Poling-induced crystallization of tetragonal $BaTiO_3$ and enhancement of optical second-harmonic intensity in $BaO-TiO_2-TeO_2$ glass system

Aiko Narazaki,[a] Katsuhisa Tanaka, and Kazuyuki Hirao
Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

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Effect of poling on surface crystallization behavior of $BaTiO_3$ in $15BaO-15TiO_2-70TeO_2$ glass and on second-harmonic generation of the resultant glass ceramics has been examined. A direct current voltage in a range of 0.3–1 kV was applied to the original glass at around 400 °C, which is above its glass transition temperature, followed by cooling of the sample to room temperature with the voltage kept constant. X-ray diffraction patterns indicate that the poling increased the fraction of crystalline phases precipitated at the glass surface and that $BaTiO_3$ crystallites were precipitated preferentially with (101)- or (110)-orientation. It is also observable that the x-ray diffraction line assigned to $BaTiO_3$ shifted from the position corresponding to bulk cubic crystal to that of ferroelectric tetragonal one when the applied voltage was increased. In other words, the poling treatment stabilizes the tetragonal $BaTiO_3$ phase, leading to a larger optical second-order nonlinear susceptibility. In fact, the second-harmonic intensity for the glass ceramic poled at 420 °C was enhanced by a factor of ten compared with the glass ceramic heat treated without an external electric field. © *1999 American Institute of Physics.* [S0003-6951(99)04247-3]

Transparent glass ceramics containing ferroelectric crystals such as $BaTiO_3$ have been quite attractive materials in the fields of optics and electronics because of their potentially large optical second-order nonlinear susceptibility and high dielectric constant as well as an easiness to fabricate.[1–6] Recently, Komatsu *et al.* succeeded in preparing transparent glass ceramics containing $BaTiO_3$ crystallites from $15BaO-15TiO_2-70TeO_2$ glass.[7] Subsequently, Tanaka *et al.* found that these glass ceramics exhibited the second-harmonic generation, although the precipitated $BaTiO_3$ are likely to be rather paraelectric cubic phase than ferroelectric tetragonal one.[8] For glass ceramics in the system $PbO-BaO-TiO_2-B_2O_3$, Lynch and Shelby[9] reported a similar result; the cubic $PbTiO_3$ was quenched to room temperature after heat treatment of glass. The lattice strain between glass matrix and precipitated crystallite restricted the phase transition of $PbTiO_3$ crystal into ferroelectric phase, which is known as crystal clamping. They also found that the effect of crystal clamping could be efficiently excluded when the glass transition temperature of the residual glass was decreased below the Curie temperature of $PbTiO_3$, i.e., 490 °C. However, as for $BaTiO_3$ crystal, this method is not available because of its lower Curie temperature of 120 °C.

In the present study, we carried out an application of a direct current (dc) voltage, i.e., poling during crystallization of $15BaO-15TiO_2-70TeO_2$ glass to fabricate transparent glass ceramics with ferroelectric properties such as large optical nonlinearity. The effect of poling on ferroelectricity and related optical nonlinearity of the precipitated crystalline phase has been little investigated thus far.[1] Therefore, we examined the effect of poling on both crystallization of $15BaO-15TiO_2-70TeO_2$ glass and optical second-order nonlinearity of the resultant glass ceramics by means of measurements of x-ray diffraction (XRD) and second-harmonic generation. The behavior of crystallization of other crystalline phases as well as $BaTiO_3$ crystal caused by an external voltage is discussed in terms of effects of both the electric field and the Joule heat.

$15BaO-15TiO_2-70TeO_2$ (in mol %) glass was prepared from reagent-grade $BaCO_3$, TiO_2, and TeO_2 as starting materials. The mixture of raw materials was melted in a platinum crucible at 1000 °C for 30 min and then was poured into an alumina boat. The glass transition temperature of the sample was determined using differential thermal analysis (Rigaku, TG-DTA 8112BH). After annealing for 30 min at 380 °C which is around its glass transition temperatures, the sample was polished with CeO_2 powders into a plate of $5\,mm \times 7\,mm \times 1\,mm$. The inside and surface of as-annealed specimen were ascertained to be amorphous by powder and bulk XRD measurements (Rigaku, RINT1400). Cu K_α radiation was used and diffraction intensity was measured at $2\theta = 10° - 70°$.

