

Host lattice materials in the system Ca_3N_2 -AlN-Si₃N₄ for white light emitting diode

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New host lattice materials whose red phosphors for white LEDs have been investigated in the ternary system $Ca_3N_2-AlN-Si_3N_4$, just as $Ca_2Si_5N_8$ and $CaSiN_2$:Eu were found in the binary system $Ca_3N_2-Si_3N_4$. A new red phosphor of $CaAlSiN_3$:Eu which is effectively excited by blue-GaN and near UV-GaInN LED chips has been synthesized at 1600 °C for 2 h and subsequently at 1800 °C for 2 h under nitrogen pressure of 1 MPa. The host-compound has an orthorhombic structure with the space group $Cmc2_1$ (No. 36), which is isotypic with $LiSi_2N_3$ and $NaSi_2N_3$. The red phosphor showed the emission peak around 650 nm which was assinged to $5d \rightarrow 4f$ of Eu^{2+} ion, and its color coordinates were estimated to be 0.667 and 0.327. The optimum concentration of Eu^{2+} ion was 1.6 mol%. The phosphor also had a high chemical stability, high quantum output, and especially a good thermal property compared to the other phosphors, $Ca_2Si_5N_8$: Eu^{2+} and $CaSiN_2$: Eu^{2+} . $CaAlSiN_3$: Eu^{2+} maintained 83% of the initial efficiency above 150 °C.

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1 Introduction

Commercially available white light emitting diodes (LEDs) which are composed of blue-GaN LED chips and an yellow-emitting phosphor, yttrium aluminum garnet doped with Ce³⁺ (YAG:Ce), have spread all over the world [1]. However the white LEDs have a poor color rendering by a deficiency of a deep red color. It can be improved by adding slightly the red phosphor to YAG:Ce. Such a combination is referred to as "warm-white LED" [2]. This wider color reproducibility range will make it possible to use warm-white LEDs not only general illumination but also in other applications, for examples backlight color liquid-crystal display (LCD) panels in mobile devices such as cell phones, medical microscopes and tools such as LED lighting goggle for surgical operation [3].

Based on early investigations, one may expect binary sulfide red phosphors, for example, CaS: Eu and SrS: Eu could be useful for the warm-white LEDs [4]. However, these sulfides have a drawback because they are unstable against humidity. Meanwhile, nitride and oxynitride have been reported as new host materials, recently.

A ternary alkali-earth silicon nitride red-emitting phosphor, $M_2Si_5N_8$: Eu^{2+} (M = Ca, Sr, Ba) has been studied in these six years or so [5]. The red phosphor has high thermal and chemical stabilities and also

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show extended excitation spectra in the wide wavelength range from UV to visible region. Therefore, OSRAM and Nichia have developed warm-white LEDs by using this-type red phosphor [6].

We have also investigated nitride phosphors to develop more efficient and stable material. Recently, we have succeeded in preparing a new-type nitride red phosphor, $CaAlSiN_3:Eu^{2+}$ in the system $Ca_3N_2-AlN-Si_3N_4$. In this paper, we are going to describe how to prepare the red phosphor, and then present its crystal structure and luminescent properties.

2 Experimental section

Chemicals were high-purity Ca_3N_2 (Cerac, 99%), α -Si₃N₄ (Ube, Tokyo, SN-E10), and AlN (Tokuyama, Tokyo, F-Grade), and used as purchased. EuN was synthesized by firing of metallic Eu in a continuous flow of NH₃ gas at 600 °C for 12 h. The four starting materials were mixed in a mortar under nitrogen atmosphere in a glove box. The mixed powder or its pellet was charged in a BN crucible and then fired at 1600 °C for 2 h and subsequently at 1800 °C for 2 h under nitrogen pressure of 1 MPa. The first firing stage was to progress the solid state reaction by a transient liquid phase and the next stage to obtaine well-crystallized products. The fired products were crushed, sieved and served for measurements. The products are stable in air and emit fluorescence even under a fluorescent lamp. The powder morphology was investigated with scanning electron microscopy, Hitach S5000.

