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Multiple Ferroic Orders and Toroidal Magnetoelectricity in the Chiral Magnet BaCoSiO$_4$

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Discovering ferroic phase transitions and their consequential physical properties are at the core of condensed matter science due to rich physics and tremendous technological promises. BaCoSiO$_4$, a chiral antiferromagnet, belongs to the tetrahedron-based chiral system, and exhibits diverse ferroic orders with coexisting chirality, polarity, trimerization, and ferro-rotational distortions, and magnetism; however, their mutual couplings remain to be explored. In this work, we used a comprehensive combination of several experimental tools: in-situ X-ray, transmission electron microscopy, magnetization, and magnetoelectric measurements of single-crystalline BaCoSiO$_4$, to investigate hierarchical phase transitions, their microscopic domain structures, and the resulting magnetoelectricity. We found that two different structural chiralities develop through distinct processes; global homochirality and local heterochirality induced by the ferro-rotational distortions on top of existing polarization. In addition, magnetic chirality, with the simultaneous presence of net magnetic moment and magnetic toroidal moment, develops below 3.2 K due to the global chirality, which leads to magnetic-field-tunable toroidal magnetoelectricity. Thus, BaCoSiO$_4$ exhibits uniquely all four types of ferroic orders and provides an avenue to explore, for example, tunable or dynamic coupling of multiple ferroic degrees of freedom.

I. INTRODUCTION

Ferroic orders refer to vector order parameters that often break spatial-inversion (SI) or time-reversal (TR) symmetries through phase transitions[1]. The ferroic orders in real materials are perennial topics for rich science and the essence for numerous technological applications. Ferroic orders can be categorized into four groups in terms of even (+) or odd (-) parity under SI and TR operations. Commonly, we have SI^-TR^+ electric polarization and SI^+TR^- magnetization in polar and ferromagnetic materials, respectively. In ferro-rotational orders, the local polarizations form a vortex-like head-to-tail arrangement with an out-of-plane axial vector, which is invariant under both SI and TR (SI^+TR^+)[2]. The ferro-toroidicity is the magnetic version of ferro-rotation by relacing rotating local polarizations with spins, and flips under both SI and TR (SI^-TR^-)[3,4]. To date, the understanding of domain configuration and cross-coupling of ferro-rotation and ferro-toroidicity are still elusive, partially due to that the material candidates of ferro-rotation and ferro-toroidicity are rather limited. To the best of our knowledge, there is no report on any materials exhibiting both ferro-rotation and ferro-toroidicity. Herein, we report that BaCoSiO$_4$ shows ferro-rotation and ferro-toroidicity at different temperatures, in addition to structural chirality and polarity. Remarkably, BaCoSiO$_4$ exhibits all of polarization, magnetization, ferro-rotation, and ferro-toroidal, corresponding to SI^-TR^+, SI^+TR^-, SI^+TR^+, and SI^-TR^- symmetry breakings, respectively.

Silica (SiO$_2$) skeleton, tetrahedron-based chirality, provides a rich family of materials that the chiral universality and polymorphic nature can be examined[5]. BaCoSiO$_4$ belongs to one exciting family, the so-called stuffed tridymite with the general formula ABXO$_4$ (A = alkali and alkaline; B and X are tetrahedrally coordinated cations). Unlike quartz with a SiO$_4$ tetrahedra chain, their corner-shared tetrahedral skeletons build six-membered rings that host the large cation A channels and are packed into a ring-over-ring two-layer structure. Ba-stuffed tridymite derivatives such as BaMnSiO$_4$[6], BaFeGaO$_4$[7], BaAl$_2$O$_4$[8], BaMSiO$_4$ (M = Co, Mg, Zn)[9], Ba(Al, Fe)$_2$O$_4$[10], and BaZnGeO$_4$[11] have been studied for their rich physical properties, including improper ferroelectricity[12,13], photodielectric effect[14], stripe domain formation[15], luminescence[16] and phonon softening[17], while BaCoSiO$_4$ has received little attention until recently[18]. BaCoSiO$_4$ crystallizes in the non-centrosymmetric $P6_3$ space group with magnetic Co^{2+} ions, and therefore exhibits several ferroic characters such as chirality, polarity, and magnetizations. Furthermore, BaCoSiO$_4$ undergoes a tripling of *ab* plane unit cell transition[9], which leads to the corrugation of the Ba^{2+} layers and tetrahedral tilting and Co-trimerization, analogous to the remarkable case of the interplay of the trimerization, magnetism, and polarization in the hexagonal rare-earth manganite family[19], while BaCoSiO$_4$ possesses the additional chiral degree of freedom.

Chirality refers to the situation where an object and its mirror image cannot overlap to each other by spatial rotation, i.e., all mirror symmetries are broken in the object. In addition to structural chirality, certain spin arrangements may also develop chirality. We define the concept "magnetic chirality" as a chirality in spin ordered states (i.e., spin ordered states with the absence of any mirror symmetry). Magnetic chirality exists in centrosymmetric lattices of frustrated antiferromagnets[20], as well as non-centrosymmetric or chiral lattices with antisymmetric Dzyaloshinskii-Moriya (DM) exchange interactions[21]. Recently, a novel type of magnetic chirality consisting of in-plane toroidal spins plus an out-of-plane canting was proposed[22], and was, afterwards, experimentally observed in $BaCoSiO_4$. In $BaCoSiO_4$, applying a magnetic field along the *c* axis can induce "-3 to -1 to 1 to 3" toroidal moment (*TM)* and *c* axis canting moment (M_c) transitions, while the magnetic chirality remains invariant[18], which makes it a fascinating system for controllable *TM*. However, several questions remain not fully understood in $BaCoSiO_4$: what the connection is between the ferro-toroidicity and lattice chirality/polarity, whether the structural domain configuration promises net ferroic quantities, and whether their couplings are experimentally detectable. In this regard, understanding the phase transition routes, revealing ferroic domains, and finding the cross-coupling are critical for the subsequent magnetic studies, optical measurements[23,24], and multifunctional applications.

In this paper, applying the laser-diode heated floating zone (LFZ) method, we obtain centimeter-size $BaCoSiO_4$ single crystals, and discuss its domain topology related to chirality, polarity, ferro-rotation, and trimerization. The real-space domain evolution involving trimerization and polarity across the structural phase transition has been revealed using in-situ X-ray structural refinement and in-situ transmission electron microscopy (TEM). Two kinds of structural chirality have been observed: a global chirality determined by a very high-temperature parent chiral lattice and a local chirality resulting from preexisting polarity plus ferro-rotational order. The sample shows a mono global chirality which protects a mono magnetic chirality below the ordering temperature of 3.2 K. Therefore, the macroscopic net *TM* can be efficiently tuned by an external magnetic field, and rich field-tunable ME behaviors have been observed in the single crystal. These findings provide structural hints and multifunctional application potential to the intriguing magnetic interactions[18]. We emphasize that $BaCoSiO_4$ is a unique material that contains ferroic orders covering all four possibilities out of breaking SI and TR.

