Supplementary material: Epitaxial $PbZrO_3$ Films from Chemical Solutions

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Supplementary Figure 1

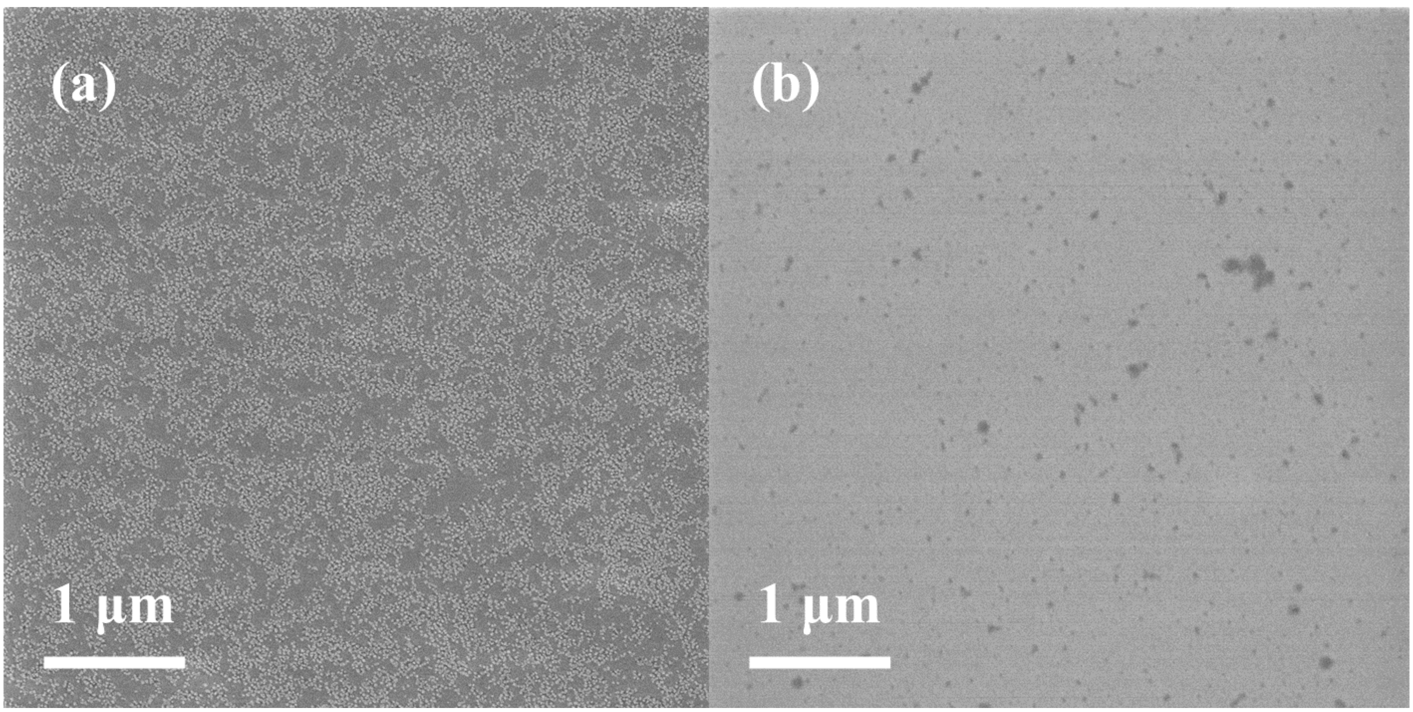

Figure 1 Helium Ion Microscopy (HIM) image of a 170 nm-thick $PbZrO_3$ film before (a) and (b) after PbO capping layer treatment

To remove the pyrochlore phase on the surface of $PbZrO_3$, a PbO capping process is used. A PbO precursor solution was synthesized from freeze dried lead(II) acetate (99.99%, Merck). The precursor was dissolved in anhydrous 2-methoxyethanol (Sigma Aldrich, 99.8%). The mixture was then refluxed for two hours under argon atmosphere. The solution was then distilled and diluted with 2-methoxyethanol until a concentration of 0.8 M. The PbO precursor solution was spin coated at 3000 rpm for 30 seconds, followed by a drying step at 130 °C for 3 minutes and a pyrolysis step at 350 °C for 3 minutes. The PbO layer was crystallized in a rapid thermal annealing furnace (AS-Master, Annealsys) at 700 °C for 5 minutes in air. The remaining PbO crystals were removed with acetic acid (99.8%, Merck). Prior to the PbO capping layer, small pyrochlore phase grains can be observed on the top of $PbZrO_3$ (Figure 1 (a)). After the PbO capping layer treatment, the pyrochlore phase disappears (Figure 1 (b)).

