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Surface crystallization of stoichiometric glass with $Bi_2ZnB_2O_7$ crystal using ultrasonic surface treatment followed by heat treatment

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Surface crystallized glass-ceramics with nonlinear optical $Bi_2ZnB_2O_7$ (BZB) crystals were prepared by ultrasonic surface treatment (UST) followed by crystallization heat treatment for stoichiometric glass with a composition of $33.3Bi_2O_3$–33.3ZnO–$33.3B_2O_3$. According to the surface XRD measurements and microscopic observations, UST technique was found to be quite effective for lower temperature precipitation of BZB, indicating the ability of crystallization control of the target phase, such as phase selectivity, small size of precipitates, high orientation and their morphology. After the optimization of the process condition parameters for improving transparency and suppressing deformation of the sample, the effective optical nonlinearity of the transparent surface crystallized glass-ceramics was estimated as 0.7 pm/V.

Key-words : Surface crystallization, Bismuth zinc borate glass, Glass-ceramics, Ultrasonic surface treatment, Optical nonlinearity

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1. Introduction

Bismuth borate-based glass systems are of interest because of their low melting glass formation, good stability and high refractive index, and therefore surveys on the glass properties[1)–4)] and structural investigations[5)–7)] were intensely conducted for various candidates for host glasses for optical applications and lead-free materials for electronic devices. Among them nonlinear optical (NLO) property induced by the corresponding crystalline phases has attracted much attention, and therefore the crystallization of non-centrosymmetric phases has been investigated so far in order to fabricate functional materials utilizing their second order optical nonlinearity.[8)–10)]

In the simple binary Bi_2O_3–B_2O_3 system, for example, monoclinic BiB_3O_6 (BIBO) crystal is a well-known NLO phase[11)] and the BIBO single crystal synthesized from the melt was already put into practical use for NLO applications. The optical nonlinearity of metastable phase $BiBO_3$, which is only prepared by crystallization of glass and is not found in the structural summary of the binary crystals by Kuzmichebva et al.,[12)] was studied based on the crystallization behaviors and NLO evaluations.[10)] It suggested that the ability of the metastable phase formation and resulting optical nonlinearity could be enhanced by substituting ternary constituent of other oxides for a part of Bi_2O_3 and B_2O_3. Thus the studies on crystalline phases in bismuth borate-based ternary systems and their crystallization behavior should give fruitful knowledge for developing new NLO materials.

In this paper, the authors focused on orthorhombic $Bi_2ZnB_2O_7$ (BZB) phase (*Pba2* space group)[13)] precipitated from ternary Bi_2O_3–ZnO–B_2O_3 glasses, which has a melilite-type structure consisting of Bi^{3+} layers and zinc borate sheets with corner-shared triangular BO_3, tetrahedral ZnO_4 and BO_4 units. The NLO evaluation was also reported for powder sample, and the effective value of 4.0 relative to KDP standard[13)] expects a considerable evaluation even in glass-ceramic form. In order to maximize the effective value of nonlinearity it is important to prepare well-controlled glass-ceramics with optical transparency. For simplicity a stoichiometric glass composition with the target phase BZB, that is $33.3Bi_2O_3$–33.3ZnO–$33.3B_2O_3$, was selected from the glass formation region of the ternary system. A novel technique of ultrasonic surface treatment (UST)[14),15)] and various effects on the surface crystallization were also investigated in order to evaluate the validity of UST as one method for controlling the crystallization behavior externally. The process condition parameters for both UST and heat treatment were optimized in terms of the target phase formation and transparency, and the NLO coefficient of BZB crystallized glass-ceramics was evaluated by second harmonic generation (SHG) measurements. Finally, the significance of UST for suppressing deformation of bulk glass-ceramics was discussed in a typical case that crystallization temperature is close to or higher than softening point of precursor glass.

2. Experimental procedure

2.1 Glass-ceramic sample preparation

The glass with a composition of $33.3Bi_2O_3$–33.3ZnO–$33.3B_2O_3$ was prepared by a conventional melt-quenching method. Commercial powders of reagent grade Bi_2O_3, ZnO and B_2O_3 were mixed thoroughly and melted in a gold crucible at 800°C for 30 min in an electric furnace. The melt was stirred every 10 min for homogenization because inhomogeneous glasses are easily formed in this glass system. The melt was poured into a brass mold preheated at about 300°C. The quenched glass was annealed for 2 h near the glass transition temperature, T_g (=390°C). The glass thus obtained was sliced with a thickness of about 1 mm and the both sides were polished to be mirror surfaces.

