Unconventional Ferroelectricity, Quantum Magnetism, and Multiferroicity of Single-Crystalline Quantum Materials

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ABSTRACT OF THE DISSERTATION

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In the first chapter, single crystal growth techniques, ferroic orders, and magnetoelectricity are introduced. In the second chapter, the phenomenological theory of ferroelectric transition is introduced. Unconventional ferroelectrics examples Sr₃Sn₂O₇, a hybrid improper ferroelectrics with high tunability, and HfO₂:Y bulk crystals showing metastable ferroelectric phase are demonstrated to show how their single-crystalline materials help to improve the ferroelectric performance and understand the physics. The third chapter shows the multiple ferroic orders, novel magnetic ground state, and toroidal magnetoelectricity in a chiral magnet BaCoSiO₄, in which the single crystal unambiguously reveals the anisotropic magnetism and magnetoelectric tensor. Beyond the experimental demonstration of BaCoSiO₄, a new concept- magnetic chirality is proposed and discussed. In the last chapter, recently
proposed unconventional crystal growth techniques are reviewed, and the growth and property of a chiral superconductor Mo$_3$Al$_2$C are introduced as a successful example of the alumina tube sealing technique. This thesis highlights the laser floating zone as a breakthrough growth technique leading to unique single-crystalline quantum materials which have not been studied before.
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Declaration

All crystals in the photograph shown in this thesis are grown by Xianghan Xu. Some parts of the thesis are from the listed work:

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1 Chapter 1 - Introduction to Single-crystalline Quantum Materials

1.1 Why Single Crystal?

In the research of experimental condensed matter physics, the real material systems are always playing important roles. With the frontier research fields going deeper and deeper into the quantum regime, single-crystalline materials are more and more desired since they reflect the most intrinsic properties of fragile quantum states. The quality of single crystals is also critical in the understanding of underlying physics. For example, recently, the finding of an ultra-high critical magnetic field in a ferromagnetic superconductor UTe$_2$ attracts great research interest as a promising candidate for triplet pairing [1]. Moreover, there are a few reports of multiple superconducting states suggesting a multicomponent superconducting order parameter [2, 3]. However, the discrepancy of experimental data among different samples, i.e., some pieces/parts show two transitions while others do not, is still blurring the underlying physics [4]. To produce high-quality single-crystalline samples and to observe the most intrinsic quantum phenomena is still a prominent direction in the condensed matter physics field. In addition, single-crystalline materials can show anisotropic properties, which reflects the underlying physics. For instance, the anisotropic magnetic susceptibilities in 4f systems like RE$_2$Ti$_2$O$_7$ facilitate the understanding of crystal electric field levels [5].
Last but not least, bulk single crystals typically have minimized strain compared to the thin film samples [6], thus are especially desired for the study of intrinsic structure domain (e.g., ferroelectric domain) configurations.

In real crystalline bulk materials, there are always defects and impurities. Therefore, for a material lab, it is important to develop straightforward and quick techniques to characterize the quality of produced crystalline materials. Typically, we use XRD, Laue diffraction, and optical microscope techniques to examine the quality of our samples. An example is shown in Fig 1.1. There are two batches of GdInO$_3$ floating zone crystals grown at different conditions. To figure out the sample quality, firstly, XRD (Fig. 1.1 (a)) is done on the ground powder of those crystals, and the one having worse quality shows an impurity (In$_2$O$_3$) peak in XRD (asterisk in the red curve) while the one having better quality doesn’t. Consistently, as shown in Fig. 1.1 (b)-(c), the back reflection Laue diffraction pattern taken along [001]$_b$ of the bad crystal shows diffused and faint spots, while the good crystal exhibits sharp and clear diffraction spots showing 6-fold symmetry. GdInO$_3$ is insulating and thus transparent in the visible light range. In this case, transmission polarized optical microscope images are obtainable on polished/cleaved crystal plates. As shown in Fig. 1.1 (d)-(e), for the bad crystal, impurities/secondary phases as opaque features can be seen, while the good crystal looks clean and well transparent even through polarized light. Moreover, by using this linearly polarized light, we also visualize the mosaic structure, which refers to a crystallographic orientation mismatch between mosaic domains. Commonly, there are also impurities stuffed at the mosaic boundaries.
Figure 1.1: **The comparison of bad and good GdInO$_3$ laser floating zone crystals.** (a) XRD of the two batches. The asterisk denotes the major peak of In$_2$O$_3$ impurity. (b)-(c) Back reflection Laue images of the two batches. (d)-(e) Transmission polarized optical microscope images of the two batches.

### 1.2 Crystal Growth Techniques

#### 1.2.1 Flux method

The basic idea of flux growth is first to heat and melt the target compound in a certain solvent, named flux. Consequently, a super-saturation is created by cooling or flux evaporating so that the crystallization takes place. It has been widely applied in the
growth of research materials as well as the production of industrial and commercial crystals. A very straightforward and practical example of flux growth is the growth of NaCl crystals from a water solution, which can be easily performed in a kitchen. In this case, the water (H₂O) works as a flux.

The choosing of the crucible is critical in the flux growth technique. For oxide materials that are stable in the air even at high temperatures, the platinum crucible (Fig. 1.2 (a)) is the best choice due to its high melting point (> 1700°C) and low reactivity with molten oxides. In the growth of intermetallic compounds, oxygen gas should be strictly avoided. Therefore, the raw materials are placed in an alumina crucible and then sealed in a purged quartz tube. In some cases, a certain amount of Ar gas is filled in the quartz tube so that the gas pressure at a high temperature can prevent the volatile material (such as S and Se) evaporation. Note that though the alumina crucible inevitably contains oxygen, it has been reported that the alumina crucible can facilitate the intermetallic compound growth by absorbing the oxide impurities in the flux [7].

![Figure 1.2: A schematic diagram of the flux growth setup](image)

(a) Platinum crucible (b) Alumina crucible in a sealed quartz tube.

To systematically learn which crystals can be grown by the flux method and which flux
should be chosen, the phase diagrams are critically important. An example is the flux growth of high-T superconductor parent phase $\text{La}_2\text{CuO}_4$ crystals. A $\text{La}_2\text{O}_3$-$\text{CuO}$ phase diagram is shown in Fig. 1.3, and it indicates that even the molar ratio $\text{La}_2\text{O}_3$: $\text{CuO} = 1:1$ in the target phase, heating the equimolar mixture will result in a $\text{La}_2\text{O}_3$ solid phase and a $\text{CuO}$ rich liquid phase, instead of a uniform molten liquid. Like $\text{La}_2\text{CuO}_4$, we call materials that decompose before melting upon heating incongruently melting materials. To grow $\text{La}_2\text{CuO}_4$, a starting mixture with CuO molar concentration of around 80% should be adopted so that the mixture can be melted into a uniform liquid without decomposition, and then the $\text{La}_2\text{CuO}_4$ crystals can be obtained upon cooling. In this case, the excessive CuO works as a flux.

Figure 1.3: **A $\text{La}_2\text{O}_3$-$\text{CuO}$ phase diagram aiming for $\text{La}_2\text{CuO}_4$ crystal growth**

From the discussion above, an excellent advantage of the flux method is that it’s very suitable to grow incongruently melting crystals. By choosing suitable flux, the co-melting point of the system could be lowered below the decomposition temperature, which facilitates the growth of the right phase.
For the compounds with high-T structural phase transition, the choosing of flux concentration can also tune the temperature at which the crystallization happens and manipulate the domain configurations of the resulting crystals. Bi$_2$WO$_6$ has a ferroelectric orthorhombic structure at room temperature, and it transits into a paraelectric tetragonal phase above 860°C. Therefore, if the Bi$_2$WO$_6$ crystal crystallizes above 860°C, it would experience the structural transition during the cooling which may produce orthorhombic twinning domains and vice versa. Na$_2$WO$_4$ is a suitable flux to grow Bi$_2$WO$_6$ crystals. From a reported phase relation shown in Fig. 1.4 (a), the crystallization point during cooling could vary depending on the flux amount ratio. I grow the Bi$_2$WO$_6$ from molten Bi$_2$WO$_6$:Na$_2$WO$_4 = 1:1$ and 1:3 having crystallization point above and below the transition point, respectively, and the 1:1 grown crystal shown in Fig. 1.4 (b) exhibit visible orthorhombic twinning domains, while the 1:3 grown crystal shown in Fig. 1.4 (c) does not. Consistently, those domains show large piezoelectric signal contrast in the in-plane PFM images in Fig. 1.4 (d), confirming that they are also 90° ferroelectric domains. No ferroelectric domains were observed in the 1:1 grown crystal (Fig. 1.4 (e)), suggesting that the crystal grown below the structure transition point tends to have a mono structure domain.
Figure 1.4: The tuning of crystallization temperature of Bi$_2$WO$_6$. (a) The mixture melting point as a function of the Bi$_2$WO$_6$ concentration in Na$_2$WO$_4$ flux from Ref. [8]. The solid and open circles represent the heating and cooling process, respectively. (b), (c) the optical microscope image of Bi$_2$WO$_6$ crystals grown from Bi$_2$WO$_6$:Na$_2$WO$_4$ = 1:1 and 1:3, respectively. (d) The PFM image of the crystal in (b) shows ferroelectric orthorhombic twinning domains. (e) The PFM image of the crystal in (c) shows no ferroelectric domains.

1.2.2 CVT method

Most crystal growth techniques are based on the liquid to solid transitions. Nevertheless, the chemical vapor transport technique involves the crystallization directly from gas to solid. A schematic diagram of a typical CVT growth setup is shown in Fig. 1.5. The raw materials and certain transport agents (like I$_2$, Cl$_2$, HCl, NH$_4$Cl, TeCl$_4$, and H$_2$O) are sealed in a vacuum quartz tube. The transport agent firstly reacts with the raw materials to form an intermediate gas phase at the starting end with temperature $T_2$, and then this gas diffuses to the other end of the quartz tube, and crystallization happens at the growth end with temperature $T_1$. Note that, unlike the liquid system in which the flux mostly has higher solubility at a higher temperature, the degree of saturation in the gas system strongly depends on the endothermic or exothermic nature of the intermediate reactions. In other words, $T_2$ is not necessarily higher than $T_1$ [9].
CVT growth has been widely applied in the growth of 2D materials [10]. Meanwhile, CVT growth has the merit to grow transition metal oxides for the following reasons. First, the $d$ orbitals of transition metal ions provide the good capability to attach halogen ions like Cl$^-$ or I$^-$ as ligands. Second, even for the materials with intermediate valence transition metal ions, the vacuumed quartz tube can avoid oxidation and facilitate the growth of the right phase. Moreover, the transition metal oxides usually have low reactivity with the quartz tube. Fig. 1.6 shows two examples of sizable crystals grown using the CVT technique.

Figure 1.6: Examples of CVT-grown crystals. (a) A FeZnMo$_3$O$_8$ crystal from one-month CVT growth. (b) A Ni$_2$V$_2$O$_7$ crystal from three-week CVT growth.

### 1.2.3 Floating zone method
In the floating zone technique, first, the polycrystalline raw materials are shaped into a rod, named feed rod, by hydrostatic pressure and following sintering. Then, a liquid zone is created by zone heating in a floating zone furnace with a proper seeding with a seed rod. During growth, the liquid zone is moved through the feed rod, and the crystallization happens at the liquid-solid boundary behind the motion of the liquid zone. Unlike all techniques mentioned above, the floating zone is the only crucible-free growth technique, so it has the advantages of avoiding impurities from the crucibles and the capability to grow ultra-high melting point materials.

