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Optical characteristics of $xSrO \cdot yAl_2O_3 : Eu$ phosphors excited by ultraviolet light emitting diodes

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Abstract–We investigated the optical characteristics of strontium aluminate phosphors excited by near ultraviolet light emitting diodes (UV LEDs). For UV LEDs applications, strontium aluminates doped with europium were prepared at high temperature in a weakly reductive atmosphere. The effect of boric acid as a flux was considered. The excitation and emission spectra of these phosphors indicated that all of them have a broad band and that the main emission peaks, situated at around 490 nm for $4SrO \cdot 7Al_2O_3 : Eu$ and 520 nm for $SrOAl_2O_3 : Eu$, are both due to the $4f^6 5d^1 \rightarrow 4f^7$ transition of Eu^{2+}. The typical brightness of a phosphor-converted LED, which was made with synthesized phosphors and a blue LED, was 712 mcd. By using the synthesized phosphors, phosphor-converted white LEDs could be well fabricated with good optical characteristics. In this case, color coordinates could be controlled from x=0.1373 and y=0.4635 to x=0.2386 and y=0.6066 at 20 mA and 3.69 V.

Key words: UV LED, Phosphor, Lighting, Efficiency, Color

INTRODUCTION

Recently, a great deal of attention has been focused on the development of white light emitting diodes (LEDs). LEDs have extremely useful characteristics, including lifetimes measured in tens of thousands of hours, ruggedness, environmental friendliness, compact size, and low power consumption [1,2]. Their low operating voltage and small size allow considerable design flexibility and applicability in consumer electronics. One example is $Y_3Al_5O_{12} : Ce$-converted LEDs, which were first used in cellular phones by Nichia [3]. In their scheme, white light is generated by mixing blue light from a blue LED and orange light from phosphors excited by the blue LED. Despite their excellent driving conditions and economy of operation, they suffered from certain disadvantages related to the quality of the light produced.

The other possible scheme of generating white light from an LED is to use a near UV LED combined with R, G, B phosphors. In this case, the color rendering index (Ra) can be dramatically enhanced. However, the problem of obtaining R, G, B phosphors with high efficiency needs to be addressed. Recently, Taguchi's group in Japan reported the development of a white LED with an efficiency of more than 30 lm/W and a CR index of 93 using $Y_2O_2S : Eu$, $ZnS : Cu$, Al, $(Sr, Ca, Ba, Mg)_{10}(PO_4)_6Cl_2 : Eu$, and orange phosphors [4]. They did not describe the longevity of their system.

Strontium aluminate phosphors were first investigated in the late 1930s. By virtue of their excellent properties, including their high quantum efficiency [5,6], highly persistent phosphorescence [8] and good stability [10], strontium aluminate phosphors have been considered as a potential candidate for various practical device applications [9]. In particular, Abbruscato studied the $SrO \cdot Al_2O_3 : Eu^{2+}$ phosphor in depth, and reported that its optical properties were dependent on the composition and that, in this system, the method of excitation of Eu^{2+} under UV irradiation would be predominantly of the charge transfer type [7]. Another comprehensive study was performed by Smet et al. for lamp applications [8]. They reported that $2SrO \cdot 3Al_2O_3 : Eu^{2+}$ (SAL) and $4SrO \cdot 7Al_2O_3 : Eu^{2+}$ (SAE) phosphors, when employed as a green and blue emitter, yield highly efficient luminescence with quantum yields of up to 90% when doped with Eu^{2+}, and could be ideally suited for use in tricolor lamps. Commercially, strontium aluminates phosphors have been regarded as useful blue and green phosphors due to their long-duration phosphorescence characteristics. The long-afterglow luminescent characteristics of $4SrO \cdot 7Al_2O_3 : Eu^{2+}, Dy^{2+}$ phosphors were well summarized by Lin et al. [10,11].

In this work, we studied the synthesis of $SrO \cdot Al_2O_3 : Eu^{2+}$ and $4SrO \cdot 7Al_2O_3 : Eu^{2+}$ and their utilization for converting near UV light into visible light. We tried to optimize the optical characteristics of strontium aluminate phosphors for white LED applications. In particular, we focused our attention on the ability of boric acid to facilitate the synthesis by acting as a flux, the influence of calcining temperature, the control of the color coordinates and the variation of the light output for the purpose of generating a new combination of white phosphors.

