

Supporting Information
***In Situ* Studies of Temperature-Dependent Surface Structure and**
Chemistry of Single-Crystalline (001)-Oriented $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$
Perovskite Thin Films

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Supplementary Methods

Pulsed Laser Deposition (PLD) Target Synthesis. $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ (LSC_{113}) powders were synthesized by a solid-state reaction using a stoichiometric mixture of La_2O_3 , SrCO_3 , and Co_3O_4 (Alfa Aesar, USA) $1,000^\circ\text{C}$ in air for 12 hours. $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_{4+\delta}$ (LSC_{214}) was prepared by the Pechini method using $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. 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. $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_2$ (GDC) was prepared in a similar fashion from $\text{Gd}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$. PLD targets of LSC_{113} , LSC_{214} , GDC with a diameter of 25 mm were fabricated by uniaxial pressing at 50 MPa and sintering at $1,350^\circ\text{C}$ in air for 20 hours.

In the following discussion, we referred the samples with 15,000 of LSC_{113} as 90 nm LSC_{113} films, and $\text{LSC}_{113/214}$ samples with a 400-pulse LSC_{214} decoration as 90 nm $\text{LSC}_{113/214}$. 90 nm LSC_{113} and 90 nm $\text{LSC}_{113/214}$ were used for XRD, EIS, XRR, and Auger experiments. 90 nm LSC_{113} , and 150-pulse LSC_{214} -decorated LSC_{113} films were used for APXPS experiments.

Microelectrodes Fabrication. Positive photoresist (MicroChem, USA) was applied on the LSC surface and patterned using a mask aligner (Karl Süss, Germany, $\lambda = 365$ nm). The photoresist was developed (MicroChem, USA) and the metal oxide thin films were etched in hydrochloric acid (HCl) to remove LSC film excess and create the circular microelectrodes. Before electrochemical testing, microelectrode geometry and morphology were examined by optical microscopy (Carl Zeiss, Germany) and atomic-force microscopy (AFM). AFM measurements after acid etching of the LSC film revealed thickness of ~ 94 nm for both the LSC_{113} and $\text{LSC}_{113/214}$ films.

Electrochemical Characterization. Electrochemical impedance spectroscopy (EIS) was collected using a microprobe station setup (Karl Süss, Germany) connected to a frequency response analyzer (Solatron 1260, USA) and a dielectric interface (Solartron 1296, USA). Pt-coated tungsten carbide probes were utilized to contact the LSC electrodes and the porous Pt counter electrode. Sample testing configuration is shown in our previous studies^{1,2}. Temperature was controlled at 550°C with a heating stage (Linkam TS1500, UK) and measured with a second thermocouple on the sample surface. EIS data were collected between 1 MHz to 1 mHz using a voltage amplitude of 10 mV

under Ar/O₂ mixtures in the range from $p(\text{O}_2)$ of 10^{-3} to 1 atm. *ZView* software (Scribner Associates, USA) was used to construct the equivalent circuit and perform complex least-square-fitting to extract the fitting parameters to describe the system. The electrical surface exchange coefficient (k^q) was determined using the Eq. S1³

$$k^q = RT / \left(4F^2 R_{LF} A_{\text{electrode}} c_o \right), \quad (\text{S1})$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature, F is Faraday's constant ($96,500 \text{ C mol}^{-1}$), R_{LF} is the low frequency real resistance, $A_{\text{electrode}}$ is the area of the microelectrode, and c_o is the lattice oxygen concentration in LSC ($c_o = (3-\delta)/V_m$, V_m is the molar volume of LSC at room temperature). Bulk LSC molar volume of $33.66 \text{ cm}^3 \text{ mol}^{-1}$ was used in the calculation of k^q under all experimental conditions, regardless of chemical expansion effects of oxygen nonstoichiometry, δ , or thermal expansion, as the influence of larger molar volumes on k^q and is less than 3%. **Figure S3** shows the $p(\text{O}_2)$ dependence of k^q .

In situ X-ray Diffraction (XRD) Characterization. The *in situ* XRD were performed on 90 nm LSC₁₁₃ and 90 nm LSC_{113/214} at room temperature (RT), 220 °C, 350 °C, and 400 °C (only for 90 nm LSC₁₁₃) in ambient air. Results of LSC₁₁₃ lattice parameters and strains are shown in **Table S1** and **S2**.

