Correlation between the temperature of molten state and the SH intensity of 30BaO·15TiO₂·55GeO₂ crystallized glass

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We have examined the dependence of the optical nonlinearity of the 30BaO·15TiO₂·55GeO₂ (BTG55) crystallized glass on the temperature at which the BTG55 glass melts are held in a molten state (called the “melt temperature” in the present paper). The absorption coefficient and the refractive index of the BTG55 precursor glass, and the second harmonic efficiency of its crystallized glass increased with increasing melt temperature of the precursor glass. We have defined the local structure similar to that of a crystal, “embryos of crystallites”, and the embryos are envisioned as the origin of precipitated Ba₂TiGe₂O₈ crystallites. The second harmonic generation efficiency of the BTG55 crystallized glass increased with increasing melt temperature. This is explained as due to an increase of the number of embryos of Ba₂TiGe₂O₈ crystallites with increasing melt temperature.

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1. Introduction

Crystallized glass is usually obtained by a heat-treatment or a laser irradiation of the precursor glass.^{1)–8)} Crystallized glass is one of the interesting glass materials for the following reasons. Since the crystallization of the precursor glass adds such extrinsic properties as optical nonlinearity^{1)–5)} or piezoelectricity,^{6)–7)} various properties of crystallized glass promise a large capacity to fabricate novel functional devices built in a glass material.

Ba₂TiGe₂O₈^{8)–9)} is one of the fersite-type (Ba₂TiSi₂O₈) phases¹⁰⁾ with the Ti cation taking up a square pyramid (TiO₅) structure and the spontaneous polarization along the *c*-axis. Halliyal et al. have reported the physical properties of both Ba₂TiGe₂O₈ crystallized glass (glass-ceramic) and a Ba₂TiGe₂O₈ single-crystal and showed that the piezoelectricity of crystallized glass is comparable to that of a Ba₂TiGe₂O₈ tetragonal single-crystal.^{6),7)} Recently, focusing on the second-order optical nonlinearity of Ba₂TiGe₂O₈ crystallized glass, our group has reported a large second order optical nonlinearity, $d_{33} = 24 \pm 3$ pm/V, observed in a surface crystallized 30BaO·15TiO₂·55GeO₂ (BTG55) glass.³⁾ Because the optical nonlinearity of the BTG55 crystallized glass was larger than that of a Ba₂TiGe₂O₈ single crystal, crystallized glass containing nonlinear optical crystals has great potential for nonlinear optical devices.^{1)–5)}

There is, however, little information about the preparation condition of the precursor BTG55 glass, especially the temperatures at which the glass melts are held in a molten state in a furnace. Here, we define this temperature as “melt temperature” in the present study. The physical properties of a glass, such as absorption coefficient, temperature of glass transition T_g , are affected by its preparation condition.¹¹⁾ Indeed, the apparent color of the BTG55 glass prepared at 1250°C was different from that prepared at 1550°C. Since the optical nonlinearity of the crystallized

glass is expected to depend on the physical properties of the precursor glass, it is worth investigating the preparation condition of the precursor glass to obtain the corresponding crystallized glass with a large optical nonlinearity.

Second harmonic generation (SHG) of the crystallized glass arises from not only micro-polarization at atomic scale but also macro-polarization generated during crystallization. One of the origins of an additional macro-polarization in the crystallized glass is the stress between glass regions and crystallites. For example, Fujiwara et al. have reported that the SHG of a SiO₂–GeO₂ thin film originates from the stress between crystallites and glass matrix;¹²⁾ this film would show no SHG without stress. One of other origins of additional macro-polarization is the orientation of the crystallized phase. Since the second harmonic (SH) intensity of the BTG55 surface crystallized glass is larger than that of the Ba₂TiGe₂O₈ single-crystal^{2),3)} and that of the BaO–TiO₂–GeO₂ crystallized glass without surface crystallized phase,⁸⁾ it is supposed that the effect of the oriented crystallized phase in the surface layer is larger than that of micro-polarization. Thus, macro-polarization that brings large dipole factor is mainly observed in the bulk sample and depends on the sample preparation.

In the present study, we have examined the correlation of the melt temperature of the BTG55 precursor glass and the SH intensity of the corresponding BTG55 crystallized glass. Using an assumption that powdered sample possesses little macro-polarization, we focused on the SHG that mainly comes from micro-polarization of the crystallized glass.

