

The photoluminescence properties of $\text{SrSi}_2\text{O}_2\text{N}_2 : \text{Eu}^{2+}$ nano oxynitride phosphor for white light emitting diodes

Seong Gwan Shin, Kyung Hwan Kim, Chung Wung Bark and Hyung Wook Choi*

Department of Electrical Engineering Gachon University, Seongnam, Gyeonggi-Do 461-701, Korea

The effect of activator on the structural and luminescent properties of $\text{Sr}_{1-x}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}_{2+x}$ nano oxynitride phosphor was investigated. In order to achieve small spherical particles with smooth and round surfaces particles, $\text{Sr}_{1-x}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}_{2+x}$ phosphors were synthesized by solid state reaction method. $\text{Sr}_{1-x}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}_{2+x}$ oxynitride phosphor was synthesized with different Eu^{2+} doping concentrations at $800^\circ\text{C} \sim 1200^\circ\text{C}$ for 6 hrs under a reducing nitrogen atmosphere containing 5% H_2 . The characteristics of the synthesized $\text{Sr}_{1-x}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}_{2+x}$ oxynitride phosphor were investigated by means of X-ray diffraction (XRD), scanning electron microscope (SEM), and photoluminescence (PL). The results of characterization showed that both of the prepared phosphors are nanosized particles. The phosphors exhibited the green to yellow emission spectrum for near excitation. The influence of Eu^{2+} content on the crystalline structure of the produced powders of $\text{Sr}_{1-x}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}_{2+x}$ phosphors was studied. As the doping concentration of Eu^{2+} was increased, there was a shift in the continuous emission spectra. The material can be a promising candidate for the potential application as a fluorescent material in a white light-emitting diodes (W-LEDs).

Key words: Oxynitride phosphor, White LEDs, Photoluminescence

Introduction

White light-emitting diodes (LEDs) have attracted much attention due to their valuable applications, such as backlight source for liquid-crystal displays and power descent lamps. [1] White LED has better luminescence efficiency than the incandescent bulb; furthermore, it poses a challenge for the fluorescent lamp. [2, 3] The rare-earth doped (oxo) nitridosilicates are generally considered to be promising materials for the luminescence down-conversion phosphors for an application in white LEDs because of their outstanding chemical, thermal, mechanical stability and excellent photoluminescence properties. [4] Due to the high covalency and crystal-field splitting effect on the luminescent centers (e.g., Eu^{2+} , Ce^{3+}) caused by the surrounding N_3 ions, the photoluminescence properties of the rare-earth ions result from the lowering gravity center of the 5d levels and decreasing Stokes shift. Recently, many rare-earth-activated oxynitride phosphors have been reported for applications in white LEDs. Especially, $\alpha\text{-SiAlON}:\text{Eu}^{2+}$, $\beta\text{-SiAlON}:\text{Eu}^{2+}$, $\text{Sr}_2\text{Si}_3\text{N}_8:\text{Eu}^{2+}$, and $\text{CaAlSiN}_3:\text{Eu}^{2+}$ have been mentioned as promising candidates for white LEDs. [5-9] However, these W-LEDs cannot be applied as indoor illumination sources because these phosphors have a lower color rendering index (CRI) value and less red than the oxynitride

phosphor. [10, 11]

In this study, we produced $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ phosphors doped with different amounts of Eu^{2+} using solid-state reaction method. The $\text{SrSi}_2\text{O}_2\text{N}_2$ compounds were identified high efficiency oxynitride phosphors, such as green to yellow phosphors, for potential applications to the blue light region in W-LEDs. The luminescence properties of the synthesized phosphors with Eu^{2+} doping concentration ratios ranging from 0.10 to 0.25 were examined by photoluminescence (PL) spectroscopy, field emission-scanning electron microscopy (FE-SEM), and X-ray diffraction (XRD).

Experimental

$\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ phosphors were prepared using the solid reaction method. Si_3N_4 (99.99%, Aldrich), SrCO_3 (99.99%, Aldrich), Eu_2O_3 (99.999%, Aldrich) were used as the starting materials. The $\text{Sr}_{1-x}\text{Si}_2\text{O}_2\text{N}_2$ phosphors were doped by Eu^{2+} with a molecular formula $\text{Sr}_{1-x}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}_{2+x}$ ($x = 0.10 \sim 0.25$). A procedure for the preparation of the phosphor powders is shown in Fig. 1. The starting materials were mixed for 24 hrs using a ball mill.

