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Growth of transparent SrB_4O_7 single crystal and its new applications

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Abstract

High-quality and transparent SrB_4O_7 single crystal has been successfully grown by the Czochralski (CZ) method. Transparency from 200 to 1100 nm and dielectric changes with the temperature ranging from 300 to 750 K are measured. Crystal quality is discussed for second harmonic generation in VUV. Sm^{2+}:SrB_4O_7 crystal has also been grown by the CZ method. Fluorescence line of Sm^{2+} close to 685.5 nm in a crystal is measured. It is revealed that Sm^{2+}:SrB_4O_7 crystal is a promising material for a pressure gauge in a diamond anvil.

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1. Introduction

Piezoelectric crystals are used for surface acoustic wave (SAW) and nonlinear optical devices in electronic and communication equipment, such as mobile telephones, televisions and solid-state lasers. With the rapid advance in information technology, there have been strong and continuing demands for improved functionality of these devices. One of the most critical issues in advancing this technology is to develop new piezoelectric crystals. Many efforts have been made to find new piezoelectric materials [1,2].

SrB_4O_7 crystal (SBO) is a piezoelectric material that belongs to the $Pnm2_1$ space group and has unit cell parameters $a = 4.4255$ Å, $b = 10.709$ Å, $C = 4.231$ Å, and $Z = 2$ [3]. Oseledchik et al. [4] reported the crystal growth of SBO crystal by the Cz method, whereas Fan et al. [5] reported the crystal growth by the Kyropolus method. One of

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most serious and common problems in borate crystal growth is the macroscopic opaque defect, in which the crystal becomes clouded [6].

Applications of SBO have been investigated since 1985 [7] and SBO has been attracting much attention as a nonlinear optical crystal with the following benefits: a transparency down to 120 nm, a high nonlinear coefficient, the highest damage threshold, and no hygroscopicity [3]. Komatsu and Ikeda [8] demonstrated that this crystal also had the highest SAW velocity among piezoelectric crystals. Recently, Petrov, one of the authors, reported the wavelength conversion of femtosecond SHG pulses down to 125 nm using SBO [9]. SBO is an attractive crystal for generating SHG pulses in the VUV region. However, crystals used in this study exhibited a different transmission. If a transparent crystal was used, valuable information, including precise SHG properties, were obtained. Thus, high-quality transparent crystals are required to determine precise SHG properties and to generate shorter pulses.

Sm^{2+}:SBO has also gained attention as a pressure gauge in a diamond anvil that can generate extremely high pressure, up to 200 GPa. The shift of the fluorescence line (685.5 nm) of Sm^{2+} in this crystal was used to determine the pressure. This shift is almost unaffected by temperature. This establishes Sm^{2+}:SBO as a superior pressure gauge material, compared to ruby and other gauge materials. An individual researcher using a diamond anvil produced Sm^{2+}:SBO polycrystals from the melt in slow cooling. Crystal size in this polycrystal is very small (only up to 10 μm). This also includes other phases such as SrB_6O_{10} and SrB_2O_4, and exhibits variations in fluorescence intensity and a broader line width leading to uncertain results. To solve this problem, we paid attention to the Sm^{2+}:SBO crystal because this crystal has uniform properties compared to polycrystals. After studying the growth of the Sm^{2+}:SBO crystal, we determined that the precise pressure choice is possible if crystal is used instead of polycrystal. P Mikhail et al. [10] reported the growth of Sm:SBO single crystals using the Cz method. However, they did not investigate the application of grown crystal to a pressure gauge.

In this study, we describe the growth of high-quality SBO crystals, and Sm^{2+} bearing SBO crystals for the above two applications. We also discuss new measurement results required for these applications.

