

Growth of $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ single crystals and behavior of Sm during growth

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$\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ has attracted much attention as a new pressure gauge in a diamond anvil that can generate extremely high pressure up to 200GPa. The shift of the fluorescence line of Sm^{2+} in SrB_4O_7 was used to determine pressure in a diamond anvil. $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ polycrystals obtained from the melt by slow cooling have usually been used. These polycrystals include other phases such as $\text{SrB}_6\text{O}_{10}$ and SrB_2O_4 , and exhibit variations in fluorescence intensity and a broader line width. In this study, we grew $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ single crystals by the CZ method and examined whether the grown crystal can be used as a pressure gauge in a diamond anvil instead of polycrystals. It was revealed that divalent Sm was predominant in the grown crystals and the grown crystals did not include other phase bearing divalent Sm such as $\text{SrB}_6\text{O}_{10}$, leading to broader line width. Therefore, it can be concluded that the grown $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ crystal is promising for precise pressure measurement.

Key words: $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$, diamond anvil cell, crystal, superior high pressure, solid liquid interface

1. Introduction

The diamond anvil cell (DAC) is a simple device capable of generating very high pressure up to 200 GPa by compressing materials between two gem-quality diamond anvils, and has been used in many research fields such as earth science and material science. For high pressure study in DAC, the fluorescence shift of ruby with pressure is commonly used as optical pressure sensor. However, fluorescence lines (R_1 and R_{29}) of ruby rapidly degrade with temperature, and R_1 peak wavelength (694.24nm) exhibits a strong temperature dependence, leading to unreliable pressure measurements above 473K. In order to determine accurately pressure at high-pressure and high-temperature ranges, new optical sensor materials whose fluorescence spectra are unaffected by temperature are required, and many efforts have been devoted to the development of new sensor materials.

Recently, $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ has attracted attention as a new pressure gauge in DAC. The shift of the $^5\text{D}_0\text{-}^7\text{F}_0$ transition (named 0-0 line) at 685.4nm of Sm^{2+} in SrB_4O_7 was used to determine the pressure. The 0-0 line is hardly affected by temperature ($d\lambda/dT=+0.001 \text{ \AA}/\text{kbar}$) [1].

To our knowledge, each researcher using a diamond anvil cell has respectively $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ polycrystals from the melt by slow cooling. These polycrystals, however, include other phases such as $\text{SrB}_6\text{O}_{10}$ and SrB_2O_4 , and exhibit variations in

fluorescence intensity and a broader line width leading to uncertain results. To solve this problem, we paid attention to the $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ single crystal because single crystal has uniform properties compared to polycrystals.

P. Mikhail et al. [2] first reported the growth of $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ single crystal using CZ method. But they did not characterize grown crystals in detail and investigate the possibility of the application of grown crystal to a pressure gauge in DAC. We have been investigating the growth of high-quality SrB_4O_7 single crystals [3-4], and thus we considered that it was possible to grow high-quality $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ crystal by means of our improved CZ furnace for borate crystals.

On the other hand, Sm in the starting materials is trivalent, whereas Sm in grown $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ crystal is divalent. This shows that a quantitative valence change from Sm^{3+} to Sm^{2+} takes place during growth. The mechanism of such a valence change during growth is not clear, and revealing this mechanism is important for the growth of high-quality $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ single crystal.

Therefore, in this paper, the growth of $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ crystals and the behavior of Sm during growth are investigated. We also show that the precise pressure determination is possible if grown crystal is used instead of polycrystal.

2. Experimental procedures

$\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ crystals were grown in air by the CZ

method. SrB_4O_7 polycrystalline powder with the molar ratio (B/Sr) of 4.00 was prepared through solid-solid reaction of SrCO_3 (99.9%), H_3BO_3 (99.9%) or B_2O_3 (99.9%) at 900°C for 10 hours. Two starting materials with different compositions were used. One (a) is SrB_4O_7 powder with excess Sm_2O_3 (2, 5, 7 wt%) and the other (b) is SrB_4O_7 powder with excess Sm_2O_3 (2, 5, 7 wt%) and B_2O_3 to keep the molar ratio (Sm/B) of 4.00. Pt crucible used was $50\phi \times 50\text{mm}$. The pulling direction was parallel to $\langle 010 \rangle$, growth rate was from 0.1 to 0.3 mm/h and rotation rate was from 5 to 20 rpm. $\text{Sm}:\text{SrB}_4\text{O}_7$ glass and $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ polycrystal were also made from the melt of the starting material (a). The melt was kept at 1050°C for 1 h in air. The glass was made by a rapid cooling rate, that is about $100^\circ\text{C}/\text{min}$ from 1050°C to room temperature. $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ polycrystal was made from the melt in the cooling rate ($10^\circ\text{C}/\text{h}$) from 1050°C to room temperature. Grown crystals, glass and polycrystal were identified by XRD.

