Anomalous Interface and Surface Strontium Segregation in \((\text{La}_{1-y}\text{Sr}_y)_2\text{CoO}_{4±}/\text{La}_{1-x}\text{Sr}_x\text{CoO}_3\) Heterostructured Thin Films.

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<td>Publisher</td>
<td>American Chemical Society (ACS)</td>
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<td>Version</td>
<td>Original manuscript</td>
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<td>Accessed</td>
<td>Tue Dec 18 01:09:27 EST 2018</td>
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Anomalous Interface and Surface Strontium Segregation in \((\text{La}_{1-y}\text{Sr}_y)_2\text{CoO}_{4\pm\delta}/\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}\) Heterostructured Thin Films

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ABSTRACT:

Heterostructured oxides have shown unusual electrochemical properties including enhanced catalytic activity, ion transport, and stability. In particular, it has been shown recently that the activity of oxygen electrocatalysis on the Ruddlesden-Popper/perovskite \((\text{La}_{1-x}\text{Sr}_x)_{2}\text{CoO}_{4\delta}/\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}\) heterostructured structure is remarkably enhanced relative to the Ruddlesden-Popper and perovskite constituents. Here we report the first atomic-scale structure and composition of \((\text{La}_{1-x}\text{Sr}_x)_{2}\text{CoO}_{4\delta}/\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}\) grown on \(\text{SrTiO}_3\). We observe anomalous strontium segregation from the perovskite to the interface and the Ruddlesden-Popper phase using direct X-ray methods, as well as with \textit{ab initio} calculations. Such Sr segregation occurred during the film growth and no significant changes were found upon subsequent annealing in air. Our findings provide insights for the design of highly active catalysts for oxygen electrocatalysis.

KEYWORDS: surface and interface, heterostructure perovskites, oxides, fuel cell, coherent Bragg rod analysis, \textit{ab initio} calculation
Interfaces in many heterostructured epitaxial materials exhibit intriguing physical, chemical, and electrochemical properties including enhanced oxygen electrocatalytic activity\textsuperscript{1-9} and electronic/ionic conductivity\textsuperscript{10-12} compared to bulk materials. The combination of a Ruddlesden-Popper (RP) (La\textsubscript{0.5}Sr\textsubscript{0.5})\textsubscript{2}CoO\textsubscript{4+δ} (LSCO\textsubscript{214})\textsuperscript{13-14} layer on top of the perovskite La\textsubscript{0.8}Sr\textsubscript{0.2}CoO\textsubscript{3-δ} (LSCO\textsubscript{113}, a mixed electronic and ionic conducting perovskite)\textsuperscript{2,10} was found to greatly enhance the activity for the oxygen reduction reaction (O\textsubscript{2} + 4e\textsuperscript{-} ↔ 2O\textsubscript{2}–) at high temperatures\textsuperscript{13,15-16}, resulting in 1~3 orders of magnitude enhancement compared to LSCO\textsubscript{113} alone.

A number of studies have been made to understand the high catalytic activity of these LSCO heterostructured catalysts using well-defined thin film systems. Density functional theory (DFT) calculations have shown that there is a large driving force for A-site cationic interdiffusion across the heterostructure interface, stabilizing Sr in LSCO\textsubscript{214} and La in LSCO\textsubscript{113} with predicted Sr concentrations ~0.75 near the interface and Sr depletion in LSCO\textsubscript{113}\textsuperscript{17}. Such interdiffusion has been postulated to result from coupling of Sr ions to the increased oxygen vacancy content near the surface\textsuperscript{18}, and is predicted to reduce the oxygen vacancy formation energy\textsuperscript{17}. The reduced enthalpy of oxidation at the interface due to the presence of Sr may play a direct role in enhancing the oxygen surface exchange\textsuperscript{17} or indirectly via the electronic activation of LSCO\textsubscript{214}\textsuperscript{9}. These findings highlight the need to determine the Sr redistribution within LSCO heterostructure films, which can provide new insights into developing catalysts with enhanced activity and stability.

However, to date there have been limited methods for obtaining the atomic-scale compositional and structural information needed to properly characterize the LSCO\textsubscript{214}/LSCO\textsubscript{113} interface. XPS\textsuperscript{18-20} and chemical etching\textsuperscript{21} have been used to great effect for studying relative
changes in Sr content before and after annealing, with high surface sensitivity. Unfortunately, these techniques lack the structural information for differentiating Sr in the LSCO$_{113}$ and LSCO$_{214}$ phases and the atomic-level of detail necessary to properly identify spatial proximity to the interface.

Recently, we have demonstrated that Coherent Brag Rod Analysis (COBRA) of LSCO$_{113}$ thin films can provide unprecedented chemical and structural details relevant to high temperature oxygen electrocatalysis.$^{22}$ COBRA is a powerful tool for providing sub-Å resolution structural information of systems composed of atoms that are well-registered to a crystal lattice, and has been successfully applied in epitaxial thin film and quantum dot systems.$^{23-25}$ The method utilizes the measured X-ray diffraction intensities along crystal truncation rods to determine the three-dimensional (3D) electron density (EDY) of a thin film structure. Employing the energy-modulated differential COBRA, which provides elemental information through the energy dependence of atomic scattering cross-sections, further allows for the determination of atomic concentrations of individual crystallographic sites. Differential COBRA has also been successfully applied to studying thin film$^{26}$ and quantum dot$^{27}$ systems.

In this Letter, we use the COBRA method to study the atomic structure and layer-by-layer strontium distribution in ~6 nm thick LSCO$_{214}$-LSCO$_{113}$ heterostructure thin films. Supported by *ab initio* calculations, we demonstrate that anomalous Sr segregation to the interface has a strong thermodynamic driving force and is present in as-deposited films. The COBRA results also reveal polar distortion of the LSCO$_{113}$ unit cell and significant A-site cationic ordering in the LSCO$_{214}$ phase, details that have not been previously considered and may contribute in part to the enhanced catalytic activity of the thin films.
A polished SrTiO$_3$(001) (10 × 10 × 1 mm$^3$, CrysTec) single crystal substrate was cleaned, acid-etched, and then O$_2$ annealed to obtain atomically flat surfaces. An epitaxial thin film of LSCO$_{113}$ on SrTiO$_3$ (STO) was prepared by pulsed laser deposition (PLD) at ~550 °C under 50 mTorr O$_2$ for 360 pulses (~2 nm). Subsequently, 450 pulses of LSCO$_{214}$ (~ 2.5 nm) were deposited on LSCO$_{113}$ to form heterostructured LSCO$_{214/113}$. To study the films under the intermediate temperature (400 °C ~ 600 °C) of the oxygen electrocatalysis condition, the LSCO film was annealed in a vacuum tube furnace (MTI GSL-1700X-KS60) at 550 °C for 1 hour in 450 Torr pure O$_2$ and quenched down to room temperature as the “frozen” working status.

