HYBRID IMPROPER FERROELECTRICS AND POLAR MAGNETS

By

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written under the direction of
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This dissertation seeks to study several polar magnets, especially hybrid improper ferroelectrics (HIF), promising candidates to realize room-temperature multiferroics. In order to realize the designed properties, high-quality single crystals are required, and the growth of single crystals is an important part of this thesis. First, we introduce the concept of hybrid improper ferroelectricity, and discuss intriguing domain features in the non-magnetic HIF, Sr-doped Ca$_3$Ti$_2$O$_7$. Second, we present the detailed studies of Ca$_3$Mn$_2$O$_7$, a prototypic magnetic HIF. Intriguing interrelation between the domain structures and polarization switching is unveiled in Ca$_3$Mn$_2$O$_7$. Finally, we select Fe$_2$Mo$_3$O$_8$ from the list of known polar magnets, and our investigation of Fe$_2$Mo$_3$O$_8$ reveals hidden ferrimagnetism and a giant magnetoelectric effect with a record high magnetoelectric coefficient. Our results shed lights into realizing room-temperature multiferroics with direct coupling between polarization and magnetization.
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# Table of Contents

Abstract ......................................................................................................................... ii

Acknowledgments ........................................................................................................ iii

List of Tables .................................................................................................................. vi

List of Figures ................................................................................................................ vii

1. Introduction ................................................................................................................. 1
   1.1. Ferroelectricity and multiferroicit ........................................................................ 1
   1.2. Proper and improper ferroelectricity ................................................................... 5
   1.3. Hybrid improper ferroelectricity .......................................................................... 7
   1.4. Polar magnets ....................................................................................................... 12
   1.5. Thesis organization .............................................................................................. 13

2. Crystal growth and domain topology in hybrid improper ferroelectric
   (Ca,Sr)$_3$Ti$_2$O$_7$ ......................................................................................................... 15
   2.1. Crystal growth ...................................................................................................... 15
       2.1.1. Preparation of polycrystalline samples ...................................................... 15
       2.1.2. Single crystal growth using the floating zone method ............................... 16
   2.2. Experimental demonstrations of switchable polarization in (Ca,Sr)$_3$Ti$_2$O$_7$ .... 20
   2.3. Domain topology and switching kinetics in (Ca,Sr)$_3$Ti$_2$O$_7$ ........................... 23
   2.4. Abundant oxygen octahedral distortions at the phase transition boundary ....... 29

3. Interrelation between domain structures and polarization switching in
   hybrid improper ferroelectric Ca$_3$(Mn,Ti)$_2$O$_7$ ......................................................... 33
3.1. Sample preparations ......................................................... 33
3.2. Domain observations and poling experiments ......................... 34
3.3. Determination of transition temperatures .................................. 36
3.4. Domain stacking along the c-axis and its interrelation with polarization switching .......................................................... 41
3.5. Complex magnetism in Ca$_3$Mn$_2$O$_7$ ........................................ 44

4. Polar magnets ........................................................................... 46
  4.1. Giant magnetoelectric effect in Fe$_2$Mo$_3$O$_8$ ......................... 46
     4.1.1. Sample growth .......................................................... 47
     4.1.2. Magnetic and dielectric measurements ............................ 48
     4.1.3. Magnetic field induced changes of polarization ................. 50
  4.2. (Lu,Sc)FeO$_3$ .................................................................... 55
     4.2.1. Crystal growth .......................................................... 55
     4.2.2. Ferroelectric domain observations ................................. 57

5. Conclusion ................................................................................. 60
List of Tables

1.1. Definition of ferroic orders. .............................................. 3
List of Figures

1.1. **First ferroelectric hysteresis loop of Rochelle salt.** Hysteresis loops of Rochelle salt at 0 °C, taken from Ref. [1]. ........................................... 2

1.2. **The number of oxide ferroelectrics discovered by year.** The plot is taken from Ref. [2]. ................................................................. 3

1.3. **Phase control in multiferroics, which is taken from Ref. [3].** The electric polarization $P$, magnetization $M$, and strain $\epsilon$ are controlled by their conjugate fields: electric field $E$, magnetic field $H$, and stress $\sigma$, respectively. In multiferroics, the cross coupling may be present like $P(M)$ can be controlled by $H(E)$. The plot is taken from Ref. [3]. ................................. 4

1.4. **Polarization flipping at 3 K by linearly varying magnetic field from 0 to 2 T in TbMn$_2$O$_5$.** The plot is taken from Ref. [4]. ................................. 5

1.5. **Structure of BaTiO$_3$ in the paraelectric and ferroelectric state.** ......................................................... 6

1.6. **The rotation pattern $a^-a^-c^+$ in ABO$_3$ perovskites with a non-polar space group $Pnma$.** (a)$a^0a^0c^+$ (b) $a^-a^-e^0$ (c) anti-polar A-site movement. The plot is taken from Ref. [5]. .................................. 7

1.7. **Two routes to induce net polarization from the ABO$_3$ perovskite building block:** (left) A-site ordered double perovskites and (right) Ruddlesden–Popper phases. The plot is taken from Ref. [5]. .............. 8

1.8. **A net polarization from noncancellation of A-site cation displacements in (Sr/Ba)$_2$Sn$_2$O$_6$ from the first-principal calculations.** (a) The sum of polarizations, $P = \sum P_{layer} = 0$ in $Pnma$ SrSnO$_3$, by symmetry; (b) Cancellation of $P_{layer}$ is not exact in (Sr/Ba)$_2$Sn$_2$O$_6$ superlattice. The plot is taken from Ref. [6]. ................................. 9
1.9. Lattice structure of Ruddlesden–Popper phase \( n = \infty \) \( \text{CaMnO}_3 \) and \( n = 2 \) \( \text{Ca}_3\text{Mn}_2\text{O}_7 \). .......................................................... 10

1.10. A net polarization from noncancellation of A-site cation displacements in \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) from the first-principal calculations. The plot is taken from Ref. [5]. .......................................................... 11

1.11. Schematic drawing of ferroelectrically induced ferromagnetism through the DM interaction. The plot is taken from Ref. [5]. ................................. 11

1.12. Numbers of published papers about multiferroics by year. ....... 12

1.13. Interrelationships of noncentrosymmetric crystal classes in both Hermann-Mauguin and Schoenflies symbols. The plot is taken from Ref. [7]. ................................. 13

2.1. The schematic drawing of the optical floating zone machine. ....... 17

2.2. The accumulation of solids around the feed rod ................. 18

2.3. Various conditions of melton zone (a) stable condition; (b) narrow neck due to overheating; (c) too much feeding; (d) not enough heating. The plot is taken from Ref. [8]. .......................................................... 19

2.4. An as-grown \( \text{Ca}_{2.4}\text{Sr}_{0.6}\text{Ti}_2\text{O}_7 \) crystal and the cleaved surface ........ 21

2.5. Circular differential interference contrast (cDIC) images of the cleaved (001) surface of a \( \text{Ca}_{2.46}\text{Sr}_{0.54}\text{Ti}_2\text{O}_7 \) single crystal. The plot is taken from Ref. [9]. .......................................................... 22

2.6. Transmission mode linear polarized optical microscopic images of the cleaved (001) surface of a \( \text{Ca}_{2.6}\text{Sr}_{0.4}\text{Ti}_2\text{O}_7 \) single crystal. (a) and (b) have different analyzer angle. .............................................. 22

2.7. Net electric polarization \( \sqrt{2}P \) vs. electric field \( E \) hysteresis loops of \( \text{Ca}_{3-x}\text{Sr}_x\text{Ti}_2\text{O}_7 \) \( (x = 0, 0.54 \text{ and } 0.85) \) single crystals. The plot is taken from Ref. [9]. .......................................................... 23

2.8. (a) PFM image and (b) C-AFM image of a \( \text{Ca}_{2.46}\text{Sr}_{0.54}\text{Ti}_2\text{O}_7 \) crystal. The plot is taken from Ref. [9]. .......................................................... 24
2.9. **The notations of the eight states in $A_3B_2O_7$.** (1+, 1–, 2+, 2–, 3+, 3–, 4+, 4–) are based on the blue octahedron in the blue circle. Notation of 1,2,3,4 represents the quadrants, which the displacements of apical oxygen ions point to. + or – indicates the rotation of octahedra along the $c$-axis, with + being clockwise and – being counterclockwise.

2.10. **Antiphase boundary (APB) in a CSTO crystal.** (a) The local distortions near an [110]$_T$–oriented APB (green line) between the 1+ and 3– states, which are identical in polarization direction but differ in structure with respect to the rotation (black curved arrows) and tilting (white arrows) by 180°. (b) A $ab$-plane DF-TEM image taken using superlattice $g_1^+ = 3/2(1,1,0)_T$ spot. (c) A DF-TEM image taken using superlattice $g_1^- = 3/2(-1,-1,0)_T$ spot. A reversed contrast in (b),(c) demonstrates the characteristic of 180°–type FE domains. (d) A DF-TEM image taken using the $g_1^-$ spot at a large tilting angle to tune contrast by enhancing excitation error. A clear boundary interference fringe can then be observed between domains ii and iii, implying an inclined nature and a strong strain gradient expected in rotation-driven FE$_r$ DWs. (e) The schematic domain configuration obtained from b–d demonstrates a typical $Z_3$ ern within the FA domain, composed of three 180°–type FE domains and three DWs: FE$_r$ (red-dotted), FE$_t$ (red-solid) DWs and APB (green-solid). White arrows denote the polarization directions in FE domains. Scale bar, 500 nm. The plot is taken from Ref. [10].
2.11. The $Z_3$-vortex patterns in Ca$_{2.55}$Sr$_{0.45}$Ti$_2$O$_7$. (a) A 2.2 $\times$ 3.9 $\mu$m$^2$ mosaic of DF-TEM images were taken using the superlattice $g_1^+$ spot (red-circled) of domain FA(i) in a CSTO crystal along $[001]_T$. The colored arrows represent polarization directions within the domain. (b) The electron diffraction pattern was taken by covering regions FA(i) and FA(ii) showing a 90$^\circ$-crystallographic-twin relation. The red/blue circled spots were contributed from the orthorhombic distortions of the FA(i) region, and the green/yellow ones were from the FA(ii) area. The color-circled spot located in each DF image is the selected superlattice Bragg spot to light up the corresponding domains at a given orientation. (c) A DF-TEM image of the white rectangular box region was taken using the blue circled superlattice $g_1^-$ spot. (d) A proposed domain configuration of c. The plot is taken from Ref. [10].

2.12. The domain switching kinetics under $e^-$ beam-induced poling. (a–e) Image sequences showing a $Z_3$ vortex-antivortex (V-AV) pair evolution during in-situ poling within a single ferroelastic domain. (a,b) The initial state. (c,d) The states during the charge dissipation process after defocusing electron beam. (e) The final state. (f) Schematic showing the 180$^\circ$ ferroelectric polarization switching via splitting or coalescence of an APB into two ferroelectric walls: APB (green line)$\leftarrow\rightarrow$FE$_t$ (red-solid)+FE$_r$ (red-dotted) DWs. (g,h) Image sequences and schematics showing 90 ferroelectric domain switching near an APB (green line). (g) The initial state. (h) The immediate image after electron beam focused at the sample edge away from the FA boundary (solid blue line). (i) Schematic showing a 90$^\circ$ ferroelectric polarization switching within an FA domain via splitting or coalescence of an APB into two ferroelastic walls: APB $\leftarrow\rightarrow$ FA$_{tr}$ (blue-solid) + FA$_t$ (blue-dotted) DWs. The plot is taken from Ref. [10].
2.13. (a) Schematic diagram of possible space groups and the corresponding Glazer notations for bi-layered perovskite $A_3B_2O_7$. Lines link the group–subgroup relations. The lattice directions are given with respect to the T state ($I4/mmm$).

(b–f) In-plane projected views of various BO$_6$ octahedral tilts/rotations. The dashed lines outline the primitive unit cells, and the red and cyan spheres represent the O and B-site ions, respectively. Black and gray arrows indicate directions of apical and basal plane oxygen displacements, respectively. (b) Un-distorted BO$_6$ octahedron in the T state. (c) A clockwise (+) rotated BO$_6$ in the O* and O'' states. The rotation can also be counterclockwise (–). In two adjacent layers within one bi-layer, an out-of-phase rotation (+ – or – +) along the c axis occurs in the O* state while in-phase (+ + or – –) rotation in the O'' state. (d) Eight possible 1±, 2±, 3± and 4± apical oxygen displacements in the O state. The azimuthal angle, $\varphi$, of an apical oxygen distortion is denoted. (e) Given tilting vectors in the O' state. (f) Four possible apical oxygen displacements (red-circled labels) along the $<100>_T$ directions in the T’ state. The plot is taken from Ref. [11].
2.14. (a) Structural phase diagram of Ca$_{3-x}$Sr$_x$Ti$_2$O$_7$ with the angles of octahedral rotation ($\theta_R$, empty squares) and tilt ($\theta_T$, cyan spheres) as a function of Sr doping, $x$. The black and cyan curves are guides for the eyes. Two structural phase transition temperatures ($T_1 = 473$ K and $T_2 = 710$ K) at $x=0.9$, marked with red spheres, are obtained from in situ TEM heating experiments. (b) Dielectric constant versus Sr content ($x$), measured at 350 K and 44 kHz. Red triangles and blue circles are from measurements on polycrystalline and single crystalline (electric field applied along the in-plane direction) specimens, respectively. The dielectric constant peaks at the O–T’ structural boundary of $x=0.9$. (c) The thermal sequence of selected area electron diffraction patterns on $x=0.9$, showing two phase transitions upon in situ heating: O (300 K)$\rightarrow$T’ (473 K)$\rightarrow$T (713 K) states. $S_1 = \frac{1}{2}(130)_T$-type superlattice spots (cyan triangles) are allowed in the O state. When the temperature reaches 473 K, additional $S_2 = \frac{1}{2}(200)_T$-type and $S_3 = \frac{1}{2}(-130)_T$-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. The plot is taken from Ref. [11]. 3.1. Large-scale polarized optical microscopy images of (a) Ca$_3$Mn$_2$O$_7$ (b) Ca$_3$Ti$_2$O$_7$ crystals. 3.2. (a) Polarized optical microscopic images of four Ca$_{3-x}$Mn$_x$O$_7$ ($x=0$, 1, 1.5 and 2) single crystals. (b) Electric polarization $P$ vs. electric field $E$ curves of the four crystals. The $P(E)$ curves are straight lines for $x=0$ and 1 even at liquid Nitrogen temperature. Good $P(E)$ hysteresis loops are evident for $x=1.5$ and 2 crystals at room temperature. 3.3. Room temperature $P(E)$ measurement of (a) $x=0$ (b) $x=1$ crystals showing huge leakage currents.
3.4. **Resistivity ρ vs. temperature T curves and in-situ and ex-situ twin domain observations after heat treatments for x=0.1 and 2.** (a) The ρ(T) curve of Ca₃Ti₂O₇ crystal shows transitions at 1063 K upon warming (red) and at 1039 K upon cooling (black). (b) Domain patterns of as-grown Ca₃Ti₂O₇ at 300 K, (c) after a 1023 K heat treatment, and (d) after a 1033 K heat treatment. (e) The ρ(T) curve of x=0.1 crystal shows transitions at 365 K upon warming (red) and at 328 K upon cooling (black). (f), (g) and (h) In-situ domain patterns of a x=0.1 crystal at 300 K, heating to 380 K, and cooled down to 364 K after heating to 380 K, respectively.

