Photoluminescence features of new Eu$^{3+}$-doped Gd$_4$Mo$_7$O$_{27}$ phosphors synthesized using glass crystallization technique

Mikiya Kotaka, Tsuyoshi Honma and Takayuki Komatsu

Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Japan

ABSTRACT

New Eu$^{3+}$-doped Gd$_4$Mo$_7$O$_{27}$ crystals (the molar ratio of Gd$_2$O$_3$/MoO$_3$ = 1/3.5) with a monoclinic structure C2/c (an inversion symmetry) were synthesized through the crystallization of xEu$_2$O$_3$·(18.89-x)Gd$_2$O$_3$·6.11MoO$_3$·15B$_2$O$_3$·1Al$_2$O$_3$ glasses (x = 0.0472 and 1.889) and photoluminescence (PL) emissions of Eu$^{3+}$ ions were measured for the first time. The crystallized glass with no Eu$_2$O$_3$ addition (x = 0) showed a blue color under the irradiation of ultra-violet light with a wavelength of λ = 254 nm, the emitting color of the crystallized glass with x = 0.0472 was pink, and that of the crystallized glass with x = 1.889 was orange. The charge transfer (CT) of O$^2-$→Mo$^{6+}$ providing broad peaks centered at around 325 nm was observed in the crystallized glasses. The peak intensity at 591 nm for the $^5D_0$→$^7F_2$ transition of Eu$^{3+}$ ions in the crystallized glasses with x = 0.0472 and 1.889 was very close to that at 615 nm for the $^5D_0$→$^7F_2$ transition for the excitation of $\lambda_{ex}$ = 394.5 nm. We propose potential of Gd$_4$Mo$_7$O$_{27}$ as a new host crystal for rare-earth-doped phosphors.

1. Introduction

Excellent photoluminescence (PL) performances of rare-earth (RE) ions in glasses and crystals have been achieved through the design of the coordination and bonding states of RE ions. RE$^{3+}$-doped molybdenum oxide (MoO$_3$)-based materials such as Eu$^{3+}$-doped CaMoO$_4$ and Gd$_{2-x}$Eu$_x$(MoO$_4$)$_2$ have been regarded as excellent phosphors emitting intense red light [1,2]. Very recently, the present authors [3] succeeded in synthesizing new crystallized glasses consisting of Gd$_4$Mo$_7$O$_{27}$ crystals (the molar ratio Gd$_2$O$_3$/MoO$_3$ = 1/3.5) using the composition designed Gd$_4$Mo$_{15}$O$_{27}$-B$_2$O$_3$ glasses with Gd$_2$O$_3$/MoO$_3$ = 1/3.5. The Gd$_4$Mo$_7$O$_{27}$ crystalline phase has not been reported in the phase diagram for the binary Gd$_2$O$_3$-MoO$_3$ system [4]. Naruke and Yamase [5] found a new crystalline phase of Gd$_4$Mo$_7$O$_{27}$ with a monoclinic structure C2/c through the pyrolysis of [Gd$_2$(H$_2$O)$_{12}$MoO$_{27}$].8H$_2$O at 750°C for 2 h in air. They also reported the synthesis of Eu$_{0.0472}$Mo$_4$O$_{27}$ crystals using a pyrolysis technique similar to the synthesis of Gd$_4$Mo$_7$O$_{27}$ [6]. From the perspectives of PL performances of RE$^{3+}$ ions, Gd$_4$Mo$_7$O$_{27}$ crystal is very attractive as host medium, because it has an inversion symmetry in the crystal structure [5] and the maximum phonon energy of this crystal based on MoO$_3$ is expected to be small [3]. RE$^{3+}$-doped Gd$_4$Mo$_7$O$_{27}$ crystals are, therefore, expected to be new phosphors emitting intense PL light.

The purpose of this study is to synthesize Eu$^{3+}$ doped Gd$_4$Mo$_7$O$_{27}$ crystals through the crystallization of Gd$_2$O$_3$-MoO$_3$-B$_2$O$_3$ glasses and to clarify PL features of Eu$^{3+}$ ions in MoO$_3$-based crystallized glasses. There has been no report on PL properties of RE$^{3+}$-doped Gd$_4$Mo$_7$O$_{27}$ crystals so far. In this study, we propose potential of Gd$_4$Mo$_7$O$_{27}$ as a new host crystal for RE$^{3+}$-doped phosphors.

