Topological defects at octahedral tilting plethora in bi-layered perovskites

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Oxygen octahedral distortions, including tilts/rotations, deformations and off-centring in (layered) perovskites, have the key role in their numerous functional properties. Near the polar-centrosymmetric phase boundary in bi-layered perovskite Ca3−xSrTi2O7 with x=1, we found the presence of abundant topological eight-state vortex-antivortex pairs, associated with four oxygen octahedral tilts at domains and another four different oxygen octahedral tilt at domain walls. Our discovery opens a new revenue to unveil real-space topological defects associated with the possible vector choices in one specific lattice mode.

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INTRODUCTION

Copious functional phenomena, including high Tc superconductivity,1 ferroelectricity,2,3 novel magnetism4–6 and giant photovoltaic effects,7,8 have been observed in perovskite (ABO3)-related compounds, where those physical properties can be closely associated with oxygen octahedral distortions, including tilts/rotations, deformations and off-centring.11 It turns out that superconductivity in (La,Ba)2CuO4 is signiﬁcantly inﬂuenced by oxygen octahedral tilts,12,13 and canted magnetic moments appear in antiferromagnetic perovskites with tilted/rotated oxygen octahedra through Dzyaloshinskii–Moriya interaction.14 High dielectric response in the vicinity of the morphotropic phase boundary is a consequence of the continuously rotating polarisation with various octahedral tilts.15,16 Crystal field split can be considerably influenced by compression or elongation of oxygen octahedra, which is the origin of the Jahn–Teller effects for B = Cu2+ or Mn3+ (refs 1,17,18). Remarkably, the simultaneous presence of oxygen octahedral tilt and rotation can result in ferroelectric polarization in perovskites with even number of layers, which is called hybrid improper ferroelectricity.19–21 It has experimentally verified that bi-layered perovskite Ca3−xSrTi2O7 (CSTO) is a hybrid improper ferroelectric with switchable polarisation of 8 μC cm−2 in bulk crystals at room temperature.20 Ferroelectricity in CSTO described by a hybridisation of two structural modes (octahedral tilt and rotation modes) turns out to be associated with an intriguing domain topology consisting of Z2 × Z2 domains and Z2 vortices with eight domains (four directional domains and two antiphase domains), abundant charged domain walls and unique zipper-like switching kinetics.22 In Z2 × Z2 domains, Z4 denotes the cyclic group of order 4 for directional variants and Z2 is for translational variants. In this article, utilising in situ heating transmission electron microscopy (TEM) studies, synchrotron powder X-ray diffraction experiments and dielectric measurements, we report the discovery of a new intermediate tetragonal state in CSTO, which demonstrates a displacive nature of hybrid improper ferroelectricity mechanism different from those predicted from the group-subgroup relation.21,23 Furthermore, we find the presence of topological eight-state vortex–antivortex defects associated with two-dimensional eight degrees of freedom for oxygen octahedral tilts in the intermediate tetragonal state.

RESULTS

Figure 1 depicts the possible octahedral tilts/rotations in bi-layered perovskite CSTO, resulting in different structural states and also domains with different directional order parameters. For each space group, the distortion axes and the corresponding Glazer notations24 are given with respect to the un-distorted tetragonal I4/mmm (T) structure (Figure 1b). The term ‘rotation’ denotes a rotation of the basal oxygen plane around the [001]T axis in a clockwise (+) or counterclockwise (−) manner (Figure 1c for +). Out-of-phase and in-phase rotation in adjacent layers within one bi-layered perovskite block lead to orthorhombic O* and O states, respectively. Note that the presence of an intermediate O* state (Figure 1c) competing with the ground-state polar O state, is responsible for uniaxial negative thermal expansion, has been confirmed in hybrid improper ferroelectric magnet Ca3Mn2O7 (refs 25, 26). The term ‘tilt’ is associated with a tilt around an in-plane axis, and it would move the basal oxygens out of the basal plane and the apical oxygen away from the c axis. In-plane tilting axes can be along <110> and <100> directions, leading to orthorhombic O’ (Figure 1e) and tetragonal T’ states (Figure 1f), respectively. Following the Glazer notation, the T’ state has the a0a0c0 pattern and the T’, O’, O” and O’’ states are described as a0a0c0, a0a0c0, a0a0c0 and a0a0c0, respectively. Two end members, Sr3Ti2O7 and Ca3Ti2O7, correspond to two extremes: the un-distorted T state of Sr3Ti2O7 and the O state with both tilt

