Afterglow improvement of high concentration Dy\(^{3+}\) co-doped SrAl\(_2\)O\(_4\):Eu\(^{2+}\) phosphor prepared by H\(_3\)BO\(_3\) free synthesis using melt quenching method

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Melt quenching method was applied to prepare the long persistent phosphor SrAl\(_2\)O\(_4\):Eu\(^{2+}\),Dy\(^{3+}\), and Dy\(^{3+}\) concentration dependence of afterglow property was investigated. Melt quenched SrAl\(_2\)O\(_4\):Eu\(^{2+}\),Dy\(^{3+}\) phosphors exhibit brighter afterglow intensity compared with these synthesized by a conventional solid-state reaction method. The afterglow property was improved with increase of Dy\(^{3+}\) concentration, and 10 mol % Dy\(^{3+}\) co-doped sample exhibits approximately 1.3 times higher afterglow intensity than commercially available phosphor.

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1. Introduction

Long persistent phosphors are materials showing continuous luminescence for several hours after ceasing excitation light irradiation and have been used as luminous pigments for watch dials and emergency signs. Dy\(^{3+}\) co-doped SrAl\(_2\)O\(_4\):Eu\(^{2+}\) (SAO:ED) phosphors are the most famous long persistent phosphor and have been widely applied over the world.\(^1\) Eu\(^{2+}\)-doped SrAl\(_2\)O\(_4\) phosphors exhibit bright green emission corresponding to 4f\(^7\) \(\longrightarrow\) 4f\(^6\)5d\(^1\) transition of Eu\(^{2+}\) ions under UV-light irradiation, and slightly afterglow.\(^2\) This phosphor slightly afterglows for a few seconds, and the Dy\(^{3+}\) co-dopant significantly extends the afterglow time to several hours.

Although various afterglow mechanisms of the long persistent phosphors have been proposed, the electron trapping-detrapping model has been widely accepted and explained below two steps (Fig. 1).\(^3\)–\(^6\) 1) Electron carriers generated by excitation light irradiation are captured in electron traps which located just below the bottom of conduction band (CB) in the band gap. Trapping and detrapping routes of electron carriers are considered to be via CB or tunneling process.\(^5\)–\(^7\) In the case of SAO:ED phosphors, Dy\(^{3+}\) ions or defects generated by adding Dy\(^{3+}\) addition can act as electron traps.\(^5\)–\(^6\),\(^8\)–\(^10\) 2) After ceasing the excitation, captured electron carriers are released from electron traps by thermal stimulation and afterglow is observed by the electron–hole recombination at luminescent centers. The thermal energy required to release electron carriers from traps corresponds to the energy gap between the bottom of CB and traps. Therefore, practical long persistent phosphors are required an appropriate trap depth that can be thermally stimulated at room temperature. In SAO:ED phosphors, Dy\(^{3+}\) co-dopant plays a role in enhancing afterglow property by charging electrons into the appropriate trap depth. In previous studies, many researchers choose 1 mol % Eu\(^{2+}\) and 2 mol % Dy\(^{3+}\) for doping rates of SAO:ED phosphors, and the information on Dy\(^{3+}\) concentration dependence of the afterglow property is limited.

The conventional synthesis method of SAO:ED phosphors is a high-temperature solid-state reaction (SSR) in a...
reducing atmosphere. Although various low-temperature synthesis methods such as a sol–gel method, a combustion method and a microwave method were also applied to the synthesis of SAO:ED phosphors, the improvement of the afterglow property cannot be realized.\textsuperscript{11) } It is widely known that the afterglow property of SAO:ED phosphors is significantly improved by adding a small amount of H\textsubscript{3}BO\textsubscript{3} flux.\textsuperscript{15),16) } In general, a flux is used to lower the calcining temperature and promote ion diffusion. Since the difference in valence and ionic radius (nine-coordination) between Sr\textsuperscript{2+} (r = 1.31 Å) and Dy\textsuperscript{3+} (r = 1.083 Å) ions, a solid solubility of Dy\textsuperscript{3+} ions for Sr\textsuperscript{2+} sites in SrAl\textsubscript{2}O\textsubscript{4} host are quite limited.\textsuperscript{17) } The Dy/Sr atomic ratio inside phosphor grains is less than 1 at.%, and Dy remains on the grain boundaries.\textsuperscript{18)–20} Considering the effect of the H\textsubscript{3}BO\textsubscript{3} flux to promote ion diffusion, the solid solubility of Dy\textsuperscript{3+} ions and the afterglow property of SAO:ED phosphors are expected to depend on their synthesis temperature.

