Single Crystal Growth and Crystal Structure Analysis of Novel Orange-Red Emission Pure Nitride CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ Phosphor

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ABSTRACT: Single crystal of novel orange-red emission CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ phosphor was grown by our original vapor phase technique, and the precise crystal structure was investigated for the first time by single crystal X-ray diffraction analysis. The crystal structure of CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ single crystal was verified to be an $α$-Si$_3$N$_4$-type trigonal structure (space group P31c) with $a = 0.79525(9)$ nm, $c = 0.57712(8)$ nm, and $z = 2$. The Ca atoms were coordinated to seven nitrogen atoms and located in the three-dimensional framework formed by (Al, Si)N$_4$ tetrahedra. The single-crystal CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ phosphors exhibited a broad reddish-yellow emission with a peak at 600 nm under near-UV and blue light excitation. When increasing the temperature up to 150 °C, the emission intensity of the CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ phosphor decreased to 88% of the initial value at 25 °C.

INTRODUCTION

In a solid-state lighting system, phosphors are the key materials regulating the luminescence emission efficiency and color rendering index of white light-emitting diodes (LEDs). The development of novel phosphors having high luminescence emission intensity under near-UV or blue light excitation and having a low thermal quenching effect is considered the most promising approach to obtain the high luminescence efficiency of white LEDs. To develop a novel phosphor for white LEDs, investigation of the crystal structure of phosphors using a single crystal is significantly important because the luminescence properties of the phosphor strongly depend on the crystal structure of the host materials. In particular, the excitation and emission band positions of Eu$^{3+}$- or Ce$^{3+}$-activated phosphors are remarkably affected by the coordination environment of the cation site replaced with an activator.

Recently, (oxy)nitride phosphors have been extensively investigated for use in white LEDs due to their excellent luminescence emission efficiency and high thermal and chemical stabilities. Some (oxy)nitride phosphors, such as CaAlSiN$_3$:Eu$^{2+}$ (CASN), Sr$_2$Si$_5$N$_8$:Eu$^{2+}$, Ca$_3$(Al$_{12-m}$Si$_m$)$_6$O$_{16-m}$N$_8$:Eu$^{2+}$ (Ca-α-SiAlON), and Si$_3$Al$_2$O$_6$:Eu$^{2+}$ (β-SiAlON) are usually used in white LEDs as commercial red- or green-emission phosphors. Additionally, the oxide and fluoride phosphors, such as NaMgPO$_4$:Eu$^{2+}$, Ca$_3$SiO$_4$:Eu$^{2+}$, La$_4$GeO$_2$:Bi$^{3+}$, K$_2$SiF$_6$:Mn$^{3+}$, and K$_2$TiF$_6$:Mn$^{4+}$ are recently reported as new red emission phosphors for use in white LEDs. The crystal structure of these phosphors has been widely studied for a long time using powder crystal structure analysis. The luminescence mechanism has been also identified in detail based on the result of crystal structure analysis. According to a recent report, the concentration of oxygen contained in the crystal lattice has a significant effect on the luminescence properties of (oxy)nitride phosphors, such as emission intensity, emission peak position, and thermal degradation. However, powder crystal structure analysis has difficulty in accurately determining the crystallographic environment around the activator in the crystal lattice.

