

Supplementary Material

Surface Matters: A Case Study of the Scale and Impact of Oxide Surfaces via Orbital Polarization

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1. Oxygen K-edge

Normalized intensity for V L_{2,3}-edge and O K-edge of strained and unstrained SrVO₃ (SVO) are presented in Figure S1. The spectra were acquired using soft x-ray absorption spectroscopy (XAS) in total electron yield (TEY) and x-ray excited optical luminescence (XEOL), and scanning transmission electron microscopy electron energy loss spectroscopy (STEM-EELS). The TEY-XAS spectrum, as elaborated in the main paper, is composed mainly of the SVO near-surface region. In contrast, the XEOL-XAS spectrum stems from the entire thickness of the film, and includes a contribution from the oxygen present in the oxide substrate. This has a small effect on the V L_{2,3}-edge, but it strongly affects the O K-edge. The STEM-EELS spectrum illustrates the SVO V L-edge and O K-edge with a minor contribution from the near-surface region, as elaborated in the main text.

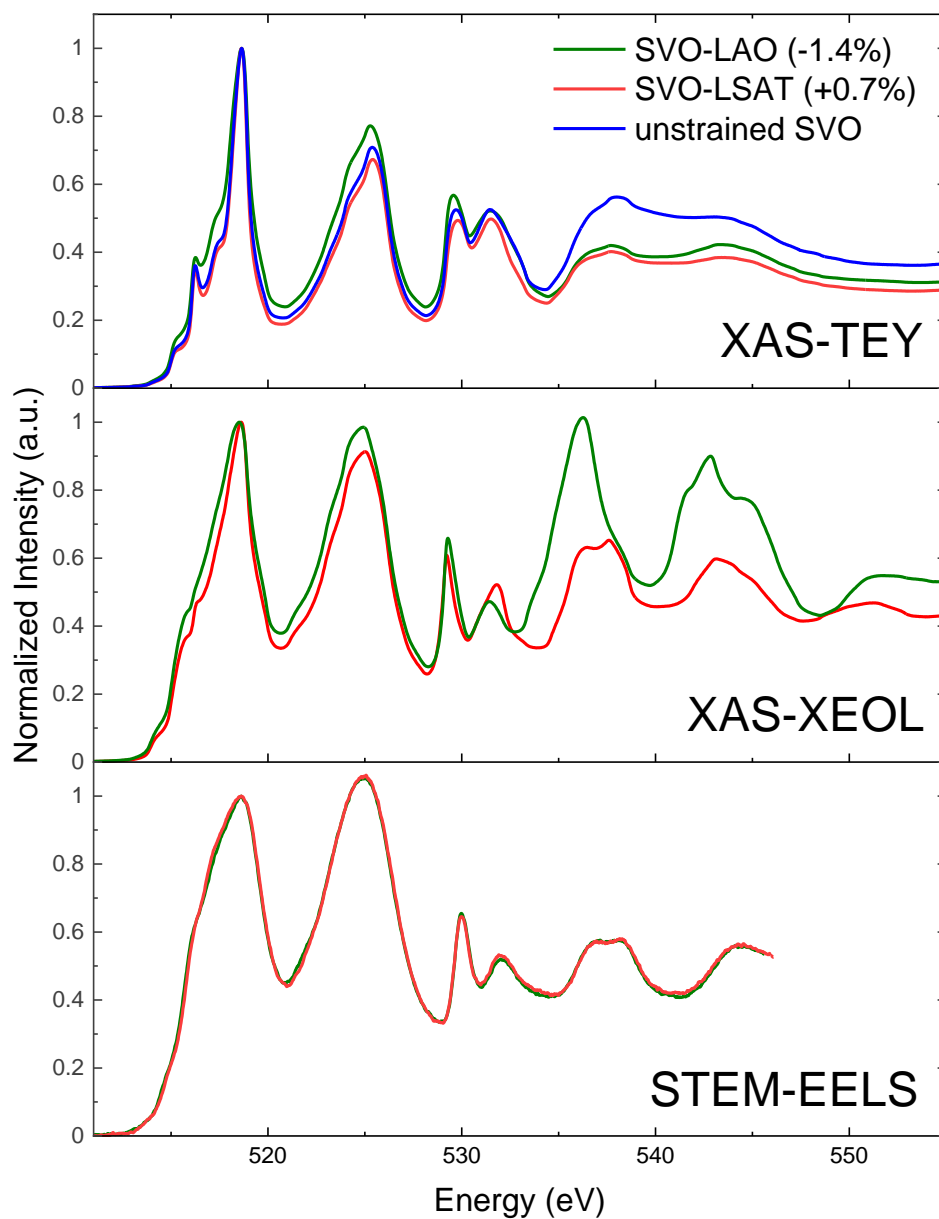


Figure S1. Comparison of the normalized V L_{2,3}-edge and O K-edge for tensile and compressive strained SVO films (SVO-LSAT and SVO-LAO, respectively) and unstrained (single-crystal) SVO. The acquisition was made using XAS in TEY and XEOL modes, and STEM-EELS.

2. Structural Characteristics

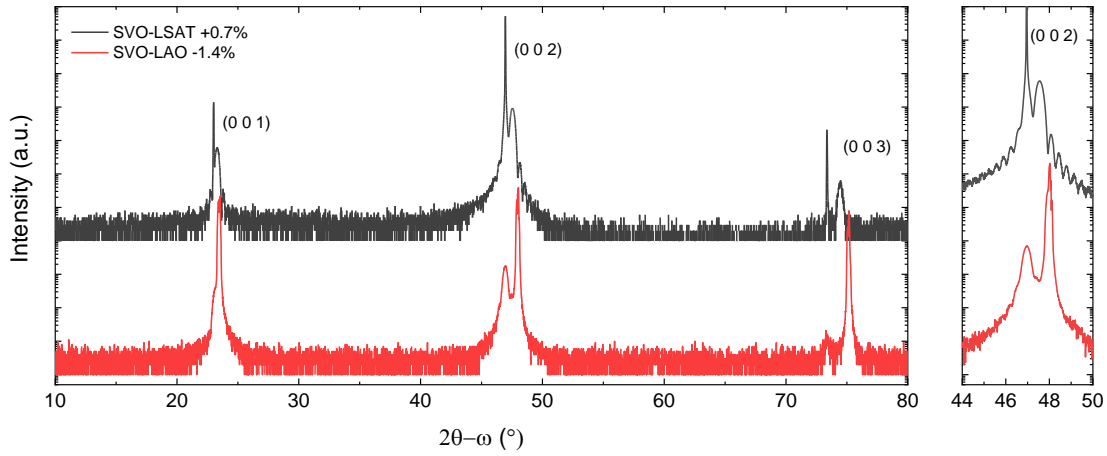


Figure S2. High-resolution 2θ - ω scans around (001), (002), and (003) peaks of LSAT (black) and LAO (red) substrates. The scans were acquired using a Rigaku SmartLab with a 2-bounce incident monochromator.

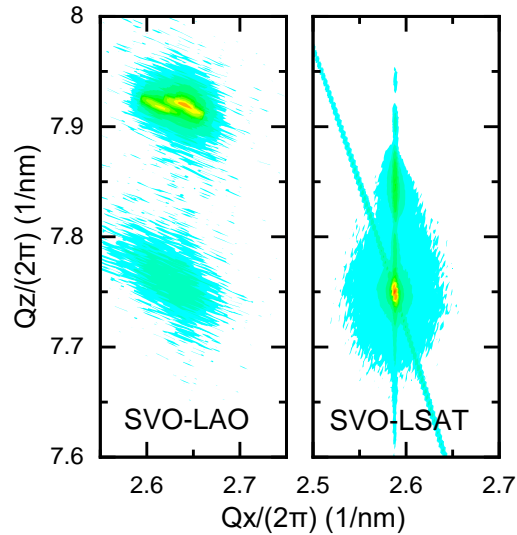


Figure S3. Reciprocal space maps (RSMs) of the strained SVO films grown on LAO and LSAT substrates taken around the cubic/pseudocubic (013) peak. The similar Q_x values of each film and substrate indicate that the films are fully strained to their substrates.

