Supplementary material

Terbium-induced phase transitions and weak ferromagnetism in multiferroic bismuth ferrite ceramics

Vladimir Koval^{1,†}, Ivan Skorvanek², Juraj Durisin¹, Giuseppe Viola^{3,4}, Alexandra Kovalcikova¹, Peter Svec jr.⁵, Karel Saksl¹, and Haixue Yan⁴

¹ Institute of Materials Research, Slovak Academy of Sciences, Kosice, Slovakia

² Institute of Experimental Physics, Slovak Academy of Sciences, Kosice, Slovakia

³ Institute of Materials Physics and Engineering, Torino, Italy

⁴ School of Engineering and Materials Science, Queen Mary, University of London, London,

United Kingdom, Mile End Road, E1 4NS

⁵ Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia

[†] Corresponding author; E-mail address: vkoval@saske.sk

Table S1. The crystal symmetry and refined unit cell parameters of the $Bi_{1-x}Tb_xFeO_3$ samples (the values obtained by Rietveld refinement of the room-temperature XRD data).

Sample	Phase Lattice parameters					
X	(wt.%)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$V(Å^3)$	
0	R3c (98%)*	5.5782(0)	5.5782(0)	13.8686(1)	373.73(0)	
0.05	R3c (99%)*	5.5716(1)	5.5716(1)	13.8426(1)	372.15(1)	
0.10	R3c (90%)	5.5630(2)	5.5630(2)	13.8061(6)	370.02(2)	
	Pnma (10%)	5.6529(15)	7.8174(32)	5.4196(12)	239.50(13)	
0.15	R3c (51%)	5.5614(2)	5.5614(2)	13.8020(8)	369.69(3)	
	Pnma (49%)	5.6272(2)	7.8115(3)	5.4325(2)	238.80(1)	
0.20	R3c (9%)	5.5604(2)	5.5604(2)	13.7984(13)	369.46(4)	
	Pnma (91%)	5.6253(3)	7.7987(4)	5.4231(3)	237.91(2)	
0.25	Pnma (100%)	5.6261(2)	7.7893(3)	5.4213(2)	237.58(1)	
0.30	Pnma (100%)	5.6249(1)	7.7789(1)	5.4152(1)	236.95(0)	

* contains *I*23-type impurity phase

Sample	x = 0.0	x =	x = 0.25	
Crystal	Rhombohedral	Bipł	nasic	Orthorhombic
system				
Space group:	R3c	R3c	Pnma	Pnma
Atomic				
coordinates:				
Bi/Tb	(0,0,0.282)	(0,0,0.278)	(0.05,0.25,0.999)	(0.05,0.25,0.993)
Fe	(0,0,0)	(0,0,0)	(0,0,0.5)	(0,0,0.5)
01	(0.771,0.662,0.28)	(0.818,0.695,0.392)	(0.479,0.25,0.09)	(0.466,0.25,0.06)
O2			(0.259, 0.563, 0.204)	(0.199,0.545,0.191)
Bond				
lengths (Å):				
Bi-O	2.435(1)	2.153(4)	2.209/2.288(1)	2.346/2.364(1)
Fe-O1	1.752(1)	1.880(1)	1.991(4)	1.983(3)
Fe-O2	2.312(1)	2.135(3)	2.029(4)	2.017(3)
Bond angles				
(deg.):				
Fe-O-Fe	153.2(4)	158.8(2)	154.8/147.1(6)	156.6/147.8(4)
R-factors:				
$R_p(\%)/R_{wp}(\%)$	9.45/12.2	9.02/	12.59	8.7/11.3
v^2	1.5	1	.4	1.4

Table S2. Refined room-temperature structural parameters for selected single phase (R3c and Pnma) and biphasic (R3c+Pnma) samples.

Table S3. Frequencies (in cm⁻¹) and assignment of the *R*3*c* signature Raman modes obtained for the Bi_{1-x}Tb_xFeO₃ ($0 \le x \le 0.20$) samples at room temperature.

	$\mathbf{x} = 0$	x = 0.05	x = 0.10	x = 0.15	x = 0.20
Mode					
<i>E</i> (TO1)	70	70	69	69	71
E(TO2)	135	137	137	138	141
$A_{l}(\text{LO1})$	167	170	171	171	171
$A_1(\text{LO2})$	215	218	224	224	233



Figure S1. Observed (black open circles), calculated (red solid line) and difference (blue solid line) patterns obtained from the Rietveld analysis of the X-ray diffraction data of Bi₁. _xTb_xFeO₃ ceramics for (a) x = 0, (b) x = 0.30, and (c) x = 0.15. The allowed Bragg reflections for the corresponding space groups (*R*3*c*, *Pnma* and *I*23) are marked by green ticks. The insets in (a) and (b) show micrographs of respective compositions. The insets in (c) illustrate the schematic representations of the crystal structures coexisting in biphasic (*R*3*c*+*Pnma*) x = 0.15 sample.



Figure S2. Comparison of the thermal behavior of the $BiFeO_3$ and $Bi_{0.95}Tb_{0.05}FeO_3$ samples; (a) heating run, (b) cooling run.



Figure S3. Two-dimensional elemental distribution maps derived from the same HAADF-STEM image (a) of $Bi_{0.7}Tb_{0.3}FeO_3$ for (b) Bi (green)/Fe (red), (c) Tb (blue)/Fe (red), and (d) composed Bi (green)/Tb (blue)/Fe (red) to confirm the occupancy of the A- sites by Bi and Tb and the B- site by Fe. The arrows indicate positions of the Tb atoms (blue) as determined by EELS.



Figure S4. The ELNES spectra acquired at the Fe $L_{2,3}$ edge of $Bi_{1-x}Tb_xFeO_3$ (x = 0, 0.15 and 0.30). The representative spectra for each composition were obtained from three different regions of the sample (scanned region 4 x 4 x 15 nm) of nearly the same thickness and the same crystallographic orientation for the limited time of exposition of 10 s in order to minimize the effects of electron irradiation on the sample materials (avoid electron-beam damage of the sample material). Other regions of samples displayed almost identical spectral features at the O K and Fe $L_{2,3}$ edges.



Figure S5. Fourier transformation of the EXAFS function $\chi(k)$ into real space for Bi_{1-x}Tb_xFeO₃ (x = 0, 0.05, 0.15 and 0.20).



Figure S6. (a) The calculated crystallographic cluster around the absorber Fe atom (5 Å radius) from the XANES data. (b) and (c) show the experimental and simulated XANES spectra of pure (x = 0) and doped (x = 0.15) BiFeO₃, respectively.