In the present study, a melt quenching (MQ) method was applied to the synthesis of SAO:ED phosphors, and the Dy\textsuperscript{3+} concentration dependence of these afterglow properties was investigated. The MQ method promotes homogeneous diffusion for a very small number of ions such as Eu\textsuperscript{2+} and Dy\textsuperscript{3+} ions by liquid-phase reaction at high-temperature. Moreover, the quenching process from melts provides metastable phases that cannot be synthesized by the SSR method. The present study suggests the solid solubility of Dy\textsuperscript{3+} ions into SrAl\textsubscript{2}O\textsubscript{4} host was increased by applying the MQ method. The high concentration Dy\textsuperscript{3+} co-doped SrAl\textsubscript{2}O\textsubscript{4}:Eu\textsuperscript{2+} phosphor exhibits brighter afterglow intensity than the commercially available SAO:ED phosphor.

2. Experimental procedure

The Sr\textsubscript{0.99-x}Al\textsubscript{2}O\textsubscript{4}:Eu\textsubscript{x}, Dy\textsubscript{y} (SAO:ED\textsubscript{y}-MQ; x = 0.02, 0.06 and 0.10) phosphors were synthesized by the MQ method using an arc-imaging furnace (SAO:ED\textsubscript{y}-MQ). The arc-imaging furnace equips a hemisphere aluminum mirror and a 6 kW xenon (Xe) arc lamp as a light source (Fig. 2). The high-energy light emitted from the Xe arc lamp is reflected and concentrated on the sample by the surrounding aluminum mirror, and the temperature of the sample reaches approximately 2000 °C instantly. Chemical reagents SrCO\textsubscript{3} (99.9 %), γ-Al\textsubscript{2}O\textsubscript{3} (99.9 %), Eu\textsubscript{2}O\textsubscript{3} (99.99 %), Dy\textsubscript{2}O\textsubscript{3} (99.99 %) and H\textsubscript{3}BO\textsubscript{3} (99.9 %) were used as starting materials. The starting materials were mixed in acetone using an agate mortar. The mixed powders were placed on a water-cooled sample stage in a sample chamber filled with reduction gas (5 vol.% H\textsubscript{2}-95 vol.% N\textsubscript{2}) and melted by the radiation of the 6 kW Xe arc lamp for 10 s. The molten samples were obtained by removing the sample stage from the focus of the mirror. The SAO:ED\textsubscript{y} (x = 0.02 and 0.10) phosphors were also synthesized by the SSR method at 1400 °C for 4 h in the same reduction atmosphere using a horizontal tube furnace (SAO:ED\textsubscript{y}-SSR).

The crystalline phase of samples was identified by X-ray diffraction (XRD) using an X-ray diffractometer (MX-Labo, Mac Science Co., Ltd.) with monochromatic Cu K\textalpha radiation (\(\lambda = 0.154056\) nm) under 25 mA and 40 kV. The microstructure and elemental mapping of the molten samples were observed using a scanning electron microscope (SEM) with an energy dispersive X-ray spectrometry (EDS) analyzer (JCM-6000 with JED-2300, JEOL). Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured at room temperature using a spectrofluorometer (FP-6500/FP-6600, Josco Inc.) with a 150 W Xenon lamp. Afterglow decay curves were also measured by using the same spectrofluorometer with a heating apparatus.

3. Results and discussion

The arc-imaging furnace melts roughly 0.05 g of raw materials at a time and the molten sample is usually obtained in a spherical shape with a diameter of 3–5 mm [Figs. 3(a) and 3(b)]. As spherical samples were obtained by rapid solidification from a melt, these samples are polycrystalline. The spherical samples were ground into powder with an alumina mortar before measurement.

Figure 3(c) shows XRD patterns of SAO:ED\textsubscript{y}-MQ (x = 0.02, 0.06 and 0.10) phosphors. SrAl\textsubscript{2}O\textsubscript{4} has hexagonal (high-temperature phase) and monoclinic (low-temperature phase) polymorphs, and phase transition from monoclinic to hexagonal occurs at 650 °C.\textsuperscript{21)} The monoclinic phase is...
generally reported as a long persistent phosphor and only monoclinic SrAl2O4 was obtained in this study. In $x = 0.06$ and 0.10, the diffraction peaks of DyAlO3 were also observed as an impurity phase. SAO:ED$_x$-SSR phosphors also show the same diffraction peaks at each $x$ value.

