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(54) Title: MONOLITHIC TRANSLUCENT BaMgAl10O17:Eu2+ PHOSPHORS FOR LASER-DRIVEN SOLID STATE LIGHTING

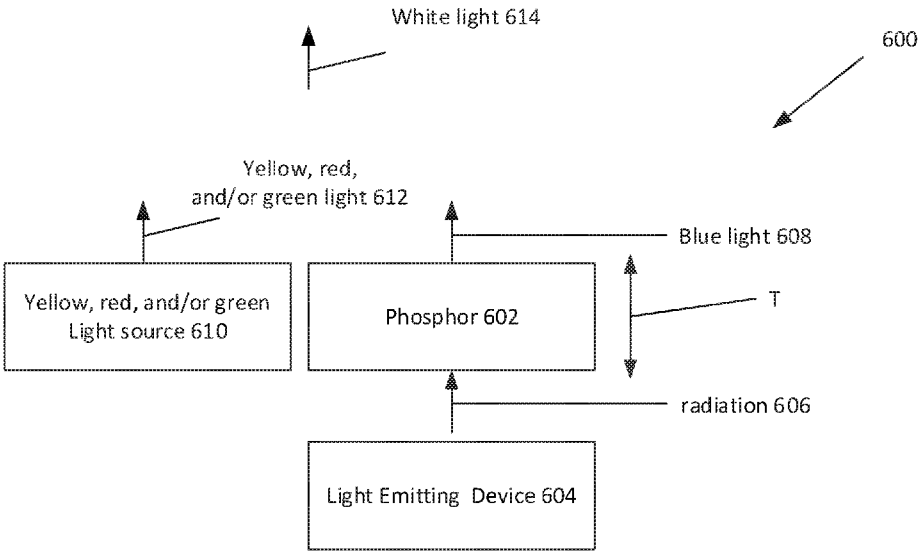


Figure 6(a)

(57) Abstract: A method for fabricating a translucent blue-emitting phosphor (e.g., $BaMgAl_{10}O_{17}:Eu^{2+}$), including sintering a phosphor powder using spark plasma sintering. The present invention also discloses the use of the translucent phosphor for laser-based applications where conversion or filtering of light is required.

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MONOLITHIC TRANSLUCENT $BaMgAl_{10}O_{17}:Eu^{2+}$ PHOSPHORS FOR LASER-DRIVEN SOLID STATE LIGHTING

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit under 35 U.S.C. Section 119(e) of co-pending and commonly-assigned to U.S. Provisional Application Serial No. 62/384,622, by Clayton J. Cozzan, Steven P. DenBaars and Ram Seshadri, filed September 7, 2016, entitled MONOLITHIC TRANSLUCENT $BaMgAl_{10}O_{17}:Eu^{2+}$ PHOSPHORS FOR LASER-DRIVEN SOLID STATE LIGHTING (Attorney's Docket No. 30794.634-US-P1 (UC ref. 2016-139-1), which application is incorporated by reference herein.

This application is related to PCT International Patent Application No. PCT/US17/44724 by Clayton J. Cozzan and Ram Seshadri, filed July 31, 2017, entitled Ce:YAG/Al_2O_3 COMPOSITES FOR LASER-EXCITED SOLID-STATE WHITE LIGHTING (Attorney's Docket No. 30794.622-US-WO, which application claims the benefit under 35 U.S.C. Section 119(e) of Provisional Application Serial No. 62/368,614, by Clayton J. Cozzan and Ram Seshadri, filed July 29, 2016, entitled Ce:YAG/Al_2O_3 COMPOSITES FOR LASER-EXCITED SOLID-STATE WHITE LIGHTING (Attorney's Docket No. 30794.622-US-P1 (UC ref. 2016-99P), which applications are incorporated by reference herein.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH AND DEVELOPMENT

This invention was made with Government support under Grant No. DE-AR0000671 awarded by the U.S. Department of Energy's Advanced Research Projects Agency -Energy (ARPA-E). The Government has certain rights in this invention.

BACKGROUND OF THE INVENTION

1. Field of the Invention.

The present invention is related to the fabrication of a phosphor for solid state lighting.

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 in 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 diode (LED) based lighting is rapidly replacing incandescent and fluorescent sources [1] and advances in semi-polar and non-polar substrates for light emitting diodes (LEDs) have pushed current densities to beyond 1000 A/cm^2 [2]. Laser diodes (LDs) have peak efficiencies at much higher operating currents than LEDs and therefore offer an alternative to the droop-limited LEDs [3]. Currently, both LEDs and LDs are being explored to generate white light using inorganic phosphors, with LDs holding the most promise for the future of high power white lighting that LEDs cannot achieve due to droop [4-6]. Two common strategies with inorganic phosphors are utilized for white light generation. Either a blue LED or LD is used in conjunction with a yellow-converting inorganic phosphor to generate a cool white light, or a near-UV or violet LED or LD is used to excite a mixture of blue, red, and green emitting inorganic phosphors to generate a warm white light [7, 8].

Additionally, recent advances in laser diodes have also enabled visible light communication [9]. Laser-based phosphor-converted white light for visible light communication has also been demonstrated, where 2 Gbit/s was achieved using a single crystal phosphor [10].

SUMMARY OF THE INVENTION

For the next generation of LED and LD-based lighting, thermally robust phosphors are required. This can be achieved by avoiding low thermal conductivity encapsulating materials altogether and creating phosphor monoliths, such as single crystals or dense ceramics.

One or more embodiments of the present invention disclose a monolithic blue-emitting phosphor suitable for converting ultraviolet (UV) light to blue light with quantum efficiencies defined by the quantum efficiency of the starting powder. Using spark plasma sintering (SPS), translucent $Ba_{1-x}Eu_xMgAl_{10}O_{17}$ ($BAM:Eu^{2+}$) has been transformed from white powder to dense (92% of theoretical density) translucent monoliths with diameters defined by the tooling used with the SPS and thicknesses on the order of millimeters (mm). These monolithic samples are phase pure and do not contain an encapsulating material, such as silicone, epoxy, or glass, and are therefore suitable for high power LED applications. They are also suitable for LD-based applications, such as for providing a blue component to generate cool or warm white light for general lighting or visible light communication. When tested against the same powder in silicone encapsulation, the silicone carbonizes (>360 °C) after 11 seconds under 3 Watts of violet laser irradiation, whereas the monolith maintains a temperature of 70 °C and is stable.

To overcome the limitations described above, and to overcome other limitations that will become apparent upon reading and understanding this specification, one or more embodiments of the present invention discloses a phosphor, comprising $Ba_{1-x}Eu_xMgAl_{10}O_{17}$ ($BAM:Eu^{2+}$), wherein $0 < x < 1$, and the $BAM:Eu^{2+}$ emits blue light and/or light having a wavelength in a range of 410 nm-510 nm in response to excitation with electromagnetic radiation having a wavelength less than 450 nanometers.

To better illustrate the composition of matter and methods described herein, a non-limiting list of examples is provided here:

In Example 1, the phosphor is a monolith.

In Example 3, the phosphor of one or any combination of the preceding examples further includes additional compatible ceramic components increasing light extraction, increasing thermal conductivity, and/or generating different types of light.

In Example 4, the phosphor of one or any combination of the preceding examples has a density of at least 70% of its theoretical density, or a density between 70% and 99.9% of the theoretical density.

In Example 5, the phosphor of one or any combination of the preceding examples is translucent.

In Example 6, the phosphor of one or any combination of the preceding examples has a thickness and/or density modulated to increase scattering of the electromagnetic radiation by the phosphor.

In Example 7, the phosphor of one or any combination of the preceding examples is phase pure and self-encapsulating.

In Example 8, the phosphor of one or any combination of the preceding examples is a single crystal or sintered ceramic.

