Epitaxy of hexagonal ABO$_3$ quantum materials

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ABSTRACT

Hexagonal ABO$_3$ oxides (A, B = cation) are a class of rich materials for realizing novel quantum phenomena. Their hexagonal symmetry, oxygen trigonal bipyramid coordination, and quasi-two-dimensional layering give rise to properties distinct from those of the cubic ABO$_3$ perovskites. As bulk materials, most of the focus in this class of materials has been on the rare-earth manganites, R MnO$_3$ (R = rare earth); these materials display coupled ferroelectricity and antiferromagnetic order. In this review, we focus on the thin-film manifestations of the hexagonal ABO$_3$ oxides. We cover the stability of the hexagonal oxides and substrates which can be used to template the hexagonal structure. We show how the thin-film geometry not only allows for further tuning of the bulk-stable manganites but also allows for the realization of metastable hexagonal oxides such as the RFeO$_3$ that combine ferroelectricity with weak ferromagnetic order. The thin-film geometry is a promising platform to stabilize additional metastable hexagonal oxides to search for predicted high-temperature superconductivity and topological phases in this class of materials.

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I. INTRODUCTION

Complex oxides display some of the most exotic physical states known. The subtle interplay of Coulomb interactions, electron–lattice coupling, and spin/orbital ordering gives rise to phenomena as diverse as high-temperature superconductivity and ferromagnetism. Synthesizing complex oxides in the thin-film form offers further opportunities to tune the ground state. Here, strain imparted from a substrate, dimensionality in a superlattice architecture, or charge transfer/coupling at an interface can unleash further emergent properties not present in the parent compounds. Moreover, complex oxide thin films not only offer opportunities to study diverse physical phenomena but also could be harnessed for a number of next-generation applications.

To date, however, much of the work on complex oxides in the thin-film form has focused on cubic perovskite oxides. This review focuses on a different class of oxides with the same ABO$_3$ stoichiometry (A, B = cations), the hexagonal oxides. As shown in Fig. 1(a), the crystal structure differs from that of the cubic perovskites: the B-site cation is surrounded by a trigonal bipyramid arrangement of oxygen atoms in contrast to the oxygen octahedra characteristic of the perovskite oxides. Planes of corner-sharing trigonal bipyramids are layered with planes of the A-site cation in a quasi-two-dimensional structure. (We refer the reader to an excellent recent review that covers a more generic class of hexagonal oxides that include face-sharing polyhedra and other structural types.) We focus on this class of materials not to generically expand the study of oxide compounds but specifically because the distinct symmetry and the crystal field environment can offer unique opportunities to realize novel properties not present in the cubic perovskite oxides.

While considerably less studied than the perovskite oxides, the hexagonal ABO$_3$ materials also display a rich array of physical phenomena (see overview in Table I). The most commonly studied hexagonal oxides are the rare-earth manganites, R MnO$_3$, where R = Sc, Y, In, and Dy–Lu. These materials display robust improper...
ferroelectricity well above room temperature as a consequence of a lattice trimerization involving a coordinated tilting of the MnO$_5$ bipyramids and a distortion of the rare-earth ion layers (see Fig. 1). Notably, at low temperature, this ferroelectric coexists and is coupled with antiferromagnetic order, as shown in Fig. 2. More recently, the hexagonal RFeO$_3$ compounds have been studied in these compounds, there is a proposed coupling of ferroelectricity with weak ferromagnetic order. In addition to the proposed uses in energy-efficient magnetoelectric spin–orbit logic devices, the ferroelectricity and ferroelectric domain walls in the hexagonal manganites and ferrites have emerged as fascinating model systems to study diverse physical phenomena. The ferroelectric domain walls display tunable metallic conductivity. The emergence of the ferroelectric domain structure, exhibiting a topologically protected vortex pattern, is further a platform to explore the Kibble–Zurek framework and spontaneous symmetry breaking in a condensed matter system. The structural phase transitions have also been proposed to display Higgs and Goldstone physics.

In addition to multiferroics, the hexagonal ABO$_3$ family offers additional prospects to stabilize emergent magnetic ground states including the elusive quantum spin liquid state. In a quantum spin liquid, spins are highly correlated and strongly frustrated due to the crystal symmetry (e.g., triangular, honeycomb, or Kagome). The resulting degeneracy between competing ground state spin configurations leads to a highly entangled state that resists macroscopic magnetic ordering to the lowest temperatures. Importantly, the “spinon” quasiparticle excitations of this system can be itinerant Majorana fermions with a gapless dispersion of relevance to quantum computing. In addition to the intrinsic triangular symmetry of the hexagonal ABO$_3$ oxides, chemical doping or lattice distortions can construct a honeycomb or Kagome lattice with additional opportunities to realize frustrated magnetism. For example, InCu$_{2/3}$V$_{1/3}$O$_3$ has both Cu$^{2+}$ and V$^{5+}$ on the B-site lattice. These cations in the 2:1 ratio arrange such that the Cu$^{2+}$ forms a honeycomb lattice, as shown in Fig. 3(b). Here, the honeycomb Cu$^{2+}$ atoms seem to order antiferromagnetically rather than behave as a quantum spin liquid. (This system could also be proximate to chiral superconductivity.) In the LaCu$_{0.5}$Mo$_{0.5}$O$_3$ compound, the 3:1 ratio of Cu$^{2+}$ to Mo$^{6+}$ generates a Kagome arrangement of copper atoms depicted in Fig. 3(c). Finally, we note that the “up–up–down” ferroelectric trimerization on the A-site generates a honeycomb arrangement as well, as shown in Fig. 3(d). In TbInO$_3$, the resulting magnetic frustration on the terbium sublattice leads to a lack of order to the lowest temperatures and TbInO$_3$ is a promising quantum spin liquid candidate.

