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LETTER TO THE EDITOR

Poling-induced structural change and second-order nonlinearity of Na^+-doped Nb_2O_5-TeO_2 glass

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Abstract. The effect of thermal/electrical poling on surface structure and poling-induced second-harmonic generation have been examined for $15Nb_2O_5 \cdot 85TeO_2$ glass. Since the poling was carried out with the $15Nb_2O_5 \cdot 85TeO_2$ glass sandwiched in between two commercial borosilicate glasses containing Na^+, penetration of Na^+ into the anode-side surface of $15Nb_2O_5 \cdot 85TeO_2$ glass took place, as revealed by x-ray photoelectron spectroscopy (XPS). XPS studies also suggest that Nb^{5+} migrates from the anode-side surface into the bulk by the poling. It is thought that the migration of Na^+ and Nb^{5+} forms an internal dc electric field, leading to the second-harmonic generation.

1. Introduction

Vigorous investigations into the optical second-order nonlinearity of poled oxide glasses have been carried out since the discovery of second-harmonic generation in Ge-doped silica glass fibre [1] and thermally/electrically poled silica glass [2]. This phenomenon, observed particularly in silica-based glasses has attracted considerable attention from both fundamental and practical viewpoints [3–13]. What is interesting from a fundamental point of view is the fact that the second-order nonlinearity is induced in a disordered solid such as glass; oxide glass has been considered to be an optically isotropic material with macroscopic inversion symmetry which precludes the second-order nonlinear optical process. An atomic origin for the lack of inversion symmetry and the mechanism which induces the second-order nonlinearity has been discussed. The potential application of glass materials with second-order nonlinearity to optoelectronics devices is of interest as well. The superiority of glasses compared with single crystals and polycrystals as optoelectronics materials lies in the fact that the glasses show a high transmittance in a broad wavelength range, and they can also be readily fabricated in any shape, such as a fibre, a waveguide, and so forth.

We found that thermally/electrically poled tellurite (TeO_2-based) glass, the optical properties of which have attracted attention because of its large optical third-order nonlinear susceptibility as well as its wide wavelength range of large gain as an optical fibre amplifier, exhibits second-harmonic generation [14]. We have studied the mechanism which induces second-order nonlinearity in poled tellurite glasses. In the course of the study, we revealed that the relaxation time for decay of second-order nonlinearity in poled $30ZnO \cdot 70TeO_2$ glass

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is as long as 9 years at room temperature [15], and that poled $20WO_3 \cdot 80TeO_2$ glass has a large second-order nonlinear susceptibility, i.e., 2.1 pm V^{-1}, which is about 40% of $\chi_{22}^{(2)}$ of $LiNbO_3$ crystal [16]. In the present investigation, we examined second-order nonlinear optical properties of thermally/electrically poled $15Nb_2O_5 \cdot 85TeO_2$ glass in connection with its surface structure. This composition is interesting because of its large third-order nonlinear susceptibility, $\chi^{(3)} = 1.0 \times 10^{-12}$ esu, larger by two orders of magnitude than the value of silica glass [17,18]. We report the effect of poling temperature on second-harmonic intensity and poling-induced surface structure of $15Nb_2O_5 \cdot 85TeO_2$ glass, which has not been clarified, although the second-harmonic generation in poled $15Nb_2O_5 \cdot 85TeO_2$ glass has already been reported [19]. The most interesting result we obtained is the poling-induced migration of Nb^{5+} from the anode-side glass surface into the bulk below the glass transition temperature.

2. Experimental procedure

Reagent-grade Nb_2O_5 (99.9%) and TeO_2 (99.9%) powders were used to prepare glass with $15Nb_2O_5 \cdot 85TeO_2$ composition. A 20 g batch composed of the raw materials was mixed thoroughly, and melted in a platinum crucible at 850 °C for 15 min in air. The melt was poured into a mould made of graphite and cooled to room temperature in air. The resultant glass was annealed for 15 min at 400 °C, higher by 20 °C than its glass transition temperature ($T_g = 380$ °C) determined by differential scanning calorimetry (Rigaku, DSC-8230B). The annealed glass was cut into a rectangular parallelepiped using a saw pasted with diamond powder, and the surfaces of the resultant glass sample were polished. The size of the glass sample was about 10 mm×10 mm ×1 mm.