In Example 9, the phosphor of one or any combination of the preceding examples is electromagnetically coupled to a light emitting device (e.g., laser) emitting the electromagnetic radiation having a wavelength less than 450 nm.

In Example 10, the phosphor of one or any combination of the preceding examples maintains a temperature under a thermal quenching regime of the phosphor (e.g., a temperature of at most 70 degrees Celsius) and emits the same intensity of blue light after absorbing the electromagnetic radiation having a power of 3 watts for 11 seconds.

In Example 11, the phosphor of one or any combination of the preceding examples is a monolith having a diameter in a range of 500 micrometers to 20 millimeters.

In Example 12, the phosphor of one or any combination of the preceding examples is coupled to a light source emitting yellow, red, and/or green light, so that a combination of the blue light and the yellow, red, and/or green light is white light characterized by CIE coordinates within 5% of pure white light.

In Example 13, the phosphor of one or any combination of the preceding examples ia a monolith that is cooler and emits the blue light with higher quantum yield as compared to the phosphor encapsulated in silicone.

In Example 14, the present disclosure further describes a method for fabricating a phosphor of one or any combination of the preceding examples, comprising mixing stoichiometric amounts of starting materials so as to obtain a powder comprising Eu-doped $BaMgAl_{10}O_{17}$ ($BAM:Eu^{2+}$); and densifying the powder to form a monolith.

In Example 15, the densifying comprises rapidly heating the powder under a pressure to a maximum temperature, the heating comprises increasing a temperature of the powder at a rate of <600 degrees Celsius per minute and holding the maximum temperature, the maximum temperature is less than the melting temperature of the constituents in the powder,
the pressure is in a range of <10 KN or 30 MPa-150 MPa, and the densifying is performed in a time of 5 hours or less.

BRIEF DESCRIPTION OF THE DRAWINGS

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

Figure 1 is a flowchart illustrating a method of fabricating a phosphor according to one or more embodiments of the present invention.

Figure 2(a) Hexagonal structure (space group $P6_3/mmc$) of $Ba_{0.985}Eu_{0.015}MgAl_{10}O_{17}$ shown with Ba atoms charcoal, O atoms orange, Al atoms green, Mg atoms purple, and Al/Mg-O polyhedra purple. Figure 2(b) shows Rietveld refinement

of synchrotron X-ray diffraction shows no impurities, with unit cell data obtained from Rietveld refinement as follows: $a = b = 5.623965$ (3) A, $c = 22.639717(22)$ A, and cell volume=620.1360(10) A (parenthesis indicate the error in refined values).

Figure 3 is a Scanning Electron Microscope (SEM) micrograph of the BAM:Eu^{2+} dense monolith SPS prepared sample according to one or more embodiments of the present invention and showing the non-perfect arrangement of the hexagonal grains. This stacking leads to translucency in these materials, as well as a density of 91.5% (black bar is 20 μm long)

Figure 4(a) Excitation (dashed line) and emission (solid line) profiles of $Ba_{0.985}Eu_{0.015}MgAl_{10}O_{17}$ show strong absorption in the UV and blue emission due to the allowed 5*d* to 4*f* transition in Eu^{2+}. Figure 4(b) shows QY (λ_{ex} =340 nm) as a function of Eu mol-% shows max quantum yield (QY) = 66% ± 5% for 1.5 mol-% Eu nominally.

Figure 5(a) is a photograph of translucent BAM:Eu^{2+} sample according to one or more embodiments of the present invention being held by carbon-tipped tweezers, and Figure 5(b) the same translucent BAM:Eu^{2+} excited by a 402 nm laser diode incident perpendicular to the surface of the sample. Under violet laser excitation, the phosphor powder in silicone Figure 5(c) exceeded 360 °C and carbonized in 11 s, whereas the translucent sample shown in Figure 5(d) only reached 70 °C. White lines on color bar mark 100 °C increments

Figures 6(a) and 6(b) illustrate the translucent phosphor used in an application where light (e.g., having a wavelength of 450 nm or less, e.g., UV) is converted to blue light and/or is filtered, according to one or more embodiments of the present invention. Figure 6(a) further illustrates further including any or all red-, green-, or yellow-emitting phosphors that absorb the converted blue light from the phosphor monolith.

Figure 6(c) illustrates an additional phosphor 610 (e.g., red-, green-, or yellow-emitting phosphor) coupled to the phosphor 602 so as to absorb the converted blue light

608 from the phosphor monolith 602 and emit yellow, red, or green light 612 in response thereto.

DETAILED DESCRIPTION OF THE INVENTION

In the following description of the preferred embodiment, reference is made to 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 Description

With high power laser-based systems for lighting applications, the high intensity light generated requires phosphor morphologies with high thermal conductivity to keep a low operating temperature of the phosphor, and to combat phosphor self-heating due to Stokes loss [11].

Spark plasma sintering (SPS) has been demonstrated to produce dense and transparent phosphor samples. In SPS, powder is placed in a carbon-coated die set, a pressure is placed on the powder by two die presses, and a current is applied to the sample to achieve temperatures up to 1700 °C with fast ramp rates (>100°C/min) [12]. SPS of the canonical yellow-emitting phosphor, Ce-doped yttrium aluminum garnet, has been previously explored [13-15]. In this cubic system, scattering is dominated by pores, and the reduction of pores leads to transparent samples. Additionally, starting with a nanoparticle powder results in transparent samples as it reduces the grain size. In hexagonal systems, like the blue-emitting phosphor Eu-doped $BaMgAl_{10}O_{17}$, the refractive index is anisotropic meaning the refractive index depends on orientation of the grains. This anisotropy leads to additional grain scattering versus cubic crystals, making hexagonal systems translucent at best, and not transparent [16].

Example Preparations

The white powder of Eu-doped $BaMgAl_{10}O_{17}$ ($BAM:Eu^{2+}$), with any level of europium (Eu) doping on the Ba site, was heated (e.g., using microwaves) and then consolidated with SPS into translucent cylindrical samples.

Figure 1 illustrates a method of fabricating the phosphor according to one or more embodiments of the present invention.

Block 100 represents thoroughly mixing and grinding stoichiometric amounts of the starting materials, to form a mixture, e.g., comprising a powder including Eu-doped $BaMgAl_{10}O_{17}$ ($BAM:Eu^{2+}$).

$BaCO_3$ (99.999% Sigma-Aldrich), MgO (99.95%, Cerac), Al_2O_3 (99.99%, Sigma-Aldrich), and Eu_2O_3 (99.99%, Sigma-Aldrich) were mixed to form a powder mixture.

Block 102 represents an optional step of heating the mixture, e.g., using microwaves, to form a heated mixture

For microwave prepared samples, the mixture pre-fired at 700 ° C in a box furnace for 12 h. Samples containing 0.5 atom %, 1.0 atom %, 1.5 atom %, 2.0 atom %, 2.5 atom %, and 3.0 atom% europium substitution levels were prepared. Samples containing 1.5 atomic % Eu ($Ba_{0.985}Eu_{0.015}MgAl_{10}O_{17}$) were prepared with 2 weight % LiF (as flux, LiF (99.995%, Aldrich), but any rare earth doping amount, with or without flux, could be used as starting powder.

The microwave heating procedure was based on work by Birkel *et al* [18]. For each preparation, 6 g of granular activated charcoal (12-20 mesh, DARCO®, Sigma-Aldrich) was used as the microwave susceptor, and placed in a 50mL alumina crucible (Advalue). Approximately 0.5 g of the unreacted sample powder was placed in a 10mL alumina crucible, which was pushed into the carbon in the 50mL crucible, covered with an alumina lid (Ad-value), and placed in a block of high temperature alumina insulation foam. The materials were heated in a domestic microwave oven (Panasonic NN-SN667B, 1200W) operating at 720W for 25 min. This power and time were found to be highly

reproducible and yielded the most efficient microwave prepared phosphors in this study. Other combinations of power and time produced the desired phase, but with phosphor efficiencies that were lower than that measured for samples prepared at 720W for 25 min. The microwave preparation method is fast due to direct heating of the reactants, and reduces the reaction time of these samples by an order of magnitude compared to conventional heating methods.

