

# Optical properties of white and multi-color light emitting diodes

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## ABSTRACT

BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>: Eu, SrGa<sub>2</sub>S<sub>4</sub>: Eu, and SrY<sub>2</sub>S<sub>4</sub>: Eu phosphors are used to emit blue, green and red emissions under excitation from a violet light emitting diode (LED), respectively. White and multi-color LEDs have been generated by mixing a violet emission from a violet LED and blue, green and red emissions from the BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>: Eu, SrGa<sub>2</sub>S<sub>4</sub>: Eu, and SrY<sub>2</sub>S<sub>4</sub>: Eu phosphors. The optical properties of white and multi-color LED are discussed.

**Key words** : white LED, multi-color LED

## Introduction

Major developments in wide band gap III-V nitride compound semiconductors have led to the commercial production of high-efficiency light emitting diodes (LEDs) (1, 2). Traditional colored LEDs are widely used in devices such as indicator lights and traffic lights. Blue InGaN technology makes possible the two-band white LED in which white light is obtained by coating Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>: Ce phosphor onto a blue LED chip (3, 4). White light is generated by additive color mixing of blue emission from the blue LED and yellow emission from the Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>: Ce phosphor. White LED has a number of advantages over incandescent and halogen lamps in power efficiency and long lifetime. However, two-band white LED with low color rendering index cannot express an actual nature-color, especially in the red region.

In order to improve color properties of the white LED, multi-band white LED should be fabricated by using multi-color emitting phosphor or mixing of various color emitting phosphors. Tricolor was generated from Ba<sub>3</sub>MgSi<sub>2</sub>O<sub>8</sub>: Eu<sup>2+</sup>,

Mn<sup>2+</sup> phosphor with near-UV LED (5). However, this phosphor has a weak blue emission. To generate the multi-color white LED pumped by near-UV LED, the combination of ZnS: Ag (blue), ZnS: Cu,Al (green), and ZnCdS: Ag (red) phosphors was used (6). SrGa<sub>2</sub>S<sub>4</sub>: Eu (green) / ZnCdS: Ag,Cl (red) systems was also used to generate the three-band white LED using a blue LED (7). The white LED of employing blue, green, and red emitting phosphors excited by a near UV LEDs can offer a higher efficiency solid-state lightening. Therefore, it is important to search for excellent blue, green, and red emitting multi-phases phosphors that can be excited efficiently under near UV range around 400 nm. In this paper, we present the optical properties of white and multi-color LED by using BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>: Eu (blue), SrGa<sub>2</sub>S<sub>4</sub>: Eu (green), and SrY<sub>2</sub>S<sub>4</sub>: Eu (red) phosphors from a violet LED.

## Experimental

Blue emitting BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>: Eu<sup>2+</sup> phosphor was obtained from Kasei Opt. Ltd. Green emitting SrGa<sub>2</sub>S<sub>4</sub>: Eu<sup>2+</sup> phosphor was synthesized by heating 0.95 mmol of strontium sulfide (SrS), 2.0 mmol of gallium dimethyldithiocarbamate (Ga[(CH<sub>3</sub>)<sub>2</sub>NCS<sub>2</sub>]<sub>3</sub>), 0.05 mmol of the europium complex ([[(CH<sub>3</sub>)<sub>4</sub>N]Eu[(CH<sub>3</sub>)<sub>2</sub>NCS<sub>2</sub>]<sub>4</sub>),

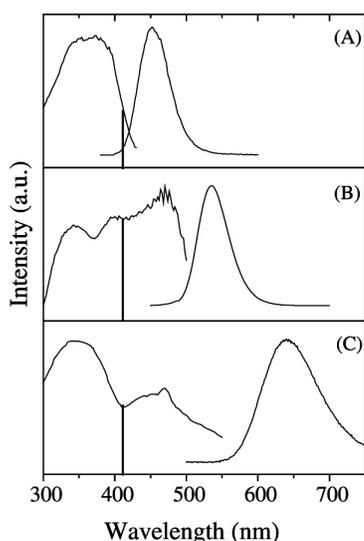
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and excess sulfur for 2 hours at 850 °C (8). Red emitting SrY<sub>2</sub>S<sub>4</sub>:Eu<sup>2+</sup> phosphor was prepared by solid-state reaction with 0.98 mmol SrCO<sub>3</sub>, 2.0 mmol Y<sub>2</sub>CO<sub>3</sub>, 0.02 mmol of Eu<sub>2</sub>CO<sub>3</sub>, and appropriate amount of Na<sub>2</sub>CO<sub>3</sub> as a flux at 1300 °C for 8 hours in H<sub>2</sub>S steam (9).

