Visualisation of polar nano-regions and chemical composition fluctuations in $BaTiO_3$ and (Ba, Sr)TiO_3 ceramics above Curie temperature

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Ferroelectric $BaTiO_3$ based materials udergo a phase transition from a non-centrosymmetric polar ferroelectric phase to a paraelectric phase at Curie temperature (Tc). The paraelectric phase is centrosymmetric (cubic) and the polarisation is lost. However, recently it have been shown that cubic $BaTiO_3$ phase exhibits breaking of nominal centric symmetry and exhibits polarization which is probably linked to the presence of polar nano-regions [Hashemizadeh et al., Journal of Applied Physics, 119, 094105, 2016].

The aim of this work was a direct visualisation of polar nano-regions in paraelectric phase of $BaTiO_3$ (BT - Tc 130 °C) and $(Ba_{0.6}Sr_{0.4})TiO_3$ (BST - Tc 0°) based on oxygen atoms displacement. We also tried to correlate the chemical composition (Ba/Sr ratio) in BST with possible appearance of polar nano-regions. The approaches used were described in recently published work where the concentration of bismuth vacancies at domain walls in $BiFeO_3$ were studied [Rojac, et al., Nature Materials 16, 322, 2017]. We will discuss the methodology and results obtained from ABF and HAADF images, acquired with Cs probe-corrected STEM.

With heating sample holder pure BT was analysed at 200 °C and 300 °C, BST was examined at room temperature (in paraelectric state).

In order to minimize the effect of the specimen drift and scanning nonlinearity during experimental image acquisition we took a stack of 20 fast frames from each area with a resolution of 5pm per pixel. After collection rigid registration was used to align images and average image was extracted. Atom column displacements were measured from ABF images while (Ba, Sr) column intensities were extracted from HAADF images and related to the chemical homogeneity of the investigated area.

For measurement errors estimation we first simulated HAADF and ABF images for BT from models based on tetragonal P4mm and cubic Pm3-m structures. In cubic model (no displacements) we measured average displacement of 2 pm with a standard deviation of 1pm. In tetragonal model (nominal displacement is 9 pm) we measured values between 8 and 11 pm with 1 pm standard deviation.

To evaluate experimental intensity distribution in BST we constructed a 200,000 atoms cubic model where we randomly occupied A sites with Ba or Sr with the probability of 0.6 and 0.4 respectively. Model in [011] zone axis is shown in Fig. 1. (only perovskite A site atoms are shown). Using multislice frozen-phonon method (QSTEM) and 30 repetitions to take thermal diffuse scattering into account we evaluated A column intensity distribution from HAADF simulated images (Fig. 2.). Normalised to the strongest intensity we obtained average intensity ratio value of 0.88 +/- 0.05 (Fig. 3).

Experimental values were very close (around 0,90 +/- 0.02) so we can conclude that the distribution of Ba and Sr at A sites are quite uniform and close to nominal ratio.

Results show that in paraelectric state BT and BST Ba or (Sr, Ba), Ti and O atom columns are displaced in a coherent way, forming noncubic few nm sized clusters, as expected for polar nano-regions (Fig. 4. shows O vs Ti in BST at RT).

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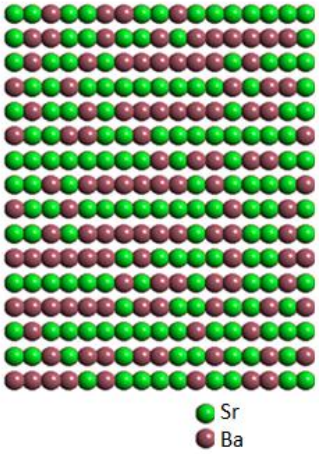

Fig. 1.
Cubic BST model

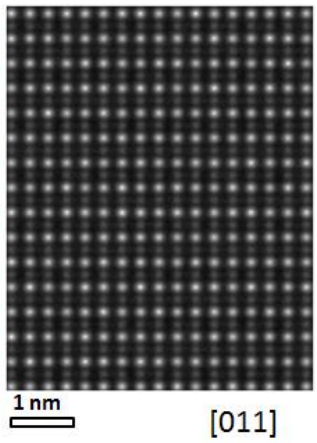

Fig. 2.
HAADF simulated image

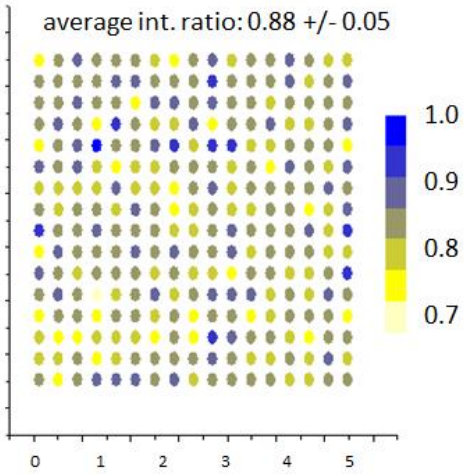

Fig. 3.
Ba/Sr column intensity

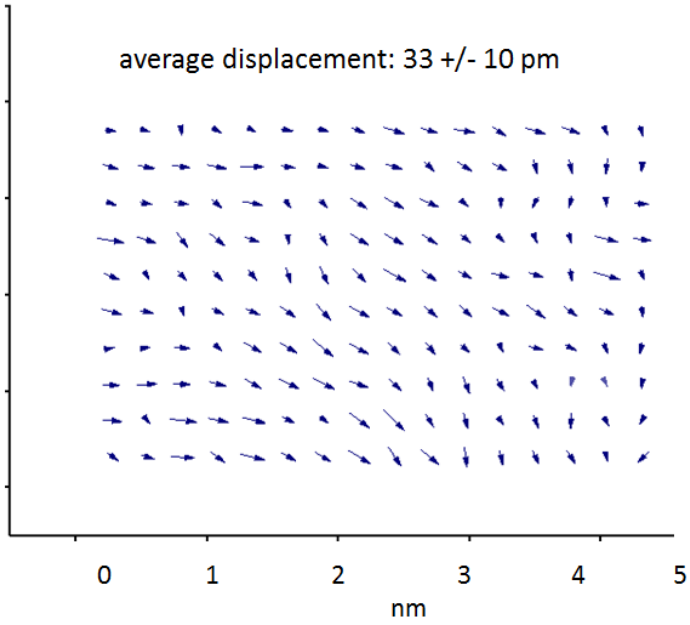

Fig. 4. Distribution of O to Ti displacements in BST sample