In the as-deposited LSCO film, terrace steps from the STO substrate surface were still visible from atomic force microscopy (AFM), indicating conformal growth (Figure S1, Supporting Information). Interestingly, there are two distinct features on the surface; films close to terrace edges are ~0.8 nm higher than the rest part on the same terraces. This observation suggests that the LSCO$_{214}$ grows by full LSCO$_{214}$ unit cells (rather than by perovskite-like and rock-salt-like building blocks), and nucleation is favored at the top of a terrace step (indicating a large Ehrlich-Schwoebel barrier). This growth mode yields a less uniform surface, and therefore poorly defined reflection high-energy electron diffraction (RHEED) oscillations during film growth (Figure S2, Supporting Information). Upon annealing to 550 °C, the surface morphology changed significantly. The AFM image (Figure S1b, Supporting Information) shows the formation of large particles (~150 nm in diameter and ~ 7 nm in height) on top of a base film, which is composed of small particles ~20 nm in diameter.

Representative experimental and COBRA-calculated diffraction intensities for the as-deposited and annealed LSCO films are in good agreement, where the diffraction intensities along the (11L) Bragg rods are shown as an example in Figure 1. Figure 2 shows EDYs along (a)
the (0,0,Z) line that passes through (La,Sr) atoms in LSCO$_{113}$ and (La,Sr)/Co/O$_{i}$ in LSCO$_{214}$, and (b) the (0.5,0.5,Z) line that passes through Co/Ti/O$_{i}$ atoms in LSCO$_{113}$ and (La,Sr)/Co/O$_{i}$ in LSCO$_{214}$. It should be noted that the stacking sequence for atoms along (0,0,Z) is A - A - A for perovskite and A - A - O - B - O … for RP, while along (0.5,0.5,Z) the sequence is O - B - O - B for perovskite and O - B - O - A - A for RP. All atoms and their positions can be clearly identified in the EDY plot, including oxygen, except those at the very surface of the film. The interface of LSCO$_{214}$-on-LSCO$_{113}$ can also be clearly identified, and the atomic structures are consistent with the previous STEM observation$^{13}$. Only one EDY peak at ~37 Å along the (0,0,Z) line (red star in Figure 2a) cannot be assigned unambiguously to either Co or La.

The small EDY fluctuations between peaks shown in Figure 2 provide a measure of the EDY uncertainty$^{28-29}$, which is generally smaller than the oxygen EDY. The EDY along the (0,0,Z) line going through the La/Sr atoms (Figure 2a) is larger in the LSCO$_{113}$ film region than in STO, as expected from the larger number of electrons in La relative to Sr. The EDY in the LSCO$_{214}$ region is smaller compared to the LSCO$_{113}$ region, indicating these films are partially covered and/or partially coherent films, which is consistent with the growth mode proposed previously from the AFM images and RHEED oscillations (Figure S1 and S2, Supporting Information).

The as-deposited and annealed diffraction intensities were found to be similar (Figure 1) and the differences between the as-deposited and annealed EDYs were found to be on the order of the experimental uncertainty (Figure S3, Supporting Information). Significant changes in the surface morphology upon annealing were nevertheless observed by AFM (Figure S1, Supporting Information). We interpret this to indicate that particulates and outgrowths are present at the
surface (without coherence to the substrate and therefore not detected by COBRA), and these features indeed change upon annealing, without effect on the majority of the material. It is proposed that surface Sr segregation rather than surface morphologies alone may play an important role in the surface oxygen exchange kinetics at elevated temperatures but further studies are needed to test this hypothesis.

The atomic positions in the Z direction were determined by fitting Gaussians to the EDY peaks in Figure 2. Using an ideal STO crystal frame of reference, extended throughout the entirety of the film, we plotted out the substrate relative displacement (SRD) profile for each element in LSCO$_{113}$ region (Figure S4, Supporting Information). Increasing polarization of the LSCO$_{113}$ unit cell was observed, with the octahedra displaced relative to the (La,Sr) ions. This polarization is identical in direction to distortions in LSCO$_{113}$ films observed recently$^{22}$, however in that work we did not observe the displacement of Co or equatorial oxygen ions. The precise physical origin is beyond the scope of this work, but merits further investigation as a potential contributor to the enhanced catalytic activity of the LSCO$_{214}$-on-LSCO$_{113}$ system.

Oxygen at the LSCO$_{214}$/LSCO$_{113}$ interface behaved differently from oxygen within the LSCO$_{113}$ or LSCO$_{214}$ film, which can be clearly visualized from the 2-dimensional folded unit cell through a number of in-plane EDYs at different depths of the film (Figure S5, Supporting Information). In these plane-cuts, the positions of oxygen atoms are well-defined for the Ti-O$_{\|}$ plane of the substrate, Co-O$_{\|}$ plane of the LSCO$_{113}$ film, and La(Sr)-O$_{\perp}$ plane of the LSCO$_{214}$ film. However, near the LSCO$_{113}$/LSCO$_{214}$ interface, the oxygen EDY is smeared in both the Co-O$_{\|}$ plane and La(Sr)-O$_{\perp}$ planes (Figure S5, Supporting Information). This observation indicates a wider distribution of in-plane positions for oxygen atoms at the interface, which can result from the displacement of oxygen atoms from the centrosymmetric crystallographic sites and/or
decrease in site occupancy. Similar behavior was observed previously at the interface of LSCO$_{113}$ films and surface SrCoO$_x$ particles. The poor registry of oxygen atoms with the substrate-defined lattice indicates the presence of oxygen vacancies and/or increased oxygen mobility at the LSCO$_{214}$-on-LSCO$_{113}$ interface.

