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Effect of Poling Temperature on Optical Second-Harmonic Intensity of Lithium Sodium Tellurite Glass

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Second-harmonic generation has been observed in poled $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass. The effect of poling temperature on the second-harmonic intensity has been examined. The second-harmonic intensity increases, attains a maximum, and then decreases as the poling temperature increases. In other words, an optimum poling temperature that results in a maximum second-harmonic intensity exists. The optimum poling temperature linearly increases as the glass-transition temperature increases for several types of tellurite glasses, including the present $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass. This fact suggests that the process to create a polarization that results in the second-harmonic generation is affected by the structural relaxation at the glass-transition range. The thermal stability of $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass is higher than that of $18Na_2O{\cdot}82TeO_2$ ($30NaO_{1/2}{\cdot}70TeO_2$) glass, as revealed via differential scanning calorimetry. As a result, the temperature range within which the poling is effective is wider for the former glass.

I. Introduction

SINCE the discovery of second-harmonic generation in germanium-doped silica (SiO_2) glass fiber[1] and thermally/electrically poled SiO_2 glass,[2] the second-order optical nonlinearity of inorganic glasses has been attracting considerable attention. Recent studies have revealed that second-order optical nonlinearity is observed in poled tellurite glasses,[3,4] as well as in SiO_2-based glasses.[5–8] This phenomenon clearly indicates that the breakdown of the macroscopic inversion symmetry is realized in a homogeneous disordered lattice such as glass. The atomistic origin for the second-order nonlinearity and the mechanism that causes second-harmonic generation are of great interest, from a fundamental perspective. Considerable attention has been given to this phenomenon from the standpoint of practical applications as well: second-order optical nonlinearity of glasses enables us to develop new types of frequency doublers and optical modulators.

Poling conditions, as well as glass compositions, significantly affect the second-order nonlinear susceptibility of glass materials. Myers *et al.*[9] examined the poling-temperature dependence of the second-harmonic intensity for SiO_2 glass and found that the second-harmonic intensity increases, attains a maximum, and then decreases as the poling temperature increases. A similar phenomenon has been observed for poled tellurite glasses.[10] We revealed that the optimum poling temperature, which is defined as the temperature at which a maximum second-harmonic intensity is attained, is proportional to the glass-transition temperature for tellurite glasses that contain ZnO, MgO, and Na_2O.[11] This phenomenon is interesting because it suggests that the process of the breakdown of macroscopic inversion symmetry in tellurite glasses is associated with structural relaxation in the glass-transition range. In this regard, the process of creating the origin of the second-harmonic generation is different in the tellurite glasses than in the SiO_2 glass, because the glass-transition temperature, in the case of SiO_2 glass, is much higher than the optimum poling temperature.[9] In the present study, we show that this proportional relationship between the optimum poling temperature and the glass-transition temperature also is valid for lithium sodium tellurite glass. In addition, we discuss the poling-temperature dependence of the second-harmonic intensity, which is associated with the thermal stability of the glasses.

II. Experimental Procedure

Glass was prepared from reagent-grade Li_2CO_3, Na_2CO_3, and TeO_2 powders, which were used as the starting materials. The raw materials were mixed thoroughly to make a $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ composition and then melted in air at 850°C for 30 min using a platinum crucible. The melt was poured onto a stainless-steel plate to obtain glass. The resultant glass was annealed at a temperature close to the glass-transition temperature, as determined by means of differential scanning calorimetry (DSC) (Model DSC-8230B, Rigaku Co., Tokyo, Japan), and cut into a rectangular parallelepiped (dimensions of ~7 mm × ~7 mm × ~1 mm) using a saw pasted with diamond powders. After the glass surfaces were polished, the platelike glass was sandwiched between two commercial borosilicate glass plates and was brought into direct contact with electrodes made of stainless steel. Then, the glass sample was poled at several temperatures for 20 min with a poling voltage of 3 kV. When the tellurite glass sample was directly sandwiched between the stainless-steel electrodes, some black precipitates were observed in the glass after the poling. Presumably, an electrical discharge occurred in a thin air layer between the cathode and the tellurite glass surface. This discharge caused some oxidation–reduction reactions, as well as an increase in the temperature of the tellurite glass surface, which resulted in precipitation from the glass; the air layer was present when the tellurite glass sample was brought into direct contact with the electrodes, because of the roughness of the tellurite glass surface. The actual voltage applied to the tellurite glass sample was <3 kV, because the borosilicate glass plate was inserted between the electrode and the tellurite glass sample.

The second-harmonic intensity of the glass samples was measured immediately after the poling by using the Maker fringe method.[12] The incident light was a *p*-polarized fundamental wave of a pulsed Nd:YAG laser (Model GCR-11, Spectra Physics, Tokyo, Japan); the wavelength was 1064 nm. A *p*-polarized second-harmonic wave of 532 nm was passed through a monochromator (Model 270M, Spex, Edison, NJ) and detected by means of a photomultiplier (Model R955, Hamamatsu Photonics, Hamamatsu, Japan). The output signals were detected and counted by using a digital oscilloscope (Model 54522A, Hewlett–Packard, Palo Alto, CA).

