

Direct Visualization of Polar Nanoregions in BaTiO₃-based Ferroelectrics Above Curie Temperature

G Drazic^{1*}, A Bencan², T Rojac² and D Damjanovic³

¹. Department of Materials Chemistry, National Institute of Chemistry, Ljubljana, Slovenia.

². Electronic Ceramics Department, Jozef Stefan Institute, Ljubljana, Slovenia.

³. Laboratory for Ferroelectrics and Functional Oxides, Swiss Federal Institute of Technology in Lausanne – EPFL, Lausanne, Switzerland.

* Corresponding author: goran.drazic@ki.si

Ferroelectric materials based on BaTiO₃ undergo a phase transition from a non-centrosymmetric polar ferroelectric phase to a cubic paraelectric centrosymmetric phase at Curie temperature (T_c) where spontaneous polarization is lost. However, recently it has been shown that cubic BaTiO₃ phase exhibits breaking of nominal centric symmetry and exhibits polarization which was explained with the presence of polar nano-regions [1].

In this work we aimed a direct visualisation of polar nano-regions in paraelectric phase of BaTiO₃ (BT, with T_c at 130 °C) and (Ba_{0.6}Sr_{0.4})TiO₃ (BST, with T_c at 0 °C) by measuring oxygen atoms displacement regarding to Ba and Ti sublattice. We also tried to correlate the chemical composition fluctuations (Ba/Sr ratio) in BST with the appearance of polar nano-regions. The approaches and methodologies used were described in recently published work where the concentration of bismuth vacancies at domain walls in BiFeO₃ were studied [2]. Briefly, the chemical composition was evaluated from the background subtracted and normalized Ba (Ba/Sr) and Ti column intensities measured from HAADF micrographs and the position of the columns were extracted by 2D Gaussian algorithm using ImageJ software [3]. Images were acquired with Cs probe-corrected STEM (Jeol ARM 200 CF) using heating and cooling in situ sample holders in the temperature range from -180 to 300 °C. To perform measurements in the paraelectric state BT was heated to 200 °C and 300 °C. BST which is paraelectric at RT was cooled down to liquid nitrogen temperature to study the paraelectric – ferroelectric transition.

In order to minimize the effect of specimen drift and scanning nonlinearity during experimental image acquisition stacks of 20 fast frames from each area with a resolution of 5pm per pixel were collected and subsequent rigid registration was used to align images. From stacks average images were extracted. Magnitude and direction of polarization was obtained from atom column displacements that were measured from ABF images.

To test the methodology capabilities and estimate the precision of measurements HAADF and ABF images were simulated for BT and BST using models based on tetragonal P4mm and cubic Pm3-m structures. Multi-slice method with frozen-phonon approximation was used for image simulations (QSTEM) [4]. In order to examine the influence of polar nano-regions overlapping we constructed a 24 nm thick model with few nm sized differently oriented polar nano-regions embedded in cubic matrix and simulated the ABF images where we varied the amounts of defocus. We found that at zero defocus information from the upper few nm sized region has the greatest impact to the final image and thus thicker samples can be used (10 – 25 nm) and still precisely measure the displacements of atomic columns.

Results show that in paraelectric state of BT and BST Ba or (Ba, Sr), Ti and O atom columns are displaced in a coherent way, forming noncubic few nm sized clusters (Figure 1). Based on shifts of Ti and O sublattice we confirm that those regions are polar and possess symmetry, which could even be lower than tetragonal.

In the presentation the possible origin of polar nano-regions formation and the correlation between the presence of polar nano-regions and chemical composition fluctuations (in the case of BST) will be presented and discussed [5].

References:

- [1] S Hashemizadeh et al., *Journal of Applied Physics* **119** (2016), p. 094105.
- [2] T Rojac et al., *Nature Materials* **16** (2017), p. 322.
- [3] J Schindelin et al., *Nature Methods* **9** (2012), p. 676.
- [4] C Koch, PhD thesis, Arizona State University (2002).
- [5] The authors acknowledge funding from the Slovenian Research Agency (P2-0393, P2-0105).

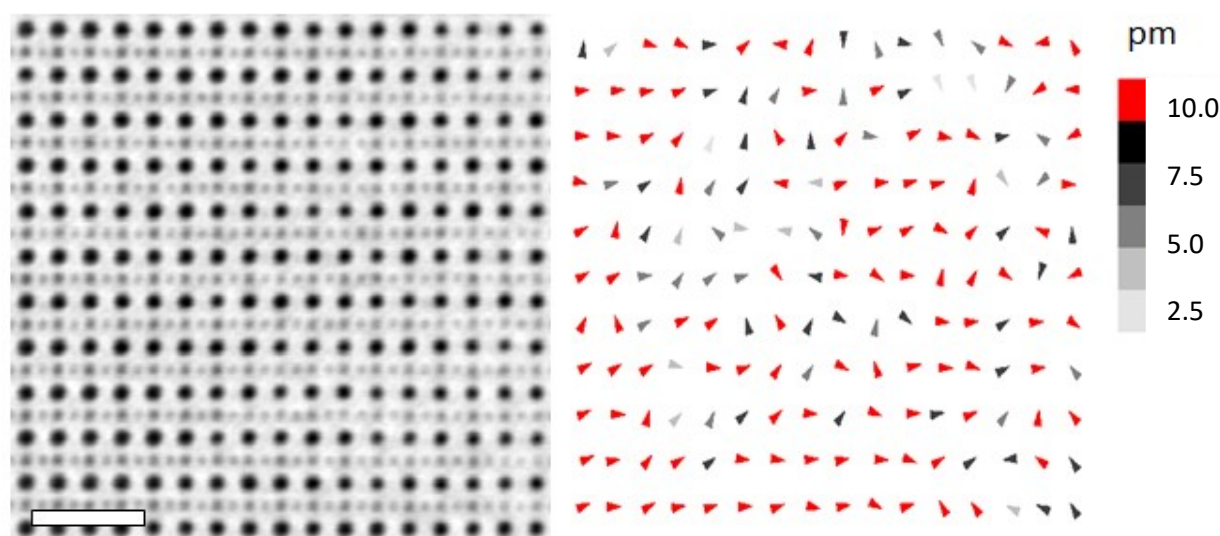


Figure 1. Experimental ABF-STEM image in [011] zone axis acquired at RT (left) and O vs Ti displacements in $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ sample (right). Scale bar is 1nm. Average absolute value of displacements was 13.4 ± 7.4 nm.