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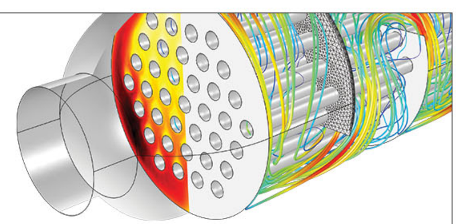

# Polarization dynamics over broad time and field domains in modified ferroelectrics

Christelle Jullian, J. F. Li, and D. Viehland[a)]
Department of Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia 24061

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The dynamics of polarization switching have been investigated over extremely broad time ($10^{-8} < t < 10^{2}$ s) and field ranges for various modified Pb-based perovskite ferroelectrics. The results unambiguously demonstrate the presence of extremely broad relaxation time distributions for switching, which can extend over decade(s) in orders of magnitude in time. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1600823]

Limiting the study of domain dynamics and polarization switching has been that current transient investigations have been performed over relatively narrow time ($t$) and electric field ($E$) ranges[1–8]—even though the current response is known to be logarithmic in time.[4,9–11] Analysis of the dynamics in the time domain of $10^{-8} < t < 10^{-6}$ s provides incomplete information, upon which to develop a mechanistic understanding. For example, it is known that the current transient peaks are skewed to longer times in the domain of $10^{-8} < t < 10^{-6}$ s.[4,6–8] Skewing has been understood by (i) a geometric model that includes domain impingement;[4] and (ii) stretched exponential functions that include the effect of random fields which broaden nucleation and growth events in the time domain.[10] Also, recent polarization versus electric ($P-E$) studies of modified Pb-based perovskites have revealed pronounced dispersion in the frequency domain of $10^{-2} < f < 10^{2}$ Hz.[11] This dispersion has also been shown to follow stretched exponential functions.

Stretched exponential behavior is well-known in disordered systems.[12–14] It is a form of hierarchial relaxation. Many modified perovskite ferroelectrics are also known to contain significant disorder, such as $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-(x)PbTiO_3$ (PMN–$x$%PT).[15–17] These systems possess random fields,[14,18] which couple to the polarization.[19] Random fields have also been shown to be important to the piezoelectric behavior of "soft" $Pb(Zr_{1-x}Ti_x)O_3$ (PZT), which are modified with higher valent substituents,[20,21,11] such as $La^{+3}$ on the $Pb^{+2}$ site (i.e., PLZT).

Investigations of the polarization dynamics over broad time and field regions would be greatly important to the study of modified ferroelectrics. It could significantly impact understanding of domain dynamics. In this letter, we report the polarization dynamics over such a broad time domain, extending from $10^{-8} < t < 10^{2}$ s. We have studied various modified Pb-based ferroelectrics. Studies were performed from $E \ll E_c$ to $E \gg E_c$, where $E_c$ is the coercive field. The results unambiguously demonstrate the presence of extremely broad relaxation time distributions for the switching process, extending over decade(s) in orders of magnitude in time, where the distribution is strongly dependent on $E$.

Polycrystalline specimens of PMN–PT 70/30 ($E_c \sim 4$ kV/cm) and PLZT 7/65/35 ($E_c \sim 6.7$ kV/cm) were prepared, as previously reported.[21] Soft PZT ($E_c \sim 11$ kV/cm) specimens were obtained from EDO Corp. (Salt Lake City, UT). In addition, a (001)-oriented single crystal of PMN–PT 70/30 was obtained from HC Materials (Urbana, IL). 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 of $0 < E < 3E_c$. In order to measure the response of the specimens over a broad time domain from $10^{-8} < t < 10^{2}$ s, three different measurements circuits were developed and built.[22] Figure 1(a) shows the measurement circuit for the short-time domain between $10^{-8}$ and $10^{-6}$ s. Figure 1(b) shows the circuit for the middle-time domain between $10^{-6}$ and $10^{-3}$ s. And, Fig. 1(c) shows the circuit for the long-time domain between $10^{-3}$ and $10^{2}$ s. For the short- and middle-time domains, the same procedure was used prior to switching. Initially the specimen was unpoled, and then an electric field of $-3E_c$ was applied to repole the specimen. 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: this is an important step that allowed for the very highest current wall between the power amplifier and the specimen. 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 $\ll 10^{-8}$ s could be achieved. For the long-time domain, this method

