Supplementary Material for the paper "Temperature dependent piezoelectric response and switching behavior of rare-earth modified bismuth ferrite ceramics"

Supplementary Materials A

Crystal structure analysis: Rietveld refinement of X-ray diffraction (XRD) patterns

Supplementary Table A1. Structural parameters, phase compositions, goodness of fitting parameters of $Bi_{0.86}Sm_{0.14}FeO_3$ (BSFO), $Bi_{0.88}Gd_{0.12}FeO_3$ (BGFO) and $Bi_{0.91}Dy_{0.09}FeO_3$ (BDFO) compositions determined by Rietveld refinement.

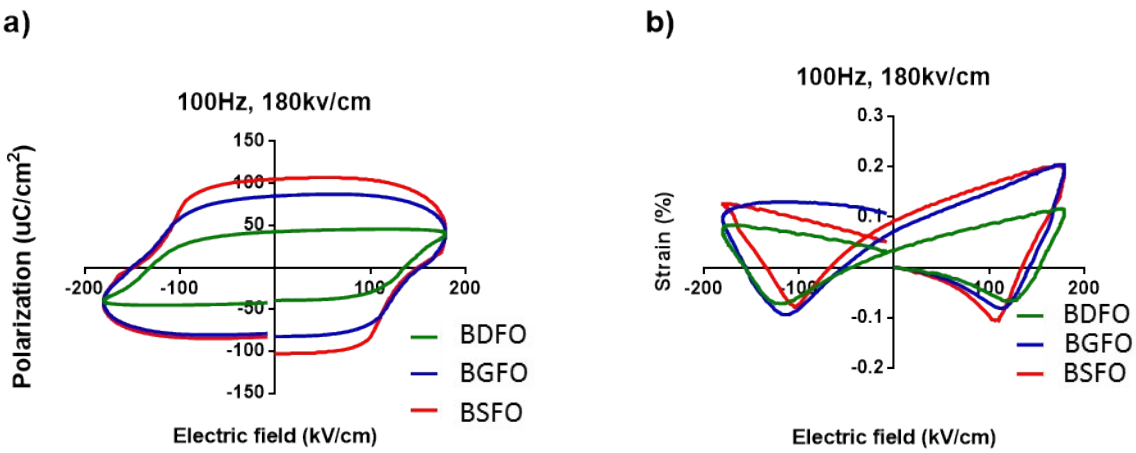
Composition (mol% RE)	Identified Phase(s)	Phase composition (wt%)	Unit cell dimensions (Å)	Atom	*x*	*y*	*z*	R factors and GOF[+]
BSFO	R3c	27	a=5.556 c=13.751	Bi Sm Fe O	0.0000 0.0000 0.0000 0.4430	0.0000 0.0000 0.0000 0.0120	0.0000 0.0000 0.2212 0.9543	GOF=1.31 Rexp=7.46 Rwp=9.79 Rp=7.24
	Pbam	73	a=5.589 b=11.213 c=7.796	Bi Sm Fe O O O O O	0.6968 0.7171 0.2372 0.2478 0.2805 0.0915 0.9534 0.0000	0.1261 0.1257 0.1261 0.1757 0.8771 0.2726 0.5171 0.0000	0.0000 0.5000 0.2549 0.0000 0.5000 0.3379 0.3169 0.2643	
BGFO	R3c	~90	a=5.561 c=13.773	Bi Gd Fe O	0.0000 0.0000 0.0000 0.4430	0.0000 0.0000 0.0000 0.0120	0.0000 0.0000 0.2212 0.9543	GOF=1.50 R_{exp}=7.12 R_{wp}=10.71 R_p=8.05
BDFO	R3c	>95	a=5.554 c=13.784	Bi Dy Fe O	0.0000 0.0000 0.0000 0.4430	0.0000 0.0000 0.0000 0.0120	0.0000 0.0000 0.2212 0.9543	GOF=4.11 R_{exp}=1.95 R_{wp}=8.02 R_p=5.33

*Note: Where a single phase made up 90% or greater of the total phase wt% only the structural parameters of the majority phase have been included.

