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Physical studies on the enhancement of photoluminescence properties for blue $BaAl_2Si_2O_8 : Eu^{2+}$ phosphors via LPP method with addition of silicate concentrations

Bong Sung Kim, Min Ji Lee[b], Takesi Abe[c], Takaki Masaki[b], Young-Hyun Song[b], Kenji Toda[c] and Dae-Ho Yoon[a,b,*]

[a]*SKKU Advanced Institute of Nanotechnology,(SAINT) Sungkyunkwan University, Suwon 440-746, Korea*

[b]*School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 440-746, Korea*

[c]*Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, Ikarashi 2 nocho 8050, Niigata 950-2181, Japan*

$BaAl_2Si_2O_8$: Eu^{2+} + $xSiO_2$ (x = 0, 1, 2 and 3) has been synthesized with phosphors via novel liquid phase precursor (LPP) method. The best crystalline $BaAl_2Si_2O_8 : Eu^{2+}$ phosphor could not be synthesized as the calcination temperature is inadequate fully to crystalize the phosphor leading to the crystal and amorphous. Albeit, the firing temperature is insufficient so as to form the fine crystal, the added excess SiO_2 could act as an additive for the crystallization of the phosphor. As a function of SiO_2, the size of the crystal has been augmented and formed fine crystals with the concentration of added SiO_2. Moreover, the added excess SiO_2 makes SiOC : Eu^{2+} phosphor as a deep blue illumination at 440 nm. Photoluminescence intensity of the phosphors is increased continuously by the addition of SiO_2 heretofore x = 3. In the present investigation, an attempt has been made to synthesize and observe carefully for photoluminescence properties with regard to the crystalline structure, optical property and surface morphology.

Key words: $BaAl_2Si_2O_8 : Eu^{2+}$, Excess SiO_2 addition, LED application, Phosphor.

Introduction

The first light emitting diodes (LEDs) in 1960, it had been a major significant advance in LEDs [1]. LEDs are a promising candidate for next generation of solid lighting due to its high energy efficiency, longer lifetime, environmental friendliness and reliability when it is compared to general light sources such as incandescent light and fluorescent lamp [2-5]. As the phosphors absorb the blue light from the LED chip, it emits the long wavelength light. While LED device is operated, lot of heat energy occurs and inducing the thermal quenching with a series of environmental reduction of luminescence property. Therefore, the high stability and efficient phosphor have been required for LED development [6].

Most of the studies related to phosphor synthesis have been carried out to conventional solid state reaction (SSR) method [7, 8]. In SSR method, the precursor is inhomogeneous owing to hand-grinding process. In contrast, the novel liquid phase precursor (LPP) method has been very quiet homogeneous process. All the raw materials are homogeneously mixed in an aqueous solution and the cellulose is impregnated into the prepared mixture solution. The nuclear of phosphor particle can grow and it will be more facile method under lower temperature than SSR [9].

Excess mount of SiO_2 has been added and studied ($MAl_2Si_2O_8$: Eu^{2+} (M = Ca, Sr)) with phosphors in earlier studies. More SiO_2 could make a good environment to help the reduction from Eu^{3+} to Eu^{2+} in forming fine crystalline structure [10, 11]. Therefore, the high concentration of SiO_2 added phosphors has been showed and enhanced the utilization efficiency since the reduced Eu^{2+} is directly related with the practical efficiency. Moreover, the crystalline structure of $MAl_2Si_2O_8$ is very quiet stable with rigid framework of tetrahedral silicates and aluminates [12, 13]. (Fig. 1)

$BaAl_2Si_2O_8 : Eu^{2+}$ has been synthesized with phosphors using novel LPP method for delivering the high performance

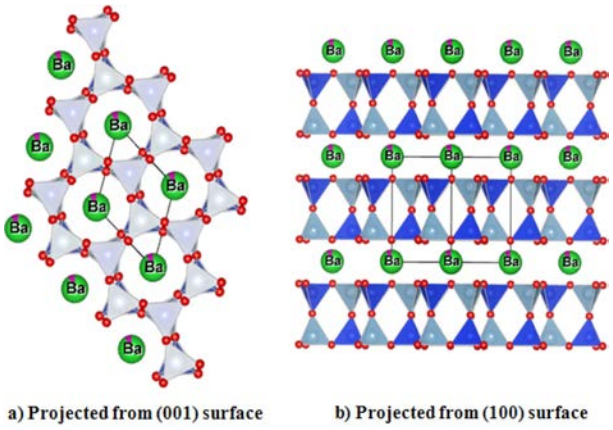

Fig. 1. The Crystalline structure of $BaAl_2Si_2O_8$.