Powder X-ray diffraction was measured with MX-Labo (MAC Science, Cu K_a = 1.540 Å) using a step scan mode with a step size of 0.02° in the range of $2\theta = 5 \sim 100^{\circ}$. Calculation of the unit cell volumes was carried out by a non-linear, least-square cell-refinement program, UNITCELL [7].

Photoluminescence spectra at room temperature were measured by an optical multi-channel analyzer, Hamamatsu Photonics PMA model C5966-31, the spectral sensitivity of which was calibrated when shipped. The wavelength resolution is 3 nm. CIE color coordinates were calculated from the luminescence spectra. Excitation source was 150 W Xe lamp coupled with a Spex 270 M monochromator. Excitation spectra were measured with the same light source and the monochromator and calibrated by light output of a rohdamin B ethyleneglycol solution. Diffuse reflectance spectra were measured by a spectro-fluorometer, JASCO FP-6500.

3 Results and discussion

The morphology of particles of a CaAlSiN₃: Eu phosphor is shown in a SEM photograph (Fig. 1). The particle size was a few micro-meters in diameter and the small particles were sintered to be larger lumps (~10 μ m) at the high temperatures ranging from 1600 to 1800 °C. When the sintered particles were strongly grinded to obtain the fine-powder, its luminescent intensity became weaker. Our synthetic technique has to be improved to produce the fine phosphorous powder without the grinding process, for example, firing at low temperature with a flux.

The host-compound has an orthorhombic structure with the space group Cmc2_1 (No. 36), which is isotypic with LiSi_2N_3 and NaSi_2N_3 [8], and it is similar to that reported by Ottinger [9]. The unit cell parameters of CaAlSiN₃ were as follows: a = 0.98020(4) nm, b = 0.56506(2) nm, and c = 0.50633(2) nm. The atomic coordinates and thermal parameters are given in Table 1. The convergent beam electron





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atom	site coordinates				$B(\text{\AA}^2)$
		x	у	Ζ	-
Ca Al/Si N(1) N(2)	4am. 8b1 8b1 4am.	0 0.1741(2) 0.21258(4) 0	0.3146(3) 0.1570(3) 0.1300(10) 0.2446(7)	0.4952(9) 0.0291(11) 0.3776(11) 0	0.678(12) 0.678 0.678 0.678

 Table 1
 Atomic coordinates and isotropic displacement parameters of CaAlSiN₃.

diffraction (CBED) measurement was carried out to confirm the point group. In accordance with the space group, Al and Si atoms in the crystal distribute randomly at 8b site.

The unit cell volume was expanded linearly with Eu concentration at least up to 20 mol%. Ca^{2+} ion in the crystal was completely replaced by Eu^{2+} ion over the region from 0 to 20 mol%.

The crystal structure of CaAlSiN₃: Eu is illustrated in Fig. 2. Six tetrahedra, MN_4 ($M = Al^{3+}$ or Si⁴⁺) form a ring by linking at their corners and Ca²⁺ ion is located in the centre of the ring. The rings consisted of the six tetrahedra form a sheet-A (see Fig. 2(a)) by linking together parallel to the *a*, *b*-plane. Another sheet B, which is equivalent to the sheet-A rotated by 21 operation, is overlaid on the sheet-A as shown in Fig. 2(b) to form a rigid three dimensional framework. In a comparison of atomic arrangements in CaAlSiN3 and AlN, the crystal structure of CaAlSiN₃ would be referred to as a super-lattice of the basic AlN or GaN (wurtzite-type). The relations between the orthorhombic lattice parameters of CaAlSiN₃ and those of the basic wurtzite-type hexagonal structure (a_w, c_w) are

$$a_{\text{CaAISiN}_3} \sim 3a_{\text{w}}$$
, $b_{\text{CaAISiN}_3} \sim a_{\text{w}}$, $c_{\text{CaAISiN}_3} \sim c_{\text{w}}$. (1)

