Structural Heterogeneity and Diffuse Scattering in Morphotropic Lead Zirconate-Titanate Single Crystals

R. G. Burkovsky, Yu. A. Bronwald, A. V. Filimonov, A. I. Rudskoy, D. Chernyshov, A. Bosak, J. Hlinka, X. Long, Z.-G. Ye, and S. B. Vakhrushev

Phys. Rev. Lett. **109**, 097603 — Published 29 August 2012

DOI: 10.1103/PhysRevLett.109.097603

Structural heterogeneity and diffuse scattering in morphotropic lead zirconate-titanate single crystals

R. G. Burkovsky,[1,2,*] Yu. A. Bronwald,[1] A. V. Filimonov,[1] A. I. Rudskoy,[1] D. Chernyshov,[3] A. Bosak,[2] J. Hlinka,[4] X. Long,[5] Z.-G. Ye,[5] and S. B. Vakhrushev[6,1]

[1]*St.Petersburg State Politekhnical University, 29 Politekhnicheskaya, 195251, St.-Petersburg, Russia*
[2]*European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France*
[3]*Swiss-Norwegian Beamlines at ESRF, BP 220, F-38043 Grenoble Cedex, France*
[4]*Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague 8, Czech Republic*
[5]*Department of Chemistry and 4D LABS, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6*
[6]*Ioffe Phys.-Tech. Institute, 26 Politekhnicheskaya, 194021, St.-Petersburg, Russia*

Complementary diffuse and inelastic synchrotron X-ray scattering measurements of lead zirconate-titanate (PZT) single crystals with composition near the morphotropic phase boundary (x=0.475) are reported. In the temperature range 293 K < T < 400 K a highly anisotropic quasielastic diffuse scattering is observed. Above 400 K this scattering disappears. Its main features can be reproduced by model of inhomogeneous lattice deformations caused by inclusions of a tetragonal phase into a rhombohedral or monoclinic phase. This observation supports the idea that PZT at its morphotropic phase boundary is essentially structurally inhomogeneous.

PACS numbers: 77.80.B-, 61.72.Dd

Lead zirconate-titanate ($PbZr_{1-x}Ti_xO_3$, PZT) is one of the most technologically important ferroelectrics [1, 2]. Being widely employed in practice PZT is also a model system representing ferroelectric solid solutions with a morphotropic phase boundary (MPB). Understanding of the mechanisms leading to very high dielectric and piezoelectric responses near the MPB is essential for strategic design of new and improved materials, particularly the ecologically friendly lead-free PZT counterparts [3]. Numerous theoretical and experimental studies performed on different lead-containing MPB ferroelectrics produce a highly complex and often controversial picture. Many of these aspects are covered in a 2006 review by Noheda and Cox [4] and references therein. More recent trends are briefly highlighted in a 2009 editorial review by Kreisel et al. [5]. Recently the morphotropic PZT single crystals of various compositions become available [6], which has opened up new experimental possibilities. The first single-crystal diffraction experiments [7, 8] did not provide the final conclusion regarding the true microscopic structure of PZT, but allowed to make several important conclusions. On the basis of neutron diffraction study of morphotropic PZT with x=0.46, it was shown [7] that low-temperature monoclinic *Cc* phase should be ruled out as a ground state and a coexistence of rhombohedral and monoclinic *Cm* domains should be considered instead. High-resolution X-ray diffraction study [8] also supports a phase coexistence model for that composition. By using 2-dimensional single-crystal scattering maps instead of 1-dimensional powder spectra the authors succeeded in resolving otherwise overlapping Bragg reflections and demonstrated the presence of more than one phase. The idea of phase coexistence was also supported by recent studies by anelastic and dielectric spectroscopy [9] and neutron powder diffraction [10].

A number of times it was also pointed out that morphotropic PZT can be inhomogeneous on the nanoscale. This point of view is supported by observation of nanometric contrast fluctuations within micrometer-scale domains in PZT by transmission electron microscopy [11, 12]. Twinned nanodomains were also considered as a cause for unusual optical isotropy [6] revealed in the tetragonal phase of PZT with x=0.46. From another point of view [13] the nanoscale heterogeneity in PZT can be connected with regions of short-range correlated monoclinic ionic displacements which on average produce the diffraction pattern compatible with rhombohedral and tetragonal symmetry at different sides of the phase diagram. It was also suggested on the basis of single-crystal inelastic X-ray scattering [14] that morphotropic PZT has similar to relaxors relaxational-type zone-boundary lattice dynamics and shares with them some intrinsic nanoscale inhomogeneity.

