Photoluminescence Properties of $Ca_2Si_5N_8:Eu^{2+}$ Nitride Phosphor Prepared by Carbothermal Reduction and Nitridation Method

Xianqing Piao,[1] Takashi Horikawa,[1] Hiromasa Hanzawa,[2] and Ken-ichi Machida*[1]
[1]Center for Advanced Science and Innovation, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871
[2]Graduate school of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531

(Received November 25, 2005; CL-051465; E-mail: machida@casi.osaka-u.ac.jp)

Eu^{2+} ion-doped nitride phosphor, $Ca_2Si_5N_8:Eu^{2+}$, was synthesized by the carbothermal reduction and nitridation (CRN) method and the photoluminescence properties were characterized. It showed a broad absorption band between 250 and 550 nm which was efficiently excited by blue LEDs (400–470 nm) and a strong emission band peaking at 600 nm with a FWHM of 80 nm. The obtained phosphor provided saturated color chromaticity (0.589, 0.407) to generate warm-white light in phosphor-converted white LEDs.

Recently, since the tremendous progress has been achieved in the development of blue-emitting semiconductors (e.g. GaN and InGaN), much attention has been paid to the white LEDs because of its low energy consumption and environmental friendliness. As a result, white LEDs are expected to replace traditional incandescent lamps.[1] The white LEDs have been realized by the combination of blue LED and yellow phosphor such as $YAG:Ce^{3+}$. However, color rendering indexes of the resultant white light are usually poor because of the deficiency of the red color component. To improve the color rendering index, the efficient red or orange-red phosphors that can be well coupled with the blue ($\lambda \approx 460$ nm) or near UV ($\lambda \approx 400$ nm) LEDs are urgently required. Currently, the nitride or oxynitride phosphors such as α- and β-type $SiAlON:Eu^{2+}$,[2,3] $LaSi_3N_5:Eu^{2+}$,[4] and $Ba_2Si_5N_8:Eu^{2+}$,[5] have shown much promising potential owing to their high thermal and chemical stability, and excellent photoluminescence properties. In the past several years, however, only a small number of nitridosilicate phosphors have been synthesized because of the technical difficulties resulting from inertness of Si_3N_4, oxygen and moisture sensitivities of the alkaline earth metal and nitride used as starting materials.

In the present work, we synthesized the ternary nitride $Ca_2Si_5N_8:Eu^{2+}$ phosphor by a convenient route, that is, carbothermal reduction and nitridation (CRN) method. As the raw materials, $CaCO_3$, Si_3N_4, Eu_2O_3, and fine graphite powder of reagent grade were mixed thoroughly in ambient atmosphere, then the mixed powder was put into a graphite crucible positioned in a high-radio frequency (RF) furnace for two-step calcination in N_2 flow. At first the above mixture was slowly heated to 1173 K and kept for 2 h to decompose $CaCO_3$ completely. Then, temperature was increased to 1823 K and maintained at the same temperature for 6 h. The reduction, nitridation, and solid-state reaction at high temperature led to the formation of coarse $Ca_2Si_5N_8:Eu^{2+}$ powder. The synthesized powder was identified by X-ray powder diffraction (RINT2000, Rigaku) with Cu Kα radiation operating at 40 kV and 30 mA. The morphology of samples was examined by SEM and EDX integration system (S-3000 HXS, Hitachi). Diffuse reflection spectrum was obtained by a UV–vis spectrophotometer (UV-2200, Shimadzu) by using $BaSO_4$ powder as the white reference. The photoluminescence spectra of samples were measured using a fluorescent spectrophotometer (F-4500, Hitachi) at room temperature. The oxygen content was measured by O/N analyzer (EMGA-550, Horiba).

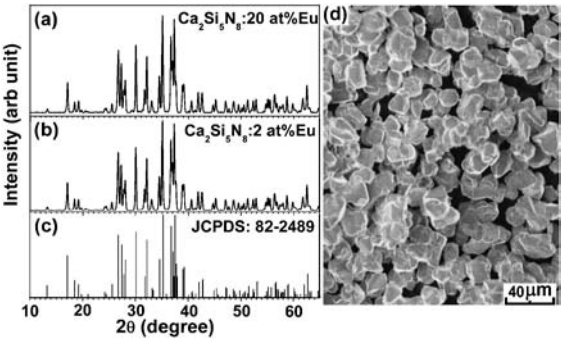

Figure 1. XRD patterns for (a) $Ca_2Si_5N_8:Eu^{2+}$ (20 atom %), (b) $Ca_2Si_5N_8:Eu^{2+}$ (2 atom %), (c) JCPDS Card No. 82-2489, and (d) SEM image of $Ca_2Si_5N_8:Eu^{2+}$ (2 atom %).

