

Supplementary information for

Surface reconstructions and related local properties of a BiFeO₃ thin film

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Supporting figures

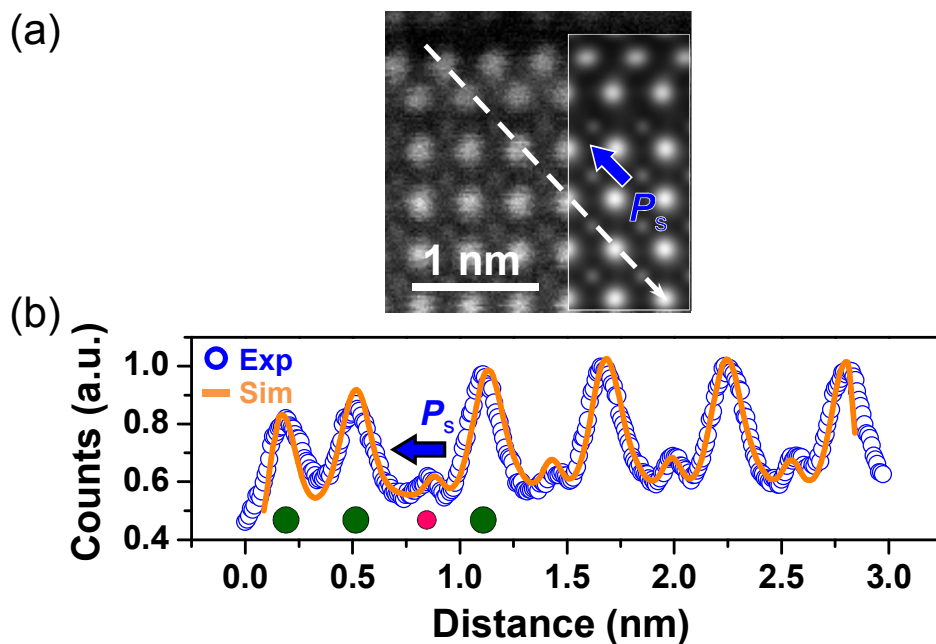


Figure S1 Comparison between experimental and simulated image based on a DFT-relaxed O8 model. (a) Atomic-resolution HAADF STEM image and simulated image. (b) Normalized intensity profile along the directions indicated by the dashed lines in (a), showing consistent modulations of a Bi (green) and an FeO (magenta) signal between the experimental and simulated images.

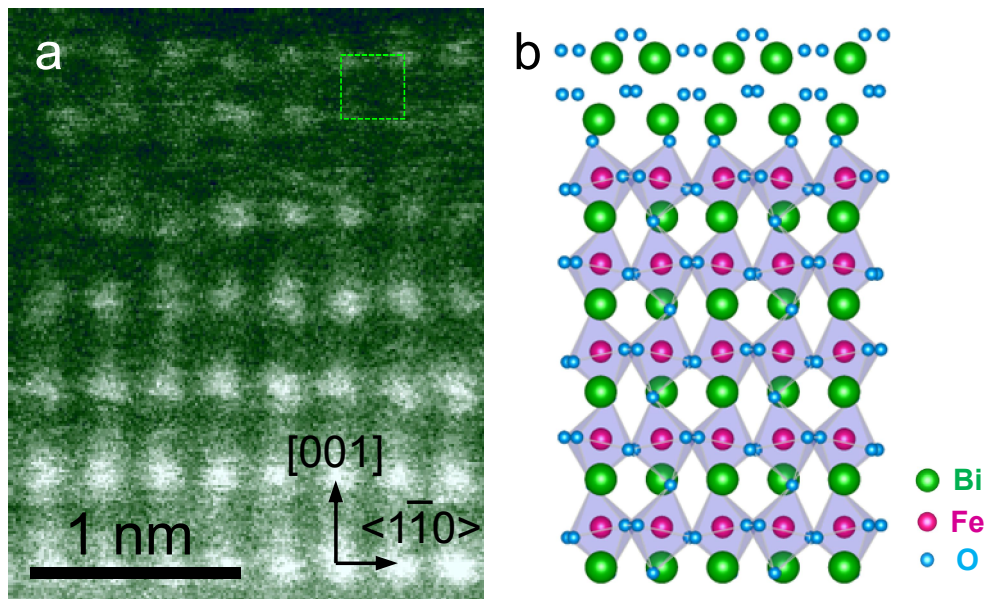


Figure S2 Atomic details of a Bi-O double-layer projected along the $\langle 110 \rangle$ pseudocubic axis. (a) HAADF STEM image showing the projection of an Aurivillius-like structure along the $\langle 110 \rangle$ direction. The Bi double-layer forms a square pattern, as indicated by the green rectangle. (b) Atomic O8 model calculated using a first-principles DFT calculation, viewed along the same orientation.