The crystal structure of inorganic materials is generally analyzed by powder or single crystal X-ray diffraction analysis. Among these two different analysis methods, single crystal X-ray diffraction analysis is well known to be suitable for accurately determining the crystal structure of inorganic materials. However, nitride materials have a high melting temperature and require elaborate atmosphere adjustment to grow the fine single crystal of nitride phosphor. Therefore, the conventional single crystal growth methods, such as Czochralski method, flux method, microwave plasma
The composition of CaAl2Si4N8:Eu2+ using a single crystal. The study. To the best of our knowledge, this is the investigated in detail using the single crystal obtained in this 586 nm.53,54 Yang et al. investigated the crystal structure of composition of phosphor shows the yellow emission peaked at 593 nm.51,52 In addition, highest solubility of Ca content was obtained for due to the inclusion of oxygen in the crystal lattice, and the composition of Ca1.99Eu0.01Al4Si8N16 reported in these papers is the theoretical composition, and it is not described as an CaSiAlON obtained from the composition equation of Ca0.99Eu0.01Al2.1Si4.3N8.7, which is normalized based on the experimental solid solubility limit for Ca content in the pure nitride-type Ca-Na2SiO4:Eu2+ phosphors, Ba2SiO4:Eu2+, and succeeded in determining the crystal structure of Ba2SiO4:Eu2+ phosphors in detail.50 In this study, we attempted to grow the nitride single crystal with a multiple mixture composition of Ca−Al−Si−Eu, in which the Eu content was fixed to be 2 mol% by our original solid–vapor hybrid synthetic technique. Among the multiple composition, we found a single crystal with a chemical composition of Ca0.99Eu0.01Al4Si8N16 (i.e., CaAl2Si4N8) in the mixture composition of Ca/Al/Si = 1.5:1:1. The theoretical chemical composition of CaAl2Si4N8 has already been reported by Jack in 1983 as pure nitride-type Ca−SiAlON−m with a multiple mixture composition of Ca−SiAlON−m−n−oAl−m−n−oN16−m−n−o.51 According to previous reports, it has an experimental solid solubility limit for Ca content in the pure nitride-type CaAl2Si4N8−m−n−oAl−m−n−oN16−m−n−o composition due to the inclusion of oxygen in the crystal lattice, and the highest solubility of Ca content was obtained for Ca1.99Eu0.01Al4Si8N16 (i.e., Ca0.99Eu0.01Al2.1Si4.3N8.7).51,52 In addition, Nagatomi et al. and Yang et al. recently reported the pure nitride-type Ca−SiAlON−Eu2+ phosphor with a composition of Ca1.99Eu0.01Al4Si8N16 (i.e., Ca0.99Eu0.01Al2.1Si4.3N8.7), and this composition of phosphor shows the yellow emission peaked at 586 nm.53,54 Yang et al. investigated the crystal structure of Ca1.99Eu0.01Al4Si8N16 by powder X-ray diffraction refinement, and the obtained lattice parameters are a = 0.78726 nm, c = 0.57226 nm, and V = 0.30716 nm3.54 The chemical composition of Ca1.99Eu0.01Al4Si8N16 reported in these papers is the theoretical composition, and it is not described as an analyzed composition of Ca1.99Eu0.01Al4Si8N16−m−n−oAl−m−n−oN16−m−n−o. In this paper, therefore, the precise crystal structure data and chemical composition of the CaAl2Si4N8:Eu2+ phosphor were investigated in detail using the single crystal obtained in this study. To the best of our knowledge, this is the first report to have verified the precise crystallographic data and chemical composition of CaAl2Si4N8:Eu2+ using a single crystal. The CaAl2Si4N8:Eu2+ powder phosphors are also synthesized by the high gas pressure sintering method based on the result of the single-crystal structure analysis as the comparison sample.