*Corresponding author:
Tel : +82-31-290-7388
Fax: +82-31-290-7371
E-mail: dhyoon@skku.edu

under low synthesizing temperature. In this present work, it is highlighted that this blue phosphor is not used on white LED but it is applicable with LED laser application due to its lighting wavelength.

Experimental

$BaAl_2Si_2O_8$: Eu^{2+}+ $xSiO_2$ phosphors (x = 0, 1, 2 and 3) are synthesized via LPP method. An aqueous metal salts are prepared by 30 weight %, $BaCl_2 \cdot 2H_2O$ (Junsei chemical Co., Japan), 50 weight % $Al(NO_3)_3 \cdot 9H_2O$ (Samchun chemical Co., 98%), 20 weight % SiO_2 (sol, 20 nm, Snotex-O, Nissan chemical) and 50 weight % $EuCl_3 \cdot 3H_2O$ (Aldrich grade). According to the composition, all the prepared solutions were mixed together and impregnated into a crystalline cellulose powder (Avicel, Asahe). The impregnated cellulose precursors are pre-calcined at 500 ºC, for 3 h and calcined at 1200 ºC for 2 hrs in air atmosphere. Finally, the obtained powders are heated at 1000 ºC for 10 hrs under N_2/H_2 (95/5) atmosphere to reduce the europium from Eu^{3+} to Eu^{2+}.

The highly crystalline phases of the obtained phosphors have been carefully examined by X-ray Diffraction (XRD, CuKα, λ = 1.5406, 40 kV, 20 mA, Rigaku, Japan). The photoluminescence (PL) properties of the phosphors are evaluated using PL spectrometer (SINCO, FS-2, Korea) and it is equipped with 500 W Xenon discharge lamp. The surface morphology of the particle has been studied by a field emission scanning electron microscopy (FESEM, JEOL, JSM7500F, Japan).

Results and Discussion

Fig. 2 depicts the synthesized crystalline structures of $BaAl_2Si_2O_8 : Eu^{2+} + xSiO_2$ (x = 0, 1, 2 and 3) phosphors through the measurement of XRD patterns. All the high intensity reflection of XRD patterns of $BaAl_2Si_2O_8$ matches perfectly with Joint Committee on Powder Diffraction Standards (JCPDS card number 012-0303 Orthorhombic) which is in good agreement with previous researches used the similar composition with other Alkali-earth based phosphors, ($CaAl_2Si_2O_8$ and $SrAl_2Si_2O_8$) [10, 11]. The XRD patterns of crystalline SiO_2 have not been shown much in Fig. 2. Therefore, SiO_2 is existed as an amorphous with other orthorhombic crystals.

Fig. 3 shows the morphologies of $BaAl_2Si_2O_8$: Eu^{2+}+ x SiO_2 phosphor particles. The surface morphology of $BaAl_2Si_2O_8$: Eu^{2+} particles (x = 0) has not been a fine crystalline particles, but it is in the mixture of crystal and amorphous. Albeit, the synthesized solution has been an exact composition, the crystals have not fully developed to the fine crystal. It implies that the calcination condition is an inadequate to synthesize the $BaAl_2Si_2O_8 : Eu^{2+}$ phosphor. At the same time, the

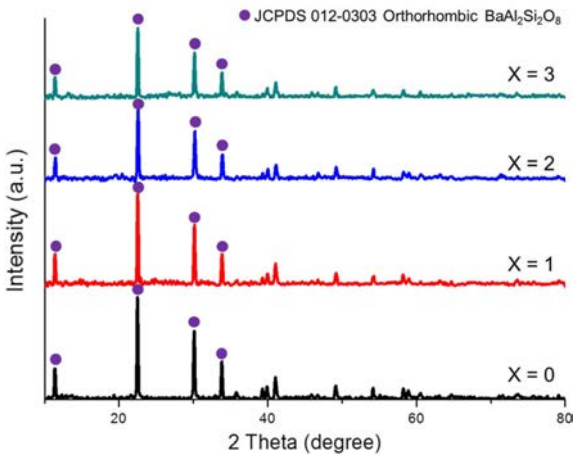

Fig. 2. XRD patterns of $BaAl_2Si_2O_8 : Eu^{2+} + xSiO_2$ (x = 0, 1, 2, and 3).

