Low temperature ammonothermal synthesis of europium-doped SrAlSiN₃: effect of mineralizers

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SrAlSiN₃:Eu²⁺ is a red-emitting phosphor that is potentially very useful in white light-emitting diodes because of its properties such as thermal stability and bright emissivity features. A limitation of this phosphor is that it is commercially synthesized at high temperature (2173 K) and pressure (190 MPa). To address this limitation, we report (1) a low-temperature (1073 K) synthesis of SrAlSiN₃:Eu²⁺ phosphors through a dissolution–precipitation process in supercritical ammonia (ammonothermal method) and (2) an investigation of the phosphors’ physical properties. All products exhibit a broad emission that is centered at approximately 580 nm, which we attribute to the 5d→4f transition of Eu³⁺, under excitation wavelengths from the ultraviolet to blue range. We used Sr as a mineralizer to synthesize a superior product in terms of a high Sr concentration in the crystals, improved crystallinity, and enhanced emission intensity.

1. Introduction

Global climate concerns have prompted much scientific research that is relevant to reducing fossil fuel use and the corresponding CO₂ emissions. Given that lighting accounts for a substantial fraction of a typical household’s energy budget, it is very important to determine how to increase the efficiency of lighting. Light-emitting diodes (LEDs) can be very useful for this purpose. Practical applications of semiconductor LEDs first emerged in 1960s. Since then, they have shown increasing promise as energy-efficient, long-lasting light sources. White LEDs are very common, most notably in GaN-based semiconductor technology.¹ These LEDs continue to replace conventional incandescent and fluorescence-based lighting because of their long life and substantial energy efficiency. White LEDs that are based on an InGaN LED chip and the phosphor (Y,Gd)₃(Al,Ga)₅O₁₂:Ce³⁺ have spread across the world. However, they exhibit suboptimal color rendering (the ability to accurately reproduce colors under optical illumination) because they do not emit a deep red color.

To solve this problem, scientists have developed white LEDs that are a combination of an InGaN LED chip with either green- or red-emitting phosphors. To the best of our knowledge, there is little published research that pertains to applications of red-emitting phosphors in InGaN-based white LEDs. Hence development of red-emitting phosphors suitable for InGaN-based white LEDs is especially promoted.² Although there are many reports on oxide and sulfide phosphors, most of the oxide phosphors exhibit weak efficiency under blue light excitation. Red-emitting oxide phosphors under blue light excitation have not been reported.² On the other hand, alkaline-earth sulfides that are activated by Eu²⁺ exhibit high-efficiency red or orange luminescence, and they can be excited with blue light because of a strong nephelauxetic effect. Unfortunately, these materials are hygroscopic and can degrade in atmospheric moisture.³ Alternatively, (oxy) nitrides that are activated by Eu³⁺ may be suitable as red-emitting phosphors, which are compatible with InGaN-based white LEDs. These materials exhibit a strong nephelauxetic effect because of the covalent bonding interactions between Eu³⁺ and the nitrogen-based ligands. Consequently, excitation level of (oxy) nitride phosphors is lower than those of oxide phosphors,⁴ and they exhibit broadband absorption between near ultraviolet and blue wavelength ranges.

It is evident from sialons, commonly used as high-temperature structural materials,⁶ that silicon-containing ternary or multinary (oxy) nitride phosphors exhibit good stability and thermal properties. Various (oxy) nitride phosphors have been reported, e.g., AE₂Si₅N₇:Eu²⁺ (AE = Ca, Sr, Ba),⁷–⁹ AEYSi₄N₇:Eu²⁺ (AE = Sr, Ba),⁹ Ca₃-Al₁On:Eu²⁺,⁹ b-SiAlON:Eu²⁺,⁶ and Ca₂Si₃O₁₂N₃0:Eu²⁺.¹⁰ In particular, Eu²⁺-activated CaAlSiN₃ exhibits noteworthy quantum efficiency, chemical stability, and thermal properties; furthermore, it emits light of a deep red wavelength under blue light excitation.¹¹ This phosphor, therefore, holds great promise for practical use in white LEDs. For lighting applications that require both high color rendering and efficiency, it is desirable to shift the deep red emission of CaAlSiN₃ to shorter wavelengths with retention of quantum efficiency. With this goal in mind, scientists have used Sr²⁺ to weaken the crystal field strength around Eu²⁺ and replace the Ca²⁺ in CaAlSiN₃ crystals on the basis of the larger atomic radius of Sr²⁺ relative to that of Ca²⁺. SrAlSiN₃:Eu²⁺ has been synthesized through solid state reaction at 2173 K and 190 MPa in an inert atmosphere, and the crystal structure and luminescence properties have been reported.¹²,¹³ Although (oxy) nitride phosphors have interesting features that are relevant to white LEDs, research on these phosphors is limited because of the challenging synthetic requirements, most notably the necessity of impractically high temperatures. Hence there is scope for further research on new (oxy) nitride phosphors and their synthesis processes. In particular, decrease of synthesis temperature is

