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

Kazuma SUGIMOTO, Sun Woog KIM, Kazuyoshi UEMATSU,*
Tadashi ISHIGAKI, Kenji TODA[†] and Mineo SATO*

Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho, Niigata 950-2181, Japan

*Department of Chemistry and Chemical Engineering, Niigata University, 8050 Ikarashi 2-nocho, Niigata 950-2181, Japan

Blue-light excitable, green-light emitting $\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ 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 $^5\text{F}_4$ and $^5\text{S}_2$ to the $^5\text{I}_8$ energy level of Ho^{3+} .

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Key-words : Ho^{3+} -doped $\text{Ba}_3\text{Sc}_4\text{O}_9$ phosphor, Melt synthesis method, White LED

[Received December 29, 2014; Accepted June 21, 2015]

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.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,²⁾⁻⁶⁾ development of a phosphor having a narrow emission band and high color purity is important.

In this study, we selected the Ho^{3+} ion as an activator of a novel green-emitting phosphor for LCD backlighting. Ho^{3+} ion has been investigated as one of promising activator for up-conversion phosphor materials, and Ho^{3+} -activated phosphors show the high up-conversion efficiency because the excited state absorption energy owing to $^5\text{I}_7 \rightarrow ^5\text{F}_4$ and $^5\text{I}_6 \rightarrow ^5\text{F}_4$ transitions of Ho^{3+} can overlap.⁷⁾⁻¹⁴⁾ However, there are scarce investigations as down-conversion phosphor for use in white LEDs because Ho^{3+} has another excited level, $^5\text{F}_5$, between the $^5\text{F}_4$ and $^5\text{S}_2$ states and $^5\text{I}_8$, and the energy gap spanning $^5\text{F}_4$, $^5\text{S}_2$, and $^5\text{F}_5$ is small (Fig. 1).¹⁵⁾⁻¹⁷⁾ Small energy band gaps generally lead to excited energy loss due to non-radiative transitions; consequently, most Ho^{3+} -doped green-emitting phosphors show low luminescence efficiency under blue light excitation. In addition, the $f-f$ transitions of Ho^{3+} are partially forbidden, and the electric dipole transitions from $^5\text{F}_4$ and $^5\text{S}_2$ to $^5\text{I}_8$, which show green emission (Fig. 1), are extremely sensitive to the symmetry of the Ho^{3+} -doping site in the host lattice.¹⁸⁾ A reduction in site symmetry generally contributes to an increase in the transition probability of the partially forbidden $4f-4f$ transitions.

Selection of a host material lacking a site of inversion symmetry in its crystal structure is important for developing a Ho^{3+} -doped phosphor with high green light emission efficiency. We

Fig. 1. Energy level diagram of Ho^{3+} .

selected $\text{Ba}_3\text{Sc}_4\text{O}_9$ as host material for the green-emitting Ho^{3+} -doped phosphor. Figure 2 shows a polyhedral representation of $\text{Ba}_3\text{Sc}_4\text{O}_9$ crystal structure illustrated by using the VESTA program.¹⁹⁾ The Sc^{3+} ions in crystal structure are coordinated by six oxygen ions and are located at sites lacking inversion symmetry.²⁰⁾ This indicates that $\text{Ba}_3\text{Sc}_4\text{O}_9$ should have a suitable structure for producing Ho^{3+} -doped phosphors. In this paper we report the preparation of novel green-emitting $\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ phosphors by a melt synthesis method using an arc imaging furnace and the characterization of their luminescence properties.

2. Experimental

BaCO_3 (purity 99.9%; Kanto Chemical, Co., Inc.), Sc_2O_3 (purity 99.99%; Shin-Etsu Chemical, Co., Ltd.), and Ho_2O_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^{3+} content was then

[†] Corresponding author: K. Toda; E-mail: ktoda@eng.niigata-u.ac.jp

[‡] This paper was submitted to the special issue of "Cutting edge research on electroceramics 2014"

Fig. 2. Polyhedral representation of the $\text{Ba}_3\text{Sc}_4\text{O}_9$ structure.

Fig. 3. (a) XRD patterns of $\text{Ba}_3\text{Sc}_4\text{O}_9$ and $\text{Ba}_3(\text{Sc}_{0.94}\text{Ho}_{0.06})_4\text{O}_9$ samples synthesized by solid-state reaction and melt synthesis methods. The XRD pattern of $\text{Ba}_3\text{Sc}_4\text{O}_9$ obtained from the crystal structure is shown for comparison. (b) Enlargement of XRD patterns in the region of $2\theta = 45$ degrees.

adjusted to between 2 and 9 mol % [$\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ ($0.02 \leq x \leq 0.09$)], 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 by using a spectrofluorometer (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-5310MVB). Elemental mapping of Ho, Sc, and Ba was carried out using an electron probe micro-analyzer (EPMA) (Shimadzu, EPMA8705).

3. 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 $\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ ($x = 0$ and 0.06) synthesized by the melt synthesis and solid-state reaction methods. The XRD simulation pattern of $\text{Ba}_3\text{Sc}_4\text{O}_9$ obtained in our previous study by Rietveld refinement analysis also is shown in Fig. 3 as a reference.²⁰⁾ The XRD patterns of the $\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$

Fig. 4. Excitation spectra (left) and emission spectra (right) of $\text{Ba}_3(\text{Sc}_{0.94}\text{Ho}_{0.06})_4\text{O}_9$ samples synthesized by melt synthesis (solid line) and solid-state reaction (dotted line) methods.