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The glass samples were placed in a polyethylene (PE) pack with a distilled water suspension of BZB crystal powder, which was synthesized by full crystallization of the corresponding glass powder and confirmed to have a wide distribution of grain size, typ. 1–10 µm by SEM observation. The volume and concentration of the suspension were 3 mL and 5 wt %, respectively, and ultrasonic wave (28 kHz) was exposed for 60 min using a commercial ultrasonic cleaner. The PE pack was shook every 10 min expecting the homogeneity of saturated UST effects. After the UST process the glass samples were placed on a flat alumina plate and subjected to the following heat treatment: heating at a rate of 10 K/min up to elevated temperatures, 400–440°C, holding for various periods, 12–96 h, and cooling down to room temperature. These heat treatments were held in an atmospheric condition.

2.2 Characterizations for crystalline phases

The crystalline phases of glass-ceramics were investigated by X-ray diffraction (XRD) analysis using Cu Kα radiation with a condition of 40 kV and 40 mA using Rigaku RINT-2100V diffractometer. The morphologies of the crystals found on the glass-ceramic surface were observed by a polarization microscope, and the thickness of them was measured based on the scanning electron microscopy (SEM) observations for the cross section by fracture.

2.3 Evaluation of optical nonlinearity

The nonlinear optical evaluations for the surface crystallized glass-ceramic samples were carried out by SHG measurements using Maker fringe technique. The radiation source was a Q-switched Nd:YAG laser operating at a wavelength of 1064 nm, and the SHG intensity at 532 nm was obtained as a function of incident angle. A *Y*-cut quartz standard plate was used as the SHG intensity reference, assuming $d_{11} = 0.3$ pm/V at 1064 nm.

3. Results

3.1 Surface crystallization behavior of BZB glass

Figure 1 shows the surface XRD patterns of the surface crystallized glass-ceramics obtained by heat treatment at 420, 430 and 440°C for 12 h, together with the powder pattern of synthesized BZB. An unknown phase was found after the heat treatment at lower temperatures, 420 and 430°C, while the stoichiometric phase of BZB was successfully precipitated at higher temperature, 440°C. According to the comparison with the diffraction pattern for the BZB powder, the BZB phase on the glass surface showed a tendency of (001) orientation with a directional dispersion.

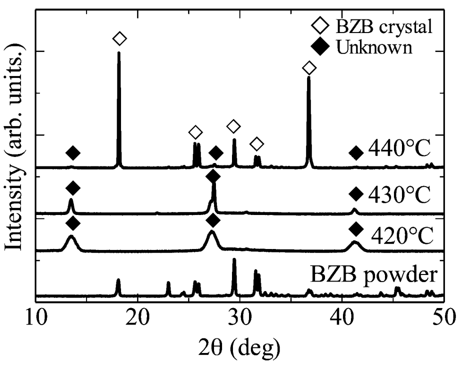

Fig. 1. Surface XRD patterns of surface crystallized glass-ceramics after heat treatment at 420–440°C for 12 h together with powder pattern of synthesized BZB.

Unfortunately, the sample plate have slightly changed in shape during the heat treatment at higher temperatures because the temperature to form BZB phase was higher than the softening point of the glass. In the present case, it is difficult to keep the precise rectangular shape of the precursor glass after the crystallization of BZB phase.

On the other hand, the XRD patterns of the surface crystallized glass-ceramics where UST were applied before the heat treatments showed a different behavior. **Figure 2** shows them for lower heat treatment temperatures, 400, 410 and 420°C. The unknown phase was also found but limited to lower crystallization temperatures, 400 and 410°C, and the temperature to form the target phase BZB was considerably lowered to 410°C. Consequently, the surface crystallized glass-ceramics with BZB as the primary phase was successfully fabricated by UST followed by heat treatment at 420°C, where the softening or deformation did not occur to keep a precise dimension.

3.2 Transparent glass-ceramics for optical evaluation

The glass-ceramic sample plate for optical evaluation was prepared by careful heat treatment at 410°C for 96 h. Since the temperature was the lowest point for the precipitation of the target phase BZB, such a long-term heat treatment was required at this temperature for the crystal growth enough to detect the SHG signal quantitatively for their nonlinearity evaluations. Nevertheless it was easy to control the transparency of the glass-ceramics rather than the case of higher temperatures.

The pictures shown in **Fig. 3** are the appearance of the surface crystallized glass-ceramics obtained by UST and subsequent heat treatment at 410°C for 96 h and the surface observation by polarization microscope with a sensitive tint plate. There are

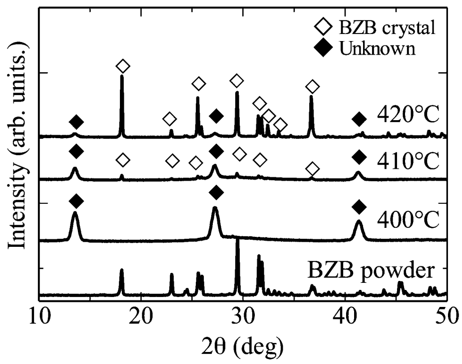

Fig. 2. Surface XRD patterns of surface crystallized glass-ceramics after UST and heat treatment at 400–420°C for 12 h together with powder pattern of synthesized BZB.

