ doped with Ce^{3+}, wherein the emission wavelength has been fixed at 630 nm.

FIG. 6(a) is a graph of an emission spectrum of the compound $Ca(Si,Al)N_2$ doped with Ce^{3+}, wherein the excitation wavelength is 475 nm.

FIG. 6(b) is a graph of an excitation spectrum of the compound $Ca(Si,Al)N_2$ doped with Ce^{3+}, wherein the emission wavelength has been fixed at 560 nm.

FIG. 7 is a schematic representation of an apparatus for solid state lighting applications, comprising an LED and a luminescent Ce compound, positioned adjacent the LED.

DETAILED DESCRIPTION OF THE INVENTION

In the following description of the preferred embodiment, reference is made to the accompanying drawings that form a part hereof, and in which is shown by way of illustration a specific embodiment in which the invention may be practiced. It is to be understood that other embodiments may be utilized and structural changes may be made without departing from the scope of the present invention.

Technical Disclosure

The subject of the present invention is the discovery of new phosphor materials for applications in white solid-state lighting based upon blue or UV LEDs. Hence, the invention covers the synthesis of an orange to red emitting material and its application as a phosphor alone or in combination with others for white LED realization, for example, in the manner shown in FIGS. 1 and 2.

The present invention covers a composition of matter comprising a luminescent Ce compound that emits orange to red light when excited by radiation and absorbs wavelengths ranging from UV to green or yellow.

This composition of matter can be described by the formula:

$$M_x(Si,Al)_yN_{z-\delta}O_\delta:Ce^{3+}$$

wherein $x \approx y \approx 1$, $z = 2$ and $0 \leq \delta < 2$. M is mainly calcium (Ca), but chemical substitution on the M site is possible with different alkaline earths, such as magnesium (Mg), strontium (Sr), and barium (Ba), as shown in Table 3 below. Table 3 also shows how substantial shifts of the emission wavelength of about 50 nm have been observed upon substitution into the M site, illustrating how the luminescent Ce compound emits orange to red light when excited by radiation. Silicon (Si) atoms may also be substituted by germanium (Ge) atoms. Yttrium (Y) or lanthanide (Ln) elements may be substituted on the M site with simultaneous replacement of Si by aluminium (Al) or gallium (Ga) atoms for charge compensation. Table 3 also shows how the compound may absorb or be excited by UV to green light.

FIG. 3 is a flowchart illustrating how these materials can be prepared.

Block 30 represents the step of mixing stoichiometric amounts of: (1) Ca_3N_2 or Ca metal, (2) AlN, (3) Si_3N_4, Si_2N_2NH or $Si(NH)_2$, and (4) a rare earth source, such as Ce, that is either a metal, a nitride, if available, or an oxide, in order to form a mixture. This step may comprise introducing an element with a larger ionic radius, such as a rare earth, on the Ca crystallographic site, and/or by the presence of vacancies or oxygen substitution in the anion sublattice.

Block 31 represents the step of weighing and grinding the mixture, which must be carried out in a glove box ($[O_2] < 1$ parts per million (ppm) and $[H_2O] < 1$ ppm) in order to prevent degradation such as oxidation or hydrolysis.

Block 32 represents the step of loading the mixture in, for example, sapphire (Al_2O_3) or boron nitride (BN) crucibles to be heated in a tube furnace under flowing nitrogen (N_2) at 0.5 to 4 liters per minute to a temperature between 1300°C and 1500°C.

All samples have been characterized using X-ray diffraction, ^{29}Si NMR spectroscopy and UV/visible emission excitation spectroscopy.

A $CaSiN_2$ phase has already been reported to crystallize with an orthorhombic symmetry (space group Pnma) and cell parameters a_o=5.1229 Å, b_o=10.2074 Å and c_o=14.8233 Å [12-14]. Synchrotron X-ray diffraction experiments have been used to characterize the new phase in the calcium silicate nitride ternary system ($CaSiN_2$), as shown in FIG. 4. The $CaSiN_2$-related phase presented herein has a cubic symmetry with possible space group F23, and a refined cell parameter of ~a = 14.88 Å. This phase can be related to the one reported in the literature according to the relations $a_c = 2\sqrt{2}a_o$, $a_c = \sqrt{2}a_o$ $a_c = c_o$. The new phase reported here can only be obtained by the introduction of an element with a larger ionic radius, such as a rare earth, on the Ca crystallographic site, and/or by the presence of vacancies or oxygen substitution in the anion sublattice (i.e., by selecting δ and the nitrogen concentration).

