

Supplementary Material

Reversal and non-reversal ferroelectric polarization in a Y-type hexaferrite

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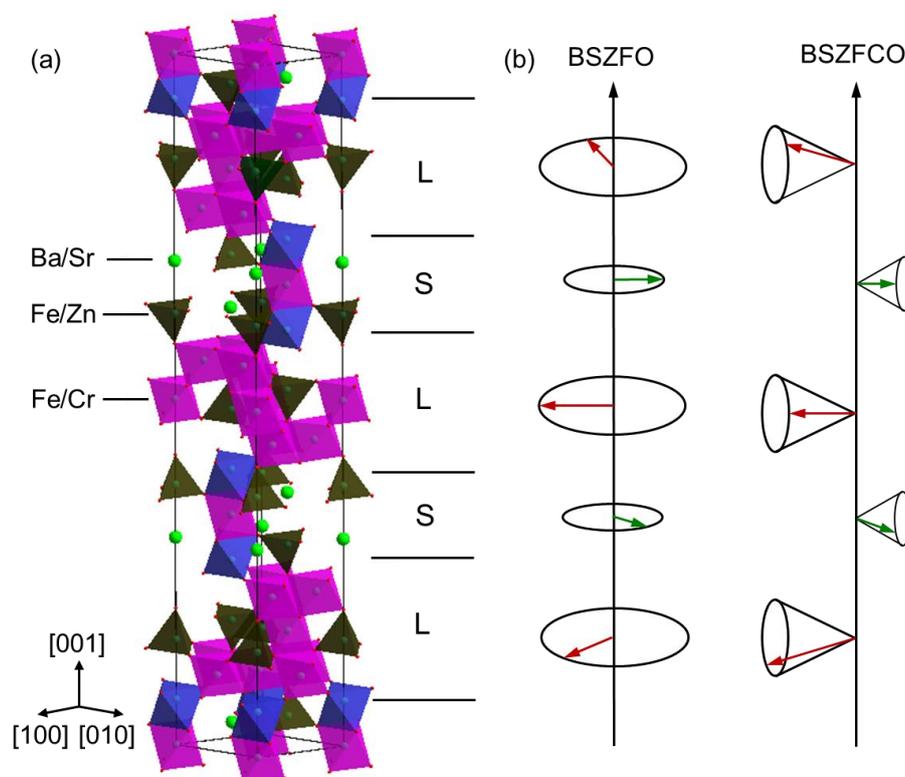


Fig. S1 (a) Crystal structure of $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{11.4}\text{Cr}_{0.6}\text{O}_{22}$. S and L represent the alternatively stacked small spin and large spin blocks, respectively. (b) Schematic illustrations of magnetic ground states of $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ (BSZFO) and

$\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{11.4}\text{Cr}_{0.6}\text{O}_{22}$ (BSZFCO).

As shown in Fig. S1(a), the unit cell of Y-type hexaferrites consists of FeO_6 octahedrons and Fe/ZnO_4 tetrahedrons. The tetrahedrons are occupied by two Fe ions and two Zn ions, while the rest Fe ions and Cr ions occupy the octahedron sites.¹ The magnetic structure can be described by alternatively arranged L and S blocks, where L and S represent large and small magnetic moments, respectively. As previously reported, the $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ (BZFO) shows collinear ferrimagnetic ground state.² To induce magnetoelectric effect, chemical doping is usually adopted to modulate the magnetic ground state. For example, with the replacement of Ba by smaller Sr ions in BZFO, the magnetic ground state of $\text{Ba}_x\text{Sr}_{(1-x)}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ (BSZFO) evolves with x from collinear ferrimagnetic state to proper screw state. For the $x=0.5$ sample, the system develops a proper screw spin structure, as shown in the left panel of Fig. S1(b).³ At the same time, the lattice parameters decrease (Table S1). Hence, the magnetoelectric effect is observed at a large in-plane magnetic field in BSZFO. However, the polarization state at zero magnetic field is still paraelectric.³

As shown in the right panel of Fig. S1(b), the Cr-doped BSZFO (BSZFCO) has a transverse conical ground state, which leads to a non-zero electric polarization at zero magnetic field and various novel magnetoelectric properties. In order to study the effect of the Cr doping on the lattice and atom positions in BSZFCO, the Rietveld refinement was performed for the powder XRD data using the GSAS program. We assumed that the doped Cr ions randomly replaced the Fe ions in octahedrons while the Ba, Sr and Zn have the same sites as BSZFO. As listed in Table S1, the lattice parameters of BSZFCO are smaller than those of BSZFO,¹ which suggests that the lattice is reduced by the Cr ions and the magnetic ground state is also tuned. The refined atom positions of BSZFCO are summarized in Table S2.