EXPERIMENTAL PROCEDURE

The starting materials were $SrCO_3$ (purity 99.99%), α-Al_2O_3 (99.99%), and Eu_2O_3 (99.99%). These powders were weighed and mixed as shown in Table 1 for the preparation of $SrO \cdot Al_2O_3 : Eu^{2+}$, $4SrO \cdot 7Al_2O_3 : Eu^{2+}$. Here, 1-10 wt% H_3BO_3 (99.99%) was added to the system as a flux. The mole fraction of the flux in the system was an independent variable for maximum light output. All samples were prepared by solid-state reaction. The weighed materials were first ball-milled for about 24 hours in ethyl alcohol (A.P.). After the ethanol was evaporated at 60 °C, the samples were pelletized

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Table 1. The experimental compositions of the $SrO \cdot Al_2O_3 : Eu^{2+}$ and $4SrO \cdot 7Al_2O_3 : Eu^{2+}$ systems

No.	Composition (mol%)	H_3BO_3(wt%)	Eu_2O_3
B10-1	$SrCO_3$:Al_2O_3=0.9:1.1	6	0.02-0.055
B10-2	$SrCO_3$:Al_2O_3=1:1	6	
B10-3	$SrCO_3$:Al_2O_3=1.1:0.9	6	
B11	$SrCO_3$:Al_2O_3=0.9:1.1	2	
G10	$SrCO_3$:Al_2O_3=3.4:7.7	6	0.02-0.055

and sintered for 3 hr at 1,000-1,200 °C in a reducing atmosphere (N_2+2% H_2). After the flux was washed, the sample was sintered again for 6 hr at 1,200-1,400 °C in a reducing atmosphere (N_2+2% H_2) to improve their crystallinity.

The crystalline structure of the particles was measured by means of an x-ray diffractometer (Scintac XDS-2000). The TG-DTA curves were recorded with a model TA-50 thermal analysis system manufactured by Shimadzu. The optical properties of the prepared phosphors, including their emission (PL) and excitation spectra (PLE), were investigated by PL measurement (ORC lighting products, LH1751300). After full characterization of the phosphors, the synthesized phosphors were mixed with epoxy (1 : 1) and coated onto a UV LED (405 nm of peak wavelength) in a vacuum oven in order to remove the air. Finally, the optical properties of the phosphor-converted light emitting diode were examined by means of a model spectro 320-116 optical spectrum analyzer (Instrument system).

RESULTS AND DISCUSSION

In the strontium aluminate system, there exist four well-known compounds: $SrO \cdot Al_2O_3$, $SrO \cdot 6Al_2O_3$, $2SrO \cdot 3Al_2O_3$, and $4SrO \cdot 7Al_2O_3$. These phases are known to be formed between 800 °C and 1,500 °C [8]. The TG-DTA curves of our sample are shown in Fig. 1. It is obvious that the two different endothermic peaks (at 450-550 °C and 900-1,100 °C) in the DTA curve correspond, respectively, to the two different weight losing processes (AB and CD) in the TG curve. An endothermic peak at 450-550 °C corresponds to the change

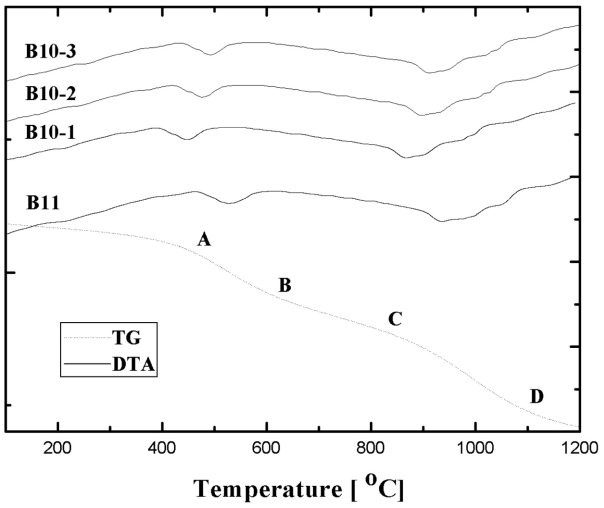

Fig. 1. TG-DTA curves of the B series phosphors.

