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Synthesis and Photoluminescence Properties of $CaAlSiN_3$:Eu^{2+} Nanocrystals

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Nanosized $CaAlSiN_3$:Eu^{2+} red phosphor was synthesized by solid-state reaction using CaH_2 as calcium source. The obtained phosphor was well crystallized and the particle size was about 200–400 nm. It showed a broad excitation band originating from the $4f^7 \rightarrow 4f^65d$ transition of Eu^{2+} ion extending to 600 nm and centering at 450 nm, and a strong emission band peaking at 660 nm. This phosphor showed low thermal quenching due to the rigid crystal structure of the host.

Generally, the "white" output light of LEDs, produced by combination of a blue LED chip with a yellow phosphor such as YAG:Ce^{3+}, is limited with high correlated color temperature (CCT) ranging from 4500 to 11000 K. To obtain high-quality warm white light output, stable complementary red-light-emitting phosphors have been intensively sought to compensate the red color deficiency or to produce white light in the three primary colors (RGB) mode. For both routes, the red phosphors that can be efficiently excited by the GaN or InGaN LED chip are in great demand.[1,2]

Among the reported Eu^{2+}-doped nitrides for LED applications,[3] $CaAlSiN_3$ (abbreviated as CASN hereafter) was found to be an excellent material for using as a red phosphor because of the adequate thermal and environmental stability, nontoxicity, high emission efficiency, and high quenching temperature.[1–6] Generally, critical preparation conditions including high temperature up to 1800 °C and 10 MPa high pressure are necessary to obtain high-quality CASN:Eu^{2+} phosphors due to the chemical and thermal inertness of the starting materials. Additionally, the method was limited to some extent because the air-sensitive and expensive Ca_3N_2 must be used as raw material. As an alternative, a self-propagating high-temperature synthesis of CASN:Eu^{2+} by CaAlSi alloy was reported.[1] However, the evaporation of Ca and Al metals during arc-melting leading to difficulty in exact control of the performance of the product. Recently, Li et al. reported the synthesis of $CaAlSiN_3$:Eu^{2+} by alloy-derived ammonometallates.[1,4] This method is useful for obtaining nanosize product. However, it is hard to obtain the homogenous phase of product by this method. Furthermore, 100 MPa pressure and at least 800 °C are necessary to obtain product. Such kinds of supercritical conditions lead to low yield and are not suitable for industrial applications.

In the present work, nanosized $CaAlSiN_3$:Eu^{2+} powders were synthesized by using CaH_2 as the raw material for the Ca component. Due to the low melting point and high activity of CaH_2, nanosized $CaAlSiN_3$:Eu^{2+} was obtained at 1300 °C under atmospheric pressure. The photoluminescence properties and thermal quenching behavior of obtained $CaAlSiN_3$:Eu^{2+} phosphors were also investigated.

Stoichiometric amounts of CaH_2 (95%), AlN (95%), α-Si_3N_4 (99.5%), Eu_2O_3 (>99.99%) were mixed thoroughly and put into a BN crucible positioned in a radiofrequency furnace using a ZrB_2 heater. The heating chamber of the furnace was pumped down to high vacuum and back filled with high purity N_2 (>99.9999%). Thereafter, the powder mixture was heated at 1300 °C for 3 h to obtain the product. Before characterizing the resultant samples, they were washed in a 10 vol % nitric acid solution for 1 h, then filtered, and dried. The total reaction was as follows: $Eu_2O_3 + CaH_2 + AlN + Si_3N_4 \rightarrow Ca_{1-x}Eu_xAlSiN_3 + H_2O\uparrow$.

