Structural fluctuations in giant c/a ratio epitaxial BiFeO3 thin films

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We study $BiFeO_3$ (BFO) thin films deposited on $LaAlO_3$ (LAO) substrate by pulsed laser deposition. Several questions remain concerning the structure of this material in the thin film geometry. A P4mm phase has been calculated [1] and experimentally observed [2, 3], although accompanied by a monoclinic distortion (and thus denoted T-like for tetragonal-like [4]), for large biaxial epitaxial strains giving a giant c/a ratio of 1.25. It has been shown [4] that this phase is accompanied by a secondary phase close to the rhombohedral bulk phase denoted R-like. We combine different approaches simultaneously in the electron microscope: energy filtered electron diffraction, high resolution electron microscopy, high angle annular dark field STEM and electron energy loss spectroscopy in order to gain insight into the structure of our BFO film. The present study is concerned with the structural characterization of the film.

In order to acquire energy filtered diffraction pattern, we use a JEOL 2200 FS equipped with a field-emission gun for small probe formation and an in-column Omega energy filter allowing the use of several detector type (CCD, Imaging-plate) depending on the nature of the signal to be recorded. Energy filtered electron diffraction drastically improves signal-to-background ratio of diffraction pattern particularly on the weak diffuse features. An energy slit of 15 eV has been used to keep a large angle of observation in the diffraction pattern while removing the important inelastic contribution of the plasmon peak. The use of Imaging Plates also improves the signal-to-noise ratio in the weak diffuse features observed.

The indexation of the zone axis diffraction pattern gives a space group of Cm with 4 pseudo-cubic unit-cells close to the tetragonal-like phase previously observed on similar samples (Fig. 1). The diffuse scattering features are generally best seen in an off-axis geometry. An electron diffraction pattern tilted a few degrees from the [010] zone-axis around the growth direction [001] is presented Fig 2. The diffuse intensity consists in a sharp streak modulated along the growth direction. Geometrical Phase Shift Analysis (GPA) of the HRTEM micrographs reveals a modulation of the monoclinic structure in the thin film and its spatial extension (Fig 3). It should be emphasized that this modulation is observed with different film thicknesses and on different substrates.

Accompanying this modulated tetragonal phase, a secondary rhombohedral-like or R-like phase can be observed in the film (4]. The mismatch between both phases is entirely compensated by distortions of the lattice planes and no misfit dislocation is observed.

The coupling of the different techniques, imaging, diffraction and spectroscopy, which can be applied in a single experiment in an electron microscope can give invaluable information on the structure of the crystal and on the chemical environment of each ion. In our film, the fluctuation of the structure described here, which has been detected in diffraction and spatially characterized in image mode, follows the fluctuation of coordination of the oxygen ions in spectroscopy [5].

References

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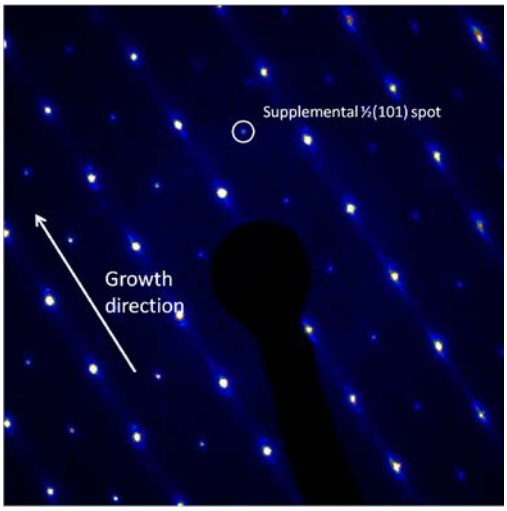


