

Preparation, Characterization and Photoluminescence Properties of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ Red-emitting Phosphors for a White LED

Hye-Jin Sung, Young-Sik Cho, Young-Duk Huh,* and Young Rag Do†

Department of Chemistry, Institute of Nanosensor and Biotechnology, Dankook University, Seoul 140-714, Korea

*E-mail: ydhuh@dankook.ac.kr

†Department of Chemistry, Kookmin University, Seoul 136-702, Korea

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A series of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) phosphors were synthesized by solid-state reactions. The $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphors have a strong absorption at 455 nm, which corresponds to the emission wavelength of a blue LED. The emission peak of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ is blue shifted from 655 to 618 nm with increasing Sr content. The characteristics of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphors make them suitable for use as wavelength-tunable red-emitting phosphors for three-band white LEDs pumped by a blue LED. In support of this, we fabricated a three-band white LED by coating $\text{SrGa}_2\text{S}_4:\text{Eu}$ and $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{S}:\text{Eu}$ phosphors onto a blue LED chip, and characterized its optical properties.

Key Words : $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphor, Three-band white LED, Photoluminescence

Introduction

There has been much interest in light emitting diodes (LEDs) with emission wavelengths in the ultraviolet to infrared range. Major developments in wide band gap III-V nitride compound semiconductors have led to the commercial production of high efficiency LEDs.¹⁻⁴ Traditional colored LEDs have proven effective in signal applications, as indicator lights, and in automotive lightning. The development of white LEDs as a cost-competitive, energy-efficient alternative to conventional electrical lightning is very important for expanding LED applications toward general white lightning.⁵⁻⁷

The first reported white light LEDs were based on blue InGaN technology, which uses a combination of blue emission from a blue LED and yellow emission from $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$. However, these two-band white LEDs suffer from limited color rendering and color temperature, and are unable to produce all nature-equivalent colors, especially in the red region. To improve the color temperatures and the rendering index of phosphor-converted white LEDs, various phosphors with different components of $(\text{Y}_{1-x}\text{Gd}_x)_3(\text{Al}_{1-y}\text{Ga}_y)_5\text{O}_{12}:\text{Ce}$ have been developed.⁸⁻¹¹ Another type of phosphor-combined white LED uses a blue chip as a pump source with a blend of a green and a red phosphor to generate high-quality white light.¹²⁻¹⁵ $\text{CaS}:\text{Eu}$ and $\text{SrS}:\text{Eu}$ are good red-emitting candidate phosphors for three-band phosphor-converted white LEDs pumped by blue LEDs, since both phosphors have a strong absorption at 455 nm due to the $4f \rightarrow 5d$ transitions of the doping Eu.^{16,17} The emission peaks of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ are located from 618 to 655 nm, and correspond to the transition from the lower $4f^65d^1$ (T_{2g}) state to the $4f^7$ ($^8S_{7/2}$) ground state. However, relatively little is known about the optical properties of solid solutions of $\text{CaS}:\text{Eu}$ and $\text{SrS}:\text{Eu}$ phosphors for use in lighting applications. In order to determine the most suitable phosphor for phosphor-converted white LEDs, it is necessary to improve our fundamental understanding of

the optical properties of tunable $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphors. In the present study, we therefore investigated the optical and structural properties of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphors, with particular focus on the photoluminescence (PL) characteristics of these phosphors and the color variations of phosphor-converted colored LEDs pumped by blue LEDs.

Experimental Section

CaS (99.9%, Aldrich) and SrS (99.9%, Strem) were used as starting materials for the host, and Eu_2O_3 (99.99%, Aldrich) was used as the activator for the synthesis of the $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphors. The concentrations of Eu and KBr were 0.1 and 3 mol %, respectively. KBr (99.9%, Aldrich) was used as a flux to decrease the calcination time and to enhance the luminescence intensity. An appropriate amount of sulfur (99.998%, Aldrich) was added. For example, to synthesize $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{S}:\text{Eu}$ phosphor, a mixture of $\text{CaS}/\text{SrS}/\text{Eu}_2\text{O}_3/\text{KBr}/\text{S}$ with a weight ratio of 9.12/10.09/0.04/0.75/2.00 was prepared and placed in an alumina crucible that was heated in a box-type furnace at 1000°C for 3 h. This heating was performed using a double crucible configuration, in which one crucible was nestled in the other with activated carbon in between, thus preventing oxidation of the phosphors.

