Chemical control of octahedral tilting and off-axis A cation displacement allows ferroelectric switching in a bismuth-based perovskite

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Supplementary information

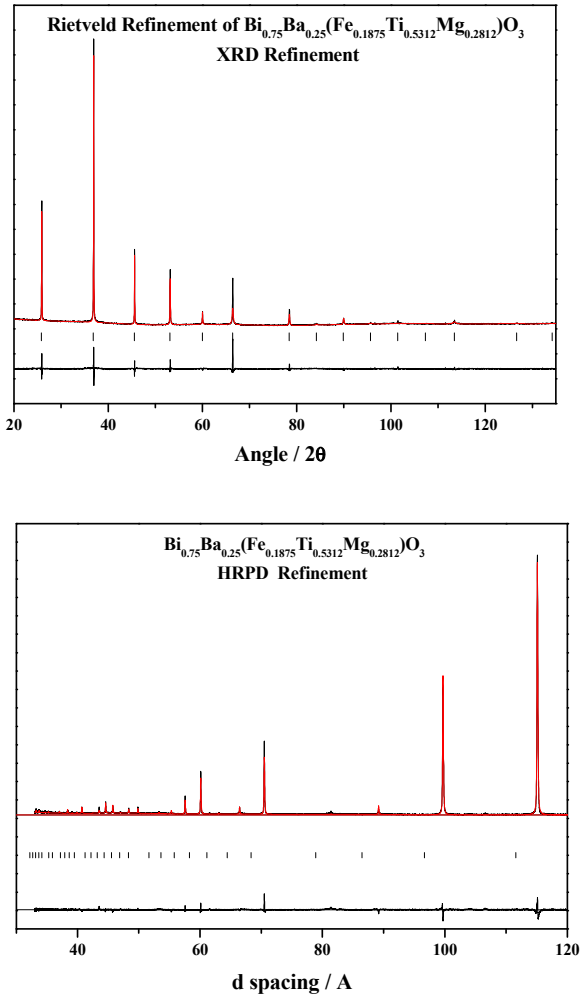


Figure S1: Room temperature Rietveld fit of 0.75BFTM-0.25BT in the $Pm\bar{3}m$ space group with the XRD data on top and the neutron data on the bottom. The XRD fit shows a mismatch in intensity for several of the peaks. The fit is better in the neutron data, but unphysical thermal parameters are the result.

Description of distorted cubic refinement

The distorted $Pm\bar{3}m$ model was based on an ideal cubic perovskite where the atoms are displaced from their special positions along disordered directions. This refinement was performed by systematically moving the cations from their corresponding special position in the [100], [110] or [111] direction without letting the position refine. First the A cation was moved separately, the best fit was taken and the B-cation displacement was added in. The R_{wp} value was recorded and plotted as in Figure S1 against the displacement to determine the distance and direction of movement from the special position. The refinement with the best fit gave an R_{wp} of 6.61.

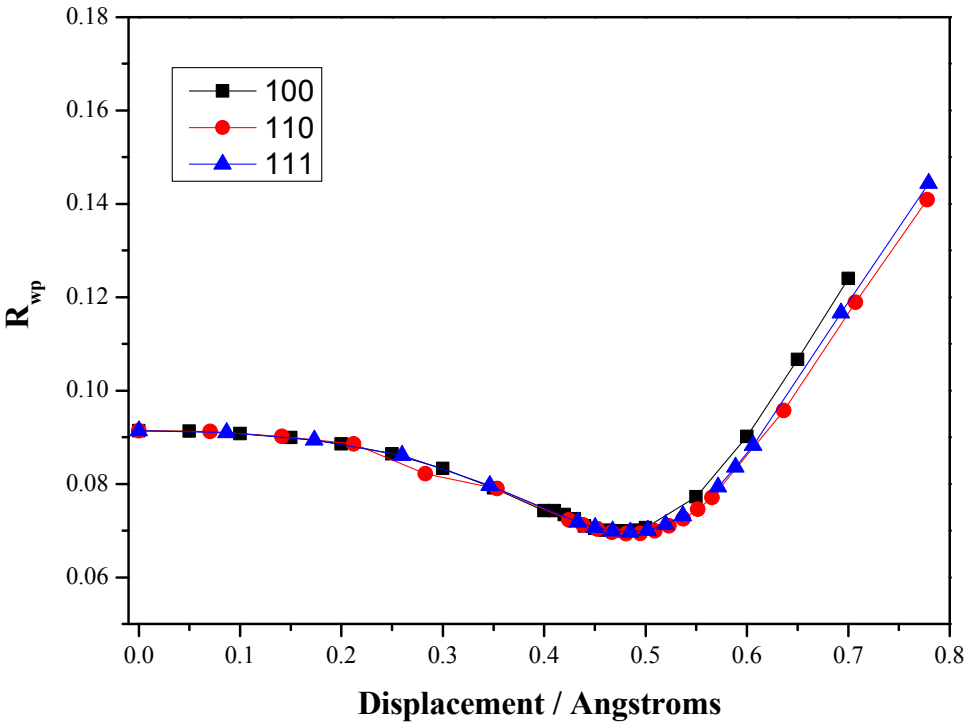


Figure S2: R_{wp} as a function of A-site displacement along the [100], [110], and [111] directions from the room temperature distorted $Pm\bar{3}m$ refinement of 0.75BFTM – 0.25BT.

