Adaptive dipolar correlation in ferroelectric $x(Ba_{0.7}Ca_{0.3})TiO_3 - (1 - x)Ba(Zr_{0.2}Ti_{0.8})O_3$

K. Datta^{1,*} Kumar Brajesh,² Rajeev Ranjan²,² and B. Mihailova^{1,†}

¹Department of Earth Sciences, University of Hamburg, Grindelallee 48, Hamburg 20146, Germany ²Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India

(Received 14 November 2019; revised 16 January 2020; accepted 3 August 2020; published 14 August 2020)

Deriving structure-property relationships for multicomponent ferroelectric materials has always been a challenging problem because the properties are mostly driven by subtle nanoscale correlations which are hard to detect. Here we have studied the famous Pb-free material $x(Ba_{0.7}Ca_{0.3})TiO_3 - (1 - x)Ba(Zr_{0.2}Ti_{0.8})O_3$ (xBCT-BZT) which has been at the center of attention for approximately the last 10 years because of its unprecedented piezoelectric properties. However, the structure-property relationship for xBCT-BZT remains elusive as neither the common concepts nor the experimental results lead to satisfactory models which can fully explain its unusual piezoelectric properties as a function of composition as well as recognize its uniqueness compared to other similar systems. Hence we have applied total neutron-scattering and Raman-scattering methods to examine the local structural correlations of xBCT-BZT in the range $0.40 \le x \le 0.60$ at ambient conditions. By refining large-box atomistic models against the neutron pair distribution functions, we have observed an emerging coherence in the polar displacements of the cations at x = 0.50, leading to an increased structural ergodicity at the key orthorhombic-tetragonal phase boundary. Given the very similar level of local structural disorder and spontaneous polarization found in the system with x, we propose that the abrupt amplification of piezoelectric properties in this material at a region of phase instability is a consequence of enhanced collaboration amongst the all cations in a strain-reduced local environment. It also indicates that the popular structure-property concept entailing a low-symmetry crystal structure cannot be a generic concept or a precondition.

DOI: 10.1103/PhysRevB.102.060102

The discovery Pb-free ferroelectric of $x(Ba_{0.7}Ca_{0.3})TiO_3 - (1 - x)Ba(Zr_{0.2}Ti_{0.8})O_3$ (xBCT-BZT) [1] was exciting not only because it exhibited exceptional piezoelectric properties ($d_{33} \sim 500-600 \text{ pC/N}$) comparable to $PbZr_{x}Ti_{1-x}O_{3}$, but more importantly, because it provided a major breakthrough in the efforts of transforming BaTiO₃-based ferroelectrics into viable Pb-free alternatives. The evidence that a composition-driven phase instability in a system without stereochemically active cations such as Pb^{2+} or Bi^{3+} or a distinct monoclinic phase can bring about enhanced piezoelectricity, further challenged the existing concepts relating structure and property in ferroelectric solid solutions. Notably it remains unclear how xBCT-BZT abruptly becomes a superior piezoelectric material at x = 0.50and why this is a unique system compared to other leading Pb-free systems, such as K_{0.5}Na_{0.5}NbO₃-, K_{0.5}Bi_{0.5}TiO₃-, and Na_{0.5}Bi_{0.5}TiO₃-based materials [2]. A number of recent reports have also challenged the original inference by Liu and Ren [1] that the presence of a tricritical triple point near room temperature in the zero-field phase diagram facilitates the polarization rotation and gives rise to a surprisingly large enhancement in the piezoelectric response. Instead, it has emerged that the combination of several physical phenomena, such as vanishing polarization anisotropy, large remnant polarization, and increased elastic softening, which facilitate extrinsic contributors such as domain-wall motions [3,4] and domain switching [5–7] may be the key here. Structural investigations on ceramics of *x*BCT-BZT have confirmed the presence of an intermediate orthorhombic (O) phase between the rhombohedral (R) and tetragonal (T) phases [8–10], and therefore revealed the existence of two phase boundaries (R-O at $x \approx 0.44$ and O-T at ≈ 0.50) of which the O-T phase boundary exhibits the largest piezoelectric response.