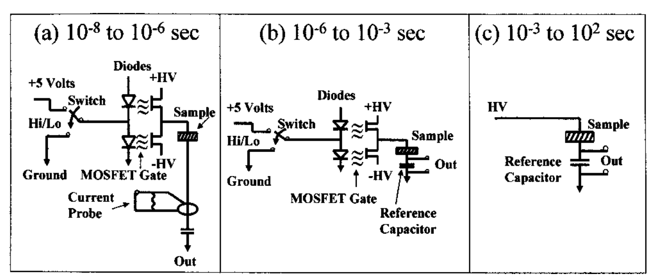


FIG. 1. Measurement circuit of switching current responses for the various time domains: (a) short-time domain between $10^{-8} < t < 10^{-6}$ s; (b) middle-time domain between $10^{-6} < t < 10^{-3}$ s; and (c) long-time domain between $10^{-3} < t < 10^{2}$ s. The circuits behind the specimen are equivalent for the short- and middle-time domains. This circuit consists of a switch, rapid response diodes, and metal–oxide–semiconductor field effect transistor gates. In the fast-time domain, a current probe is used to lower the input voltage into an oscilloscope. For the middle- and long-time domains, the circuits in front of the specimen are equivalent. The voltage is measured across a reference capacitor, using an oscilloscope operated in a time capture mode.

[a)]Electronic mail: viehland@mse.vt.edu



 

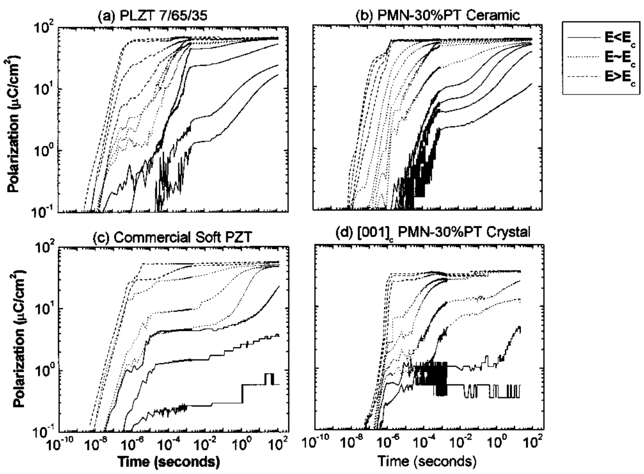


FIG. 2. Logarithm of polarization as a function of logarithm of time for various soft ferroelectrics over broad time and field ranges. (a) PLZT 7/65/35, (b) PMN–30%PT, and (c) a commercial soft PZT. Data are shown for three different field regimes of $E<E_c$, $E\approx E_c$, and $E>E_c$ regimes in each figure.

could also be used, but is not necessary as the rise time of the amplifier is significantly shorter than the measurement time. An Agilent oscilloscope operated in a time capture mode was used to measure the output voltage from each circuit.

Figure 2 shows the logarithm of the polarization as a function of the logarithm of time for (a) a PMN–PT 70/30 ceramic, (b) PLZT 7/65/35, (c) PZT, and (d) a (001)-oriented PMN–PT 70/30 crystal. All three of these specimens are soft ferroelectrics at room temperature, which have a modest $E_c$ and relatively high susceptibilities. Data are shown for over ten decades in time, taken at various applied electric fields of $3<E<20$ kV/cm. The data can be seen to be quite similar for all three compositions. It is similar for single crystals and polycrystals. Thus, the interesting general features of the data for the various compositions will be discussed together below.

The spectra can clearly be seen to be extremely broad in the time domain, extending over decade(s) of orders in magnitude. The spectra only became sharp at higher fields of $E \gg E_c$ and short times of $t<10^{-6}$ s. Unambiguously, polarization switching in soft ferroelectrics has a very broad distribution of relaxation times $\tau$. It is important to note that the results for the PMN–PT ceramic were quite similar to those of the (001)-oriented crystal, demonstrating that the broadness in the time domain is not due to a variety of extrinsic pinning sites such as grain boundaries and dislocations. The breadth of this distribution is nearly equal to that found in the weak-field susceptibility (dielectric constant) of relaxor ferroelectrics near their freezing temperature.[17,23,24] However, there is structure within the spectra that changes with $E$ and $\log(t)$. Below we use PLZT 7/65/35 as an example by which to discuss these features.

