

On the stability and reliability of $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ phosphors for white LED applications

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Abstract: $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ phosphors were synthesized using high temperature solid state reactions and the reliability of the as-synthesized phosphors for White LED applications was investigated. The oxidation resistance of the phosphors was investigated by baking the phosphors at various temperatures in air for 2 hours and also at 85 °C, 85% relative humidity for 150 hours. The photo stability of the phosphor was studied by illuminating the phosphor using a high power laser diode (450 nm) at various laser fluxes. Phosphor converted LEDs were fabricated using the as-synthesized $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0$ and 0.40) phosphors. The long term stability of the fabricated LEDs was tested by keeping the LEDs at 85 °C and 85% relative humidity for 800 hrs. Even though phosphors show high thermal and chemical stability, the electroluminescent (EL) intensity of the fabricated LEDs drops by 15% after 800 hrs of operation. The degradation of EL intensity of the device might be the result of thermally assisted photo-ionization of Eu^{2+} ions in the phosphor.

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OCIS codes: (160.2540) Fluorescent and luminescent materials; (160.5690) Rare-earth-doped materials; (250.5230) Photoluminescence.

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1. Introduction

Solid state lighting (SSL) technology has been advanced over past years due to innovations in III-Nitride (InGaN and AlGaIn) based UV/Vis light emitting diodes (LEDs) which are high power pump excitation sources in phosphor converted LEDs (pc-LEDs) [1–12]. The improved efficiency in III-Nitride LEDs is a result of the use of new types of active regions [1–3,9–12], growth and substrate technologies [4–6] and micro/nano photonic structures [11,12]. The availability of deep/mid UV LEDs as excitation sources for phosphors have opened the possibility of employing UV-excited inorganic phosphors for solid state lighting [8–12]. Moreover the development of white LEDs reported here can be solely attributed to the availability of highly efficient InGaIn based LEDs. Recently extensive research has been carried out into rare earth doped nitrides or oxynitrides based phosphors, for application in GaN/InGaIn UV or blue light emitting diodes (LEDs), owing to their remarkable characteristics such as thermal and chemical stability, high quantum efficiency (QE) and large band gap [12–44]. In order to emit light in the visible region of the electromagnetic spectrum, synthesized phosphors have to absorb in the UV to blue spectral range thereby limiting the activators that can be used in these phosphors to Eu^{2+} and Ce^{3+} . In a phosphor activated with rare earth ions such as Eu^{2+} , where the optical transitions are allowed, both absorption and emission of photons occurs via direct excitation of a localized ion without any transfer of energy from the host lattice. When an activator ion is excited by this localized absorption, the luminescence process is independent of defects or impurities in the host lattice. So, a high Q.E is expected from phosphors doped with Eu^{2+} ion, where luminescence occurs via direct localized absorption. However such a high Q.E is limited as luminescence emission is largely affected by concentration quenching and thermal quenching [13–16]. The phosphors used for solid state lighting applications and /or backlight applications should have high thermal and chemical stability. The luminescent emission of the phosphors highly depends on ambient temperature and in order to avoid variation in chromaticity and brightness of white LEDs, phosphors used should have low thermal quenching. Since luminescent emission is affected by temperature, thermal quenching of the phosphors is a really big issue that can directly result in poor reliability and/or durability of the fabricated White LEDs (w-LEDs) from these phosphors. Usually thermal quenching of Eu^{2+} doped phosphors is related to thermal ionization of the Eu^{2+} ion [13]. However, the crystal structure of the host lattice is also related to thermal stability. A rigid crystal structure of a host lattice is resistant to thermal stress where the activator ions are strongly bonded to ligands. A material consisting of a weak frame

work or chemical bonds is more susceptible to thermal stress [16]. Nevertheless excellent performance of white LEDs fabricated from the oxide/nitride based phosphors has been reported [27,28]. Among the silicon based oxynitrides, Eu doped $\text{MSi}_2\text{O}_2\text{N}_2$ ($M = \text{Sr}, \text{Ba}, \text{Ca}$) is an excellent candidate owing to better thermal and chemical stability with a broad absorption band spanning from UV to the blue region of the electromagnetic spectrum [30–41]. $\text{SrSi}_2\text{O}_2\text{N}_2$ is isotypic with $\text{EuSi}_2\text{O}_2\text{N}_2$ and crystallizes into a triclinic structure and has a $P1(1)$ space group symmetry, while its Ba and Ca counterparts crystallizes into orthorhombic and monoclinic structures respectively [33–35]. By replacing Sr with Ba or Ca the PL emission wavelength can be tuned. Both Ba and Ca substitution (for Sr), results in a red shift of the PL emission spectrum [32,35]. Owing to its excellent luminescence, high quantum efficiency and high thermal stability, $(\text{SrBa})\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ phosphors have been proved as potential candidates for solid state lighting applications [32,35,41]. Being isotypic with $\text{SrSi}_2\text{O}_2\text{N}_2$, $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Si}_2\text{O}_2\text{N}_2$ also crystallizes into a triclinic structure, the detailed crystal structure of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ has been reported on by Seibald *et al.* [35]. However the thermal oxidation resistance and the reliability of the $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ phosphors and the fabricated LEDs for commercial solid state lighting applications are still unknown. Therefore information regarding thermal degradation of the phosphors used in w-LEDs, under 450 nm illumination, is valuable from a commercial point of view. Even though several oxynitride phosphors have been investigated and studied, none of them have found application in commercial w-LEDs. Being thermally and chemically stable, the poor performance and reliability of the oxynitride phosphors (reduction in the luminescent emission (EL) intensity after several hours) in an LED package (LED PKG) is a serious issue limiting the reliability of the end product. Here a detailed investigation on the stability of $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ phosphors and fabricated LEDs using the phosphor is presented.