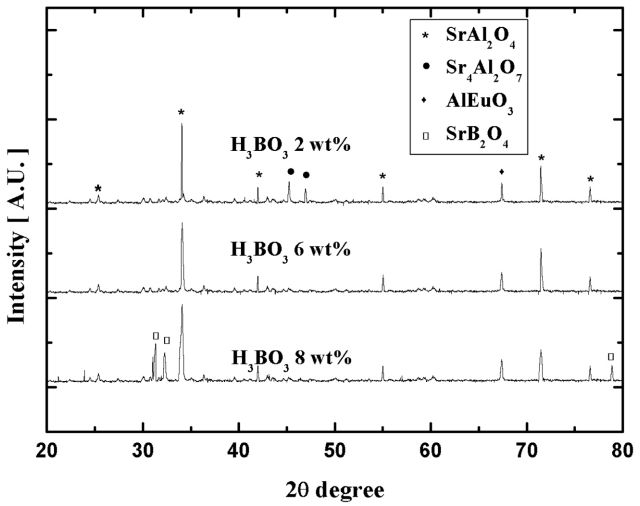

Fig. 2. The x-ray diffraction patterns of the B series phosphors.

of crystal type of $SrCO_3$. A broad endothermic peak at 900-1,100 °C indicates that $SrCO_3$ begins to decompose and strontium aluminate compounds begin to form at this time. For the DTA curves, it is clear that sample G10 with excess aluminum is decomposed at a lower temperature than the other samples. This means that the excess aluminum oxide causes the decomposition temperature to be lowered by acting as a base. The DTA curves of samples B10-1 and B10-2, which are shown in Fig. 1, indicate that H_3BO_3 accelerates the diffusion of the solid reaction and lowers the decomposition temperature.

$SrO \cdot Al_2O_3 : Eu^{2+}$ has two phases, a high temperature hexagonal phase (β-phase) and a low temperature monoclinic phase (γ-phase). The transition temperature occurs at 650 °C. The optical characteristics of $SrO \cdot Al_2O_3 : Eu^{2+}$ are known to be excellent when their structure has a hexagonal phase [14]. Shown in Fig. 2 is the x-ray diffraction data for the $SrO \cdot Al_2O_3 : Eu^{2+}$ phosphor as a function of the wt% of H_3BO_3. The synthesis conditions were 1,250 °C for 6 hr. It can be seen that there are three different diffraction peaks of $SrAl_2O_4$, $Sr_4Al_2O_7$ and $AlEuO_2$ with bad crystallinity in the case of the 2 wt% H_3BO_3 sample. When H_3BO_3 was added to the 6 wt%, sample, a single phase of $SrAl_2O_4$ was formed, and the diffraction peaks of SrB_2O_4 began to appear at a composition of 8 wt% H_3BO_3. This proved that H_3BO_3, by acting as a flux, accelerates the diffusion of the solid reaction, but that the presence of excess H_3BO_3 results in an unexpected phase such as SrB_2O_4.

The crystal structure of $4SrO \cdot 7Al_2O_3$ is known to be orthorhombic, consisting of a twinned layer containing AlO_6-octahedra or AlO_4-tetrahedra. Shown in Fig. 3 is the x-ray diffraction data of the prepared $Sr_4Al_{14}O_{25}$: Eu phosphor. It has generally been reported that the diffraction peaks of $SrAl_2O_4$ begin to appear at 1,100 °C, and that the intensity of the peaks increases with increasing calcining temperature, reaching a climax at 1,200 °C, when the diffraction peaks of $SrO \cdot 6Al_2O_3$ begin to appear [12]. As shown Fig. 3, at 1,250 °C, the number and intensity of the diffraction peaks of $SrO \cdot Al_2O_3$ and $SrO \cdot 6Al_2O_3$ decrease, while the diffraction peaks of $4SrO \cdot 7Al_2O_3$ increase rapidly, and the diffraction peaks of $4SrO \cdot 7Al_2O_3$: Eu calcined at 1,350 °C, shown in Fig. 3, show good crystallinity for a single phase.