While there may now be a consensus on the physical mechanisms responsible for the enhanced piezoelectricity at the O-T phase boundary [5,11], an atomistic description corroborating the properties is still lacking. Clearly the average structural details including the subtle changes of symmetries with xcannot fully establish the structure-property connection here considering the property anomalies across the phase diagram. Given that xBCT-BZT demonstrate distinct local structural features [12,13], we believe that there could be a missing link rooted in the adaptive atomic-scale correlations which has yet to be found. Hence our focus here is to investigate the local structural features through the analyses of neutron pair distribution functions (PDFs) and Raman-scattering data at ambient conditions. To do this we have adopted the approach applied earlier to other ferroelectric solid solutions, which evaluates the statistical trends of the relative cationic displacements derived from the refined atomistic models [14–18].

In this Rapid Communication we demonstrate that the apparent composition-induced phase transformation in xBCT-BZT originates from a local-scale change in the dipole-dipole interaction driven by an evolving structural ergodicity as a function of x. The development of analogous disorder in different types of cations at the key composition seems to

^{*}kaustuv.datta@uni-hamburg.de

[†]boriana.mihailova@uni-hamburg.de

make the system extremely susceptible to external stimuli, hence, a better piezoelectric material.

Ceramic samples of xBCT-BZT for five different x (0.40, 0.45, 0.50, 0.55, and 0.60) were prepared following the solidstate synthesis route [19]. Total scattering experiments at ambient conditions were carried out on the GEM diffractometer [20] at ISIS facility in the UK. Data correction and subsequent reduction to generate the PDFs were performed using the GUDRUN package. PDFs were then analyzed applying the reverse Monte Carlo (RMC) large-box modeling technique as implemented in the RMCPROFILE software [21]. The initial large-box models were $14 \times 14 \times 14$ supercells of the tetragonal unit cells derived from the Rietveld refinements of the powder diffraction data (see Table S1 in the Supplemental Material (SM) [22]). Each model consisted of 13 720 atoms and we applied nearest-neighbor distance-window constraints plus a weak bond-valence sum restraint in the iterations to ensure the refined models remain valid. The bond-valence sum constraint for Zr was particularly necessary to obtain chemically sensible distributions Zr-O (see also Fig. S6 in the SM). In order to produce good statistics of the structural parameters we performed 50 independent RMC runs at each composition, and an individual run was continued for approximately 10⁷ accepted moves. The analyses of the refined structural models were done using the DISCUS package [23]. Some additional details and different plots of fitted data are provided in the Supplemental Material, which further includes a description of the Raman-scattering measurements at room temperature [22].

PDFs provide an atomistic view within a system through weighted histograms of all atom-atom distances, and largebox modeling against the PDFs helps to extract those atomistic details in a quantitative manner. Given that the structure and properties of ferroelectric materials are predominantly driven by the local structural distortions, we have adopted the geometric phase approach [14] to assess the development of the respective local dipolar features (magnitude and direction) arising from different types of cations. For this purpose, cation displacement vectors ($\delta \vec{r}$) with respect to their oxygen neighbors were extracted from the refined models as follows (Fig. 1):

$$\delta \vec{r}_{\text{Ba/Ca}} = \vec{r}_{\text{Ba/Ca}} - \frac{1}{12} \sum_{i} \vec{r}_{iO},$$

$$\delta \vec{r}_{\text{Ti/Zr}} = \vec{r}_{\text{Ti/Zr}} - \frac{1}{6} \sum_{i} \vec{r}_{iO}.$$
 (1)

The directions of these vectors with respect to $[001]_{pc}$ of the pseudocubic unit cell are then mapped onto stereographic plots for the evaluation. Figure 2 presents such stereographs of the cations at different *x*, which provides a statistical description of the polar order within the system and its progress as a function of composition. It is evident that all cations except Zr, show broad distributions of directions, almost comparable to typical dipole-glass structures characterized by a divergence of fluctuations of polarization direction. The minor component Ca demonstrates highest disorder, probably because it is smaller than Ba in size and not influenced by the shifts of the neighboring cations. However, it should be noted that the



