Magnetism of β' -Gd₂(MoO₄)₃ and photoluminescence of β' -Eu₂(MoO₄)₃ crystallized in rare-earth molybdenum borate glasses

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Ferroelastic β' -Gd₂(MoO₄)₃ and β' -Eu₂(MoO₄)₃ crystals were synthesized through the crystallization of 21.25Gd₂O₃-63.75MoO₃-15B₂O₃ glass and 22.5Eu₂O₃-47.5MoO₃-30B₂O₃ glass, respectively, and their magnetism and photoluminescence properties were examined. It was demonstrated from the temperature dependence of the magnetic susceptibility and specific heat down to $T = 1.8$ K that the magnetic state of Gd³⁺ ions in the crystallized samples, i.e., in the β' -Gd₂(MoO₄)₃ crystals and the residual glasses, is paramagnetic and any magnetic interaction is not formed among Gd³⁺ ions down to $T = 1.8$ K, i.e., the effective magnetic moment of $\mu_{\text{eff}} = 7.94 \mu_B$ and Weiss constant of $\theta = -0.3$ K. Photoluminescence (PL) of Eu³⁺ ions was clearly observed in the crystallized samples, although the melt-quenched glass did not show any photoluminescence. The present study proposes that the concentration quenching among Eu³⁺ ions in β' -Eu₂(MoO₄)₃ crystals is small and β' -RE₂(MoO₄)₃ crystals would be good hosts for PL emissions of RE³⁺.

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1. Introduction

Nowadays, new phosphors have received much attention, because they are inevitable for the next generation of solid-state lighting technology applying light-emitting diodes (LED) as energy source or excitation light. Rare-earth ions (RE³⁺) such as Er³⁺ and Eu³⁺ are good activators covering various wavelengths in light emissions, and thus many RE³⁺-doped phosphors have been reported not only in crystalline materials but also in glasses so far. Because photoluminescence (PL) performances of RE³⁺ in materials depend largely on their site environments (crystal fields), it is of importance to clarify the coordination and bonding states of RE³⁺ in materials.^{1)–5)} One of the most important guidelines for the design of host materials providing excellent PL performances for doped RE³⁺ is to use materials having low phonon energies, because the degree of non-radiative relaxation of RE³⁺ in such hosts is expected to be small.^{6),7)} In this point of view, for example, PL properties of RE³⁺-doped fluoride materials having low phonon energies have been extensively studied so far.^{6),8)–11)}

RE³⁺-doped molybdates such as Gd₂(MoO₄)₃, CaMoO₄, BaGd₂(MoO₄)₄, and ZnMoO₄ have been proposed to be good candidates as phosphors.^{12)–15)} Because the single bond strength of Mo–O bonds, $B_{\text{M-O}}$, is not so strong, i.e., $B_{\text{M-O}} = 384$ kJ/mol,¹⁶⁾ it is expected that MoO₃-based materials have low phonon energies and thus would be good hosts for RE³⁺. The present authors' group has demonstrated that ferroelastic β' -RE₂(MoO₄)₃ crystals with RE = Sm, Gd, Dy, and Tb are easily synthesized through the

crystallization of RE₂O₃–MoO₃–B₂O₃ glasses.^{17)–22)} In particular, lines consisting of β' -RE₂(MoO₄)₃ crystals with high orientations have been patterned at the glass surface by cw Nd:YAG laser with a wavelength of $\lambda = 1064$ nm or Yb:YVO₄ fiber laser with $\lambda = 1080$ nm.^{17),18),21),22)} It is of interest to clarify PL properties of ferroelastic β' -RE₂(MoO₄)₃ crystals. Because a large amount of RE³⁺ ions is included in β' -RE₂(MoO₄)₃ as a main constituent, it is also of importance to clarify magnetic properties of β' -RE₂(MoO₄)₃ crystals formed in the crystallization of RE₂O₃–MoO₃–B₂O₃ glasses. Magnetic interactions between RE³⁺ ions would provide important information (e.g., the so-called concentration quenching among RE³⁺ ions) on PL properties of crystallized samples with β' -RE₂(MoO₄)₃ crystals.