The heating elements and corresponding temperature profiles are critical to the floating zone crystal quality. There are several designs of heating elements in commercial floating zone furnaces, such as induction coils, halogen lamps (Fig. 1.7 (a)), and electron beams. As a recent advanced model, the laser-diode-heated floating zone (LFZ) technique, which adopts lasers as heating elements, has innovated a great breakthrough in single crystal material science. The schematic diagram in Fig. 1.7 (b) describes the commercial LFZ model from Crystal System Corporation, Japan. The heating element includes 5 lasers with wavelength 800 – 1100 nm. Each laser has a maximum power of 200 W. This design shows many merits. First, the high-power and well-focused lasers can reach maximal 3000°C of the heating spot, which can even melt extremely refractory materials like HfO₂. Second, focused heating can significantly reduce the evaporation loss during the growth, so that facilitate the growth of crystals with volatile components such as In₂O₃ in REInO₃ and SnO₂ in Sr₃Sn₂O₇. Third, the focused heating also produces a high temperature gradient across the growth interface, which allows
rapid cooling of the crystal after crystallization and helps to stabilize metastable phases and high-temperature phases such as metastable orthorhombic phase in HfO$_2$ and high-temperature-stable BaCoSiO$_4$. Moreover, the conventional floating zone technique is mostly applied to the growth of congruently melting materials such as Silicon, Sapphire, and SrTiO$_3$. Although a traveling solvent idea, i.e. applying a flux as the molten zone, have been performed for incongruently melting crystal growth such as (La,Sr)$_2$CuO$_4$, the severe attacking from the molten zone to the feed rod limits its application to systems like La$_{2-x}$Ba$_x$CuO$_4$ (x > 0.11) and BiFeO$_3$. Instead, the large temperature gradient of the LFZ technique creates a sharp growth interface, efficiently prevents the attacking of feed rod, and facilitates the growth of incongruently melting materials by the traveling solvent method.


1.3 Ferroic orders

A ferroic order is a spontaneous switchable ordering which is associated with the breaking of symmetry. The ferroic orders in real materials are perennial topics for rich science and the essence for numerous technological applications. Ferroic orders can be categorized into four groups in terms of even (+) or odd (-) parity under SI and TR operations, which is displayed in Fig. 1.8. Commonly, we have SI’TR’ electric polarization and SI’TR’ magnetization in polar and ferromagnetic materials, respectively. In ferro-rotational orders, the local polarizations form a vortex-like head-to-tail arrangement with an out-of-plane axial vector, which is invariant under both SI
and TR (SI TR) [11]. The ferro-toroidicity is the magnetic version of ferro-rotation by relacing rotating local polarizations with spins, and flips under both SI and TR (SI TR) [12, 13]. To date, the understanding of domain configuration and cross-coupling of ferro-rotation and ferro-toroidicity are still elusive, partially due to that the material candidates of ferro-rotation and ferro-toroidicity are rather limited. Remarkably, BaCoSiO₄ discussed in Chapter 3 exhibits all four of polarization, magnetization, ferro-rotation, and ferro-toroidal orders at different temperatures.

![Four types of ferroic orders in terms of the symmetry of vector order parameters](image)

**Fig. 1.8:** Four types of ferroic orders in terms of the symmetry of vector order parameters [14].

### 1.4 Magnetoelectricity

The Magnetoelectric (ME) effect is one example of the cross-coupling of ferroic orders [15], which allows the control of polarizations by magnetic fields or magnetizations by electric fields. The first experimental demonstration of the ME effect was performed on Cr₂O₃ shown to have linear ME coefficient $\alpha_{zz} = 4.13 \text{ ps m}^{-1}$ [16-19]. In terms of
symmetry, the linear ME effect requires a spontaneously broken time reversal and a certain broken spatial symmetry, such as mirror, rotation, and inversion. Moreover, combining them generates a symmetry operation that is not broken. Using Cr₂O₃ as an example, the lattice is centrosymmetric and contains a 3-fold rotation symmetry along the c axis. The AFM order below \( T_N \approx 307 \) K breaks that rotation symmetry as well as the time-reversal symmetry. However, combining them gives an unbroken symmetry operation -3′ in the magnetic point group, which is the origin of the linear ME effect long c axis in Cr₂O₃. Subsequently, researchers have discovered various ME compounds such as TbPO₄ [20], Fe₂Mo₃O₈ [21], and Ni₃TeO₆ [22]. Unlike above materials showing induced magnetization/polarization parallel to the applied field, it was found that the magnetic toroidicity allows the control of magnetization/polarization by fields perpendicular to them [13], as illustrated in materials such as LiNiPO₄ [23], LiCoPO₄ [24], LiFeSi₂O₆ [25], and Ga₂₋ₓFeₓO₃ [26]. This off-diagonal ME effect provides an opportunity for next-generation ME devices with additional functionalities. However, besides those compounds mentioned above, the exploration of off-diagonal ME materials is very limited to date. In Chapter 3, the successful experimental demonstration of the off-diagonal ME effect induced by field-tunable toroidal moments will be discussed in detail.
2 Chapter 2 – Ferroelectric Single Crystals

2.1 Phenomenological Theory of Ferroelectric Transitions

Polar lattices allow non-zero electric polarization. We call it ferroelectricity if this polarization is switchable by an external electric field. Among 32 crystal point groups, there are 10 polar groups, which are 4, 4mm (Tetragonal), mm2 (Orthorhombic), 6, 6mm (Hexagonal), 3, 3m (Trigonal), 2, m (Monoclinic), and 1 (Triclinic). Ferroelectric materials should have symmetry belonging to the polar point groups displayed above.

After the first realization of ferroelectricity is in Rochelle salt by Pockels in Gottingen as early as 1894, numerous ferroelectric materials have been investigated and general theory for ferroelectricity has been established. Ferroelectricity always combines with a Curie temperature above which a ferroelectric material transits into a higher symmetry phase, loses its ferroelectricity, and becomes paraelectric. In other words, ferroelectricity could be regarded as spontaneous lattice instability below the Curie temperature, i.e., a non-zero minimum in free energy. In this regard, ferroelectricity can be categorized into proper ferroelectricity and improper ferroelectricity. In proper ferroelectricity, the free energy has a single minimum at $P = 0$ when the temperature is higher than Curie temperature, representing the paraelectric situation. As the temperature goes below the Curie temperature, double-well minimums develop at $\pm P \neq 0$ corresponding to the two switchable states of a ferroelectric lattice. The expression of proper ferroelectric free energy is displayed in Figure 2.1 (a) with a
schematic lattice structure of two opposite polarization states in BaTiO$_3$, which is a
typical example of proper ferroelectricity. Unlike proper ferroelectricity, improper
ferroelectricity has free energy all the way single minimum at any temperature.
However, the expression of free energy includes another order parameter $R$ coupled
with polarization, so that non-zero polarization could be induced by non-zero $R$, and
flipping $R$ can flip polarization as well. In the case of hexagonal REMnO$_3$ shown in
Fig. 2.1 (b), $R$ represents a magnetic order. In other words, improper ferroelectricity is
a byproduct of another order.

As a special type of improper ferroelectricity, hybrid improper ferroelectrics (HIFs) are
materials with spontaneous electric polarization that couples to multiple non-polar
lattice distortions e.g., $Qx_2^+$ rotation and $Qx_3^-$ tilting in R-P phase A$_3$B$_2$O$_7$ system (Fig.
2.1 (c)) - a new type of ferroelectricity that was only discovered and appreciated over
the last two decades [27-29]. Hybrid improper ferroelectricity was first realized
experimentally in 2008 in PbTiO$_3$/SrTiO$_3$ multilayers [27] and more recently in 2015
experimental switching of electric polarization in Ca$_3$Ti$_2$O$_7$ bulk crystals was
demonstrated [29]. Over the past few years, several HIF candidates have been identified
using a combination of group-theoretical symmetry analysis and first-principle
calculations [30, 31], and HIF has been revealed in Ruddlesden-Popper (RP) phases
[29, 32, 33], Dion-Jacobson layered perovskite oxides [34, 35], perovskite superlattices
[27, 36, 37] as well as metal-organic molecular perovskites [38, 39]. The potential to
cross-couple order parameters within HIFs makes them of great interest for materials
by design, for example, to realize room-temperature magnetoelectricity [40] or large
uniaxial negative thermal expansion [41]. However, the large switching barrier associated with the geometric origin of HIF still hinders the development of functional HIFs [42].

Figure 2.1: (a) The free energy as a function of the polarization of proper ferroelectricity, and the ferroelectric lattice structure of an example BaTiO$_3$. (b) The free energy as a function of the polarization of improper ferroelectricity, and the ferroelectric lattice structure of an example REMnO$_3$. (c) The free energy with the trilinear coupling of lattice modes in hybrid improper ferroelectricity, and the ferroelectric lattice structure of an example R-P phase A$_3$B$_2$O$_7$.

Recently, ferroelectricity is still a popular topic attracting huge research interest, and people have theoretically and experimentally demonstrated several novel approaches to unconventional ferroelectricity, such as low-dimension ferroelectricity in materials like CIPS [43] and stacking ferroelectricity in (twisted) bilayer materials [44]. In the following sections of this chapter, the experimental signature of highly tunable hybrid improper ferroelectricity in Sr$_3$Sn$_2$O$_7$ crystals and metastable ferroelectric phase in HfO$_2$:Y bulk crystals will be discussed.
2.2 Hybrid Improper Ferroelectric Sr$_3$Sn$_2$O$_7$ Single Crystal

2.2.1 Motivation

Recent studies have found that ferroelastic domain walls in orthorhombic HIFs mediate a 90° rotation of the polarization vector and are mobile, switchable, [45-48] and incorporated as Néel-type domain walls screening head-to-head and tail-to-tail dipoles in 180° domain walls [31]. Due to these factors, the predicted inaccessibly large switching barriers of HIFs turned out to be accessible experimentally, partially due to a multi-step switching mechanism [29, 46, 48]. For example, the ferroelectric polarization switching coercive field is 120-180 kV/cm in Ca$_{3-x}$Sr$_x$Ti$_2$O$_7$ (x=0, 0.54, 0.85) single crystal [29], 75-160 kV/cm in Ca$_3$(Ti$_{1-x}$Mn$_x$)$_2$O$_7$ ceramic [49] and single crystal [50], 150 kV/cm in Sr$_3$Sn$_2$O$_7$ polycrystalline sample [46], 100 kV/cm in Sr$_3$Zr$_2$O$_7$ polycrystalline sample [32] and 180 kV/cm in CsBiNb$_2$O$_7$ [51] polycrystalline sample. Nevertheless, these electric coercive fields are an order of magnitude larger than that those of proper ferroelectrics such as Pb(Zr,Ti)O$_3$ [52] and BiFeO$_3$ [53], which have coercive fields of 7 kV/cm and 15 kV/cm, respectively. Therefore, searching for hybrid improper ferroelectric with lower coercivity is urgently needed for further experimental investigation and industrial applications of this type of materials.