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strongly desired.

Li et al.\(^{16}\) have synthesized CaAlSiN\(_3\) for use as a multinary nitride phosphor through a low temperature liquid process in supercritical ammonia, known as an ammonothermal method. They first converted an alloy raw material (CaAlSi:Eu) into ammonometalates (metal amides, imidoamides, and their partially polymerized compounds) in ammonia–sodium amide (NaNH\(_2\)) solution and then decomposed the product into the corresponding nitride through the release of NH\(_3\) by increasing the temperature. This method requires a temperature of only 1073 K to synthesize CaAlSiN\(_3\), which is considerably lower than that which was previously reported in the high-temperature synthetic route (nitridation of metals at 1723–1823 K). We have successfully demonstrated the first example of using the ammonothermal method to synthesize SrAlSiN\(_3\) at a comparatively low temperature.\(^{15}\) In our previous study, we discussed synthesis temperature, heating rate, and Eu\(^{2+}\) concentration. In ammonothermal synthesis, mineralizers are used in order to increase the solubility of precursor in liquid ammonia by the formation of species complexed with the mineralizer. Typically, alkali metals like sodium and potassium and their amide compounds are used as mineralizers in ammonothermal synthesis.\(^{16}\) Although we used NaNH\(_2\) as a mineralizer in our previous syntheses, its use as a mineralizer has two limitations: One limitation is the solubility of sodium in the lattice of the compound. The other limitation is the lack of alkali earth ions in the lattice, which we attribute to the formation of sodium ammonometalates (sodium and alkali earth metals) as intermediates in presence of sodium amide.\(^{17}\) To solve these problems, we have synthesized SrAlSiN\(_3\) through an ammonothermal method with Sr as a mineralizer and investigated the impact of each of three mineralizers (NaNH\(_2\), Na, and Sr) on the physical properties of phosphor products.

2. Experimental

We performed all syntheses under nitrogen or argon atmospheres in a glove box (1ADB-3 type, Miwa, Japan). We prepared the starting alloy (0.008 Eu:0.992, SrAlSi) with arc discharge melting of the following powders: Eu (99.5%, Aldrich, USA), Sr (99%, Kojundo Chemical Lab., Japan), Al (99.99%, Kojundo Chemical Lab., Japan), and Si (99.999%, Kojundo Chemical Lab., Japan). The resulting alloy was milled ground in an argon atmosphere. We mixed the alloy powder and NaNH\(_2\) (95%, Aldrich, USA), metallic Na (99%, Aldrich, USA), or metallic Sr (99%, Kojundo Chemical Lab., Japan) as a mineralizer in molar ratios of 1:2 (alloy:mineralizer) and loaded them in a bottom-sealed Ni tube. The nickel tube was transferred to a vertically positioned high-pressure vessel, which was then fully filled with anhydrous liquid ammonia (99.999%, Taiyo Nippon Sanso, Japan) with a cooled condenser. An R-type thermocouple was fixed outside the surface of the pressure vessel at the bottom of the sample. The vessel was heated to 773 K at a rate of 20 K/min. After maintaining the vessel at 773 K for 20 h, it was further heated to 1073 K at a rate of 1 K/min, and the temperature was maintained for 5 h. A pressure of 100 MPa was maintained during the reaction. After cooling the reaction vessel to room temperature, the product was exposed to air, washed it with water and ethanol, and dried in air at 353 K.

We performed X-ray diffraction (XRD) analysis using a RINT-2200 (Rigaku, Japan) diffractometer; photoluminescence analysis with an FT-6500 luminescence spectrometer (JASCO, Japan), and scanning electron microscopy (SEM) analysis with a Hitachi S-5200 (Hitachi, Ltd., Japan) instrument. Chemical composition analysis was performed using inductively coupled plasma instrumentation and an O/N analyzer.

