POLAR STRUCTURES OF $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - PbTiO_3 RELAXORS: PIEZORESPONSE FORCE MICROSCOPY APPROACH

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Received 9 February 2012

Revised 7 March 2012

Published 15 June 2012

Relaxor ferroelectrics are one of the mysterious objects of the solid-state physics studied over 50 years. The physical properties of relaxors were mainly assessed by scattering and dielectric methods and revealed the importance of polarization correlations with the short-range order, so-called polarization nanoscale regions. This paper review recent progress achieved by using piezoresponse force microscopy (PFM) to analyze the spatial distribution of polarization and its evolution with time, temperature, and electric field for the most popular relaxor family: solid solutions between $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and PbTiO_3 . The PFM technique has proved to be a powerful tool for the investigation of local properties of relaxors where optical techniques obviously fail because of their lack of resolution. The PFM study of relaxors clearly helps to understand the mechanism of polarization distribution and illustrates the importance of mesoscopic polarization patterns that were until now overlooked by major theories of the relaxor state.

Keywords: Ferroelectrics; relaxors; piezoresponse force microscopy; domains.

1. Introduction

Being discovered about 60 years ago¹ relaxor ferroelectrics (relaxors for short) continue to be of significant interest for scientists and engineers due to their exceptional dielectric and electromechanical properties as well as a fascinating physics behind.^{2–4} Characteristic features of relaxors are (i) a significant frequency dependence of their peak permittivity, (ii) absence of macroscopic spontaneous polarization after zero-field cooling along with (iii) persistence of the local polarization far above the peak of the dielectric permittivity, T_m .² This local

polarization is correlated on a nanometer scale becoming apparent in polar nanoregions (PNRs), which appear at the “Burns” temperature T_D (typically $T_D \gg T_m$).⁵ Relaxor behavior has been observed for different structures ranging from disordered perovskites, e.g., $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$, to tetragonal tungsten bronzes (e.g., $(\text{Sr},\text{Ba})\text{Nb}_2\text{O}_6$) and is always accompanied by a structural disorder, i.e., occupation of the same crystallographic sites by different ions. The structural and related charge disorder is considered to be the origin of quenched electric random fields (RFs).^{3,6} On the one hand, the RFs promote nucleation of PNRs below T_D .⁶ On the

other hand, the quenched RFs conjugate to the order parameter may destroy the transition into long-range ordered state.⁷ At high temperatures the PNRs behave as dynamical entities with dipole moments thermally fluctuating between equivalent polarization directions. It is exactly the relaxation of these PNRs in a weak *ac* electric field that gives rise to the extremely large dielectric permittivity of relaxors. At low temperatures the interaction between the PNRs results in a slowing down of their dynamics and finally in a transition into a glassy-like state. In the glassy state the dipole moments of the PNRs are frozen and polar order becomes short-ranged: polarization is correlated on the nanometer scale inside the PNRs, but on a macroscopic scale the system remains nonpolar. A ferroelectric state may be induced in relaxors when poled in an electric field larger than a critical strength.⁸

Among the most studied relaxor compounds are solid solutions $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\text{PbTiO}_3$ (PMN–PT) with the perovskite type structure (general formula ABO_3). Pure PMN is often considered as a canonical relaxor. In this material PNRs are detected at ~ 600 K.⁹ According to the diffused neutron scattering experiments¹⁰ the PNRs grow on cooling from few nm near T_D to ~ 10 nm below the freezing temperature, T_f (220 K), where transformation into a glassy-like state with random orientation of the local polarization takes place.¹¹ This transformation can be described by a spherical random bond random field theory.¹² Between T_D and T_f the PNRs have a dynamical character and can be easily reoriented in a weak electric field.² To distinguish this state from paraelectric one it is termed as ergodic relaxor phase, while the state below T_f is called nonergodic relaxor state.² Recently, another characteristic temperature, so-called T^* , has been discovered above the freezing temperature.^{13,14} It was argued that this temperature corresponds to the appearance of static PNRs.¹⁴

The introduction of ferroelectrically active Ti^{4+} cations in PMN–PT solid solutions increases the size of the PNRs due to increases in off-center displacements, thereby enhancing interactions between them leading to breaking of the macroscopic cubic symmetry.¹⁵ From neutron diffraction data it is determined that the symmetry of PMN–PT remains cubic (macroscopically nonpolar) in the whole temperature range up to $x = 0.25-0.27$.¹⁶ However, diffraction studies using X-rays of variable energy revealed that for compositions as low as

