Comparisons of polarization switching in “hard,” “soft,” and relaxor ferroelectrics
Christelle Jullian, J. F. Li, and D. Viehland

Citation: Journal of Applied Physics 95, 4316 (2004); doi: 10.1063/1.1641962
View online: http://dx.doi.org/10.1063/1.1641962
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/95/8?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Electric-field-controlled interface strain coupling and non-volatile resistance switching of La1-xBaxMnO3 thin films epitaxially grown on relaxor-based ferroelectric single crystals

Mapping bias-induced phase stability and random fields in relaxor ferroelectrics
Appl. Phys. Lett. 95, 092904 (2009); 10.1063/1.3222868

Broadband inelastic light scattering of a relaxor ferroelectric 0.71 Pb ( Ni 1/3 Nb 2/3 ) O 3 - 0.29 Pb Ti O 3

Ferroelectric behavior in nominally relaxor lead lanthanum zirconate titanate thin films prepared by chemical solution deposition on copper foil

Direct piezoelectric effect in relaxor-ferroelectric single crystals
J. Appl. Phys. 95, 5679 (2004); 10.1063/1.1703829
Comparisons of polarization switching in “hard,” “soft,” and relaxor ferroelectrics

Christelle Jullian, J. F. Li, and D. Viehland

Department of Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia 24061

(Received 20 August 2003; accepted 17 November 2003)

The dynamics of polarization switching have been investigated over extremely broad time ($10^{-8} < t < 10^2$ s) and field ranges for hard, soft, and relaxor ferroelectrics based on aliovalent modified Pb(Zr$_{1-x}$Ti$_x$)O$_3$. The results unambiguously demonstrate important differences in the polarization switching mechanism for these various types of ferroelectrics. © 2004 American Institute of Physics. [DOI: 10.1063/1.1641962]

I. INTRODUCTION

Defects and substituents are known to significantly influence the electromechanical properties of ferroelectrics. Various classifications of piezoelectric behaviors have been categorized in lead zirconate titanate (PZT). The basic two types of classifications are commonly called “soft” and “hard.” In general, higher valent substituents induce soft piezoelectric behavior, while those lower valent ones induce hard. With increasing higher valent substituent concentration, a crossover between soft and relaxor ferroelectric behavior occurs.

Soft ferroelectrics have lower coercive fields, higher hysteretic losses, higher dielectric and mechanical loss factors, and lower remanent polarizations and strains, relative to hard ones. The extra contribution is designated as extrinsic, and is believed to be due to domain dynamics under weak ac fields. Hard ferroelectrics have an asymmetric polarization versus electric field ($P-E$) response, which is shifted by a built-in potential. The built-in potential is due to a pinning of the polarization by dipolar defects. Relaxor ferroelectrics have a frequency dispersive dielectric response in the audio range; the inability to sustain remanence for temperatures above a freezing temperature $T_f$ (which is notably less than that of the dielectric maximum ($T_m$)), and by the presence of a local polarization until $T > T_m$.

Previous transmission electron microscopy (TEM) studies of soft, hard, and relaxor ferroelectrics have shown dramatic differences in domain stability. Studies of hard ferroelectrics have shown fine “wavy” domains. Comparisons with dielectric property data indicated that the wavy domains result from pinning effects. Systematic studies of soft ferroelectrics have shown the development of increasingly irregular domain morphologies with increasing higher valent substituent concentrations. And, above a critical concentration, polar nanodomain (PND) form that have an average diameter between 30 and 50 Å, which is the relaxor state.

Domain dynamics are generally believed to make significant contributions to ferroelectric and piezoelectric properties. However, understanding them has proven difficult, in particular in systems containing significant concentrations of aliovalent substituents. Limiting the study of polarization switching and domain dynamics has been that current transient investigations have been performed over relatively narrow time ($t$) and electric field ($E$) ranges—even though the current response is known to be logarithmic in time. Nucleation and growth (N&G) models have previously been developed. However, analysis of the dynamics in the time domain of $10^{-8} < t < 10^{-6}$ s provides incomplete information, upon which to develop a comprehensive mechanistic understanding. Previous N&G models have been based on nucleation sites confined to existing domain walls [i.e., two-dimensional (2D)] with a subsequent restriction that during growth, the domain walls remain coherent (i.e., one-dimensional). However, it is doubtful that such a model can explain switching in a wider range of aliovalently modified ferroelectrics.

