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# Local structure heterogeneity in unique tetragonal $BaTiO_3$-based relaxor featuring ultrahigh electrostrictive effect

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## Methods

**Material preparation:** A series of (1-*x*)$BaTiO_3$-*x*($Bi_{0.5}Li_{0.5}$)$TiO_3$ (*x* = 0.10, 0.13, 0.15, 0.17, abbreviated to BT-100*x*BLT) ceramics were fabricated by a conventional solid-state sintering reaction according to the synthesis route described in reference.[1] All raw chemical powders are high-purity $BaCO_3$ (99.95%, Aladdin), $Bi_2O_3$ (99.9%, Aladdin), $Li_2CO_3$ (99.99%, Aladdin), and $TiO_2$ (99.8%, Aladdin). These oxide and carbonate powders were weighed according to the BT-100*x*BLT stoichiometric proportion. The powders were mixed by planetary ball-milling with ethanol for 12 h. Afterward, the mixed powers were dried and then calcined at 800 °C for 2 h. Subsequently, the calcined powders were ball-milled again and dried the same as the first time. The dried powers were ground with 5 wt% polyvinyl alcohol (PVA) and then pressed into disks with the thickness of ~1 mm and diameter of ~10 mm under 200 MPa. The disks covered with powders were heated to 550 °C for 2 h to remove PVA and then sintered at 1130-1350 °C in closed crucibles for 2 h. Some of the fine sintered disks were polished and sputtered with Au electrodes dielectric and ferroelectric measurements.

**Dielectric and ferroelectric Characterization:** The polarization-electric field (P-E) loops (aixACCT, TF Analyzer 1000, Aachen, Germany) was measured with a ferroelectric analyzer (aixACCT, TF Analyzer 1000, Aachen, Germany). The dielectric curves as a function of temperature(100-450K) and frequency (0.1 kHz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz, respectively) were measured by an LCR meter (E4980, Agilent, Santa Clara, CA).

**Phase structure indention**: The phase structure of ceramics was detected by X-ray diffractometer (X'pert PRO, PANalytical, Netherlands) with Cu Kα radiation (λ = 1.54 Å), and the FULLPROF software was adopted to perform Rietveld refinement.[2] The initial structure was set to P4mm below the 325 K, while the initial structure was designated as Pm-3m for the range of 325 K – 475 K.

**Total scattering and big-box refinement based Reverse Monte Carlo:** Neutron

total-scattering data were collected at the NOMAD beamline of Spallation Neutron Source (SNS), Oak Ridge National Laboratory. The pair distribution function (PDF) $G$(r) was reduced from the corrected total scattering structure factors $S$(Q) with $Q_{max}$ =31.4 Å$^{-1}$ by Fourier transform. The PDF $G$(r) fitting was executed using PDFgui.[3] The initial structure remained as P4mm for the whole temperature range. Reverse Monte Carlo refinements were performed to simulate concurrently PDF $G(r)$ and $S(Q)$ with package RMCProfile,[4] which utilizes a 20×20×20 large supercell unit cell containing 40000 atoms based on the Rietveld refined average structure. All movements of atoms position comply with the bond length constraints, the atoms valence constraints, and average coordination constraints. As depicted the insert diagram of Fig. 3a, the coordinates of 12 neighboring oxygen atoms for each *A*-site atoms could be extracted. The geometric center of the $AO_{12}$ polyhedral could be calculated. The geometric center of the $BO_6$ octahedral could be calculated as the same method. Hence, the displacement of *A*/*B*-site could be calculate by the position of *A*/*B*-site atoms minus their geometric center of oxygen cages. Moreover, the polar vectors were calculated in one perovskite unit-cell. Firstly, the coordinates of 6 neighboring oxygen atoms, and the coordinates of 8 neighboring *A*-site atoms of each *B*-site atom can be calculated as above. Subsequently, the center of oxygen and *A*-site atoms in a unit-cell can be found. Lastly, the polar could be calculated the by the displacement between the positive and negative charge centers with minus the unit-cell volume. The more detail information of the calculation polar displacement and polar vectors could refer to our previous works.[567]

**Supporting figures:**

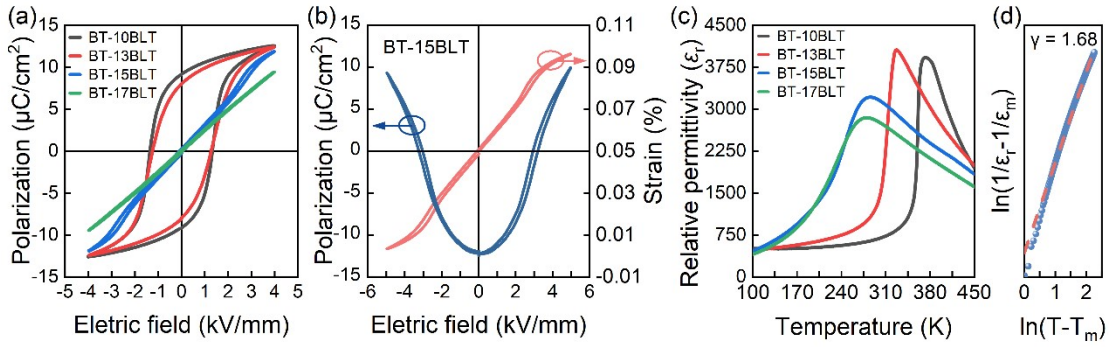


Fig. S1. (a) *P*-*E* loops of dielectric constant of BT-100*x*BLT ceramics. (b) The *P*-*E* loop and *S*-*E* curve of BT-15BLT ceramics. (c) temperature-dependent of dielectric constant of BT-100*x*BLT ceramics. (d) The modified Curie-Weiss distribution of BT-15BLT.

