

Supporting Information for:

**Epitaxially Constrained Hexagonal Ferroelectricity and Canted
Triangular Spin Order in LuFeO_3 Thin Films**

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(A) Experimental and Computational Details

Film Fabrication and Characterizations.

An epitaxial Pt (111) film as the bottom-electrode layer was grown on the Al_2O_3 (0001) substrate using RF magnetron sputtering. A pulsed laser deposition method was then used for the fabrication of a 60-nm-thick hexagonal LuFeO_3 (LFO) film layer on the Pt(111)/sapphire (Al_2O_3) substrate at a laser energy density of $\sim 1.5 \text{ J/cm}^2$ with the repetition rate of 3 Hz. The substrate temperature was held at 850 °C in an oxygen ambience of 200 mtorr. After the PLD growth, a Pt top-electrode layer was deposited to make a capacitor structure. We have subsequently performed structural analysis to confirm a hexagonal phase as well as in-plane epitaxy in the LFO layer. The hexagonal lattice parameters of LuFeO_3 as obtained from XRD patterns are $a = 5.9179 \text{ \AA}$ and $c = 11.7718 \text{ \AA}$ for the polar $P6_3cm$ phase. On the other hand, the hypothetical strain-free lattice parameters of $h\text{-LuFeO}_3$ (as obtained by density-functional theory calculations under the condition of zero pressure) are $a = 6.0057 \text{ \AA}$ and $c = 11.6767 \text{ \AA}$. Thus, the hexagonally constrained LuFeO_3 epitaxial film is compressively strained along the in-plane direction while it is under a tensile strain along the out-of-plane (thickness) direction.

The temperature-dependent spontaneous polarization was evaluated by measuring the pyrocurrent using a Keithley 487 picoammeter with a sweeping rate of 2°C/min. Starting at 100 °C, the film was cooled down under an electric poling field of 800 kV/cm along the c -axis before measuring the pyroelectric current on heating. P - E hysteresis loops with a virtual ground mode were obtained using a Precision LC system (Radiant Technologies, Inc.). Magnetic properties were examined by measuring M - H (SQUID magnetometer, Quantum Design) and $M(T)$ curves (MPMS).

First-Principles Calculations.

We have performed first-principles density-functional theory (DFT) calculations on the basis of the generalized gradient approximation (GGA) and the GGA+U method implemented in the projector augmented-wave (PAW)^{S1} pseudopotential using the Vienna *ab initio* Simulation Package (VASP).^{S2} All the DFT calculations were performed using (i) a $6 \times 6 \times 4$ Monkhorst-Pack k -point mesh centered at Γ , (ii) a 500 eV plane-wave cutoff energy, and (iii) the tetrahedron method with the Blöchl

corrections for the Brillouin zone integrations.^{S3} The Hubbard U_{eff} of 7.5 eV on Yb 4*f* and 4.5 eV on Fe 3*d* states were chosen on the basis of empirical corrections. We explicitly treated 9 valence electrons for Lu ($5p^65d^16s^2$), 16 for Fe ($3s^23p^63d^64s^2$), and 6 for oxygen ($2s^22p^4$). All the structural relaxations were performed with a Gaussian broadening of 0.05 eV.^{S4} The ions were relaxed until the forces on them were less than 0.01 eV/Å.

(B) Three Distinct LuO₈ units in the Ferroelectric $P6_3cm$ state

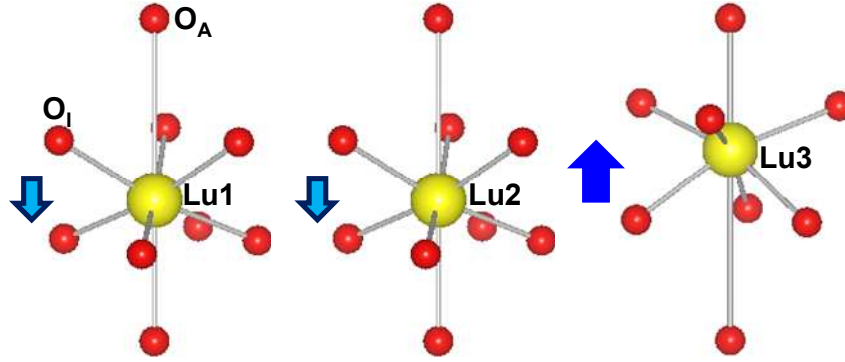


Figure S1. The three distinct LuO₈ units in the ferroelectric $P6_3cm$ state. The arrows indicate the direction of the ferroelectric off-centering displacement in each LuO₈ unit.

