Synthesis of Eu$^{2+}$-activated Rb–Ba–Sc–Si–O glass phosphors using melt synthesis technique

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Eu$^{2+}$-activated Rb–Ba–Sc–Si–O glass phosphor was synthesized by a melt synthesis technique using arc-imaging furnace and their photoluminescence properties were characterized. In addition, the obtained glass phosphors annealed in a flow of 5% H$_2$–95% Ar gas to enhance the luminescent efficiency. The emission spectra of the Eu$^{2+}$-activated glass phosphors presents yellow emission band centered at 537 nm due to the 4f$^6$5d$^1$ transitions of Eu$^{2+}$, and the emission intensity was effectively enhanced by the annealing treatment.

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1. Introduction

Phosphor-converted white light-emitting diodes (pc-white LEDs) have been widely applied in displays and lamps as an alternative to conventional incandescent and fluorescent lamps. White LEDs have a number of advantages, such as a high luminescent efficiency, a long lifetime, compactness, environmental friendliness, and desirable features. However, the pc-white LEDs have some problems because they are generally embedded in epoxy or silicone resins. The melt synthesis technique using arc-imaging furnace is suitable for synthesizing powder phosphors in epoxy or silicone resins. The large difference of refractive index between phosphors and organic resins will lead to high amount of scattering light. Furthermore, these organic resins have the poor heat- or light-resistance, which will also attribute to the degradation of luminescence emission intensity and the change of emission color. Recent years, therefore, the glass phosphors have been extensively investigated as a promising materials for white LEDs, because they have efficient luminescence, excellent heat- or light-resistance and ease of formability.

Among several phosphor materials, Eu$^{2+}$-activated phosphors are suitable for the tri-color phosphor converting white LEDs. These phosphors have excellent optical absorption at near UV and blue light region due to the 4f$^7$ → 4f$^5$5d transitions of Eu$^{2+}$ coupled to the host lattice. In particular, Eu$^{2+}$-activated silicate phosphors have been widely investigated because they can show good luminescence properties due to the strong crystal fields with the covalent Si–O bond. The strong crystal field strength around Eu$^{2+}$ in the host lattice was contribute to the increase of the energy splitting of 4f$^5$5d excited level, therefore, the silicate phosphors are expected to be obtained the excitation and emission band in the longer wavelength range.

In this study, we are synthesized the Eu$^{2+}$-activated Rb–Ba–Sc–Si–O glass phosphors by the melt synthesis technique using arc-imaging furnace. We have previously demonstrated that the RbBaScSi$_3$O$_9$:Eu$^{2+}$ powder phosphor exhibit the blue-green emission with good luminescence properties under near-UV excitation. In addition, the melt synthesis technique using arc-imaging furnace is suitable for synthesizing powder phosphors with high luminescence efficiency. This method has an interesting feature because it is a high-temperature approach for synthesis, which is rather opposite from the solid-state syntheses. The melt reactions are extremely rapid and homogeneous because of liquid mixing and rapid diffusion in the liquid phase, in contrast with the conventional solid-state reactions. Melting using arc-imaging furnace requires no container at various atmospheres up to high temperatures even greater than 2000°C. Furthermore, this method has rapid cooling process, which indicates that this method is not only suitable for synthesizing powder phosphors but also suitable for synthesizing glass phosphors.

2. Experimental

Rb$_2$CO$_3$, BaCO$_3$, SiO$_2$, Sc$_2$O$_3$ and Eu$_2$O$_3$ were mixed in a stoichiometric ratio using a mortar with acetone, in which the Eu$^{2+}$ content was adjusted between 0.5 and 5 mol %. The homogeneous mixture placed on a copper hearth, and then melted in a flow of 5% H$_2$–95% Ar gas using arc-imaging furnace. Finally, the glasses were annealed at 900 and 950°C for 12 h in a flow of 5% H$_2$–95% Ar gas. Figure 1 illustrates the schematic diagram of arc-imaging furnace. Arc-imaging furnace use the xenon lamp (6 kW) as a light source. The emitted strong light from xenon lamp was reflected by ellipsoidal aluminum mirror and the high energy light corrected on the copper sample holder. The sample can be heated rapidly up to the high temperature over 2000°C in 1 min and also cooled by removing the sample stage from the mirror focus. The cooling rate was estimated as more than 10°C/s.

