Mesoscopic structure and thermal- and bias-induced phase transitions on the surfaces of ergodic relaxors

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Ferroelectric relaxors are one of the most exciting and mysterious classes of ferroelectric materials. In the last several decades, macroscopic dielectric and electromechanical properties of relaxors have been extensively studied, illustrating rich panoply of bias- and temperature-induced phase transitions, non-exponential relaxations, and memory and spectral hole burning effects. On the nanometer and atomic levels, the atomic and phonon structure of relaxors have been studied extensively by scattering techniques. However, the mesoscopic behavior and properties of relaxors in the 5 nm to micron range is virtually unknown. Here, we summarize the results of spatially-resolved studies of several classes of materials including PMN-PT and PZN-PT solid solutions and PLZT which illustrate universal mesoscopic behaviors across families of ergodic and non-ergodic relaxors.

For ergodic relaxors including PMN, PMN-10 PT, and PLZT, piezoresponse force microscopy (PFM) imaging universally demonstrates the presence of labyrinthine 50-200 nm domains consistent with the presence of an out-of-plane polarization with no in-plane anisotropy [Fig 1(a)]. These observations are contrasted by the "cubic" symmetry of the material as determined by mono- and polychromatic focused X-ray scattering, suggesting that associated lattice deformation is small. These *frozen* domain structures coexist with and are apparently independent of *switchable* polarization. The two can be distinguished using local hysteresis loop measurements and demonstrate the presence of coupled phase transitions (first order for static polarization, second order for dynamic polarization) at temperatures ~150 K above dielectric constant maximum [Fig. 1].

Spatial variability of polarization relaxation kinetics in PMN-10PT is studied using time-resolved PFM at room temperature [Figs. 2 and 3]. Local relaxation attributed to the reorientation of polar nanoregions is shown to follow stretched exponential dependence, $\exp\left(-(t/\tau)^{\beta}\right)$, with $\beta \approx 0.4$ [Fig. 2], much larger than the macroscopic value determined from dielectric spectra ($\beta \approx 0.09$). The local distribution of activation energies is reconstructed using a combination of non-linear projection with neural network based interpolation. The spatial inhomogeneity of the activation energy illustrates distributions with the presence of mesoscopic "fast" and "slow" regions of 100-200 nm size [Fig. 3]. These results prove the presence of mesoscopic static and dynamic heterogeneous regions on the surfaces of ferroelectric relaxors in the ergodic phase. This approach is extended to map the "ergodic gap", delineating the regions of stability and metastability of the tip-induced ferroelectric state.

While the results obtained are systematic across the composition and temperature ranges and are universal for several relaxor systems, their exact interpretation remains an open issue. We believe that our data is consistent with (a) mesoscopic surface phase transitions on relaxor surfaces associated with extremely small symmetry changes and (b) coexistence of two order parameters related to *switchable* and *frozen* polarization components. This data illustrates an unexpectedly broad range of mesoscopic phenomena on relaxor surfaces that must be included in any theory of relaxor state.

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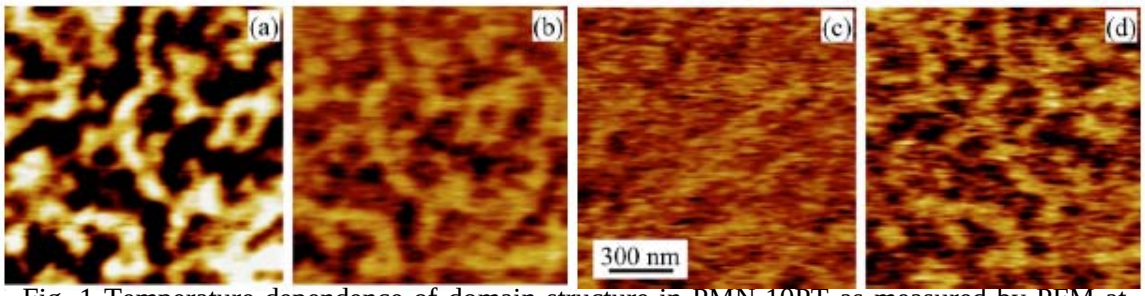

Fig. 1 Temperature dependence of domain structure in PMN-10PT as measured by PFM at (a) 295 K, (b) 335 K, (c) 385 K, and (d) 295 K after cooling.