3.5. **Resistivity ρ vs. temperature T curves and the change of the domain patterns for x=1.5 and 1 after various heat treatments.** (a) The ρ(T) curve of x=1.5 crystal shows transitions at 888 K upon warming (red) and at 871 K upon cooling (black). Domain patterns of (b) an as-grown x=1.5 crystal at 300 K, (c) after an 813 K heat treatment, and (d) after an 823 K heat treatment. (e) The ρ(T) curve of a x=1 crystal shows transitions at 717 K upon warming and at 692 K upon cooling. (f) Domain patterns of an as-grown x=1 crystal at 300 K, (g) after a 673 K heat treatment, and (h) after a 683 K heat treatment.
3.6. **Phase diagram of Ca$_3$Mn$_{2-x}$Ti$_x$O$_7$.** Red squares and black spheres mark the FE $T_c$’s determined from $\rho(T)$ measurements. Blue squares mark the Néel temperatures of several poly samples determined from $\chi(T)$ measurements. The $ab$-plane crystallographic views of intermediate $Acaa$ and the ground $A2_1am$ phases are shown. Mn/Ti-site atoms are shown in blue (green) corresponding to the upper (lower) perovskite bilayers within one unit cell. Oxygen ions are represented in red. Ca-site ions are omitted for simplification. The octahedral rotations are noted by the sign $+$ (clockwise) and $-$ (counterclockwise). Red arrows indicate the apical oxygen displacements induced by octahedral tilting. For Mn-rich side ($x < 1.3$), the phase transition goes through $Acaa$ to the ground polar $A2_1am$ phases from the parent $I4/mmmm$ phase. The blue dashed line indicates the approximate $Acaa$ to $I4/mmmm$ transition boundary. Glazer notations are labeled.

3.7. **Orthorhombicity of Ca$_3$Mn$_{2-x}$Ti$_x$O$_7$ as a function of $x$.** Lattice parameters were calculated from the refinement of X-ray diffraction data of polycrystalline Ca$_3$Mn$_{2-x}$Ti$_x$O$_7$ specimens.

3.8. **Side-views of $Acaa$ and $A2_1am$ phases, showing out-of-phase ($+ -$) and in-phase ($+ +$ or $- -$) rotation modes within each bilayer.** Octahedral rotations in $Acaa$ are represented by $(+-+)$). Rotations in $A2_1am$ can be sorted into two groups; the ferro-stacking type I $(+++)$ and $(----)$ and antiferro-stacking type II $(+--)$ and $(--+)$. Type I and type II lead to $a$-oriented and $b$-oriented domains, respectively.

3.9. **(a) DF-TEM images taken under two-beam diffraction conditions along [010]$_{orth}$ plus [100]$_{orth}$ zone in a Ca$_3$Mn$_2$O$_7$ crystal.** Blue arrows indicate the a polar directions for the image where (100)$_{orth}$ spot was taken. The left inset shows an enhanced $b$-oriented domain contrast using (010)$_{orth}$ spot in the outlined area. A high-density $90^\circ$–type FE domains along the c-axis is found in Ca$_3$Mn$_2$O$_7$. **(b) DF-TEM image of Ca$_3$Ti$_2$O$_7$.** It shows $180^\circ$–type FE domains along the c-axis. The left inset shows a magnified region with the opposite contrast due to Friedel’s pair breaking condition.
3.10. **Anisotropic magnetic properties of a Ca$_3$Mn$_2$O$_7$ crystal.** (a) Magnetization ($M$) vs. magnetic field ($H$) curves of Ca$_3$Mn$_2$O$_7$ crystals parallel (black) and perpendicular (red) to the c-axis at 5 K. (b) Enlarged display of the blue–circled area in (a). (c) $\chi(T)$ curves of Ca$_3$Mn$_2$O$_7$ crystals parallel and perpendicular to the c-axis.

4.1. **Lattice structure of M$_2$Mo$_3$O$_8$.** The plot is taken from Ref. [12].

4.2. **One large as-grown crystal of Fe$_2$Mo$_3$O$_8**. The plot is taken from Ref. [12].

4.3. **Temperature dependence of magnetic susceptibility $\chi(T)$ of Fe$_2$Mo$_3$O$_8**. The plot is taken from Ref. [12].

4.4. **Specific heat anomaly at the Néel temperature.** Red line represents the double Debye model fit. The plot is taken from Ref. [12].

4.5. **Magnetically-induced electric polarization, and the metamagnetic transition** (a) Temperature dependence of the c-axis dielectric constant $\epsilon(T)$, $f = 44$ kHz. (b) Variation of the c-axis electric polarization $\Delta P$ with temperature. (c,d) Magnetic field dependence of magnetization $M(H)$ and polarization $\Delta P(H)$ at various temperatures. In (d), solid (open) circles depict the data obtained upon sweeping the magnetic field up (down). The plot is taken from Ref. [12].

4.6. **Schematic view of the AFM and FRM orders.** Pink arrows represent the ferrimagnetic moments of the individual Fe-O layers. The plot is taken from Ref. [12].

4.7. **Magnetoelectric effect, and the associated ionic shifts.** (a,b) Magnetic field dependence of magnetization $M(H)$ and polarization $P(H)$ at $T = 55$ K. Numbers and arrows indicate the measurement sequence. The insert in (b) shows the magnetic orders and the ferrimagnetic moments of the Fe-O layers for the phases involved. (c) The calculated ionic shifts for the paramagnetic to AFM transition. The thick arrow represents the corresponding change of the electric polarization, $\Delta P$. (d) the same as (c), but for the AFM to FRM transition. The plot is taken from Ref. [12].
4.8. **Reproducible magnetoelectric control of the electric polarization and magnetization with giant ME coefficient.** (a) Periodic modulation of electric polarization (blue) induced by a magnetic field linearly varying between 3.25 T and 3.5 T (black) at 55 K. (b) Periodic modulation of magnetization (green) induced by an electric field (red) linearly varying between 16.6 kV/cm, for $T = 55$ K and $\mu_0 H = 3.345$ T. (c) Phase diagram of Fe$_2$Mo$_3$O$_8$. Black dots determined from $M(H)$, and red diamonds – from $\chi(T)$ curves. (d) Electric field dependence of magnetization for Fe$_2$Mo$_3$O$_8$ (from the panel (b), averaged), and for Ni$_3$TeO$_6$ ($\times 10$). The insert illustrates the experimental setup, with directions of the applied fields shown. In all figures, the magnetization, polarization, and the applied fields are along the $c$-axis. The plot is taken from Ref. [12].

4.9. **Crystalllographic structure of $h$–(Lu,Sc)FeO$_3$ in $P6_3cm$ space group.** Yellow balls indicate Lu or Sc atoms, while grey and blue balls stand for Fe and O atoms respectively. The black arrows show the displacement directions of Lu or Sc atoms with a two–down/one–up case. Trimerized Fe atoms are illustrated with green bonds.

4.10. **X-ray diffraction pattern of $h$-Lu$_{0.6}$Sc$_{0.4}$FeO$_3$ shows a pure hexagonal $P6_3cm$ phase**

4.11. **The ferroelectricity and vortex ferroelectric domains of $h$-Lu$_{0.6}$Sc$_{0.4}$FeO$_3$.** Room-temperature PFM images of cleaved surfaces of crystals after (a) 100 °C/h, (b) 10 °C/h and (c) 1 °C/h cooling in the 1400 °C – 1200 °C temperature range. (d) The density of defects as a function of cooling rates, compared with ErMnO$_3$ and TmMnO$_3$ from Ref. [13]. (e) Room–temperature $P(E)$ loops at 2702 Hz, which prove its robust and switchable ferroelectricity.
Chapter 1
Introduction

1.1 Ferroelectricity and multiferroicity

People have been aware of electric and magnetic phenomena since ancient times. As early as 2750 BC, ancient Egyptians had some understanding of electric phenomena through observing and interacting with Malapterurus electricus (a kind of electric fish). The compass, invented by ancient Chinese, has been used for navigation in the sea since 1000 AD, which has a great influence on the progress of civilization. Systematic studies of electricity and magnetism were begun by Ohm, Ørsted, Coulomb and Ampère. The foundation of classical electromagnetism is the Maxwell’s equations, which illustrate that a changing electric field generates a magnetic field, and vice versa. Ferroelectricity and magnetism are critical for almost all modern technologies. Finding multiferroic materials, in which the two phenomena interact with each other, is essential to develop new advanced technologies. However, the task is not easy due to the fact that the two phenomena tend to be mutually exclusive.

Ferroelectricity is a property of materials that have a spontaneous electric polarization, whose direction can be reversed by an external electric field. Ferromagnetism, the spontaneous alignment of spins in parallel directions, was observed in ancient times. However, its analogue of electric dipoles, i.e., ferroelectricity, was not observed until 1920 by J.Valasek on Rochelle salt [1]. The first ever ferroelectric hysteresis loop is shown in Fig. 1.1. The structure of Rochelle salt is relatively complicated, and its ferroelectric temperature range is very narrow [1]. The most famous ferroelectric material is BaTiO$_3$, which has been investigated by von Hippel and other physicists since 1943. The discovery of ferroelectricity in BaTiO$_3$ ceramics was very important, as it demonstrated that ferroelectricity was not always associated with hydrogen bonding, and it could exist in simple oxide materials [14]. BaTiO$_3$ has a lot of advantages compared with previous compounds. It has a very simple
perovskite structure. Its temperature range of ferroelectricity is large (below 120 °C), and it can be used as single crystals or ceramics of any shape. Since its discovery, there have been continuous researches on the fundamental studies of the phenomenon. As Arthur von Hippel said, “No longer shackled to presently available materials, we are free to dream and find answers to unprecedented challenges.” Fig. 1.2 demonstrates the developments of the oxide ferroelectric materials, showing the number of oxide ferroelectrics discovered each year. Meanwhile, the developments of various devices and applications have boosted modern electric technology. Domain structures and strained films of many typical ferroelectric materials, such as BaTiO₃, BiFeO₃ and so on, are still hot topics in condensed matter physics [15].

Our life has been influenced tremendously by the developments in the applications of ferroelectric materials [16]. Many applications of ferroelectric materials rely on dielectric, piezoelectric, pyroelectric, and photovoltaic effect properties. Ferroelectric memories and ferroelectric field-effect transistors have been used as memory devices, such as ferroelectric nonvolatile random access memories (FeRAMs). FeRAMs can be as fast as volatile dynamic random access memories (DRAMs), as small as flash devices, and more scalable [17–20].

Multiferroics was originally defined as having two or three of the “ferroic” orders, including ferroelectricity, ferromagnetism, and ferroelasticity. Later, ferrotoroidic was included,
Figure 1.2: The number of oxide ferroelectrics discovered by year. The plot is taken from Ref. [2].

but it was not easy to observe ferrotoroidic domains [21]. The correlations between electric and magnetic orders in multiferroics are shown in Fig. 1.3.

Multiferroics are of interest due to the interesting basic physics and their potential for

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<td>materials possess a spontaneous toroidal moment, which is generated by a vortex of magnetic moments. By analogy with the above examples, it is anticipated that this order parameter may be switchable.</td>
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<td>materials possess a net magnetization due to incomplete magnetic moment cancellation, and it can be switched by an applied magnetic field</td>
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Table 1.1: Definition of ferroic orders.
Figure 1.3: **Phase control in multiferroics, which is taken from Ref. [3].** The electric polarization $P$, magnetization $M$, and strain $\epsilon$ are controlled by their conjugate fields: electric field $E$, magnetic field $H$, and stress $\sigma$, respectively. In multiferroics, the cross coupling may be present like $P(M)$ can be controlled by $H(E)$. The plot is taken from Ref. [3].

Technology developments. For example, electrical polarization in ferroelectrics and magnetization in ferromagnets are utilized in data storage, with two opposite directions of the polarization or magnetization representing “1” and “0” data bits. The coupling between electric and magnetic orders could in principle permit data to be written electrically and read magnetically. This is attractive, given that it would exploit the best aspects of ferroelectric random access memory (FeRAM) and magnetic data storage while avoiding the problems associated with reading FeRAM and generating the large local magnetic fields needed to write. One example of the coupling is shown in Fig. 1.4. The reverse of ferroelectric polarization is induced by magnetic field in TbMn$_2$O$_5$ [4]. However, this coupling happens at 3 K, which is not practical for application. Searching for room-temperature multiferroics is challenging but of great importance.

Ferroelectricity requires the breaking of spatial inversion symmetry, ferromagnetism requires the breaking of time inversion symmetry, and multiferroics require the breaking of both spatial and time inversion symmetries. Magnetic ferroelectrics were expected to be
Figure 1.4: Polarization flipping at 3 K by linearly varying magnetic field from 0 to 2 T in TbMn$_2$O$_5$. The plot is taken from Ref. [4].

rare, according to an analysis by Nicola A. Hill (now known as Spaldin) [22]. The conventional mechanism of cation off-centering in ferroelectrics requires empty $d$ orbitals to form covalent bonding (electronic pairing) between the cation and neighboring oxygen ions. Meanwhile, magnetism requires partially filled $d$ orbitals. The two requirements contradict each other, and cannot be satisfied in one cation. Therefore, the atoms forming the electric dipole moments should be different from those that possess the magnetic moments, so that ferroelectricity and magnetism can coexist in a single phase. The ME couplings in this kind of multiferroics are small. In order to realize larger ME couplings, there have to be alternative mechanisms of ferroelectricity, which is the main point of this thesis.

