

Transmission Electron Microscopy and First-Principles Study on Highly Strained BiFeO₃ Grown on LaAlO₃

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BiFeO₃ (BFO) is a multiferroic material with ferroelectricity and antiferromagnetism. A great deal of recent research activity on BFO has been triggered by an article published in *Science* [1]. It demonstrated that the ferroelectricity of BFO can be enhanced more than ten times when BFO is epitaxially grown as thin film. Ever since, extensive studies have tried to further enhance its physical properties as well as to interpret the reason for physical properties enhancement found in thin film BFO.

While BFO thin films' physical properties are rather well established in terms of epitaxial growth conditions, film thickness, and the types of substrate materials, the fundamental question of “*what is the mechanism of physical property enhancement?*” still remains elusive. In order to answer this question, precise structural analysis about stress/strain effect on epitaxially grown BFO film is imperative.

When BFO grows epitaxially, it inevitably goes through lattice stress/strain imposed by the substrate materials that usually have different crystal structure and/or lattice parameter. The lattice stress/strain is known to lead to structural modification within BFO thin films. It is worth noting that a couple of recent review articles pointed out that despite extensive theoretical and experimental studies, the crystal structure(s) of BFO thin films are still unclear owing to its crystallographically complex nature [2,3]. As a result, publications dealing with the structural characterization have not waned at all over the years [3]. In this study, we investigate, for the first time, the *complete crystallographic detail* of so called “*highly strained BFO*” grown on LaAlO₃ (LAO) substrate by using multi zone-axes transmission electron microscopy (TEM), combined with first-principles calculation.

A cross-sectional TEM image show ~380 nm thick BFO layer consists of two zones, i.e., I and II. (see Fig. 1) While zone II corresponds to rhombohedral BFO, zone I turned out the *highly strained BFO*. First-principles calculation combined with multiple zone-axis electron diffraction analysis (see Fig. 2) allow us to determine the *highly strained BFO* exhibits a *monoclinic structure* with space group of *Cm* (see Fig. 3(a)). The bonding geometry between Fe and O in *highly strained BFO* turns out pyramid (see Fig. 3(a)) which is distinctively different from octahedral geometry (see Fig. 3(b)) found in rhombohedral BFO. Complete crystallographic information including the locations of all the basis atoms within the monoclinic unit cell will be presented. We will further discuss the growth mechanism responsible for zones I and II as well as electronic structure of the “*highly strained BFO*” using advanced electron microscopy techniques such as atomic resolution scanning transmission electron microscopy and electron energy loss spectroscopy.

References:

- [1] J Wang *et al*, Science **299** (2003), p. 1719.
 [2] D Sando, A Barthélémy and M Bibes, J. Phys.: Condens. Matter **26** (2014), p. 473201.
 [3] D Sando *et al*, Appl. Phys. Rev. **3** (2016) p.011106.

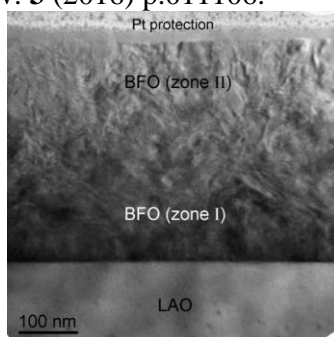


Figure 1. A cross-sectional bright-field TEM image of BFO layer along [241] zone-axis of LAO substrate. Zones I and II corresponds to *highly-strained BFO* and *rhombohedral BFO*.

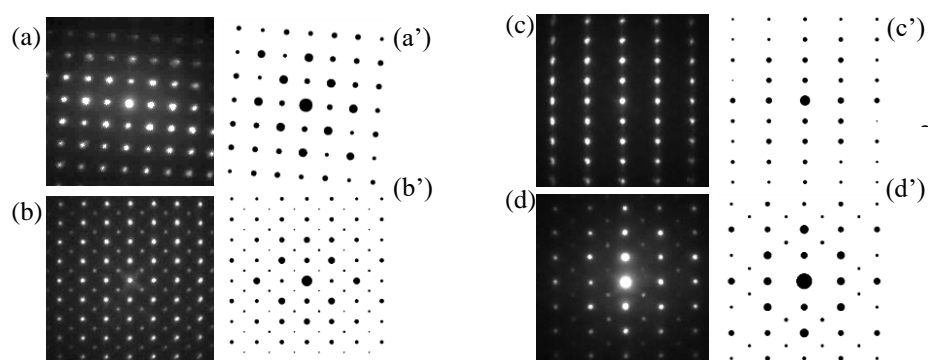


Figure 2. Transmission electron diffraction patterns from zones II and I along [241] zone-axis of LAO ((a) and (b)) as well as those along [211] zone-axis of LAO ((c) and (d)). Their corresponding structure factor calculations are shown (a'), (b') (c') and (d').

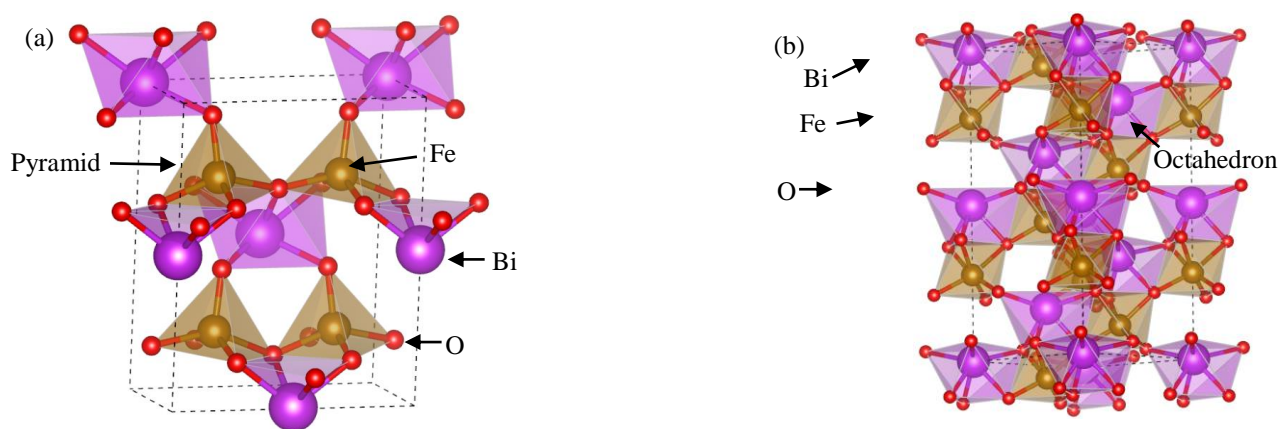


Figure 3. Atomistic models of highly strained BFO (a) and rhombohedral BFO (b) showing pyramidal and octahedral bonding geometries between Fe and O atoms, respectively.