Photoluminescent excitation and emission measurements were carried out using a spectrum analyzer (DARSA, PSI) with 0.275 m grating monochromator with an Acton Research Co., PHV400 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. A commercial SMD-type violet LED ( $\lambda_{\text{max}}=405$  nm) was used. BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu (blue), SrGa<sub>2</sub>S<sub>4</sub>:Eu (green), and/or SrY<sub>2</sub>S<sub>4</sub>:Eu (red) phosphor suspensions were coated onto the surface of the SMD-type violet LED. The suspensions was made by dispersing a phosphor in poly-vinyl-alcohol (polymerization degree: 200).

## Results and Discussion

Fig 1 shows photoluminescent excitation and emission spectra of BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu, SrGa<sub>2</sub>S<sub>4</sub>:Eu, and SrY<sub>2</sub>S<sub>4</sub>:Eu phosphors. The excitation spectra show that BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu, SrGa<sub>2</sub>S<sub>4</sub>:Eu, and SrY<sub>2</sub>S<sub>4</sub>:Eu phosphors have strong absorptions at 405 nm

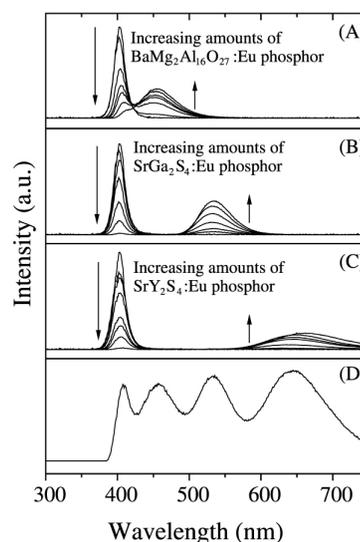


**Fig 1.** Excitation and emission spectra of (A) BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu, (B) SrGa<sub>2</sub>S<sub>4</sub>:Eu, and (C) SrY<sub>2</sub>S<sub>4</sub>:Eu phosphors. The bar at 405 nm corresponds to wavelength of the violet LED.

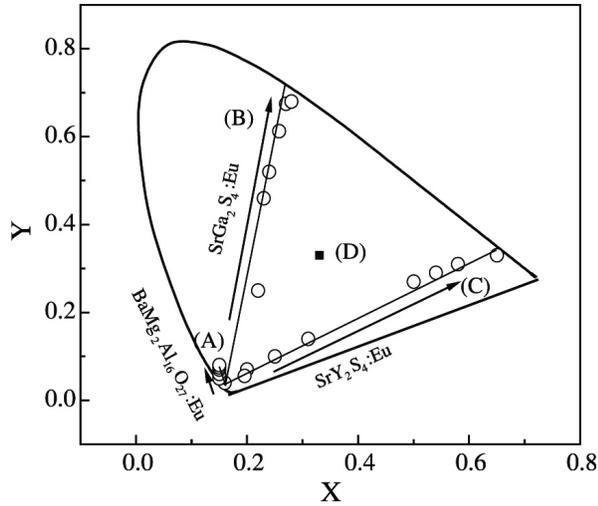
nm, which is an emission wavelength of the violet LED used. BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu, SrGa<sub>2</sub>S<sub>4</sub>:Eu, and SrY<sub>2</sub>S<sub>4</sub>:Eu phosphors emit blue (450 nm), green (535 nm), and red (640 nm) under 405 nm excitation, respectively. Therefore, BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu, SrGa<sub>2</sub>S<sub>4</sub>:Eu, and SrY<sub>2</sub>S<sub>4</sub>:Eu are suitable as blue, green, and red emitting phosphors under excitation from the violet LED.