The purpose of this study is to clarify the magnetism of β' -Gd₂(MoO₄)₃ and photoluminescence of β' -Eu₂(MoO₄)₃ synthesized through the crystallization of RE₂O₃–MoO₃–B₂O₃ glasses. In the present study, it was demonstrated from the temperature dependence of the magnetic susceptibility and specific heat down to $T = 1.8$ K that the magnetic state of Gd³⁺ ions in the crystallized sample, i.e., in the β' -Gd₂(MoO₄)₃ crystals and the residual glasses, is paramagnetic and any magnetic interaction is not formed among Gd³⁺ ions down to $T = 1.8$ K. It was also clarified that the concentration quenching among Eu³⁺ ions in β' -Eu₂(MoO₄)₃ crystals is small and β' -RE₂(MoO₄)₃ crystals would be good hosts for PL emissions of RE³⁺.

2. Experimental procedures

In the previous studies,^{17)–22)} the formation and laser patterning of ferroelastic β' -RE₂(MoO₄)₃ crystals were demonstrated in the glasses of 21.25RE₂O₃–63.75MoO₃–15B₂O₃ or 22.5RE₂O₃–47.5MoO₃–30B₂O₃. In the present study, the glasses with the

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compositions of 21.25Gd₂O₃–63.75MoO₃–15B₂O₃ (designated here as GMB glass) and of 22.5Eu₂O₃–47.5MoO₃–30B₂O₃ (designated here as EMB glass) (mol%) were prepared using a conventional melt quenching technique. Commercial powders of reagent grade Gd₂O₃, Eu₂O₃, MoO₃, and B₂O₃ were used as starting materials and 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. The glass transition, T_g , and crystallization peak, T_p , temperatures were determined using differential thermal analysis (DTA) at heating rate of 10 K/min. The as-quenched glasses were annealed at $\sim T_g$ for 30 min to release internal stresses and then polished mechanically to a mirror finish with CeO₂ powders. Densities of glasses were determined with the Archimedes method using kerosene as an immersion liquid.

Glass samples were heat-treated at around crystallization peak temperatures for 5 h in an electric furnace, and the crystalline phases present in the crystallized samples were identified by X-ray diffraction (XRD) analysis (Cu K α radiation). The temperature dependence of magnetic susceptibility was measured under both zero-field cooled (ZFC) and field-cooled (FC) conditions in an applied field (H) of $H = 0.1$ T over the temperature (T) range of $T = 1.8$ –300 K using a SQUID magnetometer (Quantum Design, MPMS-5S). Samples were contained in diamagnetic capsules, and data were corrected by extracting the contribution from diamagnetic ionic susceptibility. Specific heat measurements were performed using a relaxation technique with a commercial physical property measurement system (Quantum Design, PPMS model) in the temperature range of 1.8–300 K. Samples in the form of pellet were mounted on a thin alumina plate with Apiezon N grease for better thermal contact. Heat capacities of sample were obtained by subtracting the addenda heat capacity, which had been determined in a separate run without sample. PL spectra were measured at room temperature with a Shimadzu RF-5300PC.

3. Results and discussion

3.1 Crystallization of β' -Gd₂(MoO₄)₃ and β' -Eu₂(MoO₄)₃

In XRD measurements for the melt-quenched samples prepared in this study, only a halo pattern without any sharp peak was observed, indicating that the melt-quenched samples are fully amorphous (glasses). The DTA patterns for the bulk and powdered samples of 22.5Eu₂O₃–47.5MoO₃–30B₂O₃ glass are shown in Fig. 1. The endothermic peak due to the glass transition is detected, and in the powdered sample, two exothermic peaks are observed, implying that at least two crystalline phases would be formed in heating. The values of T_g and T_{p1} were determined to be $T_g = 552^\circ\text{C}$ and $T_{p1} = 634^\circ\text{C}$ for the bulk glass with Eu₂O₃. The values of $T_g = 540^\circ\text{C}$ and $T_p = 585^\circ\text{C}$ for the bulk glass of 21.25Gd₂O₃–63.75MoO₃–15B₂O₃ were obtained.

