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90° domain reversal in Pb(Zr_xTi_{1-x})O_3 ceramics

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A simple and direct method has been proposed, which may be used for quantitatively distinguishing the mechanisms of domain reorientation processes in polycrystalline materials. Using this method, the 90° domain reorientation in the Pb(Zr_xTi_{1-x})O_3 ceramic under an electric field was examined through the X-ray diffraction analysis. It was found that polarization switching in the PZT ceramic with a composition near the morphotropic phase boundary, is predominantly controlled by the two successive 90° domain processes rather than only the 180° domain reversal process. Experimental results also indicate that the coercive field of ferroelectric ceramics is related to the cooperative deformation associated with each grain. This cooperative deformation arises from the 90° domain-reversal process.

1. Introduction

The interrelationship between the dynamic behaviour and the microstructures (intrinsic domain structures) of ferroelectric ceramics is of great significance. The investigation of polarization reversal in ferroelectric ceramics is of both theoretical and practical interest. Recently, much effort has been directed into developing polycrystalline ferroelectric thin films as non-volatile memory devices using the capability of switching the direction of remnant polarization under the influence of an electric impulse. In fact, the polarization reorientation processes are intimately associated with the basic dynamic memory capability and the switching threshold of polycrystalline thin-film memory devices, as well as the basic fatigue and degradation behaviour of thin-film devices. With regard to this, the mechanisms of the domain reversals in PZT polycrystalline systems have a special and important aspect.

Early investigations of the dynamic behaviour of 90°-type domain walls (90° in tetragonal, 71° and 109° in the rhombohedral phase) and 180° domain walls in PZT ceramics have been carried out over the last three decades [1–7]. Based on the bias-dependence measurements of dielectric constants, polarization, and spontaneous strain in certain PLZT ceramic systems, it has been suggested that the processes of polarization reversal may be characterized by two successive 90°-type domain processes rather than by the direct 180° domain switching processes. Apparently, all previous research results seemed to be adequate; however, they are by no means quantitatively conclusive, because no direct experimental methods could distinguish the mechanisms of the polarization reversal processes in the polycrystalline materials. In general, the mechanism of polarization reversal processes in single crystals is explained by the nucleation and growth of new antiparallel domains. Ferroelectric ceramics consist of many randomly orientated grains. Therefore, the polarization reversal mechanism and switching behaviour in ferroelectric polycrystalline material is rather complicated and depends upon many conditions [8]. Usually, the polarization reversal processes in ferroelectric polycrystalline materials are substantially different from those in single crystals. In this work, a simple and direct method has been proposed, which can be used for quantitatively distinguishing the mechanisms of domain reorientation processes in polycrystalline materials. It has been directly confirmed that the polarization switching processes in PZT ceramic with the composition within the morphotropic phase boundary is predominantly dependent upon two successive 90° domain reversal processes.

2. Experimental procedure

The specimens used here are of chemical composition Pb($Zr_{0.52}$ $Ti_{0.48}$)O_3 + 0.5 wt% Nb_2O_5, which is within the morphotropic phase boundary. The ceramics were prepared by the conventional mixed-oxide process. The final sintering temperature is 1180–1250 °C for 2–3 h. The scanning electron micrographs (Fig. 1) show the average grain size of the ceramic to be 3–3.5 μm. The domain structures can be clearly observed through the environmental scanning electron microscope without coating the samples [8]. Samples were cut in the dimensions 8 mm × 8 mm × 0.5–0.8 mm, and electroded with gold

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for the dielectric and strain measurements. For the X-ray analysis measurements, the thin vacuum-deposited silver electrodes were used on the faces exposed to the X-rays in order to reduce the extra diffraction of the electrodes. Before making silver electrodes, the surfaces of the samples were polished and etched. X-ray diffraction measurements were performed on an automatic X-ray diffractometer using CuK_α radiation ($\lambda = 1.5418$ nm). The experimental data were processed with the software developed by the Materials Research Laboratory at Pennsylvania State. The X-ray patterns were recorded at a scan rate of $2\theta = 0.3° \text{ min}^{-1}$. The low scanning rate was chosen in order to enhance the intensity of the diffraction. The ceramic specimens were initially poled in two different ways in accordance with the sample shape, as shown in Fig. 2. The depth of X-ray penetration in this PZT system is estimated to be 1–2 µm.

