

# Supporting Information:

## Origin of the Critical Thickness in Improper Ferroelectric Thin Films

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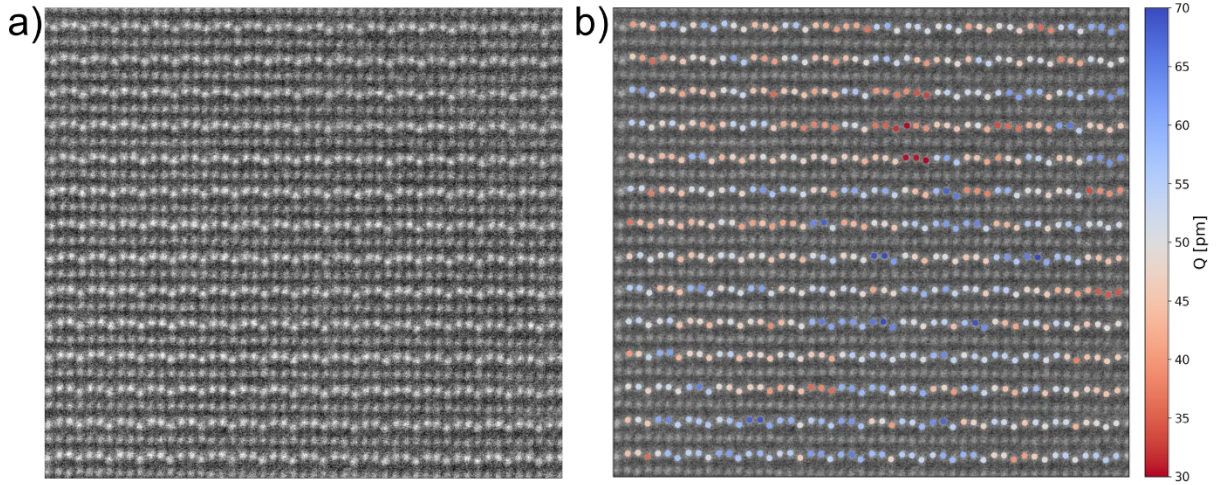
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### Supplementary Note 1: Bulk $\text{YMnO}_3$ reference

A  $\text{YMnO}_3$  (YMO) single crystal was investigated to obtain the bulk reference values for the trimerization amplitude  $Q$  and polarization  $P_s$ , using the approach described in the Methods section. Figure S1a shows a representative HAADF-STEM image of a single ferroelectric domain from the YMO single crystal. By fitting the lattice trimerization using a sinusoidal function we obtain the trimerization amplitude  $Q$  values for each Y atomic column, as plotted in Figure S1b. We obtain an average trimerization amplitude  $\langle Q \rangle = 50.2 \pm 7.2$  pm and spontaneous polarization  $P_s = 6.2 \mu\text{C cm}^{-2}$ .



**Figure S1.** Visualization of the lattice-trimerizing structural distortions in a  $\text{YMnO}_3$  single crystal. **a** HAADF-STEM image of the YMO single crystal used to extract the bulk reference values of  $Q$  and  $P_s$ . The image was filtered in Fourier space using a band-pass filter. **b** Plot of the trimerization amplitude  $Q$  in the bulk YMO reference.

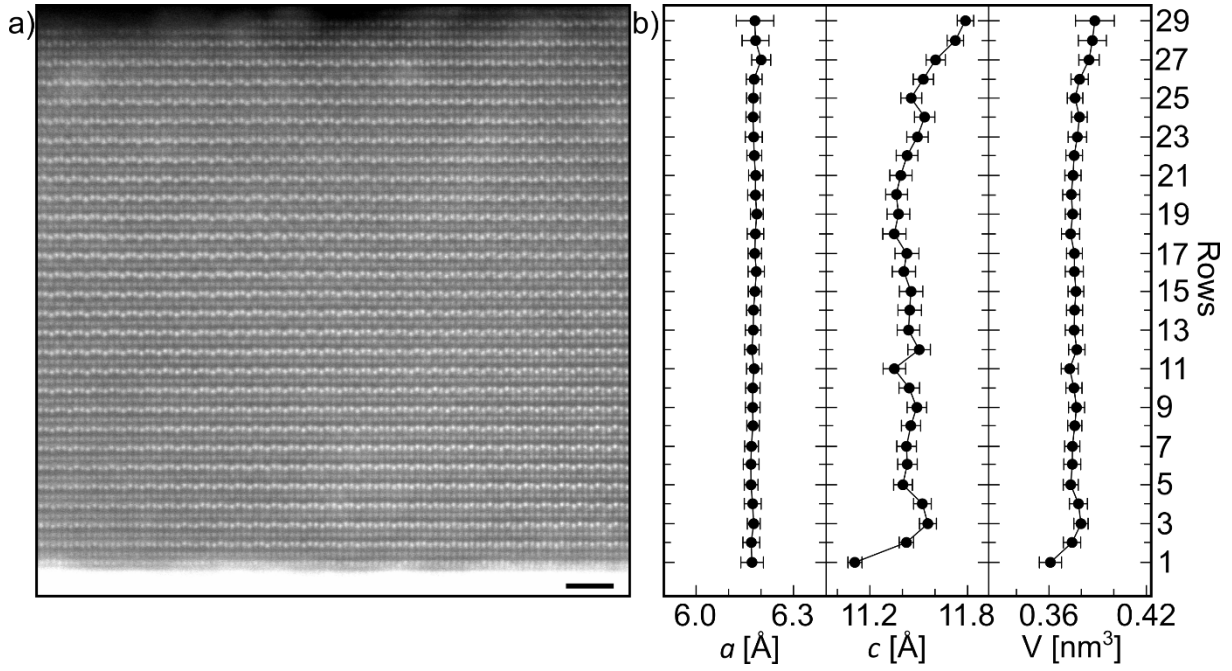
### Supplementary Note 2: Lattice-parameter characterization from HAADF-STEM images