Block 104 represents densifying the heated powder mixture, e.g., using SPS, forming a monolith.

For the SPS demonstration, an FCT Systeme GmbH SPS furnace was used. Sample powders were placed in a graphite die of 10 mm diameter with 1mm thick graphite foil lining the die, but any diameter die setup can be used. Typically, in SPS, the chamber holding the sample is pumped down to vacuum with a preload applied, with the force increased after vacuum is achieved. To achieve translucent BAM:Eu^{2+} samples, a preload of 3 kilonewtons (kN) was applied and increased to 5 kN over 30 seconds once vacuum was achieved. A heating rate of 200 °C/min was then initiated. The sample was heated to 1500 °C at a rate of 200 °C/min and held for 5 minutes (min), and cooled to room temperature in 10 min. Samples were then sanded to remove the graphite foil. Resulting samples were 9 mm in diameter and <1 mm thick. A representative sample is shown in Figure 5(a). Figure 5(b) shows the sample under 402 nm laser excitation.

Other densifying techniques and process conditions can be used. In one or more embodiments, the densifying comprises rapidly heating the powder under a pressure (e.g., typically 30 MPa-150 MPa or less than 10 KN) to a maximum temperature, and the heating comprises increasing a temperature of the powder at a fast heating rate of <300 degrees Celsius per minute or at a rate in a range of 100 °C min^{-1} - 600 °C min^{-1} and holding the maximum temperature. The maximum temperature is less than the melting temperature of the constituents in the powder, and the densifying is typically performed in a time of 5 hours or less. In one or more embodiments, the pressure applied causes

particle rearrangement, while current is supplied to achieve the fast heating rates via Joule heating. These fast heating rates mitigate sintering mechanisms with low activation energies that do not contribute to densification (evaporation and surface diffusion) and encourage densification of particles via grain boundary and volume diffusion [12].

In one or more embodiments, the phosphor is prepared from starting oxides and densified in a single step, e.g., using SPS, without the microwave heating step. However, dense monolithic phosphors cannot be made in a single step using microwave heating alone.

The quantum yield (QY) of this non-consolidated phosphor powder mixture at 1.5% Eu doping and using an excitation wavelength of 340 nm was measured as 66% (+/–5 % error), and 33% (+/–5 % error) for an excitation wavelength of 400 nm, with an excitation maximum at 337 nm and emission maximum at 447 nm. Surprisingly and unexpectedly, the powder fabricated using microwave assisted heating and SPS was determined to be phase pure using synchrotron X-ray diffraction and subsequent Rietveld refinement.

Characterization

Phase purity of Microwave prepared sample

To assess the phase purity of the microwave prepared phosphors, high resolution synchrotron powder diffraction data were collected using beamline 11-BM at the Advanced Photon Source, Argonne National Laboratory using an average wavelength of 0.459266 A. BAM:Eu^{2+} crystallizes in the hexagonal space group $P6_3/mmc$ (no. 194) [19, 20]. The refined structure showing Oxygen O, Barium Ba, Magnesium Mg, and Al/Mg-O polyhedra was visualized using the open-source crystallographic software VESTA [21] and is shown in Figure 2(a). The refined X-ray diffraction pattern for $Ba_{0.985}Eu_{0.015}MgAl_{10}O_{17}$ is shown in Figure 2(b). Rietveld refinements were performed using the General Structure Analysis System with EXPGUI [22, 23]. No impurity phases

were discovered or refined, and the R_{wp} of the fit was 11.75%. Ba and Eu occupancies were held constant at the nominal amounts. Peak shapes were handled using the pseudo-Voigt profile function, which combines Gaussian and Lorentzian components. The background was handled using a Chebyshev polynomial. The lack of impurities demonstrates the viability of microwave assisted heating for preparing phosphors.

SEM of SPS prepared sample

SEM images were collected using a FEI XL30 Sirion FEG Digital Electron Scanning Microscope in secondary electron mode using a 15 kV beam voltage. As shown in a representative SEM image (Figure 3), there are regions of densely packed layers that are oriented at different angles relative to each other. This non-perfect stacking of hexagonal grains appears to create spacing in the stacks themselves, and is also likely the source of grain scattering that makes SPS samples of this material translucent and not transparent, as well as a density 91.5% of the theoretical maximum.

Phoroluminescence

Room temperature photoluminescence spectra and external quantum yield (QY) of the initial BAM:Eu^{2+} powder were measured using a fluorescence spectrometer (Horiba, Fluoromax 4) equipped with an integrating sphere and are shown in Figure 4(a) and Figure 4(b), respectively. BAM:Eu^{2+} shows strong absorption in the UV and emission centered around 445nm (Figure 4(a)). The emission is due to the excited $4f^6 5d$ relaxing to the $4d^6$ ground state [19]. No emission is observed around 600 nm, which confirms the presence of Eu^{2+} in the lattice instead of Eu^{3+}, demonstrating the versatility of microwave assisted heating for preparing phosphor samples. QY of the starting powder was measured as a function of Eu mol% (Figure 4(b)). The maximum QY of 66% (±5 %) for λ_{ex} =340nm was achieved for the 1.5 mol% sample. The Commission Internationale de l'Eclairage (CIE) 1931 (x,y) coordinates were (0.15, 0.05) for all

samples measured. Phosphors were thoroughly mixed by 25-wt % in a silicone matrix (Momentive, RTV-615) using a high speed mixing system (FlackTek Inc., DAC 150.1 FVZ-K) at 1500 rpm for 5 min, and subsequently deposited on a fused silica substrate (Chemglass) and cured at 105 °C for 15 min in a box oven. Phosphors encapsulated in a silicone matrix were then placed in a 15 cm diameter, Spectralon R-coated integrating sphere (Horiba, Quanta ϕ-) and excited by 340nm light, which was generated by a 150W continuous output, ozone-free xenon lamp. QY was calculated based on the work by de Mello *et al* [17].

QY with Laser Diode

To demonstrate viability of the SPS prepared phosphor monoliths with a LD, photoluminescence quantum yield (PLQY) was calculated using a 50 centimeter (cm) integrating sphere with a commercial 402 nm laser mounted in a side port and the phosphor sample mounted in the center of the integrating sphere. The monolith sample surface was positioned at a slight angle from the incoming laser beam to prevent reflection back towards the laser port, and the distance between the laser and the sample was ~30 cm. The commercially available LD, with an emission wavelength λ_{max} = 402 nm, a full width at half maximum (FWHM) = 2.6 nm, threshold current of 30 mA, and wall plug efficiency of 20%, was mounted in a copper heat sink. The diode was operated at 500 mA with a voltage of 6.11 V (595 mW of laser power in output light incident on sample surface), controlled by a Keithley 2440 SourceMeter. The laser was observed to redshift with increasing current, registering 406 nm at 500 mA.

The QY (at an excitation wavelength of λ_{ex} = 400 nm) using a fluorimeter of the phase pure starting powder encapsulated in silicone was 33 % ± 5%. The same QY within error (37 % ± 5%) was calculated for the translucent ceramic monolith (no encapsulation) using both a LD and a fluorimeter, indicating that densification of the BAM:Eu^{2+} powder

into a translucent monolith does not lower the QY. External QY for λ_{ex} = 400nm is lower than λ_{ex} = 340nm as there is less absorption at 400nm (Figure 4(a)).

Better quality starting materials and lower emission wavelengths will both serve to increase the QY of the translucent samples.