In order to observe the microstructure of SAO:ED$_x$-MQ phosphors, spherical samples were polished to expose the cross section, and a backscattered electron image (BEI) and an elemental mapping were measured by using the SEM with EDS analyzer. Figures 4(a) and 4(b) shows the microstructure of SAO:ED$_{0.02}$-MQ and SAO:ED$_{0.10}$-MQ phosphors, respectively. Darker phases surrounded by brighter phases were observed from both BEI. According to the XRD patterns, SrAl2O4 was obtained in this study. In generally reported as a long persistent phosphor and only mono-

pecular transition which is allowed only in the case that Dy$^{3+}$ ions locate at the low symmetry sites without an inversion center.25-27 Since monoclinic SrAl2O4 contains low-symmetry Sr sites with C1 point group, the hypersensitive transition is due to Dy$^{3+}$ ions located at Sr sites.25

![Fig. 4. BEI and element mapping (Sr, Al, Eu, Dy) images of (a) SAO:ED$_{0.02}$-MQ and (b) SAO:ED$_{0.10}$-MQ phosphor.](image)

![Fig. 5. PLE and PL spectra of SAO:D$_x$ ($x = 0.02$ and 0.10) and DyAlO$_3$ synthesized by each method. Figure 5 shows PLE and PL spectra of SAO:D$_x$ ($x = 0.02$ and 0.10) phosphors and DyAlO$_3$ were also synthesized by each method. Figure 5 shows PLE and PL spectra of SAO:D$_x$ ($x = 0.02$ and 0.10) phosphors and DyAlO$_3$ were also synthesized by each method.](image)

| Sample | Area | Atomic ratio | Composition |
|--------|------|--------------|-------------|
| SAO:ED$_{0.02}$ | 1 | Sr 1 | 1.92 | $2.10 \times 10^{-3}$ | $4.89 \times 10^{-3}$ | Sr$_{0.9}$(Eu$_{0.01}$)Dy$_{0.09}$AlO$_4$ |
| | 2 | Al 1 | 1.63 | $7.83 \times 10^{-2}$ | 0.351 |
| SAO:ED$_{0.10}$ | 3 | Sr 1 | 1.88 | $1.84 \times 10^{-3}$ | $2.14 \times 10^{-2}$ | Sr$_{0.92}$(Eu$_{0.005}$)Dy$_{0.005}$AlO$_4$ |
| | 4 | Al 1 | 3.42 | $9.73 \times 10^{-2}$ | 2.47 |

![Table 1. Results of EDS analysis at each area in SAO:ED$_x$-MQ ($x = 0.02$ and 0.10) phosphors.](image)
SOA:D_{0.02} phosphors show broad PL spectrum which overlaps with two sharp spectra associated with \(4f^{7/2} \rightarrow \ 6H_{15/2}\) and \(4f^{9/2} \rightarrow \ 6H_{13/2}\) transition. This broad emission is considered to be due to some defects in the monoclinic SrAl\(_{2}\)O\(_{4}\) host.\(^{20,30}\) From the result of the XRD pattern, SOA:ED\(_{0.10}\)-MQ phosphor contains DyAlO\(_{3}\) as an impurity phase. In the MQ method, the emission of SOA:D\(_{0.10}\)-MQ phosphor is corresponding to Dy\(^{3+}\) ions substituting the SrAl\(_{2}\)O\(_{4}\) host because the PL intensity of DyAlO\(_{3}\) is quite lower than that of SOA:D\(_{0.10}\)-MQ phosphor. Considering the result of EDS analysis, the higher PL intensity of SOA:D\(_{0.02}\)-MQ phosphor than that of SOA:D\(_{0.02}\)-MQ phosphor is due to an increase of the amount of Dy\(^{3+}\) ions incorporated into SrAl\(_{2}\)O\(_{4}\) host. On the other hand, The PL intensities of SOA:D\(_{x}\)-SSR phosphors were lower than that of SOA:D\(_{x}\)-MQ phosphor and decreased with increasing Dy concentration. This result indicates the MQ method promotes incorporating Dy\(^{3+}\) ions into SrAl\(_{2}\)O\(_{4}\) host.

**Figure 6(a)** shows PL and PLE spectra of SOA:ED\(_{x}\)-MQ (solid line) and -SSR (dashed line) phosphors. The PLE spectra show absorption bands with some peaks in the UV-light region under 400 nm. The broad greenish emission with a maximum peak at 520 nm was observed for all SOA:ED\(_{x}\) phosphors, corresponding to \(4f^{7} \rightarrow 4f^{6}5d^{1}\) transition of Eu\(^{3+}\) ions replacing Sr sites. The emission wavelength associated with \(4f^{7} \rightarrow 4f^{6}5d^{1}\) transition depends on the crystal field strength in cation sites which Eu\(^{2+}\) ions located because the crystal field splitting of 5d orbitals is affected by ligand environment. No sharp emission spectrum corresponding to Dy\(^{3+}\) ions was observed because the transition probability of \(4f^{7} \rightarrow 4f^{6}5d^{1}\) transition in Dy\(^{3+}\) ions shows much lower than that of \(4f^{7} \rightarrow 4f^{6}5d^{1}\) transition in Eu\(^{3+}\) ions. The PL intensity decreased with increasing Dy\(^{3+}\) concentration, especially in SOA:ED\(_{x}\)-MQ phosphors.