To determine the valence of Sm, the fluorescence spectra of those samples were measured at room temperature by irradiation of an Ar^+ laser (488nm, 10mW) onto a polished thin section ($3 \times 3 \times 1\text{mm}$) made from grown crystal. The fluorescence intensity was also compared with those of $\text{Sm}:\text{SrB}_4\text{O}_7$ glass and $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ polycrystal.

3. Results and discussions

Figure 1 shows a grown $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ crystal in air by the CZ method. Grown crystals and $\text{Sm}:\text{SrB}_4\text{O}_7$ polycrystals were pale pink, and $\text{Sm}:\text{SrB}_4\text{O}_7$ glass was yellow. XRD patterns of grown crystals using the starting materials (a) and (b) are shown in Fig.2. This figure shows that these grown crystals were consisted of SrB_4O_7 and a small amount of SmBO_3 and that content of SmBO_3 in a grown crystal using the starting material (b) seems to be less than that in a grown crystal using the starting material (a). Thus, the sample for the measurement of fluorescence spectra is fabricated from the crystal grown using starting material (b). On the other hands, $\text{Sm}:\text{SrB}_4\text{O}_7$ polycrystal contains a small amounts of $\text{SrB}_6\text{O}_{10}$, SrB_2O_4 and SmBO_3 except for SrB_4O_7 as shown in Fig.3. It is revealed that there is no crystal phase in $\text{Sm}:\text{SrB}_4\text{O}_7$ glass from XRD and the polarizing microscope observation.

The fluorescence spectra (0-0 line) at 685.4nm of polycrystal (Sm_2O_3 5wt%) and grown crystal ((a) Sm_2O_3 2wt%) were shown in Fig.4. The fluorescence spectrum of grown crystal has higher intensity and narrower line width than those of polycrystal. The reason for these differences is unclear; however, the concentration fluctuation of Sm due to rapid crystallization, other phases and the strain of the

crystal lattice in the polycrystal sample may result in such differences.

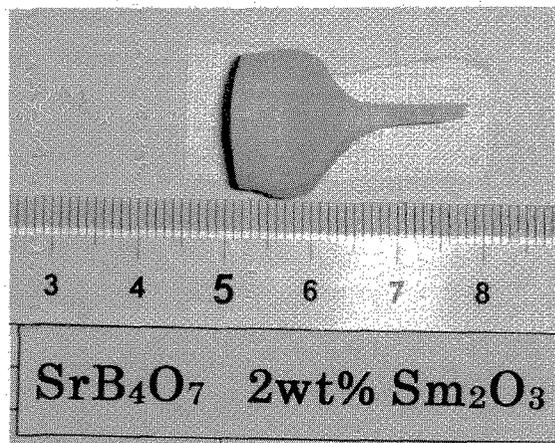


Fig.1 As-grown $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ crystal using the CZ method (seed crystal : SrB_4O_7 crystal)

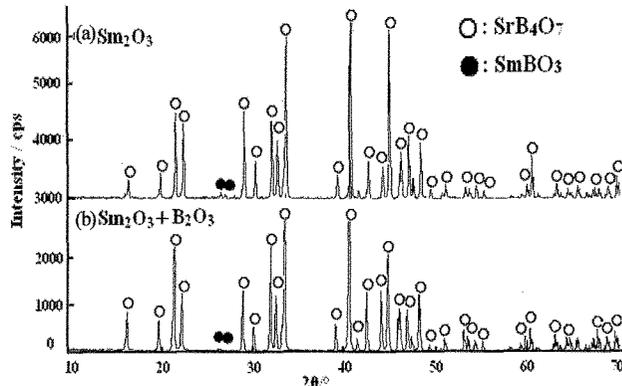


Fig.2 XRD patterns of crystals grown by adding (a) Sm_2O_3 (2wt%), (b) Sm_2O_3 (2wt%) and B_2O_3 to keep the molar ratio (Sm/B) of 4.00.

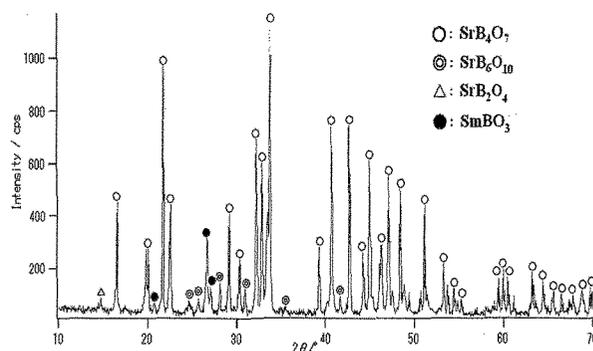


Fig.3 XRD pattern of polycrystal sample with excess 5wt% Sm_2O_3 .