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Figure 1. (a) Schematic diagram of possible space groups and the corresponding Glazer notations for bilayered perovskite A$_2$B$_2$O$_6$. Lines link the group–subgroup relations. The lattice directions are given with respect to the T state (14/mmm) and rotation (a′ a′ c′) of Ca$_3$Ti$_2$O$_7$ (Figure 1d). It is clear why orthorhombic O′ (a′ a′ c′) and O′′ (a′ a′ c′) states are the two plausible intermediate structures toward the polar O structure (a′ a′ c′) by symmetry.21,23 With the underlying square lattice, various symmetry–equivalent domains (phases) may exist in each of those states. It is convenient to define the azimuthal angle of an apical oxygen distortion, φ, as shown in Figure 1d. This φ links all possible directions of apical oxygen motions among those phases; for example, symmetry–equivalent domains of the T’ phase correspond to φ = 0°, 90°, 180°, and 270° (red-circled ➊, ➋, ➌ and ➍ in Figure 1f, respectively), whereas those in the O’ phase to φ = 45°, 135°, 225° and 315° (blue, 1, 2, 3 and 4 in Figure 1e, respectively). The domains of the polar O state has φ = 45° ± α, 135° ± α, 225° ± α and 315° ± α, where α depends on the sign and magnitude of octahedral rotation (a′ a′ c′; 1 ±, 2 ±, 3 ± and 4 ± in Figure 1d, respectively).

We have performed synchrotron powder X-ray diffraction experiments using the collimated synchrotron-radiation beam with the wavelength of 0.688 Å at the National Synchrotron Radiation Center, Taiwan. Homogeneous and phase-pure polycrystalline CSTO (0 ≤ x ≤ 3) specimens were prepared by a solid-state reaction method (Materials and methods). The general structure analysis system program using the Rietveld method with a pseudo-Voigt profile function was exploited to analyse the powder diffraction data. The evolution of octahedral rotation (θo) and tilting (θt) angles of TiO$_6$ and lattice parameters a, b and c as a function of Sr content, x, is summarised in Figure 2a and Supplementary Figure S1a. The phase diagram, constructed from these structural parameters, consists of ferroelectric O (purple, 0 ≤ x ≤ 0.9) and paraelectric T states (pink, x ≥ 1.5). The asymmetric decays of θt at x = 0.915 defines a sharp and narrow region with only non-zero θt (yellow, Figure 2a). The high-resolution X-ray diffraction data clearly display peak splitting only when x ≤ 0.9, implying a tetragonal symmetry in this narrow region (Supplementary Figure S1b). A $\sqrt{2} \times \sqrt{2}$ supercell in electron diffraction patterns from TEM (Figure 2c) is found for x = 0.915−1, confirming the stabilisation of a new tetragonal intermediate state distinct from the parent T state. The Rietveld refinement of synchrotron data provides further confirmation of the existence of the T state with the a′ a′c′ pattern (Supplementary Figure S1c). The details of X-ray refinement fits are given in Supplementary Section 1 and Supplementary Table S1. The dielectric constant also shows a marked change in magnitude upon entering the T’ state and displays almost two times larger, epsilon (ε) value at the phase boundary of x = 0.9, compared with that of low x values (Figure 2b). An increase in ε at 350 K can be understood as increasing structural fluctuations when approaching from the ferroelectric O to paraelectric T’ states. Indeed, in situ TEM heating experiments of Ca$_2$Sr$_{3-x}$Ti$_2$O$_7$ crystals exhibit a two-step transformation upon heating: O → T’ → T. Figure 2c shows that the intensity of superlattice S$_{1}$-type spots $\frac{1}{2}$(130)$_{1}$ of the O state (cyan triangles) weakens as temperature (T, defined italic T as temperature) is raised from 300 to 450 K. Two additional sets of superlattice S$_{2}$-type $\frac{1}{2}$(200)$_{1}$ and S$_{3}$-type $\frac{1}{2}$(T30)$_{1}$ spots (yellow and green triangles), corresponding to the T’ state, appear when temperature is further raised to 473 K. Finally, all superlattice spots vanish above 713 K. Thus, we have demonstrated the stabilisation of the intermediate T’ state by varying chemical composition as well as temperature. Starting from the O state at low x, Figure 2a shows a faster relaxation of the octahedral rotation (θo) than that of tilting (θt) with increasing Sr doping, which is also coupled with an increasing trend of orthorhombicity.20 The sudden suppression of octahedral rotations occurs when the azimuthal angle φ suddenly switches from ∼45° at x = 0.9 to 0° in the T’ state (Figure 1a), indicating a likely discontinuous change of the tilting order parameter and a first-order phase transition. Note that we do not observe any evidence for an intermediate
O’ (\(a\ a\ c', \varphi = 45°\)) state, reported in the solid solution of Ca\(_{3}\)Ti\(_2\)O\(_7\)-(Ca,Sr)\(_{1.15}\)Ti\(_{0.85}\)Fe\(_2\)O\(_7\) (ref. 27).

