Supporting Information

Anomalous Interface/Surface Strontium Segregation in (La₁₋ $_{y}$ Sr_y)₂CoO_{4± δ}/La_{1-x}Sr_xCoO_{3- δ} 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- δ} (LSCO₁₁₃) powders were synthesized by a solid-state reaction using a stoichiometric mixture of La₂O₃, SrCO₃, and Co₃O₄ (Alfa Aesar, USA) 1,000°C in air for 12 hours. (La_{0.5}Sr_{0.5})₂CoO_{4± δ} (LSCO₂₁₄) was prepared by the Pechini method using La(NO₃)₃·6H₂O, Sr(NO₃)₂·6H₂O, and Co(NO₃)₂·6H₂O. 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 LSCO₁₁₃ and LSCO₂₁₄ 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 SrTiO₃(001) (STO, $10 \times 10 \times 1 \text{ mm}^3$, 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 LSCO₁₁₃ (~2 nm) at 557 °C under 50 mTorr O₂, followed by 300 pulses of LSCO₂₁₄ (~2.5 nm) at the same condition. PLD was done under the following conditions: KrF excimer laser ($\lambda = 248$ nm), 10 Hz pulse rate, ~50 mJ pulse energy, and the growth rate ~ 70 pulses per LSCO₁₁₃ unit cell.

Density Functional Theory Calculations.

Spin polarized Density Functional Theory (DFT) calculations were preformed with the Vienna *Ab-initio* Simulation Package¹⁻² using the Projector-Augmented plane-Wave method³. Exchange-correlation was treated in the Perdew-Wang-91⁴ Generalized Gradient Approximation (GGA). The pseudopotential valence electron configurations for each atom are as follows: La: $5s^25p^65d^16s^2$, Sr_sv: $4s^24p^65s^2$, Ti_pv: $3p^63d^24s^2$, Co: $3d^84s^1$ and O_s: $2s^22p^4$. The GGA+U calculations⁵ are performed with the simplified spherically averaged approach⁶, 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 LSCO₂₁₄-LSCO₁₁₃ heterointerfaces and LSCO₂₁₄ surfaces are performed as follows. The LSCO₂₁₄-LSCO₁₁₃ heterointerface was simulated with a fully periodic

176-atom supercell $(2a_{113} \times 2a_{113}$ supercell in the x-y plane $(a_{113}=3.85 \text{ Å})$ with 12-layers of La_{0.75}Sr_{0.25}CoO₃ and 6-layers of $(La_{0.5}Sr_{0.5})_2$ CoO₄ 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}CoO₃ (a_{113}) . The bulk LSCO₂₁₄ structure was simulated with $2a_{214} \times 2a_{214} \times 2c_{214}$ supercell, and the bulk LSCO₁₁₃ was simulated with an 8 layer, or $2a_{113} \times 2a_{113} \times 2a_{113}$ supercell. The LSCO₂₁₄-LSCO₁₁₃ heterointerface calculations and structural model were reported previously⁷ and the simulated LSCO₂₁₄ surface slab model is provided in Figure 4.

