

Large second-order optical nonlinearity in 30BaO–15TiO₂–55GeO₂ surface crystallized glass with strong orientation

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The correlation between the orientation degree of surface crystalline phase and the second-order optical susceptibility, d coefficient for second-harmonic generation, in 30BaO–15TiO₂–55GeO₂ (BTG55) crystallized glass was investigated using x-ray diffraction measurements and a Maker fringe technique. The d coefficient in BTG55 crystallized glass was confirmed to depend on the orientation degree of the surface crystalline phase. An oriented fresnoite (Ba₂TiGe₂O₈) phase was observed in transparent BTG55 crystallized glass which had been heat treated at 720 °C for 3 h. The orientation degree along the polar c axis in the fresnoite phase increased with increasing removal thickness by polishing from the surface up to several microns. A d coefficient in transparent BTG55 crystallized glass of 24 ± 3 pm/V has been obtained, which is the largest value in crystallized glass ever reported. © 2006 American Institute of Physics. [DOI: 10.1063/1.2210173]

I. INTRODUCTION

Ba₂TiGe₂O₈, belonging to the $4mmFmm2$ group,¹ is a fresnoite-type (Ba₂TiSi₂O₈) oxide² with a phase transition temperature around 810 °C.^{1,3} In the fresnoite structure, the Ti (IV) ions take up a square pyramid (TiO₅) structure,^{4–7} which is connected to Ge₂O₇ (or Si₂O₇) to form a layered titanosilicate structure. Since fresnoite possesses ferroelastic,³ pyroelectric,^{8–11} and piezoelectric^{10,12–14} properties with its polarity along the c axis, it attracts attention for various applications, such as a surface acoustic wave device.¹⁴

Halliyal *et al.* reported piezoelectric and pyroelectric properties of both BaO–TiO₂–GeO₂ crystallized glass (glass ceramic) and Ba₂TiGe₂O₈ single crystals.^{9–11,13,14} The crystallized glass in the previous report¹⁴ was obtained by heat treatment at 1040 °C for 24 h, and it showed strong orientation along the c direction. The piezoelectric coefficient d_{33} (not to be confused with the nonlinear optical susceptibility used in the rest of the paper) of crystallized glass, 5–7 pm/V, which was measured by a capacitance bridge method, was comparable to that of Ba₂TiGe₂O₈ tetragonal single crystals (10 pm/V).¹⁴ These are efforts of crystallization that have focused on the crystallization of a whole bulk glass. It would be of great interest for applications in optical, acoustical, and actuator devices if crystallized regions can be created inside a bulk glass in a well-controlled manner.

Recently, Takahashi *et al.* focused on the second-order nonlinear optical property of BaO–TiO₂–GeO₂ (BTG) crystallized glass and reported the second harmonic generation (SHG) of the surface crystallized BTG glasses measured by a Maker fringe technique.^{15–19} In particular, the transparent

30BaO–15TiO₂–55GeO₂ (BTG55) crystallized glass showed a second-order nonlinear optical susceptibility, $d_{33} = 22 \pm 3$ pm/V, which was comparable to the value of LiNbO₃ single crystal.¹⁹ Thus, transparent BTG crystallized glass is a promising candidate for nonlinear optical devices.

The origin of this large optical susceptibility or the growth of the Ba₂TiGe₂O₈ crystallized phase in a BTG55 glass, however, remains to be clarified. For practical applications, the control of the surface crystallization as well as the second harmonic (SH) intensity is important. The objective of the present study is to examine the correlation between SH intensity and the orientation degree of the surface crystallized phase of BTG55 glass, with main emphasis on the characterization of depth direction from the surface.

II. EXPERIMENT

The 30BaO–15TiO₂–55GeO₂ (BTG55) glasses were prepared by a conventional melt-quenching method. The starting materials of the glass were BaCO₃ (45 mmol, 99.95%), TiO₂ (22.5 mmol, 99.9%), and GeO₂ (82.5 mmol, 99.99%). All the chemicals were purchased from Kojundo Chemical Laboratory Co. Ltd. Batches were mixed and melted in a platinum crucible heated at 1250 °C for 20 min in an electric furnace. After a quenching on a steel plate at 200 °C, the obtained glass was annealed at T_g , temperature of glass transition, for 30 min, and then, cut into dimensions of $10 \times 10 \times \approx 1$ mm³, and mechanically polished.