Thermal management

To study the thermal management of a translucent ceramic monolith versus phosphor powder in silicon, commercial BAM:Eu^{2+} powder encapsulated in silicone (25 wt% phosphor) and a translucent ceramic monolith prepared using the same commercial powder were thermally isolated on quartz wool, irradiated with a laser diode placed 5 cm from the sample surface, and monitored using a FLIR A310 thermal imaging camera (range
0 °C - 360 °C). Photographs of a BAM:Eu^{2+} sample without 500 and with 502 a commercial violet LD incident to its surface are shown in Figure 5(a) and 5(b), respectively. After 11 s of laser irradiation, the phosphor powder 504 in silicone (Figure 5(c)) exceeded 360 °C and carbonized. In the same time, the translucent ceramic 506 (Figure 5(d)) reached 70°C. After two minutes of laser irradiation, the translucent sample 506 reached 160 °C. Both samples had the same dimensions (6mm x 6mm x 1mm), and the laser diode was operated at the same current and voltage as the LD QY (λ_{ex}=400 nm) measurements (595 mW of optical power incident on the sample). The superior thermal management observed shows promise for BAM:Eu^{2+} ceramic monoliths as a blue component in LED- and LD-based lighting.

Geometric Density

The geometric density of the SPS prepared pellet was measured as 3.45 g/cm^3 (+/– 0.05), which is 91.5% of the theoretical density of 3.770 g/cm^3 calculated from the refined unit cell of the starting powder. The measured density of 91.5% is likely not due

to the presence of pores along grain boundaries, but is likely due to the non-perfect arrangement of hexagonal grains of the BAM:Eu^{2+}.

Example Device Structure

Figure 6(a) and 6(b) illustrate the use of the translucent phosphor monolith 300 in applications (e.g., laser based applications) where conversion or filtering of electromagnetic radiation (e.g., blue light, UV light, radiation having a wavelength of 450 nm or less, or radiation having a wavelength of 10-400 nm) is required. Specifically, Figure 6(a) and 6(b) illustrate a device 600 for converting or filtering electromagnetic radiation, comprising the phosphor 602, 300 electromagnetically coupled to a light emitting device 604 (e.g., laser or LED) that emits radiation 606, wherein the radiation 606 is incident on the surface of the phosphor 602. The phosphor 602 emits blue light 608 in response to absorbing and/or scattering the radiation 606 (e.g., having a wavelength of 450 nm or less). In one or more embodiments, the phosphor 602 also filters out the UV from the radiation 606. Figure 6(a) illustrates the device 600 in a transmission geometry and Figure 6(b) illustrates the device 600 in a reflective geometry.

In one or more embodiments, the device 600 is combined with a yellow light source 610 emitting yellow light 612, wherein the combination of the blue light 608 and the yellow light 612 is white light 614.

In one or more further embodiments, the device/light source 600 is combined/coupled with a red light source 610 emitting red light 612 and a green light source 610 emitting green light 612, wherein the combination of blue light 608, the green light 612, and the red light 612, is white light 614. In one or more examples, the white light 614 is characterized by CIE coordinates within 5% of pure white light.

In one or more embodiments, the yellow light source, the red light source, and the green light source are LEDs or LDs or phosphors.

In one example, the thermally stable blue phosphor 602 and red-, green-phosphors 610 are optically pumped by violet light emitted from the light emitting device 604 comprising a violet laser diode, wherein the combination of light 612 and 608 emitted from the phosphors 610, 602 is warm white light 614 useful for visible light communications. A summary describing phosphor combinations for generating white light used in visible light communications is given in [25], [26].

In one or more embodiments, the phosphor 602 is used as a filter in an application that requires the UV radiation 606 from the light emitting device 604 to be filtered.

Figure 6(c) illustrates an additional phosphor 610 (e.g., red-, green-, or yellow-emitting phosphor) coupled to the phosphor 602 so as to absorb the converted blue light 608 from the phosphor monolith 602 and emit yellow, red, or green light 612 in response thereto.

In one or more examples, the phosphor 602 further includes additional compatible ceramic components increasing light extraction of the phosphor 602, increasing thermal conductivity of the phosphor 602, and/or generating different types of light from the phosphor 602.

In one or more examples, the phosphor 602 has a density of at least 70% of its theoretical density, or a density between 70% and 99.9% of the theoretical density.

In one or more examples, the phosphor is translucent and a thickness T and/or density of the phosphor 602 is modulated so as to increase scattering of the electromagnetic radiation 606 by the phosphor 602. In one or more examples, the phosphor 602 is a monolith having a diameter D in a range of 500 micrometers to 20 millimeters.

In one or more embodiments, the phosphor 602 is phase pure and self-encapsulating.

In one or more embodiments, the phosphor 602 is a single crystal or sintered ceramic.

In one or more embodiments, the phosphor 602 maintains a temperature under a thermal quenching regime of the phosphor 602 (e.g., 70 degrees Celsius) and emits the same intensity of blue light 608 after absorbing the electromagnetic radiation 606 having a wavelength of 450 nm or less and a power of 3 watts for 11 seconds.

In one or more examples, the phosphor 602 is a monolith that is cooler and emits the blue light 608 with higher quantum yield as compared to the phosphor encapsulated in silicone.

Advantages and Benefits

Currently, monolithic blue-emitters do not exist. With the demand for higher power white lighting using LEDs and LDs, solutions beyond organic resins and phosphor glasses for encapsulating materials must be developed. The present invention is the first offering of a blue-emitting phosphor technology suitable for the next generation of lighting, able to withstand high heat from LEDs and LDs due to the monolithic nature of the phosphor, and wherein the phosphor is translucent (which allows reflection or transmission depending on sample thickness). With the starting phosphor powder, preparation into a dense translucent sample unexpectedly takes a short period of time (< 1 hour), (with sample diameters < 20 mm common for most SPS furnaces) which is an order of magnitude faster than techniques such as single crystal growth (which do not currently exist for this particular phosphor) and therefore provides a rapid way to fabricate encapsulation-free phosphors.

As indicated above, the QY measured of the translucent monolith under laser excitation at a wavelength of 402 nm was 37% (+/- 5% error), which is within the error of the QY measured at this same wavelength for the phosphor in the powdered unconsolidated state (prior to sintering). This demonstrates that, surprisingly and

unexpectedly, the QY of the phosphor is not decreased after the SPS process (as compared to in the powdered state).

The present invention has demonstrated reproducibility for preparation/synthesis of translucent samples, as well as conversion using a near-UV laser diode. The present invention has also demonstrated the phosphor's superior performance as compared to a phosphor in silicone, by thermally isolating the sample and monitoring laser conversion with an infrared (IR) camera. Due to the monolithic nature of the present blue-emitting phosphor, translucent phosphors prepared according to embodiments of the present invention mitigate phosphor self-heating greatly as compared to silicone encapsulation, making them extremely useful as a UV light filter and/or a blue component in warm white light generation using near-UV LEDs and LDs for general illumination and visible light communication.

Possible Modifications

Preparation parameters for maximum density samples, as well as use of higher quality and smaller particle size starting materials.

References

The following references are incorporated by reference herein:

[1] J. Brodrick, "Energy savings forecast of solid-state lighting in general illumination applications," Tech. Rep. (US Dep. Energy, Washington DC, 2014).

[2] S. Nakamura and M. R. Krames, "History of gallium–nitride-based light-emitting diodes for illumination," Proc. IEEE 101, 2211–2220 (2013).

[3] L. Y. Kuritzky and J. S. Speck, "Lighting for the 21st century with laser diodes based on non-basal plane orientations of GaN," MRS Commun. 5, 463–473 (2015).

[4] K. A. Denault, M. Cantore, S. Nakamura, S. P. DenBaars, and R. Seshadri, "Efficient and stable laser-driven white lighting," AIP Adv. 3, 072107 (2013).

