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(54) **Title**: GLASS COMPOSITE WAVELENGTH CONVERTER AND LIGHT SOURCE HAVING SAME

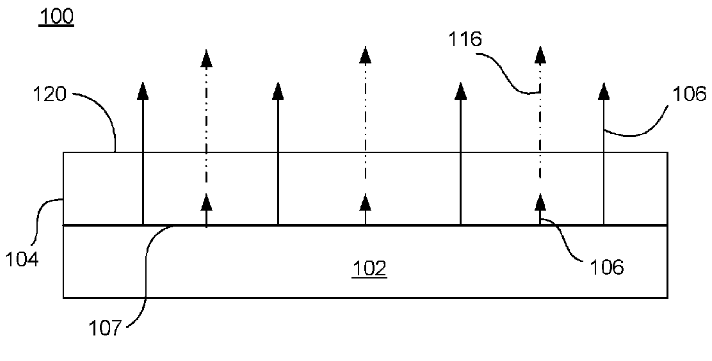

FIG. 1

(57) **Abstract**: There is herein described a glass composite wavelength converter and a light source containing same. The glass composite wavelength converter comprises phosphor particulates dispersed in a solid glass matrix. The glass matrix is comprised of a glass selected from a soda-lime glass, a Sb_2O_3-Bi_2O_3-B_2O_3 glass, a phosphate glass, a Bi_2O_3-ZnO-B_2O_3 glass, and a PbO-ZnO-B_2O_3 glass, wherein the phosphor particulates convert at least a portion of a primary light into a secondary light and the glass is substantially transparent to the primary light and the secondary light. In a preferred embodiment, the light source emits a warm white light having a CCT of about 3000K.

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Glass Composite Wavelength Converter and Light Source Having Same

Cross References to Related Applications

[0001] The present application is an international application that claims the benefit of U.S. Provisional Application No. 62/184,113 filed June 24, 2015, which is herein incorporated by reference.

Background of the Invention

[0002] In the manufacture of conventional phosphor conversion light emitting diodes (pc-LEDs), phosphor powders are normally mixed with a polymer material, such as a silicone or epoxy resin, to generate a homogenous dispersion of the phosphor particulates in the resin. The phosphor-polymer mixtures are then cast, deposited or coated on a blue-emitting (or near-ultraviolet-emitting) LED chip in an LED package. The phosphor-polymer mixture absorbs at least a portion of the light from the LED chip and converts it to light with a different peak wavelength. As a result, a pc-LED may be made that emits a light of a different color than the light emitted by the LED chip (full conversion), e.g., a red, amber or green color, or, in the case of partial conversion of the light emitted by the LED chip, a pc-LED can be made to emit a white light, e.g. a cool white or warm white light.

[0003] The phosphor-polymer mixture approach is easily implemented in LED packages, but suffers from the instability of the polymer materials which degrade under high temperatures and light intensities. Another way to create a pc-LED is to use a ceramic wavelength converter. The ceramic wavelength converters are formed by sintering a mass of inorganic phosphor particles at high temperature until the particles diffuse and stick together to form a monolithic piece. The ceramic converter is typically formed as a thin rectangular plate that is applied to the light emitting surface of the LED chip. Because of their higher thermal conductivity, ceramic wavelength converters are preferred in higher power applications over converters that are formed from dispersions of phosphor particles in epoxy or silicone resins. However, while this approach offers better stability, it can be relatively more expensive to the manufacture.

[0004] The phosphor-in-glass (PiG) approach is somewhere in between these two approaches. It has the flexibility of the phosphor-polymer approach and offers the better stability of the ceramic converter approach at a lower cost. Typically phosphor-in-glass approaches require the glass to soften or melt to assure the homogeneity of phosphor dispersion and reduce or eliminate porosity in the converter. However, because of the temperatures and duration times used in these processes, the possibility of damaging the phosphor is increased. This is less a concern for oxide-based phosphors, such as garnet phosphors, as these are less sensitive to such processing conditions. However, the damage to nitride-based phosphors can be severe, particularly because nitride-based phosphors are very sensitive to oxygen impurities and most glasses are oxide glasses, an abundant source for oxygen.

Summary of the Invention

[0005] It is an object of this invention to obviate the disadvantages of the prior art.

[0006] It is another object of the invention to provide a glass composite wavelength converter for use in pc-LED applications, including those using nitride-based phosphors.

[0007] It is a further object of the invention to provide a method of making a glass composite wavelength converter.

