

## Luminescent characteristics of a blue-emitting $\text{CaAl}_2\text{Si}_2\text{O}_8$ : $\text{Eu}^{2+}$ phosphor and the effect of boron ion substitution

**Byoung-Hwa Kwon, Sivakumar Vaidyanathan, Hui Li, Ho Seung Jang,  
Hyung Sun Yoo and Duk Young Jeon**

Dept. of Materials Science and Engineering, Korea Advanced Institute of Science  
and Technology, 335 Gwahangno, Yuseong-gu, Daejeon 305-701, Korea

TEL:82-42-350-3337, e-mail: dyj@kaist.ac.kr.

**Keywords : phosphor, luminescence, substitution**

### Abstract

Blue-emitting  $\text{CaAl}_2\text{Si}_2\text{O}_8$ : $\text{Eu}^{2+}$  (CAS: $\text{Eu}^{2+}$ ) phosphor, prepared by solid-state reaction, is described in this paper. We researched the effect of boron ion substitution in the host materials. The phase and luminescent properties were investigated using the powder X-ray diffraction (XRD) and photoluminescence (PL) spectra.

### 1. Introduction

$\text{BaMgAl}_{10}\text{O}_{17}$ : $\text{Eu}^{2+}$  (BAM: $\text{Eu}^{2+}$ ), commonly used as blue-emitting phosphor, has problems of the thermal stability and oxidation because  $\beta$ -alumina structure has an open layer in the crystal [1]. Silicates are suitable for the host lattice of phosphors because of their high physical and chemical stability. Among them,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ : $\text{Eu}^{2+}$  (CAS: $\text{Eu}^{2+}$ ) has a rigid structure and unlimited framework of silicon-oxygen and aluminum-oxygen around  $\text{Eu}^{2+}$  ions [2]. Therefore, CAS: $\text{Eu}^{2+}$  has the potential to replace BAM: $\text{Eu}^{2+}$  commonly used in color display and lamp phosphor.

Boron is usually added as a flux. It may be dissolved into the host lattice. The atomic radii of the solute must differ by no more than 15% for solid solution. Although the ionic radii of  $\text{B}^{3+}$  (0.11 Å) is much smaller than that of  $\text{Al}^{3+}$  (0.39 Å) [3], small amount of boron could displace the CAS lattice.

Here, we synthesize the single phase CAS: $\text{Eu}^{2+}$  phosphor and investigate the effect of luminescence property by substituting boron ion for the CAS: $\text{Eu}^{2+}$  host lattice.

### 2. Experimental

The phosphor was prepared by solid-state reaction.

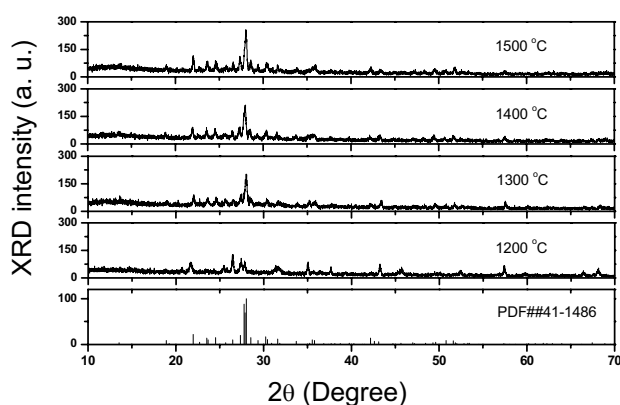
The starting materials were  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Eu}_2\text{O}_3$  and  $\text{H}_3\text{BO}_3$ . After being ground thoroughly in stoichiometric ratios by using an agate mortar, the mixed powders were sintered in a tube furnace at 1200~1400 °C for 4 h in an Ar atmosphere with 20%  $\text{H}_2$ . The crystal structures of the prepared samples were analyzed by X-ray diffraction using an X-ray diffractometer (Rigaku, D/max-III C (3kW) with  $\text{Cu-K}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ )). Photoluminescence (PL) and photoluminescence excitation (PLE) were recorded by DARSA PRO 5100 PL system with xenon lamp (500W) (PSI Co., Korea).

