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Observation of short-lived local polar states induced by applied tip biases in BaTiO₃-based relaxor ferroelectric ceramics

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Using piezoresponse force microscopy imaging and spectroscopy methods, surface polar states induced by applied tip biases in the ergodic/paraelectric phase of a BaTiO₃-based relaxor ferroelectric ceramic have been observed. The induced polar state appears to be short-lived (typical lifetime only a few seconds) and dependent on the voltages applied and their duration. The observed piezoresponse hysteresis and relaxation behavior is primarily interpreted with respect to the picture of the polar nano-region dynamics, as proposed for lead-based relaxors. Spatially resolved piezoresponse relaxation mapping reveals the presence of sub-micron correlated features, presumably due to A-site chemical inhomogeneity as supported by site-correlated elemental mapping microanalysis. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4813541>]

Relaxor ferroelectrics (relaxors) are well-known for their giant dielectric permittivity and piezoelectric properties.¹ Canonical lead-based relaxors are exemplified by, e.g., Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN) and the PbTiO₃ (PT)-doped derivatives thereof. Environment-friendly, lead-free relaxors, in particular, those derived from BaTiO₃ (BT), have gained increasing recent attention because of their use as high frequency dielectrics in field-tunable microwave devices.² The inherent compositional disorder associated with lead-based, as well as lead-free, relaxors has long been believed to be closely associated with the existence of polar nano-regions (PNRs) and characteristic relaxor behavior. As regards the local structural origins of the PNRs as well as their dynamic behavior, some differences in behavior of the lead-based from the lead-free relaxors could be envisaged as a result of the well-known fact that the Pb-ions are ferroelectric active in lead-based relaxors whereas the Ti-ions are ferroelectric active in BaTiO₃-based relaxors.

In seeking to understand the PNR-associated microstructure and dynamic behavior of relaxors, piezoresponse force microscopy (PFM) has some unique capabilities, e.g., highly localized and time-resolved detection and *in situ* application of tip bias stimuli. Previous PFM studies on several lead-based relaxors have revealed highly disordered, labyrinth-like surface domain patterns, apparently common to these materials.^{3–7} These imaged domain structures are closely related to the static PNRs that develop in certain phases of relaxors. It has also been reported that the static PFM domain contrast disappears when the Sn content is high enough to produce a relaxor state in the case of BaTi_{1–x}Sn_xO₃.⁸ Note that whether PNRs are static or dynamic here is defined relative to the PFM imaging timescale, typically of a few minutes. More involved PFM spectroscopic studies have identified dynamic PNRs and quantified their time-domain relaxation behavior with ms temporal resolution.^{9,10} All these PFM results offer

important insight into a wide spectrum of relaxors, in particular, lead-based ones. In this letter, we report PFM studies of an A-site doped, BT-based ceramic relaxor, the results of which are correlated with the structural features of the material and compared with those reported for lead-based relaxors.

0.8Ba_{0.75}Sr_{0.25}TiO₃-0.2La_{0.5}Na_{0.5}TiO₃ (BSLNT) ceramics were fabricated via a solid state reaction route. The average structure of the samples was confirmed to be cubic perovskite at room temperature using X-ray powder diffraction. Elemental mapping was performed using energy dispersive spectroscopy in a scanning electron microscope (Hitachi S4300). The dielectric properties of the ceramics were measured from 100 Hz to 1 MHz with an LCR meter (Agilent 4284). PFM investigations were carried out under ambient conditions in an atomic force microscope (Cypher, Asylum Research) using Pt-coated Si conductive probes (AC240TM, Olympus). PFM images were taken at a fixed ac signal (amplitude = 3 V, 10 kHz) well off the resonance frequencies. DC voltages were applied to the tips in contact mode for surface poling. For the dynamic piezoresponse (*PR*) switching loops and *PR* relaxation mapping measurements, we used the band excitation (BE) method, realized by incorporating external hardware: a NI PXI-5412 signal generator and a PXIe-5122 digitizer.^{11,12} A home-made LABVIEW-based BE control program was used to acquire the time domain response signals that were subsequently Fourier transformed into the frequency domain. A set of Igor Pro routines was used for data post-analysis, such as the simple harmonic oscillator model fitting.

