1940 Microsc. Microanal. 28 (Suppl 1), 2022
doi:10.1017/S1431927622007589

Atomic Imaging of Superelasticity of 2-dimensional Freestanding Perovskite Ferroelectric Films

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Perovskite ferroelectrics have attracted extensive attention in recent years because of their potential applications in the next-generation flexible electronic devices. However, bulk or thin film perovskite ferroelectrics usually have weak elasticity and high brittleness[1], imposing challenges to their application in flexible devices. Herein, we demonstrate the super elastic effect of a freestanding $BiFeO_3$ film, a classic perovskite ferroelectric, by using in-situ transmission electron microscopy and scanning transmission electron microscopy. The films exhibit superelasticity in a large range of strain[2,3], which is enabled by reversible 2-step phase transitions: rhombohedral (R)-to-tetragonal (T) and T-to-super tetragonal (ST) phase transitions. This work reveals a huge strain tolerance of freestanding $BiFeO_3$ films and elucidates the fundamental mechanisms of the super elastic effect, providing new insights for the development of advanced flexible electronic devices.

An 8-nm-thick $(001)_p$-oriented BFO thin film was grown on a $Sr_3Al_2O_6$ (SAO) sacrificial buffer layer on a (001) $SrTiO_3$ (STO) substrate (where the subscript *p* represents pseudocubic indices). The BFO freestanding (FS) film was released by dissolving SAO layer in deionized water and then scooped up by the push-to-pull chip for mechanical testing in TEM, as shown schematically in **Fig. 1a**. The low-magnification TEM image shows the region that tensile stress is applied when pushing the indenter. A time series of bright-field images (**Fig. b-e**) were recorded to show the R-to-T-to-ST phase transitions during the mechanical straining and showcase the super elastic effect. The different phases in the phase color maps were defined by fitting their corresponding diffraction patterns. To form the phase transition region, a crack is intentionally created, and local stress field is observed (**Fig. 1b**). Its phase color map shows both R and T phases exist in the belt above the orange dashed line while only the R phase appears in the bulk region below the white dashed line. In **Fig. 1c**, the belt is pulled further which results in R-to-T and T-to-ST phase transitions to compensate the large local stress. Then the mechanical load is released allowing the film to recover unaided (**Fig. 1d**). In this stage, the ST phase partially changes back to the T phase. In the last stage (**Fig. 1e**), the TEM image shows no contrast discrepancy in the belt and its phase color map shows that only the R phase exists. This self-recovery mechanism demonstrates FS BFO's super elastic effect.

To qualify the phase transitions during the mechanical test, in situ STEM was applied to a similar crack to demonstrate the evolutions of the c/a ratio and strain, and the motion of the phase boundary. In the initial stage (**Fig. 2a**), most regions are in the R phase with a small T phase region on the right side of the crack. Then, as the mechanical load increases, the R phase region on the top transitions to T phase and the R-T phase boundary moves downward, leading to an increased T phase area (**Fig. 2b** and **c**). From **Fig. 2c** to **d**, although the R-T phase boundary on the right side of the crack doesn't move, the R phase on the left side of the crack transits to the T phase to compensate the increasing local stress. Eventually, both sides of the crack turn from R phase to T phase and only the region far away from the tip head remains in the R phase (**Fig. 2e** and **f**).

In summary, in a ferroelectric FS BFO film, we performed a systematic study of the phase evolution under a mechanical stimulus by using atomic resolution in situ TEM and in situ STEM techniques. We observed a superelastic effect and explained its fundamental mechanism: it is achieved by a R-to-T-to-S 2-step phase transitions. These findings provide valuable insights into correlating mechanical properties to underlaying atomic structures, opening up a new path of designing next-generation flexible electronic nanodevices [4].