The computed local structure reveals that the ferroelectricity originates from the vertical shift of the Lu ion in the LuO₈ unit from the nonpolar centrosymmetric position. LuFeO₃ possesses three distinct LuO₈ units (i.e., Lu-ion sites) in the ferroelectric state. Among these, the first two dipoles are oriented parallel to each other but are antiparallel to the third remaining dipole (Fig. S1). Thus, the net polarization is parallel to the *c*-axis of the hexagonal $P6_3cm$.

In addition, there exist two distinct types of oxygen ions that surround the central Lu ion in each LuO₈ unit (Fig. S1). The two axial (apical) oxygen ions along the hexagonal *c*-axis (abbreviated as O_A) correspond to the first type while the six oxygen ions located at two different triangular in-planes (abbreviated as O_I) belong to the second type.

(C) Calculated Ground-State Atomic Coordinates of *h*-LuFeO₃

Both the paraelectric (PE) $P6_3/mmc$ and ferroelectric (FE) $P6_3cm$ structures were optimized by relaxing atomic positions. In calculating the PE $P6_3/mmc$ structure, we took lattice parameters and atomic coordinates of YMnO₃ (having the same $P6_3/mmc$ nonpolar symmetry) as the initial input values^{S5} with the replacement of the Mn-ion coordinates by the Fe-ion positions. In calculating the FE $P6_3cm$ structure, on the other hand, we adopted the previously reported values as the initial input values.^{S6}

Table S1. Calculated ground-state atomic positions of the hexagonal LuFeO₃ for both polar $P6_3cm$ and nonpolar $P6_3/mmc$ phases.

Atom	$P6_3cm$			$P6_3/mmc$		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Lu1	0.001	0.000	0.277	0.000	0.000	0.250
Lu2	0.667	0.334	0.233	0.667	0.333	0.250
Lu3	0.334	0.667	0.233	0.333	0.667	0.250
Lu4	0.000	0.000	0.777	0.000	0.000	0.750
Lu5	0.667	0.334	0.733	0.667	0.333	0.750
Lu6	0.333	0.667	0.733	0.333	0.667	0.750
Fe1	0.331	0.000	0.002	0.333	0.000	0.000
Fe2	0.000	0.333	0.002	0.000	0.333	0.000
Fe3	0.664	0.665	0.001	0.667	0.667	0.000
Fe4	0.335	0.334	0.501	0.333	0.333	0.500
Fe5	0.001	0.665	0.501	0.000	0.667	0.500
Fe6	0.668	0.000	0.502	0.667	0.000	0.500
O1	0.995	0.997	0.976	0.000	0.000	0.000
O2	0.666	0.333	0.022	0.667	0.333	0.000
O3	0.333	0.667	0.022	0.333	0.667	0.000
O4	0.304	0.000	0.168	0.333	0.000	0.166
O5	0.697	0.697	0.167	0.667	0.667	0.166
O6	0.000	0.304	0.167	0.000	0.333	0.166
O7	0.362	0.362	0.337	0.333	0.333	0.333
O8	0.000	0.636	0.336	0.000	0.667	0.333
O9	0.640	0.001	0.338	0.667	0.000	0.333
O10	0.003	0.998	0.476	0.000	0.000	0.500
O11	0.667	0.333	0.522	0.667	0.333	0.500
O12	0.334	0.667	0.522	0.333	0.667	0.500
O13	0.306	0.306	0.667	0.333	0.333	0.667
O14	0.000	0.696	0.667	0.000	0.667	0.667
O15	0.696	0.000	0.668	0.667	0.000	0.667
O16	0.361	0.001	0.838	0.333	0.000	0.834
O17	0.638	0.638	0.836	0.667	0.667	0.834
O18	0.000	0.361	0.838	0.000	0.333	0.834

