Imaging polarization in $BaTiO_3$ with aberration corrected instruments – Is it possible?

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Keywords: ncsi, polarization, ferroelectrics

Remarkable high resolution transmission electron microscopy (HRTEM) images of polarization-induced atomic displacements in ferroelectric materials have been recently accomplished [1]. They have been made possible by the advancements of aberration corrected instruments which allow negative values of the spherical aberration coefficient to be employed. The functional oxide structure investigated under these conditions was lead zirconate titanate (PZT). This material exhibits stable and increased ferroelectricity at room temperature due to the zirconia doping. However, lead is a well-known contaminant and thus the industry is looking to lead-free substitutes for the electronic devices based on functional oxides. One of the best candidates for ferroelectric applications is $BaTiO_3$.

$BaTiO_3$ is a perovskite crystal with a Curie temperature of 120°C that exhibits four different distinct phases. The changes in phase (first order transitions) correspond to discontinuities in the direction of spontaneous polarization. The polarization is oriented along <100> between 120°C and 0°C (Fig. 1a), along <110> between 0°C and -80°C, and along <111> below -80°C. Thus, for a room temperature experiment barium titanate is in the tetragonal phase and its polarization is oriented in the <100> direction. The relative displacement of the central titanium ions is estimated to be ~0.015 Å which leads to ~6 pm absolute off-center displacement [2]. Imaging of the Ti atom in the perovskite structure by transmission electron micrographs is convenient in the <110> orientation, as seen in Fig.1b, where Ti columns can be directly imaged.

In this study, room temperature negative spherical aberration imaging (NCSI) of single crystal $BaTiO_3$ was performed at 300 kV using a FEI Titan 80-300 equipped with an image-forming Cs corrector. A series of defocused images was acquired and they were post-processed using the TrueImage software [3] in order to retrieve the speminen's exit-plane wave function. Specimen requirements for this imaging method involve ultra-thin films (5-20 nm) with minimum surface layer amorphization. Based on these restrictions, the preferred preparation method applied was the crushing technique. Fig. 2a depicts a representative NCSI micrograph of the atomic positions along the (101) direction. The acquisition time was set to 1 sec using a 2048x2048 UltraScan Gatan camera. Though all atoms, Ba, Ti, and O are visible, there is no immediate evidence of the Ti ion displacement. Fig. 2b shows the phase of the same region as in Fig. 2a as it was reconstructed from a series of 20 images. Both the NSCI image and phase conform to the projected atom positions as calculated by JEMS [4] (Fig.1b). The phase image is much clearer than the single micrograph and slight atomic displacements are also recognized. Attributing these displacements to domain structure requires microscope conditions to remain stable during the acquisition of the focal series. Experimental considerations that can utterly inhibit HRTEM imaging of such a mechanism in $BaTiO_3$ mainly involve temperature and time dependence mechanisms of polarization. HRTEM imaging requires good signal-to-noise statistics and small pixel sizes at high magnifications. This usually leads to acquisition of time-averaged structure information which contributes to significant heating of the infinitesimal area irradiated by the electron beam. These two parameters are discussed with respect to ion displacement identification via high resolution transmission electron micrographs in perovskite type ferroelectric structures. Interpretation of micrographs with respect to the stability of the microscopes will also be discussed.