Finally, the hexagonal oxides have distinct oxygen sublattices to their perovskite counterparts. In contrast to the oxygen octahedra

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**TABLE I. Observed and predicted properties of the ABO$_3$ hexagonal materials.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMnO$_3$, R = Sc, Y, Dy-Lu</td>
<td>Multiferroic</td>
<td>12</td>
</tr>
<tr>
<td>RMnO$_3$, R = Sc, Y, Dy-Lu</td>
<td>Photovoltaic</td>
<td>37, 38</td>
</tr>
<tr>
<td>YIn$_{1-x}$Mo$_x$O$_3$</td>
<td>Blue pigment</td>
<td>39</td>
</tr>
<tr>
<td>DyMnO$_3$</td>
<td>Ion/electron conductor</td>
<td>35</td>
</tr>
<tr>
<td>RFeO$_3$, R = Lu, Yb, Sc</td>
<td>Oxygen storage</td>
<td>35, 40</td>
</tr>
<tr>
<td>DyFeO$_3$</td>
<td>Multiferroic</td>
<td>14–16</td>
</tr>
<tr>
<td>YFeO$_3$, InFeO$_3$</td>
<td>Antiferroelectric</td>
<td>41</td>
</tr>
<tr>
<td>R$_3$CuTiO$_6$, R = Y,</td>
<td>Photocatalyst/</td>
<td>42–44</td>
</tr>
<tr>
<td>Dy, Ho, Er, and Yb</td>
<td>water splitting</td>
<td></td>
</tr>
<tr>
<td>TbInO$_3$</td>
<td>Quantum spin liquid candidate</td>
<td>33, 46</td>
</tr>
<tr>
<td>YCrO$_3$, YVO$_3$</td>
<td>Predicted topological semi-metal</td>
<td>47</td>
</tr>
<tr>
<td>YNiO$_3$</td>
<td>Predicted superconductor</td>
<td>36, 48</td>
</tr>
</tbody>
</table>

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**FIG. 1.** Crystal structure and symmetry of the hexagonal ABO$_3$ compounds. The A-site, B-site, and oxygen atoms are shown in yellow, blue, and red, respectively. (a) The parent centrosymmetric P6$_3$/mmc structure that is nonpolar with point symmetry 6/mmm. (b) A slice of the half-unit-cell plane as indicated in the box in (a), projected down the [001] crystallographic zone axis. The B-site cations sit on a trigonal lattice with a locally lowered (noncentrosymmetric) symmetry compared to the full unit-cell structure, which consists of two of these B-site planes rotated 60° with respect to each other, sandwiched between the triangular rare-earth layers. (c)–(e) Displacement patterns found in hexagonal ABO$_3$ compounds and the corresponding unit-cell space (point) symmetry groups. (c) The nonpolar parent structure, for reference. (d) The polar phase has a coordinated tilting of three BO$_3$ trigonal bipyramids toward a trimerization center accompanied by a “down-up-down” displacement pattern of A site ions along the c axis. (e) The antipolar phase consists of intermediate tilt angles 30° away from the polar structure and a “down–middle–up” displacement pattern on the A site along the c axis.

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characteristic of the perovskites, the trigonal bipyramid intrinsic to the hexagonal AB\textsubscript{2}O\textsubscript{3} structure has two distinct oxygen atoms located at the apical and in-plane position. These oxygen atoms can have different bonding to the transition metal atom,\textsuperscript{34} which, in principle, can be harnessed for oxygen ion conductivity.\textsuperscript{35} There have also been theoretical predictions that the crystal field splitting surrounding the transition metal oxide could be harnessed to stabilize superconductivity in hexagonal nickelates (mimicking the electronic structure of the superconducting cuprates and pnictides).\textsuperscript{36}

Thin-film manifestations of these hexagonal oxides offer further opportunities to not only scale down the materials to fundamental thickness limits\textsuperscript{49} and heterostructure them to realize additional functional properties\textsuperscript{50} but furthermore to exploit epitaxy and layering\textsuperscript{51} to stabilize metastable compounds. Thin-film epitaxy of the hexagonal ABO\textsubscript{3} oxides offers additional challenges in comparison to the cubic perovskite oxides. In this review, we first summarize the stability of the hexagonal ABO\textsubscript{3} compounds. We then describe the thin-film deposition of the bulk-stable RMnO\textsubscript{3} compounds, including the lattice matching of the hexagonal crystal structure to commercially available substrates. We finally discuss the use of epitaxy to expand the stability of this phase.

II. STABILITY OF THE HEXAGONAL ABO\textsubscript{3} PHASE

Compounds with the ABO\textsubscript{3} stoichiometry can form a variety of cubic, orthorhombic, and hexagonal phases. The formation of the hexagonal phase is dictated by both structural stability and the electronic energy of the B-site in the trigonal bipyramid oxygen coordination complex. The structural stability of the competing cubic perovskite phase can be estimated with the tolerance factor (t), a geometric quantity based on the ionic radii (r) of constituent atoms that indicates how well a given ABO\textsubscript{3} compound fits in the cubic perovskite structure. Here, t is given by

$$t = \frac{1}{\sqrt{2}} \frac{r_A + r_O}{\text{unit-cell length}} = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}}.$$
The tolerance factor is 1 for ions which perfectly pack into the cubic perovskite structure. The well-known perovskite SrTiO$_3$ has $t = 1.01$, when calculated with $r_A = r_{Sr^{+}}(XII) = 144$ pm, $r_B = r_{Ti^{4+}}(VI) = 60.5$ pm, and $r_C = r_{O^{2-}}(eq) = 135$ pm. The tolerance factor deviates from 1, the structure becomes distorted from a cubic perovskite phase. For $t$ decreases from 1, the structure is distorted from a cubic perovskite (Fig. 4). For example, YFeO$_3$ with $t = 0.83$ forms a distorted orthorhombic perovskite phase. A tolerance factor far from 1 does not imply the stability of the hexagonal phase but instead identifies candidate compounds that are less stable in the cubic perovskite phase. YMnO$_3$ and YFeO$_3$ both with $t = 0.81$, have less structural stability in the cubic perovskite phase. Despite having the same tolerance factor, YFeO$_3$ assumes an orthorhombic perovskite structure whereas YMnO$_3$ crystallizes in a hexagonal phase.