(D) Difference in the Ferroelectric Shift among Three Typical ReMO_3 -type Hexagonal Oxides

We have compared the optimized atomic coordinates and the ferroelectric shift of $h\text{-LuFeO}_3$ with those of $h\text{-HoMnO}_3$, the most extensively studied hexagonal manganite by virtue of its strong tendency of the magnetoelectric coupling.^{S7} In addition to this, we also compared the structural features of $h\text{-LuFeO}_3$ with those of $h\text{-YbFeO}_3$, another hexagonal ferrite which had been fabricated recently.^{S8}

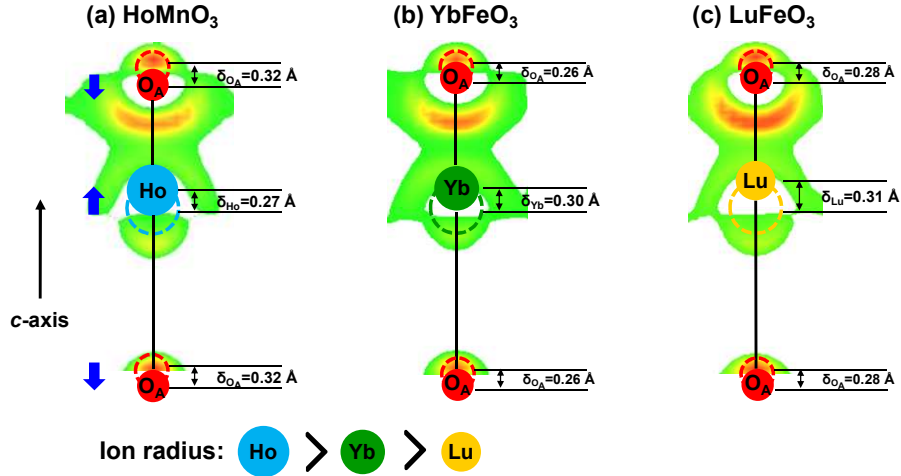


Figure S2. The differences in the computed ELF between the FE $P6_3cm$ state and the PE $P6_3/mmc$ state for three ReMO_3 -type hexagonal oxides: (a) HoMnO_3 , (b) YbFeO_3 , and (c) LuFeO_3 .

The ferroelectric (FE) shift along the hexagonal c -axis can be visualized by plotting (i) the relevant atomic positions along the c -axis and (ii) the difference in the three-dimensional (3D) electron-density contour between the polar (ferroelectric) $P6_3cm$ and nonpolar (paraelectric) $P6_3/mmc$ phases. The difference in the electron density is best represented by the difference in the electron localization function (ELF) between the two phases at an arbitrary point, $\mathbf{r}$, namely, $\Delta_{\text{ELF}}(\mathbf{r}) \equiv \text{ELF}_{\text{ferro}}(\mathbf{r}) - \text{ELF}_{\text{para}}(\mathbf{r})$.^{S9}

As shown in Fig. S2, the $\Delta_{\text{ELF}}(\mathbf{r})$ plot clearly shows asymmetric electron-density localization (along the hexagonal c -axis) associated with the para-to-ferroelectric phase transition (*i.e.*, hexagonal $P6_3/mmc$ -to- $P6_3cm$ transition). This asymmetric

localization is common to all three hexagonal ferroics examined (HoMnO_3 , YbFeO_3 & LuFeO_3) with the most pronounced asymmetric condensation in the $h\text{-LuFeO}_3$.

