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Quenching-assisted Actuation Mechanisms in Core-shell Structured $BiFeO_3$−$BaTiO_3$ Piezoceramics

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1. EXPERIMENTAL METHOD

1.1 Ceramic Processing and Electrical Measurements

1 mol% Ti-substituted ceramics were synthesised based on the chemical formula of $0.75Bi(Fe_{0.99}\ Ti_{0.01})O_3{-}0.25BaTiO_3$ by the solid state reaction method. 2 mol% Bi_2O_3 excess was also added in order to compensate for the loss of this volatile oxide during sintering. Bi_2O_3 (99%, Alfa Aesar), Fe_2O_3 (99%, Sigma Aldrich), $BaCO_3$ (99%, Alfa Aesar), and TiO_2 (99%, Huntsman Tioxide) were ball-milled in propan-2-ol for 24 h. The milled powders were dried overnight and calcined at 850 °C for 2 h. Additional milling was performed again on the calcined powders for 24 h. Polyethylene glycol (PEG1500 with an average molar mass of 1500 g mol^{-1}) solution as a lubricant was added into the calcined powders at a concentration of 2 *wt*% in order to improve compaction behaviour. The organic additive was burned-out at a temperature of 600°C for 1 h, followed by sintering at temperatures of 1025°C for 2 h in air. The sintered pellets were annealed at 800°C for 20 min and then divided into two groups based on the cooling procedure: i) a slow cooling rate of 300°C/h, and ii) air-quenched to room temperature. The types of ceramic are hereafter denoted as either *slow-cooled* and *quenched*. The relative densities of the sintered ceramics were calculated in terms of the ratio of bulk to theoretical density, which were all found to be >90% during the present study.

Microstructures of chemically-etched and non-etched surfaces were examined using a Philips XL30 FEGSEM equipped with EDS. More details on the SEM sample preparation can be found in References.[1,2] Polarisation-electric field hysteresis measurements were carried out using a function generator (HP 33120A) connected to a Chevin Research HV amplifier to generate the desired high voltage. The samples were subjected to 4 cycles of a sinusoidal electric field with a frequency of 2 Hz. The measured current waveform was integrated numerically over time to yield charge and hence the polarisation was calculated as the surface charge density.[3] Strain-electric field measurements were conducted at room temperature using AixACCT TF 2000 Ferroelectric analyser with a frequency of 0.1 Hz. Low-field dielectric measurements were carried out at fixed frequencies from 1 to 100 kHz over the temperature range from 25 to 670˚C using a HP 4284A Impedance Analyser, Carbolite CWF 12/5 furnace and a desktop computer which was operated by LabVIEW-based program. The measurements were conducted in air upon heating with a rate of 2˚C/min.

1.2 High Energy X-ray Diffraction Characterisation

The ceramic pellets for in-situ high energy x-ray diffraction experiments were prepared by cutting them into dimensions of approximately 0.5 mm (thickness) x 1 mm (width) x 4 mm (length). The experiment was performed on beamline I15 of the Diamond Light Source using high-energy, monochromatic X-rays with photon energy of 76 keV (λ =0.154982 Å). The X-ray beam size was 70 µm in diameter. A custom-designed sample holder was used to support the specimen in the beam and provide electrical contacts, the sample being immersed in silicone oil to avoid arcing during electric field application. The electric field was applied perpendicular to the beam direction using a high voltage amplifier (Matsusada ECA-10). The specimens were subjected to 2 bipolar cycles of an electric field up to 6 kV mm^{-1}, using a step size of 0.5 or 1.0 kV mm^{-1}, depending on the composition. 2D diffraction images were recorded using a Perkin-Elmer XRD 1621 flat-panel detector positioned ≈ 1.1 m from the sample, with a collection time of 10 s. Grain orientations corresponding to the azimuthal angle, Ψ, either parallel or perpendicular to the electric field direction, are denoted as Ψ=0˚ and Ψ=90˚ respectively. In addition, a specific scattering vector of 54.7° was examined, under the assumption that the ferroelectric domain orientations are in a random state (texture-free) and there is zero lattice strain along this direction.[4] The recorded 2D images were integrated into 24 sectors with a 15° interval using *DAWN* software,[5] yielding orientation-dependent 1D

XRD patterns. The converted 1D data was later analysed using TOPAS *v*5 and Matlab for structural refinement and line profile fitting analysis respectively.

