

Supporting Information

Estimating Hybridization of Transition-Metal and Oxygen States in Perovskites from O K-edge X-ray Absorption Spectroscopy

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Material Synthesis

The perovskite samples studied at the Saga Synchrotron were synthesized with a co-precipitation method. Rare and/or alkaline earth nitrate, and transition-metal nitrate (both 99.98% Alfa Aesar) in a 1:1 mole ratio were briefly mixed in Milli-Q water (18 M Ω •cm) at 0.2 M metal concentration. The solution containing rare and alkaline earth, and transition metals was titrated to 1.2 M tetramethylammonium hydroxide (100% Alfa Aesar). The precipitate was filtered, collected, and dried. The powder samples were subjected to heat treatment at 1000°C under Ar atmosphere for the La_{1-x}Ca_xMnO₃ (x = 0, 0.5) and La_{0.5}Ca_{0.5}CrO₃ samples, at 1000°C under dried air atmosphere for LaCrO₃, La_{1-x}Ca_xFeO₃ (x = 0, 0.25, 0.5), LaCoO₃, La₃Ni₂O₇, La₄Ni₃O₁₀ samples, and at 800°C under O₂ atmosphere for the LaNiO_{3- δ} sample. LaMnO_{3+ δ} was prepared from an 800°C heat treatment of LaMnO₃ in air. La₂NiO₄ was synthesized in 2 steps: 1000°C under Air atmosphere and then heated at 800°C under Ar atmosphere. All gases had ultra-high-grade purity (Airgas).

The perovskite samples studied at the ALS were prepared as followed. LaCoO₃ and LaFeO₃ were prepared from binary oxide precursors, which were La₂O₃ (99.99%, trace metal basis, Alfa Aesar), Co₃O₄ (99.7% trace metal basis, Alfa Aesar), and Fe₂O₃ (99.99% metal basis, Alfa Aesar). All binary oxide precursors were heat-dried at 800°C for 8 hours. A mixture of 1:1 La to transition metal ratio was then prepared, ground, pressed, and sintered at 1100°C for 12 hours under air atmosphere. The resulting pellet was then re-ground, pressed, and sintered a second time at the same condition. For LaNiO_{3- δ} synthesis, we applied a glycine-nitrate synthesis method. La(NO₃)₃•6H₂O (99.999% metal basis, Alfa Aesar) and Ni(NO₃)₃•6H₂O (99.999% metal basis, Sigma Aldrich) were dissolved in Milli-Q water (18 M Ω •cm), to which glycine was added. The mixture was heated and allowed to slowly evaporate, then heated at 400°C under air

atmosphere for 4 hours. The resulting powder was ground, pressed, and sintered at 800 °C under air atmosphere for 12 hours. The resulting pellet was then re-ground, pressed, and sintered a second time at the same condition. The oxygen non-stoichiometry for $\text{LaNiO}_{3-\delta}$ was verified by iodometric titration to be 2.98 ± 0.10 .

Density Functional Theory (DFT) Calculations

Density Functional Theory (DFT) calculations were performed with the Vienna *Ab-initio* Simulation Package (VASP)^{1, 2} using the Projector-Augmented plane-Wave method³ with the Perdew-Wang-91⁴ Generalized Gradient Approximation (GGA) plus Hubbard *U* method to treat the exchange-correlation interactions. The plane wave basis set was expanded up to 450 eV and the soft O_s oxygen pseudopotential was used. All calculations were performed in the ferromagnetic state in order to use a consistent and tractable set of magnetic structures, and the spin states for the calculated LaBO_3 systems (B= Cr, Mn, Fe, Co, and Ni) were: Cr: high spin; Mn: high spin; Fe: high spin; Co: intermediate spin; and Ni: low spin.

The pseudopotential configurations for each atom are as follows:

Element	VASP PAW Potential	Configuration
La	La	$5s^2 5p^6 5d^1 6s^2$
Cr	Cr_pv	$3d^5 4s^1$
Mn	Mn_pv	$3p^6 3d^6 4s^1$
Fe	Fe_pv	$3p^6 3d^7 4s^1$
Co	Co	$3d^8 4s^1$
Ni	Ni_pv	$3p^6 3d^9 4s^1$

O	O_s	$2s^2 2p^4$
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The GGA+ U calculations⁵ were performed with the simplified spherically averaged approach⁶, where an effective U parameter, $U_{eff} = U - \text{exchange } J$ is applied to the correlated $3d$ orbitals. Specifically, we use the following values: $U_{eff}(\text{Cr}) = 3.5$ eV, $U_{eff}(\text{Mn}) = 4.0$ eV, $U_{eff}(\text{Fe}) = 3.9$ eV, $U_{eff}(\text{Co}) = 3.3$ eV, $U_{eff}(\text{Ni}) = 6.4$ eV.

Fully relaxed stoichiometric bulk perovskite calculations were simulated with $2 \times 2 \times 2$ perovskite supercells based on the experimental symmetry. Relaxed lattice constants from the bulk experimental symmetry and relaxed volume for the $2 \times 2 \times 2$ supercells are provided in the table below.

System	Exp. symmetry	Relaxed Lattice Constants (Å)	Relaxed Volume for the $2 \times 2 \times 2$ supercells (Å ³)
LaCrO ₃ [7]	Orthorhombic	a = 5.57 b = 5.59 c = 7.88	490.86
LaMnO ₃ [8]	Orthorhombic	a = 5.87 b = 5.58 c = 7.77	509.10
LaFeO ₃ [9]	Orthorhombic	a = 5.62 b = 5.56 c = 7.91	494.95
LaCoO ₃ [10]	Rhombohedral	a = 5.50	469.96
LaNiO ₃ [11]	Rhombohedral	a = 5.45	458.46

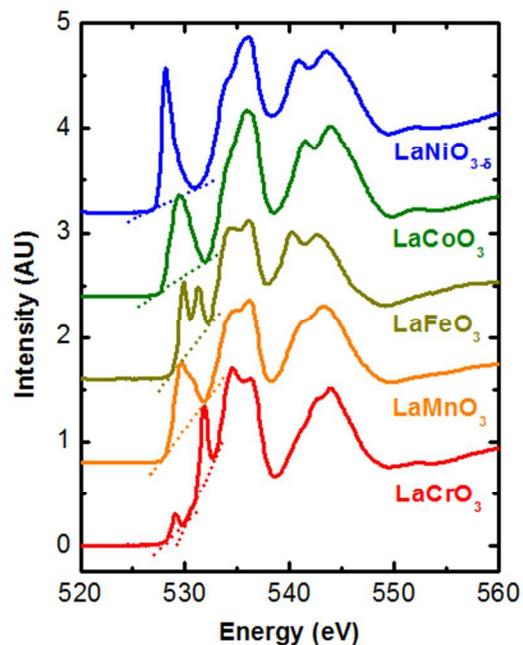


Figure S1. Linear background subtraction of O *K*-edge X-ray absorption spectra pre-edge. We extract the intensity of the excitation by first removing the linear background between the two nearest local minima to correct for the background absorption, then integrate the area underneath. Note that two linear correction regions were used for the LaCrO₃ data due to the presence of the additional peak at ~529 eV.

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