Fig 2(A) shows the photoluminescence spectra of violet and blue emitting LEDs where only BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu phosphor is coated on a violet LED. The two distinct emission peaks appear at 405 nm and 450 nm which are the wavelengths of the violet LED and blue emission from the only BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu phosphor, respectively. When the amounts of BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu phosphor is increased, the intensity of the 405 nm emission decreases, while that of the 450 nm emission increases simultaneously. The CIE (Commission International de l'Eclairage) chromaticity coordinates of the photoluminescence spectra of violet and blue emitting LEDs are shown in Fig 3(A). The CIE chromaticity coordinates of a violet LED are  $x=0.17$  and  $y=0.01$ . As the concentration of BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu phosphor is increased, CIE chromaticity coordinates approach those of the pure blue emitting BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu phosphor with  $x=0.15$ ,  $y=0.08$ .

Fig 2(B) show the photoluminescence spectra of a violet and green emitting LEDs. As the amounts of SrGa<sub>2</sub>S<sub>4</sub>:Eu phosphor



**Fig 2.** The photoluminescence spectra of (A) violet and blue emitting LEDs, (B) violet and green emitting LEDs, (C) violet and red emitting LEDs, and (D) four-band white LED, where BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu (blue), SrGa<sub>2</sub>S<sub>4</sub>:Eu (green), and/or SrY<sub>2</sub>S<sub>4</sub>:Eu (red) phosphors are coated to the violet LED.

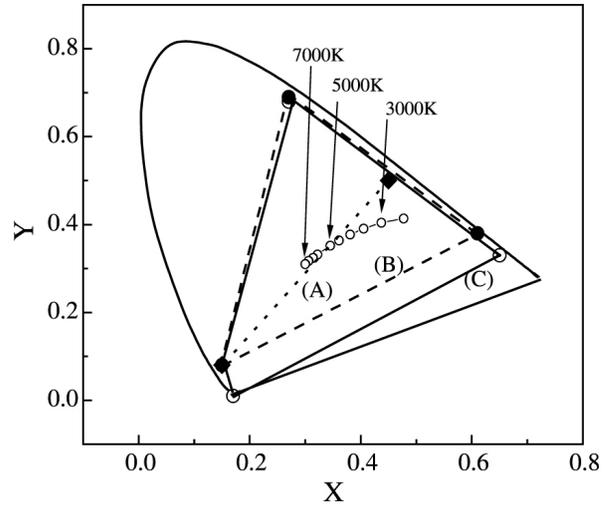


**Fig 3.** The CIE chromaticity coordinates of (A) violet and blue emitting LEDs, (B) violet and green emitting LEDs, (C) violet and red emitting LEDs, and (D) four-band white LED.

is increased, the color shifts from violet to green. The chromaticity coordinates are close to the straight line interconnecting the points of the violet LED ( $x=0.17$ ,  $y=0.01$ ) and the  $\text{SrGa}_2\text{S}_4:\text{Eu}$  phosphor ( $x=0.27$ ,  $y=0.68$ ) as in Fig 3(B). Fig 2(C) also show the photoluminescence spectra of a violet and red emitting LEDs. As in Fig 3(C), the concentration of  $\text{SrY}_2\text{S}_4:\text{Eu}$  phosphor is increased, CIE chromaticity coordinates are converged to  $x=0.65$ ,  $y=0.33$ .  $\text{SrY}_2\text{S}_4:\text{Eu}$  is an excellent red phosphor compared to  $\text{ZnCdS}:\text{Ag,Cl}$  ( $x=0.61$ ,  $y=0.39$ ) (7).

Fig 2(D) and 3(D) show the photoluminescence spectra of four-band white LED and CIE chromaticity coordinates of  $x=0.33$  and  $y=0.33$ . The color temperature is about 5500K. The amounts of  $\text{BaMg}_2\text{Al}_{16}\text{O}_{27}:\text{Eu}$ ,  $\text{SrGa}_2\text{S}_4:\text{Eu}$ , and  $\text{SrY}_2\text{S}_4:\text{Eu}$  phosphors are adjusted to generate the white color. Four distinct emission peaks are shown at 405, 450, 535, and 640 nm, which represent the violet, blue, green, and red, respectively. Therefore, we can obtain full color emitting LEDs by adjusting each amounts of  $\text{BaMg}_2\text{Al}_{16}\text{O}_{27}:\text{Eu}$ ,  $\text{SrGa}_2\text{S}_4:\text{Eu}$ , and/or  $\text{SrY}_2\text{S}_4:\text{Eu}$  phosphors. Moreover, white light can be obtained around  $x=0.33$  and  $y=0.33$ .