Figures 3a and b show a 2.7 × 1.7 μm mosaic of dark-field (DF) TEM images of the T’ state (x = 0.95 taken using S2 spot (red circle in Figure 3b) and its corresponding diffraction pattern along the [001]T direction. The curved dark-contrast lines reveal boundaries of four T’-phase domains merging at one core, which is a non-T state. With the underlying square lattice, 4 symmetry-equivalent domains, named \(Z_2 \times Z_2\) domains, may exist; four translational variants associated with the translation vectors (\(\frac{1}{2}, \frac{1}{2}, 0\)), (0, \(\frac{1}{2}, \frac{1}{2}\)) and (\(\frac{1}{2}, 0, \frac{1}{2}\)) where out-of-plane changes are involved in the latter two. However, the domain topology can be renamed as \(Z_2 \times Z_2\) domains when the in-plane order parameters (octahedral tilts) of one bilayer is considered; two directional variants ([010]-tilt producing 0 and [100]-tilt producing \(\Theta\rightarrow\Phi\)) and two translational variants associated with the in-plane translation vector (\(\frac{1}{2}, \frac{1}{2}, 0\)) between 0 and \(\Theta\rightarrow\Phi\) (Figure 1f). Our results demonstrate that four domains, corresponding to red-circled 0, \(\Theta, \Phi\) and \(\Theta, \Phi\) in Figure 1f, form an exclusive vortex-like pattern with 90°-rotating apical oxygen distortions (red arrows in Figure 3a). These four domains are represented by four values of apical oxygen azimuthal angles \(\varphi = 0°, 90°, 180°\) and 270°; for example, domains 0 and \(\Theta\) correspond to \(\varphi = 0°\) and 180°, respectively. Note that the domain network (Figure 3a) can be described by two proper colouring, i.e., two colours is sufficient to identify the domains without neighbouring domains sharing the same colour (white and green in Supplementary Figure S3a), and the vortex network can be constructed by cutting through two types of closed loops (blue and light blue in Supplementary Figure S3a) based on a graph-theoretical description. Intriguingly, those curved domain walls exhibit two distinct extinction rules in the superlattice DF-TEM images. Figure 3c shows a DF-TEM image using a S1 spot (light-blue circled in Figure 3b), revealing only a part of domain walls. A complementary domain-wall map is obtained using a S2 spot for DF-TEM imaging (blue-dotted circled in Figure 3b). The inequivalent nature of these two DF-TEM images with different superlattice peaks with ab plane components indicates an orthorhombic-like local structure at those walls, instead of, e.g., a high-symmetry T state. Considering a pure tilting nature of the matrix T’ state and the distinct extinction rules, those domain walls are likely in the O’ state (Figure 1e). The directions of oxygen octahedral tilts and apical oxygen distortions are denoted as light blue and blue arrows in Figures 3c and d, respectively—more details are discussed in Supplementary Section 2. Therefore, oxygen octahedra inside the bright-contrast domains tilt along either [100]-type and [010]-type superlattice spots appear (yellow and green triangles), indicating the appearance of a tetragonal T’ state. Above 713 K, all superlattice spots disappear, consistent with the presence of the T state at very high temperatures.
vortices. A Z4 vortex is always surrounded by antivortices and vice versa; they have the same topological charge, so both of them are antivortex defects. We emphasise that vectors in a type $i$ topological defect rotate opposite to those in a type $ii$ topological defect, but they have the same topological charge, so both of them are vortices. A Z4 vortex is always surrounded by antivortices and vice versa; for example, the vortex $i'$ in Figure 3a is connected to the antivortex $ii'$ and the antivortex $i'v$. Figure 4b illustrates the local structure around a type $i/Z_4$ vortex (Figure 4a) with red-circled $i$, $ii$, $iii$ and $iv$ domains, and domain walls of DW000 (blue-broken lines), DW000 (light-blue-broken), DW000 (blue), and DW000 (light blue). By averaging the structure of neighbouring domains, DW000 and DW000 share the same $[110]_T$-tilting axis, but are different in the origin by a half of the unit cell. Similarly, DW000 and DW000 have the same tilting axis, which is consistent with the extinction rules observed in Figures 3c and d. On the other hand, a geometric frustration of oxygen octahedral distortions between two antiphase domains occurs likely in DW000 (Figure 4c), leading to an undistorted domain wall in a T structure-like high-symmetric state. The absence of Z3 vortices where three types of domain walls merge at one point reveals the nonexistence of $(\frac{1}{2}, \frac{1}{2}, 0)$-type APB such as DW000, which, in turn, indicates a much higher energy associated with APBs.

