Magnetism of $\beta'$-Gd$_2$(MoO$_4$)$_3$ and photoluminescence of $\beta'$-Eu$_2$(MoO$_4$)$_3$ crystallized in rare-earth molybdenum borate glasses

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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 (RE$^{3+}$) such as Er$^{3+}$ and Eu$^{3+}$ are good activators covering various wavelengths in light emissions, and thus many RE$^{3+}$-doped phosphors have been reported not only in crystalline materials but also in glasses so far. Because photoluminescence (PL) performances of RE$^{3+}$ in materials depend largely on their site environments (crystal fields), it is of importance to clarify the coordination and bonding states of RE$^{3+}$ in materials. 1–5 One of the most important guidelines for the design of host materials providing excellent PL performances for doped RE$^{3+}$ is to use materials having low phonon energies, because the degree of non-radiative relaxation of RE$^{3+}$ in such hosts is expected to be small. 6–11 In this point of view, for example, PL properties of RE$^{3+}$-doped fluoride materials having low phonon energies have been extensively studied so far. 12–15 RE$^{3+}$-doped molibdates such as Gd$_2$(MoO$_4$)$_3$, CaMoO$_4$, BaGa$_2$(MoO$_4$)$_3$, and ZnMoO$_4$ have been proposed to be good candidates as phosphors. 16–19 Because the single bond strength of Mo–O bonds, $B_{\text{MoO}}$, is not so strong, i.e., $B_{\text{MoO}} = 384 \text{kJ/mol}$, 20 it is expected that MoO$_2$-based materials have low phonon energies and thus would be good hosts for RE$^{3+}$. The present authors’ group has demonstrated that ferroelastic $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals with RE = Sm, Gd, Dy, and Tb are easily synthesized through the crystallization of RE$_2$(O$_3$–MoO$_2$–B$_2$O$_3$) glasses. 17–22 In particular, lines consisting of $\beta'$-RE$_2$(MoO$_4$)$_3$ 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:YVO$_4$ fiber laser with $\lambda = 1080$ nm. 17,18,21,22 It is of interest to clarify PL properties of ferroelastic $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals. Because a large amount of RE$^{3+}$ ions is included in $\beta'$-RE$_2$(MoO$_4$)$_3$ as a main constituent, it is also of importance to clarify magnetic properties of $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals formed in the crystallization of RE$_2$(O$_3$– MoO$_2$–B$_2$O$_3$) glasses. Magnetic interactions between RE$^{3+}$ ions would provide important information (e.g., the so-called concentration quenching among RE$^{3+}$ ions) on PL properties of crystallized samples with $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals.

The purpose of this study is to clarify the magnetism of $\beta'$-Gd$_2$(MoO$_4$)$_3$ and photoluminescence of $\beta'$-Eu$_2$(MoO$_4$)$_3$ synthesized through the crystallization of RE$_2$(O$_3$–MoO$_2$–B$_2$O$_3$) glasses. In particular, it is of interest to clarify PL properties of ferroelastic $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystals and the residual glasses, is paramagnetic and any magnetic interaction is not formed among Gd$^{3+}$ 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 Eu$^{3+}$ 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 Eu$^{3+}$ ions in $\beta'$-Eu$_2$(MoO$_4$)$_3$ crystals is small and $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals would be good hosts for PL emissions of RE$^{3+}$.

2. Experimental procedures

In the previous studies, 17–22 the formation and laser patterning of ferroelastic $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals were demonstrated in the glasses of 21.25RE$_2$O$_3$–63.75MoO$_2$–15B$_2$O$_3$ or 22.5RE$_2$O$_3$–47.5MoO$_2$–30B$_2$O$_3$. In the present study, the glasses with the...
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_c, temperatures were determined using differential thermal analysis (DTA) at heating rate of 10 K/min. The as-quenched glasses were annealed at ~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 Archimedean 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 Kα 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 samples 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°C and T_p1 = 634°C for the bulk glass with Eu₂O₃. The values of T_g = 540°C and T_p1 = 585°C for the bulk glass of 21.25Gd₂O₃–63.75MoO₃–15B₂O₃ were obtained.

