Symposium on Quantum Materials Synthesis, Porto, October 22 - 24, 2025

Engineering Symmetry Breaking Interfaces in Orthorhombic Perovskite Thin Films Via Structural-Energetics

Duncan T.L. Alexander[1], Hugo Meley[2], Clémentine Thibault[2], M. Marcus Schmitt[3], Bernat Mundet[1,2], Chih-Ying Hsu[1,2], Jean-Marc Triscone[2], Philippe Ghosez[3], Stefano Gariglio[2]

[1]*Electron Spectrometry and Microscopy Laboratory (LSME), Institute of Physics (IPHYS), École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland*

[2]*Department of Quantum Matter Physics (DQMP), University of Geneva, Geneva, Switzerland*

[3]*Theoretical Materials Physics, Q-MAT, Université de Liège, Liège, Belgium*

The orthorhombic perovskite lattice with *Pnma* space group constitutes one of the most common crystal structures for transition metal oxide compounds displaying properties that are interesting for quantum materials applications. When a crystal is grown as an epitaxial thin film, the film's orientation is typically set by that which minimises its macroscopic strain energy. Nevertheless, it is well established that, when a *Pnma* orthorhombic film is grown on the (101) plane of a substrate that is also *Pnma* orthorhombic, the connectivity of oxygen octahedra across the interface plays a key role in defining the final orientation of the film.

Here, we explore the consequences of setting up an energetic conflict between these two influences, by growing films of $LaVO_3$ under ~0.5% epitaxial tensile strain on (101) $DyScO_3$, using pulsed laser deposition [1]. Under these conditions, misfit strain energy favours the film growing with its orthorhombic long axis b_{orth} out-of-plane. In contrast, oxygen octahedra connectivity favours b_{orth} remaining in-plane, as for the substrate. X-ray diffraction identifies that the film indeed keeps the substrate symmetry, up until a critical growth thickness of 60–70 unit cells. At this thickness, misfit strain energy dominates over interfacial connectivity, and the film switches to having b_{orth} out-of-plane. Detailed, "forensic", analysis of films using aberration-corrected scanning transmission electron microscopy (Cs-STEM) on different zone axes finds that the switch in orientation does not occur at the film–substrate interface, but instead at an atomically sharp plane some ~10 unit cells into the film. At this interface—that we term the *switching plane*—mismatched orthorhombic distortions tend to zero, in order to couple them between the initial intermediate layer of the film having b_{orth} in-plane, and the film bulk with b_{orth} out-of-plane. As a result, the symmetry of the parent orthorhombic lattice is inherently broken at the switching plane.

By using innovative second-principles simulations involving 1000s of atoms to investigate the structural-energetics behind this phenomenon, we successfully rationalise the experimentally observed critical thickness and switching plane behaviour. Moreover, the simulations enable us to study the modulations in local atomic structure distortions going from the intermediate layer, across the switching plane, and into the film bulk; details that compare favourably to the measurements made with Cs-STEM. The symmetry-breaking switching plane interface, that contacts two phases of the same compound that would never otherwise co-exist, presents new opportunities for creating functional properties, such as synthesizing a quantum material that is chemically uniform but magnetically inhomogeneous.

References:

[1] D.T.L. Alexander, H. Meley, M.M. Schmitt, B. Mundet, J.-M. Triscone, P. Ghosez and S. Gariglio, *ACS Nano* 2025, **19**, 10126–10137. https://doi.org/10.1021/acsnano.4c17020