

Improper Ferroelectricity at the Monolayer Limit with Undiminished Curie Temperature in h -LuFeO₃

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Abstract

Improper ferroelectrics exhibit complex crystal structures, which may allow them to circumvent the limitations of other ferroelectrics. Experiments consistently find a thickness limit below which ferroelectricity is not observed, while theoretical calculations imply the absence of such a limit in improper ferroelectrics. Here, we demonstrate that hexagonal LuFeO₃ (h -LFO) exhibits improper ferroelectricity at half-unit-cell thickness and undiminished Curie temperature. We report that the novel bottom electrode, SrCo₂Ru₄O₁₁ (SCRO), promotes the growth of the ferroelectric phase of h -LFO at low thickness, while other materials, such as yttria stabilized zirconia (YSZ), iridium, and platinum, do not. Our results demonstrate an absence of critical thickness for ferroelectricity in h -LFO and provide a framework for the fabrication of ultrathin improper ferroelectrics through epitaxial engineering.

Introduction

Ferroelectricity describes the spontaneous polarization of a material and the ability to reverse this polarization via an applied electric field [1]. It is caused by a phase transition that lowers structural symmetry below the Curie temperature, T_C [2]. In proper ferroelectricity, polarization is the primary order parameter of the phase transition, while in improper ferroelectricity, polarization is a secondary order parameter [1]. As a result, the structures of improper ferroelectrics are comparatively complex and can lend themselves to unconventional properties. In particular, improper ferroelectricity may circumvent the limit of critical thickness, or the thickness below which ferroelectricity is no longer observed. Previous studies have demonstrated that proper ferroelectrics exhibit critical thicknesses on the order of several unit cells [2], but theoretical calculations posit a lack of critical thickness for improper ferroelectrics [3].

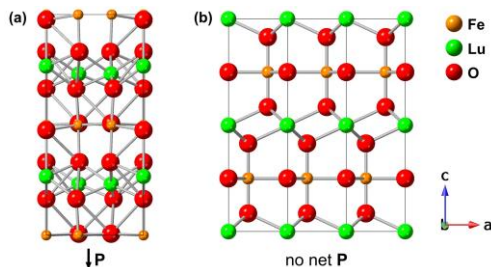


Fig. 1 Structure of h -LFO at (a) $T < T_C$, exhibiting a net downward polarization, and (b) $T > T_C$, exhibiting no net polarization.

Hexagonal LuFeO₃ (h -LFO) is a known improper ferroelectric [4]. Below its Curie

temperature, its structure undergoes a $\sqrt{3} \times \sqrt{3}$ reconstruction of the a - b plane, increasing the size of the unit cell and exhibiting net polarization (Fig. 1). On a bottom electrode that facilitates the growth of the ferroelectric phase, h -LFO might exhibit ferroelectricity at the thickness of a single formula unit, or a half unit cell.

We demonstrate a novel bottom electrode, SrCo₂Ru₄O₁₁ (SCRO). SCRO has a unit cell of comparable size to the ferroelectric phase unit cell of h -LFO [Fig. 2(a-b)], promoting the growth of this phase even at sub-unit-cell thicknesses. In contrast, other substrates and bottom electrodes, such as (111) YSZ, (111) Ir, and (111) Pt [Fig. 2(c-e)], match more closely with the unit cell of paraelectric h -LFO. Thus, epitaxial engineering can be exploited to reveal sub-unit-cell improper ferroelectricity.

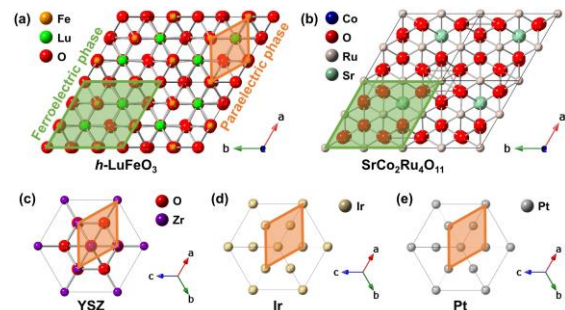


Fig. 2 Comparative sizes of unit cells in (a) h -LFO, (b) SCRO, (c) (111) YSZ, (d) (111) Ir, and (e) (111) Pt.

