

Mesoscale Domains and Nature of the Relaxor State by Piezoresponse Force Microscopy

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Abstract

Ferroelectric relaxors continue to be one of the most mysterious solid-state materials. Since their discovery by Smolenskii and coworkers, there have been many attempts to understand the properties of these materials, which are exotic, yet useful for applications. On the basis of the numerous experimental data, several theories have been established, but none of them can explain all the properties of relaxors. The recent advent of piezoresponse force microscopy (PFM) has allowed for polarization mapping on the surface of relaxors with subnanometer resolution. This development thus leads to the question of whether the polar nanoregions that contribute to diffuse X-ray scattering and a range of macroscopic properties can be visualized. This review summarizes recent advancements in the application of PFM to a number of ferroelectric relaxors and provides a tentative explanation of the peculiar polarization distributions related to the intriguing physical phenomena in these materials.

1. INTRODUCTION

Since their discovery by Smolenskii and coworkers (1) in the early 1960s, relaxor ferroelectrics (relaxors for short) have attracted continuing interest due to their exceptional dielectric and electromechanical properties as well as to their fascinating physical properties (2–5). A generic feature of relaxors is a broad maximum in the temperature dependence of the dielectric permittivity, whose position, T_m , shifts to lower temperatures with decreasing frequency (**Figure 1**). In contrast to the case for conventional ferroelectrics, this maximum does not correspond to a phase transition to a long-range ordered ferroelectric state with homogeneous polarization inside macroscopic domains. Instead, polarization is correlated on a nanometer scale within so-called polar nanoregions (PNRs), which form above the Burns temperature, T_D (6). The broad distribution of relaxation times results in the strong frequency dispersion of dielectric permittivity obeying the Vogel-Fulcher law,

$$f = f_0 \exp \left(\frac{E_a}{k(T_m - T_f)} \right), \quad 1.$$

where f is the frequency and T_f is the freezing temperature corresponding to the ultimate slowing down of PNR dynamics (7). In contrast to dipolar glasses, relaxors may undergo an irreversible transition to the ferroelectric phase by applying an electric field larger than a critical value (8).

PNRs manifest themselves in the deviation of certain physical properties from the behavior predicted for the paraelectric state. In the absence of an external electric field, local polarization of PNRs is randomly distributed, so $\sum P_i = 0$. Therefore, PNRs contribute to properties depending on P^2 , e.g., to the quadratic electro-optic effect (6, 10). Various neutron and X-ray scattering experiments indirectly confirmed the existence of PNRs (11). For example, according to high-resolution neutron diffuse scattering, the size of PNRs is ~ 1.5 nm at T_D and is almost temperature independent (12). It begins to increase on cooling at less than 300 K and reaches ~ 10 nm at 10 K. The number of PNRs estimated from the integrated intensity of scattering monotonically increases

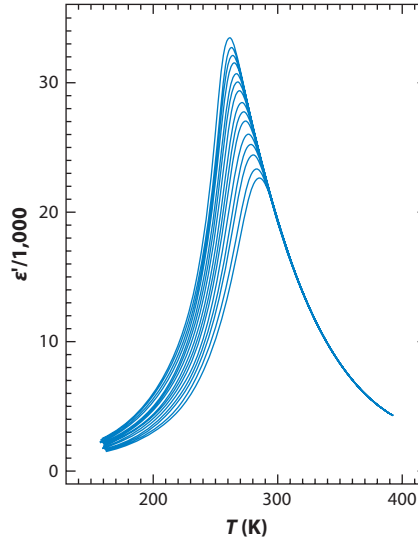


Figure 1

The dielectric permittivity of a $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) single crystal measured at frequencies of 20– 10^6 Hz. Adapted with permission from Reference 9.

on cooling and then abruptly decreases at T_f due to the merging of smaller PNRs into larger ones (12).

Another characteristic temperature, so-called T^* , was recently discovered in relaxors from anomalies in the temperature dependences of lattice parameters (13), Raman scattering (13, 14), and acoustic emission (13, 15). Researchers suggested that T^* corresponds to the appearance of static PNRs surrounded by dynamic ones and the paraelectric matrix (13) or to a transition to a nanodomain state (16). T^* may be a consequence of the local mesoscopic phase transition, which precedes the global one (17).

Relaxor behavior has been observed in a large variety of materials ranging from perovskites such as $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN), to tetragonal tungsten bronzes such as $(\text{Sr},\text{Ba})\text{Nb}_2\text{O}_6$ (SBN), to compounds with the Aurivillius structure, e.g., $\text{BaBi}_2\text{Nb}_2\text{O}_9$ (18). Such behavior is always accompanied by two essential features: structural and related charge disorder as well as the existence of relaxing entities, e.g., PNRs. Large dielectric permittivity, $\epsilon \sim 10^4$ – 10^5 , observed in many relaxors; high piezoelectric coefficients d_{33} (up to 2,500 pC N $^{-1}$); and an almost hysteresis-free strain of more than 0.6% (19) have made ferroelectric relaxors a material of choice for high-end industrial applications, e.g., electromechanical transducers (20).

The evolution of polar structures is a key element for understanding relaxor behavior. Such evolution was addressed by various experimental techniques, including diffuse neutron scattering (5, 11, 21), acoustic emission (13, 15), and dielectric spectroscopy (3, 7). In the past decade, significant progress has been achieved by using scanning probe microscopy techniques that rely on direct contact between the relaxor surface and the metallic tip. Piezoresponse force microscopy (PFM) (22–24) has been especially successful because of its intrinsically high resolution and the ability to follow the polarization statics and dynamics via a local piezoresponse. Researchers have studied several classes of relaxor materials, including single crystals [e.g., SBN (25–28), $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - PbTiO_3 (PMN-PT) (29–40), and $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - PbTiO_3 (PZN-PT) (41, 42)], ceramics [e.g., $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ (PLZT) (43–45), PMN-PT (46), and some lead-free compositions (47–49)], and thin films (50–53). This review is devoted to the recent advances in PFM studies of relaxors and to a further understanding of the mechanisms of polarization behavior in these emergent functional materials.

2. METHOD

PFM is a modification of the contact atomic force microscopy (AFM) method developed to study ferroelectric materials on the nanoscale (54). The method is based on the detection of local electromechanical vibrations of a ferroelectric/piezoelectric sample caused by an external ac electric field applied between a conducting AFM tip and a counterelectrode (**Figure 2**). The deflection of a cantilever that oscillates together with the surface of the sample is detected by using a lock-in amplifier. Ferroelectric domains are visualized by monitoring the first harmonics of the deflection signal. Its amplitude, R , is proportional to the local longitudinal piezoelectric coefficient, and the phase φ reflects the polarization direction ($\varphi \sim 0^\circ$ if the probing electric field is parallel to the local polarization and $\varphi \sim 180^\circ$ if the electric field is antiparallel). By measuring the signal corresponding to a torsional deformation of the cantilever, one can obtain information about the distribution of in-plane components of the polarization. Thus, PFM allows for full reconstruction of the local polarization distribution. In the typical PFM experiment, the sharp AFM tip plays the role of a movable top electrode. Because the thickness of studied samples is usually much greater than the tip-sample contact area (5–20 nm), the probing electric field is strongly inhomogeneous, and the measured PFM response corresponds to a small volume below the contact point. The small area investigated provides a unique spatial resolution of the PFM method of the order of

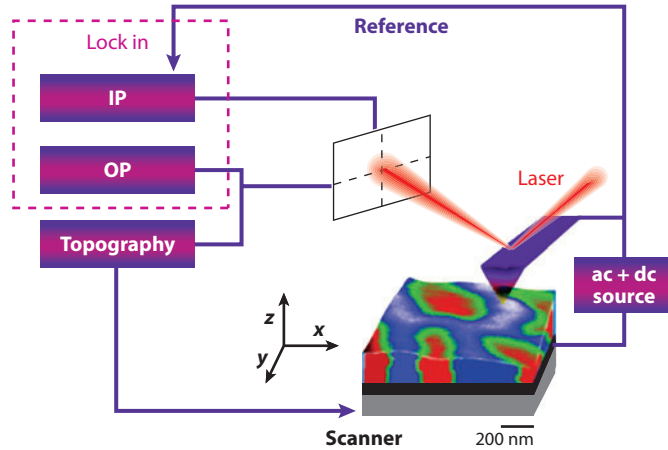


Figure 2

Schematic of the PFM setup as applied to relaxor ferroelectrics. A cantilever tip driven in the standard contact mode is used as a mobile electrode to apply ac and dc voltages and to measure out-of-plane (OP) and in-plane (IP) vibrations of the cantilever via a lock-in amplifier.

10 nm, depending on the tip and the applied force. Besides imaging, local polarization switching and corresponding hysteresis loops can be measured by sweeping the bias voltage followed by piezoresponse acquisition. Intrinsically high resolution and the possibility of temperature and temporal relaxation experiments make PFM an indispensable tool for the study of the nanoscale polar properties of relaxors.

3. PFM IN UNIAXIAL RELAXORS

3.1. Room Temperature Measurements

Strontium barium niobate ($\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$, abbreviated SBN100 x) has an unfilled tetragonal tungsten-bronze-type structure consisting of a framework of NbO_6 octahedra sharing corners in such a manner that three types of interstitial channels result: square $A1$ (occupied only by Sr^{2+}), pentagonal $A2$ (filled with both Sr^{2+} and Ba^{2+}), and triangular C ones (empty) (55). Because there are only five Sr^{2+} and Ba^{2+} atoms for six A positions, one of the A sites remains unoccupied. The randomly distributed charged vacancies result in structural and charge disorder. The most-ordered structure is expected in SBN20, in which all $A2$ sites are occupied solely by Ba^{2+} cations, whereas the Sr^{2+} ions and vacancies are randomly distributed on the $A1$ sites. Charge disorder progressively increases with increasing Sr content (56, 57); such increase correlates with the crossover from ferroelectric behavior to relaxor behavior in SBN with large x (58).