2. Experiment

The phosphors were synthesized using a high temperature solid state reaction of the constituent components: SrCO_3 , BaCO_3 (Kojundo 99.999%), Si_3N_4 (Ube, 99.99%) and Eu_2O_3 (Alfa Aesar, 99.99%). The powders were mixed stoichiometrically and ball milled in an acetone medium and calcined at 1350 °C for 6 hours in a N_2/H_2 (95:5) atmosphere to get $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$. The concentration of Ba was varied in the range of $0.1 \leq x \leq 0.7$. Finally the resultant phosphors were washed in warm water to remove the reactant residue. The crystal structure of phosphors was analyzed using Powder X-ray diffraction using Cu K_α radiation (Bruker, D8 Advance, Germany). The room temperature Photoluminescent emission (PL) and excitation (PLE) spectra were recorded using a PMT and Xenon lamp (PSI, Korea). X-ray Photoelectron Spectroscopy (XPS) spectra were recorded using a ULVAC PHI 5000 Versaprobe (Japan) with Al anode. The quantum efficiency of the phosphors was calculated using blue LEDs (460 nm, 46.1 mW) with an integrated sphere attachment. The thermal oxidation resistance of the phosphors was studied after baking the samples at various temperatures ranging from 200 – 700 °C for two hours and humidity tests were carried out by keeping the phosphors at 85% relative humidity and at 85 °C for 150 hrs. The photo-stability of the phosphors was studied by pumping high power blue Laser diode (LD) (450 nm, 1W) and the luminescent emission characteristics were studied. The experimental set up used for high power laser characterization is shown in Fig. 1. Phosphor-converted white LEDs were fabricated using green $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$ ($x = 0$) mixed with red phosphor and yellow $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$ ($x = 0.40$) phosphor. The phosphors were mixed with silicone binder in appropriate weight ratios and finally deposited over a blue InGaN chip using a conventional phosphor dispensing method. The EL characteristics were measured using a CCD and integrating sphere. (PSI, Korea).

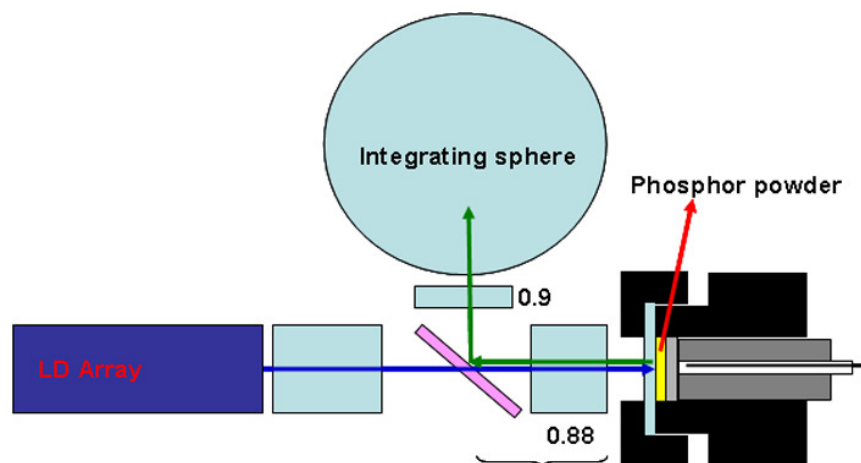


Fig. 1. Experimental set up for photo-stability studies.

3. Results and discussions

Figure 2 shows the XRD patterns of the phosphor $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0.40$) after baking/oxidizing at various temperatures.

