Phosphor Converted Three-Band White LED

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The development of wide band gap III-V nitride compound semiconductors has led to the commercial production of high-efficiency LEDs.[1,2] The recent advent of blue InGaN technology has made it possible to produce a conventional white LED in which white light is obtained by coating a $Y_3Al_5O_{12}$:Ce (or Sr_3SiO_5:Eu) phosphor onto a blue LED chip.[3-6] In this device, known as a two-band white LED, white light is generated by additive color mixing of the blue light emitted by the blue LED and the yellow light emitted by the $Y_3Al_5O_{12}$:Ce phosphor. The development of a white LED is important because it opens the way for LED applications such as light bulbs and fluorescent lamps with high durability and low energy consumption. However, the spectral composition of the light produced by the conventional two-band white LED differs from that of natural white light, particularly in the red region. The color properties of conventional two-band white LEDs can potentially be improved by adding another component to create a white LED based on three emission bands (a three-band white LED).

Full-color fluorescent display devices have been developed by using a combination of ZnS:Ag (blue), ZnS:Cu,Al (green), and ZnCdS:Ag (red) phosphors excited by a near-UV LED.[7] In addition, a white light source has been obtained by intergrating ZnS:Ag (blue), ZnS:Cu,Al (green), and Y_2O_2S:Eu (red) phosphors, and a UV-LED (350 nm).[8] White light has also been achieved by combining a blue LED (460 nm) with $SrGa_2S_4$:Eu (green) and SrS:Eu (red) phosphors.[9] Previously, we constructed a three-band white LED by combining a blue LED (465 nm) with $SrGa_2S_4$:Eu (green) and ZnCdS:Ag,Cl (red) phosphors.[10] In the present work, we investigated the optical properties of a white LED which was obtained by using a blue LED (465 nm) in conjunction with $SrGa_2S_4$:Eu (green) and SrY_2S_4:Eu (red) phosphors. The SrY_2S_4:Eu phosphor was chosen over the ZnCdS:Ag,Cl phosphor used in our previous work in order to improve the red color characteristics of the white LED.

Experimental Section

Green-emitting $SrGa_2S_4$:Eu phosphor was synthesized using a decomposition method that does not involve the use of the toxic compound hydrogen sulfide. $SrGa_2S_4$:Eu was synthesized by heating 0.95 mmol of strontium sulfide (SrS), 2.0 mmol of gallium dimethyldithiocarbamate ($Ga[(CH_3)_2NCS_2]_3$), 0.05 mmol of the europium complex $\{[(CH_3)_4N]Eu[(CH_3)_2NCS_2]_4\}$, and excess sulfur for 2 hours at 850 °C.[10,11] However, the red-emitting SrY_2S_4:Eu phosphor could not be synthesized using this decomposition method; instead, it was prepared by solid-state reaction of 0.98 mmol $SrCO_3$, 2.0 mmol Y_2CO_3, 0.02 mmol of Eu_2CO_3, and the appropriate amount of Na_2CO_3 as a flux, at 1300 °C for 8 hours in H_2S steam.[12]

Photoluminescence (PL) excitation and emission measurements were carried out using a 0.275 m monochromator, a photomultiplier tube, and a 500 W Xe lamp as an excitation source. The incident beam was perpendicular to the surface of the sample, and the observation angle was 45° to the excitation source. The PL and chromaticity of the three-band white LED were measured using a 15 cm diameter integration sphere. A blue LED (Nichia, λ_{max} = 465 nm) was used. One gram of $SrGa_2S_4$:Eu or SrY_2S_4:Eu phosphor was dispersed in an aqueous solution containing 4.0 g of polyvinyl-alcohol (polymerization degree: 200). This solution was applied onto a poly(ethylene terephthalate) (PET) film. Although, the thickness and concentration of the film were not measured, the relative amounts of phosphor could be varied by adjusting the number of phosphor flims.

Results and Discussion

Figure 1 shows the PL excitation and emission spectra of the $SrGa_2S_4$:Eu and SrY_2S_4:Eu phosphors. The excitation spectra show that both phosphors absorb strongly absorptions at 465 nm, which is the emission wavelength of the blue LED used. The emission spectra show that, under 465 nm excitation, the $SrGa_2S_4$:Eu and SrY_2S_4:Eu phosphors emit green (535 nm) and red (640 nm), respectively. Therefore, $SrGa_2S_4$:Eu and SrY_2S_4:Eu are suitable as green- and red-emitting phosphors when excited by a blue LED.