Table S1: Results from different models used in the Rietveld Refinement

Space Group	**Lebail**	**Rietveld**	**Notes**
$Pm\bar{3}m$	6.02	7.01	Negative U values.
Distorted $Pm\bar{3}m$	6.02	6.61	
R3c	6.08	6.38	Negative U values
R3c – distorted A site + separate Ti	6.08	6.14	No tilting peak can be observed in any diffraction techniques.
R3c – distorted A site, separate B sites	6.08		Refinement diverges
P4mm	6.16	6.42	
R3m+P4mm	6.10	6.37	Only 3% P4mm
R3m	6.10	6.14	

Table S2: Tolerance Factors for BFTM-BTO solid solutions. An ionic radii of 1.36 Å was used for a 12-coordinate Bi^{3+} ion.

Composition	**Tolerance Factor**	**Space Group**
BFTM	0.948	R3c
0.75BFTM-BT	0.979	R3m
0.5BFTM-0.5BT	1.003	R3m
0.25BFTM-0.75BT	1.04	R3m
BTO	1.06	P4mm

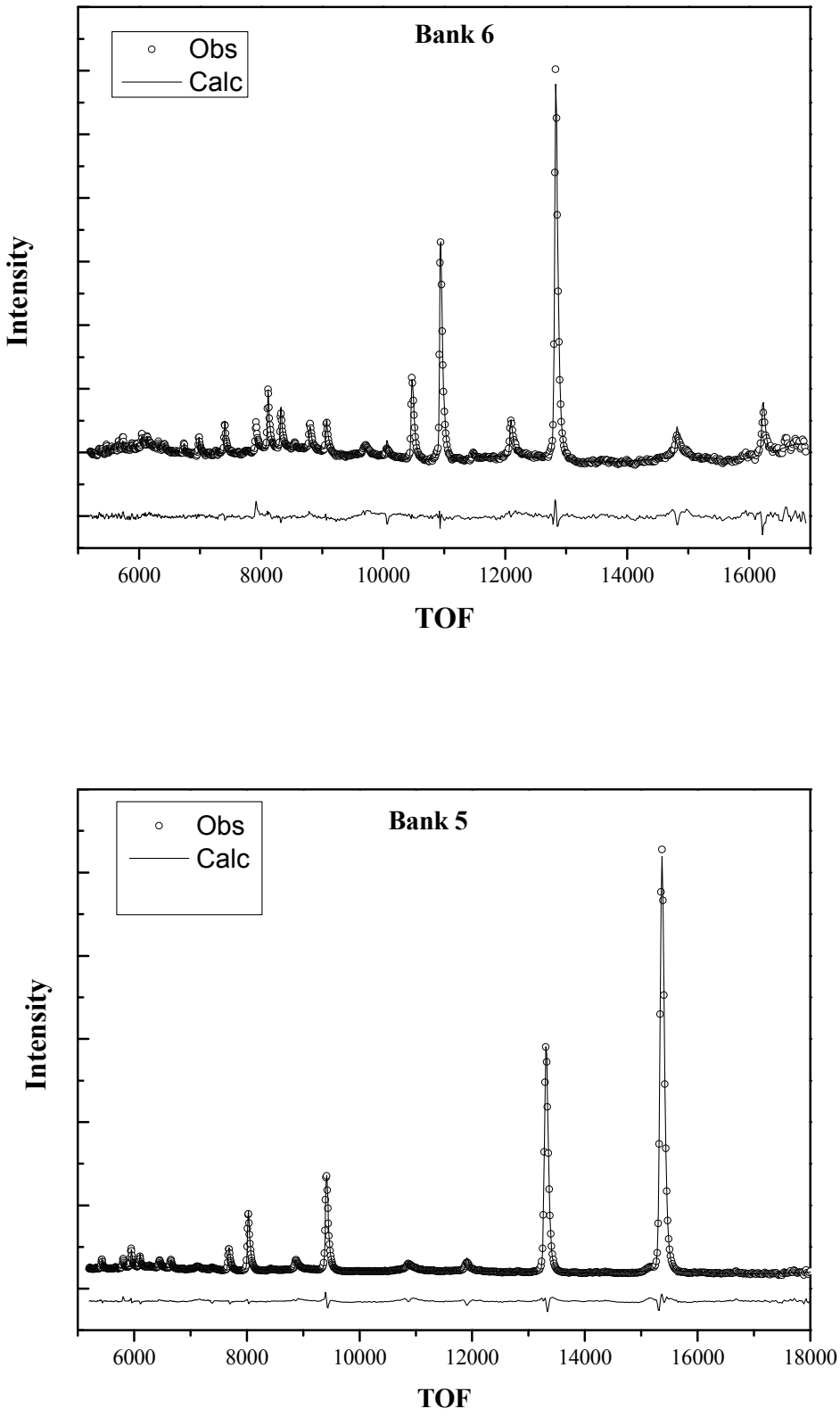


Figure S3: Low temperature (10K) neutron refinement for 0.75BFTM-0.25BT. Bank 5 and Bank 6 are shown, but the refinement was performed on all GEM banks.