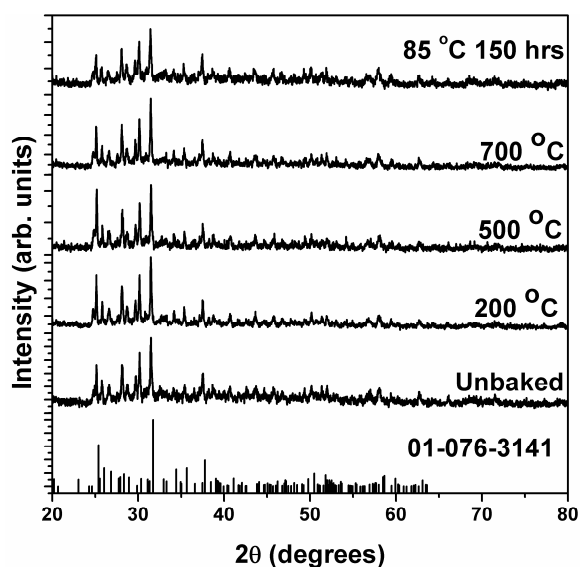


Fig. 2. XRD patterns of $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0.40$) phosphor baked at various temperatures.

The pattern for the samples baked at higher temperatures does not show much variation compared to the unbaked phosphors and matches well with standard data (PDF 01-076-3141). The calculated cell volume and lattice parameters of the unbaked and baked phosphors almost remain constant and there is no shift in the peak position of the XRD peaks even for the sample baked at 700 °C. Therefore XRD analysis shows that the crystal structure is not highly susceptible to oxidation in the range of temperatures investigated here and the samples are thermally stable.

Figure 3 shows the PL emissions of the phosphors (unbaked and baked/oxidized at various temperatures) when excited using 450 nm light from the $4f^65d \rightarrow 4f^7$ transitions in Eu^{2+} . It exhibits only a slight variation in the PL emission intensity compared to unbaked sample up to

400 °C, beyond which the emission intensity decreases. However the sample that had undergone humidity tests (85% relative humidity and 85 °C for 150 hrs) does not show much reduction in PL emission intensity, which shows the phosphors have high stability under humid environmental conditions. The decrease in the PL emission intensity at higher temperatures (500 - 700 °C) could be attributed to the thermal ionization of Eu^{2+} ions in the host lattice. Usually the temperature range in the LED package may rise up to a maximum in the range of 120 – 150 °C. Therefore the phosphor shows excellent thermal stability to oxidation in this temperature range.

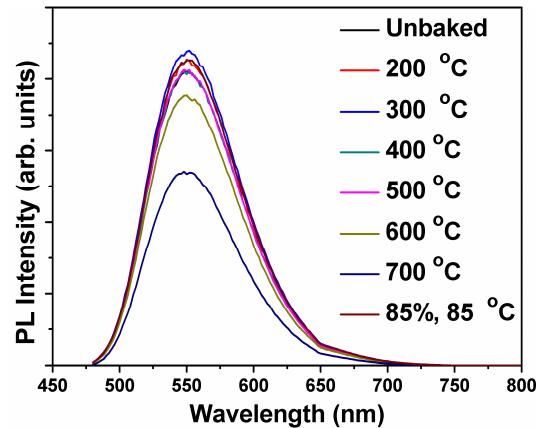


Fig. 3. PL emission spectra of $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0.40$) phosphor baked at various temperatures. ($\lambda_{\text{exc}} = 450 \text{ nm}$).

The PL excitation of the phosphors (unbaked and baked at various temperatures) is shown in Fig. 4. It is apparent from the Fig. that the PLE does not have much variation, especially, at the peak excitation wavelength. The peak excitation wavelength remains the same for different baking/oxidation temperatures. However the Commission Internationale d'Eclairage (CIE) coordinates vary with baking temperature (Fig. 5). The shifting of color coordinates is considered to be one of the serious issues in White LEDs, especially at high operating temperatures. The variation is affected by local temperature in an LED package; it cannot be reversed and results in poor quality emissions. Usually in Eu^{2+} doped phosphors such degradation is caused by thermally assisted photo-ionization [13]. Therefore if we oxidize the phosphor at higher temperatures, there exists a great chance for thermal ionization of Eu^{2+} . The CIE coordinates of the phosphors which have been baked up to temperatures of 300 °C do not show much variation.

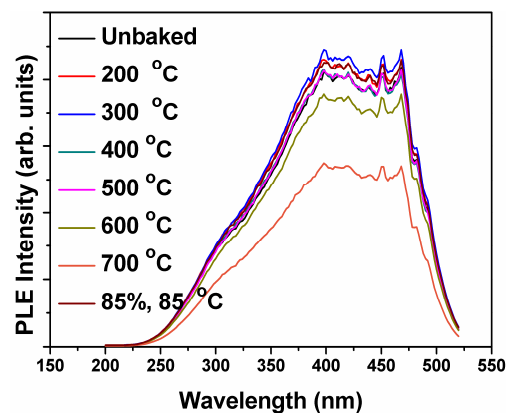


Fig. 4. PL excitation spectra of $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0.40$) phosphor baked at various temperatures ($\lambda_{\text{em}} = 560 \text{ nm}$).

However the phosphors baked at and above 400 °C shows significant variation in the coordinates which also results in low purity emissions and once again indicates the color coordinates of the phosphor do not vary with temperature in the range that usually occur in LED PKGs.