X-ray diffraction (XRD) patterns of the $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphors were obtained using an X-ray diffractometer (PW1800, Philips) with $\text{Cu K}\alpha_1$ radiation. Diffraction patterns were recorded over the range $20^\circ \leq 2\theta \leq 80^\circ$ with a scan rate of $1^\circ/\text{min}$. The shapes and sizes of the phosphor particles were recorded using scanning electron microscopy (SEM, Hitachi S-4300). PL excitation and emission were measured using a spectrum analyzer (DARSA II, PSI) with a 27.5 cm monochromator, a photomultiplier tube, and a 500-W Xe lamp as the excitation source. The incident beam was perpendicular to the surface of the sample, and the observation angle was 45° relative to the excitation source. To fabricate

phosphor-converted LEDs, a blue chip ($\lambda_{\text{max}} = 455 \text{ nm}$) was used simultaneously as a blue light source and an excitation source for the red-emitting phosphors. One gram of Ca_{1-x}Sr_xS:Eu phosphor was mixed with 2.5 g of PAS ink (800 series, Jujo), and the resulting phosphor paste was dropped onto a blue chip to make a phosphor-coated LED, with the concentration of Ca_{1-x}Sr_xS:Eu phosphor controlled by adjusting the thickness of the coating layer. To fabricate the three-band white LED, SrGa₂S₄:Eu and Ca_{0.6}Sr_{0.4}S:Eu phosphors were chosen as green and red emitting phosphors, respectively. SrGa₂S₄:Eu was synthesized using a previously reported procedure.^{15, 18}

Results and Discussion

Figure 1 shows the XRD patterns of Ca_{1-x}Sr_xS:Eu phosphors with $x = 0.0, 0.2, 0.4, 0.6, 0.8,$ and 1.0 . The XRD patterns of CaS:Eu and SrS:Eu match those in the JCPDS files for cubic CaS (08-0464) and SrS (08-0489) with the lattice parameter $a = 5.694$ and 6.020 \AA , respectively. The divalent europium

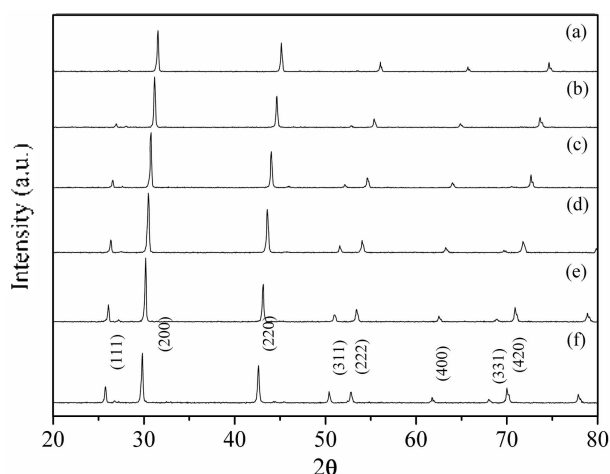


Figure 1. XRD patterns and Miller indices of Ca_{1-x}Sr_xS:Eu phosphors: (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$, and (f) $x = 1.0$.

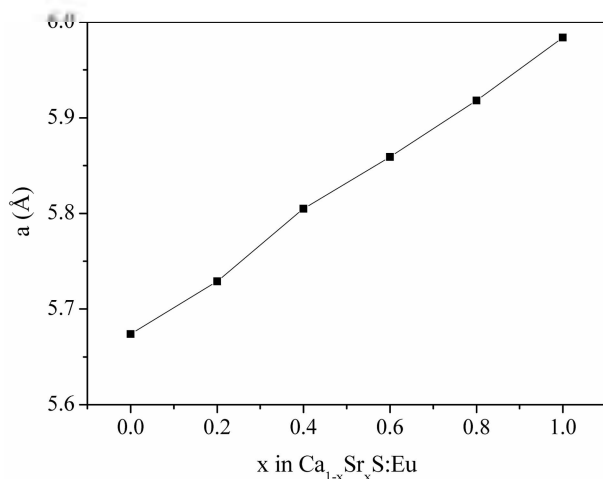


Figure 2. Lattice parameter a (Å) as a function of mole fraction of Sr in Ca_{1-x}Sr_xS:Eu phosphors.