$x = 0.05-0.10$ a transformation to a state with the rhombohedral symmetry occurs in a surface layer, which is a few tens of microns thick. At the same time the interior region of the samples remains macroscopically cubic.¹⁷ In solid solutions with $x > 0.27$ the structural phase transition is observed over the entire sample. The low-temperature state has a rhombohedral symmetry at $0.27 < x < 0.3$, a monoclinic one at $0.3 < x < 0.35$,¹⁸ and a tetragonal one at $x > 0.35$.¹⁹

The evolution of polar structures is a key element to understand relaxor behavior. It was addressed by various experimental techniques including diffuse neutron scattering,¹⁰ acoustic emission,¹⁴ etc. Recently, significant progress has been achieved in the investigation of relaxors by scanning probe microscopy techniques, namely piezoresponse force microscopy (PFM).^{20,21} Studied relaxor materials were $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ and $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3-\text{PbTiO}_3$ single crystals,^{22,23} $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ ceramics,²⁴ PMN–PT thin films, etc.²⁵ But the most thoroughly investigated were PMN–PT single crystals.^{26–35} Here we overview the most important results achieved by PFM methods in PMN–PT relaxors.

2. Method

PFM is a modification of the contact atomic force microscopy (AFM) developed to study ferroelectric materials on the nanoscale.³⁶ The method is based on the detection of local electromechanical vibrations of a ferroelectric sample caused by an external *ac* electric field applied between a conducting AFM tip and a counter electrode. The deflection of a cantilever that oscillates together with the surface of the sample is detected 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 $\sim 180^\circ$ if it is antiparallel). By measuring the signal corresponding to a torsional deformation of the cantilever one can get information about distribution of in-plane components of the polarization. Thus, PFM allows full reconstruction of the polarization distribution. The probing voltage, V_{ac} , is usually chosen to be high enough in order to cause the measurable signal but it

should be sufficiently small to prevent polarization switching and domain wall motion. In the typical PFM experiment the sharp AFM tip plays the role of a movable top electrode. Since usually the thickness of studied samples is much larger 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 around the contact point. This provides a high spatial resolution of the PFM method, 10–50 nm depending on the tip and the applied force. Besides imaging the local polarization switching and corresponding hysteresis loops can be measured applying sequences of voltage pulses with variable height and acquiring the piezoelectric signal after each pulse.

3. Polar Structure *versus* Composition: From Nanodomains to Hierarchical Structures

Already in pure PMN single crystals PFM studies carried at room temperature revealed regions of predominately negative and positive piezoresponse (Fig. 1(a)).³⁷ While having fuzzy boundaries and showing rather weak contrast against a noise background, these regions are definitely static on the

time scale of the PFM experiment (typically 5–20 min). To a certain extent they resemble “frozen” polar regions observed by PFM in other relaxor system $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ above the ferroelectric relaxor transition temperature.²² To estimate their size an autocorrelation function analysis has been applied. The autocorrelation function, $C(r_1, r_2)$, was obtained by the following transformation of the original PFM image:

$$C(r_1, r_2) = \sum_{x,y} D(x,y)D(x+r_1, y+r_2), \quad (1)$$

where $D(x,y)$ is the value of the piezoresponse signal. Positive or negative values of the autocorrelation function correspond to probabilities to find a region with parallel or antiparallel direction of the polarization after a shift on (r_1, r_2) from an arbitrary point in the original image. A two-dimensional map of the autocorrelation function (Fig. 1(b)) typically has a central peak. Width of this peak can be used as a measure of a mean size of piezoactive regions. To estimate it we averaged the autocorrelation function over all in plane directions and then approximated it by the relation

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

Fig. 1. PFM images and corresponding autocorrelation images for: (a), (b) (001)-cut of PMN; (c), (d) PMN–PT10; and (e), (f) PMN–PT20 single crystals at room temperature.

Fig. 2. (a) The azimuthally averaged autocorrelation function of (1) PFM images of the PMN, (2) PMN-PT10 single crystals at room temperature, and (3) PMN-PT20 single crystal at 415 K. (b) The autocorrelation function along a $\langle 110 \rangle$ direction for PMN-PT10 and PMN-PT20 single crystals.