1.2 Proper and improper ferroelectricity

In order to obtain a ferroelectric state, one needs to break the spatial inversion symmetry. Depending on the mechanism of symmetry breaking, there are two types of ferroelectricity, proper and improper ferroelectricity.

In the proper ferroelectrics, the main driving force of the transition is structural instability towards the polar state, associated with the electronic pairing. As in the famous BaTiO$_3$, the high-temperature cubic phase is paraelectric. Below the ferroelectric transition
temperature, the structure is tetragonal, with a polar space group $P4_{2}2_{1}2$. Each Ti$^{4+}$ cation is surrounded by six oxygen ions, and they form a TiO$_6$ octahedron. Ti$^{4+}$ has an empty 3d orbit. The virtual hopping of electrons from the filled p shell of O$^{2-}$ to the empty d shell of a Ti$^{4+}$ cation forms covalent bonding (electronic pairing). Below the ferroelectric transition temperature $T_c$, the polarization is induced when Ti$^{4+}$ cations move away from the center of TiO$_6$ octahedra, as shown in Fig. 1.5. There is an elastic-restoring force when Ti$^{4+}$ cations move away from equilibrium slightly, but the force becomes weaker when the temperature is reduced. At Curie temperature, the force is zero, which leads to an asymmetrical shift in the equilibrium ion positions and hence to a permanent dipole moment.

Improper ferroelectricity means that the phase transition is not caused by a ferroelectric order parameter, but by other order parameters, such as magnetic ordering, charge ordering, or structural transitions owing to zone-boundary instability. Polarization is only a part of a more complex lattice distortion or it appears as an accidental by-product of some other ordering. The examples are like geometric ferroelectrics caused by structure transition ($K_2SeO_4$, $Cs_2CdI_4$, hexagonal $RMnO_3$), electronic ferroelectrics caused by charge ordering ($LuFe_2O_4$), and magnetic ferroelectrics caused by magnetic ordering (Orthorhombic $RMnO_3$, $RMn_2O_5$, $CoCr_2O_4$) [23].

Why are improper ferroelectrics so important? They provide a new way to realize
Figure 1.6: The rotation pattern $a^-a^-c^+$ in ABO$_3$ perovskites with a non-polar space group $Pnma$. (a) $a^0a^0c^+$ (b) $a^-a^-c^0$ (c) anti-polar A-site movement. The plot is taken from Ref. [5].

multiferroics. Most proper ferroelectrics have an empty d shell, such as Ti$^{4+}$ in BaTiO$_3$, which has no magnetic ordering. Some of them do have a partially filled d orbit, such as Mn$^{3+}$ and Fe$^{3+}$ in BiMnO$_3$ and BiFeO$_3$. However, it is the Bi$^{3+}$ cation which moves away from the centrosymmetric position. The coupling between electric and magnetic orderings is very weak since they come from different cations. For example, BiMnO$_3$ is ferroelectric below 800 K and ferromagnetic below 110 K [24]. The two orders coexist below 110 K, and both the magnetization and polarization are quite large. However, the coupling is very weak. The dielectric constant $\epsilon$ only changes about 0.6 % by a 9 Tesla field around the $T_{FM}$.

1.3 Hybrid improper ferroelectricity

Hybrid improper ferroelectricity (HIF) was first proposed by Nicole A. Benedek and Craig J. Fennie in 2011 [25]. Its definition is that the polarization is a by-product of more than one kind of symmetry inequivalent octahedral rotations modes. The concept was proposed to provide a new way to find materials with a large polarization strongly coupled to magnetization, which is the key to producing room temperature multiferroic devices. There are several known multiferroic materials, but none of them possess a stable, single-phase in which the magnetization can be deterministically switched 180° by electric field.

The first example of HIF was discovered by Bousquet [26] on an artificial superlattice
of \((\text{PbTiO}_3)_n/(\text{SrTiO}_3)_m\). Inspired by it, Benedek focused on the most common perovskite structure \(\text{ABO}_3\) and tried to find a general way through which electric and magnetic orders could be induced by the same lattice instability. In the simple perovskite structure \(\text{ABO}_3\), A-site cations are at the corner, while B-site cations are in the center and surrounded by six oxygen ions. Depending on the size of A, B, and O ions, the high symmetry lattice structure at high temperature may not be stable at low temperature, and BO\(_6\) octahedra can have various instability modes. Here we use the Glazer notation \([27]\) to represent the lattice modes. The rotation axes used here are based on the high-temperature tetragonal phase. We can indicate the rotation modes by the superscripts \(+, -, \text{or } 0\), to show whether successive octahedra along an axis have the same tilt, opposite tilt, or no tilt about that axis. The lattice without any rotation or tilting can be represented as \(a^0a^0c^0\). The most common rotation pattern in the \(\text{ABO}_3\) perovskites is \(a^-a^-c^+\), with a non-polar space group \(\text{Pnma}\). As shown in Fig. 1.6, the pattern consists of three parts: (i) in phase BO\(_6\) octahedral rotation around \([001]\) axis, i.e., \(a^0a^0c^+\); (ii) out of phase octahedral tilting around \([110]\) axis, i.e., \(a^-a^-c^0\), with anti-polar movements of A-site cations inside each layer (iii) anti-polar A-site displacements between adjacent layers induced by the combination of \(a^0a^0c^+\) and \(a^-a^-c^0\) modes.

Inside each A-site layer, the \(a^-a^-c^+\) rotation mode induces displacements along the \([110]\) direction. However, the adjacent layers have the opposite displacements with the
Figure 1.8: **A net polarization from noncancellation of A-site cation displacements in (Sr/Ba)$_2$Sn$_2$O$_6$ from the first-principal calculations.** (a) The sum of polarizations, \( P = \sum P_{\text{layer}} = 0 \) in \( Pnma \) SrSnO$_3$, by symmetry; (b) Cancellation of \( P_{\text{layer}} \) is not exact in (Sr/Ba)$_2$Sn$_2$O$_6$ superlattice. The plot is taken from Ref. [6].

exact same amount. Therefore, there is no net macroscopic polarization due to complete cancellation. Finding ways to induce noncancellation, or “ferri-electric”, an analogue to ferrimagnetism, is the essence of hybrid improper ferroelectricity in materials built from ABO$_3$ perovskites. Fig. 1.7 shows two structural designs that allow the existence of hybrid improper ferroelectricity: A-site ordered double perovskites and Ruddlesden–Popper phases.

The goal of a double perovskite or superlattice is to create A-site ordering from different A atoms, as shown in Fig. 1.8. In SrSnO$_3$, the polarization inside each SrO layer has the same magnitude but opposite directions between adjacent layers. Therefore, the net macroscopic polarization is zero due to complete cancellation. We then introduce alternating layers of BaO and SrO, as shown in Fig. 1.8 (b). Due to the different sizes of Ba$^{2+}$ and Sr$^{2+}$ cations, the polarizations inside each BaO and SrO layers have different magnitudes and opposite directions. The small noncancellation should induce a net macroscopic polarization
and a polar space group ($Pmc_21$).

Another approach is the Ruddlesden–Popper phase $A_{n+1}B_nO_{2n+1}$. The structure of $A_{n+1}B_nO_{2n+1}$ consists of alternating $n$ layers of perovskite layers and one rock salt layer. When $n = \infty$, it is the simple $ABO_3$ perovskite. When $n = 2$, it is $A_3B_2O_7$. The structures of $CaMnO_3$ and $Ca_3Mn_2O_7$ are shown in Fig. 1.9. In $Ca_3Mn_2O_7$, the perovskite bilayers are sandwiched by rock salt layers.

From first-principal calculations, the polarizations in adjacent CaO layers in $CaMnO_3$ are opposite to each other and completely cancel out, like SrSnO$_3$. In $Ca_3Mn_2O_7$, one unit cell contains three CaO layers, with the displacements of two rock salt CaO layers in one direction and that of the perovskite CaO layer in the opposite direction. As a result, noncancellation of polarization would occur inside the unit cell.

Compared with non-magnetic $Ca_3Ti_2O_7$, $Ca_3Mn_2O_7$ is more interesting, since it can be a potential multiferroic with a large magnetoelectric effect. According to first-principle calculations from Benedek and Fennie, an enhanced magnetoelectric effect could be induced.
Figure 1.10: A net polarization from noncancellation of A-site cation displacements in Ca$_3$Mn$_2$O$_7$ from the first-principal calculations. The plot is taken from Ref. [5].

Figure 1.11: Schematic drawing of ferroelectrically induced ferromagnetism through the DM interaction. The plot is taken from Ref. [5].
by BO\textsubscript{6} octahedral rotation controlled by electric field \cite{28}. The $a^-a^-c^0$ tilting mode induces weak ferromagnetism \cite{29}, which is a small canting of antiferromagnetic spins through the Dzyaloshinskii–Moriya (DM) interaction \cite{30, 31} or crystalline anisotropy. If switchable polarizations in Ca\textsubscript{3}Mn\textsubscript{2}O\textsubscript{7} were realized in bulk crystals, it could be a multiferroic with a strong ME coupling. In HIP Ca\textsubscript{3}Mn\textsubscript{2}O\textsubscript{7} and Ca\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7}, switching either $a^0a^0c^+ \text{ or } a^-a^-c^0$ rotation mode can switch the polarization. This is quite interesting in the case of Ca\textsubscript{3}Mn\textsubscript{2}O\textsubscript{7} because of the weak ferromagnetism \cite{29}. Ferroelectrically induced weak ferromagnetism \cite{32} is the only known mechanism by which an electric field can be used to switch the direction of the magnetization $180^\circ$ in a single-phase material (see Fig. 1.11). Since $a^-a^-c^0$ induces weak ferromagnetism, if $a^-a^-c^0$ switches when the polarization is reversed, the magnetization will also switch.

1.4 Polar magnets

Since Spaldin’s explanation for magnetic ferroelectrics, people have paid more attention to multiferroics, and more papers about multiferroics have been published every year, see Fig. 1.12. In order to find more suitable candidates for multiferroics, we need to find a better way to narrow down the range of the candidates. Fig. 1.13 shows the interrelationship of

![Figure 1.12: Numbers of published papers about multiferroics by year.](image.png)
Non-Centrosymmetric Crystal Classes

Figure 1.13: Interrelationships of noncentrosymmetric crystal classes in both Hermann-Mauguin and Schoenflies symbols. The plot is taken from Ref. [7].

non-centrosymmetric crystal classes in both Hermann-Mauguin and Schoenflies symbols. In Ref. [7], the author classifies a lot of the known non-centrosymmetric oxides based on their crystal classes. Our strategy is to select the compounds that belong to polar classes and have at least 25% magnetic cations. We choose several candidates. Fe$_2$Mo$_3$O$_8$ is the first one to be studied. Its giant magnetoelectric effect is discussed in Chapter 4.

1.5 Thesis organization

Chapter 2 will discuss non-magnetic HIF, Sr-doped Ca$_3$Ti$_2$O$_7$. The first experimental demonstration of switchable polarization in this material was reported by our group. Also, we found the abundant domain features in this compound, including charged domain walls, $Z_4 \times Z_2$ domain topology with $Z_3$ vortices and anti-phase boundaries.
Chapter 3 will focus on prototypical HIF magnet Ca$_3$Mn$_2$O$_7$, which has been proposed to have large magnetoelectric coupling. However, after our systematic study, we have concluded that although there are polar domains in Ca$_3$Mn$_2$O$_7$, there is no switchable polarization. The non-switchable polarization is due to a unique domain structure along the $c$-axis. This interrelation between the domain structure and polarization switching is unprecedented.

Chapter 4 will discuss other polar magnets, including M$_2$Mo$_3$O$_8$ (M = Fe, Mn, Co, Ni) and hexagonal Sc-doped LuFeO$_3$. 
Chapter 2

Crystal growth and domain topology in hybrid improper ferroelectric \((\text{Ca, Sr})_3\text{Ti}_2\text{O}_7\)

2.1 Crystal growth

The Research of new functional material can be sometimes driven by theoretical designs. To realize the designed properties, high-quality samples are required. Since the proposal of HIF in 2011, there have been various attempts to realize the switchable polarization and the coupling between electric and magnetic orders. In 2015, our group reported the first experimental demonstration of room-temperature switchable polarization in bulk crystals of \(\text{Ca}_3\text{Ti}_2\text{O}_7\), as well as Sr-doped \(\text{Ca}_3\text{Ti}_2\text{O}_7\) \([9]\). We also obtained high-quality \(\text{Ca}_3\text{Mn}_2\text{O}_7\) crystals. The details of \(\text{Ca}_3\text{Mn}_2\text{O}_7\) will be discussed in Chapter 3.

2.1.1 Preparation of polycrystalline samples

Polycrystalline \(\text{Ca}_3\text{Ti}_2\text{O}_7\) and \(\text{Ca}_{3-x}\text{Sr}_x\text{Ti}_2\text{O}_7\) \((x < 1)\) are synthesized using the conventional solid-state method. The stoichiometric mixtures of \(\text{CaCO}_3\), \(\text{SrCO}_3\), and \(\text{TiO}_2\) powders are ground, pelletized, and sintered. The standard sintering temperatures are 1200 °C and 1400 °C for the first and second sintering, respectively. The final sintering temperatures range from 1550 °C to 1640 °C, depending on the Sr concentration. Higher Sr concentration samples require higher sintering temperature. Notice that in the case of very high temperature sintering, the pellets need to be isolated from alumina crucibles. Otherwise, they will react with each other, causing a real mess inside the furnace.
2.1.2 Single crystal growth using the floating zone method

Ceramic rod preparations

Single crystals of Ca$_3$Ti$_2$O$_7$ and Ca$_{3-x}$Sr$_x$Ti$_2$O$_7$ ($x < 1$) are grown using the optical floating zone method. For higher Sr doping samples, there will be (Ca,Sr)$_4$Ti$_3$O$_{10}$ impurity phase in the crystals, possibly due to the evaporation of Ca. To solve the problem, a little bit Ti deficiency is taken into account for the initial feed rod preparations. After the third sintering, the polycrystalline powder is pressed into a long feed rod, and sintered again at the same final sintering temperature.

