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Interplay Between Polarization and Oxygen Stoichiometry at Ferroelectric Domain Boundaries in $BiFeO_3$

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The multifaceted magnetic, electrical, and structural functionalities of perovskite ABO_3 materials derive from the subtle distortions of the crystallographic lattice from cubic prototype. These include displacements of the cations from the centers of the BO_6 oxygen octahedra (polarization), deformations of oxygen octahedral (e.g. collective Jahn-Teller effect), and collective tilts of octahedral network. Recently, much attention has been focused on new phenomena at hetero- and homointerfaces enabled by coupling between dissimilar order parameters, giving rise to new physical and applied concepts. However, almost completely ignored until recently were the effects associated with the role of local and global stoichiometry on the order parameter dynamics.

Indeed, in traditional physical description the population of cation and oxygen sublattices in perovskites is assumed to be constant and defined by the synthesis stage. However, the oxygen vacancy mobilities in these materials are known to remain measurable for temperatures as low as 400ºC (for $SrTiO_3$). Correspondingly, strong electric and strain fields present at the interfaces and domain walls can result in changes in oxygen stoichiometry over ~nm lengthscales at RT and below. Here, we systematically study the interplay between oxygen stoichiometry and ordering and ferroelectric domain wall structure in a model La-doped $BiFeO_3$ system. This system is chosen both due to its significance as multiferroic material, and high propensity for vacancy motion and ordering.

The material is studied using Nion UltraSTEM operated at 100kV; samples are grown on $DyScO_3$ in high (200 mbar) and low (10 mbar) oxygen pressure. The high-resolution data set is analyzed using the recently introduced direct polarization mapping [1,2] and column shape analysis [3]. Fig.1 (a) shows a HAADF image of the oxidized $BiFeO_3$ in the vicinity of a 109º domain wall. While the domain wall is not easily seen in the image, the corresponding Fe displacement map (Fig.1(b); also profile in (d)) shows clear contrast for the displacement parallel to the wall, while the displacement normal to the wall (Fig.1(c)) stays constant. The same analysis was performed for HAADF image of a domain wall in reduced $BiFeO_3$ (Fig. 2(a)). Here, Fe displacement parallel to the wall (Fig.2(b)) shows reduced contrast compared to the oxidized case. The normal component of Fe displacement (Fig.2(c)) is no longer constant and shows stripe-like modulation. The behavior can be clearly seen in map profiles (Fig. 2(d-e)). Ordered dipoles created by increased oxygen vacancy concentration apparently suppress polarization.

To summarize, using direct structural mapping by high-resolution STEM we explore the interplay between oxygen vacancy ordering and polarization in doped $BiFeO_3$. These studies offer a universal paradigm for probing other functional oxides and heterointerfaces at which vacancy dynamic can be the key to understanding unique and much discussed emergent physical phenomena. [4]

References

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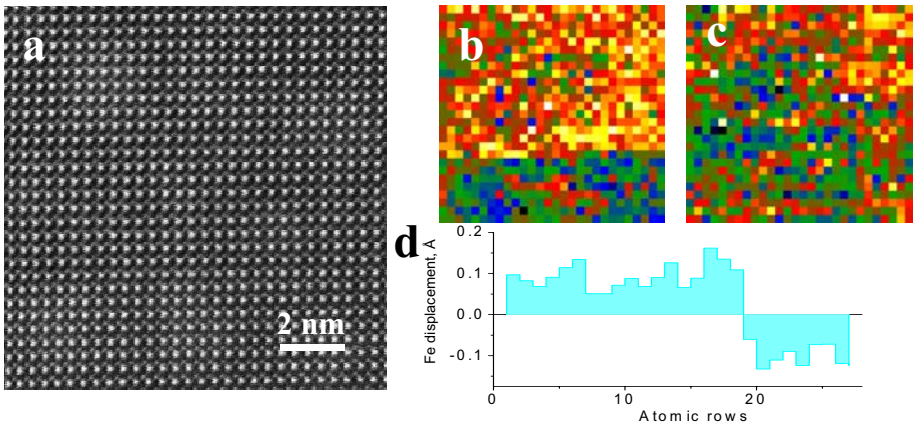

FIG.1.(a) HAADF image of a 109º domain wall in oxidized $BiFeO_3$, (b,c) corresponding Fe displacement maps for X and Y components; (d) profile of (b) showing a transition at the domain wall .

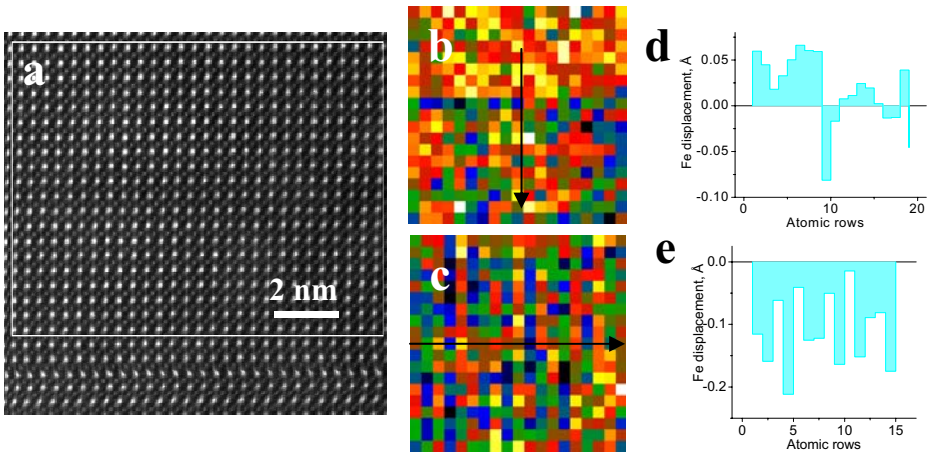

FIG. 2.(a) HAADF image of a 109º domain wall in reduced $BiFeO_3$ and (b,c) corresponding Fe displacement maps for X and Y components. (d,e) profiles of (b,c) in the directions given by arrows showing less pronounced transition at the domain wall in X component and a modulation of the displacement in Y component.

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