Investigations of the polarization dynamics over broad time and field regions would be greatly important to the study of modified ferroelectrics. In this article, we report the polarization dynamics over such a broad time domain (extending from $10^{-8} < t < 10^2$ s) for hard, soft, and relaxor ferroelectrics based on PZT. The results unambiguously demonstrate important differences in switching mechanisms between these general types of ferroelectrics.

II. EXPERIMENTAL PROCEDURE

Polycrystalline specimens of soft PZT ($E_r \sim 11$ kV/cm) and hard PZT specimens were obtained from EDO Corp. (Salt Lake City, UT). In addition, PLZT 10/65/35 relaxor specimens were prepared, as previously reported. The specimens were cut into typical dimensions of 0.3 mm in thickness and 4 mm$^2$ in area, and were electroded with gold. Measurements were performed for various fields. In order to measure the response of the specimens over a broad time domain from $10^{-8} < t < 10^2$ s, three different measurements were performed and reported. To prepare for switching, both sides of the specimen were raised to the desired switching field. Then, at time $t = 0$, one side of the specimen was taken to ground. By using these steps, we can certify that high voltage reaches its full maximum, before the polarization starts to rise. It was found that switching...
times of \( \leq 10^{-8} \) s could be achieved. An Agilent oscilloscope operated in a time capture mode was used to measure the output voltage from each circuit.

III. RESULTS AND DISCUSSION

Figure 1 shows the logarithm of the polarization as a function of the logarithm of time for [Fig. 1(a)] a soft PZT, [Fig. 1(b)] a relaxor PLZT 10/65/35, and [Fig. 1(c)] a hard PZT. These data were all taken at room temperature. Data are shown for over ten decades in time, taken at various applied electric fields. The data can be seen to be quite different for the three types of ferroelectrics.

The response of soft PZT can clearly be seen to be extremely broad in the time domain, extending over decade(s) of orders in magnitude. Two evolutionary stages in the time domain were found during polarization switching with increasing \( E \). Figure 1(a) demonstrates a broad polarization transient in the time domain of \( 10^{-6} < t < 10^{-4} \) s designated by the symbol (i) in the figure, followed by a delay, and a subsequent second broad polarization transient in the long-time domain designated by (ii). These two stages in the time domain response represent nucleation events and domain growth events, respectively. Recent investigations\(^{24}\) of poled \( \text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\%\text{PbTiO}_3 \) crystals have similarly shown two broad transients, demonstrating that the broadness in the time domain is not due to a variety of extrinsic pinning sites, such as grain boundaries and dislocations. With increasing \( E \), both transients in Fig. 1(a) shifted to shorter times, but only becoming sharp at high fields of \( E \gg E_c \) and short times of \( t < 10^{-6} \) s.

The time dependence of the polarization for soft PZT did not follow the Avarami (AV) equation, i.e.,

\[
P(t) = P_0 \exp \left(-\left(t/\tau\right)^n\right),
\]

where \( \tau \) is the relaxation time and \( n \) is a dimensionality constant. Rather, as shown in Fig. 2 (red line), it fit to a stretched exponential (SE) function, where terms in \( (t/\tau) \) in the AV equation are replaced by ones in \( \ln(t/\tau) \), i.e.,

\[
P(t) = P_0 \exp\left(-a(\ln(t/\tau))^n\right).
\]

These two stages in the time domain are designated by (ii) and (iii) in the figure, followed by a delay, and a subsequent second broad polarization transient in the long-time domain designated by (ii). These two stages in the time domain response represent nucleation events and domain growth events, respectively. Recent investigations\(^{24}\) of poled \( \text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\%\text{PbTiO}_3 \) crystals have similarly shown two broad transients, demonstrating that the broadness in the time domain is not due to a variety of extrinsic pinning sites, such as grain boundaries and dislocations. With increasing \( E \), both transients in Fig. 1(a) shifted to shorter times, but only becoming sharp at high fields of \( E \gg E_c \) and short times of \( t < 10^{-6} \) s.

