Symmetry Breaking and Direct Evidence of Polar Regions in Paraelectric Phase of $BaTiO_3$-based Ferroelectrics

Sina Hashemizadeh[1,*], Emad Oveisi[2], Sandro De Zanet[3], Andreja Bencan[4], Goran Drazic[4,5], Tadej Rojac[4], and Dragan Damjanovic[1]

1 Group for Ferroelectrics and Functional Oxides, Swiss Federal Institute of Technology in Lausanne–EPFL, 1015 Lausanne, Switzerland

2 Interdisciplinary Centre for Electron Microscopy – CIME, Swiss Federal Institute of Technology in Lausanne–EPFL, 1015 Lausanne, Switzerland

3 Computer Vision Laboratory, Swiss Federal Institute of Technology in Lausanne–EPFL, 1015 Lausanne, Switzerland

4 Electronic Ceramics Department, Jozef Stefan Institute, 1000 Ljubljana, Slovenia

5 Department of Materials Chemistry, National Institute of Chemistry, 1000 Ljubljana, Slovenia

Sina Hashemizadeh: sina.hashemizadeh@epfl.ch

Many perovskite ferroelectrics experience a temperature-driven phase transition at Curie temperature (T_C) from a non-centrosymmetric polar ferroelectric phase to a paraelectric phase, where polarization is lost. The paraelectric phase is usually centrosymmetric (often cubic) and therefore non-piezoelectric. However, ferroelectrics exhibit interesting types of electro-mechanical and electro-thermal coupling in their centrosymmetric paraelectric state, which should be forbidden by centric symmetry. Origins of the symmetry breaking are multiple and not well understood. Recently we have shown with indirect evidences that cubic phase of $BaTiO_3$ exhibits local and macroscopic breaking of nominal centric symmetry and exhibits local and global polarization. Both are likely linked to presence of polar regions/clusters [1,2].

In this work our objective is to search for direct evidence for polar regions above the T_C and understand their structure and nature by investigating the atomic structure of $Ba0_{.6}Sr_{0.4}TiO_3$ (BST60-40) ceramics at room temperature using aberration-corrected scanning transmission electron microscopy (STEM). The Curie temperature of BST60-40 during cooling is 273K, and at room temperature, material is in its paraelectric phase. To visualize local atomic displacements and departure from perfect cubic structure in the BST60-40 sample, series of high-resolution STEM images were acquired.

Our results show regions where A (Sr, Ba) and B (Ti) atoms are displaced in a coherent way, forming noncubic regions/clusters with size of about 1-3 nm, exactly as expected for polar (nano) regions. While at the moment we cannot confirm polarity of these regions, a deeper analysis which is presently underway, and which also takes into account displacement of O atoms, is expected to give an answer on their polar character.

1. Hashemizadeh, Sina, Alberto Biancoli, and Dragan Damjanovic, "Symmetry breaking in hexagonal and cubic polymorphs of BaTiO3." Journal of Applied Physics, 119, 094105 2016

2. A. Biancoli, C. M. Fancher, J. L. Jones, and D. Damjanovic, "Breaking of macroscopic centric symmetry in paraelectric phases of ferroelectric materials and implications for flexoelectricity", Nature Materials 14, 224 (2015).