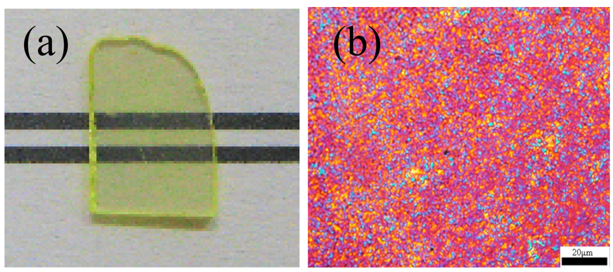

Fig. 3. (Color online) Optical observations of (a) the glass-ceramic sample appearance and (b) the surface crystallization by polarization microscope with a sensitive tint plate. The sample was obtained by UST and long-term heat treatment at 410°C for 96 h.

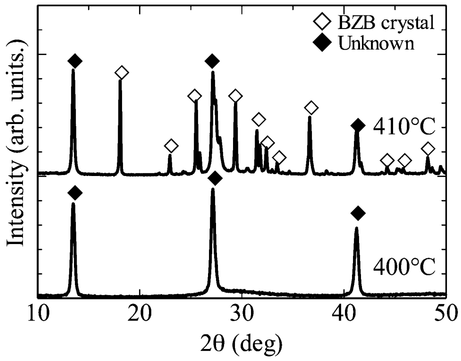

Fig. 4. Surface XRD patterns of surface crystallized glass-ceramics after UST and long-term heat treatment at 400 and 410°C for 96 h.

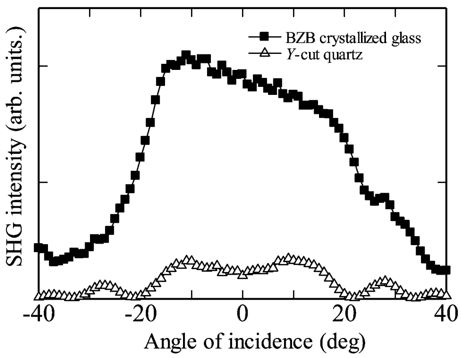

Fig. 5. Maker fringe patterns of SHG intensity for *Y*-cut quartz standard and the transparent glass-ceramics obtained by UST and long-term heat treatment at 410°C for 96 h.

innumerable crystallites with submicron diameter precipitated on the surface rather inhomogeneously. The retardation colors, blue to yellow, indicate the axis of anisotropic crystals on the surface. It was confirmed that the thickness of surface crystalline layer was approximately 3 µm by SEM observation. According to the XRD pattern (**Fig. 4**), the surface crystalline layer consists of both the target BZB and unknown phases, and the anisotropic phase shown in Fig. 3(b) was assigned to BZB.

3.3 Nonlinear optical evaluation of transparent glass-ceramics

The optical nonlinearity of the surface crystallized glass-ceramics with BZB phase was evaluated using the transparent samples. The Maker fringe pattern of SHG is shown in **Fig. 5** together with that of a *Y*-cut quartz standard plate. Although the SHG intensities varied from point to point due to the surface inhomogeneity and so did the fringe patterns, a typical pattern of them is shown here. The SHG intensity of the surface crystallized glass-ceramics was 6 times as large as the reference. The effective nonlinearity d_{eff} was estimated as 0.7 pm/V, which was approximately a half value of the reported one derived from Kurtz–Perry powder method.[13)]

4. Discussion

On the basis of these experimental results, it is obvious that UST is a quite effective process in fabricating transparent glass-ceramics with BZB crystals. It is well known that the surface crystallization behavior can be controlled by using UST technique in various glass systems[14),15)] via changing the number density of nucleation sites per unit surface area and also changing

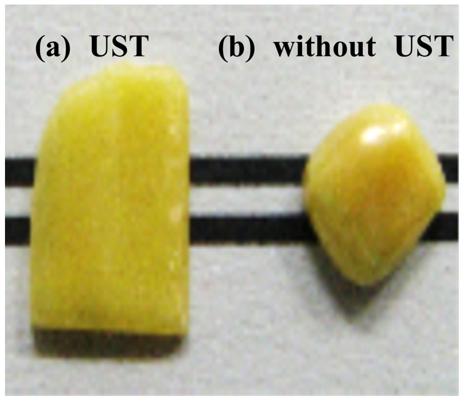

Fig. 6. (Color online) Accelerated deformation test during crystallization heat treatment at 600°C for 10 min, (a) UST applied before heat treatment, and (b) without UST.

the crystallization onset temperatures and the primary phase selected. In the case for low melting Bi_2O_3–ZnO–B_2O_3 glass system in the present study, there are difficulties found in the conventional crystallization process as follows:

1) nonlinear optical phase BZB of our target did not precipitate as a primary phase at lower temperatures,
2) crystal growth and orientation of BZB were uncontrolled, and the resulting transparency of the glass-ceramics was not adequate for optical evaluations, and
3) the glass-ceramic samples were easily deformed due to its low softening temperature.