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III. Results and Discussion

Figure 1 shows DSC curves of $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ and $18Na_2O{\cdot}82TeO_2$ ($30NaO_{1/2}{\cdot}70TeO_2$) glasses. Although an endothermic peak due to glass transition appears in both curves, an exothermic peak due to crystallization is observed only for the $18Na_2O{\cdot}82TeO_2$ glass. The exothermic peak at ~450°C in the DSC curve of $18Na_2O{\cdot}82TeO_2$ glass can be ascribed to crystallization. Namely, crystallization does not occur in the $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass when the heating temperature is <450°C. In other words, $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass has greater thermal stability than $18Na_2O{\cdot}82TeO_2$ glass. This result is coincident with the thermal-analysis data that was reported by Komatsu *et al.*[13] The glass-transition temperature of $18Na_2O{\cdot}82TeO_2$ glass (i.e., 255°C) is somewhat higher than the value reported previously (250°C[11]), because of the difference in the methods used to evaluate the glass-transition temperature. The previous value was obtained by means of differential thermal analysis (DTA).

The variation of the second-harmonic intensity with the angle of incidence is shown in Fig. 2 for $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass poled at 220°C. The Maker fringe pattern is ambiguous, which indicates that the length of the poled region is shorter than the coherence length. This fact suggests that the efficiently poled region is restricted near the anode-side glass surface.[2] The initial stage of the poling is the migration of mobile cations such as Li^+ and Na^+ ions. Because the migration of these ions leaves negative charges due to nonbridging oxide ions in the glass surface region, a space-charge layer is formed in the vicinity of the anode-side glass surface. This layer is composed of cations (such as Li^+ and Na^+ ions) and oxide ions, which are separated from each other in the direction of the external electric field. In addition, such a situation leads to a very large electric field near the anode-side glass surface.[14] It is possible that this very large electric field causes orientation of TeO_4 and TeO_3 tellurite structural units with nonbridging oxygen atoms that possess permanent electric dipoles. The breakdown of the macroscopic inversion symmetry is caused by the creation of a space-charge layer and the orientation of tellurite structural units, although the former is a major contribution.

The poling-temperature dependence of the second-harmonic intensity for $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass is shown in Fig. 3. The second-harmonic intensity increases, attains a maximum value, and then decreases as the poling temperature increases. The poling temperature that corresponds to the maximum second-harmonic intensity (i.e., the optimum poling temperature) is 220°C. The optimum poling temperatures are plotted in Fig. 4, as a function of the glass-transition temperature for several types of tellurite glasses, including the $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass. A linear relationship is observed between the optimum poling temperature and the glass-transition temperature, irrespective of the glass composition. One possible mechanism for the decrease in the second-harmonic intensity

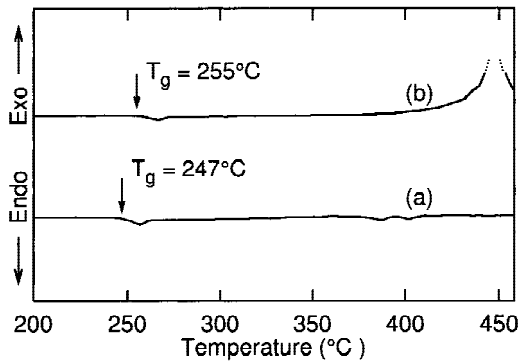

Fig. 1. DSC curves of $10Li_2O{\cdot}10Na_2O{\cdot}8TeO_2$ glass (curve ''(a)'') and $18Na_2O{\cdot}82TeO_2$ glass (curve ''(b)'').

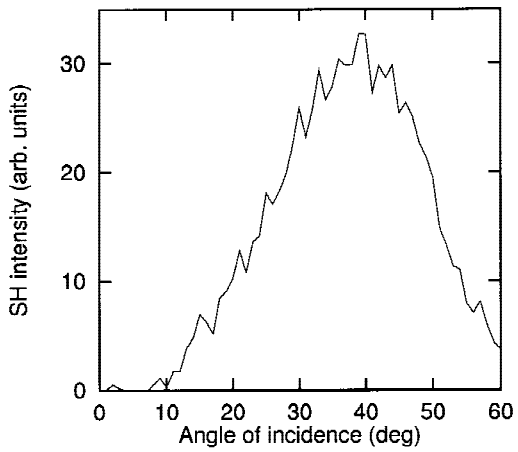

Fig. 2. Variation of the second-harmonic intensity with angle of incidence for $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass poled at 220°C for 20 min.

with increasing poling temperature near the glass-transition temperature is the migration of oxide ions. Carlson *et al.*[15] found that when a soda–lime–silicate glass is poled at its annealing temperature, with a poling electric field of 33 V/mm under vacuum (10^{-6} mm Hg), oxide ions move to the anode, so that oxygen molecules are evolved. A similar phenomenon may occur in the present tellurite glasses to reduce the electric field in the space-charge layer when the poling temperature is similar to the glass-transition temperature. Consequently, an optimum temperature that is relevant to the glass-transition temperature exists. Nevertheless, additional experiments are required to demonstrate this assumption.

