Functional Materials

MS.3.P067
Transmission electron microscopy study of defects in $BiFeO_3$ thin films

H. Deniz[1], A. Bhatnagar[1], E. Pippel[1], M. Alexe[1], D. Hesse[1]

[1]Max Planck Institute of Microstructure Physics, Halle (Saale), Germany

hdeniz@mpi-halle.de
Keywords: lattice defects, Aurivillius-type structure, $BiFeO_3$ films

A wide class of oxide materials with perovskite structure has been in the focus of intense research efforts lately due to fascinating properties they posses; such as ferroelectricity, colossal magnetoresistance, superconductivity, etc. $BiFeO_3$ (BFO) among them is the leading contender in the research of multiferroic compounds with its magnetic ordering and ferroelectric transition parameters well above room temperature. BFO has rhombohedral crystal structure that results in rich ferroelectric domain configurations in single-crystal thin films. Recently, a surface ("skin") layer has been put forward in order to elucidate some peculiar features observed for single crystals of bulk BFO [1]. Therefore, it is of great importance to grow defect-free high quality films of BFO in order to better understand/correlate structure-property relationships of this material. In this study, the surface of as-grown BFO films and defects of secondary phases were investigated by TEM to have a better understanding of its structure.

Single crystal $BiFeO_3$ thin films grown by pulsed laser deposition on scandate oxide substrates ($TbScO_3$, $GdScO_3$, etc.) have been investigated in high-resolution TEM and high angle annular dark field STEM (HAADF-STEM). Chemical composition of defects in the samples was studied using energy dispersive X-ray spectroscopy (EDX) scans in STEM. Defects having a layered structure, similar to bismuth-oxide layered perovskites [2], with a chemical composition different from the rest of the film have been observed (see figure 1a). Fast Fourier transform (FFT) analysis and image processing were used to elucidate the nature of these defects. They correspond to a new meta-stable phase in $BiFeO_3$ thin films.

EDX line scans across such defects revealed that the ratio of the atomic content of Bi to Fe is approximately 2:1 (figure 1b). High resolution HAADF images of such defects show that two rows of Bi atoms repeat themselves along the growth direction of BFO film and they are separated by a single row of Fe atoms. This structure is very different from the pseudo-cubic BFO film matrix where these defects are embedded in, closely resembling the crystal structure of Aurivillius-type ceramics, in particular Bi_2WO_6 (BWO). Layered perovskite ceramics consist of infinite 2D slabs of the ABO_3 perovskite structure which are separated by some other unit. In Aurivillius-type ceramics, separating units are Bi_2O_2 layers. BWO is the simplest case of Aurivillius-type ceramics where Bi_2O_2 layers are separated by a single WO_6 octahedron (see figure 2). BWO has an orthorhombic crystal structure with a space group *Aba2*. Its lattice parameters *a*, *b* and *c* are 5.436, 5.457 and 16.43 Å [3]. In our study, the estimated lattice parameters for the layered defects were $a \approx b \approx 5.338$ and $c = 16.18$ Å, respectively. This supports the fact that the structure of our layered defects closely matches that of BWO with a formula of Bi_2FeO_6 in our case.

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4. Financial support by the FP7 project "IFOX" is gratefully acknowledged.