Figure 6(b) shows afterglow decay curves of SOA:ED\(_{x}\)-MQ (solid line) and -SSR (dashed line) phosphors. To discharge electrons in the trap, samples were heated up to 250°C before afterglow measurement. After cooling samples to room temperature, samples were irradiated with UV-light (\(\lambda = 365\) nm) for 5 min to charge electrons in traps. Afterglow decay curves were measured immediately after ceasing UV-light irradiation by monitoring the time dependence of the emission intensity at 520 nm. The afterglow intensities of SOA:ED\(_{x}\)-SSR phosphors decreased with increasing Dy\(^{3+}\) concentration. On the other hand, SOA:ED\(_{0.02}\)-MQ phosphors exhibit superior afterglow intensity than that of SOA:ED\(_{x}\)-SSR phosphors, and afterglow intensity improved with increasing Dy\(^{3+}\) concentration. In 1000 s after ceasing excitation light irradiation, SOA:ED\(_{0.10}\)-MQ phosphor showed about 10 times higher afterglow intensity than SOA:ED\(_{0.02}\)-MQ phosphor. Considering the PL result of SOA:D\(_{x}\) phosphors (Fig. 5), these improvements in afterglow are due to the increased trap concentration caused by the increased amount of Dy\(^{3+}\) ions incorporated into the SrAl\(_{2}\)O\(_{4}\) host. Although the increasing afterglow intensity seems to contradict the decreasing PL intensity of Eu\(^{2+}\) ions in SOA:ED\(_{x}\)-MQ phosphors, the decreased PL intensity is thought to be due to prevention of electron–hole recombination by increasing trap concentration.

The comparison of afterglow decay curves between SOA:ED\(_{x}\)-SSR (\(x = 0.02\) and 0.10) phosphors synthesized by using 5 mol % \(\text{H}_2\text{BO}_3\) flux (SOA:ED\(_{x}\)-SSRB) and SOA:ED\(_{x}\)-MQ (\(x = 0.02\), 0.06 and 0.10) phosphors is shown in Fig. 6(c). The addition of a small amount of \(\text{H}_2\text{BO}_3\) flux improved the afterglow properties of SOA:ED\(_{x}\)-SSR phosphors, and in 1000 s after ceasing excitation light irradiation, afterglow intensities of SOA:ED\(_{x}\)-SSRB phosphors were comparable to that of SOA:ED\(_{0.02}\)-MQ phosphor. However, no improvement in afterglow property of SOA:ED\(_{x}\)-SSRB phosphors with increasing Dy\(^{3+}\) concentration was observed. This result suggests that a significant improvement in afterglow property of the SOA:ED phosphors with increasing Dy\(^{3+}\) concentration requires promoted ion diffusion and is observed only when synthesized by the MQ method.

In order to compare the afterglow properties, afterglow decay curves of SOA:ED\(_{x}\)-MQ (\(x = 0.02\) and 0.10) phosphors and the commercially available SOA:ED phosphor (LumiNova\(^{®}\)/G-300M, Nemoto & Co., Ltd.) are shown in Fig. 7(a). Afterglow intensities at 1000 s after ceasing excitation light irradiation of SOA:ED\(_{x}\)-MQ phosphors and the commercially available SOA:ED phosphor exhibits approximately 1.3 times higher afterglow intensity than that of LumiNova\(^{®}\), and the bright
afterglow luminescence was visible even after ceasing UV-light irradiation [Fig. 7(d)].

4. Conclusions

The Dy concentration dependence of luminescence properties in the melt quenched SAO:ED-MQ phosphors were investigated. It was found that the MQ method increased trap concentration by promoting the incorporation of Dy³⁺ ions into SrAl₂O₄ host, and SAO:ED-MQ phosphors exhibit superior afterglow intensity than those synthesized by the SSR method. The afterglow intensity of SAO:ED-MQ phosphors improved with increasing Dy³⁺ concentration, and SAO:ED₀.₁₀-MQ phosphors show brighter afterglow intensity compared with commercially available SAO:ED phosphor. The present study proposes that the afterglow intensity of SAO:ED phosphor can be improved without H₂BO₃ flux by high-temperature synthesis using the MQ method.

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