FIG. 1. (a) A schematic of the perovskite-type (ABO_3) structure. (b) Ba and Ca are at the *A* site while Ti and Zr are at the *B* site with 12 and 6 oxygen neighbors, respectively. (c) A guide stereogram looking down [001] for a cubic crystal with the major pseudocubic directions in the central part, from which the symmetry correspondence of the shift directions can be realized.

experimental data may not distinguish Ba and Ca well because of their similar neutron-scattering lengths. Zr displacements have a very clear trend along $[001]_{pc}$. Although Ti exhibits significant disorder in terms of their polarization directions, the overall trend with x seems to have a different feature from the others. At least, it shows an added preference for $[111]_{pc}$ for the composition x = 0.40 and 0.45. Hence, not only the local polar-order instability does not intuitively lead to the corresponding average crystal symmetry of the system, but also the A- and B-site cations behave distinctly. Consequently, it is hard to imagine the reported phase diagram based on these plots. This is, however, not utterly surprising or new, since symmetry-breaking cationic shifts are commonplace in ferroic solid solutions caused by the coexistence of multiple



FIG. 2. $[001]_{pc}$ stereographs with the projected directions of the relative cation displacements. Data from all 50 runs were combined to increase the statistics.



FIG. 3. (a) Centrally magnified stereographs of Ti as a function of composition. (b) Variations of mean standard deviations of positional coordinates (x, y and z) for different cations with x as defined in the text. The error bars correspond to the deviations over 50 RMC runs at each composition. While the solid lines are mere guide to the eye, the red arrow in indicates the minimum anisotropy at the critical composition. (c) Values of structural ergodicity parameter as a function of x together with the reported piezoelectric coefficient d_{33} values. The error bars correspond to the standard deviations over 50 RMC runs at each composition. Further details on this parameter can be found in the Ref. [28]. Dashed and dotted lines in the graphs are only guides to the eye. We believe that the apparent anticorrelation between the erdicity parameter and the piezoelectric coefficient d_{33} is a product of strain-polarization coupling. The tetragonality of the average structural model increases linearly with x and becomes maximum at x = 0.60.

competing phenomena [24] and in particular, distinct local polar distortions of Ba and Ti even in undoped BaTiO₃ is very well known [25-27]. The chemical substitution has indeed caused additional disorder, and apparently smeared out the differences to some extent. A close observation of these extensive fluctuations, however, reveal that there are only appreciable changes in the Ti distributions with x, while the rest seems to remain very similar in terms of their respective probability distribution functions of the polar ordering with respect to $[001]_{pc}$. In order to expose the features of Ti further, centrally magnified stereographs of Ti with equal density contours are presented in Fig. 3(a), which reveal the emergence of more symmetric distributions with respect to $[001]_{pc}$ for Ti at $x \ge 0.50$. A complementary measure of the varying Ti distribution can be obtained from Fig. 3(b) which shows the mean standard deviations of positional coordinates (x, y, z) of Ti with composition calculated from the refined models as follows: $\sigma_x = \langle \sigma_{x_i} \rangle = \langle |x_i - \langle x_i \rangle| \rangle$. Evidently the anisotropy among these sigma values shows a minima at x = 0.50, which supports the above observations. Similar plots for the rest of the cations can also be found in Fig. S9 [22], which further confirms that only B-site cations show conceivable changes as a function of composition.

