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Role of Defects and Structure Evolution across Ferroelectric Phase Transitions Studied by Quantitative Aberration-Corrected STEM

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Local structure and defects often play a decisive role in functional behavior of materials and provide a unique view at the physical characteristics of a transition, with implications for both baseline properties and dynamic response. Quantitative scanning transmission electron microscopy (STEM) has been an indispensable tool in studies of local structure in a wide range of materials, providing crucial atomic-scale information [1]. Coupled with in-depth functional characterization with scanning probe microscopy (SPM) and theoretical insights from density functional theory and Ginsburg-Landau modeling, true underpinnings of physical properties can be uncovered. In this context, variable-temperature observations of structure across the phase transitions are especially valuable.

In perovskite $BaTiO_3$ thin films, we were able to connect enhanced electromechanical response and unusual dynamic behavior to the presence of oxygen vacancies. Fully relaxed 80 nm $BaTiO_3$ thin film was grown on $SrRuO_3$ //$SrTiO_3$ (001) substrate using pulsed laser deposition. STEM imaging has uncovered areas of modulated lattice spacings within the film, as well as characteristic changes in O K EELS edge indicative of the presence of oxygen vacancies (Fig.1). Dynamic variable-temperature SPM studies combined with an array of theoretical methods point to a created internal electric field that further enhances the intrinsic electrostriction as the mechanism for enhanced electromechanical response [2].

Layered ferroelectrics of the thiophosphate family, most notably Copper Indium Thiophosphate, have garnered attention of researchers due to high potential for tunability and therefore a wealth of possible phase transitions (see e.g. [3,4]). Some 3D members of the same family such as $Sn_2P_2S_6$ possess similar ferroelectric properties with a Curie temperature of ~70°C. This material has a complex monoclinic structure [5,6] and its defect behavior is not well understood. Fig.2(a) shows HAADF STEM image of a $Sn_2P_2S_6$ crystal in (111) orientation; corresponding structure model is given in Fig. 2(b). We do not see evidence of ferroelectric domain boundaries in the 50-100 nm crystals, however we observe structural defects such as dislocations (Fig. 2(c)). Variable-temperature studies using *in situ* heating inside the STEM indicate that we can detect reversible changes in structure related to the transition at 70°C. Comparison of our observations with XRD and theoretical studies, as well as their implications for the understanding of this phase transition, will also be discussed. [7].

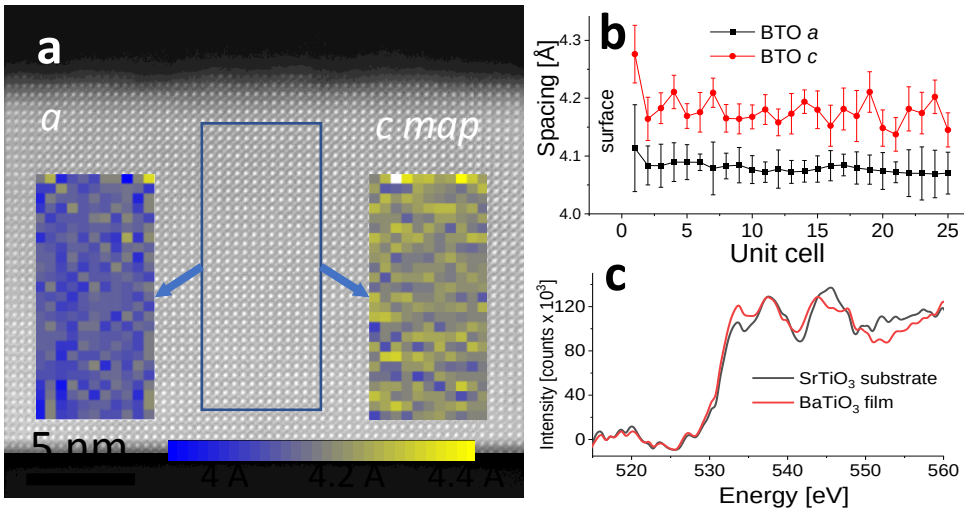
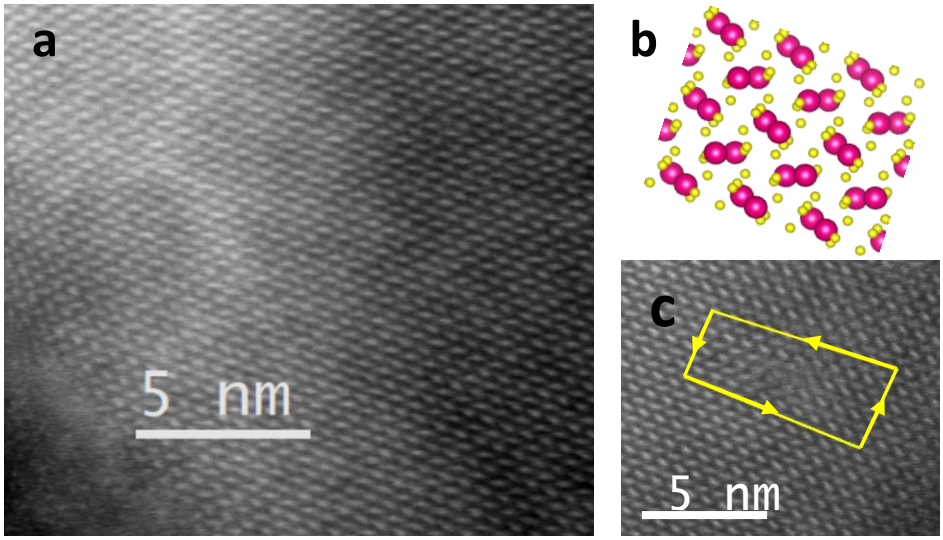


Figure 1 (a) Surface region of the $BaTiO_3$thin film; insets – lattice spacing maps from the area inside the blue box. b) Vertical profiles of the map insets from (a). c) Electron energy loss O K edge spectra for $SrTiO_3$ substrate and $BaTiO_3$ film showing differences characteristic of the presence of oxygen vacancies. (Adapted from Ref. 2)



F**igure 2.** Imaging of $Sn_2P_2S_6$ ferroelectric crystals: (a) HAADF STEM image showing tweed-like arrangement of Sn_2 dumbbells; (b) rotation-matched schematic of a suggested structure for $Sn_2P_2S_6$ (Ref. X) in (111) orientation; (c) a dislocation in $Sn_2P_2S_6$.

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