Figure 2(A) shows the PL spectra of blue- and green-emitting LEDs prepared by coating the blue LED with $SrGa_2S_4$:Eu. Two distinct emission peaks are observed at 465 nm and 535 nm, which correspond to the wavelengths of the blue LED and green emission from the $SrGa_2S_4$:Eu phosphor, respectively. As the amount of $SrGa_2S_4$:Eu phosphor is increased by increasing the number of

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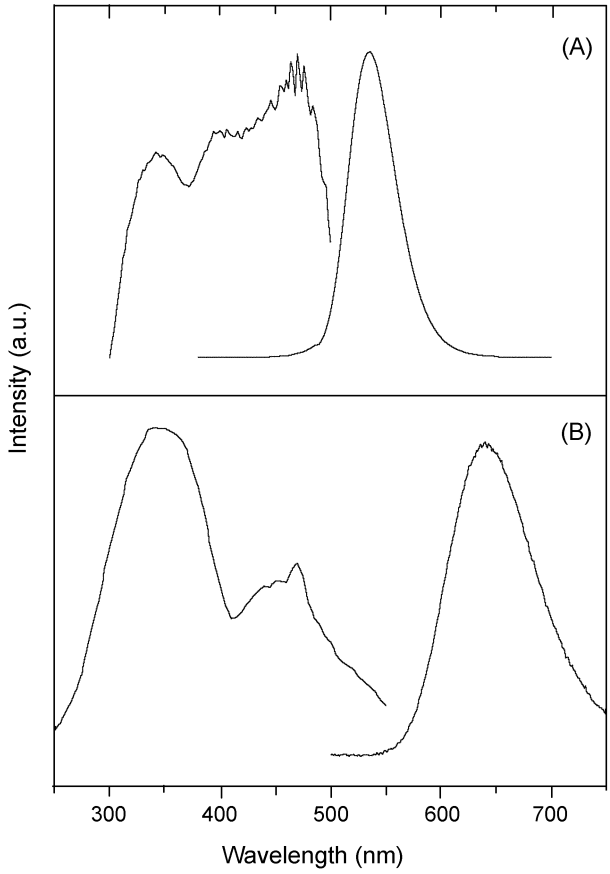

Figure 1. Excitation and emission spectra of (A) $SrGa_2S_4$:Eu and (B) SrY_2S_4:Eu phosphors. The excitation wavelength is 465 nm. The excitation spectra of (A) $SrGa_2S_4$:Eu and (B) SrY_2S_4:Eu phosphors monitor the emission at 535 nm and 640 nm, respectively.

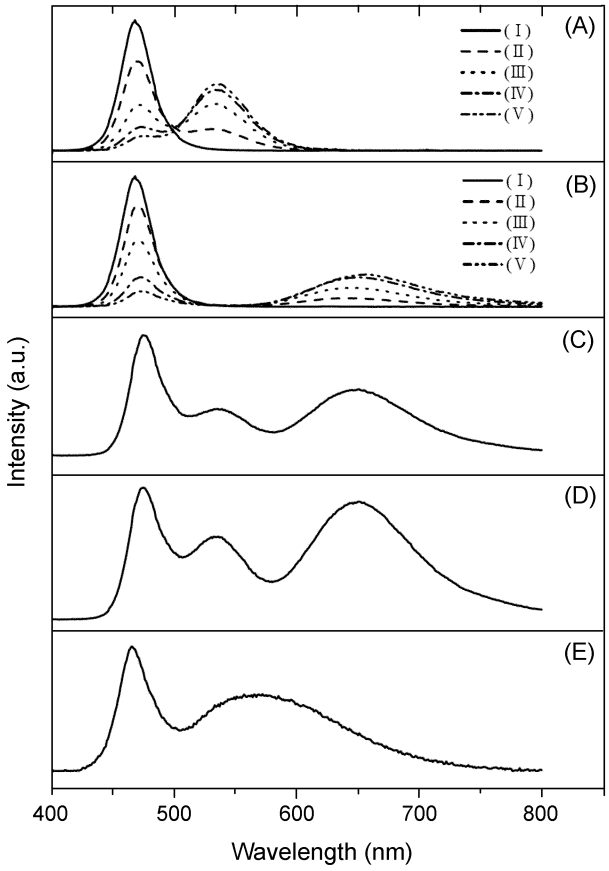

Figure 2. (A, B) Photoluminescence spectra of (A) blue- and green-emitting LEDs, and (B) blue- and red-emitting LEDs, where $SrGa_2S_4$:Eu (green) or SrY_2S_4:Eu (red) phosphor films are coated to a blue LED. No phosphor is used in (I). The amount of phosphor increases on going from (II) to (V). (C, D) Photoluminescence spectra of three-band white LEDs with color temperatures of (C) 5620 K and (D) 4550 K, where the ratio of $SrGa_2S_4$:Eu to SrY_2S_4:Eu is fixed at 0.2, and larger amounts of the phosphors are used in (D). (E) Photoluminescence spectrum of a two-band white LED with a color temperature of 5240 K in which the $(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}$:$Ce_{0.3}$ (yellow) phosphor was used.