ion is expected to occupy the calcium site in CaS:Eu and the strontium site in SrS:Eu, since the ionic radius of Eu²⁺ (1.09 Å) differs only slightly from those of Ca²⁺ (0.99 Å) and Sr²⁺ (1.12 Å).¹⁹ The (200) and (220) peaks are shifted to the lower angle as the amount of Sr increases in Ca_{1-x}Sr_xS:Eu. The correlation between the lattice parameter a (Å) and Sr mole fraction of Ca_{1-x}Sr_xS:Eu is shown in Figure 2. The XRD results indicate that the Ca_{1-x}Sr_xS:Eu phosphors were well synthesized as a single phase and that CaS:Eu is totally miscible with SrS:Eu from a crystallographic viewpoint. SEM micrographs of Ca_{1-x}Sr_xS:Eu powders are shown in Figure 3. These images show that, as the amount of Sr in Ca_{1-x}Sr_xS:Eu is increased, the particle shape changes from the multifaced morphology of CaS:Eu with an average size of $5 \mu\text{m}$ to the spherical morphology of SrS:Eu with an average size of $15 \mu\text{m}$.

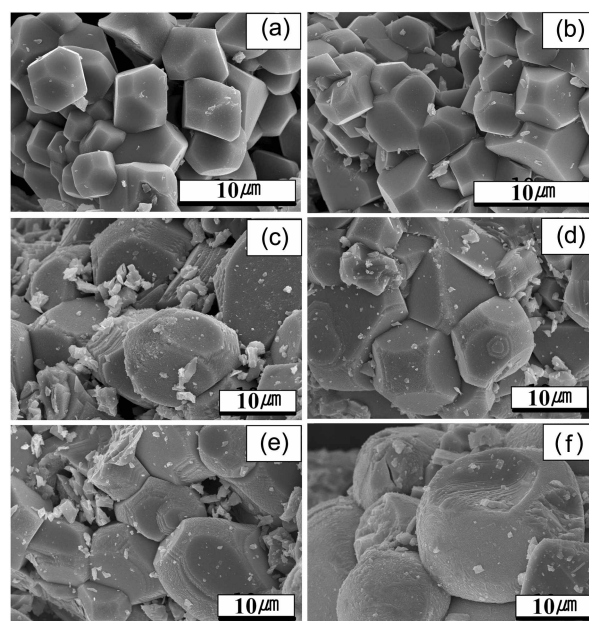


Figure 3. SEM images of Ca_{1-x}Sr_xS:Eu phosphors: (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$, and (f) $x = 1.0$.

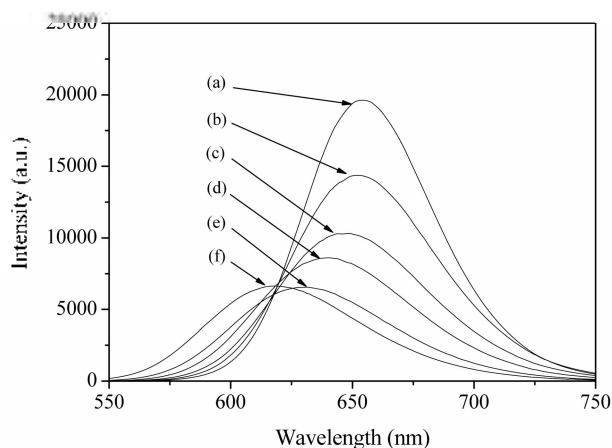


Figure 4. Photoluminescence spectra of Ca_{1-x}Sr_xS:Eu phosphors under 455 nm excitation: (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$, and (f) $x = 1.0$.