Powder XRD data were obtained using a diffractometer (MX-Labo; Mac Science Ltd.) with Cu K$_\alpha$ radiation. The photoluminescence emission and excitation spectra were measured at room temperature with a spectrofluorometer (Jasco Corp. FP-6500/6600). The transmittance curves were measured with a
The ultraviolet–visible spectrometer (Jasco Corp. V-550). The Commission International de l’Eclairage (CIE) chromaticity coordinate date for the phosphor were measured at room temperature with a luminescence colorimeter (Hamamatsu C7473-36 PMA-11).

3. Results and discussion

The XRD patterns of the \( x \) mol % \( \text{Eu}^{2+} \)-activated \( \text{Rb–Ba–Sc–Si–O} \) (0.5 \( \leq x \leq 5 \)) glass phosphors synthesized by the melt synthesis technique using arc-imaging furnace were obtained completely amorphous patterns without peaks as shown in Fig. 2. The maximum luminescent intensity was observed for 1 mol % \( \text{Eu}^{2+} \)-activated \( \text{Rb–Ba–Sc–Si–O} \) glass phosphor by the optimization of the \( \text{Eu}^{2+} \) concentration. Therefore, the \( \text{Eu}^{2+} \) concentration in the \( \text{Rb–Ba–Sc–Si–O} \) glass phosphor was fixed at 1 mol %. The photographs of the 1 mol % \( \text{Eu}^{2+} \)-activated \( \text{Rb–Ba–Sc–Si–O} \) glass phosphor before annealing treatment are shown in Fig. 3. The body color of the obtained glass phosphor was yellow, and presented the yellow emission under excitation at 365 nm light irradiation. In contrast, under excitation at 254 nm light, the obtained glass phosphor show the red emission, which is considered to be due to the \( \text{Eu}^{3+} \) existing in the glass phosphor. The emission intensity of the obtained 1 mol % \( \text{Eu}^{2+} \)-activated \( \text{Rb–Ba–Sc–Si–O} \) glass phosphor compared with that of a commercial \( \text{Y}_{3}\text{Al}_{5}\text{O}_{12}:\text{Ce}^{3+} \) (P-46) powder phosphor was attained up to only 9%, which is too low for use in white LEDs. Therefore, the \( \text{Eu}^{2+} \)-activated \( \text{Rb–Ba–Sc–Si–O} \) glass phosphor annealed in a flow of 5% \( \text{H}_{2} \)–95% \( \text{Ar} \) gas to enhance the emission intensity.

The XRD patterns of the 1 mol % \( \text{Eu}^{2+} \)-activated \( \text{Rb–Ba–Sc–Si–O} \) glass phosphors before and after annealing treatment at 900° and 950°C are shown in Fig. 4. The samples prepared before and after annealing treatment at 900°C were obtained completely amorphous patterns. In contrast, the sample annealed at 950°C observed the surface crystallization and the XRD pattern of this sample is in good agreement with that of the single phase \( \text{RbBaScSi}_{3}\text{O}_{9} \) structure. These results indicate that the crystallization of this glass phosphor has occurred beyond 900°C.

Figure 5 shows the transmittance curves of the 1 mol % \( \text{Eu}^{3+} \)-activated \( \text{Rb–Ba–Sc–Si–O} \) glass phosphors before and after annealing treatment at 900°C. Since these glass phosphors have...
yellow body color, the optical absorption behavior was observed in all samples in the region of wavelength shorter than 500 nm (i.e., in the blue region), which is the complementary color to yellow. In addition, the 1 mol % Eu\(^{2+}\)-activated Rb–Ba–Sc–Si–O glass phosphors before and after annealing treatment at 900°C shows high transmittance properties, although the transmittance of the obtained glass phosphor was slightly decreased by the annealing treatment. The transmittances of the 1 mol % Eu\(^{2+}\)-activated Rb–Ba–Sc–Si–O glass phosphors before and after annealing treatment at 900°C were 60 and 55%, respectively.

Figure 6 illustrates the excitation and emission spectra of the 1 mol % Eu\(^{2+}\)-activated Rb–Ba–Sc–Si–O glass phosphors before and after annealing treatment at 900°C and 950°C. The excitation spectra of the samples prepared before and after annealing treatment at 900°C are consisted of a broad band covering the region from the UV to blue light part. The emission spectrum under excitation at 330 nm exhibits a broad yellow emission band peaking at 500 nm, which is similar to that of RbBaSc-Si\(_3\)O\(_9\):Eu\(^{3+}\) phosphor, reported in our previous study,\(^{16}\) and the emission intensity became smaller than that of the powder phosphor, it is expected to be a suitable for material of the remote phosphor or high powder large materials. On the order hand, the sample annealed at 950°C presents the broad blue-green emission observed in the sample after annealing treatment at 900°C (solid line) and a commercial Y\(_3\)Al\(_5\)O\(_12\):Ce\(^{3+}\) (P-46) phosphor (broken line).