[0008] In accordance with an object of the invention, there is provided a glass composite wavelength converter comprising phosphor particulates dispersed in a solid glass matrix. The glass matrix is comprised of a glass selected from a soda-lime glass, a Sb_2O_3-Bi_2O_3-B_2O_3 glass, a phosphate glass, a Bi_2O_3-ZnO-B_2O_3 glass, and a PbO-ZnO-B_2O_3 glass. The phosphor particulates convert at least a portion of a primary light into a secondary light and the glass is substantially transparent to the primary light and the secondary light. Preferably, the converter has a conversion efficiency of at least about 20%, and more preferably at least about 40%.

[0009] In accordance with another object of the invention, there is provided a light source, comprising a light emitting diode (LED) that emits a primary light and a glass composite wavelength converter comprising phosphor particulates dispersed in a solid glass matrix. The glass matrix is comprised of a glass selected from a soda-lime glass, a Sb_2O_3-Bi_2O_3-B_2O_3 glass, a phosphate glass, a Bi_2O_3-ZnO-B_2O_3 glass, and a PbO-

$ZnO-B_2O_3$ glass. The phosphor particulates convert at least a portion of the primary light into a secondary light and the glass is substantially transparent to the primary light and the secondary light. Preferably, the light source emits a warm white light having a correlated color temperature (CCT) of about 3000K.

Brief Description of the Drawings

[0010] Figure 1 is a cross-sectional illustration of a light source according to this invention.

Detailed Description of the Invention

[0011] For a better understanding of the present invention, together with other and further objects, advantages and capabilities thereof, reference is made to the following disclosure and appended claims taken in conjunction with the above-described drawings.

[0012] References to the color of a phosphor, LED, laser or conversion material refer generally to its emission color unless otherwise specified. Thus, a blue LED emits a blue light, a yellow phosphor emits a yellow light and so on.

[0013] The glass composite wavelength converters of this invention are comprised of phosphor particulates that are dispersed in a solid glass matrix. The glass is selected from a soda-lime glass (e.g., Corning 0215), a $Sb_2O_3-Bi_2O_3-B_2O_3$ glass, a phosphate glass (e.g., SCV-13 SEM-COM Co.), a $Bi_2O_3-ZnO-B_2O_3$ glass, and a $PbO-ZnO-B_2O_3$ glass. Preferably, the glass has a glass transition temperature that is less than about 400°C and more preferably less than about 300°C. The glass should be substantially transparent to the primary light emitted by the excitation source, e.g. a blue LED chip, and also substantially transparent to the secondary light emitted by the phosphor as a result of the conversion of the primary light. In this context, substantially transparent means that the glass preferably transmits at least about 80%, more preferably at least about 90%, or even more preferably at least about 95% of the primary and secondary light. The glasses preferably should also be resistant to devitrification. If they easily devitrify during the manufacturing process, the formed crystalline phases may act as scattering/absorption centers, resulting light loss. It is also preferred that the glasses be humidity and weather resistant.

[0014] Non-limiting examples of suitable phosphors that may be used in the glass composite wavelength converters of this invention include phosphors such as oxide-based phosphors and nitride-based phosphors. Oxide–based phosphors may include cerium-activated garnet phosphors which may be represented by the formula $A_3B_5O_{12}$:Ce, wherein A is Y, Sc, La, Gd, Lu, or Tb and B is Al, Ga or Sc. More preferably, the oxide-based phosphor is at least one of $Y_3Al_5O_{12}$:Ce (abbr. YAG:Ce), $(Y,Gd)_3Al_5O_{12}$:Ce (abbr. YGdAG:Ce), and $Lu_3Al_5O_{12}$:Ce (abbr. LuAG:Ce). Examples of nitride-based phosphors include $MAlSiN_3$:Eu, wherein M is selected from Ca, Sr, and Ba, and $M_2Si_5N_8$:Eu, wherein M is selected from Ca, Sr, and Ba. Other possible phosphors include oxynitride phosphors such as $MSi_2O_2N_2$:Eu, wherein M is selected from Ca, Sr, and Ba, and silicate phosphors such as $BaMgSi_4O_{10}$:Eu and M_2SiO_4:Eu, wherein M is selected from Ca, Sr, and Ba.

[0015] In a preferred embodiment, the glass composite wavelength converters contain a red phosphor, and even more preferably a red narrow band phosphor. Red phosphors are very important for generating a warm white color and a high color rendering index in phosphor-converted LEDs. They can also be used for full conversion red LEDs where red phosphors absorb all the blue/UV light from LED chip and convert it to a red emission. Compared to direct InGaAlP LEDs, phosphor-converted red LEDs have much better thermal stability. However the red emission usually doesn't provide high lumens due to the spectral wavelength. The conversion between radiometric (W) and photometric units (lumens) is related to the eye sensitivity function, or the luminous efficiency function $V(\lambda)$. It has a maximum value at 555 nm and decreases drastically towards blue and red wavelengths. Luminous efficacy of radiation (LER) is the ratio of lumens output per watt of optical radiation output, describing how well a light source produces visible light. LER is dependent on a light source's emission spectral shape and position. Emissions in the red wavelength region have a very low $V(\lambda)$ value, which yield low lumens. At a similar emission wavelength, the wider the red emission, the lower the LER. For example, a red $(Ca,Sr,Ba)_2Si_5N_8$:Eu phosphor with an emission dominant wavelength Ld about 602 nm and full width at half maximum (FWHM) of 96nm has a LER of 193 lm/W. A red narrow band phosphor $Sr(Sr_xCa_{1-x})Si_2Al_2N_6$:Eu with a similar emission Ld but narrower