$SrGa_2S_4$:Eu phosphor films applied to the blue LED, the intensity of the 465 nm emission decreases and that of the 535 nm emission increases. The CIE (Commission International de l'Eclairage) chromaticity coordinates of the photoluminescence spectra are shown in Figure 3(A). The CIE chromaticity coordinates of a blue LED are x = 0.13, y = 0.08. As the amount of $SrGa_2S_4$:Eu phosphor is increased, the CIE chromaticity coordinates shift to x = 0.27, y = 0.69, which correspond to those of the pure green-emitting $SrGa_2S_4$:Eu phosphor. In addition, the trend in the chromaticity coordinates with increasing amounts of $SrGa_2S_4$:Eu phosphor is close to the straight line connecting the points of the blue LED and the green-emitting $SrGa_2S_4$:Eu phosphor. The $SrGa_2S_4$:Eu phosphor used in the present work has a better chromaticity than those of the commercial green phosphors ZnS:Cu and ZnS:Cu,Al (CIE chromaticity coordinates of x = 0.28, y = 0.53 and x = 0.29, y = 0.61, respectively).[13,14]

Figure 2(B) shows the PL spectra of blue- and red-emitting LEDs prepared by coating the blue LED with increasing amounts of SrY_2S_4:Eu phosphor. As the amount of SrY_2S_4:Eu phosphor is increased, the intensity of the 465 nm peak decreases and that of the 640 nm peak increases. The CIE chromaticity coordinates converge to those of pure red-emitting SrY_2S_4:Eu phosphor (x = 0.65, y = 0.33) as the amount of SrY_2S_4:Eu phosphor increases, as shown in Figure 3(B). Mueller-Mach *et al*. generated white light by combining a blue LED (460 nm) with $SrGa_2S_4$:Eu (green) and SrS:Eu (red) phosphors.[9] The excitation spectrum of the SrS:Eu phosphor consists of extremely broad bands that extend up to 600 nm. As a result, the SrS:Eu phosphor is excited not only by the blue LED, but also by the green-emitting $SrGa_2S_4$:Eu phosphor. Because the excitation spectrum of the SrY_2S_4:Eu phosphor used in the present work extends up to 550 nm, the SrY_2S_4:Eu phosphor is also excited by the green-emitting $SrGa_2S_4$:Eu phosphor. However, this effect is a smaller than that of the SrS:Eu phosphor on the $SrGa_2S_4$:Eu phosphor. In addition, the chromaticity coordinates of the SrY_2S_4:Eu phosphor used in the present work are better than those of the ZnCdS:Ag,Cl phosphor (x = 0.61, y = 0.39), which has also been used as the red-

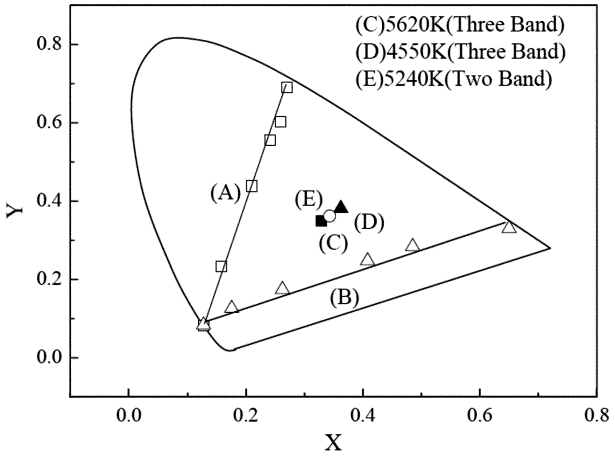

Figure 3. (A) Chromaticity coordinates (x, y) of blue- and green-emitting LEDs varies from (0.13, 0.08), correponding to the blue LED alone, to (0.27, 0.69), corresponding to the pure $SrGa_2S_4$:Eu phosphor, as the amount of $SrGa_2S_4$:Eu phosphor is increased. (B) CIE chromaticity coordinates of blue- and red-emitting LEDs, where (x, y) varies from (0.13, 0.08) to (0.65, 0.33) as the amount of SrY_2S_4:Eu phosphor is increased. (C, D) CIE chromaticity coordinates of (C) a three-band white LED with 5620 K, (D) a three-band white LED with 4550 K, and (E) a two-band white LED with 5240 K.