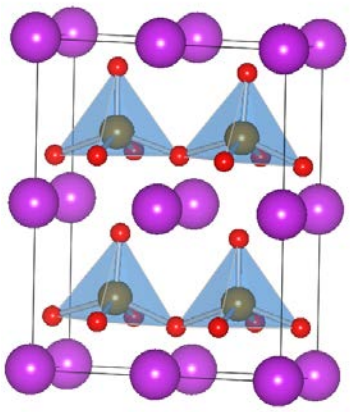
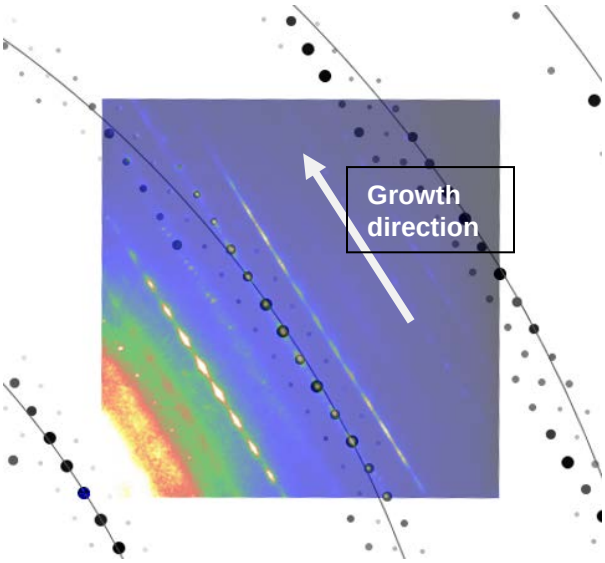


Figure 1. *Diffraction pattern of the BFO film in the [010] zone axis (all indices in pseudo-cubic lattice). On the right, unit-cell of the Cm T-like phase taking into account the supplemental spots in the DP.*



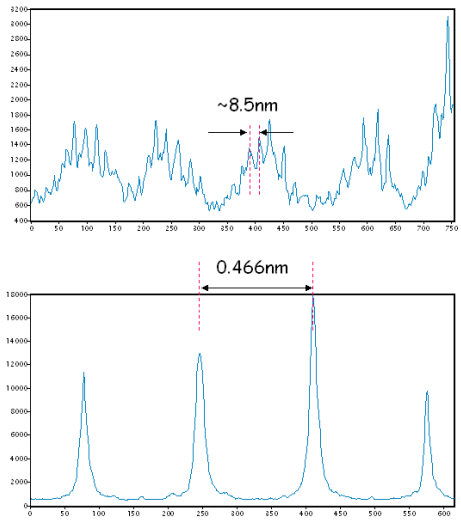
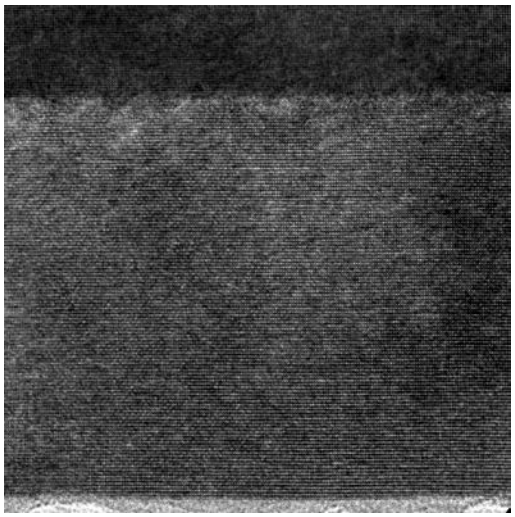


Figure 2. *Superimposition of the diffraction pattern tilted around the growth direction 8° off [010] zone axis and the corresponding simulation in the Cm phase. Profiles along the central rows show that a modulation of the structure occurs along the growth direction.*



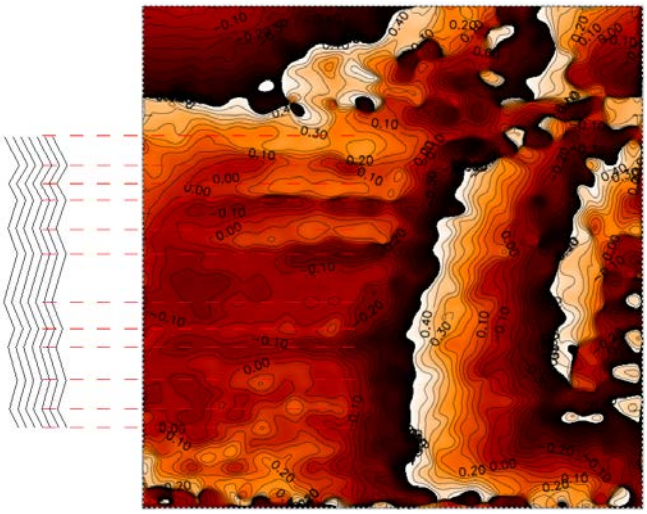


Figure 3. *HRTEM image of a T-like region. The substrate is in the upper part of the micrograph. On the right GPA image made with (100) planes. And the schematics of the modulation of the plane distorsion.*