[+]GOF=Goodness of fit

Supplementary material B

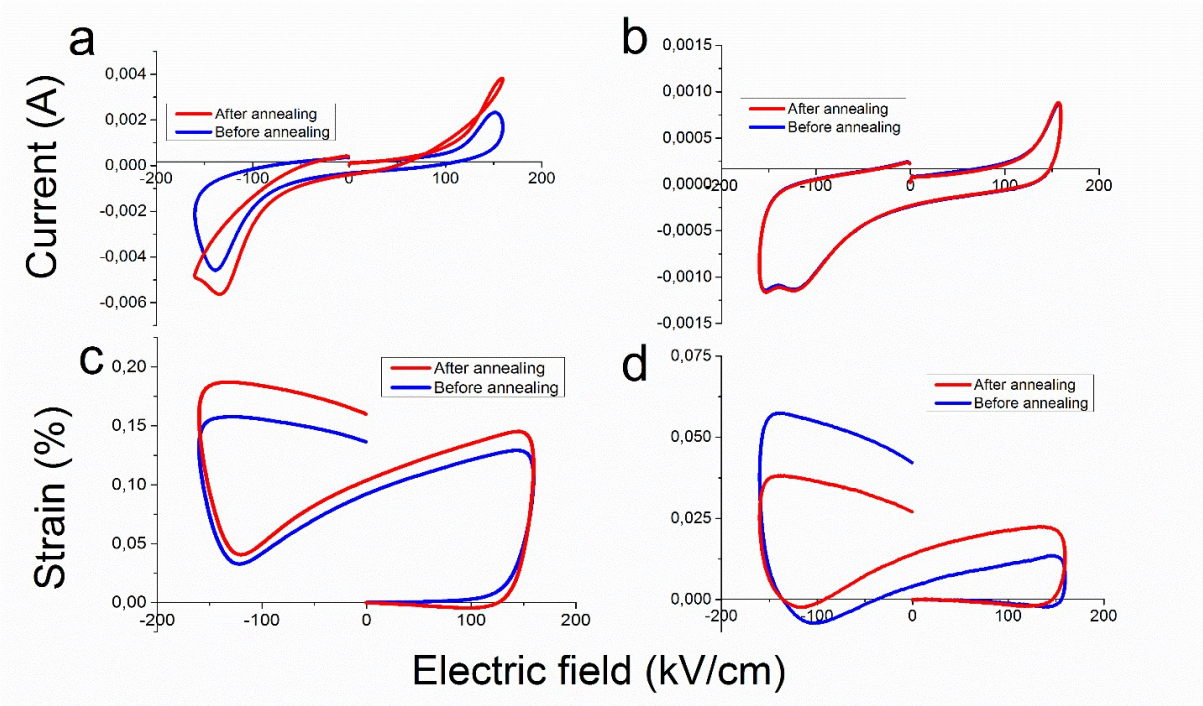
Symmetrical strain and polarization hysteresis loops were produced with the RE-BFO ceramics (**Supplementary Fig. 1**). To produce these loops the applied sinusoidal AC electric-field amplitude was increase sequentially by 10 kV/cm with each successive loop from 0 kV/cm to 180 kV/cm, with a driving electric-field frequency of 100 Hz. Hence the samples with a different electrical history to those shown in the manuscript, where above-coercive fields were directly applied to virgin samples (Manuscript **Fig 3d–f**), were able to produce symmetrical strain loops. Polarization-electric-field (P-E) loops (**Supplementary Fig. 1a**) shows rounded shaped loops giving evidence of electrical leakage currents during cycling. The shape also serves to demonstrate that in such loops the electrical leakage currents obscure many of the valuable features of the P-E loops. The strain-electric-field loops show a symmetrical shape for all three compositions (**Supplementary Fig. 1b**), in comparison to those S-E loops achieved when an electric-field of above coercive electric-field is applied directly to the ceramics (as shown in the manuscript **Fig. 3d-f**).



Supplementary Figure 1 a) Strain-electric-field, b) Polarisation-electric-field hysteresis loops for BSFO (14% Sm, red), BGFO (12% Gd, blue), BDFO (9% Dy, green) compositions at applied electric-field amplitudes of 180 kV/cm and driving frequencies of 100 Hz. The samples were exposed to increasing electric-field cycles with 10 kV/cm steps up to the maximum field of 180 kV/cm.

The virgin switched, asymmetric S-E loops produced by the BGFO and BDFO ceramics (**manuscript Fig. 3d–f**) can be reproduced in cycled samples after annealing at 400˚C (**Supplementary Fig. 2**). Note that these loops could not be reproduced for BSFO ceramics, as after the annealing the electrical conductivity significantly increased, preventing the switching behavior from being observed during the application of above coercive fields (E_c) directly to the as-annealed sample without causing dielectric breakdown. Some changes in the electrical conductivity behavior after annealing are also evident for BGFO, by the higher slope of the I-E curve after annealing (red) relative to that from before annealing (**Supplementary Fig. 2a**). Approximately reproducing the virgin S-E loop shape after annealing provides strong evidence that the strain asymmetry which develops during electric-field cycling (**manuscript Fig. 3d–f**) is unlikely to be related to cracking or microcracking. However, the small differences between before and after

annealing S-E loops suggests that the samples have indeed changed, with a likely possiblility being that the defect state has changed due to the electric-field application and the annealing. Additionally the precise nature of the phase assemblage between *R*3*c* and *Pbam* phases may have been altered due to the annealing.



Supplementary figure 2. Virgin switching loops before and after annealing above Curie temperature. a,b) Current-electric-field hysteresis loops for BGFO and BDFO respectively. c,d) Strain-electric-field hysteresis loops.