There are two ways to make the feed rods. The conventional way is to use a special pressure die. The feed rod made by this pressure die has a fixed length of 9 cm. The powder is loaded into the pressure die and pressed by a hydraulic press for 10 minutes. Sometimes, a drop of diluted (2 % wt) polyvinyl alcohol (PVA) solution is added to obtain a stronger feed rod. The feed rod can still break during the process, and sometimes it takes quite a long time to get a strong feed rod. Another method is using rubber balloon and hydrostatic pressing. The powder is loaded and compacted uniformly into a cylindrical rubber balloon, about 6 mm in diameter and 100 mm long. After evacuating air, the sealed balloon is placed into a hydrostatic presser filled with water. The hydrostatic presser is then pressurized with a pressure of 500 bars for 10 minutes. After the pressing, the feed rod is taken out of the balloon by cutting the balloon using a pair of fine scissors. The feed rod made by this method is very strong. A hole can be drilled through it using an electric drill without breaking it. A platinum wire is used to make a tie through the hole. Then the feed rod is hung on a platinum hook inside a vertical furnace for sintering. Making a strong and dense feed rod is very important for a stable and successful floating zone growth.

Set up of the floating zone growth method

A schematic drawing of the optical floating zone machine is shown in Fig. 2.1. The light from the halogen lamp is reflected from ellipsoidal mirrors, and then focused in the zone area. The feed rod hangs loosely on a hook, and the seed rod is tightened rigidly to a ceramic holder. The growth is inside a quartz tube so that gas flow and pressure can be
applied. The rotation directions of upper feed rod and lower seed rod are usually opposite to each other.

**Optimization of growth conditions**

The stability of the growth process and the quality of the obtained crystals mainly depend on the stability of the molten zone. To maintain a stable molten zone, one should make sure the following:

1. Stabilize the power of halogen lamp (controlled by the electronic panel), and change the power as slowly as possible if need to.

2. Maintain a stable gas pressure when using high-pressure gas, or a fixed flow rate when using gas flow.
(3) Translations of the feed rod shaft and mirror stage should be stable (controlled by the electronic panel), and the speed should be in a reasonable range.

(4) The feed rod should have a uniform shape with homogeneous density. Variation of density/shape of the feed rod may change the volume of the molten zone, even cause its collapse. Porous feed rod may suck up liquid from the molten zone, resulting in an “umbrella” through the accumulation of solid around the feed rod, see Fig. 2.2.

In most floating zone furnaces, the lower seed shaft does not move, and the mirror stage moves up during the growth. The relative pulling rate of lower shaft compared with the lamp is usually referred as the growth rate. The distance between two rods is controlled by adjusting the moving rate of the upper shaft. In an ideal case, the upper shaft does not move during a stable growth process. However, if the molten zone becomes smaller, or the lower seed part becomes larger due to overheating, then it is necessary to move the upper shaft downwards. Otherwise, the molten zone will collapse. Rotation speed will affect the conviction of the molten zone and should be kept at a constant value during the growth.

To maintain a stable molten zone is not easy. The supercooling rate of the crystal front, i.e., growth rate, should agree with the translation rate of the mirror stage. Also, the translation rate of the feed rod should be appropriate to keep a constant volume of the
Figure 2.3: **Various conditions of melton zone** (a) stable condition; (b) narrow neck due to overheating; (c) too much feeding; (d) not enough heating. The plot is taken from Ref. [8].
melton zone. Fig. 2.3 shows a few situations often encountered during the growth. Fig. 2.3(a) shows the stable molten zone; Fig. 2.3(b) shows the narrow neck in the molten zone and liquids below the lamp area, caused by overheating or too slow growth rate; Fig. 2.3(c) shows solids in the lamp area, caused by too much feeding; Fig. 2.3(d) shows wobbling molten zone, meaning the upper and lower solids collide with each other, caused by not enough heating. These are just general rules. For each individual material, the situation may be different, and the optimization of growth parameters needs patience and a great deal of time. Notice that all the changes of parameters from the electric panel will not affect the melton zone immediately. There will always be delays between the changes of parameters and the changes of melton zone conditions. Therefore, all the changes made from the electric panel need to be super slow.

For Ca$_3$Ti$_2$O$_7$, although feed rods are pressed for a long time at very high pressure and sintered at as high temperature as possible, there are still some problems during the growth. The accumulation of solids around the lower end of feed rod still happens, as shown in Fig. 2.2. Two kinds of treatments are used to avoid the situation. First, a slow rotation speed of the feed rod can help melt the solids, but cannot completely remove the accumulation. Second, rapid growth as fast as 20 mm/h is used to obtain a much denser rod, then it is used as a new feed rod. We call this method two-step growth. Also, 2 bar O$_2$ or air pressure is used to suppress the evaporation of Ca. The rotation speed of the seed is set to 60 rpm to make a homogeneous mixture, especially for the situation of high Sr doping. The rotation of the feed rod can be slower, about 10–20 rpm. The growth speed of the second step is quite slow, about 2–4 mm/h. At first, a poly seed is used, then the top part of the obtained crystal can be used as the seed for the next growth. Repeating the growth 2 or 3 times is necessary to obtain high-quality crystals.

2.2 Experimental demonstrations of switchable polarization in (Ca,Sr)$_3$Ti$_2$O$_7$

Since (Ca,Sr)$_3$Ti$_2$O$_7$ (CSTO) crystal has a layered structure, it can be cleaved to get the $ab$-plane, which is along the crystal boule direction, as seen in Fig. 2.4. Above the structure transition temperature, $a$- and $b$-axes are equal. When the crystal goes through the transition, $a$- and $b$-axes are not equal anymore but very close. As a result, orthorhombic twin
domains form in the $ab$-plane. At room temperature, the space group is polar $A2_1am$, with
the lattice parameters $a=5.423\,\text{Å}, b=5.417\,\text{Å}, c=19.417\,\text{Å}$. Circular differential interference
contrast (cDIC) images of a cleaved (001) surface of a $\text{Ca}_{2.46}\text{Sr}_{0.54}\text{Ti}_2\text{O}_7$ single crystal is
shown in Fig. 2.5. Dark and bright contrasts indicate the presence of orthorhombic twins.
Since the crystal is transparent, we can use transmission mode linear polarized light to
observe the twin domains. As shown in Fig. 2.6, the dark and bright contrasts of the twins
are reversed by changing the relative angle between the polarizer and analyzer.

The polarization direction is along the $a$-axis. Twin boundaries are along the [110] axis. If
the applied electric field is along the $a$-axis of one domain, it will be perpendicular to
the polarization direction in the adjacent domains. Therefore, the electric field should be
applied along the [110] direction, i.e., the twin boundary direction, in order to switch the
polarizations in all the domains simultaneously. Figure 2.7 shows the net electric polarizations
$\sqrt{2}P$ vs. electric field $E$ hysteresis loops of $\text{Ca}_{3-x}\text{Sr}_x\text{Ti}_2\text{O}_7$ ($x=0, 0.54$ and $0.85$) single
crystals, demonstrating the remanent polarizations can be switched at room temperature.
The net remanent polarizations ($P_r = \sqrt{2}P_{r,\text{exp}}$) along the [100] direction of $x=0, 0.54$ and
0.85 are 8, 4.2 and 2.4 $\mu\text{C/cm}^2$, respectively. Notice the decreasing polarizations with more
Sr doping. Sr$^{2+}$ cations have a larger radius than Ca$^{2+}$, and they preferentially occupy per-
ovskite layers. Larger A-site cation in the perovskite layers will suppress $a^{-}a^{-}c^{0}$ tilts and
Figure 2.5: Circular differential interference contrast (cDIC) images of the cleaved (001) surface of a Ca$_{2.46}$Sr$_{0.54}$Ti$_2$O$_7$ single crystal. The plot is taken from Ref. [9].

Figure 2.6: Transmission mode linear polarized optical microscopic images of the cleaved (001) surface of a Ca$_{2.6}$Sr$_{0.4}$Ti$_2$O$_7$ single crystal. (a) and (b) have different analyzer angle.
Figure 2.7: Net electric polarization $\sqrt{2}P$ vs. electric field $E$ hysteresis loops of Ca$_{3-x}$Sr$_x$Ti$_2$O$_7$ ($x$=0, 0.54 and 0.85) single crystals. The plot is taken from Ref. [9].

$a^0a^0c^+$ rotations of BO$_6$ octahedra, and thus decrease the net polarization, see Chapter 2.4 for details. Piezoresponse force microscopy (PFM) and conductive atomic force microscopy (C-AFM) images of Ca$_{2.46}$Sr$_{0.54}$Ti$_2$O$_7$ are shown in Fig. 2.8, scanned by Y.S.Oh. The images show abundant charged domain wall features. The detailed discussions can be found in Ref. [9].

2.3 Domain topology and switching kinetics in (Ca,Sr)$_3$Ti$_2$O$_7$

The charged domain walls in CSTO crystals are of particular interest. Two-dimensional electron gas has been a hot topic since it was discovered in LaAlO$_3$/SrTiO$_3$ interface [33]. Here we take a close look at the domain topology of CSTO and find antiphase boundaries (APB) in the $Z_4 \times Z_2$ domain structures.

As mentioned before, there are two structural instability modes: BO$_6$ octahedral rotation along the [001]$_T$ axis, noted as $a^0a^0c^+$; BO$_6$ octahedral tilting along the [110]$_T$ axis, noted as $a^-a^-c^0$. The combined mode $a^-a^-c^+$ has eight states, as shown in Fig. 2.9. Notice that 1+ and 3– states have the same direction of polarization, so do 1– and 3+ states, 2+ and 4– states, and 2– and 4+ states. The boundary between 1+ and 3– states is an APB. It cannot be seen in PFM since 1+ and 3– states have the same direction of
Figure 2.8: (a) PFM image and (b) C-AFM image of a Ca$_{2.46}$Sr$_{0.54}$Ti$_2$O$_7$ crystal. The plot is taken from Ref. [9].

Figure 2.9: The notations of the eight states in $A_3B_2O_7$. (1+, 1–, 2+, 2–, 3+, 3–, 4+, 4–) are based on the blue octahedron in the blue circle. Notation of 1,2,3,4 represents the quadrants, which the displacements of apical oxygen ions point to. + or – indicates the rotation of octahedra along the c-axis, with + being clockwise and – being counterclockwise.
Figure 2.10: Antiphase boundary (APB) in a CSTO crystal. (a) The local distortions near an [110]$_T$-oriented APB (green line) between the 1+ and 3– states, which are identical in polarization direction but differ in structure with respect to the rotation (black curved arrows) and tilting (white arrows) by 180°. (b) A $ab$-plane DF-TEM image taken using superlattice $g^+_1 = 3/2(1,1,0)_T$ spot. (c) A DF-TEM image taken using superlattice $g^-_1 = 3/2(-1,-1,0)_T$ spot. A reversed contrast in (b),(c) demonstrates the characteristic of 180°-type FE domains. (d) A DF-TEM image taken using the $g^-_1$ spot at a large tilting angle to tune contrast by enhancing excitation error. A clear boundary interference fringe can then be observed between domains ii and iii, implying an inclined nature and a strong strain gradient expected in rotation-driven FE$_r$ DWs. (e) The schematic domain configuration obtained from b–d demonstrates a typical $Z_3$ ern within the FA domain, composed of three 180°-type FE domains and three DWs: FE$_r$ (red-dotted), FE$_t$ (red-solid) DWs and APB (green-solid). White arrows denote the polarization directions in FE domains. Scale bar, 500 nm. The plot is taken from Ref. [10].
polarization. However, APBs can be seen by dark-field transmission electron microscopy (DF TEM), since there are local distortions at the APBs. As shown in Fig. 2.10 (a), 1+ and 3– states are separated by the green line. The two layers next to the green line are identical. If we take away one of the two layers, the two states would be identical. 1+ and 3– states have opposite tilting directions, as well as opposite rotation directions. This means that reversing the two modes simultaneously will keep the same polarization direction. By reversing only rotation or tilting direction, we can switch the polarization direction $180^\circ$. Therefore, we can define two kinds of FE domain walls, tilting-type FE$_t$ DWs and rotation-type FE$_r$ DWs, as the two adjacent states only have opposite tilting or rotation directions. For example, DWs between 1+ and 3+ are FE$_t$ DWs, and DWs between 3+ and 3– are FE$_r$ DWs. $Z_3$ vortex network forms in the $Z_4 \times Z_2$ domain structures. As shown in Fig. 2.11 (d), vortex-antivortex (V-AV) pairs are connected by an APB (green line).

Besides the $180^\circ$–FE DWs, there are $90^\circ$–ferroelastic (FA) DWs. There are two types of FA DWs. One is tilting related FA$_t$ DW, with the two states have the same rotation, like 1+ and 2+ states. Another one is tilting + rotation FA$_{tr}$ DW, across which both tilting and rotation directions change, like 1+ and 4– states.

Since CSTO crystals are insulating, we can use electron beams to induce poling and observe the in-situ DW movements using DF TEM. Focusing the electron beam ($\sim 300$nm in diameter) of the TEM creates positive charging at a thin local area near the crystal edge. As shown in Fig. 2.12, the charging reverses a 4– domain by $180^\circ$ into a 4+ domain, which is accompanied by the creation of a vortex-antivortex (V-AV) pair. A segment of APB becomes one FE$_r$ DW plus another FE$_t$ DW. After defocusing the electron beam, the 4+ domain shrinks slowly and eventually disappears (Fig. 2.12 (c–e)). Meanwhile, the V-AV pair annihilates, and the FE$_r$ DW coalesces with the FE$_t$ DW into an APB. In this process, APBs act as nucleation reservoirs for the $Z_3$ V-AV pair creation and annihilation.

