Study on the particle size control of green-emitting phosphor (Ba,Sr)2SiO4:Eu2+ via reduction firing using various flux agents

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In this study, the particle size control of (Ba,Sr)2SiO4:Eu2+, a green-emitting phosphor, was evaluated via reduction firing using various flux agents. Phosphor particles grown to ~10–50 μm in diameter and having high internal quantum efficiency of 77.3% were obtained via reduction firing at 1473 K using 10 wt % BaCl2 as a flux. To reduce the particle size, the reduction firing temperature was lowered to 1223 and 1273 K respectively and the amount of BaCl2 was increased to 20 wt %. The diameter of phosphor particles significantly reduced; however, fibrous fine particles were formed and the internal quantum efficiency decreased to 60.7%. Using BaCl2–KCl and BaCl2–CsCl mixed fluxes to increase the amount of molten flux while suppressing the dissolution of (Ba,Sr)2SiO4 into the molten flux, a phosphor with fewer fibrous fine particles was obtained. In particular, the phosphor obtained via reduction firing at 1273 K using a 10 wt % BaCl2–10 wt % CsCl mixed flux had an improved internal quantum efficiency of 73.4%. The ionic radius of Cs+(0.167 nm for CN = 6) is considerably larger than that of Ba2+(0.135 nm for CN = 6) and Sr2+(0.118 nm for CN = 6); therefore, high-quality host crystals with few defects could be possibly obtained without the substitution of Cs+ for Ba2+ and Sr2+ during reduction firing. To control the particle size of phosphor while maintaining a high internal quantum efficiency, the solubility of the host crystal into the molten flux as well as the substitution of the cation between the flux and host must be considered.

Key-words : (Ba,Sr)2SiO4:Eu2+, Green-emitting phosphor, Flux, Reduction firing

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1. Introduction

White light emitting diodes (LEDs) are used as light sources for liquid crystal backlights and solid-state lighting. Conventional white LED comprises a combination of a blue LED and a yellow phosphor; however, a combination of a blue LED, a green phosphor, and a red phosphor is used for backlights to realize high color reproducibility. The green-emitting phosphor, (Ba,Sr)2SiO4:Eu2+ (BSSE) is known to be highly efficient. In general, a phosphor is synthesized by mixing raw materials of the host crystal and activator (e.g., Eu3+) and firing them under a reduced atmosphere. To obtain a highly efficient phosphor, Eu3+(Eu2O3) must be reduced to Eu2+ to dope into the host crystal and to grow a high-quality host crystal with few defects. Previously, we investigated the reduction firing of alkaline earth silicate phosphors (yellow phosphor (Sr,Ba)2SiO4:Eu2+, green phosphor (Ba,Sr)2SiO4:Eu2+, and orange-red phosphor CaSrSiO4:Eu2+) using various flux agents and reported that the phosphors having crystal-grown particles and higher internal quantum efficiency were obtained via reduction firing at around 1473 K using SrCl2 or BaCl2 flux. The phosphors obtained using these methods had a particle size distribution of ~10–50 μm in diameter and a center particle diameter size of ~30 μm. In general, the phosphor layer of the white LED is manufactured by developing the sealing resin in which the phosphor is dispersed, dispensing the resin into the LED package and curing. To suppress the settling separation of the phosphor and the clogging of the dispenser nozzle, a coarse particle-free phosphor is required. In practical use, the particle size of the phosphor must be accurately controlled depending on the application; however, few researches have systematically investigated and reported on the particle size control of the phosphor via reduction firing using a flux agent. Therefore, we studied particle size control of BSSE via reduction firing using various flux agents.

2. Experimental procedures

Figure 1 shows the synthesis procedure of the BSSE phosphor. Based on the preliminary tests, the target composition of the BSSE phosphor was set to Ba1.41Sr0.47-
Eu0.12SiO4 which emits a green light with a peak wavelength at 528 nm when excited at 455 nm. The synthesis procedure comprised four steps: 1) precursor synthesis; 2) calcination; 3) reduction firing; and 4) cracking, washing, and drying. First, in the precursor synthesis step, H2O (deionized water), BaCO3 (KANTO CHEMICAL CO., INC., >99.9%), SrCO3, (KANTO CHEMICAL CO., INC., >99.9%), Eu2O3 (Kojundo Chemical Laboratory Co., Ltd., 99.9%), and propylene glycol-modified silane (PGMS: see reference 8 for details) as a Si source were mixed and stirred to form a slurry. The slurry was stirred until a paste-like gel was formed via hydrolytic condensation and polymerization of PGMS; then, the gel was dried at 393 K for 43.2 ks and crushed to obtain a dried gel powder. Next, in the calcination step, the dried gel powder was calcined at 1273 K for 10.8 ks in air to decompose the organic substances derived from the PGMS and carbonates to obtain the (Ba,Sr)2SiO4 phase (hereinafter referred to as calcined powder). In the reduction firing step, the calcined powder and various flux agents (BaCl2, KCl, CsCl) were mixed in an agate mortar for 300 s and fired at 1223, 1273, and 1473 K respectively for 14.4 ks under an Ar-4%H2 gas flow in a tubular furnace sealed at both ends; therein, Eu3+ (added as Eu2O3) was reduced to Eu2+ and doped into the host crystal and phosphor particles were grown. Thus, a sintered body of phosphor particles and flux was obtained. Then, in the cracking, washing, and drying step, the sintered body was cracked and stirred in water to dissolve and remove the flux and dried to obtain phosphor powder. It was confirmed that the BSSE phosphor obtained via reduction firing using BaCl2 flux have the aimed composition, crystal structure and emission peak wavelength as described in our previous study.6) Particle observation of the phosphor powder was performed using a scanning electron microscope (SEM). In addition, the emission spectrum at 455-nm excitation was measured using a spectrofluorometer (FP-6500, JASCO Corporation) equipped with an integrating sphere. The absorption, external quantum efficiency (EQE), and internal quantum efficiency (IQE) were calculated.

