

Effect of electric field on the crystallization of lead titanate in a glass

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An electric field was applied to a PbO-TiO₂-Al₂O₃-SiO₂ glass during the crystal nucleation treatment at 570°C in order to produce oriented glass-ceramics. After the crystallization treatment at 620°C of the nucleated glass, an enhanced *a*-axis preferred orientation of the lead titanate cubic perovskite, which is not ferroelectric, was developed in the surface-layer region. However, the *a*-axis orientation was difficult to develop in the interior region of the sample, possibly due to ion migration during the nucleation treatment. The degree of *a*-axis orientation on the as-heated surface showed a maximum at an optimum nucleating time t_{\max} and the t_{\max} -value decreased with an increase in the applied electric field strength.

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1. Introduction

Controlled crystallization in glasses has led to the development of glass-ceramic materials with pore-free, fine-grained microstructure and specific properties. Much of the work in the field of glass-ceramics has been done on the thermal and mechanical properties. On the other hand, few investigations were reported on the high-permittivity glass-ceramics containing a ferroelectric phase, such as BaTiO₃ [1–3], PbTiO₃ [4–6], LiTaO₃ [7], LiNbO₃ [8–10], NaNbO₃ [7, 10–13], KNbO₃ [7, 14], tungsten bronze [15–17], and bismuth-containing layered perovskites [18–20]. The ferroelectric and dielectric properties of the ferroelectric phase are usually diluted by the glass former (e.g., SiO₂, B₂O₃, etc.). However, the excellent composition and microstructure adjustability of glass-ceramics promises some advantages of high-permittivity glass-ceramics over the crystalline ferroelectric ceramics, e.g., adjustable thermal expansion, dielectric properties, and processing temperature. They also offer processing compatibility with ceramic substrates and metallized components [21, 22]. Therefore, high-permittivity glass-ceramic materials are candidates for capacitor, hybrid circuit, electrooptics, and cryogenic applications [21, 22].

According to Rüssel [23], oriented glass-ceramics may be prepared by plastic deformation (e.g., extrusion), kinetic control (e.g., surface crystallization), and thermodynamic control (e.g., via external magnetic or electric fields). Several experiments have been done on the effect of an electric field on the nucleation [24, 25] and phase separation [26, 27] in glasses. It has also been reported that crystallization of glasses can also be affected by applying an electric field [28–30]. It is suggested that this route is possibly able to fabricate

oriented glass-ceramics, esp., those containing a ferroelectric crystalline phase. In the present paper, an electric field was applied on the glass with a mol% composition of 40PbO, 25TiO₂, 10Al₂O₃, 25SiO₂ during the nucleation treatment. The orientation of the lead titanate (PbTiO₃) crystals in the resulting glass-ceramics was investigated.

2. Experimental procedures

2.1. Sample preparation

Well-mixed, dried powder containing appropriate amounts of reagent-grade PbO, TiO₂, Al₂O₃, and SiO₂ was melted in a platinum crucible for 30 min at 1200°C. The melt was quenched by pouring it onto a copper plate and pressing into plate form with a thickness of about 3 mm. The glass was annealed at 450°C for 1 h and then furnace-cooled to room temperature. The annealed glass was cut by diamond saw and ultrasonic cutter to yield disc-shaped samples with a diameter of 8 mm. After polishing the glass sample surfaces by SiC papers (#800) to a thickness of about 2.2 mm, glass-ceramics were fabricated by a two-stage heat-treatment: nucleation at 570°C for 0.5–12 h, followed by crystallization at 620°C for 1 h (Fig. 1). During the nucleating treatment, a dc electric field of 0–5.9 kV/cm was applied. platinum plates with a thickness of 0.5 mm were used as the electrodes.

2.2. Characterization

The crystallization temperatures of the glasses in bulk form were measured by differential thermal analysis (model SDT 2960, TA Instruments, Inc., DE, USA) at a heating rate of 5 K/min. X-ray diffraction (XRD)

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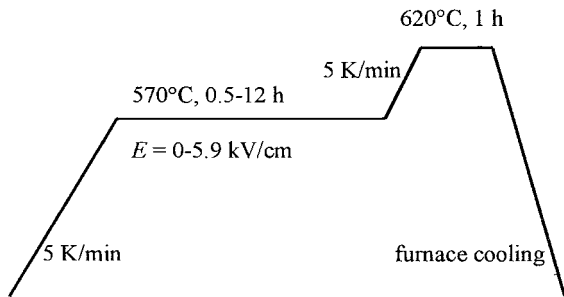


Figure 1 The heat-treatment procedure for fabricating the PbTiO₃-containing glass-ceramics.

analysis of the crystallized samples was performed on a diffractometer (Model D5000, Siemens, Germany) operating at 40 kV and 20 mA. Step scanning was used with a sampling time of 2 s for each interval of 0.03° (2θ) for phase identification or a sampling time of 1 s for each interval of 0.001° (2θ) for the measurement of integrated intensity.

