

Synthesis of CaS:Eu²⁺ Phosphor by using a Sealing Vessel and its Photoluminescence Properties

Hyoung Sun Yoo, Bong Je Park, Jong Hyuk Kang, Won Bin Im, and Duk Young Jeon^a
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea

^aE-mail : dyl@kaist.ac.kr

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We have synthesized CaS:Eu²⁺ phosphor by using a sealing vessel and evaluated its photoluminescence properties. The method using a sealing vessel is simple and economical in comparison with other methods reported up to date. As an activator concentration was increased from 0.1 mol% to 4 mol%, the main emission wavelength of the phosphor was increased from 642 nm to 651 nm due to the crystal field splitting of 5d levels of Eu²⁺ ion. Although the same amount of Eu₂O₃ was used, the concentration of the activator ions, which were reduced from Eu³⁺ to Eu²⁺ and substituted Ca²⁺ ions, was increased with increase of firing temperature. Therefore, the main emission wavelength was also shifted from 645 nm to 651 nm with increase of firing temperature from 1100 °C to 1300 °C. The critical distance ($R_{c1} = 20.65 \text{ \AA}$) between Eu²⁺ ions calculated from the critical concentration was well matched with that ($R_{c2} = 19.17 \text{ \AA}$) calculated from the Dexter formula.

Keywords : CaS:Eu²⁺, Phosphor, Luminescence, ESR

1. INTRODUCTION

Rare-earth ions doped alkaline-earth chalcogenides have been widely studied as promising phosphor materials for flat panel displays (FPDs) applications due to their excellent luminescence properties[1,2]. Among the phosphor materials, many researchers have paid their attentions to CaS:Eu²⁺ phosphor not only for electroluminescence devices but also for white light emitting diodes (LEDs) applications, because CaS:Eu²⁺ phosphor efficiently absorbs blue light and emits red light with a high color purity[3,4]. Especially, a technique producing white LEDs by combining red and green emitting phosphors, such as CaS:Eu²⁺ and SrGa₂S₄:Eu²⁺, with InGaN based blue LEDs would contribute to advances of a next generation backlight unit for liquid crystal displays (LCDs) and a lighting industry as a whole [4,5]. However, according to papers reported up to date, either toxic H₂S gas or expensive reduction gas has been used for preparing the sulfide phosphors to prevent oxidation of the phosphors during the firing step[1-4].

In this study, we have designed a new synthesis method of sulfide phosphors, which is using a sealing vessel. By using a sealing vessel, it was not needed to use atmospheric gases, reductant, and flux materials at all for preparing CaS:Eu²⁺ phosphor with high crystallinity. In addition, photoluminescence properties

depending upon a concentration of activator ions and firing temperature were investigated in detail.

2. EXPERIMENTAL

Photoluminescence properties of a phosphor are affected by synthesis methods and precursors used[6-8]. In this study, we have designed and used a sealing vessel to prepare CaS:Eu²⁺ phosphor. The sealing vessel was made of heat-resistant alloys and it was possible to assemble and disassemble the sealing vessel. Therefore, the sealing vessel was semi-permanent. CaS (Kojundo, 99.99 %) and Eu₂O₃ (Kojundo, 99.999 %) were used as raw materials, and concentration of Eu²⁺ ions was varied from 0.1 mol% to 4 mol%. After mixing of the stoichiometric raw materials, the mixture was put into a crucible. Then the sealing vessel was assembled, and subsequently it was fired at temperatures ranging from 1100 °C to 1300 °C for 4 h. The sealing vessel cooled to room temperature was disassembled, and CaS:Eu²⁺ phosphor samples were obtained. Any atmospheric gases were not used during the firing step, and other materials such as excess sulfur, flux materials, and active carbon were not used, either.

Crystalline phases of the prepared CaS:Eu²⁺ phosphor were analyzed by a Rigaku D/max - RC X-ray

