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

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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 \( \text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu} \) 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 lighting. The development of white LEDs as a cost-competitive, energy-efficient alternative to conventional electrical lighting is very important for expanding LED applications toward general white lighting.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 \( \text{Y}_2\text{Al}_2\text{O}_3\text{Ce} \). However, these two-band white LEDs suffer from limited color rendering and color temperature, and are unable to produce all-natural-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 \((Y_{1-x}\text{Gd}_x)(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_3\text{Ce} \) 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 

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

\( \text{CaS} \) (99.9%, Aldrich) and \( \text{SrS} \) (99.9%, Strem) were used as starting materials for the host, and \( \text{Eu}_2\text{O}_3 \) (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 \( \text{Eu} \) and \( \text{KBr} \) were 0.1 and 3 mol %, respectively. \( \text{KBr} \) (99.9%, Aldrich) was used as a flux to decrease the calcination time and to enhance the luminescence intensity. An appropriate amount of sulfur (99.98%, Aldrich) was added. For example, to synthesize \( \text{Ca}_{1-x}\text{Sr}_x\text{S}:\text{Eu} \) 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. The heating was performed using a double crucible configuration, in which one crucible was nested in the other with activated carbon in between, thus preventing oxidation of the phosphor.

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 Cu K\( \alpha \) radiation. Diffraction patterns were recorded over the range 20° < 2\( \theta \) < 80° with a scan rate of 1°/min. The shapes and sizes of the phosphor particles were recorded using a scanning electron microscope (SEM, Hitachi S-4300). PL excitation and emission were measured using a spectrometer analysis (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 ($\lambda_{\text{em}} = 455$ 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$_x$S: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 form a phosphor-coated LED, with the concentration of Ca$_{1-x}$Sr$_x$S:Eu phosphor controlled by adjusting the thickness of the coating layer. To fabricate the three-band white LED, SrGaS$_3$:Eu and Ca$_{1-x}$Sr$_x$S:Eu phosphors were chosen as green and red emitting phosphors, respectively. SrGa$_2$S$_4$:Eu was synthesized using a previously reported procedure.$^{15,16}$

**Results and Discussion**

Figure 1 shows the XRD patterns of Ca$_{1-x}$Sr$_x$S:Eu phosphors with $x = 0.0, 0.2, 0.4, 0.6, 0.8,$ and $1.0$. The XRD patterns of Ca$_{1-x}$Sr$_x$S: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 Å, respectively. The divalent europium ion is expected to occupy the calcium site in CaS:Eu and the strontium site in SrS:Eu, since the ionic radius of Eu$^{2+}$ (1.09 Å) differs only slightly from those of Ca$^{2+}$ (0.99 Å) and Sr$^{2+}$ (1.12 Å).$^{17}$ The (200) and (220) peaks are shifted to the lower angle as the amount of Sr increases in Ca$_{1-x}$Sr$_x$S:Eu. The correlation between the lattice parameter $a$ (Å) and Sr mole fraction of Ca$_{1-x}$Sr$_x$S:Eu is shown in Figure 2. The XRD results indicate that the Ca$_{1-x}$Sr$_x$S: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$_x$S:Eu powders are shown in Figure 3. These images show that, as the amount of Sr in Ca$_{1-x}$Sr$_x$S:Eu is increased, the particle shape changes from the multifaceted morphology of CaS:Eu with an average size of 5 μm to the spherical morphology of SrS:Eu with an average size of 15 μm.

**Figure 1.** XRD patterns and Miller indices of Ca$_{1-x}$Sr$_x$S: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 Sr mole fraction in Ca$_{1-x}$Sr$_x$S:Eu phosphors.

**Figure 3.** SEM images of Ca$_{1-x}$Sr$_x$S: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$_x$S: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 Ca$_{1-x}$Sr$_x$S:Eu phosphors. We synthesized a series of Ca$_{1-x}$Sr$_x$S:Eu phosphors at 1000°C for 3 h. These synthetic conditions were used for the optimization of CaS:Eu phosphor. Therefore, the relative intensity of Ca$_{1-x}$Sr$_x$S:Eu phosphors is not important at these conditions. The emission peaks of CaS:Eu and SrS: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 of the Eu$^{2+}$ ion in the Ca$_{1-x}$Sr$_x$S:Eu phosphors. Since CaS:Eu and SrS: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$^5$5d$^1$ electronic configuration can be split into the lower T$_{2g}$ state and the higher E$_g$ state. Since the lattice parameter of SrS:Eu is larger than that of CaS:Eu, the distance between the Eu$^{2+}$ ion and S$^2-$ ions in SrS:Eu is longer than that in CaS: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$^5$5d$^1$ electronic configuration. The emission of Ca$_{1-x}$Sr$_x$S:Eu arises from the transition from the lower 4f$^5$5d$^1$ (T$_{2g}$) state to the 4f$^7$ ($^8$S$_{7/2}$) ground state. The energy difference between these states should increase as the crystal strength of Ca$_{1-x}$Sr$_x$S:Eu decreases. Therefore, the emission peak of Ca$_{1-x}$Sr$_x$S: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 Ca$_{1-x}$Sr$_x$S: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$^5$5d$^1$ and 4f$^6$ configurations of Eu$^{2+}$ ion. Since Ca$_{1-x}$Sr$_x$S:Eu phosphors have broad spectra around 450 nm, these phosphors can be readily excited by a blue LED emitting at 455 nm.

To study the optical properties of Ca$_{1-x}$Sr$_x$S:Eu, we coated a blue LED chip emitting at 455 nm with a series of Ca$_{1-x}$Sr$_x$S:Eu phosphor pastes. Figure 7(a) shows the PL spectra of the blue LED chip coated with various amounts of CaS:Eu phosphor. As the amount of CaS: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) diagram 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 = 0.15, y = 0.08) and CaS: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 5](image5.png)

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

![Figure 6](image6.png)

*Figure 6. Excitation spectra of Ca$_{1-x}$Sr$_x$S: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 7](image7.png)

*Figure 7. PL spectra of a blue LED coated with various amounts of (a) CaS:Eu, (b) Ca$_{0.8}$Sr$_{0.2}$S:Eu, and (c) SrS: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 Ca$_{0.5}$Sr$_{0.5}$S:Eu and SrCa$_{0.5}$S: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, SrGa$_2$S$_4$: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 SrGa$_2$S$_4$: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 SrGa$_2$S$_4$:Eu phosphors on the blue LED with the weight ratio of Ca$_{0.6}$Sr$_{0.4}$S:Eu to SrGa$_2$S$_4$: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, SrGa$_2$S$_4$: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 Standards Committee). The chromaticity coordinates of the blue LED and Ca$_{0.6}$Sr$_{0.4}$S:Eu phosphor, (0.15, 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. However, the chromaticity coordinates of the SrGa$_2$S$_4$:Eu phosphor, (0.28, 0.68), are not close to those of NTSC green, (0.21, 0.71). The color range of light emitted by a three-band LED fabricated by coating SrGa$_2$S$_4$: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, SrGa$_2$S$_4$:Eu phosphor, and Ca$_{0.6}$Sr$_{0.4}$S:Eu phosphor. The area of the region inside the triangle formed by connecting the positions of the blue LED, SrGa$_2$S$_4$: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 range of the three-band white LED fabricated by coating SrGa$_2$S$_4$: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 SrGa$_2$S$_4$: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$_x$S:Eu phosphors have been synthesized by solid-state reactions. Since Ca$_{1-x}$Sr$_x$S: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 SrGa$_2$S$_4$: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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References