Substitution of smaller elements on the Ca site or larger elements on the Si site of the $CaSiN_{2-\delta}O_{\delta}:Ce^{3+}$ compound leads to a decrease of the emission wavelength towards the yellow/orange spectral region.

FIGS. 5(a) and 6(a) are further examples of the luminescent Ce compound emitting orange to red light, and FIGS. 5(b) and 6(b) are further examples of the luminescent Ce compound that has an excitation spectrum or band comprising wavelengths in the range UV to yellow.

The compound $CaSiN_{2-\delta}O_{\delta}:Ce^{3+}$ has several important properties. First, it represents the first Ce^{3+} phosphor materials showing an intense red emission (peaking at ~620 nm), as shown in FIG. 5(a). It is also one of the rare phosphors that can be excited in the yellow and green region as well as in the blue and ultraviolet, as illustrated in FIGS. 5(b) and 6(b). The red emission can be used to compensate the bluish tint of the YAG and blue LED setup by its addition as a second phosphor that converts green light into red, as shown by FIG. 5(b). Second, the green to red transition may be useful for the enhancement of plant growth by photosynthesis. Third, the tunable emission of this phosphor (see Table 3 below) makes it also very interesting as a yellow or orange phosphor by itself, as shown in FIG. 6(a), or in combination with a green emitting phosphor, which can be excited at 460 nm (with a blue LED for example), as shown in FIG. 6(b). Substitution on the Ca and Si sites leads to emission covering the visible spectra from 450 nm up to 700 nm with maxima between 500 nm and 650 nm. The excitation bands can also been tuned between 400 and 600 nm. As expected, these compounds show emission/excitation peak shapes (or spectra) that are typical of cerium compounds, with relatively broad peaks, as shown in FIGS. 5(a), 5(b), 6(a) and 6(b). The emission spectrum in FIGS. 5(a) and 6(a) may have a Full Width at Half Maximum (FWHM) of ~90 nm and comprises the entire spectrum of wavelengths associated with orange and red light.

The excitation spectrum in FIGS. 5(b) and 6(b) may have a FWHM of 60 nm. These broad emission and excitation features lead to advantageous color rendering properties.

These new phosphors may also be interesting as yellow or red phosphors in a group comprising three phosphors (red, green and blue), used with a UV LED for the design of solid-state lighting, since the luminescent Ce compounds can be excited in the UV (~380 nm) using GaN or ZnO based LEDs, as shown in FIGS. 5(b) and 6(b).

FIG. 7 is a schematic representation of an apparatus for solid state lighting applications, comprising an LED (70) and a composition of matter comprising a luminescent Ce compound (71), wherein the luminescent Ce compound is positioned adjacent the LED (70), and the luminescent Ce compound emits orange to red light (72) when excited by radiation (73) from the LED.

The luminescent Ce compound may be used in combination with one or more other phosphors (74). For example, when the LED (70) is a blue LED, the luminescent Ce compound (71) may be used with the blue LED in combination with at other phosphors (74) such as a yellow or green phosphors. Alternatively, when the LED (70) is a blue LED, the luminescent Ce compound (71) may be used with the blue LED as an orange phosphor in combination with other phosphors (74) such as a green phosphor. Also, when the LED (70) is an UV LED, the luminescent Ce compound may be used with the UV LED as a red phosphor in a group of RGB phosphors (74). The combination of radiation (73) from the LED (70) and light (75) emitted by the luminescent Ce compound in combination with the other phosphor (74) may appear as white light (76).

Other rare earths other than Ce may also be introduced or doped into the new phase of the calcium silicate nitride system, in order to form a luminescent compound or phosphor. The same cubic symmetry remains and a typical decrease of the unit cell parameter is observed along the rare earth series (see Table 1 below). The optical properties of these materials are also interesting in terms of phosphor applications (see Table 2 below). Thus, the apparatus of FIG. 7 may utilize a luminescent compound

(71) from the calcium silicate nitride ternary system having cubic symmetry (such as face center cubic), and doped with other rare earths.

References

The following references are incorporated by reference herein:

[1] S. Nakamura, G. Fasol, The Blue Laser Diode: GaN Based Light Emitters and Lasers, Springer, Berlin (1997).

[2] G. Blasse and A. Brill, Appl. Phys. Lett., 11 (1967): J. Chem. Phys., 47 (1967) 5139.