**RESULTS AND DISCUSSION**

Crystal Structure Analysis of the Single Crystal of CaAl2Si4N8:Eu2+ Phosphor. The polarized microscopy image under blue light (450 nm) excitation of the single crystal obtained from the mixture, in which the ratio of cations is Ca/Al/Si = 1.5:1:0.1:0.1, is shown in Figure 1. The obtained single crystal was formed as a hexagonal column sharp with dimensions of 0.11 mm × 0.11 mm × 0.10 mm, which makes it suitable for analysis by single-crystal X-ray diffraction. Under excitation at 365 nm, the single crystal presents a red emission. The chemical composition of the single crystal is determined by EPMA, and the result is given in Table 1. The determined chemical composition of the single crystal is Ca0.99Eu0.01Al2.1Si4.3N8.7, which is normalized based on the amount of Ca and Eu. According to the EPMA result, oxygen was not detected in the single crystal. In addition, homogeneous distribution of all elements was observed in the single crystal obtained in this study. Detailed crystallographic data and structure refinement parameters of the Ca0.99Eu0.01Al2.1Si4.3N8.7 single crystal determined by X-ray single-crystal diffraction analysis are summarized in Tables 2 and 3. The crystal structure model of CaAl2Si4N8:Eu2+, based on the crystallographic data obtained by X-ray single-crystal diffraction analysis, is illustrated in Figure 2. The crystallographic information file (CIF) of the CaAl2Si4N8:Eu2+ single crystal is given in the Supporting Information. The single crystal of CaAl2Si4N8:Eu2+ was refined in the trigonal structure with the space group of P31c (no. 159), and the lattice parameters are a = 0.79525(9) nm, c = 0.57712(8) nm, V = 0.31609(8) nm3, and Z = 2. The obtained lattice parameters of the CaAl2Si4N8:Eu2+ single crystal is larger than those of Ca1.99Eu0.01Al4Si8N16 reported by Yang et al. (a = 0.78726 nm, c = 0.57226 nm, and V = 0.30716 nm3).54 This is considered to be likely due to the inclusion of oxygen in the crystal lattice of the reported Ca1.99Eu0.01Al4Si8N16 phosphor. Since the ionic radius of O2− (0.138 nm for four coordination)55 is smaller than that of N3− (0.146 nm for four coordination),55 the

![Figure 1. Polarized microscopy images of the CaAl2Si4N8:Eu2+ single-crystal phosphor under (a) fluorescent light and (b) blue light (450 nm).](Image 384x577 to 504x749)

Table 1. Composition of the CaAl2Si4N8:Eu2+ Single-Crystal and Powder Phosphors Analyzed by the Electron Probe Microanalyzer (EPMA)

| Element | Single-crystal sample composition (wt %) | Atomic weight (wt %) | Composition ratio |
|---------|----------------------------------------|----------------------|------------------|
| Ca      | 11.529                                 | 0.288                | 0.986            |
| Eu      | 0.628                                  | 0.004                | 0.014            |
| Al      | 16.771                                 | 0.622                | 2.130            |
| Si      | 35.590                                 | 1.267                | 4.343            |
| N       | 35.483                                 | 2.533                | 8.682            |
| O       | 6.663                                  | 0.416                | 2.442            |

| Element | Powder sample composition (wt %) | Atomic weight (wt %) | Composition ratio |
|---------|---------------------------------|----------------------|------------------|
| Ca      | 6.604                           | 0.165                | 0.966            |
| Eu      | 0.875                           | 0.006                | 0.034            |
| Al      | 9.331                           | 0.346                | 2.028            |
| Si      | 26.586                          | 0.947                | 5.551            |
| N       | 49.940                          | 3.565                | 20.907           |
| O       | 6.663                           | 0.416                | 2.442            |
Table 2. Crystallographic Data of CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ Single-Crystal Phosphor

| crystallographic data |  |
|----------------------|---|
| formula              | CaAl$_2$Si$_4$N$_8$ |
| formula weight (g·mol$^{-1}$) | 319 |
| crystal system       | trigonal |
| space group          | P31c |
| hall symbol          | P3-2c |
| a (nm)               | 0.79525 (9) |
| c (nm)               | 0.57712 (8) |
| α (°)                | 90 |
| γ (°)                | 120 |
| V (nm$^3$)           | 0.31609 (8) |
| density (g·cm$^{-3}$) | 3.352 |
| Z                    | 2 |
| crystal size (mm$^3$) | 0.11 × 0.11 × 0.10 |
| diffractometer       | Rigaku XtaLAB mini diffractometer |
| radiation type       | Mo Kα radiation (λ = 0.71073 Å) |
| measurement temperature (K) | 295 |

Table 3. Bond Distances of Ca−N and Si−N in CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ Single-Crystal Phosphor

| bond | distance (nm) |
|------|---------------|
| Ca1−N2i × 1 | 0.2370 (4) |
| Ca1−N3 × 3 | 0.2576 (2) |
| Ca1−N4ii × 3 | 0.2657 (3) |
| Si2−N1 | 0.17536 (7) |
| Si2−N4ii | 0.1774 (3) |
| Si2−N4i | 0.1793 (3) |
| Si2−N3 | 0.1810 (2) |
| Si3−N2 | 0.1712 (12) |
| Si3−N4iv | 0.1794 (2) |
| Si3−N3i | 0.1796 (3) |
| Si3−N3 | 0.1803 (2) |

Symmetry codes: (i) y, x, z − 1/2; (ii) y, x + 1, z − 1/2; (iii) −x, −x + y, z − 1/2; (iv) x − y + 1, −y + 1, z − 1/2.