II. EXPERIMENTAL

The powder sample of $BaCoSiO_4$ was prepared by a direct solid-state reaction from stoichiometric mixtures of $BaCO_3$, Co_3O_4, and SiO_2 powders (Alfa Aesar, 99.99%). The mixture was calcined at 900 °C in the air for 12 hours and then re-ground, pelletized, and heated at 1200°C for 20 h and at 1250°C for 50 h with intermediate grindings to ensure a total reaction. At the end of each sintering, a quenching process, i.e., taking the sample out of the furnace quickly at the target temperature, is desired for the correct phase, since $BaCoSiO_4$ tends to decompose at intermediate temperatures. The resulting pure powder sample is supposed to be bright blue in color. Slow cooling can cause significant decomposition, visually indicated by the sample color turning purple. Large single crystals were grown using a laser-diode heated floating zone (LFZ) technique. The optimal growth conditions were growth speed of 2-4 mm/hr, atmospheric airflow of 0.1 L $\text{min}^{-1,}$ and counter-rotation of the feed and seed rods at 15 and 30 rpm, respectively. The large temperature gradient of LFZ guarantees a rapid cooling on as-grown crystal, which suppresses the decomposition at intermediate temperature. We tried to grow it by conventional optical floating zone, but the crystal quality was poor. Attempt to tailor the ionic ordering by annealing the as-grown crystal at temperature range 850ºC to 1200ºC also failed due to significant crystal decomposition.

The *in-situ* high-temperature X-ray diffraction was performed on both powder and single-crystal samples of $BaCoSiO_4$. The powder was characterized using the high-resolution X-ray diffractometer Bruker XRD D8 Discover with Cu-K_α radiation. The diffractometer is equipped with the high-temperature chamber HTK 1200N for measurements in an ambient atmosphere up to 1200°C. Structural parameters were refined by the Rietveld method using the Fullprof program [25]. Differential scanning calorimetry (DSC) data were taken on SETSYS Evolution TGA-DTA/DSC SETARAM with the DSC-800°C rod in He atmosphere, each sample (typical mass ~ 50 mg) being measured once upon warming & cooling with the rate 10 °C/min up to 780°C. Standard alumina crucibles with a diameter of 0.5 cm and a height of 0.8 cm were used. Transition temperatures were determined as the onset of the observed peaks upon warming.

Specimens for TEM studies were prepared by mechanical polishing, followed by Ar ion milling. Domain structures were studied using a JEOL-2010F transmission electron microscope equipped with a 14-bit charge-coupled-device (CCD) array detector. The in-situ heating TEM experiment was carried out using a JEOL-2000FX TEM with a high-temperature specimen holder. All images are raw data.

For pyroelectric and magnetoelectric measurements, a $BaCoSiO_4$ single crystal was oriented by the Laue method and cut and mechanically polished into an *ab* plane plate and an *ac* plane plate both with thickness of 20 μm. The electrodes were made of silver epoxy. The crystals were cooled down to 2 K with DC 50.5 kV/cm (applied by a Keithley 617 electrometer) and 2 T poling *E*, *H* fields in a PPMS-9. All isothermal ME measurements were performed by 200 Oe/s magnetic field sweeping at 2 K. The magnetic field and heating rate of all pyroelectric measurements were 1.5 T and 5 K/min. A Keithley 617 electrometer collected current signals while ε was measured in PPMS-9 with oscillating electric fields using a Quadtech 7600 LCR meter at 1V and 44 kHz. All presented figures are made by raw data.

III. RESULTS AND DISCUSSION

a. Structural characterization

$BaCoSiO_4$, the room-temperature (RT) phase ($P6_3$) [a = 9.1203 Å and c = 8.6643 Å], exhibits diverse ferroic orders including chirality, polarity, trimerization, ferro-rotational distortion, and magnetism. Fig. 1b depicts two-layered $Co^{2+}O_4$ (blue) and $Si^{4+}O_4$ (grey) tetrahedra, linked by their oxygen vertices to form triangular lattice layers. The tetrahedra are tilted to induce the Co^{2+} trimerization in each Co layer (the triangles with blue and purple bars) and the trimerization of those bridging oxygens in each O layer (the triangles with green and pink bars). These distortions result in a $\sqrt{3}\times\sqrt{3}$-type superstructure from the high-temperature (HT) phase as shown in Fig. 1a. A finite polarization exists along the c axis due to the displacement of the Co^{2+} and Si^{4+} ions from the center of the tetrahedra and the shifts of Ba^{2+} ions. Fig. 1c as the projected view of Fig. 1b illustrates the arrangement of $Si^{4+}O_4$ (D, down-pointing apices) and $Co^{2+}O_4$ (U, up-pointing apices) tetrahedra accompanied by the low distortion of two-thirds of the Ba ions (yellow balls) and the non-distortion of one-third of the Ba ions in a down-down-none configuration. A reversed $Co^{2+}O_4$(U)/$Si^{4+}O_4$(D) tetrahedra will lead to Ba^{2+} with an up-up-none configuration, as shown in Fig. 1d.