Taking into account that SBN is a uniaxial ferroelectric and cationic vacancies are sources of quenched random electric fields, SBN can be considered to be an example of a random field Ising model (RFIM) universality class (59). In this case, theory predicts the existence of a phase transition to a long-range ordered state (4). In reality, however, due to extreme, critical slowing down, the dynamic PNRs are expected to merely transform into a random field (RF)-controlled metastable domain state (4). A number of experimental works verified these theoretical predictions (59), but PFM measurements were indispensable for directly visualizing domain structure and for confirming the theoretical findings.

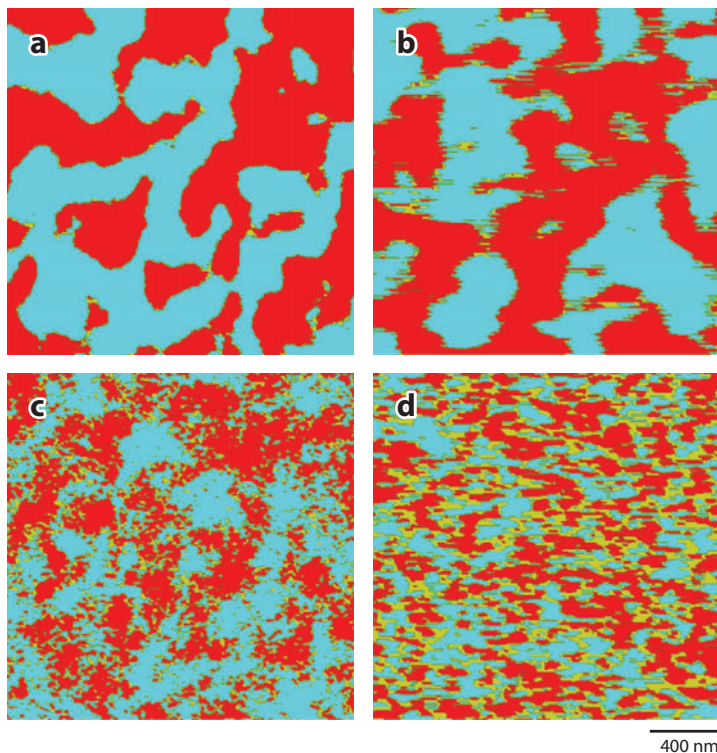


Figure 3

PFM images observed on *c*-cut SBN single crystals with various compositions: (a) SBN40, (b) SBN50, (c) SBN61, and (d) SBN75. The images are presented in a trimodal false color code. The blue and red colors correspond to domains with spontaneous polarization oriented up and down relative to the figure plane, respectively. The yellow contrast corresponds to regions with negligible piezoresponse. Reprinted with permission from Reference 22.

Figure 3 shows PFM images measured on *c*-cut SBN with different Sr/Ba ratios at room temperature (i.e., below the phase transition for all samples) (26). Ferroelectric SBN40 consists of relatively large domains with up and down polarizations. As the Sr content goes up, the domains become smaller, and their boundaries become progressively jagged; at the same time, regions with negligible piezoresponse take up a larger area. These piezoinactive regions were attributed to very fine polar structures; the PFM experimental conditions could not resolve sizes of less than 10 nm.

Although the domains are in reality three-dimensional structures, PFM probes their cross sections by a sample surface. These projections are actually two dimensional and should be described accordingly. The theory predicts that for two-dimensional RFIM systems the domain distribution, $N_S(S)$, follows the power law with exponential cutoff (60, 61):

$$N_S \sim S^{-\delta} \exp(-S/S_0). \quad 2.$$

Here $N_S dS$ is the number of domains within the range of areas $S \dots S + dS$, and S_0 corresponds to a cutoff size, above which the domains become rare. Both parameters S_0 and δ depend on the strength of RFs; i.e., S_0 decreases with increasing RFs, whereas the exponent δ approaches the value 1.55 in the limit of strong RFs.

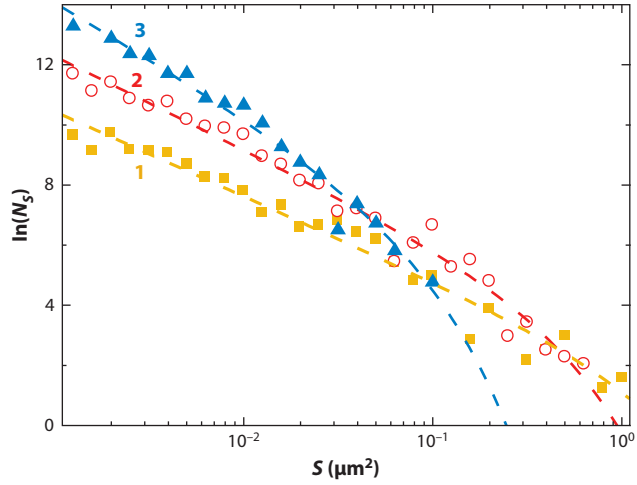


Figure 4

Domain-size distributions measured at room temperature on single crystals of SBN40 (1), SBN61 (2), and SBN75 (3). The broken lines are best fits to Equation 2. Adapted with permission from Reference 22.

Indeed, the $N_S(S)$ distributions evaluated from the PFM images can be well approximated by Equation 2 (**Figure 4**) (25, 26). Even ferroelectric SBN40 is characterized by a broad distribution of the domain sizes over three decades. With increasing Sr/Ba ratio, δ increases continuously from $\delta = 1.2$ in SBN40 to 1.6 in SBN75, whereas S_0 decreases from $1.1 \mu\text{m}^2$ in SBN40 to $0.05 \mu\text{m}^2$ in SBN75 (26). This tendency confirms that the effect of RFs becomes stronger in compositions with higher Sr content, which show stronger dielectric relaxation. Approximately the same value of the exponent δ has been found in both SBN75 (26) and SBN61 doped with only 1.1% of Ce^{3+} (25). This fact conforms to finding a substantially stronger effect of heterovalent substitution on relaxor properties due to different RFs for hetero- and isovalent doping.

As the domain boundaries in SBN are strongly jagged, they can be described by fractal analysis. For example, the domain perimeter L obeys the fractal equation $L^{1/D_H} S^{-1/2} = \text{constant}$, where the Hausdorff dimension of domain boundaries, D_H , increases with increasing Sr content (here S is domain area), as expected. A substantial deviation of D_H from the topological dimension, $D = 1$, is observed even in ferroelectric SBN40, in which 180° domains have strongly distorted shapes in comparison to those of conventional uniaxial ferroelectrics (62). Investigators thus confirmed by PFM that even compositions with low Sr/Ba ratios exhibit the behavior expected for RFIM systems with weak RFs. Apparently, polar disorder is enhanced progressively with increasing x , reflecting RF strengthening.

3.2. Polar Structures Close to T_C

PFM was then applied to investigate the evolution of polar structures around transition temperatures in SBN with $x > 0.6$ (26, 63, 64) and in Ce-doped SBN61 (25, 65, 66). For all these compositions, relatively large quasi-static regions of correlated piezoresponse were found on cooling from the paraelectric state above the nominal Curie temperature T_C (**Figure 5a,b**). The term quasi-static is applied, as both the shape and the location of these regions do not substantially change upon scanning; i.e., they are static on the PFM timescale of $t \approx 10^2\text{--}10^3$ s. The existence of correlated polarization could be easily verified by an autocorrelation analysis.

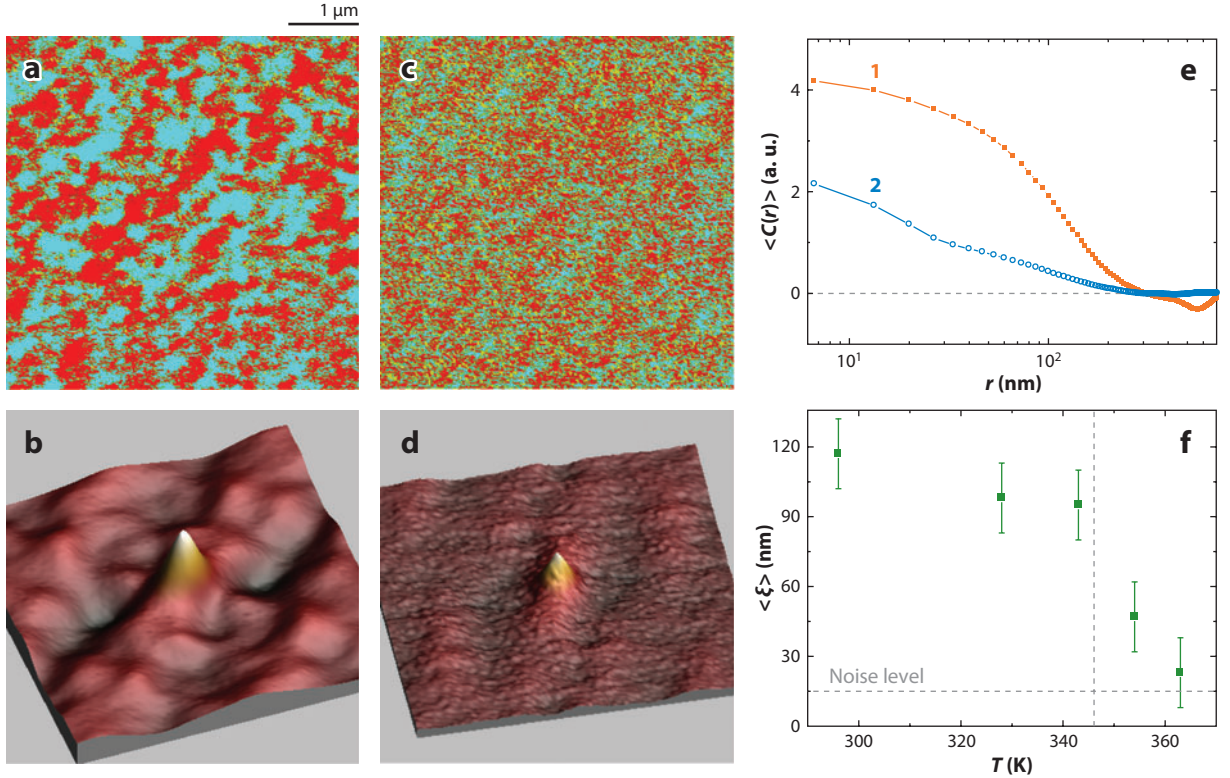


Figure 5

PFM and corresponding autocorrelation images of a SBN61 single crystal at (a,b) 295 K and (c,d) 354 K. (e) The autocorrelation function, $\langle C(r) \rangle$, averaged over all in-plane directions for SBN61 at 295 K (1) and 354 K (2). (f) Temperature dependence of the average correlation radius $\langle \xi \rangle$ of SBN61. From Reference 26.