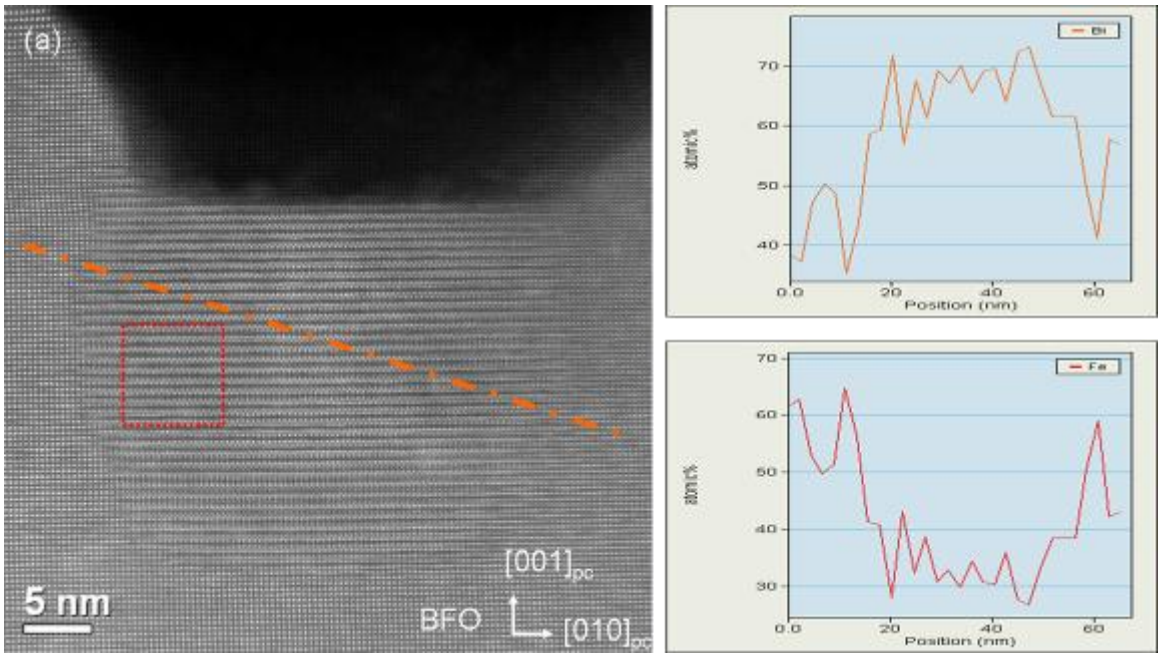

Figure 1. (a) High resolution HAADF-STEM image of a layered defect embedded in BFO film matrix. **(b)** The plots show atomic percentage of Bi and Fe contents obtained from EDX line scans along the orange colored line across the defect.

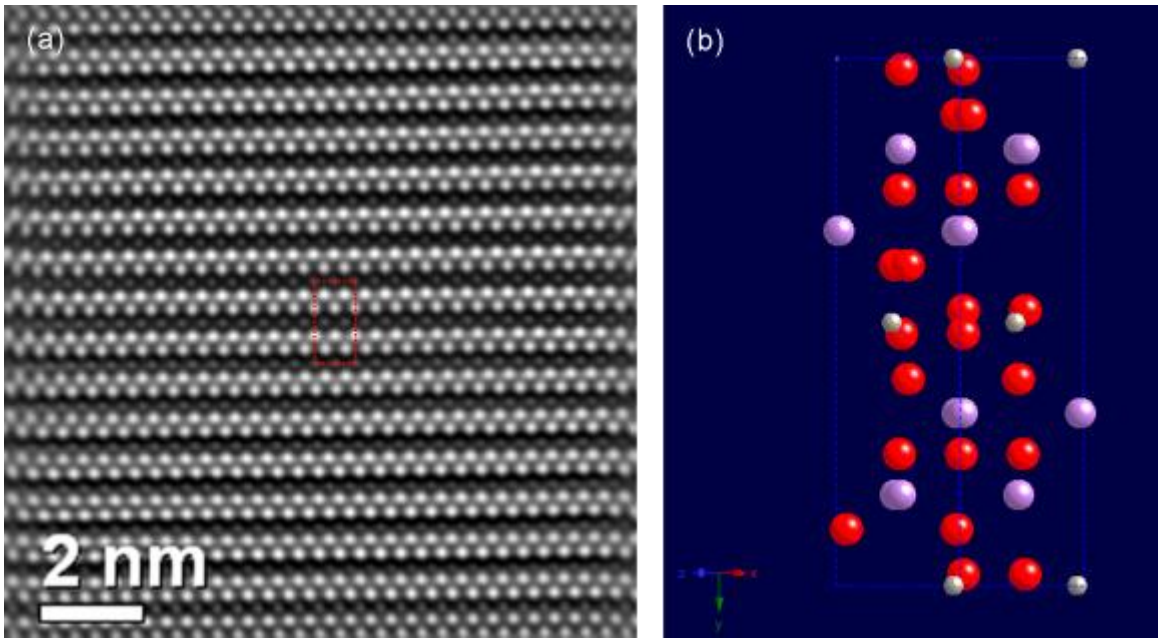

Figure 2. (a) Filtered and enlarged view of the red dotted box as-shown in the high resolution STEM image from figure 1. Bright rows of atoms and dark rows correspond to Bismuth and Iron, respectively. Red-dotted rectangle illustrates one unit cell of the new phase Bi_2FeO_6. **(b)** [101] projected crystal structure of Bi_2WO_6: Bi-lavender, W-grey and O-red.