In Fig. 3, the poling-temperature dependence of the second-harmonic intensity for $18Na_2O{\cdot}82TeO_2$ glass that has been

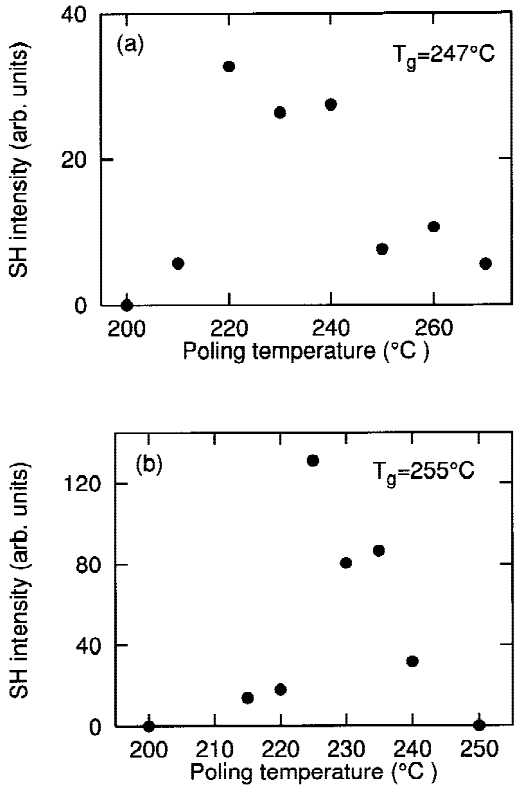

Fig. 3. Poling-temperature dependence of the second-harmonic intensity for (a) $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass and (b) $18Na_2O{\cdot}82TeO_2$ glass poled with a poling voltage of 3 kV.

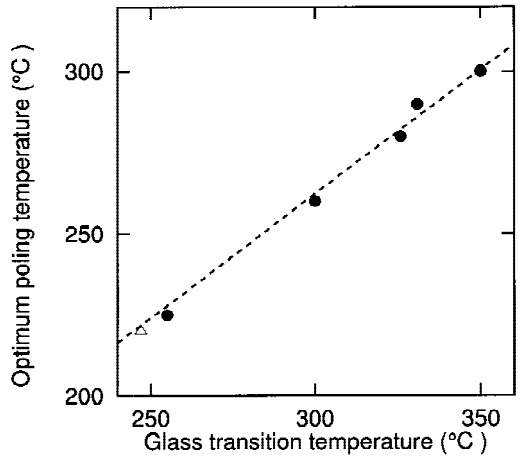

Fig. 4. Relationship between the glass-transition temperature and the optimum poling temperature for tellurite glasses, including the $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass. The datum for the $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass is indicated by an open triangle.

reported previously is also shown for comparison. The second-harmonic intensity is zero for the $18Na_2O{\cdot}82TeO_2$ glass that has been poled near the glass-transition temperature, whereas the second-harmonic generation is still observed in the $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glasses that have been poled at temperatures higher than the glass-transition temperature. This phenomenon can be associated with the thermal stability of these glasses. The $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass is more stable against heat than the $18Na_2O{\cdot}82TeO_2$ glass, as shown in Fig. 1. It is speculated that the migration of oxide ions at high temperatures, which reduces the second-harmonic intensity, is suppressed in the $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass, because of the high thermal stability of this glass.

IV. Conclusions

The poling-temperature dependence of the second-harmonic intensity for $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass exhibits an optimum poling temperature, which results in a maximum second-harmonic intensity. The linear relationship between the optimum poling temperature and the glass-transition temperature observed for tellurite glasses that contain Na_2O, MgO, and ZnO is valid for the present tellurite glasses that contain Li_2O and Na_2O as well. Thus, we conclude that the structural relaxation in the glass-transition range affects the process to break the inversion symmetry in these tellurite glasses. The thermal stability of the glass also has an influence on the poling-temperature dependence of the second-harmonic intensity. The $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass shows greater thermal stability than the $18Na_2O{\cdot}82TeO_2$ glass, as revealed from the differential scanning calorimetry measurements. Consequently, the temperature range within which the poling is effective is wider for the $10Li_2O{\cdot}10Na_2O{\cdot}80TeO_2$ glass than for the $18Na_2O{\cdot}82TeO_2$ glass.

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