

Novel yellowish-orange $\text{Sr}_8\text{Al}_{12}\text{O}_{24}\text{S}_2:\text{Eu}^{2+}$ phosphor for application in blue light-emitting diode based white LED

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Abstract: A new yellowish-orange phosphor, $\text{Sr}_8\text{Al}_{12}\text{O}_{24}\text{S}_2:\text{Eu}^{2+}$, was synthesized by the solid-state method and its photoluminescence properties were investigated by excitation and emission spectra. Its excitation band is extending from 400–500 nm, which is adaptable to the emission band of blue LED chips (450–470 nm). Upon the excitation of 450 nm light, the phosphor exhibits strong yellowish-orange emission centered at 605 nm with good thermal stability. A white light-emitting diode (W-LED) that consists of a blue LED chip (~470 nm) and a $(\text{Sr}_{0.92}\text{Eu}_{0.08})_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ phosphor is demonstrated. The CIE1931 chromaticity coordinates (x, y) are (0.34, 0.25), the correlated color temperature (CCT) is 4300 K, and the luminous efficacy of this W-LED is 14.2 lm/W at room temperature and with a forward-bias current of 400 mA.

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OCIS codes: (160.2540) Fluorescent and luminescent materials; (250.5230) Photoluminescence.

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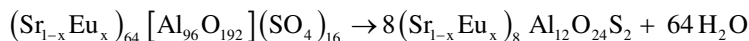
1. Introduction

Since bright blue light can be emitted from an indium gallium nitride (InGaN)–based light-emitting diode (LED) chip, efforts have continually been made to achieve solid-state lighting. There are great hopes that solid-state lighting could save electricity and thus reduce environmental problems [1,2]. One potential candidate for solid-state lighting is a white LED (W-LED). It is mercury free, and its luminous efficacy is being improved year by year. A primitive method of making white light is to mix light from red, green, and blue LED chips [3]. Even though any color can be produced by this method, its high cost is still a big problem for it to be used in white illumination.

One alternative method is to mix light from a LED chip and phosphors that can be excited by the LED chip. An excellent method using a blue LED chip and a phosphor that exhibits yellow emission under blue excitation was proposed [3–6]. The yellow phosphor is trivalent-cerium-activated yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, YAG). Alkali earth sulfide/oxy sulfide phosphors, such as $\text{CaS}:\text{Eu}^{2+}$ (red) [7], $\text{SrS}:\text{Eu}^{2+}$ (orange) [8], $\text{SrLaGa}_3\text{S}_6\text{O}:\text{Eu}^{2+}$ (yellowish-green) [9] and $\text{CaZnOS}:\text{Eu}^{2+}$ (red) [10] are also good candidates for LED applications because all of them have strong absorption in the blue region that is suitable to blue LED pumping. For this aim, we report the unprecedented yellowish-orange emitting oxy sulfide phosphor for application in blue LED based W-LED. Weller et al. have shown that the alkali earth oxy sulfide compounds $\text{M}_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ ($\text{M} = \text{Ca}, \text{Sr}$) have the structure of sodalite [11]. To our best knowledge, this is the first report of a study of Eu^{2+} -activator in $\text{Sr}_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ host. Herein, we report our investigation results on the synthesis and photoluminescence of the new yellowish-orange ($\text{Sr}_8\text{Al}_{12}\text{O}_{24}\text{S}_2:\text{Eu}^{2+}$) phosphors and the corresponding spectroscopic properties of phosphor-converted light-emitting diode (pc-LED).

2. Experimental

Polycrystalline phosphors with compositions of $(\text{Sr}_{1-x}\text{Eu}_x)_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ described in this work were prepared by a two-stage process, namely, starting with metal sulfate and carbonate and followed by hydrogen reduction. Briefly, a stoichiometric mixture of SrSO_4 (99%), SrCO_3 (99.9%), Al_2O_3 (99.99%) and Eu_2O_3 (99.99%) (all from Aldrich Chemicals, Milwaukee, WI, U.S.A) was ground together thoroughly and heated at 1200 °C for 8 h. The as-obtained products were then heated under 40% H_2 /60% N_2 atmosphere at 900 °C for 8 h. The reduction process occurred according to the following chemical equation:



These powder samples were then obtained by cooling down to room temperature in an electric furnace, ground, and pulverized for further measurements.