In situ X-ray Reflectivity Modeling and Characterization. The measured X-ray reflectivity depends on the variation in the electron density (EDY) profile, $\rho(z)$, perpendicular to the interface.^{4,5} The X-ray electron density of a material can be calculated using Eq. S2,

$$\rho_e = \frac{b_e \rho_m N_A}{M} \sum_i c_i Z_i, \quad (\text{S2})$$

where $b_e = 2.81 \times 10^{-5} \text{ \AA}$ is the scattering length of an electron, ρ_m is the mass density of the material, N_A is Avogadro's number, M is the molar mass of the material, $\sum_i c_i Z_i$ is the number of electrons per formula unit. The theoretical values of materials used in this work are listed in **Table S3**. Although the EDY profile is normally a continuously varying function, the interfacial structure can often be well approximated by a layer model in which layers of thickness, t_i , electron scattering density, ρ_i and roughness, $\sigma_{i,i+1}$ ⁶ are sandwiched between the air/vacuum and the substrate, where i is the i^{th} layer.^{4,5} In the layer model, the measured X-ray is the summation of the reflection from all interfaces and this can be calculated rigorously by using Parratt's recursion formalism⁷ or Abeles

matrix method.⁸ One can use a refinement procedure to minimize the differences between the theoretical and measured reflectivity curves, by changing the parameters that describe each layer. The goodness of the fit can be evaluated by χ^2 value, which is defined in Eq. S3,

$$\chi^2 = \sum_{n=1}^L \frac{1}{L-p} \left(\frac{y_{n,obs} - y_{n,calc}}{y_{n,error}} \right)^2, \quad (S3)$$

where L is the total number of measured data points, p is the total number of free parameters for the fit, y_{obs} is the data value with a error of y_{error} , and y_{calc} is the calculated value. The closer to unit the χ^2 value is, the better the fitting is. By fitting the XRR data, the EDY of the materials can be plotted as a function of distance^{4,5}, $\rho(z)$, by using Eq. S4,

$$\rho(z) = \sum_{i=1}^n \frac{\rho_i - \rho_{i-1}}{2} \left(1 + \operatorname{erf} \left(\left(z - \sum_{j=1}^i t_{j-1} \right) / (\sqrt{2} \sigma_i) \right) \right), \quad (S4)$$

where $\operatorname{erf}(x)$ is the error function, t_i , ρ_i , and σ_i are the thickness, EDY, and roughness of the i^{th} layer, respectively; $t_0=0$, $\rho_0=0$, and ρ_n is the substrate EDY.

For LSC₁₁₃ and LSC_{113/214}, a four-layer model was used to fit *in situ* XRR data. A five-layer model was used to further fit LSC_{113/214} *in situ* XRR data for understanding the interfacial region of LSC₁₁₃ and LSC₂₁₄. The improvement of the fitting for LSC oscillations (**Figure S5**) indicates the better structural representation for LSC films. The detailed *in situ* XRR fitting parameters for 90 nm LSC₁₁₃ are shown in **Tables S3**. Four-layer and five-layer model fitting parameters for 90 nm LSC_{113/214} films are shown in **S4 and S5**, respectively. **Figure S6** shows the surface electron density of LSC113 as a function of temperature.

Auger Spectroscopy Characterization. The Auger spectra were collected from various areas and points (shown in **Figure 3**). Area analysis ($10 \times 10 \mu\text{m}^2$) was done for as-deposited (AD) LSC₁₁₃ and LSC_{113/214} samples, and point analysis was done for annealed (AN) samples as shown in **Figure S7**. Data was analyzed using the following relative sensitivity factors (S): 0.059, 0.027, 0.226 and 0.212 for La, Sr, Co and O, respectively. In addition, the electron inelastic-mean-free-path (IMFP) was calculated to correct signal intensity for their different IMFPs (information depth). IMFPs were calculated using the NIST Standard Reference Database 71 “NIST Electron Inelastic-Mean-Free-Path Database” version 1.2. The software provides the ability to predict the IMFP for inorganic compounds when supplied the stoichiometric composition ($\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$), the number of valence electrons per molecule (assumed to be 29.8), the density (6.931 g/cm^3) and a band gap energy (for