The XRD pattern at room temperature for the sample obtained by a heat treatment at 590°C for 2 h in 21.25Gd₂O₃–63.75MoO₃–15B₂O₃ glass is shown in Fig. 2. The peaks are assigned to β' -Gd₂(MoO₄)₃ crystals (JCPDS: No. 01-070-1397). It is known that the thermodynamically stable phase in the temperatures below 800–990°C for rare-earth molybdates, RE₂(MoO₄)₃, where RE = Pr, Nd, Sm, Eu, Gd, Tb, Dy, is the α -RE₂(MoO₄)₃ phase with a monoclinic structure ($C2/c$) and the β -RE₂(MoO₄)₃ phase with a tetragonal structure ($P4_2/m$) is stable in the temperature range of $1000 < T < 1200^\circ\text{C}$.^{23–27} The β phase (paraelectric) transforms to the β' -RE₂(MoO₄)₃ phase (ferroelectric) with an orthorhombic structure ($Pba2$) below Curie temperature (T_c).²⁷

Fig. 1. DTA patterns for the bulk and powdered samples of 22.5Eu₂O₃–47.5MoO₃–30B₂O₃ glass. The heating rate was 10 K/min.

Fig. 2. XRD pattern at room temperature for the sample obtained by a heat treatment at 590°C for 2 h in 21.25Gd₂O₃–63.75MoO₃–15B₂O₃ glass. The polarization optical photograph for a crystal grain (piece) is included.

The β' -Gd₂(MoO₄)₃ phase has the value of $T_c = 163^\circ\text{C}$.²⁸ It should be emphasized that the crystalline phase formed through the crystallization of GMB glass is the ferroelectric β' -Gd₂(MoO₄)₃ phase, but not the paraelectric α -Gd₂(MoO₄)₃ phase. In Fig. 2, the polarization optical photograph for a crystal grain (piece) is included. The color is not uniform over the whole region of the grain, and the bright and dark regions with different refractive indices are formed periodically. As demonstrated from micro-Raman scattering spectra in the previous paper,¹⁹ both bright and dark regions consist of β' -Gd₂(MoO₄)₃ crystals. The XRD patterns at room temperature for the sample obtained by heat treatments at 635°C and 895°C for 5 h in 22.5Eu₂O₃–47.5MoO₃–30B₂O₃ glass is shown in Fig. 3. It is found that the first crystalline phase formed in a heat treatment at 635°C is β' -Eu₂(MoO₄)₃ crystals as similar to the case of 21.25Gd₂O₃–63.75MoO₃–15B₂O₃ glass. In the heat treatment at a high temperature of 895°C for 5 h, the formation of Eu(BO₃)₃ crystals is confirmed together with β' -Eu₂(MoO₄)₃ crystals.

The Raman scattering spectra at room temperature in the range of 300–1200 cm^{−1} for the melt-quenched glass and crystallized (635 and 895°C for 5 h) samples in 22.5Eu₂O₃–47.5MoO₃–30B₂O₃ glass are shown in Fig. 4. In the sample heat-treated at 635°C, the peaks are observed at 325, 379, 741, 813, 845, 944,

Fig. 3. XRD patterns at room temperature for the sample obtained by heat treatments at 635 and 895°C for 5 h in 22.5Eu₂O₃–47.5MoO₃–30B₂O₃ glass.

Fig. 4. Raman scattering spectra at room temperature for the melt-quenched glass and crystallized samples obtained by heat treatments at 635 and 895°C for 5 h in 22.5Eu₂O₃–47.5MoO₃–30B₂O₃ glass.

and 958 cm⁻¹. As reported by Abe et al.,¹⁷⁾ the Raman scattering spectrum at room temperature for the ferroelastic (ferroelectric) β' -RE₂(MoO₄)₃ phase with an orthorhombic structure (Pba2) is largely different from that for the paraelastic (paraelectric) α -RE₂(MoO₄)₃ phase with a monoclinic structure (C2/c), although both phases consist of REO₇ polyhedra and MoO₄ tetrahedra. It should be pointed out that the Raman peaks observed at ~741, ~813, ~845, ~944, and ~958 cm⁻¹ for the crystallized samples (Fig. 4) are assigned to stretching vibrations of Mo–O bonds in isolated (MoO₄)²⁻ tetrahedral units in β' -RE₂(MoO₄)₃ crystals,^{17)–22),29)–31)} Therefore, the Raman scattering spectra shown in Fig. 4 also indicate that the crystalline phase formed in the sample obtained by a heat treatment at 635°C for 5 h is β' -Eu₂(MoO₄)₃. It is considered that the formation of Eu(BO₂)₃ provides additional peaks at 917 cm⁻¹.