2. Experimental procedure

SBO and Sm^{2+}:SBO crystals were grown in air by the CZ method. The starting material comprised of SBO polycrystalline powder with the molar ratio (B/Sr) of 4.00 for SBO crystal growth. SrB_4O_7 powder 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 h. The pulling direction was parallel to $\langle 0\,1\,0 \rangle$, and growth and rotation rates were 0.1–0.3 mm/h and 5–20 rpm. Platinum (Pt) crucible used was $50\phi \times 50$ mmh. The transparency at wavelengths from 190 to 1000 nm (Shimazu UV160) and the dielectric constant were measured over a wide temperature range of 300–750 K (HP 4284A).

SrB_4O_7 powder with Sm_2O_3 (2, 5 wt%) added, was used as the starting material for Sm^{2+}:SBO crystal growth. Growth parameters are the same as above. The Sm content in grown crystals was measured by EPMA. The fluorescence spectra of grown crystal were also measured at room temperature by irradiation of an Ar^+ laser (488 nm, 10 mW) onto a polished thin section ($3 \times 3 \times 1\,mm^3$) made from grown crystals. The fluorescence intensity of 685.5 nm was then compared with that of Sm:SBO glass and Sm:SBO polycrystal made from the melt.

3. Results and considerations

3.1. Growth of transparent SBO single crystal

Fig. 1 shows a grown, cloudy SBO crystal. As shown in Fig. 2, microscopic observation revealed many inclusions in the cloudy crystals. Inclusions consist of voids and other phase material. Inclusions in borate crystals were caused by volatile impurities, such as water and by the deviation from the stoichiometric composition in the starting

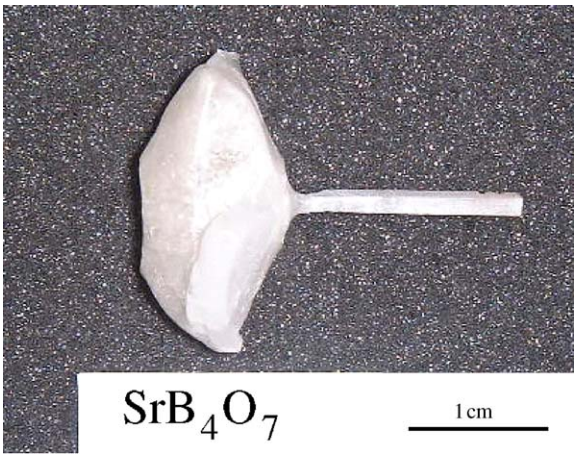

Fig. 1. As-grown cloudy SrB_4O_7 single crystal.

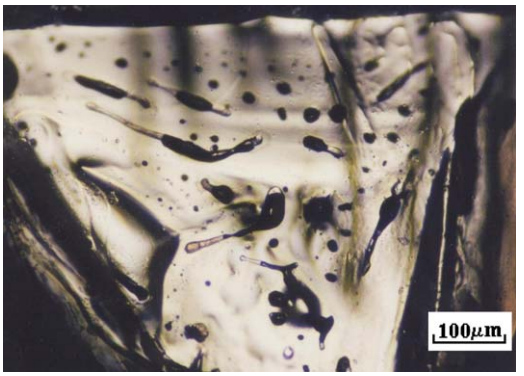

Fig. 2. Inclusions in cloudy SrB_4O_7 crystal.

material [11]. These inclusions were derived from the supersaturation of impurities in the melt, and their entrapment occurred by the sudden rate of increase in cellular growth at the solid–liquid interface [11,12]. Thus, it was important to decrease those impurities and prevent cellular growth in order to grow transparent crystals. We also adjusted the stoichiometric composition by considering the content of volatile impurities, such as water, and maintained a high-temperature gradient to avoid cellular growth by changing the hot-zone structure. As a result, transparent SBO crystal was grown (Fig. 3). Although there were micro-cracks near the surface resembling a cloud, the crystal was transparent, and inclusions could not be observed under a microscope.

Fig. 3. As-grown transparent SrB_4O_7 single crystal.