We verified the phase purity of the phosphor samples by powder X-ray diffraction (XRD) analysis with an advanced automatic diffractometer (Bruker AXS D8) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) operating at 40 kv and 20 mA. The XRD data for phase identification were collected in a 2θ range from 10 to 80°. The measurements of PL and PL excitation (PLE) spectra were performed by using a Spex Fluorolog-3 spectrofluorometer (Instruments S.A., Edison, N.J., USA) equipped with a 450 W Xe light source and double excitation monochromators. The powder samples were compacted and excited under 45° incidence, and emitted fluorescence was detected by a Hamamatsu Photonics R928 type photomultiplier perpendicular to the excitation beam. The spectral response of the measurement system is calibrated automatically on startup. To eliminate the second-order emission of the source radiation, a cutoff filter was used in the measurements. Diffuse reflectance spectra of phosphor samples were measured with a Hitachi 3010 double-beam UV-visible (vis) spectrometer (Hitachi Co., Tokyo, Japan) equipped with a $\phi 60$ mm integrating sphere whose

inner face was coated with BaSO₄ or Spectralon, and α-Al₂O₃ was used as a standard in the measurements.

In order to investigate the electroluminescent (EL) properties of our phosphor in white-light pc-LED, we have fabricated a surface mount device (SMD) LED by combining (Sr_{0.92}Eu_{0.08})₈Al₁₂O₂₄S₂ with InGaN-based LED chip with wavelength of ~470 nm. The phosphor blend was made by dispersing respective phosphor with 1:1 by wt % in a transparent silicone resin, and W-LED was then fabricated by coating the blue LED chip with the epoxy resin. The electroluminescence (EL) spectra, CIE chromaticity coordinates and luminous efficiency of pc-LED at room temperature were measured using an integrating sphere (EVERFINE PHOTO-E-INFO Co. LTD).

3. Results and discussion

3.1 XRD profile analysis and diffuse reflection spectra of Sr₈Al₁₂O₂₄S₂ and Sr₈Al₁₂O₂₄S₂:Eu²⁺

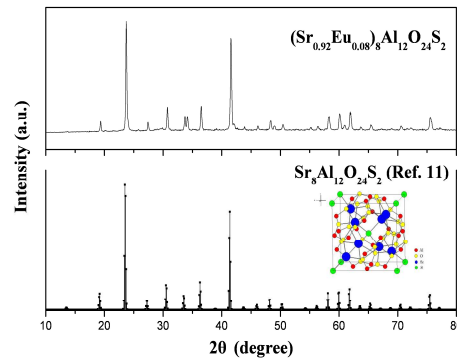


Fig. 1. XRD patterns of Sr₈Al₁₂O₂₄S₂ (Ref. 11) and (Sr_{0.92}Eu_{0.08})₈Al₁₂O₂₄S₂ sample. Inset: the body-centred cubic structure of Sr₈Al₁₂O₂₄S₂.

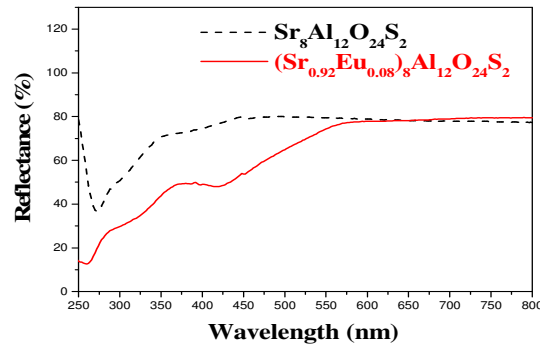


Fig. 2. Comparison of UV-Vis diffuse reflectance spectra for undoped Sr₈Al₁₂O₂₄S₂ and (Sr_{0.92}Eu_{0.08})₈Al₁₂O₂₄S₂.