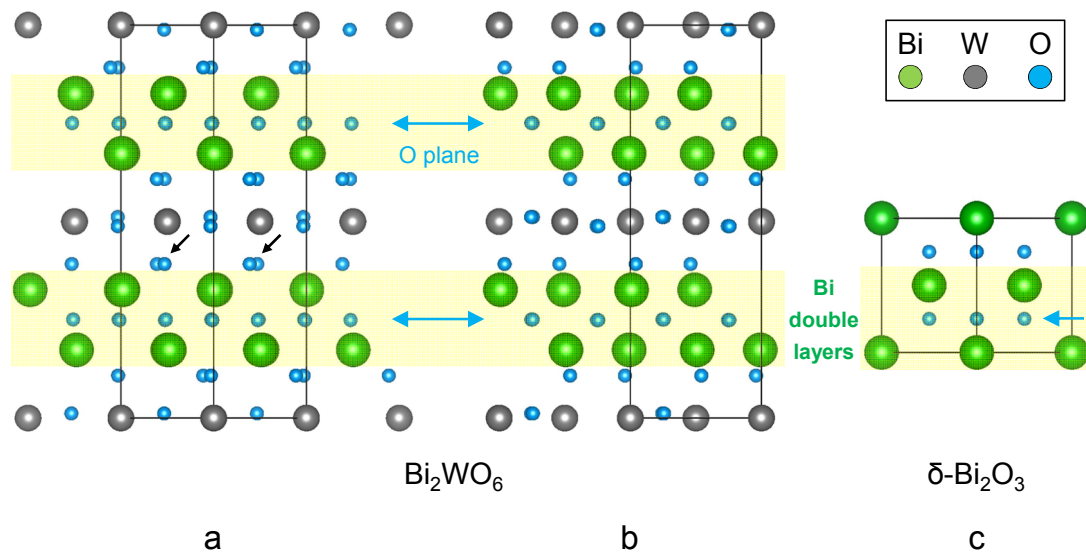


Figure S3 Crystal structure of a Bi_2WO_6 Aurivillius phase [1], including a structural unit of double Bi-O layers. (a) [110] projection and (b) [100] projection of the Bi_2WO_6 structure. An O atomic plane (marked by arrows) is located between two Bi atomic planes, as highlighted in yellow. Such a configuration is similar to the structure of $\delta\text{-Bi}_2\text{O}_3$ [2], in which 25% of the O sites are vacant. (c) Structure of $\delta\text{-Bi}_2\text{O}_3$ projected along the [110] direction.