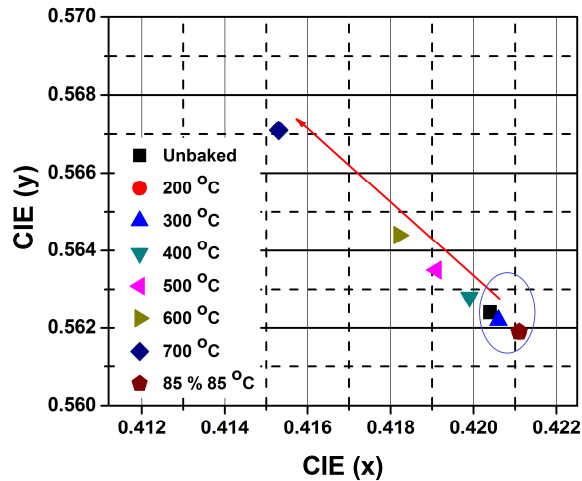


Fig. 5. Variation in CIE coordinates of PL emissions from $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0.40$) phosphor baked at various temperatures.

Figure 6 represents high resolution XPS of O 1S for various baking temperatures. The spectra can be roughly de-convoluted in to 6 peaks whose binding energy (B.E) values and full width at half maxima (FWHM) values are shown in Table 1. The major peaks were observed at ~530 eV, ~531 eV and ~532 eV, their relative intensities vary with temperature. The relative intensities of the peaks at ~530 eV and 531.3 eV decrease while that of 532.4 eV increases with temperature and the same is true for the sample that underwent humidity tests. Since oxygen is highly electronegative and, depending up on the cation that it forms bonding with, could be covalent or ionic. Therefore, usually oxides can be classified in to three types considering their ionic/covalent character, namely semi covalent oxide with a O 1S B.E in the range of 530.5 – 533 eV, normal ionic oxide with a BE range of $530 \pm 0.4\text{eV}$ and a very ionic oxide with a B.E range of 528 – 529.5 eV. Therefore the peaks at lower B.E can be assigned to Sr/Ba/Eu – O bonding. The main peaks observed at ~532 eV can be assigned to Si – O bonds in the host lattice [45,46]. However, with increases in baking temperature, we see shifts towards a higher binding energy. The sample that had undergone humidity tests shows slight shift towards higher B.E, since temperature is the factor that determines the corresponding shift. The ratio of intensities of peaks at ~532 eV to 530 eV is observed to be increased with baking temperature which means that Si is getting more and more oxidized which is also true for the sample that had undergone humidity tests. Moreover the intensity of the peak at ~532 eV increases with temperature which indicates the oxidation of the phosphor at higher temperatures. The samples baked at 85 °C and 85% relative humidity also show a similar trend which means samples are prone to oxidation even in humid conditions. However it is interesting to note that such variations in structure do not alter the PL emission characteristics of the phosphor baked at 85 °C and 85% relative humidity. However, the samples baked at higher temperatures show a reduction of PL intensity which could be due to the oxidation of samples.

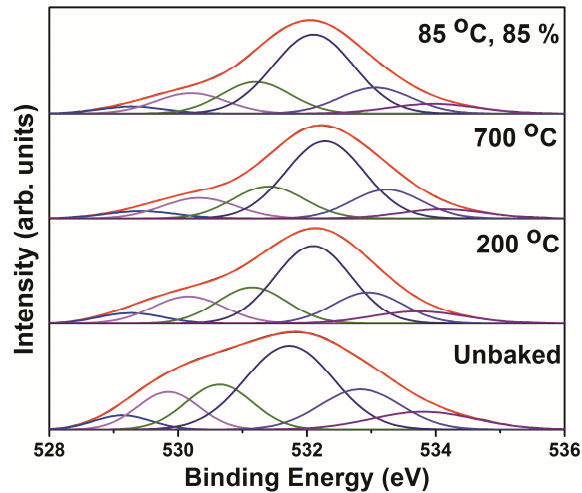


Fig. 6. O1S XPS spectra of $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0.40$) phosphor baked at various temperatures.

Table 1. The fitting parameters of the O 1S XPS peak at various temperatures

Un-baked	FWHM (eV)	Rel. Area (%)	200 °C	FWHM (eV)	Rel. Area (%)	700 °C	FWHM (eV)	Rel. Area (%)	85%, 85 °C	FWHM (eV)	Rel. Area (%)
529.2	1.05	4.4	529.3	1.18	4.7	529.4	1.31	4	529.25	1.2	3.5
529.8	1.12	12.4	530.2	1.31	13.5	530.3	1.34	13.5	530.1	1.3	10.9
530.6	1.22	16.2	531.2	1.28	17.5	531.4	1.31	17.4	531.2	1.27	16.6
531.7	1.61	39.6	532.1	1.39	41.1	532.3	1.44	45.7	532.1	1.48	48.2
532.8	1.48	17.5	533	1.3	15.3	533.2	1.28	15.4	533	1.33	14.2
533.8	1.89	9.9	533.8	1.7	7.9	534.1	1.56	6	533.9	1.62	8.1