To further understand the consequence of this development as a whole, a structural homogeneity or ergodicity function was calculated as a function of x as described by the Eqs. 9(a) and 9(b) in Ref. [28], which basically evaluates the integral of



FIG. 4. The variation of (a) mode $|\delta \vec{r}|$ and their (b) standard deviations. Dashed lines in the graphs are simply guides to the eye. Histograms of displacement values are provided in the Supplemental Material (Fig. S7).

a function considering all possible partials PDFs up to 10 Å within the RMC-refined model. The highest value of structural ergodicity would physically refer to the most structurally homogeneous system, e.g., a perfect glass or a perfect crystal. It is striking that the structural ergodicity of xBCT-BZT peaks exactly at x = 0.50, and shows a correlation with the composition-dependent piezoelectric property of the system [see Fig. 3(c)]. Therefore, x = 0.50 represents a special case where we can think of an increased correlation among the different cation dipoles within a very disordered state. This is indeed very significant, because the evidence that all cations exhibit a similar trend or an increased coherence in terms of their inherent disorder brings a new perspective in relating the structure and properties of xBCT-BZT, which suggests correlated disorder facilitates the development of enhanced coupling processes that boosts the piezoelectricity significantly at the reported O-T phase boundary of the material.

The state of the inherent polarization and the degree of local polarization distributions in terms of their magnitudes can be estimated from Figs. 4(a) and 4(b) where $|\delta \vec{r}|$ and their standard deviations are plotted respectively. Clearly both of these parameters remain unaffected in this composition window, and thus suggest that the amplification of electromechanical responses are mostly driven by the typical extrinsic factors as pointed out by several reports [5-7,29]. The variation of $|\delta \vec{r}|$ also correlates with the previous observation that the spontaneous polarization of the system remains constant over the entire intermediate phase region [7]. Nevertheless a few other characteristics of xBCT-BZT can also be drawn out here: (1) Unlike the Pb- or Bi-based ferroelectrics the overall spontaneous polarization is much smaller, and as expected, B-site cations are likely to contribute more to the ferroelectricity than the A-site cations. It is noticeable that Zr exhibits the largest relative displacements at all x when compared to the rest. (2) Given the disorder observed in Fig. 2 together with the constant polarization values, it is apparent that the composition-driven interferroelectric phase transition in *x*BCT-BZT is more of an order-disorder type. (3) Finally, neither the magnitudes (plus its sigma) nor the dipole orientation distributions as a function of x translate



FIG. 5. Experimental Raman spectra of *x*BCT-BZT ceramics, along with the assumed peaks (thin gray lines) and the resulting calculated spectrum (orange dashed line) for x = 0.4. The inset shows the composition dependence of the wave number and full width at half maximum (FWHM) of the excitation near 60 cm⁻¹, generating peak 2. The arrow marks the orthorhombic-tetragonal phase boundary. More details are given in the Supplemental Material [22].

to a distinct free-energy anisotropy model for x = 0.50, or in other words, the parameters do not quite corroborate with the predicted model of extreme flattening of the free-energy surfaces exclusively at x = 0.50 [1].

The occurrence of the O-T phase boundary may be related to the softening of the Raman-active transverse optical A-BO₃ mode near 60 cm⁻¹ (peak 2 in Fig. 5). However, for *x*BCT-BZT the respective phonon modes (peaks 1 and 2 in Fig. 5) are already strongly damped in this entire compositional range because T_c (~350–375 K) is not far away from room temperature. Equally the development of other vibrational modes with composition fails to indicate any characteristic feature from which the phase boundaries (R-O and O-T) can be identified straightaway (see Figs. S9 and S10 in the Supplemental Material [22], and references therein [30–32]). Furthermore, the phonon modes near 200–250 cm^{-1} , sensitive to the coupling among off-centered displacements of B-site cations, remain unchanged in wave number with the variation of x (Fig. S9 in the Supplemental Material [22]), which is in contrast to the observations made in the cases of Pb/Bi-containing solid solutions [33-35]. Therefore the composition-dependent dynamics of xBCT-BZT is clearly distinct compared to what

we have seen before in several Pb and Bi-containing solid solutions with morphotropic phase boundaries [33–35], and indeed support the hypothesis derived from the PDF analyses that the local polarizations and the local environments of the cations in *x*BCT-BZT remain largely invariant in the corresponding range $0.40 \le x \le 0.60$.