Regarding the polar off-centering displacement of $P6_3cm$, the FE shift of rare-earth cation (Re) increases with decreasing radius of Re ion (r_{Re}): $\delta_{\text{Lu}} = 0.31\text{\AA} > \delta_{\text{Yb}} = 0.30\text{\AA} > \delta_{\text{Ho}} = 0.27\text{\AA}$, where $r_{\text{Ho}} > r_{\text{Yb}} > r_{\text{Lu}}$. On the other hand, the FE shift of the axial oxygen (δ_{O_A}) in $h\text{-ReMnO}_3$ -type hexagonal manganites is, in general, substantially larger than the FE shift of O_A in $h\text{-ReFeO}_3$ -type hexagonal ferrites. For example, δ_{O_A} of $h\text{-HoMnO}_3 = 0.32\text{\AA} > \delta_{\text{O}_A}$ of $h\text{-YbFeO}_3 = \delta_{\text{O}_A}$ of $h\text{-LuFeO}_3 = 0.28\text{\AA}$. According to our DFT calculations, this difference in δ_{O_A} (along the hexagonal c -axis) between manganites and ferrites is closely related to the fact that the tilt angle (θ) of the MnO_5 bipyramid unit in $h\text{-ReMnO}_3$ is bigger than that of the FeO_5 bipyramid unit in $h\text{-ReFeO}_3$.

(E) Orbital Interaction Diagrams

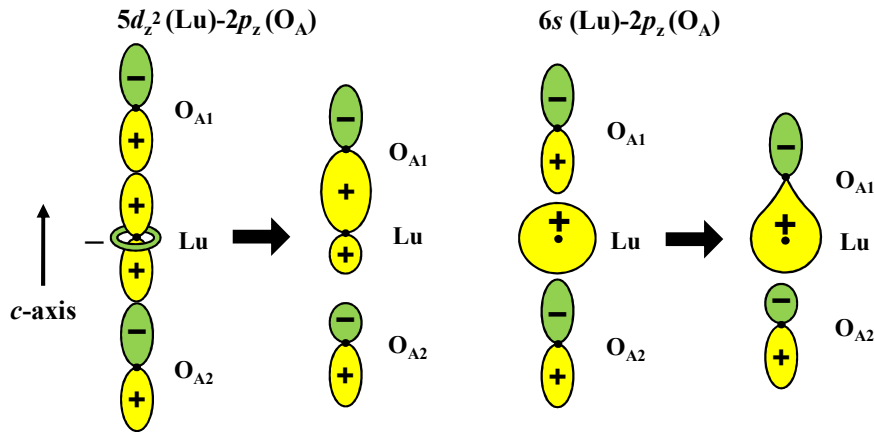


Figure S3. Schematic diagrams of the two distinct possibilities of the Lu- O_A orbital interactions, $5d_z^2 (\text{Lu})-2p_z (\text{O}_A)$ and $6s (\text{Lu})-2p_z (\text{O}_A)$.

We have considered two distinct possibilities of the Lu- O_A bonding interaction which leads to the off-centering ferroelectricity along the c -axis of $P6_3cm$: (i) empty $5d_z^2 (\text{Lu})-2p_z (\text{O}_A)$ orbital interaction and (ii) empty $6s (\text{Lu})-2p_z (\text{O}_A)$ interaction. As schematically depicted in Fig. S3, the $5d_z^2 (\text{Lu})-2p_z (\text{O}_A)$ orbital interaction induces asymmetric covalent bonding along the c -axis. In this way, the central Lu ion is now

able to make an asymmetric covalent bond with one of the two neighboring O_A ions (not simultaneously with two neighboring O_A ions), which results in a spontaneous breaking of the centrosymmetric state. Similarly, the $6s$ (Lu)– $2p_z$ (O_A) interaction is also capable of forming asymmetric covalent bonds along the c -axis of $P6_3cm$ (Fig. S3). However, the computed orbital-resolved partial density of states (PDOS) clearly indicate that the $6s$ (Lu)– $2p_z$ (O_A) hybridization is not the electronic origin of the hexagonal ferroelectricity in LuFeO_3 (see main manuscript).

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