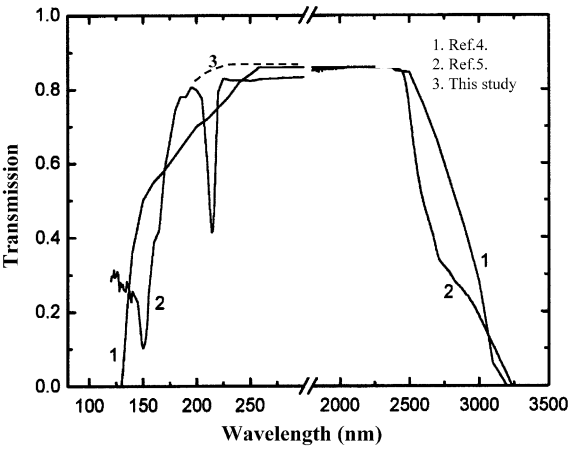

Fig. 4. Transparency of SrB_4O_7 single crystal.

Transmission from 200 to 1100 nm using (0 1 0) polished plates ($5 \times 5 \times 2\,mm^3$ and $5 \times 5 \times 3\,mm^3$) and previous results are shown in Fig. 4. Plate transparency did not differ with thickness, and our results demonstrated high transmission rates and no absorption peak at 214 nm, compared with previous results. This may indicate that high-quality transparent crystal has been successfully grown and that the grown crystal will be suitable for SHG experiments in VUV. The dielectric anomaly in the temperature range of 300–750 K was not observed, demonstrating that SBO does not exhibit ferroelectric properties [13].

3.2. Growth of Sm^{2+}:SrB_4O_7 and its fluorescence properties

Fig. 5 depicts an as-grown Sm^{2+}:SrB_4O_7 (Sm^{2+}:SBO) crystal. The crystal was clouded by its polycrystalline structure as well as many cracks and voids. Grown crystals were identified with SrB_4O_7 by X-ray diffraction. It is difficult to grow Sm^{2+}:SBO single crystals, but this should be considered further. Polished thin sections ($3 \times 3 \times 1\,mm^3$) made from grown crystals are pinkish and transparent. The light pink coloring is caused by the incorporation of Sm^{2+} into the crystal. Fig. 6 illustrates the fluorescence spectra from 625 to 690 nm at 300 K of crystal, polycrystal and glass samples. The broad band $^4Ga_{5/2} \rightarrow {}^6H_{9/2}$ transitions near 650 nm belongs to trivalent samarium, and the narrow line near 685 nm can be attributed to the $^5D_0 \rightarrow {}^7F_0$ transitions of divalent samarium [10]. From this result, it may be considered that Sm^{3+} exists predominantly in a glass state and Sm^{2+} mainly in crystal and polycrystal, whereas Sm^{3+} and Sm^{2+} coexist in Sm:SBO ceramics prepared in air under the melting point [10]. Judging from these results, Sm^{3+} seems to be more stable in the melt. 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 [11]. This reduced state is one reason for the result in the valence change of samarium.

Fig. 5. As-grown Sm^{2+}:SrB_4O_7 crystal.

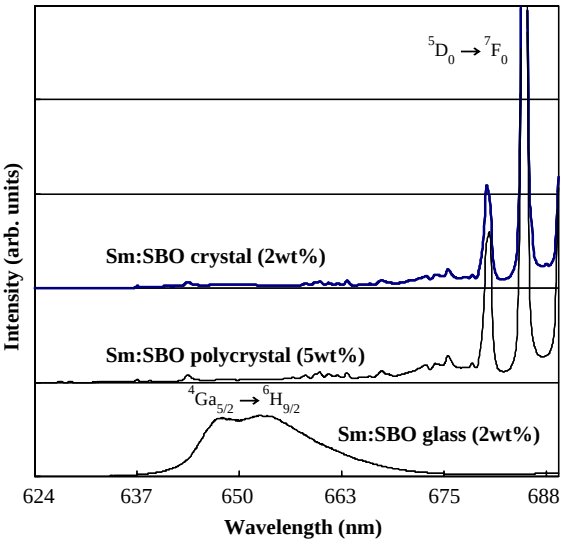

Fig. 6. Fluorescence spectra from 625 to 690 nm at 300 K of crystal, polycrystal and glass samples; Sm^{2+}:SrB_4O_7 crystal was grown from the melt including 5 wt% Sm_2O_3 and polycrystal and glass samples contain 5 and 2 wt% Sm_2O_3, respectively.