Experimental differential COBRA data and fits of the as-deposited LSCO film are in good agreement (Figure 3), from which the Sr concentration depth profile, along the corresponding thin-film structure based from ordinary COBRA, was obtained, as shown in Figure 4. The LSCO film (0—26 Å) and the topmost few layers in the STO are almost completely depleted of Sr and partially replaced by La, suggesting a La$_{1-x}$CoO$_3$/La$_{1-x}$TiO$_3$-like film chemistry at the LSCO$_{113}$/STO interface. This Sr deficiency at the film/substrate interface was also found in our previous study of LSCO$_{113}$/STO, which we attributed to the oxidizing nature of the STO substrate during the film growth. Such an interface can introduce a dipole moment that points toward the film/substrate interface, which may induce the aforementioned polarization of the LSCO$_{113}$ unit cell. More significantly, Sr was found to strongly segregate near the LSCO$_{214}$/LSCO$_{113}$ interface and in the first 2-3 layers of LSCO$_{214}$ from the surface, with a mean Sr occupancy of ~1 in LSCO$_{113}$ and ~1 in LSCO$_{214}$. As the error of Sr occupancy in each layer is approximately ±10%, the average Sr occupancy of the entire film remains consistent with the nominal Sr concentration: 0.2 in La$_{1-x}$Sr$_x$CoO$_{3-δ}$ and 0.5 in (La$_{1-y}$Sr$_y$)$_2$CoO$_{4±δ}$. This finding provides the first experimental measurements of absolute Sr atomic occupancy of LSCO$_{214}$ at the atomic scale, which reveals, for the first time, clear evidence of Sr segregation on the LSCO$_{214}$ surface, and support Sr segregation in LSCO$_{214}$ at the LSCO$_{214}$/LSCO$_{113}$ interface predicated from recent DFT studies.
To further understand the physical origin of Sr segregation in the LSCO$_{214}$-on-LSCO$_{113}$ bilayer, *ab initio* calculations were performed to understand the thermodynamic driving force for Sr substitution of La in the structures of LSCO$_{214}$ and LSCO$_{113}$. The Sr-for-La-substitution ($\text{Sr}_\text{La}$) energies for the film away from interfaces were first approximated using those found in bulk LSCO$_{113}$ and bulk LSCO$_{214}$ (dashed lines, Figure 4), which was referenced to that in LSCO$_{113}$. The substitution energy for each atomic layer near the LSCO$_{214}$/LSCO$_{113}$ interface and in LSCO$_{214}$ was then calculated (circles, Figure 4) and compared to that in LSCO$_{113}$. $\text{Sr}_\text{La}$ substitution was found thermodynamically more stable at the LSCO$_{113}$/LSCO$_{214}$ interface (up to ~ -0.8 eV/Sr), which was in agreement with our previous work$^{17}$. Moreover, the thermodynamic driving force for Sr segregation near the LSCO$_{214}$ surface was even greater than to the LSCO$_{113}$/LSCO$_{214}$ interface, with values up to ~ -1.5 eV/Sr compared to LSCO$_{113}$. This result is consistent with the strong Sr segregation in the first 2-3 layers from the LSCO$_{214}$ surface obtained from differential COBRA measurements. It should be mentioned that such segregation was present after PLD growth and also after subsequent annealing in air and no significant changes was found in the Sr distribution in the film after the annealing (Figure S6, Supporting Information). This result supports that the segregation is an equilibrium phenomenon, consistent with the DFT predicted segregation tendencies.

Differential COBRA data of both as-deposited and annealed LSCO$_{214}$-on-LSCO$_{113}$ films further revealed the presence of A-site cationic ordering in the LSCO$_{214}$ film. The alternating Sr-rich and Sr-depleted layers in LSCO$_{214}$ (Figure 4 and Figure S6) suggest that La and Sr may order in the films. Preliminary DFT results showed that there was weak thermodynamic driving force for cation ordering in LSCO$_{214}$, which can be further enhanced by strains (Figures S7 and S8) and oxygen Frenkel pair defects (Figure S9). Further studies are needed to allow the
quantitative prediction of the chemical compositions of A-site ordering by performing full LSCO$_{214}$/LSCO$_{113}$ heterointerface modeling as we have only sampled a small fraction of possible chemical configurations in this work (details can be provided in the Supplementary Information).

The Sr segregation at the LSCO$_{214}$-on-LSCO$_{113}$ revealed by the COBRA measurements provides fundamental insights that can explain the enhanced surface oxygen exchange kinetics reported previously$^{13}$. Sr segregation (Sr occupancy on the A site of $\sim$1) in the perovskite structure at the LSCO$_{214}$/LSCO$_{113}$ interface can lift the oxygen 2$p$ band center relative to the Fermi level$^{30-31}$ shown by DFT studies, which is correlated with increasing surface oxygen kinetics$^{30}$. In addition, such Sr segregation can promote oxygen ion transport kinetics as higher Sr concentrations in bulk LSCO$_{113}$ increases the oxygen vacancy concentration due to the charge imbalance from the substitution of Sr$^{2+}$ for La$^{3+}$ in the perovskite structure$^{17-18}$, which is supported by the weak EDY of oxygen ions in the LSCO$_{214}$/LSCO$_{113}$ interface in Figure 2 (indicative of a local increase in the oxygen vacancy concentration and oxygen ion mobility).

Since LSCO$_{214}$ only partially covers LSCO$_{113}$, the Sr occupancy equal to $\sim$1 in the LSCO$_{214}$/LSCO$_{113}$ interface indicates the surface layer of the LSCO$_{113}$ base film contains fully occupied Sr at the A-sites while the previously reported LSCO$_{113}$ base film (without LSCO$_{214}$) has a surface layer at lower Sr occupancy ($\sim$0.6)$^{22}$. Considering the correlation between the computed O 2$p$ band center (relative to the Fermi level) and the oxygen surface exchange kinetics for perovskites$^{30}$, here we show that the O 2$p$ band center vs. the Fermi level of LSCO$_{113}$ interface layer is lifted upwards with increasing Sr occupancy (Figure 5). In addition, although the dominant oxygen defects in LSCO$_{214}$ can be oxygen vacancies or oxygen interstitials (which dominates is dependent on the Sr concentration$^{33}$, oxygen partial pressure, and temperature) it is proposed that oxygen vacancies are the dominant anionic defect for Sr-segregated LSCO$_{214}$-on-
LSCO$_{113}$ surface under SOFC conditions based on previous findings of LSCO$_{214}$ defect concentrations. Specifically, LSCO$_{214}$ has been found to have understochiometry $\sim$ 0.1 for Sr occupancies greater than 1.5 in air at $704 \, ^{\circ}\text{C}^{34}$. Figure 5 shows the surface exchange activity as a function of the bulk O 2p band center for the LSCO$_{214}$ and select other materials, and it is seen that the fully Sr occupied top surface layer of the LSCO$_{214}$ islands on the LSCO$_{113}$ film also contains a higher O 2p band center than the surface layer of the particles on the LSCO$_{113}$ film, which could lead to higher activities. At the Sr occupancy of $\sim$1 both near the LSCO$_{214}$/LSCO$_{113}$ interface and LSCO$_{214}$ surface as detected by differential COBRA, the position of the computed O 2p band center relative to the Fermi level becomes comparable to the most active perovskites (i.e. Ba$_{1-x}$Sr$_x$Co$_{1-x}$Fe$_y$O$_{3-d}$, BSCF) for surface oxygen exchange kinetics$^{30}$. Therefore, the unique Sr occupancy changes within the LSCO$_{214}$-on-LSCO$_{113}$ heterostructure might be responsible for the enhanced surface exchange kinetics relative to LSCO$_{113}$. Caution should be given to the proposed correlation between the atomic structure information of films grown STO obtained from COBRA and surface exchange kinetics obtained from films grown on YSZ as the atomic positions and Sr segregation in LSCO$_{113}$ and LSCO$_{214}$ may vary depending on film deposition conditions and substrate$^{22}$. Nevertheless, understanding the driving forces that yield this non-uniform Sr distribution and potentially controlling surface Sr segregation represents a critical next step in designing oxides with high activities and stability for surface exchange kinetics.