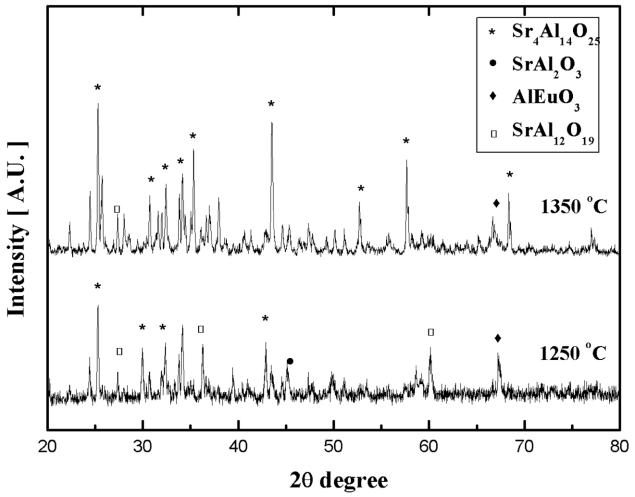

Fig. 3. The x-ray diffraction patterns of the sample G phosphor calcined at 1,250 °C and 1,350 °C for 3 hr, respectively.

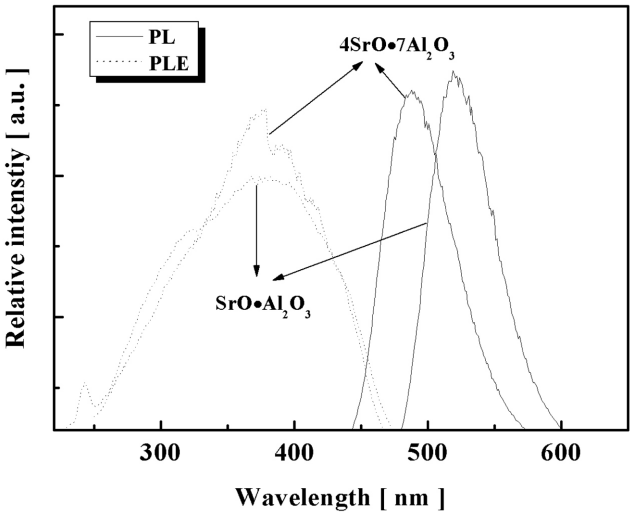

Fig. 4. Excitation and emission spectra of $SrO·Al_2O_3 : Eu^{2+}$ and $4SrO·7Al_2O_3 : Eu^{2+}$ phosphors.

In strontium aluminates, Eu^{2+} (radius: 0.112 nm) substitutes for the Sr^{2+} (radius: 0.113 nm) sites and emission from Eu^{2+} is dominant due to the $4f^7$-$4f^65d$ optical transition. The optical characteristics of phosphors doped with Eu^{2+} ions are normally dependent on their environment. Fig. 4 shows the emission (PL) and excitation (PLE) spectra of the $SrO·Al_2O_3 : Eu^{2+}$ and $4SrO·7Al_2O_3 : Eu^{2+}$ phosphors prepared in this study. The emission curve was obtained when the phosphors were excited by 405 nm radiation, which is the main emission peak of the near UV LED. The $SrO·Al_2O_3 : Eu^{2+}$ phosphor, which has an orthorhombic structure, exhibited broad band emission spectra peaking at 520 nm, while the $4SrO·7Al_2O_3 : Eu^{2+}$ phosphor, which has a hexagonal structure, exhibited broad band emission spectra peaking at 490 nm. In the case of the excitation of $SrO·Al_2O_3 : Eu^{2+}$, one excited level is observed with a maximum at 355 nm in the excitation spectrum, while in the case of the excitation of $4SrO·7Al_2O_3 : Eu^{2+}$, two excited levels may exist, since a shoulder is observed at 240 nm in the excitation spectrum, in addition to the maximum at 379 nm.

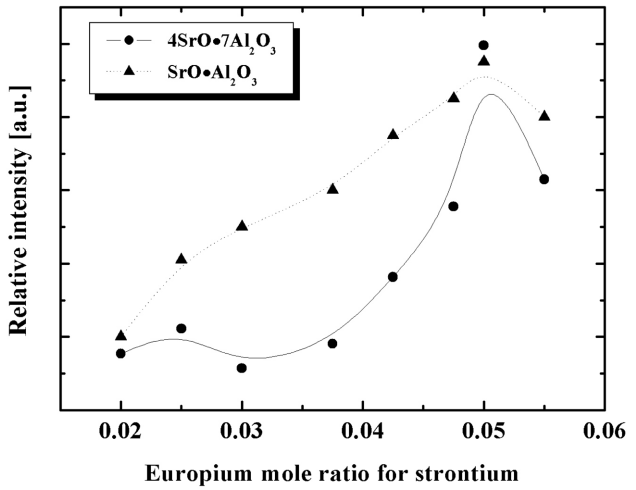

Fig. 5. Emission intensity dependence on Eu^{2+} concentration (x) for $(Sr_{1-x}Eu_x)O·Al_2O_3$ and $4(Sr_{1-x}Eu_x)O·7Al_2O_3$ phosphors (λ_{ex}=405 nm).