3. Results and discussions

3.1 Effect of the mineralizer on SrAlSiN\(_3\) phosphor purity

Figure 1 shows XRD patterns of the products that we synthesized through ammonothermal reaction at 1073 K. The results indicate that SrAlSiN\(_3\) was obtained from every sample that we synthesized using any of the mineralizers. The product synthesized with Na exhibits weak XRD lines of SrAlSiN\(_3\), which is indicative of an insufficient Sr content and impurities (Al\(_2\)O\(_3\) and an unknown phase). The patterns of the products that we synthesized with NaNH\(_2\) and Sr did not exhibit any crystallized contamination. However, we cannot exclude contamination with an amorphous compound. Such contamination would be a result of air-induced hydrolysis of ammonometalate compounds incompletely decomposed during the synthesis. The XRD line intensities of SrAlSiN\(_3\) synthesized with metal Sr are higher than those of SrAlSiN\(_3\) synthesized with sodium. This suggests that using Sr as a mineralizer facilitates SrAlSiN\(_3\) crystallization. We attribute this enhanced crystallinity to decrease of Sr defects in the SrAlSiN\(_3\) lattice, as discussed later. The lattice volume of SrAlSiN\(_3\) synthesized with Sr metal (291 Å\(^3\)) is greater than that of SrAlSiN\(_3\) synthesized with NaNH\(_2\) and metal Na (282 and 282 Å\(^3\), respectively) and is approximately equal to that of SrAlSiN\(_3\) samples synthesized by the conventional solid-state reaction (291 Å\(^3\)).\(^{18}\) The difference in the lattice volume corresponds to the number of Sr defects in the SrAlSiN\(_3\) lattice.\(^{14}\) Therefore, we conclude that the product synthesized with Sr has less defects than those estimated theoretically and a composition close to the theoretically estimated one.

Table 1 shows the chemical composition of the products. The quantities of Sr and Al in the product synthesized with Sr are greater than those in the product synthesized with NaNH\(_2\) and are approximately equal to the stoichiometric value. This corresponds to the previously noted difference in lattice volume. We attribute this chemical composition difference to different intermediates that arise because of changing the mineralizer, as discussed below.

In our previous study on the synthesis of CaAlSiN\(_3\):Eu\(^{2+}\)
through ammonothermal reaction\textsuperscript{17} we expected the sodium ammonocalciate intermediates to be more stable than other intermediates (sodium ammonoaluminate and sodium ammonosilicate). Once sodium ammonocalciate is formed, it is present until the end of the reaction. It is converted into Ca(OH)\textsubscript{2} during washing and then removed. In presence of Na in our system, absence of Ca in the CaAlSiN\textsubscript{3} lattice occurs because some of the Ca is present in the form of sodium ammonocalciate. Similarly, in synthesis of SrAlSiN\textsubscript{3}, Sr is absent in the SrAlSiN\textsubscript{3} lattice probably because of stable intermediates such as those of Na and Sr (sodium ammonostrontiate). When we used Sr as the mineralizer, the corresponding intermediate (sodium ammonostrontiate) was not formed because Na was not present in the system. Therefore, the quantity of Sr in the products increased (see Table 1). Furthermore, we formed AlN at higher NaNH\textsubscript{2}/CaAlSi:Eu\textsuperscript{2+} ratios, which we attribute to degradation of sodium ammonoaluminate. Our results indicate that sodium ammonoaluminate is stable, but not as much as sodium ammonostrontiate. Na causes less Al to be incorporated into the product through a mechanism that is analogous to the effect of Ca on Sr. Absence of these elements in the final product inhibits SrAlSiN\textsubscript{3} crystallization and instead facilitates formation of amorphous impurities. This line of reasoning corresponds to differences in XRD intensities (see Fig. 1). Eu\textsuperscript{2+} exhibits chemical characteristics that are analogous to Sr\textsuperscript{2+}; therefore, we can expect that the sodium ammonoeuropiate intermediate is approximately as stable as sodium ammonostrontiate. We expected but did not observe a difference between the quantities of Eu in products synthesized with NaNH\textsubscript{2} and those from Sr as a mineralizer. This indicates that sodium ammonoeuropiate has different chemical properties than those of sodium ammonostrontiate. However, our evaluation the difference in Eu is imprecise because the quantity of Eu in the product is small relative to those of other elements. Table 1 shows significant oxygen contamination in our products. These values include the quantity of oxygen in the SrAlSiN\textsubscript{3} lattice as well as that in amorphous compound impurities. Because the SrAlSiN\textsubscript{3} crystal structure is unstable in presence of excessive oxygen, we attribute most of the oxygen values to amorphous impurities (compounds). These amorphous compounds were formed by ammonothermal reaction and hydrolysis of the SrAlSiN\textsubscript{3}:Eu\textsuperscript{2+} surface by washing with water and/or storage in air. The quantity of oxygen in the product that we synthesized with Sr is larger than that in the product that we synthesized with NaNH\textsubscript{2}. This indicates that there is a greater extent of hydrolysis in the former product than in the latter. We attribute oxygen contamination to the minute quantity of oxygen in the mineralizers and water in the NH\textsubscript{3}.  

