

A model for the structural hysteresis in poling and thermal depoling of PZT ceramics

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A structural hysteresis associated with domain orientation during poling and thermal depoling of lead titanate zirconate (PZT) ceramics has been observed. The poled materials appear to lose their piezoelectric properties at a temperature somewhat below the Curie temperature and yet the domain configurations remain unchanged. The above phenomenon is successfully explained by a model which predicts that upon thermal depolarization, poled ceramics undergo transformation from the poled state into the antiferroelectric state before returning back to their original unpoled state.

1. Introduction

Sintered lead zirconate titanate (PZT) ceramics do not show any piezoelectric activity because domains are oriented to have a zero net dipole moment. These domains can however be aligned by poling under a high d.c. electric field. Poling usually causes 180° and 90° domain switches in the ceramics [1]: the 180° domain switch is the change of a domain orientation from antiparallel to parallel to the direction of applied field, without causing any dimensional change in the unit cell; the 90° domain switch is the change of a domain orientation from perpendicular to parallel to the direction of applied field. The 90° domain switching usually occurs by the shortening of the axis of the unit cell which is perpendicular to the applied field and elongating the axis which is parallel to the applied field, resulting in an increase in population of (001) planes and a decrease in the population of (h00) [2]. The changes of intensity of (002) and (200) peaks or (001) and (100) peaks in 2θ X-ray diffraction (XRD) pattern are frequently used to assess the degree of poling of piezoelectric ceramics and piezoelectric ceramic/polymer composites. A full reversal of these peaks usually indicates a poling saturation of the ceramics [3–6].

Aligned domains in a poled ceramic return to their unpoled state after the material is heated to temperatures above the Curie temperature [7–8]. However, we have found that the poled piezoelectric ceramics often lose their piezoelectric properties at a temperature somewhat below the Curie temperature but the domain configurations remain unchanged despite this thermal treatment. A structural hysteresis is observed during the poling and depoling of the ceramics. Cook

and colleagues [9] reported that heating of poled materials below the Curie temperature resulted in an increase in the preferred domain orientation, but these preferred orientations did not improve piezoelectric properties. This unusual behaviour was explained by assuming that heating switches the domains back to the poled state, resulting in an increase in the preferred orientation of the ceramics [7, 9]. The mechanism by which domains could switch back to the preferred orientation during heating has not been explained.

In this present study, the relationship between domain orientation and piezoelectric properties resulting from various thermal treatments is investigated.

2. Experimental procedure

Lead titanate zirconate ($\text{Pb}(\text{Ti}_{0.48}\text{Zr}_{0.52})\text{O}_3$) ceramics were used with a composition close to the morphotropic phase boundary (MPB). The ceramics have a tetragonal single phase and the Curie temperature was determined through thermal expansion measurement and was found to be 350 °C. All poling was carried out at 125 °C for 15 min using an oil-bath poling technique. Air-dry silver paint was used as temporary electrodes, which could be removed by using ethyl acetate. Samples from the poled ceramic block were heat treated at different temperatures for one hour in a furnace and cooled to room temperature. For each annealing temperature, the piezoelectric constant d_{33} (pC/N) was measured by a piezometer system PM25. The corresponding distribution of preferred orientation was investigated by X-ray diffraction (XRD) using a Rigaku X-ray diffractometer.

3. Experimental results and discussion

The changes of intensities of (002) and (200) peaks during heating are shown in Fig. 1. As the annealing temperature increases, the intensity of (002) peak increases and that of (200) peak decreases. The reversal of (002) and (200) peaks occurs at about 500 °C. The domain configuration at 800 °C is similar to that of an unpoled ceramic. The changes of d_{33} and relative intensity of (002) peak ($I_{(002)}/I_{total}$) as a function of depoling temperature is shown in Fig. 2. d_{33} decreases as temperature increases and becomes zero at about 300 °C. However, the decrease of $I_{(002)}/I_{total}$ is very small at this temperature. When d_{33} is plotted versus $I_{(002)}/I_{total}$ as a function of poling and thermal depoling, a hysteresis becomes apparent as shown in Fig. 3. Even though the ceramics lose their piezoelectric properties completely at about 300 °C, the domain configuration at 300 °C is very similar to that of the fully poled ceramic, with only a small increase in the intensity of (200) peak, as can be seen in Fig. 1. Therefore the ceramic loses its piezoelectric properties well before the domains return back to their original unpoled configurations.