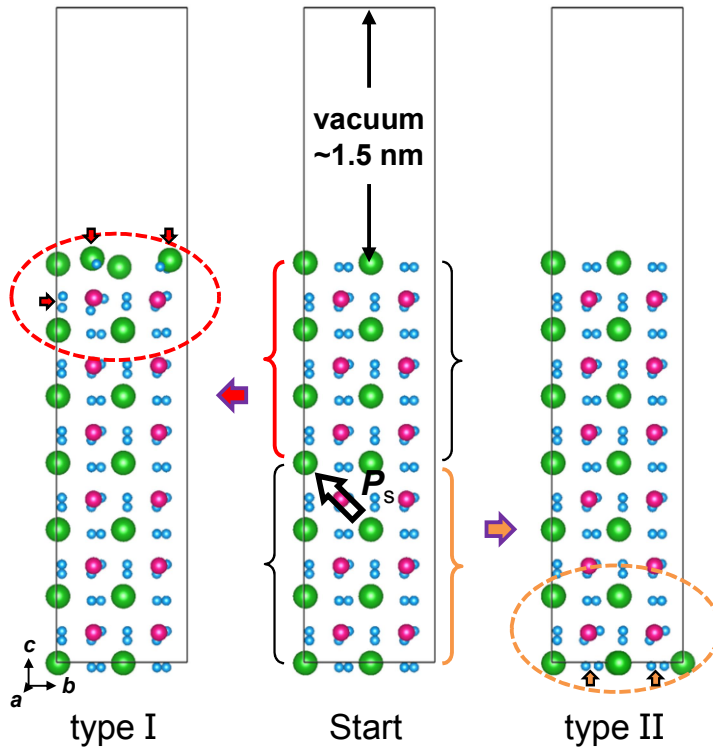


Figure S4 Free surface relaxation of strained BiFeO₃ ($c/a = 1.02$) predicted by *ab initio* calculations. Central panel: starting supercell R6 structure ($a = b = 0.773$ nm, $c = 3.865$ nm), consisting of $2 \times 2 \times 6$ BFO pseudocubic unit cells and ~ 1.5 nm of vacuum along the c -axis in order to exclude possible interactions between the top and bottom surfaces. The Fe/O atoms are displaced along the $[\bar{1}\bar{1}\bar{1}]$ axis with respect to the Bi lattice; correspondingly, P_s points towards the $[\bar{1}\bar{1}\bar{1}]$ direction. Relaxation of the structure was carried out by fixing the atoms in the 3 layers enclosed by black brackets and fully relaxing the other atoms. Left panel: Type I surface relaxation marked by a red bracket. Right panel: Type II surface marked by an orange bracket. Prominent atomic shifts are evident in the vicinity of the type I surface (enclosed by a red circle). In contrast, only a tiny O splitting from 52 to 76 pm occurs in the bc plane on the type II surface (enclosed by an orange circle), providing evidence for a strong demand to lower the energy at a charge-accumulated type I surface, when compared to a self-compensated type II surface.