which we assumed 0 eV, as LSC₁₁₃ is metallic at high temperatures; additionally, assuming an insulating band gap of 5 eV only increases the IMFP by ~ 0.03 nm). The IMFP for Sr (La) was determined to be 2.549 nm (1.337 nm). A relative depth-scaling factor (σ) was determined as:

$$\sigma_i = \int_0^{\lambda_i} \frac{1}{\lambda_i} \exp\left(-\frac{x}{\lambda_i}\right) dx, \quad (\text{S5})$$

where λ_i is the IMFP, yielding $\sigma_{\text{Sr}} = 0.41$, and $\sigma_{\text{La}} = 0.63$. The intensities from different elements were scaled using $I_{\text{scaled}} = I_{\text{measured}} * \sigma_i / S_i$. Similarly the IMFP for Sr (La) of LSC₂₁₄ was determined to be 2.668 nm (1.395 nm) by using the stoichiometric composition ((La_{0.5}Sr_{0.5})₂CoO₄), the number of valence electrons per molecule (assumed to be 38), the density (6.401 g/cm³) and a band gap energy (assumed 0). The obtained values of the relative depth-scaling factor for LSC₂₁₄ are thus approximately equal to those of LSC₁₁₃. The La and Sr concentration (c_{La} or c_{Sr}) was obtained by normalizing to the their sum, $c_i = I_i / (I_{\text{La}} + I_{\text{Sr}})$.

Experimental details of in situ APXPS. Ambient pressure and high temperature XPS spectra were collected at $p(\text{O}_2) = 1 \times 10^{-3}$ atm with the following conditions:

LSC₁₁₃ sample 1: $T = 220$ °C, $T = 370$ °C, $T = 520$ °C, $T = 370$ °C, and $T = 220$ °C.

LSC₁₁₃ sample 2: $T_1 = 520$ °C, $T_2 = 220$ °C, $T_3 = 520$ °C, $T_4 = 220$ °C, $T_5 = 520$ °C, $T_6 = 220$ °C, $T_7 = 520$ °C, and $T_8 = 220$ °C (T_x , where x represents the sequential ordering of the temperature step).

LSC_{113/214} sample: $T = 220$ °C, $T = 370$ °C, $T = 520$ °C.

In situ APXPS: The spectra for each temperature were aligned to Au 4f_{7/2} (BE = 84.0 eV). Analysis of the photoemission lines was done after subtracting a Shirley-type background using a symmetric combined Gaussian-Lorentzian line shape for fitting. Additional constraints for fitting the Sr 3d spectra include the Sr 3d_{5/2} and 3d_{3/2} doublet with an energy separation of 1.8 eV and a branching ratio of 1.5. The integrated areas (Casa XPS) for each component were then utilized for the analysis. The binding energy, full-width-half-maximum (FWHM), and integrated area for each component are provided in **Table S6**.

In situ APXPS normalization procedure. The integrated intensity of the entire elemental region (or the components) is extracted from the fitting (value shown in **Table S6**). The raw intensity values were divided by the photoionization cross-sections for the LSC thin films, as done in our previous

studies^{9,10}. The normalized intensity shown in **Figure 5c** and **5d** was performed by taking the fractional contribution of the individual Sr 3d components (after cross-section correction) normalized to the initial condition (220 °C).

In situ APXPS error analysis. Error bars for the normalized area intensities shown in **Figure 5c** and **5d** were determined using a Monte Carlo method assuming a Poisson noise distribution function (Casa XPS). The selection of the noise distribution function is generally the weakest point of the accuracy for this form of error analysis. In order to verify the validity of this assumption, a region absent of core level excitations was selected and fit to a linear function. The standard deviation of the residuals is representative of the noise distribution of the spectra and can be compared to the standard deviation of the Poisson distribution. A value near unity indicates higher reliability of the Poisson distribution assumption. Residual standard deviations were typically ~ 0.93 , which suggests that this form of error analysis is reliable.