**DISCUSSION**

The $T'$ state showing Z4 vortices occurs in a narrow compositional range of (Ca,Sr)$_3$Ti$_2$O$_7$. When octahedral rotation (thus, hybrid improper ferroelectricity) is suppressed by chemical doping/ionic ordering, Z4 vortices emerge in the narrow compositional range, where domain and domain walls are intricately intertwined with the $T'$ and O' states, arising from the active $X_3$ mode. A full isotropy subgroup analysis$^{29}$ further implies a missing intermediate orthorhombic $Pnmm$ state, representing order parameter direction $(a, b)$, which is a subgroup of both of the $T'$ and O' states, and is expected by symmetry to link domain and domain walls. A similar rule has been also applied to topological Z6 vortices in hexagonal system, h-In(Mn$_{0.9}$Ga$_{0.1}$)O$_3$, where the K3 mode is characterised by trimers of the MnO$_6$ trigonal bipyramids. Three low-symmetry possibilities derived from the parent $P6_3/mmc$ structure are allowed by the K3 mode, corresponding to 12 phases of domains and domain walls and an intermediate state link them$^{31}$. Real-space topological defects can be well classified in terms of one specific lattice mode, which leads to a valid physical insight into the phase transition and serves as a platform to uncover additional hidden symmetry and new topological defects. In addition, our new discovery of Z'$_2$ × Z$_2$ domains with Z$_2$ vortices unveils that there can be a lot more than just the topological defects (Z'$_2$ × Z$_2$ domains with Z$_2$ vortices) in hexagonal rare-earth manganites, which has been extensively investigated since the initial discovery in 2010 (ref. 32). Z'$_2$ vortices observed in improper ferroelectric rare-earth manganites$^{31,32}$ and skyrmions in low-symmetry magnets$^{33}$ have provided a new paradigm in the quest for mesoscopic self-organised structures with non-trivial topology, which can have novel functionalities. Emphasise that the octahedral distortions in the $T'$ state is also analogous to that observed in the so-called low-temperature...
High-angle annular dark-field favoured than the bi-layered A3B2O7 phase. The powder specimens for (2) S2 = Tb2Sr(Fe,Co)2O7 (refs 36 in which the CuO6 octahedra also tilt along the C directions12,13 and are governed by the X3T symmetry. Yellow-circled types i and ii are Z4 vortices and types iii and iv are Z4 antivortices. (b) Local oxygen distortions of a type i Z4 vortex with four domains (red-circled ➊) and four domain walls (blue 1−4) in the ab plane. The local apical oxygen distortions in each domain and domain wall are shown by small gray and black arrows. The gray solid squares outline the Z4 vortex core. The Glazer notations label the dominant tilting modes at the corresponding locations. (c) A schematic of the domain wall between two antiphase domains, e.g., DW➊ between domain ➊ and ➋. The open circles indicate the ideal position of oxygens of the T state.