FWHM has a LER of 221 lm/W. Thus red narrow band phosphors are preferred in some applications as they have the potential to improve lumens efficacy.

[0016] The glass composite wavelength converters preferably are made by sintering a glass/phosphor powder mixture under pressure in a spark plasma sintering (SPS) process. The sintering temperature in the SPS process is much lower than the prior art methods wherein glasses are heated to a high temperature so that they soften or melt. This reduces the potential damage to phosphors, particularly nitride-based phosphors, while keeping the porosity low by using a pressure sintering process.

[0017] In a preferred method, the glass powder and at least one type of phosphor powder are combined in a desired weight ratio and mixed thoroughly. An amount of the glass/phosphor mixture is placed into a graphite die and sintered by SPS under a N_2 atmosphere using a maximum pressure of about 50 MPa. The peak sintering temperature is held only for a few minutes to minimize damage to the phosphor.

[0018] The particle size of the glass and phosphor powders is preferably less than 100μm, and more preferably less than 25μm. The smaller particle size assures the homogeneity of mixture and color consistency of the glass composite wavelength converters. Additionally, other inorganic powders may also be added to the phosphor/glass mixtures to adjust scattering or increase thermal conductivity. In particular, TiO_2, ZrO_2, Al_2O_3, AlN, or synthetic diamond powders may be added to the phosphor/glass powder mixture prior to sintering.

<u>Example 1 – soda-lime glass/$(Ca,Sr,Ba)_2Si_5N_8$:Eu phosphor</u>

[0019] Several glass composite wavelength converters were made using a soda-lime glass powder (glass transition temperature, Tg, of about 560°C) and a $(Ca,Sr,Ba)_2Si_5N_8$:Eu phosphor powder. The glass was ground to a powder with a WC mortar and pestle and sieved with a #60 mesh sieve. The glass powder was mixed with the $(Ca,Sr,Ba)_2Si_5N_8$:Eu phosphor powder to form three mixtures having 15, 26, and 32 weight percent (wt.%) of the phosphor. A 0.8 gram amount of each mixture was SPS sintered at a temperature ranging from 520 to 600°C for several minutes under a maximum pressure of 50 MPa to form a glass composite wavelength converter in the form of a sintered disc. The sintered discs were ground and thinned to a thickness of about 120 μm. Optical performance was measured by placing the discs on a platform with 0.6 mm diameter pinhole through which blue light (448nm) from an LED was directed onto the disc. The transmitted light and converted light were measured by an integrating sphere positioned above the disc.

[0020] Table 1 gives the optical measurement results from the several samples sintered under various temperatures. Conversion efficacy is expressed in lumens/optical blue watt (lm/W) and conversion efficiency as a percentage. Color coordinates (Cx and Cy) are given including the unconverted blue excitation and without (w/o blue). L_{dom} is the dominant wavelength emitted by the converter. LER is the luminous efficacy of radiation and is the ratio of luminous flux to radiant flux (lm/W). LER can be regarded as the theoretical maximum efficacy of a light source. The SPS sintering conditions are also provided for each sample.

[0021] The data show that the conversion efficiency of the wavelength converters decreases as the sintering temperature increases. At 600°C, the conversion efficiency is almost zero, indicating severe damage to the nitride-based phosphor. A comparison of the emission spectra for the $(Ca,Sr,Ba)_2Si_5N_8$:Eu phosphor and the glass composite converter sintered at 520°C show that the emission spectrum for the converter is wider than the phosphor spectrum at left side of the spectra, indicating the phosphor may have experienced some reaction with the glass even at 520°C. Thus, a glass with a lower glass transition temperature is preferred in order to further limit any reaction between the phosphor and glass.