Autocorrelation images, $C(r_1, r_2)$ (**Figure 5b,d**), were obtained from original PFM via autocorrelation transformation:

$$C(r_1, r_2) = \sum_{x,y} D(x, y) D(x + r_1, y + r_2), \quad 3.$$

where $D(x, y)$ is the value of the piezoresponse signal. The shape of the autocorrelation function provides information about the symmetry and regularity of the polarization distribution. In particular, the width of the central peak in the two-dimensional $C(r_1, r_2)$ map is a measure of the polarization correlation radius. To obtain a measure of the short-range polar order, autocorrelation function was averaged over all in-plane directions and then approximated by the function

$$\langle C(r) \rangle = \sigma^2 \exp[-(r/\langle \xi \rangle)^{2b}]. \quad 4.$$

Here r is the distance from the central peak, $\langle \xi \rangle$ is the average correlation radius, and the exponent b ($0 < b < 1$) is a measure of the roughness of the polarization interface (**Figure 5e**) (33). The autocorrelation function of a noise image (measured without ac voltage) also exhibits a central peak of a finite width, which is determined by the image resolution as well as by PFM parameters (e.g., scanning velocity, frequency, and time constant of the lock-in amplifier). Actually,

comparison of the width of the central peak measured with and without driving voltage was used as a criterion of the appearance of correlated polarization (26).

By using this method, quasi-static polar regions were resolved in SBN single crystals 15–30 K above their transition temperature. **Figure 5f** is a representative temperature dependence of $\langle \xi \rangle$ in SBN61. It appears above the resolution limit at $T \approx T_C + 15$ K and increases on cooling when T_C is approached. Below T_C , the piezoactive regions continue to grow, but less abruptly. The regions of correlated polarization observed in SBN above T_C were attributed to relatively large mesoscale domains. The small dynamic PNRs appear in these materials at 620–650 K (67, 68). On cooling, they grow, and at certain temperatures, some of them become frozen on the experimental timescale. These mesoscopic static domains are surrounded by piezoinactive regions, which may consist of still dynamic PNRs and, probably, of smaller static PNRs not resolved in PFM experiments.

The occurrence of static PNRs above the transition temperature provides evidence that in SBN the transition from the high-temperature (ergodic) relaxor state with pure dynamic PNRs to the low-temperature ferroelectric state does not occur at a fixed temperature. Instead, in a certain temperature range above T_C , the system contains both small dynamic and large quasi-static domains. The latter ones serve as precursors of conventional ferroelectric domains. Such an intermediate state has a nonergodic character, which was verified by the observation of aging, notably an isothermal decay of the dielectric permittivity, in the same temperature range above T_C , at which frozen PNRs were visualized by PFM (65). This aging may be related to the isothermal growth of static domains at the expense of dynamic PNRs. Recent measurements on SBN75 revealed a characteristic acoustic emission signal at $T^* = 455$ K (69). This phenomenon was attributed to the appearance of long-lived or permanent PNRs. It was suggested that T^* corresponds to a local mesoscopic phase transition, which precedes the global one due to RF fluctuations (17).

The existence of quasi-static PNRs above T_C may explain a long-disputed controversy between the experimentally observed critical behavior in three-dimensional RFIM systems and theoretical predictions (65, 70–72). Specifically, the experimental values of critical exponents are close to those theoretically predicted for the two-dimensional Ising model, but these values deviate strongly from those for three-dimensional RFIM systems. Kleemann et al. (65) suggested that the appearance of stable PNRs above T_C excludes true equilibrium criticality when T_C is approached. Although these large PNRs are frozen on a finite timescale, the unfrozen interfaces can be considered to be regions with short-ranged correlation of RFs. In these two-dimensional regions, which form a percolating network through the sample, a global phase transition takes place under the constraint of a weakly disordered quasi-staggered field (65). Correspondingly, such interface systems will preserve the critical behavior of the two-dimensional Ising model.

3.3. Local Polarization Dynamics

There are several reports on local polarization switching and domain dynamics in SBN single crystals. Liu et al. (27) measured temperature dependences of local PFM hysteresis loops of SBN61. Local hysteresis was observed above the nominal T_C . The authors related such hysteresis to the alignment of PNRs by the external electric field. Importantly, the hysteresis loops attained a strongly asymmetric shape above T_C ; this asymmetry was attributed to the effect of RFs becoming notable at the local scale. Gainutdinov et al. (73) found that the local hysteresis loops in SBN61 single crystals exhibit a gradual amplitude contraction on repeated voltage cycling. This effect correlates with the well-known macroscopic behavior of SBN (74, 75): Repeated field cycling produces shrinking P - E hysteresis loops with decreasing polarization amplitude. After several

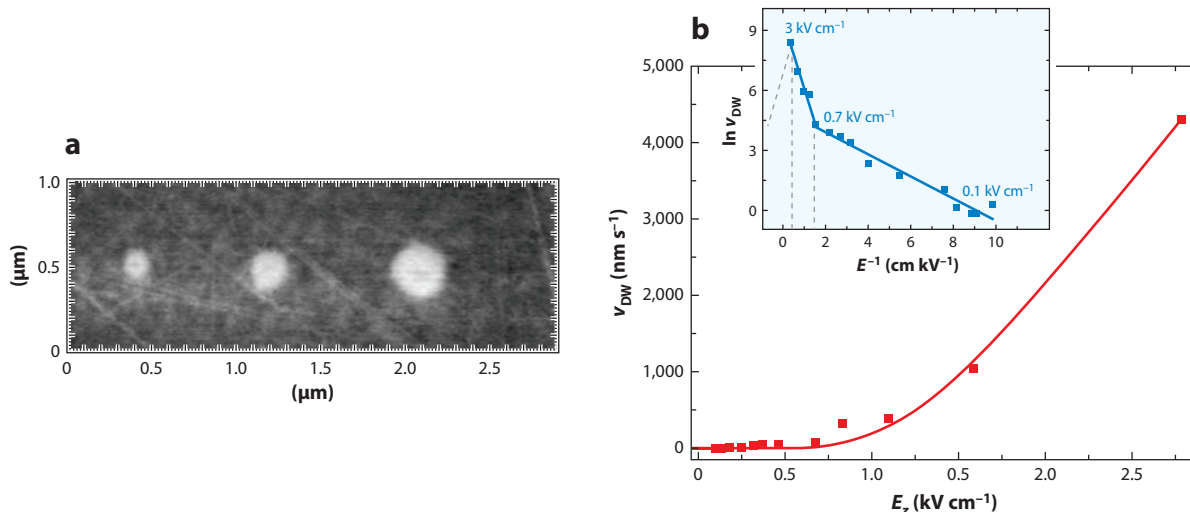


Figure 6

(a) PFM images of domains recorded in an Nd-doped SBN61 crystal sequentially with $t_p = 1, 10$, and 60 s, $U_{\text{dc}} = 10$ V. Adapted with permission from Reference 76. (b) Dependence of the velocity of lateral domain wall motion on the axial component of the electric field. The inset shows the approximation of the dependence $v_{\text{DW}}(E)$ by the activation law $v \sim \exp(-\frac{E_0}{E})$. Adapted with permission from Reference 80.

cycles, the loops become saturated with lower maximum P_s . Such a behavior was related to the domain-pinning effects characteristic of relaxors (4).

PFM experiments on domain nucleation (Figure 6) (76) revealed that the polarization reversal occurs at voltages corresponding to a field much lower than the coercive one, E_c . Moreover, the lateral expansion of the nascent domain continues even at low field ($E \ll E_c$), although it is extremely slow. Domain evolution in SBN relaxors may proceed by a mechanism different from that of domain nucleation on a plane–domain wall; the latter mechanism is postulated by the classical Miller–Weinreich model (77). The domain dynamics in relaxors are most likely affected by the RFs. Indeed, according to Kleemann (78), domain wall motion at low fields obeys the creep equation $v \sim \exp(-\frac{U_p}{kT}(\frac{E_0}{E})^\mu)$, where U_p is the characteristic pinning energy, T is the temperature, and E_0 is the depinning threshold field. The exponent μ depends on the dimensionality and nature of the pinning centers, e.g., random bond- or RF-type defects. In the RF scenario, $\mu = 1$ for two-dimensional domain walls (79). The experimental field dependence of the domain wall velocity measured by Volk et al. (80) on SBN single crystals follows $v : \exp(-\frac{E_0}{E})$, i.e., $\mu = 1$, which confirms the existence of RF-type defects in SBN61 (Figure 6). Moreover, they found an increase in the activation fields from $E_0 = 0.5$ kV cm⁻¹ to 3.3 – 3.4 kV cm⁻¹ when the applied field E exceeded E_c . This observation was interpreted as a crossover from the creep motion of domain walls in weak electric field to the motion via an activation mechanism at higher field (80).

4. PFM IN CUBIC RELAXORS

One of the largest and most-studied groups consists of cubic relaxors with the perovskite structure ABO_3 . In this case, relaxor behavior is closely related to the charge disorder caused by cations of different valencies randomly distributed over the equivalent crystallographic positions, i.e., Pb^{2+} and La^{3+} on A sites of PLZT and Mg^{2+} and Nb^{5+} on B sites of PMN.

