

Toward 3D Mapping of Octahedral Rotations at Perovskite Thin Film Heterointerfaces Unit Cell by Unit Cell

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Oxygen octahedral rotations (OOR) in perovskites couple strongly to their electronic and magnetic properties, providing another instrument of control for creating functional materials with desired properties [1]. Epitaxial thin films constitute a natural playground for manipulating OOR since the local structure and microstructure of the film can be tuned through the elastic, electrical, and chemical interactions with the substrate. It is therefore critical to characterize OOR at the heterointerface, a planar crystal defect. X-ray and neutron diffraction techniques can fully determine the octahedral rotation angles and phases, but their spatial resolution is poor [2]. On the other hand, electron microscopy imaging techniques, including HRTEM [3], bright field (BF) [4] and annular bright field (ABF)^[5] STEM can be used to directly visualize O columns and determine the rotation angle in each unit cell. However only one in-phase rotating axis can be studied at a time, therefore the full 3D rotation information is not available. This problem can in principle be solved via electron diffraction techniques, but they have their drawbacks: selected area electron diffraction (SAED) [6,7] is great for bulk samples but suffers from dynamic scattering and limited resolution in a thin film configuration; the recently introduced position averaged converged beam electron diffraction (PACBED) [8] requires extensive simulations, which become especially prohibitive for complex materials with several competing phenomena, since each sample parameter such as thickness, polarization, strain, and tilt, adds an extra dimension to the simulation phase space.

In this presentation, we will propose a simpler strategy for characterizing multiple dimensions of OOR using direct oxygen imaging in STEM, demonstrated on the example of CaTiO₃, a *Pnma* space group perovskite in the bulk. Instead of looking along the in-phase rotating axis pseudocubic [100]_{pc}, we obtain ABF STEM images from the [110]_{pc} zone, along which O atoms in one unit cell form more than one column. Because of that, the shapes of those O columns within one unit cell and their symmetry relations to adjacent unit cells contain information about the OOR system, even including information from the direction normal to the image plane. In Figure 1 the phase of OOR in the [100]_{pc} zone can be determined for a 20nm CaTiO₃ (CTO) grown on LSAT substrate, using ABF images taken in the UltraSTEM200 at ORNL.

Frozen phonon multislice image simulations [9] are then used to investigate the range of imaging and specimen conditions over which this method can be applied. As shown in Figure 2, the contrast for the ABF mode is found to be robust within a ± 2 nm defocus range and not sensitive to specimen thickness up to 40 nm, consistent with the work by Findlay *et al.* [10] We will also simulate the effect of specimen mis-tilt, which is a common practical concern. Finally, we are going to build a range of crystal models with different OOR systems and rotation angles, mapping out the range of tilt angles that can be detected. With this data in hand, a wide range of materials can be characterized from images without

extensive further simulations; it will also enable us to directly visualize out-of-plane OOR without having to remove the substrate. The prospects for using this technique on superlattices of materials with different tilt systems will also be discussed.

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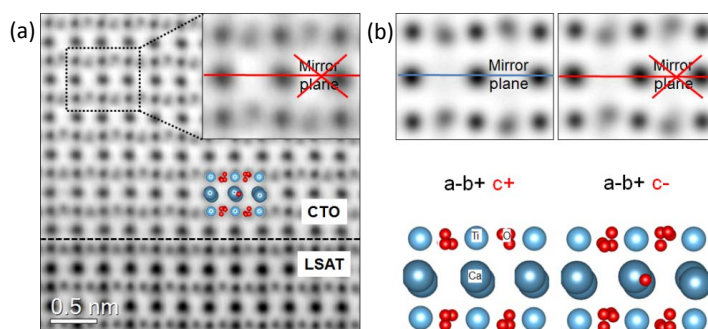


Figure 1 (a) Experimental ABF image of CTO film on LSAT substrate viewed along $[110]_{pc}$ zone axis. (b) Simulated ABF images of CTO models with different OOR systems. Notice that a mirror plane (with respect to O columns only) is present for in-phase out-of-plane rotation ($c+$) and absent for out-of-phase ($c-$). This can be used to identify the CTO film shown in (a) as $c-$.

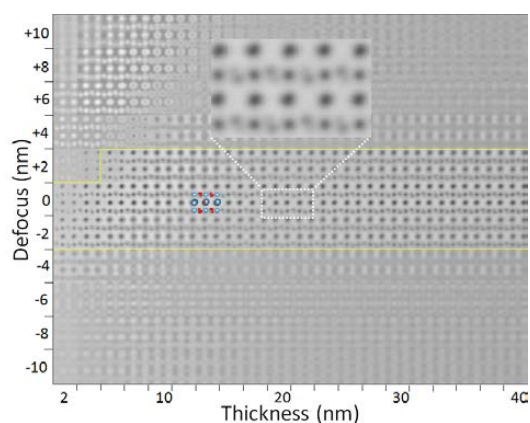


Figure 2 Frozen phonon multislice simulated defocus-thickness map of ABF imaging of CTO ($a-b+c-$) viewed along the 110 direction, using the microscope parameters of the UltraSTEM200 at ORNL. The probe size (FWHM) of 0.5Å is used. The visibility of the fine structure at the O columns is robust within ± 2 nm of defocus and is not sensitive to specimen thickness up to 40 nm.