In another situation shown in Fig. 2.12 (g-i), the APB can also be split into one FA$_{tr}$ DW plus one FA$_t$ DW. When the electron beam is focused on the edge away from FA DW, as shown in Fig. 2.12(h), it will flip a 2– domain $90^\circ$ to a 3– domain, split an APB into one FA$_{tr}$ DW and one FA$_t$ DW, and create a pair of V–AV. After defocusing, the 3– domain slowly returns to the 2– domain.
Figure 2.11: The $Z_3$-vortex patterns in $\text{Ca}_{2.55}\text{Sr}_{0.45}\text{Ti}_2\text{O}_7$. (a) A $2.2 \times 3.9 \, \mu\text{m}^2$ mosaic of DF-TEM images were taken using the superlattice $g^+_1$ spot (red-circled) of domain FA(i) in a CSTO crystal along $[001]_T$. The colored arrows represent polarization directions within the domain. (b) The electron diffraction pattern was taken by covering regions FA(i) and FA(ii) showing a $90^\circ$-crystallographic-twin relation. The red/blue circled spots were contributed from the orthorhombic distortions of the FA(i) region, and the green/yellow ones were from the FA(ii) area. The color-circled spot located in each DF image is the selected superlattice Bragg spot to light up the corresponding domains at a given orientation. (c) A DF-TEM image of the white rectangular box region was taken using the blue circled superlattice $g^-_1$ spot. (d) A proposed domain configuration of c. The plot is taken from Ref. [10].
Figure 2.12: The domain switching kinetics under e− beam-induced poling. (a–e) Image sequences showing a Z3 vortex-antivortex (V-AV) pair evolution during in-situ poling within a single ferroelastic domain. (a,b) The initial state. (c,d) The states during the charge dissipation process after defocusing electron beam. (e) The final state. (f) Schematic showing the 180° ferroelectric polarization switching via splitting or coalescence of an APB into two ferroelectric walls: APB (green line) $\rightarrow$ FE$_t$ (red-solid) + FE$_r$ (red-dotted) DWs. (g,h) Image sequences and schematics showing 90 ferroelectric domain switching near an APB (green line). (g) The initial state. (h) The immediate image after electron beam focused at the sample edge away from the FA boundary (solid blue line). (i) Schematic showing a 90° ferroelectric polarization switching within an FA domain via splitting or coalescence of an APB into two ferroelastic walls: APB $\leftrightarrow$ FA$_{tr}$ (blue-solid) + FA$_t$ (blue-dotted) DWs. The plot is taken from Ref. [10].
2.4 Abundant oxygen octahedral distortions at the phase transition boundary

As shown in Chapter 2.2, the net polarizations of CSTO decreases with increasing Sr concentration. The question is what would happen if we continue to dope more Sr. It turns out that for $0.915 < x < 1$ in $\text{Ca}_{3-x}\text{Sr}_x\text{Ti}_2\text{O}_7$, it does not form polar space group $A2_1am$ at room temperature anymore; instead, it forms a $T'$ phase with space group $P4_2/mnm$. When $1 < x < 1.5$, it would not form $\text{Ca}_{3-x}\text{Sr}_x\text{Ti}_2\text{O}_7$ phase but $(\text{Ca,Sr})_4\text{Ti}_3\text{O}_{10}$ phase. The reason for this may be that it is hard to form $(\text{Ca,Sr})_3\text{Ti}_2\text{O}_7$ phase after Sr cations fully occupy the perovskite layers. When $1.5 < x < 3$, it will form the undistorted T phase with the space group $I4/mmm$. It is not easy to synthesize $0.9 < x < 1$ samples, mainly due to Ca evaporation at the very high sintering temperature.

Fig. 2.13 shows the possible space groups due to various BO$_6$ octahedral tilts/rotations. Besides the space groups mentioned above, undistorted T phase $I4/mmmm$ ($a^0a^0c^0$), O" phase $Acam$ ($a^0a^0c^+$), O' phase $Aمام$ ($a^-a^-c^0$), and the lowest symmetry O phase $A2_1am$ ($a^-a^-c^+$), there are two more possible phases, O* phase $Acaa$ ($a^0a^0c^-$) and $T'$ phase $P4_2/mnm$ ($a^-a^0c^0$). Out-of-phase rotation inside bi-layers along $[001]_T$ leads to O* phase, and tilting along $[100]_T$ leads to $T'$ phase.

Synchrotron powder X-ray diffraction experiments were done on the polycrystalline $\text{Ca}_{3-x}\text{Sr}_x\text{Ti}_2\text{O}_7$ ($0 \leq x \leq 3$) samples using the collimated synchrotron radiation beam with the wavelength of 0.688 Å at the National Synchrotron Radiation Research Center, Taiwan. The data was analyzed using the Rietveld method with a pseudo-Voigt profile function. The angles of octahedral rotation $\theta_R$ and tilt $\theta_T$ decrease with increasing Sr concentration. $\theta_R$ suddenly drops to zero across $x=0.915$, but there is still tilting. When $0.915 < x < 1$, the room temperature phase is $T'$. For the $x=0.9$ crystal, the in-situ diffraction patterns show two transitions, O phase at room temperature, $T'$ phase between 473 K $\sim$ 713K, and T phase above 713 K, as shown in Fig. 2.14(c). The dielectric constant $\epsilon$ as a function of $x$ at 350 K shows a peak when entering the $T'$ state at $x=0.915$, with the magnitude of $\epsilon$ almost doubles compared with that of low $x$ values, as shown in Fig. 2.14(b). The peak can be understood as increasing structural fluctuations when approaching from the ferroelectric O
Figure 2.13: (a) Schematic diagram of possible space groups and the corresponding Glazer notations for bi-layered perovskite \( A_3B_2O_7 \). Lines link the group–subgroup relations. The lattice directions are given with respect to the T state \((I4/mmm)\). (b–f) In-plane projected views of various \( BO_6 \) octahedral tilts/rotations. The dashed lines outline the primitive unit cells, and the red and cyan spheres represent the O and B-site ions, respectively. Black and gray arrows indicate directions of apical and basal plane oxygen displacements, respectively. (b) Un-distorted \( BO_6 \) octahedron in the T state. (c) A clockwise (+) rotated \( BO_6 \) in the \( O^* \) and \( O'' \) states. The rotation can also be counterclockwise (−). In two adjacent layers within one bi-layer, an out-of-phase rotation (+ − or − +) along the c axis occurs in the \( O^* \) state while in-phase (+ + or − −) rotation in the \( O'' \) state. (d) Eight possible \( 1\pm, 2\pm, 3\pm \) and \( 4\pm \) apical oxygen displacements in the O state. The azimuthal angle, \( \phi \), of an apical oxygen distortion is denoted. (e) Given tilting vectors in the \( O' \) state. (f) Four possible apical oxygen displacements (red-circled labels) along the \(<100>_{T'}\) directions in the \( T' \) state. The plot is taken from Ref. [11].
state to the paraelectric T\textsuperscript{'} state. In the $x=0.95$ CSTO crystal, we also managed to observe the $Z_4$ vortex using DF-TEM, see Ref. [11] for details.
Figure 2.14: (a) Structural phase diagram of Ca$_{3-x}$Sr$_x$Ti$_2$O$_7$ with the angles of octahedral rotation ($\theta_R$, empty squares) and tilt ($\theta_T$, cyan spheres) as a function of Sr doping, $x$. The black and cyan curves are guides for the eyes. Two structural phase transition temperatures ($T_1 = 473$ K and $T_2 = 710$ K) at $x = 0.9$, marked with red spheres, are obtained from in situ TEM heating experiments. (b) Dielectric constant versus Sr content ($x$), measured at 350 K and 44 kHz. Red triangles and blue circles are from measurements on polycrystalline and single crystalline (electric field applied along the in-plane direction) specimens, respectively. The dielectric constant peaks at the O–T’ structural boundary of $x = 0.9$. (c) The thermal sequence of selected area electron diffraction patterns on $x = 0.9$, showing two phase transitions upon in situ heating: O (300 K)→T’ (473 K)→T (713 K) states. $S_1 = \frac{1}{2}(130)_T$-type superlattice spots (cyan triangles) are allowed in the O state. When the temperature reaches 473 K, additional $S_2 = \frac{1}{2}(200)_T$-type and $S_3 = \frac{1}{2}(-130)_T$-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. The plot is taken from Ref. [11].
Chapter 3

Interrelation between domain structures and polarization switching in hybrid improper ferroelectric Ca$_3$(Mn,Ti)$_2$O$_7$

So far, switchable ferroelectric polarization has been demonstrated experimentally in a number of non-magnetic HIF compounds such as Ruddlesden–Popper (RP) phases including (Ca,Sr)$_3$Ti$_2$O$_7$ [9], Sr$_3$Sn$_2$O$_7$ [34], low-Mn-doped Ca$_3$Ti$_2$O$_7$ [35], PbTiO$_3$/SrTiO$_3$ superlattice [26] and AA’B$_2$O$_6$ double perovskites [36]. In addition, the presence of polar space groups has been reported in Dion–Jacobson compounds ABiNb$_2$O$_7$ (A = Rb, Cs) [37], RP phase ferrite composites [38] and Ca$_3$Mn$_{2x}$O$_7$ [10]. In parallel, a relatively large, possibly questionable, magnetoelectric (ME) effect (72 ps/m) has been reported in polycrystalline Ca$_3$Mn$_2$O$_7$ at 4 K [39], in comparison with a low value (0.119 ps/m at 60 K) in its analogous polar ferrite composites [38]. However, no measurable FE polarization has been reported in Ca$_3$Mn$_2$O$_7$, even though the presence of polar domains, similar with those in Ca$_3$Ti$_2$O$_7$, has been confirmed using transmission electron microscopy at 300 K [10]. The preparation of high-quality Ca$_3$Mn$_2$O$_7$ and the growth of decent-size single crystals turns out to be challenging, which is a part of the reason why its ferroelectric state has not been rigorously investigated. Note that the latest investigation of the dynamics of the FE phase transition in HIFs further concludes that Ca$_3$Mn$_2$O$_7$ adopts a unique transition route distinct from other A$_3$B$_2$O$_7$ RP materials such as Ca$_3$Ti$_2$O$_7$ [11, 35, 38, 40].

3.1 Sample preparations

For the synthesis of a series of polycrystalline Ca$_3$Mn$_{2-x}$Ti$_x$O$_7$ (x=0, 0.2, 0.5, 0.75, 1, 1.2, 1.35, 1.5, 1.75 and 2), stoichiometric mixtures of CaCO$_3$, SrCO$_3$, and TiO$_2$ (MnO$_2$) powders are ground, pelletized and sintered at 1100 °C and 1300 °C for the first and second sintering, respectively. The final sintering temperatures range from 1320 °C–1550 °C with
increasing sintering temperature for higher Ti concentration. All compositions crystallize in orthorhombic space group $A2_1am$.

Single crystals of $\text{Ca}_3\text{Mn}_{2-x}\text{Ti}_x\text{O}_7$ ($x=0, 0.1, 1, 1.5, \text{and} 2$) are grown using the optical floating zone method. Since Mn$^{3+}$ is more stable than Mn$^{4+}$ in ambient pressure at high temperatures, 8 bar O$_2$ is applied to maintain the Mn$^{4+}$ valence. When doped with Mn, the crystals become brittle and have many cracks, especially for the pure Mn case. In the convenience of the experiment, $\text{Ca}_3\text{Mn}_{1.9}\text{Ti}_{0.1}\text{O}_7$ was grown to obtain better quality crystals compared with pure $\text{Ca}_3\text{Mn}_2\text{O}_7$ crystal.

3.2 Domain observations and poling experiments

The first thing we noticed is that the Mn-rich and Ti-rich single crystals possess distinct domain morphologies in the $ab$-plane. $\text{Ca}_3\text{Mn}_2\text{O}_7$ and Mn-rich single crystals exhibit a highly-unusual irregular type of orthorhombic twin structure, while $\text{Ca}_3\text{Ti}_2\text{O}_7$ and Ti-rich single crystals exhibit prototypical straight orthorhombic twins. Fig.3.1 shows the large-scale images of $\text{Ca}_3\text{Mn}_2\text{O}_7$ and $\text{Ca}_3\text{Ti}_2\text{O}_7$ taken by polarized optical microscopy. In general, twinning which often appears at structural phase transition temperature as a result of energy minimization is a widespread phenomenon and accompanies usually lamellar twin structures with straight twin domain walls. Note that $\text{Ca}_3\text{Mn}_2\text{O}_7$ possesses a large ferroelastic (FA) distortion (i.e., orthorhombicity defined by $(a - b)/(a + b)*100 \%$ is large (0.08 %)) [10],
Figure 3.2: (a) Polarized optical microscopic images of four \( \text{Ca}_3\text{Mn}_{2-x}\text{Ti}_x\text{O}_7 \) \((x=0, 1, 1.5 \text{ and } 2)\) single crystals. (b) Electric polarization \( P \) vs. electric field \( E \) curves of the four crystals. The \( P(E) \) curves are straight lines for \( x=0 \) and 1 even at liquid Nitrogen temperature. Good \( P(E) \) hysteresis loops are evident for \( x=1.5 \) and 2 crystals at room temperature.

in comparison with other compounds with straight orthorhombic twins such as \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) (0.05 %) \([9, 10]\), and Aurivillius layered \( \text{SrBi}_2\text{Ta}_2\text{O}_9 \) (0.027 %) \([41]\). To understand the origin of this unique twin structures in \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) and its physical properties associated with the twin structures, we have performed systematic and comprehensive investigations of polarization, resistivity, and magnetic property as well as real-space three-dimensional domain morphology of \( \text{Ca}_3\text{Mn}_{2-x}\text{Ti}_x\text{O}_7 \) crystals.

The single crystals are black and opaque for \( x=0, 0.1, 1 \text{ and } 1.5 \), but are transparent with brown tint at \( x=2 \). Fig. 3.2(a) shows their domain patterns under a reflection-mode
Figure 3.3: Room temperature $P(E)$ measurement of (a) $x=0$ (b) $x=1$ crystals showing huge leakage currents

The compositional dependence of orthorhombic twins in $\text{Ca}_3\text{Mn}_{2-x}\text{Ti}_x\text{O}_7$ crystals is evident. The unusual irregular orthorhombic twins with curved boundaries appear for Mn-rich compositions ($x=0$ and 1) while prototypical straight twins exist in Ti-rich ones ($x=1.5$ and 2). Interestingly, the bulk polarization can be flipped at 300 K only for Ti-rich crystals $x=1.5$ and 2 with straight twins (Figure 3.2(b)). The remnant polarizations of $x=1.5$ and 2 are 0.63 $\mu$C/cm$^2$ and 7.61 $\mu$C/cm$^2$, respectively. The $x=0$ and 1 single crystals are found to be highly leaky at 300 K (see Figure 3.3), so no meaningful $P(E)$ loops were obtained at 300 K. In order to minimize the leakage effect, we also performed the $P(E)$ measurements on $x=0$ and 1 at liquid Nitrogen temperature. Linear lines as shown in Figure 3.2(b) up to $E = 250$ kV/cm indicate that polarization of those crystals with irregular twins ($x=0$ and 1) is non-switchable in our experimental range.