Figure 7 presents the CIE chromaticity diagram for the 1 mol % Eu\(^{2+}\)-activated Rb–Ba–Sc–Si–O glass phosphor after annealing treatment at 900°C and a commercial Y\(_3\)Al\(_5\)O\(_12\):Ce\(^{3+}\) (P-46) phosphor. The emission spectrum of the 1 mol % Eu\(^{2+}\)-activated Rb–Ba–Sc–Si–O glass phosphor was slightly increased by the annealing treatment at 900°C. Results for a commercial Y\(_3\)Al\(_5\)O\(_12\):Ce\(^{3+}\) (P-46) phosphor shows high transmittance properties, although the transmittance of the obtained glass phosphor was slightly decreased by the annealing treatment. The transmittances of the 1 mol % Eu\(^{2+}\)-activated Rb–Ba–Sc–Si–O glass phosphors before and after annealing treatment at 900°C were 60 and 55% at 700 nm, respectively.

Figure 6. Excitation and emission spectra of the 1 mol % Eu\(^{2+}\)-activated Rb–Ba–Sc–Si–O glass phosphor; (a) non-annealing, (b) 900°C annealing, (c) 950°C annealing.

Fig. 5. The transmittance curve of the 1 mol % Eu\(^{2+}\)-activated Rb–Ba–Sc–Si–O glass phosphor before and after annealing treatment at 900°C. The inset shows the photographs of the 1 mol % Eu\(^{2+}\)-activated Rb–Ba–Sc–Si–O glass phosphor before and after annealing treatment at 900°C. Bottom images show the each sample during the irradiation of the excitations at 395 nm.

Fig. 6. Photoluminescence normalized emission spectra of the 1 mol % Eu\(^{2+}\)-activated Rb–Ba–Sc–Si–O glass phosphor after annealing treatment at 900°C (solid line) and a commercial Y\(_3\)Al\(_5\)O\(_12\):Ce\(^{3+}\) (P-46) phosphor (broken line).
Ba–Sc–Si–O glass phosphor after annealing treatment at 900°C and a commercial \( \text{Y}_2\text{Al}_5\text{O}_{12} : \text{Ce}^{3+} \) (P-46) phosphor. The emission band of the 1 mol% \( \text{Eu}^{2+} \)-activated Rb–Ba–Sc–Si–O glass phosphor has the larger full width at half maximum (FWHM) of emission band than that of a commercial \( \text{Y}_2\text{Al}_5\text{O}_{12} : \text{Ce}^{3+} \) (P-46) phosphor and it was widely curved in the high spectral luminous efficacy region. In addition, the glass phosphor obtained in the present study show the high transparency (Fig. 5). These results suggest that \( \text{Eu}^{2+} \)-activated Rb–Ba–Sc–Si–O glass phosphors are a suitable candidate for the yellow-emitting phosphor of near UV based white LEDs lamps using remote phosphor.\(^{20-23}\) In addition, this glass phosphor was expected to be also used in the laser excited high power optical devices.

4. Conclusions

The \( \text{Eu}^{2+} \)-activated Rb–Ba–Sc–Si–O glass phosphor was synthesized by the melt synthesis technique using arc-imaging furnace. The obtained glass phosphor was annealed in a flow of 5%\( \text{H}_2 \)–95%Ar gas to increase the reduction effect, as a result, the emission intensity was effectively enhanced by the annealing treatment. The excitation spectra of the \( \text{Eu}^{2+} \)-activated glass phosphors are consisted of broad band covering the region from 220 to 450 nm, and presents yellow emission band centered at 537 nm due to the 4f55d\(^1\) – 4f\(^7\) transition of \( \text{Eu}^{2+} \). These results indicate that \( \text{Eu}^{2+} \)-activated Rb–Ba–Sc–Si–O glass phosphors are a suitable candidate for the yellow-emitting phosphor of near UV based white LEDs lamps using remote phosphors.

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