In addition to the structural stability of competing phases, electronic stability impacts the bulk-stable crystal structure. The electronic stability of the hexagonal oxides is based on the crystal field splitting of the $d$-orbitals of the $B$-site transition metal ions with trigonal bipyramidal (fivefold) oxygen coordination. In this ligand geometry, the five $d$-orbitals split into three energy levels: two doubly degenerate lower energy levels and one non-degenerate high energy level (Fig. 5). In contrast, a perovskite with octahedral (sixfold) coordination on the $B$-site has two energy levels: the threefold degenerate $t_{2g}$ low energy level and the doubly degenerate $e_g$ high energy level. Fe$^{3+}$, with the electron configuration $[Ar]3d^5$, is more stable in the octahedral coordination, which avoids occupying the highest energy level in the trigonal bipyramidal configuration. As a result, RFeO$_3$ compounds are more stable as orthorhombic perovskites. In contrast, Mn$^{3+}$, with configuration $[Ar]3d^4$, is more stable in a trigonal bipyramidal complex where the four valence electrons populate the four lower energy orbitals. With octahedral coordination, Mn$^{3+}$ forms a degenerate high-spin state with its fourth valence electron in either of the two $e_g$ orbitals; these perovskite manganites are Jahn–Teller active. The electron in the higher energy orbitals lowers the stability of the compound. Thus, the R(MnO$_3$) compounds form a hexagonal crystal structure for small $R$ ($R = Sc, Y, Dy–Lu$), as shown in Fig. 6.

In Fig. 7, we summarize the elements which have been found in the hexagonal $ABO_3$ polymorph. In contrast to the cubic perovskites, here almost every element on the periodic table can occupy one of the three lattice sites, while the hexagonal structure can form with more limited chemical compositions. Only six cations are known to fully occupy the $B$-site although there is a much wider range of elements which can be stabilized as dopants or as partial occupants of this lattice site. We note that thin-film stabilization is a powerful platform for synthesizing phases which are metastable as bulk crystals.
various lattice constants, the most readily available oxide substrate used to stabilize hexagonal films is Al₂O₃. This substrate is not well lattice-matched to all desired hexagonal AB₃O₃ films. In addition to hexagonal oxides, cubic substrates can be used in the (111) orientation. Figure 8 shows the lattice mismatch between the prototypical hexagonal YMnO₃ and (0001)-oriented Al₂O₃, (111)-oriented cubic oxides MgO, MgAl₂O₄, (ZrO₂₀.₉₀₅(Y₂O₃)₀.₀₉₅ (9.5 mol. % yttria-stabilized zirconia, YSZ), and (111)-oriented metallic platinum. In addition to directly aligning on the substrate, YMnO₃ could also adopt a 30° rotation with respect to the substrate orientation [this would be analogous to the 45° rotation cubic perovskites might assume in the (001) direction]. Figure 9 summarizes the lattice matching between P6₃cm YMnO₃ and many commercially available substrates. While (111)-oriented cubic perovskites also have the correct symmetry, our experience is that these substrates seed the (111)-perovskite film rather than the intended hexagonal polymorph.

IV. EPITAXY OF BULK-STABLE HEXAGONAL AB₃O₃ COMPOUNDS

Epitaxial thin-film synthesis of hexagonal AB₃ materials was first achieved for the prototypical family of hexagonal rare-earth man ganites (R MnO₃). In particular, initial focus centered on the epitaxy of YMnO₃, which remains the most intensely studied member of the hexagonal AB₃O₃ materials. The first epitaxial synthesis of hexagonal YMnO₃ in 1996 was motivated by the material’s high-temperature uniaxial ferroelectricity combined with its suitability for integration with silicon as nonvolatile ferroelectric memories. Following the demonstration of magnetoelectric coupling effects in hexagonal RMnO₃ bulk crystals,¹¹,¹² interest shifted toward thin-film manifestations of such multiferroic properties and potential magnetoelectric effects. In 2006, Laukhin et al. demonstrated electrical control of magnetism in a Permalloy/YMnO₃ thin-film heterostructure⁶¹ [see Fig. 10(a)]. A giant flexoelectric effect was further observed in strained HoMnO₃ films,⁶² which could be used to tune the ferroelectric properties [Fig. 10(b)]. The discovery of the topologically protected vortex

![Image](https://example.com/image1.png)


![Image](https://example.com/image2.png)

**FIG. 7.** Periodic table indicating the elements that can be stabilized in the hexagonal AB₃O₃ phase. A-site ions are colored in yellow and B-site ions are colored in blue. We color in light yellow/blue the elements which can be found to partially occupy the site.

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FIG. 8. Lattice matching between YMnO₃ and common substrates. (a) The structure of YMnO₃ with a (0001) plane of yttrium atoms highlighted in gray. (b) Lattice matching between yttrium atoms in the (0001) plane of YMnO₃ in gray and the magnesium atoms in the (111) plane of MgO in orange. Lattice mismatch (with a factor of 2): 2.9%. (c) Lattice mismatch between YMnO₃ in gray and the magnesium atoms of MgAl₂O₄ (111) in yellow. Lattice mismatch: 7.0%. (d) Lattice mismatch of YMnO₃ with the blue aluminum atoms of Al₂O₃ (0001) in two orientations: aligned [lattice mismatch (with a factor of 3): 3.4%] and with a 30° rotation [lattice mismatch (with a factor of 3): 10.5%]. (e) Lattice mismatch between 30° rotated YMnO₃ and the zirconium atoms of yttria-stabilized zirconia (YSZ) in green. Yttrium is omitted from the YSZ crystal structure for clarity. Lattice mismatch: 2.6%. (f) Lattice mismatch between 30° rotated YMnO₃ and the platinum atoms of Pt(111). Lattice mismatch (with a factor of 3): 4.6%.

