Novel green-emitting Ho\textsuperscript{3+}-doped scandate phosphors

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Blue-light excitable, green-light emitting Ba\textsubscript{3}(Sc\textsubscript{1–x}Ho\textsubscript{x})\textsubscript{4}O\textsubscript{9} phosphors were successfully synthesized in the single-phase form by a melt synthesis method for the first time. These phosphors show sharp green light emission under blue light (455 nm) excitation. The principal green light emission peak observed at 555 nm corresponds to the transition from \textsuperscript{5}F\textsubscript{4} and \textsuperscript{5}S\textsubscript{2} to the \textsuperscript{5}I\textsubscript{8} energy level of Ho\textsuperscript{3+}.

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1. Introduction

White light emitting diodes (white LEDs) have recently attracted attention because of their advantages of high luminescence efficiency, low energy consumption, and long lifetime.\textsuperscript{1)} White LEDs are widely used in liquid crystal displays (LCDs) and lamps. Green- and red-emitting phosphor-converted blue-LED based white LEDs (pc-white LEDs) are frequently used as backlights in LCDs owing to their high luminescence efficiency and high color rendering index. To realize the high color gamut of LCDs using pc-white LEDs as backlight,\textsuperscript{2)–6)} development of a phosphor having a narrow emission band and high color purity is important.

In this study, we selected the Ho\textsuperscript{3+} ion as an activator of a novel green-emitting phosphor for LCD backlighting. Ho\textsuperscript{3+} ion has been investigated as one of promising activator for up-conversion phosphor materials, and Ho\textsuperscript{3+}-activated phosphors show the high up-conversion efficiency because the excited state absorption energy owing to \textsuperscript{5}I\textsubscript{7} → \textsuperscript{5}F\textsubscript{4} and \textsuperscript{5}I\textsubscript{6} → \textsuperscript{5}F\textsubscript{4} transitions of Ho\textsuperscript{3+} can overlap.\textsuperscript{7)–14)} However, there are scarce investigations as down-conversion phosphor for use in white LEDs because Ho\textsuperscript{3+} has another excited level, \textsuperscript{5}I\textsubscript{6}, between the \textsuperscript{5}F\textsubscript{4} and \textsuperscript{5}S\textsubscript{2} states and \textsuperscript{5}I\textsubscript{6}, and the energy gap spanning \textsuperscript{5}F\textsubscript{4}, \textsuperscript{5}S\textsubscript{2}, and \textsuperscript{5}F\textsubscript{3} is small (Fig. 1).\textsuperscript{15)–17)} Small energy band gaps generally lead to excited energy loss due to non-radiative transitions; consequently, most Ho\textsuperscript{3+}-doped green-emitting phosphors show low luminescence efficiency under blue light excitation. In addition, the f–f transitions of Ho\textsuperscript{3+} are partially forbidden, and the electric dipole transitions from \textsuperscript{5}F\textsubscript{4} and \textsuperscript{5}S\textsubscript{2} to \textsuperscript{5}I\textsubscript{6}, which show green emission (Fig. 1), are extremely sensitive to the symmetry of the Ho\textsuperscript{3+}-doping site in the host lattice.\textsuperscript{18)} A reduction in site symmetry generally contributes to an increase in the transition probability of the partially forbidden f–f transitions.

Selection of a host material lacking a site of inversion symmetry in its crystal structure is important for developing a Ho\textsuperscript{3+}-doped phosphor with high green light emission efficiency. We selected Ba\textsubscript{3}Sc\textsubscript{4}O\textsubscript{9} as host material for the green-emitting Ho\textsuperscript{3+}-doped phosphor. Figure 2 shows a polyhedral representation of Ba\textsubscript{3}Sc\textsubscript{4}O\textsubscript{9} crystal structure illustrated by using the VESTA program.\textsuperscript{19)} The Sc\textsuperscript{3+} ions in crystal structure are coordinated by six oxygen ions and are located at sites lacking inversion symmetry.\textsuperscript{20)} This indicates that Ba\textsubscript{3}Sc\textsubscript{4}O\textsubscript{9} should have a suitable structure for producing Ho\textsuperscript{3+}-doped phosphors. In this paper we report the preparation of novel green-emitting Ba\textsubscript{3}(Sc\textsubscript{1–x}Ho\textsubscript{x})\textsubscript{4}O\textsubscript{9} phosphors by a melt synthesis method using an arc imaging furnace and the characterization of their luminescence properties.