According to the conventional thermal depolarization theory, however, the loss of piezoelectric proper-

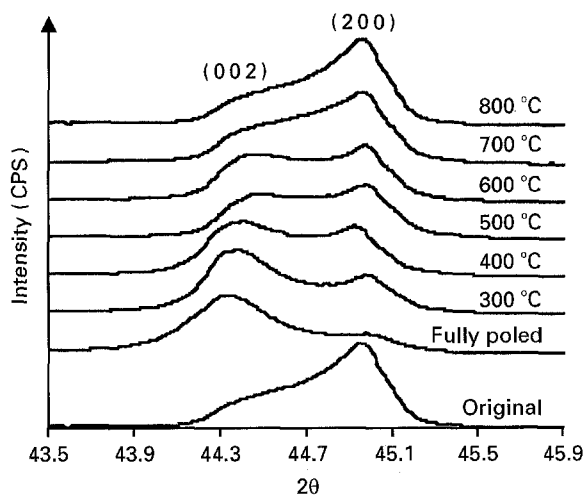


Figure 1 Changes of (002) and (200) peaks of a fully poled material with increasing depoling temperature.

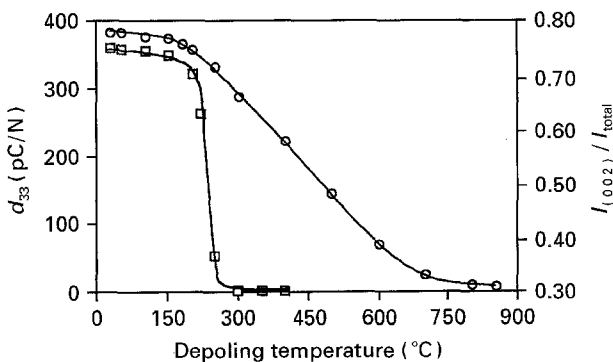


Figure 2 Variation of d_{33} (\square) and the relative intensity of (002) peak ($I_{(002)}/I_{total}$) (\circ) with depoling temperature.

ties with increasing temperature results from the aligned 180° and 90° domains returning to their original unpoled state [7, 8]. The above experimental results indicates a greater complexity of domain reorientation during heating since, although the piezoelectric ceramic loses its piezoelectric properties completely at about 300 °C, its domain configurations persist to higher temperatures. The details of the model proposed in this study follow in order to explain this phenomenon.

Poling of the ceramic causes an increase of d_{33} and $I_{(002)}/I_{total}$ as shown in Figure 3. The whole poling process can be divided into two stages: stage one corresponds to poling fields below 0.76 kV mm⁻¹ and stage two to fields above 0.76 kV mm⁻¹. In stage one, d_{33} increases quickly with a small increase of $I_{(002)}/I_{total}$ as poling voltage increases; the increases of d_{33} and $I_{(002)}/I_{total}$ are not proportional. As 180° domain switches results in an increase of d_{33} without affecting the $I_{(002)}/I_{total}$, we propose that stage one poling of lead titanate zirconate causes mainly 180° domain switches with a small degree of 90° domain switching, as well as the phase transformation from tetragonal to rhombohedral ($t \rightarrow r$). In stage two, the increase of d_{33} is almost proportional to the increase of $I_{(002)}/I_{total}$, indicating that this poling is mainly aligning the 90° domains.