Pure PMN is often considered to be a canonical relaxor. In this material, dynamic PNRs are believed to appear at $T_D \sim 600$ K (6). The interaction between PNRs and quenched random electric fields also results in a local mesoscale phase transition at $T^* \sim 500$ K; this transition is associated with the appearance of static PNRs (13, 17) coexisting with still dynamic ones. On further cooling, the slowdown of PNR dynamics—flipping of dynamic PNRs and breathing of the boundaries of static ones—results in a remarkable dielectric relaxation. Finally, at lower than the freezing temperature, T_f (220 K), the transition to a glassy-like state with a random orientation of local polarization takes place (7). A spherical random bond RF model describes this transition (81). According to diffuse neutron-scattering experiments (11), PNRs grow in size from a few nanometers near T_D to ~ 10 nm at T_f . The states above and below T_f are often termed ergodic and nonergodic relaxor states, respectively (2).

In solid-solution $(1 - x)\text{PMN}-x\text{PT}$, a crossover from relaxor to ferroelectric behavior occurs at $x > 0.35$. Compositions with $0.05 < x < 0.35$ combine both relaxor and ferroelectric features with strong dispersion of dielectric permittivity due to the existence of PNRs far above T_m in these compositions (5, 82). Interestingly, ceramics of these compositions exhibit a spontaneous transition to a ferroelectric state (83). In single crystals ($x < 0.27$), depth-resolved structural analysis revealed a cubic (unpolar) state within the bulk, whereas a rhombohedral ferroelectric phase (84) was observed within a skin layer a few tens of micrometers thick. In solid solutions with $x > 0.27$, a structural phase transition is observed over the entire sample. The symmetry of the low-temperature state changes from the rhombohedral phase at $0.27 < x < 0.3$ to the monoclinic phase at $0.3 < x < 0.35$ (85) and finally to the tetragonal phase at $x > 0.35$ (86).

4.1. PFM at Room Temperature

Figure 7 shows representative PFM images of PMN-PT100 x single crystals with different titanium concentrations at room temperature. In pure PMN, PFM reveals regions showing opposite polarization directions (**Figure 7a**) (39). Although these regions have fuzzy boundaries and show weak contrast (which is comparable to the noise level), such regions are static on the timescale of the PFM experiments (typically 5–20 min). These regions resemble frozen polar regions observed above T_C in SBN. Autocorrelation function analysis was applied to estimate the size of these regions. **Figure 7b** shows the corresponding autocorrelation image; the average correlation radius $\langle \xi \rangle$ estimated from the best fit to $\langle C(r) \rangle$ according to Equation 4 is ~ 46 nm (**Figure 8a**).

PMN-PT10 exhibits a stronger piezoresponse than pure PMN. A labyrinth-like pattern is clearly seen in **Figure 7c** (33). The size of these nanodomains varies from some tens of nanometers to 100 nm. Whereas the polarization image looks irregular, its autocorrelation counterpart shows a distinct oscillation of $C(r)$ along certain crystallographic directions, namely along $[110]_c$ (**Figure 7d**). This is a signature of the short-range order with some periodicity in this direction. In this case, the autocorrelation function can be represented as a sum of two contributions:

$$C(r) = \sigma^2 \exp \left[- \left(\frac{r}{\xi} \right)^{2b} \right] + (1 - \sigma^2) \exp \left[- \frac{r}{r_c} \right] \cos \left(\frac{\pi r}{a} \right). \quad 5.$$

Here the first term is analogous to Equation 4 and describes short-range correlations of polarization inside individual polar regions. The second term corresponds to long-range correlations whereby a is the period of the structure and r_c is the long-range correlation length, which reflects the regularity of the observed pattern. The best fit of the curve shown in **Figure 8b** yields the following values: $a = (180 \pm 40)$ nm and $r_c = (800 \pm 300)$ nm. The short-range correlation radius (averaged over all in-plane directions) is $\langle \xi \rangle \approx 70$ nm, which is $\approx 50\%$ greater than in pure

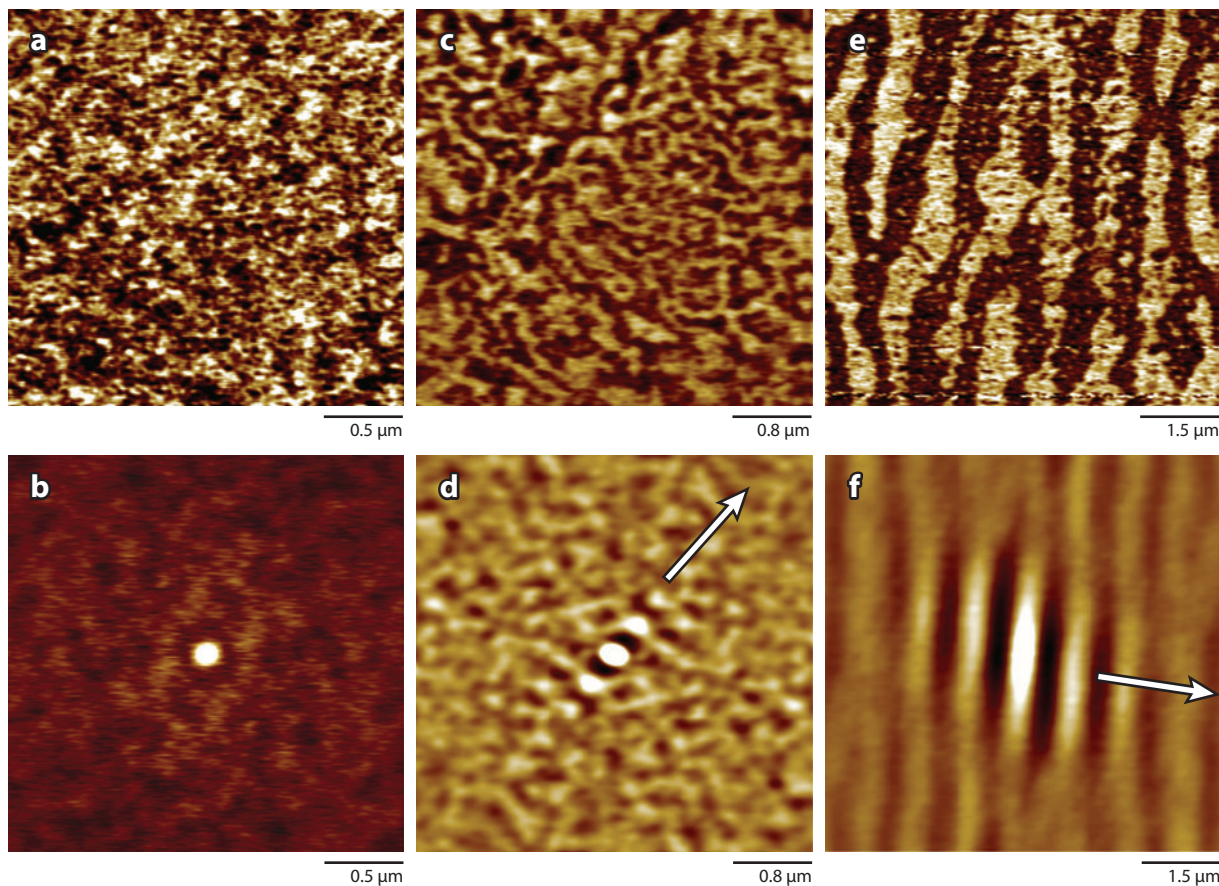


Figure 7

PFM images and corresponding autocorrelation images for (a,b) a (001) cut of PMN, (c,d) PMN-PT10, and (e,f) PMN-PT20 single crystals at room temperature. The arrows in panels d and f show the direction of pronounced oscillation of the autocorrelation function. Reprinted with permission from Reference 24.

PMN. The larger size of the polar regions is due to stronger polar correlations in PMN-PT10 [the measurements are done slightly above the transition temperature (~ 280 K for PMN-PT10)]. For compositions with $x = 0.20$, a quasi-regular domain pattern with domain walls oriented preferentially along the [110] direction was observed. A thorough inspection has revealed that these micrometer-sized domains are not uniform and consist of a large number of smaller nanometer-sized domains of opposite orientation embedded in big domains of both polarities (**Figure 7e**). The corresponding autocorrelation image is shown in **Figure 7f**. The long-range correlation length, r_c , is $\sim 2\text{--}2.5$ μm at room temperature and is approximately three times greater than that in PMN-PT10 (**Figure 8b**) due to progressively increasing ferroelectric ordering.

Domain configurations become more ordered in compositions with higher titanium content. **Figure 9** presents PFM images taken on a $\langle 001 \rangle$ cut of a PMN-PT29 crystal. On a large scale, two large twins with a width of ~ 50 μm are seen. They are composed of macroscopic micrometer-sized domains that form quasi-regular patterns. The different configurations of domain patterns—ribbon type and checkerboard type—reflect the different habit planes of the twins (**Figure 9a,b**). The magnified images reveal an internal structure that consists of smaller, less regular domains with

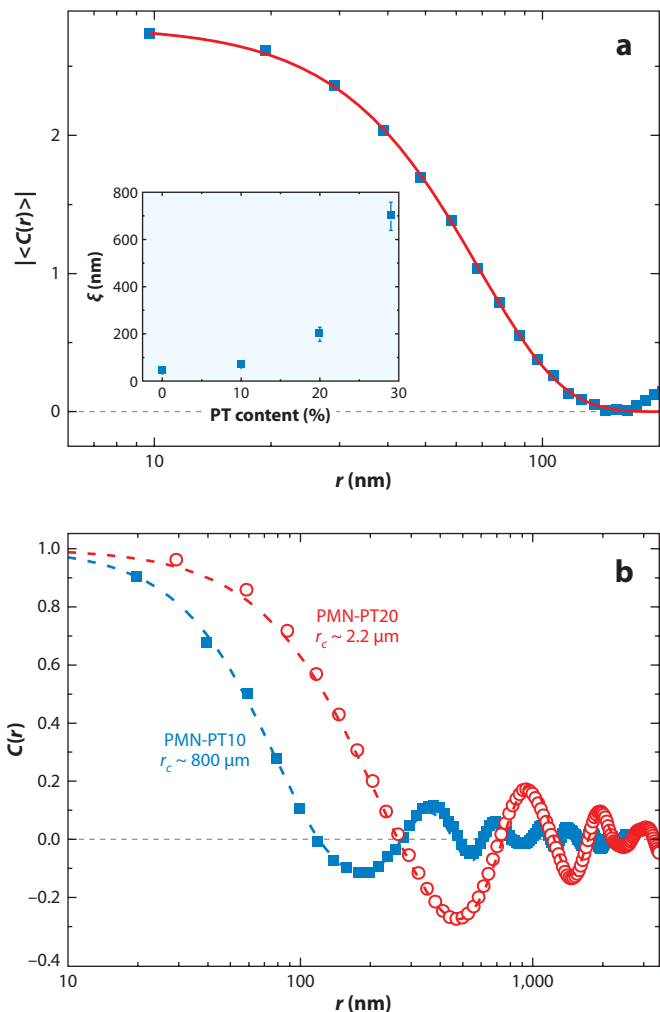


Figure 8

(a) The autocorrelation function, $\langle C(r) \rangle$, averaged over all in-plane directions for a PMN single crystal at room temperature. The solid line shows the best fit by Equation 4. The inset shows the variation of the average correlation length upon an increase in titanium content in PMN-PT% single crystals. (b) The autocorrelation function along the $\langle 110 \rangle$ direction for PMN-PT10 and PMN-PT20 single crystals. Adapted with permission from Reference 63.