2. Experimental

The nominal compositions (molar ratio) of glasses synthesized in this study were 18.89Gd$_2$O$_3$·6.11MoO$_3$·15B$_2$O$_3$·1Al$_2$O$_3$ glass (designated here as Glass #1(Eu$_2$O$_3$ = 0), 0.0472Eu$_2$O$_3$·18.8417Gd$_2$O$_3$·6.11MoO$_3$·15B$_2$O$_3$·1Al$_2$O$_3$ glass (designated here as Glass #2(Eu$_2$O$_3$ = 0.0472), and 1.889Eu$_2$O$_3$·17Gd$_2$O$_3$·6.11MoO$_3$·15B$_2$O$_3$·1Al$_2$O$_3$ glass (designated here as Glass #3(Eu$_2$O$_3$ = 1.889). In the previous paper [3], the base glass with the chemical composition of 18.89Gd$_2$O$_3$·6.11MoO$_3$·15B$_2$O$_3$·1Al$_2$O$_3$, i.e. Glass #1(Eu$_2$O$_3$ = 0), was proposed for new crystallized glasses consisting of Gd$_4$Mo$_7$O$_{27}$ crystals. The chemical compositions of Glass #2(Eu$_2$O$_3$ = 0.0472) and Glass #3 (Eu$_2$O$_3$ = 1.889) for Gd$_4$Mo$_7$O$_{27}$ crystal correspond to Eu$_{0.0472}$Gd$_{3.99}$Mo$_{14.11}$O$_{27}$ and Eu$_{1.889}$Gd$_{3.6}$Mo$_{14.4}$O$_{27}$, respectively. Commercial powders of reagent grade Eu$_2$O$_3$, Gd$_2$O$_3$, MoO$_3$, B$_2$O$_3$, and Al$_2$O$_3$ were used as starting materials, and their mixtures were melted in a platinum crucible at 1100°C for 30 min in an electric furnace. The melts were poured onto an iron plate and pressed to a thickness of ~1.5 mm by another iron plate.

CONTACT Takayuki Komatsu komatsu@mst.nagaokaut.ac.jp

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The glass transition ($T_g$) and crystallization peak ($T_p$) temperatures were determined using differential thermal analysis (DTA) at a heating rate of 10 K/min. The as-quenched glasses were annealed at $-T_g$ for 30 min to release internal stress and then polished mechanically to a mirror finish with CeO$_2$ powders. Optical absorption spectra at room temperature for the glasses were measured with a spectrometer (SHIMADZU: UV-3150). The glasses were heat-treated at different temperatures in an electric furnace, and the crystalline phases present in the crystallized samples were identified from X-ray diffraction (XRD) analysis (CuKα radiation). PL spectra at room temperature for the glasses and crystallized samples were measured with a PL spectrometer (JASCO FP-6500).

### 3. Results

#### 3.1. Formation of Eu$^{3+}$-doped Gd$_4$Mo$_7$O$_{27}$ crystals

Eu$^{3+}$-doped Gd$_4$Mo$_7$O$_{27}$ crystals were synthesized through the crystallization of the glasses in the present study. Here, as example, the results of Glass #3(Eu$_2$O$_3$ = 1.889) are described in detail. The as-quenched Glass #3(Eu$_2$O$_3$ = 1.889) has a brown color, suggesting the presence of a small amount of Mo$^{5+}$ ions [7]. The DTA patterns for bulk and powdered samples of Glass #3 (Eu$_2$O$_3$ = 1.889) are shown in Figure 1, and the values of $T_g$ = 494°C and $T_p$ = 570°C for the bulk sample and $T_g$ = 496°C and $T_p$ = 524°C for the powdered sample are obtained. A large difference in the $T_p$ values between the bulk and powder samples suggests that the surface crystallization takes place predominantly in Glass #3 (Eu$_2$O$_3$ = 1.889). The XRD patterns at room temperature for the bulk samples heat-treated at 476, 490, 590, and 640°C for 3 h in Glass #3(Eu$_2$O$_3$ = 1.889) are shown in Figure 2, suggesting the formation of the Gd$_4$Mo$_7$O$_{27}$ crystalline phase with the monoclinic structure $C2/c$ (ICDD: 01-070-9838) [5] at the surface of the samples heat-treated at 490, 590, and 640°C. The color of the sample crystallized at 640°C was white, suggesting that Mo$^{5+}$ ions present in the base glass were oxidized largely to Mo$^{6+}$ ions during the heat treatment at 640°C for 3 h in air.