3.2 Magnetism of β' -Gd₂(MoO₄)₃ in crystallized glass

The temperature dependence of the magnetic susceptibility (χ_M) and inverse susceptibility (χ_M^{-1}) for the crystallized (590°C, 2 h) sample is shown in Fig. 5, in which the magnetization is reduced against the amount of one mol Gd ions. As can be seen in Fig. 5, ZFC and FC magnetic susceptibilities have no differences, and any anomaly is not observed. The magnetic

Fig. 5. Temperature dependence of the magnetic susceptibility (χ_M) and inverse susceptibility (χ_M^{-1}) for the crystallized sample obtained by a heat treatment at 590°C for 2 h in 21.25Gd₂O₃–63.75MoO₃–15B₂O₃ glass under the zero-field cooled (ZFC) and field-cooled (FC) conditions.

Fig. 6. Plot of the magnetization (M) against $H \cdot T^{-1}$ for the crystallized sample obtained by a heat treatment at 590°C for 2 h in 21.25Gd₂O₃–63.75MoO₃–15B₂O₃ glass. The solid line is the Brillouin function for magnetic ions with $S = 7/2$.

susceptibility obeys the Curie–Weiss law, giving the effective magnetic moment (μ_{eff}) and Weiss constant (θ) of $\mu_{\text{eff}} = 7.94 \mu_B$ and $\theta = -0.3$ K. It should be pointed out that the experimental value of $\mu_{\text{eff}} = 7.94 \mu_B$ is equal to the value of Gd³⁺ ions with the 4f electron configuration of ⁸S_{7/2}, i.e., 7.94 μ_B . It was also found that the magnetic susceptibility (χ_M) for the crystallized sample in the low temperature range of 1.8–10 K indicates no differences and no anomalies in the ZFC and FC magnetic susceptibilities. Furthermore, in the measurement of the magnetic field dependence of magnetization (M) at $T = 1.8$ K for the crystallized sample, it was found that the magnetization tends to saturate and gives the value of $M = 6.89 \mu_B$ at $H = 5$ T. This value of $M = 6.89 \mu_B$ is very close to the value of $gS = 7 \mu_B$ expected for Gd³⁺ ions with $S = 7/2$, where g is the g -factor and S is the total spin quantum number. It is also pointed out that there was no hysteresis in the magnetization curve (not shown here). The plot of the magnetization against $H \cdot T^{-1}$ for the crystallized sample is shown in Fig. 6, where the Brillouin function for magnetic ions with $S = 7/2$ is also plotted (the solid line). It is found that the experimental data almost obey the Brillouin function. These results clearly demonstrate that Gd³⁺ ions in the crystallized sample consisting of β' -Gd₂(MoO₄)₃ crystals are paramagnetic down to $T = 1.8$ K. Keve et al.²³⁾ reported that ferroelectric and ferroelastic β' -Gd₂(MoO₄)₃ remains paramagnetic down to

Fig. 7. Temperature dependence of specific heat (C_p) in zero magnetic field for the crystallized sample obtained by a heat treatment at 590°C for 2 h in 21.25Gd₂O₃–63.75MoO₃–15B₂O₃ glass. The temperature region is 1.8 to 300 K.

$T = 1.4$ K and has a magnetic moment of $7.98 \mu_B$. The results for crystallized glasses obtained in this study are well consistent with those reported by Keve et al.²³⁾

The temperature dependence of specific heat (C_p) in a zero magnetic field for the crystallized sample is shown in Fig. 7. The specific heat decreases with decreasing temperature, indicating obviously the contribution of lattice vibrations in the constituent ions and structural units of β' -Gd₂(MoO₄)₃ crystals. In the temperature below $T = 5$ K, the specific heat increases with decreasing temperature. This excess specific heat would be arising from the magnetic entropy of Gd³⁺ ions. A similar behavior has been reported in Gd³⁺-containing crystals such as GdPO₄ and Gd₃Ga₅O₁₂.^{27),32)–34)} Gd³⁺ has the largest spin of $S = 7/2$ among RE³⁺ ions and is expected to have a large magnetic entropy (S_{mag}), i.e., $S_{\text{mag}} = R \ln(2S + 1) = 17.29 \text{ Jmol}^{-1} \text{ K}^{-1}$, where R is the gas constant. In the plot of C_p/T as a function of temperature, any peak such as λ -type anomaly is not observed down to $T = 1.8$ K. The results shown in Figs. 5 to 7 clearly demonstrate that the magnetic state of Gd³⁺ ions in the crystallized sample, i.e., β' -Gd₂(MoO₄)₃ crystals and the residual glassy phase, is paramagnetic and any magnetic interaction is not formed among Gd³⁺ ions down to $T = 1.8$ K.

