Ammonothermal synthesis of charge-compensated SrAlSiN₃:Ce³⁺ phosphor

Yuki MARUYAMA, Yuki YANASE and Tomoaki WATANABE

The Organization for the Strategic Coordination of Research and Intellectual Properties, Meiji University, 1–1–1 Higashimita Tama-ku, Kawasaki 214–8571, Japan
Department of Applied Chemistry, School of Science and Technology, Meiji University, 1–1–1 Higashimita Tama-ku, Kawasaki 214–8571, Japan

In this study, we successfully synthesized SrAlSiN₃:Ce³⁺ at 1073 K using the ammonothermal method. Scanning electron microscope images revealed bar-like crystals in the products. We investigated the effects of using a charge-compensating ion on the phosphor's emission of SrAlSiN₃ with Ce³⁺ and Sr²⁺ and adding Na⁺ as a charge compensator. We found that Ce³⁺-doped SrAlSiN₃ exhibited a weak emission. However, SrAlSiN₃ co-doped with Ce³⁺ approximately 550 nm for an excitation wavelength of 460 nm. We, thus, found that Na⁺ charge of Sr₂⁺ ions such as Eu²⁺, only been doped with Eu²⁺, such as SrSiN₂:Eu²⁺, Of the various nitride phosphors, silicon-based nitride phosphors are good candidates for use in white LEDs in future.

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1. Introduction

White light-emitting diodes (LEDs) are attracting attention as a potential next generation light source. Therefore, a lot of research into phosphor for white LEDs is currently being conducted. A phosphor for white LEDs should ideally have the ability to be excited using near ultraviolet or blue light, while having a high chemical stability and strong emission characteristics even at high temperatures. Unlike sulfide phosphors, nitride phosphors are excited by blue light and have a high stability. Thus, nitride phosphors are good candidates for use in white LEDs in future. Of the various nitride phosphors, silicon-based nitride phosphors such as SrSiN₂:Eu²⁺, Sr₂Si₅N₈:Eu²⁺, and SrAlSiN₃:Eu²⁺ have been studied the most because of their high chemical and thermal stability. In general, nitride phosphors are synthesized using conventional solid-state reactions, which are simple to perform. SrAlSiN₃:Eu²⁺ has been synthesized using conventional solid-state reaction at 2173 K under 190 MPa nitrogen atmosphere. Conventional synthesis method require a reaction condition at extremely high temperature and in high pressure nitrogen atmosphere. Therefore, developing a synthesis method that requires a lower temperature than conventional solid-state reactions is critical.

The ammonothermal syntheses of CaAlSiN₃:Eu²⁺(5–7) and SrAlSiN₃:Eu²⁺(8,9) were previously reported. These syntheses took place at temperatures of 1000 and 1100 K, respectively, which are below those used for conventional solid-state reactions. Additionally, CaAlSiN₃ has been doped with various emission ions such as Eu²⁺, Ce³⁺, and Pr³⁺, therefore, various CaAlSiN₃ phosphors have been reported. (10–13) Conversely, SrAlSiN₃ has only been doped with Eu²⁺; to the best of our knowledge, there are no reports of doping SrAlSiN₃ with any other emission ions.

We propose that having a SrAlSiN₃ phosphor that is doped with another emission ion would greatly expand the number of phosphor materials that can be selected for LED applications. Therefore, to search for a novel SrAlSiN₃ phosphor, we focused on Ce³⁺-doped SrAlSiN₃. This study aims to synthesize SrAlSiN₃:Ce³⁺ using the ammonothermal method. To allow Ce³⁺, which has a different valence than Sr²⁺, to replace Sr²⁺, we attempted charge compensation via Na⁺ co-doping since the ionic radius of Na⁺ is similar to that of Sr²⁺. Finally, we investigated the new material’s luminescence properties.