In summary, we have investigated the LSCO$_{214}$-on-LSCO$_{113}$ heterostructure using COBRA and ab initio calculations to provide, for the first time, atomic-scale structural and chemical information. Different COBRA analysis reveals significant Sr segregation at the interface of LSCO$_{214}$/LSCO$_{113}$ (within the rocksalt layer shared between LSCO$_{214}$ and LSCO$_{113}$) and near the surface of LSCO$_{214}$. Ab initio calculations show that such pronounced Sr segregation
can be attributed to a reduction in the Sr$_{La}$ substitution energy at the LSCO$_{113}$/LSCO$_{214}$ interface and at the surface of LSCO$_{214}$, which qualitatively agrees with the experimental Sr occupancy profile. The increased Sr content at the LSCO$_{214}$/LSCO$_{113}$ interface is coupled with a smearing of the oxygen EDY, indicative of higher local oxygen vacancy concentration and/or enhanced oxygen mobility. Our findings provide fundamental insights into unique structural and chemical information of oxide surface and interfaces that may be responsible for the enhanced catalytic activities of such oxide heterostructures for oxygen electrocatalysis at elevated temperatures.

EXPERIMENTAL AND THEORETICAL METHODS:

*Atomic Force Microscopy Characterization.* An Asylum Research MFP-3D AFM was used to examine the surface morphology of the LSCO heterostructured film at as-deposited and annealed conditions.

*Coherent Bragg Rod Analysis (COBRA).* The atomic structure and Sr depth profile of the LSCO$_{214}$-on-LSCO$_{113}$ film under as-deposited and annealed conditions were investigated at beamline ID-33 of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). Procedures for measuring the diffraction intensities along the substrate-defined Bragg rods have been described previously$^{22, 24-25}$. Ordinary COBRA measurements were performed using an incident X-ray photon energy of 16.09 keV (just below the Sr absorption edge), while energy differential COBRA were performed by modulating between 16.09 and 16.11 keV (just above the Sr absorption edge). COBRA uses the measured diffraction intensities and the fact that the complex structure factors (CSFs) vary continuously along the substrate-defined Bragg rods to
determine the diffraction phases and the CSFs. The CSFs are then Fourier transformed into real space to obtain the three-dimensional EDY of the film and substrate with sub-Angstrom resolution. Energy differential COBRA provides elemental sensitivity through the energy-dependence of the Sr atomic scattering factors above and below the absorption edge. Using the structural information directly obtained from ordinary COBRA, then varying the Sr concentration (i.e. occupancy of Sr) in each La/Sr layer to fit the differential intensity from the energy-modulated measurements, a depth profile of the Sr distribution can be determined.

*Ab-initio calculations.* Spin-polarized Density Functional Theory (DFT) calculations were performed with the Vienna *Ab-initio* Simulation Package\textsuperscript{35-36} using the Projector-Augmented plane-Wave method\textsuperscript{37} with a cutoff energy of 450 eV. Exchange-correlation was treated in the Perdew-Wang-91\textsuperscript{38} Generalized Gradient Approximation (GGA) using the soft O\_s oxygen pseudopotential (which includes 2s\(^2\) 2p\(^4\) electronic configuration). The GGA+U calculations\textsuperscript{39} were performed with the simplified spherically averaged approach\textsuperscript{40}, where the \(U_{\text{eff}}\) (\(U_{\text{eff}} = \text{Coulomb} \ U - \text{exchange} \ J\)) is applied to Co \(d\) electrons (\(U_{\text{eff}} = 3.3\) eV). All calculations were performed in the ground state ferromagnetic arrangement in order to use a consistent and tractable set of magnetic structures. While elevated temperatures used during synthesis and electrochemical testing in this study is expected to be in a paramagnetic state, such disordered moments are significantly more difficult to model and we believe that the trends and conclusions identified here would not be altered by using random spin arrangements. Multiple previous studies on LSC and related materials, e.g., LaMnO\(_3\), have obtained good agreement with experimental data at high temperatures using ferromagnetic arrangements.\textsuperscript{1,30,41}