Figure 1 shows the temperature-dependent, dielectric behavior of the BSLNT ceramics. Within the measured 100–500 K range, there is only one dielectric anomaly, i.e., the dielectric permittivity maximum at a temperature $T_{\max} = 185$ K (at 1 kHz). $T_{\max}$ is weakly frequency dependent, suggesting relaxor behavior. Fitting $T_{\max}$ as a function of measuring frequency to the Vogel-Fulcher law yields a freezing temperature T_f of 172 K and an activation energy of ~ 38 meV (435 ± 70 K). In relaxors T_f is widely regarded as marking the transition from an ergodic state to a non-ergodic

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FIG. 1. Temperature dependent dielectric permittivity spectra of the BSLNT ceramics. Inset shows the frequency dependence of $T_{\max}$ and its fit to the Vogel-Fulcher law.

glassy state.¹ In the ergodic state, the PNRs are presumed to be small in size, weakly inter-correlated, and largely of a dynamic nature. The existence of PNRs, both static and dynamic, has been confirmed by means of electron diffraction for a wide family of doped BT-based relaxors.^{13,14} On the other hand, the issue of the frequency-dependence of PNR dynamics in relation to composition, temperature, etc. has thus far mainly been studied in a few broadband dielectric spectroscopy studies for BT-based relaxors. These studies show that the onset of dielectric relaxation in the paraelectric, high temperature phase is well above MHz, typically reaching the GHz to far infrared range.^{15,16}

FIG. 2. (a) PFM phase images on a $4 \times 4 \mu\text{m}^2$ surface region of the BSLNT ceramics. The same $1/3$ parts are combined and shown for all the three states. The acquisition time is 256 s per image, and the time delay after poling is ~ 5 s. (b) Phase histograms for the full images of each state. (c) Time evolution of the PR phase signals (in the cosine form) after applications of 1 s pulses with different negative voltages, measured at a single point.

Fig. 2(a) shows typical PFM phase images acquired from the same surface region of a BSLNT ceramic for the pristine, during-poling and after-poling states. Note that during poling the PFM signal is dominated by the electrostatic effect; its phase image is given here only for reference purposes. Note that no domain patterns can be observed in the pristine phase image while, after poling, the phase image also appears rather featureless except, perhaps, for some weak features discernable on the negatively poled region. The corresponding phase histograms shown in Fig. 2(b) confirm the lack of any sharp distributions for both the pristine and as-poled states in addition to a slight spectrum weight transfer between them. These PFM observations are consistent with the fact that the material is in its paraelectric/ergodic phase at room temperature. They are similar to those made on PMN ($T_{\max} \sim 260$ K at 1 kHz),^{3,6} but substantially distinct from the case of 0.9PMN-0.1PT single crystals ($T_{\max} \sim 310$ K at 1 kHz).⁹ On the latter material, characteristic labyrinthine domain patterns can be observed in the pristine state. All the materials discussed here have metrically cubic structures at room temperature.

Fig. 1(c) shows the phase signals recorded continuously after several negative bias stimuli. In general, the measured PR signals contain contributions from the residual electrostatic effect.¹⁷ This effect can be dominant as the intrinsic PR of the material is rather weak. Here, negative biases create upwards polarized domains, for which the PR is in anti-phase with the electrostatic effect (as determined experimentally, the PR does not show a 180° phase jump/sign change after positive pulses). Typically, the PR phase measured in the bias-off states (e.g., -10 V) starts oscillating shortly after showing an initial sign change, and concurrently the PR amplitude reduces to the noise floor (data not shown). This suggests a fast decay of the PR magnitude to a level comparable to the electrostatic effect. Therefore, the stable duration of the initial phase can be defined as the lifetime of the tip-bias induced polar states. This lifetime increases from ~ 0.5 s for -5 V to ~ 3 s for -10 V but is obviously shortened when a bias larger than 20 V is applied. The latter tendency can be attributed to modified surface charge states under high biases (e.g., charge injection from the tip) leading to an enhanced electrostatic effect.^{18,19} In view of these results, we believe that the weak features observed on the after-poling phase image (see Fig. 2(a)) stem from the electrostatic effect rather than signifying any long-lived induced polar regions.

Fig. 3 shows typical dynamic switching hysteresis loops of the BSLNT ceramics. In this measurement, the PR after each 25 ms pulse is registered into 64 points in every 4 ms interval and plotted versus the applied voltage over a ± 15 V bias window. The loops measured over a higher bias window develop “noses,” i.e., self-crossings of the PR near its maxima,¹⁷ consistent with the results in Fig. 2(c). Overall, the PR loops have an average coercive voltage ~ 3.5 V, smaller than those for lead-based relaxors.^{7–10} These individual loops show clear variations in shape; the outer loops show inflection points at the smallest pulse step, ± 1.67 V, verifying a relaxation tendency for all non-zero biases. For each pulse step, the time dependence of the PR data is found to best fit the Kolrausch-William-Watts (KWW) model