The high resolution XPS spectra of Si2p at various baking temperatures is shown in Fig. 7. The spectra could be de-convoluted in to 4 peaks. The peaks shift towards higher B.E with temperature and humidity. In the layered structure of $(\text{SrBa})\text{Si}_2\text{O}_2\text{N}_2$, the Si forms tetrahedra connecting three N and one O forming SiN_3O [35]. There are three main peaks at ~ 100.5 eV, ~ 101.5 eV and ~ 103 eV for which first two peaks could be assigned to Si in a SiO_xN_y tetrahedral network [47]. The peaks at ~ 103 eV is due to Si^{4+} in the Si – O bonding, whose relative intensity is low in fresh unbaked phosphor but increases with temperature. However all the peaks shift to a higher B.E with increasing temperature. The sample that had undergone humidity tests also shows shift to higher B.E with respect to unbaked phosphor which clearly suggests that Si environment changes with temperature and humidity. The shift towards higher B.E is a clear indication of oxidation in samples with temperature which is also true for the sample that underwent humidity tests. It is quite interesting to note that even though humidity tested sample showed a change in Si environment, it does not affect the PL intensity from the samples. This leads to a conclusion that the major decrease in PL from the sample baked at 700 °C is due to thermal ionization of Eu^{2+} ions.

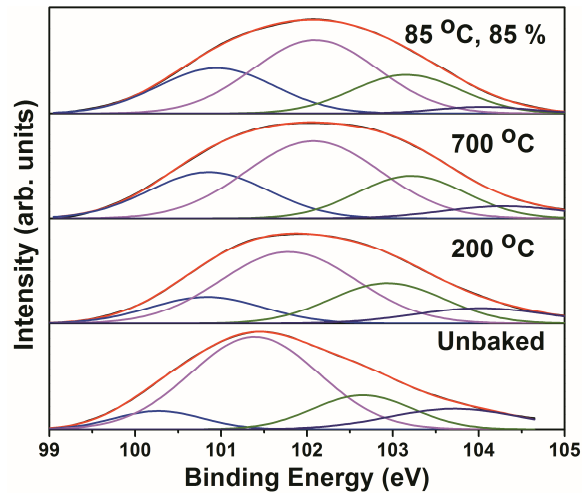


Fig. 7. Si_{2p} XPS spectra of Sr_{1-x}Ba_xSi₂O₂N₂:Eu²⁺ (x = 0.40) phosphor baked at various temperatures.

The photo stability of the phosphors was analyzed by illuminating the phosphors using a high power blue laser diode (450 nm). Figure 8 shows the luminescent emission characteristics of the phosphors when illuminated using a blue laser diode at various radiant fluxes. The corresponding variation in the emission of β -SiAlON and silicate phosphors is also shown for reference. As shown in the figure the emission from silicate phosphor begins to decrease when the input flux is 600 mW once again indicating poor stability of silicates. For β -SiAlON the emission increases almost linearly with the input radiant flux in the experimental range. It has been reported that β -SiAlON is a highly stable phosphor with low thermal quenching and high chemical stability due to its rigid crystal structure [48]. However for Sr_{1-x}Ba_xSi₂O₂N₂:Eu²⁺ (x = 0, 0.40), the emission intensity becomes saturated at higher radiant fluxes. The stability of the Sr_{1-x}Ba_xSi₂O₂N₂:Eu²⁺ phosphors are better than that of the silicates, however they are less stable than β -SiAlON. When compared to β -SiAlON, Sr_{1-x}Ba_xSi₂O₂N₂:Eu²⁺ does not have any rigid structure, which could be the reason for the lower photo-stability at higher radiant fluxes. Photo stability studies of the phosphor were also carried out by illuminating the phosphor at even higher fluxes (Fig. 9). The luminescent emission of Sr_{1-x}Ba_xSi₂O₂N₂:Eu²⁺ (x = 0, 0.40) phosphors drops above 2000 mW radiant flux. An additional experiment was carried out which retraced the laser flux and found that after reverting back to the starting/initial laser flux, there is a variation in the luminescent emission intensity from the phosphor. For low power measurements in the range 150 – 1200 mW, when one cycle is completed (from 150 mW to 1200 mW and back to 150 mW), the emission intensity drops to 90% of the initial lumen value for x = 0 phosphor while for x = 0.40 the intensity drops to 95% of the initial lumen. Interestingly for silicate, even though it shows a higher reduction in intensity at higher laser fluxes, when the laser flux reverted back to the 150 mW, its emission intensity was almost 99% of the initial value. When the experiment was carried out in a higher laser flux range (1200 – 4500 mW) all the phosphors show high degradation of their lumen value.