Eu^{2+} doped $\text{SrSi}_2\text{O}_2\text{N}_2 : \text{Eu}^{2+}$ green to yellow emitting phosphors were synthesized at different Eu^{2+} doping concentrations at $1000 \sim 1400^\circ\text{C}$ for 6 hrs under a reducing nitrogen atmosphere containing 5% H_2 . After firing, the samples were cooled to room temperature in the furnace.

The crystalline development of the resulting samples was checked by XRD (D/MAX-2200) using $\text{CuK}\alpha$ -

*Corresponding author:
Tel : +82-31-750-5562
Fax: +82-31-750-8833
E-mail: chw@gachon.ac.kr

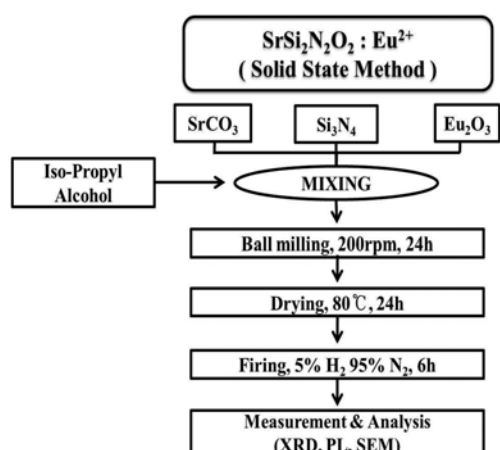


Fig. 1. Procedure for the preparation of the phosphor powders.

radiation in the range of $2\theta = 20 \sim 80^\circ$. The PL measurement was carried out with a 150 W Xe lamp (spectrofluorometer, FP-6200, Jasco). The morphology and the size of the prepared particles were investigated with FE-SEM (S-4700, Hitachi).

Results and Discussion

The XRD patterns of the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ powders at the different sintering temperatures from 1000°C to 1400°C for 6 hrs are shown in Fig. 2. It is seen that the precursor possessed mixed phases, indicating that they were not synthesized. In general, the luminescent intensity is strongly affected by the phase purity and the crystallinity of the host compound. High phase purity is needed to obtain a high luminescent intensity. When the temperature was at 1300°C , the diffraction peaks became sharper and stronger. However at 1000°C the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ peaks were markedly weakened. Therefore, in terms of phase purity, the sample prepared at 1100°C and 1300°C should show the highest luminescent intensity.

The PL excitation and emission spectra of the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ powders at the different sintering temperatures (1100°C , 1300°C) are shown in Fig. 3. At all compositions, the shape of the excitation (em = 540 nm) spectra was similar for the relative intensity. Through repeated experiments, the emission (ex = 450 nm) spectrums display the maximum luminous intensity when the sintering temperature was at 1300°C .

Fig. 4 shows the SEM images of the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ sintered at different temperatures. The surface morphologies of the phosphor sintered at 1100°C were rough. With an increased sintering temperature, the phosphor particles became spherical, because the particles condense at higher temperatures [12]. But at 1300°C , powder consists of small spherical particle with smooth and round surface with agglomerates were observed. With increased firing temperature, phosphors have spherical shape. At this point, we determined that the charac-

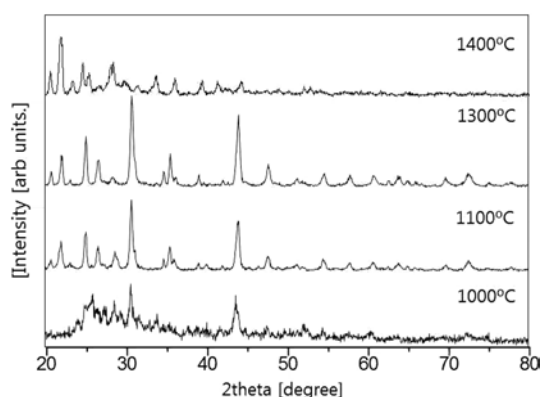


Fig. 2. XRD patterns of the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ sintered at different temperatures

