Preparation and optical properties of Eu^{2+} and Sm^{3+} co-doped glass ceramic phosphors emitting white color by violet laser excitation

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Eu^{2+} and Sm^{3+} co-doped silicate glasses were prepared under reducing atmosphere in a system $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO}$ and the glass-ceramics were obtained by heat-treatment at temperatures between 1000 and 1400°C. Broad emission band were observed between 400 and 550 nm due to the $5d \rightarrow 4f$ transition of Eu^{2+} , as well as sharp emission peaks at 563, 600, 646 and 713 nm due to the $4f \rightarrow 4f$ transition of Sm^{3+} in the samples. Emission color became white under ultraviolet or violet excitation for the glass ceramics heat-treated at above 1100°C. Ceramming temperature dependence of the color coordinates, emission spectra were investigated and discussed with the precipitated crystal phases. We have successfully obtained the glass ceramic phosphor emitting white color, suitable for a white LED without organic resin for power illumination.

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1. Introduction

In 1993, the high power output blue indium gallium nitride (InGaN) light-emitting diodes (LEDs) were developed.^{1,2)} Then nitride and phosphide LEDs achieved light's three primary colors (RGB). These LEDs applied for solid state lighting such as displays and general illumination because they have high brightness, low electric consumption and long lifetime. White LEDs have also been studied to apply for general illumination.^{3–6)} The most common white LEDs consist of blue LED-chip and YAG: Ce powder phosphor packed with organic resins.⁷⁾ The function of the phosphors in the white LEDs is to absorb the light emitted from ultraviolet or blue LED-chip and converts it into visible light. However, white LEDs have poor heat-resistance due to organic resins. The color of these resins change into yellow and cause degradation of phosphor and luminous intensity.⁸⁾ With increasing output power of LEDs for general illumination, this problem is becoming more and more serious. The commercial white LEDs also have low color rendering because these emission spectra are pseudo-white, which is a combination of blue (LED) and yellow emissions (YAG: Ce phosphor).

The glass ceramic phosphors doped with rare-earth ions are novel materials to improve these problems because they have efficient luminescence, excellent heat-resistance and ease of formability.⁹⁾ These materials are prepared by ceramization of a glass doped with rare-earth ions with a specific composition. The precipitated crystals in the glass matrix are visible phosphors, which can be used as a component of white LEDs, showing photoluminescence (PL), excited with blue or ultra violet (UV) LED.

The Eu^{2+} -doped phosphors show broad emission band with very large optical cross sections by $4f^65d^1 \rightarrow 4f^7$ transition.¹⁰⁾ The emission color in oxide hosts is usually ranging from violet to

yellow, depending on the ligand field in them. The excitation and emission spectra can be varied by changing the host lattice or chemical composition. Because their typical emission spectra covers wide wavelength range of visible, the Eu^{2+} doped phosphors become one of the most important components in the phosphor-converting white LED.

Sm^{3+} doped phosphors show orange or red emission by $4f \rightarrow 4f$ transition,¹¹⁾ which can improve color rendering in the wavelength band where many of the commercial white LEDs show low color rendering. One of the advantages of Sm^{3+} is its strong absorption peak at 405 nm where the external quantum efficiency of InGaN LEDs becomes the highest. Although the Sm ions can also take a divalent state, Sm(II), depending on the host composition and preparation condition, the tendency of reduction is much smaller than that of Eu(II) ions.¹²⁾ Therefore, it is possible to make glass and ceramic samples co-doped with Eu^{2+} and Sm^{3+} ions by choosing an appropriate reducing condition, which may lead to a phosphor material having an excellent color rendering index, CRI, including the red wavelength region.

In this study, we prepared Eu^{2+} and Sm^{3+} co-doped silicate glass ceramic phosphors and investigated the crystalline phase with X-ray diffraction. We also discuss excitation and emission spectra, the quantum yield and color coordinates of the emission of these samples.