Figure 4 shows the PL emission spectra of the $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphors. We synthesized a series of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphors at 1000°C for 3 h. These synthetic conditions were used for the optimization of $\text{CaS}:\text{Eu}$ phosphor. Therefore, the relative intensity of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphors is not important at these conditions. The emission peaks of $\text{CaS}:\text{Eu}$ and $\text{SrS}:\text{Eu}$ are located at 655 and 618 nm, respectively. Comparison of these spectra indicates that the partial replacement of Ca by Sr causes a blue shift of the emission wavelength, with a color tuning range of about 40 nm. This blue shift can be interpreted in terms of the crystal strength at the Eu^{2+} ion in the $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphors. Since $\text{CaS}:\text{Eu}$ and $\text{SrS}:\text{Eu}$ have cubic structures with point groups O_h , each Eu^{2+} ion is surrounded by six S^{2-} ions. The excited state of the Eu^{2+} ion with a $4f^65d^1$ electronic configuration can be split into the lower T_{2g} state and the higher E_g state.¹⁷ Since the lattice parameter of $\text{SrS}:\text{Eu}$ is larger than that of $\text{CaS}:\text{Eu}$, the distance between the Eu^{2+} ion and S^{2-} ions in $\text{SrS}:\text{Eu}$ is longer than that in $\text{CaS}:\text{Eu}$. Increasing the distance between the Eu^{2+} ion and S^{2-} ions will decrease the crystal strength, which should lead to a decrease in the energy difference between T_{2g} and E_g states of the $4f^65d^1$ electronic configuration. The emission of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ arises from the transition from the lower $4f^65d^1$ (T_{2g}) state to the $4f^7$ ($^8S_{7/2}$) ground state. The energy difference between these states should increase as the crystal strength of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ decreases. Therefore, the emission peak of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ would be expected to shift to shorter wavelength with increasing mole fraction of Sr. A schematic energy level of the Eu^{2+} ion as a function of the crystal field is shown in Figure 5.

The excitation spectra of the $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphors exhibit very broad and intense bands up to 500 nm, as shown in Figure 6. The excitation around 200 nm is essentially due to the valence to conduction band transition of the host, while the broad band in the visible region arises from a transition between the $4f^65d^1$ and $4f^7$ configurations of Eu^{2+} ion. Since $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphors have broad spectra around 450 nm, these phosphors can be readily excited by a

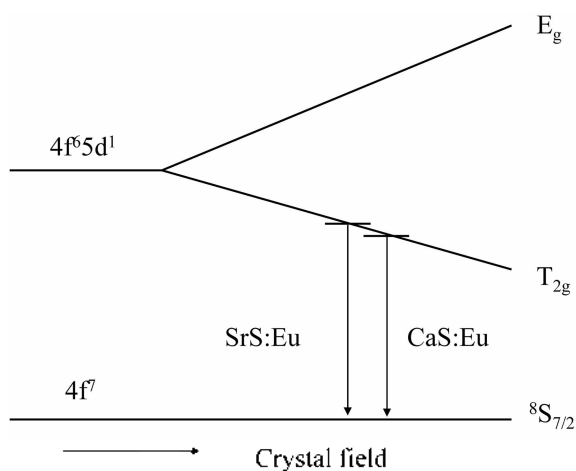


Figure 5. Schematic energy level of the Eu^{2+} ion as a function of the crystal field.

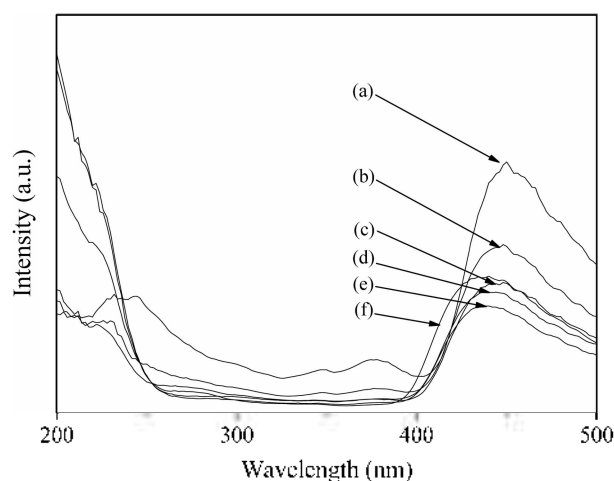


Figure 6. Excitation spectra of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphors: (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$, and (f) $x = 1.0$.

blue LED emitting at 455 nm.

