Self-powdering phenomenon of $\beta'$-RE$_2$(MoO$_4$)$_3$ formed in crystallization of glasses and its mechanism (RE: Gd, Sm, Dy)

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Some glasses in the RE$_2$O$_3$-MoO$_3$-B$_2$O$_3$ system (RE: Gd, Sm, Dy) were prepared by using a conventional melt quenching method, and the self-powdering phenomenon of $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystals, i.e., the breaking into small pieces during the crystal growth, was examined using polarized optical microscope observations in a heating stage. In Gd$_2$O$_3$-MoO$_3$-B$_2$O$_3$ glasses with Gd$_2$O$_3$/MoO$_3$ = 1/3 and with different B$_2$O$_3$ contents (15-30 mol%) such as 20Gd$_2$O$_3$-60MoO$_3$-20B$_2$O$_3$, $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystals were formed and the self-powdering phenomenon was observed irrespective of B$_2$O$_3$ content. The crack formation radiating out from the center part was clearly observed in the inside of crystals (diameter >40 $\mu$m) formed at 570°C in the glasses with Gd$_2$O$_3$ or Dy$_2$O$_3$. But, any clear crack formation was not observed in the glass with Sm$_2$O$_3$. It was found that the base glasses have larger densities at room temperature compared with $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals formed, which is a unique feature in the RE$_2$O$_3$-MoO$_3$-B$_2$O$_3$ system compared with the crystallization of other glass systems. Such differences in the density might induce the accumulation of extremely large stresses in the inside of crystals, eventually causing the breaking of crystals.

1. Introduction

Crystallization of glasses is a method for fabrication of transparent and dense condensed materials with desired shapes and functions, i.e., the development of functional glass-ceramics or crystallized glasses, and an understanding on the crystallization behavior and kinetics in glasses is one of the important topics in the glass science and technology.\(^1\)–\(^9\) One strong motivation for the development of glass-ceramics is to improve the mechanical properties of glasses, e.g., improvements of hardness and fracture toughness due to the design of the microstructure of glass/crystal composites. Another attractive motivation is to develop optical, electrical, and magnetic active glass-related materials through the crystallization of glasses. So far, various functional glass-ceramics have been proposed through the design and control of glass composition, crystal nucleation and growth.

Tsukada et al.\(^10\) found an extremely unique and curious phenomenon in the crystallization of multiferroic (ferroelectric and ferroelastic properties) $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystals in Gd$_2$O$_3$-MoO$_3$-B$_2$O$_3$ glasses. That is, crystals formed in the crystallization break into small pieces with a triangular prism or pyramidal shape having a length of 50–150 $\mu$m spontaneously during the crystallization in the inside of an electric furnace, not during the cooling in air after the crystallization. They proposed to call this phenomenon “self-powdering phenomenon”.\(^10\) To the best of our knowledge, such a self-powdering phenomenon has not been observed in the crystallization of any other glasses. The self-powdering phenomenon might mean that extremely large stresses are created in the inside of crystals and consequently crystals break into small pieces due to some stresses accumulated in crystals themselves. But, at this moment, the origin or mechanism of self-powdering phenomenon observed experimentally has not been clarified. It is of interest to clarify the mechanism itself of the self-powdering phenomenon, and furthermore, if we can depress the self-powdering phenomenon through the design of glass composition, it might be possible to develop new materials having extremely large stresses in the inside without breaking. It should be pointed out that multiferroic $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals (RE: Pr, Nd, Sm, Eu, Gd, Tb, Dy) have received much attention because of their unique physical properties and of potentials for various optical devices.\(^11\)–\(^16\) For instance, Pan and Zhang\(^16\) observed a good white up-converted luminescence in RE$^{3+}$ (e.g., Er$^{3+}$) co-doped Gd$_2$(MoO$_4$)$_3$ nanocrystals synthesized by a combustion method. The present authors’ group\(^17\)–\(^21\) succeeded in patterning $\beta'$-RE$_2$(MoO$_4$)$_3$ crystal lines with periodic refractive index changes at the glass surface by using a laser-induced crystallization technique.

