**Synthesis of Red-emitting Phosphors Based on Gadolinium Oxysulfate by a Flux Method**

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Received January 23, 2009; Accepted June 15, 2009

Red-emitting phosphors based on gadolinium oxysulfate were synthesized in a single phase form by our original flux method using alkaline metal sulfate such as Na₂SO₄ and the 0.6Li₂SO₄–0.4Na₂SO₄ eutectic mixture, and photoluminescence properties were characterized. Addition of the flux is significantly effective to enhance the emission intensity, and the luminescent peak intensity of Gd₂O₂SO₄: 10% Eu³⁺ increased double and triples by using Na₂SO₄ and 0.6Li₂SO₄–0.4Na₂SO₄, respectively. The application of the 0.6Li₂SO₄–0.4Na₂SO₄ eutectic mixture works more effectively because the melting point (600 °C) is significantly lower than that of Na₂SO₄ (887 °C).

*Key Words*: Rare Earth Oxysulfate, Phosphor, Flux Method, Eutectic Mixture, Molten Salt

1 Introduction

Phosphors have been applied in displays and lamps and are significantly important materials in our daily life. A number of rare earth activated materials have been widely studied for their applications as phosphors. As host materials for red-emitting phosphor, rare earth oxides such as Y₂O₃, which is commonly used in tricolor fluorescent lamp and color displays because of the efficient luminescence under ultraviolet and electron beam excitation, were extensively investigated. Not only rare earth oxides, but also several rare earth compounds such as borates, phosphates, and aluminates have also been extensively investigated as the host materials of phosphor.

In our previous studies, we reported red- and green-emitting phosphors based on rare earth oxycarbonates. In the series of the oxycarbonate phosphors, a green-emitting phosphor, Gd₂O₂CO₃: 15at % Tb⁺⁺⁺, exhibited the highest relative emission intensity, which was 111% of that of a commercial LaPO₄:Ce³⁺, Tb³⁺. In the case of red-emitting phosphors, however, the maximum emission intensity compared with that of the commercial Y₂O₂Eu⁺⁺⁺ phosphor was only 27% observed in Gd₂O₂CO₃: 7at % Eu⁺⁺⁺. In order to enhance the red-emission intensity in this study, we have focused on gadolinium oxysulfate as a host material of the phosphor, because rare earth oxysulfates have higher thermal durability than that of rare earth oxycarbonates where it is advantageous for obtaining phosphor particles of high crystallinity.

It is noteworthy here that rare earth oxysulfates form a layer structure similar to that of oxycarbonates, in which the (RO₂)₂⁺⁺⁺n (R: rare earths) layers are separated by the sulfate groups (SO₄²⁻) ions in the direction of the c-axis. In this layer structure, the energy transfer from an excited Eu⁺⁺⁺ ion to another Eu⁺⁺⁺ ion across the SO₄²⁻ layer is inhibited because of the long Eu⁺⁺⁺–Eu⁺⁺⁺ distance, and accordingly, phosphors based on rare earth oxysulfates should be resistant to concentration quenching.

Furthermore, it has been commonly recognized that application of molten salt (flux) is significantly effective for the synthesis of the phosphors of high emission intensity. In the flux treatment process, surface of the phosphor powders is covered with the molten salt of the flux. A part of the surface dissolves into this liquid phase, diffuses to the particle-particle contact points, and recrystallizes there again. Furthermore, surface tension of the liquid molten salt promotes the particle aggregation. Accordingly, the addition of the flux in the preparation process can promote particle growth, and surface defects of the phosphors can be eliminated effectively, leading to the enhancement of emission intensity. In this study, therefore, a new red-emitting phosphor based on gadolinium oxysulfate, Gd₂O₂SO₄: 10at % Eu⁺⁺⁺, was synthesized by our original flux method using molten alkaline metal sulfates such as Na₂SO₄ and the 0.6Li₂SO₄–0.4Na₂SO₄ eutectic mixture, and photoluminescence properties have been characterized.

2 Experimental

The Gd₂O₂SO₄: Eu⁺⁺⁺ phosphors were synthesized by the conventional solid state reaction method. Gd₂(SO₄)₃ and Eu(SO₄)·8H₂O were mixed in a stoichiometric ratio using a mortar and the amount of Eu⁺⁺⁺ in the phosphors was adjusted to be 10at %, the mixture was calcined at 900 °C in a flow of pure N₂ gas. The precursor obtained was mixed with Na₂SO₄ (m.p. 887 °C) or the 0.6Li₂SO₄–0.4Na₂SO₄ eutectic mixture (m.p. 600 °C) in a ratio of 50 mol%, and then, the mixture was heated again at 900 °C in a flow of pure N₂ gas. The sample was washed six times with deionized water and ethanol, respectively, and then dried at room temperature.

The samples were characterized by X-ray powder diffraction (XRD, Rigaku Multiflex) to identify the crystal
structure, and the sample composition was determined by X-ray fluorescence analysis (XRF, Rigaku ZSX100e). Photoluminescence excitation and emission spectra were measured at room temperature with a spectrofluorometer (Shimadzu RF-5300PC). The emission spectra were recorded for excitation at 254 nm, and the excitation spectra were recorded for emission at 617 nm. The relative emission intensity of the Gd$_2$O$_2$SO$_4$:Eu$^{3+}$ phosphor was estimated by comparing the integrated area of the emission peak at 617 nm for Eu$^{3+}$ with that of a commercial Y$_2$O$_3$:Eu$^{3+}$ phosphor.