2. RESULTS

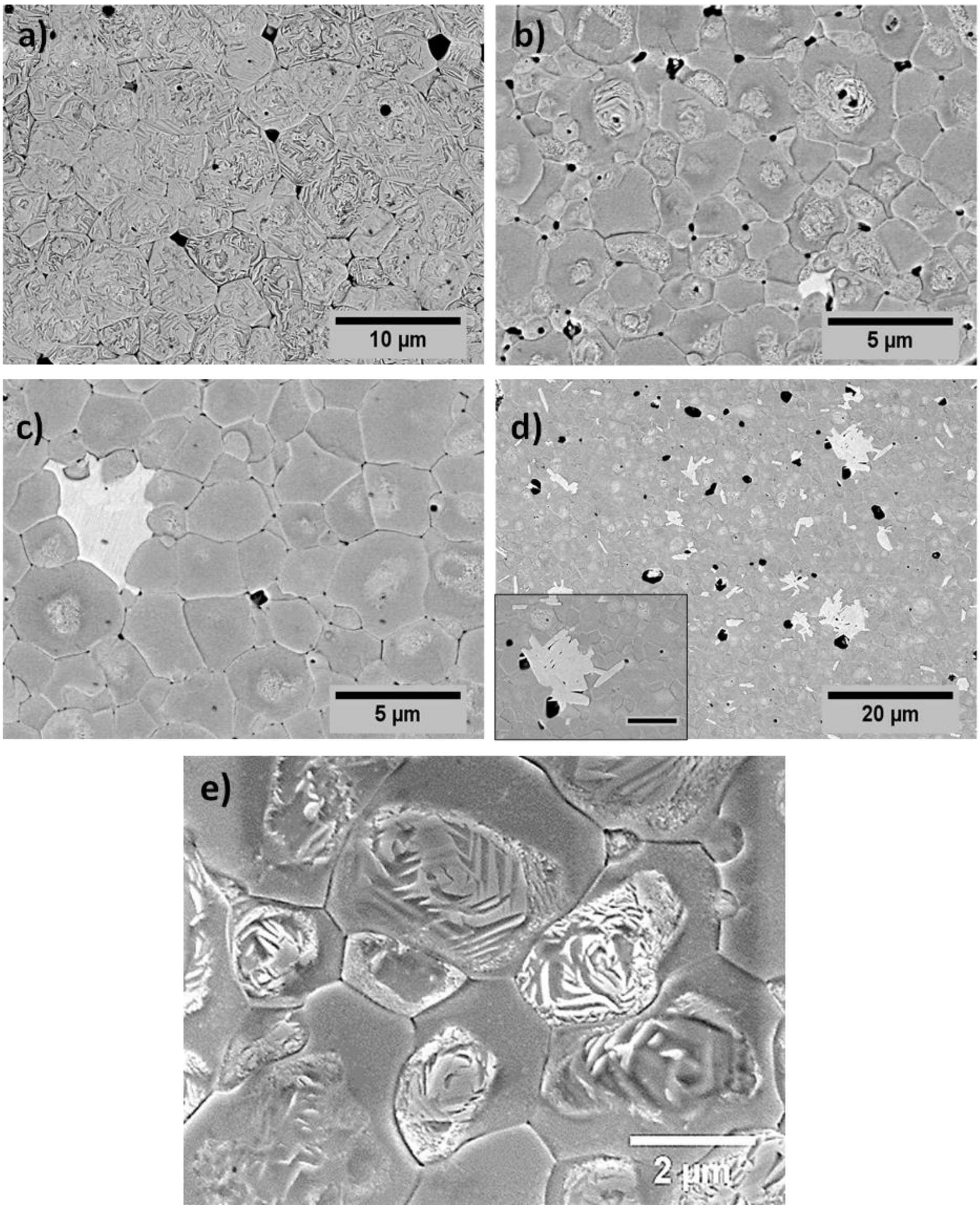

Figure S1. Microstructure of chemically-etched surfaces of **(a)** undoped, **(b)** 1 mol%, **(c)** 3 mol% and **(d)** 5 mol% Ti doped $0.75BiFeO_3$-$0.25BaTiO_3$ ceramics (slow-cooled). The scale bar shown in the inset is 5 µm. **(e)** Higher magnification of microstructure of 1 mol% Ti doped $0.75BiFeO_3$-$0.25BaTiO_3$ ceramics illustrating clear core-shell appearances within grains.