2.2.2 Crystal Growth

In the ceramic sample synthesized by conventional solid-state reaction, no hint of decomposition was observed even after 1600°C sintering. Therefore, Sr$_3$Sn$_2$O$_7$ seems a
congruently melting material, suggesting floating zone technique is feasible for the crystal growth. However, the molten liquid is not stable due to the high vapor pressure of SnO2. Actually, SnO2 sublimes above 1600°C at ambient pressure, but the melting temperature of Sr3Sn2O7 is higher than 2000°C. Utilizing LFZ could efficiently overcome those challenging and facilitate the successful growth of Sr3Sn2O7 crystal. First, LFZ is equipped with well-focused and high-power lasers, which produces enough output to melt Sr3Sn2O7 having melting point > 2000°C. Second, 9 bar oxygen pressure was applied to suppress the evaporation of SnO2. Ar pressure was also tried, however, it resulted in more evaporation and mostly Sr2SnO4 product. Therefore, the mechanism of oxygen pressure suppressing evaporation is more chemistry effect instead of simple physical increasing of the environment pressure. In other words, the Sr3Sn2O7 phase is thermodynamically favored in rich oxygen, while the Sr2SnO4 phase is more stable with oxygen deficiency. Similar mechanism that different oxygen partial pressure favors different R-P phases has also been reported in Ca_{n+1}Ru_nO_{3n+1} system [54]. Then, a test growth was done to find out the mass loss ratio, with a result suggesting that 50% excessive SnO2 should be added to compensate the evaporation loss at the growth rate 30 mm/h. This mass loss testing strategy is also reported in the floating growth of Sr_{n+1}Ru_nO_{3n+1} which similarly contains a volatile raw material RuO2 [55]. Finally, a real growth is performed with 50% excessive SnO2 in 9 bar O2 at the growth rate of 30 mm/h. The growth was all the way stable and a uniform crystal rod up to 11 cm in length was finally obtained showing in Fig. 2.2 (a). Note that 30 mm/h is a relatively fast growth rate comparing to usual examples, thus the crystal rod is not
an entire single crystal and crystal mosaics are even visible after cleaving the rod, indicating by buckling of the ab planes (Fig. 2.2 (b)). However, due to the layer nature of this material, it’s still easy to cleave and separate single crystal specimens with millimeter size. The as-grown \( \text{Sr}_3\text{Sn}_2\text{O}_7 \) single crystal is confirmed to crystallize in a polar space group \( A2_{1}am \) with lattice parameters \( a=5.733 \) Å, \( b=5.7057 \) Å, and \( c=20.6637 \) Å by XRD shown in Fig. 2.2 (c). The polarization lies along the \( a \)-axis \( (a>b) \) and comes mainly from Sr displacements. Due to the close \( a \) and \( b \) axis length, the orthorhombic twinning originated from switching \( a \) and \( b \) could happen. As shown in Fig. 2.2 (e), straight orthorhombic twinning domains are visible under polarized light on the cleaved surface of as-grown \( \text{Sr}_3\text{Sn}_2\text{O}_7 \) single crystal. In the following, it will be shown that these orthorhombic twinning domains are ferroelastic domains as well as \( 90^\circ \) ferroelectric domains.

Fig. 2.2: (a) A photo of LFZ as-grown \( \text{Sr}_3\text{Sn}_2\text{O}_7 \) crystal rod. (b) A photo of a cleaved piece. (c) The RT XRD and structure refinement results. (d) A reflection optical microscope image on a cleaved \( ab \) plane with natural light. (e) A reflection optical microscope image on a cleaved \( ab \) plane with linearly polarized light and an analyzer.
2.2.3 Low Coercivity

The ferroelectricity of Sr$_3$Sn$_2$O$_7$ is demonstrated by PUND method P-E measurement shown in Fig. 2.3 (a). The remnant polarization reaches 1.5 μC/cm$^2$ by electric field along [010], which is parallel or perpendicular to the polarizations in different orthorhombic twinning domains. Remarkably, this value is larger than the remnant polarization 1.1 μC/cm$^2$ obtained by field along [110] which is 45° to all polarizations thus supposed to have measurable polarization $P_{\text{max}}/\sqrt{2}$. This result suggests that not only 180° switching but also 90° switching occurs when applying electric field along [010], and we can conclude the $P_{\text{max}}$ is equal to 1.5 μC/cm$^2$ which is consistent with observed $P_{\text{max}}/\sqrt{2} = 1.1$ μC/cm$^2$. Surprisingly, the remnant polarization is significantly enhanced, as well as the coercive field is much suppressed. There are several reasons accounting for the different ferroelectric behaviors between the ceramic and single crystal. First, the single crystal is free of grain boundaries and thus diminishes the leakage, which ensures the applied voltage can more efficiently switch the polarization. Second, the polarization can be fully poled into one direction in the anisotropic single crystal, while the polarization is only partially saturated in ceramics with mixed crystallographic orientation grains. Moreover, the grain boundary in ceramics could pin the motion of ferroelectric domains.

The observed low coercivity of Sr$_3$Sn$_2$O$_7$ leads to an intriguing phenomenon – a small-strain-induced 90° polarization switch. As shown in Fig 2.2 (c), in-situ transmission polarized microscope images are continuously recorded in a press-and-release process
with strain applied by a tweezer along [100]/[010]. The compressive strain estimated to be linear and obtained by $\Delta L/L$ parallel to the compressive force direction. A clear change of the orthorhombic twinning domain starts to take place at a tiny coercivity < 1%. Then, the crystal becomes almost single twinning domain near the maximum strain ~ 4%. After releasing, some twinning domains recover but not all the way back to the initial ratio. Meanwhile, the strain after releasing (green star) also deviates from the state before pressing (yellow star). The observed strain-tunable twining domain, hysteresis behavior, as well as the remnant strain all indicate a ferroelasticity in addition to the ferroelectricity. Other compounds in this ferroelastic-ferroelectric crystal family include famous Rochelle salt and lead lanthanum zirconate titanate. Commonly, they all have non-180° ferroelectric domains, which are ferroelastic domains too, just like the 90° ferroelectric twinning domain in Sr$_3$Sn$_2$O$_7$.

Figure 2.3: (a) The P-E and J-E loops measured on Sr$_3$Sn$_2$O$_7$ single crystal with E along [010] (red) and [110] (blue). (b) The normalized P-E loops of Sr$_3$Sn$_2$O$_7$ crystal [010], Sr$_3$Sn$_2$O$_7$ crystal [110], Sr$_3$Sn$_2$O$_7$ poly, and (Ca,Sr)$_3$Ti$_2$O$_7$ [110]. (c) The orthorhombic twin domain ratio as a function of strain along [010], and corresponding t-POM images of each data point.

2.2.4 Discussion
To understand the small electric and stress coercivity of the Sr$_3$Sn$_2$O$_7$ single crystal, we calculate the energetics of different polarization switching paths using DFT and the nudged-elastic-band (NEB) method, as shown in Fig. 2.4 (i). Along each path, the polarization reverses by 180° as the switching coordinate changes from 0 to 1. Due to the HIF mechanism, the polarization is trilinearly coupled to the $a'^0c^0$ octahedral tilt and the $a^0a^+c^+$ octahedral rotation, so when the polarization reverses by 180°, the sense of either the tilt or the rotation also must reverse. As a result, there are several symmetry-distinct pathways to reverse the polarization. There are two ‘one-step’ paths, where the polarization and the octahedral tilt ($a'a^0c^0$, blue curve) or the octahedral rotation ($a^0a^+c^+$, green curve) amplitudes go through zero at the midpoint of the path. In addition, there are several symmetry-distinct two-step paths[48]. Here we consider ‘two-step’ paths where the polarization reverses by making two 90° steps (red curve) and where the polarization reverses by passing through a low-energy antipolar structural phase. The antipolar phase contains the same pattern of Sr displacements in each perovskite slab as in the polar ground state but the displacements in adjacent slabs are in opposite directions. The energy barriers for the switching paths in Fig. 2.4 (i) are 125 meV f.u.$^{-1}$ (reverse tilt), 41 meV f.u.$^{-1}$ (reverse rotation), and 39 meV f.u.$^{-1}$ (90° switching), and 24 meV f.u.$^{-1}$ (antipolar switching). These barriers are about a factor of two lower than the corresponding barriers for the prototypical HIF Ca$_3$Ti$_2$O$_7$ (which are 180 mev f.u.$^{-1}$, 112 mev f.u.$^{-1}$, 82 mev f.u.$^{-1}$, and 64 meV f.u.$^{-1}$, respectively), which may explain why Sr$_3$Sn$_2$O$_7$ has a lower coercive field. In addition, the energy barriers for the 90° switching and the 180° switching (reversing rotation) are quite similar,
which supports the hypothesis that both 90° and 180° polarization flipping happen in Sr₃Sn₂O₇ under an external electric field. This explains why the remnant polarization along [100] is larger than that along [110] as shown in Fig. 2.3 (a), as well as the observed small coercivity of erasing and generating FA domains. The antipolar switching path, which has the lowest energy barrier, describes polarization flipping via motion of “stacked” domain walls along the c (long) axis. This type of switching has been observed in polycrystalline Sr₃Sn₂O₇ samples [46] which is shown in Fig. 2.4 (a)-(h).
Figure 2.4: (a)-(f) A in-situ TEM observation of a 180° ferroelectric domain relaxation process in Sr₃Sn₂O₇. (g) The lattice structure of the charged head-to-head wall and non-charged shoulder-to-shoulder wall. (h) A schematic diagram showing the charged and non-charged domain wall pattern. (i) The DFT calculated energy landscape of different 180° polarization switching paths.

The experimental demonstration and theoretical investigation of highly tunable hybrid improper ferroelectricity in Sr₃Sn₂O₇ shed light on a general rule to predict and design hybrid improper ferroelectrics with low coercivity. It is well known that the Goldschmidt tolerance factor $t$ can predict octahedral rotation amplitudes in perovskites based on the ionic size mismatch [56]. A linear relationship between the tolerance factor $t$ and the Curie temperature ($T_c$) of RP-type HIFs has been empirically revealed [57], implying a possible predictive relationship between the amplitude of oxygen octahedral rotations and the ferroelectric switching barrier.

Since ferroelectric switching in HIFs requires the reversal of an octahedral rotation, it is plausible that the switching barrier correlates with the octahedral rotation amplitude. This would suggest that the HIFs with the smallest switching barriers (and coercive fields) are those with the smallest octahedral rotation amplitudes. To explore this idea further, in Table 2.1 we report the octahedral tilting and rotation amplitudes calculated from DFT and obtained from experimentally reported structures for several A₃B₂O₇ materials and the reported polar to non-polar $T_c$. As expected, the octahedral rotation amplitudes correlate with the tolerance factor of the corresponding ABO₃ perovskite so that materials with smaller tolerance factors exhibit larger octahedral rotation amplitudes (and polar distortions, due to the trilinear coupling between octahedral rotations and polarization in HIFs). The material with the tolerance factor closest to 1
is Ca$_3$Mn$_2$O$_7$. However, no meaningful polarization measurement can be obtained at room temperature due to leakiness of the sample [50]. Thus, Sr$_3$Sn$_2$O$_7$ is the experimentally switchable HIF with tolerance factor closest to 1, and thus correspondingly the smallest octahedral rotation amplitudes.

Interestingly, upon contrasting the $a^0a^c$ octahedral tilt and $a^0d^oc^+$ rotation amplitudes in Table 2.1 for Ca$_3$Ti$_2$O$_7$ and Sr$_3$Sn$_2$O$_7$ (which are both experimentally switchable HIFs) we notice that the tilt amplitudes in the two materials are almost identical, while the rotation amplitude in Sr$_3$Sn$_2$O$_7$ is significantly smaller than that in Ca$_3$Ti$_2$O$_7$. This suggests that the amplitude of the $a^0d^oc^+$ octahedral rotation, in particular, may be key for determining the energy barrier for polarization switching. To further support this idea, we note that all the low energy barrier switching paths in Fig. 2.4 (i) (the one-step rotation reversal and the two-step 90° switching and antipolar paths) involve turning the $a^0d^oc^+$ rotation off and on again. In the one-step path, the $a^0d^oc^+$ rotation reverses in all n=2 perovskite slabs, while in the two-step 90° switching and antipolar paths, the $a^0d^oc^+$ rotation sense reverses in alternating perovskite slabs in each step. The $a^0d^oc^+$ octahedral tilt axis also rotates by 90° along the 90° switching path, but this occurs while maintaining an approximately constant octahedral tilt amplitude. This analysis suggests that searching for HIFs with small $a^0d^oc^+$ octahedral rotation amplitudes may be a pathway to realizing even lower coercive fields. However, since the polarization amplitude is generally linked to the rotation amplitude, a challenge is to identify a strategy to maintain a robust polarization while reducing the octahedral rotation. Moreover, increasing the tolerance factor and decreasing the rotation amplitudes
inevitably decreases the ferroelectric $T_c$, as shown in Table 2.1. The $T_c$ of Sr$_3$Sn$_2$O$_7$ is 410 K and close to room temperature, at which experiments were performed. Thus, the low $T_c$ naturally goes together with the low switching barrier.