A powerful technique of studying structural and other types of inhomogeneities in crystals is diffuse scattering (DS). Particularly it proves itself useful in the studies of structural instabilities in ferroelectrics and related systems [15]. In PZT of different compositions the diffuse scattering planes, perpendicular to < 111 > pseudocubic directions, were observed by transmission electron microscopy [13, 16]. These planes were generally interpreted [13, 16, 17] as a result of correlated Pb displacements. In this Letter, by means of diffuse and inelastic X-ray scattering, we show that near the morphotropic phase boundary there exists a completely different type of diffuse scattering, which takes the form of rods in reciprocal space. The characteristics of this DS suggest that it originates not from correlated displacements but

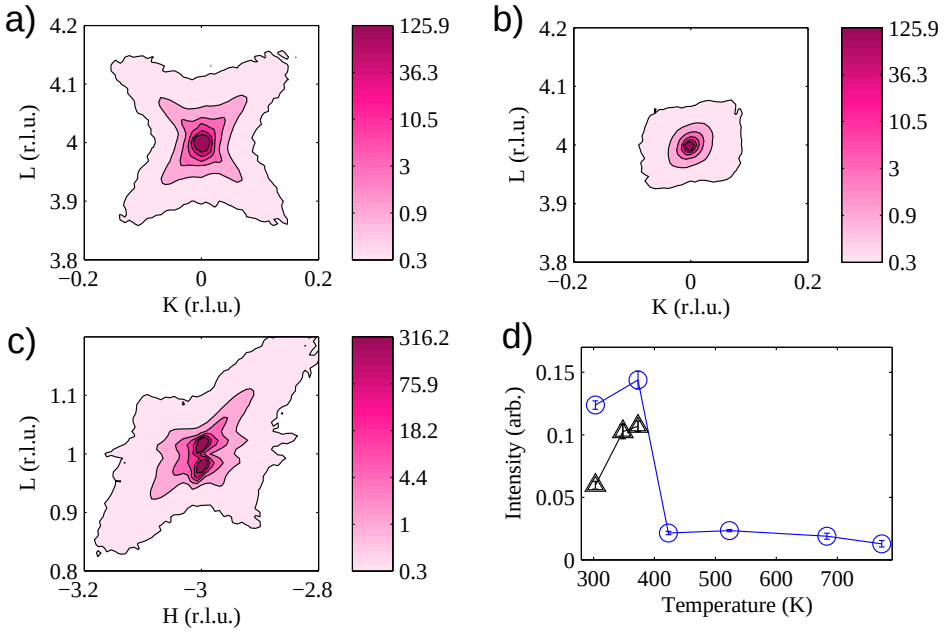

FIG. 1: Diffuse scattering (DS) distributions in the (0 0 4) zone at room temperature (a) and 683 K (b), DS distribution in the (-3 0 1) zone at room temperature (c), temperature dependence of integrated DS intensity during heating (circles) and cooling (triangles) (d).

from elastic deformations due to structural heterogeneity of PZT below MPB.

Morphotropic $PbZr_{1-x}Ti_xO_3$ single crystals with $PbTiO_3$ content x=0.475 were grown by a top-seeded solution method. For the X-ray measurements a stick-shaped sample with about 100 x 100 micrometer cross-section was prepared by slicing, polishing and subsequent etching in HCl acid. Diffraction and diffuse scattering measurements were carried out at Swiss-Norwegian beamlines at ESRF using KUMA (Oxford Diffraction) diffractometer with CCD detector. A locally constructed heat blower was used for heating up to 773 K.

At room temperature we obtained the diffuse scattering distributions in the (0 0 4) and (-3 0 1) zones (Figs. 1a, and 1c). They are highly anisotropic and appear to resemble the DS shapes in relaxors [18, 19]. On heating this strong DS disappears at temperatures between 373 K and 423 K and only weak, but also anisotropic diffuse halo remains up to 773 K. Characteristic distribution of this high-temperature DS is shown in Fig. 1b. On cooling the strong DS reappears in the same temperature region, but according to our measurements is systematically less intense than before heating. The temperature dependence of the DS intensity is presented on Fig. 1d. The intensity points on that plot correspond to the values of parameter I_0 obtained by data fits described below.

A log-log plot of diffuse scattering profile along the high-intensity direction [0 1 -1] in the (0 0 4) zone is presented in Fig. 2. The data for $q < 0.02$ r.l.u. are spoiled by Bragg scattering and not included in the plot. For larger q values a power law $I(q) = I_0 q^{-s}$ is observed with the power $s = 2 \pm 0.2$. The corresponding fit is shown by solid line. For estimation of the temperature dependence of DS intensity in Fig. 1d the value of parameter s was rounded up to be 2.