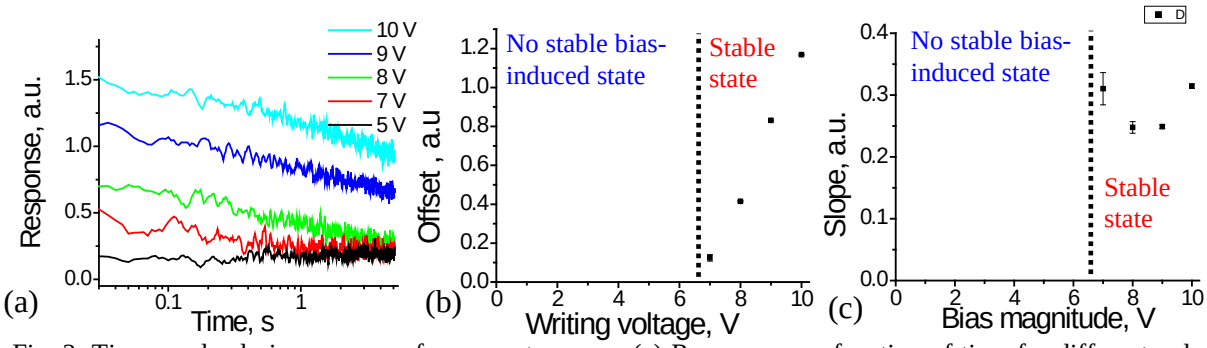

Fig. 2. Time-resolved piezoresponse force spectroscopy. (a) Response as a function of time for different pulse-bias magnitudes. (b) Offset and (c) slope as a function of bias. The data illustrates no remanent polarization below 6 V, and formation of metastable state with exponentially diverging relaxation time above 7 V.

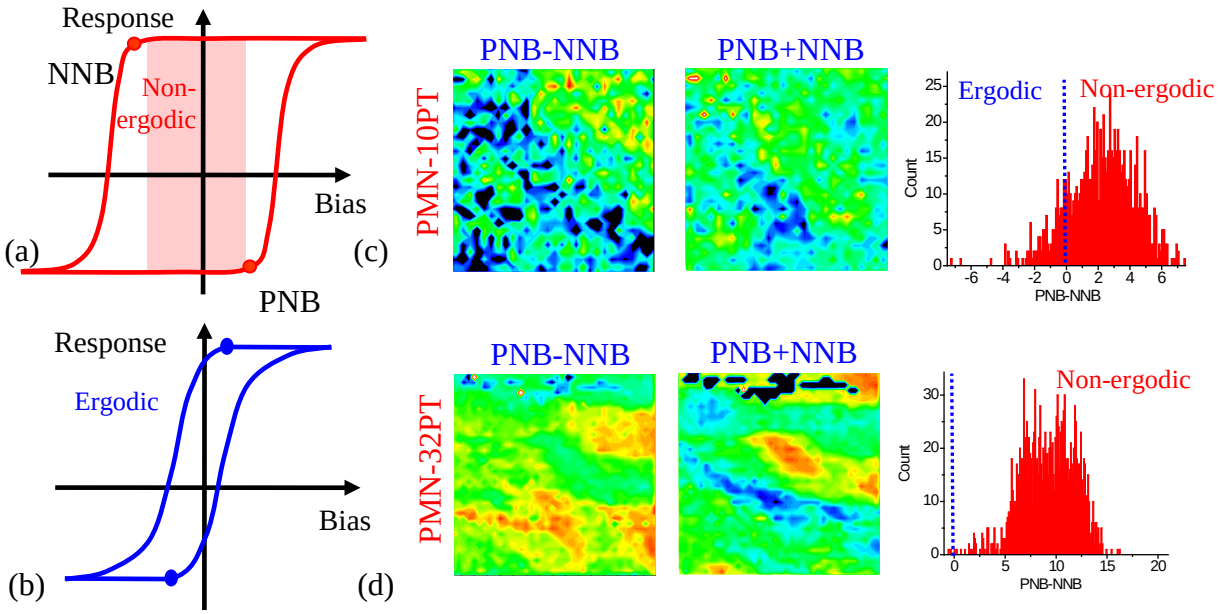

Fig. 3. Ergodic gap mapping by PFM voltage spectroscopy. (a,b) Schematics showing hysteresis loops for the cases when the ergodic gap is (a) large and (b) small. Maps of the difference and sum of positive and negative nucleation biases for (c) PMN-10PT and (d) PMN-32PT illustrating the ergodic gap (PNB-NNB) and built-in field (PNB+NNB) distributions in real space and corresponding histograms. Scan size is 1 μm.