

can be progressively distorted into a monoclinic (and perhaps even a triclinic) structure through in-plane lattice mismatch with the substrate. Ab initio calculations of the role of epitaxial strain clearly demonstrate how it can be used to drive a strain-induced structural change in  $\text{BiFeO}_3$  (Fig. 8a and b). These calculations suggest that at a certain value of epitaxial strain, in the absence of misfit accommodation through dislocation formation, the structure of  $\text{BiFeO}_3$  discontinuously changes from the distorted rhombohedral parent phase structure to a tetragonal (or slightly monoclinically distorted) structure that is characterized by a large  $c/a$  ratio of  $\sim 1.26$ . This “super-tetragonal” structure is distinctly different from the rhombohedral structure in that the coordination of the Fe ion is now five-fold instead of the usual six-fold coordination in the perovskite structure. Direct atomic resolution images of the two phases (Fig. 8c and d), clearly show the difference in the crystal coordination.

Now, an interesting question arises: what happens if one picks a substrate such as  $\text{LaAlO}_3$ , (that has  $\sim 4.5\%$  lattice mismatch with the parent rhombohedral  $\text{BiFeO}_3$  phase) and grows a film in which this epitaxial constraint is partially relaxed? Such experiments (and the corresponding theoretical aspects) have been explored in some detail.

Experimentally, it has been observed that the result is a nanoscale mixed-phase structure, typified by the AFM image and line-trace (Fig. 8e and f, respectively). Fig. 8g is an atomic resolution TEM image of the interface between these two phases and reveals one of the most provocative aspects of the structure. Although there is a large “formal” lattice mismatch between the two phases, the interface appears to be coherent, i.e. it shows no indication for the formation of interphase dislocations. Indeed, this mismatch appears to be accommodated by the gradual deformation of the structure between different phases. In a formal sense, this transformation is termed an isostructural transformation, i.e. one in which the crystal symmetry does not change, but the coordination does. Thus, one can visualize the nanoscale mixed phase ensemble as analogous to the relaxor ferroelectrics or the CMR manganites, both of which exhibit a nanoscale mixture of two phases, and perhaps presents yet another manifestation of a generic “microstructural” design criterion of creating heterophase mixtures with controllable length scales to achieve the desired properties (such as lath martensite in alloy steels, precipitation hardened Al and Ti alloys) [97,98].

Application of dc electric fields to these mixed-phase structures can give rise to large electromechanical

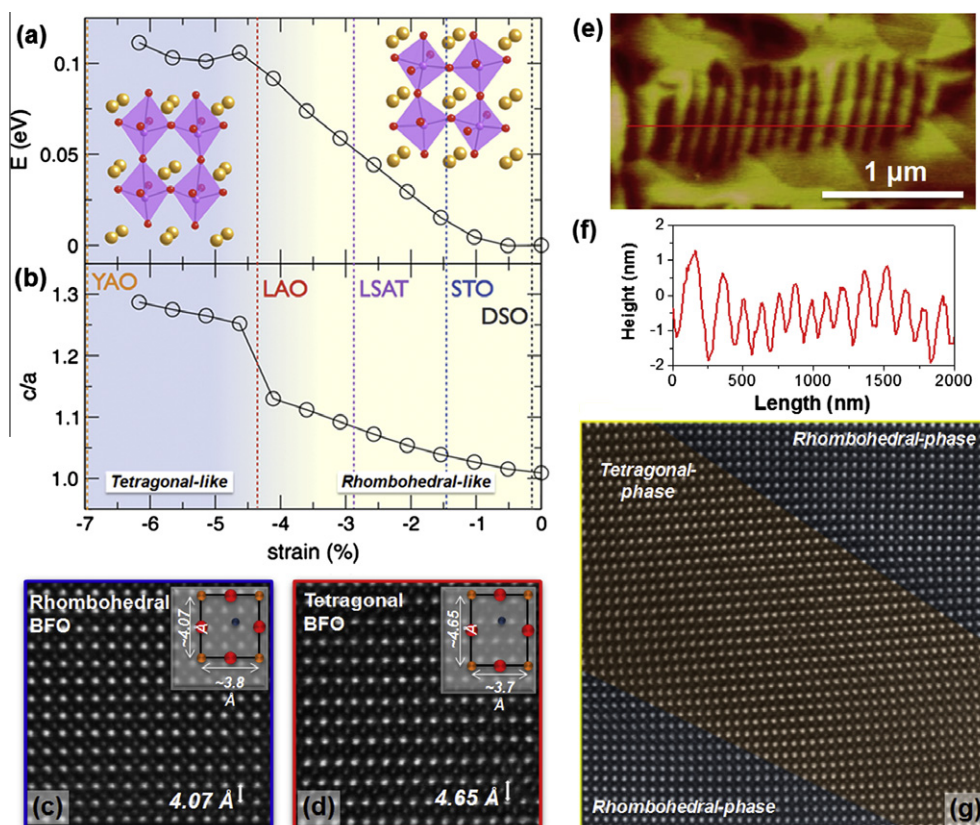


Fig. 8. Strain-induced phase complexity in  $\text{BiFeO}_3$ . First-principle calculations provide information on the strain evolution of (a) the overall energy of the system and (b) the  $c/a$  lattice parameter ratio. High-resolution transmission electron microscopy (HRTEM) reveals the presence of two phases: (c) a monoclinic version of the bulk rhombohedral phase, and (d) high-distorted monoclinic version of a tetragonal structure. These complex phase boundaries manifest themselves on the surface of the sample as imaged via (e) atomic force microscopy and these features correspond to dramatic surface height changes as shown from the line trace (f). (g) HRTEM imaging of boundaries shows a smooth transition between phases (adapted from Ref. [96]).