3. Results and discussions

3.1. Principle of X-ray analysis

It is well known that PZT ceramics contain many 90° and 180° domains. The electric field will force them to move towards the direction favourable to the total system energy. According to Friedel's law, the reversal of 180° domains during the polarization process could not be detected by the X-ray diffraction method. Therefore, it is believed that the change of ratio $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ is caused by the switching of the 90° domain alone [9, 10]. In general, the intensity of any (h, k, l) reflection, relative to that from a random specimen, is proportional to the volume fraction of domains having their $(h\,k\,l)$ planes parallel to the plate surface. Regarding this study, the intensity of the $I_{(0\,0\,2)}$ reflection is proportional to the volume fraction of the domain having the polarization direction parallel to the normal of the surface of plate specimens. Based on the general principle of X-ray diffraction, the diffractive intensity, $I(h\,k\,l)$, for the $(h\,k\,l)$ plane can be usually expressed by [10]

$$I_{(h\,k\,l)} = CAI_0L|F_{(h\,k\,l)}|^2 N_{(h\,k\,l)}\,\rho_{(h\,k\,l)} \qquad (1a)$$

where I_0 is the incident X-ray diffraction, L the Lorentz angle factor, $F_{(h\,k\,l)}$ a structure factor for the $(h\,k\,l)$ plane, $N_{(h\,k\,l)}$, the multiplicity factor, A the absorption factor, and C is known as measuring system constant. Once the measuring conditions and specimens are defined, C can be calculated. $\rho_{(h\,k\,l)}$ is the crystal plane orientation density which is defined as the volume fraction of the crystal grains with $(h\,k\,l)$ plane parallel to specimen surface.

Obviously, for a specimen with the preferred orientation of the (h, k, l) plane, its $\rho_{(h\,k\,l)}$ should be constant and can be taken as 1, therefore, one has

$$I_{\mathrm{p}(h\,k\,l)} = CAI_0L|F_{(h\,k\,l)}|^2 N_{(h\,k\,l)} \qquad (1b)$$

From the definition of diffraction intensity, it easily follows that the diffraction intensity for the $(h\,k\,l)$ planes should be proportional to the volume fraction of domains (both 90° and 180° domains) in which the $(h\,k\,l)$ planes are parallel to the surface of the plate specimens. Because there may be two possible kinds of domain reversal processes during the polarization switching, the measured $I_{(0\,0\,2)}$ and $I_{(2\,0\,0)}$ should contain the contributions of the planes (0 0 2) and (2 0 0) within both 90° reversal domains and 180° reversal domains, respectively, that is

$$I_{(0\,0\,2)} = n_1[90°]\,I_{\mathrm{p}(0\,0\,2)} + n_2[180°]\,I_{\mathrm{p}(0\,0\,2)} \qquad (2)$$

$$I_{(2\,0\,0)} = g_1[90°]\,I_{\mathrm{p}(2\,0\,0)} + g_2[180°]\,I_{\mathrm{p}(2\,0\,0)} \qquad (3)$$

and

$$n_1 + n_2 + g_1 + g_2 = 1$$

Here, n_1 and n_2 are the 90° and 180° domain volume fractions, respectively, which have the (0 0 2) plane parallel to the surface of the plate specimens. g_1 and g_2 are the 90° and 180° domain volume fractions, respectively, which have the (2 0 0) plane parallel to the surface of the plate specimens. It should be noted that n_1 and g_1 are functions of the applied electric field, whereas n_2 and g_2 are always constants during domain reversal processes because the reversal of 180° domains could not be detected by the X-ray diffraction method. The domain volume ratio between the domains with the polarization direction perpendicular

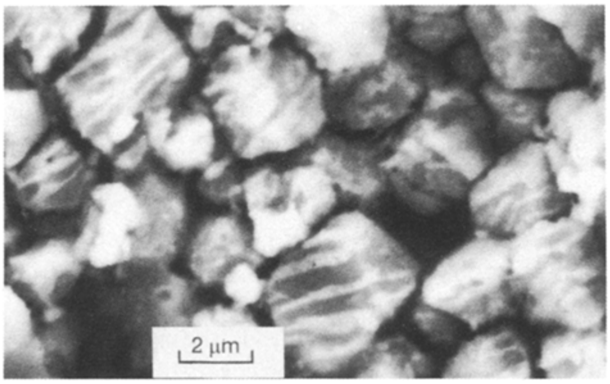

Figure 1 Scanning electron micrograph of PZT ceramic with composition near the morphotropic phase boundary.