Example 2 – Sb_2O_3-Bi_2O_3-B_2O_3 glass /$(Ca,Sr,Ba)_2Si_5N_8$:Eu phosphor

[0022] A glass composite wavelength converter was formed using a Sb_2O_3-Bi_2O_3-B_2O_3 glass and the $(Ca,Sr,Ba)_2Si_5N_8$:Eu phosphor of Example 1. The Sb_2O_3-Bi_2O_3-B_2O_3 glass has a much lower glass transition temperature (Tg of 292°C) than the soda-lime glass which means that the phosphor/glass powder mixture can be sintered at a lower temperature in the SPS process. In particular, the phosphor/glass mixture was sintered at 285°C for 4 minutes under a pressure of 50MPa. Optical measurements on the glass composite converter are given in Table 2. The conversion efficiency of converter sintered at 285°C was measured to be 25.1% which is much higher than the samples in Example 1. In addition, a comparison of the emission spectra for the

$(Ca,Sr,Ba)_2Si_5N_8$:Eu phosphor and the glass composite converter showed that they were almost identical, indicating there was essentially no damage to the phosphor in the composite converter.

Example 3 – soda-lime glass/ YAG:Ce phosphor

[0023] A glass composite wavelength converter was made using a powder mixture containing soda-lime glass powder and 30 wt.% of a YAG:Ce phosphor powdwer. The mixture was sintered at 560°C in an SPS process. The emission spectrum of the converter was substantially identical to emission spectrum of the YAG:Ce phosphor prior to sintering indicating that there was very little damage to the phosphor during the sintering. Optical measurements on the glass composite converter are given in Table 3. The conversion efficiency of the glass composite wavelength converter was measured to be 32.2%. Unlike the nitride-based phosphor of Example 1, the YAG:Ce phosphor as an oxide-based phosphor is shown to be more resistant to the damage from the soda-lime glass.

Example 4 – soda-lime glass/ $CaAlSiN_3$:Eu phosphor

[0024] A glass composite wavelength converter was made using a powder mixture of soda-lime glass and 30 wt% of a $CaAlSiN_3$:Eu phosphor. The mixture was sintered at 560°C in an SPS process. The emission spectrum of the converter was slightly wider than the emission spectrum of the $CaAlSiN_3$:Eu phosphor prior to sintering. Optical measurements on the glass composite converter are given in Table 4. The measured conversion efficiency of 11.8% is better than the $(Ca,Sr,Ba)_2Si_5N_8$:Eu phosphor in soda lime glass (Example 1) when sintered at a similar temperature.

Example 5 – soda-lime glass/ YAG:Ce/$CaAlSiN_3$:Eu phosphor (warm white)

[0025] Glass composite wavelength converters for warm white lighting applications were made using a powder mixture of soda-lime glass, 25.2 wt.% of a YAG:Ce phosphor and 16 wt.% of a $CaAlSiN_3$:Eu phosphor. Amounts of the mixture were sintered at two different temperatures, 560°C and 580°C. As may be expected, there was more damage to the $CaAlSiN_3$:Eu phosphor at 580°C than at 560°C. Optical measurements on the samples are given in Table 5. The color distribution measured from multiple points on the converters demonstrated that a warm white color temperature of 3000K is possible when the ratio of these two phosphors is optimized.

Example 6. zinc phosphate glass/(Ca,Sr,Ba)$_2$Si$_5$N$_8$:Eu phosphor

[0026] Glass composite wavelength converters were made using a zinc phosphate glass powder (SCV-13 from SEM-COM Company, Toledo, Ohio) and a (Ca,Sr,Ba)$_2$Si$_5$N$_8$:Eu phosphor powder. The zinc phosphate glass powder had a particle size distribution of 99.5% < 37μm (400 mesh) and a glass transition temperature of 292°C. The glass powder was mixed with the (Ca,Sr,Ba)$_2$Si$_5$N$_8$:Eu phosphor powder to form a mixture having 33 wt.% of the phosphor. Amounts of the mixture (0.7 to 0.8 g) were SPS sintered at temperatures ranging from 350 to 400°C for several minutes under a maximum pressure of 50 MPa to form a glass composite wavelength converters in the form of sintered discs. The sintered discs were ground and thinned to a thickness of about 76 to 121 μm.

[0027] Table 6 gives the optical measurement results from the several samples sintered under various temperatures. The data show that the conversion efficiency of the wavelength converters ranged up to 26% which was almost twice the highest value (13.9%) for the (Ca,Sr,Ba)$_2$Si$_5$N$_8$:Eu/soda-lime glass samples (Example 1). This indicates that the lower SPS temperatures reduced the damage to the (Ca,Sr,Ba)$_2$Si$_5$N$_8$:Eu phosphor, contributing to the performance improvement. A comparison of the emission spectra for the (Ca,Sr,Ba)$_2$Si$_5$N$_8$:Eu phosphor and the glass composite wavelength converter were almost identical indicating no damage to the phosphor during the process.