The purpose of this study is to clarify the mechanism of self-powdering phenomenon of $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystals observed in the crystallization of Gd$_2$O$_3$-MoO$_3$-B$_2$O$_3$ glasses. The effects of the kind of RE$_2$O$_3$ (Sm$_2$O$_3$ and Dy$_2$O$_3$) and the content of glass-forming oxide B$_2$O$_3$ on the self-powdering phenomenon were examined. From the present study, we propose that the self-powdering phenomenon is closely related to the large difference in the density between the base glass and $\beta'$-RE$_2$(MoO$_4$)$_3$ crystal.

2. Experimental procedure

Glasses with the compositions of 21.25RE$_2$O$_3$-63.75MoO$_3$-15B$_2$O$_3$ (RE: Sm, Gd, Dy), 20Gd$_2$O$_3$-60MoO$_3$-20B$_2$O$_3$, 18.75Gd$_2$O$_3$-56.25MoO$_3$-25B$_2$O$_3$, and 17.5Gd$_2$O$_3$-52.5MoO$_3$-30B$_2$O$_3$ (mol%) were prepared using a conventional melt quenching technique. Commercial powders of reagent grade Sm$_2$O$_3$, Gd$_2$O$_3$, Dy$_2$O$_3$, MoO$_3$, and B$_2$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

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poured onto an iron plate and pressed to a thickness of \( \sim 1.5 \text{ mm} \) 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 Celox powders. Densities of the glasses at room temperature were determined with the Archimedes method using distilled water as an immersion liquid.

The glasses were heat-treated at different temperatures in an electric furnace, and the crystalline phases present in the crystallized samples were identified by X-ray diffraction (XRD) analysis (Cu Kα radiation) at room temperature. Some glasses with a plate shape were heated on the heat stage, and the change in the morphology of crystals was observed with a polarized optical microscope (POM). The highest temperature in the heat stage used was limited to 600°C. The morphology of crystals was also examined from optical microscope observations.

3. Results and discussion

3.1 DTA curves for bulk and powdered glasses

The glasses prepared in this study are designated here as GdMo15B for 21.25Gd2O3–63.75MoO3–15B2O3, GdMo20B for 20Gd2O3–60MoO3–20B2O3, GdMo25B for 18.75Gd2O3–56.25MoO3–25B2O3, GdMo30B for 17.5Gd2O3–52.5MoO3–30B2O3, SmMo15B for 21.25Sm2O3–63.75MoO3–15B2O3, DyMo15B for 21.25Dy2O3–63.75MoO3–15B2O3, GdMo15B for 21.25Gd2O3–63.75MoO3–15B2O3, GdMo25B for 18.75Gd2O3–56.25MoO3–25B2O3, GdMo30B for 17.5Gd2O3–52.5MoO3–30B2O3, SmMo15B for 21.25Sm2O3–63.75MoO3–15B2O3, DyMo15B for 21.25Dy2O3–63.75MoO3–15B2O3 glasses. Heating rate was \( 10 \text{ K/min} \). The as-quenched glasses are almost independent on the content (15–30 mol%) of B2O3. That is, it is concluded that the appearance of glass has the values of \( T_g \) and \( T_p \) are summarized in Table 1. These values are almost the same, indicating that the values of \( \Delta H(\text{base}) \) are extremely small. That is, it is concluded that the appearance of \( \Delta H(\text{base}) \) in the DTA curves for Gd2O3–MoO3–B2O3 glasses is a unique behavior observed in the bulk glasses.