Fisher et al.^{35),36)} measured the specific heat of β' -Gd₂(MoO₄)₃ crystal down to $T = 0.1$ K and found that it shows antiferromagnetic properties below $T = 0.3$ K, i.e., the phase transition temperature $T_N = 0.3$ K. As shown in Fig. 5, the effective magnetic moment (μ_{eff}) and Weiss constant (θ) of $\mu_{\text{eff}} = 7.94 \mu_B$ and $\theta = -0.3$ K were obtained for the crystallized glasses with β' -Gd₂(MoO₄)₃ crystals. It is clear that the magnetic interaction between Gd³⁺ ions in β' -Gd₂(MoO₄)₃ crystals is extremely weak. In the structure of β' -Gd₂(MoO₄)₃, Gd³⁺ ions occupy a seven-coordinated oxygen environment and three different types of (MoO₄)²⁻ tetrahedra having different mean distances of Mo–O bonds form successive layers along the c -axis.²³⁾ Two independent GdO₇ polyhedra form Gd₂O₁₂ dimers by edge-sharing in β' -Gd₂(MoO₄)₃. In each GdO₇ polyhedron, the mean distance of Gd–O bonds is ~ 0.23 nm and the difference between the shortest and longest Gd–O bond distances is in the range of 0.02 nm. The Gd–Gd interatomic distances in the Gd₂O₁₂ dimers are ~ 0.39 nm and the Gd₂O₁₂ dimers are separated by MoO₄ tetrahedra. It is obvious that the large distance between Gd atoms induces extremely weak magnetic interactions, giving the paramagnetic state down to $T_N = 0.3$ K.

Fig. 8. Excitation spectra at room temperature of the crystallized (635, 895°C, 5 h) samples monitored by the emission of 616 nm in 22.5Eu₂O₃–47.5MoO₃–30B₂O₃ glass.

3.3 Photoluminescence of β' -Eu₂(MoO₄)₃ in crystallized glass

The excitation spectra of the crystallized (635, 895°C, 5 h) samples monitored by the emission of 616 nm in 22.5Eu₂O₃–47.5MoO₃–30B₂O₃ glass are shown in Fig. 8. In the crystallized samples, several sharp peaks assigned to the $4f$ – $4f'$ transitions of Eu³⁺, e.g., the peaks at 396 nm due to the ${}^7F_0 \rightarrow {}^5L_6$ transition and at 467 nm due to the ${}^7F_0 \rightarrow {}^5D_2$ transition, are observed. For the melt-quenched glass sample, any peak was not observed. The peaks shown in Fig. 8 are, therefore, related to Eu³⁺ in β' -Eu₂(MoO₄)₃ crystals formed by the crystallization of 22.5Eu₂O₃–47.5MoO₃–30B₂O₃ glass. As shown in Fig. 8, a broad and weak peak centered at ~ 270 nm is observed in the crystallized sample. This would be attributed to the Mo–O charge transfer band which is due to the energy transfer from the oxygen ligands inside the (MoO₄)²⁻ groups to the luminescence centers in β' -Eu₂(MoO₄)₃ crystals.¹⁴⁾

