Synthesis of \( \text{Ba}_3\text{Si}_6\text{O}_{12}\text{N}_2: \text{Eu}^{2+} \) and \( \text{Ba}_3\text{Si}_6\text{O}_{9}\text{N}_4: \text{Eu}^{2+} \) phosphors using \( \text{Si}_2\text{N}_2\text{O} \) as the starting material

Hidetoshi MIYAZAKI\(^1,2\) and Jun IMAGUCHI\(^1\)

\(^1\)Graduate School of Natural Science Technology, Shimane University, 1060 Nishikawatsu, Matsue 690–8504, Japan

\( \text{Ba}_3\text{Si}_6\text{O}_{12}\text{N}_2: \text{Eu}^{2+} \) and \( \text{Ba}_3\text{Si}_6\text{O}_{9}\text{N}_4: \text{Eu}^{2+} \) phosphors were synthesized by a solid-state reaction using \( \text{Si}_2\text{N}_2\text{O} \) powder as the starting material. The \( \text{Ba}_3\text{Si}_6\text{O}_{12}\text{N}_2: \text{Eu}^{2+} \) phosphor showed green photoluminescence (PL) with a peak at 517 nm, while \( \text{Ba}_3\text{Si}_6\text{O}_{9}\text{N}_4: \text{Eu}^{2+} \) showed bluish-green PL with a peak at 490 nm. Additionally, both phosphors exhibited afterglow properties.

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1. Introduction

GaN-based white-light light emitting diodes (LEDs) have been widely used for illumination in lamps, indicators, and display backlights because of their stability, long lifetimes, and high efficiency.\(^ {1,3} \) This type of white-light LED is generally fabricated using a combination of In–Ga–N blue LEDs and yellow-emitting phosphors consisting of Ce-doped YAG. Additionally, white-light LEDs fabricated using ultraviolet LEDs coupled with red, blue, and green phosphors have been developed.\(^ {3} \) Silicon oxynitride phosphors are very attractive for the fabrication of such white-light LEDs because of their high efficiency, excellent chemical stability, and thermal quenching, among other qualities.\(^ {4,5} \) These silicon oxynitride phosphors are Eu-doped MSi\(_2\)O\(_2\)N\(_2\), M\(_2\)Si\(_6\)O\(_9\)N\(_4\), and M\(_2\)Si\(_6\)O\(_{12}\)N\(_2\), where “M” corresponds to an alkaline earth metal (Mg, Ca, Sr, or Ba).

\( \text{Si}_2\text{N}_2\text{O} \) could be used as a raw material for the synthesis of alkaline earth silicon oxynitride phosphors. The crystaline structure of \( \text{Si}_2\text{N}_2\text{O} \) has \( \text{Si}_2\text{O}_2\text{N}_2 \)\(^ {2-} \) polyanion layers consisting of \( \text{SiO}_4 \) tetrahedral layers.\(^ {6} \) These polyanion layers are connected by a bridging oxygen layer. Alkaline earth silicon oxynitrides have \( \text{SiO}_4\text{N}_y \) polyanion layers and MO layers (M = Mg, Ca, Sr, or Ba); thus, the crystallographic regularity (\( \text{SiO}_4\text{N}_y \) polyanion layer) of alkaline earth silicon oxynitrides is similar to that of \( \text{Si}_2\text{N}_2\text{O} \). In a previous work, we prepared single-phase (Sr, Ba, Ca)-Si\(_2\)O\(_2\)N\(_2\)-based phosphors using Ca, Sr, and Ba carbonates and Si\(_2\)N\(_2\)O powders.\(^ {7,8} \) The resulting phosphors had few impurities and high brightness. Therefore, in this work, \( \text{Si}_2\text{N}_2\text{O} \) was considered an effective starting material in the synthesis of alkaline earth silicon oxynitride phosphors.

\( \dagger \) Corresponding author: H. Miyazaki; E-mail: miya@riko.shimane-u.ac.jp

In this study, \( \text{Ba}_3\text{Si}_6\text{O}_{12}\text{N}_2: \text{Eu}^{2+} \) and \( \text{Ba}_3\text{Si}_6\text{O}_{9}\text{N}_4: \text{Eu}^{2+} \) phosphors were synthesized by a solid-state reaction using \( \text{Si}_2\text{N}_2\text{O} \) powder as the starting material. In the case of synthesis of \( \text{BaSi}_2\text{N}_2\text{O}_2: \text{Eu} \) phosphor, the emission intensity of that increases by addition of NH\(_4\)Cl as flux.\(^ {8} \) In the present investigation, NH\(_4\)Cl was also used as flux agent for synthesizing Ba-based silicon oxynitride. The photoluminescence (PL) and afterglow properties of the resulting phosphors were evaluated.