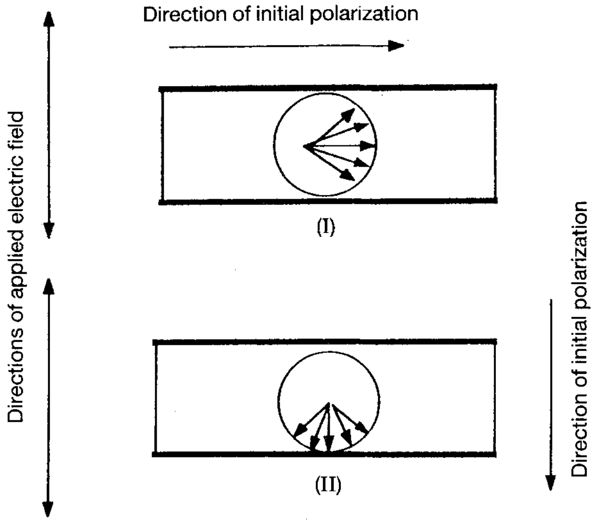

Figure 2 Shape and initial polarization orientation of specimens for two different cases: (a) the initial direction of remnant polarization parallel to the surface of the plate sample; (b) the initial direction of remnant polarization perpendicular to the surface of the plate sample.

to the surface and those having the direction of their polarizations parallel to the surface of the plate specimen could be expressed as

$$R' = K\frac{I_{(0\,0\,2)}}{I_{(2\,0\,0)}} \tag{4}$$

where, K is a special coefficient. Because the change in diffraction intensities is only caused by 90° domains, the X-ray intensities of $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ under the influence of the electric field could represent the characteristics of 90° domain reversal. The changing rate of $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ may reveal some information about the mechanism of the domain reorientations. In the following, we shall discuss two different cases of polarization reorientation to distinguish the polarization reorientation processes between 90° domain reversal and 180° domain reversal processes. It should be noted that, in reality, the domains can never be perfectly aligned. The distribution of polarization directions always obey the certain axial distribution, as shown in Fig. 3. The $I_{(0\,0\,2)}$ and $I_{(2\,0\,0)}$ are measured by their average values.

3.1.1. Case 1

For case I of Fig. 2, the initial directions of polarization in most domains are parallel to the surface of the plate specimen. If an electric field is applied to the direction normal to the surface of the plate specimen, the polarization reversal process will be expected to be following the model in Fig. 3. As the applied electric field increases, the direction of polarization will gradually be changed. With a sufficiently strong electric field, the polarization directions in the ceramic will change their distribution direction. Eventually, all polarization directions will be lined up nearly parallel to the plus direction shown at point C via the 90° domain wall reversal process. The intriguing feature is that in this process only 90° domain reorientation is involved and no 180° domain wall reversal process occurs because the initial direction of polarization is perpendicular to the applied electric field. From equations 3 and 4, one obtains

$$\begin{aligned} R|_{\text{O-C}} &= K\frac{I_{(0\,0\,2)}}{I_{(2\,0\,0)}} \\ &= K\frac{n_1[90^\circ]\,I_{\text{p}(0\,0\,2)}}{g_1[90^\circ]\,I_{\text{p}(2\,0\,0)}} \end{aligned} \tag{5}$$

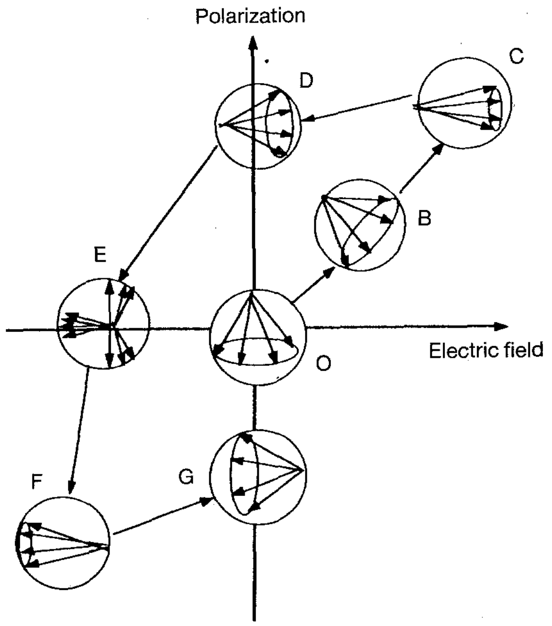

Figure 3 Two-dimensional representation of the vector model showing the spatial distribution of domains at different stages of the polarization reversal.