[5] Q.-Q. Zhu, X.-J. Wang, L. Wang, N. Hirosaki, T. Nishimura, Z.-F. Tian, Q. Li, Y.-Z. Xu, X. Xu, and R.-J. Xie, "β-Sialon:Eu Phosphor-in-Glass: a Robust Green Color Converter for High Power Blue Laser Lighting," J. Mater. Chem. C 3, 10761–10766 (2015).

[6] M. Cantore, N. Pfaff, R. M. Farrell, J. S. Speck, S. Nakamura, and S. P. DenBaars, "High luminous flux from single crystal phosphor-converted laser-based white lighting system," Opt. Express 24, A215–A221 (2016).

[7] N. C. George, K. A. Denault, and R. Seshadri, "Phosphors for Solid-State White Lighting," Annu. Rev. Mater. Res. 43, 481–501 (2013).

[8] J. Sheu, S. Chang, C. Kuo, Y. Su, L. Wu, Y. Lin, W. Lai, J. Tsai, G. Chi, and R. Wu, "White-Light Emission from Near UV InGaN-GaN LED Chip Precoated with Blue/Green/Red Phosphors," IEEE Photon. Technol. Lett. 15, 18–20 (2003).

[9] C. Lee, C. Zhang, M. Cantore, R. M. Farrell, S. H. Oh, T. Margalith, J. S. Speck, S. Nakamura, J. E. Bowers, and S. P. DenBaars, "4 Gbps direct modulation of 450 nm GaN laser for high-speed visible light communication," Opt. Express 23, 16232–16237 (2015).

[10] C. Lee, C. Shen, H. M. Oubei, M. Cantore, B. Janjua, T. K. Ng, R. M. Farrell, M. M. El- Desouki, J. S. Speck, S. Nakamura, B. S. Ooi, and S. P. DenBaars, "2 Gbit/s data transmission from an unfiltered laser-based phosphor-converted white lighting communication system," Opt. Express 23, 29779–29787 (2015).

[11] X. Luo, X. Fu, F. Chen, and H. Zheng, "Phosphor self-heating in phosphor converted light emitting diode packaging," International Journal of Heat and Mass Transfer 58, 276–281 (2013).

[12] J. Garay, "Current-activated, pressure-assisted densification of materials," Annu. Rev. Mater. Res. 40, 445–468 (2010).

[13] R. Chaim, R. Marder-Jaeckel, and J. Shen, "Transparent YAG ceramics by surface softening of nanoparticles in spark plasma sintering," Mat. Sci. Eng. A-Struct. 429, 74–78 (2006).

[14] R. Chaim, M. Kalina, and J. Z. Shen, "Transparent yttrium aluminum garnet (YAG) ceramics by spark plasma sintering," J. Eur. Ceram. Soc. 27, 3331–3337 (2007).

[15] N. Frage, S. Kalabukhov, N. Sverdlov, V. Ezersky, and M. P. Dariel, "Densification of transparent yttrium aluminum garnet (YAG) by SPS processing," J. Eur. Ceram. Soc. 30, 3331–3337 (2010).

[16] R. T. Marta Suárez, Adolfo Fernández and J. L. Menendez, Sintering to Transparency of Polycrystalline Ceramic Materials (InTech Open Access Publisher, 2012).

[17] J. C. de Mello, H. F. Wittmann, and R. H. Friend, An improved experimental determination of external photoluminescence quantum efficiency," Adv. Mater. 9, 230{232 (1997).

[18] A. Birkel, K. A. Denault, N. C. George, C. E. Doll, B. Hery, A. A. Mikhailovsky, C. S. Birkel, B.-C. Hong, and R. Seshadri, \Rapid microwave preparation of highly efficient Ce3+-substituted garnet phosphors for solid state white lighting," Chem. Mater. 24, 1198{1204 (2012)

[19] Y.-I. Kim, K.-B. Kim, M.-J. Jung, and J.-S. Hong, \Combined rietveld re_nement of BaMgAl10O17:Eu2+ using X-ray and neutron powder di_raction data," J. Lumin. 99, 91{100 (2002).

[20] K.-B. Kim, Y.-I. Kim, H.-G. Chun, T.-Y. Cho, J.-S. Jung, and J.-G. Kang, \Structural and optical properties of BaMgAl10O17:Eu2+ phosphor," Chem. Mater. 14, 5045{5052(2002).

[21] K. Momma and F. Izumi, \VESTA: a Three-Dimensional Visualization System for Electronic and Structural Analysis," J. Appl. Crystallogr. 41, 653{658 (2008).

[22] A. C. Larson and R. B. Von Dreele, \GSAS," General Structure Analysis System. LANSCE, MS-H805, Los Alamos, New Mexico (1994).

[23] B. H. Toby, \EXPGUI, a Graphical User Interface for GSAS," J. Appl. Crystallogr. 34, 210{213 (2001).

[24] C. Cozzan, M. J. Brady, N. O'Dea, E. E. Levin, S. Nakamura, S. P. DenBaars, and R. Seshadri, Monolithic translucent $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphors for laser-driven solid state lighting, AIP Adv. 6 (2016) 105005.

[25] http://www.semiconductor-today.com/news_items/2017/aug/usb_090817.shtml.

[26] Gigabit-per-second white light-based visible light communication using near-ultraviolet laser diode and RGB phosphors, *Opt. Express* **25** (2017) 17480-17487. doi: https://doi.org/10.1364/OE.25.017480.

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. It is intended that the scope of the invention be limited not by this detailed description, but rather by the claims appended hereto.

WHAT IS CLAIMED IS:

1. A phosphor, comprising:

$Ba_{1-x}Eu_xMgAl_{10}O_{17}$ ($BAM:Eu^{2+}$), wherein:

$0 < x < 1$, and

the $BAM:Eu^{2+}$ emits blue light and/or light having a wavelength in a range of 410 nm-510 nm in response to excitation with electromagnetic radiation having a wavelength less than 450 nanometers.

2. The phosphor of claim 1, wherein the phosphor is a monolith.

3. The phosphor of claim 1, further comprising additional compatible ceramic components increasing light extraction, increasing thermal conductivity, and/or generating different types of light.

4. The phosphor of claim 2, wherein the phosphor has a density of at least 70% of its theoretical density, or a density between 70% and 99.9% of the theoretical density.

5. The phosphor of any of the claims 1-3, wherein the phosphor is translucent.

6. The phosphor of claim 5, wherein a thickness and/or density of the phosphor is modulated to increase scattering of the electromagnetic radiation by the phosphor.

7. The phosphor of any of the claims 1-6, wherein the phosphor is phase pure and self-encapsulating.

8. The phosphor of any of the claims 1-7, wherein the phosphor is a single crystal or sintered ceramic.

9. A device for converting or filtering electromagnetic radiation, comprising:

the phosphor of any of the claims 1-8 electromagnetically coupled to a light emitting device emitting the electromagnetic radiation having a wavelength less than 450 nm.

10. The device of claim 9, wherein the phosphor maintains a temperature under a thermal quenching regime of the phosphor and emits the same intensity of blue light after absorbing the ultraviolet radiation having a power of 3 watts for 11 seconds.

11. The device of claims 9-10, wherein the light emitting device is a laser.

12. The device of any of the claims 9-11, wherein the monolith emits light in response to the electromagnetic radiation having the wavelength of 450 nm or less.

13. The device of any of the preceding claims, wherein the monolith has adiameter in a range of 500 micrometers to 20 millimeters.

14. The device of any of the preceding claims, wherein the device is coupled to a light source emitting yellow, red, and/or green light, so that a combination of the blue light and the yellow, red, and/or green light is white light characterized by CIE coordinates within 5% of pure white light.

15. The device of claim 14, wherein the monolith is cooler and emits the blue light with higher quantum yield as compared to the phosphor encapsulated in silicone.

16. A method for fabricating a phosphor, comprising:

mixing stoichiometric amounts of starting materials so as to obtain a powder comprising Eu-doped $BaMgAl_{10}O_{17}$ ($BAM:Eu^{2+}$); and

densifying the powder to form a monolith.