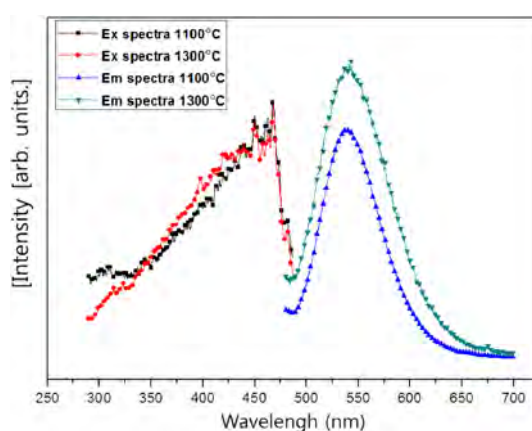


Fig. 3. PL excitation and emission spectra of the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ powders at the different sintering temperatures. (1100°C , 1300°C)

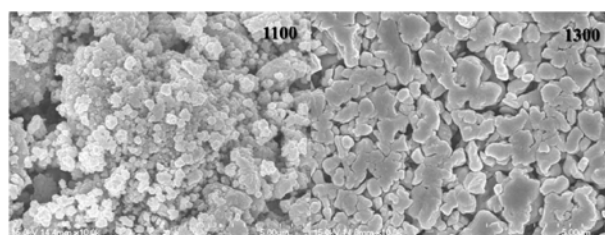


Fig. 4. SEM images of the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ sintered at different temperatures.

teristics of the phosphor powders were improved by increasing the sintering temperature. However, some defects were formed in the phosphor when it is heated beyond a critical temperature.

The XRD patterns of the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ with various concentrations of Eu^{2+} are shown in Fig. 5. The added amount of Eu^{2+} was in the range from 0.10 to 0.25. With the difference of concentration, there was no shift in the diffraction peaks toward any angle. At concentration of Eu^{2+} 0.15 the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ peaks were sharper and stronger. $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ powder peaks of phases are similar to that JCPDS card No.49-0840, $\text{Sr}_3\text{Si}_3\text{O}_9$ (JCPDS 75-2400) and $\alpha\text{-Sr}_2\text{SiO}_4$ (JCPDS 39-

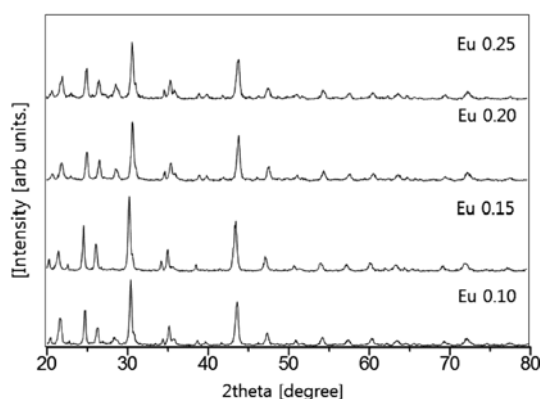


Fig. 5. XRD patterns of the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ with various concentrations of Eu^{2+} .

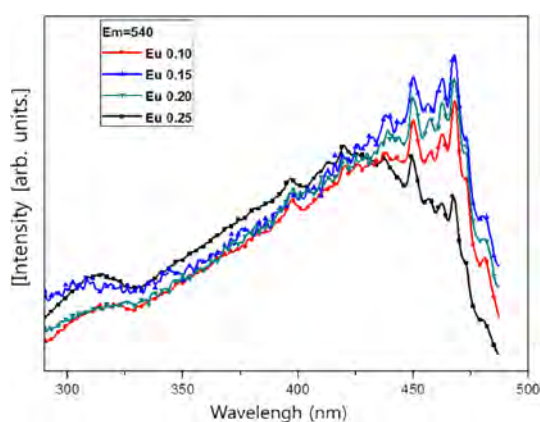


Fig. 6. The excitation spectra of the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ with various concentrations of Eu^{2+} .

1256). [13, 14] Recently, the structure of $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ was reported to triclinic unit cell with the space group P1 [15]. Low symmetry forms a combination of an orthorhombic silicate layer including pseudohexagonal metal atom layers [16].

The excitation spectra of the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ with various concentrations of Eu^{2+} are shown in Fig. 6. Several intense and sharp lines are exhibited in the range of 350 - 470 nm. When Eu content x , the intensity of the excitation band of the $\text{Sr}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}_x$ phosphor was slightly different at $x = 0.25$. The excitation intensity increased with Eu^{2+} doping concentration from 0.10 to 0.15. However, emission intensity decreased when Eu^{2+} doping concentration was 0.2. Typical broad excitation band from the crystal field splitting of the 5d orbital due to the $4f^7-4f^65d^1$ transition of the Eu^{2+} .