Figure 2. Crystal structure of CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$: (a) unit cell from the C-axis direction, (b) coordination of Si(Al)−N$_4$ polyhedra, and (c) coordination environment of Ca$^{2+}$.

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inclusion of O$^{2−}$ in the crystal lattice usually results in the reduction of the lattice parameters of nitride materials.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters are listed in Table 4. The occupancy rates of Ca, Al, and Si in the crystal lattice present 97.7(6), 0.21(8), and 1.79(8), respectively, in which the (Ca + Eu) content was normalized as 100%. The occupancy rates of each cation obtained by single-crystal structure analysis are similar to the result of EPMA (Table 1). Since the dopant amount of Eu$^{2+}$ is very small, Eu$^{2+}$ was not observed for the refinement of the crystal structure. As shown in Figure 2, Ca atoms occupy the site coordinated by seven nitrogen atoms, and Si/Al atoms occupy two different tetrahedral sites having different crystallographic environments, Si(2) and Si(3) sites, respectively. The Si2 site is fully occupied by Si atoms, and the Si3 site is replaced in part by Al atoms, in which the ratio of Si/Al was determined to be 0.79(8)/0.21(8). The Si/Al tetrahedra are linked by corner-sharing and form the three-dimensional network structure. Ca/Eu occupies the polyhedral site formed by the (Si/Al)N$_4$ tetrahedral network with strong covalent bonding. The bond distance of Ca−N consists of two broad optical absorption bands from 250 to 350 nm, with an average bond distance of 0.1783 nm 0.17712(12) nm for Si2 with an average bond distance of 0.1783 nm 0.17712(12)−0.1803(2) nm for Si3 with an average bond distance of 0.1791 nm, respectively.

Crystal Structure Analysis of the CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ Powder Phosphor. CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ phosphor was synthesized by the high nitrogen pressure sintering method based on the crystallographic data obtained by single-crystal structure analysis. Rietveld refinement analysis is carried out to determine the crystal structure of the CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ powder phosphor. The crystallographic data of the CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ single crystal are used as a starting model. Figure 3 shows the observed (red), calculated (blue), and difference (green) XRD profiles for the XRD Rietveld refinement of CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ powder. Most XRD peaks of the powder phosphor are well indexed to the XRD pattern obtained by single-crystal analysis, and a weak peak ascribed to an unknown impurity phase was observed in the powder XRD patterns. Table S1 summarizes the detailed crystallographic data and structure refinement parameters obtained by Rietveld refinement analysis. The refinement is finally converged to R$_{w}$ = 5.113%, R$_p$ = 3.205%, R$_{exp}$ = 2.208%, and S = 4.0690. The lattice parameters are a = 0.79555 nm, c = 0.57701 nm, and V = 0.31626 nm$^3$, which is larger than those of the single-crystal phosphor (Table S2). The chemical composition of the CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ powder phosphor is analyzed by EPMA, and the result is summarized in Table 1. The content of each element was detected to be different from the stoichiometric ratio, which is probably due to the existence of impurities or oxygen.

These results indicate that it is difficult to obtain the pure CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ phosphor by the conventional high nitrogen gas pressure sintering method. Although the composition and lattice volume of the CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ powder phosphor are different from the single-crystal phosphor, the crystallographic data of CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ powder phosphors are different from the conventional Ca$_{3}$-SiAlON (Ca$_{0.67}$Al$_2$Si$_{10}$O$_{4}$N$_{15.3}$ or Ca$_{1.99}$Eu$_{0.01}$Al$_{4}$Si$_{8}$N$_{16}$), which is probably due to the different contents of the Ca and O in the phosphor lattice.

