

responses (as large as 4–5%). In situ TEM studies coupled with nanoscale electrical and mechanical probing reveal that such large strains result from moving the boundaries between different phases [99]. Additional studies have shed light on the true nature of these mixed-phase structures and the mechanism for this strong electromechanical response. To begin, since the work by Zeches et al. additional information has come forth about the symmetry of these phases, including the fact that the so-called tetragonal-like phase is actually monoclinically distorted (possessing Cc , Cm , Pm , or Pc symmetry) [100–103]. Nonetheless, a thorough understanding of the complex structure of these phase boundaries in BiFeO_3 remained incomplete.

Using a combination of high-resolution X-ray diffraction and scanning-probe microscopy-based studies, however, Damodaran et al. [104] have uniquely identified and examined the numerous phases present at these phase boundaries and discovered an intermediate monoclinic phase in addition to the previously observed rhombohedral- and tetragonal-like phases. Further analysis has determined that the so-called mixed-phase regions of these films were not mixtures of the rhombohedral- and tetragonal-like phases, but intimate mixtures of a highly distorted monoclinic phase with no evidence for the presence of the rhombohedral-like parent phase. This work also provided a mechanism for the enhanced electromechanical response observed in these films, including how these phases interact at the nanoscale to produce large surface strains. This was obtained by completing detailed local electric-field-dependent switching and capturing both the topography (left

images, Fig. 9) and the out-of-plane orientation of the polarization (right images, Fig. 9) of the sample at a range of electric fields. By navigating the hysteretic nature of electric field response in this material, a number of important features of this system were revealed: (1) the large surface strains (4–5%) occur any time the material transforms from a mixed-phase structure to the highly distorted monoclinic phase, (2) these transformations between these two states are likely reversible, and (3) there are numerous pathways to achieve large electromechanical responses in these materials – including ones that do not need switching of the polar state of the sample. This, in turn, provides a plausible mechanism for the enhanced electromechanical response. The key appears to be the ability to transform between the different phases through a diffusion-less phase transition (in similar fashion to the behavior of a martensitic phase).

A number of additional studies on strain-induced phases have been reported in recent months. This includes a detailed neutron scattering study of a nearly phase-pure film of the highly distorted tetragonal-like phase which confirms antiferromagnetism with largely G-type character and a $T_N = 324$ K, a minority magnetic phase with C-type character, and suggests that the co-existence of the two magnetic phases and the difference in ordering temperatures from the bulk phase can be explained through simple Fe–O–Fe bond distance considerations [105]. Other reports suggest the possibility of a reversible temperature-induced phase transition at ~ 100 °C in the highly distorted tetragonal-like phase as studied by temperature-dependent

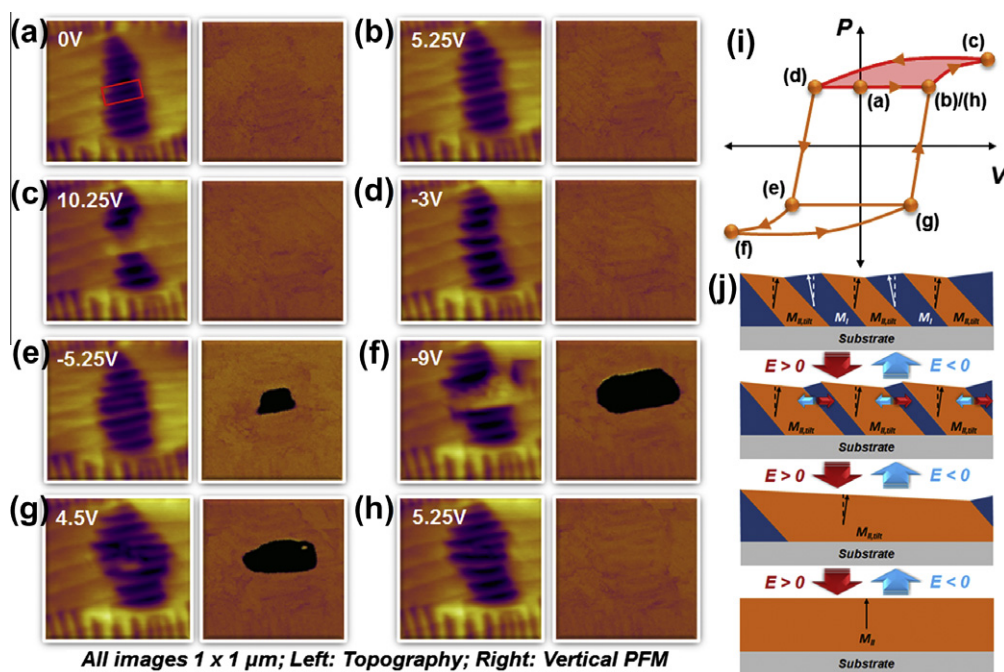


Fig. 9. AFM image (left) and vertical PFM image (right) of 100 nm $\text{BiFeO}_3/\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3/\text{LaAlO}_3$ (001) in the (a) as-grown state and after being poled in the box at (b) 5.25 V, (c) 10.25 V, (d) –3 V, (e) –5.25 V, (f) –9 V, (g) 4.5 V, and (h) 5.25 V (all images are $1 \times 1 \mu\text{m}$). (i) A schematic hysteresis loop with letters corresponding to the images in (a)–(h) shows the multiple pathways to enhanced electromechanical response. (j) Illustration of the proposed mechanism for the large electromechanical response without the need for ferroelectric switching (adapted from Ref. [104]).