Temperature Dependence of Second-Order Optical Nonlinearity in Crystallized (Sr, Ba)$_2$TiGe$_2$O$_8$ Glasses

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Second-order optical nonlinearity induced in thermally crystallized Ba$_2$TiGe$_2$O$_8$ glasses with a stoichiometric composition, 40BaO–20TiO$_2$–40GeO$_2$ (BTG–40), has been investigated for the first time. Induced second-order optical nonlinearity, $d$-coefficient, was approximately 10 pm/V in crystallized BTG–40 for the largest case in our experiment. Measured $d$-coefficient was increased with increasing temperature of heat-treatment for crystallization, and then saturated. Similar temperature dependence of $d$-coefficients was also observed in Sr-doped BTG–40 to clarify a change of $d$-coefficients by means of systematically structural modification in crystalline phase. It has been found that the increase and/or optimization of $d$-coefficients can be caused by Sr-doping, which is characterized by anisotropy of lattice constant parameter, c/a, in crystallized glasses.

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1. Introduction

Glass materials should not have second-order optical nonlinearity in principle, because of their inversion symmetry. The second-order optical nonlinearity, which is generally exhibited in ferroelectric crystal materials like LiNbO$_3$, is very useful for photonic signal processing such as switching, modulation, and wavelength conversion. Glass with second-order optical nonlinearity$^{[1-5]}$ is therefore one of the promising materials used for advanced fiber-optic information fields, since glass-based materials/components have much higher advantage to introduce them into the glass-networks rather than that by crystal-based ones.

Recently, Takahashi et al.$^{[6-8]}$ reported on the largest $d$-coefficient of second-order optical nonlinearity induced in crystallized Ba$_2$TiGe$_2$O$_8$ (BTG) glass with fresnoite-type structure.$^{[9]}$ The BTG glass had a composition of 30BaO–15TiO$_2$–55GeO$_2$ (BTG–55) that is close to the stoichiometric of BTG crystal,$^{[9]}$ and showed induced $d$-coefficient with 22 pm/V in crystallized BTG–55,$^{[10,11]}$ which is almost comparable to $d_{33}$ ($\sim 28$ pm/V) of LiNbO$_3$ crystal. It was suggested that micro-texture and crystal-structure of surface crystallized BTG glass are the main origin of large $d$-coefficient,$^{[6-8,12]}$ and such crystallized glasses are also excellent for long-term stability with no degradation of the induced effect, in contrary with that in poled glasses.$^{[13]}$ Crystallized BTG glasses with just the composition with stoichiometry, 40BaO–20TiO$_2$–40GeO$_2$ (BTG–40), may be expected to have possible larger $d$-coefficient than that in crystallized BTG–55, due to smaller amount of “impurity phases” introduced in pure crystalline phase.$^{[13]}$ However, crystallization of stoichiometric BTG glasses has not reported yet at the moment.

We investigated second-order optical nonlinearity induced in crystallized BTG–40 for the first time, and experimentally characterized temperature dependences of $d$-coefficient in BTG–40, and in addition, crystalline structural modification of $d$-coefficients in Sr-doped BTG–40.

2. Sample preparation and experimental

Glasses with the compositions of xSrO–(40–x)BaO–20TiO$_2$–40GeO$_2$ (x = 0, 4, 8) were prepared using a conventional melt-quenching method. These samples are called hereafter as BTG–40 (x = 0), SBTG–4 (x = 4), and SBTG–8 (x = 8). Commercial powders of reagent grade SrCO$_3$, BaCO$_3$, TiO$_2$ and GeO$_2$ were mixed and melted in a platinum crucible at 1250°C for 1 h in an electric furnace. The batch weight was 20 g. The liquids with mixed compounds were poured onto an iron plate heated at 200°C in advance and pressed to a thickness of about 1 mm with another iron plate. The glass transition, $T_g$, crystallization onset, $T_c$, crystallization peak, $T_p$, and melting, $T_m$, temperatures were determined using differential thermal analyses (DTA) at a heating rate of 10 K min$^{-1}$. The glasses were mechanically polished to get mirror surface using diamond slurry and then were heat-treated at various temperatures for 3 h to obtain transparent crystallized glasses. The micro-texture of crystallized samples was observed by scanning electron microscope (SEM) and polarization optical microscopy. The crystalline phases present in the heat-treated samples were examined by X-ray diffraction (XRD) analyses at room temperature using CuK$\alpha$ radiation. Using the $\alpha$-quartz peaks as an external calibration standard, the lattice constant of the surface crystalline phases was estimated from the top positions of BTG (221), (311) and (002) reflection peaks. The second-harmonic (SH) intensity of crystallized glasses was quantitatively evaluated by using a fundamental wave of a Q-switched Nd$^3+$ doped yttrium-aluminum-garnet (Nd:YAG) laser at a wavelength of 1064 nm as a function of the angle of the incident light (Maker fringe technique). Z-cut $\alpha$-quartz with a thickness of 0.6 mm was used as a reference in a Maker fringe technique for transparent crystallized glasses. As a polarization on SH intensity measurements, the combination of p excitation and p detection was used for all cases.

