

Table 1: (Supporting Information) Values of the structural parameters of BiFeO<sub>3</sub>. T stands for temperature, a and c are the lattice constants (in the hexagonal setting of space group *R3c*),  $z_{Fe}$ ,  $x_O$ ,  $y_O$  and  $z_O$  are the fractional coordinates of the Fe<sup>3+</sup> and Bi<sup>3+</sup> ions, respectively.  $R_B$  and  $\chi^2$  are the Bragg factor and goodness-of-fit indicator  $\chi^2$  (Rodríguez-Carvajal et al., 1993), respectively.

T [K]	a [Å]	c [Å]	$z_{Fe}$	$x_O$	$y_O$	$z_O$	$R_B$ [%]	$\chi^2$
298	5.57882(5)	13.86932(16)	0.22021(09)	0.44694(28)	0.01814(35)	0.95183(14)	3.03	1.44
473	5.58829(5)	13.90400(17)	0.22067(10)	0.44744(28)	0.01764(36)	0.95256(14)	3.51	1.19
503	5.58986(5)	13.90943(17)	0.22084(10)	0.44743(28)	0.01747(36)	0.95279(14)	3.50	1.14
543	5.59227(5)	13.91782(17)	0.22083(10)	0.44824(29)	0.01773(36)	0.95266(14)	3.52	1.09
623	5.59771(6)	13.93538(18)	0.22126(10)	0.44813(29)	0.01710(37)	0.95306(15)	4.07	1.04
643	5.59922(6)	13.94046(18)	0.22155(10)	0.44859(29)	0.01755(36)	0.95339(15)	4.08	1.00
663	5.60065(6)	13.94476(18)	0.22153(10)	0.44825(29)	0.01717(37)	0.95319(15)	3.61	0.98
723	5.60456(6)	13.95570(19)	0.22182(11)	0.44852(30)	0.01720(39)	0.95364(16)	4.14	0.98
823	5.61135(6)	13.97082(21)	0.22236(11)	0.44893(32)	0.01676(40)	0.95434(17)	4.24	0.89
923	5.61853(7)	13.98240(21)	0.22288(12)	0.45020(34)	0.01695(43)	0.95544(18)	4.45	0.83

Table 2: (Supporting Information) Values of the anisotropic temperature parameters  $U_{ij}$  [ $\text{\AA}^2$ ] refined for  $\text{BiFeO}_3$  as a function of temperature. The form of the temperature factor is  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \dots)]$ .

T [K]	Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
298	Bi	0.0081(7)	0.0081(7)	0.0000(9)	0.0040(7)	0.0	0.0
	Fe	0.0044(6)	0.0044(6)	0.0053(9)	0.0022(6)	0.0	0.0
	O	0.0101(3)	0.0079(3)	0.0062(2)	0.0034(3)	0.0016(3)	-0.0011(3)
473	Bi	0.0158(8)	0.0158(8)	0.0031(9)	0.0079(8)	0.0	0.0
	Fe	0.0069(6)	0.0069(6)	0.0111(10)	0.0035(6)	0.0	0.0
	O	0.0163(3)	0.0120(3)	0.0083(2)	0.0055(3)	0.0016(3)	-0.0031(3)
503	Bi	0.0171(8)	0.0171(8)	0.0047(9)	0.0085(8)	0.0	0.0
	Fe	0.0078(6)	0.0078(6)	0.0094(10)	0.0039(6)	0.0	0.0
	O	0.0178(3)	0.0120(3)	0.0098(2)	0.0055(3)	0.0013(3)	-0.0031(3)
543	Bi	0.0188(8)	0.0188(8)	0.0056(9)	0.0094(8)	0.0	0.0
	Fe	0.0082(6)	0.0082(6)	0.0109(10)	0.0041(6)	0.0	0.0
	O	0.0196(3)	0.0136(3)	0.0105(3)	0.0064(3)	0.0014(3)	-0.0032(3)
623	Bi	0.0219(9)	0.0219(9)	0.0075(10)	0.0110(9)	0.0	0.0
	Fe	0.0099(6)	0.0099(6)	0.0121(10)	0.0050(6)	0.0	0.0
	O	0.0232(3)	0.0149(4)	0.0125(3)	0.0079(3)	0.0023(3)	-0.0038(3)
643	Bi	0.0236(9)	0.0236(9)	0.0075(10)	0.0118(9)	0.0	0.0
	Fe	0.0104(6)	0.0104(6)	0.0132(10)	0.0052(6)	0.0	0.0
	O	0.0234(3)	0.0152(4)	0.0130(3)	0.0076(3)	0.0017(3)	-0.0043(3)
663	Bi	0.0245(9)	0.0245(9)	0.0081(10)	0.0123(9)	0.0	0.0
	Fe	0.0105(6)	0.0105(6)	0.0132(11)	0.0053(6)	0.0	0.0
	O	0.0246(3)	0.0161(4)	0.0141(3)	0.0083(3)	0.0032(3)	-0.0040(3)
723	Bi	0.0272(10)	0.0272(10)	0.0085(10)	0.0136(10)	0.0	0.0
	Fe	0.0123(7)	0.0123(7)	0.0159(10)	0.0062(7)	0.0	0.0
	O	0.0266(4)	0.0167(4)	0.0159(3)	0.0085(3)	0.0021(4)	-0.0051(3)
823	Bi	0.0320(11)	0.0320(11)	0.0144(12)	0.0160(11)	0.0	0.0
	Fe	0.0144(7)	0.0144(7)	0.0155(11)	0.0072(7)	0.0	0.0
	O	0.0322(4)	0.0184(4)	0.0200(4)	0.0094(4)	0.0019(4)	-0.0061(4)
923	Bi	0.0380(11)	0.0380(11)	0.0172(12)	0.0190(11)	0.0	0.0
	Fe	0.0161(7)	0.0161(7)	0.0190(12)	0.0081(7)	0.0	0.0
	O	0.0373(5)	0.0200(4)	0.0233(4)	0.0097(4)	0.0015(5)	-0.0071(4)