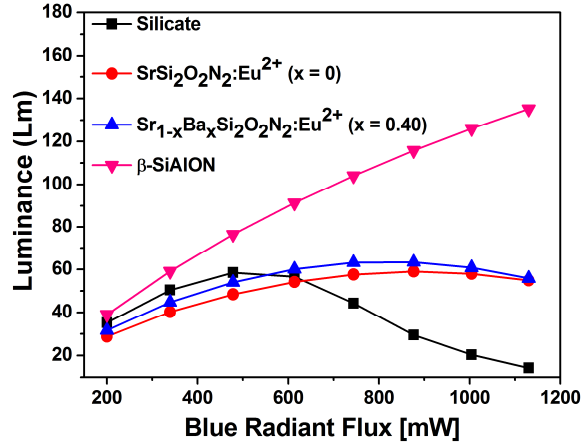


Fig. 8. Variation in luminescence of $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0$ and $x = 0.40$) phosphor at various laser fluxes.

For $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0, 0.40$) phosphors the lumen value drops to 29% and 37% of the initial value, respectively, while for silicate the luminescent intensity drops to 68% of the initial value. From the high power laser experiments it is clear that photo ionization of Eu^{2+} occurs at higher laser fluxes and once ionized the phosphor does not revert back to its original state. Even though in $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0, 0.40$) phosphors, 450 nm light does not excite the electrons from the Eu^{2+} ground state to the conduction band of the host, at higher laser flux, multi-photon absorption could take place which may excite electrons to the conduction band of the host lattice. Therefore, multi photon absorption could be the reason for the reduction in luminescence at higher laser fluxes. However, in Silicates the reason for thermal quenching has been identified as phonon assisted non-radiative transitions from excited states of the Eu^{2+} to ground state [13]. Since the experiment was carried out at room temperature, there is no thermal assistance for such non-radiative transitions. Therefore multiphoton absorption could be the reason for the degradation of luminescent intensity in silicates. However the process of conversion of Eu^{2+} to Eu^{3+} is optically reversible via a photo reduction process [49]. Therefore it reverts back to an original state keeping the luminescent intensity at 99% of the initial value. At higher laser fluxes, the intensity reduces to 68% of the initial value, which means that photo reduction is not so efficient in bringing the luminescence of the phosphor back to its original value. The photo ionization that occurs in the $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0, 0.40$) phosphor is permanent, resulting in the poor performance of the phosphor.

Two-phosphor converted (2-pc) LEDs were fabricated using a blue LED chip, $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0$) and commercial $\text{CaAlSiN}_3:\text{Eu}^{2+}$ phosphor. Similarly a 1-pcLED was fabricated using $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0.40$). For the 2-pcLED, $\text{CaAlSiN}_3:\text{Eu}^{2+}$ was used as a red phosphor to cover the red-region of the visible spectrum.

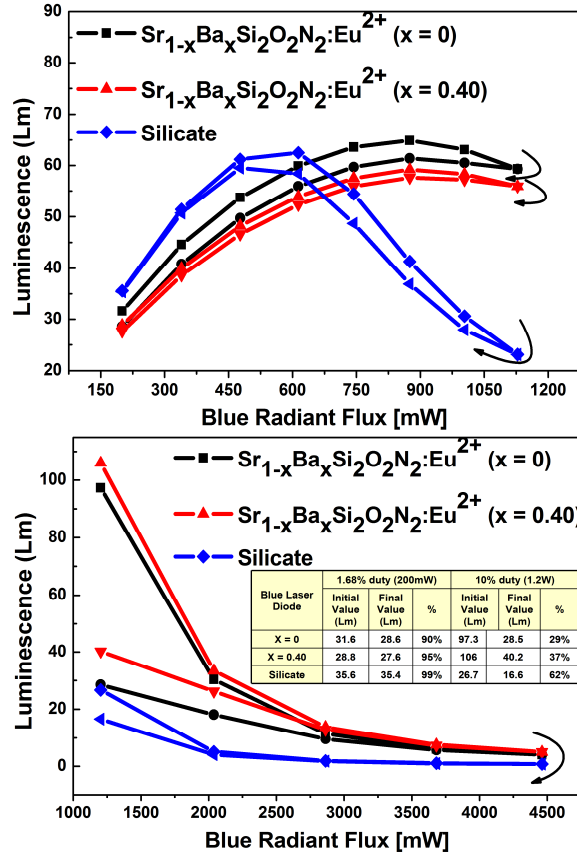


Fig. 9. Luminescence of $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0$ and $x = 0.40$) phosphor at various higher laser fluxes.

The optical parameters of the LED package (PKG), measured at 20 mA drive current, is summarized in Table 2. The fabricated LED has a correlated color temperature (CCT) of 5953 for the $x = 0$ + red-nitride LED PKG and 6290 for the $x = 0.40$ LED PKG. The CIE values of the w-LEDs fabricated are shown in Fig. 10(a). Figure 10(b) shows the variation of CIE(x) values for various fabricated w-LEDs (by changing the binder – phosphor molar ratio) with different EL intensities (Lumen).