sizes in the range from 100 nm to a few micrometers (**Figure 9c**). Similar hierarchical structures were reported for other PMN-PT crystals with high PT content (shown in **Figure 9d-f**) (30, 31, 37). For example, in monoclinic PMN-PT35 and tetragonal PMN-PT40, polar nanodomains self-assembled into $\langle 110 \rangle$ - and $\langle 001 \rangle$ -oriented striations, respectively, on a scale of $< 1 \mu\text{m}$ (30). These striations of alternating polarity in turn assembled into macrodomain plates, which are oriented close to the $\langle 001 \rangle$ direction. Hierarchical domain structures were also observed in relaxor $(1-x)\text{PZN}-x\text{PT}$ single crystals with $x \geq 0.045$ (41, 42, 87).

Bai et al. (31) argued that the observed complex domain hierarchy in perovskite relaxors is a result of interplay between three factors: mechanical stress relief, polarization compensation,

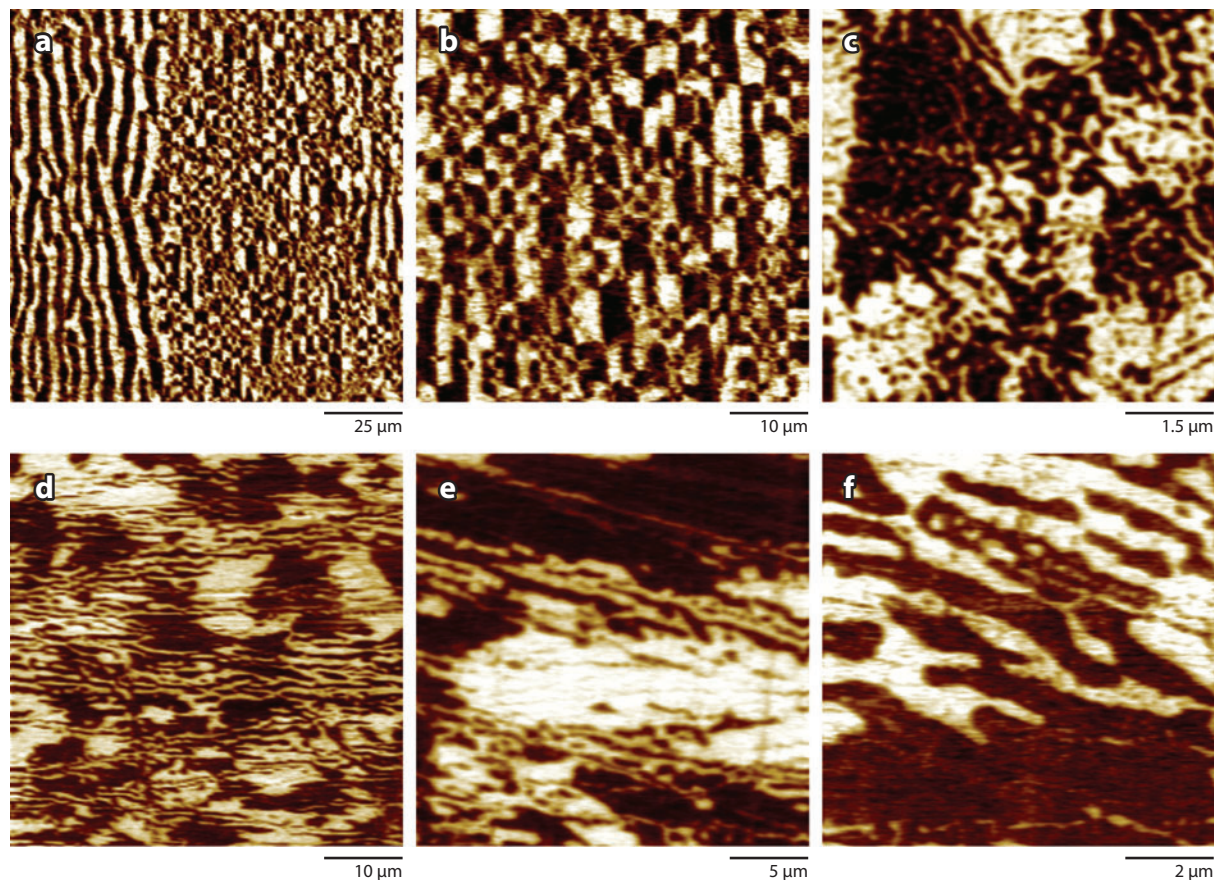


Figure 9

PFM images of (001)-cut (*a–c*) PMN-PT29 and (*d–f*) PMN-PT35 single crystals.

and random electric fields. Local rhombohedral distortions result in a mechanical mismatch between PNRs with different polarization orientations. Mechanical stress can be relieved by self-organization of PNRs into ordered patterns. At lower x (<0.2), self-organization is limited by RFs, and only mesoscale domains are observed with a short-range order. At higher x , to minimize the elastic energy, the domains assemble into colonies with different morphologies depending on macroscopic symmetry. Boundaries of these colonies are oriented along directions parallel to invariant planes: $\langle 110 \rangle$ and $\langle 010 \rangle$ for rhombohedral and tetragonal compounds, respectively (31). For PMN-PT, this pattern is observed starting from $x = 0.2$. It should be mentioned that the bulk of PMN-PT20 retains a cubic structure; however, its surface layer (actually probed by PFM) is rhombohedrally distorted. Complete strain accommodation in compositions with large titanium content is achieved via the formation of macrodomain plates and twins.

4.2. PFM Versus Temperature

Similar to the case for uniaxial SBN, the static nanodomains in perovskite cubic relaxors are observed above the nominal transition or freezing temperature, but in a substantially wider

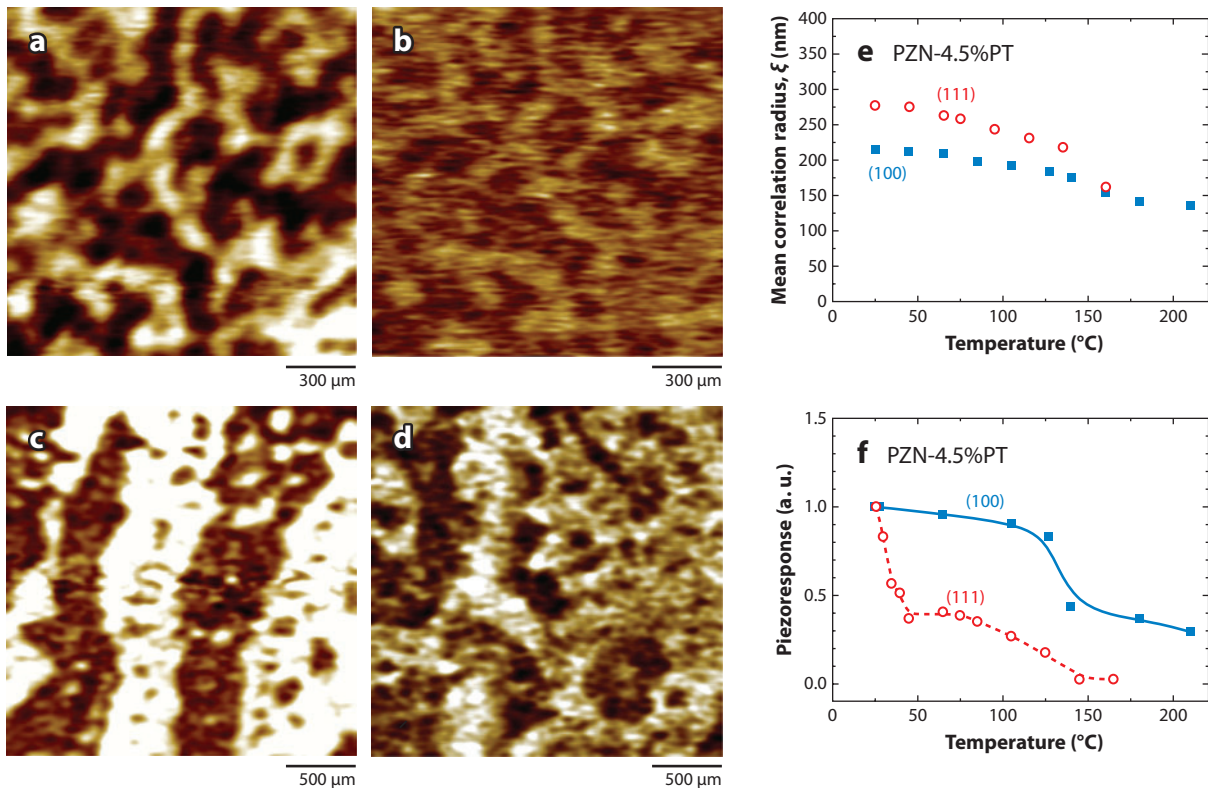


Figure 10

PFM images of a PMN-PT10 single crystal ($T_C = 280$ K) at (a) 295 K and (b) 335 K. PFM images of a PMN-PT20 single crystal ($T_C = 360$ K) at (c) 295 K and (d) 405 K. Panels *a–d* reprinted with permission from Reference 24. Temperature dependences of (e) correlation length and (f) local piezoresponse of PZN-4.5%PT single crystals with (100) and (110) orientations. Panels *e* and *f* adapted with permission from Reference 23.

temperature range. For example, in PMN the transition to the glassy state with frozen polarization is expected at 80 K below room temperature, but the domains are seen at room temperature.

