Low-temperature synthesis of CaAlSiN$_3$:Ce$^{3+}$ using the ammonothermal method

Yuki MARUYAMA and Tomoaki WATANABE$^\dagger$

Department of Applied Chemistry, Meiji University, 1-1-1 Higashi-Mita Tama-ku, Kawasaki 214-8571, Japan

In this study, we successfully synthesized CaAlSiN$_3$:Ce$^{3+}$ at 1073 K using the ammonothermal method. The synthesis temperature was 900 K lower than that in the conventional solid-state reaction. The product exhibited a broad emission band that was centered at approximately 550 nm by irradiation of 440 nm blue light. Furthermore, we investigated the effects of the reaction temperature and mineralizers on the products synthesized using the ammonothermal method. The results of X-ray diffraction analysis indicated that the optimal temperature for CaAlSiN$_3$:Ce$^{3+}$ synthesis was 773 K because the sample treated at this temperature exhibited the highest diffraction intensity and the smallest half-value width. The product prepared using NaNH$_2$ as a mineralizer exhibited the highest emission intensity. Moreover, the products prepared using the ammonothermal method had a plate-like crystal morphology.

Key-words: Ammonothermal, Nitride, Phosphor, Low temperature process, CaAlSiN$_3$

1. Introduction

White light-emitting diodes (LEDs) save energy and live long. Therefore, they are of particular interest under today’s energy challenge. In general, white LEDs exhibit a white color by combining the yellow phosphor with a blue LED. YAG:Ce$^{3+}$ phosphor, which is generally used as a phosphor for white LEDs, exhibits a yellow emission by excitation with blue light. However, the emission intensity of YAG:Ce$^{3+}$ phosphor decreases at high temperature. Therefore, instead of YAG:Ce$^{3+}$, CaAlSiN$_3$:Ce$^{3+}$ yellow phosphor is expected to be a phosphor for white LEDs. CaAlSiN$_3$:Ce$^{3+}$ has a three-dimensional crystal structure, where the Si or Al tetrahedral is connected with the nitrogen. Because of the presence of Si, the AlN$_4$ tetrahedral has a rigid host lattice; CaAlSiN$_3$:Ce$^{3+}$ exhibits high chemical stability and excellent thermal stability. CaAlSiN$_3$:Ce$^{3+}$ was synthesized by a solid-state reaction. However, it required a high reaction temperature, which generated a nitrogen defect, diminishing the luminescence efficiency. It is therefore important to synthesize CaAlSiN$_3$:Ce$^{3+}$ at a lower temperature.

The ammonothermal synthesis of Eu$^{2+}$-doped CaAlSiN$_3$ was previously reported in a synthesis study of nitride phosphor. Using the ammonothermal method, CaAlSiN$_3$:Eu$^{2+}$ was synthesized at 1000 K below the temperature of the conventional solid-state reaction. Moreover, SrAlSiN$_3$:Eu$^{2+}$ synthesis was reported using the same method, at 1100 K below the temperature of the conventional solid-state reaction. In the above syntheses, the effects of the reaction temperature and mineralizers on the products were investigated. However, there is no report on CaAlSiN$_3$:Ce$^{3+}$ synthesis using the ammonothermal method, although it is expected that this synthesis would require a lower temperature as well. In the present study, we synthesized CaAlSiN$_3$:Ce$^{3+}$ using the ammonothermal method, and investigated the effects of the reaction temperature and mineralizers on the products.

2. Experimental procedures

Ca (99%, Kojundo Chemical Lab., Japan), Ce (99%, Junsei Chemical., Japan), and Li (Kanto Chemical., Japan) were weighed under argon atmosphere in a glove box (1ADB-3 type, Miwa, Japan). According to the reference, Li$^+$ was used as the charge compensator. Li$^+$ has important role for charge compensator of Ca$^{2+}$ and Al$^{3+}$; Al (Kojundo Chemical Lab., Japan) and Si (Kojundo Chemical Lab., Japan) were weighed in air. The starting alloy (Ca:Ce:Li:Al:Si = 0.968:0.016:0.08:1:1) was prepared using the arc discharge melting method. The alloy was ground using a small-sized mill (SK-M2 type, Kyritsu Riko, Japan) in argon atmosphere. The alloy powder was mixed with NaNH$_2$ (95%, Aldrich, USA), K (99%, koujundo Chemical Lab., Japan), or Ca as a mineralizer in molar ratios 1:2 (alloy: mineralizer) and loaded on a bottom-sealed nickel tube. The nickel tube was transferred to a vertically positioned high-pressure vessel, which was then fully 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 position of the sample bottom. The samples were heated to 573–773 K at a rate of 20 K/min. After maintaining the samples at 573–773 K for 20 h, they were further heated to 1073 K at a ratio of 1 K/min and the temperature was maintained for 5 h. A pressure of 100 MPa was maintained during the entire reaction. An ammonia-releasing valve was used to reduce the pressure whenever necessary. After the samples were naturally cool down to room temperature, the products were exposed to air, washed with ethanol and diluted chloric acid (0.2 M), and dried in air at 353 K. The crystal structures of the products were determined by X-ray diffraction (XRD, Rigaku RINT-2200 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.

