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Multi-scale Visualization of Ferroelectric Domains in a Magnetically Frustrated $TbInO_3$ Thin Film

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Novel physical properties may be realized in materials hosting frustrated magnetic phases such as quantum spin liquids and spin ices [1]. While the search for such materials has focused on bulk crystals with the prerequisite frustrated-lattice geometries [2, 3], thin-film growth and epitaxial stabilization offer exciting opportunities for not only realizing but also manipulating these exotic magnetic phases. Hexagonal $TbInO_3$ is a recent candidate for quantum spin liquids due to its magnetically frustrated rare-earth sublattice [2, 3]. The triangular Tb^{3+} sublattice is modulated by unit-cell-tripling ion distortions which lead to a stuffed honeycomb lattice geometry. This lattice distortion, also known as trimerization, is accompanied by an improper ferroelectric polarization along the c-axis. In thin films of $TbInO_3$, epitaxial constraints may further enrich the structural and magnetic landscapes, by modulating lattice strain, ferroelectric domains and atomic-scale distortions. Therefore, visualizing the local structure of the ferroelectric distortions and domains in these films is key for understanding and tuning their magnetic ground states.

Here we use advanced scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) to visualize the atomic- and nano-scale structures of the ferroelectric domains in $TbInO_3$ thin films. We stabilize a ~25 nm hexagonal $TbInO_3$ film on a YSZ substrate by reactive oxide molecular beam epitaxy. A thin layer of TbO_x between the substrate and the TbInO3 film serves as a buffer that stabilizes the remainder of the growth. The microscopy is performed on a Titan Themis Z operating at 200 kV.

Figure 1a shows a HAADF-STEM image of the $TbInO_3$ film, the buffer layer, and the YSZ substrate. We identify the atomic planes using the HAADF intensity profile in Fig. 1b-c where the Tb atomic planes show higher HAADF contrast than the In planes. EELS mapping at the interface (Fig. 1d) further shows the Tb and In layers, where the Tb planes are co-located with the modulated layers in the HAADF images. Analysis of the Tb-$M_{4,5}$ edges indicates that the buffer layer consists predominantly of Tb^{4+}, whereas Tb^{3+} is found in the $TbInO_3$ film (Fig. 1e). The lower HAADF contrast at the buffer layer coincides with the reduced signal in the Tb-M EELS map, indicating a possible Tb-deficiency. The Tb-deficiency may be related to a stress-relieving mechanism at the interface which helps to stabilize the hexagonal $TbInO_3$ film on top.

The lattice trimerization is apparent via the large displacement of Tb atoms in a down-up-up pattern, as shown in the red box in Fig. 2a,b. The resulting unit-cell tripling leads to extra satellite peaks in the Fourier transform in Fig. 2d. This displacement pattern can take on six different domain states, each associated with a 180° reversal of the polarization direction (Fig 2b,c). While such polarization domains can appear in strain-free regions, parts of the film exhibit lattice strain (or rotation) which correlates with

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reversals of the polarization, indicating that strain can pin polarization domains. To understand the interplay between strain and improper ferroelectric domains over a larger length scale, we imaged the films at lower collection angles and acquired three 360 kX magnification (~280 nm lateral field of view) images which are stitched together in Fig. 2e. At low collection angles, the contrast is more sensitive to the channeling for the electron beam and can therefore detect strain fields inside the film and atomic displacements which may be associated with improper ferroelectric distortions. The largest domain, which appears with contiguous bright contrast, is ~270 nm but other smaller domains (~70 nm) also occur. A combination of picometer-precision atom tracking, phase and strain mapping, and differential phase contrast further reveal in greater detail the interplay between strain and polarization domains over a micrometer length scale [4, 5]. Such multidomain structures in the $TbInO_3$ epitaxial thin film have fundamental implications for the realization of frustrated magnetic phases, especially at the domain walls where novel excitations may emerge [3, 6].