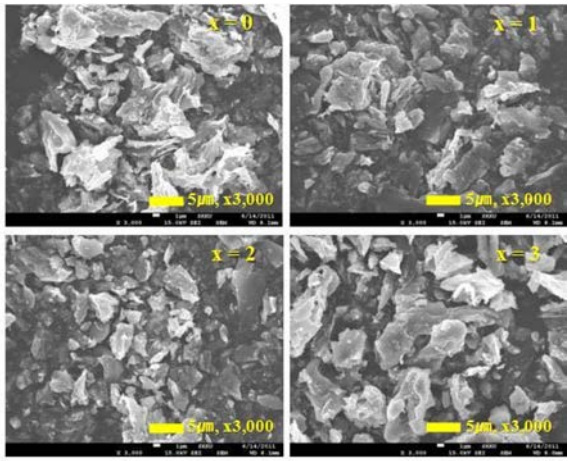

Fig. 3. FE-SEM images of $BaAl_2Si_2O_8 : Eu^{2+} + xSiO_2$ (x = 0, 1, 2 and 3).

amorphous phase is eclipsed and the sizes of the particles are augmented with the concentration of the added excess SiO_2. Exactly, an addition of 3 M of SiO_2 with $BaAl_2Si_2O_8 : Eu^{2+}$, it shows the biggest particles of phosphor. An addition of excess amount of SiO_2 can help the nucleation of $BaAl_2Si_2O_8$ crystals and it is existed resulting in the formation of the amorphous and covering the surface of the phosphor particles.

Fig. 4 illustrates the excitation and emission spectra of $BaAl_2Si_2O_8$: Eu^{2+} + x SiO_2 (x = 0, 1, 2 and 3) phosphors have been measured by PL spectra. The emission spectra of $BaAl_2Si_2O_8$: Eu^{2+} shows the emission spectra with broad or amorphous excitation has been centered at 290 and 470 nm. The broad excitation spectra (Fig. 5) exhibits a couple of overlapping peaks is centered at 320 (t_{2g}) and 370 nm (e_g), may be due to the result of 5d orbital separation is caused by crystal field splitting.

Despite, low PL intensity for $BaAl_2Si_2O_8$: Eu^{2+} phosphor, an excess amount of SiO_2 depicts lucidly the enhanced PL intensities. There are several genuine reasons in this regard. First of all, the light emits the phosphor

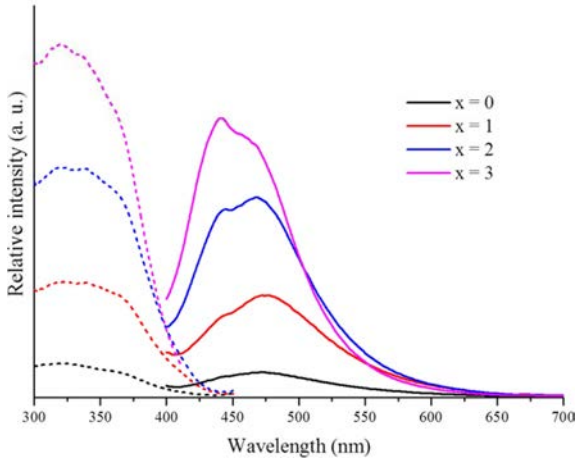

Fig. 4. Photoluminescence spectra of $BaAl_2Si_2O_8 : Eu^{2+} + xSiO_2$ (x = 0, 1, 2 and 3).