Table 2.1: Tolerance factors, structural distortion amplitudes, and $T_c$ of A$_3$B$_2$O$_7$ materials with symmetry $A2_1am$.

<table>
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<tbody>
<tr>
<td>Ca$_3$Mn$_2$O$_7$</td>
<td>0.977</td>
<td>0.87</td>
<td>0.79</td>
<td>0.66</td>
<td>0.73</td>
<td>270-320 K</td>
</tr>
<tr>
<td>Sr$_3$Sn$_2$O$_7$</td>
<td>0.957</td>
<td>1.18</td>
<td>0.76</td>
<td>0.89</td>
<td>0.67</td>
<td>410 K</td>
</tr>
<tr>
<td>Ca$_3$Ti$_2$O$_7$</td>
<td>0.946</td>
<td>1.20</td>
<td>0.87</td>
<td>1.01</td>
<td>0.83</td>
<td>1100 K</td>
</tr>
<tr>
<td>Sr$_3$Zr$_2$O$_7$</td>
<td>0.942</td>
<td>1.27</td>
<td>0.86</td>
<td>1.07</td>
<td>0.78</td>
<td>700 K</td>
</tr>
<tr>
<td>Ca$_3$Ru$_2$O$_7$</td>
<td>0.937</td>
<td>1.40</td>
<td>1.11</td>
<td>1.38</td>
<td>1.10</td>
<td>&gt;1073 K</td>
</tr>
<tr>
<td>Ca$_3$Sn$_2$O$_7$</td>
<td>0.905</td>
<td>1.88</td>
<td>1.17</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ca$_3$Zr$_2$O$_7$</td>
<td>0.891</td>
<td>1.94</td>
<td>1.22</td>
<td>-</td>
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Perovskite tolerance factor $t$, $Q_T[DFT]$ of the $a'ac^0$ octahedral tilt and $Q_R[DFT]$ of the $a^0d^0c^+$ octahedral rotation from DFT calculation, $Q_T[Exp]$ of the $a'ac^0$ octahedral tilt and $Q_R[Exp]$ of the $a^0d^0c^+$ octahedral rotation from experimentally determined structure, and reported $T_c$ for several A$_3$B$_2$O$_7$ materials with symmetry $A2_1am$. The DFT distortion amplitudes are reported for a 24 atom cell, and the distortion amplitudes and lattice parameters are given in Å.

### 2.3 Metastable Ferroelectric Phase in HfO$_2$:Y Bulk

**Single Crystal**
2.3.1 Motivation

HfO$_2$ is a famous “high-k” material which has been widely applied in the gate materials as an alternative to thin silicon dioxide gate insulators in silicon technology since 2007 (Fig. 2.5). Remarkably, the continued dimensional scaling-down led to the observation of unexpected ferroelectricity (FE) in ultrathin HfO$_2$ films in both pure and doped forms [58-60]. The good CMOS-compatibility, as well as the robust ferroelectricity down to few layers [61], has strongly suggested hafnia as a promising candidate for the next generation of non-volatile memory devices beyond the PZT-based ferroelectrics [62-64]. In parallel, the application of hafnia-based ferroelectrics as gate insulators into negative capacitance transistors offers an avenue for extending Moore’s law [65, 66].

![Standard silicon transistor vs. High-k insulator + metal gate transistor.](image)

The finding of ferroelectricity in HfO$_2$ based thin films is totally unexpected since all the polymorphs of previous reported HfO$_2$ in bulk form, including high-temperature and high-pressure phases, are all centrosymmetric. These six phases (shown in Fig. 2.6)
include the room temperature monoclinic (m) P21/c phase, the high-temperature tetragonal (t) P42/nmc and cubic (c) Fm-3m phases, and the high-pressure fluorite CaF2-type antipolar orthorhombic Pbcn (o-AP or o-I), disordered Pbcn (o-DO) phases and the cotunnite (PbCl2)-type Pmnb (o-II) phase.

Figure 2.6: (a) Phase diagram of bulk HfO2 at various temperature and pressure. (b) The space groups and conditions of bulk HfO2 polymorphs.

Various work has been done to figure out the origin of ferroelectricity in HfO2-based thin films. For example, in Gd-doped HfO2 thin film, Sang et al. proposed a Pca21 polar orthorhombic phase as the origin of ferroelectricity. On the other hand, by using a different substrate LSMO, Noheda group shows experimental evidence of a new R3m rhombohedral phase as a potential ferroelectric origin of Hf0.5Zr0.5O2 film. Perplexities and confusions arise primarily from the polymorphic nature of hafnia and also from to the challenges associated with the characterization of the mixed/complex phases in ultrathin films at small length scales [67]. The different sets of growth conditions, including dopant species [58, 59, 68-70], substrates [71-74], and capping electrodes [59, 68, 75] all add some degree of uncertainty in these characterizations. Furthermore, various extrinsic factors such as stress [76], oxygen vacancies [77-79], surface energy
and electric fields have been put forward to provide a rationale for the ferroelectricity. Under these circumstances, bulk materials with metastable ferroelectric phase are highly desired.

2.3.2 Crystal Growth

To stabilize the metastable phases in bulk, whose appearance cannot be anticipated from the traditional phase diagrams, the non-equilibrium growth through a quenching process is the key. Laser-Diode-heated Floating Zone furnace (LDFZ) having the merit of well-focused laser diodes as heating sources, resulting in a high maximum temperature around 3,000°C and a steep temperature gradient at the growth interface that enables a much higher quenching rate than the conventional Infrared-Lamp FZ technique. Stoichiometric and high-purity powders of HfO₂ and Y₂O₃ (900°C overnight baked) were mixed in a mortar, pelletized and sintered at 1,500°C in a box furnace for 20 hours with one intermediate grinding. The sintered pellet was grinded into powder, poured into a rubber tube, and pressed into a 3-mm-diameter rod under 8,000 PSI hydrostatic pressure. The compressed rod was sintered at 1,600°C in a box furnace for 10 hours. The crystals were grown at the speed of 20 mm/hour in 0.5 L/min flowing O₂. This growth speed is fast enough to prevent phase separation and slow enough to guarantee good crystallinity. 95% laser power is needed to melt the refractory HfO₂. As shown in Fig. 2.7, crystal rods longer than 10 cm are obtained. The Laue diffraction on pseudo cubic [100] shows clear 4-fold pattern but broad peaks, suggesting the existing of nano domains, which will be discussed later. Consistently,
complex twinning-like feature is observed in transmission polarized microscope of polished crystals (Fig. 2.8). As shown in Fig. 2.9, the XRD of as-grown crystal is much different with the poly crystalline sample which is simply mixture of monoclinic phase and cubic phase, indicating the formation of metastable phases. Annealing the as-grown crystal at 1600°C will result in the decomposition of the metastable phase back into monoclinic and cubic phase. Utilizing neutron diffraction, the metastable phase is confirmed to be polar orthorhombic [86].

Figure 2.7: (a) The photo of as-grown 12% Y HfO2 crystal rods. (b) The photo of molten zone during LFZ growth. (c) A back-reflection Laue image taken on a pseudo cubic [100] oriented as-grown crystal.
Figure 2.8: Transmission polarized optical microscope (tPOM) of HfO$_2$:Y crystals. (a)-(b), 12 % HfO$_2$:Y and (c)-(d), 8 % HfO$_2$:Y, showing distinct crisscross of needle-like domains of one cutting surface. 12 % HfO$_2$:Y belongs to the pure $\alpha$-FE phase while a mixed phases of cubic, monoclinic and $\alpha$-AP phases contribute to the complicated local features in 8 % HfO$_2$:Y.

Figure 2.9: (a) The XRD of polycrystalline, as-grown crystal, and 1600C 10h annealed crystal of 12 % Y HfO2 shown by black, red, and blue curves, respectively. (b) The zoomed-in region near the main peaks. The vertical dashed lines denote the two main peaks belongs to monoclinic phase.

2.3.3 Structural Phase Diagram

Fig. 2.10 shows the X-ray diffraction pattern (XRD) for pristine HfO$_2$:Y crystals with
different Yttrium doping concentrations. As revealed, the ground state of non-doped HfO\(_2\) crystal is monoclinic, and Y-rich ends in the cubic phase, similar to the famous Yttrium-stabilized Zirconia (YSZ). Surprisingly, new peaks appear (at \(2\theta = 35^\circ, 43.5^\circ, \text{ and } 75^\circ\)) within the 8-12 % Y doping while they disappear after a high-temperature (1,600°C) annealing, indicating the meta-stability of the new phases (Supplementary Figure 1). 12 % HfO\(_2\):Y is particularly interesting as the monoclinic phase is fully suppressed, accompanying the disappearance of (11-1)\(_m\) and (111)\(_m\) reflections at \(2\theta = 28.5^\circ\) and 31.7° (Figure 1a). The profile fitting leads to tetragonal/orthorhombic unit cells with aspect ratio \(c/a\) or \(2b/(a+c)\) \(\approx\) 1.01 and possible candidates of either \(t\), \(o\)-AP, \(o\)-DO, or \(o\)-FE phases. The similarity comes that \(o\)-AP can be considered alternate stacks of \(o\)-FE domains and resulting in the \(a\)-lattice doubling while the \(o\)-DO can be treated as a macroscopic average of \(o\)-FE domains [87].

Figure 2.10: The XRD of 0%, 7%, 8%, 10%, 11%, 12%, and 20% Y-doped HfO2 LFZ
as-grown crystals. The vertical dashed line denotes a fingerprint peak from metastable orthorhombic phase, which doesn’t overlap with peaks from other phases.