2. Materials and methods

\( \text{Si}_2\text{N}_2\text{O} \) powder was prepared by a solid-state reaction in which Si (Kojundo Chemical Laboratory Co. Ltd.) and SiO\(_2\) (Quartz, Kojundo Chemical Laboratory Co. Ltd.) powders were mixed in a 3:1 molar ratio and fired at 1450°C for 1 h under N\(_2\) atmosphere. The \( \text{Si}_2\text{N}_2\text{O} \) powder synthesis procedure has been described in a previous report.\(^ {9} \) The resulting \( \text{Si}_2\text{N}_2\text{O} \), SiO\(_2\), BaCO\(_3\) (Wako Pure Chemical Industries, Ltd.), and Eu\(_2\)O\(_3\) (Nippon Yttrium Co. Ltd.) powders were used as starting materials for synthesizing \( \text{Ba}_3\text{Si}_6\text{O}_{12}\text{N}_2: \text{Eu}^{2+} \) and \( \text{Ba}_3\text{Si}_6\text{O}_{9}\text{N}_4: \text{Eu}^{2+} \) phosphors. The source materials, taken in their stoichiometric ratios, were mixed properly in an agate mortar. The Eu/Ba ratio of the source was fixed to 1/99. Subsequently, NH\(_4\)Cl (Wako Pure Chemical Industries Ltd.) was added at an outer percentage of 5wt % and the mixing in the agate mortar was continued. The mixture was heat-treated in a carbon boat in H\(_2\)/N\(_2\) atmosphere (90% N\(_2\), 10% H\(_2\)) under the conditions given in Table 1. The resulting powders were grounded in the agate mortar and washed using ion-exchanged water for further analysis.

The structures of the resulting powders were characterized using X-ray diffraction (XRD, Rigaku Miniflex, Japan) with Cu K\( \alpha \) radiation (30 kV, 15 mA). Their microstructures were observed using a scanning electron microscope (SEM, JCM-6000 Plus, JEOL Ltd., Japan). The
nitrogen and the oxygen contents in the phosphors were evaluated by LECO ON836 analyzer (nitrogen and oxygen content analyzer designed by LECO Corp). The PL and afterglow properties of the powders were evaluated at room temperature using a conventional fluorescence spectrophotometer (Shimadzu RF 5300PC) with a Xe lamp.

3. Results and discussion

3.1 Ba₃Si₆O₁₂N₂:Eu²⁺ phosphor

Ba₃Si₆O₁₂N₂:Eu²⁺ was synthesized using the conditions given in Table 1. Figure 1 shows the XRD pattern (a), SEM image (b), and PL spectrum (c) of the phosphor after washing. A single Ba₃Si₆O₁₂N₂ phase with ICSD-421322 was observed. A temperature of 1350°C resulted in the melting of the powders. When the heat-treatment time was 2 h, the reaction did not progress sufficiently; however, the reaction time of 6 h resulted in the formation of other phases. The resulting granular particles were in the size range of 5–10 μm. The washing procedure successfully removed the reaction residues. Similar to the BaSi₂N₂O₂ phosphor, the results revealed that Ba₃Si₆O₁₂N₂:Eu²⁺ was chemically resistant to water and could be washed using this solvent. The analytical composition of the phosphor was Ba₃Si₆O₁₁.5N₂.1:Eu²⁺. The nitrogen content was slightly larger and the oxygen content was slightly lower than the stoichiometric composition of Ba₃Si₆O₁₂N₂.

Upon exciting Ba₃Si₆O₁₂N₂:Eu²⁺ at 327 nm, green PL was observed with the peak position at 517 nm. The PL was attributed to the transition of Eu²⁺ from 4f⁶5d¹ to 4f⁷. The excitation spectra at 517 nm showed two broad excitation peaks at approximately 327 and 434 nm. Green PL was observed by 365-nm ultraviolet (UV) irradiation, as seen in the inset photograph in Fig. 1(c). Mikami calculated the electronic structure of Ba₃Si₆O₁₂N₂:Eu²⁺ and reported the PL peak of the phosphor to be at 530 nm. The PL peak of the phosphor obtained in this work was located at a slightly smaller wavelength (517 nm) than that from calculated data. The PL properties of Ba₃Si₆O₁₂N₂:Eu²⁺ were assumed to vary depending on the synthesis method and the composition of the phosphor.