3. Results

3.1. Differential thermal analysis (DTA)

Fig. 2 shows the DTA thermograms for the glasses nucleated at 540–590°C for 2 h. Two exothermic peaks were observed. According to XRD analysis, the low-temperature peak (T_{P1}) was caused by the crystallization of cubic PbTiO₃ from the glass matrix and the high-temperature peak (T_{P2}) was associated with the formation of PbTi₃O₇ and PbAl₂Si₂O₈ phases. It can be seen that the T_{P1} -value decreased from 632° to 612°C when the nucleating temperature was increased from 540 to 590°C, indicating an increasing number-density of PbTiO₃ nuclei. Moreover, the peak area for the glasses nucleated at $\leq 570^\circ\text{C}$ was nearly the same, while that for the glasses nucleated at $\geq 580^\circ\text{C}$ decreased because some crystal growth has occurred during the nucleating treatment. Therefore, the optimum nucleating-temperature for the PbTiO₃ phase was 570°C. It was also noted that the T_{P2} -value was nearly insensitive to the nucleating temperature because no PbTi₃O₇ and PbAl₂Si₂O₈ nuclei were formed during the nucleating treatment. Therefore, in the following experiments, the glass-ceramics were obtained by nucleating at 570°C for 0.5–12 h, then crystallizing at 620°C for typically 1 h.

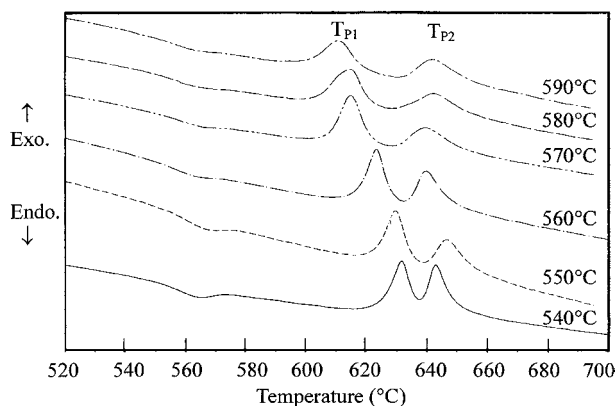


Figure 2 DTA patterns of the glasses nucleated at 540–590°C for 2 h.

It was found that the glass was easily damaged due to electrical breakdown because of its high electrical conductivity when the electric field was applied at the crystallizing temperature (620°C). This situation can be avoided if the electric field was applied at the nucleating temperature (570°C). As a result, the heat-treatment schedule as shown in Fig. 1 was determined.

3.2. X-ray diffraction analysis (XRD)

Fig. 3 shows the typical XRD patterns for the glass-ceramics. Pattern (a) was obtained from the powder of the sample crystallized at 620°C for 3 h without applying electric field. In the present study, all glass-ceramics contained cubic PbTiO₃ as the single crystalline phase. It has been shown in our previous paper [6] that tetragonal PbTiO₃, PbTi₃O₇, and PbAl₂Si₂O₈ can form when the glass was crystallized at higher temperatures (e.g., 830°C). The phase- and microstructure-developments have also been discussed. It can also be seen in pattern (a) that the broad scattering intensity around 25°–35° still remained, indicating a considerable amount of residual glass phase. Pattern (b) was obtained from the as-heated surface of the sample nucleated at 570°C for 9 h with a dc electric field strength (E) of 1.8 kV/cm, followed by crystallized at 620°C for 1 h. Using (111) line of each pattern as a reference, it can be seen that the relative intensities of the ($h00$) lines increased as compared with that of the powder pattern (a), implying that there is a -axis preferred orientation of cubic PbTiO₃ phase on the sample surface.