A representative crystal image of 12% HfO₂:Y is presented in Fig. 2.7 (a). Up to 50 mm long HfO₂:Y transparent crystal boule can be grown. Transmission polarized optical microscope (Fig. 2.8) reveals a tweed texture on a cutting surface, namely a crisscross of needle-like domains, which is typical in orthorhombic systems with fine orthorhombic twins. The twin character can be recognized in the fact that domain contrast reversal by manipulating the analyzer under transmission polarized optical microscope. We notice 8-12 % HfO₂:Y crystals share some general features of tweed textures but whose details can vary (Fig. 2.8). The orthogonal nature of the tweed textures is further confirmed by selected area electron diffraction (SAED) patterns under TEM (Fig. 2.11 (b)-(d)) which rule out the presence of the t phase. The cell-doubling superlattice peaks, i.e. o-AP, persist in 8-11 % range which can be clearly identified through a sequence of SAED patterns, whereas they disappear in the 12 % HfO₂:Y crystal (Fig. 2.11 (c)). A closer examination of those SAED patterns in the 12 % HfO₂:Y crystal reveals no peak splitting or diffuse streaking attributing to the formation of mixed phases or defects. The comprehensive structural analysis leads to the non-equilibrium phase diagram (Fig. 2.11 (a)), which is distinct from the known HfO₂-Y₂O₃ binary phase diagram reflecting equilibrium states [88]. In other words, the polycrystalline ceramics and the LFZ single crystals can have quite different phases even they have the same Y doping concentration (Fig. 2.9), because of different thermal histories.
2.3.4 Ferroelectric Domains and Ferroelectricity

The bulk orthorhombicity which defined by $\epsilon = \frac{(c-a)}{(c+a)}*100\% = 0.017\%$ in present work is about six times smaller than the reported value 0.099 % in the HfO$_2$:Gd thin film [89]. The small orthorhombicity explains in part the tweed textures observed in Transmission polarized optical microscope (Fig. 2.8). Those fine ac tweeds occur because of the ferroelastic spontaneous strain and are characterized by a crosshatching up to a few hundred nanometers in length. The atomically resolved positions of the projected Hf atom sublattice and the tweed boundary are readily determined using high-angle annular dark-field (HAADF) STEM which displays strong contrast associated with the heavy Hf atoms (Fig. 2.12 (a)-(b)). Fig. 2.12 (c)-(d) indicate a 90° rotation of the diffractograms by fast Fourier transform (FFT) operations of green and red selected areas in Figure 3a. In real space, the periodic short-long Hf-Hf bonding along the $a$-axis revealed by overlaid color-coded o-FE unit cells also rotates 90° across the tweed.
boundary oriented along [101]₀-FE. Since the polarization is along the c-axis, these ac tweed walls are 90°-type FE domain walls. Consequently, the microstructures perpendicular to [010]₀-FE, i.e. [100]₀-FE and [001]₀-FE are similar, with abundant irregular shaped ab and bc twin domains within a few hundred nanometers in size. There is almost an equal distribution of ab and bc domains. A further zoomed-in HAADF-STEM image of one ab/bc twin wall (Fig. 2.12 (b)) shows an atomically coherent wall along the longest b-axis. The crystallographic orientation of ab/bc domains is confirmed by the diffractograms of purple and blue selected areas (Fig. 2.12 (c)-(f)) by FFT operations. Inside those ferroelastic ac/ab/bc domains, there exist 180°-type FE domains in a hundred nanometer scale or less. Fig. 2.12 (g)-(h) display the DF-TEM images of FE domains with bright and grey contrasts viewing along [111]₀-FE direction, resulting from the non-equal diffraction intensity due to the broken space-inversion of the o-FE phase. The domains with two different contrasts are associated with the ±c polar axes as indicated by white arrows. The yellow arrows mark the ferroelastic domain walls, in which the contrast remains deep-dark when ±g = (11\overline{2}) spots were excited (Fig. 2.12 (g)-(h)). Our DF-TEM images demonstrate consistently the presence of 180° and 90° FE domains.
Figure 2.12: (a) and (b), High-angle annular dark-field (HAADF)–STEM images taken on [010]$_{o}$-FE and [001]$_{o}$-FE cut crystals, respectively. (c) to (f), the diffractograms of selected area shown by colored squares in (a) and (b). (g) and (f), the Friedel pair breaking of 180° ferroelectric domains seen by dark field TEM on [111]$_{o}$-FE cut crystal.

A pristine [100]/[001]$_{o}$-FE oriented 12 % HfO$_2$:Y crystal was mechanically polished into a 2.7-μm-thick piece fixed on a back electrode made by Silver epoxy. The top electrode
with area 15,000 µm² was made by Silver epoxy after polishing. The $P-E$ loop in Fig. 2.12 (i) was measured by the “PUND” method provided in the Ferroelectric Material Test System (RADIANT TECHNOLOGIES INC.) with $V_{\text{max}} = 1,600$ V and $f = 500$ Hz. Wake-up test in Fig. 2.13 was performed on another piece of pristine $[100]/[001]_{\text{o-FE}}$ 12 % HfO$_2$:Y crystal with thickness 3 µm and electrode area 18,000 µm². The hysteresis loops were measured by the “PUND” method provided in the Ferroelectric Material Test System (RADIANT TECHNOLOGIES INC.) with $V_{\text{max}} = 1,400$ V and $f = 500$ Hz. Fig. 2.12 (i) shows polarization vs electric field $P$-$E$ hysteresis loop of a pristine $[100]/[001]_{\text{o-FE}}$ oriented 12 % HfO$_2$:Y crystal at room temperature. The complete current density peaks indicate a fully saturated switching with remnant polarization $2P_r = 6$ µC/cm$^2$ and coercive field $E_c = 4$ MV/cm. Generally, $90^\circ$ switching of ferroelectric domains has higher energy barriers compared to $180^\circ$ switching. In addition, zero remnant polarization was observed when measuring along [010], which strongly suggests that $90^\circ$ switching doesn’t occur here. Therefore, due to abundant $90^\circ$ polar domains in the $ac$ plane, only 50% of the total polarization can be detected when measuring along $[100]/[001]_{\text{o-FE}}$. Based on this assumption, the total $2P_r$ is estimated to be 12 µC/cm$^2$. Compared with previous studies which showed $P_r$ values 45 µC/cm$^2$, 14-17 µC/cm$^2$ and 5 µC/cm$^2$ of 15 nm epitaxial, 10-930 nm polycrystalline and 1 µm epitaxial 7% HfO$_2$:Y films [90-92], respectively, our $P_r$ value is on the same order of magnitude as the 1 µm epitaxial 7% HfO$_2$:Y films. The $E_c$ here seems larger than the reported $E_c$ for those films (2 MV/cm), but it may not reflect the intrinsic difference since $D$-$E$ loops generally give smaller $E_c$ values than $P$-$E$ loops.
Figure 2.13: (a) The first ten P-E loops (\(E_{\text{max}} = 4.67 \text{ MV/cm}, f = 500 \text{ Hz}\)) and the loop after 1E4 cycles (\(E_{\text{max}} = 4.67 \text{ MV/cm}, f = 10,000 \text{ Hz}\)) on a pristine crystal. (b) The first five P-E loops showing slight increasing of \(P\) from 1\(^{\text{st}}\) loop to 3\(^{\text{rd}}\) loop. (c) The first five J-E loops showing sharpening peaks and slight increasing of \(E_c\) from 1\(^{\text{st}}\) loop to 3\(^{\text{rd}}\) loop.

Wake-up effects refer to the remnant polarization increasing or current loop shape
changing after electric field cycles, and have been widely observed in HfO$_2$-based ferroelectric films. The first ten PUND measurements are performed on another [100]/[001]$_{o-FE}$ piece of pristine 12 % HfO$_2$:Y crystal to test possible wake-up effects (Fig. 2.13). Note that the maximum electric field used in the wake-up test (4.67 MV/cm) is slightly lower than the maximum electric field in Figure 3i (5.93 MV/cm) to avoid sample breakdown. Nevertheless, 4.67 MV/cm is still higher than the coercive field 4 MV/cm derived from Fig. 2.12 (i), thus supposed to be enough to activate wake-up effects, if there are any. Fig. 2.13 reveals that $2P_r$ is enhanced by 15 % (4.68 μC/cm$^2$ to 5.38 μC/cm$^2$) as well as $E_c$ slightly increases from 3.69 MV/cm to 3.79 MV/cm in the first three loops. Afterward, both $P_r$ and $E_c$ don’t show any measurable change even after applying a series of 10,000 Hz and 4.67 MV/cm pulses for 1 second. The change of polarization is negligible compared with typically reported wake-up effects in HfO$_2$-based ferroelectric films [93].

Generally, the ferroelectricity always accompanies a well-defined Curie temperature ($T_c$). In Fig. 2.14, the $\alpha$-FE to cubic Curie transition at $T_c \approx 800\pm50^\circ$C is demonstrated utilizing in-situ heating TEM. The clear thermal hysteresis during warming and cooling cycles is the characteristic of a first-order phase transition. $T_c = 450^\circ$C has been observed in 15 nm epitaxial 7 % HfO$_2$:Y films [90]. Recently, the study on $T_c$ of HfO$_2$:Y films with various thickness revealed that thicker films tend to have higher $T_c$, and 550°C has been achieved in 1-μm-thick films [94]. In this sense, $T_c \approx 850^\circ$C for bulk crystals is in agreement with the observed trend while an orthorhombic to cubic, instead of tetragonal, transition is found distinct from what has reported in HfO$_2$:Si and HfO$_2$:Y
thin films[90, 95].

Figure 2.14: (a)-(c), In-situ thermal sequence of SAED patterns of 12 % HfO$_2$:Y along [001]$_{o}$-FE, indicating a $o$-FE to cubic structural transition at ~800±50°C. The clear thermal hysteresis during warming and cooling cycles is the characteristic of first-order phase transition. (d)-(f), A second round in-situ experiment was performed and tilted to [103]$_{o}$-FE zone axis, which is 17° away from the [001]$_{o}$-FE. The SAED pattern observation along [103]$_{o}$-FE ambiguously excludes the existence of tetragonal (t) phase as commonly assigned to be the high-temperature phase in doped HfO$_2$ thin films. Superlattice spots related to $o$-FE phase disappear and reappear upon warming and cooling across the transition. (g) Intensity profiles of the $g = 111$ and $\overline{3} 0 \overline{1}$ peaks as a function of temperature.

2.3.5 Discussion

In contrary to the present work, degrading orthorhombic phase portion and
ferroelectricity with increasing thickness has been widely observed in HfO$_2$-based films [96], which is possibly due to strain relaxation and phase separation. The bulk crystal growth technique provides an alternative to overcome those bottlenecks. HfO$_2$:Y solid solution with uniform Yttrium distribution crystallizes from a molten liquid at temperatures above 2,700°C. After a subsequent rapid cooling, the Yttrium diffusion is frozen resulting in a supersaturation state. The huge chemical pressure from Yttrium supersaturation drives the formation of metastable orthorhombic phases. 1,600°C annealing on pristine HfO$_2$:Y crystals results in the decomposition of the orthorhombic phase into cubic and monoclinic phases (Fig. 2.9), probably because the Yttrium diffusion is activated again at 1,600°C. Annealing with moderate temperatures such as 1,000°C doesn’t change the phase.

In summary, $Pbc2_1$ ferroelectric phase is stabilized in HfO$_2$:Y bulk single crystals for the first time, with switchable polarization $2P_r = 6 \, \mu C/cm^2$ and coercive field $E_c = 4 \, MV/cm$. Abundant 90°/180° ferroelectric domain nature is unveiled in atomic imaging. Our findings break the upper length-scale limit for ferroelectric HfO$_2$, provide insights for an alternative route for polymorphic phase controlling of HfO$_2$, and pave the road for the further exploitation of hafnia-based science and technologies. The large sample size ensures several measurement techniques (such as neutron diffraction) feasible, and is sufficient for the use as substrate material. Moreover, the $Pbca$ phase crystal at room temperature and ambient pressure provides a great opportunity to study the possible antiferroelectricity and field-induce transitions in future. A recent work suggests that the $Pbca$ plays an important role as the intermediate phase of polarization switching.
[97]. A deeper investigation on the $Pbca$ phase in future could be the key to unravel the robust low-dimension ferroelectricity mystery in HfO$_2$. 
3 Chapter 3 – Multiple Ferroic Orders and Toroidal Magnetoelectricity of BaCoSiO$_4$ Single Crystal

3.1 Stuffed Tridymite BaCoSiO$_4$ – a Playground for Ferroic Orders

Silica (SiO$_2$) skeleton, tetrahedron-based chirality, provides a rich family of materials that the chiral universality and polymorphic nature can be examined [98]. BaCoSiO$_4$ belongs to one exciting family, the so-called stuffed tridymite with the general formula ABXO$_4$ (A = alkali and alkaline; B and X are tetrahedrally coordinated cations). Unlike quartz with a SiO$_4$ tetrahedra chain, their corner-shared tetrahedral skeletons build six-membered rings that host the large cation A channels and are packed into a ring-over-ring two-layer structure. Ba-stuffed tridymite derivatives such as BaMnSiO$_4$ [99], BaFeGaO$_4$ [100], BaAl$_2$O$_4$ [101], BaMSiO$_4$ (M = Co, Mg, Zn) [102], Ba(Al, Fe)$_2$O$_4$ [103], and BaZnGeO$_4$ [104] have been studied for their rich physical properties, including improper ferroelectricity [105, 106], photo-dielectric effect [107], stripe domain formation [108], luminescence [109] and phonon softening [110], while BaCoSiO$_4$ has received little attention until recently [111]. BaCoSiO$_4$ crystallizes in the non-centrosymmetric $P6_3$ space group with magnetic Co$^{2+}$ ions, and therefore exhibits several ferroic characters such as chirality, polarity, and magnetizations. Furthermore, BaCoSiO$_4$ undergoes a tripling of $ab$ plane unit cell transition [102], which leads to the corrugation of the Ba$^{2+}$ layers and tetrahedral tilting and Co-trimerization, analogous to the remarkable case of the interplay of the trimerization, magnetism, and polarization.
in the hexagonal rare-earth manganite family [112], while BaCoSiO$_4$ possesses the additional chiral degree of freedom.