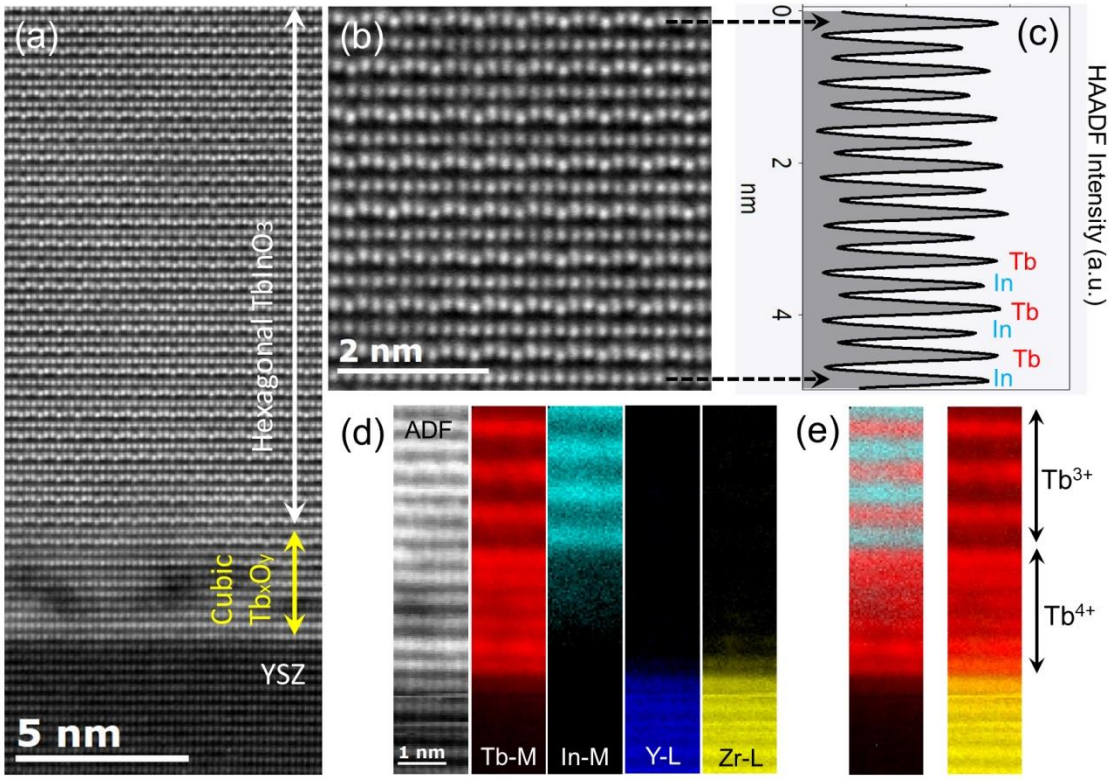

Figure 1. Atomic-scale visualization of $TbInO_3$ thin films stabilized on YSZ substrate. (a) STEM-HAADF image shows a buffer layer at the interface. (b) high magnification STEM-HAADF image at the middle of the thin film. The corresponding HAADF intensities are shown to the right in (c) with an arbitrary scale. (d) EELS maps acquired at the atomic scale at the $TbInO_3$–YSZ interface show a Terbium oxide buffer layer with Tb^{4+} at the interface. (e) color composition maps for In and Tb (right), and Tb and Zr (left) with an illustration of Tb^{4+} at the interface.

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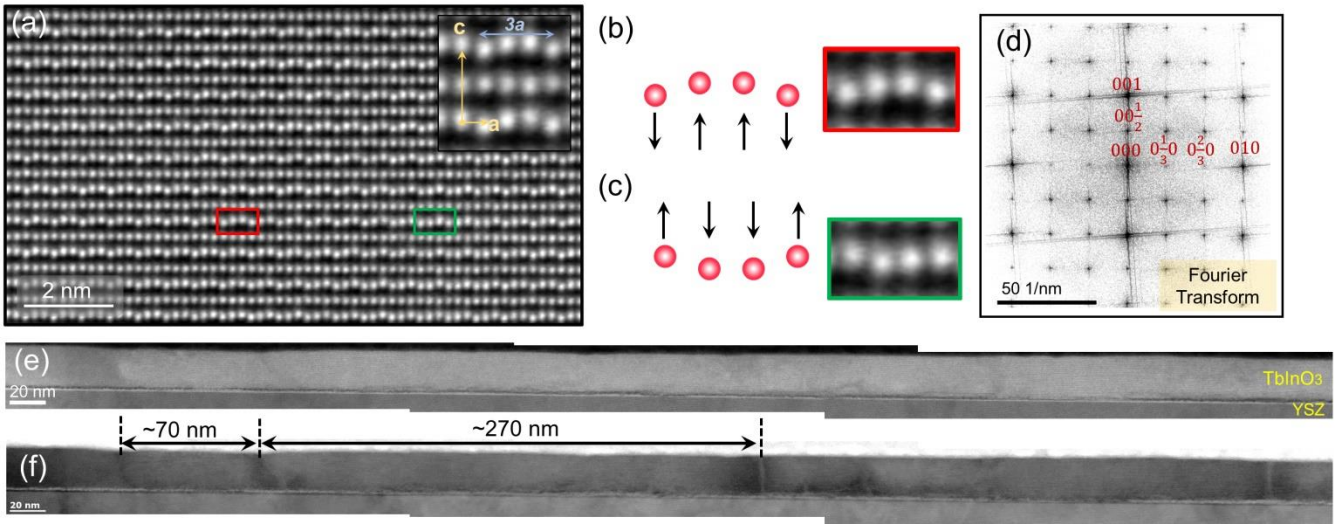

Figure 2. Improper ferroelectric domains in the $TbInO_3$ thin film. (a) high magnification high-angle annular dark field (HAADF) image shows displacement pattern across the image. The top-right insert shows and magnification of the unit cell. (b,c) Illustration of the down-up-up and up-down-down displacement pattern, respectively. The right inserts in (b-c) are zoom-ins from the HAADF image in (a). (d) Fast Fourier transformation of a HAADF image shows the lattice reflections. Peaks with wavevector **Q**=1/3 **a*** are visible, indicating the tripling of the unit cell due to the trimerization displacements. (e) HAADF, and (f) low-angle ADF images. The images are composite of stitching of 3 frames of ~270 nm each. Several domains inside the films are visible in the low-angle ADF images.

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