Poling treatment was performed as follows. The glass specimen was sandwiched in between two commercial borosilicate glass plates with a size of $18\,mm \times 18\,mm \times 0.15\,mm$ and contacted with electrodes made of stainless steel. The borosilicate glasses were used for the suppression of leakage current at the sample surface. The glass specimen with electrodes was put in an electric furnace and heated to an aimed temperature which ranged from 380 to 420 °C. Then, a dc voltage of 0–1 kV was applied at the temperature for 3 h, followed by gradual cooling to room temperature with the voltage applied. It should be noted that the actual voltage applied to the specimen was smaller than the intentionally applied external voltage due to the use of borosilicate glass plates. The XRD pattern for the surface of the resultant specimen was measured in order to identify crystalline phases if precipitated.

Second-harmonic generation was examined for all the heat-treated specimens at room temperature using the Maker

[a]Electronic mail: aiko@curl1.kuic.kyoto-u.ac.jp

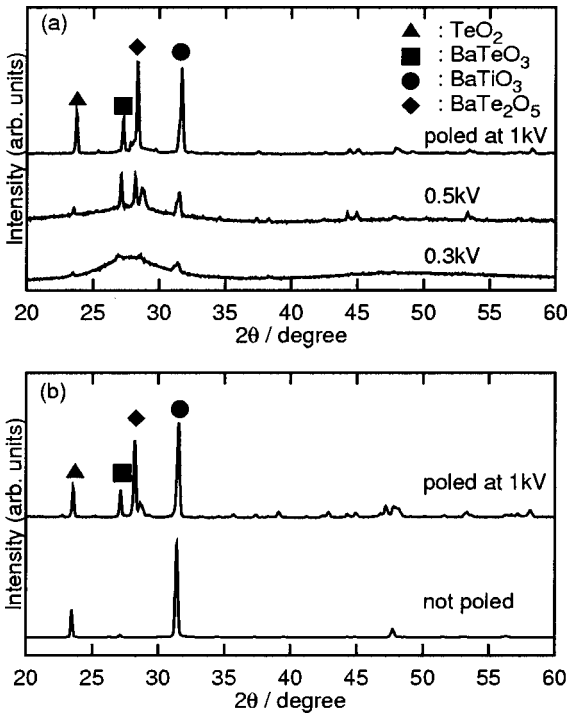

FIG. 1. XRD patterns for the specimens prepared by heat treatment at (a) 400 and (b) 420 °C, respectively. The patterns from bottom to top in (a) correspond to the samples heat treated at an applied voltage of 0.3, 0.5, and 1 kV/mm. The upper and lower patterns in (b) represent the XRD lines for the glass ceramics heat treated with a voltage of 1 kV and without a voltage.

fringe method.[10] The *p*-polarized fundamental light at 1064 nm from a *Q*-switched pulsed Nd:yttrium–aluminum–garnet laser (Spectra-Physics, GCR-11) was incident on the sample. The fundamental wave which passed through the sample was eliminated by two infrared cut filters and a monochromator (Spex, 270M), whereas the *p*-polarized second-harmonic light at 532 nm generated in the sample was detected by using a photomultiplier (Hamamatsu Photonics, R955). The signal from the photomultiplier was accumulated using a digital oscilloscope (Hewlett Packard, 54522A). The input fundamental light power was estimated by measuring the second-harmonic intensity of *Y*-cut quartz as a reference material.

Figures 1(a) and 1(b) show XRD patterns for an anode-side surface of the bulk specimens heat treated at 400 and 420 °C, respectively. The XRD patterns in Fig. 1(a) correspond to the samples poled at several voltages indicated in the figure during the heat treatment. In the case of the poling voltage of 1 kV, the diffraction lines were observed at around $2\theta = 23.6°$, 27.2°, 28.2°, and 31.7°. These lines can be assigned to TeO_2, $BaTeO_3$, $BaTe_2O_5$, and $BaTiO_3$ crystalline phases, respectively. The intensity of these diffraction lines was decreased with a decrease in the applied voltage. The diffraction lines eventually disappeared for the sample without poling which was identified as an amorphous phase by XRD. Here, it should be noted that the powder XRD patterns of all the heat-treated samples, irrespective of poling conditions, exhibited only a broad hallow peak characteristic of an amorphous material. This fact indicates that the crystallization did not occur uniformly inside the bulk $15BaO–15TiO_2–70TeO_2$ glass, but took place only at the surface region of the glass. Thus, it can be said that the surface crystallization was promoted by the application of a dc voltage during the heat treatment. The application of voltage possibly has an influence on the crystallization behavior through effect of an electric field or Joule heat. Whereas the former is considered to bring about the transfer of ions, the latter causes an increase in actual sample temperature. Based on the measured specific heat of about 0.4 $J g^{-1} K^{-1}$ at 400 °C for $15BaO–15TiO_2–70TeO_2$ glass and the measured poling current of less than 0.1 μA, the increase of sample temperature due to the Joule heat was estimated to be about 10 K at most when the glass was poled at an external voltage of 1 kV. Therefore, it is plausible that the increase in sample temperature is possibly one of the important factors for the occurrence of crystallization at this temperature.