Example 7. zinc phosphate glass/LuAG:Ce phosphor

[0028] Glass composite wavelength converters were made using the zinc phosphate glass powder of Example 6 and a LuAG:Ce phosphor powder. The glass powder was mixed with the LuAG:Ce phosphor powder to form a mixture having 27.4 wt.% of the phosphor. Amounts of the mixture (0.7 to 0.8 g) were SPS sintered at 320°C and 340°C for several minutes under a maximum pressure of 50 MPa to form glass composite wavelength converters in the form of sintered discs. The sintered discs were ground and thinned to a thickness of about 120μm.

[0029] Table 7 gives the optical measurement results from the samples sintered at the different temperatures. In both cases, the conversion efficiency was about 50% with a conversion efficacy of about 140 lm/W.

Example 8. zinc phosphate glass/ $CaAlSiN_3$:Eu phosphor

[0030] Glass composite wavelength converters were made using the zinc phosphate glass powder of Example 6 and a $CaAlSiN_3$:Eu phosphor powder. The glass powder was mixed with the $CaAlSiN_3$:Eu phosphor powder to form a mixture having 30.2 wt.% of the phosphor. Amounts of the mixture (0.7 to 0.8 g) were SPS sintered at 320°C and 340°C for several minutes under a maximum pressure of 50 MPa to form glass composite wavelength converters in the form of a sintered discs. The sintered discs were ground and thinned to a thickness of about 104 to 123μm.

[0031] Table 8 gives optical measurement results from the samples sintered at the different temperatures. The highest conversion efficiency of the wavelength converters was 23.3%. A comparison of the emission spectra of the $CaAlSiN_3$:Eu phosphor and the glass composite wavelength converter showed that the spectra were almost identical indicating no damage to the phosphor during the process.

Example 9. LuAG:Ce + $CaAlSiN_3$:Eu in zinc phosphate glass

[0032] A glass composite wavelength converter for warm white lighting applications was made using a powder mixture of the zinc phosphate glass of Example 6 and 37 wt.% of a mixture of LuAG:Ce and $CaAlSiN_3$:Eu phosphors. The phosphor mixture had a LuAG:Ce to $CaAlSiN_3$:Eu weight ratio of 3.5 to 1. The mixture was sintered at 340°C. Optical measurements on the samples are given in Table 9. The color distribution measured from multiple points demonstrated that a converter with a high efficiency, high color rendering index (CRI), and warm white color temperature of 3000K is possible when the ratio of these two phosphors is optimized. In particular, a correlated color temperature of 2821K, a high CRI of 93 and a conversion efficacy of 78.7 lm/W was demonstrated.

Example 10. $Sr(Sr_aCa_{1-a})Si_2Al_2N_6$:Eu in zinc phosphate glass

[0033] The zinc phosphate glass powder of Example 6 and a red narrow band $Sr(Sr_aCa_{1-a})Si_2Al_2N_6$:Eu phosphor powder are combined and mixed in weight ratio of

2:1. About 0.8 grams of mixed powder is put into a graphite die with 15 mm inner diameter. The samples are sintered by spark plasma sintering (SPS) with a maximum force of 50kN and a maximum current of 1500A. The sample is sintered under N_2 atmosphere, at peak temperature for a few minutes with the pressure applied.

[0034] One sample of the $Sr(Sr_aCa_{1-a})Si_2Al_2N_6$:Eu phosphor in zinc phosphate glass is sintered at 350°C for half minute under 50 MPa pressure. The sintered disc was ground and thinned to a thickness of about 115 µm to form the converter. The color of the sample was red, indicating the phosphor survived SPS process. Its optical performance was measured by placing the disc on a platform with 0.6 mm diameter pinhole through which blue light (448nm) from a LED was directed onto the disc. The transmitted light and converted light were measured by an integrating sphere positioned above the disc. Optical measurements on the converter sample are given in Table 10. The shape of the emission spectrum of the phosphor-in-glass converter was almost identical to powdered phosphor, showing the $Sr(Sr_aCa_{1-a})Si_2Al_2N_6$:Eu phosphor survived the SPS process with almost no damage from the glass. The left side of converter emission spectrum was slightly shifted to the red compared to powdered phosphor, which is likely caused by the self absorption from scattering in converter. Due to the self-absorption, the emission width of phosphor-in-glass converter is even narrower than the phosphor. Conversion efficacy (CE) was 44.3 lm/W.

[0035] Figure 1 illustrates the use of a glass composite wavelength converter according to this invention in a phosphor-converted LED (pc-LED) configuration. In particular, a light source 100 in the form of a pc-LED having a glass composite wavelength converter 104 is shown. The glass composite wavelength converter is comprised of particulates of at least one phosphor that are dispersed in a solid matrix of a glass. Preferably, the phosphor is a nitride-based phosphor. The composite converter 104 generally has a thickness of between 20µm and 500µm and preferably between 100µm and 250µm. In a preferred embodiment, the composite converter has the shape of a flat plate, although it is not limited to such.