References

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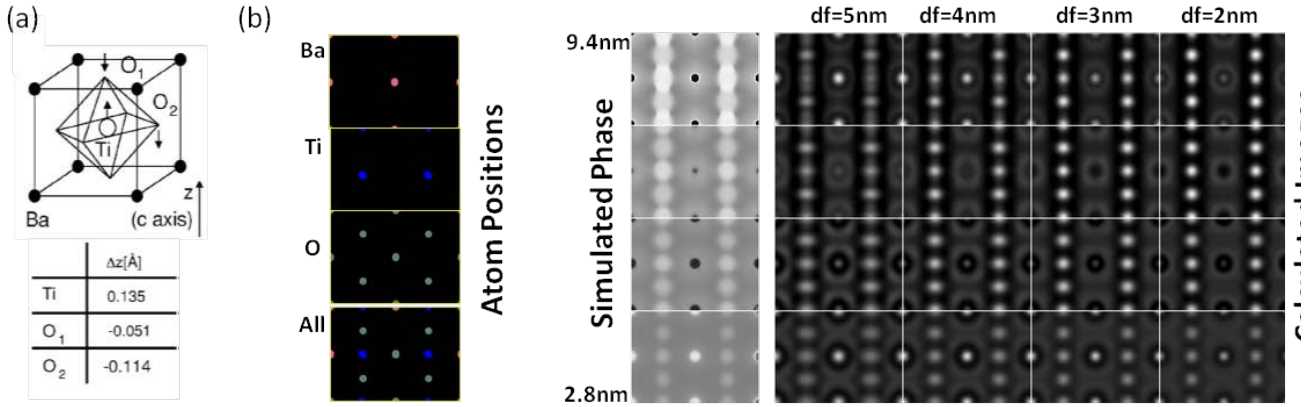

Figure 1. *(a) Model view of $BaTiO_3$ in the tetragonal phase with the polarization vector oriented along the c axis. Also shown are the relative displacements of the Ti atom and the two oxygen atoms around it. (b) JEMS atomic positions, phase simulations, and calculated HREM images for thicknesses ranging from 2.8 to 9.4nm and defocus values of 2, 3, 4, and 5nm.For the HREM simulations the spherical aberration coefficient Cs was set to -0.015mm.*

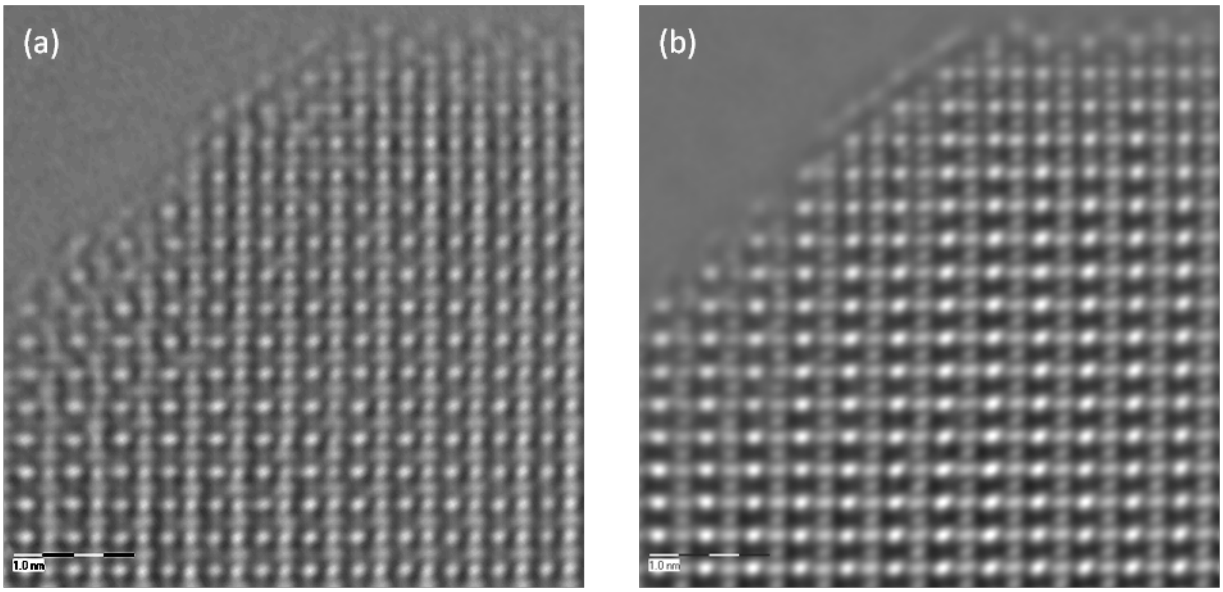

Figure 2. *(a) High resolution transmission electron micrograph of $BaTiO_3$ imaged along the <110> zone axis. Operating parameters: 300kV, Cs=-0.015mm, df=7nm, t_{aq}=1sec.(b) Reconstructed phase from a series of 20 defocused HRTEM images including (a).*