One of the most significant problems is that the temperature to form BZB phase, 440°C is high enough to soften the bulk glass during crystallization, and therefore it is difficult to maintain the original rectangular shape of glass samples. However, UST process caused the lower crystallization onset for BZB phase, and was utilized as a powerful method for controlling BZB crystallization. In other words, this target phase was formed at lower temperature 410°C where no deformation occurs. Consequently, the glass-ceramic samples kept a definite quality in dimension for the following optical and other evaluations. The formation of the unknown phase was also influenced, but both of short (12 h) and long-term (96 h) heat treatments at this temperature did not yield a single-phase crystallization of BZB as shown in Figs. 2 and 4. It is necessary to optimize the parameters for UST and heat treatment for this purpose.

Here an accelerated test is demonstrated for softening and deformation during heat treatment at much higher temperature. As for the crystallization at 600°C for 10 min, the difference in shape between glass-ceramic samples (a) UST applied and (b) without UST is obvious as shown in **Fig. 6**. The former kept its original rectangular shape while the latter changed into round one although both samples were subjected to the same thermal history above. This fact is explained by the formation of crystalline shell on the glass surface at the beginning of the heat treatment. For the UST applied glass sample, BZB phase was easily formed on the surface at lower temperatures 410°C. The shell thus formed should play an important role for keeping rectangular shape because it is rigid and lower surface energy than glassy state. On the other hand for the heat treatment without UST, the BZB layer shell did not form on the glass surface (otherwise the unknown phase only formed) before reaching softening point (see **Fig. 7**). It can be concluded that UST technique is quite effective for precise fabrications of surface crystallized glass-ceramics at higher temperature and/or in lower melting glass systems.

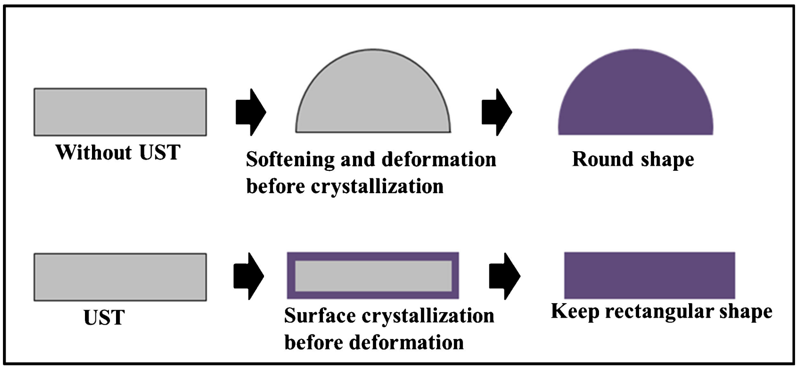

Fig. 7. (Color online) Schematic change in shape of the sample due to softening and deformation during crystallization heat treatment.

The Maker fringe profile shows the definite optical nonlinearity of the surface crystallized glass-ceramics with transparency. It consists of two kinds of crystals on the glass surface, BZB and the unknown phases. However the estimated value of d_{eff} is assigned to that of BZB phase instead of the unknown phase because no SHG was observed for the single phase sample with the unknown phase prepared by heat treatment at 400°C. Unfortunately, the surface crystallized glass-ceramics with BZB single phase is not yet prepared for all the conditions of UST and heat treatments. Increasing the amount or fraction of BZB phase on the glass surface would maximize the effective value of the optical nonlinearity, which is expected to be accomplished in the future work.

5. Conclusion

Surface crystallized glass-ceramics with nonlinear optical $Bi_2ZnB_2O_7$ (BZB) phase were prepared by UST process followed by precise heat treatment for bismuth zinc borate glass with a stoichiometric composition with BZB. The crystallization onset of BZB phase was lowered by the notable effect of UST, from 440 to 410°C, which successfully suppressed the bulk glass deformation near the softening temperature. The optical nonlinearity was estimated for the transparent surface crystallized glass-ceramics obtained by long-term and precisely controlled heat treatment at 410°C, and d_{eff} value 0.7 pm/V is comparable with other practical materials in borate systems and also indicating that BZB crystallized glass-ceramics thus obtained is one of promising candidates for nonlinear optical applications.

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