After the precise atomic column fitting using a 2-dimensional Gaussian function in the Python library Atomap<sup>1</sup> we extract the in-plane lattice parameter  $a$  from the HAADF-STEM images as

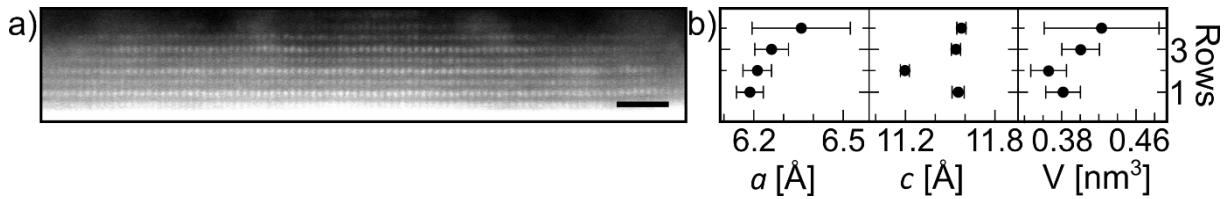
$$a = \frac{3d}{\cos \pi/6}, \quad (\text{S1})$$

where  $d$  is the in-plane distance between Y ions obtained from the atomic column fitting. The out-of-plane lattice parameter  $c$  is extracted as twice the distance between neighboring Y layers. Finally, the volume of the hexagonal unit cell is defined as

$$V = c \cdot a^2 \sin \frac{\pi}{3}. \quad (\text{S2})$$



**Figure S2.** Analysis of the lattice parameters and unit-cell volume of a 14 u.c. YMnO<sub>3</sub> film. **a** HAADF-STEM image of the film. The scale bar is 1 nm. **b** Line profiles of the in-plane and out-of-plane lattice parameters  $a$  and  $c$ , respectively, averaged per atomic row. The unit cell volume is then calculated as  $V = c \cdot a^2 \sin \pi/3$ .



**Figure S3.** Analysis of the lattice parameters and unit-cell volume of a 2 u.c. YMnO<sub>3</sub> film. **a** HAADF-STEM image of the film. The scale bar is 1 nm. **b** Line profiles of the in-plane and out-of-plane lattice parameters  $a$  and  $c$ , respectively, averaged per atomic row. The unit cell volume is then calculated as  $V = c \cdot a^2 \sin \pi/3$ .

### Supplementary Note 3: Layer charges in *h*-YMnO<sub>3</sub>

The total polarization of a material is defined by the ferroelectric polarization  $P_{\text{FE}}$  plus the polarization of the lattice  $P_{\text{lattice}}$ , which results from the formal charges of the ionic layers. In *h*-YMO, there are positively charged  $\text{Y}^{3+}$  and  $\text{MnO}^+$  layers, which are separated by two negatively charged layers of apical oxygens  $\text{O}^{2-}$ . Summing up the total dipole density of the layers along the *c*-axis, we obtain

$$P_{\text{lattice}} = \frac{1}{\Omega} \sum_i c_i Z_i, \quad (\text{S3})$$

where  $c_i$  is the *c*-axis coordinate of each layer,  $Z_i$  is the corresponding formal charge and  $\Omega$  is the unit cell volume. Performing this sum within the periodic boundary conditions of an infinite solid, we obtain a multivalued solution for  $P_{\text{lattice}}$  given by

$$P_{\text{lattice}} = \left(\frac{1}{2} \pm n\right) \frac{e}{S}, \quad (\text{S4})$$