The DTA curves for the bulk samples of SmMo15B and DyMo15B glasses are shown in Fig. 1. All glasses show endothermic dips due to the glass transition and exothermic peaks due to the crystallization are observed. In the present study, the values of \( T_g \) and \( T_p \) were determined by a usual method, in which the intersection of two tangent lines at the endothermic dips was used. The values of \( T_g \) and \( T_p \) are summarized in Table 1. It is seen that the glasses have the values of \( T_g \approx 530°C \) and \( T_p \approx 580°C \), indicating that the glass transition and crystallization peak temperatures of the glasses are almost independent on the content (15–30 mol%) of B2O3. It should be pointed out that just only one crystallization peak is detected in the temperatures below 700°C in each glass, as shown in Fig. 1. Furthermore, it is noted that all glasses show a similar shape in DTA curves. The DTA data shown in Fig. 1 and Table 1 are, therefore, strongly suggest that similar crystallization behaviors are taking place in GdMo15B, GdMo20B, GdMo25B, and GdMo30B glasses, irrespective of the content of glass-forming B2O3.

As shown in Fig. 1, the position of the base line in the before side of the crystallization is different largely from that in the after side of the crystallization. In this paper, we designate this difference as \( \Delta H(\text{base}) \). To the best of our knowledge, this kind of DTA curves with a unique \( \Delta H(\text{base}) \) shown in Fig. 1 has not been reported in other glasses. In order to confirm the appearance of \( \Delta H(\text{base}) \) in the bulk samples of Gd2O3–MoO3–B2O3 glasses, DTA experiments were carried out for the powdered (pulverized) samples and the results are shown in Fig. 2. Only one sharp exothermic peak is observed in each glass, as similar to the bulk sample (Fig. 1). In the DTA curves shown in Fig. 2, the positions of the base lines in the before and after sides of the crystallization are almost the same, indicating that the values of \( \Delta H(\text{base}) \) is extremely small. That is, it is concluded that the appearance of \( \Delta H(\text{base}) \) in the DTA curves for Gd2O3–MoO3–B2O3 glasses is a unique behavior observed in the bulk glasses.

The DTA curves for the bulk samples of SmMo15B and DyMo15B glasses are shown in Fig. 3. The bulk SmMo15B glass has the values of \( T_g = 530°C \) and \( T_p = 571°C \) and the bulk DyMo15B glass shows the values of \( T_g = 533°C \) and \( T_p = 586°C \). These values are close to the values for the bulk GdMo15B glass. In DyMo15B glass, the presence of \( \Delta H(\text{base}) \) is
transition and crystallization peak temperatures, respectively. As reported by Ida et al.,\textsuperscript{22)\textsuperscript{22} the shape of the DTA curves with a large exothermic peaks are observed in each glass and also any clear difference was not observed, although its degree is small compared with GdMo15B glass. On the other hand, any clear $\Delta H$(base) is not detected in SmMo15B glass. The DTA curves for the powdered samples of SmMo15B and DyMo15B glasses are shown in Fig. 4. Sharp exothermic peaks are observed in each glass and also any clear $\Delta H$(base) is not detected as similar to the case of GdMo15B glass (Fig. 2). As reported by Ida et al.,\textsuperscript{21,22)\textsuperscript{21} the shape of the DTA curves for the bulk and powdered samples of RE$_2$O$_3$-BaO-Nb$_2$O$_5$-B$_2$O$_3$ glasses is almost the same, i.e., the values of $\Delta H$(base) are almost zero for both bulk and powdered glasses. In their report,\textsuperscript{22)\textsuperscript{22} ferroelectric Ba$_x$RE$_{2-x}$Nb$_2$O$_6$ nanocrystals are formed in the crystallization and glass-ceramics obtained keep not only optical transparency but also the original bulk shape (no breaking into small pieces). The present study, therefore, indicates that the bulk RE$_2$O$_3$-Mo$_2$O$_3$-B$_2$O$_3$ glasses (RE: Gd, Dy) show unique DTA curves with a large $\Delta H$(base).

### 3.2 XRD patterns for crystallized samples

In the previous study,\textsuperscript{10)\textsuperscript{10} the self-powdering phenomenon observed in the crystallization of $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystals was for 21.25Gd$_2$O$_3$-63.75MoO$_3$-15B$_2$O$_3$ glass (GdMo15B) with the ratio of Gd$_2$O$_3$/MoO$_3$ = 1/3. In the present study, other glasses with different compositions were prepared to clarify the mechanism of the self-powdering phenomenon, i.e., 20Gd$_2$O$_3$-60MoO$_3$-20B$_2$O$_3$ glass (GdMo20B), 18.75Gd$_2$O$_3$-56.25MoO$_3$-25B$_2$O$_3$ glass (GdMo25B), and 17.5Gd$_2$O$_3$-52.5MoO$_3$-30B$_2$O$_3$ glass (GdMo30B) with the same ratio of Gd$_2$O$_3$/MoO$_3$ = 1/3. Prior to the study of the self-powdering phenomenon, it is necessary to confirm the formation of $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystals in all glasses prepared in this study.