The PL spectra of the melt-quenched EMB glass and crystallized (635, 895°C, 5 h) samples in an excitation of $\lambda_{\text{ex}} = 396$ nm are shown in Fig. 9. Any detectable PL peak is not observed in the melt-quenched glass. For the crystallized samples, however, the PL peaks typical to the $4f$ – $4f'$ transitions of Eu³⁺, i.e., ${}^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2, 3, 4$), are observed, indicating that these PL peaks are attributed to Eu³⁺ in β' -Eu₂(MoO₄)₃ crystals. Indeed, Buijs et al.³⁷⁾ and Machon et al.³⁸⁾ observed PL peaks due to the transitions of ${}^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2, 3, 4$) in β' -Eu₂(MoO₄)₃ single crystals. It is clear from Fig. 9 that the peak intensity of the ${}^5D_0 \rightarrow {}^7F_2$ emission is strong compared with other emissions with $J = 1, 3$, and 4. It is well known that the ${}^5D_0 \rightarrow {}^7F_2$ emission band is due to the electric-dipole transition and thus largely depends on the local symmetry of coordination environments around Eu³⁺. It is known that three different types of (MoO₄)²⁻ tetrahedra having different mean distances of Mo–O bonds are present in β' -RE₂(MoO₄)₃ crystals, i.e., type-I, II, and III, three crystallographically independent (MoO₄)²⁻ tetrahedra form successive layers along the c -axis.^{23),29)–31)} Each (MoO₄)²⁻ tetrahedron is discrete, and each oxygen atom in (MoO₄)²⁻ is bonded only to one Mo atom, in addition to either one or two Eu atoms. On the other hand, the peak intensity of the ${}^5D_0 \rightarrow {}^7F_1$ emission related to the magnetic-dipole transition is weak, as shown in Fig. 9. The magnetic moment of Eu³⁺ in the ground state is zero. Furthermore, even in β' -Eu₂(MoO₄)₃ crystals, it is considered that EuO₇ polyhedra would be distributed independently each other without having any magnetic interaction, as demonstrated in β' -Gd₂(MoO₄)₃ crystals (Figs. 5 to 7). That is,

Fig. 9. Photoluminescence spectra at room temperature of the melt-quenched glass and crystallized (635, 895°C, 5 h) samples in 22.5Eu₂O₃-47.5MoO₃-30B₂O₃ glass in an excitation of $\lambda_{\text{ex}} = 396$ nm. All peaks are assigned to the 4f-4f transitions of Eu³⁺ ions.

Fig. 11. Photoluminescence spectra at room temperature of the melt-quenched glass and crystallized (750°C, 5 h) sample in 2Eu₂O₃-20.5Gd₂O₃-47.5MoO₃-30B₂O₃ glass in an excitation of $\lambda_{\text{ex}} = 396$ nm. All peaks are assigned to the 4f-4f transitions of Eu³⁺ ions.

Fig. 10. Photoluminescence spectra at room temperature of the melt-quenched glass and crystallized (635, 895°C, 5 h) samples in 22.5Eu₂O₃-47.5MoO₃-30B₂O₃ glass in an excitation of $\lambda_{\text{ex}} = 467$ nm. All peaks are assigned to the 4f-4f transitions of Eu³⁺ ions.

the crystallized glasses are paramagnetic and any magnetic interaction is not formed among RE³⁺ ions down to $T = 1.8$ K. These features of Eu³⁺ ions in β' -Eu₂(MoO₄)₃ crystals would result in the strong PL peak due to the ⁵D₀ → ⁷F₂ emission and the weak PL peak due to the ⁵D₀ → ⁷F₁ emission. The PL spectra of the melt-quenched EMB glass and crystallized (635, 895°C, 5 h) samples in an excitation of $\lambda_{\text{ex}} = 467$ nm are shown in Fig. 10. The PL spectrum patterns are almost the same as those (Fig. 9) obtained in $\lambda_{\text{ex}} = 396$ nm. The PL spectra of the melt-quenched glass and crystallized (750°C, 5 h) sample for 2Eu₂O₃-20.5Gd₂O₃-47.5MoO₃-30B₂O₃ in an excitation of $\lambda_{\text{ex}} = 396$ nm are shown in Fig. 11. It should be pointed out that the PL spectrum pattern (Fig. 11) for the sample of 2Eu₂O₃-20.5Gd₂O₃-47.5MoO₃-30B₂O₃ with a small amount (2 mol %) of Eu₂O₃ is almost the same as those (Fig. 9) for the samples of 22.5Eu₂O₃-47.5MoO₃-30B₂O₃ with a large amount (22.5 mol %) of Eu₂O₃. Furthermore, it was found that the peak intensities of ⁵D₀ → ⁷F₁ peaks shown in Fig. 11 are almost the same as those of ⁵D₀ → ⁷F₁ peaks shown in Fig. 9.