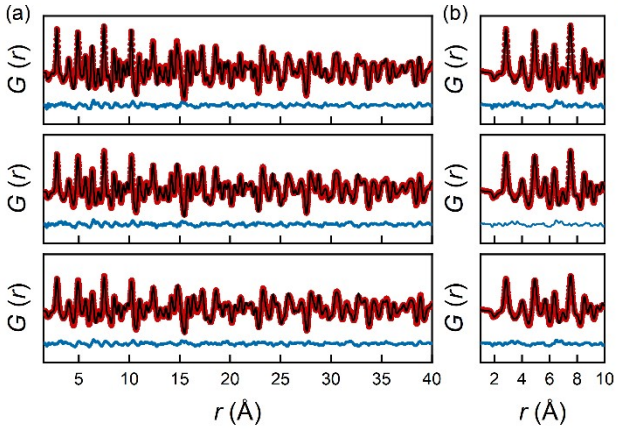


Fig. S2. (a) The 1-40 Å long-range and (b) 1-10 Å short-range PDF fitting at 100 K, 300 K, and 500 K are shown from top to bottom. Red points, black lines, and blue lines indicate the experiment data, calculated data, and residual curves, respectively.

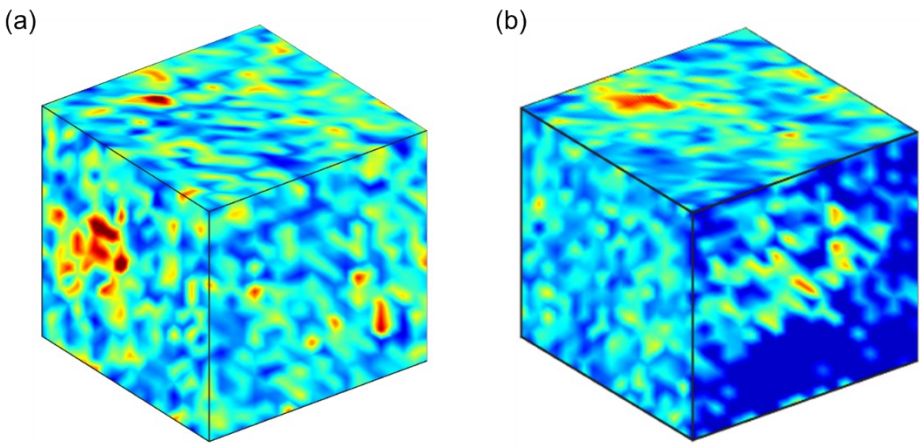


Fig. S3. The 3D distribution of magnitude of polar vector at (a) 100 K, and (b) 500 K, relatively.

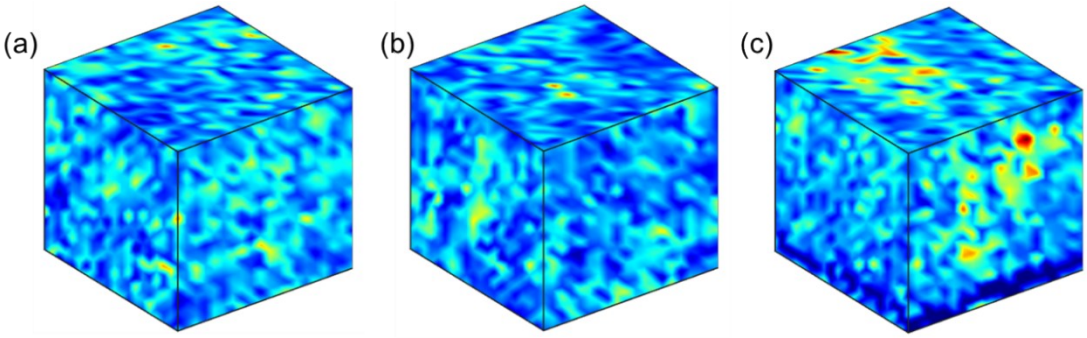


Fig. S4. The 3D polar displacements distribution of B-site atoms at (a) 100 K, (b) 300 K, and (c) 500 K, relatively.

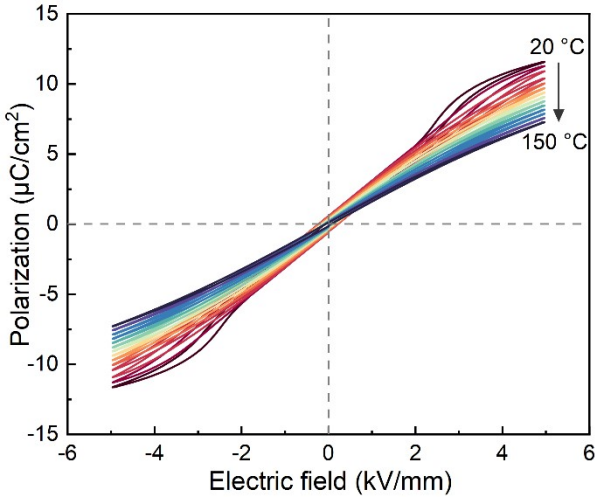


Fig. S5. The bipolar P–E loop measured at different temperatures from 20 ℃ to 150 ℃.

**References**

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