[3] U.S. Patent No. 5,998,925, to Y. Shimizu. et al., issued December 7, 1999, and entitled "Light emitting device having a nitride compound semiconductor and a phosphor containing a garnet fluorescent material."

[4] T. Justel, H. Nikol, C. Ronda, Angew. Chem. Int. Ed., 1998, 37, 3084-3103.

[5] G. Blasse, B. C. Grabmeier, Luminescent Materials, Springer, Berlin (1994).

[6] J. W. H. van Krevel, H. T. Hintzen, R. Metselaar, A. Meijerink, J. Alloys Compd. 268 (1-2), 272-277 (1998).

[7] U.S. Patent No. 6,717,353, to G. O. Mueller et al., issued April 6, 2004, and entitled "Phosphor converted light emitting device."

[8] J. W. H. van Krevel, J. W. T. van Rutten, H. Mandal, H. T. Hinzen, R. Metselaar, J. Solid State Chem. 165 (1) 19-24 (2002).

[9] U.S. Patent No. 6,670,748, to A. Ellens et al., issued December 30, 2003, and entitled "Illumination unit having at least one LED as light source."

[10] U.S. Patent No. 6,682,663, to G. Botty et al., issued January 2004, and entitled "Pigment with day light fluorescence."

[11] U.S. Patent Publication No. 20030006702, by R. B. Mueller-Mach et al., published January 9, 2003, and entitled "Red deficiency compensating phosphor light emitting device."

[12] Z. A. Gal, P. M. Mallinson, H. J. Orchard, S. J. Clarke. Inorg. Chem. 2004, 43, 3998-4006.

[13] S. S. Lee, S. Lim, S. S. Sun, J. F. Wagner. Proc. SPIE Int. Soc. Opt. Eng. 3241, 1997, pp. 75-79.

[14] E. A. Pugar, J. H. Kennedy, P. D. Morgan, J. H. Porter, J. Am. Ceram. Soc. 71 [6] C-288 (1988).

[15] S. P. Den Baars, in Solid State Luminescence Theory, Materials and Devices, edited by A. H. Kitai, Chapman and Hall, London (1993).

Conclusion

This concludes the description of the preferred embodiment of the present invention. The foregoing description of one or more embodiments of the invention has been presented for the purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed. Many modifications and variations are possible in light of the above teaching without fundamentally deviating from the essence of the present invention. It is intended that the scope of the invention be limited not by this detailed description, but rather by the claims appended hereto.

Table 1: Cubic unit cell parameters for different rare earth ions (RE) doped on Ca site with the same percentage - the refinement has been carried out in the space group *F23*.

$Ca_{1-x}RE_xSiN_2$	RE= Ce^{3+}	RE=Pr^{3+}	RE= Sm^{3+}	RE=Eu^{2+}	RE=Tb^{3+}	RE=Er^{3+}
Cubic unit cell parameter	14.8822 Å	14.8720 Å	14.8463 Å	14.8419 Å	14.8587 Å	14.8517 Å

Table 2: Optical properties of $CaSiN_2$ doped with several rare earth ions (RE) - for line emitter rare earth, only the strongest peak is presented.

$Ca_{1-x}RE_xSiN_2$	RE= Ce^{3+}	RE=Pr^{3+}	RE= Sm^{3+}	RE=Eu^{2+}	RE=Tb^{3+}	RE=Er^{3+}
Body color	pink/red	white	white	orange	white	grey
Wavelength (λ) emission maximum (nm)	630	425	610	605	550	420
Wavelength (λ) excitation maximum (nm)	535	330	400	400	275	325

Table 3: Optical properties of Ce^{3+} doped $CaSiN_2$ substituted with different cations on the Ca and Si site

Ce^{3+} doped compound	Emission wavelength maximum (nanometers)	Excitation Wavelength maximum (nanometers)	Body color
$CaSiN_2$	630	535	pink/red
$Ca(Al,Si)N_2$	560	475	orange
$(Ca,Sr)SiN_2$	640	500	orange
$(Ca,Mg)SiN_2$	540	460	yellow

WHAT IS CLAIMED IS:

1. An apparatus for solid state lighting applications, comprising:

a light emitting diode (LED); and

a luminescent cerium (Ce) compound that emits orange to red light when excited by radiation from the light emitting diode.

2. The apparatus of claim 1, wherein the light emitting diode is a blue light emitting diode and the luminescent cerium compound is used with the blue light emitting diode in combination with a yellow or green phosphor.