### Table 1. Atomic Compositions of two samples synthesized by ammonothermal reaction and a reference sample

| Sample     | Sr    | Al    | Si    | Eu    | N    | O    |
|------------|-------|-------|-------|-------|------|------|
| NaNH\textsubscript{2}\textsuperscript{a} | 0.668 | 0.887 | 1 | 0.012 | 1.582 | 2.374 |
| metal Sr\textsuperscript{b} | 0.811 | 0.966 | 1 | 0.011 | 1.199 | 5.233 |
| reference\textsuperscript{c} | 0.98  | 1.00  | 1 | 0.01  |      |      |

a) Synthesized by ammonothermal reaction with NaNH\textsubscript{2}. b) Synthesized by ammonothermal reaction with metal Sr. c) Synthesized via the high-temperature process\textsuperscript{13}.

3.2 Effect of mineralizer on SrAlSiN\textsubscript{3} phosphor luminescence and crystal quality

**Figure 2** shows the emission spectra (\(\lambda_{\text{ex}} = 460\) nm) of phosphor products. All of the products exhibit a broad emission spectrum, with a maximum emission at approximately 580 nm that arises from the transition of Eu\textsuperscript{2+} from the 5d\textsuperscript{0} excited state to the 4f\textsuperscript{0} ground state. This emission intensity trend corresponds with the XRD intensity trend. The emission intensity of the product synthesized from Sr is much stronger than those of our products synthesized by ammonothermal reaction when excited by 320–500 nm. **Figure 3** shows the excitation spectra of phosphor products. SrAlSiN\textsubscript{3}:Eu\textsuperscript{2+} synthesized through an ammonothermal reaction has an excitation range that is suitable for InGaN-based white LEDs. The product synthesized with Sr showed the strongest emission compared to those of our products synthesized by ammonothermal reaction when excited by 320–500 nm. **Figure 4** shows SEM images of phosphor products. The
particle sizes of products synthesized with NaNH₂ and Sr are 20 and 40 nm, respectively. From this size difference, we infer that the product synthesized with Sr is more strongly water resistant than the other. However, chemical composition analysis shows that the product synthesized with Sr leads to more significant oxygen contamination in the phosphor product. SEM observations clearly indicate preferential crystallization. We observed needle-like crystals in the product synthesized with Sr: see in Fig. 4(d). We believe that this difference in shape is due to the Sr concentration in the system. Sr atoms are abundant in (002) and (001) planes. When Sr is used as a mineralizer, the Sr concentration in the system is relatively high, which facilitates crystal growth along the c-axis.

4. Conclusions

We synthesized a SrAlSiN₃:Eu²⁺—a red-emitting phosphor—at a comparatively low temperature (1073 K) through an ammonothermal reaction. The specific mineralizer had obvious effects on crystallinity, lattice constants, and chemical composition of the SrAlSiN₃:Eu²⁺ phosphors. The phosphors that we synthesized with Sr have an emission maximum at approximately 590 nm when illuminated with 460 nm light. The crystal morphology varied in accordance with the specific mineralizer. We observed bar- and plate-like crystals when with Sr as the mineralizer and needle-like crystals with NaNH₂ as the mineralizer. Our improved low-temperature synthetic protocol will assist with research and development that is aimed at using SrAlSiN₃:Eu²⁺ phosphors in white LEDs.

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