High color rendering white light-emitting-diode illuminator using the red-emitting Eu^{2+}-activated CaZnOS phosphors excited by blue LED

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Abstract: A red phosphor CaZnOS:Eu^{2+} was synthesized by solid state reaction and has been evaluated as a candidate for white LEDs. For this material, the XRD, PL, PL excitation (PLE) and diffuse reflection spectra have also been investigated. CaZnOS:Eu^{2+} reveals a broad absorption band and good color purity. By utilizing a mixture of red-emitting CaZnOS:Eu^{2+}, green-emitting $(Ba,Sr)_2SiO_4$:Eu^{2+} and yellow-emitting $Y_3Al_5O_{12}$:Ce^{3+} as light converters, an intense white InGaN-based blue-LED (~460 nm) was fabricated to exhibit a high color-rendering index Ra of 85 at a correlated color temperature of 4870 K. Based on the results, we are currently evaluating the potential application of CaZnOS:Eu^{2+} as a red-emitting blue-chip convertible phosphor.

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

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1. Introduction

The white light-emitting diodes (LEDs), featuring the advantages of high light efficiency, low energy consumption, and long service lifetime, have drawn much attention because of their wide applications. Currently, the most common approach to produce white light is to combine a blue LED chip with a yellow phosphor, and some detailed studies on the combination of the InGaN blue-emitting LED and Ce^{3+}-doped yttrium aluminum garnet (YAG) yellow phosphor are presented [1,2]. However, the "white" output light of such an LED is limited with high correlated color temperature (CCT) ranging from 5000 to 10000 K; that is, the cold white light is usually obtained. To obtain the warm white light output, a complementary red light is necessary to compensate the red color deficiency or to produce white light in the blue-green-red (BGR) mode. For both routes, the red phosphors that can be efficiently excited by the GaN or InGaN LED chip are in great demand.

As the 4f-5d transition of Eu^{2+} ion is sensitive to the crystal field and covalency, the Eu^{2+} doped phosphors have a strong absorption in the UV to the visible spectral region and exhibit broad emission bands covering the color from blue to red [3,4]. Alkali earth sulfide phosphors, such $CaS:Eu^{2+}$ (red) and $SrS:Eu^{2+}$ (orange) 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 [5–7]. From the above-mentioned considerations, it can be anticipated that novel oxysulfide compounds may be promising host materials for Eu^{2+}. The compound CaZnOS was first discovered by Petrova et. al. [8] in 2003 and subsequently its synthesis, structure, and electrical properties were investigated in detail by Clarke et al. in 2007 [9]. Very recently, the $CaZnOS:Mn^{2+}$ phosphor was reported by Hintzen et al. in 2009 [10]. However, there has been no paper reporting the luminescence properties of Eu^{2+}-activated CaZnOS and applied to high color rendering index (CRI) LEDs, to our knowledge. The aim of this work is to report our investigation results on the synthesis and photoluminescence of the new red $CaZnOS:Eu^{2+}$ phosphor and their corresponding optical properties of phosphor-converted LEDs (pc-LEDs).

2. Experimental

Polycrystalline phosphors with compositions of $(Ca_{1-x}Eu_x)ZnOS$ described in this work were prepared by a solid-state reaction. Briefly, the constituent raw materials CaS (99.9%), ZnO (99.99%) and Eu_2O_3 (99.9%) (all from Aldrich Chemicals, Milwaukee, WI, USA) were weighed in stoichiometric proportions and intimately ground, and were then sintered under a reducing atmosphere at 900 °C for 8 h. The products 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 as prepared by powder X-ray diffraction (XRD) analysis with an advanced automatic diffractometer (Bruker AXS D8) with Cu Kα radiation (λ = 1.5418 Å) operating at 40 kv and 20 mA. The XRD data for phase identification were collected in a 2θ range from 10 to 80°. 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 ø60 mm integrating sphere whose inner face was coated with $BaSO_4$ or Spectralon, and α-Al_2O_3 was used as a standard in the measurements. 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. The CIE chromaticity coordinates for all samples were determined by a Laiko DT-100 color analyzer equipped with a charge coupled device (CCD) detector (Laiko Co.,

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Tokyo, Japan). The quantum efficiency (QE) was measured by an integrating sphere whose inner face was coated with Spectralon equipped with a spectrofluorometer (Horiba Jobin-Yvon Fluorolog 3–22 Tau-3).