3. The apparatus of claim 1, wherein the light emitting diode is a blue light emitting diode and the luminescent cerium compound is used with the blue light emitting diode as an orange phosphor in combination with a green phosphor.

4. The apparatus of claim 1, wherein the light emitting diode is an ultraviolet (UV) light emitting diode and the luminescent cerium compound is used with the ultraviolet light emitting diode as a red phosphor in a group of red, green and blue (RGB) phosphors.

5. A composition of matter, comprising:

a luminescent cerium (Ce) compound that emits orange to red light when excited by radiation.

6. The composition of matter of claim 5, wherein the luminescent Ce compound is excited by wavelengths ranging from ultraviolet (UV) to green.

7. The composition of matter of claim 5, wherein the luminescent Ce compound is described by the formula:

$M_x(Si,Al)_yN_{z-\delta}O_\delta:Ce^{3+}$

wherein $x \approx y \approx 1$, $z = 2$, $0 \leq \delta < 2$ and M is calcium (Ca), magnesium (Mg), strontium (Sr) or barium (Ba).

8. The composition of matter of claim 7, wherein germanium (Ge) is substituted for silicon (Si).

9. The composition of matter of claim 7, wherein M is yttrium (Y) or lanthanide (Ln) elements, and silicon (Si) is replaced by aluminum (Al) or gallium (Ga) for charge compensation.

10. The composition of matter of claim 7, wherein the luminescent Ce compound is a new phase in the calcium silicate nitride ternary system that crystallizes in a cubic unit cell.

11. The composition of matter of claim 10, wherein the luminescent Ce compound comprises $CaSiN_{2-\delta}O_{\delta}:Ce^{3+}$.

12. The composition of matter of claim 11, wherein substitution of smaller elements on the Ca site or larger elements on the Si site leads to a decrease of the emission wavelength towards the yellow or orange region.

13. The composition of matter of claim 7, wherein the luminescent Ce compound is made using the following steps:

(a) mixing stoichiometric amounts of: (1) Ca_3N_2 or Ca metal, (2) AlN, (3) Si_3N_4 Si_2N_2NH, or $Si(NH)_2$, and (4) Ce as a rare earth source either as a metal, a nitride, or an oxide, in order to form a mixture;

(b) weighing and grinding the mixture in conditions of $[O_2] <1$ parts per million (ppm) and $[H_2O] < 1$ ppm in order to prevent oxidation or hydrolysis; and

(c) heating the mixture under flowing N_2 in conditions of 0.5 to 4 liters per minute to a temperature between 1300°C and 1500°C.

14. The composition of matter of claim 5, wherein the luminescent compound is used with a blue light emitting diode in combination with a yellow or green phosphor.

15. The composition of matter of claim 5, wherein the luminescent Ce compound is used with a blue light emitting diode as an orange phosphor in combination with a green phosphor.

16. The composition of matter of claim 5, wherein the luminescent Ce compound is used with an ultraviolet (UV) light emitting diode as a red phosphor in a group of red, green and blue (RGB) phosphors.

17. A method for creating a luminescent compound, comprising the steps of:

(a) mixing stoichiometric amounts of: (1) Ca_3N_2 or Ca metal, (2) AlN, (3) Si_3N_4 Si_2N_2NH, or $Si(NH)_2$, and (4) a rare earth source either as a metal, a nitride, or an oxide, in order to form a mixture;

(b) weighing and grinding the mixture in conditions of $[O_2]$ <1 parts per million (ppm) and $[H_2O]$ < 1 ppm in order to prevent oxidation or hydrolysis; and

(c) heating the mixture under flowing N_2 in conditions of 0.5 to 4 liters per minute to between 1300°C and 1500°C.

18. The method of claim 17, wherein the rare earth source is cerium (Ce).

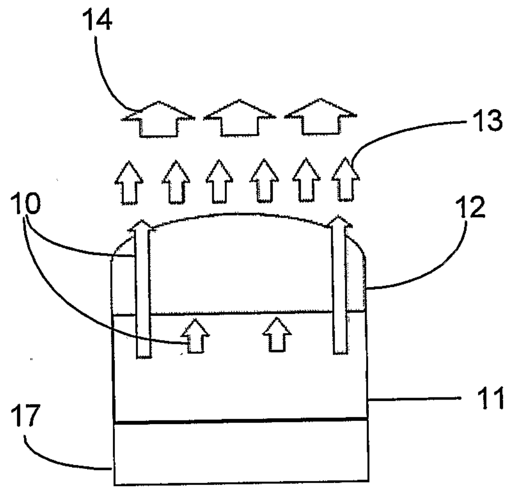


FIG. 1(a)