FIG. 9. In-plane lattice matching for hexagonal materials. Vertical lines indicate substrate (0001) (dotted-dashed lines) and (111) (dashed lines) in-plane lattice parameters. The intersection between a vertical line and scaling factor indicates a possible effective substrate lattice parameter. The horizontal line at 6.14 Å represents YMnO₃ and the boundaries for ±2% lattice mismatch are labeled. The gray region indicates typical hexagonal film lattice parameters. Colored dots correspond to the lattice matching diagrams in Fig. 8. The thickness of the scaling factor lines roughly matches their likelihood of being realized, with 1 and √3 the most common.
domain patterns in bulk crystal RMnO₃ compounds in 2010 and their related domain-wall functionalities sparked a renewed interest in the multiferroic domain structure and thickness scaling in hexagonal RMnO₃ thin films. Furthermore, the improper nature of the ferroelectric order in hexagonal ABO₃ oxides, which is driven by a non-ferroelectric structural distortion, suggests novel avenues for stabilizing and controlling spontaneous ferroelectric polarization in the ultrathin limit.

To date, the hexagonal phase has been realized as thin films for the entire bulk-stable rare-earth manganite series (R = Dy–Lu). Epitaxial stabilization additionally extended the series to lighter rare-earth ions down to samarium (Sm–Tb) that normally would crystallize in the orthorhombic Pnma phase as further discussed in Sec. V. Here, hexagonal SmMnO₃ has been achieved only on an isostructural YMnO₃ substrate, whereas the other members can be grown epitaxially on commercially available substrates such as YSZ(111). In addition to the rare-earth series and yttrium, the A-site of hexagonal manganites can accommodate both scandium and indium. However, to our knowledge, only the (epitaxially stabilized) orthorhombic phase of ScMnO₃ has been reported in thin films; growth of hexagonal InMnO₃ remains limited to polycrystalline films reported in the literature. In bulk InMnO₃, carefully tuning the defect chemistry or the thermal history of the crystals selects between trimerized domains of either $P6_{3}cm$ symmetry [see Fig. 1(d)], just as in the other rare-earth manganites, or anti-polar $P/\bar{1}c$ symmetry [Fig. 1(e)], as seen at the domain walls between the polar trimerization domains in RRMnO₃, all the while retaining the vortex domain pattern. Epitaxial realization of single-crystalline hexagonal InMnO₃ thus provides an interesting opportunity for studying the thin-film manifestation of these complementary symmetry properties.

**FIG. 10.** Ferroelectric properties of hexagonal RMnO₃ thin films. (a) Voltage control of exchange bias in a Permalloy layer through interfacial magnetic exchange in epitaxial multiferroic YMnO₃ grown on Pt(111)/SrTiO₃(111). Reprinted with permission from Laukin et al., Phys. Rev. Lett. 97, 227201 (2006). Copyright 2006 American Physical Society. (b) Modification of ferroelectric hysteresis loops in hexagonal HoMnO₃ films on Pt(111)/Al₂O₃(0001) caused by the strain-gradient-induced flexoelectric effect. Reprinted with permission from Lee et al., Phys. Rev. Lett. 107, 057602 (2011). Copyright 2011 American Physical Society. (c) Improper ferroelectric domain pattern mapped at the atomic scale in hexagonal YMnO₃ on Pt(111)/YSZ(111) using HAADF-STEM. Each color represents one of six total trimerization domain states, with polarization pointing either up or down. (d) Improper ferroelectric transition temperatures in hexagonal YMnO₃ films grown on YSZ(111) as function of film thickness. (c) and (d) reprinted with permission from Nordlander et al., Nat. Commun. 10, 5591 (2019). Copyright 2019 Author(s), licensed under a Creative Commons Attribution 4.0 License.
As mentioned in Sec. III, a major challenge in thin-film growth of the hexagonal manganites is the lack of instructural or lattice-matching substrates. Added to this is a tendency to form crystallographic domains and defects due to close lattice matching between multiple crystallographic orientations of the hexagonal RMnO₃ structure itself and between RMnO₃ and the corresponding binary oxide R₂O₃. Indeed, the higher symmetry of cubic substrates such as YSZ compared to that of the layered hexagonal ABO₃ phase impedes nucleation of a completely single-domain crystalline film and can cause defects such as antiphase boundaries. Thus, careful attention to substrate surface termination may play an important role in reducing the occurrence of these types of defects. The epitaxial quality of RMnO₃ films is also strongly dependent on substrate temperature during deposition. The hexagonal phase crystallizes down to 690 °C; however, the highest crystalline quality is achieved in the range 750–900 °C. Although hexagonal manganite thin films have been grown on a range of substrates including YSZ(111), Si(111), Pt(111), MgO(111), GaN(0001), ZnO(0001), and c-plane Al₂O₃, resulting in various degrees of crystallinity, not nearly as many options are commercially available as for their perovskite ABO₃ counterparts.

Over the past decade, significant improvement of the thin-film crystalline quality of RMnO₃ has been achieved and epitaxial layer-by-layer thin-film growth with sub-unit-cell thickness precision has recently been demonstrated. Such improvement of structural quality has been crucial to the investigation into the ultrathin manifestation of improper ferroelectric properties and domain structure in this class of materials [Fig. 10(c)]. In particular, the structural distortion transforming the nonpolar P₆₃/mmc phase to the polar P₆₃cm phase and leading to the secondary ferroelectric polarization was shown to be significantly modified by substrate-interface proximity, as demonstrated by a combination of in situ high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and optical second harmonic generation (SHG). The resulting threshold thickness for room-temperature polarization in YMnO₃ on an insulating substrate was determined to be two unit cells [Fig. 10(d)].

In hexagonal RMnO₃, the improper ferroelectric order coexists with antiferromagnetic order on the Mn¹⁺⁺ sublattice below 70–120 K, leading to multiferroicity. Because of the fully compensated nature of this antiferromagnetic order (i.e., lack of net magnetic moment), its thin-film manifestation has been challenging to study. Although neutron diffraction on thicker films of YMnO₃ (thickness exceeding 400 nm) shows Néel temperatures that closely match the bulk values, similar neutron measurements on thinner films are precluded due to the limited thin-film volume. Moreover, SQUID magnetometry has revealed spin-glass states in oxygen-deficient YMnO₃ films, indicating the strong influence of oxygen off-stoichiometry on the magnetic order. Hence, further work is needed to fully characterize the intrinsic magnetic state of ultrathin hexagonal RMnO₃. Additionally, the antiferromagnetic domain size is expected to be significantly reduced in thin films compared with bulk crystals, hampering real-space characterization. Thus, the enigmatic multiferroic coupling of ferroelectric and antiferromagnetic domain patterns observed in RMnO₃ bulk crystals remains a topic for future investigations in RMnO₃ thin films.