Table S1. Crystallographic parameters obtained from Rietveld analysis for slow-cooled and quenched ceramics. *Goodness of Fit (R_{wp}/R_{exp}).

Parameters	**Slow-cooled**		**Quenched**	
Phases	$R3c^{Core}$	$R3c^{Shell}$	$R3c^{Core}$	$R3c^{Shell}$
Fraction (%)	24.6(9)	75.4(9)	39.4(3)	60.5(3)
Unit cell parameters (Å)				
a_h	5.3325(7)	5.3625(6)	5.3263(4)	5.3651(5)
c_h	13.2020(20)	13.1460(20)	13.2034(12)	13.1649(16)
a_{pc}	3.7841	3.7929	3.7813	3.7959
Lattice distortion (%) η_{rh}	1.07	0.08	1.2	0.18
Inter-axial angles (°)				
α_{rh}	59.53	59.96	59.47	59.92
α_{pc}	89.59	89.97	89.54	89.93
B–O–B (°)	152.3	178.8	157.4	178.9
U_{iso} (Å^2)				
Bi/Ba	4.85(13)	5.12(12)	5.20(17)	4.24(11)
Fe/Ti	1.25(9)	0.95(8)	0.56(10)	0.18(12)
O	2.1(12)	1.45(8)	0.84(7)	1.27(8)
Reliability-factors				
R_{wp} (%)	3.78		2.76	
R_{exp}(%)	2.17		2.19	
GoF*	1.74		1.26	

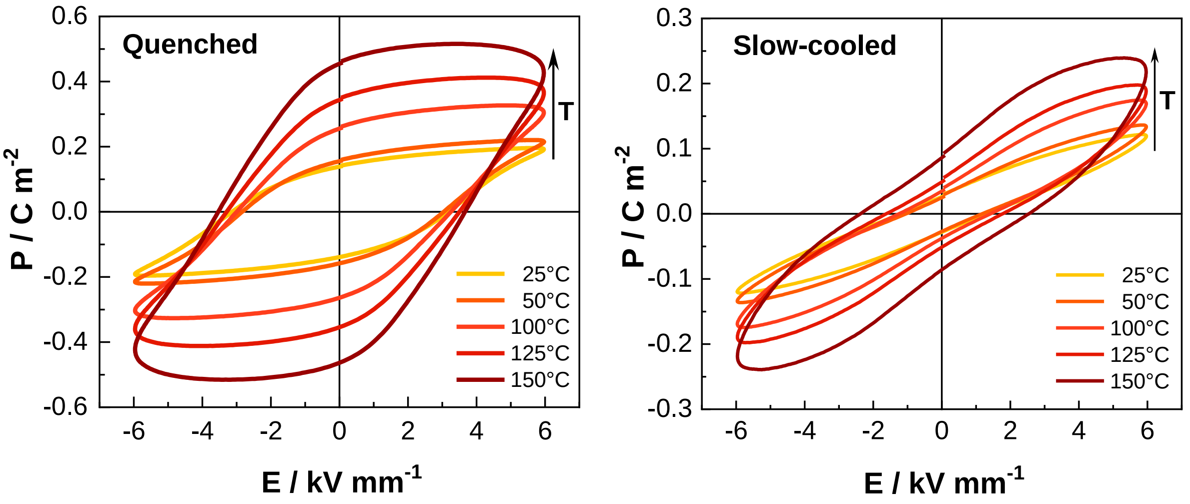

Figure S2. Temperature-dependent P-E hysteresis loops for quenched and slow-cooled BF-BT-1Ti ceramics.