where $n_1 + g_2 = 1$, and $n_2 = g_2 = 0$. Equation 5 means that the diffraction intensity ratio $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ is equal to the diffraction intensity ratio $\{n_1[90^\circ]\, I_{\text{p}(0\,0\,2)}/g_1[90^\circ]\, I_{\text{p}(2\,0\,0)}\}$ within the unit volume of 90° domain. In this case, the number of 90° domains per unit volume is equal to the number of domains per unit volume because only 90° domain reorientation is involved in this process. It should be noted that, in general, the number of 90° domains per unit volume is not necessarily equal to the number of domains per unit volume, when considering the coexistence of both 90° and 180° domains. We will explain this later. From Equation 5, the rate of changing R as a function of electric field can be expressed as

$$\left.\frac{\mathrm{d}R}{\mathrm{d}E}\right|_{\text{O-C}} = \frac{\mathrm{d}(Kn_1[90^\circ]\,I_{\text{p}(0\,0\,2)}/g_1[90^\circ]\,I_{\text{p}(2\,0\,0)})}{\mathrm{d}E} \tag{6}$$

where R is the measured value of the ratio $I_{(0\,0\,2)}/I_{(2\,0\,0)}$. $\mathrm{d}R/\mathrm{d}E$, the rate of change of $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ from point O to point C reflects only the feature of 90° domain wall reorientation.

3.1.2. Case 2

When the intensity of the electric field is decreased from the point C to point D, the domain polarization turns back to the nearest easy direction in favour of lowering the internal energy. If the applied electric field is increased further in the negative direction from point D to point F, the domain polarizations pointing in the positive direction are reversed. This process may involve both the 90° and 180° domain switching processes. Therefore, from Equations 2 and 3, we have

$$\begin{aligned} R|_{\text{D-F}} &= K\frac{I_{(0\,0\,2)}}{I_{(2\,0\,0)}} \\ &= K\frac{n_1[90^\circ]\,I_{\text{p}(0\,0\,2)} + n_2[180^\circ]\,I_{\text{p}(2\,0\,0)}}{g_1[90^\circ]I_{\text{p}(2\,0\,0)}} \end{aligned} \tag{7}$$

where $n_1 + n_2 + g_1 = 1$, and $g_2 = 0$. It should be noted that no 180° domain reversal occurs in the direction perpendicular to the applied field. Therefore, Equation 7 can be expressed as

$$\begin{aligned} R|_{\text{D-F}} &= K\frac{I_{(0\,0\,2)}}{I_{(2\,0\,0)}} \\ &= K\frac{n_1[90^\circ]\,I_{\text{p}(0\,0\,2)} + n_2[180^\circ]\,I_{\text{p}(0\,0\,2)}}{g_1[90^\circ]I_{(2\,0\,0)}} \\ &= (n_1 + g_1)[90^\circ]K\alpha \end{aligned} \tag{8}$$

where

$$\alpha = \frac{\{n_1[90^\circ]\,I_{\text{p}(0\,0\,2)} + n_2[180^\circ]\,I_{\text{p}(0\,0\,2)}\}}{g_1[90^\circ]I_{\text{p}(2\,0\,0)}(n_1 + g_1)}$$

and $(n_1 + g_1) = (1 - n_2)$, which is the volume fraction of total 90° domains in the material. α is the ratio of diffractive intensity per unit volume of 90° domain, which reflects the feature of 90° domain reversal. α is also a function of electric field and dependent upon the entire domain polarization reversal process. Precisely speaking, because only the $(n_1 + g_1)$ portion of 90° domains contribute to the diffraction intensity of R [or $I_{(0\,0\,2)}/I_{(2\,0\,0)}$] in Equation 8, thus, the contribution of 90° domains to R in the process from point D to point F should not be exactly the same as that of the intensity R in the process from point O to point C. In order to compare the features of these two domain reversal processes, we can define the changing rate of diffraction intensity as the same within the unit volume of 90° domains with respect to these two domain switching processes. Therefore, from Equation 8, one should have

$$\left.\frac{\mathrm{d}R}{\mathrm{d}E}\right|_{\mathrm{D-F}} = (n_1 + g_1)[90°]\,K\,\frac{\mathrm{d}\alpha}{\mathrm{d}E} = (n_1 + g_1)[90°]\left.\frac{\mathrm{d}R}{\mathrm{d}E}\right|_{\mathrm{O-C}} \qquad (9)$$