2. Experimental procedure

Sr (99%, Kojundo Chemical Lab., Japan), Ce (99%, Junsei Chemical., Japan), and Na (99%, Sigma-Aldrich, USA) were weighed in an Ar atmosphere in a glove box (IADB-3 type, Miwa, Japan). Al (Kojundo Chemical Lab., Japan) and Si (Kojundo Chemical Lab., Japan) were weighed in air. The starting alloys (Sr:Ce:Al:Si = 0.984:0.016:1:1, Sr:Ce:Na:Al:Si = 0.968:0.016:0:08:1:1) were prepared using the arc-discharge melting method. The alloys were ground using a small-sized mill (SK-M2 type, Kyoritsu Riko, Japan) in an Ar atmosphere. The alloy powder was mixed with Sr as a mineralizer in a 1:2 (alloy:mineralizer) molar ratio and loaded into a bottom-sealed nickel tube. The nickel tube was transferred to a vertically positioned high-pressure vessel, which was then completely filled with anhydrous liquid ammonia via a cooled condenser. An R-type thermocouple was fixed to face the outer surface of the pressure vessel at the bottom of the sample. The samples were heated to 773 K at a rate of 20 K/min. After maintaining the samples at 773 K for 20 h, they were further heated to 1073 K at a rate of 1 K/min and that temperature was maintained for 5 h. A constant pressure of 100 MPa was applied during the entire reaction. An ammonia-releasing valve was used to reduce the pressure whenever necessary. After the samples were naturally cooled down to room temperature, the products were exposed to air, washed with

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deionized water and ethanol, and dried in air at 353 K. The crystal structures of the products were determined via X-ray diffraction (XRD, Rigaku Rint TTRIII diffractometer using Cu Kα radiation and operating at 40 kV and 40 mA). Scanning electron microscope (SEM) images were obtained using a Hitachi S-5200. Photoluminescence spectra were measured using a JASCO FT-6500 luminescence spectrometer.

3. Results and discussion

Figure 1 shows the XRD patterns of the products prepared via the nitridation of the SrAlSi:Ce and SrAlSi:Ce, Na precursor alloys. These patterns agree with the pattern for Sr0.962AlSiN3 reported in ICDD data 01-077-9189.14) A small amount of Al2O3 impurity phase was detected in the XRD pattern of Ce3+ and Na+ co-doped product. Table 1 shows the lattice parameter calculated by Cellcalc.15) The ionic radii of Sr2+ and Na+ (both Sr2+ and Na+ have six-fold coordination) are 1.32 and 1.16 Å, respectively. As Na+ has a smaller ionic radius than Sr2+, it can be replaced by Sr2+. This causes the cell volume of the Ce3+ and Na+ co-doped product to be slightly smaller than that of the Ce3+ doped product.

Further, the diffraction intensity of the Ce3+ and Na+ co-doped product was slightly decreased compared with that of the Ce3+ doped product. Previous studies related to the ammonothermal synthesis of SrAlSiN3:Eu2+ predicted that the intermediates incorporating Na (sodium ammonometallates) should be more thermally stable than the intermediate without Na (ammonometallates).8),9) As sodium ammonometallates may not be easily converted to SrAlSiN3, the diffraction intensity of the Ce3+ and Na+ co-doped product was slightly decreased due to the incorporation of Na.

Figure 2 presents the SEM images of the products. The morphologies of the products showed bar-like crystals around 1–2 μm in length. No morphological changes of the product were observed regardless the presence or absence of Na as a charge compensator. Ammonothermal synthesis of SrAlSiN3:Eu2+ reportedly yield products with bar- and plate-like crystal morphologies.8) The crystal structure of SrAlSiN3 is identical to that of CaAlSiN3, i.e., space group 36 (Cmc21), and the Sr atom is exposed in the a-axis direction. As Sr is used as a mineralizer, the Sr concentration in the reaction system is relatively high, which facilitates crystal growth along the a-axis; this is what causes the formation of the bar-like crystals.

Figure 3 shows the emission spectra of the products synthesized using the ammonothermal method. The Ce3+ doped product exhibited a weak emission. On the other hand, the Ce3+ and Na+ co-doped product exhibited a broad emission band centered at 550 nm with an excitation wavelength of 460 nm. Although a small amount of Al2O3 impurity phase was detected in the XRD pattern of Ce3+ and Na+ co-doped product, it seems that a small amount of Al2O3 impurity phase may not be an origin of lumi-

| Sample           | a/Å (standard deviation) | b/Å (standard deviation) | c/Å (standard deviation) | V/Å³ (standard deviation) |
|------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Ce3+ doped       | 9.854 (0.006)            | 5.747 (0.005)            | 5.183 (0.004)            | 293.5 (0.402)            |
| Ce3+, Na+ Co-doped | 9.846 (0.006)            | 5.756(0.005)             | 5.175 (0.004)            | 293.2 (0.397)            |
| Reference9       | 9.843                    | 5.760                    | 5.177                    | 293.5                    |

Fig. 1. XRD patterns of the products synthesized using the ammonothermal method and the standard XRD pattern for ICDD data 01-077-9189.