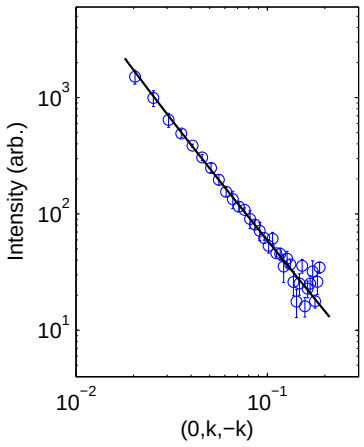

FIG. 2: Diffuse scattering profile along the [0 1 -1] direction in the (0 0 4) Brillouin zone at room temperature together with the results of fit by expression $I(q) = I_0 q^{-s}$.

Diffuse scattering distributions obtained at SNBL in-

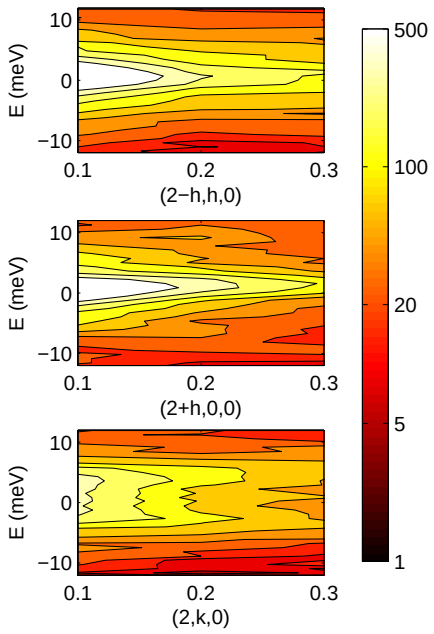

FIG. 3: Inelastic X-ray scattering intensity maps for the diagonal, longitudinal and transverse directions in the (2 0 0) Brillouin zone.

clude both the elastic and inelastic contributions. To distinguish the nature of this DS we additionally performed an inelastic X-ray scattering (IXS) experiment at ID28 ESRF beamline. The resolution was about 3 meV. The IXS maps along the diagonal (2-h,h,0), longitudinal (2+h,0,0) and transverse (2,k,0) directions are presented in Fig. 3. These maps apparently demonstrate that the maximum signal corresponds to elastic scattering (E=0) for diagonal and longitudinal directions but no elastic line is observed for transverse direction. This contrasts with the DS in relaxors where temperature-dependent DS exists in the transverse direction but is almost absent in the longitudinal direction [20].

Surprisingly, we do not see any increase of X-ray DS intensity near T=663 K, where the cubic-to-tetragonal transition takes place. In fact this transition is accompanied by a strong central peak in Brillouin scattering [21], most possibly associated with ferroelectric fluctuations. We do not see such fluctuations by X-rays near high-temperature transition and thus do not expect to observe them near low-temperature transition. This way we see the strong increase of DS intensity below 423 K as a sign of developing heterogeneity. A starting point for interpreting this heterogeneity can be set up on the basis of previous results, that indicate the simultaneous presence of multiple phases. We start from an assumption that a host phase of specific symmetry contains clusters of a different symmetry. In this case the DS can be described by the terms corresponding to the form factor of the clusters and the factor describing the impact of these clusters on the matrix [22]:

$$I = N_d e^{-2W} \frac{1}{v^2 \lambda} \sum_{\alpha=1}^{\lambda} |s_\alpha(\vec{q})|^2 |\Delta f - f \vec{Q} \vec{A}_{\vec{q}\alpha}|^2. \qquad (1)$$

The intensity is proportional to the number of defect centers N_d, Debye-Waller factor e^{-2W} and a sum of λ additives. Each additive describes the scattering due to particle of orientation α. The shape of particle is represented by Fourier transform of corresponding shape function $s_\alpha(\vec{q})$, where $\vec{q} = \vec{Q} - \vec{\tau}$. Δf represents the difference between the structure factors of the host phase and the clusters. The term $f\vec{Q}\vec{A}_{\vec{q}\alpha}$ describes the scattering due to elastic deformations caused in matrix by particles. This latter term is assumed to be dominant in comparison with Δf since the structures of matrix and particles in PZT are expected to be very close.

