Reinvestigation on polarization and strain response of electrically poled lead titanate zirconate ceramics under low-to-medium electric field loading

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Abstract

The polarization and strain response of electrically poled lead zirconate titanate ceramics was reinvestigated under low-to-medium electric field loading. A phenomenon that is usually ignored was pointed out and discussed. That is, under low-to-medium cyclic electric field loading, remnant strains measured under a negative electric field loading are larger than those measured under a positive electric field loading. Here, ‘positive’ and ‘negative’ mean that the applied electric field is aligned or antiparallel to the pre-poling direction of the material, respectively. Moreover, a reverse trend was observed for remnant polarizations. Texture-dependent domain switching, defect dipole reorientation, and interactions between them were used to rationalize this phenomenon. In addition, the equation \( a = \pm \frac{1}{2} E^2 \) which is used to describe the strain response, was modified by taking the asymmetry of the electric field versus strain curve into consideration. The modified equation can better describe the strain response than the original equation.

1. Introduction

In ferroelectrics, the direction of spontaneous strains changes along with the reorientation of the polarization direction, particularly a non-180° domain switching [1]. Normally, under electric field loading, polarization changes nearly proportionally with strain. In fact, such a proportionality has been explored to minimize the effect of strain hysteresis in piezoelectric actuators on controlling the input charges [2, 3]. However, in this study, when we tested the polarization and strain response of pre-poled soft lead zirconate titanate (PZT) ceramics, the remnant polarizations and remnant strains under positive and negative electric field loading revealed a very interesting phenomenon: the measured remnant polarizations under the positive electric field were larger than those measured under the negative electric field, and a reverse trend was observed for the remnant strains. These findings are in contradiction to previous understanding, which implies that, except domain switching, other physical processes happen in the material, and these processes play an important role in the polarization and strain response. In this paper, we pointed out these phenomena and propose a possible mechanism to explain it. Furthermore, as the measured remnant strains were different under positive and negative loading, we modified the equation \( S = (d_{\text{init}} + \alpha E_0) \alpha E \pm \frac{1}{2} (E_0^2 - E^2) \) by taking the asymmetry of the electric field versus strain curves into consideration. The results show that the modified equation can better describe the strain response than the original equation.

2. Materials and experimental procedure

The test was performed on electrically poled PZT ceramics, with a composition of \( \text{Pb}_{1.0}[Zr_{0.5}\text{Ti}_{0.49}\text{Fe}_{0.25}\text{La}_{0.25}\text{Sb}_{0.5}]_{0.05}\text{O}_3 \). Its crystal structure is at the morphotropic phase boundary, where the
tetragonal and rhombohedral phases coexist [1]. The specimen was first electrically poled at 120 °C and then aged for 24 h. After aging, the evolution of the polarizations and longitudinal strains was measured under low-to-medium cyclic electric field at 20 °C with a loading frequency of 1 Hz. The polarizations were measured by the typical Sawyer–Tower circuit. Then, the longitudinal strains were monitored using strain gages.

3. Results and discussion

Figures 1(a) and 1(b) display the measured electric field versus polarization (E–P) curves and electric field versus strain (E–S) curves, respectively. As reported by previous studies [4–9], the polarizations and strains show a nonlinear response with respect to the applied electric field, even under very low electric fields, e.g., 0.2 kV/mm. With the increase in the electric field, the nonlinearity of the E–P and E–S curves becomes increasingly significant. Simultaneously, the areas of the E–P and E–S curves become larger. According to previous investigations [4–9], these phenomena demonstrate that more irreversible domain switching happens at high electric fields.

Figure 1(a) also shows that the measured $P_{\text{max}}^-$ is normally larger than $P_{\text{max}}^+$. Here, $P_{\text{max}}^-$ and $P_{\text{max}}^+$ represent the maximum polarizations measured under a negative electric field loading and positive electric field loading, respectively. Their definitions are given in Fig. 1(a). Similarly, the measured $S_{\text{max}}^-$ is larger than $S_{\text{max}}^+$. Here, $S_{\text{max}}^-$ and $S_{\text{max}}^+$ represent the maximum strains measured under a negative electric field loading and positive electric field loading, respectively. Furthermore, Fig. 1 shows that with the increase in the electric field, the E–P and E–S curves change from symmetric to asymmetric.