Fig. 2. SEM images of the products synthesized using the ammonothermal method.

Fig. 3. Emission spectra of the products synthesized using the ammonothermal method.
nescence. These emissions arise from the transition of Ce\(^{3+}\) from the 5d\(^1\) excited state to the 4f\(^0\) ground state. For Ce\(^{3+}\)-doped SrAlSiN\(_3\), charge compensation of the Sr defect is required when replacing Ce\(^{3+}\) with Sr\(^{2+}\), as shown in the following equation.

\[ 3\text{Sr}^{2+} \rightarrow 2\text{Ce}^{3+} + V_{\text{Sr defect}} \]  

Since a weak emission was observed for the Ce\(^{3+}\) doped product, it was thought that a small amount of Ce\(^{3+}\) was doped in the product. Conversely, we propose that the emission observed from the Ce\(^{3+}\) and Na\(^{+}\) co-doped product is caused by the Sr\(^{2+}\) site being replaced by Ce\(^{3+}\) and Na\(^{+}\), as shown in the following equation.

\[ 2\text{Sr}^{2+} \rightarrow \text{Ce}^{3+} + \text{Na}^{+} \]  

Previously, emission from CaAlSiN\(_3\):Ce\(^{3+}\) was observed at 580 nm with an excitation wavelength of 460 nm.\(^{11}\) The peak emission wavelength of SrAlSiN\(_3\):(Ce\(^{3+}\), Na\(^{+}\)) prepared using the ammonothermal method shifts toward blue in comparison with the peak emission wavelength of CaAlSiN\(_3\):Ce\(^{3+}\) prepared using solid-state reaction.\(^{11}\) Dorenbos (2003) reported that the peak emission wavelength of a phosphor with a long bond length between the emission ion and the anion is shifted toward a shorter wavelength when the crystal field splitting is decreased.\(^{16}\) The peak emission wavelength of SrAlSiN\(_3\):Eu\(^{2+}\) is shorter than that of CaAlSiN\(_3\):Eu\(^{2+}\). Additionally, the cell volume of the SrAlSiN\(_3\) host crystal (\(V = 293.5\;\text{Å}^3\)) is larger than that of the CaAlSiN\(_3\) host crystal (\(V = 278.3\;\text{Å}^3\)).\(^{11}\) The peak emission wavelength of SrAlSiN\(_3\):Eu\(^{2+}\), which has a long Eu–N bond length, is blue-shifted due to a decrease in the 5d orbital splitting of Eu\(^{2+}\). Similarly, the peak emission wavelength of SrAlSiN\(_3\):(Ce\(^{3+}\), Na\(^{+}\)) (\(V = 293.2\;\text{Å}^3\)) is blue-shifted in comparison with the peak emission wavelength of CaAlSiN\(_3\):Ce\(^{3+}\) (\(V = 279.8\;\text{Å}^3\)).\(^{11}\) To summarize, we found that SrAlSiN\(_3\):(Ce\(^{3+}\), Na\(^{+}\)) synthesized using the ammonothermal method exhibited a broad emission band centered at 550 nm when excited with white light; thus, it is a promising phosphor for fabricating white LEDs.

4. Conclusion

In the present study, we successfully synthesized SrAlSiN\(_3\):Ce\(^{3+}\) using the ammonothermal method at 1073 K under 100 MPa. The material’s morphology is characterized by bar-like crystals having lengths of 1–2 μm. We propose that SrAlSiN\(_3\):Ce\(^{3+}\) was generated via a dissolution–crystallization process. We investigated the effect of the emission on the presence or absence of Na\(^{+}\) as a charge compensator between the Sr\(^{2+}\) and Ce\(^{3+}\) ions. As a result, the Ce\(^{3+}\) doped product exhibited a weak emission, while the product with Na\(^{+}\) as a charge compensator exhibited a broad emission band centered at 550 nm when excited with a wavelength of 460 nm. As the ionic radius of Sr\(^{2+}\) is quite similar to that of Na\(^{+}\), Na\(^{+}\) is easily substituted at the Sr\(^{2+}\) site. We propose that the emission of SrAlSiN\(_3\):(Ce\(^{3+}\), Na\(^{+}\)) is caused by Na\(^{+}\) functioning as a charge compensator. Thus, we have demonstrated the synthesis of a novel SrAlSiN\(_3\):Ce\(^{3+}\) phosphor and revealed that Na\(^{+}\) plays an important role in this material by acting as a charge compensator between Sr\(^{2+}\) and Ce\(^{3+}\).

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