

Imaging Local Polarization and Domain Boundaries in Multiferroic $(\text{LuFeO}_3)_m/(\text{LuFe}_2\text{O}_4)_n$ Superlattices

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Materials that couple strong ferroelectric and ferromagnetic order hold tremendous promise for next-generation memory devices. However, many so-called multiferroics have properties that are either weak, emerge well below room temperature, and/or lack coupling between the electric and magnetic domains, stymieing technological applications. The atomic-scale design of new multiferroics, usually realized as heterostructures or interface phases, requires a local probe of physical properties and structure inside the material. This atomic-scale feedback on ferroelectric polarization and domain structure has helped lead us to a new strong ferrimagnet-ferroelectric with the highest known simultaneous transition temperatures. These $(\text{LuFeO}_3)_m(\text{LuFe}_2\text{O}_4)_n$ superlattices (Fig 1) are constructed by integrating the ferroelectric, antiferromagnetic LuFeO_3 and paraelectric, ferrimagnetic LuFe_2O_4 . The hexagonal LuFeO_3 is an improper ferroelectric where the Lu-O buckles into a polar structure [1]. We quantify the polar structure—manifest as a displacement of the lutetium atoms—with atomic precision for different superlattice layerings. Our ferroelectric domain measurements show large polarization and regular domain walls correlate with improved magnetic moment and critical temperature, T_C .

Aberration-corrected scanning transmission electron microscopy (STEM) can provide atomic column positions with sub-picometer precision [2]. Here we apply atomic mapping with picometer precision to find local polarization and domain structure in $(\text{LuFeO}_3)_m(\text{LuFe}_2\text{O}_4)_n$ as a function of m, n in a 100 keV NION Ultra-STEM. Each image was formed from many (>20) cross-correlated fast acquisitions. 2D Gaussian fitting located the center of the lutetium columns, from which the displacement, and thereby polarization, was measured (Fig 2ab). After analyzing over 100 images, or > 4000 nm² of the material, we find that the $(\text{LuFeO}_3)_m(\text{LuFe}_2\text{O}_4)_1$ superlattices with $m \geq 2$ display a ferroelectric structure. The polarization is damped for lutetium rows adjacent to the LuFe_2O_4 layers for $2 \leq m \leq 5$, thus we would expect net polarization to grow with layer width. Indeed, the polarization of the parent-compound LuFeO_3 is reached for $m \geq 3$ multilayers and surprisingly is exceeded for $m = 7, 8$ (Fig 2c).

We collected domain sizes and boundary type statistics from the local polarization data. We found that domain size grows with m , increasing the width in the growth plane but limited in height by the LuFe_2O_4 layers, for up to $m=7$. At $m=7$, the domain height stabilizes at half the height of the $(\text{LuFeO}_3)_7$ layer, and forms regular domains with tail-to-tail walls at the LuFe_2O_4 layer and head-to-head walls in the middle of the $(\text{LuFeO}_3)_7$ layer. First-principle calculations suggest that the doping associated with this particular domain configuration leads to the increase in magnetic moment, which we have observed (Fig 3). T_C is also seen to increase, approaching room temperature. STEM analysis combined with first-principles results suggests pursuing strongly ferroelectric domains with regular domain boundaries will lead to enhanced magnetization and T_C in these multiferroics. [3]

References:

[1] H Das, *et al*, Nat. Comm. **5** (2014) 2889.[2] A Yankovich *et al*, Nat. Comm. **5** (2014) 4155.

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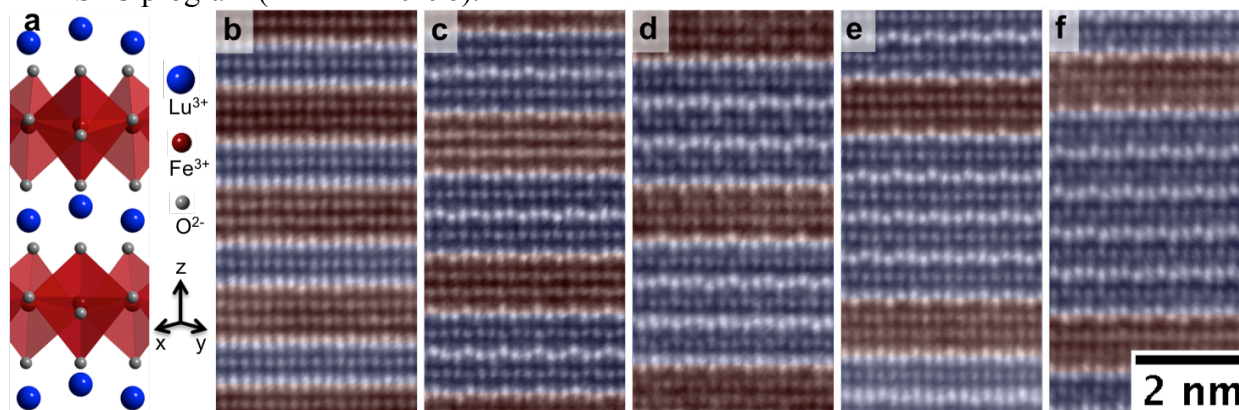