Materials and Methods

Eleven high-quality polycrystalline specimens of Ca3−xSr2Ti2O7 (x = 0, 0.3, 0.5, 0.6, 0.8, 0.85, 0.9, 1, 1.5, 2 and 3) were prepared using a solid-state reaction method. Stoichiometric mixes of CaCO3 (Alfa Aesar 99.9%), SrCO3 (Alfa Aesar 99.9%) and TiO2 (Alfa Aesar Puratronic 99.995%) powders were ground, pelleted and then sintered at 1,550–1,660 °C for 30 h. In the range of 1.1 ≤ x < 1.5, we found a triple-layered A3B3O10 phase is more stable and favoured than the bi-layered A3B2O7 phase. The powder specimens for acquiring synchrotron X-ray powder diffraction data were sealed in 0.2-mm-diameter capillary quartz tubes. All synchrotron X-ray experiments were performed on beamline BL01C2 at the National Synchrotron Radiation Research Center, Taiwan. The powder diffraction patterns were acquired using a collimated synchrotron-radiation beam with the wavelength of 0.688 Å (18 KeV). Powdered sample were loaded into a 0.2-mm capillary for uniform absorption and faster rotation during data collection. The general structure analysis system program using the Rietveld method with a pseudo-Voigt function was exploited to analyse the X-ray powder diffraction data. Specimens for transmission electron microscope (TEM) studies were prepared by chemical polishing, followed by Ar-ion milling, and studied using a JEOL-2010F TEM at Rutgers University, NJ. We observed Z4 vortex domains with superlattice DF-TEM imaging taking (1) S1 = ½(130) = (120)superl., (2) S2 = ½(020) = (110)superl., and (3) S3 = ½(T30) = (210)superl. spots. In situ heating TEM experiment was carried out using a JEOL-2000FX TEM with a high-temperature specimen holder at National Taiwan University in Taiwan. High-angle annular dark-field scanning TEM imaging with atomic-column resolution was carried out using a JEOL-2100F microscope equipped with a spherical aberration Cs-correction at National Taiwan University in Taiwan. High-angle annular dark-field images were acquired in the condition: 512 × 512 with 0.024 nm per pixel with collection angle between 80 and 210 mrad. For dielectric constant measurements, two electrodes were prepared using Au sputtering on polished specimens with a capacitor condition: 512 × 512 with 0.024 nm per pixel with collection angle between 80 and 210 mrad. For dielectric constant measurements, two electrodes were prepared using Au sputtering on polished specimens with a capacitor geometry, and an LCR metre at f = 44 kHz was utilised.

Data availability

The authors declare that all source data supporting the findings of this study are available within the article and the file.

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Contributions

F.-T.H. and M.-W.C. conducted the (S)TEM experiments. B.G. and X.L. synthesised the work at Postech was supported by the Max Planck POSTECH/KOREA Research Initiative Program (grant no. 2011-0031558) through NRF of Korea funded by MSIP.

Competing interests

The authors declare no conflict of interest.

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