In addition to dimensionality scaling and heterostructure integration, thin-film realization of quantum oxide materials offers the opportunity to use epitaxial constraints to further tune their functionality. The lattice mismatch with respect to the substrate can impart epitaxial strain in the thin film or induce interface defects, which affect both electronic and magnetic properties. In hexagonal RMnO₃, strain engineering can, in principle, be used to tune the improper ferroelectricity in terms of both domain configuration and polarization magnitude. Although thin-film RMnO₃ is often grown on substrates with large lattice mismatch exceeding 2% (see Fig. 9), the resulting epitaxial strain is not obvious. Rather than inducing a coherently strained thin-film lattice, several other mechanisms are often at play that accommodate this mismatch. For example, misfit dislocations are frequently seen at the substrate–film interface, allowing bulk-like lattice constants to persist in the thin-film limit. Structural or chemical mismatch at interfaces can additionally be accommodated through oxygen off-stoichiometry, in-plane lattice rotation, or interface reconstruction, as shown in Fig. 11. It is possible that coherently strained epitaxial films could be achieved in hexagonal RMnO₃ films if grown on substrates with smaller lattice mismatch. This, however, would require the design and development of new substrates that offer better compatibility with the family of hexagonal ABO₃ materials.

An alternative route to achieve coherently strained heterostructures is demonstrated through the recent realization of mutual lattice matching between RMnO₃ and In₂O₃-based transparent conducting layers such as indium–tin oxide (ITO). Straining the conducting layer to the RMnO₃ lattice, rather than vice versa, offers a new opportunity for epitaxial integration of hexagonal ABO₃ into functional oxide-electronic heterostructures and superlattices [Figs. 12(a)–12(c)].

The layered structure of hexagonal ABO₃ further distinguishes this class of oxides as prospective quantum materials. As already seen in Sec. I, the triangular sublattice of each half-unit-cell layer breaks inversion symmetry [see Fig. 1(b)]. Given the half-unit-cell layer-by-layer growth mode achieved by PLD, the symmetry of the ultrathin thin-film system can be alternatingly controlled between preserved and broken inversion symmetry, purely based on either an even or odd total number of half-unit-cell layers. This effect was demonstrated using in situ SHG during hexagonal RMnO₃ epitaxial growth [Fig. 12(d)]. Similar to 2D-layered van-der-Waals materials, such layer-dependent symmetry control in thin films could, furthermore, be used to not only tune nonlinear optical responses but also may present an avenue to engineer, e.g., magnetoelectric, nonreciprocal, chiral, or topological effects in the general class of hexagonal ABO₃ materials and their heterostructures.

Beyond the hexagonal manganites, the polar hexagonal P₆₃cm phase has been achieved as bulk crystals for certain gallates (AGaO₃, A = Y, Er, Ho19) and indates (Al₂O₃, A = Y, Sm–Ho,49,50). The nonpolar P₆₃/mmc hexagonal structure is furthermore the bulk-stable phase of InFeO₃. Although thin films of hexagonal gallates and indates remain little explored so far, thin films of InFeO₃ have been grown by PLD on both ZnO(0001) and Ta:SnO₂-buffered Al₂O₃ substrates. InFeO₃ films have been proposed as candidates for water-splitting and photoelectrode applications due to their beneficial bandgap placement. Additionally, epitaxial InFeO₃ has been used as structurally compatible nonpolar spacer layers in hexagonal LuFeO₃-based superlattices grown by oxide MBE. The high volatility of indium and its sub-oxides at the elevated temperatures required for crystallization of the hexagonal phase, however, renders the thin-film synthesis of the indium-based hexagonal compounds challenging.

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such challenges can also be expected for hexagonal gallates given the similar volatility of gallium.

We note, however, that epitaxy of indates and gallates offers interesting opportunities to study the thin-film functional properties of hexagonal oxides in the absence of transition metal ions and magnetism on the $B$ site. This enables, for example, isolating the physics of frustrated rare-earth magnetism on the hexagonal $A$-site lattice. Moreover, in contrast to the transition-metal-based hexagonal $ABO_3$ oxides, which are mixed electronic and ionic conductors, the indates and gallates are electronically insulating and could, thus, support pure oxygen-ion conductivity.

V. EPITAXY OF METASTABLE HEXAGONAL $ABO_3$ COMPOUNDS

Thin-film epitaxy is also a powerful platform for exploring metastable hexagonal oxides. During crystal growth, the phase that is deposited minimizes the global energy of the system. The Gibbs free energy of formation for a crystal nucleating on a...
substrate is comprised of a volume term, which will prefer the thermodynamically stable structure; a surface term, which is determined by the surface energy between the material and the substrate; and a stress term, which discourages the growth of highly stressed states. In the early stages of growth, the crystal nucleating on the substrate has a high surface-to-volume ratio, making the interface between the substrate and nucleating crystal a critical component in film growth. Because coherent crystalline interfaces require less energy to form than non-coherent ones, the film often adopts a structure which resembles the crystallographic structure of the substrate in epitaxial thin film growth. One of the powerful consequences of this minimization of interfacial energy between the substrate and film—known as epitaxial stabilization—is that a metastable crystal structure, not the lowest energy structure, can be grown. By careful choice of substrate, epitaxial stabilization enables the exploration of compounds in their metastable and nonequilibrium structures, opening the door to novel materials with new functionalities.

In the case of rare-earth manganites, RMnO₃, the ground-state structure depends largely on the R-site radius, as discussed in Sec. II. As the radius of the R-cation is decreased, the lower energy structure goes from orthorhombic (La–Dy) to hexagonal (Ho–Lu). The small energy difference in the bulk stable state near the crossover between the substrate and film usually orthorhombic in their ground state, due to the crystal field stabilization. For example, Bosak et al. demonstrated that EuMnO₃, GdMnO₃, and DyMnO₃ could form the hexagonal phase by epitaxial stabilization on YSZ(111), and that HoMnO₃, TmMnO₃ and LuMnO₃ could form the orthorhombic phase using LaAlO₃(001) or SrTiO₃(001) substrates (Table II).