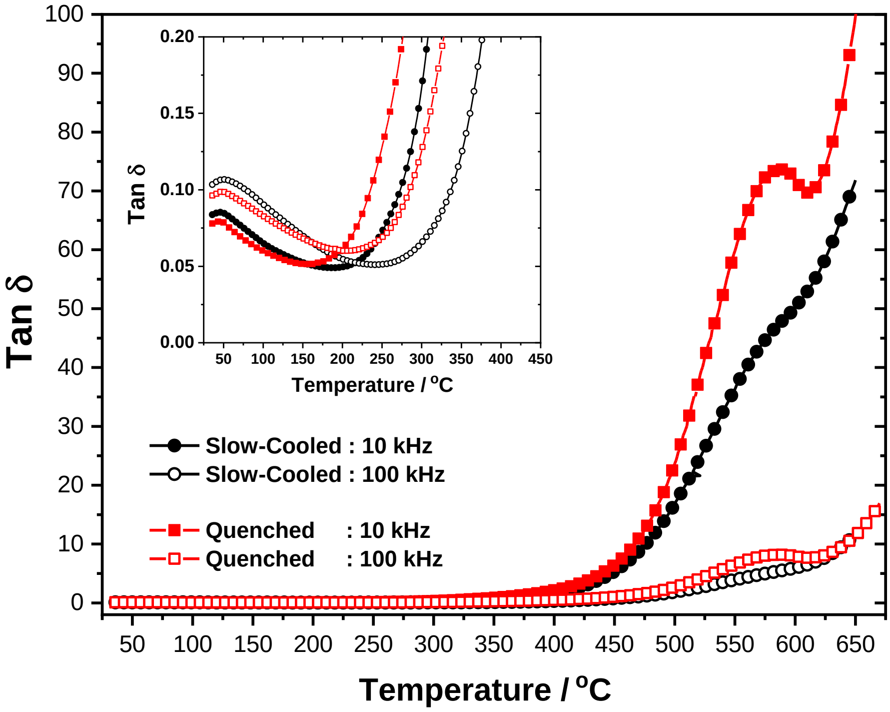

Figure S3. Dielectric loss (tan δ) as a function of temperature and frequency for quenched and slow-cooled BF-BT-1Ti ceramics.

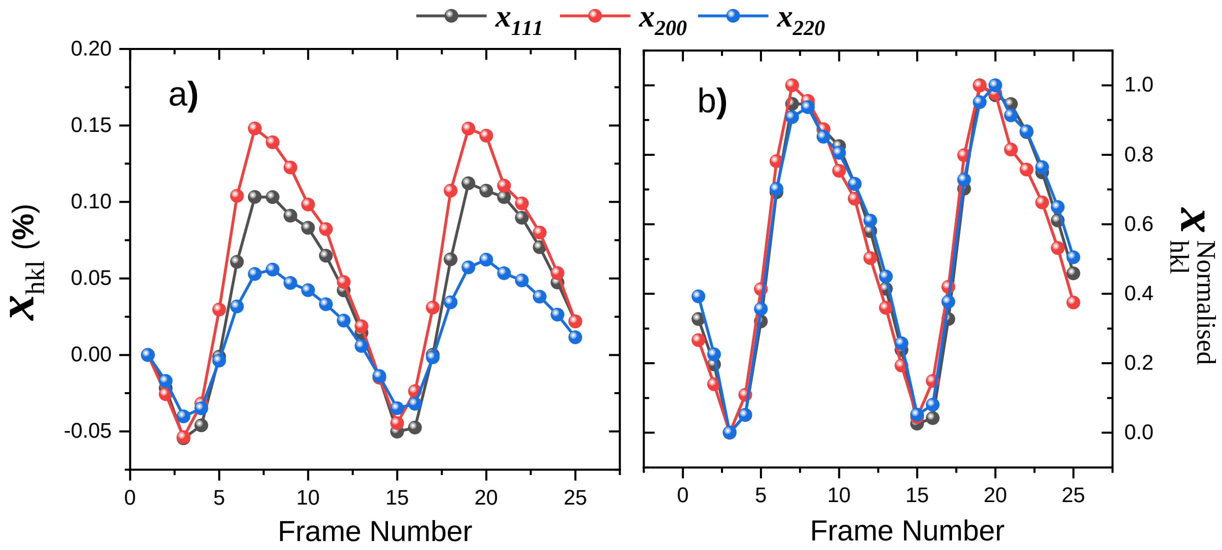

Figure S4. **(a)** Cyclic variations in strain for {111}, {200} and {220} grain families as a function of frame number in response to one bipolar electric field cycle, for ψ = 0°. **(b)** Normalised strain variations of associated *hkl* planes given in (a).

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