Sr substitution (i.e. Sr replaces La) energy calculations of bulk LSCO\(_{113}\), LSCO\(_{214}\), LSCO\(_{113}\)-LSCO\(_{214}\) heterointerfaces, and LSCO\(_{214}\) surfaces were performed as follows. The
LSCO$_{113}$-LSCO$_{214}$ heterointerface was simulated with a fully periodic 176-atom supercell ($2a_{113} \times 2a_{113}$ supercell in the $x$-$y$ plane ($a_{113}$=3.85 Å) with 12 layers of LSCO$_{113}$ and 6 layers of LSCO$_{214}$ along $z$ where $c_{113}$=3.83 Å). The in-plane lattice parameter for the interface calculation was fixed to that of LSCO$_{113}$ ($a_{113}$). Calculations of LSCO$_{214}$ (001) free surfaces were performed using a symmetric slab with 72 atoms (the primitive LSCO$_{214}$ cell has 14 atoms) with $2a_{214} \times 2a_{214}$ in the $x$-$y$ direction and both surfaces terminating with rocksalt AO-AO layers in the $z$-direction. Bottom AO-AO layers were fixed to the bulk and all other layers were internally relaxed. The bulk LSCO$_{214}$ structure was simulated with $2a_{214} \times 2a_{214} \times 2c_{214}$ supercell, and the bulk LSCO$_{113}$ was simulated with a 4 layer, or $2a_{113} \times 2a_{113} \times 2a_{113}$ supercell. The LSCO$_{113}$-LSCO$_{214}$ heterointerface structural model were reported previously\textsuperscript{17} and the simulated bulk LSCO$_{113}$, LSCO$_{214}$, and LSCO$_{214}$ surface slab model are provided in Figure 4 below. Sr substitution energy was calculated by taking the total energy change from the stoichiometric supercell after one La ion is replaced by Sr. More details of the calculation methods in this study can be found in the SI.
Figure 1. A representative example of the dependence of diffraction intensity on the momentum transfer measured on (La$_{0.5}$Sr$_{0.5}$)$_2$CoO$_{4+\delta}$ (LSC$_{214}$) / La$_{0.8}$Sr$_{0.2}$CoO$_{3+\delta}$ (LSC$_{113}$) / SrTiO$_3$(001) for as-deposited and annealed conditions, shown for the (11L) Bragg rod.
Figure 2. The COBRA-determined electron density (EDY) of as-deposited \( \text{LSCO}_{214}/\text{LSCO}_{113}/\text{STO} \) along: (a) the \((0\ 0\ Z)\) line; (b) the \((0.5\ 0.5\ Z)\) line.
Figure 3. Differential COBRA data (black circles) and fit (green lines) for the as-deposited sample.
Figure 4. Top panel: Layer-by-layer Sr concentration vs. depth profile determined from differential COBRA for the as-deposited LSCO thin film. The double arrow on the top-right corner indicates the uncertainty in Sr concentration. The region between two dashed black lines close to $Z = 30$ Å and the dashed line at $Z = 0$ Å represent the $(\text{La}_{1-x}\text{Sr}_x)_2\text{CoO}_4$ and $(\text{La}_{1-x}\text{Sr}_x)_2\text{CoO}_3$ heterointerfaces, respectively. Middle panel: The schematic atomic model of the heterostructured film reflects results obtained by ordinary COBRA. Bottom panel: Ab initio Sr for La substitution energies (relative to that of bulk La$_{0.75}$Sr$_{0.25}$CoO$_3$) of bulk La$_{0.75}$Sr$_{0.25}$CoO$_3$ (dark blue dashed line), the $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ heterointerface (filled circles between $Z= 20$ Å and $Z = 35$ Å), bulk $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ (light blue dashed line), and $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ surface (filled circles at $Z > 52$ Å). The horizontal dashed lines represent data from bulk supercell calculations of the relevant phases and therefore have no influence from the interfaces. The calculated La for Sr substitution...
energy in SrTiO\textsubscript{3} (not shown in the figure) is found to be +2.4 eV relative to that of La\textsubscript{0.75}Sr\textsubscript{0.25}CoO\textsubscript{3}. The schematics in the bottom figure represent the simulated supercells for the bulk La\textsubscript{0.75}Sr\textsubscript{0.25}CoO\textsubscript{3}, (La\textsubscript{0.5}Sr\textsubscript{0.5})\textsubscript{2}CoO\textsubscript{4}/La\textsubscript{0.75}Sr\textsubscript{0.25}CoO\textsubscript{3} heterointerface, and (La\textsubscript{0.5}Sr\textsubscript{0.5})\textsubscript{2}CoO\textsubscript{4} surface.
Figure 5. The figure shows surface exchange coefficients $k^q$ or $k^*$ vs. the calculated O 2$p$ band centers (relative to the Fermi level) calculated for bulk unit cells. The specific details for each data point are as follows. $k^q$ values are shown for uncoated $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ films ($LSCO_{113}$, red diamonds) and ($La_{0.5}Sr_{0.5})_2CoO_{4+\delta}$ ($LSCO_{214}$, blue squares) covered LSCO$_{113}$ films, both on the yttria-stabilized zirconia (001) single crystals buffered by a gadolinium-doped ceria layer at $T=550$ °C, $P(O_2)=1$ bar$^{13}$. Each of these cases has associated with two separate O 2$p$ band center values corresponding to two possible compositions used in the bulk calculations for each case, which compositions are estimated from COBRA measurements of the most relevant active surface or interface layers. Although the compositions are estimated from surface or interface
compositions, the O 2p band center calculations are done with bulk unit cells. For uncoated LSCO$_{113}$ film$^{22}$ we use a bulk composition of La$_{1-x}$Sr$_x$CoO$_3$ at $x=0.625$ (red filled diamond), as previous COBRA measurements reveal Sr segregation on the LSCO$_{113}$ film surface to $x=0.59$. $^{22}$ For the LSCO$_{214}$-on- LSCO$_{113}$ film we use a bulk composition of La$_{1-x}$Sr$_x$CoO$_3$ at $x=1$ (blue filled squares), as the interface layer of the LSCO$_{214}$-on-LSCO$_{113}$ heterostructure is near $x=1$ as revealed in Figure 4. The possible error in the COBRA measurement for the Sr occupancy (~10%) is represented by the thin horizontal bars. Bulk DFT calculations have been done to estimate the O 2p band centers at the end points of these bars, which represent compositions of $x=0.5$ (left) and $x=0.75$ (right) for the uncoated LSC$_{113}$ film and $x=0.875$ (left) and $x=1.0$ (right) for the LSCO$_{214}$-on-LSCO$_{113}$ film. A similar assessment for $k^*$s of the uncoated LSCO$_{113}$ and LSCO$_{214}$-on-LSCO$_{113}$ film vs. the calculated O 2p band centers (relative to the Fermi level) of bulk La$_{1-x}$Sr$_x$CoO$_3$ and (La$_{1-y}$Sr$_y$)$_2$CoO$_4$ based on the compositions of the top surface of Sr-segregated particles on the LSCO$_{113}$ film$^{22}$ ($x=0.875$, open red triangle) and the top surface layer of LSCO$_{214}$ islands on the LSCO$_{113}$ of LSCO$_{214}$-on-LSCO$_{113}$ ($y=1.0$, open blue square), respectively. Again, the possible error in the COBRA measurement for the Sr occupancy (10%) represented by the horizontal dashed bars. The endpoints of the bars represent compositions of $x=0.75$ (left) and $x=1.0$ (right) for the uncoated LSC$_{113}$ film and $x=0.875$ (left) and $x=1.0$ (right) for the LSCO$_{214}$-on-LSCO$_{113}$ film. The black circles are the reported experimental $k^*$ of bulk LSCO$_{113}$$^{42}$ and Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (BSCF)$^{43}$ at $p$(O$_2$) = 1.0 bar at T = 600 °C vs. the calculated bulk O 2p band centers$^{30}$. The dashed circle is the estimated $k^*_{eq}$ of bulk LSCO$_{214}$ at $y=0.5$ at T=600 °C and $p$(O$_2$) = 1.0 bar$^{17}$ (based on the reported interfacial conductivity of the porous LSCO$_{214}$ electrode$^{44}$) vs. the calculated bulk (La$_{0.5}$Sr$_{0.5}$)$_2$CoO$_4$ O 2p band center. The structures used for calculating the O 2p band centers of LSCO$_{113}$ and LSCO$_{214}$ are provided in Figure S10.
ASSOCIATED CONTENT

**Supporting Information.** Details about sample preparation, ordinary and differential COBRA analysis, error analysis, and octahedral distortion and ab-initio calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

This work was supported in part by DOE (SISGR DESC0002633) and King Abdullah University of Science and Technology. The authors like to thank the King Fahd University of Petroleum and Minerals in Dharam, Saudi Arabia, for funding the research reported in this paper through the Center for Clean Water and Clean Energy at MIT and KFUPM. This research was supported by the Israel Science Foundation under grant No. 1005/11. Support for Y.-L. Lee provided by Department of Energy (DOE), National Energy Technology Laboratory (NETL), Solid State Energy Conversion Alliance (SECA) Core Technology Program, Funding Opportunity Number DEFE0009435 and for M. Gadre by U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award number DESC0001284. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. Authors thank the support from the beamline
scientists including Zhan Zhang, Christian M. Schlepuetz and Lynette Jirik at ID-33 of APS. Samples were synthesized at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. DOE under Contract No. CNMS2012-284.
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Supporting Information

Anomalous Interface/Surface Strontium Segregation in \((\text{La}_{1-y} \text{Sr}_y)_{2}\text{CoO}_{4+\delta}/\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}\) Heterostructured Thin Films

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Supplementary Methods

Pulsed Laser Deposition (PLD) Target Synthesis and Growth.

