Poling temperature dependence of optical second-harmonic intensity of $MgO–ZnO–TeO_2$ glasses

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Poling temperature variation of optical second-harmonic intensity induced by electrical poling has been examined for $30ZnO·70TeO_2$, $5MgO·25ZnO·70TeO_2$, and $10MgO·20ZnO·70TeO_2$ glasses. The Maker fringe pattern of these glasses indicates that the orientation of electric dipoles presumably due to TeO_4 trigonal bipyramids and TeO_3 trigonal pyramids is not restricted within the glass surface but extends into the inside of bulk glass. The poling temperature dependence of second-harmonic intensity manifests a maximum in all the glasses. There exists a tendency that the poling temperature which corresponds to the maximum of second-harmonic intensity is higher in the glass with higher glass transition temperature. This fact suggests that the orientation of tellurite structural units occurs as a result of the structural relaxation of tellurite network at around the glass transition temperature. © *1996 American Institute of Physics.* [S0021-8979(96)00107-3]

The optical second-harmonic generation in poled oxide glass materials, which was originally discovered for Ge-doped silica glass fiber[1] and electrically poled bulk silica glass,[2] is a very interesting phenomenon, because this phenomenon clearly indicates that an optical anisotropy is induced in oxide glass which has been considered to be a prototype of optically isotropic material. As for the second-harmonic generation induced by electrical poling, much attention has been focused on silica and silicate glasses.[2–11] The authors found that the optical second-harmonic generation also takes place in poled tellurite glasses.[12–14] One of the interesting results obtained experimentally for poled tellurite glasses is the relationship between glass structure and second-harmonic intensity. For instance, the second-harmonic intensity increases monotonically with an increase in the concentration of ZnO in the binary $ZnO–TeO_2$ system.[13] This phenomenon was explained on the basis of the flexibility of glass network structure. The increase in the concentration of ZnO increases the number of TeO_3 trigonal pyramids and nonbridging oxygen and, consequently, increases the flexibility of glass network structure. In the glass where the flexibility of the glass network structure is large, the orientation of TeO_4 trigonal bipyramid and TeO_3 trigonal pyramid, which presumably yield electric dipole moments because of their structure lacking in the center of symmetry, can take place more readily. As a result, the second-harmonic intensity becomes high in the glass with ZnO-rich composition. Another interesting result for poled tellurite glasses is the fact that the second-harmonic generation is scarcely observed in the tellurite glasses containing cations with large electron polarizability such as Ba^{2+} ion.[13] It was speculated that the poling process mainly brings about the electron polarization of the cation with large electron polarizability. The electron polarization cannot contribute to the freezing of orientation of electric dipoles after the poling process because of its rapid relaxation.

Although the compositional dependence of second-harmonic intensity and second-order nonlinear coefficient has been investigated for the poled tellurite glasses, the effect of poling conditions on the second-harmonic generation is less clear. Such a study is important not only for the evaluation of the mechanism by which the orientation of electric dipole moments is attained but also for the determination of the best poling condition to obtain maximum second-harmonic intensity. The latter is particularly important for the application of poled glass to a second-order nonlinear optical device. In the present study, the poling temperature dependence of second-harmonic intensity for poled $MgO–ZnO–TeO_2$ glasses is examined. The choice of this system comes from the fact that the tellurite network structure of binary $MgO–TeO_2$ glasses is identical to that of $ZnO–TeO_2$ glasses when the glass compositions are the same as each other according to the previous Raman studies.[15,16]

Glasses were prepared from MgO, ZnO, and TeO_2 as starting materials by using the conventional melt-quenching method. The raw materials were mixed thoroughly to make prescribed compositions shown in Table I. The mixture was melted in a platinum crucible at 800–900 °C for 20–40 min in air. The melt was poured onto a stainless-steel plate and cooled in air. The as-quenched glass was annealed for 30 min at around glass transition temperature determined by means of differential thermal analysis (DTA). It was ascertained that the resultant specimens were amorphous by using x-ray-diffraction analysis with Cu $K\alpha$ radiation.

Both sides of the glass specimen were polished so that the thickness of the platelike glass specimen became about 1 mm. The glass specimen was put between two commercial glass plates for an optical microscope and contacted physically to electrodes made of stainless steel. Two commercial glass plates were used to prevent discharge between electrodes and electrochemical reaction between electrodes and glass surfaces during the poling process.[14] After the external dc electric field of 3 kV was applied, the specimen was heated to a chosen temperature in an electric furnace, and kept for 20 min. Then, the specimen was taken out from the furnace and cooled in air while the applied voltage was maintained to be constant. The applied voltage was removed after the specimen was cooled to the room temperature.