### 3. Results and discussion

Figure 1 shows XRD patterns of CAS: $\text{Eu}^{2+}$  phosphors with variation of the sintering temperature from 1200 to 1500 °C. The structure of CAS host lattice is monoclinic (JCPDS file #41-1486) and belong to the space group of P-1(2). The peak pattern of the prepared at 1200 °C is quite different from JCPDS 41-1486 because impurity phase exist. On the other hand, as increasing the temperature higher than 1300 °C, all the peaks are well matched due to the single phase formation.

Before the boron substitution in host lattice, we optimized the activator concentration. At 1500 °C, the CAS: $\text{Eu}^{2+}$  phosphor forms a glass phase depending upon the  $\text{Eu}^{2+}$  concentration. In considering the result, the experiment of boron substitution were proceeded at 1300 and 1400 °C.

To investigate the effects of boron substitution, CAS: $\text{Eu}^{2+}$  phosphor samples were prepared with varying boron concentration at 1300 and 1400 °C.

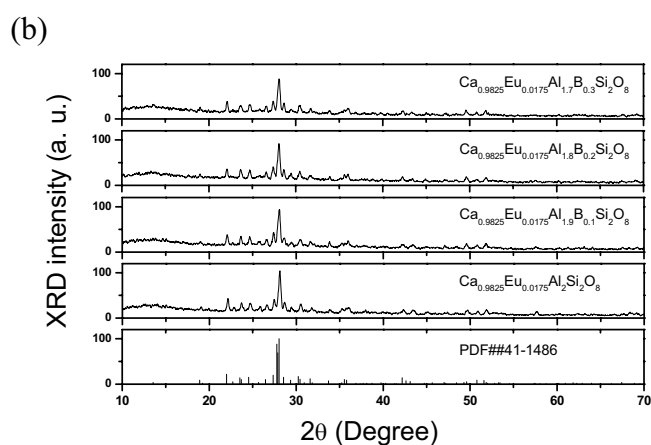
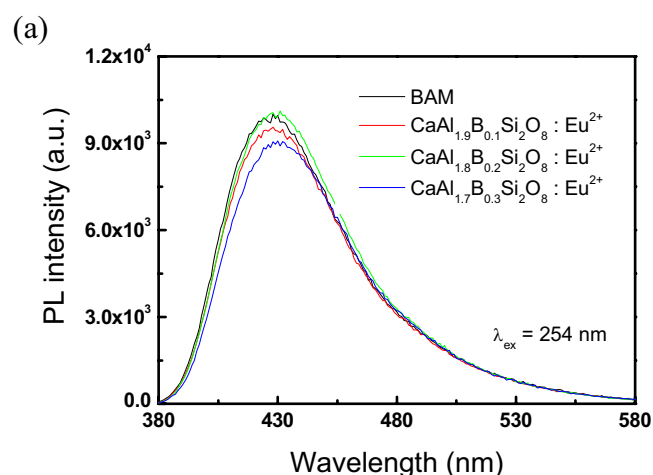