Notably, unlike the manganites, there are no known bulk-stable hexagonal oxides besides InFeO₃. Instead, the RFeO₃ ferrites are usually orthorhombic in their ground state, due to the crystal field splitting of the orbitals as discussed in Sec. II. However, many of the RFeO₃ structures have been epitaxially stabilized for R with smaller cation radius (Y, Sc, Eu, and Tb–Lu), as summarized in Table II. In addition to epitaxial stabilization, "stromataxic stabilization" can be used to further increase the number of compounds which can be synthesized in the thin film form. Garten et al. showed that by using sequential atomic layering they could form hexagonal ScFeO₃ with the YMnO₃-like structure. In the same growth conditions, co-deposition of scandium and iron yielded the bixbyite polymorph. Stromataxic stabilization is a powerful technique that could likely be used to construct other metastable hexagonal oxides, beyond those which can be constructed by epitaxial stabilization alone.

Stabilizing these hexagonal AFeO₃ ferrites opens the door to further engineering their ferroelectric, magnetic, and multiferroic properties. Here, we will focus on LuFeO₃, since it has seen as a recent surge in interest—for an overview of the other AFeO₃ compositions, refer to

| TABLE II. Summary of the RMnO₃ and RFeO₃ structures where R = rare earth, Sc, In, and Y. The bulk-stable phase is listed in addition to the structures which can be epitaxially stabilized on the listed substrate or template. o, h, and b refer to orthorhombic, hexagonal, and bixbyite, respectively. |

<table>
<thead>
<tr>
<th>Mn</th>
<th>Epitaxially stabilized</th>
<th>Fe</th>
<th>Epitaxially stabilized</th>
</tr>
</thead>
<tbody>
<tr>
<td>La o⁵⁵,¹¹⁶</td>
<td>Pbnnm</td>
<td>o¹⁷</td>
<td>Pbnnm</td>
</tr>
<tr>
<td>Ce o¹¹⁸</td>
<td>Pbnnm</td>
<td>o¹⁹</td>
<td>Pnma</td>
</tr>
<tr>
<td>Pr o¹²⁰</td>
<td>Pbnnm</td>
<td>o¹⁷</td>
<td>Pbnnm</td>
</tr>
<tr>
<td>Nd o¹²⁰,¹²¹</td>
<td>Pbnnm</td>
<td>o¹⁷</td>
<td>Pbnnm</td>
</tr>
<tr>
<td>Sm o⁵⁵,¹²¹</td>
<td>Pnma</td>
<td>o¹⁷</td>
<td>Pbnnm</td>
</tr>
<tr>
<td>Eu o¹²⁰,¹²¹</td>
<td>Pnma</td>
<td>o¹⁷</td>
<td>Pbnnm</td>
</tr>
<tr>
<td>Gd o¹²¹</td>
<td>Pnma</td>
<td>o¹⁷</td>
<td>Pbnnm</td>
</tr>
<tr>
<td>Tb o¹²³</td>
<td>Pnma</td>
<td>o¹⁷</td>
<td>Pbnnm</td>
</tr>
<tr>
<td>Dy o⁵⁵,¹²⁰,¹²¹</td>
<td>Pnma</td>
<td>o¹⁷</td>
<td>Pbnnm</td>
</tr>
<tr>
<td>Ho h⁴,¹²¹</td>
<td>Pnma</td>
<td>o¹⁷</td>
<td>Pbnnm</td>
</tr>
<tr>
<td>Er h⁴,⁵⁵,¹²⁵</td>
<td>Pnma</td>
<td>o¹⁷</td>
<td>Pbnnm</td>
</tr>
<tr>
<td>Tm h⁴,¹²¹</td>
<td>Pnma</td>
<td>o¹⁷</td>
<td>Pbnnm</td>
</tr>
<tr>
<td>Yb h⁴,⁵⁵,¹²¹</td>
<td>Pnma</td>
<td>o¹⁷</td>
<td>Pbnnm</td>
</tr>
<tr>
<td>Lu h⁴,¹²¹</td>
<td>Pnma</td>
<td>o¹⁷</td>
<td>Pbnnm</td>
</tr>
<tr>
<td>Sc h¹²⁷</td>
<td>Pnma</td>
<td>h¹²²,¹²³</td>
<td>Pnma</td>
</tr>
<tr>
<td>In h¹²⁹</td>
<td>Pnma</td>
<td>h¹²²,¹²³</td>
<td>Pnma</td>
</tr>
<tr>
<td>Y h⁵⁵</td>
<td>Pnma</td>
<td>h¹²²,¹²³</td>
<td>Pnma</td>
</tr>
<tr>
<td></td>
<td></td>
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</tbody>
</table>
an earlier review of hexagonal ferrites. While LuFeO$_3$ is stable in the orthorhombic structure in the bulk, it can be epitaxially stabilized to be isostructural to YMnO$_3$, as shown in Table II. In addition to YSZ(111), LuFeO$_3$ has been epitaxially stabilized on the basal plane of Al$_2$O$_3$, Ir(111), Pt(111), Fe$_3$O$_4$(111), and GaN. Figures 13(a) and 13(b) show high-resolution HAADF-STEM images of epitaxially stabilized LuFeO$_3$ synthesized by MOCVD [Fig. 13(a)] and MBE [Fig. 13(b)]. This hexagonal structure is an improper ferroelectric with $P6_3/mcm$ symmetry (similar to what was discussed in Sec. IV) with a polarization of 6.5 $\mu$C/cm$^2$ (Ref. 133) and a Curie temperature around 1020 K. The switching of the polarization by piezoresponse force microscopy is shown in Fig. 13(c). The high symmetry of the structure produces a magnetically frustrated system, which results in two-dimensional arrangements of spins in the iron planes, as shown in Fig. 2, resulting in an antiferromagnet. Below approximately 145 K, the spins cant in the [0001] direction, producing a net magnetic moment, displayed in Fig. 13(d). Due to the simultaneous existence of ferroelectricity and a weak ferromagnetic moment, LuFeO$_3$ is a promising candidate for multiferroic materials. In particular, compared to the hexagonal manganites, the hexagonal ferrites promise higher magnetic transition temperatures and magnetoelectric coupling due to the additional occupied orbital (the five $d$ electrons in Fe$^{3+}$ half fill each of the orbitals in Fig. 5). While LuFeO$_3$ itself only has a net magnetic moment at cryogenic temperatures, LuFeO$_3$ can be synthesized in a superlattice with other materials in an effort to enhance the magnetism. The first attempts included cobalt-doped LuFeO$_3$ depicted in Fig. 14(a). It was found that these materials showed a decrease in the magnetic ordering temperatures with respect to LuFeO$_3$ and LuFe$_2$Co$_{0.5}$O$_4$. More recently, LuFeO$_3$ was grown in a superlattice structure with formula-unit-thick layers of LuFe$_2$O$_4$, a hexagonal ferrite with a 240 K ferrimagnetic transition temperature, to create a room-temperature multiferroic. In these superlattices shown in Fig. 14(b), the ferroelectric distortion from the LuFeO$_3$ reduced the magnetic frustration in the LuFe$_2$O$_4$, increasing the magnetic transition temperature to 281 K. The material further demonstrated electric field control of magnetism—creating a magnetoelectric multiferroic (Fig. 15). This opens doors to the new engineering of multiferroic materials based on these epitaxially stabilized, improper ferroelectrics. We further note that LuFeO$_3$ can be epitaxially stabilized on intergrown spinel Fe$_3$O$_4$ (magnetite). The very high magnetic ordering temperature of Fe$_3$O$_4$ and other spinel compounds could provide a pathway to create a ferroelectric multiferroic with simultaneous transitions well above room temperature.

