doi:10.1017/S1431927617008698
Microsc. Microanal. 23 (Suppl 1), 2017

Understanding the Effect of Doping and Epitaxial Strain on the Ferroelectric Polarization of Layered Perovskite Thin Films

Marco Campanini[1], Morgan Trassin[2], Claude Ederer[2], Rolf Erni[1] and Marta D. Rossell[1]

[1.] Electron Microscopy Center, Empa – Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland.
[2.] Department of Materials, ETH Zurich, Switzerland.

Multiferroic magnetoelectric materials, which offer the possibility of manipulating the magnetic order by a low energy consuming electric field, have been attracting considerable attention during the last decade. However, materials that exhibit multiferroic properties above room temperature, and are thus suitable for future device applications, are very rare. First-principles calculations based on density functional theory have become of high relevance in exploring and predicting novel multiferroic materials. Likewise, the experimental validation of the magnetoelectric phenomena both at the atomic and macroscopic scales is crucial to improve our insight into the microscopic mechanisms underlying the predicted phenomena.

Here, in this context, we study the effect of doping and epitaxial strain on the structure and the ferroelectric properties of the promising Aurivillius-phase compounds [1]. In particular, we investigate the potential multiferroic behavior of $Bi_5FeTi_3O_{15}$ as predicted by ab-initio calculations [2, 3]. Its crystal structure consists of 4 perovskite layers stacked periodically along the [001] direction and separated by fluorite-like $(Bi_2O_2)^{2+}$ layers. This phase has been predicted to have a large response of in-plane polarization under biaxial strain, and a preferential occupation of the inner (outer) perovskite site with the Fe^{3+} for tensile (compressive) strain.

The experimental characterization of this system is very challenging, dealing with the requirement of very high spatial resolution (< 1Å). In fact, while the detection of the Fe substitutional species in preferential lattice sites requires analytical investigations with atomic resolution, the estimation of the local polarization at the atomic scale is nevertheless more demanding, being the typical atomic displacements involved in the polar distortions in the 10-50 pm range [4, 5]. To perform the abovementioned investigations at sub-Ångstrom resolution we use probe-corrected scanning transmission electron microscopy (STEM). Specifically, we exploit high-angle annular dark-field (HAADF) and annular bright-field (ABF) images to get access to both heavy and light atomic columns.

In order to investigate the microscopic properties of strained and doped Aurivillius phases we have implemented an analytical algorithm able to retrieve the polarization at the atomic scale from the structural distortions, *i.e.* from atomic or charge's center of mass displacements. In addition, other distortions like tilting of the oxygens octahedrons, tetragonal deformation and metal-oxygen-metal bonding angle bending, that play a pivotal role in determining the ferroelectric/ferromagnetic ordering are measured by our algorithm. Combining the HAADF and ABF signals, the accurate positions of all the different atomic species in the structure are precisely measured fitting the peaks of the images with 2D asymmetric Gaussians [6]. The polarization at the atomic scale can therefore be computed as the displacement of the B cation with respect to the center of mass of the cell or, alternatively, by the offset between the centers of mass of the cationic and anionic charges. As an example, a map of the local

polarization in a strain-free $Bi_5FeTi_3O_{15}$ single-crystal thin film is reported in Figure 1, as obtained from the offset between the centers of mass of the oxygen octahedron and the cell given by the Bi cations.

Finally, energy dispersive X-ray (EDX) spectroscopy is successfully applied to investigate the occupation of the magnetic ions in the $Bi_5FeTi_3O_{15}$ structure. We unambiguously identify a preference of the Fe^{3+} cations to occupy the outer or mixed sites within the perovskite-like layers depending on the applied biaxial strain [7].

References:

[1] L Keeney *et al*, Journal of the American Ceramic Society**96** (2013), 2339.
[2] AY Birenbaum and C Ederer, Physical Review B **90** (2014), 214109.
[3] AY Birenbaum and C Ederer, Applied Physics Letters **108** (2016), 082903.
[4] AK Yadav *et al*, Nature **530** (2016), p. 198
[5] R Guzman *et al*, Nano Letters **16** (2016), p. 2221.
[6] AB Yankovich *et al*, Nature Communications **5** (2014), 4155.
[7] The authors acknowledge funding through NCCR MARVEL, funded by the Swiss National Science Foundation.

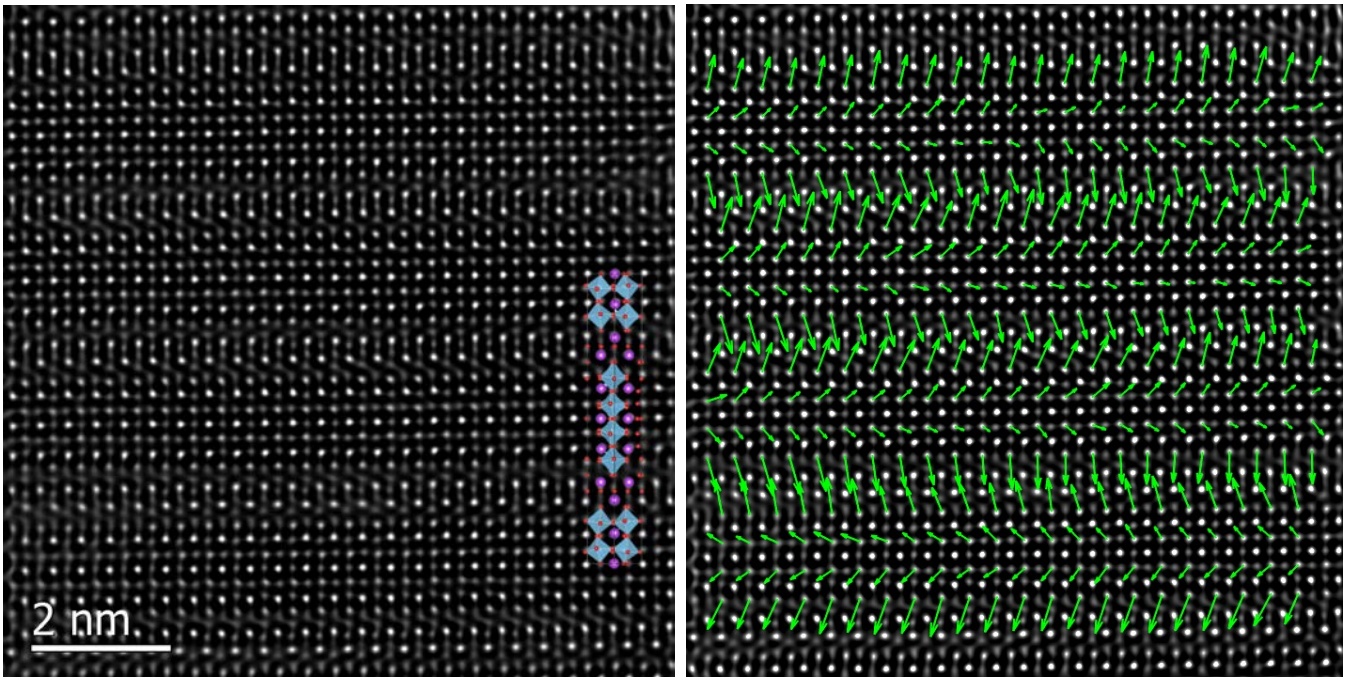

Figure 1. Inverted ABF-STEM image with overlaid ball-and-stick model (left) and superimposed polarization map (right) of a strain-free Aurivillius $Bi_5FeTi_3O_{15}$ thin film.

https://doi.org/10.1017/S1431927617008698 Published online by Cambridge University Press