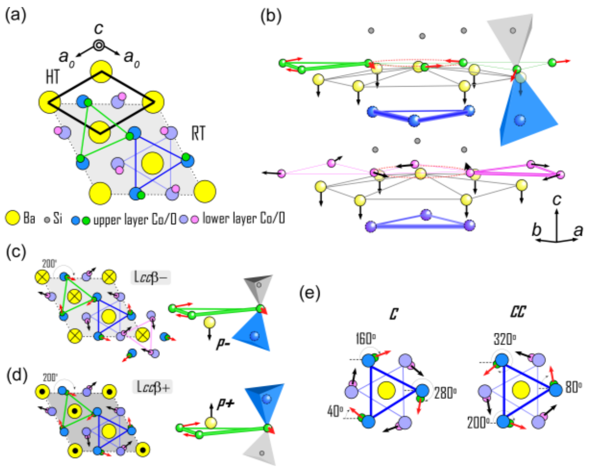

Figure 1. Room temperature crystal structure of $BaCoSiO_4$. (a) The thick solid line and dashed line represent the high-temperature ($a_0\times a_0$) and the room temperature ($\sqrt{3}a_0\times\sqrt{3}a_0$) unit cells, respectively. The triangles with green/blue/purple bars correspond to Co/O trimers. (b) Three-dimensional crystallographic structure of $BaCoSiO_4$, showing double-layer lattices of SiO_4 and CoO_4 tetrahedra. The large/yellow and small/grey spheres represent the Ba and Si ions. The blue/green spheres display the upper CoO_4 layer and purple/pink ones for the lower CoO_4 layers. The tetrahedral tilting leads to the Ba ion displacements and the trimerization of Co and O ions. (c) The projection of L*cc*β- state. L*cc* unit stands for left chiral with counterclockwise oxygen distortions. α/β/γ antiphase relations correspond to 80°, 200°, and 320° oxygen in-plane rotations. The Ba^{2+} downward distortion arises from the up-pointing apice of CoO_4 tetrahedron (blue) and the squeezing O trimer (green bar) from the top. The large yellow circles show the positions of Ba ions, with crosses or dots indicating displacement into or out of the plane within one unit cell. Sign "-" attributes from a net Ba^{2+} downward polar distortion along the c axis. (d) The projection of L*cc*β+ state with a net Ba^{2+} upward distortion. (e) Clockwise (c) and counterclockwise (cc) ferro-rotational distortion of bridging oxygens and their angles, which are closely related with antiphase domains.

Besides, we note that the projected displacement map of those bridging oxygen reveals a circular rotational pattern surrounding the non-distorted Ba ion (small green and pink spheres around yellow spheres in Fig. 1e). Consequently, two propeller-like orientations of those bridging oxygens, termed ferro-rotational distortion, are denoted as c (clockwise) and cc (counterclockwise). The ferro-rotational order, whose order parameter is an axial vector invariant under both time-reversal and spatial-inversion operations, has only been realized recently in $RbFe(MoO_4)_2$ [2]. Those ferroic orders lead to 24 possible domain configurations of the RT phase as summarized in Fig. 2, combining L and R chirality preserved from the HT phase, + or − polarity (up- or down-orientation of the polar displacement), c or cc ferro-rotation of the bridging oxygens, and three possible translation variants of trimerization (α, β and γ represent different origins for the trimerization). For example, the domain depicted in Fig. 1c is labeled as L*cc*β-, in which L*cc*β represents a left-chiral unit in a counterclockwise oxygen distortion with β-type antiphase domain while sign + or − indicate the net up- or down-orientation of the Ba^{2+} ions. Six symmetry-equivalent domains of the L*cc* unit are shown in Fig. S1 [26].

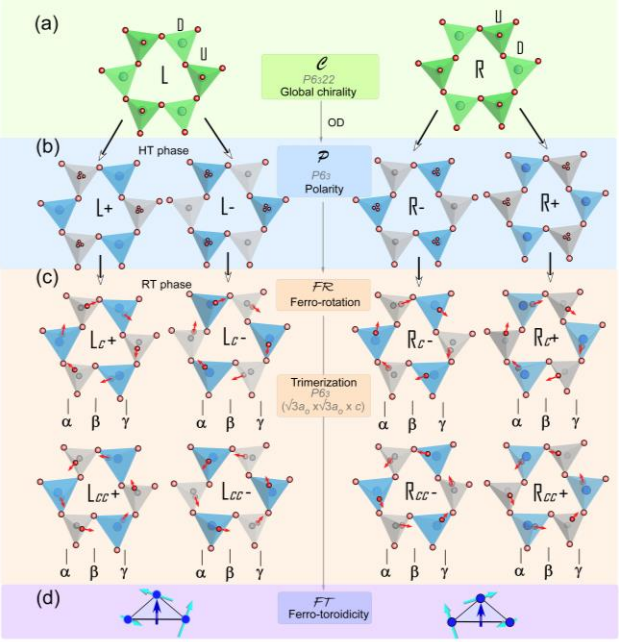

Figure 2. Phase transition hierarchy of $BaCoSiO_4$. (a) The parent chiral phase ($P6_322$), showing the left-handedness of DUDUDU and the right-handedness of UDUDUD six-membered rings of tetrahedra point alternating up (U) and down (D). (b) A Co^{2+}/Si^{4+} order-disorder (OD) transition leads to the breaking of in-plane 2-fold rotation and the HT phase with a chiral and polar symmetry ($P6_3$). The grey, blue, and red spheres represent the Co, Si, and O ions. The apical O atoms are shifted off the threefold axes and split over three equivalent positions to eliminate linear Si—O—Co linkages. Signs + or − indicate the net up or down polar distortion related to down and up CoO_4 tetrahedral geometries. (c) The 24 domain configurations of the RT phase as a result of chirality, polarity, trimerization (α/β/γ antiphase displacements), and ferro-rotation (c and cc ferro-rotational distortion of bridging oxygens). L*c*α+ represents a left-chiral unit in a clockwise oxygen distortion with α-type antiphase domain and an upward polar distortion. (d) Below 3.2 K, rotating Co^{2+} spins in each triangle form a toroidal moment pointing c. This magnetic structure with a canting magnetization M_c is also chiral, and this magnetic chirality is determined by the parent chiral lattice described in (a).

b. Chirality

First, we start $BaCoSiO_4$ on the point of chirality. Fig. 2a illustrates two six-membered rings of $BaCoSiO_4$ tetrahedra with DUDUDU or UDUDUD orientations, in which up (U) and down (D) stand for the pointing direction of the tetrahedral apices along the *c* axis. A mirror operation relates two orientations that preserve the chiral tetrahedral unit, thus labeled as left-chiral (L) and right-chiral (R). The absolute chirality determination requires to be confirmed. It appears the chirality comes with the Co^{2+}/Si^{4+} site mixing (Fig. 2a), a paraelectric structure of space group $P6_322$ develops with a linear tetrahedral string oriented along the *c* axis since the up and down tetrahedral apices remain at the high symmetric position. The crystallographic structure is already chiral even above the Co^{2+}/Si^{4+} order-disorder (OD) process as illustrated in Fig. 2b, and, herein we name its chiral origin as parent chiral lattice. With the settle down of Co^{2+}/Si^{4+}site ordering from cooling, CoO_4 and SiO_4 tetrahedral tilts occur due to sizeable ionic size differences, resulting in the broken in-plane 2-fold axes and a lower symmetry (space group $P6_3$). We find that the parent lattice chirality, i.e., the global chirality, is preserved in the following room-temperature (RT) phase.