3. Results and discussion
3.1 Reduction firing at 1473 K using BaCl2 flux
Figure 2 shows the SEM image of the BSSE phosphor obtained via reduction firing at 1473 K after adding 10 wt % BaCl2 to the calcined powder. Figure 3 shows the SEM image of the calcined powder before reduction firing was performed for comparison purposes. The calcined powder was agglomerated powder comprising ~1 μm primary particles, but the particles obtained via reduction firing at 1473 K were spherical crystal particles of ~10–50-μm diameter.

As an example of ceramics crystal growth using BaCl2 flux, the growth of a single crystal of BaTiO3 has been observed.
studied since a long time. Phase diagrams of the BaTiO3–BaCl2 system have also been studied, and the system is reported to be eutectic with a eutectic point at 2.5 mol% of BaTiO3 at 1211 K.9) A phase diagram of the (Ba,Sr)2SiO4–BaCl2 system has not been reported yet; however, in our previous study,6) we performed reduction firing of the mixture of claimed powder [(Ba,Sr)2SiO4] and BaCl2 at various reduction firing temperature and confirmed that BaCl2 melts at 1173 K, which is lower than its melting point (1235 K). Furthermore, we confirmed that (Ba,Sr)2SiO4 and BaCl2 are the only phases confirmed by XRD after the reduction firing, and that the composition of BSSE phosphor hardly changes after reduction firing. Thus, the (Ba,Sr)2SiO4–BaCl2 system is also considered to be eutectic type as schematically shown in Fig. 4 (Note that this phase diagram is schematically inferred based on various experimental phenomena and further investigation is necessary to determine an accurate eutectic point) and (Ba,Sr)2SiO4 slightly dissolves into molten BaCl2. Crystal growth presumably occurs due to the mass transfer through molten BaCl2 during reduction firing and due to the precipitation of dissolved (Ba,Sr)2SiO4 on the particle surface, which is driven by supercooling (Fig. 5).

Figure 6 shows the SEM image of the fracture surface of the sintered body (before BaCl2 removal) after reduction firing at 1473 K. The phosphor particles are covered with a BaCl2 flux layer. Thus, the crystallinity of the phosphor particle surface was improved by crystal growth through the molten BaCl2 and a high internal quantum efficiency, as shown in Table 1, can be obtained.

3.2 Particle size control by lowering the reduction firing temperature

BSSE phosphor obtained via reduction firing at 1473 K had high internal quantum efficiency, but coarse particles of ≥40 μm diameter were observed. As the simplest approach to reduce the particle size, lowering the reduction firing temperature was attempted. To reduce the particle size while maintaining a high internal quantum efficiency and to improve the crystallinity of the surface, the molten flux must be spread on phosphor particle surface during reduction firing. The central particle size of the phosphor obtained via reduction firing at 1473 K was ~30 μm in diameter. It is well known \( V = \frac{4}{3}\pi r^3 \), \( S = 4\pi r^2 \) (where \( V \) is volume, \( S \) is surface area, \( r \) is radius of a sphere), so we have \( S/V = 3/r \). If the diameter was reduced from 30 to 15 μm, the surface area per volume of the phosphor particles would double. Thus, if the amount of flux is doubled and the reduction firing temperature is accurately lowered, the surface of the phosphor particles can be covered with flux and the particle size can be reduced.

| Absorption (%) | EQE (%) | IQE (%) |
|---------------|---------|---------|
| 86.2          | 66.6    | 77.3    |

Table 1. Quantum efficiency of the BSSE phosphor obtained via reduction firing at 1473 K using 10 wt% BaCl2.
Based on this idea, reduction firing was performed, wherein the amount of BaCl₂ was doubled and the reduction firing temperature was lowered to 1223 and 1273 K, respectively. Figure 7 shows the SEM image of the obtained BSSE phosphor particles. Phosphor particles grown to about ~5–20 μm were obtained at both firing temperatures. The particle diameter was then reduced significantly compared with the phosphor obtained via reduction firing at 1473 K. However, fibrous fine particles, which were not found at 1473 K, were observed and their presence was remarkable at 1223 K. The fibrous fine particles exhibited a distinctly different particle shape from the calcined powder shown in Fig. 3 and the phosphor powder obtained via reduction firing at 1273 K without flux shown in Fig. 8. The reason for the formation of fibrous fine particles is not known; however, we assumed that the lowered firing temperature and doubled amount of BaCl₂ influenced crystal growth during the cooling process. The crystal growth mode changed from precipitation on the phosphor particle surface to the multinucleation generation-fibrous fine particle growth in the flux phase. These fibrous particles remained on the surface of the phosphor particles even after flux removal.