The change of the fluorescence spectra (0-0 line) of grown crystals with the content of Sm_2O_3 in the starting material (b) is shown in Fig.5. This figure shows that the intensity was proportional to the content of Sm_2O_3 . The intensity of the fluorescence spectra hardly changes in the crystal grown with the same content of Sm_2O_3 . Therefore, it may be

considered that the fluorescence intensity depends upon the content of Sm^{2+} ion and that the fluctuation of Sm content in a grown crystal is small, expecting from impurity distribution during the crystal growth from the melt.

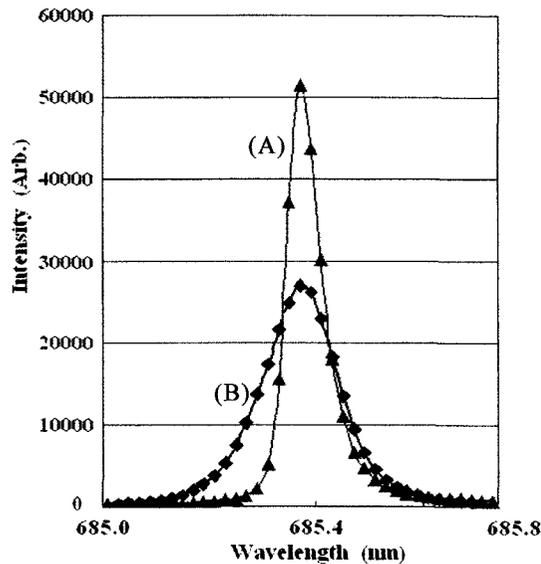


Fig.4 Fluorescence spectra (0-0 line) of a grown crystal (Sm_2O_3 2wt% and B_2O_3) (A) and polycrystal (Sm_2O_3 5wt%) (B).

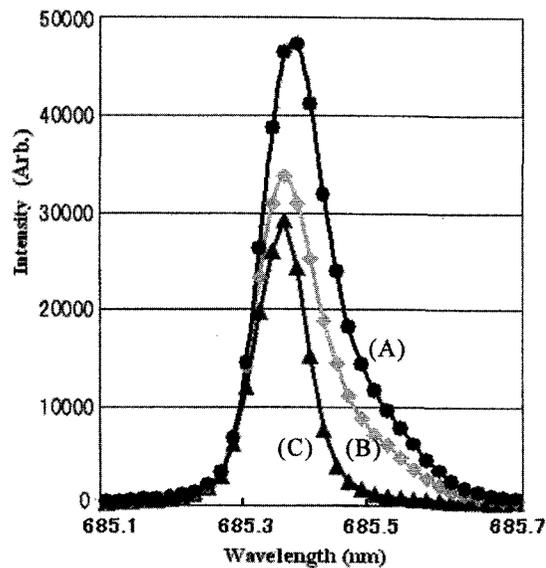


Fig.5 Fluorescence spectra (0-0 line) of grown $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ crystal using the starting material (b) with excess Sm_2O_3 (7wt%) (A), Sm_2O_3 (5wt%) (B) and Sm_2O_3 (2wt%) (C). B_2O_3 were also added to keep the molar ratio (Sm/B) of 4.00 in each starting material.

The fluorescence spectra from 625 to 690nm at 300K of grown crystal are shown in Fig.6 together with those of polycrystal, ceramics[2] and glass. The broad band $^4\text{G}_{5/2}-^6\text{H}_{9/2}$ transitions near 650nm belongs to trivalent samarium, whereas narrow line near 685nm

can be attributed to the $^5\text{D}_0-^7\text{F}_0$ transitions of divalent samarium [5]. Sm^{2+} exists predominantly in crystal and polycrystal samples, whereas both Sm^{2+} and Sm^{3+} exist in ceramic sample and only Sm^{3+} exists in glass sample. $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ has been required for the pressure gauge in DAC, and thus it is considered that ceramics and glass samples are not proper for this gauge because of a considerable content of Sm^{3+} in those samples.