$^\dagger$ Corresponding author: T. Watanabe; E-mail: tomowata@meiji.ac.jp

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3. Results and discussions

Figure 1 shows the XRD patterns of the products prepared at 573–773 K in the first stage of the experiment, maintaining a stable temperature and using NaNH₂ as a mineralizer. The XRD patterns of the products agreed with the pattern for CaAlSiN₃ reported in the ICDD data 00-039-0747. The results of XRD analysis indicated that the optimal temperature for CaAlSiN₃ synthesis was 773 K because the sample treated at this temperature exhibited the highest diffraction intensity and the smallest half-value width. The full width at half maximum (FWHM) value of (002) line obtained at 573, 673, and 773 K are 0.47, 0.33, and 0.27°, respectively.

Figure 2 presents the SEM images of the products. The crystal morphologies of the products were plate-like, and their sizes were 500 nm. Because euhedral crystals were observed, it was thought that the products may be generated via the dissolution–crystallization process. In previous studies related to the synthesis of CaAlSiN₃:Eu²⁺ using ammonothermal process, it was reported that CaAlSiN₃ is formed by a two-step reaction. In ammonothermal synthesis, an alloy is converted to ammonometallates and then decomposed into CaAlSiN₃. CaAlSiN₃ is also formed at temperatures ≥ 773 K by a single-step reaction. However, CaAlSiN₃ is insoluble in ammonia solutions and cannot grow via a dissolution–crystallization process after formation. The crystal growth of CaAlSiN₃ requires a two-step reaction consisting of a formation reaction step and a decomposition reaction step. It is important to investigate the first-stage holding temperature to determine the crystal growth pattern of CaAlSiN₃ through intermediate formation and decomposition. In addition, the present synthesis of CaAlSiN₃:Ce³⁺ proceeds following a similar reaction. Because we used NaNH₂ as a mineralizer in the present study, the intermediate was predicted to be sodium ammonometallates. Indeed, the generation of sodium ammonometallates was promoted because the crystallinity of the product obtained at 773 K was the highest. Consequently, the crystal growth from sodium ammonometallates to CaAlSiN₃ was also probably promoted. The SEM images indicated that the product size at 773 K was the greatest. The crystal growth of CaAlSiN₃ was observed in the product obtained at 773 K.

Figure 3 shows the emission spectra of the products prepared at 573–773 K in the first-stage holding temperature with NaNH₂ as a mineralizer. The products exhibited a broad emission band centered at approximately 550 nm by irradiation of 440 nm blue light. These emissions arise from the transition of Ce³⁺ from the 5d¹ excited state to the 4f⁰ ground state. The highest emission was observed from CaAlSiN₃:Ce³⁺ at 580 nm under irradiation of 460 nm light source. The peak emission wavelength of the products prepared using the ammonothermal method shifts toward blue in comparison with the peak emission wavelength of CaAlSiN₃:Ce³⁺ prepared using solid-state reaction. Dorenbos reported that the peak emission wavelength of phosphor with a high covalent anion shifts toward a longer wavelength by an increase in the centroid shift. Because oxygen is lesser covalent than nitrogen, the peak emission wavelength shifts toward a shorter wavelength in this case. Incorporating oxygen therefore creates a Ce–O bond, which is lesser covalent than the Ce–N bond. Consequently, the peak emission wavelength shifts toward blue by a decrease in the centroid shift of Ce³⁺. In the present study, the oxygen could originate from the absorbed water in NaNH₂ and/or the water in NH₃.

Compared with the products prepared at different temperatures, the product obtained at 773 K exhibits the highest emission intensity. In the synthesis of SrAlSiN₃:Eu²⁺ using the ammonothermal method, high-crystallinity product exhibited a high emission intensity. In the present study, the product obtained at 773 K exhibited a higher crystallinity and emission intensity than the products obtained at different temperatures. Table 1 shows the lattice parameters calculated by Cellcalc. The cell
volume of the products, which are obtained at 573 or 673 K, is smaller than the that of the product obtained at 773 K. This suggests that crystal defects are present due to the Ca deficiency.

