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Statistical Measurement of Polar Displacements in Complex Oxides

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Ferroelectrics are crystals with a spontaneous, switchable electrical polarization [1]. According to the modern theory of ferroelectricity, the polarization is a function of the polar displacement and the Born effective charge [2]. In complex oxides this is defined as second-order Jahn–Teller displacements in proper ferroelectrics, where the primary order parameter is the *B* site displacement with respect to the oxygen octahedral cage in ABO_3 perovskites [3]. In improper ferroelectrics, this is a first order Jahn–Teller distortion, where the rotation of the oxygen octahedral cages results in the absence of inversion symmetry [4]. Sub-Ångström resolution imaging with aberration correction has allowed the direct measurement of atom positions with scanning transmission electron microscopy [5]. Aberration corrected scanning transmission electron microscopy (STEM) has been used to image the evolution of domain walls in $BiFeO_3$ thin films, and have been used to image the presence of novel phenomena like polarization vortices in oxide superlattices [6, 7].

Scanning distortions like jitter and non-linear scan drift in STEM can cause the local displacement measurement prone to error [8]. To overcome these challenges we use a relative statistical measurement to quantify sub 10pm displacements in complex oxides. An average summation of atom positions generates a measurement with reduced random noise and jitter. Secondly, a relative measurement between the neighboring atomic species minimizes the contribution of non-linear drift. Finally, a statistical sampling leads to significantly higher accuracy in the displacement measurement, with the accuracy being inversely proportional to the square root of the number of sampling points according to the central limit theorem [9].

Figure 1a shows the annular dark field STEM image of $CaFeO_{2.5}$–$SrFeO_{2.5}$ thin films grown on a $SrTiO_3$ substrate. Density functional theory predicts three structures with equal energy, distinguished by the orientation of Fe tetrahedral layers [10]. Statistical measurement of the horizontal displacements of the B–sites which are the tetrahedral and octahedral Fe layers in film and the Ti atoms in the substrate is shown in Figure 1b. This shows no horizontal displacements in the substrate, and chiral tetrahedral displacements in the film. The overlaid predicted displacements from density functional theory demonstrate strong agreement between the statistically sampled experimental measurements and theoretical predictions. Through properly summing the unit cell displacements, we also demonstrate the horizontal displacements maintaining their chirality, while the smaller magnitude demonstrates the effect of the substrate on the polar displacement. Another example pertains to probing the atomic structure in $LiNbO_3$ across a 180° domain wall (Fig. 1c). Through summing the unit cells and quantifying the average displacements in $LiNbO_3$, statistical measurements parallel and perpendicular to the domain wall indicate that Ising nature of the domain wall with 30pm relative displacement of NbO_6 octahedra across the wall. Additionally, the NbO_6 octahedra also indicate displacements on the order of 10pm perpendicular to the wall, demonstrating the presence of a Néel wall. This research will present our statistical metrology approach allowing quantification of the displacements beyond the resolution limit of the microscope [11].

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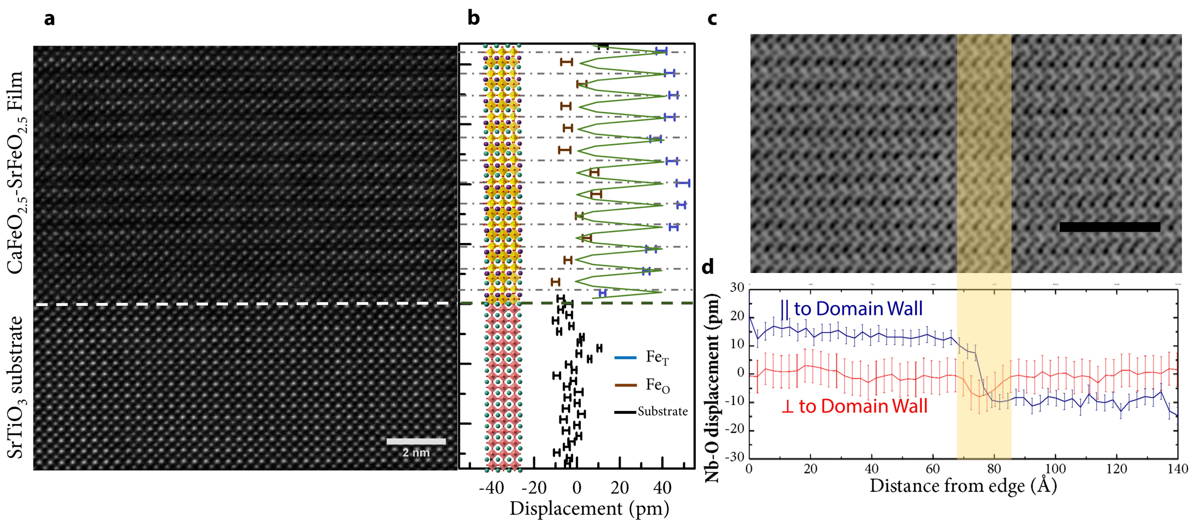

Figure 1. (***a***), ADF-STEM image of $CaFeO_{2.5}$ – $SrFeO_{2.5}$ film grown on a $SrTiO_3$ substrate. (***b***) Statistical measurement of horizontal displacements Fe displacements with respect to Ca and Sr positions, compared with DFT predictions (in green). (***c***) ABF-STEM image of $LiNbO_3$ showing Nb and O atoms. The scale bar is 2nm. (***d***) Statistical measurements of NbO_6 displacements ǀ and ⊥ to the domain wall demonstrating a mixed domain wall.

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