Synthesis of Eu$_2$O$_3$-doped CaAlSiN$_3$ for Red Light-Emitting Phosphor by Two-step Carbothermal Process

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Abstract: CaAlSiN$_3$: Eu$^{2+}$ red phosphors with different concentration of Eu$^{2+}$ addition were prepared by two-step carbothermal process. Eu$_2$O$_3$ dopant with nitrogen gas instead of EuN directly was utilized. The phase purity, morphology and particle distribution, and luminescence properties were investigated. Synthesized powders have a pure CaAlSiN$_3$ phase and consist of fine size particles. It showed a broad excitation band originating from UV region to 600 nm with centering at 450 nm, and indicated a strong emission peak at 645 nm. This phosphor showed chemical stability and low thermal quenching due to the rigid crystal structure of the host.

Keywords: Red-emitting phosphor, White LEDs, Nitride phosphor, Two-step solid state reaction.

1. INTRODUCTION

Recently, Eu$^{2+}$- doped nitride phosphors, such as CaAlSiN$_3$:Eu$^{2+}$ [1,2] and M$_2$Si$_5$N$_8$:Eu$^{2+}$ (M= Ca, Sr, Ba) [3,4] have drawn much interest for optical wavelength conversion because of their outstanding thermal and chemical stability and attractive photoluminescence properties. CaAlSiN$_3$:Eu$^{2+}$ in particular, which is more efficient than M$_2$Si$_5$N$_8$:Eu$^{2+}$ [5,6], has many advantages, including good resistance to many chemicals, good thermal stability, crystallographic framework for wide band gap, etc... Consequently, many investigations have aimed to develop a reproducible stable synthesis fabrication. Li et al. [7] reported the synthesis of CaAlSiN$_3$:Eu$^{2+}$ phosphor from ammonetamulates. However, it was hard to obtain homogenous phase of fine size phosphor powder. Jung et al. [8] also reported a synthetic method to obtain CaAlSiN$_3$:Eu$^{2+}$ phosphor using Ca$_3$N$_2$, AlN, Si$_3$N$_4$, and EuN as raw materials. But this method was prepared by high gas-pressure sintering furnace. Most of previous researches used EuN, which is so expensive and need extra synthesis equipment as starting material for doping in the host lattice instead of EuN. The crystal structure, morphology and particle size distribution of the synthesized CaAlSiN$_3$:Eu$^{2+}$ phosphors were investigated. Furthermore, luminescence properties compare and temperature dependence on emission intensity of the prepared phosphors were evaluated and discussed.

2. EXPERIMENTAL

Ca$_{1-x}$Eu$_x$AlSiN$_3$ phosphor samples with various concentration of Eu$^{2+}$ addition ($x = 0$~10 mol. %) were prepared by two-step carbothermal procedure starting from the raw materials of Ca$_3$N$_2$, AlN, Si$_3$N$_4$, Eu$_2$O$_3$ (high purity chemical, 99.9%), and activated charcoal powder (C, 99.9%). They were stoichiometrically weighed and mixed thoroughly in a glove box filled with nitrogen. Mixtures were charged in graphite crucible placed into an induction furnace and then fired at 1500°C for 4 h under N$_2$ gas flow rate of 1500ml/min. Finally, the samples were finely ground and transferred into a BN crucible, and then fired at 1500°C for 4 h under N$_2$ gas flow rate of 1500ml/min. After sintering, the synthesized phosphors were cooled to room temperature in a furnace. Before characterizing the resultant samples, prepared phosphors were washed in a nitric acid solution (10 wt. %) and stirred for 1h to remove residual impurities, which remained in the samples of two-step carbothermal process, then filtered and dried at 60°C in the oven for two hours.