Being similar to the glass ceramics poled at 400 °C, the XRD pattern of the poled glass ceramic in Fig. 1(b) show sharp peaks at around 23.6°, 27.2°, 28.2°, and 31.6°. On the other hand, the glass ceramic prepared with no voltage applied shows the Bragg reflection lines at 23.6°, 27.2°, and 31.4°, but does not exhibit any lines assignable to $BaTe_2O_5$ crystalline phase. The fact that $BaTe_2O_5$ was observed for only the poled glass ceramics suggests that the electric field, i.e., movement of ions brought about the change in the crystallization behavior.

The XRD peaks due to the Bragg reflection from (101) and (110) plane of $BaTiO_3$ crystalline phase are shown for the glass ceramics prepared at 400 and 420 °C in Figs. 2(a) and 2(b), respectively. The higher the applied voltage was during heat treatment, the larger shift in 2θ these peaks experienced, whereas the diffraction lines attributable to the other crystalline phases exhibited no change in their peak position. According to Joint Committee on Powder Diffraction Standards (JCPDS) cards, the paraelectric cubic phase of $BaTiO_3$ crystal shows the XRD line from (110) plane at $2\theta = 31.4°$. On the other hand, the ferroelectric tetragonal $BaTiO_3$ has the diffraction peaks corresponding to (101) or (110) plane at 31.50° and 31.64°, respectively. Therefore, it can be pointed out that the poling made $BaTiO_3$ crystallites rather close to tetragonal phase than cubic phase.

Figure 3 shows the variation of second-harmonic intensity with angle of incidence, i.e., Maker fringe pattern for the glass ceramic prepared at 400 °C with poling at 1 kV. Whereas the second-harmonic generation was observable for the glass ceramics poled at 0.5 and 1 kV, no second-harmonic signals were detected from the specimens heat treated with a voltage in the range of 0–0.3 kV applied. This observation indicates that in the present experiments the surface crystallization is necessary for the second-harmonic generation. Here, we can consider two possibilities as a source of the second-order nonlinearity induced by the surface crystallization of $15BaO–15TiO_2–70TeO_2$ glass. One of them is the $BaTiO_3$ crystallites the tetragonal phase of which has large second-order nonlinearity. Another is a stress caused during the cooling process from heat treatment temperature to room temperature because of difference in thermal expansion coefficient between glass and precipitated crystals. However, this kind of stress leads to $C_{\infty\nu}$ symmetry like poled glass materials which show no second-harmonic generation at 0° but have a maximum intensity at a larger angle.[11] According to the Maker fringe pattern in Fig. 3, such