In β' -Eu₂(MoO₄)₃ crystal, a large amount of Eu³⁺, i.e., Eu³⁺ / (Eu³⁺ + Mo⁶⁺) = 0.4, is contained. The appearance of clear PL peaks in the crystallized samples shown in Figs. 9 and 10, therefore, suggests that the concentration quenching among Eu³⁺ ions in β' -Eu₂(MoO₄)₃ crystal and also in the crystallized samples

would be small. The present study proposes that β' -Eu₂(MoO₄)₃ and β' -RE₂(MoO₄)₃ crystals are good hosts for PL emissions of Eu³⁺ and also RE³⁺ ions, because of homogeneous distributions of RE³⁺ ions without having significant magnetic interaction between RE³⁺ ions. Very recently, Suzuki et al.³⁹⁾ examined the magnetic properties of 21.25Gd₂O₃-63.75MoO₃-15B₂O₃ glass itself and clarified that Gd³⁺ ions in the glass are distributed homogeneously and randomly as paramagnetic ions down to $T = 1.8$ K without inducing any strong magnetic interactions. As can be seen in Figs. 9 to 11, any detectable PL peak for Eu³⁺ ions is not observed in the melt-quenched glass. This suggests that RE³⁺ ions in the glass are surrounded partly by BO_n polyhedra ($n = 3$ or 4) with high vibration frequencies,⁴⁰⁾ i.e., the formation of RE³⁺-O-B bonds, and consequently the contribution of non-radiative relaxation process in the f - f transitions of RE³⁺ ions is becoming large. On the other hand, it should be emphasized again that RE³⁺ ions in β' -RE₂(MoO₄)₃ crystals are surrounded only by (MoO₄)²⁻ tetrahedra with relatively low vibration frequencies.

4. Conclusion

Ferroelastic β' -Gd₂(MoO₄)₃ and β' -Eu₂(MoO₄)₃ crystals were synthesized through the crystallization of 21.25Gd₂O₃-63.75MoO₃-15B₂O₃ glass and 22.5Eu₂O₃-47.5MoO₃-30B₂O₃ glass, respectively, and their magnetism and photoluminescence properties were examined. It was demonstrated from the temperature dependence of the magnetic susceptibility and specific heat down to $T = 1.8$ K that the magnetic state of Gd³⁺ ions in the crystallized samples, i.e., in the β' -Gd₂(MoO₄)₃ crystals and the residual glasses, is paramagnetic and any magnetic interaction is not formed among Gd³⁺ ions down to $T = 1.8$ K, i.e., the effective magnetic moment of $\mu_{\text{eff}} = 7.94 \mu_B$ and Weiss constant of $\theta = -0.3$ K. Photoluminescence (PL) of Eu³⁺ ions was clearly observed in the crystallized samples, although the melt-quenched glass did not show any photoluminescence. The present study proposes that the concentration quenching among Eu³⁺ ions in β' -Eu₂(MoO₄)₃ crystals is small and β' -RE₂(MoO₄)₃ crystals would be good hosts for PL emissions of RE³⁺.