In addition to their coupled electric and magnetic orders, hexagonal ferrites, like the hexagonal manganites, host topological defects such as their ferroelectric domain walls and vortices where six ferroelectric domains come to a point. The superlattice construction of (LuFeO$_3$)$_m$/LuFe$_2$O$_4$ provides an avenue to manipulate these topological textures in hexagonal ferroelectrics. As the confinement of the ferroelectric layer...
is increased, the material goes from stabilizing charged domain walls with threefold and fivefold fractional vortices, to having irregular domains with neutral domain walls. As the confinement approaches one monolayer of LuFeO₃, the ferroelectricity is suppressed—reminiscent of the ferroelectric to paraelectric transition with temperature.

VI. OUTLOOK

The hexagonal ABO₃ materials are a rich class of quantum materials. In addition to the well-studied multiferroicity in the hexagonal manganites, there has been recent interest in stabilizing the elusive quantum spin liquid and predicted topological semimetal states and unconventional superconductivity. Thin-film epitaxy provides a powerful platform for both studying these materials at the fundamental limits as well as potentially stabilizing new materials. More recent work has used precise chemical layering to access compounds that were not accessible with epitaxial stabilization alone. Combined, thin-film epitaxy should allow additional emergent phenomena to be uncovered in the hexagonal oxides.

![Image](image_url)

**FIG. 14.** STEM micrographs of LuFeO₃ thin films combined with other materials. (a) HAADF STEM and atomic resolution EDS of a small region of cobalt-doped LuFeO₃, nominally LuFe₀.₇Co₀.₃O₃. Republished with permission from Akbashev et al., CrystEngComm 14, 5373–5376 (2012). Copyright 2012 The Royal Society of Chemistry. (b) HAADF-STEM micrographs of the m = 1–5 members of the (LuFeO₃)ₙ/(LuFe₂O₄) series imaged along the LuFeO₃ [100] zone axis. The leftmost image shows the position of lutetium (teal) and iron (yellow) atomic columns. Reprinted with permission from Mundy et al., Nature 537, 523–527 (2016). Copyright 2016 Springer Nature. (c) HAADF-STEM micrograph of an iron-rich LuFeO₃ film with ingrown epitaxial Fe₃O₄ nanolayers. The inset shows a HAADF-STEM simulation of Fe₃O₄ along with white dots that mark the imaged iron positions. Reprinted with permission from Akbashev et al., Sci. Rep. 2, 672 (2012). Copyright 2012 Springer Nature.

![Image](image_url)

**FIG. 15.** Magneto-electric coupling in (LuFeO₃)ₙ/LuFe₂O₄ superlattices. Left, a HAADF-STEM micrograph of a (LuFeO₃)ₙ/LuFe₂O₄ superlattice showing one period of the layered structure. (a) An out-of-plane PFM image at 300 K of an electrically poled region of the m = 9 superlattice film showing a pattern of up (teal) and down (red) c-axis polarized domains. (b) An XMCD PEEM image of the Fe L₃ edge of the poled region in (a) taken at 200 K. (c) The same image as (b) collected at 320 K. (d) Line profiles of the XMCD signal along the yellow lines in (b) and (c). The correspondence between the PFM and PEEM images demonstrates the coupling between improper ferroelectricity and ferrimagnetism in the film. Reprinted with permission from Mundy et al., Nature 537, 523–527 (2016). Copyright 2016 Springer Nature.
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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Johanna Nordlander: Data curation (equal); Visualization (equal); Writing – original draft (lead); Writing – review and editing (lead). Margaret A Anderson: Data curation (equal); Visualization (equal); Writing – original draft (equal); Writing – review and editing (equal). Charles M Brooks: Visualization (equal); Writing – original draft (equal); Writing – review and editing (equal). Megan E Holtz: Data curation (equal); Visualization (equal); Writing – original draft (equal); Writing – review and editing (equal). Julia Mundy: Data curation (equal); Visualization (equal); Writing – original draft (equal); Writing – review and editing (equal).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