2. Experimental

The 30BaO·15TiO₂·55GeO₂ (BTG55) glasses were prepared by a conventional melt-quenching method using BaCO₃ (99.95%), TiO₂ (99.9%) and GeO₂ (99.995%) as the starting materials. Mixed batches were melted in a platinum crucible at 1250°C, 1400°C and 1550°C for 1 h in an electric furnace, and quenched on a steel plate at 200°C. The obtained glass was annealed at its glass transition temperature, T_g , for 30 min, and

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then, cut and mechanically polished. The BTG55 glasses were heat-treated at 830°C for 5 h on the alumina plate in an ambient atmosphere, and the corresponding BTG55 crystallized glasses were obtained.

The T_g , crystallization onset temperature, T_x , and the crystallization peak temperature, T_p , were determined by differential thermal analysis (DTA) at a heating rate of 10 K/min. The quantity ΔT , $T_x - T_g$, is defined as the stability parameter for crystallization of the glass. In the present study, the bulk crystallized glass was crashed to obtain powder crystallized sample. With this process we assumed that the effect of macro-polarization that is observed the surface of bulk crystallized sample was removed. To examine the crystalline phases in the crystallized glass, we performed X-ray diffraction (XRD) measurements with Cu K α radiation on the powdered BTG55 crystallized glasses with the grain diameter of 20–32 μm . The same powdered samples were also used for second harmonic generation (SHG) to neglect the contribution from the surface crystalline phase. Densities of glasses were determined with the Archimedes method using distilled water as an immersion liquid. The refractive index was measured using a He–Ne laser ($\lambda = 633 \text{ nm}$), and the error bar of this measurement is ± 0.0001 . Raman scattering spectra were obtained using a laser microscope with an Ar⁺ laser ($\lambda = 488 \text{ nm}$).

Figure 1 shows the schematic measuring system for an evaluation of SH intensities of the powdered BTG55 crystallized glasses. A fundamental wavelength of a YAG laser at 1064 nm is used as an incident light source, and the beam line is split into two to irradiate both the powdered crystallized glass and the reference. The powdered BTG55 crystallized glass with the grain diameter classified as 20–32 μm was used for the SH measurement. On the other hand, a Z-cut quartz (thickness 0.6 mm) sample was used as the reference for the normalization of the incident beam intensity. The signal intensity was monitored after integration for 8 sec with the rotation of the sample holder to obtain the average value. Each measurement had 31 monitored points and the measurement was performed three times per one sample.

3. Results and discussion

3.1 BTG55 precursor glasses prepared at different melt temperature

The 30BaO-15TiO₂-55GeO₂ (BTG55) glasses were prepared at different melt temperatures. All the samples turned out to be transparent and visually homogeneous. The apparent color of the BTG55 glasses changes with the melt temperature: from yellowish (1550°C) to colorless (1250°C). **Figure 2** shows the absorption spectra in the energy region 2.7 to 3.5 eV of the BTG55 glasses prepared at 1250°C, 1400°C and 1550°C for 1 h. The absorption coefficient of the BTG55 glasses increases with

increasing melt temperature. Since the absorption band originating from Ti³⁺ around 550 nm¹³⁾ is hardly observed in any of the spectra, the increasing of absorption coefficient is thought to be mainly caused by absorption of heterogeneous parts such as some defects. The preparation effects on the UV optical properties of GeO₂ glasses have reported, and the paper suggested the formation of defects in the GeO₂ glass.¹⁴⁾ In the present case, it is prospective that similar formation brings the increasing of optical property of the BTG55 glasses. **Table 1** shows T_g , T_x , T_p , ΔT , and the refractive index at 633 nm of the BTG55 bulk glasses prepared at 1250°C, 1400°C and 1550°C for 1 h. The T_g and ΔT of the three BTG55 glasses are nearly constant. This indicates that the melt temperature has no effect on the thermodynamic property of the BTG55 precursor glasses. On the other hand, the refractive index of the BTG55 precursor glasses increases with increasing melt temperature. It has been reported that the refractive index of the BTG55 crystallized glass is higher than that of its precursor glass prepared at 1300°C.¹⁾ It follows that the refractive index of the BTG55 glass prepared at higher temperatures is closer to that of the Ba₂TiGe₂O₈ crystallite²⁾ than the BTG55 glass prepared at lower temperatures.