Table 2. The LED package parameters of $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}_{0.07}^{2+}$ phosphors

Phosphor	EL (%)	CIE x	CIE y	CCT	Luminance efficacy (lm/W)	CRI
Silicate Yellow (reference)	100	0.3143	0.3375	6370	165	59.1
$\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}_{0.07}^{2+}$ ($x = 0.40$)	96	0.3159	0.3379	6290	158	56.2
$\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}_{0.07}^{2+}$ ($x = 0$) + $\text{CaAlSiN}_3:\text{Eu}^{2+}$	91	0.3220	0.3501	5953	151	89.4

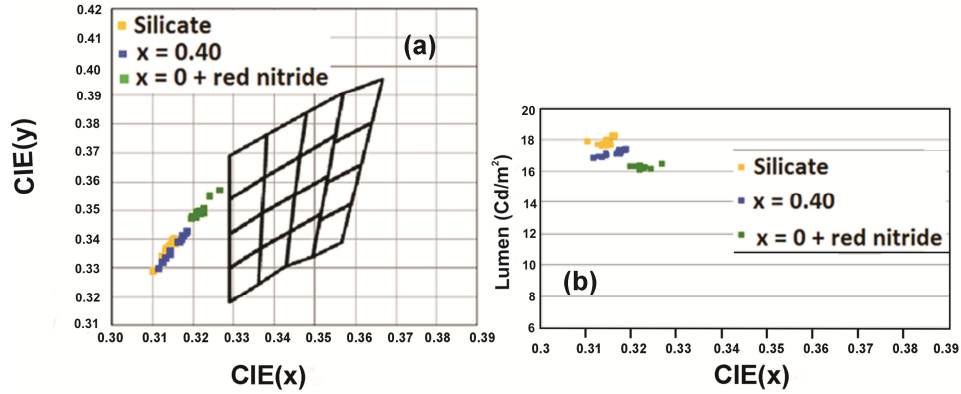


Fig. 10. (a) CIE coordinates of fabricated w-LEDs (b) variation of CIE(x) coordinate with luminescent intensity for various devices fabricated.

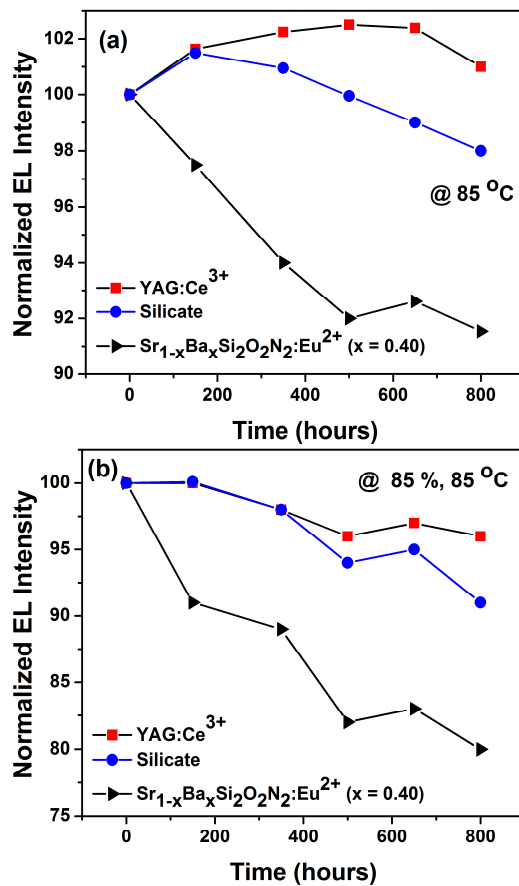


Fig. 11. Variation of EL emission from the fabricated w-LEDs with time (a) at 85 °C (b) at 85 °C and 85% relative humidity.

Figure 11(a) shows the temporal variation of EL emissions from the fabricated w-LED at 85 °C and Fig. 11(b) shows the corresponding variation at 85 °C and 85% relative humidity. The phosphor shows high degradation of emission intensity with time, reducing to 90% of the maximum within 800 hours for the device kept at 85 °C while for the one kept at 85 °C and