Figure 4 shows the XRD patterns of the products prepared at 773 K in the first-stage holding temperature with various mineralizers. The XRD patterns of all the products prepared using the different mineralizers agreed with the pattern for CaAlSiN3 reported in the ICDD data 00-039-0747. Using K or Ca, the Ca(OH)2 peak was detected in the XRD patterns of the products. The diffraction peaks at 2θ = 28.6°, 34.1°, and 47.1° from Ca(OH)2 crystal corresponded to Miller indices of (100), (101), and (102), respectively. Formed Ca(OH)2 may be oriented in the direction of (100), (101), (102) faces, respectively. Since more Ca atom is exposed at (100) face, it is thought that the growth rate of (100) face is higher than that of (101), (102) faces by using Ca as a mineralizer. We observed that the products prepared using K or Ca drastically reacted with water. Then, the intermediates potassium and calcium ammonometallates remained in the final products. It seems that the hydroxide in the product is formed by the reaction of these intermediates with water. In contrast, we did not observe a similar reaction with water when using NaNH2. Compared with potassium or calcium ammonometallates, the CaAlSiN3 formation reaction proceeded easily from sodium ammonometallates. Consequently, the sodium ammonometallates did not remain in the final product, and the product did not drastically react with water.

The crystallinity of the products prepared using NaNH2 was greater than that of the products prepared using K or Ca. The diffraction peak of the starting alloy was not detected in the XRD patterns of the products. The first-stage reaction proceeded using any mineralizers. When K or Ca was used, potassium or calcium ammonometallates remained in the final products. It is assumed that the generation of CaAlSiN3 from these ammonometallates is insufficient. The potassium and calcium ammonometallates are stable in supercritical ammonia. Sodium ammonometallates are not stable. Therefore sodium ammonometallates may be easily converted to CaAlSiN3. The high crystallinity of the product prepared using NaNH2 is due to the promotion of CaAlSiN3 generation from sodium ammonometallates. Figure 5 shows the SEM images of the products prepared using various mineralizers. The SEM images show that the particle size of the product prepared using NaNH2 was greater than that of the products prepared using K or Ca. CaAlSiN3 crystal growth was observed in the product prepared using NaNH2.

Figure 6 shows the emission spectra of the products prepared at 773 K in the first-stage holding temperature with various mineralizers. The products prepared using NaNH2 did not exhibit any emission. CaAlSiN3:Ce3+ prepared using K or Ca exhibited a larger half-value width in the XRD spectra than the products prepared using NaNH2. This suggests that CaAlSiN3:Ce3+ prepared using K or Ca has low crystallinity. CaAlSiN3:Ce3+ crystal defects, when synthesized using K or Ca, did not show emission.

Figure 7 presents the excitation spectra of the products prepared at 773 K in the first-stage holding temperature with various mineralizers. CaAlSiN3:Ce3+ synthesized using NaNH2 has an excitation range that is suitable for InGaN-based white LEDs. CaAlSiN3:Ce3+ synthesized using the ammonothermal method a promising phosphor for white LEDs.

| Sample | a/A | b/A | c/A | V/A³ |
|--------|-----|-----|-----|------|
| 573 K  | 9.625 | 5.608 | 5.003 | 270.1 |
| 673 K  | 9.744 | 5.596 | 5.014 | 273.4 |
| 773 K  | 9.880 | 5.594 | 4.998 | 276.2 |
| Reference2) | 9.795 | 5.647 | 5.059 | 279.8 |

Fig. 4. XRD patterns of the products treated with various mineralizers.

Fig. 5. SEM images of the products treated with various mineralizers.

Fig. 6. Emission spectra of the products treated with various mineralizers.
4. Conclusion

In the present study, we successfully synthesized CaAlSiN$_3$:Ce$^{3+}$ using the ammonothermal method at a temperature 900 K lower than that of the conventional solid-state reaction. The CaAlSiN$_3$:Ce$^{3+}$ crystallinity was affected by the first-stage holding temperature and mineralizer. The product prepared using NaNH$_2$ at 773 K exhibited a high crystallinity. CaAlSiN$_3$:Ce$^{3+}$ synthesized using the ammonothermal method exhibited a broad emission band that is centered at approximately 550 nm when illuminated with 440 nm light. The product prepared using NaNH$_2$ at 773 K exhibited high emission intensity. CaAlSiN$_3$:Ce$^{3+}$ synthesized using the ammonothermal method is a promising phosphor for white LEDs.

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