**Fig. 1. XRD patterns of CAS:Eu<sup>2+</sup> phosphors with various sintering temperature.**

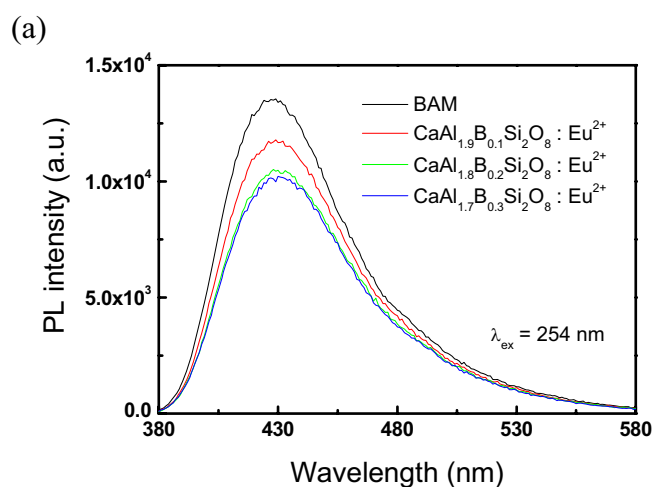
Fig. 2. (a) shows the PL spectra of CAS:Eu<sup>2+</sup> phosphor with 0.1, 0.2, 0.3 mol of boron concentration at 1300 °C. In the case of 0.1 and 0.3 mol of B<sup>3+</sup> substitution, the emission intensity decrease a little. However, in the case of 0.2 mol of B<sup>3+</sup>, the PL intensity increase. Fig. 2. (b) is the XRD pattern of the same samples. As the boron concentration increases from 0.1 to 0.3 mol, the peak well matched JCPDS 41-1486, but the intensity ratio of peaks present in each diffraction pattern decrease. It means that the impurity phase does not exist, but the degree of crystallinity deteriorate as increasing the boron concentration.

The presence of boron in phosphor lattice can remove the electron traps such as oxygen vacancies [4]. Therefore, the luminescence intensity is enhanced with 0.2 mol of boron concentration in spite of decrease of the crystallinity.

As shown in Fig 3, CAS:Eu<sup>2+</sup> phosphor samples were synthesized in higher temperature at 1400 °C. As the boron concentration increased, the PL intensity decreased. Because H<sub>3</sub>BO<sub>3</sub> powder usually acts as a flux, it can give an effect of increasing the temperature more than 1400 °C. Therefore, it is supposed that the deterioration of crystallinity was accelerated and the emission intensity decrease.



**Fig 2. CAS:Eu<sup>2+</sup> phosphor samples synthesized at 1300 °C. (a) PL spectra (b) XRD patterns with 0.1, 0.2, 0.3 mol of B<sup>3+</sup> concentration.**

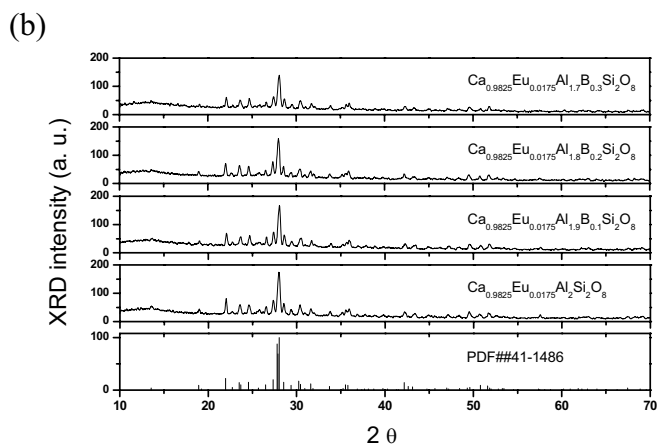


#### 4. Summary

The single phase of CAS:Eu<sup>2+</sup> phosphor for display device were synthesized by conventional solid-state reaction. We investigated the boron substitution in CAS host materials. Although there is a big difference in the ionic radii between boron and aluminium, small amount of boron can dissolve in host lattice. The boron substitution can enhance the luminescence properties by removing oxygen vacancies acting as the electron trap in proper range of boron amount and sintering temperature that do not decrease the crystallinity.

#### 5. References

1. S. Oshio, T. Matsuoka, S. Tanaka and H. Kobayashi, *J. Electrochem. Soc.* 145, 3903 (1998).
2. W. B. Im, Y. I. Kim, J. H. Kang and D. Y. Jeon, *Solid State Commun.* 134, 717 (2005).
3. R. D. Shannon, *Acta Crystallogr. A* 32, 751 (1976).
4. J. Niittykoski, T. Aitasalo, J. Holsa, H. Jungner, M. Lastusaari, M. Parkkinen and M. Yukiä, *J. Alloys Compd.* 374, 108 (2004).



**Fig 3. CAS:Eu<sup>2+</sup> phosphor samples synthesized at 1400 °C. (a) PL spectra (b) XRD patterns with 0.1, 0.2, 0.3 mol of B<sup>3+</sup> concentration.**