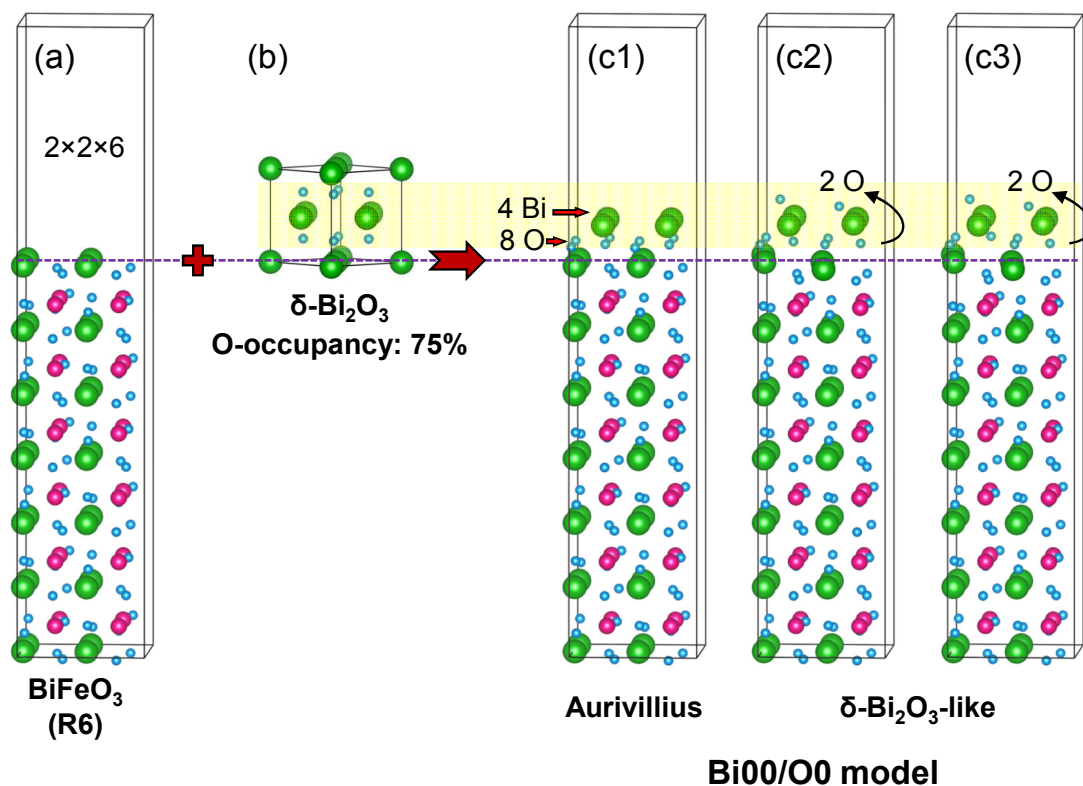


Figure S5 Construction of a Bi100/O0 supercell. (a) and (b) show the BFO R6 and δ -Bi₂O₃ components used to construct a supercell. (c1)-(c3) show three different models by considering the atomic site occupation of 8 O for (c1) an Aurivillius-like geometry, i.e., with 8 O located in the Bi-Bi interlayer (fully occupied) and (c2) and (c3) δ -Bi₂O₃-like occupation, i.e., with only 6 O located on the 8 atomic sites of the Bi-Bi interlayer. After relaxation, the c/a ratio is essentially the same, with the δ -Bi₂O₃-like occupation possessing much higher system energy (by at least 0.75 eV) than the Aurivillius-like configuration.

