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Influence of Bulk Polarization and Surface Polarity on Surface Reconstructions and Related Local Properties of Multiferroic $BiFeO_3$ Film

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The surfaces of perovskite oxides undergo surface relaxation and reconstruction owing to the breaking of translational symmetry. Coupling between lattice and order parameters, such as polarization ($\boldsymbol{P}_s$) in ferroelectrics and/or polarity in polar structures, has a strong impact on surface relaxation and reconstruction. The resulting surface structures can affect samples with large surface to volume ratios and devices that rely on interfacial coupling or interaction. Until now, surface structures that involve the termination of both matrix $\boldsymbol{P}_s$ and polar atomic planes have received little attention, in particular on the atomic scale. Here, we present an atomic-scale study of the surfaces of multiferroic $BiFeO_3$ (BFO) thin films using atomic-resolution scanning transmission electron microscopy (STEM) and spectroscopy combined with first-principles density functional theory (DFT) calculations. Two distinct surface structures are revealed and the local ferroelectric and magnetic properties are deduced on the basis of atomic positions in a DFT-calculated model. Our results provide a structural basis for tuning the local multiferroic properties of BFO by controlling electrical boundary conditions and promise to stimulate wide interest in research on the behavior of surface reconstructions in other ferroelectric oxides with odd valences of cations, such as $LiNbO_3$.

BFO is a prototypical material that possesses ferroelectric $\boldsymbol{P}_s$ and polar atomic planes simultaneously. As illustrated in Fig. 1a, $(BiO)^+$ and $(FeO_2)^-$ layers stack alternately along the $\boldsymbol{c}$-axis, leading to the formation of a polar {001} surface. In addition, off-center displacements of the Fe and O atoms with respect to the Bi sub-lattice result in a large $\boldsymbol{P}_s$ of approximately 0.9 – 1.0 C/m^2 along the direction of the tensile-distorted [111] body diagonal [1]. In this material, $\boldsymbol{P}_s$ contains an <001> component that interacts with charges on the terminating surface, resulting in four possibilities for surface structures.

Figure 1b shows a high-angle annular dark-field (HAADF) STEM image of a BFO (001) thin film on a $DyScO_3$ $(110)_o$ (where o denotes orthorhombic) substrate, recorded along an <010> direction. The chosen sample area contains two domains. A 180º domain wall, which is marked by yellow dashed lines, can be traced by following a reversal in the shifts of FeO columns with respect to Bi columns (brighter dots). Such reversal can be revealed more clearly in Fig. 1c by mapping displacement vectors pointing from the centers of four Bi columns to FeO columns. The in-plane components of $\boldsymbol{P}_s$ in the two domains are denoted by arrows in Fig. 1b.

Two types of surface structure are evident in Fig. 1b, depending on the $\boldsymbol{P}_s$ of the underlying ferroelectric domain. On domains that have an upward polarization component (Type I), a layer with an Aurivillius-Bi_2O_2-like structural unit is observed. Dramatic changes in local properties are measured directly below the surface layer. On domains that have a downward polarization component (Type II), no reconstructions are visible. DFT calculations show that for the type I surface the structural unit of the Aurivillius phase acts as a reservoir for negative charges from an excess of O in the outer Bi plane, which stabilizes the surface structure. The negative charges contribute to the compensation of positive charges associated with the upward component of polarization and the $(BiO)^+$ polar surface termination. In contrast, the negative surface bound charges induced by the downward component of $\boldsymbol{P}_s$ on the type II surface can be self-compensated by the positive charges of the $(BiO)^+$ termination layer and therefore do not require an additional Bi_2O_2-like structure [2].

References:

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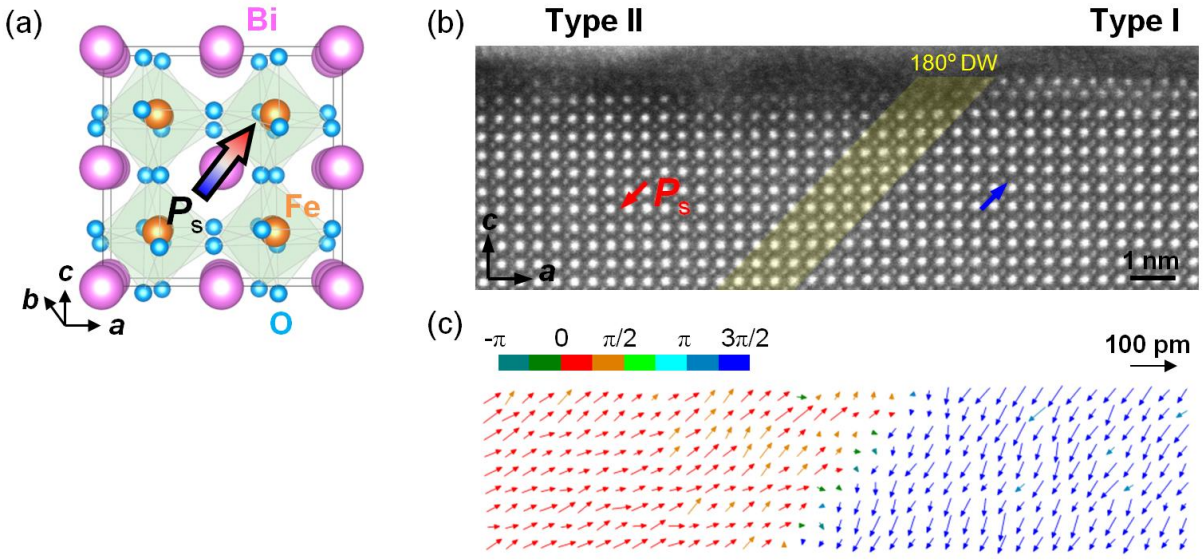

Figure 1. (a) 2×2×2 pseudocubic unit cells of room temperature BFO, showing displacements of Fe (orange) and O (blue) atoms along the $[\overline{111}]$ axis with respect to the Bi sub-lattice (pink). The displacements lead to a spontaneous polarization $\boldsymbol{P}_s$ pointing towards the [111] body diagonal. The $(BiO)^+$ and $(FeO_2)^-$ atomic planes have positive and negative net charges and stack alternately along the [001] axis. Four configurations of the (001) surface can be expected, depending on the $\boldsymbol{P}_s$ direction and the termination of the atomic planes. (b) Atomic-resolution HAADF STEM image showing two BFO ferroelectric domains separated by a 180° domain wall (marked by yellow dashed lines). The polarization vectors are marked in red in the left domain and in blue in the right domain. The surface structure on the left domain can be distinguished from that on the right domain. (c) Displacement map between the center of four Bi columns and FeO columns, showing a reversal in $\boldsymbol{P}_s$.