3. Results and discussions

Thermal properties in bulk BTG–40 (x = 0), SBTG–4 (x = 4), and SBTG–8 (x = 8) glasses measured by DTA are listed in Table 1. Anomalous values of $T_c$ and $T_p$, especially in SBTG–4 should be pointed out in relation with those values of other Sr-concentrations, even very good reproducibility of those. It seems to be affected by possible phase transition due to solid solution of Sr ions into fresnoite crystalline structure. Measured XRD patterns in BTG–40 obtained at several crystallized temperatures are shown in Fig. 1. A XRD pattern obtained in BTG polycrystals is also shown in Fig. 1 as references. It is clearly seen that (002), i.e. along with c-axis, is the primary orientation in crystallized BTG–40 (x = 0), and the orientation of crystalline phase becomes stronger with higher process temperatures. These tendencies accompanied with crystallization in BTG–40 are exactly the same as those meas-
Table 1. Thermal Properties Measured by DTA in Bulk BTG–40, SBTG–4, and SBTG–8 Glasses

<table>
<thead>
<tr>
<th></th>
<th>Glass transition temperature, $T_g$ (°C)</th>
<th>Crystallization onset, $T_m$ (°C)</th>
<th>Crystallization peak, $T_p$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTG–40</td>
<td>670</td>
<td>771</td>
<td>784</td>
</tr>
<tr>
<td>SBTG–4</td>
<td>677</td>
<td>794</td>
<td>818</td>
</tr>
<tr>
<td>SBTG–8</td>
<td>682</td>
<td>786</td>
<td>817</td>
</tr>
</tbody>
</table>

![XRD patterns for BTG–40 heat-treated at 665, 670, and 680°C for 3 h.](image1)

![Temperature dependence of $d$-coefficients in crystallized BTG–40, SBTG–4, and SBTG–8 glasses.](image2)

Fig. 1. XRD patterns for BTG–40 heat-treated at 665, 670, and 680°C for 3 h.

Fig. 2. Temperature dependence of $d$-coefficients in crystallized BTG–40, SBTG–4, and SBTG–8 glasses.

ured in surface crystallized BTG–55. In these fresnoite-type crystals, it is known that an electric polarization caused by TiO$_2$ unit is parallel with c-axis of crystalline structure. Therefore, crystallized BTG–40 glass has also a texture of surface layer for highly effective on macroscopic second-order optical nonlinearity.

Temperature dependences of $d$-coefficient values are presented in Fig. 2 for crystallized BTG–40, SBTG–4, and SBTG–8 glasses. All Maker-fringe patterns in the experiment were observed to present symmetric curves for positive and negative incident angles without any SH intensities at null degree (not shown). This is also one of optical properties reported in BTG–55, and experimental evidence of polarization which is textured normal to the surface, thus measured $d$-coefficient must be denoted to $d_{33}$. Increases of $d$-coefficients with increasing heat-treatment temperatures for crystallization in all crystallized glasses are obviously found in Fig. 2. Two data points equivalent to the same temperature condition for each SBTG–4 (665°C) and SBTG–8 (700°C) are shown in the figure. Those data points were obtained from different glass samples, cut from the same batch and applied with the same heat treatments. This means that there might be a sort of dispersion of $d$-coefficient values occurred by non uniformity of crystallized glasses and measurement error of SHG. Increase tendency of $d$-coefficient is seen to be saturated for higher crystallization temperatures. The largest values of $d$-coefficient obtained in our experiment are about 10, 13, and 15 pm/V for BTG–40, SBTG–4, and SBTG–8, respectively, and it should be noted that another crystallized glass system with larger than 10 pm/V of $d$-coefficients is successfully fabricated with following BTG–55.

As shown in Fig. 1, orientation degree to c-axis in crystallized glass is becoming stronger with higher temperature for crystallization. It is suggested from this result that strong orientation is one of the origin for increase of $d$-coefficients with increasing crystallization temperatures. In previous statement, $d$-coefficient in fresnoite-type crystallized glasses is supposed to be governed by the polarization of TiO$_2$ unit. As an alternative way to characterize the increase of $d$-coefficients, it
is quite interesting to take account of anisotropy of lattice constants using an indicator of c/a, based on the above assumption in crystalline structure. Temperature dependences of lattice constants of a- and c-axes for three samples are shown in Fig. 3-a) and b). Both lattice constants are estimated from measured XRD patterns in crystallized glasses, and they increase with increasing crystallization temperature, and then decrease for higher temperatures as shown in the figures. Such behaviors can be seen similarly for all crystallized glasses. Heat-treatment temperatures corresponding to the peaks of a- and c-axes in Fig. 3 are very close to the glass transition temperatures, $T_g$, listed in Table I for every case. Although these non-monotinous changes of lattice constants against heat-treatment temperatures are not fully understood yet at present, the other factors to act on change of lattice constants during crystallization process, (e.g.) structural relaxation, thermal expansion etc., must be existing in this surface crystallized mechanism including the intrinsic proceed of crystallinity. Change of $d$-coefficients against c/a is plotted in Fig. 4 for three crystallized BTG–40, SBTG–4, and SBTG–8 glasses. All $d$-values in crystallized glasses are uniquely characterized by c/a, in this figure, optimization of c/a to give the largest $d$-coefficient for all crystallized glasses is exhibited, and both the largest value and peak position of $d$-coefficients are systematically depending on Sr-concentrations. These behaviors are very interesting to develop a novel photonic crystallized glass with larger second-order optical nonlinearity, in addition, characterization by parameter c/a can be used for designing optimum crystalline structure in the crystallized glass.

4. Conclusion
Second-order optical nonlinearity induced in fresnoite-type crystallized $\text{xSrO.(}40-x\text{BaO-}20\text{TiO}_2-40\text{GeO}_2$ ($x = 0, 4, 8$) glasses with stoichiometric composition to the BTG crystal was investigated for the first time. Large $d$-coefficients, larger than 10 pm/V, were successfully obtained in these crystallized glasses, and change of $d$-coefficients against crystallization temperatures was cleared experimentally. It was found that increase and optimization of $d$-coefficients were performed by Sr-doping in BTG crystallized glasses. This compositional method in glass can be used to fabricate the novel photonic glasses with larger second-order optical nonlinearity.

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References