Figure 10b shows a PFM image of a PMN-PT10 single crystal taken at 335 K (55 K above nominal T_C). Although the piezoresponse contrast is weaker and domain boundaries are more diffuse than those at room temperature, long-range correlations in the $\langle 110 \rangle$ direction are still observed. Individual regions of correlated polarization exist even at higher temperatures (≈ 385 K), while the average correlation radius, $\langle \xi \rangle$, drops from 70 nm (at room temperature) to 20 nm (at 385 K). Similarly, in PMN-PT20 (29), PMN-PT25 (32), and PMN-PT32 (34), nanodomains are found at up to 50–70 K above nominal T_C (**Figure 10d**). Such nanodomains are not arbitrarily distributed and form structures resembling domains observed at lower temperatures.

Kholkin et al. (23) performed a series of temperature- and depth-resolved experiments on PZN-4.5%PT single crystals and relaxor PLZT ceramics. These researchers confirmed that static nanodomains can be seen at ~ 100 K above the phase transition in PLZT8/65/35 ceramics being stabilized by the surface. The nanodomain patterns remained almost invariant during the variable temperature measurements, and no reconfiguration of the static labyrinthine domains

was observed. The correlation radius in both materials is only weakly temperature dependent. **Figure 10e** exemplifies the temperature dependence of the correlation radius in PZN-4.5%PT crystals. In comparison, the amplitude of the PFM contrast shows a more complex temperature dependence, with rapid decreases at ~ 320 K for the (111) surface and at ~ 405 K for the (100) surface and a high-temperature tail above these temperatures (**Figure 10f**). This behavior is explained by the existence of both the static and dynamic components of polarization. Static polarization corresponds to the amplitude of piezoresponse inside mesoscale domains, and dynamic polarization is related to the dc bias-induced piezoresponse, which relaxes with time after the bias is switched off. For the (111) orientation, the remanent dynamic polarization (derived from hysteresis loops) disappears at ~ 360 K. At the same time, for the (100) termination, the dynamic polarization persists to a much higher temperature. These observations clearly illustrate that surface termination strongly affects both the static and dynamic components of polarization in ergodic relaxors. The polarization correlations in relaxors with the perovskite structure are thought to develop in the (111) orientation. Correspondingly, on (111) surfaces, there are two possible up and down orientations that couple strongly to the normal electric fields (either due to the tip or due to the surface terminations), and there are six components with a much smaller normal polarization component. At the same time, on (100) surfaces, four equivalent up-oriented and four equivalent down-oriented polarization components are degenerate. Correspondingly, the near-surface electric fields can lift the degeneracy of possible polarization states for the (111) orientation, but not for the (100) termination (23).

One should also take into account that the relaxor single crystals (PMN-PT, PZN-PT) are spatially inhomogeneous materials. In PMN-PT ($0.05 < x < 0.27$) and PZN-PT, the transition to the rhombohedral state occurs in a surface layer, whereas the bulk remains macroscopically cubic. The nature of this phenomenon is unclear. The phenomenon may be related to a large mechanical strain existing near the surface in these materials (88). Such strain may stabilize the ordered state and shift the phase transition to higher temperatures such as those observed in PFM experiments.

The static nanodomains in relaxors, e.g., in PMN-PT10 single crystals and PLZT ceramics, are barely affected by an external electric field (23, 36, 38). At the same time, the applied bias substantially increases the PFM signal, which decays with time after the bias is switched off. This observation led to the proposal that two types of polarization, static (as observed via PFM contrast) and dynamic, coexist (36). The static mesoscale nanodomains were attributed to spatial fluctuations of polarization caused by the density fluctuations of PNRs having up or down dipole moment directions. The additional dynamic component of polarization is due to the response from dynamic PNRs, which are invisible on PFM images but contribute to a piezoresponse during the application of dc electric field. The static and dynamic polarization components demonstrate similar thermal behavior; however, the corresponding transition temperatures are different. The dynamic polarization is associated mainly with the surface, whereas static domains penetrate deeply into the crystal bulk (23). As mentioned above, the coexistence of the dynamic and static polarization components can be related to surface-induced phase transition and symmetry breaking due to strain relaxation, electric interaction, or more complicated coupling. Kholkin et al. (23) argued that the presence of the surface breaks the symmetry between possible polarization orientations in PNRs due to elastic interactions. This favors up and down dipole orientation, resulting in a transition from the cubic phase to the tetragonal phase. The associated lattice deformations are small, and hence the new state looks macroscopically cubic. The electrical interaction results in secondary breaking of symmetry in plane and the formation of 180° nanodomains (23). The formation of mesoscale nanodomain patterns was subsequently explained in the framework of Landau-Ginzburg thermodynamic theory (23). Although the domain walls are destabilized by RFs, a quasi-periodic domain structure is then formed as the result of the interplay between renormalized negative gradient

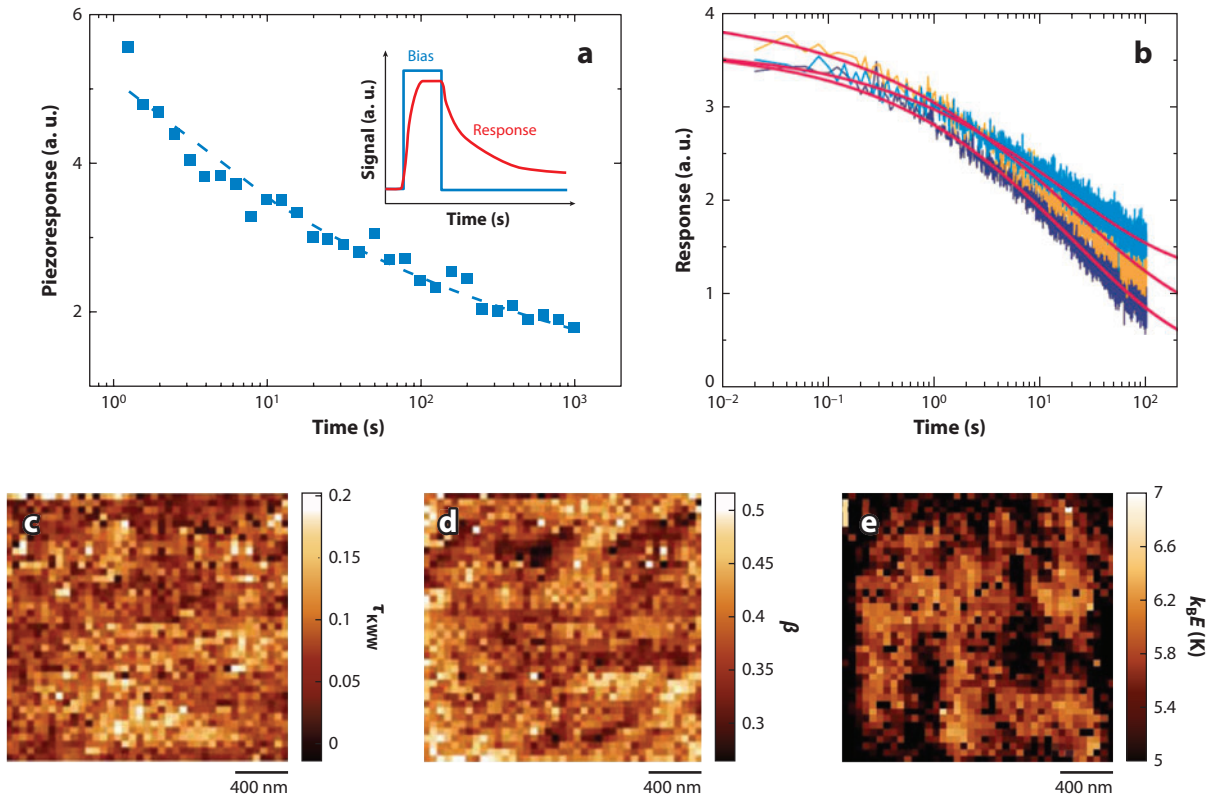


Figure 11

(a) Relaxation of the induced piezoresponse in a PMN single crystal after poling by a dc bias of 60 V for 1 s. The dashed line shows the best fit by Curie–von Schweidler dependence. The inset schematically demonstrates the concept of time-resolved spectroscopic PFM. Adapted from Reference 39. (b) Relaxation of the induced piezoresponse in a PMN-PT10 single crystal after poling by a dc bias of 10 V for 1 s fitted by the Kohlrausch-Williams-Watt (KWW) law. Adapted with permission from Reference 36. Spatially resolved mapping of (c) KWW relaxation time, (d) KWW exponent β , and (e) activation energy for a PMN-PT10 single crystal. Panels c–e reprinted with permission from Reference 36.

terms and higher-order terms (which become relevant) in the free-energy expansion of the order parameter. Thus, PFM measurements revealed a new mechanism of polarization ordering on the surfaces of relaxors.

4.3. Local Polarization Dynamics

Conventional PFM images are acquired at low field as static or quasi-static polar structures. To probe dynamic PNRs, which are mainly responsible for the large dielectric permittivity in relaxors, a time-resolved spectroscopic PFM mode has been applied. In this case, a dc bias pulse of specified magnitude and duration is applied locally, and the relaxation of the induced piezoresponse signal is measured either in an on (writing) state or in an off (readout) state (see inset in **Figure 11a**).