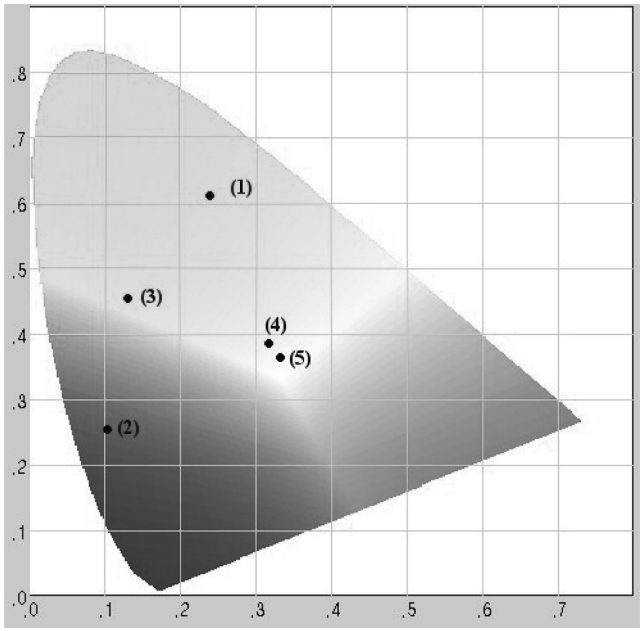

Fig. 6. CIE coordinates of phosphor converted LEDs.

The emission intensity dependence on the Eu^{2+} concentration under 405 nm excitation for the $(Sr_{1-x}Eu_x)O·Al_2O_3$ and $4(Sr_{1-x}Eu_x)O·7Al_2O_3$ phosphors (where x varies from 0.02 to 0.055) is shown in Fig. 5. The emission intensities of the $SrO·Al_2O_3 : Eu^{2+}$ and $4SrO·7Al_2O_3 : Eu^{2+}$ phosphors constantly increase with increasing Eu^{2+} concentration. It is not until the Eu^{2+} concentration exceeds about x=0.055 that the emission intensity begins to decrease with increasing Eu^{2+} concentration, which indicates that the emission center is quenched due to the high Eu^{2+} concentration. In terms of the heat-treatment, the maximal PL intensity was obtained at 1,250 °C for $SrO·Al_2O_3 : Eu^{2+}$ and 1,350 °C for $4SrO·7Al_2O_3 : Eu^{2+}$.

To assess the feasibility of using these phosphors in white LED applications, the PL characteristics of phosphor converted LEDs fabricated with $SrO·Al_2O_3 : Eu^{2+}$ and $4SrO·7Al_2O_3 : Eu^{2+}$ phosphors

were examined. In our work, we used a 405 nm near-UV LED as our excitation source. The phosphor was mixed with epoxy (1 : 1) and the resulting mixture was stirred at 60 °C for one hour. Once the air present in the mixture was removed by heating it in a vacuum oven, it was injected into the UV LED Chip using a syringe. Briefly, a small quantity of the mixture was drawn up into the syringe, and then the syringe was placed above the UV LED chip. Next, the plunger was pressed down so as to allow a droplet to form at the tip of the syringe, which was then allowed to fall onto the surface of the chip and, after allowing time for the droplet to be adsorbed into the chip, this operation was repeated until the entire contents of the syringe had been so "injected" into the chip. Finally, the chip was annealed at 140 °C for one hour.

Fig. 6 shows the CIE coordinates of the $SrO \cdot Al_2O_3 : Eu^{2+}$ phosphor-converted LED (1), the $4SrO \cdot 7Al_2O_3 : Eu^{2+}$ phosphor-converted LED (2) and the LED which was filled with a 1 : 1 mixture of the two phosphors (3) LEDs were (0.2386, 0.6066) for LED (1), (0.1003, 0.263) for LED (2) and (0.1373, 0.4635) for LED (3). As the mixing ratio of the two strontium aluminates phosphors varies, the color of the fabricated LED changes from blue to green.