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References

- 1) C. K. Jørgensen and R. Reisfeld, *J. Less-Common Met.*, **93**, 107–112 (1983).
- 2) E. W. J. L. Oomen and A. M. A. van Dongen, *J. Non-Cryst. Solids*, **111**, 205–213 (1989).
- 3) S. Tanabe, T. Ohyagi, N. Soga and T. Hanada, *Phys. Rev. B*, **46**, 3305–3310 (1992).
- 4) H. Ebendorff-Heidepriem and D. Ehrt, *J. Non-Cryst. Solids*, **248**, 247–252 (1999).
- 5) N. Maruyama, T. Honma and T. Komatsu, *J. Chem. Phys.*, **128**, 184706 (2008).
- 6) Y. Wang and J. Ohwaki, *Appl. Phys. Lett.*, **63**, 3268–3270 (1993).
- 7) H. Oishi, Y. Benino and T. Komatsu, *Phys. Chem. Glasses*, **40**, 212–218 (1999).
- 8) M. J. Dejneka, *J. Non-Cryst. Solids*, **239**, 149–155 (1998).
- 9) Y. Kishi and S. Tanabe, *J. Alloys Compd.*, **408–412**, 842–844 (2006).
- 10) M. Kusatsugu, M. Kanno, T. Honma and T. Komatsu, *J. Solid State Chem.*, **181**, 1176–1183 (2008).
- 11) M. Kanno, T. Honma and T. Komatsu, *J. Am. Ceram. Soc.*, **92**, 825–829 (2009).
- 12) F. Lei and B. Yan, *J. Solid State Chem.*, **181**, 855–862 (2008).
- 13) C. Gao, H. K. Yang, Z. Fu, L. Li, B. C. Choi and J. H. Jeong, *J. Am. Ceram. Soc.*, **92**, 1713–1718 (2009).
- 14) J. Wan, L. Cheng, J. Sun, H. Zhong, X. Li, W. Lu, Y. Tian, H. Lin and B. Chen, *J. Alloys Compd.*, **496**, 331–334 (2010).
- 15) X. Ju, X. Li, W. Li, W. Yang and C. Tao, *Mater. Lett.*, **65**, 2642–2644 (2011).
- 16) K. J. Rao, “Structural Chemistry of Glasses”, Elsevier, Amsterdam (2002) pp. 39.
- 17) M. Abe, Y. Benino, T. Fujiwara, T. Komatsu and R. Sato, *J. Appl. Phys.*, **97**, 123516 (2005).
- 18) Y. Tsukada, T. Honma and T. Komatsu, *Appl. Phys. Lett.*, **94**, 059901 (2009).
- 19) Y. Tsukada, T. Honma and T. Komatsu, *J. Solid State Chem.*, **182**, 2269–2273 (2009).
- 20) F. Suzuki, T. Honma and T. Komatsu, *J. Solid State Chem.*, **183**, 909–914 (2010).
- 21) F. Suzuki, T. Honma and T. Komatsu, *Mater. Chem. Phys.*, **125**, 377–381 (2011).
- 22) Y. Wang, T. Honma and T. Komatsu, *Mater. Chem. Phys.*, **133**, 118–125 (2012).
- 23) E. T. Keve, S. C. Abrahams and J. L. Bernstein, *J. Chem. Phys.*, **54**, 3185–3194 (1971).
- 24) K. Nassau, H. J. Levinstein and G. M. Loiacono, *J. Phys. Chem. Solids*, **26**, 1805–1816 (1965).
- 25) K. Nassau, J. W. Shiever and E. T. Keve, *J. Solid State Chem.*, **3**, 411–419 (1971).
- 26) W. Jeitschko, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, **28**, 60–76 (1972).
- 27) V. Dimitriev, V. Sinitsyn, R. Dilanian, D. Machon, A. Kuznetsov, E. Ponyatovsky, G. Lucazeau and H. P. Weber, *J. Phys. Chem. Solids*, **64**, 307–312 (2003).
- 28) K. Aizu, A. Kumada, H. Yumoto and S. Ashida, *J. Phys. Soc. Jpn.*, **27**, 511 (1969).
- 29) F. G. Ulman, B. J. Holden, B. N. Gauguly and J. R. Hardy, *Phys. Rev. B*, **8**, 2991–2998 (1973).
- 30) S. S. Saleem, G. Arulhas and H. D. Bist, *J. Solid State Chem.*, **48**, 77–85 (1983).
- 31) L. Guy and M. Denis, *J. Raman Spectrosc.*, **37**, 189–201 (2006).
- 32) R. E. Rapp, M. El Massalami, A. Elzubair and P. H. Domingues, *J. Magn. Magn. Mater.*, **226–230**, 1106–1107 (2001).
- 33) T. Numazawa, K. Kamiya, T. Okano and K. Matsumoto, *Physica B*, **329–333**, 1656–1657 (2003).
- 34) C. Thiriet, P. Javorsky and R. J. M. Konings, *Solid State Commun.*, **134**, 409–412 (2005).
- 35) R. A. Fisher, E. W. Hornumg, G. E. Brodale and W. F. Giauque, *J. Chem. Phys.*, **56**, 193–212 (1972).
- 36) R. A. Fisher, E. W. Hornumg, G. E. Brodale and W. F. Giauque, *J. Chem. Phys.*, **59**, 5796–5809 (1973).
- 37) M. Buijs, G. Blasse and L. H. Brixner, *Phys. Rev. B*, **34**, 8815–8821 (1986).
- 38) D. Machon, V. P. Dmitriev, V. V. Sinitsyn and G. Lucazeau, *Phys. Rev. B*, **70**, 094117 (2004).
- 39) F. Suzuki, T. Honma, Y. Doi, Y. Hinatsu and T. Komatsu, *Mater. Res. Bull.*, **47**, 3403–3406 (2012).
- 40) J. S. Wang, E. M. Vogel and E. Snitzer, *Opt. Mater.*, **3**, 187–203 (1994).