3.3 Determination of transition temperatures

In order to determine ferroelectric transition temperature (FE $T_c$), two sets of experiments were performed on our single crystals; the temperature dependence of resistivity $\rho(T)$ and the in-situ and ex-situ twin domain observations during various heat treatments. Fig. 3.4 (a-d) and (e-h) are the results for $x=2$ and $x=0.1$. First, we can identify structural
Figure 3.4: Resistivity $\rho$ vs. temperature $T$ curves and in-situ and ex-situ twin domain observations after heat treatments for $x=0.1$ and 2. (a) The $\rho(T)$ curve of Ca$_3$Ti$_2$O$_7$ crystal shows transitions at 1063 K upon warming (red) and at 1039 K upon cooling (black). (b) Domain patterns of as-grown Ca$_3$Ti$_2$O$_7$ at 300 K, (c) after a 1023 K heat treatment, and (d) after a 1033 K heat treatment. (e) The $\rho(T)$ curve of $x=0.1$ crystal shows transitions at 365 K upon warming (red) and at 328 K upon cooling (black). (f), (g) and (h) In-situ domain patterns of a $x=0.1$ crystal at 300 K, heating to 380 K, and cooled down to 364 K after heating to 380 K, respectively.
transitions from large resistivity anomalies (Fig. 3.4 (a) and (e)) in both warming (red) and cooling (black) curves. For example, the FE $T_c$ determined from $\rho(T)$ curves are 1063 K (warming) and 1039 K (cooling) in $x=2$ (Fig. 3.4 (a)). Next, we further confirm $T_c$ by means of ex-situ observations of twin patterns after heating up one thin single crystal near $T_c$. Twin patterns remain intact with heat treatments up to 1023 K (Fig. 3.4 (b) and (c)), but rearrange completely after heat treatment to 1033 K (Fig. 3.4 (d)). The obtained $T_c$s of Ca$_3$Ti$_2$O$_7$ from the two methods are consistent with each other, and also with the reported one (1100 K) [35]. Thanks to a lower FE $T_c$ of $x=0.1$, in-situ observation of twin pattern change with varying temperature can be made under a polarized optical microscope with a thermal stage (Fig. 3.4 (f-h)). We observed the sudden disappearance of those irregular twins above 380 K (Fig. 3.4 (g)), which can be understood as a first-order transition from orthorhombic ($A2_1am$) to nearly-tetragonal ($Acaa$) symmetry [40]. The irregular twins reappeared when cooled down to 364 K with a pattern different from the pattern before heating. FE $T_c$ determined from this heat treatment (364 K-380 K) is consistent with $T_c$ (365 K in warming and 328 K in cooling) determined from $\rho(T)$ curves (Fig. 3.4(e)). Emphasize that the appearance of a completely different irregular twin pattern through the heat treatment across $T_c$ (Fig. 3.4 (f) and (h)) indicates that the irregular twin patterns are not simply due to pinning by disorders such as chemical defects or dislocations. More heat treatment results of twin patterns for $x=1$ and 1.5 are shown in Fig. 3.5.

Based on the above $T_c$ determination together with recent reports on different pathways to stabilize the polar $A2_1am$ symmetry of Ca$_3$Mn$_2$O$_7$ and Ca$_3$Ti$_2$O$_7$ [40], the temperature-concentration phase diagram of Ca$_3$Mn$_{2-x}$Ti$_x$O$_7$ (Fig. 3.6) is constructed. For the Ti-rich side ($x=1.5$ and 2), the high-symmetry structure, tetragonal $I4/mmm$, goes directly to polar $A2_1am$ symmetry upon cooling [35] while the structural transition processes via an additional intermediate $Acaa$ symmetry for the Mn-rich side ($x=0$, 0.1 and 1) [40]. The dashed line as shown in Fig. 3.6 indicates the approximate $Acaa$ to $I4/mmm$ phase boundary near $x=1.3$. Our measured orthorhombicity, obtained using powder X-ray diffraction, as a function of Ti concentration shows a drop of orthorhombicity at $x=1.3$ (Fig. 3.7).

Relevant space groups are directly associated with various distortion modes of BO$_6$ octahedral rotation and tilting. Here, we define $[001]_T$ as the octahedral rotation axis and
Figure 3.5: Resistivity $\rho$ vs. temperature $T$ curves and the change of the domain patterns for $x=1.5$ and $1$ after various heat treatments.  (a) The $\rho(T)$ curve of $x=1.5$ crystal shows transitions at 888 K upon warming (red) and at 871 K upon cooling (black). Domain patterns of (b) an as-grown $x=1.5$ crystal at 300 K, (c) after an 813 K heat treatment, and (d) after an 823 K heat treatment.  (e) The $\rho(T)$ curve of a $x=1$ crystal shows transitions at 717 K upon warming and at 692 K upon cooling.  (f) Domain patterns of an as-grown $x=1$ crystal at 300 K, (g) after a 673 K heat treatment, and (h) after a 683 K heat treatment.
Figure 3.6: Phase diagram of Ca$_3$Mn$_{2-x}$Ti$_x$O$_7$. Red squares and black spheres mark the FE $T_c$'s determined from $\rho(T)$ measurements. Blue squares mark the Néel temperatures of several poly samples determined from $\chi(T)$ measurements. The ab-plane crystallographic views of intermediate Aca$\alpha$ and the ground A$\alpha 2_1am$ phases are shown. Mn/Ti-site atoms are shown in blue (green) corresponding to the upper (lower) perovskite bilayers within one unit cell. Oxygen ions are represented in red. Ca-site ions are omitted for simplification. The octahedral rotations are noted by the sign + (clockwise) and – (counterclockwise). Red arrows indicate the apical oxygen displacements induced by octahedral tilting. For Mn-rich side ($x < 1.3$), the phase transition goes through Aca$\alpha$ to the ground polar A$\alpha 2_1am$ phases from the parent $I4/mmm$ phase. The blue dashed line indicates the approximate Aca$\alpha$ to $I4/mmm$ transition boundary. Glazer notations are labeled.
Figure 3.7: Orthorhombicity of Ca$_3$Mn$_{2-x}$Ti$_x$O$_7$ as a function of $x$. Lattice parameters were calculated from the refinement of X-ray diffraction data of polycrystalline Ca$_3$Mn$_{2-x}$Ti$_x$O$_7$ specimens.

two [110]$_T$ directions as octahedral tilting axes. The ground polar $A2_1am$ symmetry results from the hybridization of octahedral rotation and tilting relative to the undistorted $I4/mmm$ symmetry. The intermediate $Acaa$ symmetry is associated only with octahedral rotations and exhibits opposite octahedral rotations in two layers within each bilayer. Fig. 3.8 depicts the octahedral rotations of two adjacent bilayers: out-of-phase octahedral rotations (+−−+) of $Acaa$ and four possible combinations of in-phase octahedral rotations (+ + +, −−−, + + −− and −−−−) of $A2_1am$. The signs + and − represent the clockwise or counterclockwise rotation of each BO$_6$ octahedron about [001]$_T$ axis, respectively. The type-I (+ + + + and −−−−) and type II (+ + −− and −−−−) of in-phase octahedral rotations define orthorhombic $a$-oriented and $b$-oriented domains, respectively.

3.4 Domain stacking along the $c$-axis and its interrelation with polarization switching

In order to understand the origin of the irregular twin structures and the non-switchable polarization of Mn-rich crystals, superlattice dark-field transmission electron microscope (DF-TEM, JEOL-2010F) images were taken on the side surface of Ca$_3$Mn$_2$O$_7$ (Fig. 3.9
Figure 3.8: Side-views of *Acaa* and *A21am* phases, showing out-of-phase (+ –) and in-phase (+ + or – –) rotation modes within each bilayer. Octahedral rotations in *Acaa* are represented by (+ – – +). Rotations in *A21am* can be sorted into two groups; the ferro-stacking type I (+ + + +) and (– – – –) and antiferro-stacking type II (+ + – –) and (– – + +). Type I and type II lead to *a*-oriented and *b*-oriented domains, respectively.

Figure 3.9: (a) DF-TEM images taken under two-beam diffraction conditions along [010]_{orth} plus [100]_{orth} zone in a *Ca3Mn2O7* crystal. Blue arrows indicate the *a* polar directions for the image where (100)_{orth} spot was taken. The left inset shows an enhanced *b*-oriented domain contrast using (010)_{orth} spot in the outlined area. A high-density 90°–type FE domains along the *c*-axis is found in *Ca3Mn2O7*. (b) DF-TEM image of *Ca3Ti2O7*. It shows 180°–type FE domains along the *c*-axis. The left inset shows a magnified region with the opposite contrast due to Friedel’s pair breaking condition.
Superposed diffraction patterns of [010]orth and [100]orth zones were always observed, suggesting that 90° type twin domains are uniformly present in the crystal. Alternating black-white bands with typical 50-100 nm widths in Fig. 3.9 (a) inset are due to stacking of two orthorhombic variants with twin \( a \) (black) and twin \( b \) (white), rotated 90° along the \( c \)-axis. The DF-TEM image (Fig. 3.9 (a)) using a (100)orth spot produces a-few-unit-cells-wide \( +a \) (dark) and \( -a \) (light) domains in the \( a \) area while \( b \) domains (gray) are invisible here since they have the polarization into the plane. The consequence of alternating 90°–type FE domains is an interchanged FA tensor along the \( c \)-axis. Note that \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) has a rather simple configuration of alternating 180°–type FE domains \((+a \text{ and } -a)\) along the \( c \)-axis (Fig. 3.9 (b)).

The density of alternating 90°–type FE domains along the \( c \)-axis decreases with increasing Ti concentration. This also matches with the trend of the in-plane irregular twins in optical microscope images presented earlier. Therefore, the occurrence of in-plane irregular twins appears to be the consequence of a continuous cancellation of the FA tensor in the presence of an extremely high density of the \( ab \)-domain stacking along the \( c \)-axis. In-plane FA energy is reduced significantly at the expense of those \( ab \)-domain stacking inside a crystal. As a consequence, the in-plane twin domains can be random and large, and in-plane domain walls can be highly wavy in Mn-rich crystals. In contrast, in Ti-rich crystals, lamellar twin patterns develop in the \( ab \)-plane in order to reduce the in-plane FA energy.

Following the rotation modes discussed earlier, B-site octahedral rotations need to be rearranged during the symmetry-changing transition from \( Acaa \) to \( A2_1am \) in Mn-rich crystals: octahedral rotations \((++-+)\) in the \( Acaa \) phase can switch to either a-oriented (type I: ++ + + and -- -- --) or b-oriented (type II: + + -- and -- + +). This degeneracy evidently results in the random stacking of high-density 90°–type FE twins along the \( c \)-axis. We note that two low-energy paths for polarization switching have been proposed for \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) in a recent first-principle study; switching via a local antipolar stacking domain walls or via a two-step orthorhombic twin domains [42]. The former is relevant for 180°–type FE domains along the \( c \)-axis while the latter is for \( ab \)-plane 90°–type FE domains. Here, we discover an unexpected and different domain morphology, 90°–type FE domains along the \( c \)-axis, in \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) and Mn-rich crystals, and this domain morphology appears
3.5 Complex magnetism in Ca$_3$Mn$_2$O$_7$

The magnetic phase diagram of Ca$_3$Mn$_{2-x}$Ti$_x$O$_7$ is also shown in Fig. 3.6. Néel temperature ($T_N$) decreases roughly linearly as $x$ increases and reaches zero before $x=1$, which excludes any possible ME coupling in Ti-rich specimens. The temperature dependence of zero-field-cooled (ZFC) DC magnetic susceptibility of Ca$_3$Mn$_2$O$_7$ single crystals along two crystallographic directions, shown in Fig. 3.10 (c) exhibits a clear anomaly at 115 K, consistent with an earlier neutron diffraction study that claims $G_cF_bC_a$–type magnetic order below 115 K [29]. Magnetization ($M$) vs. field ($H$) measurement perpendicular to the $c$-axis at 5 K (Fig. 3.10 (a) and (b)) appears consistent with the $G_cF_bC_a$–type magnetic order;
the presence of spin flop transition at 3.5 Tesla (i.e., the direction of staggered moments changes from the $c$-axis to the $ab$-plane in 3.5 Tesla) and the existence of a canted magnetic moment in the $ab$-plane. Considering the coexistence of huge $a^- a^- c^+$ octahedral distortions (rotation 18.57° and tilting 13.41°) and $G_c$ spin configuration, the small magnitude of spin canting angle (about 0.01°), estimated from the remnant magnetization of 0.0015 $\mu$B per formula unit, perhaps indicates a tiny spin-orbit coupling and very weak Dzyaloshinskii-Moriya (DM) interaction [30, 31]. The DM interaction in Ca$_3$Mn$_2$O$_7$ seems even weaker than that of La$_2$CuO$_4$, where the spin canting angle is 0.22°, and the octahedral rotation angle is 2.75° [43]. Another puzzling feature is the presence of a magnetic hysteresis loop along the $c$-axis, which is almost identical with that perpendicular to the $c$-axis. In fact, peculiar $\chi(T)$ behavior along the $ab$-plane below $T_N$ is also similar with that along the $c$-axis. Overall, this isotropic canted magnetic moment and small spin-orbit coupling are not in favor of large ME coupling.