The glasses of GdMo15B, GdMo20B, GdMo25B, and GdMo30B were heat-treated at 570°C (−$T_g$) for 3 h in air, and the XRD patterns for the crystallized samples are shown in Fig. 5. It is seen that all glasses show the formation of $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystals, irrespective of the content (15–30 mol %) of B$_2$O$_3$. However, it is seen that the intensity of the peak around 2θ = 23.8° is becoming strong with increasing the content of B$_2$O$_3$. The peak at 2θ = 23.8° corresponds to the (022) or (202) plane in $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystal (ICPDS: No. 01-070-1397). B$_2$O$_3$ is not a constituent oxide in $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystal, suggesting that B$_2$O$_3$ would affect the diffusion of Gd$^{3+}$ and Mo$^{6+}$ ions and consequently the formation behavior (i.e., size and morphology) of $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystals. The results shown in Figs. 1, 2, and 5 clearly demonstrate that $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystals are formed easily in Gd$_2$O$_3$-Mo$_2$O$_3$-B$_2$O$_3$ glasses. The formation of $\beta'$-Sm$_2$(MoO$_4$)$_3$ and $\beta'$-Dy$_2$(MoO$_4$)$_3$ crystals in SmMo15B and DyMo15B glasses were also confirmed from XRD analyses for the heat-treated samples.

As reported by Imaoka,\textsuperscript{23)\textsuperscript{23} it is difficult to form glasses in the binary system of MoO$_3$-B$_2$O$_3$. Furthermore, as reported by Chakraborty et al.,\textsuperscript{24)\textsuperscript{24} glasses are not formed in the binary Gd$_2$O$_3$-B$_2$O$_3$ system. It is, therefore, considered that the addition of both Gd$_2$O$_3$ and MoO$_3$ to B$_2$O$_3$ enables to form glasses, i.e., the glass formation in the ternary Gd$_2$O$_3$-Mo$_2$O$_3$-B$_2$O$_3$ system. It is expected that strong chemical bonds of Mo-O-B and Gd-O-B would not be formed in the Gd$_2$O$_3$-Mo$_2$O$_3$-B$_2$O$_3$ glasses prepared in the present study, and such a feature in the glass formation might be an important reason for the formation of RE$_2$(MoO$_4$)$_3$ crystals in RE$_2$O$_3$-Mo$_2$O$_3$-B$_2$O$_3$ glasses. Nakajima et al.\textsuperscript{25)\textsuperscript{25} measured Raman scattering spectra of 21.25RE$_2$O$_3$-63.75MoO$_3$-
$\text{Gd}_3 \text{MoO}_15 \text{B}_2 \text{O}_3$ (RE: Gd, Sm, Dy) glasses and suggested that $\text{MoO}_4$ tetrahedral units are formed in these glasses containing a large amount (63.75 mol %) of $\text{MoO}_4$ and act as network glass formers. Very recently, Suzuki et al. measured the magnetic susceptibility and specific heat of $21.25 \text{Gd}_2 \text{O}_3 - 63.75 \text{MoO}_4 - 15 \text{B}_2 \text{O}_3$ glass in the temperature range of $T = 1.8 - 300 \text{K}$ and proposed that $\text{Gd}^{3+}$ ions are distributed homogeneously and randomly as paramagnetic ions down to $T = 1.8 \text{K}$ without inducing any strong magnetic interaction. Wang et al. proposed that ferroelastic $\beta^-\text{Gd}_3 \text{MoO}_4$ crystals synthesized through the crystallization of a glass (GdMo15B glass) is paramagnetic and any magnetic interaction is not formed among Gd$^{3+}$ ions down to $T = 1.8 \text{K}$. These previous studies suggest that the coordination state of Gd$^{3+}$ ions in the short-range structure of Gd$_2$O$_3$-$\text{MoO}_3$-$\text{B}_2\text{O}_3$ glasses is close to that in $\beta^-\text{Gd}_3 \text{MoO}_4$ crystals, and this might be another reason for the crystallization of Gd$_3$(MoO$_4$)$_3$ in Gd$_2$O$_3$-$\text{MoO}_3$-$\text{B}_2\text{O}_3$ glasses.