Here r is the distance from the central maximum and $\langle \xi \rangle$ is an average correlation radius and the exponent h ($0 < h < 1$) is related to the roughness of a “polarization interface” (Fig. 2(a)). It should be mentioned that autocorrelation functions of “noise” images (measured without a probing voltage) also exhibit the central peak of a finite width, which is determined by the image resolution as well as by scan parameters: scanning velocity, probing frequency and time constant of the lock-in amplifier. This instrumental contribution should be subtracted to get correct values of $\langle \xi \rangle$ and h . For PMN the best fit gave the average correlation radius $\langle \xi \rangle \sim 46$ nm.

$(1-x)$ PMN- x PT (PMN-PT100 x) single crystals with a moderate Ti content (10%) show a more complex pattern consisting of nanodomains with positive and negative piezoresponse with size varying from some tens to hundred nanometers (Fig. 1(c)).³⁰ The PFM contrast is more distinct as compared to the PMN single crystal. The nanodomains form a labyrinth-like structure, which looks irregular at first glance. However, the autocorrelation analysis reveals a pronounced interchange of positive and negative values of the autocorrelation function along a $[110]$ -crystallographic direction (Fig. 1(d)). Such behavior points out some regularity of the polar structures in this direction with a characteristic well-defined period. In order to describe it, the autocorrelation function along a certain direction can be represented as a sum of two contributions:

$$C(r) = \sigma^2 \exp \left[- \left(\frac{r}{\xi} \right)^{2h} \right] + (1 - \sigma^2) \times \exp \left[- \frac{r}{r_c} \right] \cos \left(\frac{\pi r}{a} \right). \quad (3)$$

Here the first term is analogous to Eq. (1) and describes short-distance correlations of the polarization inside individual polar regions. The second term corresponds to long-range correlations related to the regularity of the observed pattern. Correspondingly, r_c is the long-range correlation length, a is the period of the structure. The best fit of the curve shown in Fig. 2(b) with Eq. (2) yields values of $a = (180 \pm 40)$ nm and $r_c = (800 \pm 300)$ nm. The short-range correlation radius obtained after averaging over all in plane directions is $\langle \xi \rangle \approx 70$ nm, which is approximately 1.5 times larger than one for the PMN samples. The larger size of the polar regions is due to stronger polar correlations in vicinity of the transition temperature, which is ~ 280 K for PMN-PT10, while for PMN the bulk transition into the nonergodic relaxor state occurs only at 220 K.

For composition with $x = 0.20$ (PMN-PT20) quasi-regular domain pattern with domain walls oriented preferentially along a $[110]$ direction has been observed. Thorough inspection has revealed that these micron-sized domains are not uniform. Namely, a large number of small nanometer-sized domains of opposite orientation are embedded in micron-sized domains of both polarities (Fig. 1(e)). Similar structures were reported also for some other relaxors.²³ The corresponding autocorrelation structure is shown in Fig. 1(e). The long-range correlation length, r_c , is about 2–2.5 μm at room temperature, which is approximately three times larger than that in PMN-PT10 (Fig. 2(b)). This signifies more regular character of domain patterns as compared to the PMN-PT10 single crystals. It should be mentioned however that even in PMN-PT10 besides labyrinth nanodomains some “islands” with more regular patterns, similar to

those observed in PMN–20PT but with smaller period (~ 500 nm) were observed.³⁸ These “islands” occupy 15%–25% of the surface. Nature of these “inclusions” is not clear, e.g., they may correspond to regions with a larger Ti content due to compositional fluctuations. Otherwise, local electric fields or mechanical strain in vicinity of free surface may stimulate an ordering of nanodomains in larger entities.

Domain configuration becomes more ordered in compositions with higher Ti content. Figure 3 shows the PFM images taken on $\langle 001 \rangle$ -cut of a PMN–PT29 single crystal. On a large scale two large twins are seen with width ~ 50 μm . Inside they are composed of “macroscopic” micron size domains forming quasi-regular patterns. Different configurations of domain patterns: ribbon- and checker-board-type, reflect, most probably, different habit planes of the twins (Figs. 3(a) and 3(b)). The magnified images reveal that these macrodomains in

turn have an internal structure, consisting of smaller less regular domains with sizes in range from 100 nm to few microns (Figs. 3(c) and 3(d)). Such hierarchy of domain structures on length scales varying from nano- to millimeters was reported for other PMN–PT single crystals with high Ti content.^{27,28,34} So, in monoclinic PMN–PT35 and tetragonal PMN–PT40 miniature polar nanodomains are self-assembled into $\langle 110 \rangle$ - and $\langle 001 \rangle$ -oriented striations, respectively, of a scale < 1 μm . These striations of alternating polarity in turn are assembled into macrodomain plates of micron size, which are oriented close to $\langle 001 \rangle$ directions.

