Electronic Supplementary Information

Intrinsic multiferroics in an individual single-crystalline $Bi_5Fe_{0.9}Co_{0.1}Ti_3O_{15}$ nanoplate

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Fig. S1. XRD patterns of samples prepared under different temperatures (200°C and 180°C).



Fig. S2. SEM image of sample prepared under 180°C for 48h.



Fig. S3. SEM image of BFCTO nanoplates.



Fig. S4. XRD patterns of samples prepared under different [OH-] using NaOH as mineralizing agent.



Fig. S5. SEM images of samples prepared under different [OH-] using NaOH as mineralizing agent.



Fig. S6. XRD patterns of samples prepared under different [OH-] using KOH as mineralizing agent.

	Name	Туре	Ref/damp	Fractional coordinates			Mult	Occupancy	Uiso
1	01	O-2	000	0.331000	0.325200	0.000000	4	1.0000	0.00870
2	02	O-2	000	0.008200	-0.007500	0.250500	8	1.0000	0.00670
3	O3	O-2	000	0.327100	0.188200	0.094770	8	1.0000	0.01380
4	O4	O-2	000	0.291800	0.302600	0.194550	8	1.0000	0.01130
5	O5	O-2	000	0.041900	0.031000	0.039880	8	1.0000	0.01390
6	O6	O ⁻²	000	0.590050	0.454212	0.045511	8	1.0000	0.01190
7	07	O-2	000	0.369051	0.173954	0.175145	8	1.000	0.01320
8	08	O ⁻²	000	0.547143	0.533598	0.153263	8	1.000	0.00960
9	Ti1	Ti ⁺⁴	000	0.295100	0.251400	0.048710	8	0.7500	0.00370
10	Fel	Fe ⁺³	000	0.295100	0.251400	0.048710	8	0.2250	0.00370
11	Ti2	Ti ⁺⁴	000	0.291600	0.258200	0.152920	8	0.7500	0.00280
12	Fe2	Fe ⁺³	000	0.291600	0.258200	0.152920	8	0.2250	0.00280
13	Bi1	Bi ⁺³	000	0.250000	0.755900	0.000000	4	1.0000	0.01630
14	Bi2	Bi ⁺³	000	0.232200	0.730400	0.219250	8	1.0000	0.00950
15	Bi3	Bi ⁺³	000	0.247000	0.754800	0.104680	8	1.0000	0.01090
16	Co2	Co ⁺³	000	0.291600	0.258200	0.152920	8	0.0250	0.02500
17	Col	Co ⁺³	000	0.295100	0.251400	0.048710	8	0.0250	0.02500

 Table S1 Final refined parameters for the XRD patterns of BFCTO nanoplates.



Fig. S7. (a) Topographic image of the white rectangle on the single plate; (b) The out of plane phase image near to resonance conditions; (c) the corresponding phase profile.



Fig. S8. Raman spectrum of BFCTO nanoplates.

Fig. S8 displays the Raman spectrum of BFCTO nanoplates. For Raman spectrum of bismuth layer structured crystals, it is generally recognized that their phonon modes can be classified into two categories^{1, 2}: low frequency modes below 200 cm⁻¹ and high frequency modes above 200 cm⁻¹. The modes below 200 cm⁻¹ are related to heavy mass Bi^{3+} ions,³ for example, the mode at ~60 cm⁻¹ reflects the vibration of Bi^{3+} ions in $(Bi_2O_2)^{2+}$ layers which cannot be observed due to the instrument limiting and the mode in 80–160 cm⁻¹ arises from the vibration of Bi^{3+} ions at A-sites in the perovskite layer. The high frequency modes above 200 cm⁻¹ (256 cm⁻¹, 545 cm⁻¹, 699 cm⁻¹, 718 cm⁻¹ and 863 cm⁻¹) with A_{1g} character are resulted from the torsional bending and the stretching modes of BO₆ octahedral. The mode at 256 cm⁻¹ belongs to the torsional bending of TiO₆ octahedra. The mode at 545 cm⁻¹ is originated from the torsional vibration of FeO₆ and CoO₆ octahedra. The torsional bending mode at 699 cm⁻¹ indicates that Fe (Co) exist in the form of Fe(Co)O₆ octahedra. The observation of the mode at 718 cm⁻¹ proves that Co³⁺ enters the lattice. The stretching mode of 863 cm⁻¹ shifts to a lower frequency compared with 865 cm⁻¹ of the SrBi₄Ti₄O₁₅,⁵ because Fe³⁺ ions are heavier than Ti⁴⁺ ions, indicating that the FeO₆ octahedra are inserted

successfully into $Bi_4Ti_3O_{12}$. The mode at ~315 cm⁻¹ corresponds to ferroelectric phase-transition, coinciding well with that of $Bi_5FeTi_3O_{15}$. From the Raman spectra results, we can conclude that $BiFe_{0.9}Co_{0.1}O_3$ is successfully inserted to $Bi_4Ti_3O_{12}$ and forms the four-layered perovskite BFCTO structure.

Besides, XPS was also measured to determine the valances of the metal elements in the BFCTO singlecrystalline nanoplates. The binding energies obtained by referencing the C1s line to 284.5 eV. The survey XPS spectrum (Fig. S9(a)) reveals that the nanoplates are composed of Bi, Fe, Co, Ti and O. Fig. S9(b) illustrates Bi 4f core-level spectra of BFCTO. The peaks located at 159.3 eV (Bi 4f_{7/2}) and 164.6 eV (Bi 4f_{5/2}) are referenced by Bi₂O₃. Fig. S9(c) shows the Fe 2p core-level spectrum of BFCTO. The binding energies at 710.7 eV and 725.9 eV, corresponding to the spin-orbit split Fe 2p_{3/2} and 2p_{1/2} peaks, respectively, are comparable to those in Fe₂O₃,⁶ suggesting that Fe ions in BFCTO plates are +3 valence states. Furthermore, the core-level spectra of Co 2p and the deconvoluted curve in BFCTO are shown in Fig. S9(d) The peaks located at 781.9 eV and 796.8 eV correspond to the binding energy of Co 2p_{3/2} and Co 2p_{1/2} in Co₂O₃,⁷ implying that the doped Co ions in the BFCTO is +3 valence states. The peaks of Ti 2p_{1/2} and Bi 4d_{3/2} are partially overlapped (Fig. S9(e)), leading to a broad bump in the vicinity of 463.4 eV. The Ti 2p_{3/2} and Ti 2p_{1/2} peaks with a typical spin orbit doublet of 5.7 eV are at 457.7 eV and 463.4 eV, respectively, which are characteristic of Ti⁴⁺. Therefore, the XPS results confirm the metal elements in the BFCTO single-crystalline nanoplates exist in the form of Bi³⁺, Fe³⁺, Co³⁺ and Ti⁴⁺, respectively.



Fig. S9. (a) Survey XPS spectrum of BFCTO plates. High-resolution XPS spectra of (b) Bi 4f, (c) Fe 2p,
(d) Co 2p, Bi 4p_{1/2}, and (e) Ti 2p, Bi 4d_{3/2}.



Fig. S10. (a)-(c) Sketchers of the three main distortions; Purple, blue and red balls represent Bi, Ti/Fe/Co and O atoms, respectively. The displacement amplitudes of the various ions are indicated by the arrows;
(d) HADDF image along [110] direction (inset: the corresponding SAED pattern); (e) the enlarged HAADF image of Figure 4 (d), red circles represent Bi cations, orange and green circles represent *B*-site cations (Ti, Fe, or Co) deviating along different directions respectively.

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