Figure 3(A) shows Raman spectra of the BTG55 glasses prepared at 1250°C for 1 h. Dash lines show five peaks after signal deconvolution using the Gauss function, and each peak is named as (α)–(ϵ). The center of peak position and the half width at half maximum (HWHM) of these peaks are fixed for the deconvolution, and these parameters are listed in **Table 2**. **Figure 3(B)** shows peak area ratios of three BTG55 glasses after peak deconvolution. We fixed peak area of (α) at 1 as a reference, and other peak ratios are normalized by the peak (α) that is mainly assigned to Ba–O symmetric vibration mode.¹⁵⁾ In **Fig. 3(B)**, peaks (β) and (δ) show certain values whereas the values of (ϵ) and (γ) peaks change with melt temperature of the BTG55 glass. The peak intensity of (ϵ) increases with increasing melt tem-

Fig. 2. Absorption spectra of BTG55 glasses prepared at 1250°C, 1400°C and 1550°C for 1 h.

Fig. 1. Schematic measuring system for an evaluation of second harmonic (SH) intensities of powdered BTG55 crystallized glasses.

Table 1. Physical Properties of the BTG55 Glass Prepared at Different Melt Temperature

Melt temperature/°C	T_g /°C	T_x /°C	T_p /°C	$\Delta T (= T_x - T_g)$ /°C	Refractive index n (at 633 nm)
1250	669	796	830	127	1.8281
1400	672	794	835	122	1.8283
1550	668	796	831	128	1.8308

Fig. 3. (A) Raman spectra of BTG55 glass prepared at 1250°C for 1 h. Dash line shows deconvoluted peaks (α), (β), (γ), (δ), and (ϵ). (B) Peak area ratios of three BTG55 glasses after peak deconvolution using the peak (α) as a reference.

Table 2. Used Fitting Parameters in Deconvolution of Raman Spectra

	Center of peak position/cm ⁻¹	HWHM/cm ⁻¹
α	301	55
β	373	35
γ	515	125
δ	715	65
ϵ	815	85

perature whereas that of (γ) decreases. The bands of (γ) and (ϵ) are assigned to modes of the Ge–O–Ge symmetric vibration and Ti–O stretching vibration, respectively.¹⁴⁾ Since Raman spectra of the Ba₂TiGe₂O₈ crystal shows a strong Ti–O vibration at 840 cm⁻¹, the increase of the Ti–O vibration peak (ϵ) indicates an increase of characteristics of the Ba₂TiGe₂O₈ crystallites, and that the decrease of Ge–O–Ge vibration peak (γ) works as a counterpart of the increase of Ti–O vibration. A structural similarity between the 40BaO–20TiO₂–40GeO₂ glass and the Ba₂TiGe₂O₈ single crystal has been suggested.¹⁵⁾ We define the local structure similar to that of a crystal, “embryos of crystallites” which envision as an origin of the precipitated crystallites. We suggest that a crystalline embryo is a kind of heterogeneous part in the glass matrix. Since the Ti–O vibration shows that the BaO–TiO₂–GeO₂ glass contains the embryo of Ba₂TiGe₂O₈ crystallite, we conclude that an increase of Ti–O intensity in the

Raman spectra in the present study indicates the formation of the embryo of Ba₂TiGe₂O₈ crystallite.

Since viscosity affects the compositional homogeneity of glass melt, a glass melt prepared at higher temperatures (lower viscosity) is generally thought to be more homogeneous than that with lower temperatures (higher viscosity). However, the obtained results conflict with this assumption, that is, the heterogeneous part was observed in the glass prepared at higher melt temperature. According to the above description classification, it is thought that the heterogeneity observed in the Raman spectra (Fig. 3) is mainly caused by the heterogeneity during the cooling process from a glass melt. Since the formation of Ba₂TiGe₂O₈ embryos is observed in the glass with higher melt temperature as shown in the Fig. 3, it is speculated that a higher melt temperature is more favorable for the crystalline nucleation from the glass melt than lower temperatures. Note that this increase of the embryos of Ba₂TiGe₂O₈ crystallites in the BTG55 glass correlates with the increase of refractive index as well as melt temperature. The present result indicates that the formation of Ba₂TiGe₂O₈ embryos affects the refractive index of the BTG55 glass. Since we observed both increasing of absorption coefficient and increasing refractive index, the formation of Ba₂TiGe₂O₈ embryo raises increasing of the absorption coefficient. Although XRD pattern of BTG55 glass prepared at 1550°C showed amorphous without clear diffraction peak of Ba₂TiGe₂O₈, it is thought that the generated embryo was too small or less ordered structure than conventional Ba₂TiGe₂O₈ crystallites.