Following the previous reports by our group,^{15,19} the glass sample was heat treated at 720 °C for 3 h on an alumina plate in an ambient atmosphere to obtain transparent surface crystallized glass. The heating rate was 10 K/min from room temperature to 690 °C and reduced to 1 K/min from 690 to 720 °C. After a heat treatment at 720 °C for 3 h, the furnace was cooled down without temperature control. Since the crystalline phase was observed at both the

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front side (air side) and the backside (alumina side) of a heat-treated sample, the backside was mechanically polished to remove the crystalline phase completely and to obtain a mirror surface. Only the crystalline phase at the air side of the heat-treated sample was used for characterization in the present study, in which x-ray diffraction (XRD) and SHG were conducted step by step after each stage of stepwise surface polishing at the same spot of the sample. All mechanical polishing was carried out using DOCTOR LAP ML-180 (Maruto Instrument Co. Ltd.).

The temperatures of glass transition T_g , crystallization onset T_x , and crystallization peak T_p were determined by differential thermal analysis (DTA) operated at a heating rate of 10 K/min using TG8120 (Rigaku). The microstructure of the crystallized region was observed with a scanning electron microscope (SEM), JSM-5310LVB (JEOL). The crystalline phases in the glasses were examined by measurements with Cu $K\alpha$ radiation. SH intensities of the crystallized glass were evaluated by a Maker fringe technique²⁰ and its d coefficient was determined, in which Z-cut quartz (thickness of 0.6 mm) was used as a reference. The crystallized side of the sample was irradiated with the fundamental wavelength of 1064 nm of an Yttrium-aluminum-garnet (YAG) laser (GCR-130-10, Spectra Physics).

The analysis of experimental SHG fringe patterns was carried out according to the Maker fringe theory.²⁰ The Maker fringe pattern is described using the intensities of SH wave $P_{2\omega}$ and incident light P_ω ,

$$P_{2\omega} = C d_{\text{eff}}^2 t_\omega'^4 T_{2\omega}'' R(\theta) P_\omega^2 \frac{\sin^2 \Psi}{(n_\omega^2 - n_{2\omega}^2)^2}, \quad (1)$$

where t_ω' and $T_{2\omega}''$ are the transmission factors of the incident light and SH wave, respectively. d_{eff} is the effective second-order nonlinear optical susceptibility, and $R(\theta)$ is the multiple reflection factor. n_ω and $n_{2\omega}$ are the refractive indices of the incident light and the SH wave of the crystallized glass matrix, respectively. C is a constant. ψ is defined by Eq. (2),

$$\psi = \frac{2\pi L}{\lambda} (n_\omega \cos \theta_\omega' - n_{2\omega} \cos \theta_{2\omega}'), \quad (2)$$

where L is the thickness of the nonlinear medium, λ is the wavelength of the incident light, and θ_ω' and $\theta_{2\omega}'$ are the reflection angles of the incident light and SH wave, respectively. The second-order nonlinear susceptibility, d_{33} , of a uniaxially oriented sample was estimated by using $d_{\text{eff}} = d_{33} \sin \theta_\omega'$.

The refractive index of the SH wave $n_{2\omega} = 1.855$ was used as in a previous report.¹⁶ n_ω was used as a fitting parameter. The thickness L of the BTG55 crystallized phase was obtained by subtracting the removal thickness from the total thickness of the crystallized phase. The total thickness of the crystallized phase was experimentally determined to be equal to the maximum removal thickness at which the XRD pattern was observable. The removal thickness was measured using a micrometer (error $\pm 1 \mu\text{m}$). The d_{11} value of Z-cut quartz 0.503 pm/V was used for comparison with a previous report.¹⁸