Indeed, Fig. 3a shows a single chiral domain of our $BaCoSiO_4$ single crystal under transmission-polarized optical microscopy (*t*-POM) for the light propagating along the chiral *c* axis. The size of the observed chiral domains is on a cm-sized scale. The single chiral domain is robust and does not change when a polycrystalline seed is applied during the crystal growth or post-annealing below the decomposition temperature (~850^{o}C). Namely, either left- and right-handed crystals already exist during the crystal growth while it governs the handedness and the robustness of the single chiral domain observed here. In this regard, we narrow it down to 12 domain configurations in our $BaCoSiO_4$ crystals (Fig. 2).

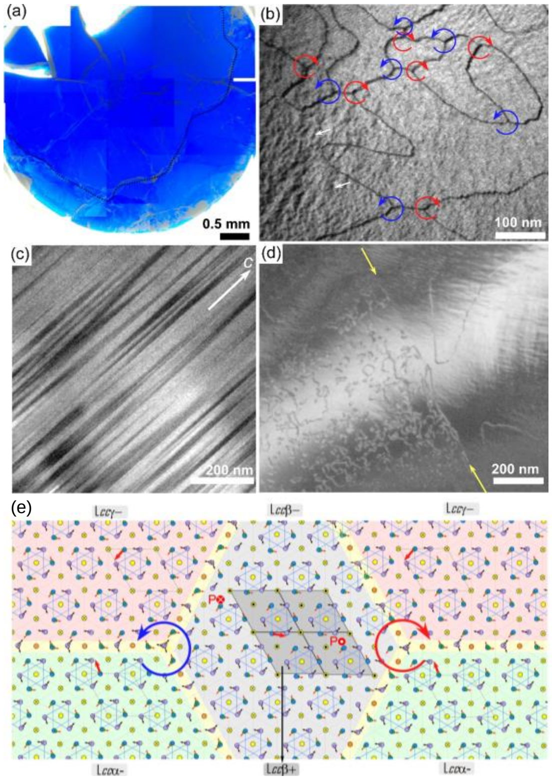

Figure 3. Four ferroic orders in $BaCoSiO_4$. (a) Polished cross-section of a LFZ crystal boule of $BaCoSiO_4$ of (001) surface with two mosaic domains and a single chiral domain and its natural deep blue color under transmission mode Axio-Imager optical microscope (t-POM). (b) In-plane DF-TEM showing antiphase boundaries as dark lines. Three symmetry-equivalent antiphase domains exist because of trimerization. Triple-point junctions are marked in blue and red arrows. Many nanometer-sized dark speckles appear inside antiphase domains as pointed by white arrows, indicating nanoscale lateral polar domains. (c) Side-view DF-TEM of polar domains elongating along the *c* axis. Dark and bright regions corresponding to two different polar domains appear by selecting the (2$\bar{2}$2) spot along [110]. (d) In-plane DF-TEM of ferro-rotational domains demonstrates the discontinuation of trimerization at the ferro-rotational boundary indicated by yellow arrows. (e) The schematic of a pair of Z_3 vortex-antivortex by the 120° apical oxygen rotations (red arrows) across antiphase boundaries. The blue/purple triangles correspond to the top and bottom Co trimers, and the arrows on the atoms depict the in-plane oxygen rotation. The yellow dots and crosses represent the upward and downward distortions of Ba^{2+} ions. Big central red and blue arrows indicate the vorticities obtained by counting the rotating directions in the clockwise direction. A portion of the L*cc*β+ region exists in the central L*cc*β- region due to local Co^{2+}/Si^{4+} ordering.

c. Trimerization and ferro-rotational orders

Next, a clear structural transition takes place around 530°C, identified using differential scanning calorimetry (DSC) shown in Fig. S2a and S2b. In-situ powder XRD measurements in Fig. S2c shows the temperature dependence of the lattice parameters derived from the Rietveld refined plots of $BaCoSiO_4$ in the temperature region between RT and 800^{o}C. The transition temperature from XRD seems slightly lower than that from DSC, while the small discrepancy is

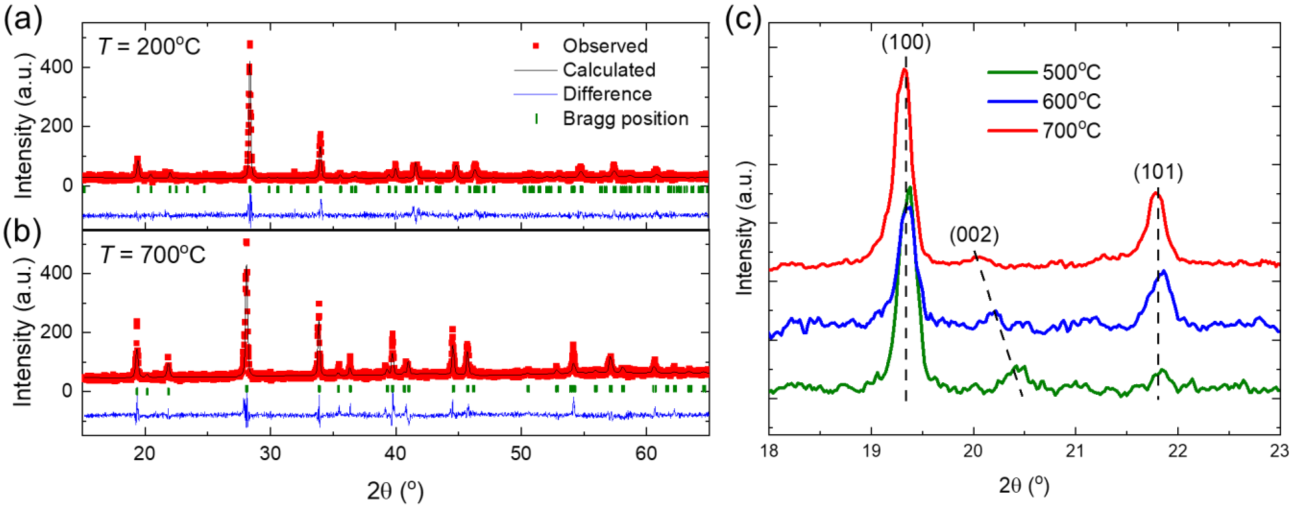

Figure 4. Powder XRD refinement data of RT and HT structures. (a) The refinement data at 200°C. The observed, calculated, and difference profiles are shown by red square, black line, and blue line, respectively. The green bars indicate the positions of the Bragg reflections. (b) The refinement at 700°C. Symbols have same meanings as in (a). (c) The evolution of Bragg reflections (002), and (101) from 500°C to 700°C.

within the DSC-measurement error ~5°C. The HT phase is free from superlattice reflections, while the RT phase shows $a = \sqrt{3} \cdot a_0$ ($a_0 \sim 5.29$ Å) superstructure within the hexagonal plane. The transition is accompanied by an increase of the lattice parameter c by ~1.4 % (from 8.6936 Å at 500°C to 8.8148 Å at 700°C) upon warming. Fig. 1 displays the refined chiral and polar RT structure that is consistent with the literature[9], and the powder XRD refinement data of RT and HT phases are displayed in Fig. 4a and 4b.