Chirality refers to the situation where an object and its mirror image cannot overlap to each other by spatial rotation, i.e., all mirror symmetries are broken in the object. In addition to structural chirality, certain spin arrangements may also develop chirality. We define the concept “magnetic chirality” as a chirality in spin ordered states (i.e., spin ordered states with the absence of any mirror symmetry). Magnetic chirality exists in centrosymmetric lattices of frustrated antiferromagnets [113], as well as non-centrosymmetric or chiral lattices with antisymmetric Dzyaloshinskii-Moriya (DM) exchange interactions [114]. Recently, a novel type of magnetic chirality consisting of in-plane toroidal spins plus an out-of-plane canting was proposed [115], and was, afterwards, experimentally observed in BaCoSiO$_4$. In BaCoSiO$_4$, applying a magnetic field along the $c$ axis can induce “-3 to -1 to 1 to 3” toroidal moment ($TM$) and $c$ axis canting moment ($M_c$) transitions, while the magnetic chirality remains invariant [111], which makes it a fascinating system for controllable $TM$. However, several questions remain not fully understood in BaCoSiO$_4$: what the connection is between the ferrotoroidicity and lattice chirality/polarity, whether the structural domain configuration promises net ferroic quantities, and whether their couplings are experimentally detectable. In this regard, understanding the phase transition routes, revealing ferroic domains, and finding the cross-coupling are critical for the subsequent magnetic studies, optical measurements [116, 117], and multifunctional applications.
3.2 Crystal Growth

We synthesize the BaCoSiO$_4$ single crystal sample using the laser floating zone technique. The powder sample of BaCoSiO$_4$ was prepared by a direct solid-state reaction from stoichiometric mixtures of BaCO$_3$, Co$_3$O$_4$, and SiO$_2$ powders (Alfa Aesar, 99.99%). The mixture was calcined at 900 °C in the air for 12 hours and then re-ground, pelletized, and heated at 1200°C for 20 h and at 1250°C for 50 h with intermediate grindings to ensure a total reaction. At the end of each sintering, a quenching process, i.e., taking the sample out of the furnace quickly at the target temperature, is desired for the correct phase, since BaCoSiO$_4$ tends to decompose at intermediate temperatures. The resulting pure powder sample is supposed to be bright blue in color. Slow cooling can cause significant decomposition, visually indicated by the sample color turning purple. Large single crystals were grown using a laser-diode heated floating zone (LFZ) technique. The optimal growth conditions were growth speed of 2-4 mm/hr, atmospheric airflow of 0.1 L min$^{-1}$, and counter-rotation of the feed and seed rods at 15 and 30 rpm, respectively. The large temperature gradient of LFZ guarantees a rapid cooling on as-grown crystal, which suppresses the decomposition at intermediate temperature. We tried to grow it by conventional optical floating zone, but the crystal quality was poor. Attempt to tailor the ionic ordering by annealing the as-grown crystal at temperature range 850°C to 1200°C also results in significant crystal decomposition (Fig. 3.2 (b)-(c)).
Figure 3.1: (a) The lattice structure of BaCoSiO$_4$. Only one layer (half $c$) is shown for clarity. (b) A photo of LFZ as-grown BaCoSiO$_4$ crystal.

Figure 3.2: (a) The XRD of polycrystalline BaCoSiO$_4$ sintered at 1250C for 10 h
followed by furnace cooling (red curve) and quenching (blue curve). The red asterisks denote peaks from a decomposition product \( \text{Ba}_2\text{CoSi}_2\text{O}_7 \). (b)-(c) The t-POM images of as-grown and annealed crystals.

### 3.3 Multiple Structural Orders

Fig. 3.1 (a) shows the photo of an as-grown LFZ crystal rod, the transmission polarized microscope image of a polished crossection at RT (Fig. 3.4 (a)) shows the crystal is bluish transparent, which is consistent with the insulator nature. More importantly, no chiral domains with different optical activity are observed, suggesting a mono chirality. Analysis of the crystallographic structure can give clue of this mono chirality. At HT, a mixing ionic disorder of Co and Si is expected, showing by the schematic in Fig. 3.3 (a). Note that in the HT phase each site is equal and alternatingly outside and inside the screen, just like a propeller. The symmetry of this HT phase is \( P6_3\overline{2}2 \), still chiral but non-polar, so it can be either mono L or mono R. Therefore, it can be concluded that the mono chiral HT skeleton creates a mono global chirality even at RT. Then, during the cooling of the HT phase, a Co-Si ionic order transition happens, and the mirror symmetry parallel to the screen is broken creating an out-of-plane polarization denoted by + or – shown in Fig. 3.3 (b). For example, in the L+ case, three Si are outside the screen and three Co are inside the screen. Switching the Si and Co will flip the polarization from + to –. Consistently, stripy polar domains are observed in TEM at RT shown in Fig. 3.4 (c). The small length scale of the polar domains is limited by the quenching process. Note that the polarization is actually fixed by the ionic order, so normally this type of polarization is not switchable by electric field, indeed, no hysteresis loop in the RT P-E measurement is obtained, so this material is polar, has
polar domains, but not ferroelectric. During cooling, besides the polar transition, another FR transition takes place as well, which means the apical oxygen atoms tend to deviate or distort from the highest symmetry position, and they form \( c \) clockwise or \( cc \) counterclockwise ferorotation domains shown by yellow arrows in Fig. 3.4 (d). In addition, there are three equal distortion sites to take for each oxygen, therefore \( Z_3 \) vortices are expected to exist, and are observed in TEM at RT as shown in Fig. 3.4 (b).

In total, \( \text{BaCoSiO}_4 \) has two kinds of global chirality L and R, two kinds of polarity + and −, two kinds of ferorotation \( c \) and \( cc \), and three types of vortex domain \( \alpha \beta \gamma \) with \( 120^\circ \) phase difference, resulting \( 2 \times 2 \times 2 \times 3 = 24 \) kinds of domains at RT. Importantly, combining the coexisting of polarity and ferorotations at RT also gives an effective local chirality. This local chirality has many mixed L and R small domains. The key information is that this material has a mono global chirality from the HT prototype lattice, and various local chirality consisting of polarity and ferorotaion.
Figure 3.3: (a) High-temperature prototypic \( \text{P6}_3 \text{22} \) chiral lattice. (b) Two +/- polarities created by Co-Si ionic ordering. (c) Clockwise (c) and Counterclockwise (cc) ferro-rotation and \( 120^\circ \) antiphase domains (\( \alpha, \beta, \gamma \)). (d) The magnetic ferro-toroidicity.
3.4 Non-collinear Magnetism and Magnetic Chirality

BaCoSiO$_4$ holds magnetic Co$^{2+}$ ions forming a triangle lattice (Fig. 3.1 (a)), creating interesting quantum magnetism as well. First, from the anisotropic susceptibility vs. temperature curves shown in Fig. 3.5, there is an in-plane AFM order below 3.2 K, with a large ferromagnetic moment out-of-plane. With large single crystals, our collaborators from ORNL figure out the magnetic structure below the ordering temperature using neutron techniques [111]. For each Co triangles, the spin in-plane component rotates $120^\circ$ with each other, producing a magnetic toroidal moment (TM). In addition, there is
an out-of-plane canted moment for each Co triangle. This magnetic object cannot be overlapped with itself after mirror operation, so it holds a so-called magnetic chirality. There are three Co triangles in each unit cell. At zero field, two of them have same $TM$ and canted moment, while the rest one is opposite. Therefore, it could be interpreted as a ferrimagnetic and ferritoroidal state at zero field. As shown in Fig. 3.6 (a), if applying magnetic field along $c$, a metamagnetic transition at 1.2 T can happen and all three $TM$ and canted moment in each unit cell can be poled into a same direction, generating a ferromagnetic and ferrotoroidal state. Applying field parallel to $ab$ plane seems to have a metamagnetic transition as well. As shown in Fig. 3.6 (b), the in-plane $M-H$ exhibits weak feature starting at around 2 T, which may come from an in-plane spin flop transition suppressing the toroidicity. For the whole crystal, If the magnetic chirality is mono, a net $TM$ can show up. Otherwise, the $TM$ will cancel out.

![Graph](image)

**Figure 3.5:** Anisotropic magnetic susceptibility vs. temperature of BaCoSiO$_4$ single
crystal. The red and black curves represent applied field along \( c \) and \( ab \), respectively. The field is 1000 Oe for both measurements.

Figure 3.6: Anisotropic isothermal (2 K) magnetization vs. magnetic field of BaCoSiO\(_4\) single crystal. (a) Magnetization as a function of applied field along \( c \). The inset shows the hysteresis loop from the \( c \) axis ferrimagnetism at low field regime. (b) Magnetization as a function of applied field along \( ab \).

3.5 Toroidal Magnetoelectricity
Figure 3.7: Magnetoelectricity of BaCoSiO$_4$ single crystal. (a)-(b) Schematic diagrams of cutting and measurement setup of $ab$-plane and $ac$-plane crystal plates. (c) Magnetoelectric polarization as a function of applied fields measured on $ab$ plane (upper panel) and $ac$ plane (lower panel) single crystals at 2 K with magnetic field along various orientations shown in legends. The color of each curve corresponds to the field indicated with same color of arrows in (a) and (b). (d) The 2 K isothermal $M_c(H_c)$ data (magenta), and magnetoelectric polarization as a function of fields pointing 45° in between $c$ and $a$ (olive). The field is normalized by dividing $\sqrt{2}$ to make $c$-component $H_c$ as the $x$ axis. (e) Schematics of the magnetic structure of one Co sublattice. Blue spheres represent Co ions, and cyan and blue arrows show spins and resulting TM and $M_c$, respectively. (f) A schematic showing the “-3 to -1 to 1 to 3” TM and $M_c$ change with applied field along $c$. Polarizations (olive arrows) along $a^*$ are induced with the presence of the magnetic field component along $a$. The narrow shadow area near zero field denotes the tiny hysteresis regime.

As above mentioned, we note two-step structural chirality in BaCoSiO$_4$: (1) the mono global chirality fixed by the very high-temperature parent chiral lattice, and (2) the various local chirality induced by the ferro-rotation with existing polarization, i.e., nanoscale lateral polar domains. Though ferro-rotation, which does not break space inversion, does not induce optical activity, but has symmetry operation similarity (SOS) with a structural chirality in the presence of polarization [117, 118]. Then, the structural chirality can generate magnetic chirality through DM interactions. If the global structural chirality determines magnetic chirality, the whole crystal shall show a mono ferro-toroidal domain when applying magnetic field along the $c$ axis, and TM induced ME effects should be observed [13]; otherwise, not.