La$_{0.8}$Sr$_{0.2}$CoO$_{3-\delta}$ (LSCO$_{113}$) powders were synthesized by a solid-state reaction using a stoichiometric mixture of La$_2$O$_3$, SrCO$_3$, and Co$_3$O$_4$ (Alfa Aesar, USA) 1,000 °C in air for 12 hours. (La$_{0.5}$Sr$_{0.5}$)$_2$CoO$_{4\delta}$ (LSCO$_{214}$) was prepared by the Pechini method using La(NO$_3$)$_3$$\cdot$6H$_2$O, Sr(NO$_3$)$_2$$\cdot$6H$_2$O, and Co(NO$_3$)$_2$$\cdot$6H$_2$O. The precursors were dissolved in deionized water with citric acid, and ethylene glycol (Sigma-Aldrich, USA) mixture. After esterification at 100 °C, the resin was charred at 400 °C and then calcinated at 1000 °C in air for 12 hours. PLD targets of LSCO$_{113}$ and LSCO$_{214}$ with a diameter of 25 mm were fabricated by uniaxial pressing at 50 MPa and sintering at 1,350 °C in air for 20 hours.

Polished SrTiO$_3$(001) (STO, 10 × 10 × 1 mm$^3$, CrysTec) single crystal substrates were acid-etched in buffered HF solution for 30 s and subsequently annealed in oxygen at 1050 °C for 2 hours to obtain atomically flat surfaces. Heterostructured thin films of LSCO on STO were prepared first by pulsed laser deposition (PLD) of 360 pulses of LSCO$_{113}$ (~2 nm) at 557 °C under 50 mTorr O$_2$, followed by 300 pulses of LSCO$_{214}$ (~2.5 nm) at the same condition. PLD
was done under the following conditions: KrF excimer laser ($\lambda = 248$ nm), 10 Hz pulse rate, $\sim 50$ mJ pulse energy, and the growth rate $\sim 70$ pulses per LSCO$_{113}$ unit cell.

**Density Functional Theory Calculations.**

Spin polarized Density Functional Theory (DFT) calculations were preformed with the Vienna *Ab-initio* Simulation Package$^{1,2}$ using the Projector-Augmented plane-Wave method$^3$. Exchange-correlation was treated in the Perdew-Wang-91$^4$ Generalized Gradient Approximation (GGA). The pseudopotential valence electron configurations for each atom are as follows: La: $5s^25p^65d^6$, Sr$_{sv}$: $4s^24p^6$, Ti$_{pv}$: $3p^63d^4$, Co: $3d^84s^1$ and O$_s$: $2s^22p^4$. The GGA+$U$ calculations$^5$ are performed with the simplified spherically averaged approach$^6$, where the $U_{eff}$ ($U_{eff} = $ Coulomb $U$ - exchange $J$) is applied to Co 3 $d$ electrons ($U_{eff}$(Co) = 3.3 eV)$^7$. All calculations are performed in the ground state ferromagnetic arrangement in order to use a consistent and tractable set of magnetic structures.

Sr-La substitution energy of LSCO$_{214}$-LSCO$_{113}$ heterointerfaces and LSCO$_{214}$ surfaces are performed as follows. The LSCO$_{214}$-LSCO$_{113}$ heterointerface was simulated with a fully periodic 176-atom supercell ($2a_{113} \times 2a_{113}$ supercell in the x-y plane ($a_{113}$=3.85 Å) with 12-layers of La$_{0.75}$Sr$_{0.25}$CoO$_3$ and 6-layers of (La$_{0.5}$Sr$_{0.5}$)$_2$CoO$_4$ along z where $c_{113}$=3.83 Å). The in-plane lattice parameter for the interface calculation was fixed to that of La$_{0.75}$Sr$_{0.25}$CoO$_3$ ($a_{113}$). The bulk LSCO$_{214}$ structure was simulated with $2a_{214} \times 2a_{214} \times 2c_{214}$ supercell, and the bulk LSCO$_{113}$ was simulated with an 8 layer, or $2a_{113} \times 2a_{113} \times 2a_{113}$ supercell. The LSCO$_{214}$-LSCO$_{113}$ heterointerface calculations and structural model were reported previously$^7$ and the simulated LSCO$_{214}$ surface slab model is provided in Figure 4.

Calculations for Sr-La substitution energy at (001)-LaO-terminated LSCO$_{214}$ free surfaces are performed using a symmetric supercell with 72 atoms (the primitive LSCO$_{214}$ cell has 14 atoms) with $2a_{214} \times 2a_{214}$ in the x-y direction and both surfaces terminating with rocksalt AO-AO layers in the z-direction. Bottom AO-AO layers are fixed to the bulk and all other layers are internally relaxed. The reference supercell contains 0.5 Sr in each AO plane parallel to the free surface, with two Sr atoms arranged as second nearest neighbors. The slab used for the surface calculation is shown in Figure 4.

Calculations for Sr-La swapping energy in bulk SrTiO$_3$ were performed using a $2 \times 2 \times 2$ cubic supercell structure of SrTiO$_3$ (using relaxed lattice parameter of 3.93 Å with DFT-GGA)
with $2\times2\times2$ k-point mesh and 500 eV plane-wave energy cut-off. The Sr-La swapping energy for SrTiO$_3$ bulk was taken as the difference in energies of a perfect STO bulk and the supercell with one of the Sr replaced with a La.