Upon increasing temperature, the evolution of peaks (002) and (101) (at $2\theta = 20.1^{\circ}$ and 21.8°) in the HT powder XRD data are evident (Fig. 4c). Several structures ($BaAl_2O_4$, $BaZnGeO_4$, $BaGa_2O_4$) [8,27,28] were tested to describe the HT phase described by the space group $P6_322$ (#182), and the (002) and (101) peaks can be described by the β-$BaGa_2O_4$ structure reasonably with a single tetrahedral site of disordered Co^{2+}/Si^{4+}. The apical oxygen O_2 6h (x, $2x$,¼) connecting tetrahedra are also shifted off the 3-fold axes and split over three equivalent positions from the high-symmetric position 2d (⅓, ⅔, ¼) to avoid linear linkages. A significant splitting of the bridging oxygen over three statistically occupied sites implies the local ordering of Co^{2+}/Si^{4+}. Although refinement using the $P6_3$ space group with ordered Co^{2+}/Si^{4+} did not result in any improvement; however, considering the same R factors within the error margin, significant bond length difference (Si—O: 1.62 Å and Co—O: 1.97 Å), and the relatively large values of the U_{eq} parameters, the refined result with $P6_322$ symmetry of disordered Co^{2+}/Si^{4+} is not against the possibility that $P6_322$ symmetry serves as an average symmetry only.

On the other hand, the tripling unit cell structural phase transition at 530°C is confirmed. The bridging oxygen distortion comes in so that the trimerization and ferro-rotation are closely related with those bridging oxygens, as depicted in Figs. 1b-1c. Based on the XRD results alone, we cannot decide whether the structural transition at 530°C is a trimerization/ferro-rotational transition, i.e., $P6_3$ ($a_0 \times a_0$) to $P6_3$ ($\sqrt{3}a_0 \times \sqrt{3}a_0$) or a polar coupled phase transition, i.e., $P6_322$ ($a_0 \times a_0$) to $P6_3$ ($\sqrt{3}a_0 \times \sqrt{3}a_0$).

d. Polarity

To gain insight into the structural change at 530°C, the microstructure observations were performed using Dark-Field (DF) TEM, in which domain contrasts of dynamical diffraction can occur based on the Friedel pair breaking in a non-centrosymmetric structure[29,30]. Specifically, we can examine the polar domains using a suitable reflection with at least a component along the polarization direction, i.e., c axis in addition to three types of antiphase domains (α, β, and γ) from the trimerization. In a polar coupled with trimerization/ferro-rotational transition phase transition, one may expect a similar cloverleaf pattern observed in the hexagonal rare-earth manganite due to the interlocked polar and structural antiphase boundaries (APBs); otherwise, not. Fig. 3b shows a DF-TEM image taken the g = $(4\bar{3}2)$ along $[\bar{1}02]$, tilted from [001], by 27° to incorporate c axis (polar) component. We observe three antiphase domains emerging from one point instead of six domains with alternating dark and light contrast. Numerous nanoscale speckles indicated with white arrows in Fig. 3b distribute within each antiphase domain. The DF-TEM image clearly shows the decoupled nanoscale lateral polar domains and the structural antiphase domains, whose size can be about a few hundred nm. The correlation of nanoscale lateral polar domains is long along the c axis, as shown in Fig. 3c along [110].

The microstructures revealed by DF-TEM support a trimerization/ferro-rotational transition at 530°C and the scenario of disordered $P6_322$ symmetry being an average HT phase. The local polar regions also indicate a short-range positional order of Co^{2+}/Si^{4+} tetrahedra in the entire $BaCoSiO_4$ single crystal at RT, determined by Co^{2+}/Si^{4+} order-disorder process at a temperature far above 530°C. The phase transition hierarchy shown in Fig. 2 reveals that the paraelectric to polar transition coincides with the Co^{2+}/Si^{4+} order-disorder (OD) process and then follows the trimerization/ferro-rotational transition at 530°C. Indeed, the picture of local polar regions is consistent with the necessary quenching process during the polycrystalline preparation and the rapid growth rate in the L-FZ method to stabilize Co^{2+} ion. The polarization cannot be flipped at room temperature, indicating pyroelectricity, which can be understood as the obstacle of the migration of Co^{2+}/Si^{4+} cations in the ferroelectric reversal path.

e. Trimerization and Domain evolution

The presence of antiphase boundaries (APBs), as shown in Fig. 3b, is the consequence of trimerization, resulting in three possible translation variants. The APBs, visible as narrow dark curved lines, tend to form a network of triple junctions named Z_3, as there are plenty at RT and start to disappear above 540°C in Fig. 5. Fig. 3e illustrates a pair of Z_3 vortex-antivortex of L*cc*α-, L*cc*β- and L*cc*γ- domains, where α, β, and γ represent different origins for the trimerization. An oxygen distortion vector (bold red arrows in Fig. 3e) rotates every 120 degrees around a vortex core. In a clockwise cycle, an increment in an angle of $+2\pi$ is counted as a vortex and a decrement of -2π as an antivortex. Yellow atomically sharp structural domain walls and two vortex cores surround the central L*cc*β- domain. Local polar up regions (L*cc*β+) exist within the central polar down region (L*cc*β-) in the presence of nanoscale Co^{2+}/Si^{4+} ionic ordering. Since only the discontinuation of trimerization occurs at the APBs, it leads to a local lattice compensation at those APBs, i.e., the HT phase.

We study the domain evolutions in a warming-up process through the trimerization/ferro-rotational transition at 530°C. This can be inspected using in-situ heating DF-TEM by selecting the superlattice peaks. The domain evolution at elevated temperatures is captured by incrementally raising the temperature. The coexistence of HT and RT phases can be identified during the in-situ heating, manifesting as dark and light areas, as shown in Figs. 4a-4e. The light areas exhibit the Z_3 network while no feature within the dark areas. Continuing to raise the temperature leads to the vanishing of light areas as the $\sqrt{3}a_0\times\sqrt{3}a_0$-type superlattice peaks disappear. Figs. 4g-4i show clearly that the HT phase is evolved from those dark lines of APBs that correspond to the growth of the HT phase from those APBs of the RT phase. Fig. 5f demonstrates the reversible process and a completely different Z_3 pattern after further cooling the specimen temperature below 530°C.

