Ceramic **Processing Research** 

# Synthesis of green-emitting $SrSi_2O_2N_2$ : boron-coated $Eu_2O_3$ phosphor with different crucible

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To synthesize green-emitting SrSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub> phosphor, boron-coated Eu<sub>2</sub>O<sub>3</sub> was used as an activator with different crucibles. This phosphor showed higher emission intensity than phosphor obtained using boron nitride and an alumina crucible. The synthesized green-emitting phosphors obtained using a carbon crucible were crystallized much better and showed higher emission intensity. The emission spectra typically showed a single broad green emission band corresponding to the  $5d \rightarrow 4f$ transition of Eu<sup>2+</sup> ions under excitation of 450 nm. This green-emitting phosphor is expected to be applied to next-generation white LEDs.

Key words: SiSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub> : Eu<sup>2+</sup> phosphor, White LEDs, Boron-coated Eu<sub>2</sub>O<sub>3</sub>.

#### Introduction

Recently, phosphor-converted LEDs have drawn significant attention due to their several advantages over incandescent lamps, such as high conversion efficiency, environmentally friendliness, high reliability, compact size, and long life time [1-3]. Generally, white LEDs can be realized with  $Y_3Al_5O_{12}$ : Ce<sup>3+</sup> (YAG) vellow phosphor and InGaN-based blue chips. These white LEDs have disadvantages of low thermal quenching, low color rendering index (CRI) value, and high correlated color temperature (CCT) [4]. So, these LEDs are not usually applied as indoor illumination sources. An alternative to overcome these problems is to use green and red oxynitride phosphors with InGaNbased blue chips [5]. Oxynitride phosphors have received considerable attention because of their excellent properties, such as thermal and chemical stability [6]. Also, rare-earth-activated oxynitride hosts are flexible in that their emission wavelengths can be changed so that desired colors can be obtained. Oxynitride phosphor is synthesized by conventional solid-state reaction at high temperature over 1500 °C under critical conditions, but if a new synthetic route with no spray pyrolysis or sol-gel methods can be developed, the synthesis of oxynitride phosphor would be feasible at low temperature. Oxynitride phosphor is well suited for application as host lattices because of its high quantum efficiency and small Stokes shift, which are possible due to the rigidity of its silicate substructures [7].

In this study, we focused on Eu<sup>2+</sup>-activated SrSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub>

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phosphor with a perfect single phase and high photoluminescence properties. This phosphor was synthesized using different conditions and a very simple route. We already reported on the new synthetic route using  $R(a)B_2O_3$  (R = Eu<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>) and obtained high-quality phosphor [8].

We report on a new approach to enhance the luminescence efficiency of green-emitting Eu<sup>2+</sup>-activated SrSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub> phosphor. Eu<sup>2+</sup>-activated SrSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub> phosphors were successfully synthesized by a simple synthetic route using various crucibles under a reducing nitrogen atmosphere with 5% H<sub>2</sub> gas. The crystal structure and luminescence properties of the green-emitting Eu<sup>2+</sup>activated SrSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub> phosphor were analyzed using powder X-ray diffraction (XRD) and photoluminescence spectrometry (PL).

#### **Experimental**

Boron-coated  $Eu_2O_3$  was prepared with 10 g of Eu<sub>2</sub>O<sub>3</sub> (High Purity Chemicals, 99.99%) and 3.65 g of H<sub>3</sub>BO<sub>3</sub> (High Purity Chemicals, 99.9%). These were magnetically stirred with de-ionized water at 60 °C for 3 hrs and then dried at 100 °C for 24 hrs. The dried sample was ground using an agate mortar and then fired at 600 °C for 7 hrs.

SrCO<sub>3</sub> (High Purity Chemicals, 99.9%), SiO<sub>2</sub> (Sigma Aldrich, -325 mesh), Si<sub>3</sub>N<sub>4</sub> (Sigma Aldrich, -325 mesh), and boron coated Eu<sub>2</sub>O<sub>3</sub> were then used as raw materials for synthesizing the  $SrSi_2O_2N_2$ :  $Eu^{2+}$  phosphor. These were homogeneously mixed with an agate mortar for 1 hr and then fired with different types of crucibles (alumina, carbon, and boron nitride) at 1400 °C for 5 hrs under 5%H<sub>2</sub>/95%N<sub>2</sub> atmosphere.

The phase determination of the obtained samples was

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carried out by X-ray diffraction (XRD, Rigaku, Japan) using a Cu K<sub> $\alpha$ </sub> target in the 2 $\theta$  range of 20-80 °. The photoluminescence spectra were recorded using a spectrometer (SCINCO, FS-2, Korea) with a xenon lamp excitation source (150 W).

#### **Results & Discussion**

Fig. 1 shows the powder XRD patterns of the asprepared phosphor samples obtained at 1350 °C under reducing atmosphere. The XRD patterns of the samples were investigated in the range of 20 °C <  $2\theta$  < 80 °. The crystal structure of the samples is triclinic structure (space group P1) with lattice constants of  $a = 0.708 \ 02(2) \ nm$ ,  $b = 0.723 \ 06(2) \ nm, \ c = 0.725 \ 54(2) \ nm, \ \alpha = 88.767(3),$  $\beta = 84.733(2), \gamma = 75.905(2), V = 0.35873(2) \text{ nm}^3$ , and Z = 4. All samples were indexed to a reference [9]. The crystal structure of SrSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub> was similar to that of CaSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub>. These materials showed a similar layered structure to that of  $(Si_2O_2N_2)^2$ , consisting of SiON<sub>3</sub> tetrahedra. The N atom bridges three Si atoms, while the O atom is bound with two Si atoms. There are four different crystallographic sites for the  $Sr^{2+}$  ions [10, 11]. Most of the XRD peaks of the synthesized samples are well indexed to the SrSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub> phase. Fig. 1 indicates that all samples showed good crystallization. We suggest that the boron-coated Eu<sub>2</sub>O<sub>3</sub> plays a significant role in the formation of a single phase during the synthesis procedure.