3.2 BTG55 crystallized glasses prepared at different melt temperature

It has been reported that the BTG55 glass crystallizes into fresnoite Ba₂TiGe₂O₈ by a heat-treatment.^{1)–4)} Figure 4(A) shows the powder XRD patterns of the BTG55 crystallized glasses heat-treated at 830°C for 5 h together with the JCPDS pattern of Ba₂TiGe₂O₈ (No. 01–077–0389). The temperature in the figure shows the melt temperature of each precursor BTG55 glass. The closed circles are assigned to the peak of BaGe₄O₉. The precipitated phase was a kind of benitoite (BaTiGe₃O₉) that was observed previously in the BTG55 crystallized glasses.^{1)–4)} The diffraction angle and peak intensity ratio of the crystallized glass correspond to that of JCPDS pattern of Ba₂TiGe₂O₈ single crystal, except for the diffraction peaks of BaGe₄O₉. We can label four diffraction peaks as peak fresnoite or benitoite in the Fig. 4(A). For examples, f_{311} and f_{002} assign fresnoite (311) and (002) peaks, respectively. On the other hand, b_{11-1} and b_{220} assign benitoite (11-1) and (220) peak, respectively. Using these peak intensities, we can assume the ratio between fresnoite and benitoite. Figure 4(B) shows a correlation between melt temperature of the mother glass and the peak ratio of fresnoite/benitoite using these four peaks. It indicates that the diffraction intensities of fresnoite increased with increasing melt temperature of the precursor glass. Although a quantitative discussion on the amount of the crystallites is difficult, we use an interpretation that the amount of Ba₂TiGe₂O₈ embryos in the BTG55 glass observed in the Raman spectra (see Fig. 3) determines the number density of the Ba₂TiGe₂O₈ crystallites.

Figure 5 shows the distribution charts concerning the SHG of the present BTG55 crystallized glasses heat-treated at 830°C for 5 h. The ordinate shows the number of the data points and the abscissa shows the relative SH intensity, where the SHG intensity is normalized by the average intensity of the BTG55 crystallized glass prepared at 1250°C. In the present study, we assume that the SH intensity from benitoite is small enough to be neglected.⁴⁾

The obtained SH distribution of the BTG55 crystallized glasses shows that the SH intensity of the BTG55 crystallized glass increases with increasing melt temperature and that the highest

Fig. 4. (A) Powder XRD patterns of BTG55 crystallized glasses heat-treated at 830°C for 5 h together with that of Ba₂TiGe₂O₈ (JCPDS No. 01-077-0389). The BTG55 glasses were prepared at 1250°C, 1400°C and 1550°C for 1 h. (B) (311) diffractions in XRD patterns of BTG55 crystallized glasses.

Fig. 5. Dispersion curves of BTG55 crystallized glasses heat-treated at 830°C for 5 h as a function of SH intensity. The BTG55 glasses were prepared at 1250°C, 1400°C and 1550°C for 1 h.

SH intensity is observed in the crystallized glass with the highest number density of crystallites. It follows that the difference of SH intensity among three BTG55 crystallized glasses reflects the difference of the crystallite density, in other words, the difference of the density of crystalline embryos in the precursor glass.

The correlation between the refractive index of the mother glass and the SHG of crystallized glass can be explained by an alternative interpretation from the viewpoint of refractive index and the pyroelectricity. Since fresnoite Ba₂TiGe₂O₈ was reported as pyroelectric material,⁷⁾ the refractive index is expected to depend on the polarization of the matrix. If SHG of a crystallized glass is correlated to the refractive index of the mother glass, it can be a guide for making the crystallized glass with large optical nonlinearity, even if the origin of the increase of refractive index is not well clarified.

4. Conclusion

In this study, we focused on the SHG of the BTG55 crystallized glass and examined its correlation with the melt temperature and the SHG. The absorption coefficient and refractive index increase with increasing melt temperature. Although the mother glass was seem to be isotropic, the Raman signal attributable to the Ti–O vibration and refractive index of the BTG55 glass increases with increasing melt temperature of the BTG55 precursor glasses. Increase of these properties in the mother glass correlate with Ba₂TiGe₂O₈ crystallites that is precipitated after heat-treatment. Thus, we suggest that melt temperature of the precursor glass affect the formation of embryos of the Ba₂TiGe₂O₈ crystallites that affect the SH intensity of the BTG55 crystallized glasses.

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