Luminescence Properties. The excitation and emission spectra of the CaAl$_2$Si$_4$N$_8$:Eu$^{2+}$ single crystal and powder phosphors are presented in Figure 4. The excitation spectrum consists of two broad optical absorption bands from 250 to 500 nm, which can be covered by the region from UV to visible light part due to the 4f → 5d transition of Eu$^{2+}$. A strong optical absorption in the near-UV and blue light region
Table 4. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Displacement Parameters of CaAl2Si4N8:Eu2+ Single-Crystal Phosphor

| phosphor | x     | y     | z     | U(eq)/U(eq) (nm²) | occ. (-1) |
|----------|-------|-------|-------|-------------------|-----------|
| Ca1      | 0.3333| 0.6667| 0.41446 (18) | 0.0082 (3)     | 0.977 (6) |
| Si2      | 0.0786 (9) | 0.24910 (9) | 0.64435 (12) | 0.00535 (15) | 1.000     |
| Si3      | 0.51177 (9) | 0.42589 (9) | 0.43212 (14) | 0.0052 (3)     | 0.79 (8)  |
| Al3      | 0.51177 (9) | 0.42589 (9) | 0.43212 (14) | 0.0052 (3)     | 0.21 (8)  |
| N1       | 0     | 0     | 0.6433 (8)   | 0.0088 (7)     | 1.000     |
| N2       | 0.6667 | 0.3333| 0.5038 (8)   | 0.0087 (8)     | 1.000     |
| N3       | 0.3407 (3) | 0.3976 (3) | 0.6551 (5)   | 0.0079 (4)     | 1.000     |
| N4       | −0.0071 (4) | 0.3188 (3) | 0.8932 (5)   | 0.0082 (4)     | 1.000     |

Figure 3. Observed (red + symbol) and calculated (blue line) X-ray powder diffraction data of the CaAl2Si4N8:Eu2+ powder phosphor prepared the difference profile (green line) between them, and Bragg reflection peak positions are shown as vertical bars.

Figure 4. Normalized excitation (broken line) and emission (solid line) spectra of CaAl2Si4N8:Eu2+ powder (black line) and single-crystal phosphors (red line).