3 Results and Discussion

Figure 1 shows the XRD patterns for the Gd$_2$O$_2$SO$_4$:10at %Eu$^{3+}$ samples prepared in the absence or presence of the flux such as Na$_2$SO$_4$ and the 0.6Li$_2$SO$_4$–0.4Na$_2$SO$_4$ eutectic mixture. All the XRD patterns can be assigned as a single phase of the orthorhombic Gd$_2$O$_2$SO$_4$ structure and no other phase was observed. In addition, the composition of the samples was confirmed by the XRF analysis and sodium was not detected. There is a possibility that a nominal amount of lithium is contained in the samples, but it has been elucidated in our previous studies on the oxy carbonate phosphors that the luminescent properties was not affected by the existence of a nominal amount of alkaline metal compounds, which were not detected in the XRD patterns.\(^\text{27}\)

Figure 2 illustrates the excitation spectra for the Eu$^{3+}$ emission at 617 nm in the Gd$_2$O$_2$SO$_4$:10at %Eu$^{3+}$ phosphors prepared in the absence or presence of Na$_2$SO$_4$ and the 0.6Li$_2$SO$_4$–0.4Na$_2$SO$_4$ eutectic mixture. The excitation spectra of Gd$_2$O$_2$SO$_4$:10at %Eu$^{3+}$ consists of a strong broad peak from 230 to 330 nm, corresponding to charge transfer state (CTS) between Eu$^{3+}$ and O$^\text{2-}$. In addition, a number of relatively weaker peaks were observed between 300 and 500 nm, corresponding to the f$f$ transitions of Eu$^{3+}$ ion between the ground state and the excited levels of 4$^\text{f}$ configuration. Application of Na$_2$SO$_4$ or 0.6Li$_2$SO$_4$–0.4Na$_2$SO$_4$ as the flux in the preparation process was effective to enhance the intensity of the excitation peaks, particularly in the case of the 0.6Li$_2$SO$_4$–0.4Na$_2$SO$_4$ eutectic mixture.

Figure 3 depicts the emission spectra of the Gd$_2$O$_2$SO$_4$:10at %Eu$^{3+}$ phosphors prepared without flux and in the presence of Na$_2$SO$_4$ and 0.6Li$_2$SO$_4$–0.4Na$_2$SO$_4$ for the excitation at 254 nm. Characteristic luminescence corresponding to the $^5$D$_{0}$→$^7$F$_{J}$ (J = 0, 1, 2, 3, and 4) transitions of Eu$^{3+}$ is observed. Similar to the results obtained for the excitation spectra shown in Fig. 2, the emission peak intensity increased by employing the flux in the preparation process. In particular, the effect is more significant when the 0.6Li$_2$SO$_4$–0.4Na$_2$SO$_4$ eutectic mixture is employed, because the melting point of this eutectic mixture (600°C) is considerably lower than that of Na$_2$SO$_4$ (887°C) and this feature is advantageous to synthesize the phosphor of high-crystallinity, which usually shows high brightness emission. The relative emission intensities of the Gd$_2$O$_2$SO$_4$:10at %Eu$^{3+}$ phosphors prepared in this study are compared with that of a commercial Y$_2$O$_3$:Eu$^{3+}$ phosphor. As summarized in Table 1, the
Table 1  Relative emission intensity of the Gd$_2$O$_3$:SO$_4$: 
10at% Eu$^{3+}$ samples prepared in the absence and the presence of flux, in comparison with that of a commercial Y$_2$O$_3$:Eu$^{3+}$ phosphor.

<table>
<thead>
<tr>
<th>Flux</th>
<th>Relative emission intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>16</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>37</td>
</tr>
<tr>
<td>0.6Li$_2$SO$_4$-0.4Na$_2$SO$_4$</td>
<td>49</td>
</tr>
</tbody>
</table>

intensities were 16%, 37%, and 49% for the samples prepared without flux, using Na$_2$SO$_4$, and using the 0.6Li$_2$SO$_4$-0.4Na$_2$SO$_4$ eutectic mixture, respectively, and the maximum emission intensity (49%) obtained for the last sample is obviously higher than that of the oxycarbonate Gd$_2$O$_3$:CO$_2$:7at% Eu$^{3+}$ phosphor (27%).

Furthermore, the emission corresponding to the $^3$D$_{0}$→$^7$F$_{2}$ electric-dipole transition at 617 nm is more dominant than that of the $^3$D$_{0}$→$^7$F$_{1}$ magnetic-dipole transition at 586 nm and 595 nm, which indicates that Eu$^{3+}$ occupies the Gd$^{3+}$ site with no inversion symmetry. This indicates that the crystal structure of gadolinium oxysulfate is suitable for the host material of the red-emitting phosphor, because the ideal emission for a rich red color is a narrow band around 610 nm.\(^{13}\)

4 Conclusion

New red-emitting phosphors based on gadolinium oxysulfate were synthesized in a single phase by our original flux (molten salt) method using Na$_2$SO$_4$ and the 0.6Li$_2$SO$_4$-0.4Na$_2$SO$_4$ eutectic mixture. Addition of the flux is significantly effective to enhance the luminescent peak intensity of the Gd$_2$O$_3$:SO$_4$:10at% Eu$^{3+}$ phosphor. In particular, the peak intensity increased triples by using the 0.6Li$_2$SO$_4$-0.4Na$_2$SO$_4$ eutectic mixture, because the melting point (600 °C) is significantly lower than that of Na$_2$SO$_4$ (887 °C).

Acknowledgement

This research was partially supported by a Grant-in-Aid for Science Research (No. 19750171) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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