The emission spectra of the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ with various concentrations of Eu^{2+} are shown in Fig. 7. The photoluminescence emission spectra were measured for the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ powders under an excitation of 450 nm. It is shown that these phosphors exhibit an intense and green to yellow emission. The emission spectra show a broad band from 525 to 560 nm when the excitation wavelength was monitored at 450 nm. The

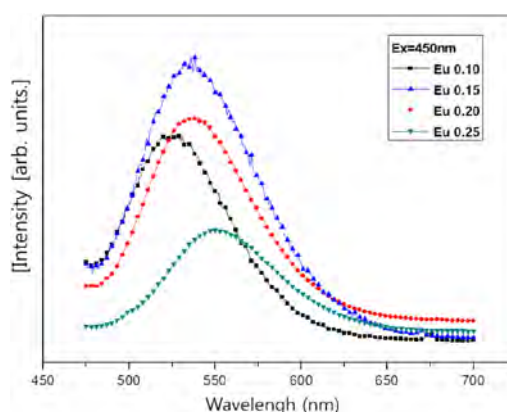


Fig. 7. The emission spectra of the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ with various concentrations of Eu^{2+} .

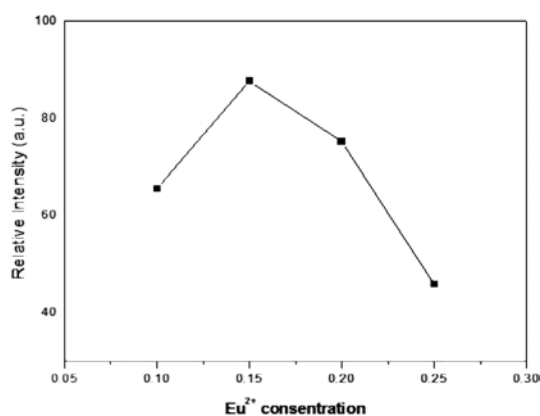


Fig. 8. The variation of the intensity to the Eu^{2+} concentration for the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$.

emission intensity increasing Eu^{2+} concentration up to $x = 0.15$, and then decreased at $x = 0.20$ due to concentrations. This emission, located at 525 ~ 550 nm (excited at 450 nm), is attributed to the typical $4f^65d^1-4f^7$ transition of Eu^{2+} [17].

Fig. 8 shows the variation of the intensity to the Eu^{2+} concentration for the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$. The emission peak showed with highest intensity occurred at $\text{Sr}_{0.85}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}_{0.15}$. With an increasing Eu^{2+} content x , the intensity of the emission band of the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ phosphor was 525-560 nm, the intensity increased until the Eu^{2+} concentration reached to $x = 0.15$. However, it was found that the intensity started to decrease from the Eu^{2+} concentration at $x = 0.20$ in the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ phosphor.

Conclusion

Eu^{2+} doped $\text{SrSi}_2\text{O}_2\text{N}_2$ green to yellow emitting phosphors were synthesized at different Eu^{2+} doping concentrations at 1000 ~ 1400°C for 6 hrs under a reducing nitrogen atmosphere containing 5% H_2 using a conventional solid-state reaction method. The XRD peaks of phosphors became sharper and stronger at the sintering temperature of 1300°C. PL measurement of

the $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ firing at different temperatures (1100°C, 1300°C) shows that for all compositions, the shapes of the excitation spectra were similar for the relative intensity. Through repeated experiments, the maximum luminous intensity of emission spectrums was obtained from the phosphor sintered at 1300°C. The $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ powder consists of small spherical particle with smooth and round surface. With increased firing temperature, phosphors particles had the spherical shape. The PL emission spectra of the $\text{Sr}_{1-x}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}_x$ with different concentrations of Eu^{2+} were measured. The emission intensity increased with an increasing Eu^{2+} concentrations up to $x = 0.15$. The emission, located at 525 ~ 550 nm (excited at 450 nm), is attributed to the typical $4f^65d^1-4f^7$ transition of Eu^{2+} .

As a result, an increase of the quenching concentration played a key role in enhancing the luminescent intensity. Therefore, it can be concluded that the optimized $\text{Sr}_{0.85}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}_{0.15}^{2+}$ phosphor is expected to be successfully used as the green to yellow emitting phosphor for blue pumped WLEDs.

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