### 3.3 Self-powdering behavior in the crystallization

The optical photographs at room temperature for the samples obtained by heat treatments of GdMo15B, GdMo20B, and GdMo30B glasses at 570°C for 3 h in an electric furnace are shown in Fig. 6. In these experiments, the samples were cooled in an electric furnace after the heat treatments. As seen in Fig. 6, the original bulk glasses with a plate shape break into small pieces. Even in this study, it was confirmed experimentally that the breaking into small pieces takes place during the crystallization in the inside of an electric furnace, not during the cooling process after heat treatments. That is, the self-powdering phenomenon is observed in the crystallization of $\beta^-\text{Gd}_3 \text{MoO}_4$ crystals in all Gd$_2$O$_3$-$\text{MoO}_3$-$\text{B}_2\text{O}_3$ glasses examined in this study. Small pieces have triangular prism, pyramid, and rectangular shapes with sharp edges and their length is in the range of 100–600 µm.

The results for the SmMo15B and DyMo15B glasses are shown in Fig. 7. The self-powdering phenomenon being similar to Gd$_2$O$_3$-containing glasses (Fig. 6) is observed in the crystallization of $\beta^-\text{Dy}_3 \text{MoO}_4$ crystals in DyMo15B glass. In the case of SmMo15B glass, a breaking of the plate-shape glass is observed, but the size of each piece is large compared with the case of GdMo15B and DyMo15B glasses. Further, it is obvious that the degree of self-powdering, i.e., the size of each pieces, changes depending on the kind of RE$_2$O$_3$ and also on the content of glass-forming B$_2$O$_3$.

### 3.4 Crystallization in heat stage and crystal morphology

The self-powdering phenomenon of RE$_2$(MoO$_4$)$_3$ crystals, i.e., the breaking into small pieces, takes place during the crystallization in the inside of an electric furnace, not during the cooling process after heat treatments. It is considered that extremely large stresses are accumulated in the inside of crystals and consequently some cracks providing breaks are created. It is, therefore, important to observe directly the formation and growth of crystals and also the crack formation in the heat treatment at high temperatures. For this purpose, the glasses with a plate shape were heated on the heat stage, and the change in the morphology of crystals was examined with POM observations, i.e., in-situ observations of crystal growth. In this study, the glasses were heated at the heating rate of 30 K/min in the temperature range of room temperature (RT) to 560°C and at 2 K/min from 560 to 600°C.