A schematic diagram of the domain orientation during poling is shown in Fig. 4 from state (i) to (ii) in (a), (b) and (c). The solid line in Fig. 4 represents the original domain configuration and the dashed line the changed configuration. The 180° domain switch occurs by 180° flipping of the component antiparallel to

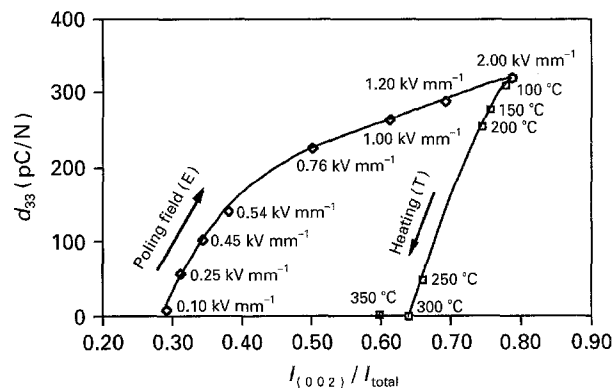


Figure 3 The change of d_{33} with $I_{(002)}/I_{total}$ during poling (\diamond) and thermal depoling (\square) of PZT ceramics.

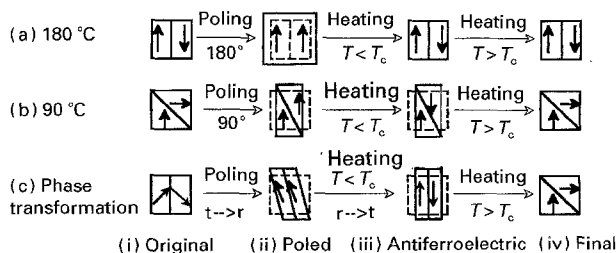


Figure 4 Schematic diagram for the proposed model.

the applied field as shown in Fig. 4 (a) (i) and (a) (ii). These 180° domain switches do not affect the X-ray diffraction pattern. The small expansion of the domain shown in Fig. 4 (a) is probably due to the sublattice interaction in the electrostrictive effect [10]. The 90° domain switching, however, causes a dimensional change of the unit cell, and the domain configurations are shown in Fig. 4 (b) (i) and (b) (ii). These changes result in an increase in population of (001) planes and a decrease in the population of (h00) in the XRD diffraction pattern. The phase transformation, as shown in Fig. 4 (c) (i) to (c) (ii), was explained by Kakegawa *et al.* [11] in terms of electrostatic free energy $-P_s E$, where P_s is the spontaneous polarization of a unit cell and E is the applied electric field. If the $\langle 100 \rangle$ axis of the tetragonal unit cell is parallel to the applied field, the vector of P_s is either antiparallel or parallel to the applied field (i.e. 180° domains). If the spontaneous polarization is parallel to E , then the free energy is a minimum. However, owing to the random distribution of the direction of crystallites, it is possible that any direction of a tetragonal phase unit cell is parallel to the applied field. Therefore phase transformation occurs if the energy required for phase transformation is less than energy required for the domain switching [11]. Indeed, it has been reported that the poling can cause single phase PZT to become two phase [12, 13]. Even grinding the surface of PZT has been reported to cause the phase transformation [14]. The rhombohedral phase is assumed to be easier to pole than tetragonal phase, as the 109–71° domain reorientation for a rhombohedral phase has a crystal distortion about one-third that of the 90° domain in the tetragonal phase [9, 15].

Therefore, we propose that in stage one poling, 180° domain switches dominate, possibly with a small degree of the 90° domain switching and phase transformation. The increase of $I_{(002)}/I_{\text{total}}$ during this stage is a combined result of the phase transformation and the 90° domain reorientation. In stage two, the piezoelectric response of the material comes from the 90° domain alignment solely. After poling, domains of the materials change from state (i) to state (ii) in (a), (b) and (c) in Fig. 4.

Upon heating, the poled material loses its piezoelectric properties at 300°C with a small decrease in $I_{(002)}/I_{\text{total}}$, as shown in Fig. 3. We propose that the domain reorientation during thermal depoling is similarly divided into two stages depending on the depoling temperature. The first stage is that below the Curie temperature during which phase transformation and the switching back of 180° domains occurs. Thus, as the depoling temperature approaches the Curie temperature, the ceramics progressively form an antiferroelectric state. The second stage occurs above the Curie temperature and is characterized by the switching back of 90° domains. Therefore heating during the first stage causes the poled materials to change from state (c) (ii) to state (a) (ii) in Fig. 4 through phase transformation. Some of the transformed domains form a pair of 180° antiparallel domains and the ceramics start losing part of their piezoelectric properties. When all the aligned domains are in the form of