It was argued that the observed complex domain hierarchy in PMN–PT single crystal results from interplay of three essential ingredients: mechanical stress accommodation, polarization compensation, and random electric fields.²⁸ Rhombohedral cell distortion inside PNRs results in a mechanical

Fig. 3. PFM images of the $\langle 001 \rangle$ -oriented PMN–PT29 single crystal at room temperature.

mismatch between regions with different polarization orientation. The corresponding mechanical strain can be accommodated by self-organization of PNRs into ordered patterns. At lower titanium content ($x < 0.2$) the self-organization is limited by random fields and only nanodomain patterns are observed, while having certain regularity. However, in compounds with more PT the unit cell becomes more distorted and stress accommodation between nanodomains may become critical. To minimize the elastic energy, they may begin to assemble into colonies with a morphology oriented along directions parallel to invariant planes: $\langle 110 \rangle$ and $\langle 010 \rangle$ for rhombohedral and tetragonal PMN–PT, respectively. This is observed starting from the PMN–PT20. While bulk of PMN–PT20 retains cubic structure, a surface layer actually probed by PFM is rhombohedral distorted. A more complete stress accommodation in composition with large Ti

content is achieved via formation of macrodomain plates.

4. PFM versus Temperature: Nanodomains above the Freezing Temperature

It is intriguing that both in PMN–PT10 and PMN single crystals the static nanodomains were observed at temperatures above the nominal transition or freezing temperature. For example, for PMN the transition into the glassy state with frozen polarization is expected only at 80 K below room temperature. Moreover, PFM measurements done at different temperatures on other PMN–PT single crystals reveal that these nanodomains do exist in a broad temperature interval above $T_C(T_f)$.

Figure 4(b) shows PFM image of the PMN–PT10 single crystal taken at 335 K (55 K

Fig. 4. PFM images of a PMN–PT10 single crystal ($T_C = 280$ K) at (a) 295 K and (b) 335 K and of a PMN–PT20 single crystal ($T_C = 360$ K) at (c) 295 K and (d) 405 K.

above nominal T_C). While the piezoresponse contrast is weaker and domain boundaries are more diffused in comparison to those at room temperature, the long-range correlations in $\langle 110 \rangle$ directions 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 (at RT) to 20 nm (at 385 K). Similarly, in PMN–PT20 (Ref. 26) and PMN–PT25 (Ref. 29) regions with nonzero piezoresponse were found up to 50 K above the nominal T_C (Fig. 4(d)). They are not arbitrarily distributed, but form structures resembling the domains observed at lower temperatures. The corresponding correlation radius is larger in compounds with more PT, e.g., for PMN–PT20, $\langle \xi \rangle \approx 110$ nm at $T_C + 45$ K (Fig. 2(a)).

Origin of these steady nanodomains and their relation to PNRs are still a matter of discussion. On one hand, it is accepted now that static PNRs may appear in relaxors at T^* , which is much above than T_C (or T_f).^{13,14} However, these PNRs are expected to be still relatively small, one order of magnitude smaller as those entities found in the PFM experiments. It was suggested that nanodomains observed in PMN–PT single crystals may correspond to self-assembled agglomerates of PNRs.³⁹ The driving force of such self-organization is the minimization of the free energy related to mechanical strains resulting from the rhombohedral distortion of unit cell. It is also not excluded that mechanical strain existing near to the surface⁴⁰ may stabilize the ordered state and shift the phase transition to higher temperatures. If we suppose a gradient of the strain across the outer layer, then the shift of the Curie temperature will also be nonuniform and the transition point in a very thin sub-surface layer, which gives the main contribution to the PFM signal, may be considerably higher than nominal T_C .

Recently Kholkin *et al.*²¹ have performed a series of temperature and depth-resolved experiments on relaxor $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ –4.5% PbTiO_3 (PZN–4.5% PT) single crystals and $(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$ (PLZT) ceramics in the broad temperature range. It was confirmed that the surface phase transition occurs at about 100 K above the bulk transition in PLZT 8/65/35 ceramics and the polarization is stabilized by the surface. The evolution of domain structure during the variable temperature measurements illustrates that the domain patterns remain almost