The XRD pattern at room temperature for the powder (the heat-treated bulk sample was pulverized) sample heat-treated at 640°C for 3 h is shown in Figure 3, indicating that Gd$_4$Mo$_7$O$_{27}$ crystals are formed even in the inside of Glass #3 (Eu$_2$O$_3$ = 1.889). The lattice constants of the Gd$_4$Mo$_7$O$_{27}$ crystalline phase formed in the crystallization (640°C, 3 h) of Glass #3(Eu$_2$O$_3$ = 1.889) were estimated to be $a = 2.3021$ nm, $b = 1.4707$ nm, and $c = 1.4394$ nm. The crystals of Gd$_4$Mo$_7$O$_{27}$ and Eu$_2$Mg$_2$O$_{27}$ have the same structure with the monoclinic structure $C2/c$. The following lattice constant values have been reported: $a = 2.3034$ nm, $b = 1.4677$ nm, and $c = 1.4348$ nm for Gd$_4$Mo$_7$O$_{27}$ [5] and $a = 2.3031$ nm, $b = 1.4720$ nm, and
c = 1.4410 nm for Eu₄Mo₂O₂₇ [6]. It should be pointed out that the difference in the lattice constant values b and c between Gd₄Mo₂O₂₇ and Eu₄Mo₂O₂₇ is relatively large compared with the difference in the lattice constant a. Therefore, the lattice constants estimated for the crystallized sample (Figure 3) in Glass #3(Eu₂O₃ = 1.889) suggest the incorporation of Eu³⁺ ions into Gd₄Mo₂O₂₇, i.e. the formation of Eu³⁺-doped Gd₄Mo₂O₂₇ crystals. Glass #2(Eu₂O₃ = 0.0472) (bulk) has the values of \(T_g = 496°C\) and \(T_p = 570°C\), and the crystallization of Gd₄Mo₂O₂₇ was confirmed from XRD analysis as similar to Glass #3(Eu₂O₃ = 1.889).

As seen in Figure 3, the XRD peaks for the fully crystallized (640°C, 3 h) sample are still broad. At this moment, the composition design for the crystallization of RE₄Mo₂O₂₇ in Gd₄O⁷/Eu₂O₃-MoO₃-B₂O₃-Al₂O₃ glasses might not be optimal. In order to draw the decisive conclusion for the incorporation of Eu³⁺ ions into Gd₄Mo₂O₂₇ crystals from the lattice constant, further XRD analyses would be required. The formation of Eu³⁺-doped Gd₄Mo₂O₂₇ crystals in the crystallized samples of both Glass #2 (Eu₂O₃ = 0.0472) and Glass #3(Eu₂O₃ = 1.889) will be discussed more clearly from PL spectra of the crystallized samples, which will be described in the following sections.

### 3.2. PL properties of Gd₄Mo₂O₂₇ crystals

Glass #1(Eu₂O₃ = 0) with no Eu₂O₃ addition has the values of \(T_g = 507°C\) and \(T_p = 572°C\) for the bulk glass sample and was heat-treated at 580°C for 3 h in air in order to form Gd₄Mo₂O₂₇ crystals [3]. Glass #1 (Eu₂O₃ = 0) shows a brown color due to the presence of Mo⁵⁺ ions, providing not steep absorption edges. The absorption edges of \(\lambda = 468\) nm were estimated from the optical absorption spectra at room temperature for the bulk glass and heat-treated (510°C for 3 and 10 h) samples. The PL excitation spectra at room temperature for the glass and crystallized (580°C, 3 h) sample of Glass #1(Eu₂O₃ = 0) are shown in Figure 4(a), in which the wavelength of the monitoring emission light (\(\lambda_{em}\)) was 420 nm. The PL emission spectra at room temperature for these samples are shown in Figure 4(b), in which the wavelength of the excitation light (\(\lambda_{ex}\)) was 280 nm. The optical photograph for the crystallized sample during the irradiation of ultraviolet (UV) light with a wavelength of 254 nm is included in Figure 4(b), showing a blue color. In the PL emission spectrum for the crystallized sample, a broad emission peak centered at around 420 nm is observed. Furthermore, several sharp peaks are observed at around 420 and 470 nm. It is obvious that these emissions are related to the generation of blue color in the crystallized sample as shown in Figure 4(b).

![Figure 4](image_url)

**Figure 4.** PL excitation (a) (the monitoring emission: \(\lambda_{em} = 420\) nm) and emission (b) (the excitation light: \(\lambda_{ex} = 280\) nm) spectra at room temperature for Glass #1 (Eu₂O₃ = 0) and crystallized (580°C, 3 h) sample.