85% relative humidity the EL intensity reduces to 80% of the maximum in 800 hours. Comparatively, YAG:Ce³⁺ which shows poor thermal stability is much more stable and reliable than oxynitride phosphors. This is a serious drawback of the Sr_{1-x}Ba_xSi₂O₂N₂:Eu²⁺ phosphors even though they show excellent thermal stability when under no photo irradiation. The quenching of the luminescence with temperature of the 5d – 4f emission of Eu²⁺ has been a matter of investigation for several decades. Various quenching models have been suggested in literature. Blasse et al reported that quenching is due to the large displacement between excited and ground states of Eu²⁺ in the configuration coordinate diagram [50]. Thermally excited holes from the Eu²⁺ ground state to the valence band of the host semiconductor has also been suggested as the reason for quenching of the luminescence in certain thiogallates [51]. However, Dorenbos concluded that the most likely mechanism for the quenching of luminescence is thermally assisted excitation of electrons from the Eu²⁺ excited state to the conduction band of the host and in most of the hosts the excited state of Eu²⁺ lies within about 1 eV from the bottom of the conduction band [51]. However, thermal quenching of Sr_{1-x}Ba_xSi₂O₂N₂:Eu²⁺ phosphors is very high which means the quenching of luminescence occurs at high temperatures. Therefore, it is hard for an electron to excite from excited states of Eu²⁺ to the conduction band with thermal assistance only, especially at 85 °C.

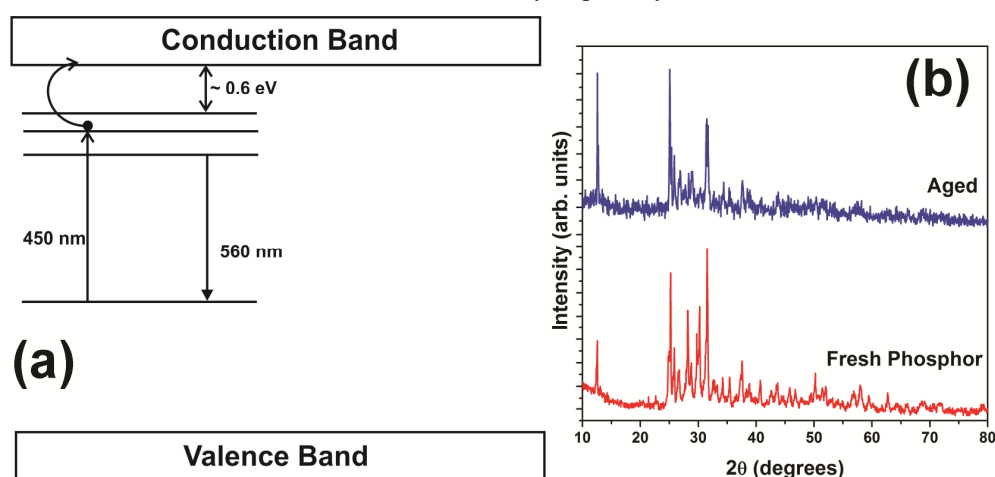


Fig. 12. (a) Schematic diagram of thermally assisted photo-ionization in Sr_{1-x}Ba_xSi₂O₂N₂:Eu²⁺ (x = 0.40) phosphor (b) The XRD pattern of aged and fresh phosphor.

Moreover the crystal structure and peak emission wavelength do not vary with temperature, as can be seen from our experimental results. XRD analysis of phosphor that had undergone ageing (800 hrs) was also carried out (Fig. 12(b)). Other than some noise due to silicone binder in the material, the peak positions and patterns were similar to that of fresh phosphor. Therefore structural changes of the phosphors that may cause the poor performance can be ruled out. In order to verify for any change in the local environment, the XPS of the aged samples was also analyzed (figure not shown). When compared to fresh phosphor, aged phosphor does show some oxidation, as observed in the case of the baked phosphors. Therefore, a plausible explanation for the degradation mechanism of the phosphor could be thermally assisted photo-ionization of electrons from Eu²⁺ excited states to the conduction band of the host. (The schematic model for thermally assisted photo-ionization is shown in Fig. 12(a)). However more studies are necessary to elucidate the reason for poor performance of the phosphors in a PKG.

4. Conclusion

In summary the long term reliability of Sr_{1-x}Ba_xSi₂O₂N₂:Eu²⁺ (x = 0 and x = 0.40) oxynitride phosphors made using solid state synthesis were investigated. The phosphor exhibits high oxidation resistance. The luminescent intensity of the phosphors becomes saturated when

irradiated using a laser diode emitting at 450 nm and at high laser fluxes the PL emission reduces drastically. After irradiating the phosphors using high laser flux, the luminescent emission of the phosphor drops significantly causing serious damage to the phosphor efficacy. Phosphor converted LEDs were fabricated using $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x = 0$ and $x = 0.40$) phosphors. A 2-pc-LED was fabricated with $x = 0$ phosphor and $\text{CaAlSiN}_3:\text{Eu}^{2+}$ (used as a red phosphor), while a 1-pc LED was fabricated with $x = 0.40$ phosphor. Even though the fabricated LEDs show high luminance, the luminance decreases over time. The luminance of the fabricated pc-LED drops by 20% in 800 hrs at 85 °C and 85% relative humidity making it impossible to use in commercial lighting systems. The possible reason for the degradation of the phosphor may be thermally assisted photo-ionization of the Eu^{2+} ions.

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