17. The method of claim 16, wherein:

the densifying comprises rapidly heating the powder under a pressure to a maximum temperature,

the heating comprises increasing a temperature of the powder at a rate of <600 degrees Celsius per minute and holding the maximum temperature,

the maximum temperature is less than the melting temperature of the constituents in the powder,

the pressure is in a range of <10 KN or 30 MPa-150 MPa, and

the densifying is performed in a time of 5 hours or less.

18. The method of claim 17, wherein the densifying uses spark plasma sintering.

19. The method of claim 17, wherein the monolith has a density of at least 70% of its theoretical density, or a density between 70% and 99.9% of the theoretical density.

20. The method of claim 17, wherein the monolith is translucent.

21. The method of claim 17, wherein the monolith is phase pure and self-encapsulating.

22. The method of claim 17, wherein the phosphor is a single crystal or sintered ceramic.

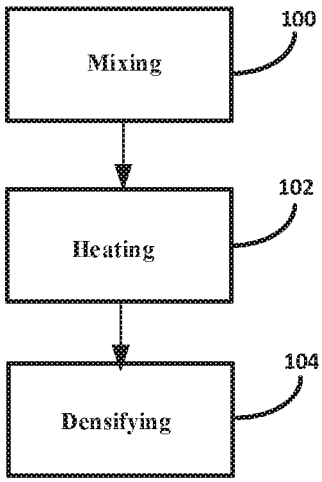


Figure 1

Figure 2(a)

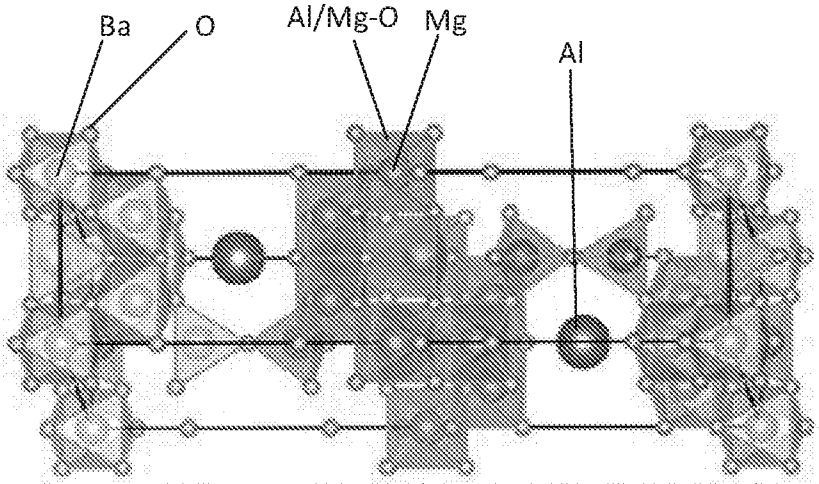
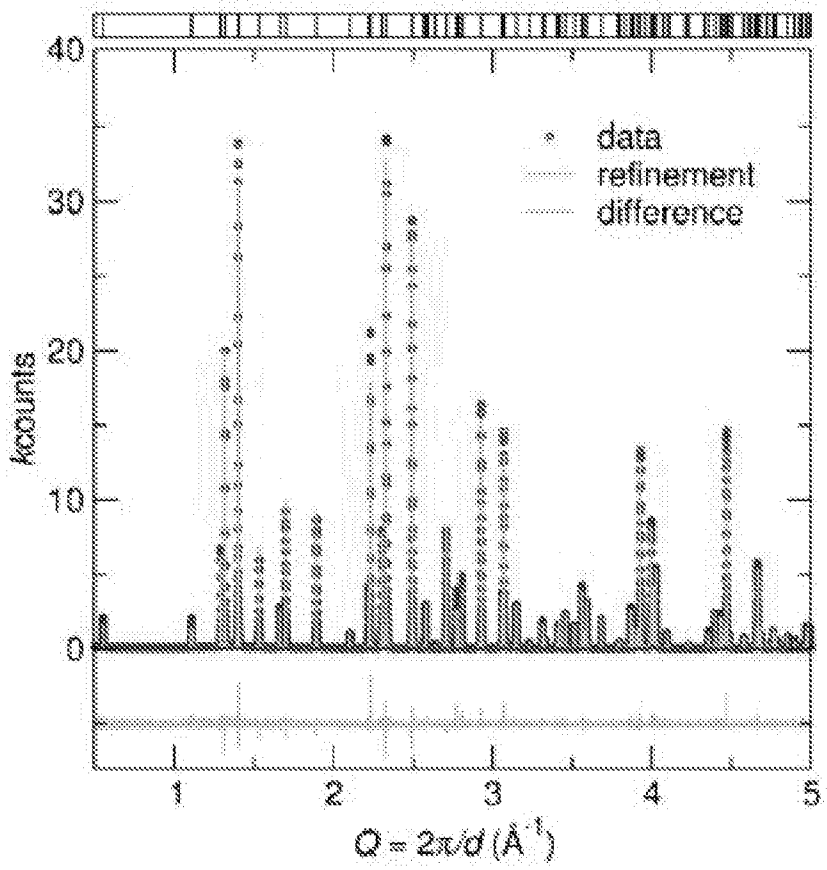


Figure 2(b)