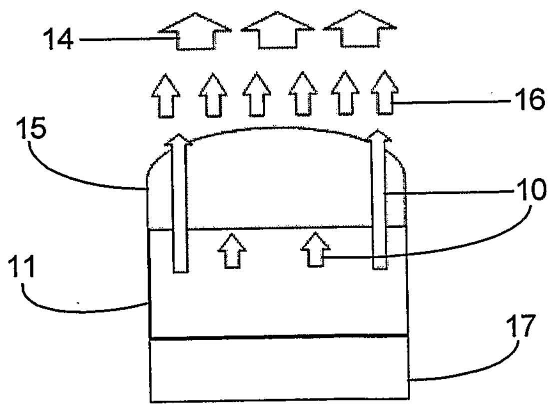


FIG. 1(b)

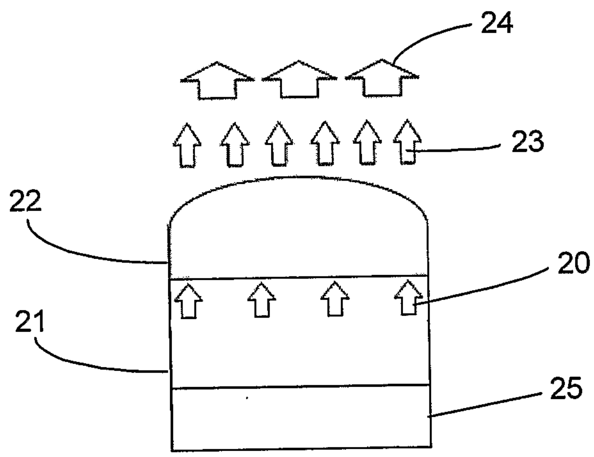


FIG. 2

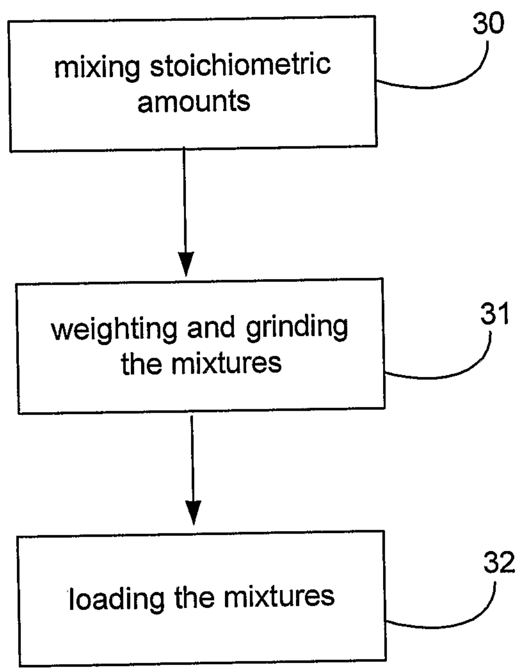
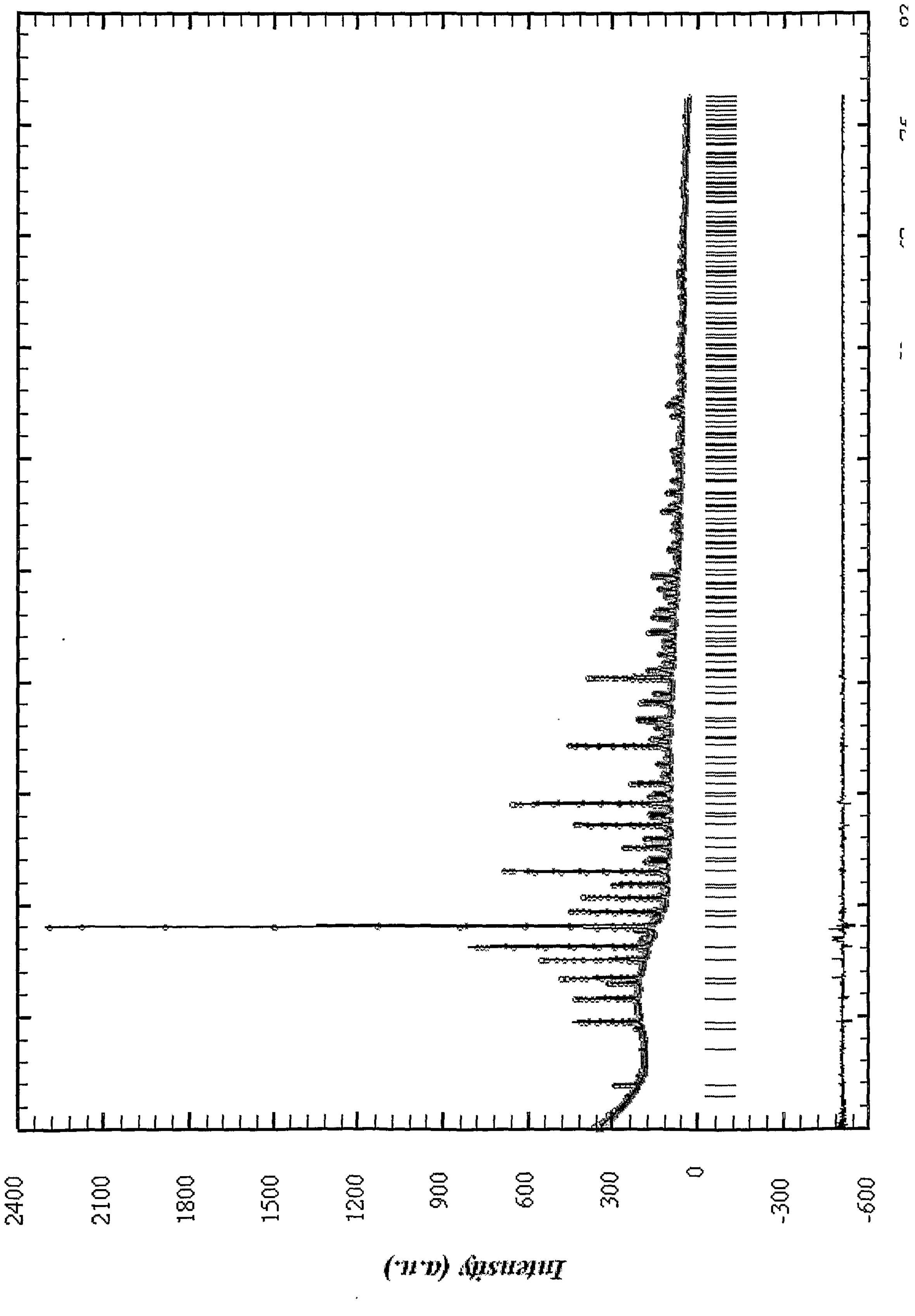