[0036] Primary light 106 emitted from light-emitting surface 107 of blue-emitting LED die 102 passes into composite converter 104 which converts at least a portion of the blue light into a secondary light 116 having a different peak wavelength, e.g., a yellow or red light. Preferably, the blue primary light 106 has a peak wavelength in the range of 420nm to 490nm. The color of the light eventually emitted from the light-emitting surface 120 of composite converter 104 will depend on the ratio of the amount of unconverted primary light 106 that passes through the converter to the amount of primary light that is converted to secondary light 116 within the converter. In some applications, all of the primary light 106 is absorbed and only converted light 116 is emitted (full conversion.)

[0037] While there have been shown and described what are at present considered to be preferred embodiments of the invention, it will be apparent to those skilled in the art that various changes and modifications can be made herein without departing from the scope of the invention as defined by the appended claims.

Table 1 - $(Ca,Sr,Ba)_2Si_5N_8$:Eu phosphor in soda lime glass

Sample (wt% of phosphor)	Thickness (µm)	Cx	Cy	CE (lm/W)	Conv. Eff.	w/o blue				SPS condition (°C/Min/MPa)
						L_{dom}(nm)	Cx	Cy	LER	
1-1 (15%)	119	0.2270	0.0716	24.0	13.9%	598.1	0.6171	0.3809	212	520/3.5/50
1-2 (26%)	124	0.1771	0.0327	18.9	9.6%	595.2	0.5989	0.3946	223	530/5/25
1-3 (32%)	129	0.4233	0.2118	13.2	8.0%	601.6	0.6337	0.3655	190	530/5/50
1-4 (15%)	122	0.2048	0.0548	15.9	7.9%	597.3	0.6119	0.3849	215	550/5/25-38
1-5 (32%)	127	0.1921	0.0467	0.5	0.2%	597.2	0.6087	0.3849	203	600/5/20

Table 2 - $(Ca,Sr,Ba)_2Si_5N_8$:Eu phosphor in Sb_2O_3-Bi_2O_3-B_2O_3 glass

Sample (wt% of phosphor)	Thickness (µm)	Cx	Cy	CE (lm/W)	Conv. Eff.	w/o blue				SPS condition (°C/Min/MPa)
						L_{dom}(nm)	Cx	Cy	LER	
2-1 (32%)	128	0.6109	0.3399	40.6	25.1%	602.9	0.6395	0.36	190	285/4/50

Table 3 – YAG:Ce in soda lime glass

Sample (wt% of phosphor)	Thickness (µm)	Cx	Cy	CE (lm/W)	Conv. Eff.	w/o blue				SPS condition (°C/Min/MPa)
						L_{dom}(nm)	Cx	Cy	LER	
S1170 (30%)	135	0.3201	0.2865	86.8	32.2%	573.2	0.4605	0.5241	420	560/3/50

Table 4 - $CaAlSiN_3$:Eu phosphor in soda lime glass

Sample (wt% of phosphor)	Thickness (µm)	Cx	Cy	CE (lm/W)	Conv. Eff.	w/o blue				SPS condition (°C/Min/MPa)
						L_{dom}(nm)	Cx	Cy	LER	
S1169 (30%)	140	0.4162	0.1942	14.5	11.8%	605	0.6474	0.3514	142	560/3/50

Table 5 - YAG:Ce + $CaAlSiN_3$:Eu in soda lime glass

Sample	Thickness(µm)	Cx	Cy	CE (lm/W)	Conv. Eff.	w/o blue				SPS condition (°C/Min/MPa)
						L_{dom}(nm)	Cx	Cy	LER	
5-1	141	0.5214	0.4201	27.4	11.3%	585.8	0.5459	0.4476	285	560/5/50
5-2	133	0.4529	0.4404	40.6	12.5%	577.6	0.4923	0.4979	385	580/5/50

Table 6 - $(Ca,Sr,Ba)_2Si_5N_8$:Eu phosphor in zinc phosphate glass

Sample (wt% of phosphor)	Thickness(µm)	Cx	Cy	CE (lm/W)	Conv. Eff.	w/o blue				SPS condition (°C/Min/MPa)
						L_{dom}(nm)	Cx	Cy	LER	
6-1 (33%)	121	0.6230	0.3464	41	25.4%	603.2	0.6407	0.3588	188	400/1/10
6-2 (33%)	76	0.6026	0.3439	39.2	23.12%	601.5	0.6326	0.3659	199	350/2/50
6-3 (33%)	109	0.6319	0.3549	42.5	26.0%	602.9	0.6392	0.3601	191	350/1/50