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Supplementary Figure 2

The lattice vectors for the commonly accepted *Pbam* structure or $PbZrO_3$ (subscript 'o') are given as a function of the lattice vectors of the parent perovskite cubic cell (subscript 'pc') as

$$\begin{cases} \vec{a}_{\mathrm{o}} &= \vec{a}_{\mathrm{pc}} + \vec{c}_{\mathrm{pc}} \\ \vec{b}_{\mathrm{o}} &= -2\vec{a}_{\mathrm{pc}} + 2\vec{c}_{\mathrm{pc}} \\ \vec{c}_{\mathrm{o}} &= 2\vec{b}_{\mathrm{pc}} \end{cases} \tag{1}$$

The point group lowering from $m\bar{3}m$ to mmm comes with the formation of 6 orientational ferroelastic domains. Figure 2 below aims at clarifying the orientation of these domains with respect to the cubic substrate, whose cubic lattice vectors match those of pseudo-cubic $PbZrO_3$. This can be obtained in this particular case by simply considering all permutations of $(\vec{a}_{\mathrm{pc}}, \vec{b}_{\mathrm{pc}}, \vec{c}_{\mathrm{pc}})$ in the equations above. A more systematic approach is to derive the orientation of all domains from the symmetry operations lost at the phase transition (coset decomposition).

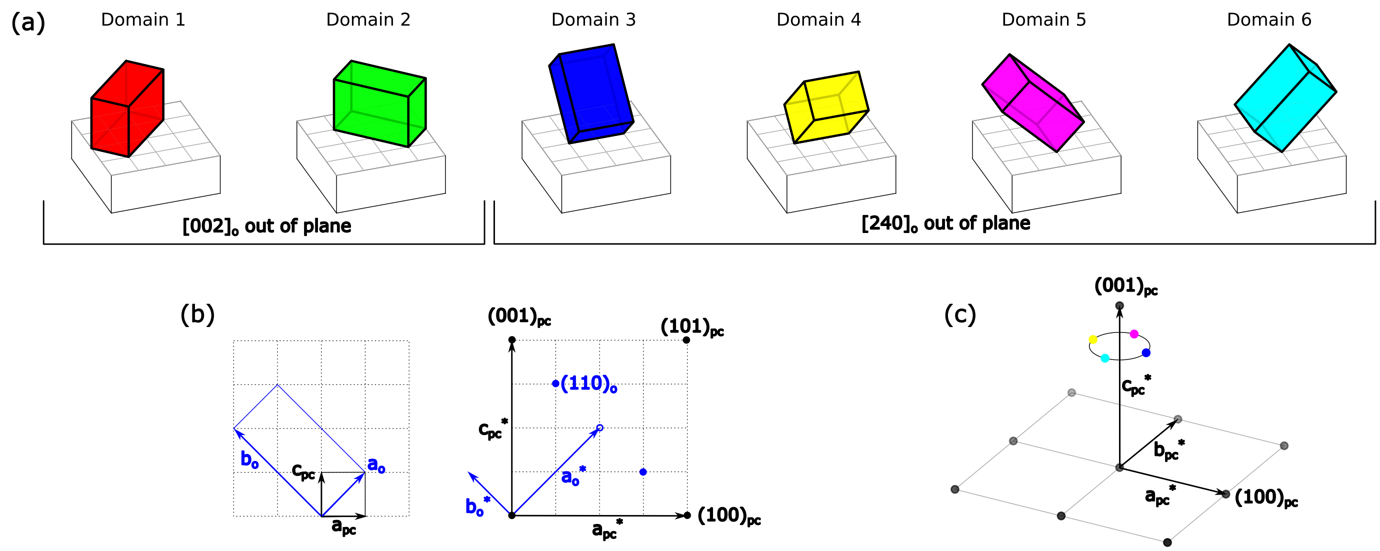

Figure 2 (a) Orientations of the 6 ferroelastic domains of $PbZrO_3$ that satisfy an epitaxy relation with the cubic $SrTiO_3$ substrate. (b) Relation between the direct (left) and reciprocal (right) lattice vectors of the *Pbam* phase of $PbZrO_3$ for the vectors given in equation (1). The $(110)_{\mathrm{o}}$ (open circle) is a forbidden reflection. (c) Positioning of the $(110)_{\mathrm{o}}$ reflection for domains 3 to 6, as they are measured during the ϕ-scan shown in the Figure 1(c) of the main text.