The structure was checked by X-ray powder diffraction (RINT2200, Rigaku) with Cu Kα radiation. The room temperature photoluminescence spectra of the powder phosphor were measured by fluorescence spectrophotometry (Model F-4500, Hitachi). Rhodamine B, a light diffuser, and a standard light source were used as references to correct the spectral distribution. The temperature-dependent luminescence spectra were measured by USB Ocean 2000 between RT and 200 °C. The morphology of the products was observed by a field emission scanning electron microscope (FE-SEM; ERA-8800, ELIONIX, Tokyo, Japan) equipped with an energy-dispersive X-ray (EDX) system. The sample was coated with thin films of sputtered gold to reduce electrical charge-up.

Figure 1a shows the XRD patterns of the product heated at 1300 °C for 3 h. The sample crystallized in single-phase crystal structure of the CASN. All the diffraction peaks are consistent with these previous reports.[1,6,7] Due to the size effect, the broadening of the Bragg peak width of the nanosized CASN can be observed in Figure 1a. The averaged grain size of the powder can be calculated using the Debye–Scherrer equation: $D = K\lambda/\beta\cos\theta$. By using the fitted information of different diffraction peaks (by MDI JADE), the calculated averaged grain size of the sample is about 72 nm. Figure 1b presents the SEM morphology of the synthesized phosphor. It is clear from Figure 1b that the powder obtained in the present work is fine

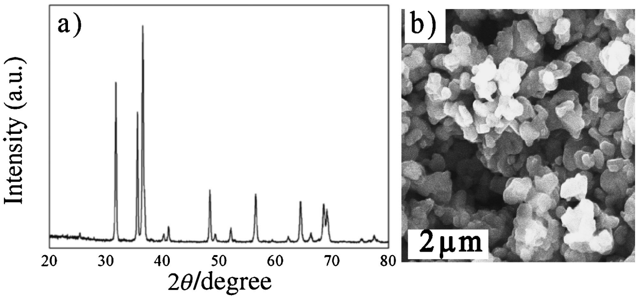

Figure 1. XRD pattern (a) and SEM image (b) of CASN:2%Eu^{2+} phosphor.

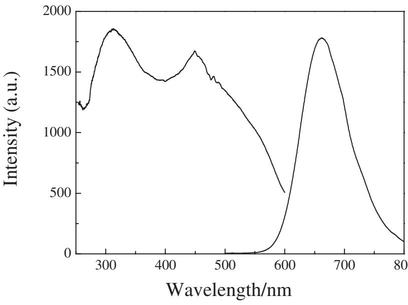

Figure 2. Excitation (left, $\lambda_{em} = 660$ nm) and emission (right, $\lambda_{ex} = 450$ nm) spectra of CASN:2%Eu^{2+} phosphor.

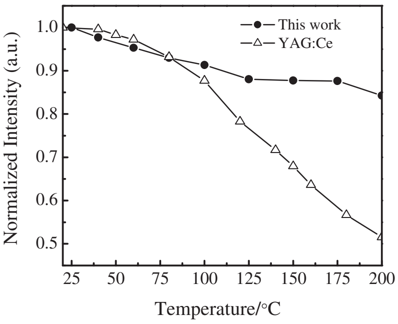

Figure 3. Temperature dependences of the emission intensity of CASN:2%Eu^{2+} and YAG:Ce^{3+} phosphor.

and uniform. The mean edge diameter of the particles is about 200–400 nm, which is larger than the calculated grain size value. This difference is reasonable because it is hard to extract precise FWHM values from the XRD patterns and the inevitable aggregation effect of the particles during the firing process.

Figure 2 shows the excitation and emission spectra of the 2% Eu^{2+}-doped CASN phosphor. It is clear that the emission spectrum exhibits an intense broad band ranging from 550 to 800 nm peaking at 660 nm, which is attributed to the transition from the lowest component of the 5d excited states to the ground state ($^8S_{7/2}$) of Eu^{2+} ion. Monitored at 660 nm, at least two intense broad excitation bands ranging from 200 to 600 nm were observed in the excitation spectrum. The first one is caused by the transition between the valence and conduction bands of CASN host. The latter one centered at ca. 450 nm is attributed to the direct excitation of Eu^{2+} ion via the $4f^7 \rightarrow 4f^65d^1$ parity-allowed transition. This intense broad excitation band located at the near-UV and visible light spectral range provides the basis for developing this kind of phosphors for lighting-emitting diode (LED) conversion applications.[1,5,6] Upon irradiation at different wavelengths within the excitation spectrum, the emission spectra exhibit similar emission of Eu^{2+} in peak shape and position, indicating the occurrence of energy transfer between the matrix and the Eu^{2+} activators.