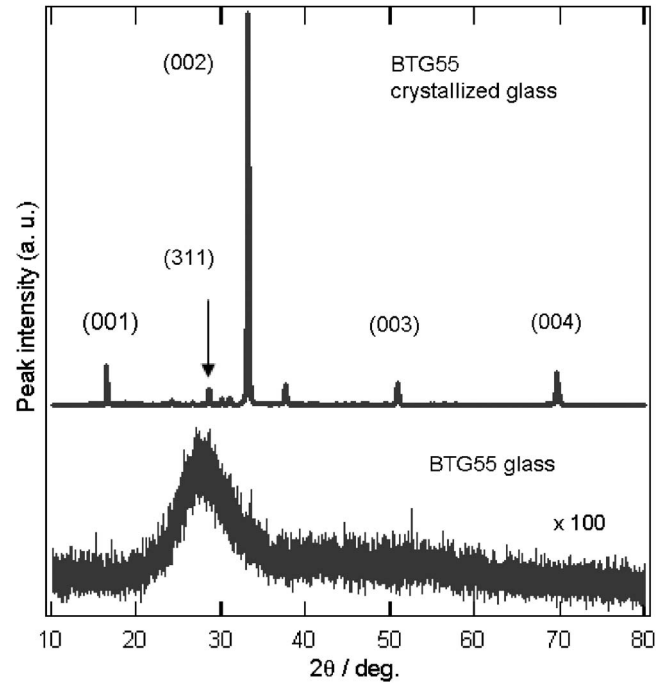


FIG. 1. XRD patterns of BTG55 glass and BTG55 crystallized glass heat treated at 720 °C for 3 h.

III. RESULTS AND DISCUSSION

A. BTG55 glass and BTG55 crystallized glass

The T_g , T_x , and T_p of transparent BTG55 bulk glass were determined as 665, 812, and 827 °C, respectively. The mirror surface of the sample became slightly rough after crystallization. Figure 1 shows the XRD patterns of BTG55 glass and BTG55 crystallized glass heat treated at 720 °C for 3 h. In the present study, the $\text{Ba}_2\text{TiGe}_2\text{O}_8$ crystal is considered as orthorhombic, because it was heat treated at a temperature (720 °C) lower than the ferroelastic phase transition temperature (810 °C).⁵ According to the JCPDS card (No. 01-077-0389), the strongest diffraction peak of fresnoite appears at $2\theta = 28.3^\circ$, corresponding to the (311) diffraction. In Fig. 1, the c -axis oriented peaks, (001), (002), (003), and (004), of fresnoite were clearly observed, indicating that the BTG55 crystallized glass has undergone a surface crystallization with a strong c orientation. The ratio of the intensity of the 002 peak I_{002} , to that of the 311 peak I_{311} , was used for an estimation of the relative degree of orientation. In an as-heat-treated sample, the I_{002}/I_{311} ratio of BTG55 crystallized glass in the present study was about 20, higher than that of BTG55 crystallized glass in a previous report.¹⁵ It was previously reported that the benitoite ($\text{BaTiGe}_3\text{O}_9$) phase, which crystallizes at a temperature lower than the fresnoite phase, initially crystallized at the surface, and then the fresnoite phase propagated around the benitoite region.¹⁵ Since benitoite exhibits a smaller optical susceptibility than fresnoite,¹⁵ generation of a benitoite phase near the surface is undesirable in obtaining a crystallized glass with a large optical susceptibility. In the present study, however, only a small amount of the benitoite phase was observed at the crystallized surface, suggesting that fresnoite can crystallize without the assistance of benitoite phase, which is thought to be a nucleus of fresnoite.

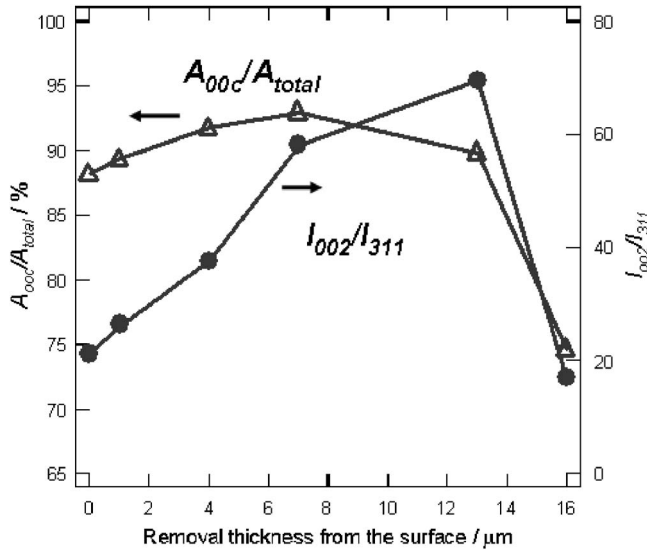


FIG. 2. A_{00c}/A_{total} ratio and I_{002}/I_{311} ratio as a function of removal thickness from the surface of BTG55 crystallized glass heat treated at 720 °C for 3 h.