Fig. 2 shows the PEL and PL spectra of the samples of boron-coated  $Eu_2O_3$  and the  $Eu_2O_3$  used as an activator. The emission spectra display excitation and broad emission bands, which is in good agreement with the room-temperature spectra of general  $SrSi_2O_2N_2 : Eu^{2+}$  phosphor. The sample obtained using the boron-coated  $Eu_2O_3$  indicated the highest excitation and emission intensity compared to  $Eu_2O_3$ . The use of boron-coated  $Eu_2O_3$  as an activator is believed to lead to highly efficienct luminescence properties due to the improvement of the diffusion coefficient of boron-coated  $Eu_2O_3$  mateirals in the  $SrSi_2O_2N_2$  host lattice.

Fig. 3 indicates the PEL and PL spectra of the asprepared phosphor obtained using different crucibles (all samples are obtained with boron-coated  $Eu_2O_3$ ). The boron-coated Eu<sub>2</sub>O<sub>3</sub> concentration is 0.07 mol. The broad excitation spectra in all samples were shown in range of the UV region to the blue region, corresponding to the  $4f \rightarrow 5d$  electronic transition of Eu<sup>2+</sup> ions. The emission spectra of all samples under excitation of 450 nm show a single broad band at 533 nm with a full width of half maximum of 80 nm, which is ascribed to the  $4f^65d^1 \rightarrow 4f^7$  transition of Eu<sup>2+</sup> ions [12]. The sample obtained using the carbon crucible indicated the highest excitation and emission intensity compared to samples obtained using other crucibles. This phenomenon implies that the carbon crucible plays a role in making a strong reducing



Fig. 1. The X-ray diffraction pattern of the as-prepared  $SrSi_2O_2N_2$ :  $Eu^{2+}$  obtained with different crucibles.



Fig. 2. Excitation and emission spectra of  $SrSi_2O_2N_2$  :  $Eu^{2+}$  as a function of activator conditions.



Fig. 3. Excitation and emission spectra of  $SrSi_2O_2N_2$ :  $Eu^{2+}$  phosphor obtained with different crucibles.

atmosphere. These results indicate that the boroncoated  $Eu_2O_3$  obtained with a carbon crucible plays a highly important role in the enhancement of the luminescence properties in synthesized oxynitride phosphor.

Figs. 4 (a) and (b) show the PL spectra of the  $SrSi_2$  $O_2N_2$ :  $Eu^{2+}$  phosphor as a function of  $Eu^{2+}$  concentration. The emission intensity is increased with increasing  $Eu^{2+}$  contents from 0.01 to 0.07 mol. However, the



**Fig. 4.** Emission spectra of synthesized  $SrSi_2O_2N_2$ :  $Eu^{2+}$  phosphor as a function of boron-coated  $Eu_2O_3$  contents.

emission intensity under excitation of 450 nm is decreased when the Eu<sup>2+</sup> contents is 0.9 mol. Concentration quenching occurs as a result of non-radiative energy transfer among Eu<sup>2+</sup> ions [13]. This non-radiative energy transfer occurs as a result of an exchange interaction and multipole-multipole interaction. Also, the emission intensity can be affected by the contents of the activator as a result of changes in the local surroundings of the Eu<sup>2+</sup> sites. The highest emission intensity is observed at 536 nm when the  $Eu^{2+}$  content is 0.07 mol. In addition, a peak shift toward the red region was observed with increasing Eu<sup>2+</sup> contents. A single broad emission band in  $Sr_{1\text{-}x}Si_2O_2N_2:Eu^{2+}{}_x$  was observed from 529 to 545 nm, as shown in Fig. 4. This is attributed to the probability of energy transfer between the Eu<sup>2+</sup> ions, and it might increase as the distance between Eu<sup>2+</sup> ions becomes shorter with increasing Eu<sup>2+</sup> doping concentration. Therefore, the increase in non-radiative energy transfer to the 5d level can allow for a continuous emission peak shift to the red region, the same as a lower energy, with increasing  $Eu^{24}$ contents [14].

## Conclusions

In this study, boron-coated  $Eu^{2+}$  activated  $SrSi_2O_2N_2$  green phosphors have been successfully synthesized by solid-state reaction as a function of  $Eu^{2+}$  contents with various crucibles. The optical properties of the phosphors have also been evaluated. As a result,  $SrSi_2O_2N_2$ : boron-coated  $Eu^{2+}$  phosphors obtained with a carbon crucible can be effectively excited by UV to blue light and emit green light with a single broad band at 529 nm to 545 due to the 4f-5d transition of  $Eu^{2+}$ . These results are expected to potentially lead to new concepts for the synthesis of oxynitride phosphor for generating white lighting and display applications.

### Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2013R1A1A2059280).

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