Therefore, we define

$$R_i(E) = I_{100}(E)/I_{111}(E) \quad (1)$$

where $I_{100}(E)$ and $I_{111}(E)$ are the integrated intensities for the (100) and (111) lines, respectively, for the sample treated by an electric field strength of E , and $i = P, S$, or B denoting that the XRD pattern was obtained from powder, as-heated surface, or bulk region

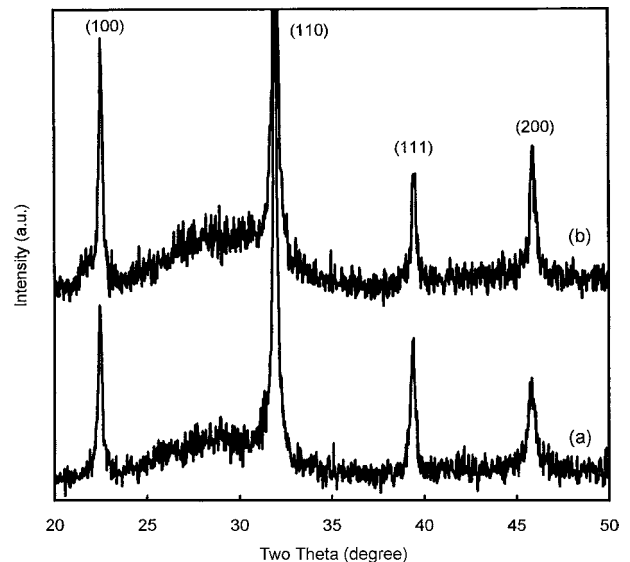


Figure 3 Typical XRD patterns for the samples: (a) crystallized at 620°C for 3 h (powder form) and (b) nucleated at 570°C for 9 h with $E = 1.8$ kV/cm, then crystallized at 620°C for 1 h (free surface).

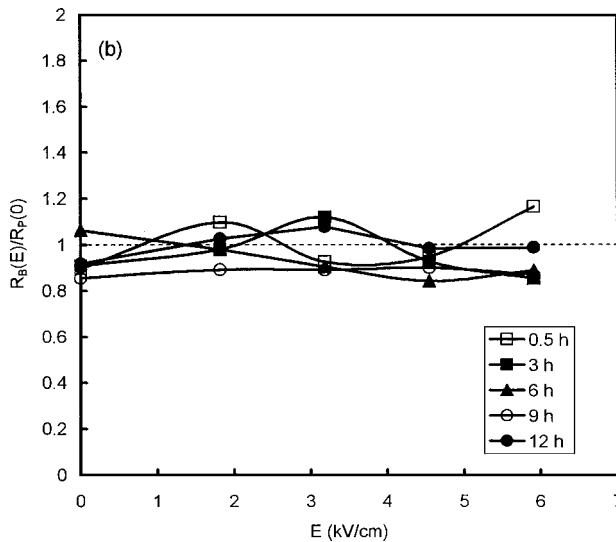
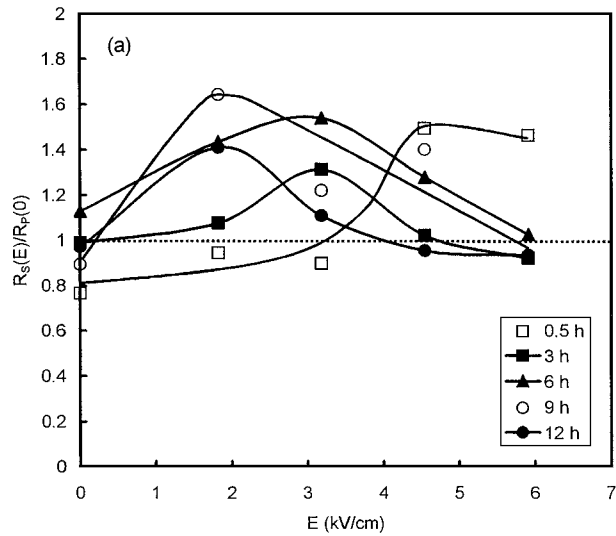


Figure 4 Effect of electric field strength on the (a) $R_S(E)/R_P(0)$ and (b) $R_B(E)/R_P(0)$ ratios.