![Figure 3](image_url)

**Figure 3.** XRD pattern at room temperature for the powdered (the heat-treated bulk sample was pulverized) sample heat-treated at 640°C for 3 h in Glass #3(Eu₂O₃ = 1.889).
3.3. PL spectra of Eu\(^{3+}\)-doped Gd\(_4\)Mo\(_7\)O\(_{27}\) crystals

The PL excitation spectra of Eu\(^{3+}\) ions for the crystallized (590°C and 630°C, 3 h) samples of Glass #2 (Eu\(_2\)O\(_3\) = 0.0472) are shown in Figure 5, in which the monitoring emission \(\lambda_{\text{em}}\) was 615 nm corresponding to the \(5D_0 \rightarrow 7F_2\) transition of Eu\(^{3+}\) ions. The broad bands having the peaks at around 260 and 325 nm are observed. The sharp peaks are observed in the range of 350–500 nm, corresponding to the 4f\(\rightarrow\)4f transitions of Eu\(^{3+}\) ions, i.e. \(7F_0 \rightarrow 5D_4\), \(7F_0 \rightarrow 5D_7\), \(7F_0 \rightarrow 5D_{40}\), \(7F_0 \rightarrow 5D_3\), and \(7F_0 \rightarrow 5D_2\) transitions.

The PL emission spectra under the excitation of \(\lambda_{\text{ex}} = 280\) nm for the base glass and the crystallized samples are shown in Figure 6. Any clear intense PL peak is not observed in the base glass. For the crystallized samples, however, the PL peaks typical to the 4f-4f transitions of Eu\(^{3+}\) ions are observed, indicating that Eu\(^{3+}\) ions are incorporated into Gd\(_4\)Mo\(_7\)O\(_{27}\) crystals, i.e. the formation of Eu\(^{3+}\)-doped Gd\(_4\)Mo\(_7\)O\(_{27}\) crystals. The PL emission peak at 591 nm corresponds to the \(5D_0 \rightarrow 7F_1\) transition of Eu\(^{3+}\), i.e. the magnetic dipole (MD) transition, and that at 615 nm corresponds to the \(5D_0 \rightarrow 7F_2\) transition of Eu\(^{3+}\), i.e. the electric dipole (ED) transition. Furthermore, the broad bands together with several sharp peaks are also observed clearly in the range of 350–550 nm. Since these broad bands are not observed in the base glass (Figure 6), the origin of the PL emissions at 350–550 nm would be related to the Eu\(^{3+}\)-doped Gd\(_4\)Mo\(_7\)O\(_{27}\) crystals. The optical photograph for the crystallized (630°C, 3 h) sample under the UV light (\(\lambda = 254\) nm) irradiation is included in Figure 6, showing a pink color. It is considered that the appearance of the pink color is the results of the combination of the PL emissions at 350–550 nm and due to the 4f-4f transitions of Eu\(^{3+}\) ions. The PL emission spectra under the excitation of \(\lambda_{\text{ex}} = 394.5\) nm for the crystallized samples are shown in Figure 7. The emission peaks corresponding to the \(5D_0 \rightarrow 7F_1\) and \(5D_0 \rightarrow 7F_2\) transitions of Eu\(^{3+}\) ions are clearly detected. It should be pointed that the peak intensity of the \(5D_0 \rightarrow 7F_1\) transition is very close to that of the \(5D_0 \rightarrow 7F_2\) transition for the excitation of \(\lambda_{\text{ex}} = 394.5\) nm. That is, the ratio (\(R\)) of the peak intensity (615 nm) of the \(5D_0 \rightarrow 7F_2\) transition to that...
(591 nm) of the $^5D_0 \rightarrow ^7F_1$ transition for Eu$^{3+}$ ions in the crystallized glasses is $R = 1.05$.

The PL excitation spectra of Eu$^{3+}$ ions for the crystallized samples of Glass #3(Eu$_2$O$_3 = 1.889$) are shown in Figure 8, in which the monitoring emission ($\lambda_{em}$) was 615 nm corresponding to the $^5D_0 \rightarrow ^7F_2$ transition. The sharp peaks corresponding to the $4f \rightarrow 4f$ transitions of Eu$^{3+}$ ions are observed, being similar to the case of Glass #2 (Eu$_2$O$_3 = 0.0472$) with a small addition of Eu$_2$O$_3$. In the PL emissions in the range of 250–350 nm, the broad band with a strong intensity appeared at about 325 nm, but it is noted that the intensity of the band at around 260 nm is weak. The excitation spectra shown in Figures 5 and 8 indicate that the PL emission in the range of 250–350 nm changes depending on the content of Eu$^{3+}$ ions in Eu$^{3+}$-doped Gd$_5$Mo$_{10}$O$_{27}$ crystals.

