Exploring the local structure of stress-written phases in polymorphic $BiFeO_3$

Holsgrove, K.[1], Duchamp, M.[2], Moreno, S.[3], Bernier, N.[4], Browne, N.[1], Mazumdar, D.[5], Gregg, J.M.[1], Kumar, A.[1] and Arredondo, M.[1]

[1] Queen's University Belfast, United Kingdom, [2] Nanyang Technological University, Singapore, [3] Bariloche Atomic Centre, San Carlos de Bariloche, Argentina, [4] University of Grenoble Alpes, France, [5] Southern Illinois University, United States

Multiferroic, magnetoelectric, piezoelectric and lead-free - $BiFeO_3$ (BFO) thin films exhibit exciting physics and fascinating properties for tuning their functionality [1-4]. Over the past two decades, an upsurge of interest has been witnessed in the growth of epitaxially strained BFO. The realisation of a morphotropic phase boundary (MPB) in highly-strained BFO leads to a functionally active mixture of two ferroelectric phases, one being rhombohedral-like (R) and the other tetragonal-like (T), whose response can, in principle, be controlled by external stimuli. Here, we reveal the subtle differences in crystal and electronic structure in native phases and phases created through the application of electrical bias and localised stress using an atomic force microscope (AFM) tip.

In a novel exploration of the local structure of these newly-written phases, in particular stress-written regions which display enhanced conductivity as measured by conducting-AFM, we combine state-of-the-art scanning transmission electron microscopy (STEM), see Figure 1, and electron energy loss spectroscopy (EELS) to provide an insight into the origin of the enhanced conductivity. To do this, we have examined three distinct regions consisting of: native (as-grown) R and T phases, an electrically-written (pure) T phase and stress-written R' and T' phases. We highlight the benefit of using nano-beam electron diffraction (NBED) to directly compare strain gradients across the R/T interfaces in the native and stress-written regions. By examining the Fe-$L_{2,3}$ and O-K edges we reveal changes in ELNES features which suggest octahedral distortion variations between native and stress-written phases (see O-K edges in Figure 2). Using multiple-scattering calculations based in the FEFF9 code we correlate ELNES spectral features in the O-K and Fe-$L_{2,3}$ edges (using BFO unit cells varying in strain levels) with the experimental spectra. Furthermore, by precisely measuring the energy onset of the O-K and Fe-$L_{2,3}$ edges we demonstrate that the stress-written regions (R' and T') contain a higher distribution of onset energies compared to a native region of R and T phases, providing a possible rationalisation for increased conductivity in the stress-written regions as originating from an enhanced level of defect energy levels in the bandgap at these highly-strained interfaces.

By revealing the local structure of stress-written R' and T' phases at the atomic scale, we provide a valuable insight into the possible mechanisms responsible for enhanced interfacial conductivity in BFO thin films at the microscale, thus advancing our understanding of the phases created by external stimuli and allowing us to gain control over ferroelectric mixed-phase systems to tune their functional behaviour for broader applications.

The authors acknowledge funding support from the EPSRC.
[1] J. Wang, J. Neaton, H. Zheng, V. Nagarajan, S. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. Schlom, U. Waghmare, N. Spaldin, K. Rabe, M. Wuttig, R. Ramesh, *Science.* **2003**, *299*(5613), 1719-1722.
[2] J. Li, J. Wang, M. Wuttig, R. Ramesh, N. Wang, B. Ruette, A. Pyatakov, A. Zvezdin, D. Viehland, *Appl. Phys. Lett.* **2004**, *84*(25), 5261-5263.
[3] S. Y. Yang, J. Seidel, S. J. Byrnes, P. Shafer, C. Yang, M. D. Rossell, P. Yu, Y. Chu, J. F. Scott, Ager, J.W.III, L. W. Martin, R. Ramesh, *Nature Nanotechnology.* **2010**, *5*(2), 143-147.
[4] J. Seidel, L. W. Martin, Q. He, Q. Zhan, Y. -. Chu, A. Rother, M. E. Hawkridge, P. Maksymovych, P. Yu, M. Gajek, N. Balke, S. V. Kalinin, S. Gemming, F. Wang, G. Catalan, J. F. Scott, N. A. Spaldin, J. Orenstein, R. Ramesh, *Nature Materials.* **2009**, *8*(3), 229-234.

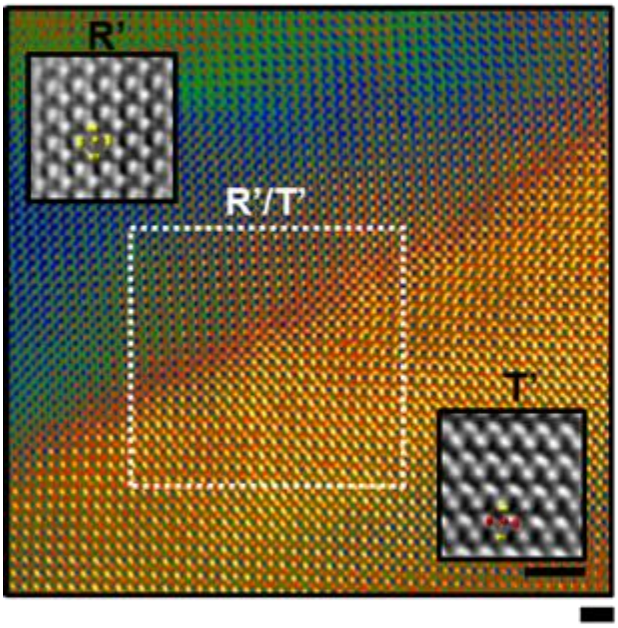

Figure 1: Bright-field STEM image of a representative stress-written region displaying an interface between an R' and T' phase. Insets display higher magnification images with schematics of the oxygen positions overlaid. Scale bars represent 1 nm.

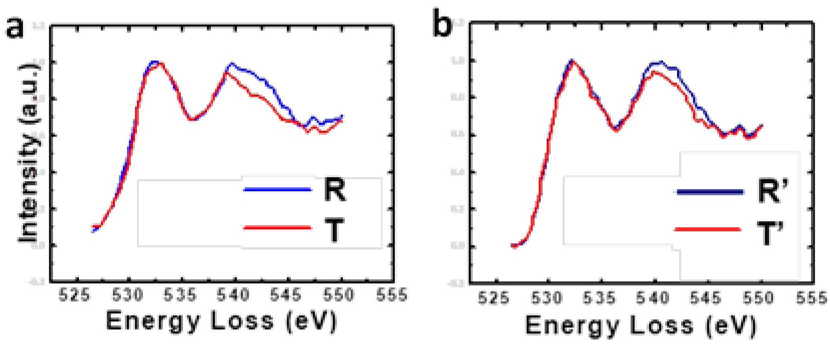

Figure 2: Oxygen K-edge corresponding to native (a) R and T phases and stress-written (b) R' and T' phases.