mixing stoichiometric amounts
30
weighting and grinding the mixtures
31
loading the mixtures
32

FIG. 3



Intensity (a.u.)
2400
2100
1800
1500
1200
900
600
300
0
-300
-600

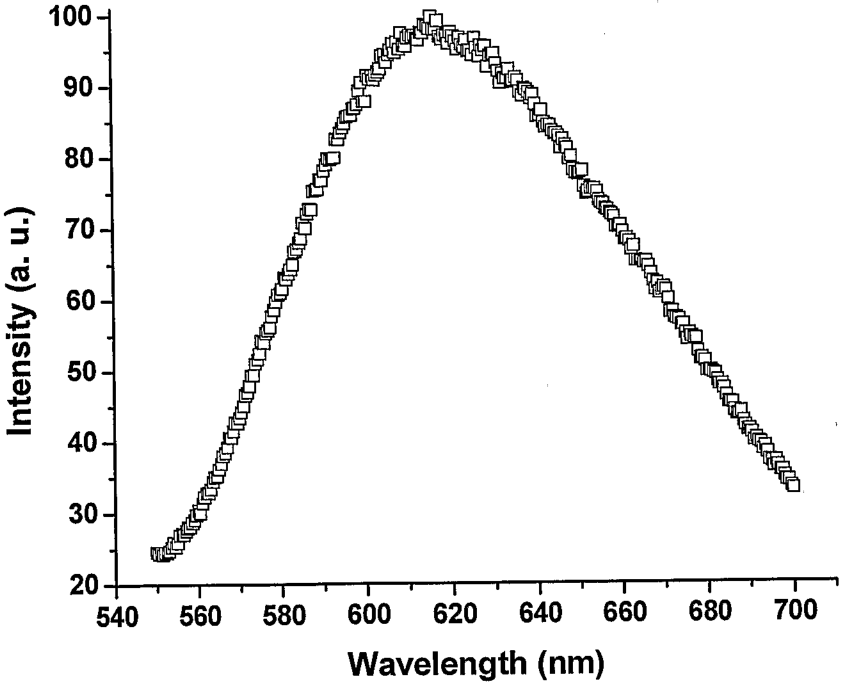

Intensity (a. u.)
100
90
80
70
60
50
40
30
20
540
560
580
600
620
640
660
680
700
Wavelength (nm)