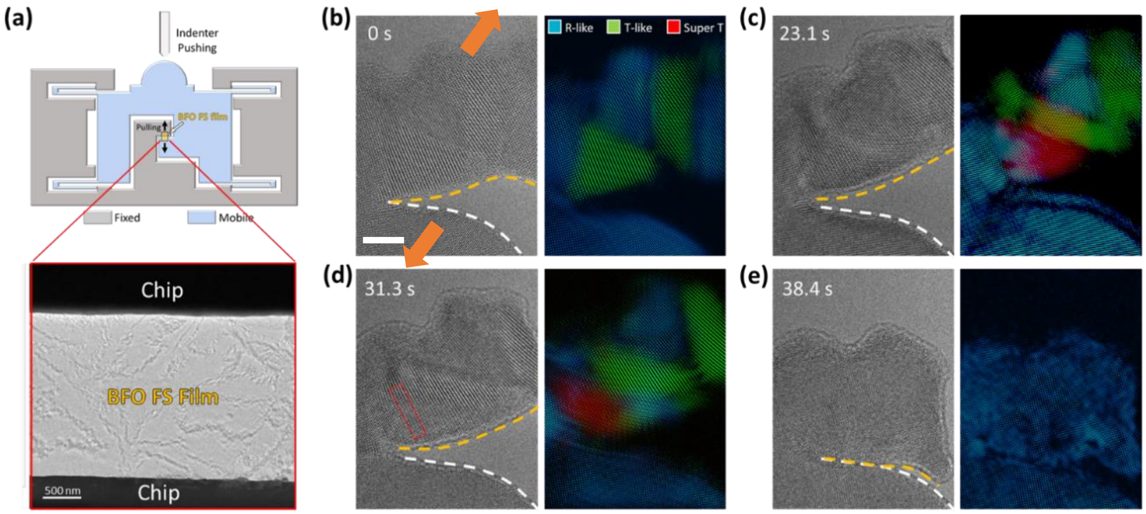

Figure 1. Mechanically induced phase transitions probed by in-situ TEM. (a) A schematic of the push-to-pull chip setup with a mobile indenter used for the mechanical pulling of the FS BFO films, and a low-magnification TEM image of the film. The contrast in the film comes from bend contours. **(b-e)** TEM bright field image time series acquired while applying mechanical load along with their corresponding phase color maps. The white and orange dashed lines represent fixed and mobile edges of the crack, respectively. The arrows represent the local stress direction. In the phase color maps, the blue, green, and red colors denote R, T, and ST phases, respectively.

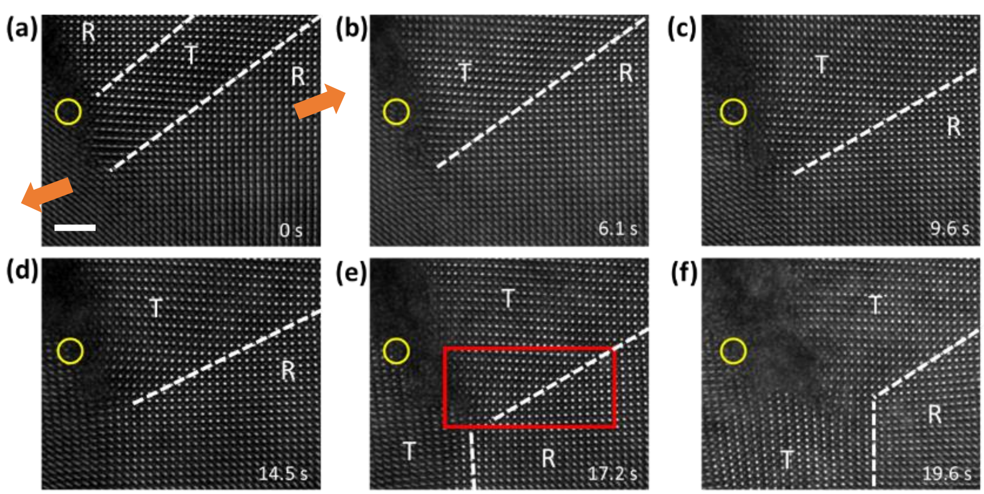

Figure 2. Observation of phase transitions at atomic scale by in-situ STEM. **(a-f)** HAADF-STEM image time series collected while applying mechanical load. The white dashed lines represent the phase boundaries

https://doi.org/10.1017/S1431927622007589 Published online by Cambridge University Press

between R and T phases. The region in the yellow circle is used as reference point because it didn't move during the mechanical test. The orange arrows indicate the mechanical stress direction. Scale bar, 2 nm.

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[4] This work was supported by the Department of Energy (DOE) under Grant DE-SC0014430. TEM experiments were conducted using the facilities in the Irvine Materials Research Institute (IMRI) at the University of California-Irvine