The DTA 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 (ICPDS: No. 01-070-1397). It is known that the thermodynamically stable phase in the temperatures below 800–900°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°C. The β phase (paraelectric) transforms to the β'-RE₂(MoO₄)₃ phase (ferroelectric) with an orthorhombic structure (Pnma) below Curie temperature (T_C). 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 β'-Gd₂(MoO₄)₃ phase has the value of T_C = 163°C. It is known that the thermodynamically stable phase in the temperatures below 800–900°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°C. The β phase (paraelectric) transforms to the β'-RE₂(MoO₄)₃ phase (ferroelectric) with an orthorhombic structure (Pnma) below Curie temperature (T_C).

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. 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 Eu₄(B₂O₅)₃ crystals is confirmed together with β'-Eu₂(MoO₄)₃ crystals.

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. The heating rate was 10 K/min.

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,
and 958 cm\(^{-1}\). As reported by Abe et al.,\(^{17}\) the Raman scattering spectrum at room temperature for the ferroelastic (ferroelectric) \(\beta\'-\text{RE}_2\text{(MoO}_4\text{)}_3\) phase with an orthorhombic structure (Pba\(_2\)) is largely different from that for the paraelastic (paraelectric) \(\alpha\)-\(\text{RE}_2\text{(MoO}_4\text{)}_3\) phase with a monoclinic structure (C2/c), although both phases consist of \(\text{REO}_7\) polyhedra and \(\text{MoO}_4\) tetrahedra. It should be pointed out that the Raman peaks observed at \(\sim741, \sim813, \sim845, \sim944,\) and \(\sim958\) cm\(^{-1}\) for the crystallized samples (Fig. 4) are assigned to stretching vibrations of Mo–O bonds in isolated \(\text{MoO}_4^{2-}\) tetrahedral units in \(\beta\'-\text{RE}_2\text{(MoO}_4\text{)}_3\) 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 \(\beta\'-\text{Eu}_2\text{(MoO}_4\text{)}_3\). It is considered that the formation of \(\text{Eu(BO}_2\text{)}_3\) provides additional peaks at 917 cm\(^{-1}\).

3.2 Magnetism of \(\beta\'-\text{Gd}_2\text{(MoO}_4\text{)}_3\) in crystallized glass

The temperature dependence of the magnetic susceptibility \((\chi_M)\) and inverse susceptibility \((\chi_M^{-1})\) 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 susceptibility obeys the Curie–Weiss law, giving the effective magnetic moment \((\mu_{\text{eff}})\) and Weiss constant \((\theta)\) 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 Gd\(^{3+}\) ions with the \(4f\) electron configuration of \(8\text{S}_{7/2}\), i.e., 7.94 \(\mu_B\). It was also found that the magnetic susceptibility \((\chi_M)\) 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 \(\mu_S = 7\) \(\mu_B\) expected for Gd\(^{3+}\) 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 \(H^{-1}\) 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 Gd\(^{3+}\) ions in the crystallized sample consisting of \(\beta\'-\text{Gd}_2\text{(MoO}_4\text{)}_3\) crystals are paramagnetic down to \(T = 1.8\) K. Keve et al.\(^{23}\) reported that ferroelectric and ferroelastic \(\beta\'-\text{Gd}_2\text{(MoO}_4\text{)}_3\) remains paramagnetic down to
$T = 1.4$ K and has a magnetic moment of 7.98 $\mu_B$. The results for crystallized glasses observed in this study are well consistent with those reported by Keve et al.\textsuperscript{(25)}

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 increasing temperature, indicating a phase transition at $T = 0.3$ K, i.e., $S = 7/2$ among RE\textsuperscript{3+} ions and thus is expected to have a large magnetic entropy ($S_{mag}$), i.e., $S_{mag} = R \ln(2S + 1) = 17.29$ Jmol\textsuperscript{-1}K\textsuperscript{-1}, where $R$ is the gas constant. In the plot of $C_p/T$ as a function of temperature, any peak such as $\lambda$-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 Gd\textsuperscript{3+} ions in the crystallized sample, i.e., $\beta'$-Gd\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} crystals and the residual glassy phase, is paramagnetic and any magnetic interaction is not formed among Gd\textsuperscript{3+} ions down to $T = 1.8$ K.