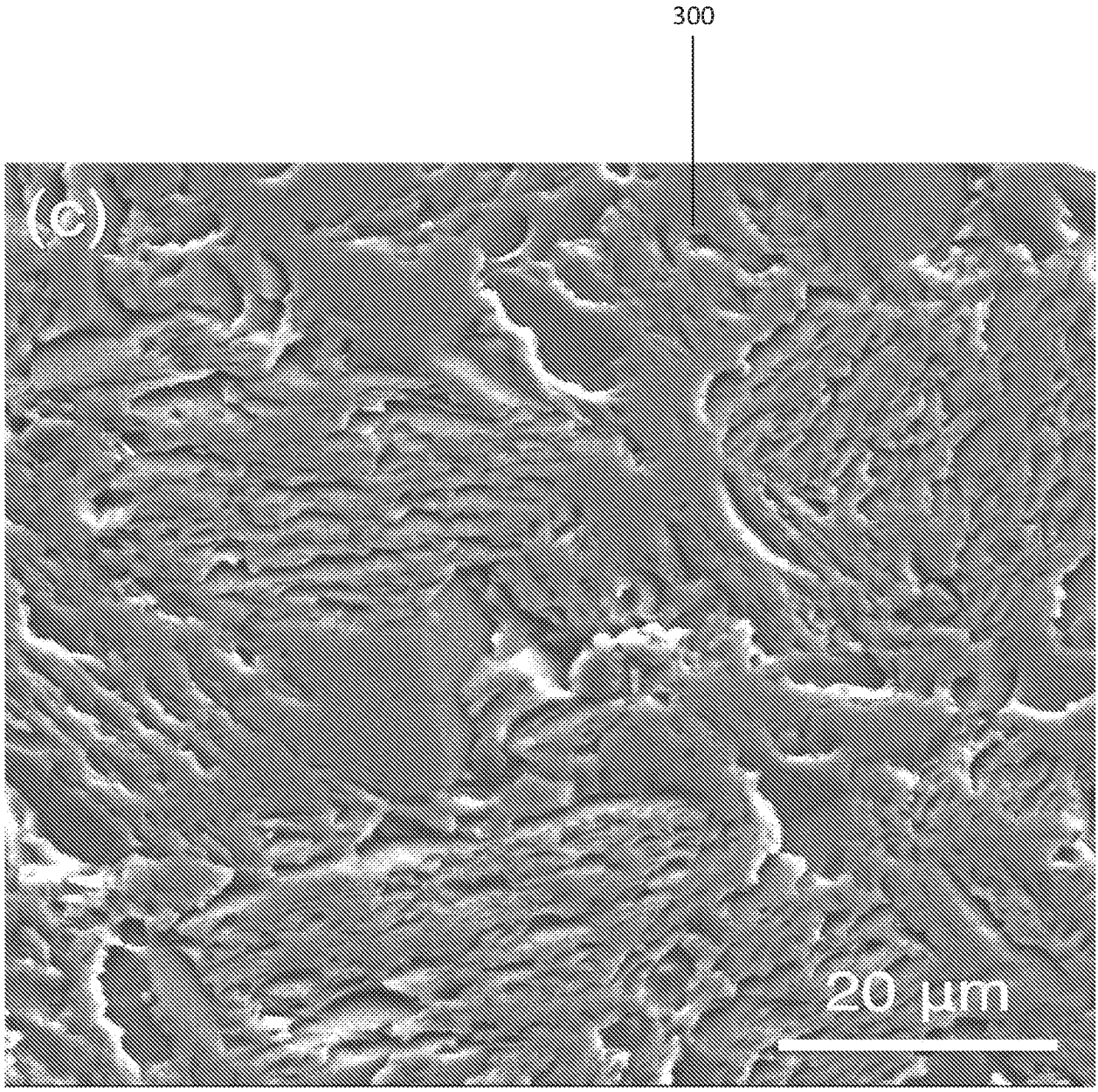


Figure 3

Figure 4(a)

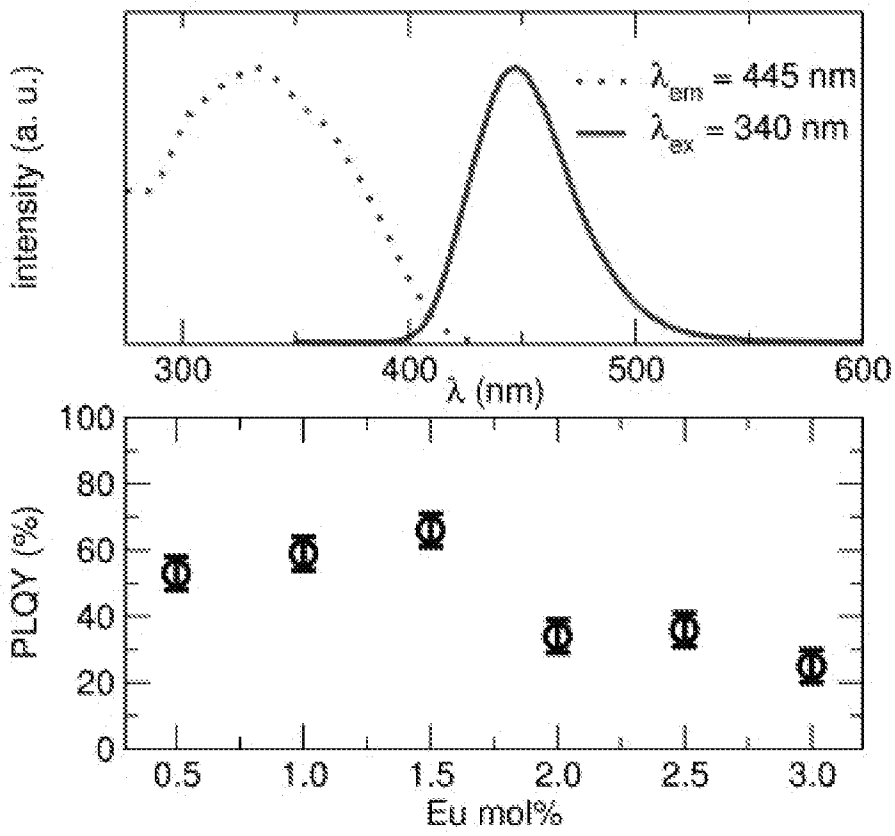


Figure 4(b)

Figure 5(a)

Figure 5(b)

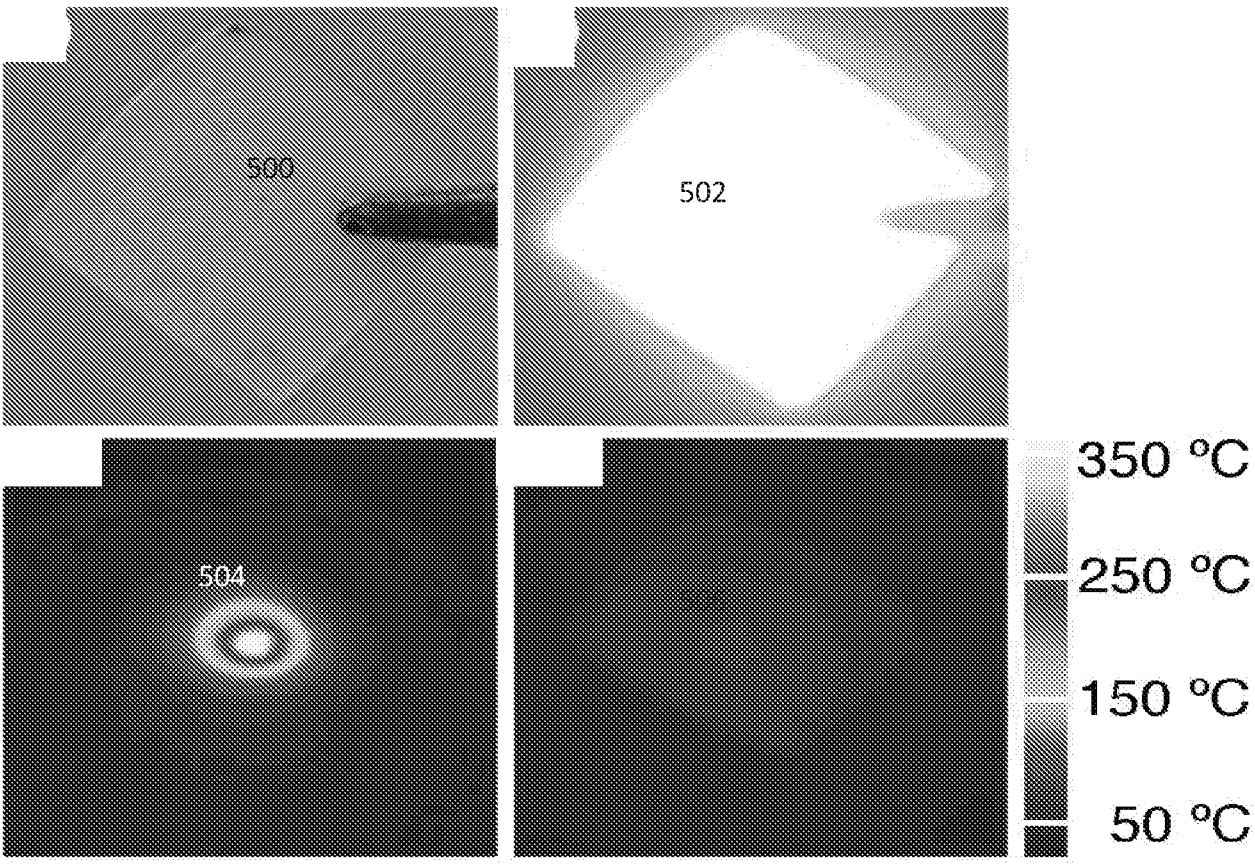


Figure 5(c)

Figure 5(d)