The poled glass specimens thus obtained were subjected to measurements of second-harmonic intensity by using a

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TABLE I. Composition and glass transition temperature of $MgO–ZnO–TeO_2$ glasses prepared in the present study.

Glass composition (mol %)	Glass transition temperature (°C)
$30ZnO·70TeO_2$	326
$5MgO·25ZnO·70TeO_2$	331
$10MgO·20ZnO·70TeO_2$	350

pulsed Nd:yttrium-aluminum-garnet (YAG) laser with a pulse width of about 10 ns. The fundamental wave with the wavelength of 1064 nm was used as an incident light. The beam area was about 1 mm in diameter. The output light from the specimen was passed through a prism to divide the second-harmonic wave with 532 nm from the fundamental wave. The second-harmonic wave was detected with a monochromator equipped with a photomultiplier. The situation of polarization was *p* excitation and *p* detection. The output signal was accumulated by using a boxcar integrator. The measurements were carried out at several angles of incidence from $-65°$ to 65°. A schematic illustration of equipment for measurements of optical second-harmonic intensity is shown in Fig. 1.

Table I shows the glass composition and glass transition temperature. The glass transition temperature tends to increase with a displacement of ZnO by MgO. Figure 2 shows the Maker fringe pattern[17] for $5MgO·25ZnO·70TeO_2$ glass poled at 320 °C. The fringe pattern is clearly observed. This fact suggests that the poled region is longer than the coherent length. It is known that the poled region is restricted to only the glass surface in the case of poled silica glasses.[2–6] In contrast, the region where the orientation of electric dipoles takes place extends into the inside of bulk glass in the case of the present poled tellurite glasses.

In Fig. 3 is shown variation of second-harmonic intensity with poling temperature for $30ZnO·70TeO_2$, $5MgO·25ZnO·70TeO_2$, and $10MgO·20ZnO·70TeO_2$ glasses. The second-harmonic intensity increases, experiences a maximum, and decreases with an increase in the poling temperature for all the specimens. A similar phenomenon was observed in the poling temperature dependence of

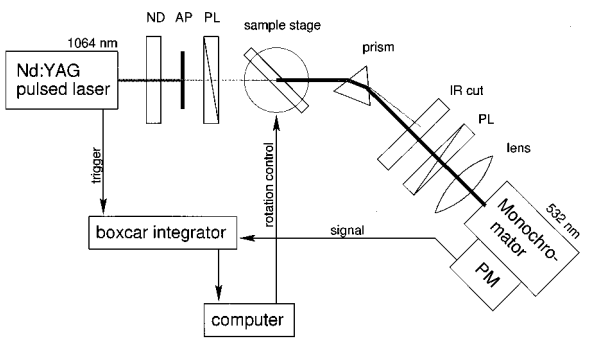

FIG. 1. Schematic illustration of equipment for measurements of optical second-harmonic intensity. The thich and thin lines represent second-harmonic and fundamental waves, respectively. The notation of symbols indicated in the figure is as follows. ND: ND filter; AP: aperture; PL: polarizer; IR cut: IR cut filter; and PM: photomultiplier.

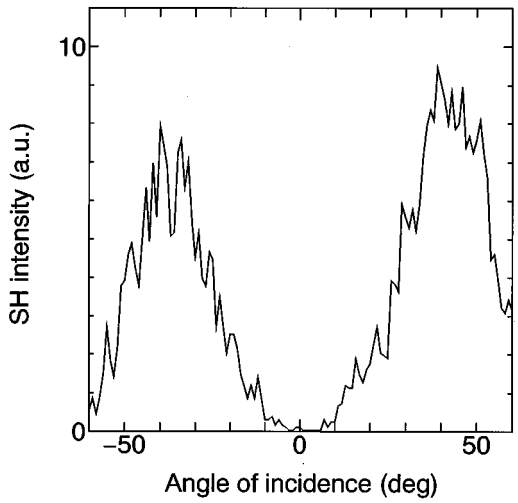

FIG. 2. Maker fringe pattern of $5MgO·25ZnO·70TeO_2$ glass poled at 320 °C. The fringe pattern is clearly observed.

second-harmonic intensity for poled silica glass.[8] The appearance of maximum in the poling temperature dependence of second-harmonic intensity is explainable in terms of the competition effect between thermal fluctuation and external dc electric field. As the poling temperature increases, the thermal energy becomes large enough to promote the orientation of electric dipole moments in the direction of external dc electric field; however, when the poling temperature is too high, the thermal fluctuation overcomes the external dc electric field. Consequently, the poling becomes less effective as the poling temperature increases, leading to the smaller second-harmonic intensity. Thus, the maximum of the second-harmonic intensity appears in its poling temperature dependence.