The PL emission spectrum under the excitation of $\lambda_{ex} = 280$ nm for the crystallized (630°C, 3 h) sample of Glass #3(Eu$_2$O$_3 = 1.889$) is shown in Figure 9. The PL emissions due to the $4f \rightarrow 4f$ transitions of Eu$^{3+}$ ions, i.e. the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions of Eu$^{3+}$ ions, are clearly observed. However, it should be pointed out that any clear peak is not detected in the range of 350–500 nm, being extremely different from the PL emission spectra observed in the crystallized samples of Glass #2(Eu$_2$O$_3 = 0.0472$) with a small addition of Eu$_2$O$_3$. The optical photograph for the crystallized (630°C, 3 h) sample under the UV light (\(\lambda = 254 \text{ nm}\)) irradiation is included in Figure 9, showing an orange color. The PL emission spectra under the excitation of $\lambda_{ex} = 394.5$ nm for the crystallized samples of Glass #3(Eu$_2$O$_3 = 1.889$) are shown in Figure 10. The PL emissions due to the $4f \rightarrow 4f$ transitions of Eu$^{3+}$ ions in Eu$^{3+}$-doped Gd$_5$Mo$_{10}$O$_{27}$ crystals are clearly observed in the crystallized (590 and 630°C) samples of Glass #3(Eu$_2$O$_3 = 1.889$). It should be pointed out that the peak intensity of the $^5D_0 \rightarrow ^7F_1$ transition is very close to that of the $^5D_0 \rightarrow ^7F_2$ transition for the excitation of $\lambda_{ex} = 394.5$ nm. The value of the peak intensity ratio is $R = 1.06$. This behavior observed in the crystallized samples of Glass #3(Eu$_2$O$_3 = 1.889$) is similar to that observed in the crystallized samples of Glass #2(Eu$_2$O$_3 = 0.0472$).
4. Discussion

Prior to the discussion of the PL features of the crystallized glasses consisting of Gd₄Mo₇O₂₇ crystals observed in the previous section, the structural features of Gd₄Mo₇O₂₇ crystal (a monoclinic structure C2/c) are described. Gd₄Mo₇O₂₇ crystal has a structure consisting of MoO₄, MoO₃₁₁, and Gd-containing layers (these layers are stacked along the c-direction) [5,6]. Looking at the structural units in more detail [5,6], seven types of MoO₄ units are present and MoO₃₁₁ group is composed of trigonal bipyramidal MoO₃ units connected to two MoO₄ tetrahedral units. Gd₄Mo₇O₂₇ is, therefore, a double-layer compound consisting of MoO₄ and MoO₃₁₁-containing layers parallel to the bc plane. Gd³⁺ ions are present at the interstitial sites between two different MoO₄- and MoO₃₁₁-containing layers and have four different oxygen coordination sites. Three different Gd³⁺ structural units are surrounded by eight oxygens with the distorted square-antiprismatic coordination, i.e. GdO₆, and one Gd³⁺ structural unit has the seven-fold oxygen coordination with an approximate monocapped trigonal prism, i.e. GdO₇. Therefore, it is regarded that Gd₄Mo₇O₂₇ has an extremely unique crystal structure compared with other RE molybdates. Furthermore, it should be pointed out that Eu₄Mo₇O₂₇ crystal has the same crystal structure and structural features as Gd₄Mo₇O₂₇ crystal [5,6], indicating the possibility of the formation of Eu₄Gd₄-Mo₇O₂₇ crystals.

In the present study, the incorporation of Eu³⁺ ions into Gd₄Mo₇O₂₇, i.e. the formation of Eu³⁺-doped Gd₄Mo₇O₂₇ crystals (Eu₄Gd₄-Mo₇O₂₇), was confirmed from PL properties. At this moment, however, the amount of Eu³⁺-doped Gd₄Mo₇O₂₇ crystals formed in the crystallized samples has not been determined, and thus, the following discussion on the PL performance obtained in the present study is qualitative. Again, we emphasize that the present study is the first report on PL properties of Eu³⁺-doped Gd₄Mo₇O₂₇ crystals.