In conclusion, our systematic study of Ca$_3$Mn$_{2-x}$Ti$_x$O$_7$ reveals unique orthorhombic twin domain morphology both in the $ab$-plane and along the $c$-axis in the Mn-rich single crystals. The phase transition route through an $Acaa$ phase only with octahedral rotations results in the stacking of 90° twin domains along the $c$-axis, which appears to be responsible for non-switchable polarization. In addition, the complex magnetism of Mn$^{4+}$ spins in Ca$_3$Mn$_2$O$_7$ accompanies a tiny and isotropic canted magnetic moment despite huge structure distortions, which is not in favor of large ME coupling. The discovered interrelationship between domain morphology, phase transition path, and polarization/magnetization switching paves a new avenue to design novel multiferroics with room-temperature magnetoelectricity.
4.1 Giant magnetoelectric effect in Fe$_2$Mo$_3$O$_8$

The first series of compounds we selected from the list in Ref. [7] are M$_2$Mo$_3$O$_8$ (M=Fe, Zn, Mn, Co, Ni). This series of compounds was first synthesized by McCarroll et al [44]. The crystal structure and magnetic properties of polycrystalline samples were studied by Varret, Bertrand [45]. In 1982, single crystals were prepared, and the magnetism was investigated by McAlister and Strobel [46]. M$_2$Mo$_3$O$_8$ crystallizes in a polar $P6_3mc$ space group at room temperature. The hexagonal structure is an alternating stacking of honeycomb-like M-O layers and sheets of Mo$^{2+}$ ions along the $c$-axis, as seen in Fig. 4.1. The Mo atoms form a diamagnetic MO$_3$ trimer, and all the magnetic properties are coming from the transition metal cations. The transitional metal cations in M-O layer have two different sites, i.e., octahedral site and tetrahedral site, each forming an MO$_6$ octahedron and MO$_4$ tetrahedron. The two sites are not in the same plane perpendicular to the $c$-axis. The vertical displacement between the two sites is about 0.6 Å. The nearest magnetic neighbors of the octahedral M$^{2+}$ site in the M-O layers are three tetrahedral M$^{2+}$ sites, vice versa. At low temperature, M$_2$Mo$_3$O$_8$ compounds present different magnetic orders. Fe$_2$Mo$_3$O$_8$ and Co$_2$Mo$_3$O$_8$ are antiferromagnetic, Mn$_2$Mo$_3$O$_8$ is ferrimagnetic, Zn$_2$Mo$_3$O$_8$ is diamagnetic, and Ni$_2$Mo$_3$O$_8$ is paramagnetic. Although recently we found that Ni$_2$Mo$_3$O$_8$ is not paramagnetic at very low temperature, I will not discuss it here. The magnetic properties of Fe$_2$Mo$_3$O$_8$, Co$_2$Mo$_3$O$_8$, and Mn$_2$Mo$_3$O$_8$ are highly anisotropic, suggesting that the spins are preferentially along the $c$-axis below the transition temperature.

The space group $P6_3mc$ belongs to a polar point group 6mm, which is pyroelectric. However, it is not ferroelectric, meaning that the polarization cannot be reversed. The whole crystal has one single domain. As polar magnets, the magnetoelectric effect of these
compounds has never been studied before. The initial test is to measure the temperature
dependence of dielectric constant. We found anomalies at the magnetic transition temper-
atures in the $\epsilon(T)$ curves of Fe$_2$Mo$_3$O$_8$ and Mn$_2$Mo$_3$O$_8$ and nothing for Co$_2$Mo$_3$O$_8$.

Here I present the comprehensive study of ME effect in single crystalline Fe$_2$Mo$_3$O$_8$.

4.1.1 Sample growth

Mo$^{4+}$ has a reduced valence state in the M$_2$Mo$_3$O$_8$ compounds. Sintering at high tempera-
tures in the air will induce Mo$^{6+}$. Therefore, the sample growth has to be done in evacuated
quartz tubes.

Polycrystalline powders of M$_2$Mo$_3$O$_8$ samples are grown using the standard solid-state
reaction method: the stoichiometric mixtures of MO$_x$ (Fe$_2$O$_3$, ZnO, MnO$_2$, CoO, NiO),
Mo and MoO$_3$ powders are ground, pelletized and sintered in evacuated quartz tubes. The
standard sintering temperatures are 1000 °C and 1100 °C for the first and second sintering,
respectively. Here we use Mo and MoO$_3$, not MoO$_2$, so we can adjust the ratio between Mo
and MoO$_3$ to make the total oxygen concentration to the right amount. In practical, we
found Mo$^{6+}$ impurity, such as FeMoO$_4$. The reason is that the surface of fine Mo powder
is oxidized. After several trials, we found that X-ray diffraction patterns of $\text{M}_2\text{Mo}_3\text{O}_{8-x}$, $x=0.3\sim0.4$, present the clean single phase.

Single crystals are grown by chemical vapor transport (CVT). The temperatures of hot end and cold end are set to 1000 °C and 650 °C $\sim$ 850 °C (depending on different compounds) for 300 hours, using either a two-zone tube furnace or a single zone tube furnace with the known temperature gradient. $\text{I}_2$ chucks and $\text{Cl}_2$ gas were used as transport agents first. Small crystals of $\text{M}_2\text{Mo}_3\text{O}_8$ and $\text{MoO}_2$ can be found at the cold end. $\text{MoO}_2$ crystals are purple and have a different shape from $\text{M}_2\text{Mo}_3\text{O}_8$. It is easy to distinguish them from $\text{M}_2\text{Mo}_3\text{O}_8$. Later $\text{TeCl}_4$ powder was used as the transport agent and bigger crystals were obtained. The biggest single crystal of $\text{Fe}_2\text{Mo}_3\text{O}_8$ is shown in Fig. 4.2.

4.1.2 Magnetic and dielectric measurements

The temperature dependence of magnetic susceptibility $\chi(T)$ is measured along the $c$-axis and perpendicular to the $c$-axis both in zero-field-cooled (ZFC) and field-cooled (FC) processes, as shown in Fig. 4.3. The different behaviors between two directions suggest that the
spins are preferentially oriented along the c-axis below $T_N$. The spins of two different Fe$^{2+}$ sites have different values and opposite directions. Fe$_O$ has a larger spin than Fe$_t$. Therefore, each Fe-O layer is ferrimagnetic. Along the c-axis, the nearest Fe spins are aligned in the same direction, implying ferromagnetic interlayer coupling. However, along the c-axis, the nearest Fe site of Fe$_O$ is Fe$_t$, vice versa. So the magnetic moments of adjacent Fe-O layers are opposite, as seen in Fig. 4.6. This results in vanishing macroscopic magnetic moment along the c axis. We call this state AFM.

The temperature dependence of the dielectric constant $\epsilon$ along the c-axis is also measured, as seen in Fig. 4.5 (a). A large anomaly presents at $T_N$. A similar anomaly is shown in the $C_p(T)$ curve (Fig. 4.4). So we suspect that there is a simultaneous structure transition associated with the magnetic transition at $T_N$. This is further confirmed by the measurements of the variation of the electric polarization $\Delta P(T) = P(T) - P(T = 120K)$ along the c-axis, in particular, the jump of $\Delta P$ at $T_N$, as shown in Fig. 4.5 (b). The magnitude of this jump, $\sim 0.3 \ \mu C/cm^2$, is quite large, and we have not found any other polar magnets with even larger measured $\Delta P$. $\Delta P$ was measured by integrating the pyroelectric
current on warming after cooling down to $T = 5$ K in zero electric field. The advantage of this compound is that we do not need to pole the crystal to observe the changes shown in Fig. 4.5, as it has a single polar domain.

### 4.1.3 Magnetic field induced changes of polarization

Next, we measured magnetic field $H$ dependence of magnetization $M$ at different temperatures. Metamagnetic transitions signaled by sharp magnetization $M$ jumps present between the temperature range of 50 K~60 K, see Fig. 4.5 (c). Also, we measured the magnetic field $H$ dependence of the changes of polarization, as shown in Fig. 4.5(d). Clearly, the magnetic transition is accompanied by a structural transition indicated by the corresponding jumps in the electric polarization. A small hysteresis is observed in the $\Delta P(H)$ curves. The $\Delta P \equiv P(H) - P(H = 0 \text{ T})$ vector points to the negative c-axis direction, and its value at $T = 50$ K is roughly twice as small as the $\Delta P$ induced at $T_N$ for $H = 0$ T. Mn$_2$Mo$_3$O$_8$ [47] and (Fe,Zn)$_2$Mo$_3$O$_8$ [48] are known to possess a ferrimagnetic (FRM) state, compared with the AFM ground state in Fe$_2$Mo$_3$O$_8$. In the FRM state, the AFM order in the Fe-O layers is preserved, but all the spins in every second layer are flipped, see Fig. 4.6. The ferrimagnetic moments of the Fe-O layers are aligned in the same direction, resulting in a
Figure 4.5: Magnetically-induced electric polarization, and the metamagnetic transition (a) Temperature dependence of the c-axis dielectric constant $\varepsilon(T)$, $f = 44$ kHz. (b) Variation of the c-axis electric polarization $\Delta P$ with temperature. (c,d) Magnetic field dependence of magnetization $M(H)$ and polarization $\Delta P(H)$ at various temperatures. In (d), solid (open) circles depict the data obtained upon sweeping the magnetic field up (down). The plot is taken from Ref. [12].

Figure 4.6: Schematic view of the AFM and FRM orders. Pink arrows represent the ferrimagnetic moments of the individual Fe-O layers. The plot is taken from Ref. [12].
macroscopic magnetization. If we extrapolate the high-field $M(H)$ data of Fig. 4.5 (c) to zero field, it would give a positive intercept of $\sim 0.5 \, \mu B/\text{f.u.}$ at $T = 50 \, \text{K}$, indicating the ferrimagnetic nature of the high-field state. This assumption is confirmed by the Moessbauer measurements of FeO and Fe\text{t} moments [45] (4.83 $\mu B$ and 4.21 $\mu B$, respectively), from which we can calculate the net ferrimagnetic moment for a single Fe-O layer to be 0.6 $\mu B/\text{f.u.}$.

Now the question is what is the origin of the change of polarization. When the magnetic structure transits from PARA to AFM, there are ionic shifts relative to the original positions. The same thing happens during the transition from AFM to FRM state. The ionic shifts can be calculated from the experimental paramagnetic structure and the calculated AFM and FRM structures. Although the total polarization can have multiple values, the relative change of polarization is definite. The positive $c$-axis is defined as the direction which the vertices of the FeO\text{4} tetrahedra point to. The change of polarization can be calculated using the formula $\Delta P = \frac{1}{V} \sum_j (z^i_j - z^f_j)Q_j$, where $z^i_j$ and $z^f_j$ are ionic coordinates along the $c$-axis for the initial and final structures, respectively, $Q_j$ are the ionic charges, $V$ is the volume of the unit cell, and the sum is taken over the unit cell. See Ref. [49] for the details of the calculation. From the calculation, $\Delta P$ values are 0.60(11) $\mu C/\text{cm}^2$ and -0.55(11) $\mu C/\text{cm}^2$ for the PARA to AFM and AFM to FRM transition, respectively. The ionic shifts from AFM to FRM state are opposite to those from PARA to AFM state.

Both a positive and a negative magnetic field along the $c$-axis can induce the FRM state. The only difference is an 180° rotation of every spin in the system. $\Delta P$ induced by exchange striction should be identical, although the field-induced magnetizations should be opposite for the opposite fields. This is confirmed by the data in Fig. 4.7 (a,b). Fig. 4.7 (d) shows the calculated ionic shifts for the transition from AFM to FRM, which have a smaller value but opposite direction compared with those occurring at the transition from PARA to AFM, see Fig. 4.7 (c). This means the lattice tends to relax towards the paramagnetic structure in the FRM state. This is because there is a magnetic energy loss due to the interlayer interactions in the FRM phase. Also, in the AFM state, there is already a relaxation of the lattice distortion. As a result, during the transition from AFM to FRM, $\Delta P$ is negative.

At $T = 55 \, \text{K}$, the field-induced transitions shown in Figs 4.5(d) and 4.7 (a,b) are very sharp. Therefore, the values of the differential ME coefficient $dP/dH$ near the transition
Figure 4.7: **Magnetoelectric effect, and the associated ionic shifts.** (a,b) Magnetic field dependence of magnetization $M(H)$ and polarization $P(H)$ at $T = 55$ K. Numbers and arrows indicate the measurement sequence. The insert in (b) shows the magnetic orders and the ferrimagnetic moments of the Fe-O layers for the phases involved. (c) The calculated ionic shifts for the paramagnetic to AFM transition. The thick arrow represents the corresponding change of the electric polarization, $\Delta P$. (d) the same as (c), but for the AFM to FRM transition. The plot is taken from Ref. [12].
Figure 4.8: Reproducible magnetoelectric control of the electric polarization and magnetization with giant ME coefficient. (a) Periodic modulation of electric polarization (blue) induced by a magnetic field linearly varying between 3.25 T and 3.5 T (black) at 55 K. (b) Periodic modulation of magnetization (green) induced by an electric field (red) linearly varying between 16.6 kV/cm, for $T = 55$ K and $\mu_0 H = 3.345$ T. (c) Phase diagram of $\text{Fe}_2\text{Mo}_3\text{O}_8$. Black dots determined from $M(H)$, and red diamonds – from $\chi(T)$ curves. (d) Electric field dependence of magnetization for $\text{Fe}_2\text{Mo}_3\text{O}_8$ (from the panel (b), averaged), and for $\text{Ni}_3\text{TeO}_6$ ($\times10$). The insert illustrates the experimental setup, with directions of the applied fields shown. In all figures, the magnetization, polarization, and the applied fields are along the $c$-axis. The plot is taken from Ref. [12].
field are giant, reaching almost $\sim 10^4$ ps/m. Notice the small hysteresis (0.02 T at 55 K, 0.007 T at 58 K). Also, it does not require poling. The variation of $P$ with $H$, as shown in Fig. 4.8(a) for $T = 55$ K is almost linear, reproducible, and giant. When $H$ oscillates between 3.25 to 3.5 T, $\Delta P$ also oscillates between 0 and $-0.08 \mu C/cm^2$. The inverse effect, the change of magnetization by applying the electric field ($E$) is also linear, giant, and reproducible, as shown in Fig. 4.8(b). At $H = 3.345$ T and $T = 55$ K, when the electric field oscillates between $\pm 16.6$ kV/cm, the magnetization varies between $\pm 0.175 \mu B/f.u.$, resulting in the $dM/dE$ of $-5700$ ps/m. At other points on the AFM-FRM transition boundary shown in Fig. 4.8 (c), we can observe similarly large differential ME coefficients $dP/dH$ and $dM/dE$. Compared with the polar magnet $\text{Ni}_3\text{TeO}_6$ [50], these coefficients are more than an order of magnitude larger, see Fig. 4.8 (d).