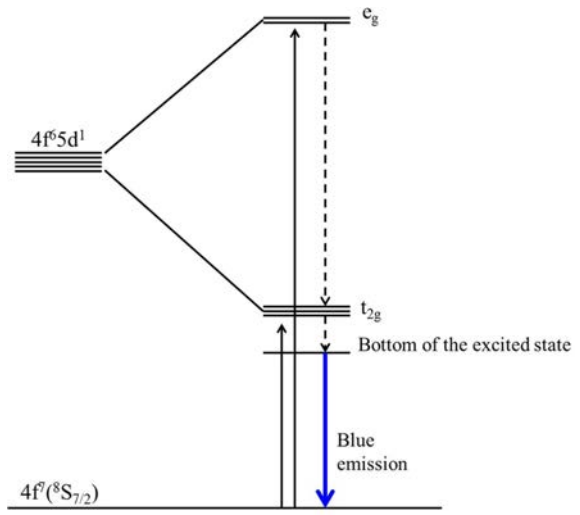

Fig. 5. The effect of crystal field splitting on energy level of Eu^{2+} in $BaAl_2Si_2O_8$.

crystal which could be formed in helping the nucleation with the concentration of the SiO_2. Secondly, more electrons are at the verge of tetrahedral silicate crystal leading to form a very strong reduced environment to help the reduction of activator from Eu^{3+} to Eu^{2+} [14]. Therefore, the enhanced emission is occurred owing to the high ratio of Eu^{2+} in phosphor. $BaAl_2Si_2O_8$:Eu^{2+} has emitted the blue light due to the Eu^{2+} activator bestowing the various illuminations depends on the crystal field splitting from the lattice structure, whereas Eu^{3+} induces a weak red emission in the most of the cases. Moreover, the common phosphors do not show any PL enhancement caused by SiO_2 addition. It is well evident to know that Eu^{2+} can be easily oxidized in the air atmosphere. As a result of re-oxidation, the amount of Eu^{3+} still remains in the phosphor as an activator. However, $BaAl_2Si_2O_8 : Eu^{2+}$ phosphor could avoid the re-oxidization process caused by a special crystalline structure. It is evident that oxygen cannot penetrate into the lattice structure to react with Eu^{3+} as reduced Eu^{2+} to be surrounded by a narrow cave of tetrahedral SiO_4^{4-} and AlO_6^{9-} lattice [12, 13]. In view of the above, all the preliminary investigations suggest that Eu^{2+} is reduced which could be preserved inside the lattice structure for avoiding the re-oxidization process.

On the other hand, it is quite interesting to note that the second peak is seen and it is centered at 440 nm which is motivated by Eu^{2+} doped SiOC [15]. Notwithstanding, the cellulose possesses an aqueous metal salts in the fiber cell and it is vanished during the decomposition at high temperature with amount of carbon and Eu^{2+} forming SiOC upon the calcination process. It is understood in the resulting formation of $SIOC : Eu^{2+}$, a slight rising in the concentration of the added excess amount of SiO_2. As a result of $SiOC : Eu^{2+}$, the intensity of PL has been increased at 440 nm with the concentration of excess SiO_2. Therefore, $SIOC : Eu^{2+}$ could be an apt and promising candidate to assist the blue emission of $BaAl_2Si_2O_8 : Eu^{2+}$ phosphor.

Conclusions

$BaAl_2Si_2O_8 : Eu^{2+} + xSiO_2$ (x = 0, 1, 2 and 3) phosphors have been synthesized through LPP method. All the high intensity X-ray diffraction patterns confirm the phosphors are having the same crystalline structure. FESEM images exhibit the mixture of crystalline particles and amorphous phases in the exact composition of $BaAl_2Si_2O_8$: Eu^{2+} phosphor.

Excess amount of SiO_2 phosphors exhibits large and disordered crystalline particles. Each crystal of amorphous of $BaAl_2Si_2O_8$: Eu^{2+} and SiOC: Eu^{2+} are found to be an emission centered at 470 nm and at 440 nm. Thus, the photoluminescence intensity of $BaAl_2Si_2O_8 : Eu^{2+}$ has been investigated and enhanced with increase of SiO_2 concentration. The enhancement of PL intensity may be due to increase of the number of light emitting phosphors with an increase of more reduced Eu^{2+} doped $BaAl_2Si_2O_8$ phosphor and Eu^{2+} doped SiOC amorphous phase structure.

Acknowledgments

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