Table 7 - LuAG:Ce phosphor in zinc phosphate glass

Sample (wt% of phosphor)	Thickness(µm)	Cx	Cy	CE (lm/W)	Conv. Eff.	w/o blue				SPS condition (°C/Min/MPa)
						L_{dom}(nm)	Cx	Cy	LER	
7-1 (27.4%)	123	0.2405	0.2390	138	49.4%	559.7	0.364	0.5734	458	320/3/50
7-2 (27.4%)	122	0.2416	0.2420	140	50.0%	559.5	0.363	0.5715	456	340/3/50

Table 8 - $CaAlSiN_3$:Eu phosphor in zinc phosphate glass

Sample (wt% of phosphor)	Thickness(µm)	Cx	Cy	CE (lm/W)	Conv. Eff.	w/o blue				SPS condition (°C/Min/MPa)
						L_{dom}(nm)	Cx	Cy	LER	
8-1 (30.2%)	104	0.6097	0.3077	19	17.3%	608.3	0.6599	0.3395	129	320/3/50
8-2 (30.2%)	123	0.6127	0.3061	25	23.3%	609.1	0.6624	0.3371	125	340/3/50

Table 9- LuAG:Ce + $CaAlSiN_3$:Eu in zinc phosphate glass

Sample (wt% of phosphor)	Thickness(µm)	Cx	Cy	CE (lm/W)	Conv. Eff.	w/o blue				SPS condition (°C/Min/MPa)
						L_{dom}(nm)	Cx	Cy	LER	
9-1 (37%)	128	0.4369	0.3818	78.7	34.4%	581.0	0.5021	0.4672	277	340/1/50

Table 10 - $Sr(Sr_aCa_{1-a})Si_2Al_2N_6$:Eu in zinc phosphate glass

Sample (wt% of phosphor)	Thickness(μm)	Cx	Cy	CE (lm/W)	Conv. Eff.	w/o blue				SPS condition (°C/Min/MPa)
						L_{dom}(nm)	Cx	Cy	LER	
10-1 (33%)	115	0.5983	0.3127	44.3	26.6%	605.9	0.6515	0.3481	198	350/0.5/50

Claims

What is claimed is:

1. A glass composite wavelength converter comprising phosphor particulates dispersed in a solid glass matrix, the glass matrix comprising a glass selected from a soda-lime glass, a Sb_2O_3-Bi_2O_3-B_2O_3 glass, a phosphate glass, a Bi_2O_3-ZnO-B_2O_3 glass, and a PbO-ZnO-B_2O_3 glass, wherein the phosphor particulates convert at least a portion of a primary light into a secondary light and the glass is substantially transparent to the primary light and the secondary light.

2. The converter of claim 1 wherein the glass has a glass transition temperature that is less than about 400°C.

3. The converter of claim 1 wherein the glass has a glass transition temperature that is less than about 300°C.

4. The converter of claim 1 wherein the phosphor particulates comprise at least one phosphor selected from:

$A_3B_5O_{12}$:Ce, wherein A is Y, Sc, La, Gd, Lu, or Tb and B is Al, Ga or Sc;
$MAlSiN_3$:Eu, wherein M is selected from Ca, Sr, and Ba;
$M_2Si_5N_8$:Eu, wherein M is selected from Ca, Sr, and Ba;
$MSi_2O_2N_2$:Eu, wherein M is selected from Ca, Sr, and Ba;
$BaMgSi_4O_{10}$:Eu; and
M_2SiO_4:Eu, wherein M is selected from Ca, Sr, and Ba.

5. The converter of claim 4 wherein the glass is a zinc phosphate glass and the phosphor is selected from:

$M_2Si_5N_8$:Eu, wherein M is selected from Ca, Sr, and Ba; and
$MAlSiN_3$:Eu, wherein M is selected from Ca, Sr, and Ba.

6. The converter of claim 4 wherein the glass is a Sb_2O_3-Bi_2O_3-B_2O_3 glass and the phosphor is $M_2Si_5N_8$:Eu, wherein M is selected from Ca, Sr, and Ba.

7. The converter of claim 4 wherein the glass is a soda-lime glass and the phosphor is $MAlSiN_3$:Eu, wherein M is selected from Ca, Sr, and Ba.

8. The converter of claim 7 wherein the converter further contains particulates of a YAG:Ce phosphor.

9. The converter of claim 1 wherein the converter has a conversion efficiency of at least about 20%.

10. The converter of claim 1 wherein the converter has a conversion efficiency of at least about 40%.

11. The converter of claim 1 wherein the phosphor particulates comprise a $Sr(Sr_aCa_{1-a})Si_2Al_2N_6$:Eu phosphor.

12. The converter of claim 11 wherein the glass is a zinc phosphate glass.

13. A light source, comprising:

a light emitting diode (LED) that emits a primary light; and

a glass composite wavelength converter comprising phosphor particulates dispersed in a solid glass matrix, the glass matrix comprising a glass selected from a soda-lime glass, a Sb_2O_3-Bi_2O_3-B_2O_3 glass, a phosphate glass, a Bi_2O_3-ZnO-B_2O_3 glass, and a PbO-ZnO-B_2O_3 glass, wherein the phosphor particulates convert at least a portion of the primary light into a secondary light and the glass is substantially transparent to the primary light and the secondary light.