4.2 (Lu,Sc)FeO$_3$

Hexagonal rare earth manganites are improper ferroelectrics with antiferromagnetism. Various studies have been done on hexagonal REMnO$_3$, including its FE domain structures, magnetism, and the coupling between ferroelectric and magnetic orders. Its Fe analogue, hexagonal REFeO$_3$, however, has not been studied well simply because the hexagonal phase is not stable in bulk. $h$-LuFeO$_3$ can be stabilized in films [51–54], which shows weak ferromagnetism and a higher magnetic ordering temperature $T_N=150$ K, compared with $T_N=86$ K in $h$-LuMnO$_3$ [55]. Recently, Masuno [56] report the stabilization of bulk $h$-LuFeO$_3$ using Sc doping into the Lu site, providing a new way to study the multiferroics in $h$-LuFeO$_3$.

4.2.1 Crystal growth

Bulk LuFeO$_3$ usually forms orthorhombic space group $Pnma$, which is centrosymmetric. Lu$^{3+}$ is the smallest cation of rare earth series (La $\sim$ Lu). To form the hexagonal phase, an even smaller A-site cation is needed. However, Sc$^{3+}$ is too small. ScFeO$_3$ forms cubic space group $Ia\bar{3}$, which is also centrosymmetric. The idea is to mix Lu and Sc to get the proper radius of A-site cations.

Polycrystalline samples are prepared using the conventional solid-state method. The
Figure 4.9: **Crystallographic structure of h–(Lu,Sc)FeO₃ in P6₃cm space group.** Yellow balls indicate Lu or Sc atoms, while grey and blue balls stand for Fe and O atoms respectively. The black arrows show the displacement directions of Lu or Sc atoms with a two–down/one–up case. Trimerized Fe atoms are illustrated with green bonds.

Stoichiometric mixtures of Lu₂O₃, Sc₂O₃, and Fe₂O₃ powders are ground, pelletized and sintered. The standard sintering temperatures are 1200 °C, 1400 °C and 1450 °C for the first, second and final sintering, respectively. However, the sample preparation is not straight forward, since there are always impurity phases in the X-ray diffraction pattern. Both LuFeO₃ and ScFeO₃ peaks are present even after very fine grinding and sintering at very high temperature. Finally, we figured out the trick: both Lu₂O₃ and Sc₂O₃ are hygroscopic. Mixing all three powders together would make some Lu₂O₃ powder sticking with Fe₂O₃, and also some Sc₂O₃ powder sticking with Fe₂O₃. Once this happened, it would be impossible to mix Lu and Sc well at the atomic level. The solution is to grind Lu₂O₃ and Sc₂O₃ powder first for about half an hour to mix them well, then add Fe₂O₃ powder and grind. In this way, we can obtain the pure hexagonal phase in Lu₁₋ₓScₓFeO₃, x ranging from 0.35 ~ 0.65. Fig. 4.10 presents the X-ray diffraction pattern of an x = 0.4 crystal, which shows a cleaner phase than the sample reported in Ref. [56].

Single crystals of Lu₁₋ₓScₓFeO₃ (x=0.5, 0.4) are grown using the optical floating zone method. Lu₀.₆Sc₀.₄FeO₃ are grown because less Sc concentration would improve the crystal
Figure 4.10: X-ray diffraction pattern of $h$-Lu$_{0.6}$Sc$_{0.4}$FeO$_3$ shows a pure hexagonal $P6_3cm$ phase

quality. The maximum rotation speed of shafts is used to help obtain a homogeneous melton zone. Due to the low viscosity of the melton zone, special cares are required to maintain a stable melton zone.

4.2.2 Ferroelectric domain observations

The FE domain structures of $h$-REMnO$_3$ are well studied in recent years. Topological defects are discovered in real space domain topology and even linked to cosmology [13]. The crystal structure as shown in Fig. 4.9 displays the trimerization of Fe$^{3+}$ cations and the displacement directions of Lu$^{3+}$/Sc$^{3+}$ cations with the one–up/two–down case. The crystals were cooled down across the phase transition temperature at different cooling rates and different sizes of topological defects were obtained. For our $h$-Lu$_{0.6}$Sc$_{0.4}$FeO$_3$ single crystals, we tried different cooling rates (1 °C/h, 10 °C/h, and 100 °C/h) from 1400 °C to 1200 °C and observed different sizes of topological defects, in this case, vortices, as shown in Fig. 4.11. Clearly, slower cooling causes lower defects density. The relation between the density of defects and cooling rates follows the Kibble–Zurek mechanism discussed in Ref. [13]. Also, room temperature $P(E)$ hysteresis loops shown in Fig. 4.11 demonstrate the switchable polarization in $h$-Lu$_{0.6}$Sc$_{0.4}$FeO$_3$. 

![X-ray diffraction pattern of h-Lu$_{0.6}$Sc$_{0.4}$FeO$_3$](image)
Figure 4.11: The ferroelectricity and vortex ferroelectric domains of $h$-$\text{Lu}_{0.6}\text{Sc}_{0.4}\text{FeO}_3$. Room-temperature PFM images of cleaved surfaces of crystals after (a) 100 °C/h, (b) 10 °C/h and (c) 1 °C/h cooling in the 1400 °C–1200 °C temperature range. (d) The density of defects as a function of cooling rates, compared with ErMnO$_3$ and TmMnO$_3$ from Ref. [13]. (e) Room–temperature $P(E)$ loops at 2702 Hz, which prove its robust and switchable ferroelectricity.
We also performed measurements of magnetic properties, showing a weak ferromagnetism (WFM) with $T_N=150$ K. Magnetic domain structures are obtained by low-temperature magnetic force microscopy (LT-MFM), which show the decoupling of FE and WFM domains. Detailed discussions are in Dr. Kai Du’s paper submitted to Advanced Materials.
Chapter 5
Conclusion

This thesis presents a systematic study of hybrid improper ferroelectric materials and two hexagonal polar magnets synthesized in our lab. In Chapter 1, we discussed the concepts of ferroelectricity, multiferroics, and hybrid improper ferroelectricity, as well as their applications. Multiferroics are materials with coexisting ferroelectricity and magnetism. The possibility to manipulating one order parameter with the conjugate filed for the other is of great interest for device applications. The ideal case is to switch the direction of magnetization by changing the electric field so that we can write electrically and read magnetically. Electric and magnetic orders are mutually exclusive in proper ferroelectrics. Therefore, alternate mechanisms of ferroelectricity are designed to realize the coupling between electric and magnetic orders. Ferroelectricity induced indirectly through charge ordering, magnetic ordering, or structure transition is called improper ferroelectricity. There are several improper ferroelectrics, but we still cannot find one stable single phase in which the magnetization can be switched $180^\circ$ by electric field. Hybrid improper ferroelectricity was proposed to solve this problem. Nicole A. Benedek and Craig J. Fennie were inspired by the unusual ferroelectric behaviors in the artificial superlattice of $(\text{PbTiO}_3)_n/(\text{SrTiO}_3)_m$, where two non-polar octahedral rotation modes are responsible for the polarization. The most common perovskite $\text{ABO}_3$ with space group $Pnma$ and rotation pattern $a^-a^-c^+$ is used as the building block. Theoretical calculations show that there are antiparallel displacements of A-site cations between adjacent layers, which cancel out each other. Two routes are introduced to induce the non-cancellation, double perovskites (superlattices) and Ruddlesden–Popper phases ($\text{A}_3\text{B}_2\text{O}_7$). $\text{Ca}_3\text{Ti}_2\text{O}_7$ and $\text{Ca}_3\text{Mn}_2\text{O}_7$ are proposed as the prototypical HIF. $\text{Ca}_3\text{Mn}_2\text{O}_7$ is more interesting due the presence of weak ferromagnetism related with one of the two rotation modes. If there is switchable polarization in $\text{Ca}_3\text{Mn}_2\text{O}_7$, then
we can use electric field to flip the direction of magnetization, which is a huge breakthrough.

In Chapter 2, we discussed the interesting results in the non-magnetic HIF, Sr-doped Ca$_3$Ti$_2$O$_7$. Switchable polarization is confirmed in Ca$_{3-x}$Sr$_x$Ti$_2$O$_7$ ($x < 0.9$). We also find abundant domain features in Ca$_{3-x}$Sr$_x$Ti$_2$O$_7$ crystals. Four tilting directions and two rotation directions of the octahedra result in the $Z_4 \times Z_2$ domain structures. $Z_3$ vortices and antiphase boundaries are observed using dark-field TEM. APBs connect the vortex and anti-vortex pairs. In-situ domain switching observations using $e^-$ beam poling show that the switching process is accompanied by the creation and annihilation of vortex and anti-vortex pairs. APBs act as nucleation reservoirs for the $Z_3$ V-AV pair creation and annihilation. 180° (90°) ferroelectric (ferroelastic) polarization switching happens via splitting or coalescence of an APB into two ferroelectric (ferroelastic) walls. Besides the polar orthorhombic phase ($x < 0.9$) and undistorted tetragonal $I4/mmm$ phase ($x > 1.5$), there are other possible octahedral tilts/rotations in the bi-layered perovskite CSTO. The rotation and tilting angles decrease with increasing Sr concentration. In a small region (0.915 < $x$ < 1), the rotations are totally suppressed by chemical doping, and only tilts of the octahedra exist. In this new tetragonal T’ phase with the space group $P4_2/mnm$, we observed $Z_4$ vortex domain structures using DF-TEM, which could lead to further studies of topological defects. This T’ phase has been reported in other materials, and the tilting could be related to magnetism.

In Chapter 3, we discussed the most interesting HIF Ca$_3$Mn$_2$O$_7$, which is a potential multiferroic. Ferroelectrically induced weak ferromagnetism is the only known mechanism by which magnetization can be switched 180° by electric field. Although switchable polarization has been reported in some non-magnetic HIF, such as Sr-doped Ca$_3$Ti$_2$O$_7$ discussed in Chapter 2 and Sr$_3$Sn$_2$O$_7$, there is no report of switchable polarization in Ca$_3$Mn$_2$O$_7$. we managed to synthesize high-quality single crystals of Ca$_{3-x}$Mn$_{2-x}$Ti$_x$O$_7$ for the first time. We first noticed the unusual twin domain structures in the $ab$-plane in Mn-rich crystals. Also, there is no switchable polarization in Mn-rich crystals. Ti-rich crystals possess the regular orthorhombic twin domains and switchable polarization. The relation between the domain structures and polarization switching is apparent. The ferroelectric transition temperatures
of the series of compounds are determined by two methods; one is the resistivity vs temperature measurements, and the other is the changes of domain patterns after heat treatments. The FE transition temperature increases linearly as the function of Ti concentration. TEM images reveal that Mn-rich crystals have an unprecedented $90^\circ$ a- and b-domain stacking along the c-axis, due to an intermediate $Acaa$ phase during the phase transition. It is a pity that this stacking causes the non-switchable polarization in Mn-rich crystals. The occurrence of in-plane irregular twins appears to be the consequence of a continuous cancellation of FA tensors in the presence of an extremely high density of a- and b-domain stacking along the c-axis. Meanwhile, there is no magnetic ordering down to 0 K in Ti-rich crystals, which rules out any magnetoelectric effect in this series of compounds.

In Chapter 4, we select one candidate, Fe$_2$Mo$_3$O$_8$, from the list of known polar magnets, and present the giant magnetoelectric effect in the hidden ferrimagnetic state. The polarization behaviors of many polar magnets in our list have not been studied before. From our systematic studies, we have discovered that there are two changes of crystal structure, associated with two magnetic transitions in Fe$_2$Mo$_3$O$_8$. The second structure change is induced by the metamagnetic transition, which provides a playground for the magnetoelectric effect. The advantage of Fe$_2$Mo$_3$O$_8$ is that it does not need poling since it is pyroelectric. The ME coefficient $dM/dE$ in Fe$_2$Mo$_3$O$_8$ from our measurements is record high, $-5700$ ps/m. Other M$_2$Mo$_3$O$_8$ (M=Ni, Mn, Co, Zn) compounds also have intriguing magnetic and physical properties, and we are investigating them in details. Also, I present our work on bulk hexagonal LuFeO$_3$ crystals. While hexagonal REMnO$_3$ has been studied thoroughly, its ferrite analogue h-REFeO$_3$ has not been studied well, because the hexagonal phase is not stable in bulk. We managed to synthesize bulk single crystals of Sc-doped LuFeO$_3$ in hexagonal phase for the first time. Room temperature $P(E)$ hysteresis loops and FE vortex domain patterns demonstrate its ferroelectricity. The Kibble–Zurek mechanism, i.e., the relation between the density of topological defects and cooling rates across the transition temperature, is also observed in the (Lu,Sc)FeO$_3$ single crystals.

In every chapter, I present the details of sample preparations. As a sample grower, I must say that it is not easy to synthesize high quality samples, especially single crystals. The experimental demonstration of switchable polarization in (Ca,Sr)$_3$Ti$_2$O$_7$ was published
in 2015, four years after the proposal of HIF in 2011. I am sure many groups tried to synthesize this compound, but only our group succeeded. Synthesizing high quality single crystals requires the perfection in every step of the process and also creative thinking. Meanwhile, advanced equipments are also important. Recently, the first laser floating zone machine in the US was installed in our lab. Now it is possible to obtain single crystals of many intriguing compounds which cannot be synthesized before.

The main topic of this thesis is hybrid improper ferroelectricity. It is a good example of how theoretical calculations and experimental results affect each other. The idea of HIF was inspired by the unusual ferroelectric behaviors in \((\text{PbTiO}_3)_n/(\text{SrTiO}_3)_m\) superlattice, and the calculations predicted the prototypical HIF \(\text{Ca}_3\text{Mn}_2\text{O}_7\) and \(\text{Ca}_3\text{Ti}_2\text{O}_7\). The successful demonstration of switchable polarization in \(\text{Ca}_3\text{Ti}_2\text{O}_7\) proves the validity of theoretical calculations. However, it is unfortunate that \(\text{Ca}_3\text{Mn}_2\text{O}_7\) does not process switchable polarization as expected. Otherwise, we would realize 180° switching of magnetization by electric field, which is significant for device applications. As a matter of fact, \(\text{Ca}_3\text{Mn}_2\text{O}_7\) is very close to be the first compound which processes this property. The only obstacle is the 90° \(a\)- and \(b\)-domain stacking along the \(c\)-axis. This study is enlightening and important for the future research of multiferroics.
Bibliography