The diffuse reflectance spectra of CaAlSiN₃ and CaAlSiN₃:0.8 mol% Eu²⁺ are shown in Fig. 3. The absorption edge was estimated to be about 320 nm in the diffuse reflectance spectrum (dotted line) of the undoped CaAlSiN₃. An apparent increase in the reflectance over the fundamental absorption, which was observed in the reflectance spectrum (solid line) of Eu²⁺ doped CaAlSiN₃, was due to a red emission of Eu²⁺ detected together with the reflected light. A broad absorption band ranging from near UV to visible region was observed by subtracting the solid spectrum from the dotted one. The broad peak can be assigned to the 4f \rightarrow 5d transition of Eu²⁺.

The excitation and emission spectra of CaAlSiN₃:0.8 mol% Eu^{2+} are presented in Fig. 4(a). In the excitation spectrum, a small absorption peak was observed below 300 nm. In comparison to the reflection spectrum of CaAlSiN₃ which was shown in Fig. 3, it clearly showed the peak was due to the absorption of the host-lattice. A broad absorption band was extended over the region from ultraviolet (UV) to 600 nm with two peaks. The broad band can be assigned to the transitions from 4f to 5d orbits of Eu^{2+} . In the crystal structure of CaAlSiN₃, the Ca atom is coordinated by five nitrogen atoms with Ca–N dis-



Fig. 2 Crystal structure of CaAlSiN₃ projected on the *a*, *b*- and *b*, *c*-plane.

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Fig. 3 Diffuse reflectance spectra of $CaAlSiN_3$ and $CaAlSiN_3:0.8 \text{ mol}\% \text{Eu}^{2+}$.

tances, 0.2490(5), $0.2405(3) \times 2$, 0.2539(5) and 0.2586(5) nm. As shown in Fig. 4(b), the symmetry of nitrogen ion arrangement around the Eu²⁺ ion which is located at the Ca²⁺ site can be regarded as tetrahedral or Td symmetry when the four nearest neighbor nitrogen ions are only taken into account. Accordingly, 5d levels of Eu²⁺ will be divided to two crystal field components as shown in Fig. 4(c). Two broad peaks observed in the broad excitation band can be ascribed to the transitions from 4f to each crystal field component.

On the other hand, the red emission peak was observed around 650 nm. The red emission was assigned to the 5d \rightarrow 4f transition of Eu²⁺ ion. The color coordinates were estimated to be 0.667 and 0.327. As shown in Fig. 4, one can say the new red phosphor, CaAlSiN₃: Eu has optical properties really suitable to the excitation at 450 nm and 405 nm which is emitted from blue and near UV LED chips.

Figure 5 shows change in luminescent color of CaAlSiN₃:Eu phosphors with various Eu²⁺ contents. With increase in Eu²⁺ concentration, the red emission peak was uniformly shifted to long wave-length. As shown in Fig. 5, the changing in luminescent color was practically observed in the photograph of CaAlSiN₃:*x* mol Eu²⁺ ($x = 0.05 \sim 6.40$) under irradiation with UV lamp. This shift is similar to the case of CaS doped with Eu²⁺ ion, CaS:Eu. It has been discussed in our previous report [10]. The red emission intensity of CaAlSiN₃:Eu²⁺ was decreased above 1.6 mol% of Eu²⁺ concentration. Concentration quenching was observed above 1.6 mol%. The optimum concentration of the activator, Eu²⁺ was 1.6 mol% for CaAlSiN₃:Eu²⁺ red phosphor.



Fig. 4 Excitation and emission spectra of $CaAlSiN_3:0.8 \text{ mol}\% Eu^{2+}(a)$, the coordination geometry around the Ca^{2+} ion in $CaAlSiN_3$ (b) and the simplified energy-level scheme of the Eu^{2+} ion at the Ca^{2+} site (c).

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Fig. 5 (online colour at: www.pss-a.com) Emission of spectra of $CaAlSiN_3:x$ mol% Eu^{2+} phosphors ($x = 0.05 \sim 20.0$) and the picture of them with $LaO_3S:Eu^{3+}$ phosphor taken under UV irradiation.