Figure 1 shows the XRD pattern of (Sr_{0.92}Eu_{0.08})₈Al₁₂O₂₄S₂ that was body-centred cubic structure and in good agreement with the literature ($a_0 = 9.257 \text{ \AA}$) [11]. Figure 2 shows the diffuse reflectance spectra of the Sr₈Al₁₂O₂₄S₂ and (Sr_{0.92}Eu_{0.08})₈Al₁₂O₂₄S₂. The spectrum of the (Sr_{0.92}Eu_{0.08})₈Al₁₂O₂₄S₂ displays absorption bands between 400 and 500 nm attributed to the absorption of Eu²⁺ ion with the f→d transition, which was consistent with the corresponding excitation spectrum (Fig. 3).

3.2 Photoluminescence properties of Sr₈Al₁₂O₂₄S₂:Eu²⁺

Figure 3 shows the PL and PLE spectra of (Sr_{0.92}Eu_{0.08})₈Al₁₂O₂₄S₂ at room temperature. The PL emission spectrum under 450 nm light excitation exhibits a well-known characteristic Eu²⁺

emission. The emission band is due to the $4f^65d^1-4f^7$ transition of the Eu^{2+} ion. No emission peaks of Eu^{3+} are observed in the spectra, which proves that Eu^{3+} in the matrix crystals have been reduced to Eu^{2+} completely. The wavelength of the emission maximum is situated at $\lambda_{\text{max}} = 605$ nm, corresponding to chromaticity coordinates at (0.61, 0.38). The PLE spectra of $(\text{Sr}_{0.92}\text{Eu}_{0.08})_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ show broad band ranging from 400 to 500 nm, attributed to the $f \rightarrow d$ transition of Eu^{2+} ions. The broad excitation band well matches with the emission spectral range of blue LED chip (450–470 nm).

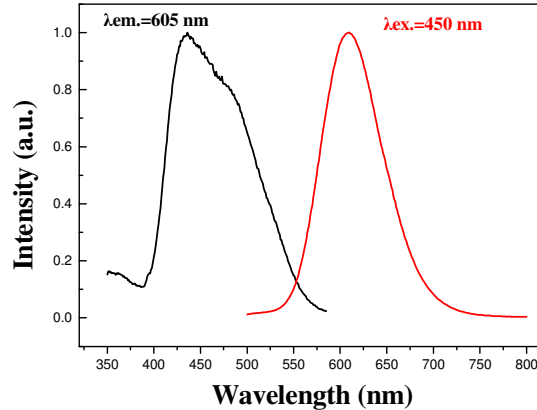


Fig. 3. PLE and PL spectra of $(\text{Sr}_{0.92}\text{Eu}_{0.08})_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ phosphor. ($\lambda_{\text{ex.}} = 450$ nm, $\lambda_{\text{em.}} = 605$ nm).

Figure 4 shows the emission intensity as a function of the Eu^{2+} concentration (x) for the $(\text{Sr}_{1-x}\text{Eu}_x)_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ phosphors. The data indicated that $(\text{Sr}_{0.92}\text{Eu}_{0.08})_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ is the optimized-composition. A percolation model [12,13] can be applicable to the concentration quenching of the compound on the following two assumptions: (1) The interaction between the Eu^{2+} ions occurs only among the nearest-neighbor sites in the rare earth sublattice. (2) The concentration quenching is due to the energy transfer from a percolating cluster of the Eu^{2+} ions to killer centers. In oxide phosphors, the energy transfer via a percolating cluster of the Eu^{2+} ions to killer centers is unlikely. The energy transfer occurs actually within the nearest Eu^{2+} ions [9,14]. When considering the mechanism of energy transfer in oxide phosphors, Blasse [15] pointed out that if the activator is introduced solely on Z ion sites, x_c is the critical concentration, N the number of Z ions in the unit cell and V is the volume of the unit cell, then there is on the average one activator ion per $V/x_c N$. The critical transfer distance (R_c) is approximately equal to twice the radius of a sphere with this volume:

$$R_c \approx 2\left(\frac{3V}{4\pi x_c N}\right)^{1/3} \quad (1)$$

Taking the values of V (793.3 \AA^3), N (8), and x_c (0.08), the R_c was calculated to be 13 \AA . It was believed that the decrease in the PL intensity for samples with x of 0.08 was mainly due to the non-radiative transition among the Eu^{2+} ions, which may occur because of exchange interaction, radiation reabsorption, or multipole–multipole interaction [16,17]. The $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} is allowed while exchange interaction is responsible for the energy transfer for forbidden transitions and typical critical distances are then about 5 \AA [17]. This indicates that the mechanism of exchange interaction plays no role in energy transfer between Eu^{2+} ions in $\text{Sr}_8\text{Al}_{12}\text{O}_{24}\text{S}_2:\text{Eu}^{2+}$ phosphor. The mechanism of radiation reabsorption comes into effect only when there is broad overlap of the fluorescent spectra and in the view of the emission and excitation spectra of $\text{Sr}_8\text{Al}_{12}\text{O}_{24}\text{S}_2:\text{Eu}^{2+}$ phosphor is unlikely to be occurring in this case. Therefore, the multipolar interaction dominated the concentration quenching mechanism of Eu^{2+} emission [18,19].

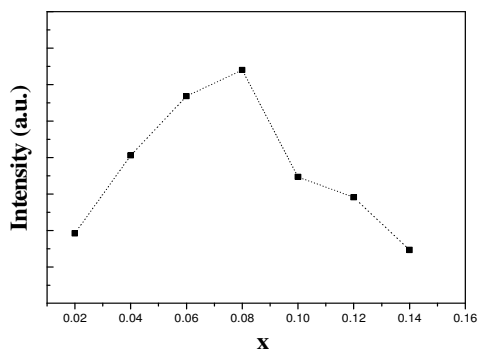


Fig. 4. Emission intensity as a function of Eu^{2+} concentration (x) for $(\text{Sr}_{1-x}\text{Eu}_x)_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ ($x = 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14$) phosphors ($\lambda_{\text{ex}} = 450 \text{ nm}$).

3.3 Thermal quenching properties of $\text{Sr}_8\text{Al}_{12}\text{O}_{24}\text{S}_2:\text{Eu}^{2+}$

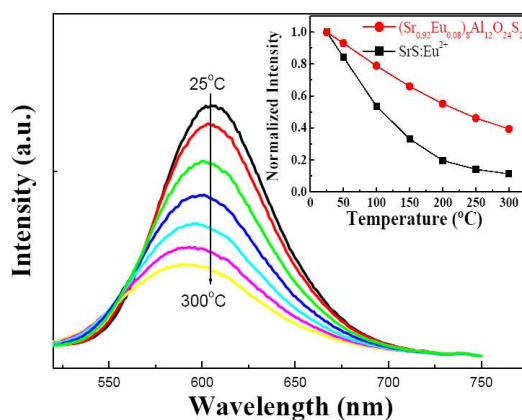


Fig. 5. PL spectra of $(\text{Sr}_{0.92}\text{Eu}_{0.08})_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ phosphor excited at 450 nm with different temperatures. The inset shows the normalized PL intensity as a function of temperatures. For comparison, thermal quenching data of commercial phosphor ($\text{SrS}:\text{Eu}^{2+}$) excited at 450 nm were also measured as a reference.

For the application of high power LEDs, the thermal stability of phosphor is one of important issues. Temperature dependence of luminescence for $(\text{Sr}_{0.92}\text{Eu}_{0.08})_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ phosphor under 450 nm excitation is shown in Fig. 5. The activation energy (E_a) can be expressed by:

$$\ln \frac{I}{I_0} = \ln A - \frac{E_a}{kT} \quad (2)$$

where I_0 and I are luminescence intensity of $(\text{Sr}_{0.92}\text{Eu}_{0.08})_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ phosphor (by integrating the area of each spectrum) at room temperature and testing temperature, respectively; A is constant; k is Boltzmann constant ($8.617 \times 10^{-5} \text{ eV/K}$). The E_a was obtained to be 0.0494 eV/K. The inset of Fig. 5 displayed the thermal quenching of $(\text{Sr}_{0.92}\text{Eu}_{0.08})_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ at $\lambda_{\text{em}} = 605 \text{ nm}$ and $\text{SrS}:\text{Eu}^{2+}$ at $\lambda_{\text{em}} = 616 \text{ nm}$ (excited at 450 nm, U-color Co. LTD). As shown in Fig. 5, $(\text{Sr}_{0.92}\text{Eu}_{0.08})_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ phosphor exhibited much higher thermal stability than that of $\text{SrS}:\text{Eu}^{2+}$ commodity. The results indicate that $(\text{Sr}_{0.92}\text{Eu}_{0.08})_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ phosphor could be a promising phosphor for high power LED application.