Naturally, unlike Equation 6, Equation 9 describes a pure 90° domain wall reorientation process. From Equation 9, it can be found that the changing rate of R as a function of the electric field will also be affected by $(n_1 + g_1)$. Obviously, if $(n_1 + g_1)$ is equal to 1, the polarization reversal process will be a pure type of 90° domain reversal process. Thus, Equation 9 should become exactly the same as Equation 6. In contrast, if $(n_1 + g_1)$ is equal to zero, this means that no 90° domain reversal will occur, and no X-ray information can be obtained. Equation 9 is an approximate expression which is precisely valid only if large amounts of 90° domains are involved in the polarization switching processes. Detailed discussions can be found elsewhere [8]. Compared to Equations 9 and 6, it could be asserted that if 90° domain wall reorientation is the main process in the polarization reversal from point D to point F, the changing rate of the measured ratio $\mathrm{d}R/\mathrm{d}E$ would be slightly less than those from point O to point C according to Equation (9). In other words, the feature of domain reversal process from point D to point F is most likely a pure type of 90° domain reorientation process. Conversely, if 180° domains are predominantly involving the polarization reversal process from point D to point F, the measured changing rate, $\mathrm{d}R/\mathrm{d}E$, would be much smaller than that from point O to point C because $(n_1 + g_1)$ is small in this case. Here, we assume the internal energy states at points O and D to be the same. This assumption means that the polarization distributions of ceramics are the same at both points O and D, which is almost fulfilled in reality. In short, Equation 9 could be used as the criterion for qualitatively evaluating the characteristics of the dynamic behaviour of domain reorientation processes in ceramics in terms of X-ray analysis techniques.

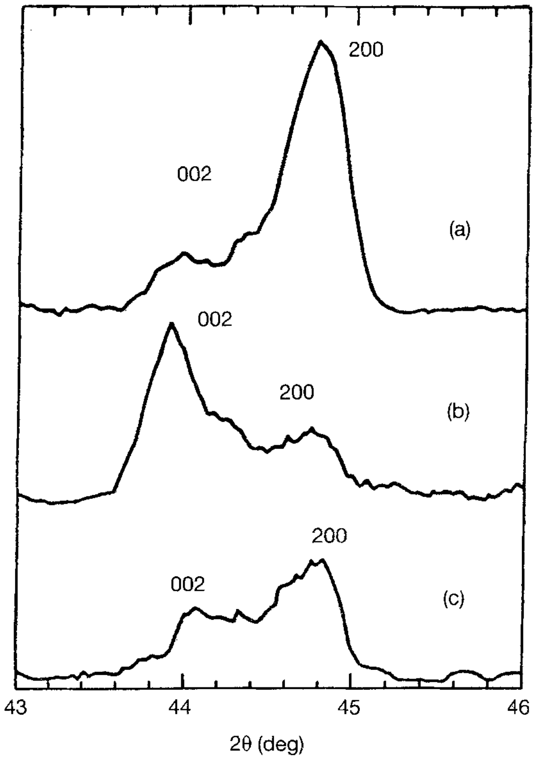

Figure 4 The XRD profiles of (0 0 2) and (2 0 0) peaks for plate PZT samples of different orientation of polarization. (a) X-ray intensity profile of a poled ceramic plate sample with its normal direction perpendicular to the poling direction. (b) X-ray intensity profile of a poled ceramic plate sample with its normal direction parallel to the poling direction. (c) X-ray intensity profile of an unpoled ceramic sample.

3.2. Results and conclusions

In practice, in order to sort out the mechanisms of domain reorientation in the ceramic specimens, we have to examine both the dependence of $I_{(h\,k\,l)}$ as a function of applied electric fields and the changing rate of $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ as a function of the applied electric field (or $\mathrm{d}\{I_{(0\,0\,2)}/I_{(2\,0\,0)}\}/\mathrm{d}E$) in some details. Fig. 4 shows the XRD profiles of (0 0 2) and (2 0 0) peaks for plate PZT samples in the case of different polarization orientations.It can be seen from Fig. 4a that when the normal direction of the plate is perpendicular to the polarization direction, the (2 0 0) peak is much higher than the (0 0 2) peak of the sample. Conversely, for samples with the normal direction of the plate parallel to the poling direction, as shown in Fig. 4b, the (0 0 2) peak is much higher than (2 0 0) peak. Fig. 4c is the case of an unpoled sample. Because no preferred orientation exists, the intensity of the (2 0 0) peak is about twice that of the (0 0 2) peak. Fig. 5 presents the ratio $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ as a function of the applied electric field in case II of Fig. 2. In Fig. 5, the magnitude of the applied electric field at points D and D′ are almost exactly equal to the coercive fields of the P–E (polarization–electric field) hysteresis loop and S–E (strain–electric field) hysteresis loop measured at ultra-low frequency. Because the ratio $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ represents the characteristics of 90° domain reversal, it indicates that the coercive field of polarization switching is closely related to the 90° domain reversal in this ceramic sample. Fig. 6 presents the ratio of $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ as a function of the applied electric field from point O to point D′ for Case I of Fig. 2. As