diffractometer with Cu K_{α} ($\lambda = 1.542 \text{ \AA}$) radiation operating at 40 kV and 45 mA. The scan rate was $1^{\circ}/\text{min}$ and the measurement range was from 20° to 80° . Excitation and emission spectra of the prepared CaS:Eu^{2+} phosphor were obtained using a standard spectrometer setup from DARSA PRO 5100 PL system (Professional Scientific Instrument Co., Korea), which utilize a Xenon lamp as an excitation source. The electro spin resonance (ESR, JES-FA200) measurements at room temperature were carried out at X-band frequency to observe the amount of Eu^{2+} ions in the phosphor samples. The decay time of prepared CaS:Eu^{2+} phosphor was measured by a Tektronix TDS 340A with a xenon flash lamp.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the prepared CaS:Eu^{2+} phosphor. All of the peaks in the XRD pattern corresponded to the cubic structured CaS (JCPDS # 65-0894) phase as indexed in the figure. It meant that the prepared phosphor sample was not oxidized during the firing step and the crystallinity of the prepared phosphor sample was good. Figure 2 shows the PLE/PL spectra of the prepared CaS:Eu^{2+} phosphor. The excitation band of the phosphor ranged from 420 nm to 620 nm, and the phosphor emitted a red emission ranged from about 600 nm to 730 nm.

Figure 3 shows the relative PL intensity and the main emission wavelength of the prepared phosphor samples depending upon the concentration of Eu^{2+} ion. All of the phosphor samples were fired at 1200°C . As can be seen from the figure, when the concentration of Eu^{2+} ion was 1 mol%, the relative PL intensity was maximum. When the concentration of Eu^{2+} was higher than 1 mol%, the relative PL intensity was decreased due to a well-known

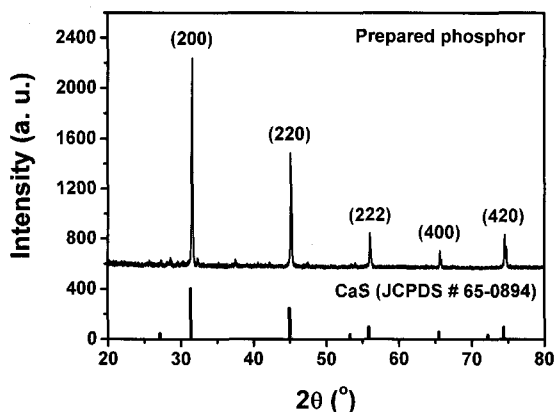


Fig. 1. The XRD pattern of the prepared CaS:Eu^{2+} phosphor at 1200°C .

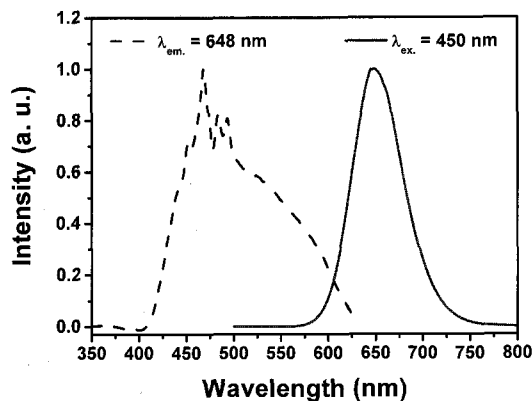


Fig. 2. The PLE/PL spectra of the prepared CaS:Eu^{2+} phosphor.

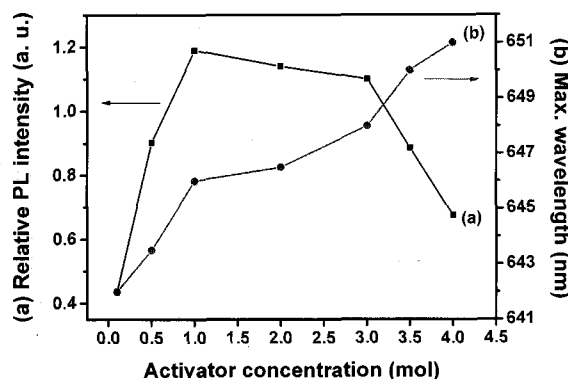


Fig. 3. (a) The relative PL intensity and (b) the main emission wavelength of the prepared CaS:Eu^{2+} phosphor depending upon the concentration of Eu^{2+} ion.

concentration quenching. In addition, the main emission wavelength was increased from 642 nm to 651 nm with increase of the Eu^{2+} ion concentration from 0.1 mol% to 4 mol%. It was due to increase of the crystal field strength, which Eu^{2+} ions felt, with increase of the Eu^{2+} ion concentration. Because the ionic radii of Eu^{2+} ion (1.17 \AA) is bigger than that of Ca^{2+} ion (1.00 \AA), Eu^{2+} ions felt stronger crystal field with increase of the Eu^{2+} ion concentration[9]. Eu^{2+} ion has an electronic configuration of $4f^7$. Red emission of CaS:Eu^{2+} phosphor is owing to the $4f-5d$ transition of Eu^{2+} ions, and the splitting of the 5d levels is strongly dependant on the crystal field strength. As shown in Fig. 4, the splitting of the 5d levels was increased with increase of the crystal field. Therefore, as the concentration of Eu^{2+} ion increased, the energy difference between bottom of 5d level and top of 4f level of Eu^{2+} ions decreased, and subsequently the main emission wavelength was shifted to the longer wavelength.

