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Spatial distribution of relaxation behavior on the surface of a ferroelectric relaxor in the ergodic phase

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Spatial homogeneity of polarization relaxation behavior on the surface of 0.9Pb(Mg1/3Nb2/3)O3–0.1PbTiO3 crystals in the ergodic relaxor phase is studied using three-dimensional time-resolved spectroscopic piezoresponse force microscopy. The number of statistically independent components in the spectroscopic image is determined using principal component analysis. In the studied measurement time interval, the spectra generally exhibit logarithmic behavior with spatially varying slope and offset, and the statistical distribution of these parameters are studied. The data illustrate the presence of mesoscopic heterogeneity in the dynamics of the relaxation behavior that can be interpreted as spatial variation in local Vogel–Fulcher temperatures. © 2009 American Institute of Physics. [doi:10.1063/1.3242011]

Unique dielectric and electromechanical properties of relaxor ferroelectrics have attracted broad attention to the polarization switching and relaxation mechanisms in these materials.1 Macroscopic techniques such as dielectric spectroscopy2–3 and light scattering4–5 unambiguously indicate the broad distribution of relaxation times,6,7 related to the interactions and dynamics of polar nanoregions (PNRs). The link between the PNRs and the unusual properties of relaxors has stimulated a number of spatially resolved studies using piezoresponse force microscopy (PFM).7–10 Even though the spatial resolution is significantly larger than the pre-existing domain contrast, these studies have provided insights into the relationship between disorder and static mesoscopic (~100 nm) polar structure. At the same time, little is known about the mesoscopic dynamics behavior. Here, we analyze the spatial variability of polarization relaxation in an ergodic ferroelectric relaxor using spatially resolved piezoresponse spectroscopy.11

The (1–x)Pb(Mg1/3Nb2/3)O3–xPbTiO3 crystal with x =0.1 (PMN-10PT) is grown using a flux method.12 The dielectric maximum occurs at $T_{\text{max}}=310$ K (at 1 kHz) and the crystal undergoes a macroscopically cubic to rhombohedral ferroelectric phase transition on cooling at $T_C \approx 280$ K (as determined by x-ray diffraction measurements).13 The transition is observed only near the surface of the crystal while the bulk structure remains nearly cubic (as determined by neutron diffraction measurements).14 The Burns temperature is $\sim650$ K and the Vogel–Fulcher temperature is $\sim270$ K. The absence of macroscopic piezoelectric effects15 and aging16 at $T>T_C$ suggests that the bulk room-temperature state in PMN-10PT is ergodic. The PFM measurements are performed using a commercial atomic force microscope (AFM) (Veeco MultiMode with Nanonis controller) on the mirror-polished and annealed (500 °C for 30 min) (100) surface. The spatially resolved relaxation measurements are performed using a homebuilt MATLAB/LABVIEW data acquisition system, as described elsewhere.11

The surface topography and domain structure before and after the switching experiment are shown in Fig. 1. The PFM amplitude and phase images indicate that a labyrinthine domain structure is ubiquitously present on the surface. The presence of these domain patterns indicates the deviation of symmetry from cubic to transversally isotropic. The presence of switchable polarization is clearly established from the contrast change after the switching experiment [Figs. 1(d)–1(f)]. Note that the switched contrast is significantly larger than the pre-existing domain contrast.

To probe polarization relaxation locally, dc bias pulses of specified magnitude and duration are applied to the conducting AFM tip in contact with the sample, and the resulting vertical electromechanical response is measured as a func-

![FIG. 1. (Color online) [(a) and (d)] Surface topography and piezoresponse [(b) and (e)] amplitude and [(c) and (f)] phase images before [(a), (b), and (c)] and after [(d), (e), and (f)] switching.](image-url)
tion of time. The measurements are performed on a densely-
spaced grid of points, yielding the three-dimensional (3D) 
PR(x,y,t) data arrays, where PR is the piezoresponse signal, 
(x,y) is the coordinate, and t is time. Here, the measurements 
are performed with a 30 ms, 10 V setting pulse, and a 300 ms 
detection window (4000 time samples) on a 40×40 spatial 
grid with 50 nm pixel spacing.