Note that the 530°C transition is also the ferro-rotational transition ascribed to the *c* or *cc* displacements of the bridging oxygens. As shown in Fig. 1d, defining this *cc* in-plane rotating angle to be 200°, symmetry-equivalent structures are obtained for rotating angles of 320° and 80°. We likewise obtain 40°, 160°, and 280° for clockwise in-plane rotating angles. Because of the non-integer relation of those *c* and *cc* in-plane rotating angles, we observe the interruption of the Z_3 network at ferro-rotational domain walls as shown in Fig. 3d. Experimentally, a continuous Z_3 network tends to extend over a large area, indicating a larger scale of ferro-rotational domains. It can be understood in terms of symmetry. Above the 530°C transition, the apical O atoms are split over three equivalent positions (Fig. 2b) while the 3-fold symmetry along the *c* axis is maintained. A condensation to multiple *c* and *cc* ferro-rotation domains below the transition will undoubtedly break the 3-fold symmetry and unfavored it. The lateral domain sizes among four ferroic orders of our BaCoSiO$_4$ crystals are domains of chirality (cm-size) > ferro-rotation (a few hundred μm) > antiphase (a few μm to a few hundred nm) > polarity (tens of nm laterally).

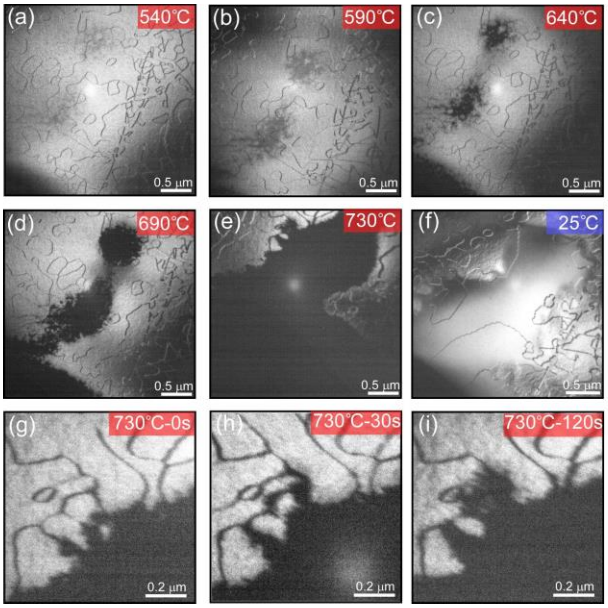

Figure 5. Dark-field TEM images of BaCoSiO$_4$ at different temperatures. (a-e) Black regions, the nucleated HT phase, are observed above 530°C. Bright regions with dark lines of antiphase boundaries are the residual RT phase. (f) A different Z_3 pattern forms after a warming-cooling cycle. (g-i) The HT phase is evolved from those dark lines, APBs, during in-situ heating.

f. Magnetic chirality and magnetoelectric effect

Magnetoelectric (ME) effect can occur in ferroic materials[31]. The first experimental demonstration of magnetoelectricity was performed on Cr$_2$O$_3$, in which electric-field-induced magnetization and magnetic-field-induced polarization with linear ME coefficient α_{zz} = 4.13 ps m^{-1} were observed[32-35]. Subsequently, researchers have discovered various ME compounds such as TbPO$_4$[36], Fe$_2$Mo$_3$O$_8$[37], and Ni$_3$TeO$_6$[38]. Unlike above materials showing induced magnetization/polarization parallel to the applied field, it was found that the magnetic toroidicity allows the control of magnetization/polarization by fields perpendicular to them[4], as illustrated in materials such as LiNiPO$_4$[39], LiCoPO$_4$[40], LiFeSi$_2$O$_6$[41], and Ga$_{2-x}$Fe$_x$O$_3$[42]. Besides those compounds, the exploration of *TM* induced ME materials is very limited to date.

Ni_3TeO_6 has a polar and chiral structure, but the magnetic ground state is collinear without toroidicity or magnetic chirality. Therefore, $BaCoSiO_4$ is great candidate showing both structural and magnetic chirality, which could lead to a robust and field-tunable ME effect induced by *TM*.

We note two-step structural chirality in $BaCoSiO_4$: (1) the mono global chirality fixed by the very high-temperature parent chiral lattice, and (2) the various local chirality induced by the ferro-rotation with existing polarization, i.e., nanoscale lateral polar domains. Though ferro-rotation, which does not break space inversion, does not induce optical activity, but has symmetry operation similarity (SOS) with a structural chirality in the presence of polarization[24] [43]. Then, the structural chirality can generate magnetic chirality through DM interactions. If the global structural chirality determines magnetic chirality, the whole crystal shall show a mono ferro-toroidal domain when applying magnetic field along the *c* axis, and *TM* induced ME effects should be observed[4]; otherwise, not.