pairs of 180° antiparallel domains, the ceramic will lose its piezoelectric properties completely, (as shown in Fig. 4 state (iii) in (a), (b) and (c)) i.e. the ceramic changes from a poled state into an antiferroelectric state, (from state (ii) to state (iii) in (a), (b) and (c) in Fig. 4). This distinguishes a thermally depoled ceramic from unpoled material (state (i)), even though both do not show any piezoelectric properties. When the temperature is further increased, the aligned domains undergo transformation from the antiferroelectric state into final state, i.e. domains return to their original unpoled configuration, as shown in Fig. 4 state (iii) and (iv) in (a), (b) and (c). Therefore upon heating, the poled ceramics undergo a phase transformation back to the tetragonal and then an antiferroelectric state before returning to their original unpoled state.

When the depoling temperature is below 300°C, the rhombohedral phase transforms back to tetragonal phase, i.e. from state (c) (ii) to state (a) (ii) or (b) (ii) in Fig. 4. Some of the domains form pairs of antiparallel domains (state (a) (ii) to state (a) (iii) in Fig. 4), resulting in the decrease of d_{33} shown in Fig. 3. As the temperature approaches 300°C, all the aligned domains form pairs of antiparallel domains (state (iii) in (a), (b) and (c) in Fig. 4), and the ceramic loses its piezoelectric properties completely. As the flip of 180° domains does not cause any dimensional change in the unit cell, the domain configuration remains similar to that of a poled ceramic, as shown in Fig. 1. Therefore the relative intensity of (002) peak of the ceramic remains high even though d_{33} drops to zero at 300°C, as shown in Fig. 3. While the phase transformation from rhombohedral to tetragonal will cause an increase of $I_{(002)}/I_{\text{total}}$, this ratio will decrease when the 90° domains switch back to their original state. Therefore the small decrease of $I_{(002)}/I_{\text{total}}$ observed indicates probably that some of the 90° domains do switch back but the amount of phase transformation is small. Any further increase of temperature will cause these antiparallel domains to go back to their original unpoled state, as shown in Fig. 4 from stage (iii) to stage (iv) in (a), (b) and (c). Once heated to 800°C, the ceramic has a very similar domain orientation to that of unpoled ceramic, as shown in Fig. 1.

In order to test this model, two specimens were cut from the same piece of poled ceramic and heat treated at 800 and 300°C respectively. These two specimens were then successively repoled to saturation. The changes in the domain orientation are indicated by the intensity of (002) and (200) peaks as shown in Figs 5 and 6. It is apparent that upon repoling the reversal of the (002) and (200) peaks occurs for the 800°C heat-treated sample whilst there is no peak reversal for the 300°C heat-treated sample. This difference indicates that the 800°C heat treatment of the poled material results in a random distribution of the aligned domains while the 300°C heat treatment brings the poled material into an antiferroelectric state. From Fig. 5, the repoling of 800°C heated ceramics causes an increase of intensity of the (002) peak as the electrical field increases. The reversal of the (002) and (200) peaks occurs when the poling field is about 0.56 kV mm⁻¹. According to the proposed

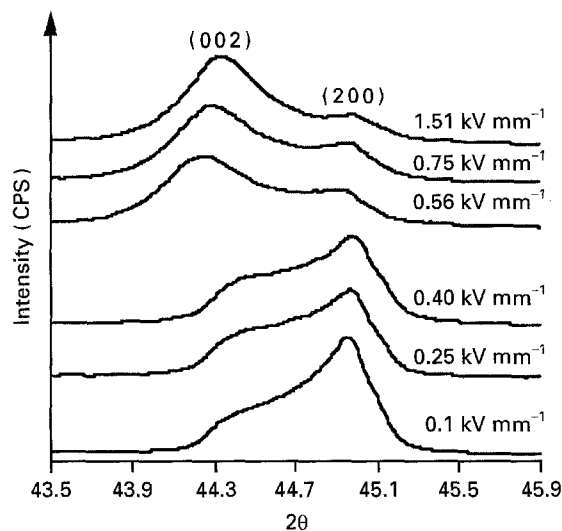


Figure 5 Changes of (002) and (200) peak intensities for the 800 °C heat-treated sample as the field strength increases.