Analysis of the resulting PR(x,y,t) using the functional 
fit, PR(t)=f(x,y), where α=α_1,⋯,α_n is an n-dimensional 
parameter vector, allows maps of α_k(x,y) describing the spa-
tial variability of the relaxation behavior to be constructed.
As an example, a fit using the stretched exponential law, 
PR(t)=A_0−A_1 exp[−(t/τ)^β] with n=4 yields spatially re-
solved maps of relaxing, A_1, and nonrelaxing, A_0, polariza-
tion components, relaxation time, τ, and exponent, β.17 How-
ever, such analysis is prone to errors, since the functional 
form of the relaxation law, its physical interpretation, and 
the number of statistically independent variables are a priori un-
known. As a result, fitting can lead to a strong interdepen-
dence of the derived parameters, α, yielding poorly interpre-
table maps.

To avoid this problem and to establish unambiguously 
the veracity of the fitting procedure, we analyze spectro-
scopic PFM data using principal component analysis 
(PCA).18–20 The spectroscopic image of N×M pixels formed 
by spectra containing P points is represented as a superposi-
tion of the eigenvectors w_j,

\[ PR(t) = a_k w_k(t), \]

where a_k=α_k(x,y) are position-dependent expansion coeffi-
cients, PR(t)=PR(x,y,t) is the image at a selected time, 
and t is the discrete times at which the response is mea-
sured. The eigenvectors, w_k(t), and the corresponding eigen-
values, λ_k, are found from the covariance matrix, C=AA^T, 
where A is the matrix of all experimental data points A_{ij} 
=PR(t), i.e., the rows of A correspond to individual grid 
points (i=1⋯N×M), and the columns correspond to time 
points, j=1⋯P. The eigenvectors, w_j(t), are orthogonal 
and are chosen such that the corresponding eigenvalues 
are placed in descending order, λ_1>λ_2>⋯.

The spatial maps of the first three PCA components of 
the piezoresponse data arrays and the corresponding eig-
evectors and eigenvalues are shown in Fig. 2. The shape of 
λ_k(k) dependence (scree plot) indicates that the first two PCA 
components contain 99.9% of the significant information 
within the 3D spectral image, whereas the remaining P−2 
=3998 components are dominated by noise. This behavior 
is also evident from the eigenvectors, w_j(t), where first two 
eigenvectors illustrate a clear time dependence, while the 
third and subsequent eigenvectors are noiselike. Finally, spa-
tially resolved maps of the first and second PCA components 
clearly illustrate long-range contrast and discernible spatial 
features, whereas the third and subsequent PCA maps are 
essentially random.

This analysis suggests that with the given experimental 
offset and measurement time interval, the 3D spectro-
scopic relaxation image can be represented as a system 
with 2 degrees of freedom, PR(x,y,t)=A_1(x,y)w_1(t) +A_2(x,y)w_2(t)+Y(t), where Y(t) is a spatially uncorrelated 
noise term. Therefore, functional fits with more than two 
independent parameters will invariably lead to strong param-
ter dependence, and provide unrealistic results. Note that 
the PCA analysis is a purely statistical method and does not 
employ any assumption regarding the underlying physical 
behavior, ensuring its fidelity.

The detailed analysis of the eigenvectors and single-
point relaxation data suggest that the observed behavior is 
close to logarithmic, PR(t)=B_0+B_1 ln t. Given the results of 
the PCA analysis, the use of more complex functional fits is 
not expected to provide better description of the data. Hence, 
3D PR(x,y,t) data arrays were fitted using a logarithmic 
function and the resulting spatial maps of offset, B_0(x,y), 
and slope, B_1(x,y), are shown in Figs. 3(a) and 3(b). Note 
that both maps indicate the presence of mesoscopic struc-
tures and contain a number of uncorrelated features, indica-
tive of the validity of the analysis.