4.1. PL features of Gd₄Mo₇O₂₇ crystals

The generation of blue color observed in the crystallized sample under the UV light (λ = 254 nm) (Figure 4) in Glass #1(Eu₂O₃ = 0) is interest. The wavelength (λ = 254 nm) of UV light is much shorter than that (λ = 468 nm) of the optical absorption edge in the heat-treated sample, suggesting the excitation of electrons in the valence band to the conduction band in Gd₄Mo₇O₂₇ crystals. The blue emission would be, therefore, closely related to the CT model [8]. That is, the CT from 2p orbitals of O²⁻ ions to 4d orbital of Mo⁶⁺ ions with the 4d⁴ electronic configuration in MoO₄ and/or MoO₅ units in Gd₄Mo₇O₂₇ is induced, and the excited electrons relax to O2p orbitals through the radiative transition, generating the broad peak centered at around 420 nm and consequently radiating blue light.

At this moment, the origin of the sharp peaks at around 420 and 470 nm (Figure 4) is not clear. However, it should be pointed out that Gd₄Mo₇O₂₇ crystal has a unique double-layer structure consisting of seven different MoO₄, MoO₅, GdO₂ and GdO₆ units. Furthermore, it is known that Gd³⁺ ions show the f-f transitions of 8S₇/₂→8I₉/₂ at around 270 nm and 8S₇/₂→8P₇/₂ at around 310 nm [9]. It is, therefore, expected that the excitation of 4f electrons in Gd³⁺ ions in Gd₄Mo₇O₂₇ crystal would be induced under the UV light (λ = 254 nm) irradiation. One possible mechanism for the origin of the sharp peaks at around 420 and 470 nm shown in Figure 4 might be related to the energy transfer between Gd³⁺ ions and MoO₄/MoO₅ structural units in Gd₄Mo₇O₂₇ crystals formed in the crystallization of 18.89Gd₂O₃·66.11MoO₃·15B₂O₃·1Al₂O₃ glass.

4.2. PL features of Eu³⁺-doped Gd₄Mo₇O₂₇ crystals

Many studies on the excitation spectra of Eu³⁺-doped molybdates suggest that the broad peak at about 240–260 nm are assigned to the CT transition from O²⁻ ions to Eu³⁺ ions, i.e. O²⁻→Eu³⁺ CT, and the broad peaks at about 260–400 nm are due to the CT transition from O²⁻ ions to Mo⁶⁺ ions in (MoO₄)²⁻, i.e. O²⁻→Mo⁶⁺ CT [10–12]. Considering the previous assignments of PL peaks of Eu³⁺ ions [8–10], the broad bands at around 260 and 325 nm in the excitation spectra (Figure 5) obtained for the crystallized samples of Glass #2(Eu₂O₃ = 0.0472) would be assigned to mainly the O²⁻→Eu³⁺ CT and O²⁻→Mo⁶⁺ CT transitions, respectively. It is noted that the intensity of the peak at around 260 nm is stronger than that at around 325 nm as shown in Figure 5, suggesting that the O²⁻→Eu³⁺ CT transition is taking place largely in Eu³⁺-doped Gd₄Mo₇O₂₇ crystals with a small amount of Eu³⁺ ions. On the other hand, as shown in Figure 8, in Eu³⁺-doped Gd₄Mo₇O₂₇ crystals formed in the crystallized glasses of Glass #3(Eu₂O₃ = 1.889) with a large amount of Eu³⁺ ions, the relative intensity of the peak at around 260 nm against the peak at around 325 nm is small. This suggests the concentration quenching of the O²⁻→Eu³⁺ CT transitions in Eu³⁺-doped Gd₄Mo₇O₂₇ crystals with a double-layered structure.

In all glasses of Glass #1(Eu₂O₃ = 0), Glass #2 (Eu₂O₃ = 0.0472) and Glass #3(Eu₂O₃ = 1.889), any detectable PL emissions of Eu³⁺ ions were not observed, and this would be due to the multi-phonon relaxation related to B₂O₃ (15 mol%) having large maximum phonon energies (1350–1480 cm⁻¹)
[13] in the glasses. The PL emissions of Eu$^{3+}$ ions are clearly detected in the crystallized samples of Glass #2(Eu$_2$O$_3$ = 0.0472) and Glass #3 (Eu$_2$O$_3$ = 1.889) under the excitations of $\lambda_{ex}$ = 280 and 394.5 nm as shown in Figures 6, 7, 9 and 10. That is, Eu$^{3+}$ ions in Eu$^{3+}$-doped Gd$_2$Mo$_5$O$_{27}$ crystals formed in the crystallization of the glasses show clear PL emissions. In the previous paper [3], the Raman scattering spectra at room temperature for the crystallized samples of the base glass, and it was found that the Raman band peaks of Gd$_2$Mo$_5$O$_{27}$ crystals appear below 1000 cm$^{-1}$ and the peak at 947 cm$^{-1}$ shows the strongest intensity. It is suggested that the maximum phonon energy of Gd$_2$Mo$_5$O$_{27}$ crystal would be around 950 cm$^{-1}$, generating clear PL emissions of Eu$^{3+}$ ions.