Figure 2 presents the evolution of $P_{\text{max}}^-$, $P_{\text{max}}^+$, $S_{\text{max}}^-$, and $S_{\text{max}}^+$ as functions of the applied electric field. We can see that they all increase nonlinearly with the increase in the electric field. Simultaneously, $P_{\text{max}}^- - P_{\text{max}}^+$...
difference between the maximum polarizations measured under the positive and negative electric fields, increases with the increase in the electric field. A similar evolution trend was also observed for $S_{\text{max}}^- - S_{\text{max}}^+$. These phenomena can be rationalized by the domain-switching ability difference during positive and negative electric field loading. After electric field poling, most of the domains have been aligned into the direction in parallel to the applied electric field [10, 11]. Thus, under subsequent positive electric field loading, only a small volume of domains can be reoriented. However, under a negative electric field loading, more domains can be reoriented by a non-180° or 180° domain switching. Therefore, the measured $P_{\text{max}}^-$ and $S_{\text{max}}^-$ are normally larger than $P_{\text{max}}^+$ and $S_{\text{max}}^+$, respectively. When the applied electric field is small, only a few domains can be reoriented. As a result, the $E$–$P$ and $E$–$S$ curves initially show a symmetry behavior. At a high electric field, more domains can be reoriented under negative electric field loading. Consequently, the shape of the $E$–$P$ and $E$–$S$ curves change from symmetric to asymmetric. Meanwhile, $P_{\text{max}}^- - P_{\text{max}}^+$ and $S_{\text{max}}^- - S_{\text{max}}^+$ increase with the increase in the electric field.

When the applied electric fields decrease to zero, the measured polarizations and strains are called remnant polarization and remnant strain, respectively. As more domains can be reoriented during a negative electric field loading, the measured remnant polarizations and remnant strains under a negative electric field should be larger than those measured under a positive electric field. As expected, the measured $S_{\text{r}}^-$ is larger than $S_{\text{r}}^+$. However, the measured $P_{\text{r}}^-$ is smaller than $P_{\text{r}}^+$. That is, the measured remnant polarization during negative and positive loading show a contrary behavior with the evolution of the measured remnant strains, which is consistent with our expectation. Here, it should be noted that in the experiments, the applied electric fields were smaller than $E_c$. If the applied field is large enough, e.g., $\gg E_c$, then the electric field could drive several domains to reorient their directions; consequently, a larger $P_{\text{r}}^-$ should be observed during a negative electric field loading than $P_{\text{r}}^+$ measured during a positive electric field loading.

Figure 2. (a) Evolution of $P_{\text{max}}^+, P_{\text{max}}^-, P_{\text{r}}^+$, and $P_{\text{r}}^-$ as functions of the applied electric field. (b) Evolution of $S_{\text{max}}^-, S_{\text{max}}^+, S_{\text{r}}^-$, and $S_{\text{r}}^+$ as functions of the applied electric field. The definitions of $P_{\text{max}}^+, P_{\text{max}}^-, P_{\text{r}}^+, P_{\text{r}}^-$, $S_{\text{max}}^+, S_{\text{max}}^-, S_{\text{r}}^+$, and $S_{\text{r}}^-$ are given in Fig. 1.
In fact, the phenomenon that \( P_r^- \) is smaller than \( P_p^+ \) has been reported by others, although not pointed out specifically. For instance, Jones et al reported the E–P curves of pre-poled PZT films under a cyclic electric field loading [12]. Their results show that \( P_r^- \) is smaller than \( P_p^+ \).

A 180° domain switching does not influence the strain response, and one possible explanation for the contradicting result mentioned above is that a domain switching of more than 180° happened under a positive electric field. However, this explanation cannot be always true because the material was pre-poled. During a negative electric field loading, a domain switching of more than 180° can happen, which will also induce a larger \( P_r^- \) than \( P_p^+ \).

This finding indicates that, except domain switching, other physical processes also happen under electric field loading, which induce the response difference for the remnant polarization and remnant strain. We believe that the most likely physical mechanism is defect reorientation. In the case of Fe-doped PZT ceramics, \( \text{Fe}^{3+} \), compensating either an A or B site of higher valency in the perovskite structure, is compensated by oxygen vacancies, which was found to result in defect dipoles, such as \( (\text{Fe}^{3+} - V_O) \). Similar with domain switching, the direction of the defect dipoles can also be reoriented by an electric field [13] or mechanical stresses [14]. Normally, the domains and defect dipoles are randomly distributed in the materials. Figure 4(a) illustrates the state of the domain structure and defect dipoles in an unpoled PZT ceramics. During an electric field loading, most of the domains and defect dipoles can be driven into the direction parallel to the electric field. Thus, after electric poling, a net electric field will form in the PZT ceramics. The direct proof is the existence of an internal bias electric field [13, 14]. That is, for electrically poled PZT ceramics, the coercive electric field measured under a negative electric field loading is larger than that measured under a positive electric field loading. Figure 3 shows the hysteresis loop of the material used in this study. The coercive electric field measured under a positive electric field loading is 0.88 kV mm \(^{-1}\), whereas that measured under a negative electric field loading is 0.93 kV mm \(^{-1}\), demonstrating the existence of polar defects in the test materials.

Figure 4(b) illustrates the possible state of domains and defect dipoles in an electrically poled and aged PZT specimen. In ceramics, the specimen cannot be poled into a single domain state due to the grain interaction. As a result, some domains with polarization direction perpendicular to the poling direction exist. In addition, for polar defects, some polar defects with direction antiparallel or perpendicular to the poling directions also exist to reduce the depolarization electric field. If we applied positive electric field on the specimen, then some domains reorient their direction to the applied electric field. Simultaneously, the defects with polar direction antiparallel to the applied electric field can also reorient into the direction along the electric field. Compared with domain switching, the reorientation of defect dipoles only induces the polarization change and will not influence the macro strain. During an electric field unloading, some domains switch back. However, the defects reoriented during loading may remain their state. This is because the energy state of polar defects reduces if their orientation is in parallel with the polarization directions of the surrounding domains. Thus, the measured remnant strain is caused only by domain switching, whereas for the remnant polarization, it is caused by two physical processes: domain switching and defect dipole reorientation.