Fisher et al.\textsuperscript{(35,36)} measured the specific heat of $\beta'$-Gd\textsubscript{2}(MoO\textsubscript{4})\textsubscript{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 ($\mu_{eff}$) and Weiss constant ($\theta$) of $\mu_{eff} = 7.94 \mu_B$ and $\theta = -0.3$ K were obtained for the crystallized glasses with $\beta'$-Gd\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} crystals. It is clear that the magnetic interaction between Gd\textsuperscript{3+} ions in $\beta'$-Gd\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} crystals is extremely weak. In the structure of $\beta'$-Gd\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}, Gd\textsuperscript{3+} ions occupy a seven-coordinated oxygen environment and three different types of (MoO\textsubscript{4})\textsuperscript{2-} tetrahedra having different mean distances of Mo–O bonds form successive layers along the c-axis.\textsuperscript{(25)} Two independent GdO\textsubscript{2} polyhedra form Gd\textsubscript{2}O\textsubscript{12} dimers by edge-sharing in $\beta'$-Gd\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}. In each GdO\textsubscript{2}-polyhedron, the mean distance of Gd–O bonds is $\sim 0.23$ 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 Gd\textsubscript{2}O\textsubscript{12} dimers are $\sim 0.39$ nm and the Gd\textsubscript{2}O\textsubscript{12} dimers are separated by MoO\textsubscript{4} 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.

$3.3$ Photoluminescence of $\beta'$-Eu\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} in crystallized glass

The excitation spectra of the crystallized (635, 895°C, 5 h) samples monitored by the emission of 616 nm in 22.5Eu\textsubscript{2}O\textsubscript{3}–47.5MoO\textsubscript{3}–30B\textsubscript{2}O\textsubscript{3} glass are shown in Fig. 8. The crystallized samples, several sharp peaks assigned to the 4f–4f transitions of Eu\textsuperscript{3+}, e.g., the peaks at 396 nm due to the $^5D_0 \rightarrow ^7F_2$ transition and at 467 nm due to the $^5D_0 \rightarrow ^7F_1$ transition, are observed. For the melt-quenched glass sample, any peak was not observed. The peaks shown in Fig. 8 are, therefore, related to Eu\textsuperscript{3+} in $\beta'$-Eu\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} crystals formed by the crystallization of 22.5Eu\textsubscript{2}O\textsubscript{3}–47.5MoO\textsubscript{3}–30B\textsubscript{2}O\textsubscript{3} glass. As shown in Fig. 8, a broad and weak peak centered at $\sim 270$ 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 (MoO\textsubscript{4})\textsuperscript{2-} groups to the luminescence centers in $\beta'$-Eu\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} crystals.\textsuperscript{(41)}

The PL spectra of the melt-quenched EMB glass and crystallized (635, 895°C, 5 h) samples in an excitation of 465 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 Eu\textsuperscript{3+}, i.e., $^5D_0 \rightarrow ^7F_2$ ($J = 1, 2, 3, 4$), are observed, indicating that these PL peaks are attributed to Eu\textsuperscript{3+} in $\beta'$-Eu\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} crystals. Indeed, Buijs et al.\textsuperscript{(37)} and Machon et al.\textsuperscript{(38)} observed PL peaks due to the transitions of $^5D_0 \rightarrow ^7F_1$ ($J = 1, 2, 3, 4$) in $\beta'$-Eu\textsubscript{2}(MoO\textsubscript{4})\textsubscript{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 Eu\textsuperscript{3+}. It is known that there are three different types of (MoO\textsubscript{4})\textsuperscript{2-} tetrahedra having different mean distances of Mo–O bonds are present in $\beta'$-RE\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} crystals, i.e., type-I, II, and III, three crystallographically independent (MoO\textsubscript{4})\textsuperscript{2-} tetrahedra form successive layers along the c-axis.\textsuperscript{(23,29-31)} Each (MoO\textsubscript{4})\textsuperscript{2-} tetrahedron is discrete, and each oxygen atom in (MoO\textsubscript{4})\textsuperscript{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 Eu\textsuperscript{3+} in the ground state is zero. Furthermore, even in $\beta'$-Eu\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} crystals, it is considered that Eu\textsubscript{O} polyhedra would be distributed independently each other without having any magnetic interaction, as demonstrated in $\beta'$-Gd\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} crystals (Figs. 5 to 7). That is,
the crystallized glasses are paramagnetic and any magnetic interaction is not formed among RE$^{3+}$ ions down to $T = 1.8$ K. These features of Eu$^{3+}$ ions in $^{15}$B$_2$O$_3$ crystals would result in the strong PL peak due to the $^5D_0 \rightarrow ^7F_2$ transition and the weak PL peak due to the $^5D_0 \rightarrow ^7F_1$ transition. The PL spectra of the melt-quenched EMB glass and crystallized (63.5 $\pm$ 0.5 $\mathrm{g/cm^3}$, 5 h) samples in an excitation of $\lambda_{ex} = 396$ nm, is shown in Fig. 10. The PL spectrum patterns are almost the same as those obtained in $\lambda_{ex} = 396$ nm. The PL spectra of the melt-quenched glass and crystallized (750°C, 5 h) sample in 2Eu$_2$O$_3$–20.5Gd$_2$O$_3$–47.5MoO$_3$–30B$_2$O$_3$ glass in an excitation of $\lambda_{ex} = 396$ nm. All peaks are assigned to the $4f$–$4f$ transitions of Eu$^{3+}$ ions.