Experimental

16 nm SCRO was grown on Sr_{1.03}Ga_{10.81}Mg_{0.58}Zr_{0.58}O₁₉ (SGMZ) substrates with

molecular beam epitaxy (MBE). Two samples of *h*-LFO were grown on the SCRO bottom electrodes via MBE. During *h*-LFO growth, shutters for iron and lutetium sources were alternately opened to grow one monolayer of iron oxide or lutetium oxide at a time. Film surface quality was monitored via reflection high-energy electron diffraction (RHEED). RHEED intensity line profiles were plotted to obtain the positions of brightness peaks. Atomic force microscopy (AFM) images were compared before and after growth to confirm film uniformity.

Results and Discussion

The RHEED data reveals tripling in the *h*-LFO lattice below one unit cell thickness. Fig. 3(a) displays line profiles from the growth of the first sample, with ferroelectric tripling evident at as low as 0.75 unit cells. Since the distance between peaks in the RHEED is inversely proportional to a material's in-plane lattice constant, comparing the peak spacing gives insight into the type of material being observed. Calculating the difference in pixel spacing between the outermost peaks of SCRO and 0.75-unit-cell *h*-LFO results in a 2.3% mismatch. This result concurs with the expected difference, since the lattice mismatch between bulk SCRO and bulk *h*-LFO is calculated to be 2.3% based on literature values for in-plane lattice constants [5,6]. The calculation corroborates the assertion that the tripling observed at 0.75 unit cells is from ferroelectric *h*-LFO, and not simply a residual RHEED signal from SCRO.

Fig. 3(b) shows the RHEED data for the growth of the second sample. We again observe ferroelectric tripling, in this case starting at 0.5 unit cells (1 formula unit). Although this sample is fully strained to SCRO, the presence of tripling indicates ferroelectricity.

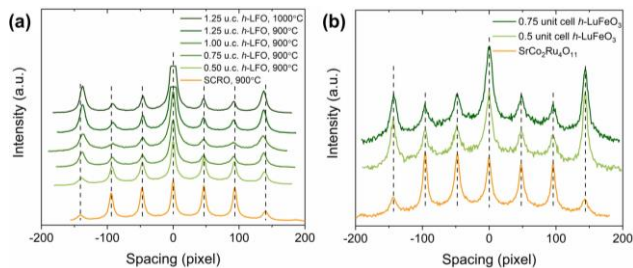


Fig. 3 Line profiles for growth of (a) the first sample (1.25 unit cells thick) and (b) the second sample (0.75 unit cells thick). RHEED tripling appears in both, indicating ferroelectricity.

AFM images (Fig. 4) of the samples reveal uniform, smooth growth. Both samples display root mean squared roughness values below 0.6 nm before and after growth, as well as the preservation of terraces. These results are consistent with uniform

film growth and support the assertion that the observed tripling is due to sub-unit-cell-thick *h*-LFO, rather than uncovered regions of SCRO or thicker islands of *h*-LFO.

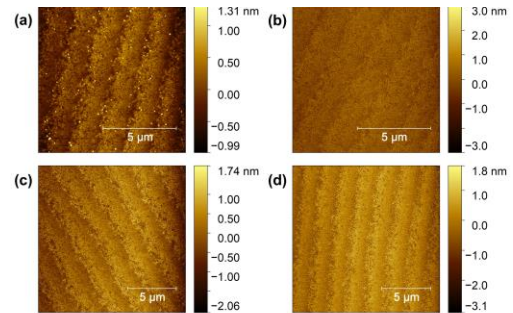


Fig. 4 AFM images of (a) bare SCRO before growth of the first sample (RMS=0.33 nm), (b) the first sample after growth (RMS=0.43 nm), (c) bare SCRO before growth of the second sample (RMS=0.59 nm), (d) the second sample after growth (RMS=0.59 nm).

Conclusion

We observed ferroelectricity in *h*-LFO at half unit cell thickness and undiminished Curie temperature. Our results support the theoretical work that suggests there is no critical thickness for improper ferroelectricity, and we provide a framework for the fabrication of ultrathin improper ferroelectrics through epitaxial engineering. In the future, we hope to observe polarization switching in *h*-LFO films below one unit cell thickness and obtain scanning transmission electron microscopy (STEM) images for this ultrathin improper ferroelectric.

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