Bulk $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ calculations to investigate its Sr ordering tendency are performed using $\sqrt{2} a_{214}\times\sqrt{2} a_{214}\times c_{214}$ supercells (where $a_{214}$ is the in-plane cubic lattice parameter, and $c_{214}$ is oriented along the stacking of (La,Sr)O and CoO$_2$ planes, which we will designate the (001) $z$ direction) with $2\times2\times1$ k-points and 450 eV plane-wave energy cut-off. Six investigated Sr-La arrangements on the A-sites of the simulated $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ supercell along with the $a_{214}$ and $c_{214}$ relaxed from the experimental structural parameters ($a_{214}=3.085$ Å, $c_{214}=12.489$ Å) $^8$ are provided in Figure S7. We note the use of the GGA+U method generally gives rise to overestimated lattice parameters than the experiments$^9$, which is also seen in our results. Three ordered $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ phases with alternating Sr-O and LaO rocksalt layers were calculated, as shown in Figure S7a~c, and the disordered phase treated with the special quasi-random structure approximations $^{10}$ (the first to third nearest neighbor (up to $\sim$ 4 Å) pair correlations equal to 0) for random La-Sr arrangement in the $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$, as shown in Figure S7c and S7d. In addition an ordered phase with each rocksalt layer composition equal to $(\text{La}_{0.5}\text{Sr}_{0.5})\text{O}$ layers is also included as a reference for comparing the relative stability, as shown in Figure S7f. Strained calculations are performed by fixing the in-plane lattice constant $a$ to the relaxed lattice constant of STO (3.93 Å with the GGA-PW91), while the c/a ratio is constrained to 3.2 based on the experimental COBRA information, instead of using relaxed $c_{214}$ parameters among the various investigated configurations under the in-plane epitaxial strain of STO. Figure S8 shows the relative stability of the bulk and strained LSCO$_{214}$ configurations shown in Figure S7, including perfect bulk, bulk containing oxygen-vacancy, and bulk containing oxygen-interstitial. Three configurations of the LSCO$_{214}$ containing oxygen Frenkel pair defects are simulated using the $\sqrt{2} a\times\sqrt{2} a\times2c$ supercells with $2\times2\times1$ kpoints, as illustrated in Figure S9a-S9c, and the calculated relative stabilities are shown in Figure S9d.

The ordering energy required to overcome the configurational entropy for the A-site disorder under the PLD conditions within the $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ structure has to be larger or at least comparable to 100 meV per formula unit (i.e., $2k_B T \ln(1/2)$, where $k_B$ is the Boltzmann constant, $T$ is temperature, and a factor of 2 is to account for the total number of A-site per
formula unit of \((\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4\). We note that if one takes into account the maximum experimental error of Sr concentration in each layer (~±0.1), the layered ordered phase can be stabilized by ~46 meV per formula unit (i.e., \(2k_B T\times[0.1\times\ln(0.1)+0.9\times\ln(0.9)]\)), which reduces the required ordering energy from ~100 meV to ~54 meV per formula unit for the layered ordered phase with partial occupancy 0.9 of Sr or La in each layer. In the discussions and stability results below, the ordered phase is treated as full layered ordering (occupation 1 of Sr or La in each layer) to assess the maximum possible value of the A-site ordering energy, and we note the ordering tendency may be equal to or smaller than the assessed ordering energy results discussed below.

To understand the influence of epitaxial strain on the A-site ordering tendency, both relaxed bulk and strained \((\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4\) calculations are performed to assess the La-Sr ordering tendency. The ordered phase with each rocksalt layer composition equal to \((\text{La}_{0.5}\text{Sr}_{0.5})\text{O}\) layers (Figure S7f) is used as a reference for comparing the relative stability of the layered A-site ordered vs. the disordered phases. The increase in stability with ordered, or ordering tendency, in the relaxed bulk is found to be ~20 meV/FU (FU=formula unit) relative to the most stable SQS and the reference structure (Figure S8a). On the other hand, the strained \((\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4\) shows a significantly enhanced ordering tendency to 40~80 meV/FU, suggesting strain may contribute to the A-site ordering in \((\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4\) (Figure S8a). This ordering tendency is comparable to the disordering entropy, suggesting that some ordering may occur in the strained films. Furthermore, it has previously been shown that A-site ordering can occur in the 0.5 Sr-doped \(\text{LSCO}_{113}\) on an STO substrate at \(T=650\ \text{K}\)\(^{11}\), which ordering was suggested to originate from the interplay between epitaxial strain imposed by STO and coupling to oxygen vacancy content and ordering. We therefore investigated the ordering tendency in the bulk and strained \(\text{LSCO}_{214}\) with anionic defects, including oxygen vacancy (Figure S8b), oxygen interstitial (Figure S8c), and the oxygen vacancy-interstitial Frenkel pair (the calculated three \((\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4\) configurations with the oxygen Frenkel pair defects are shown in Figure S9a, S9b, and S9c), as all these oxygen defects may possibly exist in the \(\text{LSCO}_{214}\)\(^{12}\). With an oxygen interstitial (Figure S8c) or oxygen interstitial-vacancy Frenkel pair (Figure S9d) present in the calculation at a concentration of 0.125 per FU, the change in relative stability between the ordered and the disordered \((\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_{4+\delta}\) can be increased to 100~140 meV/FU for the bulk and the strained film,
while the A-site ordering tendency for the (La$_{0.5}$Sr$_{0.5}$)$_{2}$CoO$_{4-\delta}$ with oxygen vacancy alone shows relatively weaker enhancement. Our results suggest the A-site ordering may be significantly enhanced by coupling to strain and both oxygen interstitials and oxygen Frenkel defect pairs in the LSCO$_{214}$ film. Further work is still needed for quantitative prediction of chemical distribution of LSCO$_{214}$/LSCO$_{113}$ interfaces, as we have only sampled a small fraction of possible configurations, and the A-site cation ordering observed in LSCO$_{214}$ LSCO$_{214}$/LSCO$_{113}$ heterointerfaces could further be altered by the LSCO$_{214}$ being only a few nanometers thick and having extensive regions affected by both interface and free surface energetics.
Figure S1. (a) AFM (1 × 1 μm²) images: (a) as-deposited and (b) annealed 2 unit cells \((\text{La}_{0.5}\text{Sr}_{0.3})_2\text{CoO}_{4±δ}\) on 7 unit cells \(\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3±δ}\) film. The annealing was carried out in a tube furnace at 550 °C for 1 hour in pure \(\text{O}_2\) at 450 Torr. Although the terraces originating from the STO substrate surface (Figure S1) were still visible after film deposition and annealing, particles can be identified after anneal (~150 nm lateral size, ~7 nm height).
Figure S2. RHEED oscillations (intensity of the specular reflection measured as a function time) recorded during growth of (a) LSCO$_{113}$ on STO and (b) LSCO$_{214}$ on LSCO$_{113}$. These oscillations indicate the layer-by-layer growth of LSCO$_{113}$ and then islands or mixed islands and layer-by-layer growth mode for LSCO$_{214}$. 
Figure S3. The electron density (EDY) along two lines shown in the crystal model insets. (a) The EDY along the (0 0 Z) line, (b) the EDY along the (0.5 0.5 Z) line for as-deposited (dark color) and annealed (grey/light color) samples. The topmost four unit cells of the substrate are
included in the structure determination. The dashed line represents the nominal LSCO$_{113}$/STO interface and LSCO$_{214}$/LSCO$_{113}$ interface, respectively.
**Figure S4.** COBRA-determined atomic positions of each type of atoms for (a) as-deposited and (b) annealed samples. The positions are shown as displacements relative to the corresponding atoms in an ideal STO lattice used as a frame of reference.

