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Robust thermal performance of $Sr_2Si_5N_8:Eu^{2+}$: An efficient red emitting phosphor for light emitting diode based white lighting

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An important component to the advent of solid state lighting technology is the development of inorganic crystalline phosphors for efficient conversion of photons from blue light emitting diodes (LEDs) to other visible wavelengths for greater color rendering and "warmer" white lighting. We present the results of a recently developed rare earth doped nitride-based red emitting phosphor, $Sr_2Si_5N_8:Eu^{2+}$, combined with GaN-based blue emitting LEDs and YAG:Ce phosphor for improved white lighting applications. A unique remote phosphor packaging approach was used in all testing to isolate LED performance from phosphor performance. Luminous efficacies were achieved at 94 lm/W with an improved color rendering index (CRI) of 72, mixing red phosphor with YAG:Ce. The $Sr_2Si_5N_8:Eu^{2+}$ red emitting phosphor was found to have a low temperature sensitivity (only 28% power reduction at 150 °C) and greater luminous performance at low concentrations in the encapsulant by weight relative to other typical red emitting phosphors. © *2011 American Institute of Physics*. [doi:10.1063/1.3666785]

Light emitting diodes (LEDs) are steadily replacing conventional incandescent and fluorescent-based lighting as a standard form of illumination due to the progression of gallium nitride (GaN) based semiconductor technology.[1–4] Equally important to the deployment of LED-based white lighting has been the advancement of inorganic phosphors for photon conversion.[5] Solid state lighting utilizes highly efficient GaN-based near UV or blue emitting LEDs (BLEDs) in conjunction with green, yellow, and red emitting inorganic phosphors to achieve a fuller color gamut and allow colored objects to be properly rendered as well as to have desirable color temperature.[6]

With a need for efficient phosphors for blue photon down conversion, phosphors in various material systems have been developed by chemists, chemical engineers, and material scientists.[7–9] Concerns that continue to drive development of inorganic phosphors for lighting applications are the desire to reduce the energetic costs of Stokes' shift and maintain performance under elevated temperature operation. The commercial standard developed for GaN-based lighting has been YAG:Ce owing to its high conversion and luminous efficacy and ability to meet basic spectral needs for white light.[5,10]

However, BLEDs paired with yellow emitting phosphors suffer the same color rendering and aesthetic deficiencies that were cited in the utilization of fluorescent lighting. To solve this issue, yellow and/or green emitting phosphors are combined with red emitting phosphors to produce a "warmer" white light. Unfortunately, adding additional phosphors results in a reduction of the system efficiency despite the improvement in color rendering capability. Furthermore, common red emitting phosphors, such as sulphide based materials, suffer from chemical instability and strong thermal quenching. Phosphor utility depends on the ability to deliver photon conversion at as low an efficiency and stability cost as possible while still providing photon wavelengths for applications where a large color gamut is required.

We present the results of a nitride-based red emitting phosphor, $Sr_2Si_5N_8:Eu^{2+}$, to further elaborate on existing data.[11,12] All testing was performed using commercially available BLEDs (nominally 450 nm) as an excitation source for the red and yellow emitting phosphors considered. The red emitting phosphor was deployed alone as well as mixed with YAG:Ce for measuring color rendering capabilities of a white lighting package.

For the purposes of this study, a unique approach was taken to control for the emission and efficiency properties of the LEDs separately from the phosphors. Often, LEDs are combined with phosphors where the phosphor is placed directly on the LED and then encapsulated in a silicone or epoxy resin. In this direct contact configuration, the LED degrades its own performance through self heating but also negatively impacts the performance of the phosphor. Less frequently, phosphors are deployed in a remote configuration to reduce some of the phosphor heating from the LED and prevent lossy optical processes.[13–15] The configuration presented here improves upon these methods in that the packaging for the LED and the phosphor are distinct, separate, and modular.

We use electroplated silver headers as a reflective heat sink and conduction path as well as large area (1 mm^2) LEDs and encapsulate both in a silicone hemispherical dome

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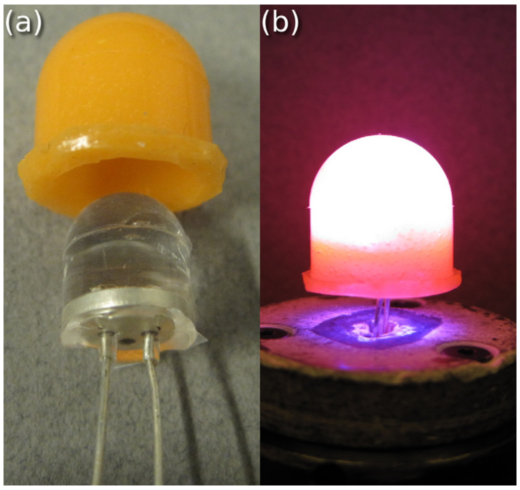

FIG. 1. (Color online) (a) Picture of silicone hemispherical packaging used to encapsulate 1 mm^2 blue LED and a phosphor containing silicone cap. (b) Picture of biased LED with a silicone cap containing $Sr_2Si_5N_8:Eu^{2+}$ phosphor.