We prepared *ab*-plane and *ac*-plane single crystalline plates and tested their ME properties by applying magnetic fields along various directions and collecting the induced current signal. The setup of electrodes and external magnetic field directions is shown in Fig. 6a and 6b for *ab* plane and *ac* plane plates, respectively. For the *ab* plane crystal, the pyroelectric current shows a much clearer anomaly at Neel temperature ~ 3.2 K (from the χ(T) in Fig. S2d) when applying magnetic field along the *c* axis rather than the *a* axis (Fig. S3a). Consistently, at 2 K, magnetic field sweeping along the *c* axis induces a large ME current signal up to 2 pA (Fig. S3c) and a polarization up to 90 $\mu C/m^2$ (Fig. 6c upper panel). The anomaly and tripled slope in the polarization curve at $H_c = \pm 1.2$ T agree with the reported field-induced “1 to 3” M_c transitions[18]. Therefore, in the *ab* plane crystal, the dominated ME effect happens when both *P* and *H* parallel to the *c* axis. This behavior is not surprising considering $BaCoSiO_4$ a non-centrosymmetric hexagonal system with polarization and net magnetization along the *c* axis[37,38]. As shown in Fig. S4, the fitting of $P_c(H_c)$ by $P_c = C + \alpha H_c + \beta {H_c}^2$ yields α = 5.42(2) *ps/m*, β = $2.01(6) \times 10^{-18}$ *s/A* for high-field region (1.5 T to 7 T), and α = 6.13(7) *ps/m*, β = $-1.96(4) \times 10^{-18}$ *s/A* for low-field region (0 T to 0.9 T). The linear term has the same order of magnitude with the reported α = 4.13 *ps/m* in Cr_2O_3, and the quadratic term is comparable with the reported β = 2.959×10^{-18} *s/A* in another non-centrosymmetric antiferromagnet $Co_2Mo_3O_8$[44]. This coexisting of linear term and quadratic term ME effect has also been observed in the high-field region of non-centrosymmetric hexagonal magnet $Ni_2Mo_3O_8$[45]. In $Ni_2Mo_3O_8$, it has been suggested that the low-field AFM state has a symmetry that does not allow the linear term, while field-induced ferromagnetic moments in high fields could contribute to a linear term. It should be noticed that the magnetic space group of $BaCoSiO_4$ and high-field $Ni_2Mo_3O_8$ both contain *c*-rotation operation ***6***. Since the space inversion and time reversal are all broken by polar lattices and ferromagnetic moments in ***6***, it allows both linear and quadratic ME effects along the *c* axis. Our results show that the linear term α remains almost invariant below and above the “1 to 3” transition, while the quadratic term β flips its sign, which suggests that the quadratic term depends more on the net magnetic moments while the linear term stays almost unaffected. In addition, although a significant ME effect is observed in $P_c(H_c)$, the dielectric constant ε(*T*) along *c* axis doesn’t show clear anomaly at T_N at various magnetic fields along *c* axis (Fig. S5c and d). The reason is unknown yet.

More interesting behaviors come with the *ac* plane crystal. As shown in Fig. S3b, among H parallel to a (orange), c (wine), and $a*$ (cyan) axes, the pyroelectric current when $H /\!/ a$ shows the clearest peak at Neel temperature 3.2 K. Accordingly, the observed polarization at 2 K with $H /\!/ a$ sweeping is much larger than $H /\!/ a*$ and $H /\!/ c$ cases (Fig. 6c lower panel). For a *TM* along the *c* axis, the induced ME effect requires $H \perp c$, $P \perp c$, and $H \perp P$, which is precisely consistent with the P, H assignment in which the significant ME effect was detected on the *ac* plane crystal. Therefore, we can conclude that the observed off-diagonal ME effect ($P /\!/ a*$, $H /\!/ a$) origins from a magnetic toroidicity contribution. In the low-field region (-2 T to 2 T), the induced polarization is nearly linear to the applied field, and it decreases when field larger than 4 T. The reason of this behavior could be that large in-plane magnetic field tends to co-align spins through a spin-flop transition and suppress the *TM*. Consistently, we also observed the disappearance of the magneto-dielectric effect at magnetic field larger than 3 T, as shown in Fig. S5a and b.

Note that even if the magnetic field was applied along the *a* axis, practically, there could always exist a tiny *c* component of the magnetic field due to misalignment. This tiny *c* component could flip the magnetization, especially considering the reported coercive field of $BaCoSiO_4$ M_c is extremely small, which is only around 50 Oe[18]. To investigate this possibility, a *TM* induced ME measurement within a low field range -2000 Oe to 2000 Oe was performed and displayed in Fig. 7. Clear peaks at around ±800 Oe and “butterfly” hysteresis behavior confirm the flipping of M_c by a tiny *c* component of applied field, as well as the ferroic nature of *TM*. From the reported coercive field of M_c 50 Oe, the misalignment of the magnetic field can be estimated to be 3.5°, which is reasonably small enough. We notice that the induced polarization P_{a*} is markedly linear to applied magnetic field H_a within -2000 Oe to 800 Oe (ascending) and 2000 Oe to -800 Oe (descending) ranges, with a linear ME coefficient α = 1.03(4) *ps/m*.

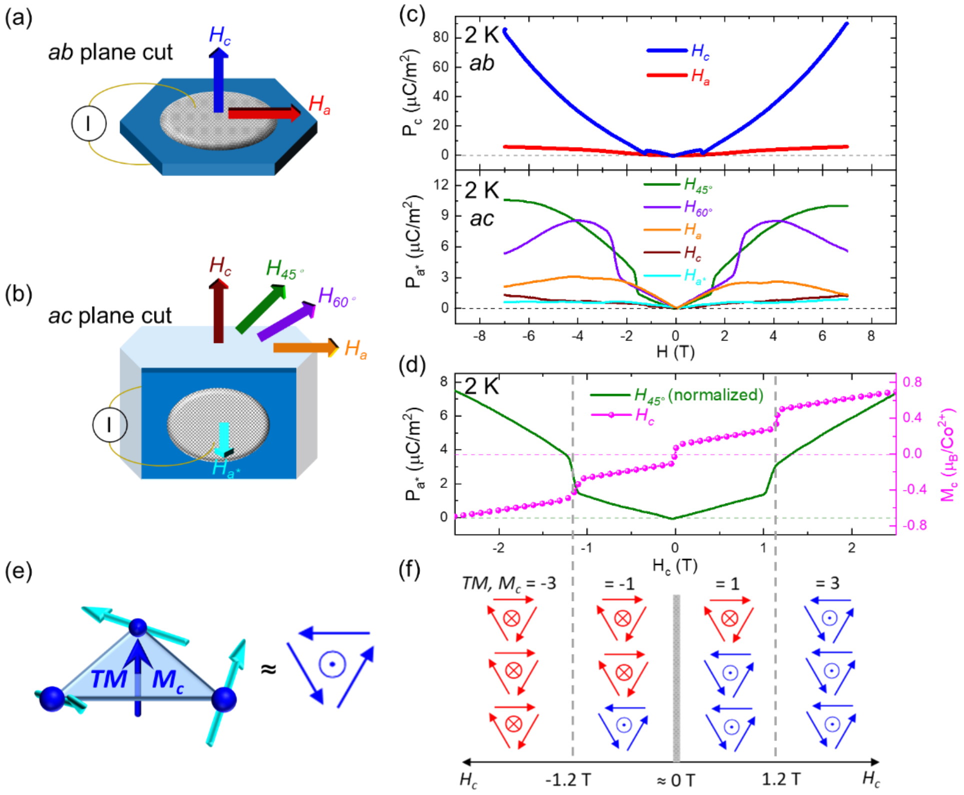

Figure 6. Magnetoelectric effect of $BaCoSiO_4$. (a), (b) Schematics of electrodes and magnetic field directions on *ab* plane (a) and *ac* plane (b) single crystals. (c) Magnetoelectric polarization as a function of applied fields measured on *ab* plane (upper panel) and *ac* plane (lower panel) single crystals at 2 K with magnetic field along various orientations shown in legends. The color of each curve corresponds to the field indicated with same color of arrows in (a) and (b). (d) The 2 K isothermal $M_c(H_c)$ data (magenta), which is from ref.[18], and magnetoelectric polarization as a function of fields pointing 45° in between *c* and *a* (olive). The field is normalized by dividing $\sqrt{2}$ to make *c*-component H_c as the *x* axis. (e) Schematics of the magnetic structure of one Co sublattice. Blue spheres represent Co ions, and cyan and blue arrows show spins and resulting *TM* and M_c, respectively. (f) A schematic showing the "-3 to -1 to 1 to 3" *TM* and M_c change with applied field along *c*. Polarizations (olive arrows) along *a** are induced with the presence of the magnetic field component along *a*. The narrow shadow area near zero field denotes the tiny hysteresis regime.