![COBRA-determined atomic positions](image)

**Figure S5.** Electron density on various planes parallel to the surface of LSCO\textsubscript{214}/LSCO\textsubscript{113} on STO substrate. The upper panel shows the representative electron density of as-deposited LSCO\textsubscript{214}/LSCO\textsubscript{113}/STO with a crystal model inset as the guide (blue and black are curves along...
the (0 0 Z) and (0.5 0.5 Z) lines, respectively). Black arrows indicate the positions of the in-plane cuts. (b) Substrate Ti/O$_{II}$ plane. The lower panel shows the in-plane cuts at different depths.

Figure S6. (a) Layer-by-layer Sr concentration vs. depth profile determined from differential COBRA method for LSCO$_{214}$/LSCO$_{113}$/STO as-deposited (dark blue) and annealed (light blue) sample. The double arrow indicates the error bar. The black dashed lines represent the nominal LSCO$_{113}$/substrate interface and LSCO$_{214}$/LSCO$_{113}$ interface, respectively.
(a) \(a_{214} = 3.84\,\text{Å}; c_{214} = 12.58\,\text{Å}\)

(b) \(a_{214} = 3.82\,\text{Å}; c_{214} = 12.80\,\text{Å}\)

(c) \(a_{214} = 3.81\,\text{Å}; c_{214} = 12.92\,\text{Å}\)

(d) \(a_{214} = 3.84\,\text{Å}; c_{214} = 12.64\,\text{Å}\)

(e) \(a_{214} = 3.83\,\text{Å}; c_{214} = 12.71\,\text{Å}\)

(f) \(a_{214} = 3.82\,\text{Å}; c_{214} = 12.62\,\text{Å}\)
Figure S7. The investigated La (green spheres)/Sr (blue spheres) arrangements from ab initio calculations for the relaxed bulk and strained (La\textsubscript{0.5}Sr\textsubscript{0.5})\textsubscript{2}CoO\textsubscript{4}. For the oxygen defect calculations, oxygen vacancy is placed at the oxygen lattice site (0.75, 0.75, 0.50) and oxygen interstitial is placed at the rocksalt layer interstitial site (0.25, 0.25, 0.25) in the fractional coordinate of the simulated $\sqrt{2}a\times\sqrt{2}a\times c$ supercell. Configurations (a), (b), and (c) represent different arrangement for the full Sr and full La rocksalt layers, configuration (d) and (e) are the special quasi-random structures with the A-site (1st to 3rd nearest pair correlations equal to 0), and configuration (f) represents the structure with half Sr and half La evenly distributed in each rocksalt layer, which is used a reference for comparing the relative stability of the (La\textsubscript{0.5}Sr\textsubscript{0.5})\textsubscript{2}CoO\textsubscript{4}. For the strained (La\textsubscript{0.5}Sr\textsubscript{0.5})\textsubscript{2}CoO\textsubscript{4} calculations, the c/a ratio is constrained to 3.2 based on the experimental COBRA information and $a$ is fixed to the calculated STO lattice constant (3.93 Å with GGA-PW91).
**Figure S8.** The relative stability of the relaxed (blue) and strained (red) bulk $(La_{0.5}Sr_{0.5})_2CoO_4$ configurations in Figure S7, where the configuration in Figure S7f is chosen as the reference and positive (negative) energy indicates less (more) stable. Relaxed bulk $(La_{0.5}Sr_{0.5})_2CoO_4$
calculations are performed with full relaxation. Strained LSCO\textsubscript{214} calculations are performed by fixing the in-plane lattice constant \(a\) to the relaxed lattice constant of STO (3.93 Å with the GGA-PW91), while the \(c/a\) ratio is constrained to 3.2 based on the experimental COBRA information. The disordered phase treated with the special quasi-random structure (SQS) approximations. For the oxygen defect calculations, oxygen vacancy is placed at the oxygen lattice site (0.75, 0.75, 0.50) and oxygen interstitial is placed at the rocksalt layer interstitial site (0.25, 0.25, 0.25) in the fractional coordinate of the simulated \(\sqrt{2} a \times \sqrt{2} a \times c\) supercells shown in Figure S7. We note the energy shown in Figure S8 does not include -0.1 eV per formula unit for the SQS and the reference configurations to account for the A-site configurational entropy (i.e., \(2k_bT \ln(1/2)\), where \(k_b\) is the Boltzmann constant, \(T\) is the PLD temperature \(\sim 550\) C, and a factor of 2 is to account for the total number of A-site per formula unit of \((\text{La}_{0.5}\text{Sr}_{0.5})\text{CoO}_4\), which will further stabilize the A-site disordered phase).
**Figure S9.** The investigated (La$_{0.5}$Sr$_{0.5}$)$_2$CoO$_4$ configurations containing oxygen Frenkel pair defects. The configuration (c) contains the same A-site arrangement as the configuration of...
Figure S7f. An oxygen vacancy is placed at the oxygen site indicated by the arrow, while an oxygen interstitial is placed in the rocksalt layer near the bottom of the supercell and is presented by the red filled circle. Figure S9d shows the relative stability of the three configurations of the relaxed and strained bulk \((\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4\). The strain condition is described in the caption of Figure S7. We note the energy shown in Figure S9 does not include \(-0.1\) eV per formula unit for the SQS and the reference configurations to account for the A-site configurational entropy (i.e., \(2k_b T \ln(1/2)\), where \(k_b\) is the Boltzmann constant, \(T\) is the PLD temperature \(~550\) C, and a factor of 2 is to account for the total number of A-site per formula unit of \((\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4\), which will further stabilize the A-site disordered phase).
**Figure S10.** The bulk supercells used to calculate the O 2p band centers of La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ (LSCO$_{113}$) (a) x=0.5, (b) x=0.625, (c) x=0.75, (d) x=0.875, (e) x=1.0, and (La$_{1-y}$Sr$_y$)$_2$CoO$_{4+\delta}$ (LSCO$_{214}$) (f) y=0.875 (g) y=1.0 for Figure 5 of the main manuscript. The dark blue octahedra, light blue, green and red spheres represent Co centered octahedra, Sr, La, and O ions, respectively.
References