2. Experimental

BaCO\textsubscript{3} (purity 99.9%; Kanto Chemical, Co., Inc.), Sc\textsubscript{2}O\textsubscript{3} (purity 99.99%; Shin-ETSu Chemical, Co., Ltd.), and Ho\textsubscript{2}O\textsubscript{3} (purity 99.9%; Wako Pure Chemical Industries, Ltd.) were mixed in a stoichiometric ratio with acetone using a mortar to obtain a homogeneous chemical mixture. The Ho\textsuperscript{3+} content was then
Elemental mapping of Ho, Sc, and Ba was carried out using an electron microscope (SEM; JEOL Ltd. JSM-5310MVB). The microstructure of the sample powder was examined with a scanning electron microscope (SEM; NanoTechnology, SEA1200VX). The emission and excitation spectra were measured at room temperature by using a spectrometer (Jasco Corp. FP-6500). The X-ray powder diffraction (XRD; Mac Science Ltd. MX-Labo) analysis to be in the correct stoichiometric ratio.

### Results and discussion

The composition of each sample was confirmed by XRF analysis to be in the correct stoichiometric ratio. Figure 3 shows the XRD patterns of Ba$_3$(Sc$_{1-x}$Ho$_x$)$_4$O$_9$ ($0.02 \leq x \leq 0.09$), and the homogeneous mixture was melted in an arc imaging furnace. For comparison, phosphor samples were also synthesized by a conventional solid-state reaction method that involved heating in air at 1500°C for 12 h.

The samples were characterized by X-ray powder diffraction (XRD; Mac Science Ltd. MX-Labo). The sample composition was analyzed by X-ray fluorescence spectroscopy (XRF; SII NanoTechnology, SEA1200VX). The emission and excitation spectra were measured at room temperature using a spectrophotometer (Jasco Corp. FP-6500/6600). The emission spectrum was obtained upon excitation at 455 nm, and the excitation spectrum was obtained by monitoring emission at 555 nm. The microstructure of the sample powder was examined with a scanning electron microscope (SEM; JEOL Ltd. JSM-5310MVX). Elemental mapping of Ho, Sc, and Ba was carried out using an electron probe micro-analyzer (EPMA) (Shimadzu, EPMA8705).

#### Figure 4

Figure 4 shows the excitation and emission spectra of Ba$_3$(Sc$_{1-x}$Ho$_x$)$_4$O$_9$ (x = 0 and 0.06) samples synthesized by the melt synthesis and solid-state reaction methods and melt synthesis methods. The excitation spectra are composed of sharp peaks arising from the following 4f–4f transitions of Ho$^{3+}$: 363 nm ($^1I_6 \rightarrow ^3H_4$, $^3D_2$), 388 nm ($^1I_6 \rightarrow ^3G_4$), 422 nm ($^1I_6 \rightarrow ^3G_5$), 455 nm ($^1I_6 \rightarrow ^5F_2$, $^5F_2$, $^5K_4$), and 491 nm ($^1I_6 \rightarrow ^2F_3$). The emission spectra are composed of sharp peaks at 555 nm ($^3F_4$, $^3S_2 \rightarrow ^1I_6$) and 662 nm ($^3F_4 \rightarrow ^1I_6$) due to 4f–4f transitions of Ho$^{3+}$. The emission peak intensities of the sample synthesized by the melt synthesis method are 1.79 times greater than those of the sample synthesized by solid state reaction. The reason for this improvement is attributed to the high dispersion of Ho$^{3+}$ in the sample prepared by melt synthesis.