FIG. 5(a)

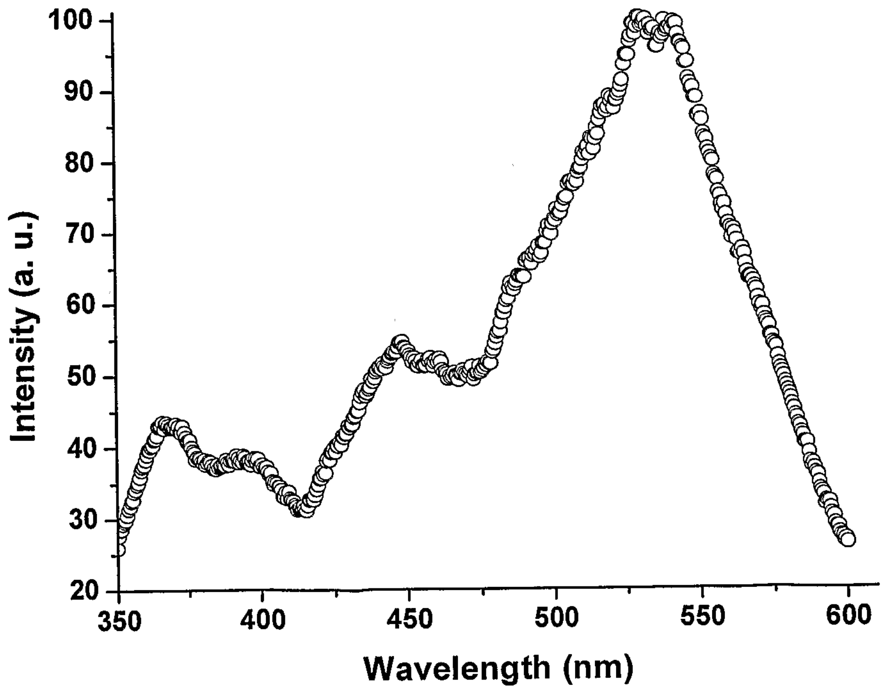
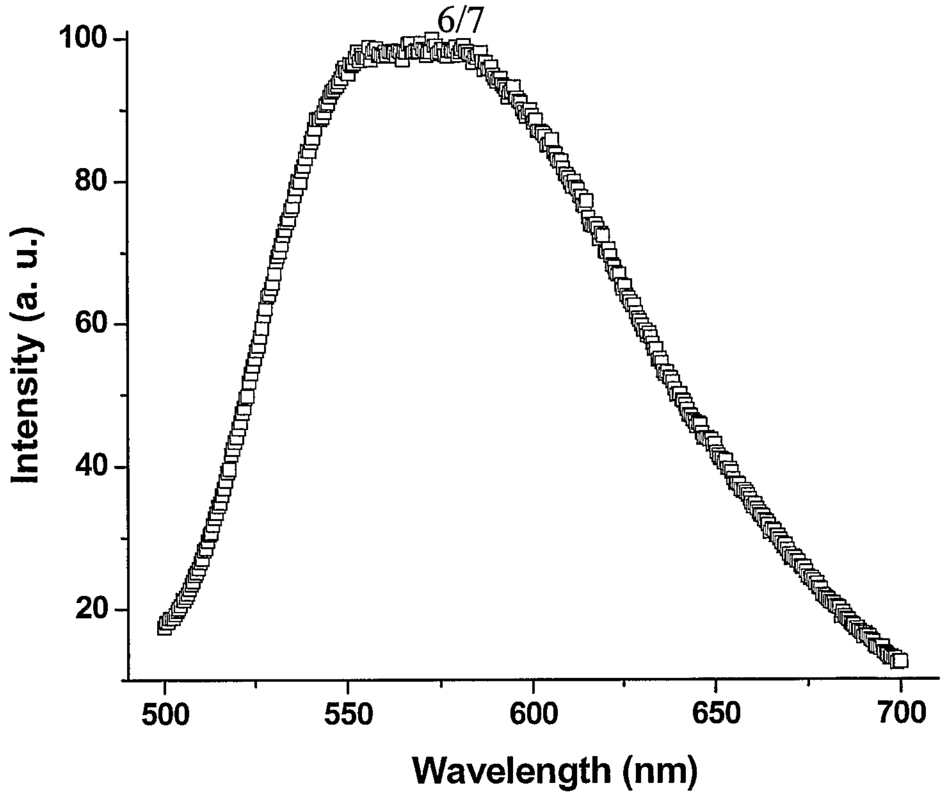
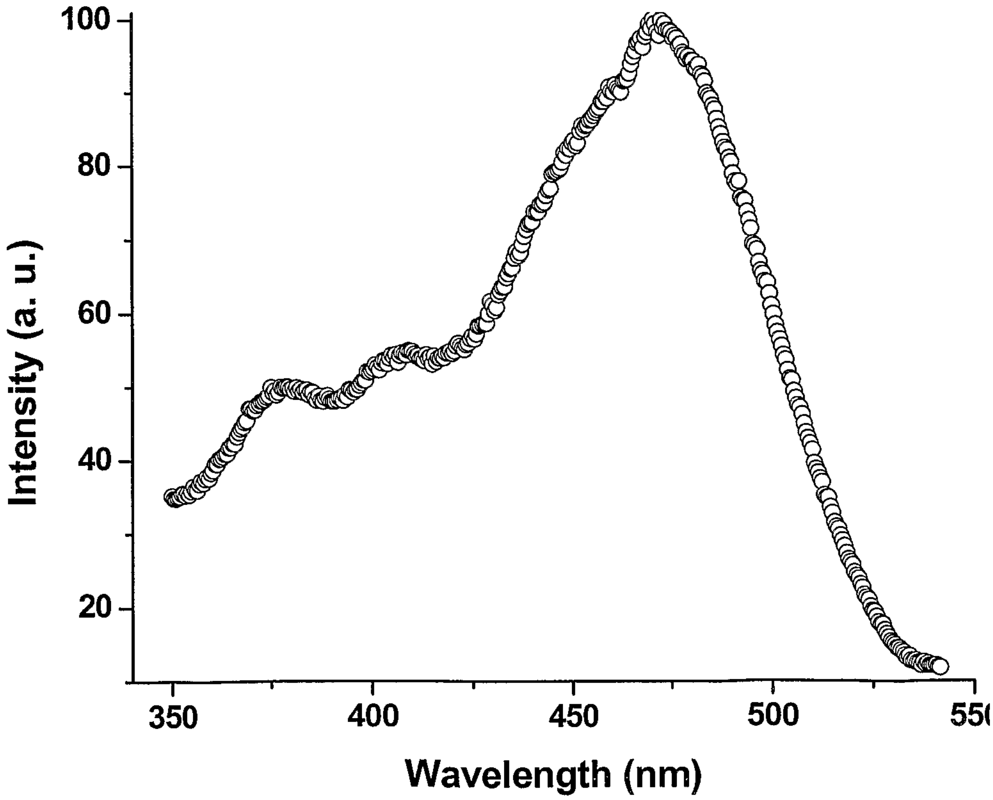