indicates that the phosphor is suitable for a color converter of white LED-based near-UV or blue LED. The emission spectra of the CaAl2Si4N8:Eu2+ single-crystal and powder phosphors exhibit a broad orange-red emission. The emission band position of powder phosphor (590 nm) was obtained at a shorter wavelength side than that of the single-crystal phosphor (600 nm), which can be explained by the oxygen content in the phosphor lattice (Table 4). For the emission band shift of the Eu2+-activated phosphors, it is usually explained by the centroid shift ($ε_c$) and the crystal field splitting ($ε_{df}$) of the 5d energy level of Eu2+. In the host lattice, the 5d energy level will split due to the crystal field strength, which depends on the distance between the luminescence ion and anions and the ionic radius of the cation and coordination number of cation ion polyhedral. The centroid shift represents the nephelauxetic effect, which depends on the bonding strength between the luminescence ion (Eu2+) and the anion ligands of the host lattice. With increasing bonding strength, the emission band of Eu2+-activated phosphor shifts to a longer wavelength side due to a low energy shift of the 5d energy level center. Since the formation energy of N3+ from atomic N (+2300 kJ mol⁻¹) is higher than that of O2⁻ from atomic O (+700 kJ mol⁻¹), the bonding strength of Eu2+-N3+ is stronger than that of Eu2+-O2-. Therefore, the oxygen atom included in the crystal lattice of nitride phosphors leads to a reduction of the bonding strength of Eu2+-anion ligands, which usually results in the 5d energy level center shifts to the higher energy side. Thus, the emission band of the powder phosphor shifted to a shorter wavelength side compared with the single-crystal phosphor. A small amount of oxygen was detected in the powder phosphor; consequently, the powder phosphor shows a shorter wavelength emission than the single-crystal phosphor. Although the CaAl2Si4N8:Eu2+ powder phosphor included a small amount of oxygen, the emission band position of the powder phosphor is located at a longer wavelength side compared to the commercial Ca-α-SiAlON phosphor (Ca0.625Eu0.025Si10.675Al1.325O0.025N15.975; λem = 580 nm). The internal quantum efficiency of the CaAl2Si4N8:Eu2+ powder phosphor was 78% under excitation at 450 nm, which is similar to that of a commercial red-emission phosphor Sr2Si5N8:Eu2+ (~80%). The CIE chromaticity coordinate values for the CaAl2Si4N8:Eu2+ powder phosphor were x = 0.54 and y = 0.46 under excitation at 365 nm. The CIE values of the CaAl2Si4N8:Eu2+ indicate that this phosphor has higher color purity of red emission than that of the conventional Ca-α-SiAlON (x = 0.491, y = 0.497) and pure nitride-type Ca-α-SiAlON (x = 0.521, y = 0.473). The emission intensity of a phosphor generally decreases with increasing temperature due to the thermal quenching effect. Therefore, the temperature dependence of the phosphor is significantly important in white LED applications. Figure 5 presents the temperature dependence of the emission intensity of the CaAl2Si4N8:Eu2+ powder phosphor under excitation at 450 nm, normalized with respect to the value at 25 °C. The CaAl2Si4N8:Eu2+ powder exhibits a thermal quenching behavior similar to that of CaAlSiN3:Eu2+ and Sr2Si5N8:Eu2+, which are commercial red-emission phosphors for white LEDs. The emission intensities of the CaAlSiN3:Eu2+ and Sr2Si5N8:Eu2+ phosphors measured at 150 °C are 86–90% of that at 25 °C. When increasing the temperature up to 150 °C, the emission intensity of CaAl2Si4N8:Eu2+ powder phosphor decreases to 88% of the initial value at 25 °C. These results indicate that the CaAl2Si4N8:Eu2+ powder is expected to find application as a red emission phosphor for use in white LEDs.
A high-purity single crystal of the CaAl₂Si₄N₈:Eu²⁺ phosphor was successfully grown by the solid–vapor hybrid technique using a high nitrogen pressurized sintering furnace. From the X-ray single crystal diffraction analysis, the CaAl₂Si₄N₈:Eu²⁺ single crystal phosphor has a trigonal structure with the space group of P31c. In the crystal structure of CaAl₂Si₄N₈:Eu²⁺, (Si, Al)−N₄ and Si−N₄ tetrahedral corner-connected to form a three-dimensional network structure, and Ca²⁺ and Eu²⁺ are taken into a three-dimensional framework. The CaAl₂Si₄N₈:Eu²⁺ single crystal and powder phosphor exhibited a broad orange-red emission with a peak at 600 and 590 nm, respectively, and the internal quantum efficiency of the powder phosphor under blue excitation (λₑᵣ = 450 nm) was 78%. The major advantage of this study is that it has verified for the first time the chemical composition and the detailed crystallographic data of the pure nitride-type Ca-α-SiAlON:Eu²⁺ phosphor, CaAl₂Si₄N₈:Eu²⁺. This paper could also provide new avenues for growing the high-purity single crystal of nitride phosphor.

EXPERIMENTAL SECTION

Solid-Vapor Hybrid Synthetic Technique. We developed a new type single-crystal growth technique to easily and reliably grow the phosphor single crystal. This method is a kind of chemical vapor deposition that does not require the high purity of target materials or a high vacuum system. It used the vaporization of one or two raw materials to make a gas phase, and the reaction between the vaporized raw material gas and substrate material, which is a mixture of other raw materials, occurred on the surface of substrate materials. Furthermore, it can control the atmosphere such as air, neutral (e.g., N₂ or Ar), or reduction (e.g., H₂−N₂ or H₂−Ar mixed gases). Therefore, this method is expected to be suitable to obtain the Eu²⁺-activated phosphor single crystal besides trivalent rare earth (e.g., Eu³⁺, Er³⁺, Yb³⁺, etc.)-doped phosphors. Additionally, this method can control the size of the single crystal by controlling the content of the vaporized raw material gas, which can be controlled by the temperature or atmosphere. The single-crystal size generally increases with increasing content of the vaporized raw material gas.