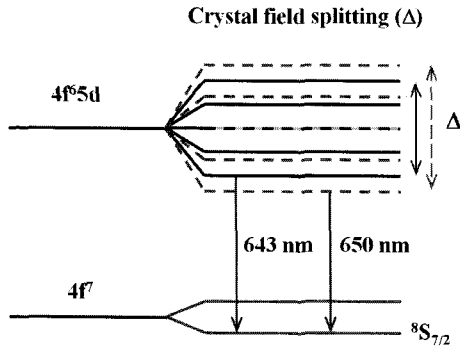


Fig. 4. The energy level diagram of the Eu²⁺ ion in the CaS:Eu²⁺ phosphor. 5d levels of the Eu²⁺ ion split by the crystal field.

Figure 5 shows the relative PL intensity and the main emission wavelength of the prepared phosphor samples depending upon the firing temperature.

The concentration of Eu₂O₃ was fixed at 0.5 mol%. The phosphor sample fired at 1200 °C showed the maximum relative PL intensity among the ones experimented. In addition, the main emission wavelength was also shifted from 645 nm to 650 nm with increase of the firing temperature from 1100 °C to 1300 °C. It was similar to the result which was related to a variation of Eu²⁺ ion concentration. From the result, it was expected that the change of the main emission wavelength depending upon the firing temperature was also dependant on the concentration of Eu²⁺ ion which substituted Ca²⁺ ion. In order to investigate the reason, the ESR analysis was carried out. The difference between the electronic configuration of Eu²⁺ ion and that of Eu³⁺ ion exists. The Eu²⁺ ion has an electronic configuration of 4f⁷ (⁸S_{7/2}) which is paramagnetic, while the Eu³⁺ ion has an electronic configuration of 4f⁶ (⁷F₀) which is non-paramagnetic[10]. Therefore, only Eu²⁺ ions, which substituted Ca²⁺ ions, responded to a magnetic field. Because Eu ions in Eu₂O₃ were Eu³⁺ ions,

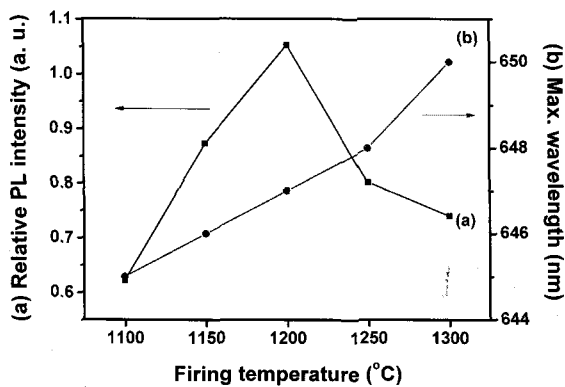


Fig. 5. (a) The relative PL intensity and (b) the main emission wavelength of the prepared CaS:Eu²⁺ phosphor depending upon the firing temperature.

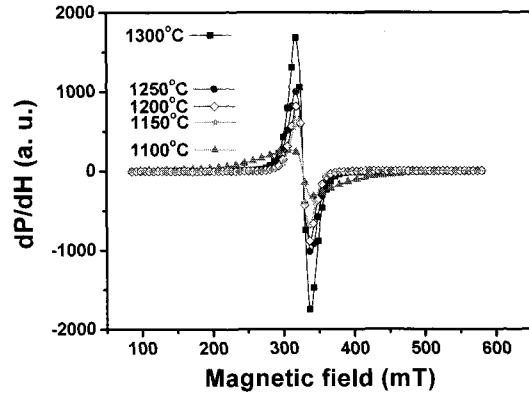


Fig. 6. The ESR spectra of the prepared CaS:Eu²⁺ phosphor samples with different firing temperatures.