To study the optical properties of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$, we coated a blue LED chip emitting at 455 nm with a series of $\text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu}$ phosphor pastes. Figure 7(a) shows the PL spectra of the blue LED chip coated with various amounts of $\text{CaS}:\text{Eu}$ phosphor. As the amount of $\text{CaS}:\text{Eu}$ phosphor coated on the chip is increased, the intensity of the 455 nm peak decreases whereas that of the 655 nm peak increases simultaneously, causing the LED to shift from blue to deep red emission. The Commission Internationale de l'Eclairage (CIE) diagrams of the PL spectra of the blue- to deep red-emitting LEDs are shown in Figure 8(a). The CIE chromaticity coordinates of the blue- to deep red-emitting LEDs appear in the diagram as a straight line connecting the positions of the blue LED ($x = 0.13$, $y = 0.08$) and $\text{CaS}:\text{Eu}$ phosphor ($x = 0.70$, $y = 0.30$). Figure 7(b) and 7(c) show the PL spectra of the blue- and red-emitting LEDs prepared by coating the blue LED with

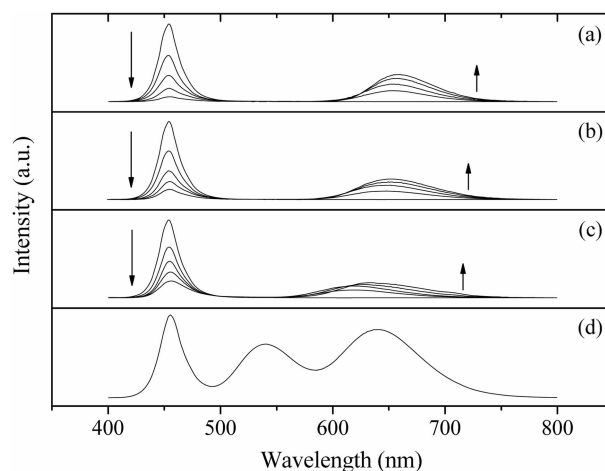


Figure 7. PL spectra of a blue LED coated with various amounts of (a) $\text{CaS}:\text{Eu}$, (b) $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{S}:\text{Eu}$, and (c) $\text{SrS}:\text{Eu}$ phosphors. Arrows indicate the changes in the spectra when the amount of phosphor is increased. (d) PL spectra of a three-band white LED in which $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{S}:\text{Eu}$ and $\text{SrGa}_2\text{S}_4:\text{Eu}$ phosphors are coated on a blue LED.

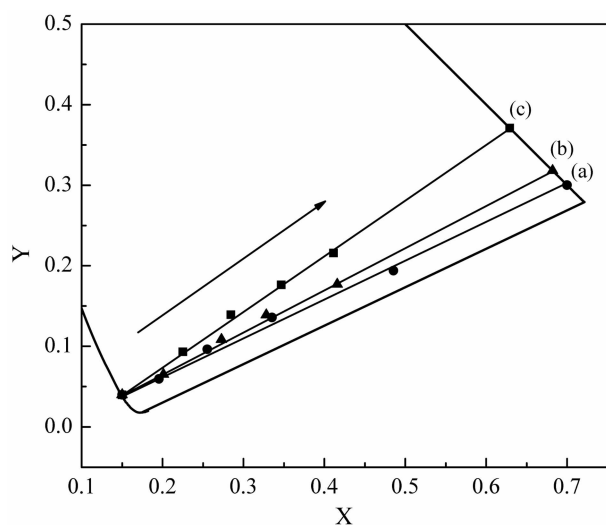


Figure 8. CIE chromaticity coordinates of PL spectra produced by a blue LED coated with various amounts of (a) CaS:Eu, (b) Ca_{0.6}Sr_{0.4}S:Eu, and (c) SrS:Eu phosphors. Arrows indicate the changes in chromaticity coordinates as the amount of phosphor is increased.

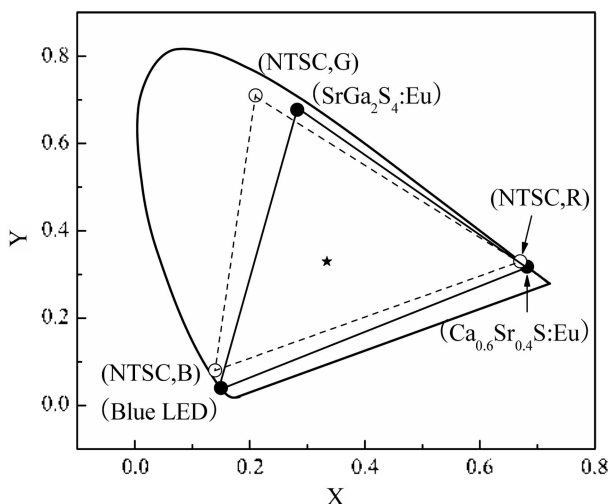


Figure 9. CIE diagram and chromaticity coordinates of the blue LED, SrGa₂S₄:Eu, and Ca_{0.6}Sr_{0.4}S:Eu, as well as NTSC blue, NTSC green, and NTSC red. ★ represents the chromaticity coordinates of the three-band white LED fabricated by coating SrGa₂S₄:Eu and Ca_{0.6}Sr_{0.4}S:Eu phosphors onto a blue LED chip; the color temperature of the three-band white LED is 5500 K.

