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Atomic Level View at the Ferroelectric-Antiferroelectric Transition and Phase Coexistence at Morphotropic Phase Boundary by Quantitative Aberration-Corrected STEM

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Phase transitions in solids can be often described through order-parameter based thermodynamic theories. However, for materials with competing or multidimensional order parameters the competition between close ground states often results in mesoscopic structural instabilities and associated complex nanoscale morphologies, such as monoclinic phases in the vicinity of morphotropic phase boundaries (MPB)[1] in ferroics and ferroelectric-antiferroelectric (FE-AFE) boundaries[2]. Almost invariably, spatially-resolved studies of these low-symmetry transitional phases reveal the presence of nanoscale domain structures of coexisting orientational variants, phases, or compositional gradients, with maximal complexity close to the MPB or FE-AFE boundary and simplifying away from it. However, the detailed internal structure of the domains, and especially the size and atomic structure of boundaries between them cannot be addressed with diffraction-based or mesoscopic approach. Here, we report direct atomically-resolved mapping of structural transformations at the ferroelectric-antiferroelectric boundary in Sm-doped $BiFeO_3$ using quantitative aberration-corrected Scanning Transmission Electron Microscopy (STEM) [3,4].

Sm-doped $BiFeO_3$ exhibits FE-AFE morphotropic phase boundary at ~14% Sm substitution.[2,5] We focused our attention on the 4x modulated phase for antiferroelectric (10% Sm) and MPB (14% Sm) compositions. Shown in Fig. 1 (a) is the high angle annular dark field (HAADF) image of the 10% doped sample in the [100] pseudocubic orientation. Figs. 1 (b,c) show two-dimensional maps of out-of-plane (X) lattice spacings calculated from Fig. 1 (a) for Bi and Fe sublattices. A considerable modulation of the Bi spacings in (1 10) direction is observed in the central area of the map in 1(b), while upper left and lower right corners have uniform spacings, showing the coexistence of the modulated AFE phase and parent FE phase. In contrast, the map of Fe spacings in Fig. 1 (c) appears quite featureless, suggesting uniform spacings for both modulated and unmodulated areas. Fig. 1(d) shows the corresponding profile of Bi displacements taken along diagonal direction shown by the blue arrow. We can see oscillating displacements in the modulated area and non-zero displacements outside it (in the FE matrix). Fig. 2(a) shows a HAADF image taken from MPB composition (14% Sm), while the Bi and Fe lattice spacing maps are shown in Fig. 2(b,c). In this image, recorded in a uniformly ordered area, both Bi and Fe sublattice spacings appear modulated. In fact, they are exactly in phase with each other and have comparable moduli, which results in considerable suppression of the relative Bi displacements (Fig. 2(d)).

These observations suggest that the bridging phase is a complex interplay of polarization and strain. For lower rare earth concentrations, patterns of oscillating Bi displacements are formed, while Fe sublattice is undisturbed. As A cation radius is reduced with Sm doping, Fe sublattice is also driven

to distort to accommodate increasingly asymmetric environment. These conjectures are corroborated by O-K NEXAFS data on the two compositions.[6]

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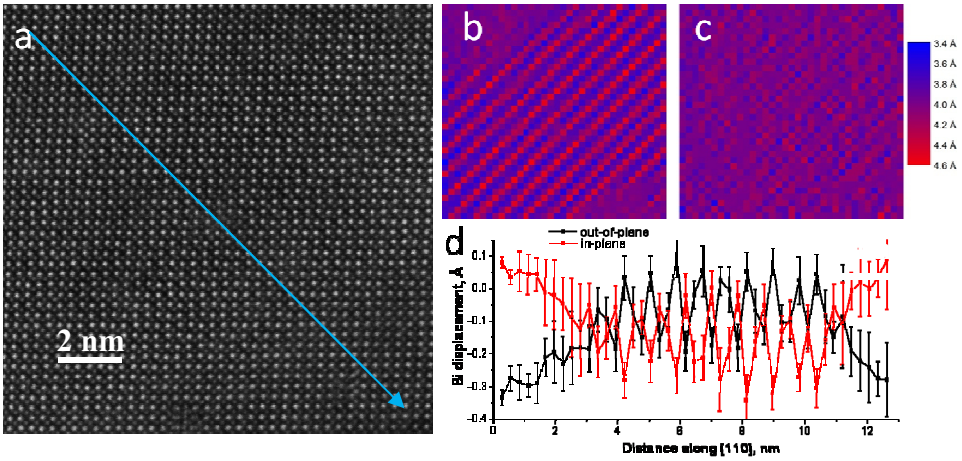

FIG.1 (a) HAADF image of the 10% Sm-doped composition (AFE) and (b,c) lattice parameter maps obtained from (a) showing strong lattice modulation in the Bi sublattice(b) and no contrast in the Fe sublattice (c). The ordered area exhibits oscillating Bi displacements (d)

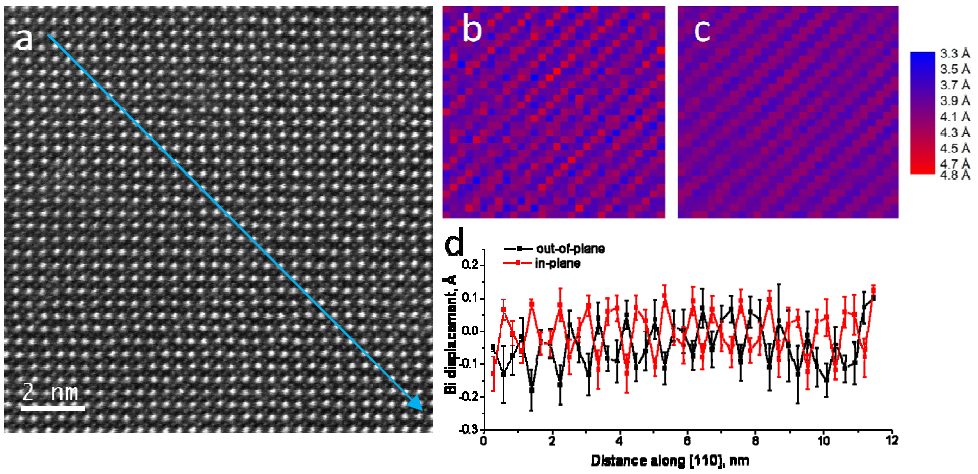

FIG.2(a) HAADF image of the 14% Sm-doped composition (at the MPB) and (b,c) lattice parameter maps obtained from (a showing lattice modulation in both Bi sublattice(b) and Fe sublattice (c). The modulations occur in-phase, suppressing the relative cation displacements (d).

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