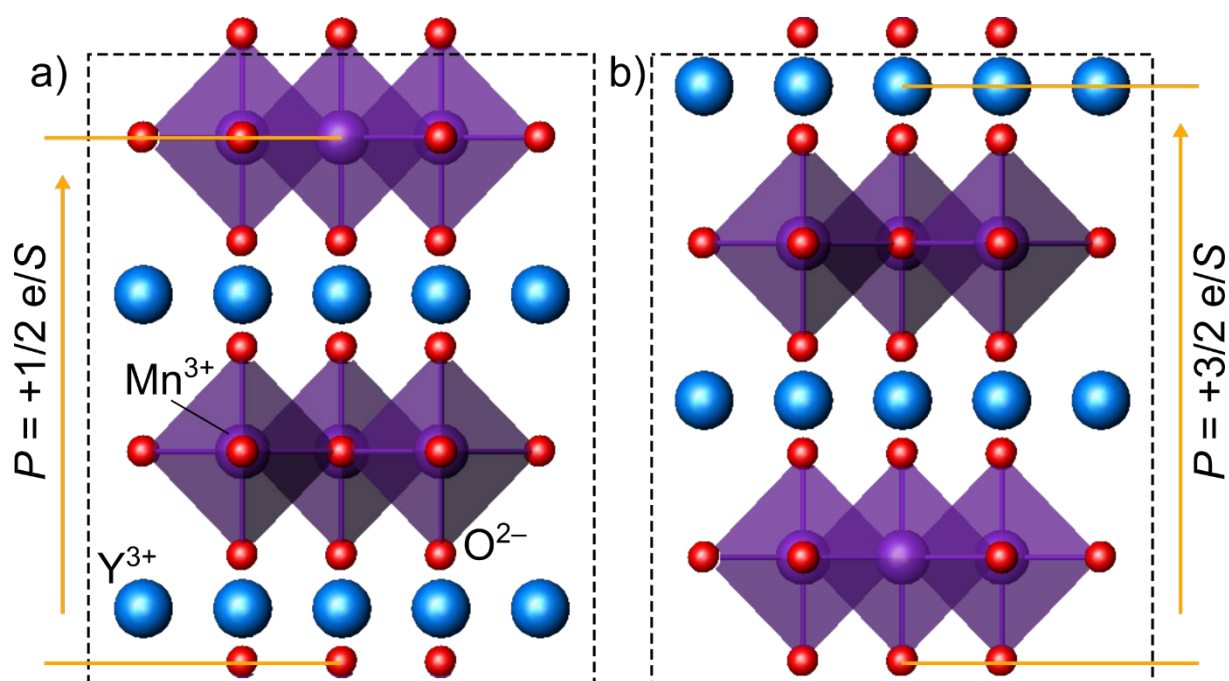
where  $n$  is an integer,  $e$  is the charge of an electron and  $S$  is the surface area of the unit cell perpendicular to the charged layers (see for example Figure S4). Using  $S \approx 11 \text{ \AA}^2$  ( $P6_3/mmc$  phase), this results in a layer polarization of approximately

$$P_{\text{lattice}} = (75 \pm n \cdot 150) \mu\text{C cm}^{-2}, \quad (\text{S5})$$

which is one order of magnitude larger compared to its spontaneous polarization of about  $6 \mu\text{C cm}^{-2}$  we measure in the bulk single crystal. In ultrathin films, the lattice polarization becomes highly important as it corresponds to the surface charge, with the surface termination selecting a specific value of the quantum  $n$ . Analogously to the ferroelectric depolarizing field, the lattice polarization also induces a large electric field in the material if its surface charges remain unscreened. In order to minimize the electrostatic energy cost, the material thus favors terminations that lead to the smallest possible value of  $P_{\text{lattice}}$ , thus in this case  $n = 0, -1$ , which corresponds to a termination on the  $\text{MnO}^+$  layers; see Figure S4a. Instead, for  $n = 1$ , which

corresponds to a termination on the  $Y^{3+}$  layer, a larger value of  $P_{\text{lattice}}$  is obtained as displayed in Figure S4b.

The electric field emerging from the surface charges directly interacts with the ferroelectric polarization of the material, favoring an anti-parallel alignment of the lattice polarization and ferroelectric polarization, in order to reduce the net electric field and electrostatic energy. Such behavior has been observed in thin films of  $\text{BiFeO}_3$ , where  $|P_{\text{FE}}| \approx |P_{\text{lattice}}|^2$ . However, in  $h$ -YMO, the spontaneous polarization is one order of magnitude smaller than the layer polarization and thus is not able to fully compensate the electric field from the layer polarization. Instead, screening charges need to be induced at the surface in order to prevent divergence of the electrostatic potential. In the MnO-terminated YMO slab ( $P = \frac{1}{2} e/S$ ), this amounts to a compensating charge of  $-0.5 e/S$ , which corresponds to the one-half electron per manganese atom. This is fully consistent with the EELS measurements, which show a reduction of  $\text{Mn}^{3+} \rightarrow \text{Mn}^{2.5+}$  at the top interface, and could for example be introduced by the formation of neutral oxygen vacancies.



**Figure S4.** Two possible polarization lattices of an infinite crystal arising from different origins of the unit cell. **a** The unit cell terminates with a  $\text{MnO}^+$  layer, resulting in  $P_{\text{lattice}} = 1/2 \text{ e/S}$ . **b** The unit cell terminates with a  $\text{Y}^{3+}$  layer, resulting in  $P_{\text{lattice}} = 3/2 \text{ e/S}$ .

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