In this present work, red phosphors, CaAlSiN$_3$:Eu$^{2+}$, were prepared by two-step carbothermal process under the normal pressure of nitrogen gas. Eu$_2$O$_3$ was used as starting material for doping in the host lattice instead of EuN. The crystal structure, morphology and particle size distribution of the synthesized CaAlSiN$_3$:Eu$^{2+}$ phosphors were investigated. Furthermore, luminescence properties compare and temperature dependence on emission intensity of the prepared phosphors were evaluated and discussed.
morphology was examined via scanning electron microscopy (SEM, JSM 5410, JEOL). The particle size distribution was measured with a laser particle size analyzer using a CILAS 1064. The photoluminescence spectra were measured by Hitachi F-4500 fluorescent spectrophotometer at room temperature. The temperature dependence of photoluminescence was measured with a multichannel spectrophotometer (model MCPD-7000; Otsuka Electronics) equipped with temperature-controlled sample holders and a Xe lamp.

3. RESULTS AND DISCUSSION

The crystal structure of CaAlSiN$_3$ host contains a highly condensed network structure build-up on SiN$_4$ and AlN$_4$ tetrahedra and showed an orthorhombic structure with the space group $Cmc2_1$ as reported by Ottinger [9]. Figure 1 gives the XRD patterns of the washed sample with various concentration of Eu$^{2+}$ (x=1; 2; 3 mol. %) compared by first heated sample and second heated sample. In this figure, all of the XRD patterns were indexed to reference [11,12]. As the Eu$^{2+}$ concentration increased and heating process again, and washing process in acid, there was no shift in the diffraction peaks toward any angle. This suggests that the incorporation of Eu$^{2+}$ and heating again, and washing in acid did not cause any change in the lattice parameter of the host lattice. Furthermore, from Figure 1a, the resultant consisted of CaAlSiN$_3$:Eu$^{2+}$ phosphor and the impurity phase in first heated sample and then heating again, no appearance of the impurity phase (Figure 1b). After the washing in a nitric acid solution (10 wt. %), CaAlSiN$_3$:Eu$^{2+}$ phosphors without C were obtained in a high-quality form (Figure 1c).

Figure 2 shows the SEM morphology of phosphors obtained by first heated sample (a) and second heated sample (b). In the both figure, particles of powder samples show well-crystallize and contain good dispersion with uniform morphology, the particle size of images with average size of about 1-2 µm in diameter (Figure 2a) and about 1.5-2.5 µm in diameter (Figure 2b) were observed separately. This can also be seen from the measurements of particle size distribution as how in Figure 3. The powder particles of second heated sample showed narrow size distribution with average particle size of about 1.74 µm, indicating that the powder have fine average size, however, experience some slightly agglomerations in the both images.

Figure 1: XRD patterns of Ca$_{1-x}$Eu$_x$AlSiN$_3$: a) first heated sample, b) second heated sample, and c), d), e) washed samples with concentration of Eu$^{2+}$: 1; 2; 3 mol. %, respectively.

Figure 2: SEM morphology comparison first heated sample (a) with second heated sample (b).

Figure 4 shows the excitation and emission spectra of the washed sample, together with first heated sample and second heated sample as comparison. It is clear that the emission spectrum exhibits a broad band.
ranging from 550 to 800 nm peaking at 645 nm, which is attributed to the transition from the lowest component of the 5d excited states to the ground state of Eu\(^{2+}\) ion. The broad excitation spectrum covers the wavelength ranging from UV region to 600 nm and consists of at least two broad bands. The first band is caused by the electronic transition between the valence and the conduction band of the CaAlSiN3 host. The excitation energy can be transferred nonradiatively from the host to the activator to emit red light. The latter band peaking at 455 nm is responsible for direct excitation of the Eu\(^{2+}\) ion (4f\(^7\) - 4f\(^6\)5d\(^1\)). In this work, the emission intensity of washed sample showed about 5% intensity increase of second heated sample and 14% intensity increase of first heated sample, respectively, at the same excitation of 455 nm. These results indicated that the impurities were removed after heating again and washing in acid nitric (10 wt. %) solution.