X-ray diffraction patterns of grown crystals coincided with that of SrB_4O_7, although grown crystals include a small amount of Sm. This indicates that Sm^{2+} replaces the Sr site in SBO crystal. Fig. 7 illustrates the fluorescence spectra of 685.5 nm ($^5D_0 \rightarrow {}^7F_0$ transition) of crystals, grown from the melt with 2 and 5 wt% Sm_2O_3. The content of Sm in each crystal was about 0.8 and 2.5 wt% Sm_2O_3, respectively. The fluorescence intensity was dependent upon the Sm content, and the intensity variation in crystal samples was almost undetectable. However, the fluorescence intensity and line width in Sm^{2+}:SBO polycrystal may fluctuate greatly, compared with the grown crystal. The reason for these differences is unclear; it is possible, however, that the concentration fluctuation of Sm due to rapid crystallization and other phase in the melt, and the strain of the crystal lattice due to the polycrystal structure, result in such differences. In addition, Sm^{2+}:SBO polycrystal contains SrB_6O_{10} as secondary phases and SrB_6O_{10} includes Sm^{2+}. The fluorescence

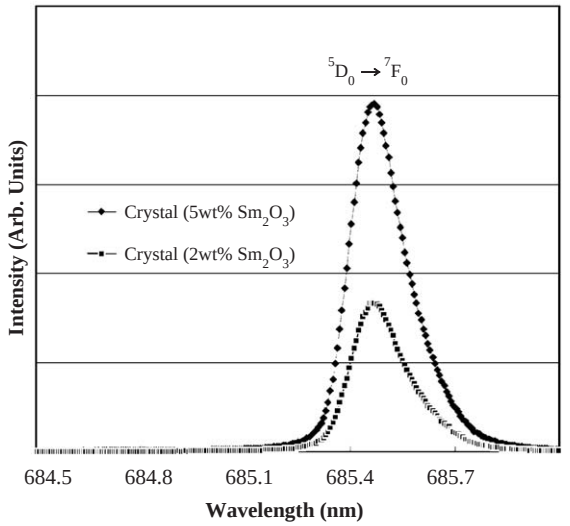

Fig. 7. Fluorescence spectra (685.5 nm) at room temperature of Sm^{2+}:SrB_4O_7 crystal, grown from the melt with 2 and 5 wt% Sm_2O_3, respectively.

spectra of $^5D_0 \rightarrow {}^7F_0$ transitions of divalent samarium in SrB_6O_{10} at room temperature overlap that in Sm^{2+}:SBO [14]. The pressure shift of this 0–0 emission line (685.5 nm) in Sm^{2+}:SrB_6O_{10}, however, is not the same as in Sm^{2+}:SBO. This makes the pressure measurement vague. Therefore, we conclude that crystal samples are more promising than Sm^{2+}:SBO polycrystal.

4. Conclusions

A high-quality transparent SBO crystal was successfully grown by avoiding cellular growth and by reducing impurities, such as water and deviation from stoichiometric composition. The grown crystal showed high transmission and no absorption peak of 214 nm. SBO was the paraelectric material in the temperature range 300–750 K.

Sm^{2+} exists predominantly in grown Sm:SBO crystals. The intensity fluctuation of 0–0 line was almost not observed in a thin section taken from this crystal. This result demonstrates that Sm^{2+}:SBO crystal is promising as a pressure gauge material, and some earth science researchers have already confirmed pressures up to 40 GPa using this sample.

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