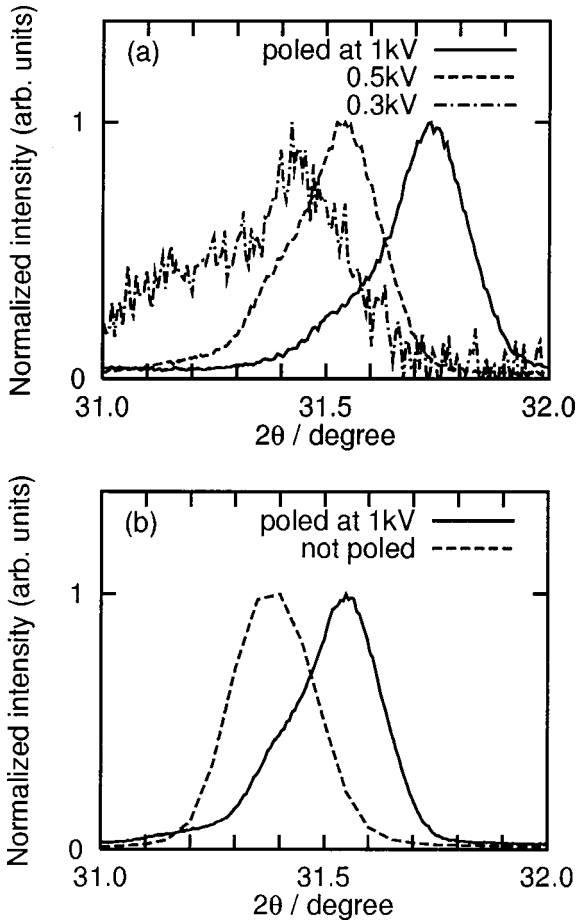

FIG. 2. XRD lines, which can be assigned to $BaTiO_3$ crystal, for the glass ceramics fabricated via heat treatment at (a) 400 and (b) 420 °C, respectively. According to the JCPDS cards, diffraction line at around $2\theta = 31.4°$ is due to the Bragg reflection from (110) plane of cubic phase, whereas diffraction peaks at 31.50° and 31.64° are attributable to (101) and (110) planes of tetragonal one, respectively.

a stress can be excluded from the origins for second-harmonic generation in the present glass ceramics.

The Maker fringe patterns of the glass ceramics heat treated at 420 °C are demonstrated in Fig. 4. The solid curve and closed circles represent the second-harmonic intensity

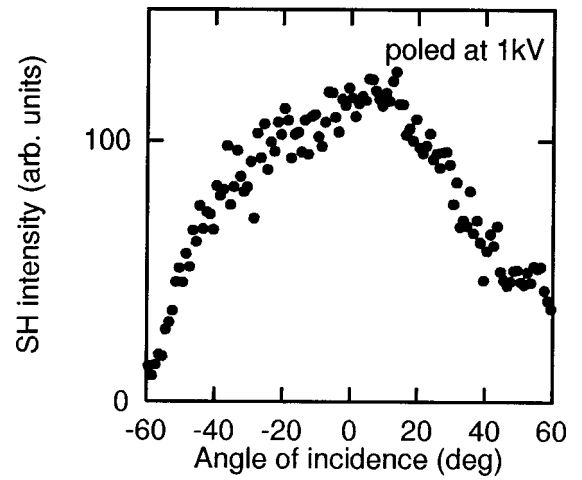

FIG. 3. Variation of the second-harmonic intensity with incident angle, i.e., Maker fringe pattern for the glass ceramic prepared at 400 °C with an applied voltage of 1 kV.

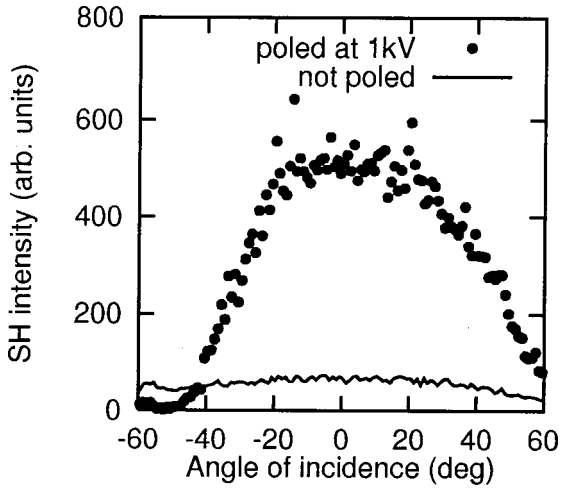

FIG. 4. Maker fringe patterns for the glass ceramics heat treated at 420 °C. The solid curve and closed circles denote the second-harmonic intensity for the specimens crystallized without and with an external voltage, respectively.

from the glass ceramics without and with poling, respectively. The latter intensity is ten times larger than the former one, indicating that the poling treatment enhanced the second-harmonic generation. The possible explanation for this enhancement is an increase in amount or tetragonality of precipitated $BaTiO_3$. On the other hand, it was revealed by scanning electron microscopy observations that the longer-period heat treatment made the crystallized layer thicker; the thickness varied from a few to more than 100 μm, resulting in an increase in the amount of precipitated $BaTiO_3$. However, the glass ceramic with a thicker surface-crystallized layer showed smaller intensity of second-harmonic light because of a decrease in transparency. Therefore, it takes a more important role in the enhancement of second-harmonic generation by poling that $BaTiO_3$ crystal precipitates as the tetragonal phase.

In conclusion, the effect of poling on both the surface crystallization behavior of $BaTiO_3$ in $15BaO–15TiO_2–70TeO_2$ glass and the second-harmonic generation in the resultant glass ceramics was investigated. The poling proceeded not only the surface crystallization of $BaTiO_3$ at lower temperature but also the stabilization of tetragonal $BaTiO_3$ phase. The poled glass ceramics exhibited larger second-harmonic intensity, which can be ascribed to the increase in tetragonality of $BaTiO_3$ crystalline phase.

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