We do not see any distinct deviation of scattering profile from q^{-2} law in the whole region with acceptable signal/noise ratio, up to $q \approx 0.1$ r.l.u., which means that the clusters dimensions should not exceed 10 unit cells. Neither we see any contribution from the Bragg peaks of the tetragonal phase. These observations allow to conclude that the particles are small and we can consider the form factor $s_\alpha(\vec{q})$ as constant and model the DS as being solely due to elastic deformations. Fourier components of the lattice deformation fields in Eq.(1) are calculated as

$$A_{\alpha i}(\mathbf{q}) = \frac{1}{q} N_d C^{-1}_{ij}(\mathbf{q}) p_{\alpha j l} n_l, \qquad (2)$$

where $\mathbf{n} = \mathbf{q}/q$. The tensors $C_{ij}(\mathbf{q}) = c_{iljm} n_l n_m$ and $p_{\alpha ij} = \sum c_{ijlm} L_{\alpha lm}$ are calculated from the crystal elastic constants c_{ijlm}. The tensor $L_{\alpha jl}$ describes the contribution of point-like defects to the strain of the lattice. We find that the best agreement is achieved with defects of tetragonal symmetry described by characteristic tensor L with only non-zero elements $L_{xx} = L_{yy} = -2L_{zz}$. The defects of this type tend to compress the surrounding lattice in x and y directions while elongating it in the remaining z direction or vice versa. The volume of unit cell tends to be preserved. The elastic constants of morphotropic PZT single crystals, needed for calculations, have not yet been determined experimentally, but ceramics data (see Ref. 23 and references therein) and theoretical estimations [24] are available. Pseudocubic elastic constants extracted from ceramics data [23] allow us to get a satisfactory qualitative description of DS distributions. However the best agreement we find with slightly changed constants $c_{11} = 135$, $c_{12} = 75$ and $c_{44} = 70$ GPa. Corresponding calculations and comparison with experiment are presented in Fig. 4.

Despite apparent simplicity of our model we find it very reasonable. While we do not know the exact symmetry of the host phase we may assume it to be close

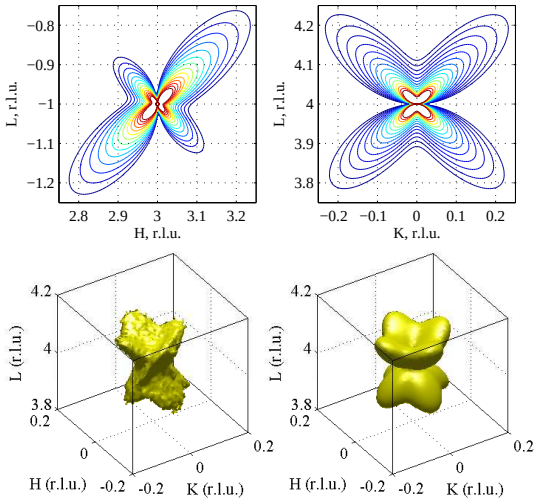

FIG. 4: Model calculations of Huang scattering due to tetragonal defects in (0 0 4) and (-3 0 1) Brillouin zones (upper row) and three-dimensional comparison of experiment and calculations in (0 0 4) zone (bottom row)

to cubic. First because the deviations from cubic structure at least for compositions close to MPB are rather small. Secondly, after averaging over all possible orientations of monoclinic/rhombohedral domains the matrix will appear effectively cubic. The assumption of tetragonal symmetry of clusters is also well-founded since previous studies indicate the signs of tetragonal phase in the MPB region. And, at last, this model perfectly reproduces all the main peculiarities of the DS revealed by our experiments. It gives a zero-intensity transverse plane in high-symmetry (0 0 L) zones and a non-zero longitudinal scattering. Also it reproduces the observed q^{-2} scattering law. This combination could not be reproduced by purely form-factor based models such as the ones, proposed in Ref. 25.

In this Letter we have shown that morphotropic PZT single crystals are characterized by strong anisotropic diffuse scattering below ferroelectric-ferroelectric transition point. The shape of DS is visually similar to that in relaxors, but the exact topology of DS is essentially different for these two. This observation implies different microscopic origins. Indeed we show that Huang scattering formalism, which seems inapplicable for DS in relaxors, adequately describes key details of DS in PZT. The topology of this DS indicates the presence of elastic deformations induced by the defect centres of tetragonal symmetry, which fits well to the concept of "survival" of small clusters of tetragonal phase after cooling below T_{MPB}.

