

LaBGeO₅ single crystals in glass and second-harmonic generation

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Abstract

Flower-shaped crystals with diameters of 100–200 μm consisting of LaBGeO₅ (LBGO) single crystals similar to petals were observed in the interior of transparent LBGO surface-crystallized glasses. Each flower-shaped crystal was radially grown from the surface of the included bubbles. A more intense second-harmonic generation was observed from the LBGO crystallized glasses with the flower-shaped LBGO single crystals compared to the samples without such crystals based on the Maker fringe technique and second-harmonic (SH) generation microscopy. The SH intensity for the flower-shaped LBGO single crystals monotonically decreased with increasing temperature up to $\sim 350^\circ\text{C}$, less than the Curie temperature reported so far ($\sim 530^\circ\text{C}$). It is considered that the internal compressive stress induced by the difference in the thermal expansion between the LBGO single crystal and the corresponding glass affect the ferroelectric property of the flower-shaped LBGO single crystals in glass.

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1. Introduction

Ferroelectric LaBGeO₅ (LBGO) crystals with a Curie temperature of $T_c \sim 530^\circ\text{C}$ have attracted much attention, because Nd-doped LBGO crystals have the possibility of cw laser emission in the green region by self-frequency doubling [1,2]. The LBGO crystal has a hexagonal stillwellite (CeBSiO₅)-type structure, in which the BO₄ tetrahedra form screw chains along the c-axis and the La atoms are in the nine-fold vertices arranged under and over the slightly distorted GeO₄ tetrahedra [1]. The crystal structure of LBGO is shown in Fig. 1. It is known that a glass with a stoichiometric composition (i.e., 25La₂O₃·25B₂O₃·50GeO₂) corresponding to the LBGO crystal can be prepared using a conventional melt-quenching technique and the LBGO crystalline phase is formed by crystallization of the glass [3–5]. Recently, Takahashi et al. succeeded in fabricating transparent surface-crystallized glasses with various nonlinear optical

crystals and examined their second-order optical nonlinearities [6–10]. Particularly, it was suggested that a transparent surface-crystallized glass fabricated from the precursor glass with the exact or very close composition of stoichiometry of the target crystal directly reflects the optical nonlinearity of the corresponding single crystal in the research of transparent LBGO surface-crystallized glass, demonstrating that glass crystallization processing is a noble techniques for the fabrication and exploitation of optical functional materials [8,11].

In a previous study, it was found that bubbles, which were included during the glass molding process, effectively act as nucleating sites for the formation of LBGO crystals in the interior of the 25La₂O₃·25B₂O₃·50GeO₂ glass [12]. The shape of the LBGO crystals surrounding the bubbles looks like a flower. However, the details of the formation and second-harmonic generation (SHG) of the flower-shaped LBGO crystals have not yet been clarified. Therefore, the aim of this study is to examine the morphology and the second-order optical nonlinear properties of the flower-shaped LBGO crystals in the transparent LBGO surface-crystallized glass.

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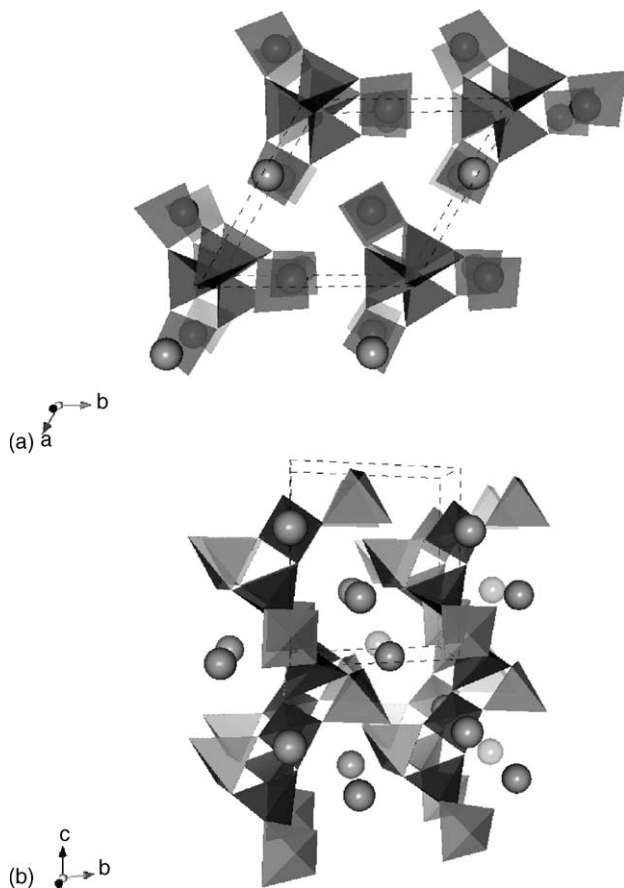


Fig. 1. Crystal structure of LBGO: (a) a view in the (001) direction. Sphere and polyhedra of bright and dark colors correspond to La atom and GeO_4 and BO_4 tetrahedral units, respectively, and (b) a view in the (100) direction. These figures were drawn using VENUS by Dilanian and Izumi.