Therefore both PDF and Raman-scattering results suggest that the anomalous properties of *x*BCT-BZT in the region of phase instability ought to be dictated by some other factors beyond the canonical factors, since polarizability, dipole rotational instability, dielectric instability, phase degeneracy, and adaptive strain distribution, etc., seem to remain very similar across the phase boundary. While all of these factors are responsible for the better properties in this composition range, the emerging dipolar coherence at x = 0.50 as described above is unique, and could be linked to the extraordinary piezoelectricity of the system at this composition. Nevertheless, it also explains why the leading mechanism in this case cannot be the typical polarization rotation phenomena, and should be the processes like synchronous domain switching effect instead [5].

In summary, we have presented statistical descriptions of the atomic-level polar ordering in piezoelectric xBCT-BZT as a function of composition, which can be related to an increased coherence among the different types of cations at the critical composition. The coherence should be appreciated as an overall dipole-dipole accord-not limited to nearest neighbors, which facilitates coupled macroscopic responses in the system under external stimuli, and therefore plays the pivotal role in the exhibition of very high piezoelectricity. Surely this observation and the complying concept not only provide an answer to the mysterious behavior of xBCT-BZT at x = 0.50, but also creates a new paradigm where underlying disorder-polarization coupling effects would be considered to manipulate the physical properties of ferroelectric systems. It is therefore expected that the current results will evoke further investigations to understand the specific roles of different chemical constituents in other promising Pb-free and Pbbased systems to build robust structure-property relationships and develop novel systems in general.

Financial support from Deutsche Forschungsgemeinschaft (MI 1127/8-2) is gratefully acknowledged. R.R. acknowledges the Science and Engineering Research Board (SERB), Ministry of Science and Technology, India for financial support (Grant No. EMR/2016/001457). We are hugely grateful to David Keen (GEM, ISIS Facility, UK) for the assistance with data collection and correction. K.D. would like to thank Matt Tucker (ORNL) for helpful discussions regarding RM-CPROFILE.

- W. Liu and X. Ren, Large Piezoelectric Effect in Pb-Free Ceramics, Phys. Rev. Lett. 103, 257602 (2009).
- [2] J. Roedel, W. Jo, K. T. P. Seifert, E.-M. Anton, T. Granzow, and D. Damjanovic, Perspective on the development of leadfree piezoceramics, J. Am. Ceram. Soc. 92, 1153 (2009).
- [3] G. Tutuncu, B. Li, K. Bowman, and J. L. Jones, Domain wall motion and electromechanical strain in

lead-free piezoelectrics: Insight from the model system $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3-x(Ba_{0.7}Ca_{0.3})TiO_3$ using in situ high-energy x-ray diffraction during application of electric fields, J. Appl. Phys. **115**, 144104 (2014).

[4] J. Gao, X. Hu, Le Zhang, F. Li, L. Zhang, Yu Wang, Y. Hao, L. Zhong, and X. Ren, Major contributor to the large piezoelectric response in (1-x)Ba(Zr_{0.2}Ti_{0.8})O₃-x(Ba_{0.7}Ca_{0.3})TiO₃ ceramics: Domain wall motion, Appl. Phys. Lett. **104**, 252909 (2014).