The difference of crystallization behavior between the two phases is attributed to be the difference of their crystallization temperatures and the crystal growth rates. For further discussion on the correlation between a heat-treatment temperature, a heat-treatment profile, and the crystallized phase of BTG55 glass will be given in a separate paper.

B. Crystalline orientation and SH generation of BTG55 crystallized glass

It has been clearly shown that the surface crystallized phase of BTG55 glass in the present study mainly consists of *c*-axis oriented fresnoite $Ba_2TiGe_2O_8$, in which the *c* axis is a SH active orientation. The average thickness of the crystallized phase on the surface was estimated as approximately 12 μm by a scanning electron microscopy (SEM) measurement of the cross section of BTG55 crystallized glass. The fresnoite phase was, however, observed by XRD measurement even after polishing 13 μm from the surface, which was beyond the average thickness of the crystallized phase. The thickness of the total crystallized phase of the present measured area was estimated to be about 17 μm , the value beyond which no crystalline phase was observed by XRD.

Figure 2 shows the correlation between the removal thickness from the surface of BTG55 crystallized glass and the ratio of the sum of 00c peak areas A_{00c} to that of the total sum of all peaks A_{total} with 2θ ranging from 5° to 80°. The I_{002}/I_{311} ratio was also used to estimate the relative degree of orientation. Both the A_{00c}/A_{total} ratio and the I_{002}/I_{311} ratio increased with increasing removal thickness from the surface and showed their maximum value after 7 and 13 μm of polishing, respectively. In both estimates of the phase orientation, the orientation degree of the *c* axis showed its maximum after polishing of several microns. Takahashi *et al.* reported that, in an initial stage, the growth of $Ba_2TiGe_2O_8$ crystals at the glass surface generated in several orientations, and that the 002 direction, which is normal to the surface and the preferential direction for the crystal growth, survived after surface polishing.¹⁶ In the present study, stepwise polish-

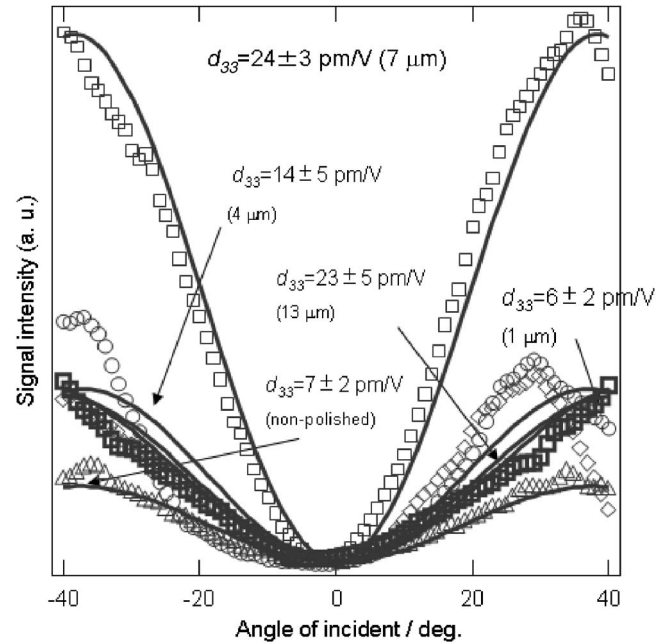


FIG. 3. Maker fringe patterns of BTG55 crystallized glasses together with the d_{33} value and removal thickness from the surface.

ing has shown that other orientations of fresnoite or other crystalline phases near the surface of the BTG55 glass were removed gradually by polishing. It indicated that the thickness of *c*-axis fresnoite phase was larger than that of other phases, and as a consequence the ratio of the *c*-axis oriented peak increased as surface polishing progressed. The difference of phase thickness was attributed to the difference of the crystal growth rate in each direction or a crystalline phase. The incremental orientation of *c*-axis fresnoite after stepwise polishing confirms the previous reports,^{11,16} in which highly *c*-oriented fresnoite in the crystalline phase was observed at the depth of several microns from the surface.