2. Experimental procedure

Glass with composition of $30\text{SiO}_2\text{--}30\text{Al}_2\text{O}_3\text{--}40\text{CaO}$: $0.1\text{Eu}_2\text{O}_3$, $0.1\text{Sm}_2\text{O}_3$ was prepared by using SiO_2 , Al_2O_3 , CaCO_3 , Eu_2O_3 and Sm_2O_3 . NH_4Cl was added as a flux at 5 mass%. All the chemical powders were 99.9%–99.99% purity. Batches of about 25 g materials were well mixed in an alumina mortar. The mixed materials were first heated in an alumina crucible at 900°C for 1 h using an electric furnace. The crucible was placed in a larger alumina crucible that was filled with graphite powder to reduce Eu^{3+} into Eu^{2+} . And then the mixed materials were melted at

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1600°C for 1.5 h under the same condition. The melt was poured onto a pre-heated stainless-steel mold. The glasses obtained were annealed for 30 min at the glass transition temperature (T_g) determined by a differential scanning calorimeter (DSC) (Rigaku, Thermo plus, DSC8270) at a heating rate of 10°C/min. The annealed glasses (As-made glasses) were cut into 5 mm × 5 mm × 7 mm size and then heat-treated at various temperatures between 1000 and 1400°C for 2 h. X-ray diffraction (XRD) measurement was carried out to identify crystal phases of these samples with (Shimadzu XRD6000) using Cu K α radiation. The PL and photoluminescence excitation (PLE) spectra were measured by using a fluorescence spectrophotometer (Shimadzu, RF-5000). The total radiant flux of the PL were measured under 378 nm LD excitation (Nichia, NDHU110APAE3) by using an integrating sphere (Labsphere, LMS-100) which was connected to a CCD detector (Ocean Optics, USB2000) with an optical fiber. A standard halogen lamp (Labsphere, CLS-600) was used for calibration of this measurement system. With the power distribution spectrum of total flux obtained, the quantum yield (QY) of the samples was evaluated by the following equation,

$$\text{Quantum yield (QY)} = \frac{\text{Emission photon number}}{\text{Absorption photon number}} \times 100\%, \quad (1)$$

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

The color coordinates (x , y) of CIE-1931 chromaticity diagram¹³⁾ were obtained under 378 nm LD excitation (Nichia, NDHU110APAE3) with a software (Ocean Optics, Spectra Suite) from the calibrated spectra obtained.

3. Results

The colors of glasses and glass ceramics prepared from the batch composition were yellow or yellowish white due to the $4f^65d^1 \leftarrow 4f^7$ absorption transition of Eu^{2+} in the violet to blue wavelength region. Surface crystallization was observed for the samples heat-treated above 1100°C.

The DSC curve of the as-made glass is shown in **Fig. 1**. The T_g and the onset crystallization temperature (T_x) were 860°C and 980°C, respectively. One small exothermic peak was observed at 1280°C. The X-ray diffraction patterns of these glass ceramics that were heat-treated between 1000 and 1400°C are shown in

Fig. 1. DSC curve of Eu^{2+} - Sm^{3+} co-doped glass.

Fig. 2. The $\text{CaAl}_2\text{SiO}_6$ and $\text{Ca}_2\text{Al}_2\text{SiO}_7$ crystals were precipitated at temperature range of 1000–1200°C and 1300–1400°C, respectively. The heat-treatment temperature variations of PL spectra of the as-made glass and the glass ceramics under 378 nm excitation are shown in **Fig. 3**. The broad emission bands peaking between 420 nm and 520 nm originate from the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} . The narrow emission bands peaked at 563 nm, 600 nm, 646 nm and 713 nm originate from the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$ transition of Sm^{3+} , respectively. The heat-treatment temperature variations of PLE spectra of the as-made glass and the glass ceramics are shown in **Fig. 4**. The λ_{em} is the monitoring wavelength of Eu^{2+} emission peak. The peak wavelengths of broad excitation bands were located between 330 nm and 420 nm. The peaks of the glass and the glass ceramics heat-treated at 1000–1100°C and 1200–1400°C were 420, 330 and 360–380 nm, respectively. The Stokes shifts of the samples were 70 nm for as-made, 100 nm for 1000–1100°C and 140 nm for 1200–1400°C.

The QY of the samples under 378 nm excitation is plotted as a function of ceramming temperature in **Fig. 5**. The maximum value of QY was 11% at 1000°C. The QY values of the samples heat-treated above 1100°C were approximately 4%.

The color coordinates of the samples under 378 nm excitation are plotted in the chromaticity diagram in **Fig. 6**. All the samples

Fig. 2. X-ray diffraction patterns of Eu^{2+} - Sm^{3+} co-doped glass ceramics heat treated at 1000–1400°C.