FIG. 3. Typical dynamic *PR* switching hysteresis loops of the BSLNT ceramics, consisting of 64 loops acquired at 4 ms intervals after 25 ms pulse voltages in 36 steps. Inset shows the *PR* relaxation trend after the 15 V pulse, along with a KWW fit to the measured data.

$$R(t) = R_0 + R_1 \times \exp(-(t/\tau)^\beta), \quad (1)$$

where R_0 denotes the non-relaxing component, R_1 the relaxing component, and β and τ are fitting parameters.^{3,9} This KWW model describes thermally activated relaxation in disordered systems where a spread of relaxation times is present, in contrast to the single relaxation time of the Debye model (the $\beta=1$ case of the KWW model). The inset in Fig. 3 shows an example fit for the 15 V pulse step, the obtained parameters being $R_0 = 3.54(14)$, $R_1 = 5.74(20)$, $\beta = 0.49(3)$, and $\tau = 40(3)$ ms. The fitted β and τ values vary slightly for biases larger than 5 V. The lower bias *PR* data generally show larger fitting uncertainties, and a clear monotonic trend is not always found, probably because of the high noise inherent to them.

As mentioned previously, our PFM investigations were made at a temperature at least 100 K higher than the T_f of the BSLNT ceramics. At this temperature, the material has certainly not developed any macroscopic polarization. The expected local polarization, i.e., the PNRs, are thus still highly dynamic. PFM is essentially a low frequency technique that measures sub-MHz electromechanical responses of a material. In our case, therefore, the appearance of measurable *PR* after tip bias stimuli requires a substantial slowing-down of the PNR dynamics, consistent with their condensing and merging into the larger volumes required for PFM detection. This scenario is consistent with those conjectured for lead-based relaxors, despite the different structural origins of PNRs.^{2,13} Upon switching off the tip biases, these induced local polar clusters break up and quickly return back to the equilibrium state due to thermal agitation. In this respect, the fast relaxation of the induced polar states is quite consistent with the rather small (close to 300 K/26 meV) Vogel-Fulcher activation energy deduced for BSLNT. By contrast, under tip biases with the same voltage and duration, the induced polar state in PMN (with an activation energy of ~ 70 meV (Ref. 20)) is much more long-lasting (up to a few hundred seconds).^{3,6}

It is interesting to note here that Dul'kin *et al.* recently reported the emergence of static PNRs even in the paraelectric phase of pure BT crystals at temperatures below $T^* \sim 506$ K using acoustic emission spectroscopy,²¹ also a low frequency technique. Nevertheless, in the case of our BSLNT ceramics, the population of static PNRs at the measuring temperature of 300 K appears to be too low to assemble into the labyrinth-like domain patterns as observed in 0.9PMN-0.1PT.^{9,20}

Note that although the above conjecture had been rationalized by phenomenological analyses for certain relaxor systems,^{9,10} a conclusive structural validation of it via a local structure sensitive diffraction or spectroscopic tool (e.g., presumably, micro-focused X-ray diffuse scattering) is still lacking due to obvious experimental difficulties. On the other hand, well-defined *PR* (more accurately, electromechanical response) hysteresis loops have recently been reported for several non-polar oxides, e.g., doped-ZrO₂, SrTiO₃, and TiO₂.^{22,23} We have also measured similar dynamic hysteresis loops on a (001)-SrTiO₃ single crystal under the same conditions as used for BSLNT (see Fig. S1 in supplementary material²⁴). In these cases, the formation of the *PR* loops relies on ionic transport processes, and their *PR* hysteresis behavior thus reflects the extent of ionic diffusion. The bulk ion activities of the studied BSLNT sample are rather weak judging from its weak field dielectric behavior showing the absence of low frequency dielectric dispersion within 300–500 K. However, under a strong, concentrated electrical field (which may well be in excess of 10^6 V/cm) in PFM, the surface ion activities, e.g., oxygen vacancy creation/annihilation can indeed be triggered leading to a modification of the defect state of the probed sample volume.²² These ion activities very likely couple to the dynamics of the PNRs via electrostatic and elastic interactions or may even act themselves in mediating a hysteretic *PR* behavior. After all, we stress that a definitive attribution of the intrinsic/extrinsic microscopic nature or their combination to the observed *PR* hysteresis and relaxation remains intractable in our current experiment.