only reduced and substituted Eu ions were Eu²⁺ ions. Figure 6 shows the ESR spectra of the prepared phosphor samples with different firing temperatures. The ESR signal centered on 327 mT was caused not by Eu³⁺ ions but by Eu²⁺ ions, and the signal was increased with increase of the firing temperature. It meant that the amount of the Eu²⁺ ions, which were reduced and substituting Ca²⁺ ions, was varied with the firing temperature. Although the same amount of Eu₂O₃ was used in these samples, the amount of Eu²⁺ ions in these samples was increased with increase of the firing temperature. Therefore, the crystal field splitting was increased with increase of the firing temperature, and subsequently the main emission wavelength was also increased. On the other hand, Fig. 7 shows the decay curves of the prepared phosphor samples with the different firing temperatures. The decay time of the samples was decreased with increase of the firing temperature, which represented that non-radiative transitions between Eu²⁺ ions were promoted. Generally, when the distance between Eu²⁺ ions decrease, the non-radiative transitions increase[11]. Therefore, from the decay curves, it was confirmed that the distance between

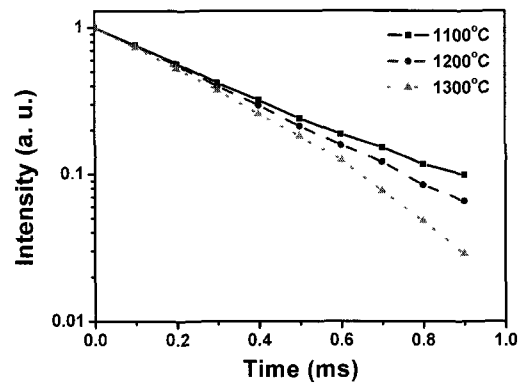


Fig. 7. The decay curves of the prepared CaS:Eu²⁺ phosphor samples with the different firing temperatures.

Eu^{2+} ions was decreased and thus concentration of the Eu^{2+} ion was increased with increase of the firing temperature.

It is possible to calculate the critical distance (R_{c1}) from the critical concentration (X_c) and number of cation (N) present in the unit cell. In this case, the X_c is the optimized concentration of Eu^{2+} ion and the R_{c1} is equal to the average shortest distance between Eu^{2+} ions corresponding to the X_c [12]. The R_{c1} obtained from the experimental data of concentration quenching is represented as

$$R_{c1} \approx 2 \left(\frac{3V}{4\pi X_c N} \right)^{1/3} \quad (1)$$

where, V is a volume of the unit cell. Taking the values of V (184.327 \AA^3), N (4), and X_c (0.01, from the Fig. 3), the R_{c1} turned out to be 20.65 \AA . In addition, the critical distance (R_{c2}) could be obtained from the Dexter's formula[13]. Assuming the electric dipole-dipole interaction between Eu^{2+} ions, the R_{c2} could be given as

$$R_{c2} = \left(0.63 \times 10^{28} \frac{4.8 \times 10^{-16} \cdot P}{E^4} SO \right)^{1/6} \quad (2)$$

where, P is the oscillator strength of the Eu^{2+} ion. E is the energy of maximum spectral overlap and SO is the spectral overlap integral, which represents the product of normalized spectral areas of emission and emission spectra[14]. For P corresponding to the broad $4f^7 \rightarrow 4f^6 5d$ absorption band, a value of 10^{-2} was taken[14]. Taking the values of E (2.06 eV) and SO ($0.5 \times \text{height} \times \text{width} = 0.5 \times 0.23 \times 0.25 = 0.0284 \text{ eV}^{-1}$) from the spectra, the value of R_{c2} was calculated as 19.17 \AA . It was well matched with the R_{c1} . From the results, it was confirmed that the energy transitions between Eu^{2+} ions in CaS:Eu^{2+} phosphor were mainly electric dipole-dipole interaction, and the optimized concentration (0.01 mol%) obtained in this study was accurate.

4. CONCLUSION

Equations We have prepared a highly efficient CaS:Eu^{2+} phosphor by using a sealing vessel. The method proposed in this study was very simple and economical. As concentration of Eu^{2+} ion was increased, the crystal field was increased, and subsequently the main emission wavelength was also increased. Although the same amount of Eu_2O_3 was used, the amount of Eu^{2+} ions which were reduced and also substituted Ca^{2+} ions was increased. Therefore, the main emission wavelength

was also increased with increase of the firing temperature. The critical distance ($R_{c1} = 20.65 \text{ \AA}$) between Eu^{2+} ions calculated from the critical concentration was well matched with that ($R_{c2} = 19.17 \text{ \AA}$) calculated from the Dexter formula. From the results, it was confirmed that the energy transitions in CaS:Eu^{2+} phosphor were mainly electric dipole-dipole interaction between Eu^{2+} ions, and the optimized concentration (0.01 mol%) obtained in this study was accurate.

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