O_9 ($x = 0$ and 0.06) samples synthesized by the melt synthesis and solid-state reaction methods were well indexed to a single-phase rhombohedral $\text{Ba}_3\text{Sc}_4\text{O}_9$ structure. Peak shifts to lower diffraction angle were observed for both $\text{Ba}_3(\text{Sc}_{0.94}\text{Ho}_{0.06})_4\text{O}_9$ samples relative to un-doped $\text{Ba}_3\text{Sc}_4\text{O}_9$. The above results indicate that Ho^{3+} ions have been successfully substituted in the Sc^{3+} sites of the host $\text{Ba}_3\text{Sc}_4\text{O}_9$ lattice to form solid solutions. The ionic radius of Ho^{3+} (0.0901 nm for six-coordination)²¹⁾ is larger than that of Sc^{3+} (0.0745 nm for six-coordination),²¹⁾ whereas it is much smaller than that of Ba^{2+} (0.1470 nm for 9-coordination and 0.1570 nm for 12-coordination).²¹⁾ Even though the $\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ samples exhibited similar compositions, the XRD peaks of the melt synthesis sample are located at a lower diffraction angle compared to those of the sample synthesized by solid state reaction [Fig. 3(b)]. This is attributed to the rapid cooling that occurs in the melt synthesis using an arc imaging furnace.^{22,23)}

Figure 4 shows the excitation and emission spectra of $\text{Ba}_3(\text{Sc}_{0.94}\text{Ho}_{0.06})_4\text{O}_9$ phosphors synthesized by the solid-state reaction and melt synthesis methods. The excitation spectra are composed of sharp peaks arising from the following $4f-4f$ transitions of Ho^{3+} : 363 nm ($^1\text{I}_8 \rightarrow ^3\text{H}_6, ^3\text{D}_2$), 388 nm ($^5\text{I}_8 \rightarrow ^3\text{G}_4, ^3\text{K}_7$), 422 nm ($^5\text{I}_8 \rightarrow ^5\text{G}_5$), 455 nm ($^5\text{I}_8 \rightarrow ^5\text{G}_6$), 468 nm ($^5\text{I}_8 \rightarrow ^5\text{F}_2, ^3\text{K}_8$), and 491 nm ($^5\text{I}_8 \rightarrow ^5\text{F}_3$). The emission spectra are composed of sharp peaks at 555 nm ($^5\text{F}_4, ^5\text{S}_2 \rightarrow ^5\text{I}_8$) and 662 nm ($^5\text{F}_5 \rightarrow ^5\text{I}_8$) due to $4f-4f$ transitions of Ho^{3+} .²⁴⁾ 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 the solid-state reaction. The reason for this improvement is attributed to the high dispersion of Ho^{3+} in the sample prepared by melt synthesis.^{22,23)}

To investigate the dispersion of Ho^{3+} ions in both $\text{Ba}_3(\text{Sc}_{0.94}\text{Ho}_{0.06})_4\text{O}_9$ samples, X-ray mapping images of Ba, Sc, and Ho were measured by EPMA. The results are shown in **Fig. 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.²⁵⁻²⁸⁾

Figure 6 shows the dependence of emission intensity on Ho^{3+} concentration in $\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ 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

Fig. 5. EPMA images of $\text{Ba}_3(\text{Sc}_{0.94}\text{Ho}_{0.06})_4\text{O}_9$ samples synthesized by solid-state reaction (a) and melt synthesis (b).

Fig. 6. Dependence of emission intensity on Ho^{3+} concentration in $\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ samples (filled squares: solid-state reaction method, $0.03 \leq x \leq 0.09$; filled circles: melt synthesis method, $0.02 \leq x \leq 0.08$).

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 $\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ 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 $\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ samples prepared by melt synthesis.

Figure 7 shows the temperature dependence of the relative emission intensities of $\text{Ba}_3(\text{Sc}_{0.94}\text{Ho}_{0.06})_4\text{O}_9$ 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.²⁹⁾ At 150°C the emission

Fig. 7. Temperature dependence of relative emission intensities for $\text{Ba}_3(\text{Sc}_{0.94}\text{Ho}_{0.06})_4\text{O}_9$ samples prepared by melt synthesis and solid-state reaction methods.

Fig. 8. SEM images of $\text{Ba}_3(\text{Sc}_{0.94}\text{Ho}_{0.06})_4\text{O}_9$ samples synthesized by solid-state reaction (a) and melt synthesis (b) methods.

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 $\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ phosphor prepared by melt synthesis method has a greater resistance to the thermal quenching effect.

Figure 8 shows SEM images of $\text{Ba}_3(\text{Sc}_{0.94}\text{Ho}_{0.06})_4\text{O}_9$ 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

$\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ phosphors were successfully synthesized in a single-phase form by a melt synthesis method. The photoluminescence of $\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ phosphors shows green light emission under blue light irradiation. The emission intensity of the phosphor prepared by melt synthesis is greater than that of the phosphor prepared by solid-state reaction. The $\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ phosphor synthesized by melt synthesis has excellent stability relative to the thermal quenching effect. Based on these results, the $\text{Ba}_3(\text{Sc}_{1-x}\text{Ho}_x)_4\text{O}_9$ 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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