In the white LED application, a low-temperature quenching effect of phosphors is an important requirement to keep the stability of the chromaticity and brightness of white light output of the white LEDs at high temperature.[1,8] The dependence of PL intensity on temperature was measured, as illustrated in Figure 3. For comparison, the temperature-dependent emission intensity of YAG:Ce^{3+} (P46-Y3) phosphor is also given. As the temperature increased from room temperature to 200 °C, the emission band peaking at 660 nm showed about 10 nm blue shift, and the intensity was decreased slowly. With heating the samples up to 150 °C at which the white LEDs usually work, the emission intensity of CASN:2%Eu remains at about 87.7% of that measured at room temperature, while at about 63.6% for the YAG:Ce^{3+} (P46-Y3) phosphor, as shown in Figure 3. Generally, there are abundant surface defects in the nanosized phosphor due to its low crystallinity and high specific surface area. In this case, the thermal quenching of nanosized phosphor is significantly worse than that of the bulk sample. However, as shown in Figure 3, the thermal stability of nanosized CASN:2%Eu^{2+} prepared in the present work is equivalent to that prepared by CaAlSi alloy.[1] Based on the high quenching temperature and small stokes shift of the Eu^{2+} ion luminescence in the rigid CASN host, the low thermal quenching effect is closely related the thermally activated ionization from the $4f^65d$ to the conduction band.[1,9]

In conclusion, excellent nanosized CASN:Eu^{2+} red phosphor is prepared by solid-state reaction under lower temperature (1300 °C) without using traditional Ca_3N_2 raw material. The particle size of the obtained phosphor is in a range of 200–400 nm. As expected, the obtained phosphor is efficiently excited by the blue light (400–470 nm) of InGaN-based LEDs and gives an intense emission band peaking at 660 nm. Furthermore, the thermal stability (87.7% at 150 °C) is better than that of YAG:Ce^{3+} (P46-Y3) and is equivalent to that prepared from CaAlSi alloy although there are abundant surface defects in the nanosize phosphor.

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References

1 X. Piao, K. Machida, T. Horikawa, H. Hanzawa, Y. Shimomura, N. Kijima, *Chem. Mater.* **2007**, *19*, 4592.

2 J. Li, T. Watanabe, H. Wada, T. Setoyama, M. Yoshimura, *Chem. Mater.* **2007**, *19*, 3592.

3 R. Xie, N. Hirosaki, *Sci. Technol. Adv. Mater.* **2007**, *8*, 588.

4 J. Li, T. Watanabe, N. Sakamoto, H. Wada, T. Setoyama, M. Yoshimura, *Chem. Mater.* **2008**, *20*, 2095.

5 H. Watanabe, H. Wada, K. Seki, M. Itou, N. Kijima, *J. Electrochem. Soc.* **2008**, *155*, F31.

6 K. Uheda, N. Hirosaki, Y. Yamamoto, A. Naito, T. Nakajima, H. Yamamoto, *Electrochem. Solid-State Lett.* **2006**, *9*, H22.

7 K. Uheda, N. Hirosaki, H. Yamamoto, *Phys. Status Solidi A* **2006**, *203*, 2712.

8 Y.-S. Tang, S.-F. Hu, C. C. Lin, N. C. Bagkar, R.-S. Liu, *Appl. Phys. Lett.* **2007**, *90*, 151108.

9 V. Bachmann, T. Jüstel, A. Meijerink, C. Ronda, P. J. Schmidt, *J. Lumin.* **2006**, *121*, 441.