Figure 5

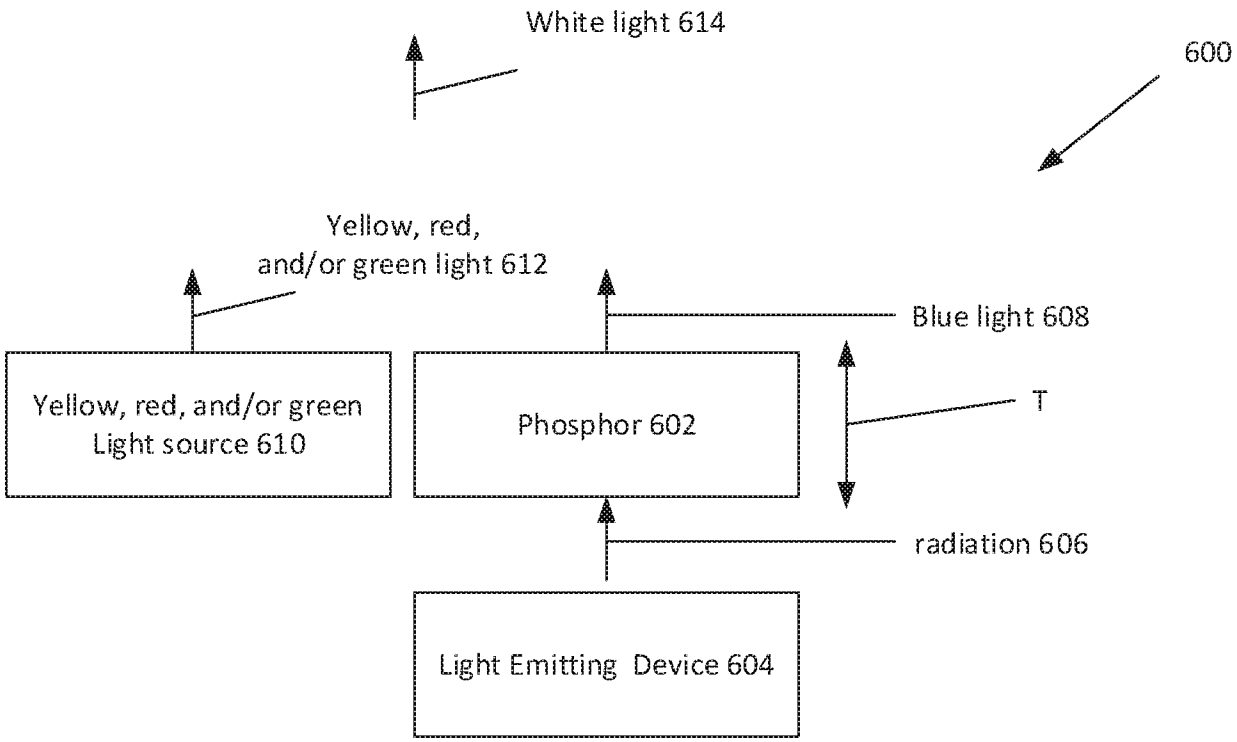


Figure 6(a)

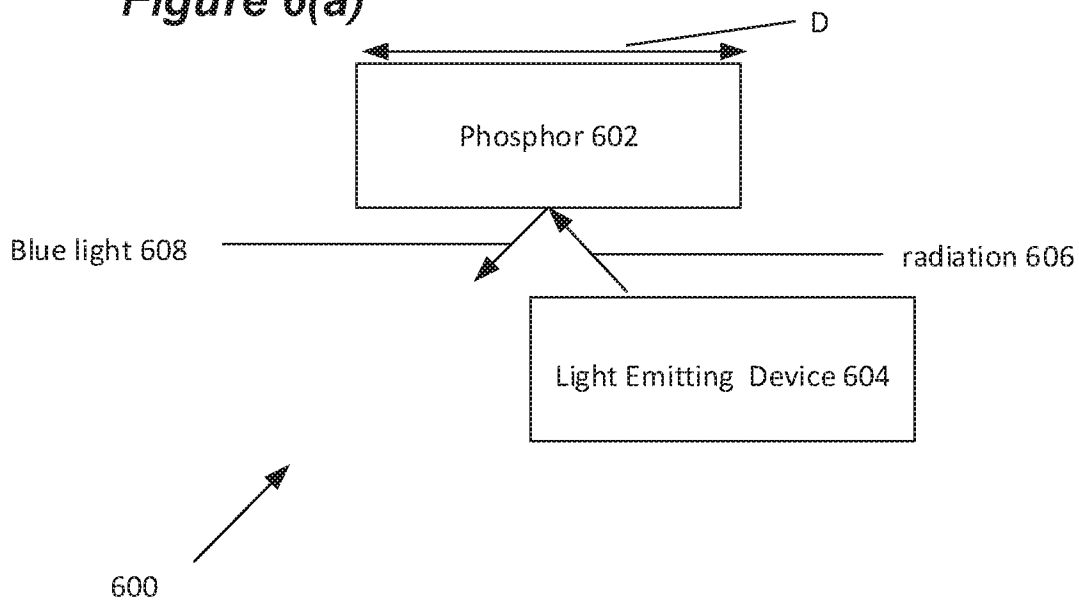


Figure 6(b)

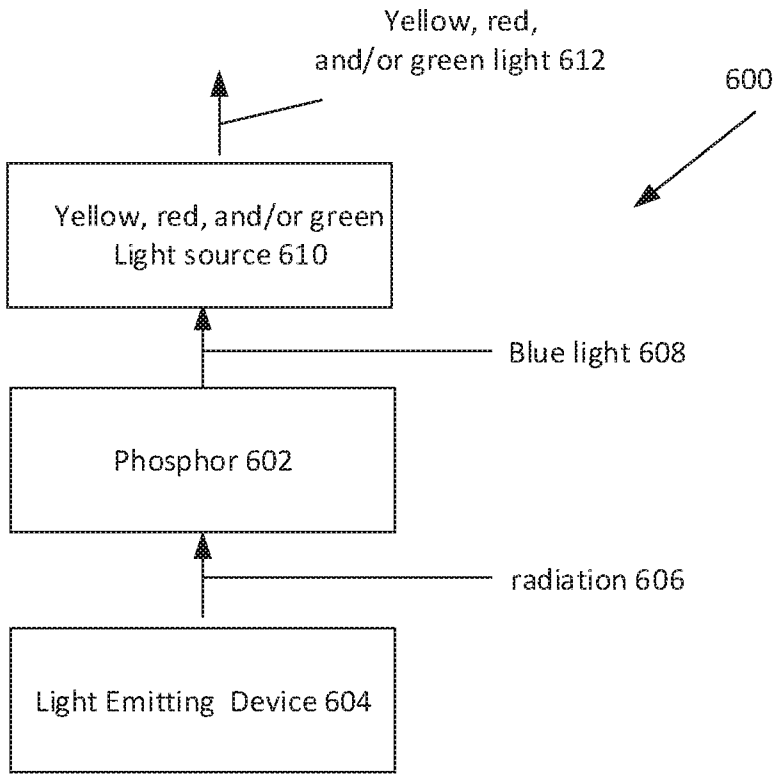

Yellow, red,
and/or green light 612
600
Yellow, red, and/or green
Light source 610
Blue light 608
Phosphor 602
radiation 606
Light Emitting Device 604

Figure 6(c)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/050512

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C09K 11/64; C09K 11/02; C09K 11/08; C09K 11/55 (2017.01)
CPC - C09K 11/576; C09K 11/02; C09K 11/025; C09K 11/643 (2017.08)

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)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 252/584; 252/586; 252/588 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2005/0145854 A1 (SETO et al) 07 July 2005 (07.07.2005) entire document	1 --- 2-6
X --- Y	US 2007/0138438 A1 (HAMPDEN-SMITH et al) 21 June 2007 (21.06.2007) entire document	16 --- 17-22
Y	US 2010/0142181 A1 (SCHMIDT et al) 10 June 2010 (10.06.2010) entire document	2-6, 20
Y	US 2015/0132585 A1 (NITTO DENKO CORPORATION) 14 May 2015 (14.05.2015) entire document	17-22
A	US 2008/0116421 A1 (WANG et al) 22 May 2008 (22.05.2008) entire document	1-6, 16-22

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 October 2017	13 NOV 2017
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/050512

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 7-15
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.