Table 2 compares the quantum output for three phosphors under excitation at 460 nm. By comparing the integrated quantum output of the other phosphors with that of YAG: Ce phosphor [11], we estimated the quantum output for $Ca_2Si_5N_8:0.8 \text{ mol}\% \text{ Eu}^{2+}$ to be 102% and for $CaAlSiN_3:0.8 \text{ mol}\% \text{ Eu}^{2+}$ to be 155%.

Finally, a comparison of the thermal quenching in three phosphors, $CaAlSiN_3:0.8 \text{ mol}\% Eu^{2+}$, $Ca_2Si_5N_8:0.8 \text{ mol}\% Eu^{2+}$ and $CaSiN_2:0.3 \text{ mol}\% Eu^{2+}$ is presented in Fig. 6. In the temperature dependence of $Ca_2Si_5N_8:Eu^{2+}$, its efficiency was strongly decreased with temperature, and then reached 66% of the initial efficiency above 150 °C. $CaSiN_2:Eu^{2+}$ also showed the largest quenching, 26% of the initial efficiency. In contrast, $CaAlSiN_3:Eu^{2+}$ kept 83% of the initial efficiency above 150 °C. It was a small decrease in the red emission intensity up to 150 °C. Using $CaAlSiN_3:Eu^{2+}$ as a red phosphor for white LEDs, the out of color registration would not occur by regarding the red phosphor around 80 °C which is supplied from a blue-GaN chip.

Two thirds of N atoms are coordinated with three Si atoms $(N-Si_3)$ and the rest of N atoms with two Si atoms $(N-Si_2)$ in the crystal structure of CaAlSiN₃: Eu²⁺. In CaSiN₂: Eu²⁺, however, all the N atoms are coordinated with two Si atoms. Accordingly CaAlSiN₃: Eu (CaAlSiN₂^[3]N^[2]) has more rigid structure of the MN₄ (M = Al or Si) cross-linking structure as compared to the structures of Ca₂Si₅N₈ (Ca₂Si₅N₄^[3]N₄^[2]) and CaSiN₂: Eu²⁺ (CaSiN₂^[2]). The difference in thermal quenching among three phosphors would be considered to depend on the degree of condensed three dimensional MN₄ networks.

4 Summary

In this work, we have succeeded to synthesize the new nitride red phosphor, $CaAlSiN_3:Eu^{2+}$ for warmwhite LEDs, in the system $Ca_3N_2-AlN-Si_3N_4$. The red phosphor has a broad excitation band in the range from UV to visible region, and will be also efficiently excited by blue-GaN and near UV-InGaN LEDs. The red emission showed color coordinates of 0.667 and 0.327, and the optimum concentration of

Table 2Relative quantum output under excitation at 460 nm.

	relative quantum output/%
$\begin{array}{c} (Y,Gd)_{3}Al_{5}O_{12}{:}Ce^{3+}\\ Ca_{2}Si_{5}N_{8}{:}0.8\ mol\%\ Eu^{2+}\\ CaAlSiN_{3}{:}0.8\ mol\%\ Eu^{2+} \end{array}$	100* 102 155

*According to M. Yoshino et al. [11], the external quantum efficiency of $(Y, Ga)_3Al_5O_{12}$: Ce^{3+} is 49%.

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Fig. 6 (online colour at: www.pss-a.com) Thermal quenching of the red emission of CaAlSiN₃:0.8 mol% Eu^{2+} , Ca₂Si₅N₈:0.8 mol% Eu^{2+} and CaSiN₂:0.3 mol% Eu^{2+} in air. (Proportion of efficiency was the proportion of an efficiency which was measured above room temperature to the efficiency at room temperature).

the activator, Eu^{2+} was 1.6 mol%. In the near future, the red phosphor is expected to be suitably used with high power LEDs for application of general lighting, car headlamps and so on, because it has a high chemical stability, high quantum output, and small thermal quenching.

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