It appears from Figure 2(a) that the 6 ferroelastic domains can be separated into two groups. Two domains (1 and 2) have their $[002]_{\mathrm{o}}$ normal to the substrate while four domains (3 to 6) have their $[240]_{\mathrm{o}}$ out of plane. In both cases, the domains are related by C_4 rotations around the normal to the substrate. Figure 2(b) shows the position of the $(110)_{\mathrm{o}}$ for domain 3. Note that this reflection is a $(1/4\ 0\ 3/4)_{\mathrm{pc}}$ superstructure that reflects the 'up-up-down-down' antiparallel arrangement of Pb ions. When performing a ϕ-scan for this reflection, the scan will meet all 4 domain variants (3 to 6) as depicted schematically in Figure 2(c), which also shows that these reflections are found at the same ϕ angle as the cubic substrate peaks.

Supplementary Figure 3

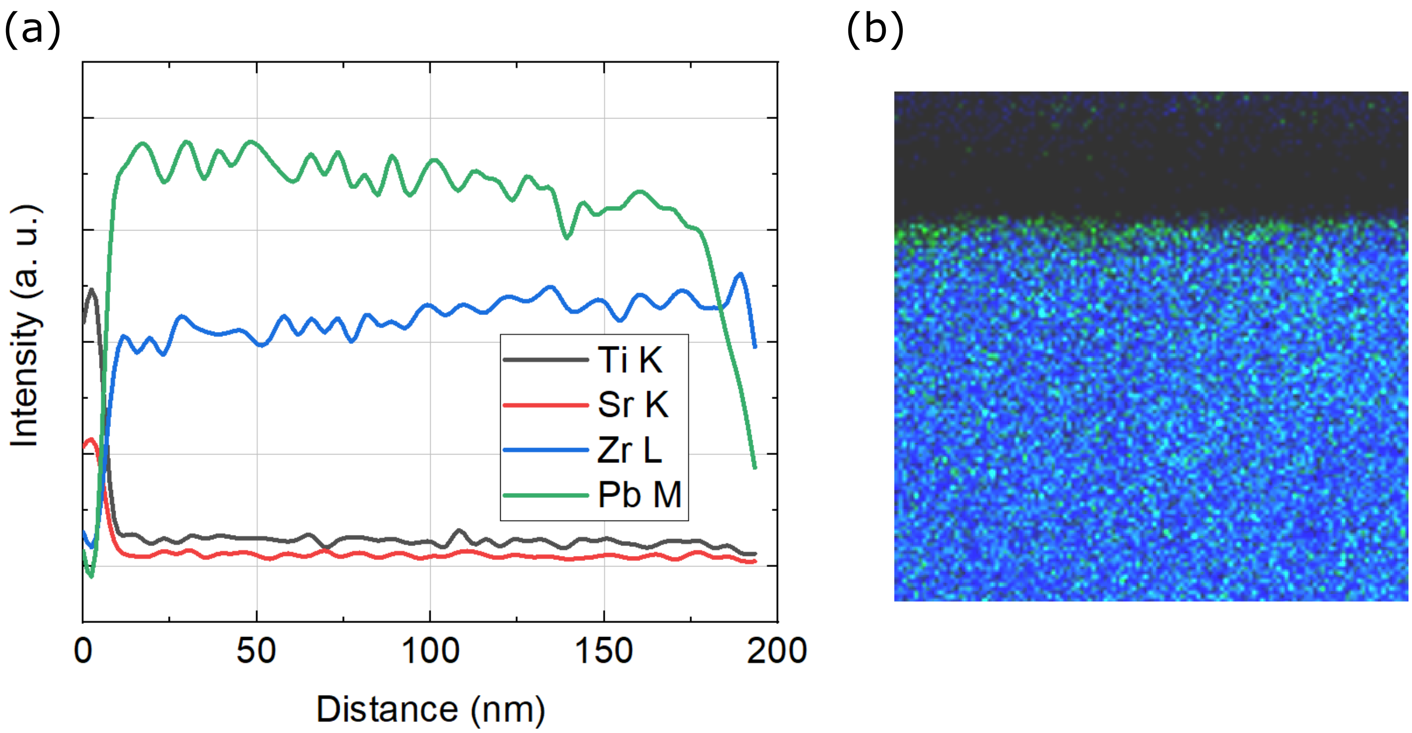

Figure 3 (a) EDXS line profiles of Ti K, Sr K, Zr L, and Pb M signals. (b) Composite EDXS image showing a Zr-rich layer at the top surface of the 170 nm-thick $PbZrO_3$ film using Zr K (green) and Pb M lines (blue).

To better understand the chemical inhomogeneities produced during the solution-processing of $PbZrO_3$, Figure 3 (a) shows the EDXS line profile of Pb and Zr in the $PbZrO_3$ film. A gradient of lead and zirconium content along the films is observed. The composite EDXS image (Figure 3 (b)) clearly shows Zr-rich layer at the top surface of the 170 nm-thick film.