Figure 1. Diagram of the Lu-O buckling in LuFeO_3 (a), which leads to the ferroelectric structure [1]. ADF-STEM of the $(\text{LuFeO}_3)_m (\text{LuFe}_2\text{O}_4)_n$ viewed along the $[110]$ zone axis, the $(\text{LuFeO}_3)_n$ blocks highlighted in blue, for the $m, n = 1, 1$ structure (b), 2, 1 (c), 3, 1 (d), 4, 1 (e) and 5, 1 (f).

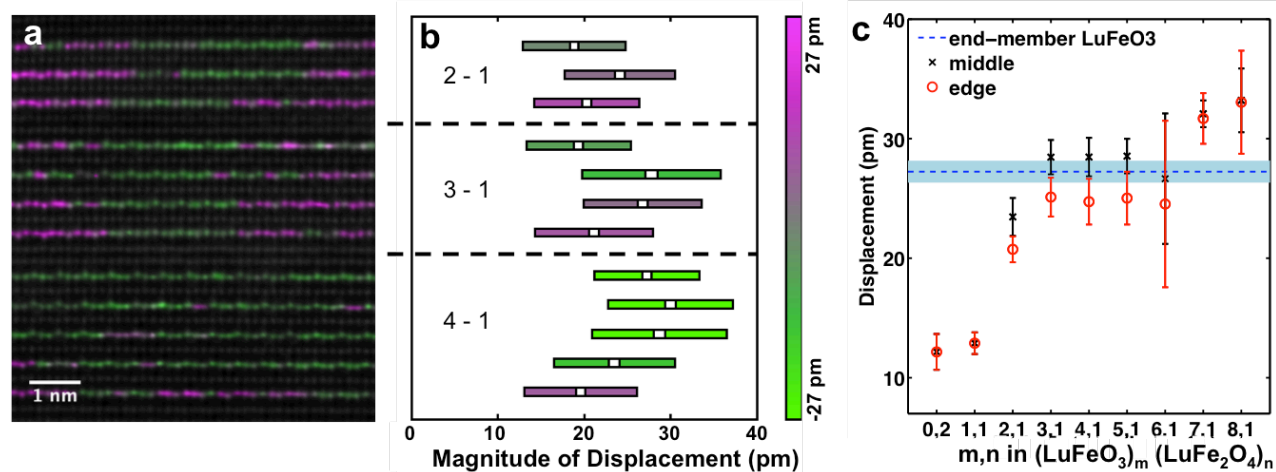


Figure 2. (a) STEM image of $(\text{LuFeO}_3)_m (\text{LuFe}_2\text{O}_4)_n$ with color overlays for the magnitude and direction of the local ferroelectric displacements. (b) r.m.s. displacement (square) for each lutetium row. Color indicates mean polarization, with lengths corresponding to 20-80% of the distribution. (c) r.m.s. displacement averaged over many images for varying (m,n) , distinguishing between layers on the edge bordering the double iron layer and in the middle. Blue line is for LuFeO_3 .

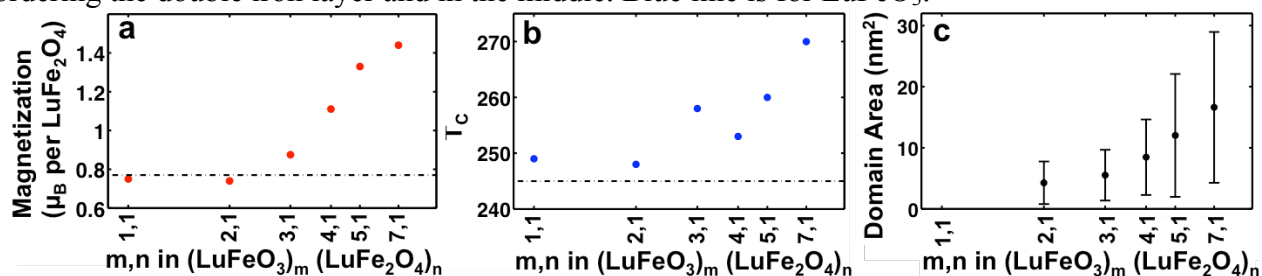


Figure 3. Magnetization and critical temperature for the $(\text{LuFeO}_3)_m (\text{LuFe}_2\text{O}_4)_n$, plotted alongside ferroelectric domain area. Larger domain area correlates to higher magnetization.