Various reports concern the functional form of piezoresponse relaxation in relaxors. For example, in PFM experiments performed on 0.9PMN-0.1PT crystals (35, 36) and on PMN thin films (51), Kohlrausch-Williams-Watt (KWW)-type, $d_{zz}(t) \sim \exp[-(t/\tau)^\beta]$, or logarithmic

$d_{zz}(t) \sim d_0[1 - b\ln(t/t_0)]$ time dependences of induced piezoresponse were observed (see **Figure 11b**). This relaxation was attributed to flipping of dynamic PNRs aligned by applied bias back to the initial disordered state. KWW-type behavior is a result of the distribution of relaxation times of elementary Debye processes. The exponent $0 < \beta < 1$ is a measure of the width of this distribution; smaller β implies broader relaxation spectra. In particular, the β value obtained in PFM experiments on 0.9PMN-0.1PT single crystals is considerably larger ($\beta = 0.3\text{--}0.4$) than the macroscopic β value evaluated from the dielectric relaxation experiments (36). This finding is expected because PFM yields local parameters that characterize the relaxation time distribution inside the nanoscale volumes of ~ 30 nm in depth. At the same time, a heterogeneous spatial distribution of local relaxation characteristics provides a broad macroscopic distribution of relaxation times.

To gain insight into the spatial variations of relaxation parameters and to relate them to observed static nanodomains, Kalinin and coworkers (36) performed extensive PFM relaxation experiments on a densely spaced grid of points (with 50–100-nm mesh size) in PMN-PT10 crystals. Piezoresponse relaxation followed KWW-type dependence. For the writing experiments, distributions of the relaxation parameters, τ_{KWW} and β , are featureless, indicating a spatially uniform relaxation process. At the same time, relaxation upon polarization readout is characterized by the coexistence of fast and slow relaxations on the length scale of ~ 100 nm (**Figure 11c**). The characteristic relaxation time differs by one order of the magnitude between these regions. The distribution of the exponent β for the zero-field experiments (**Figure 11d**) is also broad. From the obtained relaxation parameters, the distribution of activation energies can also be evaluated (**Figure 11e**). As we discuss above, the induced piezoresponse in relaxors is due mainly to the reorientation and coarsening of dynamic PNRs under writing dc field. These PNRs relax back to their initial disordered state, and spatial variation of the local relaxation parameters is thus a signature of the frozen random electric and elastic fields as well as of random interactions between the PNRs themselves (36).

Another type of relaxation was recently observed in PMN crystals (39). Specifically, the piezoresponse follows a power or Curie–von Schweidler (CvS) dependence, $f(t) = (t/\tau_{\text{CvS}})^n$ (**Figure 11a**) (39). Similar CvS time decay was seen in macroscopic birefringence studies of polarization relaxation in PMN single crystals (89). A crossover from KWW-type relaxation to a faster power law on increasing poling voltage was found in PMN thin films (51).

Switching spectroscopy PFM was recently performed on PMN-PT relaxors (37, 38). In these experiments, the local hysteresis loops are acquired on a grid of points, and the spatial distributions of several parameters, such as remanent piezoresponse, work of switching, and positive nucleation bias (PNB) and negative nucleation bias (NNB), are analyzed. In ferroelectrics, polarization switching occurs via domain nucleation and subsequent domain growth through domain wall motion. However, in relaxors, the polarization reorientation proceeds through the gradual evolution and decay of PNRs driven by the external dc field. Therefore, the local hysteresis loops have a characteristic diamond shape, with a relatively constant response at small dc biases and a linear increase in response at larger field (37). By comparing PNB and NNB, one can define a stability gap, $\text{PNB} - \text{NNB}$, or a built-in electric field, $\text{PNB} + \text{NNB}$. The first parameter is a measure of the stability of the bias-induced state. It is close to zero and may be even negative in relaxors above the freezing temperature, indicating that the induced polar state is unstable. In contrast, in ferroelectrics the stability gap is always positive. The built-in fields are related to local defects, e.g., frozen electric RFs and mechanical stresses. The spatial distribution of these fields does not reveal a direct correlation to the static nanodomain pattern (38). This distribution may indicate that these static nanodomains are not necessarily coupled to the random electric fields and may have another origin, as is discussed above.

4.4. Polycrystalline Relaxors by PFM

The investigation of polar structures in polycrystalline relaxors is of special interest. In this case, the microstructure of the samples, e.g., grain size effect and grain boundaries, plays an important role, thus allowing PFM to be used to study these effects via apparent domain structure. It has long been known that the dielectric properties of ferroelectric ceramics are dependent on their average grain size. For example, Arlt et al. (90) reported that the dielectric constant in BaTiO_3 ceramics first increases with decreasing grain size d , then passes a pronounced peak at $d \approx 1 \mu\text{m}$, and finally sharply declines in a fine-grained material. This effect imposed a serious limitation on the application of these materials in multilayer capacitors, in which submicrometer grain size is required to decrease the separation between inner metallic electrodes. Ferroelectric behavior is also strongly influenced by the grain/particle size; specifically, the ferroelectric properties disappear at some critical size, accompanied by a strong decrease in T_C (91). Why properties strongly deteriorate with decreasing grain/particle size is not well understood, as many extrinsic and intrinsic factors influence this behavior (91). For example, the dielectric constant effect has been attributed either to increased residual internal stress in submicrometer grains (92) or to enhanced domain wall contributions to the dielectric response (90). Also, severe damage during the prolonged milling or sintering processing steps and the formation of a surface layer with reduced properties, the so-called dead layer (93), are apparent sources of size-induced phenomena.

The situation is much more complicated in relaxor ceramics. Because PNRs are extremely small, relaxors, at first sight, should not be susceptible to size effects, even in fine-grained ceramics. However, there are contradictory experimental data on grain size dependencies of macroscopic properties, such as dielectric permittivity and the piezoelectric effect, in thin films and fine-grained ceramics. Tyunina et al. (94) found that 150–450-nm-thick 0.68PMN-0.32PT relaxor thin films have properties similar to those of single crystals. Nagarajan et al. (95) reported that decreased thickness of 0.9PMN-0.10PT thin films is accompanied by an increase in dielectric permittivity. In PMN-PT ceramics with relatively large (>20%) titanium content, a crossover from ferroelectric-like to relaxor-like dielectric behavior occurred for decreasing grain size (96, 97). In contrast, the progressive disappearance of relaxor-specific relaxation below a grain size of $\sim 30 \text{ nm}$ as well as a decrease in permittivity were observed in pure PMN ceramics. These observations were interpreted as a consequence of the transition from interacting PNRs to independent relaxing entities (98). The ability of PFM to probe local properties inside grains provides an excellent opportunity to study various size effects at a scale down to several tens of nanometers and to reveal their underlying mechanisms.

Figure 12a shows an example of the polar structure observed by PFM in PLZT ceramics with a lanthanum concentration of $x = 9.75\%$ (43, 44). As the figure shows, 180° nanodomains form a complex labyrinth structure. Applying the autocorrelation function analysis (see the above sections), one can determine the correlation radius, ξ , within an individual grain. The relatively large grain size of the PLZT ceramics allows one to determine ξ as a function of the coordinate inside the grain. The correlation radius varies: The value is greater in the center of the grain and gradually decreases as the grain boundary is approached (**Figure 12b**) (44). Such behavior indicates that polarization disorder notably increases at the grain boundary (the most significant variation is at $\sim 1\text{--}1.5 \mu\text{m}$). Several reasons can qualitatively explain this observation. First, there is a compressive mechanical stress that arises at the grain boundaries upon cooling from the sintering temperature. The stress is due to directional differences in thermal expansion coefficients, plastic deformation, or elastic properties. In ferroelectric materials, the stress may also appear due to structural distortion arising upon the ferroelectric phase transition. As Samara (99, 100) showed, the application of compressive hydrostatic pressure to relaxors leads to an apparent decrease in

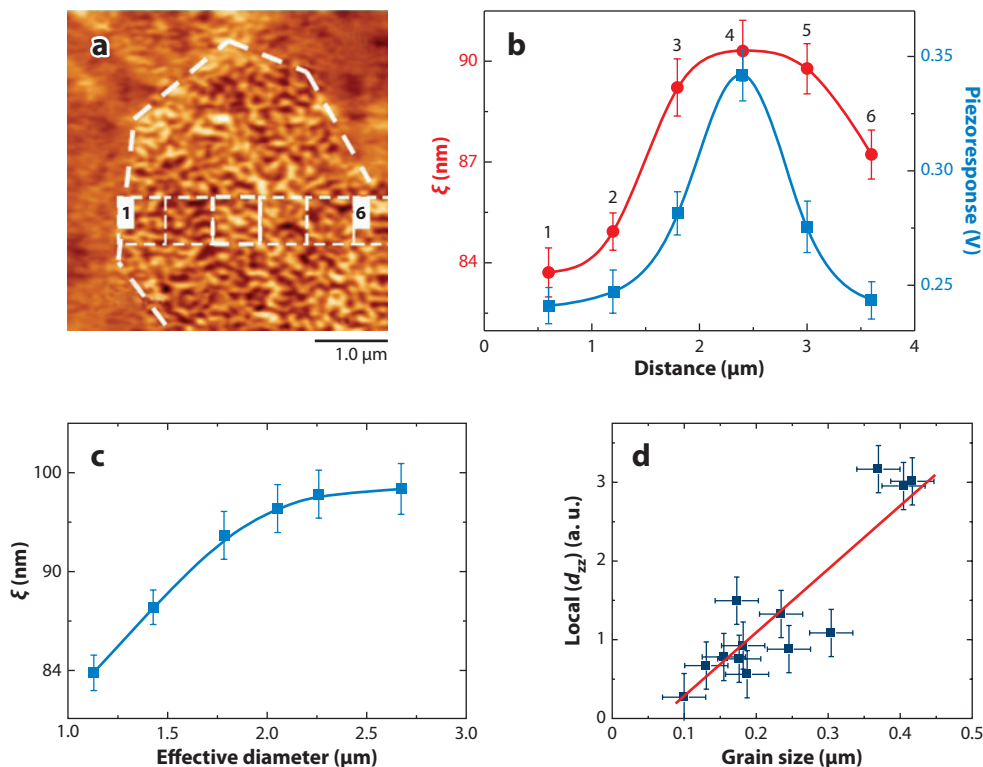


Figure 12

(a) Representative PFM image of the relaxor grain in PLZT9.75/65/35 ceramics with marked squares 1–6 for the autocorrelation analysis. (b) Spatial dependence of the average piezoresponse (blue squares) and correlation radius (red circles) across the grain shown in panel a. (c) Average correlation radius versus grain diameter in PLZT9.75/65/35. (d) Size effect in PMN-PT10 thin films prepared by pulsed laser deposition. Adapted with permission from References 44 (panels a–c) and 49 (panel d).

the correlation radius, i.e., to decreased PNR size. This results in a shift and broadening of the dielectric maximum in several relaxor systems, including PLZT (100). The spatial dependence of the correlation radius reported by Kiselev et al. (44) is consistent with the mechanical pressure effect (100) and may thus be responsible for the grain size effect in PLZT ceramics: Fine-grained PLZT ceramics exhibit a much more diffuse phase transition than do coarse-grained samples (101). An alternative explanation for the observed spatial dependence of the correlation radius is the composition gradients across the grain. Indeed, Lin & Chang (102) reported the segregation of defects and second phases at PLZT grain boundaries during hot pressing under PbO excess. This resulted in a gradient of the lanthanum concentration as the grain boundary was approached. This behavior may, in turn, lead to a variation in the correlation radius, as lanthanum substitution disrupts long-range ferroelectric order and leads to a pronounced diffuseness of the phase transition.