Under a negative electric field loading, more domain switching happens (Figs. 4(d) to 4(e)). After electric field unloading, only partial domains switch back (Figs. 4(e) to 4(f)). As a result, the measured \( S_r^- \) is larger than \( S_p^+ \). Conversely, for the defect dipoles, only a few defect dipoles may change their direction during a negative
electric field loading because of the constraint coming from their surrounding domains. Even if some defect dipoles can be reoriented by the applied electric field, they will also switch back. Thus, although more domain switching happens during a negative electric field loading, the remnant polarization measured under a negative electric field loading is still smaller than that measured during a positive electric field loading due to the asymmetry of the defect reorientation ability under positive and negative electric field loading.

Furthermore, as the measured remnant polarizations and remnant strains are asymmetric under positive and negative electric field loading, the equations

\[ P = (\varepsilon_{\text{init}} + \beta E_0)_a \pm \frac{1}{2}(E_0^2 - E^2) \]  

and

\[ S = (d_{\text{init}} + \alpha E_0)_a E \pm \frac{1}{2}(E_0^2 - E^2) \]  

which are used to describe the polarization and strain response, should take this kind of asymmetry into consideration. That is, they should be modified into

\[ P = (\varepsilon_{\text{init}} + \beta E_0)_a \pm \frac{1}{2}(E_0^2 - E^2) + \Delta P / 2 \]  

and

\[ S = (d_{\text{init}} + \alpha E_0)_a \pm \frac{1}{2}(E_0^2 - E^2) - \Delta S / 2, \]  

respectively, where \( P \) and \( S \) are the instantaneous polarizations and strains; \( E_0 \) and \( E \) are the peak field and instantaneous field, respectively; and \( \varepsilon_{\text{init}}, \beta, d_{\text{init}}, \) and \( \alpha \) are the Rayleigh parameters. The second term is either positive or negative, depending on the decrease or increase in the electric field.

In Fig. 5(b), we show the evolution of \( \Delta P / 2 \) and \( \Delta S / 2 \). The definitions of \( \Delta P \) and \( \Delta S \) are given in Fig. 5(a), which can be calculated by \( \Delta P = P^+ - P^- \) and \( \Delta S = S^+ - S^- \), respectively. The results show that \( \Delta P / 2 \) is proportional to \( E^2 \), whereas \( \Delta S / 2 \) increases nearly linearly with the increase in the electric field. Figure 5(a) presents the measured dielectric permittivity \( \varepsilon_{33} \), which is calculated by \( \varepsilon_{33} = (P_{\text{max}}^+ - P_{\text{max}}^-) / 2E_0 \) and piezoelectric coefficient \( d_{33} \), which is calculated by \( d_{33} = (S_{\text{max}}^+ - S_{\text{max}}^-) / 2E_0 \). Under certain electric fields, both of them linearly increase with the increase in the electric field. As reported by others, this finding indicates that \( \varepsilon_{33} \) and \( d_{33} \) obey the Rayleigh behavior. By fitting the experimental results using the Rayleigh equations, \( \varepsilon_{33} = \varepsilon_{\text{init}} + \beta E_0 \) and \( d_{33} = d_{\text{init}} + \alpha E_0 \), respectively, and the parameters \( \varepsilon_{\text{init}}, \beta, d_{\text{init}}, \) and \( \alpha \), can be obtained. Figures 5(c) and 5(d) show the measured and calculated \( P \)–\( P \) and \( S \)–\( S \) curves under an electric field of 0.5 MV/m. Figure 5(d) shows that by taking the response asymmetry into account, the calculated strains can fit the experimental results better than the unmodified equations. Conversely, for the polarization, as \( \Delta P / 2 \) is still very small at 0.5 MV/m, the unmodified and modified equations can fit the experimental results well.

4. Conclusions

In summary, the polarization and strain response in the electrically poled PZT ceramics under low-to-medium electric field loading were reinvestigated. A phenomenon normally ignored was proposed by checking the polarization and longitudinal strain response of pre-poled soft PZT ceramics in scrutiny. That is, under low-to-medium cyclic electric field loading, the measured remnant strain under a negative electric field loading is larger than that measured under a positive electric field loading. Moreover, a reverse trend was observed for the remnant polarization. This phenomenon was explained by the texture-dependent domain switching, defect
dipole reorientation, and interactions between them. Furthermore, as the remnant strains are asymmetrical under positive and negative loading, the equation \( a = \pm \frac{E}{E_{\text{init}} 0^2} \) was modified by taking the asymmetry of the electric field versus strain curves into consideration to describe the strain response better.

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