The time dependence of the polarization for soft PZT did not follow the Avarami (AV) equation, i.e.,

\[
P(t) = P_0 \exp \left(-\left(t/\tau\right)^n\right),
\]

where \( \tau \) is the relaxation time and \( n \) is a dimensionality constant. Rather, as shown in Fig. 2 (red line), it fit to a stretched exponential (SE) function, where terms in \( (t/\tau) \) in the AV equation are replaced by ones in \( \ln(t/\tau) \), i.e.,

\[
P(t) = P_0 \exp\left(-a(\ln(t/\tau))^n\right).
\]

These two stages in the time domain are designated by (ii) and (iii) in the figure.
for relaxor PLZT was found to be well fit to the AV equation, as shown in Fig. 2 (blue line). Analysis yielded \( n = 3 \) and \( \tau = 4.8 \times 10^{-8} \) s. No indication of a domain growth region was found. These results demonstrate that polarization reversal in the relaxors for \( T > T_f \) occurs entirely by nucleation. The results are consistent with prior TEM studies that have shown pre-existing polar nuclei or PNR, somewhat similar to the relaxor, which then exhibits a broad polarization transient in the time domain of \( 10^{-8} < \tau < 10^{-6} \) s designated as (i) in the figure. This transient was similar to that observed in soft PZT. Analysis with the SE equation yielded a value of \( n = 3 \), as shown in green in Fig. 2. Then, at \( \tau \approx 10^{-6} \) s, a sharp increase in \( P \) was found, which is designated as (ii). The sharpness of this peak is similar to that observed for the relaxor, but \( \tau = 10^{-6} \) s, rather than \( 10^{-8} \) s. This portion of the time domain response was found to be well fit by the AV equation with \( n = 3 \), and its position in the time domain did not shift with increasing \( E \). Finally, a weak long-time polarization transient for \( \tau > 1 \) s was found at higher \( E \), designated by (iii). It is analogous to that in soft PZT, but was much weaker and was only noticeable at much higher \( E \). This long-time transient was well fit by the SE equation with \( n = 2 \), again in analogy with soft PZT.

The results for hard PZT demonstrate that the switched polarization is mainly due to nucleation. The data show a switchover from SE type nucleation events to AV ones. It is important to note that the fraction of polarization switched by nucleation is much higher for hard PZT, than soft. This is because domain growth is not significant for hard PZT. The switchover to AV-type nucleation near \( t = 10^{-6} \) s may reflect a transition to a state with a high density of stable polar nuclei or PNR, somewhat similar to the relaxor, which then do not grow readily into fully formed domain variants with a reversed polarization due to built-in dipolar fields.

We also found that nucleation is only slightly dissipative, whereas domain growth is strongly so. This is illustrated in the \( P-E \) curves given in Figs. 3(a)–3(c), respectively, for hard PZT with \( E = 15 \) kV/cm, relaxor PLZT, and hard PZT with \( E = 25 \) kV/cm. The \( P-E \) response for both Figs. 3(a) and 3(b) were nearly anhysteretic and nondissipative over the frequency range of \( 10^{-2} < f < 10^5 \) Hz. Clearly, nucleation is not significantly dissipative. However, for hard PZT with \( E = 25 \) kV/cm, hysteresis became evident with decreasing frequency.

The development of a long-time polarization transient in the time domain data with increasing \( E \). These results indicate that nucleation events occur against a small anisotropy barrier. In this regard, nucleation events may be similar to polarization rotation in poled PMN–PT crystals, with gradual structural evolution. However, in our case, rotation clearly must be an inhomogeneous process.

IV. CONCLUSIONS

In summary, the polarization response of hard, soft, and relaxor ferroelectrics have been investigated over broad time and field ranges. The results unambiguously demonstrate important differences in the polarization switching mechanism between these family of materials.

ACKNOWLEDGMENTS

This research was supported by the Office of Naval Research under Grant Nos. N000140210340, N000140210126, and MURI N000140110761.