APPENDIX: A NOTE ON HEXAGONAL GEOMETRY

The effective hexagonal in-plane lattice parameter of a (111)-oriented cubic crystal depends on the type of cubic structure the material forms. The simplest structure is the simple cube. For a crystal with cations on the corners of a cube, the (111) lattice parameter is given by the length of the face diagonal of the cube:

\[ a_{\text{hex}} = a_{\text{SC}} \sqrt{2}. \]

Materials that follow this formula include cubic perovskites (e.g., SrTiO3, KTaO3, and LaAlO3). Most of the common substrates and bottom electrode materials considered in this review have a face-centered cubic (FCC) structure. For this structure, the hexagonal lattice parameter is given by (1/2) of the face diagonal of the cubic unit cell:

\[ a_{\text{hex}} = \frac{a_{\text{FCC}} \sqrt{2}}{2}. \]

Various single elements (e.g., Ir, Pt, Pd, Ag, Si) crystallize in an FCC lattice. Spinel (e.g., MgAl2O4) and rock salt-type structures (e.g., MgO) also follow the FCC formula. Other materials with an FCC-type configuration include 3C-SiC, CaF2, and yttria-stabilized zirconia (YSZ). Some elements crystallize as a body-centered cubic (BCC) lattice (e.g., Cr, Mn, Fe, Mo). The hexagonal lattice parameter for this structure is the length of the face diagonal, just as in the simple cubic case, because the central atom lies slightly out of the (111) plane that includes three corner atoms. For the more complicated bixbyite structure, the true (111) lattice parameter follows the simple cubic formula \( a_{\text{hex}} = a_{\text{bixbyite}} \sqrt{2}. \) However, there are cations in a slightly distorted hexagonal lattice with average spacing \( a_{\text{hex}}/4. \) For this reason, the hexagonal lattice parameter of the bixbyite compound In2O3 is reported as 3.58 Å above while the cubic lattice parameter is 10.12 Å, giving 14.31 Å between identical lattice sites in the (111) plane. Other bixbyite materials include R2O3, Y2O3, and Mn2O3.

Lattice matching between hexagonal crystals is more complicated than that of cubic or orthorhombic structures. While both structures can accommodate matching between crystals with integer ratios between their lattice parameters (e.g., \( a = 2a_{C14} \)), hexagonal films can also incorporate scaling factors like \( \sqrt{3} \) or \( \sqrt{2} \) as well as a 30° rotation between the film and substrate. The rotation effectively scales the lattice parameter by \( \sqrt{3} \). This possible rotation, along with a scarcity of substrates with proper lattice parameters, complicates studies of strain engineering in hexagonal thin films. As with cubic thin films, the lattice mismatch between substrate and film is quantified as

\[ \text{lattice mismatch} \% = \frac{a_{\text{film}} - a_{\text{substrate}}}{a_{\text{film}}} \times 100. \]

For many materials, this simple formula can accurately predict which substrates and films are compatible and how they will align. However, this calculation is imperfect. Especially for large lattice mismatch, the

### TABLE III. Equivalent hexagonal lattice parameters for the substrate materials considered in Fig. 8.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Orientation</th>
<th>Hexagonal lattice constant (Å)</th>
<th>30° Rotated lattice constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Al2O3</td>
<td>(0001)</td>
<td>4.76</td>
<td>8.24</td>
</tr>
<tr>
<td>YSZ</td>
<td>(111)</td>
<td>3.64</td>
<td>6.30</td>
</tr>
<tr>
<td>GaN</td>
<td>(0001)</td>
<td>3.19</td>
<td>5.52</td>
</tr>
<tr>
<td>SCAM</td>
<td>(0001)</td>
<td>3.25</td>
<td>5.62</td>
</tr>
<tr>
<td>4H-SiC</td>
<td>(0001)</td>
<td>3.07</td>
<td>5.32</td>
</tr>
<tr>
<td>ZnO</td>
<td>(0001)</td>
<td>3.25</td>
<td>5.63</td>
</tr>
<tr>
<td>Graphite</td>
<td>(0001)</td>
<td>2.46</td>
<td>4.26</td>
</tr>
<tr>
<td>In2O3</td>
<td>(111)</td>
<td>14.31 (3.58)</td>
<td>24.79 (6.20)</td>
</tr>
<tr>
<td>CaF2</td>
<td>(111)</td>
<td>3.86</td>
<td>6.69</td>
</tr>
<tr>
<td>KTaO3</td>
<td>(111)</td>
<td>5.64</td>
<td>9.77</td>
</tr>
<tr>
<td>LaAlO3</td>
<td>(111)</td>
<td>5.37</td>
<td>9.30</td>
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<tr>
<td>MgAl2O4</td>
<td>(111)</td>
<td>5.71</td>
<td>9.90</td>
</tr>
<tr>
<td>CoFe2O4</td>
<td>(111)</td>
<td>3.67</td>
<td>6.36</td>
</tr>
<tr>
<td>MgO</td>
<td>(111)</td>
<td>2.98</td>
<td>5.16</td>
</tr>
<tr>
<td>3C-SiC</td>
<td>(111)</td>
<td>3.08</td>
<td>5.33</td>
</tr>
<tr>
<td>SrTiO3</td>
<td>(111)</td>
<td>5.52</td>
<td>9.56</td>
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<td>Pt</td>
<td>(111)</td>
<td>2.78</td>
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<td>Pd</td>
<td>(111)</td>
<td>2.75</td>
<td>4.76</td>
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<tr>
<td>Ir</td>
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<td>2.72</td>
<td>4.70</td>
</tr>
<tr>
<td>Si</td>
<td>(111)</td>
<td>3.84</td>
<td>6.65</td>
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</tbody>
</table>
difference in lattice parameters does not tell the whole story. The exact termination of the substrate and structure of the sublattice—the positions and identities of atoms that lie within the cations that define the hexagonal unit cell—can change how the substrate and film will align to reduce energy at the interface. Furthermore, the tendency of hexagonal crystals to adopt a 30° rotation or unusual scaling factor between film and substrate complicates the quantification of the lattice mismatch because the alignment can dramatically affect the effective lattice parameter of the substrate.

We tabulate the lattice parameters used for substrate and film materials (Tables III and IV, respectively) shown in Fig. 9.

REFERENCES