The valence states of all metal ions were studied by the X-ray photoelectron spectroscopy (XPS) on a Thermo ESCALAB 250Xi spectrometer operating in fixed analyser transmission mode (30 eV), and an Al $K\alpha$ anode was employed. Other than the Ba, Sr and Zn ions (which are definitely in the +2 valence state), we mainly study

the valence states of Fe and Cr ions. As shown in Fig. S2, both of Fe and Cr ions show +3 valence. This result is consistent with the octahedral occupation in the XRD analysis. Therefore, in the Y-type ferrite structure, Fe³⁺ is believed in the high spin state (S=5/2) and Cr³⁺ is in the S=3/2 state.

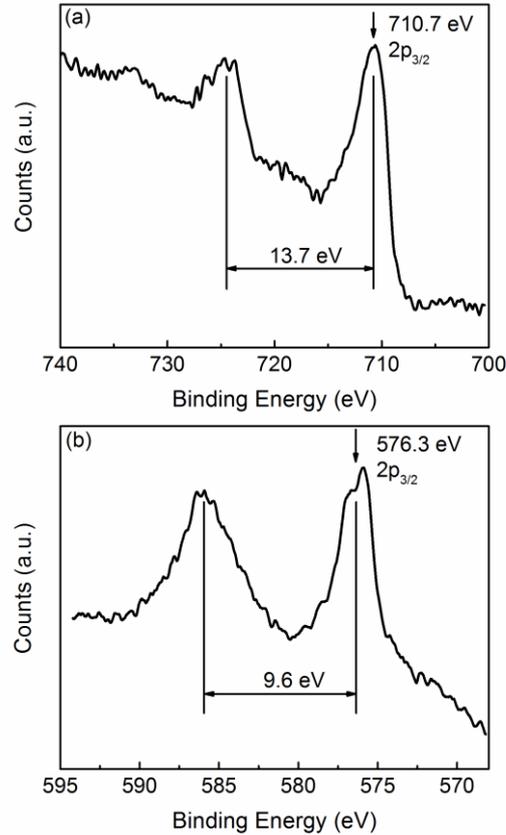


Fig. S2 X-ray photoelectron spectroscopy of the (a) Fe and (b) Cr ions taken on the fresh cross-section of the as-grown BSZFCO polycrystalline sample.

Table S1. Lattice parameters of BSZFCO, BSZFO and BZFO.

	a (Å)	c (Å)	
BSZFCO	5.8581	43.3970	present paper
BSZFO	5.863	43.433	Ref. 1
BZFO	5.876	43.558	Ref. 2

Table S2. Refined atom positions in Ba_{0.5}Sr_{1.5}Zn₂Fe_{11.4}Cr_{0.6}O₂₂.

Ion	Coordination	x	y	z
Ba/Sr		0	0	0.29798
Fe/Zn	Tetrahedral	0	0	0.37543
Fe/Zn	Tetrahedral	0	0	0.15228
Fe/Cr	Octahedral	0	0	0.0652

Fe/Cr	Octahedral	0	0	0.5
Fe/Cr	Octahedral	0.50301	0.497	0.10939
Fe/Cr	Octahedral	0	0	0
O		0	0	0.4195
O		0	0	0.19805
O		0.1602	0.8398	0.02919
O		0.8302	0.1698	0.0843
O		0.1776	0.8224	0.13834

1. M. Nobuyuki and Y. Yasuo, *J. Phys. Soc. Jpn.*, 1993, **62**, 1292-1304.
2. W. D. Towns and J. H. Fang, *Zeitschrift für Kristallographie*, 1970, **131**, 196.
3. T. Kimura, G. Lawes and A. P. Ramirez, *Phys Rev Lett*, 2005, **94**, 137201.