As one of the PL features of Eu$^{3+}$ ions in Eu$^{3+}$-doped Gd$_2$Mo$_5$O$_{27}$ crystals, it is noted that the peak intensity of the $^5_{D0} \rightarrow ^7_{F2}$ transition is very close to the intensity of the $^5_{D0} \rightarrow ^7_{F1}$ transition for the excitation of $\lambda_{ex}$ = 394.5 nm (Figures 7 and 10), i.e. R = 1.06 for Glass #2(Eu$_2$O$_3$ = 0.0472) and R = 1.06 for Glass #3(Eu$_2$O$_3$ = 1.889). Furthermore, it should be also pointed out that the increase in the Eu$^{3+}$ content, i.e. the Eu$_2$O$_3$ contents of 0.0472 mol% and 1.889 mol%, does not change the shape and peak positions of the PL emission spectra of Eu$^{3+}$ ions in the crystallized samples. Since the $^5_{D0} \rightarrow ^7_{F2}$ transition of Eu$^{3+}$ ions observed at around 615 nm is the ED transition, its peak intensity is sensitive for the local symmetry of coordination environments around Eu$^{3+}$. That is, in the coordination environments with the non-inversion site symmetry (i.e. large electric field gradients sites) for Eu$^{3+}$ sites, the intensity of the $^5_{D0} \rightarrow ^7_{F2}$ transition would be strong, and contrary, Eu$^{3+}$ ions present in the inversion symmetry sites would have weak intensities for the $^5_{D0} \rightarrow ^7_{F2}$ transition. On the other hand, the $^5_{D0} \rightarrow ^7_{F1}$ transition observed at around 591 nm is the MD transition, being not sensitive for the site symmetry of Eu$^{3+}$ ions. The crystal structure of Eu$^{3+}$-doped Gd$_2$Mo$_5$O$_{27}$ has an inversion symmetry and this structural feature would be an origin for the weak intensity of the $^5_{D0} \rightarrow ^7_{F2}$ transition, consequently providing the peak intensity ratio close to one (R~1.0) in Eu$^{3+}$-doped Gd$_2$Mo$_5$O$_{27}$ crystals formed in the crystallized samples of Glass #2 (Eu$_2$O$_3$ = 0.0472) and Glass #3(Eu$_2$O$_3$ = 1.889).

As seen in Figures 5 and 8, under the excitation of $\lambda_{ex}$ = 394.5 nm, the 4$f$ electrons of Eu$^{3+}$ ions in Eu$^{3+}$-doped Gd$_2$Mo$_5$O$_{27}$ crystals are mainly excited from the ground state $^7_{F0}$ to the excited states such as $^5_{I8}$ in which it is not necessary to consider seriously the CT transitions from O$^{2-}$ ions to Eu$^{3+}$ ions and from O$^{2-}$ ions to Mo$^{6+}$ ions, and thus the possibility of energy transfer from CT transition to the excited level of 4$f$ electron of Eu$^{3+}$ ions. In other words, PL emission spectra under $\lambda_{ex}$ = 394.5 nm shown in Figures 7 and 10 provide information on the site symmetry of Eu$^{3+}$ ions in Eu$^{3+}$-doped Gd$_2$Mo$_5$O$_{27}$ crystals more clearly compared with PL emission spectra under $\lambda_{ex}$ = 280 nm (Figures 6 and 9). The relative strong intensity of the $^5_{D0} \rightarrow ^7_{F2}$ transition for the $^5_{D0} \rightarrow ^7_{F1}$ transition of Eu$^{3+}$ ions, i.e. large R values of the peak intensity ratio, has been observed in many Eu$^{3+}$-doped molybdenum compounds such as $\beta$'-Gd$_2_3$Eu$_{242}$Mo$_{27}$ (Eu$_2$O$_3$ = 395 and 396 nm) [11,14], Eu$_2$Gd$_2$Mo$_5$O$_6$ (Eu$_2$O$_3$ = 393 nm) [15], Y$_2$(MoO$_3$)$_3$:Eu$^{3+}$ (Eu$_2$O$_3$ = 394 nm) [16], and $\alpha$-ZnMoO$_4$; Eu$^{3+}$ (Eu$_2$O$_3$ = 397 nm) [7] under the excitation of around $\lambda_{ex}$ = 395 nm. For example, Wang et al. [14] reported that Eu$^{3+}$-doped $\beta$'-Gd$_2$(MoO$_3$)$_3$ crystals synthesized through the crystallization of Eu$_2$O$_3$-Gd$_2$Mo$_5$O$_{27}$-MoO$_3$-B$_2$O$_3$ glasses show the intense PL emissions corresponding to the $^5_{D0} \rightarrow ^7_{F2}$ transition of Eu$^{3+}$ ions under $\lambda_{ex}$ = 396 nm. It should be pointed out that $\beta$'-Gd$_2$(MoO$_4$)$_3$ crystal has an orthorhombic structure and shows ferroelectric and second-order non-linear optical properties due to the birefringence, i.e. the non-inversion symmetry of host material, which is different largely from Gd$_2$Mo$_5$O$_{27}$ crystal with the inversion symmetry. Furthermore, compared with $\beta$'-Gd$_2$(MoO$_4$)$_3$ with the molar ratio of Eu$_2$O$_3$/MoO$_3$ = 1/3, it should be pointed out that Gd$_2$Mo$_5$O$_{27}$ crystal with Gd$_2$O$_3$/MoO$_3$ = 1/3.5 includes more MoO$_3$ content, i.e. the relatively weak single bond strength (384 kJ/mol) of Mo-O bonds [17] and probably low maximum phonon energies [3], which will be an advantage as host materials for PL performance of doped RE$^{3+}$ ions.