($\frac{1}{2}$ sample thickness). According to the powder pattern (a) in Fig. 3, the intensity ratio $R_P(0)$ was calculated ($=1.084$) and was used in the experiment as the reference value without preferred orientation. Therefore, the $R_i(E)$ -value obtained from each XRD pattern was divided by $R_P(0)$ in order to represent the degree of $[h00]$ preferred orientation.

Fig. 4a and b show the effect of dc electric field strength (E) on the $R_S(E)/R_P(0)$ and $R_B(E)/R_P(0)$ ratios, respectively. It can be seen from Fig. 4a that the $R_S(E)/R_P(0)$ ratios for the samples nucleated for 0.5–12 h with $E = 0$ were around 1. However, the $R_S(E)/R_P(0)$ ratios for most of the samples with $E > 0$ were larger than 1. According to Fig. 4b, the $R_B(E)/R_P(0)$ ratios for most samples were around 1.

Further information was obtained by stepwisely polishing the sample surface to the desired depth and measuring the $R(E)/R_P(0)$ -value, as shown in Fig. 5. The samples were nucleated at 570°C for 6 h with $E = 0$ and 3.18 kV/cm, then crystallized at 620°C for 1 h. The $R(E)/R_P(0)$ -value for the sample with $E = 3.18$ kV/cm was remarkably higher than that for the sample with $E = 0$ for the depth range from 0–90 μm ,

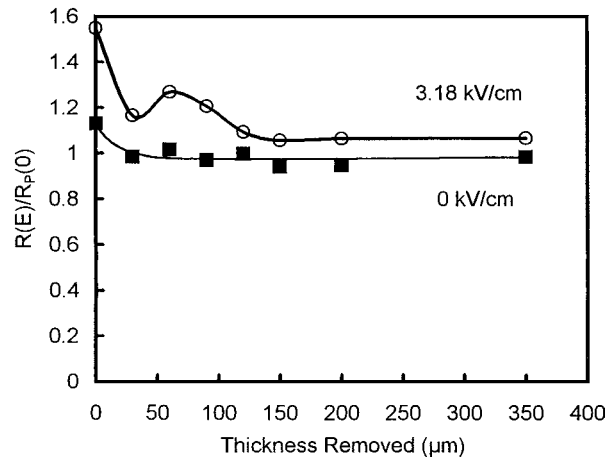


Figure 5 Variation of $R_S(E)/R_P(0)$ with the thickness removed for the samples nucleated at 570°C for 6 h with $E = 0$ and 3.18 kV/cm, then crystallized at 620°C for 1 h.

and was only slightly higher for the depth ≥ 150 μm . For the sample with $E = 0$, the $R(E)/R_P(0)$ value was slightly > 1 only in the sample surface, then decreased to ~ 1 when the thickness removed was ≥ 30 μm .

4. Discussion

According to Figs 4 and 5, applying a dc electric field during nucleating treatment can develop some degree of a -axis preferred orientation of the PbTiO_3 crystals near the sample surface. However, the preferred orientation was difficult to develop in the interior region of the sample and only a very slight orientation was seen. Although in Fig. 5 a thin layer of very slight preferred orientation has also developed on the surface of sample with $E = 0$, this behavior is common for glass-ceramic materials due to surface crystallization.

Pernice *et al.* [28] have reported that in $\text{K}_2\text{O-Nb}_2\text{O}_5\text{-SiO}_2$ glasses the KNbSi_2O_7 crystals can grow along the dc field direction at the sample surface. The KNbSi_2O_7 phase is ferroelectric up to 1180°C . In the present study, since the electric field was applied at the temperature higher than the Curie temperature of lead titanate (490°C), no ferroelectric domains should exist in the cubic perovskite nuclei. Therefore, the development of crystal orientation can not be attributed to domain reorientation under electric field. It is suggested that some nuclei of cubic perovskite with more or less random a -axis orientation would form in the absence of electric field during the continuous heating stage (Fig. 6a). When the glass was heated at 570°C , the applied field would induce an electric dipole along the a -axis of these nuclei (ionic polarization). The newly formed nuclei at this temperature would also have the a -axis oriented dipole being parallel with the applied field (Fig. 6b). As shown in Fig. 6c, the a -axis oriented dipole of pre-existed nuclei might be able to align with the applied field without constraint due to the viscous nature of the glass matrix (dipole polarization). After the nucleation treatment at 570°C , the applied field was removed and thus the dipoles would relax (Fig. 6d). However, the a -axis preferred orientation was retained, even when the glass was further heated to 620°C to grow the nuclei.

