Synthesis of green-emitting SrSi$_2$O$_3$N$_2$: boron-coated Eu$_2$O$_3$ phosphor with different crucible


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To synthesize green-emitting SrSi$_2$O$_3$N$_2$ phosphor, boron-coated Eu$_2$O$_3$ 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 → 4f transition of Eu$^{2+}$ ions under excitation of 450 nm. This green-emitting phosphor is expected to be applied to next-generation white LEDs.

Key words: SrSi$_2$O$_3$N$_2$: Eu$^{2+}$ phosphor, White LEDs, Boron-coated Eu$_2$O$_3$

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$_3$Al$_5$O$_{12}$ : Ce$^{3+}$ (YAG) yellow 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 InGaN-based 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$^{2+}$-activated SrSi$_2$O$_3$N$_2$ 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@B$_3$O$_3$ (R = Eu$_2$O$_3$ and CeO$_2$) and obtained high-quality phosphor [8].

We report on a new approach to enhance the luminescence efficiency of green-emitting Eu$^{2+}$-activated SrSi$_2$O$_3$N$_2$ phosphor. Eu$^{2+}$-activated SrSi$_2$O$_3$N$_2$ phosphors were successfully synthesized by a simple synthetic route using various crucibles under a reducing nitrogen atmosphere with 5% H$_2$ gas. The crystal structure and luminescence properties of the green-emitting Eu$^{2+}$-activated SrSi$_2$O$_3$N$_2$ phosphor were analyzed by using powder X-ray diffraction (XRD) and photoluminescence spectrometry (PL).

Experimental

Boron-coated Eu$_2$O$_3$ was prepared with 10 g of Eu$_2$O$_3$ (High Purity Chemicals, 99.99%) and 3.65 g of H$_2$BO$_3$ (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$_3$ (High Purity Chemicals, 99.9%), SiO$_2$ (Sigma Aldrich, ~325 mesh), Si$_3$N$_4$ (Sigma Aldrich, ~325 mesh), and boron coated Eu$_2$O$_3$ were then used as raw materials for synthesizing the SrSi$_2$O$_3$N$_2$: 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$_2$/95%N$_2$ atmosphere.

The phase determination of the obtained samples was
carried out by X-ray diffraction (XRD, Rigaku, Japan) using a Cu Kα target in the 2θ 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 as-prepared phosphor samples obtained at 1350°C under reducing atmosphere. The XRD patterns of the samples were investigated in the range of 20°C < 2θ < 80°. The crystal structure of the samples is triclinic structure (space group P1) with lattice constants of

\[
a = 0.70802(2) \text{ nm}, \quad b = 0.72306(2) \text{ nm}, \quad c = 0.72554(2) \text{ nm}, \quad \alpha = 88.767(3)^\circ, \quad \beta = 84.733(2)^\circ, \quad \gamma = 75.905(2)^\circ, \quad V = 0.35873(2) \text{ nm}^3, \quad Z = 4.
\]

All samples were indexed to a reference [9]. The crystal structure of SrSi₂O₂N₂ was similar to that of CaSi₂O₂N₂. These materials showed a similar layered structure to that of (Si₂O₂N₂)₂, consisting of SiON₃ 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 Sr²⁺ ions [10, 11].

Most of the XRD peaks of the synthesized samples are well indexed to the SrSi₂O₂N₂ phase. Fig. 1 indicates that all samples showed good crystallization. We suggest that the boron-coated Eu₂O₃ 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 Eu₂O₃ and the Eu₂O₃ 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 SrSi₂O₂N₂ : Eu²⁺ phosphor. The sample obtained using the boron-coated Eu₂O₃ indicated the highest excitation and emission intensity compared to Eu₂O₃. The use of boron-coated Eu₂O₃ as an activator is believed to lead to highly efficient luminescence properties due to the improvement of the diffusion coefficient of boron-coated Eu₂O₃ materials in the SrSi₂O₂N₂ host lattice.

Fig. 3 indicates the PEL and PL spectra of the as-prepared phosphor obtained using different crucibles (all samples are obtained with boron-coated Eu₂O₃). The boron-coated Eu₂O₃ 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→5d electronic transition of Eu²⁺ 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 4f⁵5d¹ → 4f⁶ transition of Eu²⁺ 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 atmosphere. These results indicate that the boron-coated Eu₂O₃ 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 SrSi₂O₂N₂ : Eu²⁺ phosphor as a function of Eu²⁺ concentration. The emission intensity is increased with increasing Eu²⁺ contents from 0.01 to 0.07 mol. However, the
emission intensity under excitation of 450 nm is decreased when the Eu$^{2+}$ content is 0.9 mol. Concentration quenching occurs as a result of non-radiative energy transfer among Eu$^{2+}$ 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$^{2+}$ 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$^{2+}$ contents.

Conclusions

In this study, boron-coated Eu$^{2+}$ activated SrSi$_2$O$_2$N$_2$ 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$_2$O$_2$N$_2$: 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 nm 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).

References


Fig. 4. Emission spectra of synthesized SrSi$_2$O$_2$N$_2$: Eu$^{2+}$ phosphor as a function of boron-coated Eu$_2$O$_3$ contents.