It is known that Gd$^{3+}$ ion has a very high absorption coefficient in the UV region due to the excitations to the excited levels such as $^6$P$_1$ (usually centered at about $\lambda$ = 275 nm) and $^4$I$_{1}(\text{at about } \lambda = 310 \text{ nm})$ from the ground state $^8$S$^7/2$ and can transfer energy to other RE$^{3+}$ ions such as Eu$^{3+}$ ions [9,18,19]. Eu$^{3+}$-doped Gd$_2$Mo$_5$O$_{27}$ crystals contain both Gd$^{3+}$ and Eu$^{3+}$ ions. The effect of Gd$^{3+}$ ions on PL emissions of Eu$^{3+}$ ions in Eu$^{3+}$-doped Gd$_2$Mo$_5$O$_{27}$ crystals is, however, unclear from the present study. It is desired to synthesize Eu$_2$Mo$_5$O$_{27}$ crystals using the glass crystallization technique and to clarify PL performances of Eu$^{3+}$ ions.

5. Conclusions

The Eu$^{3+}$-doped Gd$_2$Mo$_5$O$_{27}$ crystals were synthesized through the crystallization of xEu$_2$O$_3$-(18.89-x)Gd$_2$O$_3$-66.11MoO$_3$-15B$_2$O$_3$-1Al$_2$O$_3$ glasses, i.e. Glass #1(Eu$_2$O$_3$ = 0), Glass #2(Eu$_2$O$_3$ = 0.0472), and Glass #3(Eu$_2$O$_3$ = 1.889), and PL emissions of Eu$^{3+}$ ions were measured for the first time. The crystallized
glasses showed the following colors under the irradiation of UV light with \( \lambda = 254 \) nm; blue for the base glass, pink for the Glass \#2(\( \text{Eu}_2\text{O}_3 = 0.0472 \)), and orange for Glass \#3(\( \text{Eu}_2\text{O}_3 = 1.889 \)). The CT of \( \text{O}^2- \rightarrow \text{Mo}^{6+} \) providing broad peaks centered at around 325 nm was observed in the crystallized glasses. The peak intensity of the \( ^3\text{D}_0 \rightarrow ^7\text{F}_2 \) transition of Eu\(^{3+} \) ions in the crystallized glasses with Eu\(^{3+} \)-doped \( \text{Gd}_2\text{MoO}_7\text{O}_{27} \) crystals was very close to that of the \( ^3\text{D}_0 \rightarrow ^7\text{F}_2 \) transition for the excitation of the \( \lambda_{ex} = 394.5 \) nm, resulting from the structural features of \( \text{Gd}_2\text{MoO}_7\text{O}_{27} \) crystals with an inversion symmetry. We propose potential of \( \text{Gd}_2\text{MoO}_7\text{O}_{27} \) as a new host crystal for RE\(^{3+} \)-doped phosphors.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

This work was supported by JSPS KAKENHI Grant No. 17H03387.

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