Dependence of emission intensity and peak emission wavelength on Eu\(^{2+}\) concentration of the Ca\(_{1-x}\)Eu\(_x\)AlSiN3 phosphor is shown in Figure 5. Enhanced emission intensity was observed by 2 mol. % Eu\(^{2+}\) adding. With an increase of Eu\(^{2+}\) concentration exceeds 2 mol. %, emission intensity of Ca\(_{1-x}\)Eu\(_x\)AlSiN3 phosphor showed rather a little bit decline. Emission intensity decline beyond critical concentration level is ascribed to the concentration quenching effect, which is mainly caused by the energy transfer between two Eu\(^{2+}\) ions. Namely, in the condition of excitation and emission band overlap at 550-620 nm, if Eu\(^{2+}\) ions are allowed for 4f\(^6\)5d\(^1\) → 4f\(^7\) transition, energy transfer may occur as a result of multipolar interaction and radiation reabsorption. On the other hand, with increasing Eu\(^{2+}\) concentration from 0 to 10 mol.%, peak emission intensity of Ca\(_{1-x}\)Eu\(_x\)AlSiN3 phosphor showed long wavelength side (red shift) shift from 625 to 690 nm.

The emission spectra of the CaAlSiN\(_3\) : Eu\(^{2+}\) phosphors with various amounts of C powder were shown in Figure 6. The emission spectra were peaking at about 645 nm and the relative emission intensity of CaAlSiN\(_3\) : Eu\(^{2+}\) phosphor was maximized on the sample prepared with 100 mol.% C powder. This result may be caused by a decrease in impurities due to the reaction of carbon with oxygen to product carbon monoxide, which increase emission intensity. However, with an increase.
of C powder continues, the emission intensity would be decreased. We guess that prepared phosphor has been contaminated by residue of carbon. Furthermore, the emission wavelength of synthesized phosphors was red shifted with an increase amount of carbon powder.

![Figure 6: Effect of content of carbon powder on the emission intensity of CaAlSiN3: Eu2+ phosphors.](image)

For white LED application, a low temperature quenching effect of phosphors is an important requirement to keep the stability of chromaticity and brightness of the white light output of white LEDs at high temperature. Temperature dependence on emission intensity of Sr2Si3N6: Eu2+ phosphor has been previously reported by us [13]. Comparing synthesized CaAlSiN3:Eu2+ phosphor with former result and commercial YAG: Ce3+ phosphor are illustrated in Figure 7. As the temperature increases from room temperature to 200°C, the intensity of CaAlSiN3:Eu2+ phosphor and Sr2Si3N6:Eu2+ phosphor is decreased by 12% and 18% of that measured at room temperature. At 150°C, the emission intensity of CaAlSiN3: Eu2+ phosphor, Sr2Si3N6: Eu2+ phosphor and YAG: Ce3+ remains at about 94%, 92% and 64%, respectively. CaAlSiN3: Eu2+ phosphors showed less thermal quenching value than Sr2Si3N6: Eu2+ phosphors. This result might be ascribed to the rigid network of host and [AlN4] tetrahedra in its crystal structure.

4. CONCLUSIONS

Red nitride phosphor, CaAlSiN3:Eu2+ has been successfully synthesized by using Eu2O3 as raw material with two-step carbothermal process. Synthesized CaAlSiN3: Eu2+ phosphors have single-phase crystal structure of CaAlSiN3 and consist of fine size particle with average particle size of about 1.74 µm. It showed a broad excitation band originating from UV region to 600 nm and centering at 455 nm, and a strong emission band peaking at 645 nm. The relative emission intensity of CaAlSiN3: Eu2+ phosphor was maximized on the sample prepared with 100 mol.% C powder. This phosphor was chemically stable as well and thermal quenching is lower than Sr2Si3N6: Eu2+ phosphor and commercial YAG: Ce3+ phosphor.

REFERENCES


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