invariant and no reconfiguration of the static labyrinthine domains is indeed observed. The correlation length depends on the temperature relatively weakly and this dependence can be (partially) attributed to the decay of image contrast with temperature. Figure 5 illustrates the temperature dependences of static (i.e., measured under weak *ac* field) and dynamic (induced by a *dc* bias) polarization parameters in PZN–4.5% PT single crystals for both (100) and (111) orientations. Similar to PLZT, the correlation length slowly decays with temperature without any observable anomalies at the bulk transition temperatures. In comparison, the static polarization component (i.e., the amplitude of the PFM contrast in labyrinthine structures) shows more complex temperature dependence, with rapid decreases at ~ 320 K for (111) surface and ~ 420 K for (100) surface and a high-temperature tail above. The behavior of the dynamic polarization component is illustrated in Figs. 5(c) and 5(d). For (111) orientation, the remanent polarization disappears at ~ 360 K. The corresponding nucleation bias (i.e., the measure of energy for nucleating the polar phase) decreases with temperature and becomes zero at the same temperature. At the same time, for (100) termination both remanent dynamic polarization and nonzero switching bias persist to much higher temperature. These observations clearly illustrate that both static and dynamic components of polarization in ergodic relaxors are strongly affected by surface termination, in agreement with studies by Ozgul *et al.*⁴¹ While the full explanation of the observed phenomena clearly requires more extensive structural studies, it was believed that the polarization correlations in PMN and similar materials develop in the (111) orientations. Correspondingly, on the (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 six components with much smaller normal polarization component. At the same time, on the (100) surfaces four equivalent up-oriented and four down-oriented polarization components are degenerated. Correspondingly, the near-surface electric fields can lift the degeneracy of possible polarization states for (111) orientation, while it is not the case for (100) termination.

The observed mesoscopic behavior is consistent with the presence of the frozen and switchable

Fig. 5. Temperature dependences of (a) correlation length, (b) static polarization amplitude, (c) effective coercive bias, and (d) switchable polarization obtained from local PFM hysteresis loops of the PZN–4.5% PT single crystals with (100) and (111) orientations.

polarization components. The order parameters demonstrate similar thermal behavior (comp. temperature behavior of static and dynamic polarization for (100) and (111) surfaces of PZN–PT). However, within experimental error (finite sensitivity, nonzero probing bias) the corresponding transition temperatures are different. This suggests that the dynamic and static polarization components coexist giving rise to the surface-induced phase transition and symmetry breaking due to strain relaxation, electric interaction or more complicated coupling. Dynamic polarization is shown to be associated with surface; however, static domains deeply penetrate into the crystal bulk. Possible origin of this polarization patterns were analyzed, while the domain walls are destabilized by the random fields, quasi-periodic domains structure are then formed as the results of interplay between renormalized negative gradient terms and higher-order terms (which become relevant) in the free energy expansion.²¹

5. Polarization Dynamics Probed by PFM

The usual PFM imaging measures static or quasi-static polar structures. To probe response of 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 relaxation of induced piezoresponse signal is measured either in “on” or in “off” state.

There are different reports concerning the functional form of the piezoresponse relaxation after bias is switched off. So, in PFM experiments done on 0.9PMN–0.1PT single crystals^{32,33} and PMN thin films⁴² Kohlrausch–Williams–Watt (KWW) type, $d_{zz}(t) \sim \exp[-(t/\tau)^\beta]$,^{33,42} or logarithmic $d_{zz}(t) \sim d_0[1 - b \ln(t/t_0)]$ ³² time dependences of induced piezoresponse were reported (Fig. 6(a)). This relaxation was attributed to a flipping of dynamic PNRs

Fig. 6. (a) Relaxation of the piezoresponse in the PMN thin film follows KWW time dependence after poling by a moderate bias (Ref. 42); (b) relaxation of the piezoresponse in the PMN single crystal follows CsV time dependence after poling by a strong bias (Ref. 37).

aligned by applied bias back to the initial disordered state. The KWW behavior results from a 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 spectrum. In particular, it has been found that β value obtained in PFM experiments for 0.9PMN–0.1PT single crystals is considerably larger ($\beta = 0.3 - 0.4$) than the macroscopic one evaluated from dielectric relaxation experiments.³³ This is expected because the PFM values are the local parameters which characterize the relaxation-time distribution inside the probed regions with the typical dimensions of ~ 30 nm. At the same time heterogeneous spatial distribution of local relaxation characteristics provides broad macroscopic distribution of relaxation times.