Because the correlation radius is sensitive to the position inside the grain, it is natural to expect that its value taken on a larger scale (of several micrometers) will also depend on the grain size. The correlation radius as a function of the grain size is shown in **Figure 12c**. The correlation radius is ~ 80 nm for fine grains and rapidly increases to ~ 100 nm for 2–3- μm grains. These data are consistent with those shown in **Figure 12b**, which demonstrate the spatial

dependence of the correlation radius. These results are in perfect agreement with previous reports on the dielectric size effect in PLZT ceramics (101). Thus, the PFM measurements in relaxor ceramics give a clear insight into the origin of the deterioration of the dielectric response with decreasing grain size. Indeed, in small grains one can expect a smaller average correlation radius and greater variation across the grain. Therefore, the local phase transition and freezing temperatures should also be inhomogeneous inside the material, giving rise to a broad distribution of relaxation times and thus to a broad dielectric peak. Recently, this technique was further improved by using local two-dimensional fast Fourier transform (FFT) on a $3,000 \times 3,000$ -pixel PFM image (45). Local FFT parameters, such as PFM amplitude, correlation radius, width of the spectrum of spatial correlations, and eccentricities, were mapped in PLZT along with the conventional topography. The results are important for understanding the role of grain boundaries and the inhomogeneous defect distribution in the macroscopic response.

4.5. Visualization of the Relaxor-Ferroelectric Phase Transition

Understanding the effect of the electric field on the relaxor state is important for both fundamental physics and applications. Indeed, the reported giant piezoelectric effect in relaxor-based compounds was connected with so-called polarization rotation, which results in the appearance of a large strain under the applied electric field when the boundary between the tetragonal and rhombohedral phases through the intermediate monoclinic phase is traversed in the compositional phase diagram (103). Interestingly, the piezoelectric coefficients were maximal not at zero field but rather at a finite electric field value (104). The presence of the maximum of the piezoeffect versus E was explained by the critical behavior of the system near the quasi-vertical phase boundary and by the critical end point in the E - T phase diagram (105). In case of PMN, a ferroelectric phase transition can be induced below ~ 210 K (which is very close to T_f) when an electric field higher than a threshold value $E > E_t \cong 1.8 \text{ kV cm}^{-1}$ is applied along the $[111]$ direction (7). This effect is not only temperature dependent but also time dependent, and the appearance of the ferroelectric state was confirmed by both low-temperature hysteresis and time-dependent dielectric measurements in PMN single crystals (106, 107).

By using PFM, it was possible not only to detect the transition but also to visualize the shape of the ferroelectric island embedded into the sea of PNRs and to follow the island's temporal and electric field evolutions (108, 109). This approach was followed in PMN-0.23PbSc $_{1/2}$ Nb $_{1/2}$ O $_3$ solid solutions, which have properties intermediate between those of relaxors and ferroelectrics. Indeed, in this system a ferroelectric phase can be easily triggered by a rather weak electric field applied between the tip and the bottom electrode. The locally applied electric field is believed to increase the temperature of the ferroelectric phase transition, as expected in the case of a first-order-like transition. More interestingly, after the poling with an inhomogeneous (local) field produced by the tip, well-defined ferroelectric domains exhibiting a strong piezoelectric response were observed (**Figure 13**). In particular, the domains appear as sectors with a cylindrical domain in the center initiated by the electric field produced by the tip. This cylindrical domain is surrounded by four domains in which a $[111]$ -type polarization is stabilized and compensated by the charge provided by the tip. These findings show that domain engineering is feasible at a local scale, which opens up new perspectives. These studies (108) also revealed that the domain structure is more compact in the case of long poling pulses than in the case of short ones and that the increase in the pulse duration results in two distinct jumps of the domain size above certain threshold values. This behavior resembles that reported by X-ray diffraction measurements in the nonergodic state of PMN (110) below the freezing temperature. Indeed, by keeping the sample at fixed temperature

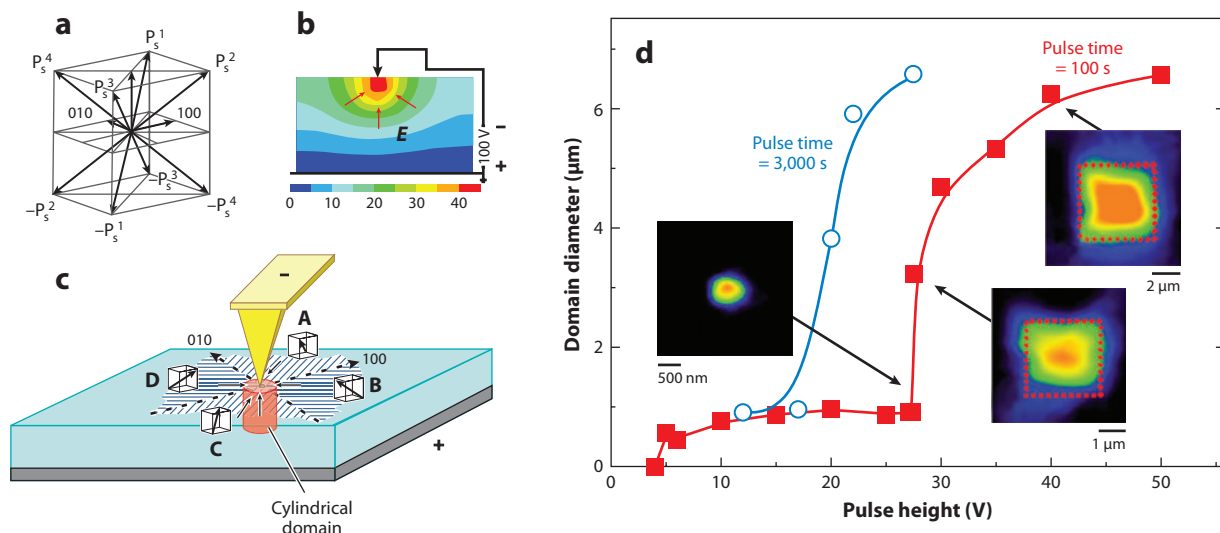


Figure 13

(a) Schematic of the possible polarization orientations in a (001)-oriented rhombohedral crystal. (b) Electric field distribution in PMN-23PSN explaining a local phase transition. (c) Possible domain orientations (A–D) after poling along the [001] direction by the tip. (d) Field-induced domain size versus applied voltage. Insets show the corresponding out-of-plane PFM images. Adapted with permission from Reference 109.

and electric field values, the nucleation of new domains with similar size occurs until a percolation-like effect occurs, allowing for domain size growth after an incubation time.

5. CONCLUSIONS

Thanks to the recent advancements in PFM methods, it is now possible to visualize peculiar mesoscale domain patterns and to follow the temperature evolution, time evolution, and electric field evolution of the polarization on the relaxor surface. PFM studies have unambiguously revealed the relevance of such mesoscale polar correlations to the underlying phenomena in ferroelectric relaxors such as the coexistence of several order parameters, the complex interactions between reorientable PNRs, static mesoscale domains, and true ferroelectric long-range polarization complicated by interactions between them and random electric fields and strains. The observed complex domain structure with a labyrinthine-like arrangement that coexists (in solid solutions) with more organized ferroelectric domains seems to be chaotic at first glance. However, image processing revealed polar correlations that indicate a subtle organization of the polarization contrast. This organization is affected by (a) the crystallographic orientation, (b) the strain/stress arising near the surface (the so-called skin effect), (c) the grain boundaries and the atomic arrangements, and (d) the random electric fields due to the inherent random ionic distribution.

A proper understanding of the relaxor state requires consideration of both PNRs and the quenched random electric fields arising by ionic distribution. When polarization appears at T_D , it is purely dynamic. By cooling toward room temperature, static (at least on the PFM measurement timescale) PNRs and dynamic PNRs coexist. Static PNRs are believed to form at T^* and to be accompanied by local strains. This state survives several tens of degrees above the temperature of the critical phase transition or the freezing temperature. Interestingly, static (or frozen) PNRs are not (or are hardly) switchable under an external electric field compared with dynamic PNRs (23).

Frozen PNRs arrange themselves by accommodating the inherent random electric fields and strains. It is believed that the presence of the surface breaks the symmetry between possible orientations of the PNRs due to elastic interactions. As a result, the mesoscopic behavior needs to be described by two effective order parameters to take into account both static polarization and dynamic polarization (23). RFs destabilize classical domains, which break into smaller domains. The slow dynamics of these small domains are directly responsible for the relaxation behavior in the induced polarization and hysteresis loops observed above the transition temperature. As we show above for two major classes of relaxor materials, a novel method—PFM—can serve as an excellent tool for studying the complex interplay of polarization, stress/strain, and various defects on the relaxor surface.

DISCLOSURE STATEMENT

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