We have learned that applying magnetic field along the *c* axis can triple the *TM* as well. However, detecting the corresponding ME effect requires a magnetic field component perpendicular to the *c* axis. Therefore, to reach the ME effect with tripled *TM*, applied *H* should contain both *c* and *a* components. The olive and violet curves in Fig. 6c lower panel display ME current and polarization measured in such a way that magnetic field orients 45° and 60° to the *c* axis, respectively. Consistently, "1 to 3" *TM* transitions are observed around 1.6 T (expected to be 1.2 / *cos*(45°) T) for H_{45}° and 2.4 T (expected to be 1.2 / *cos*(60°) T) for H_{60}°. We normalize the $P_{a*}(H_{45}°)$ data into $P_{a*}(H_c)$ and combine it with published $M_c(H_c)$ curve in Fig. 6d, and the anomalies in $P_{a*}(H_c)$ precisely coincide with the metamagnetic transitions at ± 1.2 T. The *TM* induced polarization is nearly linear just below and above the transitions. The tripled *dP/dH* and magnetization confirm the "1 to 3" *TM* and M_c change. A maximum ME coefficient *dP/dH* = 26.22(6) *ps/m* is obtained at the metamagnetic transition point. Fig. 6e shows an example of magnetic structure of a Co triangle sublattice with *TM* = +1 and M_c = +1, which is also an object of magnetic chirality. The schematics in Fig. 6f shows how the three sublattices evolve with H_c, i.e., "-3 to -1 to 1 to 3" *TM* and M_c transitions. Clearly, the field-invariant magnetic chirality, which is fixed by global structural chirality, is the essence of $BaCoSiO_4$ to achieve field-tunable *TM* and ME effect.

Overall, $BaCoSiO_4$ single crystal shows not only a conventional $H /\!/ P$ type ME effect, but also an exotic $H \perp P$ type *TM* induced ME effect. These findings strongly suggest that each bulk crystal has a single and invariant magnetic chiral domain, and the mono structural global chirality is possibly the root cause. Note that both global and local chiral structures have very low symmetry and permit nonzero DM interactions. However, the local chiral contribution is supposed to be canceled out due to the multiple domains. Thus, the observed magnetic chirality only couples with the global chirality. In addition, the observed multistep and low-barrier control of magnetization and polarization provides insights into next-generation ME and memory devices.

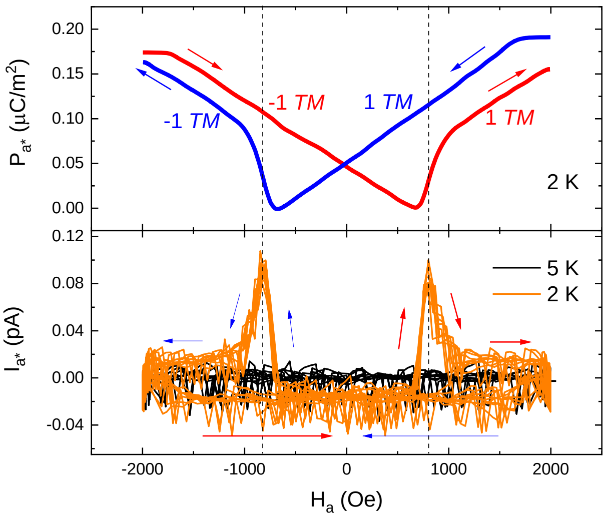

Figure 7. The low field (-2000 Oe to 2000 Oe) region of $I_{a*}(H_a)$ (lower panel) and $P_{a*}(H_a)$ (upper panel). In the lower panel, orange and black lines represent magnetoelectric current $I_{a*}(H_a)$ at 2 K (below transition) and 5 K (above transition), respectively. The red and blue arrows mark the ascending and descending magnetic field H_a sweeping loop. In the upper panel, the red and blue curves show the polarization P_{a*} as a function of ascending and descending magnetic field H_a, respectively.

IV. CONCLUSION

A new triangular lattice antiferromagnet $BaCoSiO_4$ single crystal with a chiral and polar crystal structure (RT space group $P6_3$) was synthesized by the LFZ method. We identify diverse ferroic orders of $BaCoSiO_4$ at room temperature and explore their hierarchial phase transitions through domain observations. We discover the formation of Z_3 (anti)vortices driven by a trimerization-type structural instability, the ferro-rotational domains from the in-plane distortion of bridging oxygens, and lateral nano-sized polar domains limited to the Co^{2+}/Si^{4+} ionic ordering process. Our results reveal a trimerization coupled with the ferro-rotational transition at 530ºC instead of a polar-coupled transition, which differs distinctly from other tridymite derivatives, e.g., $BaAl_2O_4$. $BaAl_2O_4$ has been proposed as an improper ferroelectric from the analysis of group theory, in which the primary order parameter M_2 vibration mode is coupled with the secondary Γ_2 polar mode [46]. The decoupling of polar mode and the detailed symmetry analysis in $BaCoSiO_4$ found in this work call for further attention.

Interestingly, two-step chirality develops. We found that the single global chirality possibly locks the single magnetic chirality below 3.2 K, so a net *TM* can exist and be tunable by an external magnetic field along the *c* axis. As a result, the magnetic-toroidicity-induced ME effect has been successfully observed with a maximum ME coefficient 26.22(6) *ps/m*. Our results unveil the complex structures and phase transitions, the critical role of domain configuration for macroscopic properties, and the tunable coupling between magnetization and polarization. $BaCoSiO_4$ is a unique playground for studying the multifaceted coupling of structural and magnetic ferroic orders and promising material for next-generation multifunctional electronic devices.

V. ACKNOWLEDGMENT

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