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IFSM-PL-1670 From Atomic Structure to Properties of Oxides: Applications of Aberration-corrected Transmission Electron Microscopy

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Functional oxides provide an important part of the material basis for multifunctional devices as a result of their exceptional range of physical properties. These properties, in turn, depend strongly on the crystal structures, chemical compositions and defect configurations of the materials, which can be characterized on the atomic scale.

In a high-resolution transmission electron microscope equipped with an aberration corrector, the spherical aberration coefficient CS of the objective lens can be tuned to either a positive or a negative value. The use of a negative value of CS combined with an overfocus setting of the objective lens is used in the negative CS imaging (NCSI) technique [1]. Images obtained using the NCSI technique show superior atomic column contrast and intensity than corresponding positive CS images [2], especially for weakly scattering oxygen columns that are in close proximity to strongly scattering cation columns.

Using the NCSI technique, we have investigated the atomic details near 180° domain walls in thin films of PbZr0.2Ti0.8O3 [3,4]. The relative displacements of ions have been measured and on this basis the local polarization across the wall has been calculated. Using this technique we have studied the atomic structure of LaO-TiO2-type interfaces in epitactic LaAlO3/SrTiO3 heterostructures [5]. The prominent result is the oxygen octahedron rotation and the TiO6 octahedra distortion induced by LaAlO3 in SrTiO3 at the interface. The cation-oxygen octahedra represent the prominent structural element of perovskites, which can be modified by distortions, rotations, and particular atomic shifts. Small atomic rearrangements as they are expected to occur at the interfaces between perovskites of different structure can change dramatically the electronic system.

We have recently used the NCSI technique to perform quantitative comparisons between experimental and simulated images on an absolute intensity basis after taking into account the effects of the modulation transfer function of the camera and additional image spread [6]. This absolute intensity matching approach not only allows atomic column positions and defect structures to be determined with picometer precision, but also allows the local chemistry and the three-dimensional morphology of a crystal to be determined on the atomic scale.

Figure 1 shows results obtained from a study of the relationship between the atomic structure and properties of BiFeO3, a room temperature multiferroic material. In the rhombohedrally-distorted perovskite unit cell of BiFeO3 (shown in Fig. 1a), characteristic structural features include relative shifts between the cations and the oxygen anions along the [111] axis and rotations of oxygen octahedra about the [111] axis, which are related to the ferroelectric polarization and the antiferromagnetic properties of the material, respectively. Both the atomic shifts and the rotations of the octahedra can be quantified using the NCSI and ACM techniques and used to understand the electrical and magnetic properties of the material. Figure 1b shows an atomic-resolution image of a 109° domain boundary (thick arrow) between two domains. The use of NCSI conditions and a particular specimen thickness result in the atomic columns appearing bright on a dark background. The domains in the material can then be distinguished by measuring the positions of the atomic columns inside individual unit cells.

In Fig. 1(b), the domain above the boundary is oriented along the [110] direction. The O column positions are shifted upward and downward (Fig. 1c), corresponding to alternating rotations of octahedra. A corresponding off-centre displacement of Fe with respect to the middle point of the line connecting two neighbouring (left and right) O positions is visible and oriented in a downward direction. In this orientation, the [001] component (red arrow) of the [111] polarization vector can be measured and the octahedron rotation can be revealed. Below the boundary (Fig. 1d), the domain is viewed along the [1¯10] direction. The octahedron rotation is now not visible due to the overlap of atoms (Fig. 1d). However, the full vector (red arrow) of the atomic column displacement is now revealed. In this way, the polarization of the domain can be determined unambiguously.