The XRD patterns of samples doped with 2 and 20 atom % of Eu^{2+} ions are shown as Figures 1a and 1b, respectively. All the peaks are indexed as $Ca_2Si_5N_8$ (JCPDS 82-2489, Figure 1c). The Eu^{2+} ions are uniformly introduced into the $Ca_2Si_5N_8$ crystal lattice until $Eu_2Si_5N_8$ appears as an impurity phase at about 40 atom % dopant concentration. The Eu^{2+} ions, which take the position of Ca^{2+} ions, are located in channels formed by Si_6N_6 rings along [010] orientation in the vertex-linked SiN_4 tetrahedron-based networks.[6] The host lattice, in which large alkaline earth cations form linear chains, contributes to a long-wavelength Eu^{2+} emission with a large Stokes shift.[7] Figure 1d shows the SEM image of the $Ca_2Si_5N_8:Eu^{2+}$ (2 atom %) phosphor. The powder consists of well-crystallized and well-dispersed grain with a mean size of 20 μm. Additionally, the oxygen content, which may reduce the emission intensity by taking the place of N^{3-} to form the O_N^{+} trap level or by forming other impurity phases, is effectively suppressed less than 0.72 wt %. This oxygen content value is even lower than that of samples prepared from Ca_3N_2, Si_3N_4, and EuN by conventional solid-state reaction.

Figure 2 shows the reflection and photoluminescence spectra of $Ca_2Si_5N_8:Eu^{2+}$ (2 atom %). For the excitation and reflection spectra, two absorption bands are observed in the regions of 250–325 and 325–550 nm. The first one is caused by the transition between the valence and conduction bands of $Ca_2Si_5N_8$ host. The absorption of high-energy photons by the host can be transferred to the Eu^{2+} ions nonradiatively and followed by the emission of $Ca_2Si_5N_8:Eu^{2+}$. The other one is attributed to the direct excitation of Eu^{2+} ions ($Eu^{2+}:4f^7 \rightarrow 4f^65d$). The strong absorption in the range of 400–470 nm indicates that

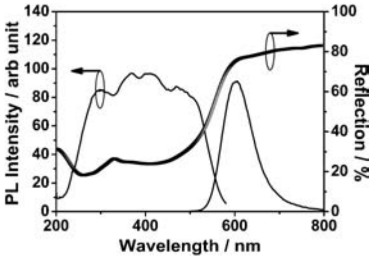

Figure 2. Photoluminescence and reflection spectra of $Ca_2Si_5N_8:Eu^{2+}$ (2 atom %). The excitation spectrum is monitored at 600 nm and the emission spectrum is excited at 450 nm.

the $Ca_2Si_5N_8:Eu^{2+}$ phosphor is efficiently excited by the InGaN-based LEDs. The extension of reflection spectrum to the long wavelength side yields all of the samples with orange-red color.

The emission spectrum (excited at 450 nm) exhibits an intense band (FWHM ≈80 nm) peaking at 600 nm which is assigned to the allowed $4f^65d \rightarrow 4f^7$ transition of Eu^{2+} ion. The emission intensity is competitive (≈92%) with that of the commercially available $YAG:Ce^{3+}$ (P46-Y3) under the same excitation of 450 nm. Compared with other Eu^{2+} ion-doped phosphors, the emission band of $Ca_2Si_5N_8:Eu^{2+}$ locates at fairly longer wavelength range. Furthermore, in the Eu^{2+} ion-doped oxynitride or nitride hosts the emission occurs at longer wavelengths with increasing the nitrogen content,[4,5] which is attributed to the higher electronegativity of N^{3-} and the nephelauxetic effect which effectively lower the center of gravity of 5d orbitals of Eu^{2+} ions.[8]

Dependence of the emission intensity and peak position of samples on Eu^{2+} ion concentration is shown in Figure 3. The emission intensity is maximized at 2 atom % dopant of Eu^{2+} ions. At the same time, the peak position of emission band shows a red shift (≈450 cm^{-1}) behavior with increasing Eu^{2+} ion concentration up to 20 atom %. Dexter[9] has pointed out the mechanism of energy transfer in phosphors. A nonradiative energy transfer among Eu^{2+} ions usually occurs as a result of exchange interaction, radiation reabsorption, or multipolar interaction. The exchange interaction is mainly responsible for forbidden transitions and the typical critical distance is about 5 Å,[9] whereas Eu^{2+}:4f → 5d transition is allowed in the $Ca_2Si_5N_8$ host, so that the exchange interaction hardly plays any roles in $Ca_2Si_5N_8:Eu^{2+}$. Thus, the nonradiative energy transfer among Eu^{2+} ions takes place mainly as a result of radiation reabsorption and multipolar interactions. With increasing Eu^{2+} ion concentration, the reabsorption begins to reduce the high-energy wing of Eu^{2+} emission band, while the red-shifted emission band gains intensity. Furthermore, the overlap of excitation and emission spectra between 530–580 nm indicates the energy migration which also contributes to the concentration quenching. Consequently, the emission intensity is lowered and the peak position is red-shifted with increasing Eu^{2+} ion concentration.