Some results for GdMo20B and SmMo15B glasses, as examples, are shown in Fig. 8. The temperatures of 585 and 591°C for GdMo20B glass ($T_p = 578°C$) and of 579 and 585°C for SmMo15B glass ($T_p = 571°C$) are higher than the crystallization peak temperatures of these glasses. It is seen that in both glasses many crystals with spherical shapes are formed and their sizes increase with increasing heating temperature. It is also observed that many crystals contact or collide each other. Looking POM photographs more in detail, in the case of GdMo20B glass, the center part of crystals shows a black color, but in the case of SmMo15B glass such a black color is not observed in each crystal. The POM photographs in the expanded scale for crystals formed in GdMo15B, GdMo20B, and SmMo15B glasses are shown in Fig. 9. It is found that many cracks are created in the crystals formed in GdMo15B and GdMo20B glasses on the
other hand, in the case of crystals formed in SmMo15B glass, any crack is not observed. The optical microscope photographs for crystals formed in the heating of GdMo15B glass is shown in Fig. 10, in which the samples were obtained by cooling to RT after the heating in the heating stage. It is seen that cracks are present and are radiating out from the center part. These results shown in Figs. 8 to 10 clearly demonstrate that cracks are created in each Gd₂(MoO₄)₃ crystal formed in the crystallization of Gd₂O₃-MoO₃-B₂O₃ glasses even at high temperatures. That is, Gd₂(MoO₄)₃ crystals are formed easily in Gd₂O₃-MoO₃-B₂O₃ glasses and crystals having a large diameter of >50 μm break into small pieces spontaneously (voluntary). The crack formation similar to the case of Gd₂O₃-MoO₃-B₂O₃ glasses was observed in Dy₂(MoO₄)₃ crystals in DyMo15B glass. Although any cracks are not observed in the inside of each Sm₂(MoO₄)₃ crystal (Fig. 9), some cracks are observed at the boundary between crystalline particles as shown in Fig. 8. It is obvious that the crack creation radiating out from the center part in Gd₂(MoO₄)₃ and Dy₂(MoO₄)₃ crystals provides small pieces having mainly triangular prism with sharp edges (Figs. 6 and 7).

### 3.5 Mechanism of self-powdering phenomenon

β'-RE₂(MoO₄)₃ crystals exhibit ferroelastic and ferroelectric properties, i.e., multiferroic crystals. In the ferroelastic state, spontaneous strains are present within crystals like spontaneous magnetic moments in ferromagnetic crystals. The Curie temperatures of RE₂(MoO₄)₃ crystals in the phase transition from the ferroelastic state [β'-RE₂(MoO₄)₃] to the paraelastic state [β-RE₂(MoO₄)₃] are around Tₑ = 150–200°C, e.g., Tₑ = 159°C for β'-Gd₂(MoO₄)₃ and Tₑ = 197°C for β'-Sm₂(MoO₄)₃. The self-powdering phenomenon observed in the crystallization of RE₂(MoO₄)₃ in RE₂O₃-MoO₃-B₂O₃ glasses takes place at high temperatures of >570°C. Such high temperatures are obviously higher than the Tₑ values of RE₂(MoO₄)₃ crystals. It is, therefore, considered that crystals formed in the crystallization of RE₂O₃-MoO₃-B₂O₃ glasses are paraelastic β'-RE₂(MoO₄)₃ crystals with no spontaneous strains. In other words, we can say that the self-powdering phenomenon would not be related directly to ferroelastic spontaneous strains.

It is obvious that extremely large stresses causing the breaking of crystals are accumulated in the inside of crystals. Furthermore, the formation of cracks means the creation of new open spaces. Considering these points, we focus on the difference in the density (ρ) between β'-RE₂(MoO₄)₃ crystals and the residual glassy phase. Because the chemical compositions of the residual glassy phases in the crystallization process in RE₂O₃-MoO₃-B₂O₃...
glasses are not clear, we use the densities of the base glasses. The densities of $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals and the base glasses at RT (not at 570–600°C) are summarized in Table 2. The data on the density at RT of $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals are taken from Ref. 29). It is found that the base glasses have larger densities compared with the corresponding $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals, e.g., $d = 4.762$ g/cm$^3$ for GdMo15B glass and $d = 4.555$ g/cm$^3$ for $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystal. The chemical compositions of the base glasses and $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals are different, but the content of B$_2$O$_3$ is not so large. For instance, in GdMo15B glass, B$_2$O$_3$ of just only 15 mol % is added to the composition corresponding to $\beta'$-RE$_2$(MoO$_4$)$_3$.