Table S3: Atomic parameters for 0.75BFTM-0.25BT at 10K from GEM Rietveld refinement.

	x	y	z	Occ
Bi/Ba	-0.0572(6)	-0.0572(6)	-0.0572(6)	0.75/0.25
Fe/Mg/Ti	0.4649(6)	0.4649(6)	0.4649(6)	0.1875/0.2812/0.5312
O1	0	0.185(2)	0.349(1)	1

The displacements in the low temperature phase for 0.75BFTM-0.25BT are 0.26Å in the <111> direction for the A-site and 0.11 Å in the <111> direction for the B-site.

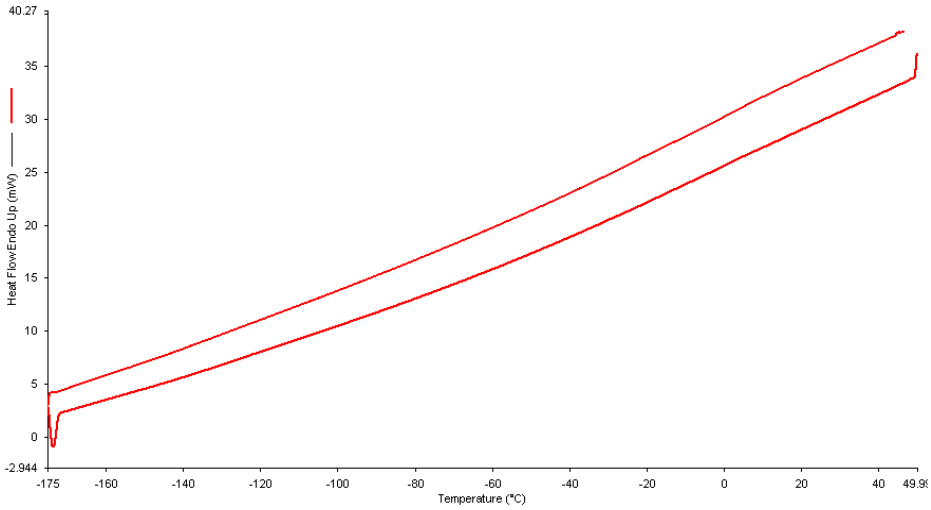
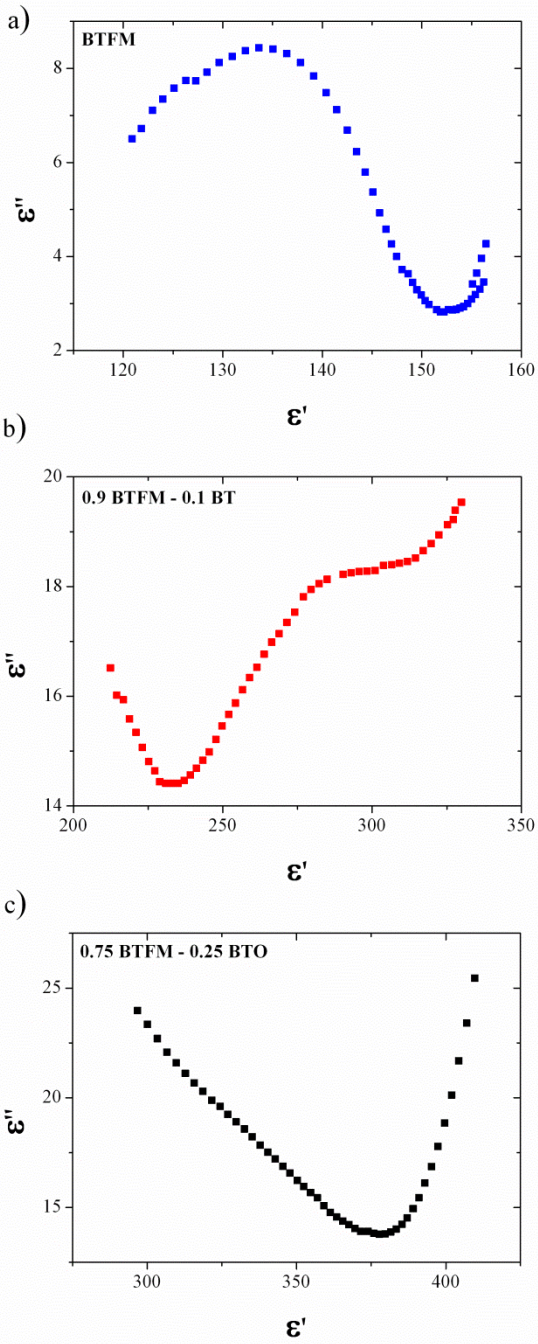


Figure S4: Low temperature DSC data from room temperature down to 100K.



Figures S5: Cole-Cole plots for a) BFTM, b) 0.9BFTM-0.1BT, and c) 0.75BFTM-0.25BT.