3. Results and discussion

3.1 XRD profile analysis

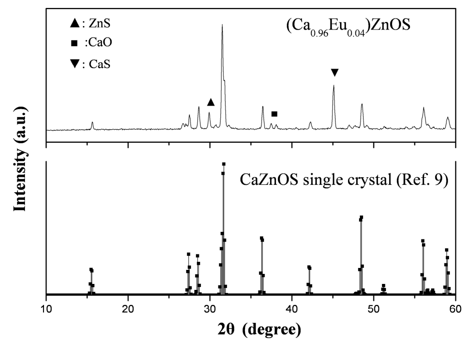

Fig. 1. XRD pattern of $(Ca_{0.96}Eu_{0.04})ZnOS$ powder sample.

Figure 1 shows the powder XRD pattern of $(Ca_{0.96}Eu_{0.04})ZnOS$ sample. $(Ca_{0.96}Eu_{0.04})ZnOS$ phosphor is shown to be the main phase of the CaZnOS sample combined with a small amount of impurities, i.e. in particular CaS, plus ZnS, and CaO phases. Compared to the reported preparation method using a sealed tube, relatively more impurities have been detected for our Eu^{2+}-doped CaZnOS samples [8,9]. The result was similar to that reported for CaZnOS:Mn^{2+} [10]. According to the literature [11], Xia et al. synthesized BaZnOS:Mn^{2+} by sealed tube method, the impurity phases could be reduced. Therefore, we synthesized $(Ca_{0.96}Eu_{0.04})ZnOS$ by sealed tube method and confirmed that the luminescence properties of $(Ca_{0.96}Eu_{0.04})ZnOS$ keep the same after reducing the impurity phases.

3.2 Diffuse reflection spectra of CaZnOS and CaZnOS:Eu^{2+}

Figure 2 displays the diffuse reflectance spectra of the CaZnOS and $(Ca_{0.96}Eu_{0.04})ZnOS$. The spectrum of the $(Ca_{0.96}Eu_{0.04})ZnOS$ displays absorption bands between 450 and 550 nm attributed to the absorption of Eu^{2+} ion with the f→d transition, which was consistent with the corresponding excitation spectra (Fig. 3).

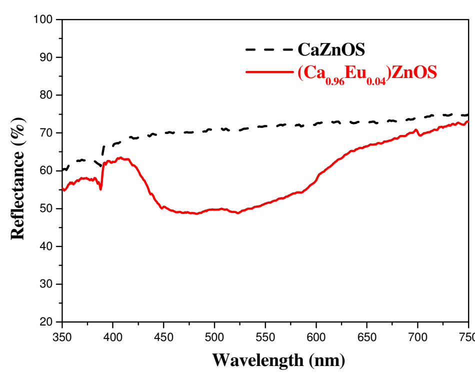

Fig. 2. Diffuse reflection spectra of CaZnOS and $(Ca_{0.96}Eu_{0.04})ZnOS$ powder samples.

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3.3 Photoluminescence properties of CaZnOS:Eu^{2+}

Figure 3 shows the PLE and PL spectra of $(Ca_{0.96}Eu_{0.04})ZnOS$ at room temperature. It exhibits a broad emission band extending from 600 to 700 nm, which corresponds to the allowed $4f^6 5d \rightarrow 4f^7$ electronic transitions of Eu^{2+}. The PLE spectra of $(Ca_{0.96}Eu_{0.04})ZnOS$ show broad band ranging from 450 to 550 nm, attributed to the f→d transition of Eu^{2+} ions. The broad excitation band well matches with the emission spectral range of blue-LED (450–470 nm).

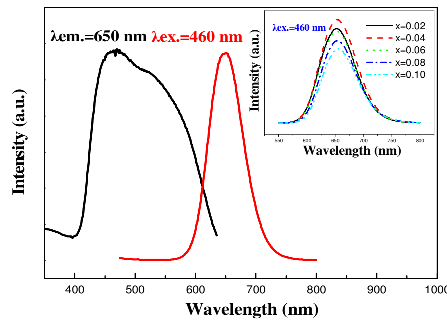

Fig. 3. PLE and PL spectra of $(Ca_{0.96}Eu_{0.04})ZnOS$ phosphor. ($\lambda_{ex.}$ = 460 nm, $\lambda_{em.}$ = 650 nm). Inset: PL intensity of $(Ca_{1-x}Eu_x)ZnOS$ as a function of Eu^{2+} content.