[Fig. 1(a)]. The phosphor is dispersed and separately molded using the same silicone resin into a "cap" that can be easily taken on and off of the aforementioned LED packaging, first demonstrated in Im *et al.*[16] [Fig. 1(b)].

By packaging and characterizing the LED and phosphor separately, there is no need for ambiguous statistical analysis to separate the properties of the materials and devices. The external quantum efficiency (EQE) of the LED is measured first in a calibrated integrating sphere to ascertain the baseline efficiency without a phosphor. Subsequently, we place phosphor caps on the LED packaging and measure them in the same integrating sphere and characterize the additional loss induced by inclusion of the phosphor/silicone mixture.

Additionally, the LED efficiency is evaluated as a function of ambient temperature. We can quantify the band-gap shrinkage, which results in a spectral red-shift, and the thermal droop, for the LED. After the LED temperature characteristics are measured, the phosphor cap can be included to determine the thermal properties of the phosphor where changes due to the LED are removed from the data.

Temperature-dependent data were taken using a hotplate and a large brass enclosure for the LED and phosphor cap to create harsh ambient thermal conditions. Typically, these measurements are performed using thermoelectric stages, but these can often lack sufficient thermal contact to accurately test phosphors in a remote configuration. An optical fiber was used to collect light from the enclosure. A thermocouple was used to measure the temperature of the LED or phosphor cap, while an Ocean Optics 2000+ photodetector was used to collect spectra at 5 °C intervals. The photodetector was calibrated using a known blackbody source for accurate relative wavelength intensities. The LED was operated at a peak EQE current density of 5 A/cm^2 for all of the temperature measurements, which ranged from 22 °C to 150 °C.

Measurements were first taken of the $Sr_2Si_5N_8:Eu^{2+}$ phosphor with a BLED to determine the phosphor properties. The cap, made by mixing 1% phosphor of the total phosphor/silicone mixture (by weight), was mounted on the LED and placed in a calibrated integrating sphere where the DC current density was varied from 0.1 A/cm^2 to 50 A/cm^2. The collected spectra are shown in Fig. 2. The encapsulated LED package was measured to have an EQE of 60%. The approximate energy efficiency of the phosphor when used with a BLED at room temperature in the described implementation was stable at 52%, while the quantum yield was measured at 80% with a 457 nm laser excitation wavelength. This energy efficiency includes the conversion and scattering efficiency of the phosphor (including Stokes' loss) as well as the extraction efficiency of the phosphor cap. This phosphor efficiency is calculated as being, $\eta = P_{Phosp}/(P_{LED} - P_{LED+Phosp})$, where P_{Phosp} is the integrated radiometric power of the phosphor emission, and $P_{LED+Phosp}$ and P_{LED} are the integrated radiometric powers of the blue photon emission spectra with and without the phosphor cap, respectively.

Typically, phosphor efficiencies are reported in terms of quantum yield.[17] However, the phosphor efficiency calculation described previously gives a more accurate depiction of phosphor performance in conjunction with an LED excitation source. We have observed that phosphors with high values for quantum yield do not necessarily result in high values in the system level efficiency measurement. Furthermore, quantum yield is likely somewhat wavelength and temperature dependent and, given the methodology for obtaining this value, will have only limited utility in predicting phosphor performance in a full solid state lighting implementation.

Figure 2 shows that the phosphor is very stable under normal levels of photon flux as there is negligible saturation of the phosphor, even to high excitation levels. There is also no indication of thermal degradation or photo-bleaching during our monitoring of many measurements spanning several hours at elevated temperatures. We measured a stable full-width-at-half-maximum of approximately 100 nm and the inset of Fig. 2 shows little variation in chromaticity. The small variation in chromaticity is due to blue shifting of the