The glass sample was sandwiched in between two commercial borosilicate glass plates the thickness of which was 0.1 mm, and physically contacted with electrodes made of stainless steel. The glass sample was heated at various temperatures for 20 min with a dc voltage of 3 kV applied. The commercial borosilicate glass plates were used to prevent crystallization and/or fracture on the tellurite glass surface, which might be brought about by an electric discharge in thin air layers between electrodes and tellurite glass surface when the tellurite glass sample was directly sandwiched in between the electrodes made of stainless steel.

The Maker fringe method [20] was utilized to measure second-harmonic intensity for the poled glass samples. The p-polarized fundamental wave of a pulsed Nd:YAG laser (Spectra Physics, GCR-11), the wavelength of which was 1064 nm, was used as an incident light. The p-polarized second-harmonic wave with wavelength 532 nm was passed through a monochromator (Spex, 270M), and detected using a photomultiplier (Hamamatsu Photonics, R955). The intensity of the second-harmonic wave was determined by means of a digital oscilloscope (Hewlett Packard, 54522A).

The as-annealed and poled glasses were subjected to x-ray photoelectron spectroscopy (XPS) to clarify the surface state. The measurements were carried out for the anode-side surface of poled glasses as well as as-annealed glass by using a spectrometer (ULVAC- phi, MT-5500) with MgKα radiation as the excitation source in a pressure range 10^{-9} to 10^{-8} Torr.

3. Results and discussion

Figure 1 shows dependence of second-harmonic intensity on poling temperature. It is found that the second-harmonic intensity increases, shows a maximum at 260 °C, and decreases with an increase in the poling temperature. A similar tendency was observed for other tellurite [21–24] and silica [25] glasses. As for tellurite glasses containing monovalent and/or divalent cations

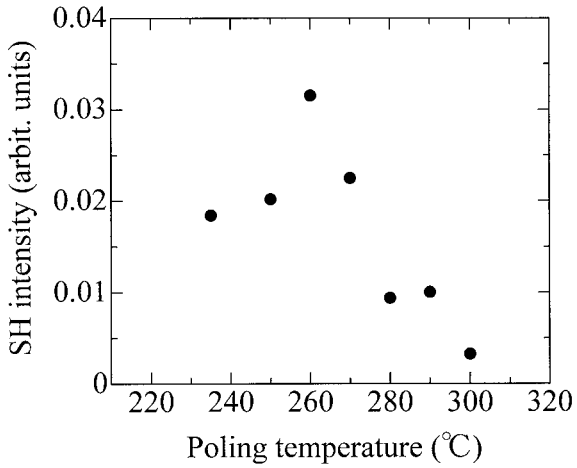

Figure 1. Dependence of second-harmonic (SH) intensity on poling temperature for $15Nb_2O_5 \cdot 85TeO_2$ glass.

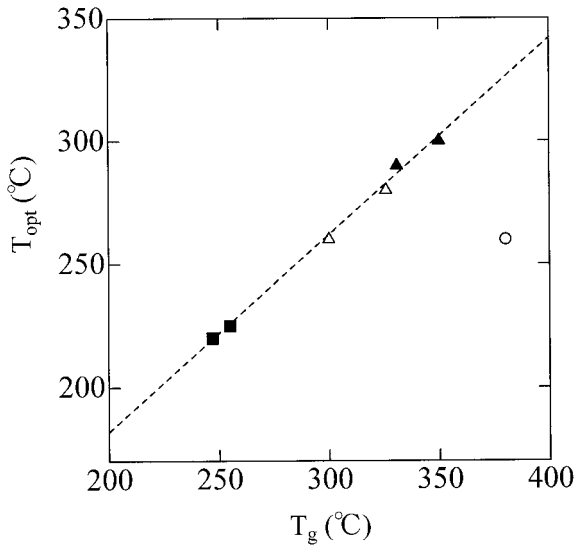

Figure 2. Relation between optimum poling temperature (T_{opt}) and glass transition temperature (T_g) for several tellurite glasses.