We prepared $ab$-plane and $ac$-plane single crystalline plates and tested their ME properties by applying magnetic fields along various directions and collecting the induced current signal. The setup of electrodes and external magnetic field directions is shown in Fig. 3.7 (a) and (b) for $ab$ plane and $ac$ plane plates, respectively. All
measurements are performed at 2 K in a PPMS. For the \textit{ab} plane crystal, magnetic field sweeping along the \textit{c} axis induces a large ME polarization up to 90 \( \mu \text{C/m}^2 \) (Fig. 3.7 (c) upper panel). The anomaly and tripled slope in the polarization curve at \( H_c = \pm 1.2 \text{ T} \) agree with the reported field-induced “1 to 3” \( M_c \) transitions [111]. Therefore, in the \textit{ab} plane crystal, the dominated ME effect happens when both \( E \) and \( H \) parallel to the \textit{c} axis. This behavior is not surprising considering BaCoSiO\(_4\) a non-centrosymmetric hexagonal system with polarization and net magnetization along the \textit{c} axis[21, 22]. As shown in Fig. 3.8, the fitting of \( P_c(H_c) \) by \( P_c = C + \alpha H_c + \beta H_c^2 \) yields \( \alpha = 5.42(2) \) \( \text{ps/m} \), \( \beta = 2.01(6) \times 10^{-18} \text{ s/A} \) for high-field region (1.5 T to 7 T), and \( \alpha = 6.13(7) \text{ ps/m}, \beta = 1.96(4) \times 10^{-18} \text{ s/A} \) for low-field region (0 T to 0.9 T). Note that the \( \alpha \) here is actually the \( \alpha_{zz} \) in the ME tensor. The linear term has the same order of magnitude with the reported \( \alpha_{zz} = 4.13 \text{ ps/m} \) in Cr\(_2\)O\(_3\), and the quadratic term is comparable with the reported \( \beta = 2.959 \times 10^{-18} \text{ s/A} \) in another non-centrosymmetric antiferromagnet Co\(_2\)Mo\(_3\)O\(_8\) [119]. This coexisting of linear term and quadratic term ME effect has also been observed in the high-field region of non-centrosymmetric hexagonal magnet Ni\(_2\)Mo\(_3\)O\(_8\) [120]. In Ni\(_2\)Mo\(_3\)O\(_8\), it has been suggested that the low-field AFM state has a symmetry that does not allow the linear term, while field-induced ferromagnetic moments in high fields could contribute to a linear term. It should be noticed that the magnetic space group of BaCoSiO\(_4\) and high-field Ni\(_2\)Mo\(_3\)O\(_8\) both contain \( c \)-rotation operation \( \mathbf{6} \). Since the space inversion and time reversal are all broken by polar lattices and ferromagnetic moments in \( \mathbf{6} \), it allows both linear and quadratic ME effects along the \( c \) axis. Our results show that the linear term \( \alpha \) remains almost invariant below and
above the “1 to 3” transition, while the quadratic term $\beta$ changes its sign, which suggests that the quadratic term depends more on the ferromagnetic moments while the linear term stays almost unaffected.

Figure 3.8: The fitting of $P_c(H_c)$ curve in the low field (0 T to 0.9 T, inset) and high field (1.5 T to 7 T) regions. Blue and cyan represent polarization $P_c$ and corresponding fitting curves by $P_c = C + \alpha H_c + \beta H_c^2$, respectively. The fitting parameters $\alpha$ and $\beta$ are displayed in the figure.

More interesting behaviors come with the $ac$ plane crystal. As shown in Fig. 3.7 (c) lower panel, among $H$ parallel to $a$ (orange), $c$ (wine), and $a^*$ (cyan) axes, the observed polarization at 2 K with $H//a$ sweeping is much larger than $H//a^*$ and $H//c$ cases. For a
TM along the c axis, the induced ME effect requires \( H \perp c, P \perp c, \) and \( H \perp P, \) which is precisely consistent with the \( P, H \) assignment in which the significant ME effect was detected on the \( ac \) plane crystal. Therefore, we can conclude that the observed off-diagonal ME effect (\( P/\alpha^*, H/\alpha \)) origins from a magnetic toroidicity contribution. In the low-field region (-2 T to 2 T), the induced polarization is nearly linear to the applied field, and then it starts to decrease with larger field. The reason of this behavior could be that large in-plane magnetic field tends to co-align spins and suppress the TM, which may correspond to the weak feature observed in in-plane \( M-H \) curve (Fig. 3.6 (b)). Consistently, we also observed the disappearance of the magneto-dielectric effect at high fields, such as 7 T, as shown in Fig. 3.9.

![Figure 3.9](image)

**Figure 3.9: Dielectric constant versus temperature \( \varepsilon(T) \).** (a) 2 K to 300 K \( \varepsilon(T) \) (black) and dissipation (red) curves measured along \( \alpha^* \) axis with zero magnetic field. (b) 2 K to 6 K \( \varepsilon(T) \) along \( \alpha^* \) axis with 0 T, 1 T, 1.5 T, and 7 T magnetic fields along \( \alpha \), shown by black squares, red circles, blue up-triangles, and green down-triangles, respectively.

Note that even if the magnetic field was applied along the \( \alpha \) axis, practically, there could always exist a tiny \( c \) component of the magnetic field due to misalignment. This tiny \( c \) component could flip the magnetization, especially considering the reported coercive
field of BaCoSiO$_4$ $M_c$ is extremely small, which is only around 50 Oe [111]. To investigate this possibility, a $TM$ induced ME measurement within a low field range -2000 Oe to 2000 Oe was performed and shown in Fig. 3.10. Clear peaks at around ±800 Oe and “butterfly” hysteresis behavior confirm the flipping of $M_c$ by a tiny $c$ component of applied field, as well as the ferroic nature of $TM$. From the reported coercive field of $M_c$, 50 Oe, the misalignment of the magnetic field can be estimated to be 3.5°, which is reasonably small enough. We notice that the induced polarization $P_{a^*}$ is markedly linear to applied magnetic field $H_a$ within -2000 Oe to 800 Oe (ascending) and 2000 Oe to -800 Oe (descending) ranges, with a linear ME coefficient $\alpha = 1.03(4)$ ps/m.

![Figure 3.10](image)

**Figure 3.10:** The low field (-2000 Oe to 2000 Oe) region of $I_{a^*}(H_a)$ (lower panel) and $P_{a^*}(H_a)$ (upper panel). In the lower panel, orange and black lines represent magnetoelastic current $I_{a^*}(H_a)$ at 2 K (below transition) and 5 K (above transition), respectively. The red and blue arrows mark the ascending and descending magnetic
field $H_a$ sweeping loop. In the upper panel, the red and blue curves show the polarization $P_{a*}$ as a function of ascending and descending magnetic field $H_a$, respectively.

We have learned that applying magnetic field along the $c$ axis can triple the $TM$ as well. However, detecting the corresponding ME effect requires a magnetic field component perpendicular to the $c$ axis. Therefore, to reach the ME effect with tripled $TM$, applied $H$ should contain both $c$ and $a$ components. The olive and violet curves in Fig. 3.7 (c) lower panel display ME current and polarization measured in such a way that magnetic field orients $45^\circ$ and $60^\circ$ to the $c$ axis, respectively. Consistently, “1 to 3” $TM$ transitions are observed around 1.6 T (expected to be $1.2 / \cos(45^\circ)$ T) for $H_{45^\circ}$ and 2.4 T (expected to be $1.2 / \cos(60^\circ)$ T) for $H_{60^\circ}$. We normalize the $P_{a*}(H_{45^\circ})$ data into $P_{a*}(H_{c})$ and combine it with $M_{c}-H_{c}$ curve in Fig. 3.7 (d), and the anomalies in $P_{a*}(H_{c})$ precisely coincide with the metamagnetic transitions at $\pm 1.2$ T. The $TM$ induced polarization is nearly linear just below and above the transitions. The tripled $dP/dH$ and magnetization confirm the “1 to 3” $TM$ and $M_{c}$ change. A maximum linear ME coefficient $\alpha = 26.22(6)$ $ps/m$ is obtained at the metamagnetic transition point. Fig. 3.7 (e) shows an example of magnetic structure of a Co triangle sublattice with $TM = +1$ and $M_{c} = +1$, which is also an object of magnetic chirality. The schematics in Fig. 3.7 (f) shows how the three sublattices evolve with $H_{c}$, i.e., “-3 to -1 to 1 to 3” $TM$ and $M_{c}$ transitions.

In summary, BaCoSiO$_4$ single crystal shows not only a conventional $H_{\parallel}P$ type ME effect, but also an exotic $H_{\perp}P$ type $TM$ induced ME effect. These findings strongly suggest that each bulk crystal has a single and invariant magnetic chiral domain, and the mono structural global chirality is possibly the root cause. Note that both global and
local chiral structures have very low symmetry and permit non-zero DM interactions. However, the local chiral contribution is supposed to be canceled out due to the multiple domains. Thus, the observed magnetic chirality only couples with the global chirality. In addition, the observed multi-step and low-barrier control of magnetization and polarization provides insights into next-generation ME and memory devices.

3.6 Discussion on Magnetic Chirality

Clearly, the field-invariant magnetic chirality, which is fixed by global structural chirality, is the essence of BaCoSiO$_4$ to achieve field-tunable TM and ME effect. Therefore, a systematic study on the magnetic chirality could put new insights in the condensed matter physics and point out future study directions. Chirality refers the situation where an object and its mirror image cannot overlap to each other by spatial rotation, i.e., all mirror symmetries are broken in the object even if any spatial rotation is freely allowed. Magnetic chirality means chirality in spin ordered states or (atomic-scale or mesoscopic) spin textures. In addition, chirality should not change with time, so time reversal is unbroken in chirality.

Summarizing all reported spin textures with chirality, there are four types of magnetic chirality: (1) helical spin order, (2) toroidal spin state with a canted moment, (3) Type-I magnetic quadrupole state with alternating canted moments, and (4) Bloch-type skyrmions. Fig. 3.11 is the schematic diagram showing these four cases. (1) exists in compounds like (Ba$_3$NbFe$_3$Si$_2$O$_{14}$) [121], Cr$_{1/3}$TaS$_2$ [122], and Co/Mn-doped Ni$_3$TeO$_6$ [123, 124]. (2) is the case of BaCoSiO$_4$. (3) has been observed in Pb(TiO)Cu$_4$(PO$_4$)$_4$
and Er$_2$Ge$_2$O$_7$ [125, 126], and (4) mostly appears in B20-structure compounds such as MnSi [127].

