Preparation of BaSi$_2$O$_5$:Eu$^{2+}$ Glass Ceramic Phosphors and Luminescent Properties

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ABSTRACT

Eu$^{2+}$-doped BaSi$_2$O$_5$ glasses were prepared by melting method and the glass-ceramics (GCs) were obtained by heat-treatment at various temperatures between 800 °C and 1000 °C. The single phase of BaSi$_2$O$_5$ micro-crystal precipitated in the GCs by heat-treatment above 950 °C, and the quantum yield (QY) of Eu$^{2+}$ fluorescence became higher than that of other GCs, in which other crystal phases precipitated. When the BaSi$_2$O$_5$ precipitated, the QY increased drastically.

KEYWORDS: glass ceramics, phosphor, alkaline earth silicate

1. Introduction

The visible luminescent phosphors that are excited by blue or near UV light have been used as the next-generation light sources such as a white LED. For example, the yttrium aluminum garnet (YAG): Ce$^{3+}$ phosphor has been put into practical use in a white LED. The blue light (~460 nm) from an InGaN LED chip is absorbed by the Ce$^{3+}$ ion by the 5d$\leftrightarrow$4f transition in the YAG structure, and the YAG: Ce$^{3+}$ phosphor produces the yellow emission. The luminous efficiency of this type of white LEDs is better than other types of white LEDs, such as RGB-LED or RGB phosphor-converting LED that is excited by UV-light.

Recently, the alkaline-earth orthosilicate phosphors have been reported to show desirable luminescent properties for white LED. The Ba$_2$SiO$_4$: Eu$^{2+}$ (M = Ca, Sr, Ba) is called BOS phosphor, which shows broad photoluminescence (PL) band between 470 nm to 530 nm. Photoluminescence excitation (PLE) spectra also have a broad band between 220 nm and 460 nm, which is suitable for InGaN LED or LD excitation system.

The glass-ceramic (GC) process, which is prepared by the cerammization of a glass with a specific composition, is a new method of phosphor synthesis. We have reported the Ce$^{3+}$:YAG GC, which shows excellent luminescent performance by 460 nm LED excitation. Among the alkaline earth silicate binary systems, the BaO-SiO$_2$ system has the widest compositional range for glass formation (BaO:SiO$_2$ = 0.27) and the lowest melting point. The BaSi$_2$O$_5$: Eu$^{2+}$ powder phosphor has wide blue-green emission band at 508 nm, and we can easily fabricate the glass, which has the composition of that crystal. In this study, the Eu$^{2+}$-doped GC samples were obtained by heat-treatment of barium silicate glasses at various temperatures, and luminescent properties of the GC were investigated.

2. Experimental

The glass samples with the chemical composition of Ba$_{1-x}$Eu$_x$Si$_2$O$_5$ (x=0.001, 0.005, 0.007, 0.01, 0.02, 0.05) were prepared by a conventional melting method. The starting materials were BaCO$_3$ (3N), SiO$_2$ (3N), and Eu$_2$O$_3$ (3N). 5 wt% of NH$_4$Cl (3N) was added as flux. The materials were well mixed in an alumina mortar, and sintered at 1200 °C for 2h in an alumina crucible under the N$_2$ atmosphere. The crystal phases were identified by X-ray diffraction (XRD) measurement (Shimadzu, XRD6000). The PL and PLE spectra of Eu$^{2+}$ in the as-made glass and the GCs were measured by a spectrophotometer (Shimadzu, RF-5000). The total radiant flux of PL was measured by 378 nm LD excitation (Nichia, NDHU110APAE3) in an...
3. Results and discussions

Figure 1 shows the DSC curve of the as-made glass of Ba0.99Eu0.01Si2O5 (x=0.01). The Tg and the Tx were estimated to be 690 °C and 810 °C, respectively. Two small exothermic peaks are observed at 950 °C and 1000 °C.