different amounts of Ca_{0.6}Sr_{0.4}S:Eu or SrS:Eu phosphor. As the amount of Ca_{0.6}Sr_{0.4}S:Eu or SrS:Eu phosphor is increased, the intensity of the 455 nm peak decreases and that of the 649 nm or 618 nm peak increases, respectively, such that the CIE chromaticity coordinates converge to those of the Ca_{0.6}Sr_{0.4}S:Eu or SrS:Eu phosphor as shown in Figure 8(b) and 8(c). Figure 7(d) shows the PL spectrum of a three-band LED fabricated by coating Ca_{0.6}Sr_{0.4}S:Eu and SrGa₂S₄:Eu phosphors on the blue LED with the weight ratio of Ca_{0.6}Sr_{0.4}S:Eu to SrGa₂S₄:Eu of 3.3. The CIE chromaticity coordinates of this three-band LED are $x = 0.33$ and $y = 0.33$, and its color temperature is about 5500 K as shown in

Figure 9.

Figure 9 shows the CIE diagram and chromaticity coordinates of the blue LED, SrGa₂S₄:Eu and Ca_{0.6}Sr_{0.4}S:Eu phosphors, as well as the blue, green, and red coordinates specified by the NTSC (National Television Standard Committee). The chromaticity coordinates of the blue LED and Ca_{0.6}Sr_{0.4}S:Eu phosphor, (0.13, 0.08) and (0.68, 0.32), almost coincide with the NTSC blue and red coordinates, (0.14, 0.08) and (0.67, 0.33), respectively, indicating that the blue LED and Ca_{0.6}Sr_{0.4}S:Eu phosphor have excellent color purities.²⁰ However, the chromaticity coordinates of the SrGa₂S₄:Eu phosphor, (0.28, 0.68), are not close to those of NTSC green, (0.21, 0.71).²⁰ The color range of light emitted by a three-band LED fabricated by coating SrGa₂S₄:Eu and Ca_{0.6}Sr_{0.4}S:Eu phosphors on a blue LED is the region inside the triangle formed by connecting the CIE chromaticity coordinate positions of the blue LED, SrGa₂S₄:Eu phosphor, and Ca_{0.6}Sr_{0.4}S:Eu phosphor. The area of the region inside the triangle formed by connecting the NTSC blue, green, and red coordinates is used as the reference value for the color purity of a display panel. The area of the triangle formed by connecting the positions of the blue LED, SrGa₂S₄:Eu, and Ca_{0.6}Sr_{0.4}S:Eu phosphors is 96.5% of that of the NTSC triangle. Given that a typical display panel is required to have a color purity of at least 80%, the color purity of the three-band white LED fabricated by coating SrGa₂S₄:Eu and Ca_{0.6}Sr_{0.4}S:Eu phosphors onto the blue LED chip is much better than that typically required for display panels. Within this triangle, the CIE chromaticity coordinates of the three-band white LED can be adjusted by controlling the amount of phosphors and the ratio of SrGa₂S₄:Eu to Ca_{0.6}Sr_{0.4}S:Eu. Therefore, the color temperatures of the three-band white LED can be easily adjusted simply by using the different amounts of phosphors.

Conclusion

Ca_{1-x}Sr_xS:Eu phosphors have been synthesized by solid-state reactions. Since Ca_{1-x}Sr_xS:Eu phosphors exhibit strong absorption at the emission wavelength of 455 nm, the emission wavelength of a blue LED, these phosphors can be used as wavelength tunable red-emitting phosphors from 618 to 655 nm under the blue LED excitation. The present results show that the three-band white LED fabricated by coating SrGa₂S₄:Eu and Ca_{0.6}Sr_{0.4}S:Eu phosphors on a blue LED has high luminescence and good color properties, and is suitable for use as a backlight source for color display LED devices.

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