A number of relaxation curves extracted from regions of 
dissimilar contrast in Figs. 3(a) and 3(b) are shown in Figs. 
3(c) and 3(d). Note that the relaxation behavior varies be-
tween adjacent locations, illustrating the presence of meso-
copic dynamic inhomogeneity on the surface of the PMN-
10PT relaxor crystal. The histograms of the slope and offset 
are shown in Figs. 3(e) and 3(f). The slope distribution is 
relatively narrow, B_1=−0.10±0.02 within the image, and 
close to Gaussian. In comparison, the distribution of offsets 
is much broader, B_0=1.5±0.5, and is strongly asymmetric.

The observed point-to-point variations in the amplitude of 
the pulse-induced polarization can be attributed to a variation.
of PNR density, the presence of lattice defects and surface contamination (the latter factor is probably responsible for the distribution asymmetry), and (possibly) topographic cross-talk, while the distribution of logarithmic slope suggests nonuniform relaxation kinetics.

To get insight into the origins of the observed mesoscopic dynamic heterogeneities, we consider standard relaxation dynamics, \( dp/dt = -p/\tau \), equivalent to relaxation, \( P = P_0 \exp(-t/\tau) \). To relate the parameters to the relaxation law we assume that the local relaxation time is determined by the activation energy, \( E \), and depends on temperature in accordance with the Vogel–Fulcher relationship, \( \tau(E) = \tau_0 \exp[E/(T - T_f)] \). Then, in terms of a distribution function of energies, \( G(E) \), the relaxation law is expressed as

\[
\langle P \rangle = P_0 \int_{E_{\text{min}}}^{E_{\text{max}}} dE G(E) \exp \left[ -\frac{t}{\tau(E)} \right].
\]

Equation (2) leads to \( G(E) = (T - T_f)^{-1} \tau(E) g[\tau(E)] \). For systems with logarithmic relaxation the energy distribution is almost uniform, \( G(E) \approx (E_{\text{max}} - E_{\text{min}})^{-1} \) and Eq. (2) can be integrated in the analytical form. For \( \tau_{\text{min}} \ll t \ll \tau_{\text{max}} \) where \( \tau_{\text{min,max}} = \tau_0 \exp[E_{\text{min,max}}/(T - T_f)] \), we obtain

\[
\langle P(t) \rangle \approx -P_0 \left[ \frac{T - T_f}{E_{\text{max}}} \right]^{\gamma - 1} \left[ 1 + \frac{T - T_f}{E_{\text{max}}} \ln \left( \frac{t}{\tau_0} \right) \right],
\]

where the Euler constant \( \gamma = 0.577 \). Hence, the spatial variation of slope in response-time dependence for the logarithmic model can be interpreted as the fluctuations of the local Vogel–Fulcher temperature. This interpretation is in agreement with the experimental observation of the distribution of the Vogel–Fulcher temperatures related to various segments of the dielectric relaxation spectrum in the relaxor crystal (higher values of \( T_f \) correspond to slower segments of the spectrum). These segments can be related to various mesoscopic regions of the crystal.

To summarize, the spatial variability of relaxation behavior in the ergodic relaxor phase of a PMN-10PT crystal surface is studied using time-resolved piezoresponse spectroscopy. The principal component analysis of the 3D spectroscopic imaging data sets indicates that within the image (40 x 40 pixels, 2 x 2 \( \mu m^2 \)), the spectra in the time domain (0.3 s, 4000 pixels) can be represented as a sum of two statistically independent components, imposing the limit on the number of independent parameters that can be determined in a functional fit. The two-parameter logarithmic fit allows a nearly-ideal description of experimental relaxation behavior within the image. Spatially resolved maps of logarithmic function slope and offset illustrate the presence of mesoscopic dynamic heterogeneities on the surface of the relaxor crystal. These heterogeneities can be interpreted as spatial variations of the Vogel–Fulcher temperature.

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