To investigate the dispersion of Ho$^{3+}$ ions in both Ba$_3$(Sc$_{0.94}$Ho$_{0.06}$)$_4$O$_9$ samples, X-ray mapping images of Ba, Sc, and Ho were measured by EPMA. The results are shown in Figure 5. A homogeneous distribution of all elements was observed in the sample synthesized by the melt synthesis method, whereas the sample synthesized by the solid-state reaction showed localized aggregations. A high dispersion of activator in a sample typically enhances the emission intensity of a phosphor by effectively preventing concentration quenching.

#### Figure 6

Figure 6 shows the dependence of emission intensity on Ho$^{3+}$ concentration in Ba$_3$(Sc$_{1-x}$Ho$_x$)$_4$O$_9$ samples prepared by the melt synthesis ($0.02 \leq x \leq 0.08$) and solid state reaction ($0.02 \leq x \leq 0.09$) methods. The emission intensities of phosphors prepared by both methods increased with increasing Ho$^{3+}$ concentration.
until an optimum value was reached, beyond which the emission intensity decreased with increasing Ho$^{3+}$ content, probably due to concentration quenching. At all compositions samples prepared by melt synthesis showed greater emission intensities than the solid state reaction samples. Furthermore, the Ho$^{3+}$ content at which an optimum emission intensity is observed in Ba$_3$(Sc$_{1-x}$Ho$_x$)$_4$O$_9$ phosphors occurs at a lower concentration in the melt synthesis versus solid state reaction samples. The reason for these behaviors is increasing inhomogeneous dispersion of Ho$^{3+}$ in the host lattice of Ba$_3$(Sc$_{1-x}$Ho$_x$)$_4$O$_9$ samples prepared by melt synthesis.

Figure 7 shows the temperature dependence of the relative emission intensities of Ba$_3$(Sc$_{0.94}$Ho$_{0.06}$)$_4$O$_9$ samples prepared by the melt synthesis and solid-state reaction methods. The temperature dependence of luminescence intensity is important in the development of white LEDs, because it has a significant influence on the light output and color-rendering index. The emission intensities of phosphors usually decrease with increasing temperature due to thermal quenching. At 150°C the emission intensity of the sample prepared by melt synthesis has fallen to 83% of its initial value at 20°C, which is a smaller decrease than that exhibited by the sample prepared by the solid-state reaction method (76% of 20°C value at 150°C). This result indicates that the Ba$_3$(Sc$_{1-x}$Ho$_x$)$_4$O$_9$ phosphor prepared by melt synthesis method has a greater resistance to the thermal quenching effect.

Figure 8 shows SEM images of Ba$_3$(Sc$_{0.94}$Ho$_{0.06}$)$_4$O$_9$ samples prepared by the solid-state reaction and melt synthesis methods. In the case of the solid-state reaction method, an aggregation of particles was observed. On the other hand, no particle aggregation was observed in the sample prepared by the melt synthesis method, and the particle size was smaller than that of the sample synthesized by the solid-state reaction method. It is evident that the particle morphology of the sample prepared by melt synthesis is more uniform than that of the sample prepared by the conventional solid-state reaction method. Uniform particle morphology contributes to the enhanced emission intensity and thermal stability of phosphors.

4. Conclusion

Ba$_3$(Sc$_{1-x}$Ho$_x$)$_4$O$_9$ phosphors were successfully synthesized in a single-phase form by a melt synthesis method. The photoluminescence of Ba$_3$(Sc$_{1-x}$Ho$_x$)$_4$O$_9$ phosphors shows green light emission under blue light irradiation. The emission intensity of the phosphor prepared by melt synthesis has increased to 83% of its initial value at 20°C, which is a smaller decrease than that exhibited by the sample prepared by the solid-state reaction method. The Ba$_3$(Sc$_{1-x}$Ho$_x$)$_4$O$_9$ phosphor synthesized by melt synthesis has excellent stability relative to the thermal quenching effect. Based on these results, the Ba$_3$(Sc$_{1-x}$Ho$_x$)$_4$O$_9$ phosphor prepared by melt synthesis is expected to find excellent application as a green-light emitting phosphor for white LED backlights.

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