Figure 2 shows the XRD patterns of the glass and the GC by heat-treatment between 800 °C and 1000 °C. For each heat-treated sample from (b) 800 °C to (f) 1000 °C in Figure 2, we name as below, (b) GC800, (c) GC850, (d) GC900, (e) GC950, (f) GC1000. It can be seen that BaSi2O5 and BaSi5O13 crystals, which have slightly barium-richer compositions than the BaSi2O5, were precipitated in the GC800 and the GC850. The single phase of the BaSi2O5 was precipitated in the GC950 and the GC1000. The BaSi2O5 single phase was obtained by heat-treatment above 950 °C. The XRD patterns of GC900 could not be identified by the database of the BaO-SiO2 binary system of JCPDS files. While the
Figure 3 shows PL and PLE spectra of Eu\(^{2+}\) in the glass and the GCs heat-treated at 800 °C–1000 °C. The as-made sample shows an emission band peak at 550 nm. The emission peaks of GC800 and GC850, in which multiple phases precipitated, were at 530 nm and at 510 nm, respectively and the full widths at half maximum (FWHM) of both were about 150 nm. The emission peak of GC900 was the shortest at 490 nm and the FWHM was about 100 nm. The GC950 and GC1000, in which the single phase of BaSi\(_2\)O\(_5\) crystal precipitated, show the emission peaks at 520 nm and 508 nm, respectively. The FWHMs of both were about 100 nm. The emission spectrum of the GC1000 is similar to that of BaSi\(_2\)O\(_5\) phosphor prepared by the conventional solid-state reaction (peak at 504 nm). Since the Ba-sites of the polycrystalline BaSi\(_2\)O\(_5\) phosphor are substituted by Eu\(^{2+}\) ions, those of GC950 are also considered to be substituted by the Eu\(^{2+}\) ions. The PLE intensity increased with increasing heat-treatment temperature above 900 °C.

The QY of the samples was evaluated by the following equation,

\[
QY = \frac{\text{Emission photon number}}{\text{Absorption photon number}} \times 100 \%\, (1)
\]

where the emission photon number and the absorption photon number were calculated by integral of photon distributions, which were obtained from the spectral power distribution. In order to correct the effects of reabsorption by the reflection of excitation-light from the inner wall of the sphere, the spectrum by indirect excitation was subtracted from that by direct excitation.

Figure 4 shows the heat-treatment temperature dependence of QY. The QY increased rapidly with increasing heat-treatment temperature above 900 °C. The value is about 68% to 70%.

The spectral power distributions of the samples pumped by 18.5 mW excitation of 378 nm LD are shown in Figure 5. The Eu-concentration dependence of the total radiant flux is shown in Figure 6. The total radiant flux of x=0.01 was the highest, 4.03 mW, among the six samples.

The Eu concentration-dependence of QY is shown in Figure 7. As the Eu concentration increases, the QY decreases monotonically from 76 % to 26 %. It can be confirmed that the concentration quenching started below the x=0.01.

The Eu-concentration dependence of the color coordinates of emission spectra by 378 nm excitation in the CIE chromaticity diagram are shown in Figure 8.
The $y$-coordinate slightly shifts to higher side with increasing Eu-concentration in the range of $(x, y) = (-0.25, 0.4 \sim 0.5)$. In the spectral power distribution of Figure 5, the PL emission peak slightly shifts for longer side with increasing Eu-concentrations probably because of reabsorption of shorter wavelength light and alteration of the ligand field splitting states. The red-shift of dominant wavelength can result in the change of $y$-coordinate.

4. Conclusions

The BaSiO$_3$: Eu single-phase GC phosphors were fabricated by a conventional GC process. The PL and PLE spectra of the GC950 and GC1000 were similar to those of the referenced BaSiO$_3$ powder phosphor. When the single phase of BaSiO$_3$ was precipitated, the QY increased drastically. The BaSiO$_3$: Eu precipitated GC of $x=0.01$ showed the highest total radiant flux among six samples with different Eu concentration and its QY was 68%.

References


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