The inset of Fig. 3 displays the PL spectra as a function of the Eu^{2+} concentration (x) for the CaZnOS:xEu^{2+} phosphors. The data indicated that $(Ca_{0.96}Eu_{0.04})ZnOS$ is the optimized-composition. When considering the mechanism of energy transfer in oxide phosphors, Blasse [12] 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_cN. The critical transfer distance (R_c) is approximately equal to twice the radius of a sphere with this volume:

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

Taking the values of V (139.388 Å^3), N (2), and x_c (0.04), the R_c was calculated to be 15 Å. It was believed that the decrease in the PL intensity for samples with x of 0.04 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 [13,14]. The exchange interaction is generally responsible for the energy transfer of forbidden transitions and the typical distance is about 5 Å [14]. Because the $4f\,^6 5d \rightarrow 4f^7$ transition of the Eu^{2+} ion is allowed as well as the excitation and emission band overlap at 600–630 nm, the energy transfer may occur as a result of multipolar interaction and radiation reabsorption [15].

In order to further determine the absolute quantum efficiency of photo-conversion for the novel phosphor, herein we have used integrated sphere method for the measurements of optical absorbance (A) and quantum efficiency (Φ) of phosphor samples. The absorbance and quantum efficiencies of $(Ca_{0.96}Eu_{0.04})ZnOS$ phosphor can also be calculated by using these following equations,

$$A = \frac{L_0(\lambda) - L_i(\lambda)}{L_0(\lambda)} \tag{2}$$

where $L_0(\lambda)$ is the integrated excitation profile when the sample is diffusely illuminated by the integrated sphere's surface; $L_i(\lambda)$ is the integrated excitation profile when the sample is directly excited by the incident beam. Furthermore, quantum efficiency (Φ) of $(Ca_{0.96}Eu_{0.04})ZnOS$ phosphor can be calculated by

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$$\Phi = \frac{E_i(\lambda) - (1 - A) \bullet E_0(\lambda)}{L_e(\lambda) \bullet A} \quad (3)$$

where $E_i(\lambda)$ is the integrated luminescence of the powder upon direct excitation, and $E_o(\lambda)$ is the integrated luminescence of the powder excited by indirect illumination from the sphere. The term $L_e(\lambda)$ is the integrated excitation profile obtained from the empty integrated sphere (without the sample present). The absorbance of $(Ca_{0.96}Eu_{0.04})ZnOS$ and $SrS:Eu^{2+}$ (U-color Co. LTD) were found to be 76.1 and 64.5 at the excitation wavelength of 460 nm, respectively, and the corresponding QE was found to be 35.5% and 60.8%. The corresponding excitation wavelengths, emission wavelengths, CIE coordinates, absorbance and QE's are summarized in Table 1.

Table 1. The comparison of commodity phosphor and $(Ca_{0.96}Eu_{0.04})ZnOS$.

Composition	Excitation (nm)	Emission (nm)	CIE (x, y)	Relative Absorbance	Relative QE
$(Ca_{0.96}Eu_{0.04})ZnOS$	460	650	(0.69, 0.31)	76.1	35.5
$SrS:Eu^{2+}$	460	616	(0.61, 0.38)	64.5	60.8

3.4 Thermal quenching properties of CaZnOS:Eu^{2+}

For the application of high power LEDs, the thermal stability of phosphor is one of important issues to be considered. Temperature dependence of PL spectra for $(Ca_{0.96}Eu_{0.04})ZnOS$ under excitation at 460 nm is shown in Fig. 4. The activation energy (*Ea*) can be expressed by

$$\ln \frac{I}{I_0} = \ln A - \frac{E_a}{kT} \quad (4)$$

where I_0 and I are the luminescence intensity of $(Ca_{0.96}Eu_{0.04})ZnOS$ at room temperature and the testing temperature, respectively; A is a constant; k is the Boltzmann constant (8.617×10^{-5} eV K^{-1}). E_a was obtained to be 0.1461 eV K^{-1}. Figure 4 inset displays and compares the thermal quenching properties of $(Ca_{0.96}Eu_{0.04})ZnOS$ and $SrS:Eu^{2+}$. As shown in the inset of Fig. 4, the thermal stability of $CaZnOS:Eu^{2+}$ is superior than that of $SrS:Eu^{2+}$ commodity in the range of 50 °C to 125 °C, which is within LED operating temperature [16].