Generally, the crystallization of glasses induces the increase in density, because the crystallization means atomic rearrangements from random structure in the glass to more regular (periodic) structure. In Table 2, some data on the densities at room temperature for the base glasses and crystals formed in the crystallization reported so far are shown. In the combination of the glasses and isochemical (stoichiometric composition) crystals, the densities of the precipitated crystals are larger than those of the base glasses, e.g., $d = 2.35$ g/cm$^3$ for Li$_2$O–2SiO$_2$ glass and $d = 2.45$ g/cm$^3$ for Li$_2$Si$_2$O$_5$ crystals and $d = 4.294$ g/cm$^3$ for 40BaO–20TiO$_2$–40SiO$_2$ glass and $d = 4.446$ g/cm$^3$ for Ba$_2$TiSi$_3$O$_9$ crystal. In the combination of the glasses and non-isochemical (non-stoichiometric) crystals, densities of the precipitated crystals are also larger than those of the base glasses, e.g., $d = 3.772$ g/cm$^3$ for 40Li$_2$O–32Nb$_2$O$_5$–28SiO$_2$ glass and $d = 4.64$ g/cm$^3$ for LiNbO$_3$ crystals and $d = 4.267$ g/cm$^3$ for 16SrO–16BaO–32Nb$_2$O$_5$–36B$_2$O$_3$ glass and $d = 5.42$ g/cm$^3$ for Sr$_6$Ba$_8$Nb$_2$O$_{19}$ crystal.

From the viewpoints of densities of the base glasses and precipitated crystals, it should be emphasized that RE$_2$O$_3$–MoO$_3$–B$_2$O$_3$ glasses providing the formation of $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals are extremely unique. The self-powdering phenomenon (Figs. 6 to 10) takes place at high temperatures of 570–600°C. At this moment, the densities at these high temperatures for the glassy phase and RE$_2$(MoO$_4$)$_3$ crystals have not been determined. However, because the differences in the densities between the base glasses and crystals are large (Table 2), it would be expected that even at high temperatures the residual glassy phases base have larger densities compared with the precipitated RE$_2$(MoO$_4$)$_3$ crystals. If so, large stresses would be accumulated in the inside of RE$_2$(MoO$_4$)$_3$ crystals, and the degree of accumulated stresses would be increased with increasing the size of crystals (crystal growth). Eventually, accumulated stresses induce cracks in crystals in order to release stresses. Considering the unique DTA curves with ΔH(base) (Fig. 1), the release of accumulated stresses might induce not only cracks but also some heat release. It should be pointed out that any clear self-powdering phenomenon was not observed in the crystallization of SmMo15B glass (Fig. 7) showing no clear ΔH(base) in the DTA curve (Fig. 3).

In the present study, it was demonstrated that the self-powdering phenomenon of $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals (RE: Gd and Dy) is a common feature in the crystallization of RE$_2$O$_3$–MoO$_3$–B$_2$O$_3$ glasses. And, the mechanism of self-powdering phenomenon was discussed. As reported by Tsukada et al. [30], $\beta'$-Gd$_2$(MoO$_4$)$_3$ crystals patterned by laser irradiations show an extremely unique crystal growth providing a periodic refractive index change. The crystallization of RE$_2$O$_3$–MoO$_3$–B$_2$O$_3$ glasses is, therefore, including some new and interesting scientific points in comparison with the crystallization of other glasses. Further studies, in particular on the relationship between the crystal growth and crack formation, crystal growth kinetics, and also the origin of ΔH(base) (Fig. 1) are required.

4. Conclusion

The self-powdering phenomenon of $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals in RE$_2$O$_3$–MoO$_3$–B$_2$O$_3$ glasses (RE: Gd, Sm, Dy), i.e., the breaking into small pieces during the crystal growth, was examined using polarized optical microscope observations in a heating stage. The crack formation radiating out from the center part was clearly observed in the inside of crystals (diameter >40 μm) formed at 570°C in the glasses with Gd$_2$O$_3$ or Dy$_2$O$_3$ such as 21.25Gd$_2$O$_3$ (or Dy$_2$O$_3$–63.75MoO$_3$–15B$_2$O$_3$). The base glasses have larger densities at room temperature compared with $\beta'$-RE$_2$(MoO$_4$)$_3$ crystals formed, which is a unique feature in the RE$_2$O$_3$–MoO$_3$–B$_2$O$_3$ glasses. Such differences in the density might induce the accumulation of extremely large stresses in the inside of crystals, eventually causing the breaking of crystals.

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