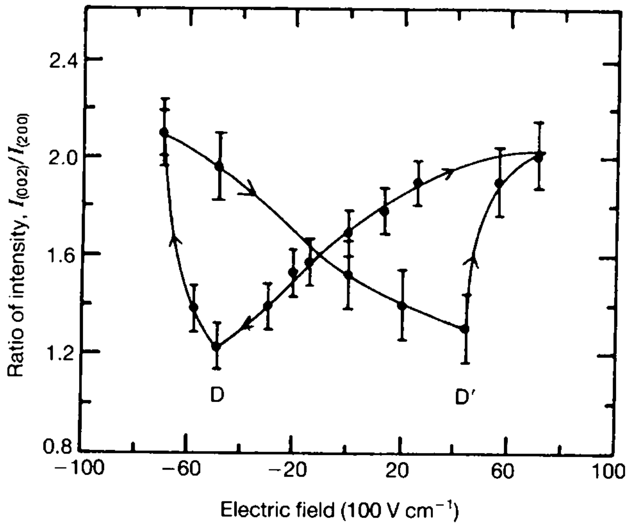

Figure 5 The ratio of $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ as a function of the applied electric field for Case II of Fig. 2.

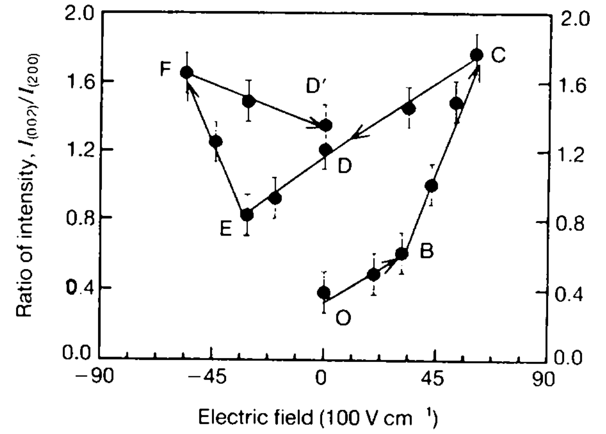

Figure 6 The ratio of $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ as a function of the applied electric field for Case I of Fig. 2.

TABLE I Changing rate of $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ with applied electric field for the cases in Fig. 6

Lines	Slopes
O–B	$(0.95 \pm 0.2) \times 10^{-2}$ (100 V cm^{-1})$^{-1}$
B–C	$(4.2 \pm 0.3) \times 10^{-2}$ (100 V cm^{-1})$^{-1}$
D–E	$(1.1 \pm 0.2) \times 10^{-2}$ (100 V cm^{-1})$^{-1}$
E–F	$(3.2 \pm 0.3) \times 10^{-2}$ (100 V cm^{-1})$^{-1}$

discussed above, from point O to point C, the domain reorientation is a pure 90° domain type. If polarization reorientations involving both the 180° and 90° domain reversal processes from point D to point F, then the slopes of $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ as a function of electric fields from point D to point F should be substantially smaller than those from point O to point C. The slopes of dR/dE in Fig. 6 are listed in Table I, from which it can be clearly found that there is no substantial difference in the absolute values of the slopes between the O B line and the D–E line or between the B–C line and the E–F line. This argument strongly suggests that the entire polarization reorientation process from point O to point F is predominantly controlled by the 90° domain reversal process. In other words, Equation 9 could be approximately satisfied by the experimental data. The estimated value $(n_1 + g_1)$ is around 0.7–0.8 from comparing the slopes between the line B–C and the line E–F in Table I. This result indicates that in PZT ceramics, 80% domains within total reversal domains are 90° domains. Therefore, it can be concluded that the 90° domain reorientation plays a major role in terms of the polarization switching in the PZT bulk ceramic with the composition within the morphotropic phase boundary.

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