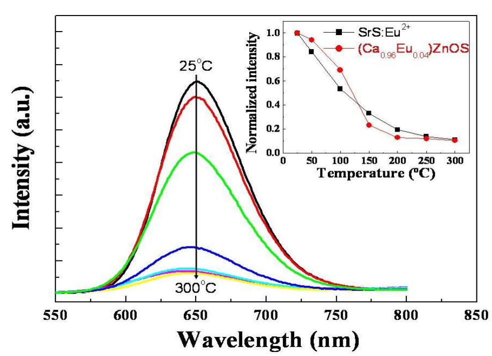

Fig. 4. Temperature-dependent PL spectra of $(Ca_{0.96}Eu_{0.04})ZnOS$ phosphor excited at 460 nm. Inset: normalized PL intensity as a function of temperature. For comparison, thermal quenching data of $SrS:Eu^{2+}$ excited at 460 nm were also measured as a reference.

3.5 Electroluminescence properties of CaZnOS:Eu^{2+}

$(Ca_{0.96}Eu_{0.04})ZnOS$ was selected with 460 nm InGaN as the pumping light source for red light LED packaging. As revealed by chromaticity simulations, $Y_3Al_5O_{12}:Ce^{3+}$(YAG),

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$(Ba,Sr)_2SiO_4:Eu^{2+}$(BOS) and $(Ca_{0.96}Eu_{0.04})$ZnOS were selected with 460 nm InGaN as the pumping light source for white light pc-LED package demonstration. The pc-LED was chosen for its high light extraction efficiency, the resulting luminous efficiency of white light pc-LED hence was found to reach as high as 25.6 lm/W under 400 mA driving current. Red and white pc-LEDs electroluminescence (EL) spectra are shown in Fig. 5. A qualitative criterion of the ability to display the colors of an irradiated object in a natural way is the color rendering index (CRI) [17]. The CIE coordinates, CRIs, and luminous efficiency of pc-LEDs are summarized in Table 2. Table 2 displayed the CRIs of the combination of blue-LED with YAG, BOS and $(Ca_{0.96}Eu_{0.04})$ZnOS, which gives a Ra of 85, which was found to be higher than that of commercial pc-LED (Harvatek Co. LTD, HT-P278BPV) that combining blue-LED with YAG (Ra = 75).

The insets of Fig. 5 show the appearance of well-packaged single-phosphorconverted-LED and three-phosphorconverted-LED lamps in operation. These results demonstrate that CaZnOS:Eu^{2+} is a potential red phosphor for applications in display and illumination because of its high luminous efficiency and excellent color purity.

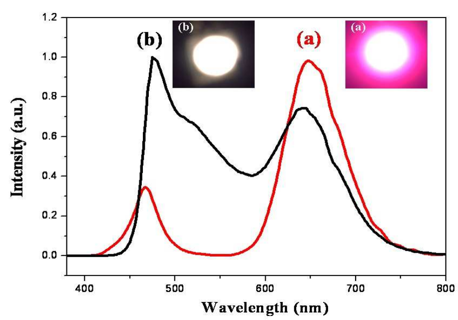

Fig. 5. EL spectra of (a) red pc-LED fabricated with $(Ca_{0.96}Eu_{0.04})$ZnOS and (b) white pc-LED fabricated with YAG, BOS and $(Ca_{0.96}Eu_{0.04})$ZnOS. The inset shows the red pc-LED and white pc-LED, both driven by a 400 mA current.

Table 2. The comparison of commercial pc-LED and those were prepared by combining (a) $(Ca_{0.96}Eu_{0.04})$ZnOS and (b) $(Ca_{0.96}Eu_{0.04})$ZnOS + YAG + BOS with blue LED.

pc-LED	Power (watt)	CIE (x, y)	Ra	Luminous efficiency (lm/W)
(a)	1.1	(0.49, 0.23)	–	15.2
(b)	1.1	(0.34, 0.40)	85	25.6
HT-P278BPV	2.3	(0.32, 0.33)	75	28.1

4. Conclusion

In summary, an intense red-emitting CaZnOS:Eu^{2+} phosphor has been synthesized by a conventional solid state reaction. The phosphor shows a broad absorption band and good color purity under blue light pumping. The white LEDs fabricated with an blue chip, green/yellow-emitting phosphors and red-emitting $(Ca_{0.96}Eu_{0.04})$ZnOS generate white light with high color rendering index (Ra = 85). These results indicate that CaZnOS:Eu^{2+} is a promising red phosphor for application in white light LEDs (excited by blue LEDs).

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