2. Experimental

The glass with a composition of $25\text{La}_2\text{O}_3 \cdot 25\text{B}_2\text{O}_3 \cdot 50\text{GeO}_2$ was prepared using a conventional melt-quenching method. Commercial powders of reagent La_2O_3 , B_2O_3 and GeO_2 were mixed and melted in a platinum crucible at 1300°C for 20 min in an electric furnace. The batch weight was 40 g. The melts were poured into Al_2O_3 molds (tube: inner radius, 11 mm; outer radius, 16 mm; height, 10 mm) heated at 300°C and then gradually cooled (not pressed) in air. The glass plates with a thickness of 1 mm obtained by cutting the mold glasses were heat-treated to precipitate the LBGO crystals. The shape of the crystals formed in the interior of the glass was observed using a polarization microscope. SHG measurement was carried out using the Maker fringe technique [13], in which a fundamental wave of a pulsed Nd: YAG laser at $\lambda = 1064\text{ nm}$ was used as the incident light and the intensity of the generated green light at $\lambda = 532\text{ nm}$ was measured as a function of the incident light angle. The SHG at $\lambda = 532\text{ nm}$ of α -quartz was used as a reference. In addition, the SHG microscope was also utilized for the observation of LBGO crystals in the in-

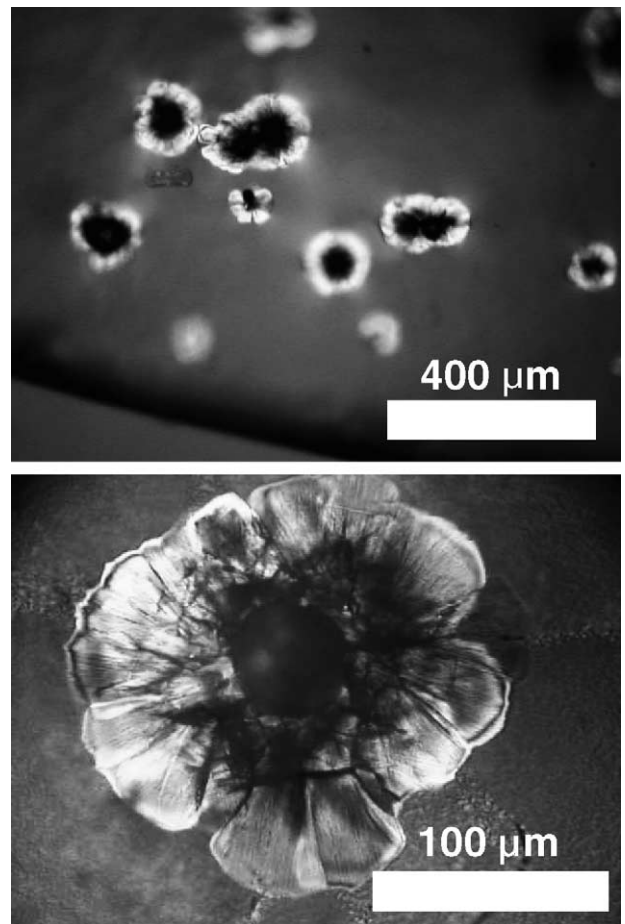


Fig. 2. The polarization micrographs for the interior region of the transparent LBGO surface-crystallized glasses.

terior of the glass. SHG microscopy is a powerful tool for observing the domain structure in nonlinear optical single crystals [14]. The laser source and its wavelength for the SHG microscopy were same as those for the Maker fringe technique.

3. Results

3.1. Formation of flower-like shape crystals

The polarization micrographs for the interior region of the transparent LBGO surface-crystallized glasses obtained in the present study are shown in Fig. 2. This sample was fabricated by a two-step heat-treatment (670°C , 10 h + 730°C , 3 h) [6,12]. It is seen that many crystalline particles are formed even in the interior. This kind of crystallization has not been observed in transparent LBGO surface-crystallized glasses obtained in previous studies [5,6]. From Fig. 2, it is clear that crystals with diameters of about $100\text{--}200\text{ }\mu\text{m}$ are precipitated from the surface of the bubbles. The crystals have a flower-shape, looking like the familiar “pansy” flower. Furthermore, it is seen that each crystal radially grows

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