Numerous new experiments and emergent properties associated with magnetic chirality are proposed/predicted; for example, (a) natural optical activities associated with magnetic chirality need to be further explored, and circular dichroism due to magnetic chirality, especially in the cases without bulk net magnetic moment, needs to be studied, (b) magnetochiral effects (i.e. the directional nonreciprocity in the presence of external magnetic fields) of "toroidal moment + a canted moment" and "Type-I magnetic quadrupole moment + alternating canted moments" need to be investigated, (c) the true magnetic ground state of some compounds with chiral crystallographic lattices, especially triangular lattices, should be carefully reexamined – an example is RENi$_3$(Al,Ga)$_9$, (d) magnetoelectric properties of Er$_2$Ge$_2$O$_7$ need to be studied, (e) the magnetic chirality of helical spin states in centrosymmetric crystallographic lattices can

Figure 3.11: A schematic diagram of four types of magnetic chirality. (a) Helical spins. (b) Toroidal moment + a canted moment. (c) Type-I magnetic quadrupole + alternating canted moments. (d) Bloch-type skyrmions. Blue arrows are spins and red plates are broken mirror symmetries.
be controlled by circularly-polarized light or vortex beams, (f) how vortex beams with orbital angular momentum can couple with either crystallographic chirality or magnetic chirality, etc..
4 Chapter 4 - Outlook

4.1 Unconventional Growth Techniques

4.1.1 Flux Growth in a Horizontal Configuration

The demand for high quality bulk single crystal research materials is still rapidly growing in fields of material science, condensed matter physics, and solid chemistry. For example, the current research interest of quantum spin liquids includes a fingerprint experimental signature i.e., the fractional excitations of the correlated spins. Inelastic neutron scattering is the most direct and convincing technique to detect the fractional excitations, which typically requires grams of bulk single crystals. To meet the growing requirements of new and sizable quantum materials, people never stop to investigate new crystal growth ideas and setups. In 2017, Yan et al. reported a flux growth in a horizontal configuration as an analog to vapor transport growth [128]. The idea is to seal the raw materials and flux into a quartz tube, and the quartz tube is placed horizontally in a tube furnace with a temperature gradient between two ends. The crystallization happens in the space with temperature at which certain phases are stable. Comparing with conventional flux method without temperature gradient, this method has advantages of higher yield and better controllability to grow phases with narrow stable temperature window. Actually, a similar liquid transport idea was also performed in the growth of quantum spin liquid herbertsmithite $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ [129] utilizing water as flux.
4.2.2 Alumina Tube Sealing Technique – The growth of a Chiral Superconductor Mo₃Al₂C

To grow materials that can be oxidized or are highly volatile, an enclosed crucible is needed. The quartz tube is commonly used for this purpose due to its easily shapable nature, however, there are still some limitations. First, the highest working temperature of quartz tubes is only around 1200°C, and the softening of quartz can fail at a higher temperature. Second, the oxide nature of quartz makes it highly reactive with some other oxides such as alkali metal oxides. Third, the relatively low mechanical strength of quartz tubes makes the growth of volatile materials risky. In 2018, the J. F. Mitchell group proposed a growth technique including sealing the raw materials inside an alumina tube by a floating zone furnace [130]. They successfully obtained millimeter-sized Na₄Ir₃O₈ single crystals, and a vapor growth inside the alumina tube is believed to be the growth mechanism, which is facilitated by the volatility of NaO and IrO₂. The Alumina tube can endure much higher temperature and inner pressure than a conventional quartz tube, thus this idea brings tons of opportunities to investigate the growth of air-sensitive or volatile materials at high temperatures. Utilizing laser floating zone, the sealing of Alumina tube can also be easily done at optional oxygen or inert gas atmosphere. In the following, we’ll show an example of the growth of Mo₃Al₂C single crystal in a sealed alumina tube utilizing the laser floating zone.

Chiral superconductors are intriguing quantum materials that are great platforms to study topological non-trivial superconducting states. One of the chiral superconductor candidates Mo₃Al₂C has been reported to crystallize in β-Mn type P4₁32 or P4₃32,
with a superconducting transition around 9 K [131, 132]. There are also reported attempts to grow crystals of Mo₃Al₂C [133], but the sample quality looks poor and no anisotropic measurements or Laue diffractions are shown. Here we show that utilizing the sealed alumina tube technique, high-quality Mo₃Al₂C single crystals can be grown. First, an end of the alumina tube is heated and melted in the laser floating zone furnace. With a little bit of overheating, the viscosity of the molten liquid decreases, and the ring-shaped liquid shrinks into one whole drop. A slow cooling process taking 30 minutes is necessary to prevent the cracking of the alumina tube due to thermal expansion. After solidification, the first end is sealed. Then, small pieces of Mo: Al: C = 3: 4: 1 in the molar ratio are placed into the alumina tube. The excessive Al can work as a flux, but more Al will result in Al₅Mo instead of Mo₃Al₂C as the major product. The filled alumina tube is placed back into the laser floating zone furnace. The chamber is gently pumped and filled with Ar three times to expel the air inside the alumina tube. Then, the second end is sealed under 1 bar Ar gas. A photo of the both-end sealed alumina tube is shown in Fig. 4.1 (a). The sealed alumina tube is heated to 1650°C, and 5°C/h cooled down to 1450°C, then 100°C/h cooled down to RT. Note that such a high temperature is necessary to melt the mixture, and it is impossible to do with a quartz tube. The millimeter-size Mo₃Al₂C crystals with metal luster are mechanically separated after breaking the alumina tube. Fig. 4.1 (b) shows the reflection optical microscope image and the photograph of an as-grown crystal. The crystal quality is confirmed by back-reflection Laue diffraction. Clear 4-fold peaks are observed with cubic [100] direction (Fig. 4.1 (c)). The transport measurement shown in Fig. 4.1 (d)
unveils a superconducting transition at around 8 K as well as a charge density wave transition at around 150 K denoting by the asterisk. Consistently, the superconducting transition is observed in the zero-field-cooling susceptibility vs. temperature curve in Fig. 4.1 (e), while field cooling suppresses the superconducting transition.

Figure 4.1: The growth and superconducting properties of Mo₃Al₂C single crystal. (a) A photo of a sealed alumina tube with Mo, Al, and C inside. (b) The reflection optical microscope image of an as-grown Mo₃Al₂C single crystal. The inset is a camera photo of the same piece of crystal. (c) A back-reflection Laue image taken with cubic [100] orientated crystal. (d) The heating (red) and cooling (blue) four-probe resistivity vs. temperature curves measured with current flowing along [100]. The inset shows the temperature region near the SC transition. The asterisk denotes the charge density wave transition. (e) The zero-field-cooling (black) and field-cooling (red) susceptibility vs. temperature measured with 20 Oe magnetic field along [110]. The inset shows the temperature region near the SC transition.

Our results show that the sealing alumina tube technique not only works for volatile
oxides growth but also works well for high-temperature intermetallic compound growth. In principle, the alumina tube may release oxygen at high temperatures, but practically it is not a serious enough problem that can disturb the crystal growth. Typically, the alumina tube should have much lower reactivity with the molten metals than molten oxides, which provides additional value to extend its application into more high-temperature intermetallic flux growths.

4.2 Future Directions

The projects discussed in this thesis also point out several important future research directions.

(1) The highly tunable ferroelectricity and stress-induced 90° domain switching in Sr₃Sn₂O₇ single crystals suggest that it could show good piezoelectric behaviors as well. A quantitative study of piezoelectricity is needed for future research.

(2) A recent calculation work emphasizes the contribution of free carriers to the polarizations in layered hybrid improper ferroelectrics [134]. Especially, the Ba₂SrSn₂O₇ compound is predicted to hold a free-carrier-induced polar phase. Thus, post-annealing or chemical doping to tune the carrier density of Sr₃Sn₂O₇ and its effect on the ferroelectric behaviors should be experimentally studied.

(3) The metastable ferroelectric phase is experimentally demonstrated in HfO₂:Y bulk single crystal. However, the remnant polarization value (~3 μC/cm²) is smaller than the reported thin films (>10 μC/cm²). The conditions such as dopant concentration and cooling rate may need to be further optimized for larger
remnant polarization value. Other rare earth elements as dopants and their effects on structure and ferroelectricity should also be investigated.

(4) We propose four prototypes of spin texture with magnetic chirality: helical spin order, toroidal spin state with a canted moment \((\text{BaCoSiO}_4)\), type-I magnetic quadrupole state with alternating canted moments, and Bloch-type skyrmions. Numerous new experiments and emergent properties associated with magnetic chirality are proposed/predicted in 3.6 and are desired for future research.

(5) In terms of crystal growth, the laser floating zone technique still has great potential in the synthesis of new quantum materials. For example, the Ce\(^{3+}\) system is interesting due to the single electron and effective S-1/2 which is favored by quantum spin liquid (QSL) states. However, Ce\(^{3+}\)-included oxides are hard to synthesize. In fact, Ce\(_2\)O\(_3\) can be rapidly oxidized to CeO\(_2\) even at ambient conditions. From a chemical point of view, the higher temperature generally favors the lower elemental valence. Therefore, the ultra-high temperature in the laser floating zone could facilitate the stabilization of Ce\(^{3+}\) compounds. As a successful example, we have grown Ce\(_2\)Zr\(_2\)O\(_7\) and Ce\(_2\)Hf\(_2\)O\(_7\) pyrochlore single crystals by laser floating zone with reducing gas flow and a high-temperature molten zone (> 2200°C). Even the feed rod contains room-temperature-stable Ce\(^{4+}\) ions, they are spontaneously and in-situ reduced into Ce\(^{3+}\) during the high-temperature melting process. The crystals show high quality, and no spin freezing is observed down to 0.1 K [135]. Following the same idea, we recently synthesized single crystals of more Ce\(^{3+}\) single-crystalline materials such as B-.
site-disordered pyrochlore Ce$_2$ScNbO$_7$ and 2D triangle magnetic lattice CeMgAl$_{11}$O$_{19}$. The seeking of novel magnetism in those materials is still going on.
Appendix A
Measurement Method

A.1 P-E loop

The idea of measuring P-E is to make a parallel plate capacitor with the sample as the
dielectrics. During applying the electric field, the current signal is recorded and
integrated to get the corresponding polarization change. In real materials, this current
signal contains various contributions including the capacitor component, leakage
component, and ferroelectric polarization switching component. In order to learn the
pure ferroelectric contribution in the obtained P-E loop, the PUND method which can
cancel out the non-remnant component is preferred.

First, the sample is cut and polished into a thin plate with thickness typically less than
100 μm. Silver epoxy is uniformed applied on both surfaces and then carefully cured to
make two electrodes. The electrode area and sample thickness are measured by a ZEISS
optical microscope with a CCD camera connected to a computer.

In the P-E measurement of HfO$_2$:Y single crystals, thinner sample is preferred due to
the large coercive field. An unconventional sample preparation is performed. First, the
crystal is polished into 20 μm. Then, one side is fix on a piece of Silicon substrate with
silver epoxy as back electrode. The fixed crystal is further polished into desired
thickness, typically less than 5 μm. The supporting of Silicon substrate prevents sample
from cracking. Finally, top electrode is made by silver epoxy. Due to the small thickness,
this setup is still approximately a parallel plate capacitor.
The $P-E$ loop is measured by the “PUND” method provided in the Ferroelectric Material Test System (RADIANT TECHNOLOGIES INC.). As shown in Fig. A.1 and A.2, the logic 1 loop has preset pulse and measurement pulse opposite to each other, so it contains both remnant and non-remnant parts. Differently, the logic 0 loop presets the polarization into the same direction with the measurements, so it will not be switched, and only non-remnant part is in the logic 0 loop. The difference of logic 1 and logic 0 gives the loop with pure ferroelectric contribution. Fig. A.3 gives an example.
Figure A.1: Logic 1 loop construction
Figure A.2: Logic 0 loop construction
A.2 Dielectric property

A similar parallel plate capacitor preparation of sample is used for dielectric measurements. The sample is mounted and connected to a multi-functional sample probe adapting PPMS-9, and the temperature and magnetic field control is performed in the PPMS. A Quadtech 7600 LCR meter is used for permittivity $\varepsilon$ measurements. A Keithley 617 electrometer is used to collect pyroelectric and magnetoelectric current signals.

A.3 Magnetic property

$\chi(T)$ and $M(H)$ are performed in a Quantum Design MPMS-XL7.
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