Paraelectric Behavior of $0.75(Na_{0.5}Bi_{0.5})TiO_3$ -$0.25SrTiO_3$ Under Induced Electric-Field

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Perovskite compounds, such as lead zirconate titanate $Pb(Zr,Ti)O_3$ or PZT, have attracted significant interest for applications in actuators, capacitors, sensors, and transducers, where high strain, dielectric constant and piezoelectric coefficient are desired. PZT is commercially available in a variety of products, however, the lead content remains an environmental concern, which has motivated researchers to seek alternative, lead-free perovskite compounds. Sodium bismuth titanate, $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT), among other lead-free perovskites, has been recognized as a potential replacement for PZT in some commercial applications. NBT exhibits ferroelectric behavior at room temperature, and becomes paraelectric at temperatures above 520 °C, which manifests through a crystallographic phase change from rhombohedral (ferroelectric) to tetragonal (paraelectric).

Early investigations revealed that when strontium titanate is added to NBT in certain ratios, denoted by NBT-xST where xST represents the relative amount of strontium titanate, results in superior strain output at reduced electric fields compared to other lead-free materials, thus leading to a high normalized strain d_{33}^* compared to pure NBT. [1] However, large hysteresis has plagued efforts to use it in commercial products. The high strain at reduced electric field has been attributed to a core-shell microstructure, thus understanding the microstructure-functional properties relationships may lead to the successful implementation of lead-free materials [2]. It was demonstrated that NBT-xST core shell bulk materials showed strain values of 0.3% in the presence of a 4 kV/cm E-field at room temperature, in situ TEM revealed that reorientation of the domain walls within the core also occurs. However, high temperature investigations of the ferro- and paraelectric properties of NBTs under an adequate E-field have not been reported.

Protochips recently introduced new in situ capability based on their Fusion heating and electrical biasing system, which can apply heat and electrical bias simultaneously. To better understand the behaviour of the NBT-xST in situ, this new capability was used to probe the microstructure of the core shell particles under different temperatures and electric fields. The experiment was done using a FEI Titan ChemiSTEM at 200 kV with a quad-EDS (SuperX) system for element analysis. High angle annular dark field (HAADF), as well as bright-field (BF) and dark-field (DF) scanning transmission electron microscopy (STEM) modes were used to analyze and quantify the reactions.

We show that the ferroelectric phase transforms into the cubic paraelectric phase at temperatures above ~520 °C. At 700 °C no domain contrast is visible, which confirms the paraelectric state of the particle, Fig. 2. However, after applying a 0.15 kV/cm e-field, the particle became polarized and domain contrast appears. The width of one set of polarization was measured at 3nm. The polarization width increased to 10nm at ~3 kV/cm. When the polarization was reversed domains shrank in width, and upon removal of the e-field at 700 °C the domain contrast faded, which implies the polarization of the particles returns to zero. The results offer new insight into fundamental phenomena such as diffusion paths, degradation and aging mechanisms in various fields of energy-related materials and electronics.

References
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[4] Authors would like to acknowledge analytical instrumentation facility at North Carolina State University for Titan ChemiSTEM instrument.
[5] Authors would like to acknowledge the synthesis and comments from Matias Acosta, Department of Geo- and Materials Science, Technische Universität Darmstadt, 64287 Darmstadt, Germany

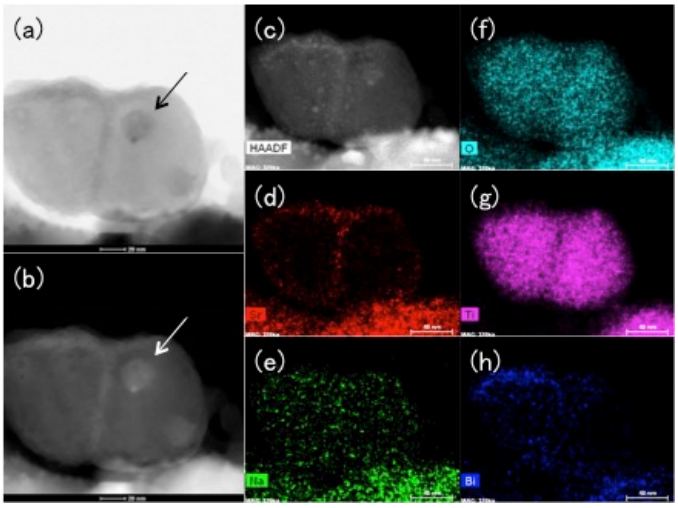

Figure 1. Formation of core-shell structure upon calcination at 700 °C. (a) and (b) represent the BF- and DF-STEM images, respectively, of the calcined core-shell structure, indicated with arrows. (c-h) represent the HAADF image and elemental mapping of the particles.

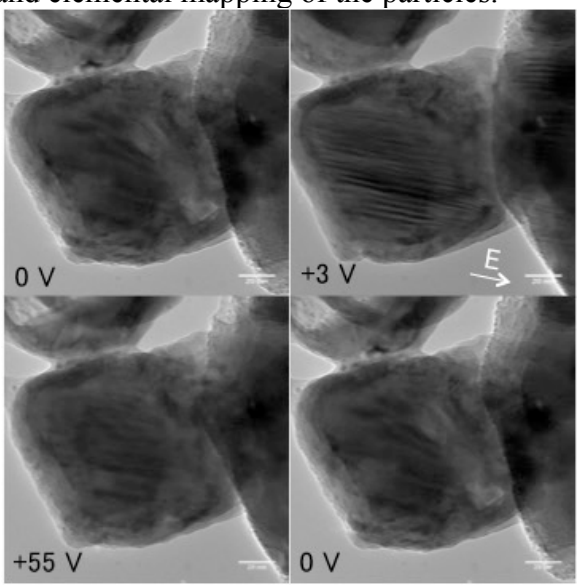

Figure 2. Evolution of domains at 700 °C upon application of e-field.