To reveal the spatial variation in the relaxation behavior of the BSLNT ceramics, single point *PR* relaxation curves were acquired on a 40×40 point grid evenly spaced over a $2 \times 2 \mu\text{m}^2$ region. Each of these curves includes 150 points measured in 4 ms intervals after a fixed 25 ms, 15 V pulse, and is fitted to the KWW model with the resultant parameters constructed into the maps shown in Figs. 4(a)–4(d). These maps show the existence of relatively large (up to several hundred nm) correlated features. Overall, the average R_1 value is ~ 4 times larger than the average R_0 value, verifying a dominant relaxing component to the *PR* within the probed timescale. Most of the high value R_1 regions (see e.g., the lower left part of Fig. 4(b)) also correspond to low value R_0 regions in Fig. 4(a). There are, however, also regions with high R_0/R_1 ratios (see e.g., the area circled in Fig. 4(b)). This may suggest that the induced polar states in this region are relatively more stable or long-lived than elsewhere. In Fig. 4(e)), a calculated map of R_1/R_0 is shown to enable a visualization of the distribution of relaxation strength. The contrast observed on the β and τ images of Figs. 4(c) and 4(d) are relatively weak, especially for the τ image which is essentially featureless. On the other hand, statistically both

FIG. 4. Spatially resolved maps (40×40 pixels, $2 \times 2 \mu\text{m}^2$) of the PR relaxation parameters obtained from fittings to the KWW model: (a) R_0 , (b) R_1 , (c) τ , (d) β , and (e) R_1/R_0 . Map (e) has been smoothed with a 3×3 single-pass median filter. (f) The histograms of τ and β (inset), along with their Gaussian fits.

the β and τ distributions are satisfactorily Gaussian as is apparent from Fig. 4(f).

It is of interest to know what the contrast observed in these relaxation maps reflects. The features revealed have little correlation with the associated topography (not shown). They are also quite different from the grain contrast of the sample both in shape and size ($1\text{--}2 \mu\text{m}$), so that a direct crystal orientation origin seems unlikely. We infer that the features must be related to the frozen chemical inhomogeneity of the BSLNT ceramics, as prompted by a careful elemental mapping analysis. As shown in Fig. S2 in supplementary material,²⁴ the distribution of the various A -site elements is clearly not uniform with some sub- μm sized segregation discernable, in contrast to a much finer fluctuation of the B -site, Ti element. That the distributions of Na and La appear highly correlated, as required by local charge balance considerations, suggests a marginal effect of mesoscopic space charges on the observed PR relaxation behavior. In fact, it has been argued that the PNRs in doped-BT relaxors derive

from the frustration of local strains set by the dopants rather than charge disturbance.^{13,14} Macroscopically, it is well verified that BT-solutions develop stronger relaxor characteristics with increasing doping levels.^{2,14} How does such a composition-property relationship behave at the sub- μm length scale? To explore this question, site-correlated measurements have been performed with the aid of focused ion beam (FIB) etched micro-marks. As shown in Fig. 5, the two types of mapping results obtained correlate reasonably well. Here we have only considered the Ba and Sr ions of the A -site, neglecting the Na and La ions as their distribution patterns appear far less correlated to the PR relaxation maps. By comparing Figs. 5(b) and 5(d), one finds an obvious tendency for Ba-rich regions to have high R_1/R_0 ratios that largely result from high R_1 components (cf., Fig. 5(a)). This only partially follows the macroscopic trend described above in the sense that the Ba-rich regions can be more polarizable under applied biases but are expected to be less capable of relaxing. Nevertheless, here we refrain from further speculation about the exact origin of this observation.

To summarize, we have found that the surface phase of a BT-based relaxor can be stimulated into a local and temporary polar state by applied tip biases and well-defined PR hysteresis loops can thereby be formed. Fast relaxation of the measured PR is believed to indicate the instability of the induced polar state as a result of the PNR dynamics. Spatially resolved relaxational mapping shows the existence of correlation features at the sub-micron scale, attributed to the chemical inhomogeneity of the investigated ceramic sample. These results complement our current PFM observations of the nanoscale dynamic behavior of relaxors and provide clues for further development of BT-family dielectric materials.

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FIG. 5. Spatial distributions of the PR relaxation parameters: (a) R_1 and (b) R_1/R_0 , and the corresponding elemental parameters: (c) A -site occupancy of Sr and (d) Ba/Sr ratio. Maps (a) and (b) have been smoothed with a 3×3 single-pass median filter.

¹A. A. Bokov and Z. G. Ye, *J. Mater. Sci.* **41**, 31 (2006).

²V. V. Shvartsman and D. C. Lupascu, *J. Am. Ceram. Soc.* **95**, 1 (2012).