3.2 Ba₃Si₆O₉N₄:Eu²⁺ phosphor

Ba₃Si₆O₉N₄:Eu²⁺ phosphors were also synthesized under the conditions given in Table 1. Figure 2 shows the XRD pattern, SEM image, and PL spectrum of the resulting phosphor after washing. A single Ba₃Si₆O₉N₄ phase with ICSD-415918 was observed. Similar to the case of Ba₃Si₆O₁₂N₂:Eu²⁺, a temperature of 1400°C melted the powder, whereas at 1250°C a second Ba₃Si₆O₁₂N₂ phase appeared. Under a heat-treatment time of 2 h the reaction did not progress sufficiently. The resulting particles were granular, ranging in size from 3 to 15 μm; thus, the size distribution of Ba₃Si₆O₉N₄:Eu²⁺ phosphor particles was slightly larger than that of Ba₃Si₆O₁₂N₂:Eu²⁺ phosphor particles. As with other Ba Si oxynitride phosphors, water washing can also be employed for a Ba₃Si₆O₉N₄:Eu²⁺ phosphor. The analytical composition of the phosphor was Ba₃Si₆O₇.₅N₄.₅:Eu²⁺. The nitrogen content was slightly larger and the oxygen content was slightly lower than the stoichiometric composition of Ba₃Si₆O₉N₄.
The excitation of Ba₃Si₆O₉N₄:Eu²⁺ at 441 nm resulted in a bluish-green PL with a peak at 490 nm; the PL was attributed to the transition of Eu²⁺ from 4f⁶5d¹ to 4f⁷. The excitation spectrum was also measured at 490 nm; three broad excitation peaks were observed at approximately 296, 385, and 441 nm. As seen in the inset in Fig. 1(c), a bluish-green PL was observed upon irradiation with 365-nm UV light. The PL peak position was slightly shorter than that in previous reports (520 nm). Mikami also calculated the electronic structure of Ba₃Si₆O₉N₄:Eu²⁺ and reported the PL peak to be at 480 nm. The PL properties of this phosphor were also assumed to vary depending on the synthesis method and the composition of the phosphor.

The Ba₃Si₆O₁₂N₂:Eu²⁺ and Ba₃Si₆O₉N₄:Eu²⁺ phosphors were successfully synthesized using Si₂N₂O as the starting material. Figure 3 illustrates the crystal structures of Si₂N₂O, Ba₃Si₆O₁₂N₂, and Ba₃Si₆O₉N₄. The Si₂N₂O crystal structure comprises SiON₃ tetrahedral units with a bridging oxygen layer. This bridging oxygen layer replaces the barium oxide layer ((Si₂O₂N₂)n²⁻ polyanion layer [poly]), replacing part of the SiO₃N in Si₂N₂O with SiO₂N₂ or SiO₃N units, resulting in the formation of the crystal structures of Ba₃Si₆O₁₂N₂ and Ba₃Si₆O₉N₄. Ba₃Si₆O₁₂N₂ and Ba₃Si₆O₉N₄ could be easily synthesized using Si₂N₂O as the starting material because their crystal structures are very similar to that of Si₂N₂O.

3.3 Afterglow properties of Ba₃Si₆O₁₂N₂:Eu²⁺ and Ba₃Si₆O₉N₄:Eu²⁺

Figure 4 depicts the afterglow properties of Ba₃Si₆O₁₂N₂:Eu²⁺ and Ba₃Si₆O₉N₄:Eu²⁺ evaluated at the PL peak wavelength (Ba₃Si₆O₁₂N₂:Eu²⁺: 517 nm, Ba₃Si₆O₉N₄:Eu²⁺: 490 nm) using UV irradiation with an excitation wavelength of 250 nm for 10 s. The half-lives of Ba₃Si₆O₁₂N₂:Eu²⁺ and Ba₃Si₆O₉N₄:Eu²⁺ were 3.4 and 1.9 s, respectively. In a previous report, the Ba₅Si₂O₆N₂:Eu²⁺ phosphor showed afterglow characteristics. Since the crystal structures of Ba₃Si₆O₁₂N₂ and Ba₃Si₆O₉N₄ were similar to that of Ba₅Si₂O₆N₂, they also showed afterglow properties due to the formation of electron traps.

4. Conclusions

Ba₃Si₆O₁₂N₂:Eu²⁺ and Ba₃Si₆O₉N₄:Eu²⁺ phosphors were synthesized using Si₂N₂O powder as starting mater-
Both the nitrogen content in the resulting phosphors were slightly larger than the stoichiometric composition of the phosphor. The former showed green PL with a peak at 517 nm, whereas the latter showed bluish-green PL with a peak at 490 nm. In addition, both phosphors exhibited afterglow properties. Furthermore, their crystal structures were similar to that of Si2N2O, because of which Ba3Si6-O12N2 and Ba3Si6O9N4 could be easily synthesized using Si2N2O as the starting material.

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