To get insight into spatial variations of relaxation parameters and relate them to observed static nanodomains Kalinin and co-workers performed PFM relaxation experiments on a densely-spaced grid of points (with 50–100 nm mesh size) on PMN–PT10 single crystals.³³ Relaxation in both field on (writing) and field off (reading) states was found to follow the KWW-type dependence. For the writing processes distributions of the relaxation parameters, τ_{KWW} and β , are featureless indicating a spatially uniform relaxation process. At the same time, in zero-field experiments fast and slowly relaxed regions could be distinguished on the length scale ~ 100 nm. The characteristic relaxation time differs approximately on one order of the magnitude between these regions. The distribution of the exponent β for the zero-field experiments is also broader than for the relaxation under the field and it

is shifted to lower values of β . From the obtained relaxation parameters the distribution of activation energy was evaluated. As we have mentioned already the induced piezoresponse in relaxors is mainly due to reorientation and coarsening of dynamic PNRs under writing *dc* field. After switching off the bias these PNRs relax back to the initial disordered state. Spatial variation of the local relaxation parameters can be attributed to frozen random electric and elastic fields existing in inherently disordered structure of relaxors as well as to random interactions between the dynamic PNRs.³³

In experiments done on PMN single crystals another type of the relaxation has been observed, namely, the induced piezoresponse which followed a power or Curie–von Schweidler (CvS) law, $f(t) = (t/\tau_{\text{CvS}})^n$ (Fig. 6(b)).³⁷ However, in that case substantially larger bias voltage has been applied (40–80 V) than in aforementioned studies (1–10 V). Similar CvS time dependence was observed by macroscopic birefringence studies of the polarization relaxation in PMN single crystals.⁴³ A cross-over from the KWW-type relaxation to a faster power law on increasing the poling voltage was observed in PMN thin film.⁴² These findings may indicate that on increasing the strength of the poling field a cross-over from KWW- (or logarithmic-) type to CvS-type relaxation occurs.

Remarkably, the static nanodomains, e.g., in PMN–10PT single crystal, were found to be barely affected by applied *dc* electric field.^{33,35} Based on this observation Kalinin *et al.*^{32,33} suggested a coexistence of two types of PNRs: static and dynamic, above the freezing temperature in this material. The static labyrinth nanodomains were

attributed to frozen spatial fluctuations of polarization caused by the density fluctuations of static PNRs having dipole moment directions up or down. On the other hand, the dynamic PNRs are not visible on PFM images, but might be aligned by the applied *dc* bias.

There are several reports on switching spectroscopy PFM (SS-PFM) on PMN–PT relaxors.^{34,35} In these experiments the local hysteresis loops are acquired on a grid of points and spatial distribution of parameters like the reversible polarization, the work of switching, and positive (PNB) and negative nucleation bias (NNB) are analyzed. In ferroelectrics the polarization switching occurs via domain nucleation and subsequent domain growth by wall motion, whereas in relaxors, the polarization reorientation proceeds through a gradual evolution and decay of field-induced state. Therefore, the local hysteresis loops have a characteristic “diamond” shape with a relatively constant response at small *dc* biases and a linear increase of response at larger bias.³⁴ Kalinin *et al.* argued that shape of the local hysteresis in relaxors is controlled by local properties (e.g., local relaxation time spectrum), while in ferroelectrics it is defined by nonlocal polarization wall dynamics.³⁴ By comparison of PNB and NNB one can define a stability gap, PNB–NNB, or a built in electric field, PNB + 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 pointing that the induced polar state is unstable. On contrary, in ferroelectrics the stability gap is definitely positive. The built in fields are related to local defects, e.g. frozen electric random fields. It is intriguing that the spatial distribution of these fields does not reveal a direct correlation to the static PNRs pattern. These may indicate that these static PNRs are not necessarily coupled to the random electric fields and may have another origin as it was discussed in Sec. 4.

6. Conclusion

Relaxor ferroelectrics continue to be a fascinating object of the solid-state physics. Besides their attractive dielectric and electrooptic properties, they represent an example of the hierarchical system with controlled degree of disorder and distinct change of the phase transition and order parameter at the surface. The PFM study of relaxors clearly

helps to understand the mechanism of polarization distribution and illustrates the importance of mesoscopic polarization patterns that were until now overlooked by major theories of relaxor states. Significant progress has been achieved in understanding the appearance of the piezoelectric contrast on the surface of nominally cubic relaxors and those having intermediate properties between relaxors and “normal” ferroelectrics. It has been shown that nanodomains (actually static part of order parameter) may exist above the transition point in a nonergodic state. The mean size of the nanodomains is 50–150 nm at room temperature and weakly decrease upon heating. The results can be interpreted as an evidence of coexisting static and dynamic polarization and symmetry breaking at the surface.

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