- ³V. V. Shvartsman, A. L. Kholkin, M. Tyunina, and J. Levoska, *Appl. Phys. Lett.* **86**, 222907 (2005).
- ⁴H. R. Zeng, H. F. Yu, S. X. Hui, R. Q. Chu, G. R. Li, H. S. Luo, and Q. R. Yin, *Solid State Commun.* **133**, 521 (2005).
- ⁵V. V. Shvartsman and A. L. Kholkin, *Z. Kristallogr.* **226**, 108 (2011).
- ⁶A. Kholkin, A. N. Morozovska, D. Kiselev, I. Bdikin, B. Rodriguez, P. Wu, A. Bokov, Z.-G. Ye, B. Dkhil, L. Chen, M. Kosec, and S. V. Kalinin, *Adv. Funct. Mater.* **21**, 1977 (2011).
- ⁷Q. Li, Y. Liu, R. L. Withers, Y. Wan, Z. Li, and Z. Xu, *J. Appl. Phys.* **112**, 052006 (2012).
- ⁸V. V. Shvartsman, W. Kleemann, J. Dec, Z. K. Xu, and S. G. Lu, *J. Appl. Phys.* **99**, 124111 (2006).
- ⁹S. V. Kalinin, B. J. Rodriguez, J. D. Budai, S. Jesse, and A. N. Morozovska, *Phys. Rev. B* **81**, 064107 (2010).
- ¹⁰B. J. Rodriguez, S. Jesse, A. N. Morozovska, S. V. Svechnikov, D. A. Kiselev, A. L. Kholkin, A. A. Bokov, Z.-G. Ye, and S. V. Kalinin, *J. Appl. Phys.* **108**, 042006 (2010).
- ¹¹S. Jesse, A. P. Baddorf, and S. V. Kalinin, *Nanotechnology* **17**, 1615 (2006).
- ¹²A. kumar, Y. Ehara, A. Wada, H. Funakubo, F. Griggio, S. Troler-Mckinstry, S. Jesse, and S. V. Kalinin, *J. Appl. Phys.* **112**, 052021 (2012).
- ¹³Y. Liu, R. L. Withers, B. Nguyen, and K. Elliott, *Appl. Phys. Lett.* **91**, 152907 (2007).
- ¹⁴Y. Liu, R. L. Withers, X. Wei, and J. D. F. Gerald, *J. Solid State Chem.* **180**, 858 (2007).
- ¹⁵T. Tsurumi, J. Li, T. Hoshina, H. Kakemoto, M. Nakada, and J. Aakedo, *Appl. Phys. Lett.* **91**, 182905 (2007).
- ¹⁶D. Nuzhnyy, J. Petzelt, M. Savinov, T. Ostapchuk, V. Bovtun, M. Kempa, J. Hlinka, V. Buscaglia, M. T. Buscaglia, and P. Nanni, *Phys. Rev. B* **86**, 014106 (2012).
- ¹⁷S. V. Kalinin and D. A. Bonnell, *Phys. Rev. B* **65**, 125408 (2002).
- ¹⁸Q. Li, Y. Liu, J. Schiemer, P. Smith, Z. Li, R. L. Withers, and Z. Xu, *Appl. Phys. Lett.* **98**, 092908 (2011).
- ¹⁹Q. Li, Y. Liu, D. Wang, R. L. Withers, Z. Li, H. Luo, and Z. Xu, *Appl. Phys. Lett.* **101**, 242906 (2012).
- ²⁰A. A. Bokov, B. J. Rodriguez, X. Zhao, J. Ko, S. Jesse, X. Long, W. Qu, T. H. Kim, J. D. Budai, A. N. Morozovska, S. Kojima, X. Tan, S. V. Kalinin, and Z. Ye, *Z. Kristallogr.* **226**, 99 (2011).
- ²¹E. Dul'kin, J. Petzelt, S. Kamba, E. Mojaev, and M. Roth, *Appl. Phys. Lett.* **97**, 032903 (2010).
- ²²A. Kumar, F. Ciucci, A. N. Morozovska, S. V. Kalinin, and S. Jesse, *Nat. Chem.* **3**, 707 (2011).
- ²³Y. Kim, A. N. Morozovska, A. Kumar, S. Jesse, E. A. Eliseev, F. Alibart, D. Strukov, and S. V. Kalinin, *ACS Nano* **6**, 7026 (2012).
- ²⁴See supplementary material at <http://dx.doi.org/10.1063/1.4813541> for the SrTiO₃ single crystal PFM data and a full data set of elemental mapping.