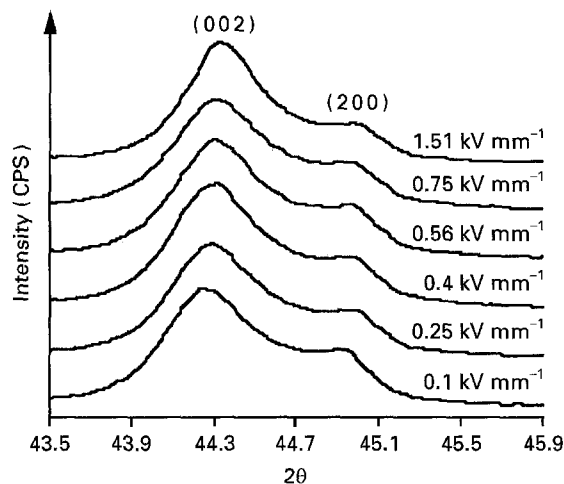


Figure 6 Changes of (002) and (200) peak intensities for the 300 °C heat-treated sample as the field strength increases.

model, this reversal is a result of phase transformation ($t \rightarrow r$) and 90° domain alignment (state (i) to state (ii) in (b) and (c) in Fig. 4). However, for the 300 °C heat-treated specimen, as shown in Fig. 6, the repoling of the 300 °C heated sample only aligns the 180° domains, i.e. from state (a) (i) to state (a) (ii) in Fig. 4. As a result, the 300 °C heat-treated specimen has a higher d_{33} value than the 800 °C heat-treated specimen at each poling voltage, as shown in Fig. 7. The 300 °C heat-treated specimen reaches its poling saturation at about 1.0 kV mm^{-1} while the saturation poling field for the 800 °C heat-treated specimen is about 1.5 kV mm^{-1} . These experimental results correlate well with the proposed model.

According to this proposed model, the change of the intensity of the (002) peak is a combined result of the phase transformation and preferred orientation. Therefore an increase in the intensity of the (002) peak in the X-ray diffraction pattern could originate from either effect. After heating poled materials to 250 °C and cooling down to room temperature, a small increase of relative intensity of (002) peak in

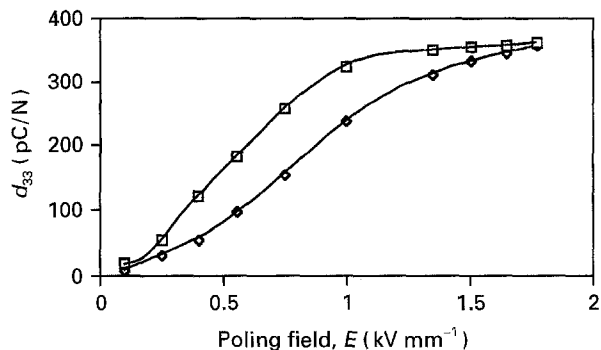


Figure 7 d_{33} varies with repoling field strength for 300 °C (\square) heat-treated and 800 °C (\diamond) heat-treated samples.

a subsequent heating had been observed by Cook *et al.* [9]. This increase was explained by Jaffe [7] and Cook *et al.* [9] by assuming that some of the re-oriented domains switch once more to their poled direction with increasing temperature. However, we believe that the increase of relative intensity of the (002) peak is more likely due to the phase transformation from rhombohedral to tetragonal during the heating, and so has no direct contribution to the piezoelectric properties of the ceramic [9].

4. Conclusions

The proposed model provides a consistent explanation for the structural hysteresis during poling and thermal depoling of lead titanate zirconate ceramics. In this model, the loss of piezoelectric properties upon heating below the Curie temperature is because the ceramic changes to a metastable antiferroelectric state from a poled ferroelectric state, while the increase of preferred orientation of the ceramic upon heating is due to the phase transformation from rhombohedral to tetragonal ($r \rightarrow t$).

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