Calculations for Sr-La substitution energy at (001)-LaO-terminated LSCO₂₁₄ free surfaces are performed using a symmetric supercell with 72 atoms (the primitive LSCO₂₁₄ 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 SrTiO₃ were performed using a $2\times2\times2$ cubic supercell structure of SrTiO₃ (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 SrTiO₃ 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 (La_{0.5}Sr_{0.5})₂CoO₄ 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 CoO₂ planes, which we will designate the (001) *z* direction) with 2×2×1 k-points and 450 eV plane-wave energy cut-off. Six investigated Sr-La arrangements on the A-sites of the simulated (La_{0.5}Sr_{0.5})₂CoO₄ 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 experiments⁹, which is also seen in our results . Three ordered (La_{0.5}Sr_{0.5})₂CoO₄ 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 approximations¹⁰ (the first to third nearest neighbor (up to ~ 4 Å) pair correlations equal to 0) for random La-Sr arrangement in the (La_{0.5}Sr_{0.5})₂CoO₄, as shown in Figure S7c and S7d. In addition an ordered phase with each rocksalt layer composition equal to $(La_{0.5}Sr_{0.5})O$ 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 LSCO₂₁₄ configurations shown in Figure S7, including perfect bulk, bulk containing oxygen-vacancy, and bulk containing oxygen-interstitial. Three configurations of the LSCO₂₁₄ containing oxygen Frenkel pair defects are simulated using the $\sqrt{2} a \times \sqrt{2} a \times 2c$ supercells with $2 \times 2 \times 1$ 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 $(La_{0.5}Sr_{0.5})_2CoO_4$ structure has to be larger or at least comparable to 100 meV per formula unit (i.e., $2k_bT\bullet ln(1/2)$, 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 $(La_{0.5}Sr_{0.5})_2CoO_4$). We note that if one takes into account the maximum experimental error of Sr concentration in each layer ($\sim \pm 0.1$), the layered ordered phase can be stabilized by ~ 46 meV per formula unit ((i.e., $2k_bT\bullet [0.1\bullet ln(0.1)\pm 0.9\bullet ln(0.9)$), 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 $(La_{0.5}Sr_{0.5})_2CoO_4$ calculations are performed to assess the La-Sr ordering tendency. The ordered phase with each rocksalt layer composition equal to $(La_{0.5}Sr_{0.5})O$ 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 $(La_{0.5}Sr_{0.5})_2CoO_4$ shows a significantly enhanced ordering tendency to 40~80 meV/FU, suggesting strain may contribute to the A-site ordering in (La_{0.5}Sr_{0.5})₂CoO₄ (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 LSCO₁₁₃ on an STO substrate at T=650 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 LSCO₂₁₄ with anionic defects, including oxygen vacancy (Figure S8b), oxygen interstitial (Figure S8c), and the oxygen vacancy-interstitial Frenkel pair (the calculated three $(La_0 Sr_0 Sr_0)_2CoO_4$ 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 $LSCO_{214}^{12}$. 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 $(La_{0.5}Sr_{0.5})_2CoO_{4\pm\delta}$ can be increased to 100~140 meV/FU for the bulk and the strained film, while the A-site ordering tendency for the $(La_{0.5}Sr_{0.5})_2CoO_{4-\delta}$ 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 LSCO₂₁₄ film. Further work is still needed for quantitative prediction of chemical distribution of LSCO₂₁₄/LSCO₁₁₃ interfaces, as we have only sampled a small fraction of possible configurations, and the A-site cation ordering observed in LSCO₂₁₄ LSCO₂₁₄/LSCO₁₁₃ heterointerfaces could further be altered by the LSCO₂₁₄ being only a few nanomateres thick and having extensive regions affected by both interface and free surface energetics.



Figure S1. (a) AFM $(1 \times 1 \ \mu m^2)$ images: (a) as-deposited and (b) annealed 2 unit cells $(La_{0.5}Sr_{0.5})_2CoO_{4\pm\delta}$ on 7 unit cells $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ film. The annealing was carried out in a tube furnace at 550 °C for 1 hour in pure O₂ 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 LSCO₁₁₃/STO interface and LSCO₂₁₄/LSCO₁₁₃ 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.



Figure S5. Electron density on various planes parallel to the surface of $LSCO_{214}/LSCO_{113}$ on STO substrate. The upper panel shows the representative electron density of as-deposited $LSCO_{214}/LSCO_{113}/STO$ 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.



Figure S7. The investigated La (green spheres)/Sr (blue spheres) arrangements from *ab initio* calculations for the relaxed bulk and strained $(La_{0.5}Sr_{0.5})_2CoO_4$. 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 $(La_{0.5}Sr_{0.5})_2CoO_4$. For the strained $(La_{0.5}Sr_{0.5})_2CoO_4$ 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).

(a)



Figure S8. The relative stability of the relaxed (blue) and strained (red) bulk $(La_{0.5}Sr_{0.5})_2CoO_{4\pm\delta}$ 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 $(La_{0.5}Sr_{0.5})_2CoO_{4\pm\delta}$ calculations are performed with full relaxation. Strained LSCO₂₁₄ 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 interstiatial 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., $2k_bT \cdot \ln(1/2)$, 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 $(La_{0.5}Sr_{0.5})_2CoO_4$), which will further stabilize the A-site disordered phase).



Figure S9. The investigated $(La_{0.5}Sr_{0.5})_2CoO_4$ 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 suprecell and is presented

by the red filled circle. Figure S9d shows the relative stability of the three configurations of the relaxed and strained bulk $(La_{0.5}Sr_{0.5})_2CoO_4$. 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., $2k_bT\bullet ln(1/2)$, 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 $(La_{0.5}Sr_{0.5})_2CoO_4$), which will further stabilize the A-site disordered phase).





(d)





(e)







(g)

Figure S10. The bulk supercells used to calculate the O 2p band centers of $La_{1-x}Sr_xCoO_{3-\delta}$ (LSCO₁₁₃) (a) x=0.5, (b) x=0.625, (c) x=0.75, (d) x=0.875, (e) x=1.0, and $(La_{1-y}Sr_y)_2CoO_{4\pm\delta}$ (LSCO₂₁₄) (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.

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