Intensity (a. u.)
100
90
80
70
60
50
40
30
20
350
400
450
500
550
600
Wavelength (nm)

FIG. 5(b)



100
80
60
40
20
Intensity (a. u.)
500
550
600
650
700
Wavelength (nm)

FIG. 6(a)



100
80
60
40
20
Intensity (a. u.)
350
400
450
500
Wavelength (nm)

FIG. 6(b)

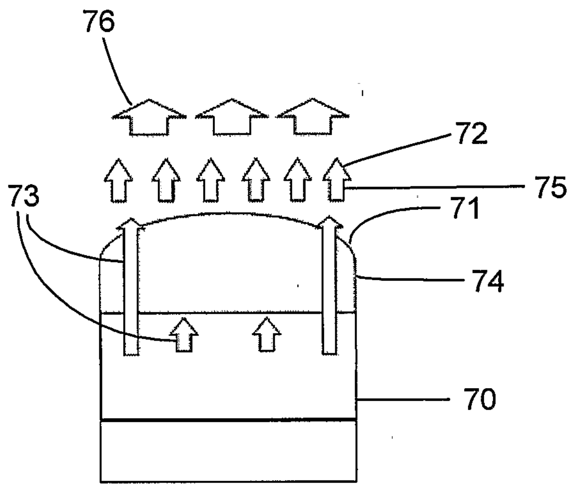


FIG. 7