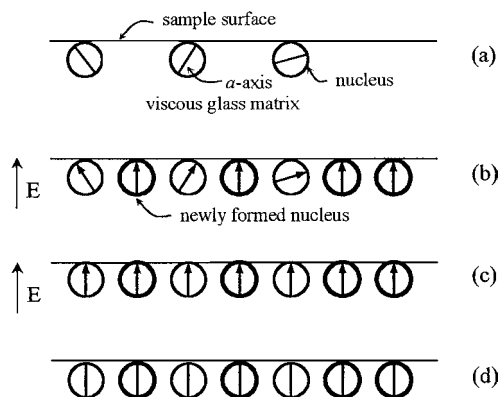


Figure 6 Schematic drawing to show the development of preferred orientation: (a) before, (b, c) during, and (d) after heating at 570°C.

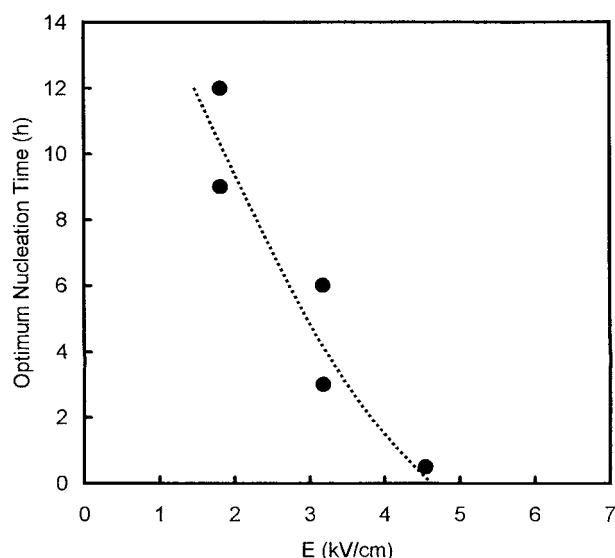


Figure 7 Dependence of optimum nucleation time on the electric field strength.

The more or less absence in preferred orientation in the interior region of the sample was possibly caused by the migration of modifier ions (e.g., Ti^{3+} [30] or Pb^{2+}) under the applied electric field, developing a concentration gradient and thus an internal field in the opposite direction. This reverse internal field partially offset the external field. Evidence supporting this point is given by the fact that the $R_S(E)/R_P(0)$ ratio for a fixed E did not increase with the increase in nucleating time (see Fig. 4a), but showed a maximum at an optimum nucleating time t_{max} . Fig. 7 shows that t_{max} decreased with the increase in E . It is suggested that when a higher field was applied the time required for setting up the internal field reduced, i.e., a decreased t_{max} . The above mentioned composition gradient would gradually disappear when the external field was removed during the samples being crystallized at 620°C for 1 h. We have examined the Pb- and Ti-distributions from both sides toward the center of the sample with the highest degree of orientation in this study. No composition gradients were found between the two sample surfaces. According to Pernice *et al.* [28], the depth of propagation of textured $KNbSi_2O_7$ crystals into glass may reach about 0.5 mm from the surface.

It is suggested that the degree of orientation can be further enhanced by using glasses which have the higher electrical resistivity at crystallizing temperature (usually alkali-free glasses) and the crystalline phase formed in the glass has ferroelectric domains. Thus, alkali-free glass-ceramics containing a ferroelectric phase with a Curie temperature higher than the crystallizing temperature is preferred.

5. Conclusions

The effect of applied electric field on the preferred orientation of lead titanate in the $PbO-TiO_2-Al_2O_3-SiO_2$ glass-ceramics was investigated. The following results have emerged:

(1) Glass-ceramics, nucleated at 570°C for 0.5–12 h and then crystallized at 620°C for 1 h, exhibited cubic $PbTiO_3$ as the single crystalline phase.

(2) Applying a dc electric field during nucleating treatment can enhance a -axis preferred orientation in a surface-layer region. However, the a -axis orientation was difficult to develop in the interior region of the sample, possibly due to the formation of a reverse internal field which partially offset the applied field.

(3) The degree of a -axis orientation on the as-heated surface showed a maximum at an optimum nucleating time t_{max} and the t_{max} -value decreased with the increase in the applied electric field strength. This result is also explained in terms of the formation of reverse internal field.

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