Figure 3 shows the typical Maker fringe patterns of BTG55 crystallized glasses together with the d_{33} value and the removal thickness from the surface. The d_{33} value of each glass was calculated by using Eqs. (1) and (2) together with the thickness of the crystallized phase. The obtained d_{33} values are plotted as a function of removal thickness from the surface in Fig. 4, together with the I_{002}/I_{311} ratio. The d_{33} value increased with increasing removal thickness, and after 7 μm polishing (thus thickness of the crystallized phase, L , of approximately 10 μm) it exhibited a maximum nonlinear susceptibility, $d_{33}=24\pm 3$ pm/V ($n_\omega=1.812$, $n_\omega=1.855$). The d_{33} value of the present study is comparable to that of the previous report, and it also shows the largest nonlinear susceptibility of the BTG55 crystallized glass. In addition, the tendency of d_{33} with the removal thickness from the surface was similar to those of the I_{002}/I_{311} ratio and the A_{00c}/A_{total} ratio (see Fig. 2), indicating that the d_{33} value strongly depends on the orientation of fresnoite crystallized phase.

The results presented confirm that the orientation of *c*-axis fresnoite in its crystallized phase is the dominant factor for the nonlinear susceptibility of BTG55 surface crystallized glass. The optical susceptibility of transparent BTG55 crystallized glass, which possesses a strongly *c*-oriented

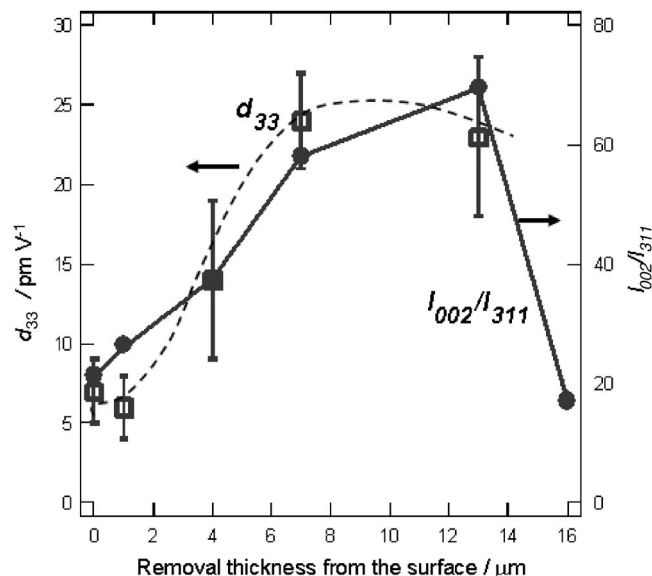


FIG. 4. The d_{33} value and the I_{002}/I_{311} ratio of BTG55 crystallized glasses as a function of removal thickness from the surface. (A broken line is the guide for the eye.)

crystallized phase, showed a maximum value, $d_{33} = 24 \pm 3$ pm/V, comparable to that of LiNbO_3 single crystal. Transparent BTG55 crystallized glass, therefore, has been shown to be a candidate for nonlinear optical materials.

IV. CONCLUSION

The orientation of the surface crystalline phase and the second-order nonlinear susceptibility, d_{33} , of transparent $30\text{BaO}-15\text{TiO}_2-55\text{GeO}_2$ (BTG55) crystallized glass were investigated using XRD and Maker fringe techniques. The orientation of the fresnoite ($\text{Ba}_2\text{TiGe}_2\text{O}_8$) phase with the polar c -axis in surface crystallized BTG55 glass was increased by polishing several microns from the surface. The d_{33} value

of BTG55 crystallized glass depends on the orientation of fresnoite with c -axis direction and showed a maximum value of optical susceptibility, $d_{33} = 24 \pm 3$ pm/V, which is the largest value in crystallized glasses ever reported.

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