3.4 Electroluminescence properties of $\text{Sr}_8\text{Al}_{12}\text{O}_{24}\text{S}_2:\text{Eu}^{2+}$

$(\text{Sr}_{0.92}\text{Eu}_{0.08})_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ was selected with 470 nm InGaN as the pumping light source for white light LED package. The pc-LED was chosen for its high light extraction efficiency, the resulting luminous efficiency of W-LED hence was found to reach as high as 14.2 lm/W under 400 mA driving current. Blue LED and W-LED electroluminescence (EL) spectra are shown in Fig. 6. The CIE coordinates of blue LED and W-LED are (0.13, 0.09) and (0.34, 0.25), respectively. The luminous efficiency of blue LED and pc-LED ($\text{SrS}:\text{Eu}^{2+}$ was selected with 470 nm InGaN) are 8.1 lm/W and 22.8 lm/W, respectively. The insets of Fig. 6 show the appearance of blue LED and well-packaged single-phosphorconverted-LED lamps in operation. These results demonstrate that $\text{Sr}_8\text{Al}_{12}\text{O}_{24}\text{S}_2:\text{Eu}^{2+}$ is a potential yellowish-orange phosphor for applications of display and illumination because of its good thermal stability.

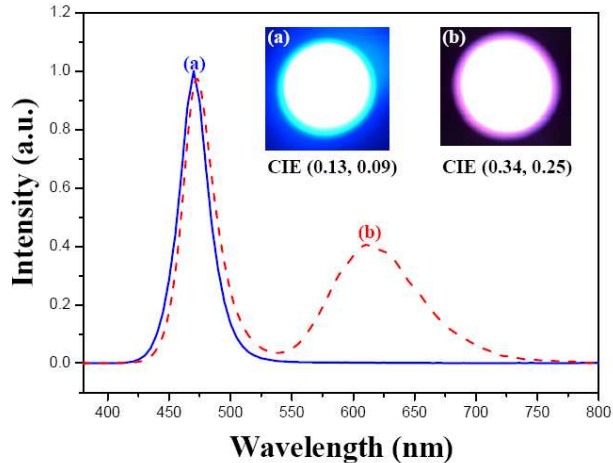


Fig. 6. (a) EL spectra of an InGaN-based blue-LED driven with a 400 mA current. (b) EL spectra of a white emitting InGaN-based blue-LED comprising of $(\text{Sr}_{0.92}\text{Eu}_{0.08})_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ phosphor driven with a 400 mA current. Inset: blue-LED and W-LED photos.

4. Conclusion

In summary, we have synthesized a series of novel yellowish-orange $\text{Sr}_8\text{Al}_{12}\text{O}_{24}\text{S}_2:\text{Eu}^{2+}$ phosphors by solid-state reactions. The excitation and emission spectra of these phosphors show that all are broadband, which can be viewed as the typical emission of Eu^{2+} ascribed to the 4f–5d transitions. Because of their broadband absorption in the region 400–500 nm, these phosphors meet the application requirements for blue LED chips. The critical quenching concentration of Eu^{2+} in $\text{Sr}_8\text{Al}_{12}\text{O}_{24}\text{S}_2:\text{Eu}^{2+}$ phosphor is determined as 8%. Moreover, a white light LED was fabricated through the integration of a 470 nm chip and a yellowish-orange phosphor $(\text{Sr}_{0.92}\text{Eu}_{0.08})_8\text{Al}_{12}\text{O}_{24}\text{S}_2$ into a single package, which shows a white light of 4300K, color coordinates of (0.34, 0.25), and luminous efficiency of 14.2 lm/W. The results indicate that $\text{Sr}_8\text{Al}_{12}\text{O}_{24}\text{S}_2:\text{Eu}^{2+}$ is a promising yellowish-orange phosphor for the application in blue LED chips based white-light LEDs.

Acknowledgments

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