Fig. 3. Heat-treatment temperature variations of photoluminescence spectra of Eu^{2+} - Sm^{3+} co-doped glass and glass ceramics under excitation at 378 nm LD.

Fig. 4. Heat-treatment temperature variations of photoluminescence excitation spectra of Eu^{2+} - Sm^{3+} co-doped glass and glass ceramics at emission peak wavelength of Eu^{2+} .

Fig. 5. Heat-treatment temperature dependence of quantum yield of Eu^{2+} - Sm^{3+} co-doped glass and glass ceramics under excitation at 378 nm LD.

except that heat-treated at 1000°C were in the range of $(x, y) = (0.27\text{--}0.33, 0.3\text{--}0.4)$ corresponding to white or greenish white.

4. Discussion

As indicated from Fig. 1 and Fig. 2, the exothermic peaks of 1000 and 1280°C in Fig. 1 correspond to the precipitation of $\text{CaAl}_2\text{SiO}_6$ and $\text{Ca}_2\text{Al}_2\text{SiO}_7$, respectively. Both crystals, doped with Eu^{2+} ions, showed broad emission spectra in the visible range.

As shown in Fig. 3 and Fig. 4, the PL and PLE spectra of Eu^{2+} were largely changed between the glass and the glass ceramics. This is probably because the Eu^{2+} was doped into the precipitated aluminosilicate crystal phase. The coordination environment of Eu^{2+} should be different between silicate glass matrix and crystal.¹⁰⁾ The emissions of Eu^{2+} and Sm^{3+} are originated from the $5d \rightarrow 4f$ transition and the $4f \rightarrow 4f$ transition, respectively. The $4f$ orbital is shielded from the surroundings by the filled $5s^2$ and $5p^6$ orbitals. On the other hand, the $5d$ orbital is the outershell orbital. Therefore the influence of coordination environment in $5d \rightarrow 4f$ transition is much larger than that in the $4f \rightarrow 4f$ transition. The change of coordination environment influences optical properties of Eu^{2+} than that of Sm^{3+} .

From Fig. 3, the peak wavelengths of Eu^{2+} were changed from 420 nm to 520 nm by ceramming at 1000–1200°C, which correspond to the precipitation temperature of $\text{CaAl}_2\text{SiO}_6$. The color

Fig. 6. Chromaticity color coordinates of Eu^{2+} - Sm^{3+} co-doped glass and glass ceramics.

of sample's surface was white, while the inside was yellow. Actually, in the samples heat-treated at 1100–1400°C the surface crystallization occurred. The relative intensity of Sm^{3+} was increased with increasing heat-treatment temperature and the emission of Eu^{2+} between 470 nm and 500 nm was decreased.

From Fig. 4, the excitation peak wavelengths of the glass ceramics were shorter than that of the glass.

As shown in Fig. 6, the samples except that heat-treated at 1000°C showed white or greenish white emission. Although the QY of the glass ceramics ceramming at above 1100°C are still only 4%, if the relative emission of Sm^{3+} is increased, the color coordinates shift to red region, resulting in warm white. In the lighting technologies including white LEDs for the next generation, achievement of warm white color having low correlated color temperatures, CCT, around 3000 K, are becoming an important issue. Therefore, the optimization of the intensity ratio of $\text{Sm}^{3+}/\text{Eu}^{2+}$ can be one of the simple routes to solve this important issue.

Further improvement of QY is expected by optimization of preparation conditions of glass and glass ceramics in this co-doped silicate system.

5. Conclusions

Eu^{2+} and Sm^{3+} co-doped silicate glass ceramic phosphors were obtained by heat-treating a glass of SiO_2 - Al_2O_3 - CaO system. The DSC and XRD results showed that $\text{CaAl}_2\text{SiO}_6$ and $\text{Ca}_2\text{Al}_2\text{SiO}_7$ crystals were precipitated at 1000°C and 1280°C, respectively. The emission wavelengths of Eu^{2+} in the glass ceramics were changed from that of the glass because Eu^{2+} was doped into the crystal phases. The emission intensity of Sm^{3+} was increased with increasing heat treatment temperature. The convolution of emissions from Eu^{2+} and Sm^{3+} resulted in white emission. The Eu^{2+} and Sm^{3+} co-doped glass ceramic phosphors showed a potential as phosphor candidate for white LEDs having an excellent CRI and low CCT.

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