Single-Crystal Growth of CaAl₂Si₄N₈:Eu²⁺. Ca₃N₂ (Taiheiyo Cement, Corp.), AlN (Tokuyama, Corp.), Si₃N₄ (Shin-Etsu Chemical Co., Ltd.), and EuCl₃ (Alfa Aesar, A Johnson Matthey Company) were mixed using a mortar in Ar-filled glove boxes in a mixture ratio of Ca/Al/Si = 1.5:1.0:1.0. The Eu²⁺ content was at 2 mol %. The homogeneous mixture was heated in a nitrogen atmosphere of 0.9 MPa at 1800 °C for 2 h using a vacuum and a pressurized sintering furnace “VESTA” (Shimadzu Mectem, Inc.). In this process, we used Ca₃N₂ as the raw material for making the gas phase. In our previous study, we verified the vaporization of Ca₃N₂ as a function of the heating temperature and the nitrogen gas pressure, as shown in Figure S1. The content of the vaporized Ca₃N₂ gas is increased with increasing heating temperature and is decreased with increasing nitrogen gas pressure. From the result of the optimization of the condition of temperature (1400−1600 °C) and gas pressure (0.1−0.9 MPa), the best of the conditions is 1800 °C and 0.9 MPa, respectively, to grow the single crystal of the CaAl₂Si₄N₈:Eu²⁺ phosphor. Additionally, the CaAl₂Si₄N₈:Eu²⁺ powder phosphor was also synthesized by a conventional high nitrogen gas pressure sintering method based on the result of crystal structure analysis of the single crystal of the CaAl₂Si₄N₈:Eu²⁺ phosphor.

Characterization. The surface of the single crystals was observed using an optical microscope (Olympus, Corp. BX-60). Quantitative analysis of Ca, Eu, Al, Si, N, and O was carried out using an electron probe microanalyzer (EPMA) (Shimadzu, Corp. EPMA8705). The precise crystallographic data of CaAl₂Si₄N₈:Eu²⁺ was verified by single-crystal X-ray diffraction using a Rigaku XtaLAB mini diffractometer. A single crystal is placed on a glass capillary, and data collection and cell refinement were outputted by the Crystal Clear-SM Auto 2.0 rl (Rigaku, 2010). Detailed analysis conditions for the determination of the crystal structure of the CaAl₂Si₄N₈:Eu²⁺ single crystal are listed in Table S1. After the measurement, structural analysis was performed using the structural analysis software WinGX. The structure refinement was carried out using direct methods with SHELXS97 program. The crystal structure of CaAl₂Si₄N₈:Eu²⁺ was drawn by VESTA based on the crystallographic data obtained by single-crystal structure analysis. The powder sample was characterized by X-ray powder diffraction (XRD; Bruker Corp. D2 PHASE) analysis, and the crystal structure analysis was carried out via Rietveld refinement of powder XRD data using the program “RIETAN-FP”. The emission and excitation spectra were measured at room temperature by using a spectrofluorimeter (Jasco, Corp. FP-6500/6600). The emission spectrum was obtained upon excitation at 410 nm, and the excitation spectrum was obtained by monitoring the emission at 590 nm. The Commission International de l’Eclairage (CIE) chromaticity coordinate data for the phosphors were measured at room temperature with a luminescence colorimeter (Hamamatsu C7473-36 PMA-11).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00606.

The chemical composition of the CaAl₂Si₄N₈:Eu²⁺ single crystal and powder phosphor analyzed by EPMA and the crystallographic data of CaAl₂Si₄N₈:Eu²⁺ powder phosphor from the Rietveld refinement using X-ray powder diffraction data (PDF)

X-ray structure report for Ca₃N₂.N₄.4th (ZIP)

X-ray crystallographic information file obtained by single-crystal structure analysis (CCDC 1917874) (CIF)
The authors would like to thank Taiheiyo Cement Corporation for their cooperation in providing the high-purity complex nitride materials. The authors would also like to thank Shimadzu Mectem Inc. for their cooperation in providing the high-purity rare-earth based silicon nitride based phosphors.

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