14. The light source of claim 13 wherein the glass has a glass transition temperature that is less than about 400°C.

15. The light source of claim 13 wherein the glass has a glass transition temperature that is less than about 300°C.

16. The light source of claim 13 wherein the phosphor particulates comprise at least one phosphor selected from:

$A_3B_5O_{12}$:Ce, wherein A is Y, Sc, La, Gd, Lu, or Tb and B is Al, Ga or Sc;

$MAlSiN_3$:Eu, wherein M is selected from Ca, Sr, and Ba;

$M_2Si_5N_8$:Eu, wherein M is selected from Ca, Sr, and Ba;

$MSi_2O_2N_2$:Eu, wherein M is selected from Ca, Sr, and Ba;

$BaMgSi_4O_{10}$:Eu; and

M_2SiO_4:Eu, wherein M is selected from Ca, Sr, and Ba.

17. The light source of claim 16 wherein the glass is a zinc phosphate glass and the phosphor is selected from:

$M_2Si_5N_8$:Eu, wherein M is selected from Ca, Sr, and Ba; and

$MAlSiN_3$:Eu, wherein M is selected from Ca, Sr, and Ba.

18. The light source of claim 16 wherein the glass is a Sb_2O_3-Bi_2O_3-B_2O_3 glass and the phosphor is $M_2Si_5N_8$:Eu, wherein M is selected from Ca, Sr, and Ba.

19. The light source of claim 13 wherein the light source emits a warm white light having a CCT of about 3000K.

20. The light source of claim 13 wherein the converter contains a first phosphor having a formula $A_3B_5O_{12}$:Ce, wherein A is Y, Sc, La, Gd, Lu, or Tb and B is Al, Ga or Sc, and a second phosphor selected from:

$M_2Si_5N_8$:Eu, wherein M is selected from Ca, Sr, and Ba; and

$MAlSiN_3$:Eu, wherein M is selected from Ca, Sr, and Ba.

21. The light source of claim 13 wherein the converter has a conversion efficiency of at least about 20% and the converter contains a nitride-based phosphor.

22. The light source of claim 13 wherein the converter has a conversion efficiency of at least about 40%.

23. The light source of claim 13 wherein the phosphor particulates comprise a $Sr(Sr_aCa_{1-a})Si_2Al_2N_6$:Eu phosphor.

24. The light source of claim 23 wherein the glass is a zinc phosphate glass.

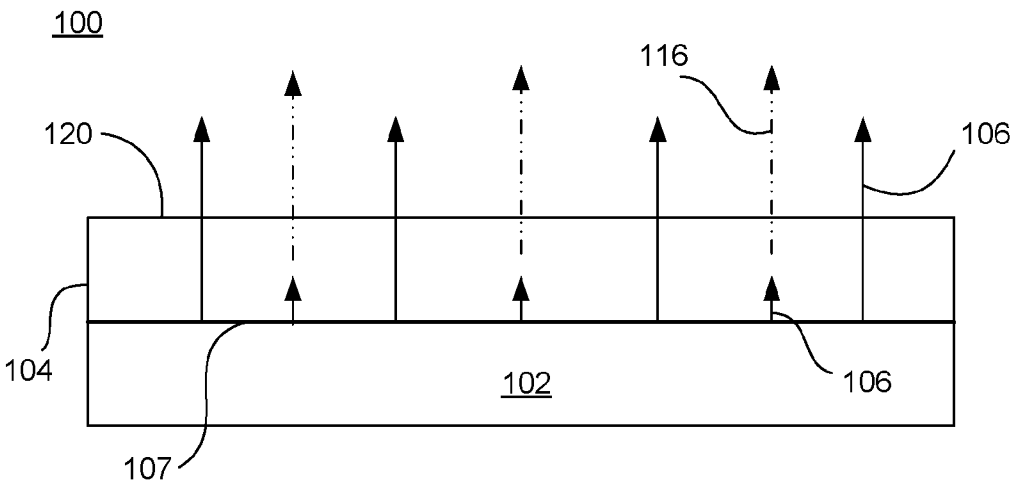

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/038632

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/77 C03C4/12
ADD. C04B35/597 C03C8/14 C03C3/12 H01L33/50 C03C14/00 C03B19/06

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)
H01L C04B C09K C03C C03B

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 practicable, search terms used)

EPO-Internal, INSPEC, WPI Data, COMPENDEX

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
15 August 2016	22/08/2016

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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