Complementary scanning transmission electron microscopy (STEM) analysis ruling out octahedral rotation of the VO_6 octahedra is reported elsewhere.¹

3. XAS by Total Fluorescence Yield (TFY)

A common approach for extending the probing depth of TEY is TFY. However, in some cases, TFY can have several issues: (i) it can lead to self-absorption for concentrated samples, which makes the L_3 -edge smaller than the L_2 . (ii) The TFY is not always equivalent to the x-ray absorption spectra.² And, finally, (iii) depending on the edge investigated and the strength of background fluorescence, it can lead to negative peaks in the measured absorption.³ This does not apply to all samples measured by TFY. For our films, the large O TFY signal from the film and substrate can be observed in Figure S4 to interfere with the V- $L_{2,3}$ spectral region.

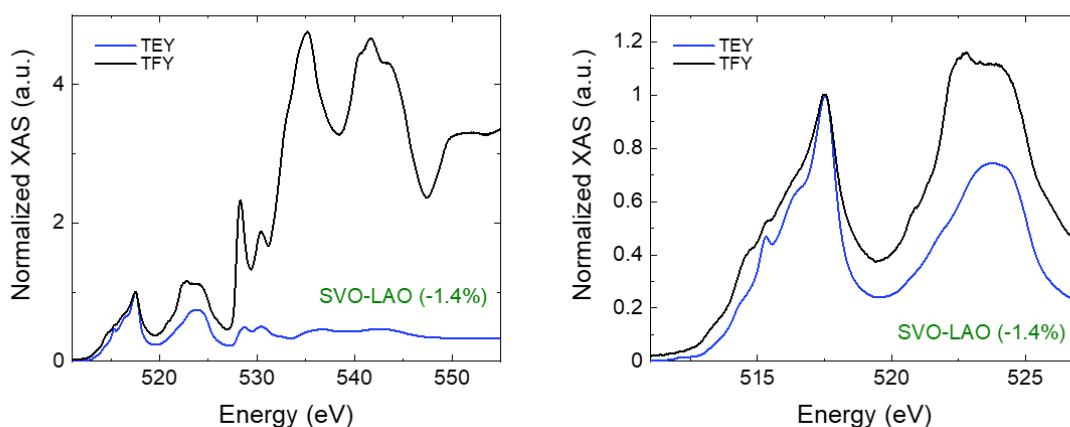


Figure S4. Comparison of the V $L_{2,3}$ -edge and O K-edge for compressive strained SVO (SVO-LAO) acquired in TEY and TFY modes.

4. Reduced High Harmonic Contamination for XEOL

To obtain a reliable XLD spectrum by XEOL, we used the monochromator setting with $c_{\text{ff}}=1.5$ in order to drastically reduce high harmonic contamination.⁴ Using more standard values of c_{ff} (such as 2.25 or 5.0), we always observed a different spectrum that looked more like the XAS spectrum. We believe this comes from the fact that the flux for linearly polarized x-rays in the second harmonic is drastically different if the polarization is horizontal or vertical. However, more measurements are needed to be sure.

References

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- ² B. Liu, C. Piamonteze, M.U. Delgado-Jaime, R.P. Wang, J. Heidler, J. Dreiser, R. Chopdekar, F. Nolting, and F.M.F. De Groot, “Sum rule distortions in fluorescence-yield x-ray magnetic circular dichroism,” *Phys Rev B* **96**(5), 054446 (2017).
- ³ F.M.F. de Groot, “Dips and peaks in fluorescence yield X-ray absorption are due to state-dependent decay,” *Nat Chem* **4**(10), 766–767 (2012).
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