For $E<E_c$, as shown in Fig. 3(a), two regimes of different polarization responses were found. At short times of $10^{-5}<t<10^{-3}$ s, the polarization logarithmically increased with $t$, exhibiting significant fluctuation (Barkhaussen-like)[14] events. With increasing $E$ the randomness of the fluctuations decreased, and a plateau was found for $10^{-3}<t<10^{-1}$ s. At longer times of $10^{-1}<t<10^{2}$ s, the polarization smoothly and gradually increased with $\log(t)$. For $E<E_c$, polarization

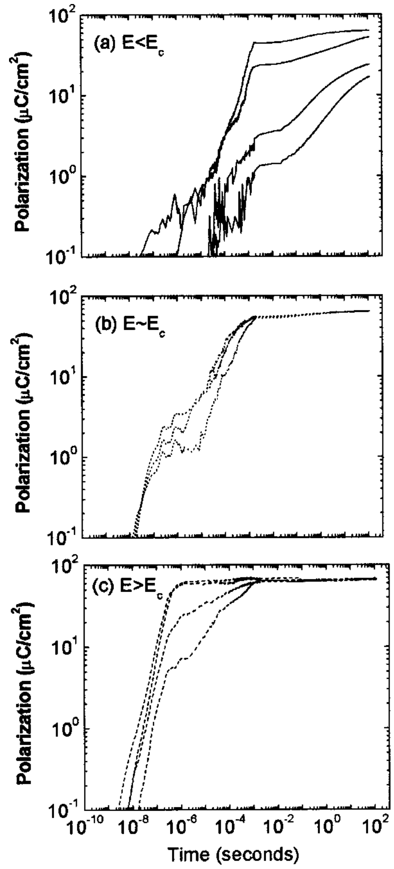


FIG. 3. Logarithm of polarization as a function of logarithm of time for PLZT 7/65/35 for various field ranges. (a) $E<E_c$ (3, 4, 5, and 6 kV/cm), (b) $E\approx E_c$ (6.4, 6.7 7 kV/cm), and (c) $E\gg E_c$ (10, 15, 17, and 19 kV/cm). The fields shown in the brackets represent data from lower right to upper left in each figure.

saturation seemingly would eventually be achieved, but only at times many orders of magnitude longer than $10^2$ s. For $E\approx E_c$, two regimes of polarization response were again present, as shown in Fig. 3(b). With increasing $E$, the regimes became increasingly indistinguishable in the time domain of $10^{-7}<t<10^{-3}$ s. Complete saturation was only gradually approached for $t>10^{-3}$ s. For $E>E_c$, the polarization response became increasingly sharp with increasing $E$, as shown in Fig. 3(c). For $E\gg E_c$, saturation was reached at $\sim 10^{-7}$ s.

We discuss our results in terms of a double well potential that is under an applied electric field $E$ and that has a rugged fine structure, which is somewhat like that of a relaxor.[17,23,24] For small $E$, Barkhaussen-like events occur as the system moves between rugged fine structures, towards the other variant—a polarization creep develops over long times. This creep occurs by stretched exponential functions,[10,11] due to the hierarchial nature of relaxation within a rugged landscape.[12,13] With increasing $E$, the system moves more freely within this landscape, and thus the breadth of the $\tau$ distribution and $\tau_{\mathrm{average}}$ both decrease. At high fields of $E \gg E_c$, polarization switching occurs rapidly and the $\tau$ distribution is sharp. In this field range, the dynamics can be described by an Avarami-type relationship,[1–8] as the rugged landscape presents no impediments to switching.

Previous electron microscopy studies of soft ferroelectrics[20,21] have shown domain breakdown with increasing ac electric field. Furthermore, fractal domains have recently been used to understand long-time polarization dynamics in various modified PZTs.[10,11,25] The results of our investigation demonstrate that soft ferroelectrics contain such heterogeneities under field for $E \leqslant E_c$, which control the dynamics of polarization switching. These heterogeneities are conceptually similar to the long-lived ones observed in relaxor ferroelectrics under weak field drive. At higher fields of $E \geqslant E_c$, switching occurs by a mechanism similar to conventional ferroelectric domain nucleation and growth.[1–8]

In summary, the polarization response of various modified Pb-based perovskites has been investigated over broad time and field ranges. The results unambiguously demonstrate the presence of extremely broad relaxation time distributions for switching, which can extend over decade(s) in orders of magnitude in time. With increasing field for $E \geqslant E_c$, the breadth of the distribution is significantly sharpened, revealing that the switching mechanism is dependent on $E$.

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