Fig. 11. Photoluminescence spectra at room temperature of the melt-quenched glass and crystallized (750°C, 5 h) sample in 2Eu$_2$O$_3$–20.5Gd$_2$O$_3$–47.5MoO$_3$–30B$_2$O$_3$ glass in an excitation of $\lambda_{ex} = 396$ nm. All peaks are assigned to the $4f$–$4f$ transitions of Eu$^{3+}$ ions.

In $^{15}$B$_2$O$_3$ crystals, a large amount of Eu$^{3+}$, i.e., Eu$^{3+}$ / (Eu$^{3+}$ + Mo$^{6+}$) $= 0.4$, 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 Eu$^{3+}$ ions in $^{15}$B$_2$O$_3$ crystals is small and would be small. The present study proposes that $^{15}$B–Eu$_2$(MoO$_4$)$_3$ and $^{15}$B–RE$_2$(MoO$_4$)$_3$ crystals are good hosts for PL emissions of Eu$^{3+}$ and also RE$^{3+}$ ions, because of homogeneous distributions of RE$^{3+}$ ions without having significant magnetic interaction between RE$^{3+}$ ions. Very recently, Suzuki et al. examined the magnetic properties of 21.25Gd$_2$O$_3$–63.75MoO$_3$–15B$_2$O$_3$ glass self and clarified that Gad$^{3+}$ 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 Eu$^{3+}$ ions is not observed in the melt-quenched glass. This suggests that RE$^{3+}$ ions in the glass are surrounded partly by BO$_x$ polyhedra ($n = 3$ or $4$) with high vibration frequencies, i.e., the formation of RE$^{3+}$–O–B bonds, and consequently the contribution of non-radiative relaxation process in the $f$–$f$ transitions of RE$^{3+}$ ions is becoming large. On the other hand, it should be emphasized again that RE$^{3+}$ ions in RE(RE$_2$(MoO$_4$)$_3$) crystals are surrounded only by (MoO$_x$)$^2$– tetrahedra with relatively low vibration frequencies.

4. Conclusion

Ferroelastic $^{15}$B–Gd$_2$(MoO$_4$)$_3$ and $^{15}$B–Eu$_2$(MoO$_4$)$_3$ crystals were synthesized through the crystallization of 21.25Gd$_2$O$_3$–63.75MoO$_3$–15B$_2$O$_3$ glass and 22.5Eu$_2$O$_3$–47.5MoO$_3$–30B$_2$O$_3$ 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 Gad$^{3+}$ ions in the crystallized samples, i.e., in the $^{15}$B–Gd$_2$(MoO$_4$)$_3$ crystals and the residual glasses, is paramagnetic and any magnetic interaction is not formed among Gad$^{3+}$ ions down to $T = 1.8$ K, i.e., the effective magnetic moment of $\mu_{eff} = 7.94 \mu_B$ and Weiss constant of $\theta = -0.3$ K. Photoluminescence (PL) of Eu$^{3+}$ 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 Eu$^{3+}$ ions in $^{15}$B–Eu$_2$(MoO$_4$)$_3$ is small and $^{15}$B–RE$_2$(MoO$_4$)$_3$ crystals would be good hosts for PL emissions of RE$^{3+}$.

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