For commercial white LEDs (two-band white LEDs), different components of yttrium aluminum garnet (YAG),  $(\text{Y}_{1-x}\text{Gd}_x)_3\text{Al}_5\text{O}_{12}:\text{Ce}$ , must be synthesized to obtain white LEDs with different color temperatures (10). When the content of Gd is increased in  $(\text{Y}_{1-x}\text{Gd}_x)_3\text{Al}_5\text{O}_{12}:\text{Ce}$  phosphors, peak wavelength of emission shifts from 530 nm to a longer wavelength



**Fig 4.** The CIE chromaticity coordinates of (A) blue LED with  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$  phosphor for two-band white LED, (B) blue LED with  $\text{SrGa}_2\text{S}_4:\text{Eu}$  and  $\text{ZnCdS}:\text{Ag,Cl}$  phosphors for three-band white LED, (C) violet LED with  $\text{BaMg}_2\text{Al}_{16}\text{O}_{27}:\text{Eu}$ ,  $\text{SrGa}_2\text{S}_4:\text{Eu}$ , and  $\text{SrY}_2\text{S}_4:\text{Eu}$  phosphors for four-band white LED. The Planckian locus and color temperatures are also shown.

up to 570 nm. When white light of stronger red shade for lower color temperatures, it can be achieved by increasing the amount of Gd added 'in  $(\text{Y}_{1-x}\text{Gd}_x)_3\text{Al}_5\text{O}_{12}:\text{Ce}$ . Whereas the content of Ga is increased in  $\text{Y}_3(\text{Al}_{1-x}\text{Ga}_x)_5\text{O}_{12}:\text{Ce}$  phosphors, peak wavelength of emission shifts to a shorter wavelength. The white light of stronger blue shade with higher color temperatures can be achieved by increasing the amount of Ga added in  $\text{Y}_3(\text{Al}_{1-x}\text{Ga}_x)_5\text{O}_{12}:\text{Ce}$  phosphors. However, various color temperatures in four-band white LED can be easily made by simply mixing the different amounts of phosphors. The white light for lower and higher color temperatures can be obtained by coating higher amounts of red and green emitting phosphors onto a violet LED, respectively. This is the one of main advantages of the four-band white LED over the two-band white LED.

Fig 4 is a chromaticity diagram in which the two-band, three-band, and four-band LEDs are shown. The color of light emitted by a two-band LED in the chromaticity diagram is shown as the line by connecting two positions of a blue LED and  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$  (yellow) phosphor (10). The color range of light emitted by a three-band LED is shown as the region inside each triangle which is drawn by connecting the positions of a blue LED,  $\text{SrGa}_2\text{S}_4:\text{Eu}$  (green), and  $\text{ZnCdS}:\text{Ag,Cl}$  (red) phosphors (7). The color range of a four-band LED is the region

connecting the four positions of a violet LED,  $\text{BaMg}_2\text{Al}_6\text{O}_{27}:\text{Eu}$  (blue),  $\text{SrGa}_2\text{S}_4:\text{Eu}$  (green), and  $\text{SrY}_2\text{S}_4:\text{Eu}$  (red) phosphors. In Figure 4, the color range of four-band LED is the widest. This means that the four-band LED shows much better color purity in comparison with two-band and three-band LED. We are convinced that the four-band white LED has better color properties. Four-band white LED will be a good backlight source when it is used in full color display devices such as personal digital assistants.

### Conclusions

A four-band white LED was fabricated by using a violet LED with  $\text{BaMg}_2\text{Al}_6\text{O}_{27}:\text{Eu}$  (blue),  $\text{SrGa}_2\text{S}_4:\text{Eu}$  (green), and  $\text{SrY}_2\text{S}_4:\text{Eu}$  (red) phosphors. Full color emitting LEDs and four-band white LEDs with different color temperatures can be obtained by simply adjusting each amounts of  $\text{BaMg}_2\text{Al}_6\text{O}_{27}:\text{Eu}$ ,  $\text{SrGa}_2\text{S}_4:\text{Eu}$ , and  $\text{SrY}_2\text{S}_4:\text{Eu}$  phosphors. The four-band LED shows better color purity compared to two-band and three-band LED.

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*(Received Jan 10, 2006; Accepted Feb 15, 2006)*