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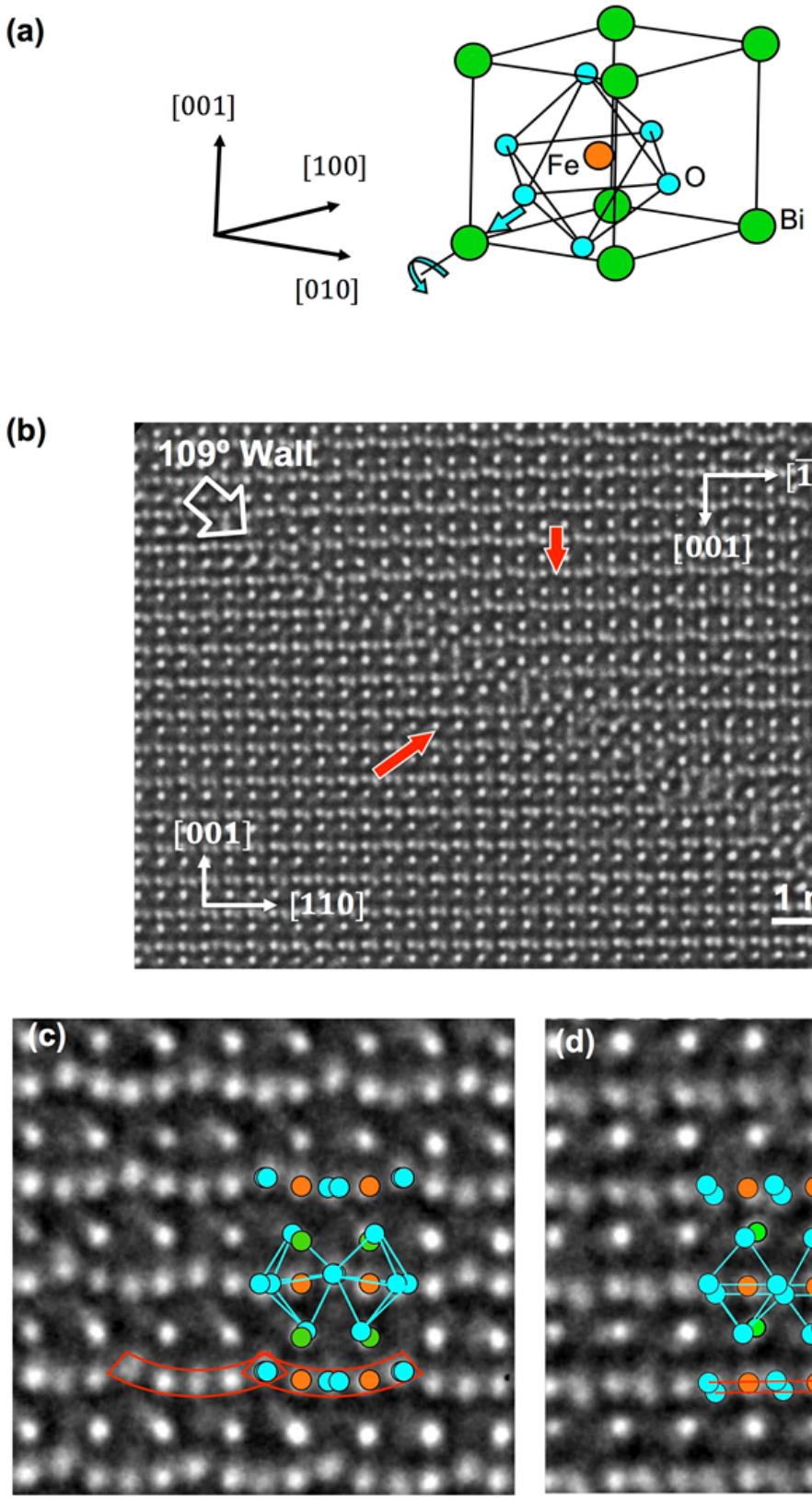

Fig. 1: (a) Schematic diagram of the pseudocubic unit cell of BiFeO3. (b) Atomic-resolution image of a 109° domain wall (thick arrow) separating two domains: the domain above the wall and the magnification in (c) correspond to a [110] viewing direction, while the domain below the wall and the magnification in (d) correspond to a [1$\bar{1}$0] viewing direction. The red arrows denote the polarization.