- [5] M. Acosta, N. Novak, G. A. Rossetti, Jr., and J. Rödel, Mechanisms of electromechanical response in (1-x)Ba(Zr_{0.2}Ti_{0.8})O₃-x(Ba_{0.7}Ca_{0.3})TiO₃ ceramics, Appl. Phys. Lett. **107**, 142906 (2015).
- [6] M. Acosta, N. Khakpash, T. Someya, N. Novak, W. Jo, H. Nagata, G. A. Rossetti, Jr., and J. Rödel, Origin of the large piezoelectric activity in $(1 - x)Ba(Zr_{0.2}Ti_{0.8})O_3$ - $x(Ba_{0.7}Ca_{0.3})TiO_3$ ceramics, Phys. Rev. B **91**, 104108 (2015).
- [7] S. Zhukov, M. Acosta, Y. A. Genenko, and H. Von Seggern, Polarization dynamics variation across the temperatureand composition-driven phase transitions in the lead-free Ba(Zr_{0.2}Ti_{0.8})O₃-x(Ba_{0.7}Ca_{0.3})TiO₃ ferroelectrics, J. Appl. Phys. **118**, 134104 (2015).
- [8] D. S. Keeble, F. Benabdallah, P. A. Thomas, M. Maglione, and J. Kreisel, Revised structural phase diagram of (Ba_{0.7}Ca_{0.3}TiO₃)-(BaZr_{0.2}Ti_{0.8}O₃), Appl. Phys. Lett. **102**, 092903 (2013).
- [9] Y. Tian, X. Chao, L. Jin, L. Wei, P. Liang, and Z. Yang, Polymorphic structure evolution and large piezoelectric response of lead-free (Ba, Ca)(Zr, Ti)O₃ ceramics, Appl. Phys. Lett. 104, 112901 (2014).
- [10] K. Brajesh, K. Tanwar, M. Abebe, and R. Ranjan, Relaxor ferroelectricity and electric-field-driven structural transformation in the giant lead-free piezoelectric (Ba, Ca)(Ti, Zr)O₃, Phys. Rev. B 92, 224112 (2015).
- [11] M. Acosta, N. Novak, V. Rojas, S. Patel, R. Vaish, J. Koruza, G. A. Rossetti, and J. Rödel, BaTiO₃-based piezoelectrics: Fundamentals, current status, and perspectives, Appl. Phys. Rev. 4, 041305 (2017).
- [12] L. Zhang, X. Ren, and M. A. Carpenter, Influence of local strain heterogeneity on high piezoelectricity in 0.5Ba(Zr_{0.2}Ti_{0.8})O₃-0.5(Ba_{0.7}Ca_{0.3})TiO₃ ceramics, Phys. Rev. B **95**, 054116 (2017).
- [13] Y. Nahas, A. Akbarzadeh, S. Prokhoreko, S. Prosandeev, R. Walter, I. Kornev, J. Íñiguez, and L. Bellaiche, Microscopic origins of the large piezoelectricity of leadfree (Ba, Ca)(Zr, Ti)O₃, Nat. Commun. 8, 16172 (2017), corrigendum.
- [14] R. Resta, "Macroscopic polarization in crystalline dielectrics: The geometric phase approach," Rev. Mod. Phys. 66, 899 (1994).
- [15] I. Grinberg, V. Cooper, and A. Rappe, Relationship between local structure and phase transitions of a disordered solid solution, Nature (London) 419, 909 (2002).
- [16] D. S. Keeble, E. R. Barney, D. A. Keen, M. G. Tucker, J. Kreisel, and P. A. Thomas, Bifurcated polarization rotation in bismuth-based piezoelectrics, Adv. Funct. Mater. 23, 185 (2013).
- [17] N. Zhang, H. Yokota, A. M. Glazer, Z. Ren, D. A. Keen, D. S. Keeble, P. A. Thomas, and Z.-G. Ye, The missing boundary in the phase diagram of $PbZr_{1-x}Ti_xO_3$, Nat. Commun. **5**, 5231 (2014).
- [18] K. Datta, A. Richter, M. Göbbels, D. A. Keen, and R. B. Neder, Direct mapping of microscopic polarization in ferroelectric $xBiScO_3$ - $(1 x)PbTiO_3$ throughout its morphotropic phase boundary, Phys. Rev. B **93**, 064102 (2016).
- [19] K. Brajesh, M. Abebe, and R. Ranjan, Structural transformations in morphotropic-phase-boundary composition of the lead-

free piezoelectric system Ba(Zr_{0.2}Ti_{0.8})O₃-(Ba_{0.7}Ca_{0.3})TiO₃, Phys. Rev. B **94**, 104108 (2016).

