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Supporting information for article:

New method to measure domain-wall motion contribution to piezoelectricity: the case of $\text{PbZr}_{0.65}\text{Ti}_{0.35}\text{O}_3$ ferroelectric

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S1. Determination of the lattice symmetry and lattice parameters from the splitting of sub-peaks

We use the measured radial reciprocal space separation of the sub-peaks (equivalent to the separation in the 2θ axis) to reconstruct the deviation of the lattice parameters / the elements of the metric tensor ($G_{ij} = \mathbf{a}_i \mathbf{a}_j$). The deviation of the elements of the metric tensor from the cubic one $G_{ij} = a^2 \delta_{ij}$ defines the pattern of splitting in that particular family of peaks. Therefore, initial assessment of the symmetry can be made by the evaluation of the number of split peaks in each family $\{hkl\}_{m\bar{3}m}$ (the subscript $m\bar{3}m$ denotes all the reflections, which are related to hkl by the $m\bar{3}m$ point symmetry group operations). Table S1 shows the number of split peak components, corresponding to cubic, tetragonal, rhombohedral and monoclinic (MA/MB and MC) lattice symmetries.

Symmetry	Lattice parameter (pseudo-cubic cell setting)	$\{h00\}_{m\bar{3}m}$	$\{hh0\}_{m\bar{3}m}$	$\{hk0\}_{m\bar{3}m}$	$\{hhh\}_{m\bar{3}m}$	$\{hkk\}_{m\bar{3}m}$	$\{hkl\}_{m\bar{3}m}$
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	1	1	1	1	1	1
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	2	2	3	1	2	3
Rhombohedral	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	1	2	2	2	3	4

Monoclinic (MA/MB)	$a = b$ $\neq c$ $\alpha = \beta$ $\neq \gamma$	2	4	6	3	7	12
Monoclinic (MC)	$a \neq b$ $\neq c$ $\alpha = \beta$ $\neq \gamma$	3	4	8	2	6	12

Note that the actual number of separated sub-peaks around could be lower as the appearance of the peaks is subject to the presence of corresponding ferroelastic domains in the X-ray beam.

Plausible models of the lattice symmetries are selected from the observed splitting pattern, and the procedure of the lattice parameters' refinement follows the algorithm below. The algorithm resembles the Pawley / Le Bail methods (for the determination of lattice parameters from powder diffraction data) but is modified for the analysis of partially-complete data only with some sub-peaks / ferroelastic domains absent.

- Three-dimensional Cartesian coordinates H_x, H_y, H_z of the sub-peaks in each family of reflections is marked according to the description in §6.1. The length of the reciprocal lattice vector, corresponding to each sub-peak $L_{obs} = \sqrt{H_x^2 + H_y^2 + H_z^2}$ is calculated.
- For the given trial lattice parameters (restrained according to the tested model of the symmetry) the set of the reciprocal lattice vectors' lengths is calculated:

$$L_{calc}^2 = (h \ k \ l)_{m\bar{3}m} [G^*] \begin{pmatrix} h \\ k \\ l \end{pmatrix}_{m\bar{3}m}$$

Here $[G^*] = [G]^{-1}$ and $G_{ij} = \mathbf{a}_i \mathbf{a}_j$.

- The observed sub-peaks are indexed in a way by which the smallest error sum is achieved:

$$\chi^2 = \frac{1}{\sigma^2} \sum_m (L_{calc,m} - L_{obs,m})^2$$

The index m runs over all the sub-peaks of the individual reciprocal space volume. σ is the nominal standard uncertainty of $L_{obs,m}$ (defined by the resolution of the experiment). It is set globally to $\sigma = 0.2 \cdot 10^{-3} \text{ \AA}^{-1}$ for each sub-peak.

- The lattice parameters / the elements of the metric tensor are determined by global optimization, providing the least value of the error sum (the sum runs over all the collected reciprocal space maps)

$$\chi^2 = \sum_n \chi_n^2$$

Table S2 below summarizes the details of the lattice parameters' refinement for seven split reflections of the PZT35 crystal

Parameter	Value
Number of reflections measured	7
Total number of sub-peaks	55
Number of model parameters (R, M, R+M)	2, 4, 6
Global error sums (R, M, R+M)	200, 26, 8

S2. Figure 4 for all the measured reflections $\bar{3}00, \bar{1}11, \bar{1}20, \bar{2}20, \bar{1}21, \bar{2}11, \bar{3}01$.

Attached as a separate seven-page PDF file, kc5109sup2.pdf.

S3. Animation 1: electric field dependence of the diffraction intensity distribution

Animation 1 shows how the distribution of X-ray diffraction intensities in the reciprocal space volumes around all the measured families of twinned peaks ($\bar{3}00, \bar{1}11, \bar{1}20, \bar{2}20, \bar{1}21, \bar{2}11, \bar{3}01$) depend on electric field. Files kc5109sup3.mp4 and kc5109sup4.mp4.

S4. Animation 2: field-dependence of the diffraction intensity distribution

Animation 2 shows the distribution of X-ray diffraction intensities in the reciprocal space volumes around all the measured families of twinned peaks as the function of electric field with the position of the mass centres shown by the larger circle. The cross follows the position of the mass centre reconstructed by using rotation tensor alone. File kc5109sup5.mp4.

S5. Figure 7 for all the measured reflections.

Attached as a separate seven-page PDF file, kc5109sup6.pdf.