Table 2 shows the measurement results of quantum efficiency. The internal quantum efficiency decreased for both 1223 and 1273 K. The absorption of excitation/emission light by coexisting fibrous fine particles may possibly be one of the reasons for the reduced quantum efficiency.

### Table 2. Quantum efficiency of the BSSE phosphor obtained via reduction firing at 1223 and 1273 K using 20 wt % BaCl₂

| Reduction firing temperature | Absorption (%) | EQE (%) | IQE (%) |
|-----------------------------|----------------|---------|---------|
| 1223 K                      | 70.3           | 39.7    | 56.0    |
| 1273 K                      | 72.1           | 43.8    | 60.7    |

#### 3.3 Reduction firing using mixed flux

After lowering the reduction firing temperature and increasing the amount of BaCl₂, fibrous fine particles were formed and a high quantum efficiency could not be obtained. To reduce the amount of dissolved (Ba,Sr)₂SiO₄ in the molten flux while securing the amount of molten flux required to spread over the surface of the phosphor particles, a mixed flux of BaCl₂ and a flux into which (Ba,Sr)₂SiO₄ did not dissolve was selected and reduction firing was performed. As a preliminary test, KCl and CsCl were each mixed with calcined powder and subjected to reduction firing at 1273 K. It was confirmed that these fluxes did not have a crystal growth promoting effect, i.e., (Ba,Sr)₂SiO₄ did not dissolve into these fluxes. Hence, KCl and CsCl were chosen; each were mixed with BaCl₂ and calcined powder, and reduction firing at 1273 K was conducted.

Figure 9 shows the SEM image of BSSE phosphor particles obtained via reduction firing using a mixed flux of 10 wt % BaCl₂–10 wt % KCl and 10 wt % BaCl₂–10 wt % CsCl. In each case, the formation of fibrous fine particles was suppressed and particles grown to ~5–20 μm were obtained. Figure 10 shows the emission spectra of the BSSE phosphor obtained via reduction firing using a mixed flux compared with the reference (at 1473 K using 10 wt % BaCl₂). When the BaCl₂–KCl mixed flux was used, the emission peak wavelength was the same as the reference, but when the BaCl₂–CsCl mixed flux was used, the emission peak wavelength became slightly shorter. Table 3 shows the measurement results of quantum effi-
used, the concentration of the impurities and defects in the host was considered to be close to the reference and the external quantum efficiency was decreased as a result of controlling the phosphor particles to be small. However, when BaCl$_2$–KCl was used, the internal quantum efficiency decreased remarkably. Considering the ion radius of Cs$^+$ (0.167 nm for CN = 6); K$^+$ (0.138 nm for CN = 6); Ba$^{2+}$ (0.135 nm for CN = 6); and Sr$^{2+}$ (0.118 nm for CN = 6), it is likely that Cs$^+$ does not substitute for the Ba$^{2+}$ and Sr$^{2+}$ sites during reduction firing and high-quality host crystals with few defects can be obtained. However, since K$^+$ has an ionic radius almost equal to that of Ba$^{2+}$, it is likely that K$^+$ slightly substitutes for the Ba$^{2+}$ site, which may cause the decrease in internal quantum efficiency. The same relationship between the ion radius, the substitution of cation during flux reduction firing, and the influence on internal quantum efficiency had been confirmed in our previous study on CaSrSiO$_4$:Eu$^{2+}$ orange-red phosphor.

4. Summary

We studied the particle size control of (Ba,Sr)$_2$SiO$_4$:Eu$^{2+}$ green phosphor via reduction firing using a flux agent. An ideal sintered structure in which the phosphor crystal particles were covered with the flux layer was obtained. Therefore, phosphor particles grown to ~10–50 μm in diameter and having high internal quantum efficiency of 77.3% were obtained via reduction firing at 1473 K using 10 wt % BaCl$_2$ as a flux. To reduce the diameter, the reduction firing temperature was reduced to 1223 and 1273 K and the amount of BaCl$_2$ was increased to 20 wt %. The phosphor particles were significantly reduced in diameter, but fibrous fine particles were formed and the internal quantum efficiency decreased. Using BaCl$_2$–KCl and BaCl$_2$–CsCl mixed fluxes to increase the amount of molten flux while suppressing the dissolution of (Ba,Sr)$_2$SiO$_4$ into the molten flux, a phosphor with smaller particles and fewer fibrous fine particles was obtained. In particular, the phosphor obtained via reduction firing at 1273 K using the 10 wt % BaCl$_2$–10 wt % CsCl mixed flux had an internal quantum efficiency of 73.4% which is close to that obtained via reduction firing at 1473 K. To control the size of phosphor particles while maintaining a high internal quantum efficiency, it is important to consider the solubility of the host crystal into the molten flux and the substitution of the cation between flux and host.

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