- [20] P. Day, J. Enderby, W. Williams, L. Chapon, A. Hannon, P. Radaelli, and A. Soper, Scientific reviews: Gem: The general materials diffractometer at ISIS-multibank capabilities for studying crystalline and disordered materials, Neutron News 15, 19 (2004).
- [21] M. G. Tucker, D. A. Keen, M. T. Dove, A. L. Goodwin, and Q. Hui, RMCProfile: Reverse Monte Carlo for polycrystalline materials, J. Phys.: Condens. Matter 19, 335218 (2007).
- [22] See Supplemental Material http://link.aps.org/supplemental/ 10.1103/PhysRevB.102.060102 for additional figures and details on the adopted methodology for the data analyses, which includes Refs. [23,30–32].
- [23] R. B. Neder and T. Proffen, Diffuse scattering and defect structure simulations—A cook book using the program DISCUS (Oxford University Press, London, UK, 2007).
- [24] T. Egami, Local structure of ferroelectric materials, Annu. Rev. Mater. Res. 37, 297 (2007).
- [25] G. H. Kwei, S. J. L. Billinge, S.-W. Cheong, and J. G. Saxton, Pair-distribution functions of ferroelectric perovskites: Direct observation of structural ground states, Ferroelectrics 164, 57 (1995).
- [26] B. Ravel, E. A. Stern, R. I. Vedrinskii, and V. Kraizman, Local structure and the phase transitions of BaTiO₃, Ferroelectrics 206, 407 (1998).
- [27] S. Hashemizadeh, A. Biancoli, and D. Damjanovic, Symmetry breaking in hexagonal and cubic polymorphs of BaTiO₃, J. Appl. Phys. **119**, 094105 (2016).
- [28] A. R. Oganov and M. Valle, How to quantify energy landscapes of solids, J. Chem. Phys. 130, 104504 (2009).
- [29] A. P. Turygin, M. M. Neradovskiy, N. A. Naumova, D. V. Zayats, I. Coondoo, A. L. Kholkin, and V. Ya. Shur, Domain structures and local switching in lead-free piezoceramics Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O₃, J. Appl. Phys. **118**, 072002 (2015).
- [30] A.-M. Welsch, B. J. Maier, B. Mihailova, R. J. Angel, J. Zhao, C. Paulmann, J. M. Engel, M. Gospodinov, V. Marinova, and U. Bismayer, Transformation processes in relaxor ferroelectric PbSc_{0.5}Ta_{0.5}O₃ heavily doped with Nb and Sn, Z. Kristallogr. 226, 126 (2011).
- [31] V. Buscaglia, S. Tripathi, V. Petkov, M. Dapiaggi, M. Deluca, A. Gajović, and Y. Ren, Average and local atomic-scale structure in Ba $Zr_xTi_{1-x}O_3$ (x = 0.10, 0.20, 0.40) ceramics by high-energy x-ray diffraction and Raman spectroscopy, J. Phys.: Condens. Matter **26**, 065901 (2014).
- [32] I.F. Chang and S.S. Mitra, Long wavelength optical phonons in mixed crystals, Adv. Phys. 20, 359 (1971).
- [33] K. Datta, R. B. Neder, J. Chen, J. C. Neuefeind, and B. Mihailova, Atomic-level structural correlations across the morphotropic phase boundary of a ferroelectric solid solution: $xBiMg_{1/2}Ti_{1/2}O_3$ -(1 x)PbTiO₃, Sci. Rep. 7, 471 (2017).
- [34] K. Datta, R. B. Neder, J. Chen, J. C. Neuefeind, and B. Mihailova, Favorable Concurrence of Static and Dynamic Phenomena at the Morphotropic Phase Boundary of *x*BiNi_{0.5}Zr_{0.5}O₃-(1-*x*)PbTiO₃, Phys. Rev. Lett. **119**, 207604 (2017).
- [35] K. Datta, R. B. Neder, A. Richter, M. Göbbels, J. C. Neuefeind, and B. Mihailova, Adaptive strain prompting a pseudo-morphotropic phase boundary in ferroelectric (1 x)Na_{0.5}Bi_{0.5}TiO₃-xBaTiO₃, Phys. Rev. B **97**, 184101 (2018).