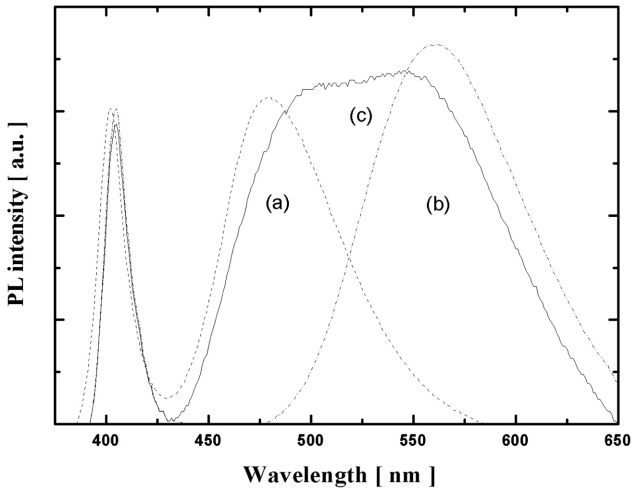

Fig. 7. EL spectra of phosphor converted white LEDs fabricated with $4SrO \cdot 7Al_2O_3 : Eu^{2+}$ and commercial strontium orthosilicate phosphors, respectively.

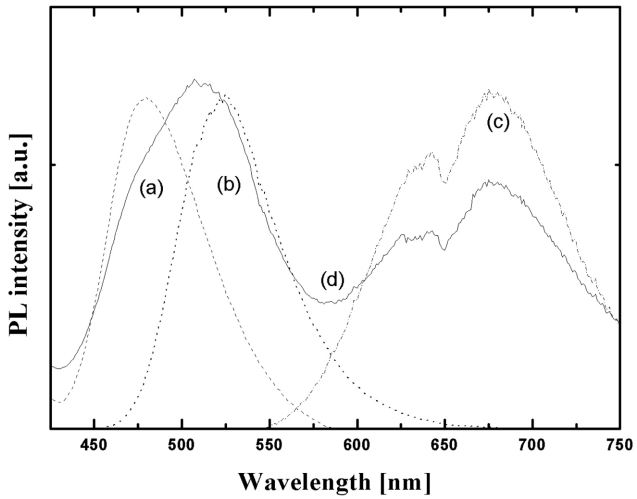

Fig. 8. EL spectra of phosphor converted white LEDs fabricated with $SrO \cdot Al_2O_3 : Eu^{2+}$, $4SrO \cdot 7Al_2O_3 : Eu^{2+}$ and commercial zinc sulfide phosphors, respectively.

In order to fabricate a phosphor-converted white LED, a mixture of a commercial orange phosphor (strontium ortho-silicate) and our blue phosphor ($SrO \cdot Al_2O_3 : Eu^{2+}$) or a mixture of a commercial phosphor (zinc sulfide) and our two phosphors ($4SrO \cdot 7Al_2O_3 : Eu^{2+}$ and $SrO \cdot Al_2O_3 : Eu^{2+}$) were injected into the near UV LED. The phosphors were mixed according to the ratio (B): 1 (O): 1 in the former case, and (B): 1 (G): 1 (R): 2 in the latter case, before injection into the LED. The overall emission spectrums of the two phosphor converted white LEDs are shown in Fig. 7 and Fig. 8, respectively. For convenience, we compared the emission color of the LEDs by means of their CIE values. The CIE values of the two LEDs were (0.3204, 0.3872) and (0.3295, 0.3724), respectively, as shown in (4) and (5) of Fig. 6. The former white LED has a bad color rendering index (<70) but good brightness (700 mcd), whereas the latter white LED has a good color rendering index (>95) but bad brightness (413 mcd). The latter white LED is slightly bluish-green in color, due to a lack of red color. Both LEDs were driven at 3.69 V and 20 mA.

CONCLUSION

In this work, $SrO \cdot Al_2O_3 : Eu^{2+}$ and $4SrO \cdot 7Al_2O_3 : Eu^{2+}$ phosphors were synthesized and their UV-light to visible light conversion properties were studied. It was found that the two phosphors have strong absorption bands between 380 and 410 nm and can be satisfactorily excited by a 405 nm UV LED. It is worth noticing that the luminescent materials which have absorption band near visible light are hardly found. In this point, $SrO\text{-}Al_2O_3$ material systems showed good optical characteristics appropriate to LED application. Also, we demonstrated the phosphor converted white LEDs by using $SrO\text{-}Al_2O_3$ system. However, more work on the control emission light from the $SrO\text{-}Al_2O_3$ system has to be done for achieving successful solid state lighting sources.

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