

Investigation of Local A-site Chemistry in Barium Strontium Titanate Using Aberration Corrected STEM, EELS and EDS

Matthew J. Burch¹, Jing Li¹, Lauren Garten², Xiahan Sang¹, James Lebeau¹, Susan Trolier-Mckinstry², Jon-Paul Maria¹, and Elizabeth C. Dickey¹

¹North Carolina State University, Materials Science and Engineering, Raleigh, NC USA

²Pennsylvania State University, Materials Science and Engineering, University Park, PA USA

Barium strontium titanate (BST) is an important dielectric material because of its high tunability (dielectric constant as a function of applied voltage) and low loss, with specific applications in tunable microwave circuits. However, regardless of processing technique, additives, or synthesis temperatures some remnant ferroelectricity is always observed beyond the paraelectric phase transition [1]. One possible explanation for this remnant ferroelectricity, which has been hotly debated, is that the local stoichiometry of the A-site cations (Ba and Sr) is not globally and locally homogeneous. This hypothesis surmises that local areas, which are barium rich, may result in remnant polarization [1]. However, this hypothesis has never been experimentally shown. In this work, we use an aberration corrected scanning transmission electron microscope (STEM), electron energy loss spectroscopy (EELS), and energy dispersive X-ray spectroscopy (EDS) to investigate the local stoichiometry of arguably the best-engineered barium strontium titanate samples ever fabricated [2] in comparison to BST thin films showing some of the best tunability in thin-film form.

The experiments were performed on a monochromated and probe-corrected FEI Titan G2 60-300 kV S/TEM. The STEM images obtained were taken with and processed with RevSTEM, an imaging technique used to correct for drift during imaging [3]. Figures 1 and 2 are examples of images taken with RevSTEM. EELS was used to measure nano-scale changes in stoichiometry by measuring the ratio's of barium and titanium (strontium is not used because of the lack of intensity in the L-edge and its distance from the barium M-edges), and assuming a 1:1 ratio from the A-site cation's to the B-site Ti cation. The EELS maps were 16x6 with pixel size of 2.05 nm x 2.05 nm. Atomic resolution EDS was also performed to observe any local changes in the Sr-map, which could indicate clustering in the BST.

The first sample we examined was fabricated in the 1990's by Texas Instruments (TI) and later given to Dr. Cross at Penn State for electrical characterization [2]. It has long been deemed as one of the best-engineered bulk BST sample ever synthesized and shows excellent electrical properties, including a very sharp phase transition. We used this sample as a baseline and compared the result to modern-day synthesized BST thin films on a ceramic alumina substrate, which show a much broader phase transition than the TI sample.

As shown in Figure 4, EELS shows that a variation of the Ba/Ti ratio of 2-3% in the TI sample and as much as 8-10% in the BST thin film across 10's of nanometers. This is consistent with the increased broadening of the phase transition in the modern thin film when compared to the TI sample. However, the variation may exist across smaller length scales than has been identified by EELS. Thus we continued our investigation by utilizing atomic resolution EDS, which traditionally is avoided in BST, because of the serious Ba L-edge overlap with the Ti K-edge. However, by finding the correct zone axis and using the Sr edge it may be possible to observe any atomic-level disorder. The results are not conclusive on the level of Sr being in-homogenous across the atomic scale as shown in Figure 3. In

addition RevSTEM maybe utilized to observe the lattice distortion, which will result from the difference in unit cell size with Ba or Sr on the A-site. These experiments are still ongoing.

References:

- [1] L. Szymczak, Z. Ujma, J. Hańderek, and J. Kapusta, *Ceramics International* **30** (2004), p. 1003
 [2] Wenhui Ma and L. Eric Cross, *Applied Physics Letters*, **81** (2002), p. 3440
 [3] Xiahan Sang and James M. LeBeau, *Ultramicroscopy* **138** (2014), p. 28
 [4] The authors acknowledge funding by Defense MicroElectronics Activity (H94003-10-0-1002). This material is based upon work supported by the National Science Foundation Graduate Research Fellowship for M.J. Burch under Grant No. DGE-0946818. Any opinion, findings, and conclusions or recommendations expressed in this material are those of the authors(s) and do not necessarily reflect the views of the National Science Foundation.

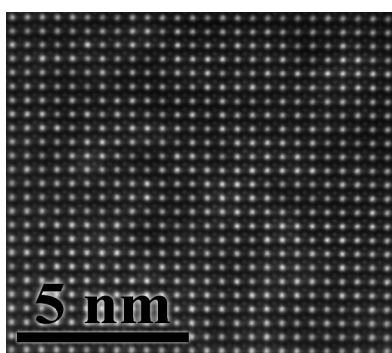


Figure 1. A RevSTEM image of the bulk BST fabricated by Texas Instruments.

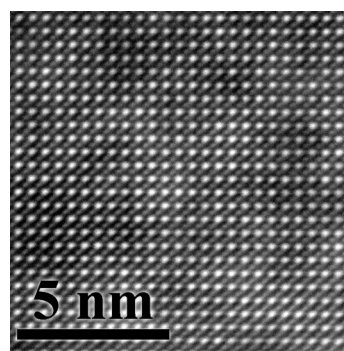


Figure 2. A RevSTEM image of thin-film BST on ceramic alumina fabricated recently.

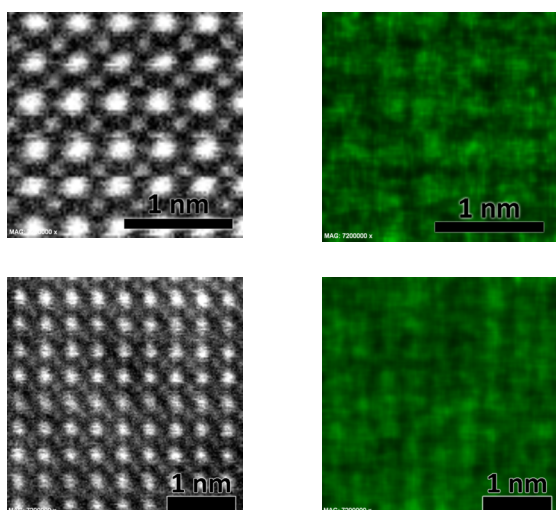


Figure 3. (a) STEM image of the bulk TI BST sample with (3b) the corresponding EDS map of the integrated Sr $K\alpha$ emission line. (3c) STEM image of the thin-film BST with (3d).corresponding Sr map

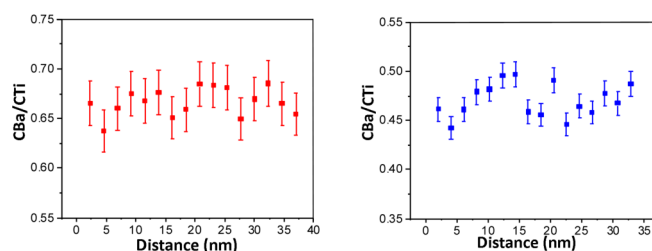


Figure 4. (a) Nano-scale EELS profile across the bulk TI BST sample. (b) Corresponding nano-scale EELS profile across the thin film BST sample.