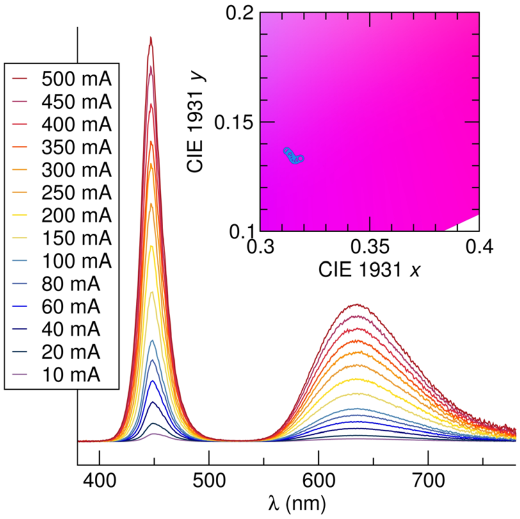

FIG. 2. (Color online) Plot showing $Sr_2Si_5N_8:Eu^{2+}$ emission spectra from a 1% phosphor containing silicone cap and encapsulated LED at drive current ranging from 1 mA to 500 mA (0.1 A/cm^2 to 50 A/cm^2). The inset shows the movement of the chromaticity coordinates with electrical bias across the 1931 CIE diagram (right to left with increasing current).

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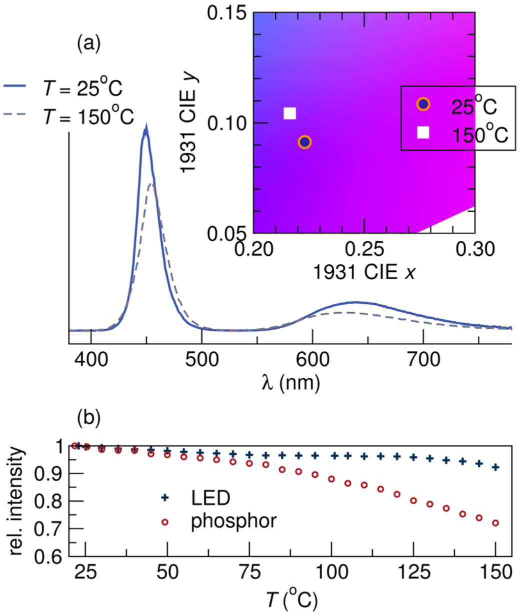

FIG. 3. (Color online) (a) Shows the spectra collected for $Sr_2Si_5N_8$:Eu^{2+} measured at room temperature and 150 °C. The inset shows the change in chromaticity with temperature. (b) The relative intensity decrease of the $Sr_2Si_5N_8$:Eu^{2+} phosphor and the LED based on the integrated intensity measured at each temperature compared to room temperature.

LED emission with increasing current due to the quantum confined Stark effect.

As can be seen in Fig. 3(a), temperature measurements showed that the $Sr_2Si_5N_8$:Eu^{2+} phosphor performed very well with only a 28% reduction in intensity (corrected for LED thermal droop) at 150 °C. The room temperature chromaticity coordinates of Fig. 3(a) inset differ from Fig. 2 because a different phosphor concentration was used to prevent saturation of the photodetector by the LED. The shift in chromaticity in Fig. 3(a) is, however, due to thermal effects rather than LED polarization effects. Figure 3(b) shows the impact of heating on performance for the $Sr_2Si_5N_8$:Eu^{2+} phosphor from room temperature to 150 °C. As expected, the phosphor suffers thermal quenching but with performance comparable to YAG:Ce. This is remarkably good for a red emitting phosphor. The LED shows low thermal droop, which we attribute to the low current density at which it was operated. Thermal quenching of any phosphor can be exacerbated when used with a broad spectrum source (i.e., LED), as its operation changes with thermal stress too (unlike in Ref. 7). This result should be kept in mind for more successful phosphor deployment.

To demonstrate the performance of our red emitting phosphor in producing white light, it was formed into a cap with commercially available YAG:Ce and tested in a calibrated integrating sphere, in conjunction with a BLED, to calculate the luminous efficacy, Commission Internationale de l'Eclairage (CIE) color coordinates, and color rendering index (CRI). The peak luminous efficacy was measured to be 94 lm/W with a correlated color temperature of 3791.58 K, x and y chromaticity coordinates of 0.39474 and 0.39738, respectively, and a CRI of 72. Variations on the ratio of YAG:Ce to red phosphor (by weight) in the caps produced the expected trade offs in efficiency and color rendering.

We find $Sr_2Si_5N_8$:Eu^{2+} red emitting phosphor to be suitable for use in solid state lighting. An important difference in the utilization of the $Sr_2Si_5N_8$:Eu^{2+} phosphor, as compared to other phosphors developed and tested in our lab, is that we were able to use very little phosphor (by volume and by weight) to produce warm white light. We also show that quantum yield measurements may not be sufficient to assess the efficiency of phosphors in a full solid state lighting implementation. Furthermore, the strontium-based phosphor demonstrates low thermal quenching, useful in applications where such environmental or ambient conditions would require such resilience.

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