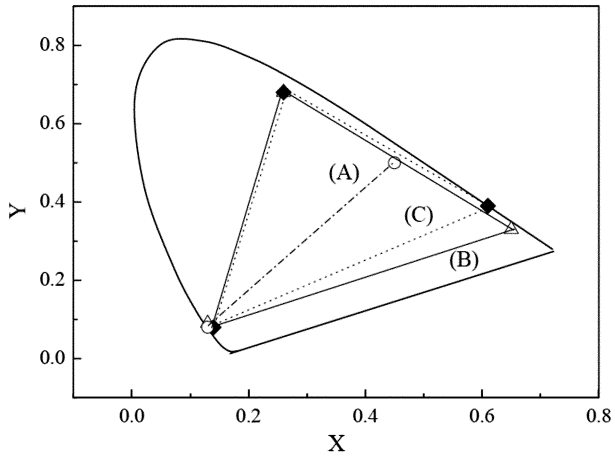

Figure 4. CIE chromaticity coordinates of (A) a two-band LED (blue LED + $Y_3Al_5O_{12}$:Ce), (B) a three-band LED (blue LED + $SrGa_2S_4$:Eu + SrY_2S_4:Eu), and (C) another three-band LED (blue LED + $SrGa_2S_4$:Eu + ZnCdS:Ag,Cl).

emitting phosphor in a three-band LED.[10] Therefore, SrY_2S_4:Eu phosphor is an excellent red-emitting phosphor for use in conjunction with a blue LED and a green-emitting $SrGa_2S_4$:Eu phosphor to generate a three-band white LED.

Figures 2(C) and 2(D) show the PL spectra of three-band white LEDs in which the ratio of $SrGa_2S_4$:Eu to SrY_2S_4:Eu was fixed at 0.2, and where the total amount of phosphors used in (D) is 1.25 times of that in (C). The CIE chromaticity coordinates of these LEDs are x = 0.33, y = 0.35 and x = 0.36, y = 0.38, as shown in Figure 3(C) and 3(D), respectively. The colors of white light sources are generally expressed in terms of the color temperatures with CIE chromaticity coordinates. The color temperatures of the three-band white LEDs in Figure 2(C) and 2(D) are 5620 K and 4550 K, respectively. Therefore, by controlling the relative amounts of $SrGa_2S_4$:Eu and SrY_2S_4:Eu phosphors as well as the total combined amount of the two phosphors, we can vary the color temperature of the white emitting LED.

Adjusting the color temperature of a conventional two-band white LED entails preparing a new sample of yttrium aluminum garnet (YAG), $(Y_{1-X}Gd_X)_3(Al_{1-Y}Ga_Y)_5O_{12}$:Ce with different proportions of the various components. When the content of Gd is increased in $(Y_{1-X}Gd_X)_3Al_5O_{12}$:Ce phosphors, the peak emission wavelength is red shifted from 530 nm to wavelengths up to 570 nm. On the other hand, increasing the Ga content in $Y_3(Al_{1-Y}Ga_Y)_5O_{12}$:Ce phosphors causes a blue shift in the peak emission wavelength. Therefore, the color temperature of the white light can be decreased by increasing the amount of Gd and decreasing the amount of Ga in the $(Y_{1-X}Gd_X)_3(Al_{1-Y}Ga_Y)_5O_{12}$:Ce phosphor coated onto the blue LED, and vice versa.[15] Figure 2(E) shows the PL spectrum of a two-band white LED comprised of a blue LED and $(Y_{0.6}Gd_{0.4})_{2.7}Al_5O_{12}:Ce_{0.3}$ phosphor, which has a color temperature of 5240 K. Its CIE chromaticity coordinates are shown in Figure 3(E). In contrast to the effort required to vary the color temperature of a two-band white LED, the color temperature of the three-band white LED reported here can be easily varied by simply mixing the different amounts of phosphors and/or varying the total amount of phosphor coated onto the blue LED. This represents a key advantage of the three-band white LED over the two-band white LED.

Figure 4 shows a chromaticity diagram depicting the chromaticity coordinates of a two-band LED (blue LED + $Y_3Al_5O_{12}$:Ce), the three-band LED developed in the present work (blue LED + $SrGa_2S_4$:Eu + SrY_2S_4:Eu), and a three-band LED developed previously (blue LED + $SrGa_2S_4$:Eu + ZnCdS:Ag,Cl).[10,15] The color range of the light emitted by the two-band LED is shown in the chromaticity diagram as a line connecting the positions of the blue LED and $Y_3Al_5O_{12}$:Ce (yellow) phosphor. Similarly, the color range of each three-band LED is shown as the region inside the triangle drawn by connecting the positions of the blue LED, the green phosphor, and the red phosphor. Of the three LEDs shown in Figure 4, the color range of the blue LED + $SrGa_2S_4$:Eu + SrY_2S_4:Eu three-band LED is the widest, and hence this LED has the best color purity. The superior color properties of the three-band LED developed in the present work (blue LED + $SrGa_2S_4$:Eu + SrY_2S_4:Eu) make it a good candidate for use as a backlight source in small full-color display devices such as personal digital assistants.

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