studied previously, there exists a linear relationship between glass transition temperature and optimum poling temperature, which corresponds to the temperature of maximum second-harmonic intensity, as shown in figure 2. This phenomenon was explained in terms of the idea that a certain electrochemical reaction relevant to viscous flow of glass, such as migration of O^{2-} followed by evolution of O_2 [26], as well as possible oxidation of Te^{4+} at the anode-side glass surface, reduces the magnitude of internal dc electric field which contributes to the second-harmonic generation. In figure 2, the open circle, closed squares, open triangles, and closed triangles represent the present $15Nb_2O_5 \cdot 85TeO_2$ glass, Li_2O–Na_2O–TeO_2 system [21], Na_2O–ZnO–TeO_2 system [22], and MgO–ZnO–TeO_2 system [23, 24], respectively. It is clear that

the datum point for $15Nb_2O_5 \cdot 85TeO_2$ glass significantly deviates from the linear relationship which holds for the other tellurite glasses. It is thought that for the $15Nb_2O_5 \cdot 85TeO_2$ glass the presence of optimum poling temperature is not attributable to the viscous flow of the whole bulk glass because the optimum poling temperature is much lower than the glass transition temperature. This fact suggests that the mechanism to induce second-order nonlinearity is different in $15Nb_2O_5 \cdot 85TeO_2$ glass than in the other tellurite glasses containing monovalent and/or divalent cations.

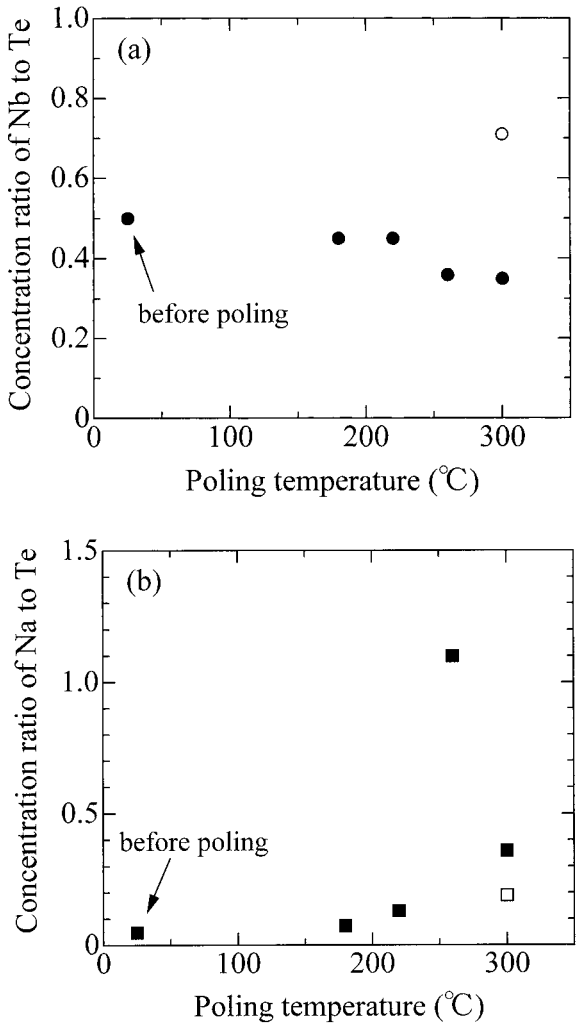

Figure 3. Poling temperature dependence of concentration ratio of (a) Nb to Te and (b) Na to Te on the anode-side glass surface. The concentration ratio for glass surface before poling is also shown. The open symbols (open circle and square) represent the concentration ratio measured after the anode-side surface was mechanically etched to 10 μm in depth.

In order to evaluate the mechanism to induce second-harmonic generation, we carried out XPS measurements on the glass surface. The poling temperature dependence of concentration ratio of Nb to Te and Na to Te on the anode-side glass surface is shown in figures 3(a) and