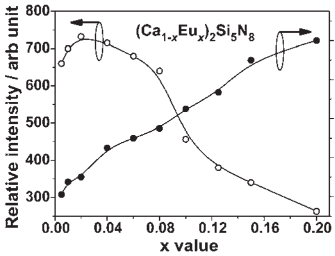

Figure 3. The dependence of emission intensity and peak position of $Ca_2Si_5N_8:Eu^{2+}$ on Eu^{2+} ion concentration.

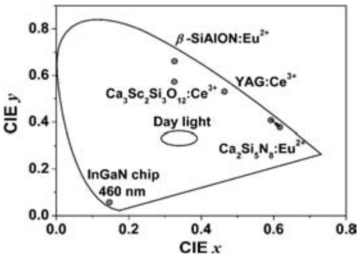

Figure 4. Chromaticity coordinates of Eu^{2+} ion-doped $Ca_2Si_5N_8$.

The CIE (Commission International del' Eclairage) 1931 chromaticity of $Ca_2Si_5N_8:Eu^{2+}$ phosphors is shown in Figure 4. The chromaticity index (x, y) shifts from (0.589, 0.407) to (0.613, 0.378) by varying the Eu^{2+} ion content from 2 to 20 atom %, while the index of $YAG:Ce^{3+}$ (P46-Y3) is (0.461, 0.525). The characteristic index of $Ca_2Si_5N_8:Eu^{2+}$ with high color saturation indicates that the CIE coordinates of white light are possibly generated by coupling with a blue LED together with suitable green phosphor such as β-SiAlON: Eu^{2+} (0.32, 0.64)[3] or $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ (0.32, 0.57).[10] Therefore, the $Ca_2Si_5N_8:Eu^{2+}$ phosphor can be used to compensate the color deficiency of current $YAG:Ce^{3+}$ phosphor-converted white LEDs or to create warm-white light by combining with blue LED and suitable green phosphor.

In conclusion, the excellent orange-red phosphor $Ca_2Si_5N_8:Eu^{2+}$ has been prepared by the CRN method without using any air or moisture sensitive raw material. This phosphor contains well-crystallized grains with mean size of 20 µm, and the oxygen content is effectively suppressed below 0.72 wt %. The powder sample doped with Eu^{2+} ions at the optimized concentration of 2 atom % is efficiently excited by the blue lights (400–470 nm) of InGaN-based LEDs and gives an intense emission at 600 nm which is competitive (≈92%) with that of $YAG:Ce^{3+}$ (P46-Y3). It is believed to be a potential candidate for the phosphor-converted white LEDs.

References

1 M. G. Craford, *Commercial Light Emitting Diode Technology*, Kluwer, Dordrecht, **1996**.
2 R. J. Xie, N. Hirosaki, K. Sakuma, Y. Yamamoto, M. Mitomo, *Appl. Phys. Lett.* **2004**, *84*, 5404.
3 N. Hirosaki, R. J. Xie, K. Kimoto, T. Sekiguchi, Y. Yamatoto, T. Suehiro, M. Mitomo, *Appl. Phys. Lett.* **2005**, *86*, 211905.
4 K. Uheda, H. Takizawa, T. Endo, H. Yamane, M. Shimada, C. M. Wang, M. Mitomo, *J. Lumin.* **2000**, *87–89*, 967.
5 H. A. Hoppe, H. Lutz, P. Morys, W. Schnick, A. Seilmeier, *J. Phys. Chem. Solids* **2000**, *61*, 2001.
6 T. Schlieper, W. Milius, W. Schnick, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1037.
7 S. H. M. Poort, G. Blasse, *J. Lumin.* **1997**, *72–74*, 247.
8 G. Blasse, B. C. Grabmaier, *Luminescent Materials*, Springer, Berlin, **1994**.
9 D. L. Dexter, *J. Chem. Phys.* **1953**, *21*, 836.
10 Y. Shimomura, T. Honma, M. Shigeiwa, T. Akai, N. Kijima, *Rare Earths* **2005**, *46*, 116.

Published on the web (Advance View) March 5, 2006; DOI 10.1246/cl.2006.334