It is a pleasure to acknowledge P. M. Gehring and A. K. Tagantsev for many useful discussions and various suggestions. The work at SPbSPU was supported by Federal Program "Research and development on high-priority directions of improvement of Russia's scientific and technological complex" for 2007-2013 years and by grant of the St.-Petersburg government. The work at Ioffe institute was supported by RFBR grant 11-02-00687-a. The work at Institute of Physics was supported by the Czech Science Foundation (GACR P204/10/0616). The work at SFU was supported by the U.S. Office of Naval Research (Grants No N00014-06-1-0166 and N00014-11-1-0552) and the Natural Sciences and Engineering Research Council of Canada.

* Electronic address: rg.burkovsky@mail.ioffe.ru

[1] G. H. Haertling, Journal of the American Ceramic Society **82**, 797 (1999).
[2] J. F. Scott, Science **315**, 954 (2007).
[3] E. Cross, Nature **432**, 24 (2004).
[4] B. Noheda and D. E. Cox, Phase Transitions **79**, 5 (2006).
[5] J. Kreisel, B. Noheda, and B. Dkhil, Phase Transitions **82**, 633 (2009).
[6] A. A. Bokov, X. Long, and Z.-G. Ye, Phys. Rev. B **81**, 172103 (2010).
[7] D. Phelan, X. Long, Y. Xie, Z.-G. Ye, A. M. Glazer, H. Yokota, P. A. Thomas, and P. M. Gehring, Phys. Rev. Lett. **105**, 207601 (2010).
[8] S. Gorfman, D. S. Keeble, A. M. Glazer, X. Long, Y. Xie, Z.-G. Ye, S. Collins, and P. A. Thomas, Phys. Rev. B **84**, 020102 (2011).
[9] F. Cordero, F. Trequattrini, F. Craciun, and C. Galassi, Journal of Physics: Condensed Matter **23**, 415901 (2011).
[10] N. Zhang, H. Yokota, A. M. Glazer, and P. A. Thomas, Acta Crystallographica Section B **67**, 386 (2011).
[11] K. A. Schönau, L. A. Schmitt, M. Knapp, H. Fuess, R.-A. Eichel, H. Kungl, and M. J. Hoffmann, Phys. Rev. B **75**, 184117 (2007).
[12] T. Asada and Y. Koyama, Phys. Rev. B **75**, 214111 (2007).
[13] A. M. Glazer, P. A. Thomas, K. Z. Baba-Kishi, G. K. H. Pang, and C. W. Tai, Phys. Rev. B **70**, 184123 (2004).
[14] J. Hlinka, P. Ondrejkovic, M. Kempa, E. Borissenko, M. Krisch, X. Long, and Z.-G. Ye, Phys. Rev. B **83**, 140101 (2011).
[15] P. M. Gehring, H. Hiraka, C. Stock, S.-H. Lee, W. Chen, Z.-G. Ye, S. B. Vakhrushev, and Z. Chowdhuri, Phys. Rev. B **79**, 224109 (2009).
[16] K. Z. Baba-Kishi, T. R. Welberry, and R. L. Withers, Journal of Applied Crystallography **41**, 930 (2008), URL http://dx.doi.org/10.1107/S0021889808026253.
[17] T. R. Welberry, D. J. Goossens, R. L. Withers, and K. Z. Baba-Kishi, METALLURGICAL AND MATERIALS TRANSACTIONS A-PHYSICAL METALLURGY AND MATERIALS SCIENCE **41A**, 1110 (2010).
[18] G. Xu, G. Shirane, J. R. D. Copley, and P. M. Gehring, Phys. Rev. B **69**, 064112 (2004).
[19] A. Bosak, D. Chernyshov, S. Vakhrushev, and M. Krisch, Acta Crystallographica Section A **68**, 117 (2012).
[20] S. Vakhrushev, A. Nabereznov, S. Sinha, Y. Feng, and T. Egami, Journal of Physics and Chemistry of Solids **57**, 1517 (1996).
[21] T. H. Kim, J.-H. Ko, S. Kojima, A. A. Bokov, X. Long,

and Z.-G. Ye, Applied Physics Letters **100**, 082903 (pages 4) (2012), URL http://link.aip.org/link/?APL/100/082903/1.

[22] M. A. Krivoglaz, *X-Ray and Neutron Diffraction in Nonideal Crystals* (Springer-Verlag, 1996).

[23] J. Ouyang and A. Roytburd, Acta Materialia **54**, 5565 (2006), ISSN 1359-6454, URL http://www.sciencedirect.com/science/article/pii/S1359645406005556.

[24] R. Cohen, E. Heifets, and H. Fu, in *AIP Conference Proceedings* (2001), vol. 582, p. 11.

[25] G. Xu, Z. Zhong, H. Hiraka, and G. Shirane, Phys. Rev. B **70**, 174109 (2004).