(b), respectively. The anode-side surface was examined because a second-harmonic wave was generated only from a thin layer just below the glass surface in contact with the anode during the poling. The concentration of each element was estimated from the integrated intensity of XPS spectra by taking the sensitivity of each element into account. The concentration ratio for glass surface before poling is also shown in these figures as indicated by an arrow. In addition, in both figures, the open symbols (open circle and square) represent the concentration ratio measured after the anode-side surface was mechanically etched to 10 μm in depth. Na^+ ions were detected because they might be present as an impurity in the raw materials and/or they migrated from the borosilicate glass plate and penetrated the $15Nb_2O_5 \cdot 85TeO_2$ glass sample. Figure 3(b) shows that as the poling temperature is increased, the concentration of Na^+ increases below 260 °C. The concentration of Na^+ on the anode-side surface decreases as the poling temperature is varied from 260 °C to 300 °C. This is presumably because most of the Na^+ ions do not remain on the surface but migrate into the bulk of the $15Nb_2O_5 \cdot 85TeO_2$ glass at 300 °C. Indeed, the concentration of Na^+ on the anode-side surface after mechanical etching by 10 μm of the glass poled at 300 °C is still large. In addition, some electrochemical reactions at the anode-side and the cathode-side glass surfaces may affect the distribution of Na^+ at 300 °C. The variation of concentration of Na^+ with poling temperature shows behaviour similar to the poling temperature dependence of second-harmonic intensity shown in figure 1. In other words, the optimum poling temperature depends on the concentration of Na^+ on the anode-side surface. Here, it should be noted that the method of poling is the same for all the tellurite glasses shown in figure 2; the tellurite glass sample was sandwiched in between two commercial borosilicate glass plates during the poling. However, in the tellurite glasses containing monovalent and/or divalent cations, the effect of penetration of Na^+ from the borosilicate glass is slight. In fact, our XPS measurements of poled $30ZnO{\cdot}70TeO_2$ glass revealed that the concentration ratio of Na to Te in this glass is small compared with the present $15Nb_2O_5 \cdot 85TeO_2$ glass [27]. Besides, the migration of Zn^{2+} from the anode-side surface was detected by means of the XPS measurements. The migration of Zn^{2+} is thought to form the internal electric field, i.e., the origin of the second-harmonic generation, in the poled $30ZnO{\cdot}70TeO_2$ glass. On the other hand, in the case of sodium-containing tellurite glasses, the large amount of Na^+ in the original glass makes the effect of penetration of Na^+ less. In such a sense, the mechanism for the second-harmonic generation is different for the $15Nb_2O_5 \cdot 85TeO_2$ glass than for the other tellurite glasses. Consequently, the datum point for $15Nb_2O_5 \cdot 85TeO_2$ glass deviates from the linear relationship between glass transition temperature and optimum poling temperature, as shown in figure 2.

The XPS studies also indicate that Nb^{5+} is forced to migrate by the poling in spite of its high valence state; the concentration ratio of Nb to Te clearly decreases as the poling temperature is varied from 220 °C to 260 °C, as shown in figure 3(a). It should be noted that the glass transition temperature of $15Nb_2O_5 \cdot 85TeO_2$ glass is 380 °C. Hence, figure 3(a) suggests that the migration of a cation with high valence such as Nb^{5+} took place far below the glass transition temperature. The ionic conduction of Nb^{5+} is not plausible because of its high valence. We speculate that the penetration of a large amount of Na^+ ions decreases the glass transition temperature of the local part just below the anode-side surface of $15Nb_2O_5 \cdot 85TeO_2$ glass, and the Nb^{5+} ions migrate as a result of viscous flow-like relaxation in the part near the glass surface, where the practical glass transition temperature is lowered by the addition of Na^+ ions. Thus, on the anode-side surface, a decrease in the concentration of Nb^{5+} as well as an increase in the concentration of Na^+ take place, and the excess or lack of positive charge on the anode-side glass surface leads to the formation of internal dc electric field which can bring about the second-order nonlinearity.

4. Conclusion

The thermal/electrical poling-induced structural change and the resultant second-harmonic generation were examined for Na^+ doped $15Nb_2O_5 \cdot 85TeO_2$ glass. The penetration of Na^+ at the anode-side surface of the glass took place during the poling because the glass was sandwiched in between commercial borosilicate glasses containing Na^+ ions. The migration of Nb^{5+} from the anode-side surface into the bulk was also observed. We speculate that the incorporation of Na^+ lowers the glass transition temperature of the anode-side surface and makes the migration of a cation with high valence such as Nb^{5+} easy, even below the glass transition temperature of the whole bulk glass.

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