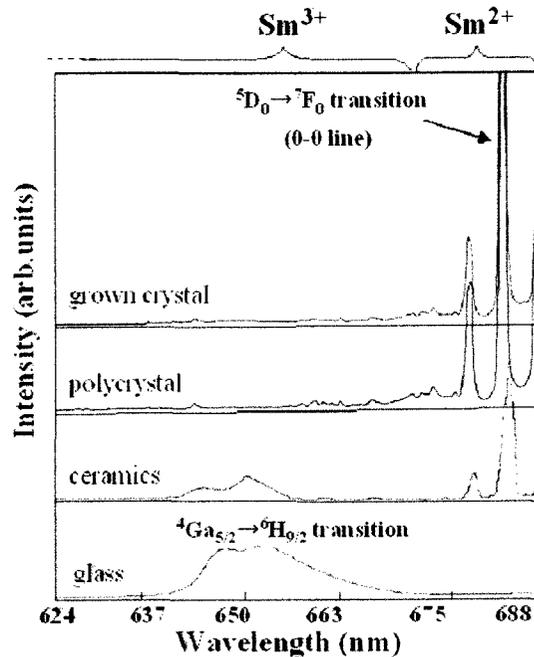


Fig.6 Fluorescence spectra from 625 to 690nm at 300K of each $\text{Sm}:\text{SrB}_4\text{O}_7$ samples.

Valence of Sm and coexisting other phases were given in Table.1. Polycrystal contains $\text{SrB}_6\text{O}_{10}$ and SrB_2O_4 including Sm^{2+} as secondary phases. The fluorescence line of $^5\text{D}_0-^7\text{F}_0$ transitions of Sm^{2+} in those phases overlaps with that in $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ at room temperature [5]. The pressure shift of this 0-0 line at 685.4nm in $\text{Sm}^{2+}:\text{SrB}_6\text{O}_{10}$ and $\text{Sm}^{2+}:\text{SrB}_2\text{O}_4$ however, is not the same as in $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$. This makes the pressure measurement vague. Therefore, we conclude that grown crystals are more promising than $\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ polycrystals because polycrystal sample includes secondary phases including Sm^{2+} .

Table 1 Valence of Sm and coexisting other phases in each sample.

Sample	Valence of Sm	Other phase
Glass	Sm^{3+}	—
Polycrystal	Sm^{2+}	$\text{SrB}_6\text{O}_{10}$, SrB_2O_4 , SmBO_3
Grown crystal	Sm^{2+}	SmBO_3 (trace)

predominantly in a glass state. Judging from this

result, Sm^{3+} seems to be more stable in the melt. Divalent Sm is predominant in the grown crystals although excess Sm_2O_3 (Sm^{3+}) and B_2O_3 were added to the starting material. Thus, we conclude that a quantitative valence change from Sm^{3+} to Sm^{2+} takes place at the solid-liquid interface during growth. In the solid-liquid interface, its state is slightly reduced compared with the melt around the interface [6]. This reduced state is one reason for the valence change of samarium. It may be considered that Sr^{2+} , Sm^{2+} and Sm^{3+} ions exist at the solid-liquid interface. Furthermore, the ionic radii of Sr^{2+} , Sm^{2+} and Sm^{3+} are 1.31, 1.32 and 1.13 Å, respectively, for the coordination number of nine [7], and thus it may be estimated that only Sm^{2+} , with similar radius to Sr^{2+} , substitutes easily Sr^{2+} site in the SrB_4O_7 crystal.

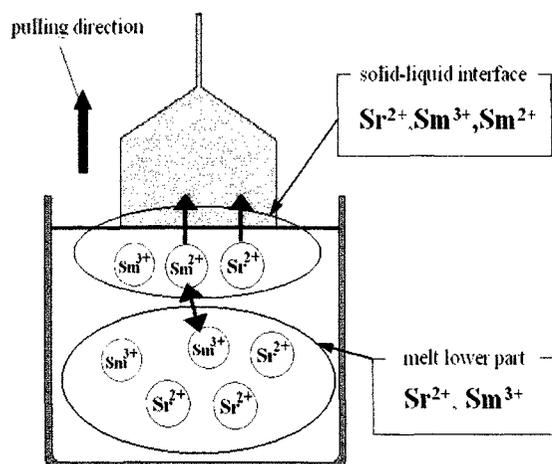


Fig.7 Schematic diagram of valence change of Sm from Sm^{3+} to Sm^{2+} in the solid-liquid interface.

4. Conclusions

$\text{Sm}^{2+}:\text{SrB}_4\text{O}_7$ crystal was grown in air by the CZ method. The fluorescence intensity was proportional to the content of Sm in starting material.

From the fluorescence measurements, Sm^{2+} exists predominantly in grown crystals although Sm_2O_3 (Sm^{3+}) and B_2O_3 was added to the starting material to keep the molar ratio (Sm/B) of 4.00. It may be considered that this change from Sm^{3+} to Sm^{2+} is due to the reduction state in the solid-liquid interface.

The grown crystals are suitable for precise high pressure measurement, compared with polycrystals including $\text{SrB}_6\text{O}_{10}$ and some earth science researchers have already confirmed pressures up to 40GPa using those single crystal samples.

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