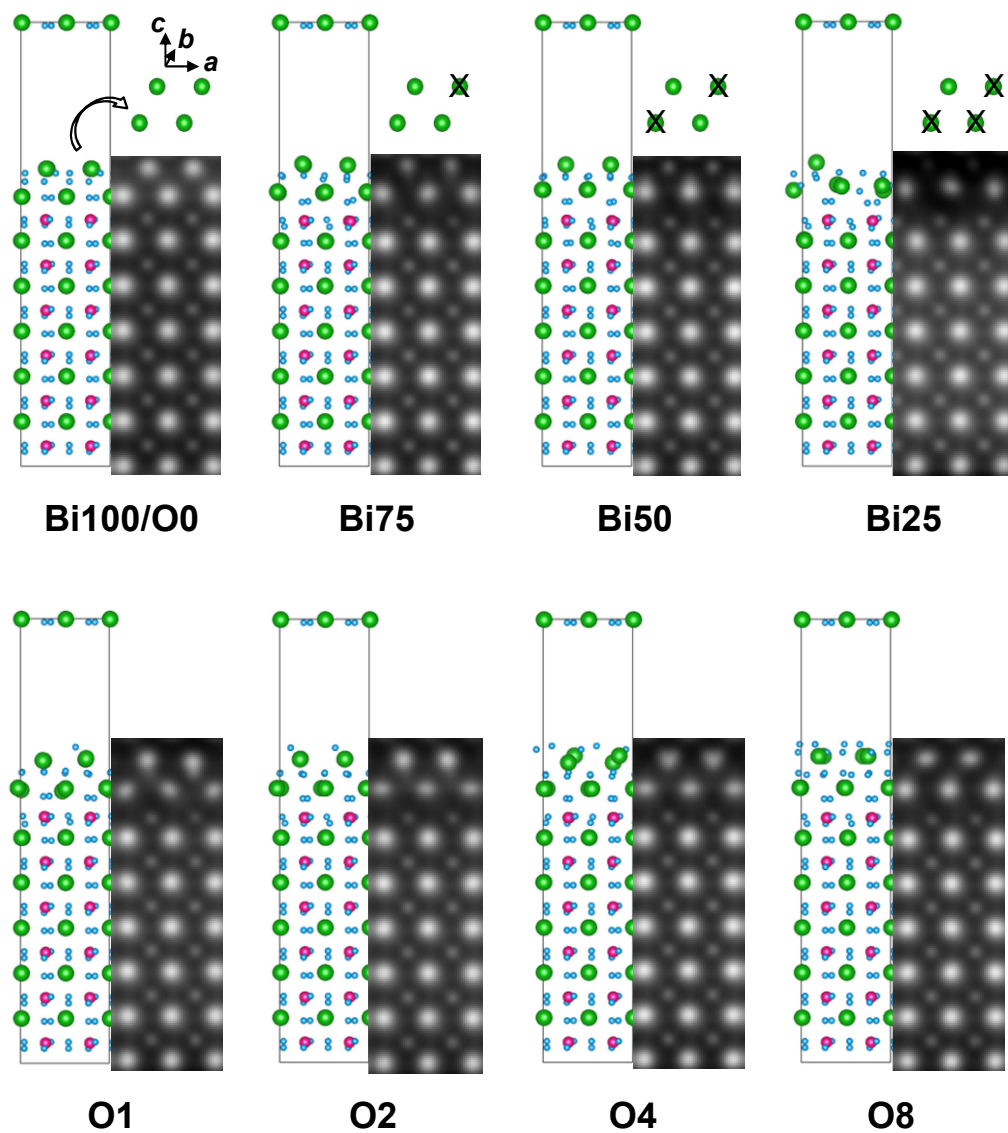


Figure S6 Relaxed atomic models and corresponding HAADF STEM simulated images. The construction of a Bi100/O0 model was described in supplementary Figure S5 for an Aurivillius-like surface geometry. Bi75, Bi50 and Bi25 models were constructed by removing 1, 2 and 3 surface Bi atoms (marked by crosses) on the basis of the Bi100/O0 model. O1 to O8 models were constructed by adding 1 to 8 O atoms on the outer Bi surface of the Bi100/O0 model.

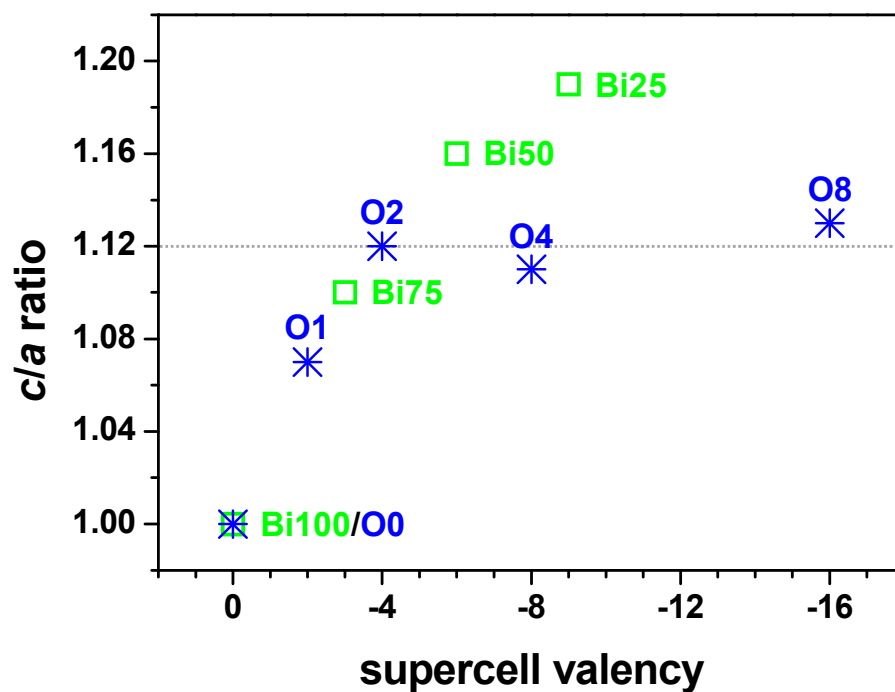


Figure S7 Plot of the calculated c/a ratio as a function of the net valency of the **entire supercell**. The c/a ratio was calculated on the basis of simulated HAADF images, as shown in supplementary Figure S6. In order to ensure measurement accuracy, the sampling rate was set to 0.0086 nm for the simulation, which is identical to the experimental value shown in Figure 2(b) in the main text. A plateau is present for the O2-O8 models, indicating saturation of negative charge compensation for O.

Supplementary references:

- [1] Deniz, H. *et al.* Nanoscale $\text{Bi}_2\text{FeO}_{6-x}$ precipitates in BiFeO_3 thin films: a metastable Aurivillius phase. *J. Mater. Sci.* **49**, 6952-6960 (2014).
- [2] Zhong, G., Wang, Y., Dai, Z., Wang, J. & Zeng, Z. Oxygen vacancy configuration of $\delta\text{-Bi}_2\text{O}_3$: an *ab initio* study. *Phys. Status Solidi B* **246**, 97-101 (2009).