As seen from Fig. 3 there is a tendency that the poling temperature corresponding to the maximum of second-harmonic intensity increases with an increase in the concen-

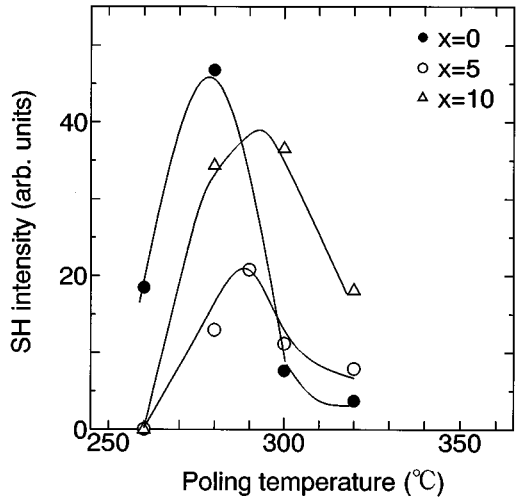

FIG. 3. Variation of second-harmonic intensity with poling temperature for $30ZnO·70TeO_2$, $5MgO·25ZnO·70TeO_2$, and $10MgO·20ZnO·70TeO_2$ glasses. The solid curves are to guide the eye.

tration of MgO. This means that the effect of thermal fluctuation increases in the order of $10MgO \cdot 20ZnO \cdot 70TeO_2$, $5MgO \cdot 25ZnO \cdot 70TeO_2$, and $30ZnO \cdot 70TeO_2$ glasses. The thermal effect is also evident in the behavior of second-harmonic intensity at poling temperatures above 300 °C. The second-harmonic intensity increases in the order of $30ZnO \cdot 70TeO_2$, $5MgO \cdot 25ZnO \cdot 70TeO_2$, and $10MgO \cdot 20ZnO \cdot 70TeO_2$ when the poling temperatures are 300 and 320 °C. This fact clearly indicates that the thermal fluctuation is the most efficient in the $30ZnO \cdot 70TeO_2$ glass and the thermal effect is the least in the $10MgO \cdot 20ZnO \cdot 70TeO_2$ glass among the present tellurite glasses. Besides, Fig. 3 shows that the second-harmonic generation is not observed for the $5MgO \cdot 25ZnO \cdot 70TeO_2$ and $10MgO \cdot 20ZnO \cdot 70TeO_2$ glasses but takes place for the $30ZnO \cdot 70TeO_2$ glass when the poling temperature is 260 °C. This fact also suggests that the thermal effect is the most prominent in the $30ZnO \cdot 70TeO_2$ glass. As shown in Table I, the glass transition temperature increases with an increase in the concentration of MgO. These facts imply that the thermal effect is more outstanding in the glass with lower glass transition temperature. Hence, it is considered that the orientation of electric dipoles in the direction of external electric field, which induces the optical anisotropy in the glass, takes place as a result of the structural relaxation of glass network at around the glass transition temperature. As the present authors argued in previous articles, the electric dipoles are attributed to TeO_4 trigonal bipyramids and TeO_3 trigonal pyramids which are lacking in the center of symmetry. Therefore, it is thought that the orientation of these structural units results from the relaxation of tellurite network structure at around the glass transition temperature.

In conclusion, optical second-harmonic generation was observed in the poled $MgO–ZnO–TeO_2$ glasses. The Maker fringe pattern indicates that the poled region, where the orientation of electric dipoles ascribed to TeO_4 trigonal bipyramids and TeO_3 trigonal pyramids takes place, is not restricted to the glass surface but extends over the glass network structure. From the poling temperature dependence of second-harmonic intensity for the present three kinds of glasses in the $MgO–ZnO–TeO_2$ system it is proposed that the orientation of tellurite structural units takes place as a result of the structural relaxation of the tellurite network at around the glass transition temperature.

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