The Monte Carlo method was used to estimate the Hessian matrix of the fitted parameters, which was then used to determine the standard deviations for the binding energies, FWHM, and integrated intensity areas for each component (Casa XPS). Normalized intensity areas were calculated by assuming no error for the XPS photoionization cross-sections. The general formula Eq. S6 was used to propagate the error bars determined for the initial integrated area intensities to the changes of the individual components of Sr and O relative to the total Sr and O, and the Sr concentration relative to the combined Sr and O in the lattice.

$$\sigma_f^2 = \sum_{i=1}^n \left(\frac{\partial f}{\partial x_i} \right)^2 \sigma_i^2 \quad (\text{S6})$$

Table S1: Constrained and relaxed lattice parameters of 90 nm LSC₁₁₃ films extracted from normal and off-normal *in situ* XRD data. The constrained out-of-plane and in-plane lattice parameters of the LSC₁₁₃ in LSC₁₁₃ films were calculated from combining the interplanar distances of the (002)_{pc} and (202)_{pc} peaks. For determining the relaxed film lattice parameter $\hat{a}$, we used the equation:

$$\frac{\Delta c}{\hat{c}} = \frac{-2\nu}{1-\nu} \frac{\Delta a}{\hat{a}}$$

Assuming $\hat{a} = \hat{c}$ and $\nu = 0.25^{11}$.

Electrode System	Constrained LSC ₁₁₃ in-plane lattice parameter a (Å)	Constrained LSC ₁₁₃ out-of-plane lattice parameter a (Å)	Relaxed LSC ₁₁₃ film lattice parameter $\hat{a}$ (Å)	In-plane strain $\epsilon_{xx} = \frac{(a - \hat{a})}{\hat{a}}$	Out-of-plane strain $\epsilon_{zz} = \frac{(c - \hat{c})}{\hat{c}}$
RT	3.868	3.813	3.835	0.87	-0.57
220 °C	3.857	3.847	3.851	0.16	-0.10
350 °C	3.863	3.869	3.866	-0.09	0.06
400 °C	3.868	3.878	3.874	-0.15	0.10

Table S2: Constrained and relaxed lattice parameters of 90 nm LSC_{113/214} films extracted from normal and off-normal *in situ* XRD data.

Electrode System	Constrained LSC ₁₁₃ in-plane lattice parameter a (Å)	Constrained LSC ₁₁₃ out-of-plane lattice parameter a (Å)	Relaxed LSC ₁₁₃ film lattice parameter $\hat{a}$ (Å)	In-plane strain $\varepsilon_{xx} = \frac{(a - \hat{a})}{\hat{a}}$	Out-of-plane strain $\varepsilon_{zz} = \frac{(c - \hat{c})}{\hat{c}}$
RT	3.863	3.814	3.834	0.77	-0.51
220 °C	3.870	3.867	3.869	0.05	-0.03
350 °C	3.871	3.890	3.882	-0.29	0.19

Table S3: Parameters obtained from *in situ* XRR fits of 90 nm LSC₁₁₃/GDC/YSZ, where ρ is experimental and ρ_i (i = Y = YSZ, G = GDC, L1 = LSC₁₁₃, L2 = LSC₂₁₄) is the bulk or theoretical electron density of the corresponding material, t is the thickness with unit nm and σ is the roughness in nm. The number in the bracket of each parameter is the last digit error. The theoretical electron density or scattering length density of each material is: $\rho_Y = \rho_{YSZ} = 46.05$, $\rho_G = \rho_{GDC} = 50.5$, $\rho_{L1} = \rho_{LSC113} = 51.7$ and $\rho_{L2} = \rho_{LSC214} = 46.7$, with unit $10^{-6} \text{ \AA}^{-2}$.

T (°C)	Interfacial Layer			GDC			LSC ₁₁₃			Surface Layer			χ^2
	t	σ	ρ/ρ_Y	t	σ	ρ/ρ_G	t	σ	ρ/ρ_{L1}	t	σ	ρ/ρ_{L1}	
25	0.9(1)	0.3(1)	0.94(2)	6.6(1)	0.2(1)	0.98(7)	88.1(4)	0.3(1)	0.83(8)	4.4(8)	1.5(1)	0.82(8)	9.8
220	1.3(5)	0.5(2)	0.99(2)	5.8(2)	0.1(1)	0.99(4)	90(1)	0.2(4)	0.83(4)	3(1)	1.4(5)	0.83(8)	3.8
350	0.6(3)	0.1(5)	0.9(2)	5.8(4)	0.3(1)	0.96(9)	92(1)	0.9(1)	0.84(7)	2.3(9)	0.8(2)	0.7(2)	1.5
400	0.3(3)	0.2(1)	0.9(2)	6.9(2)	0.2(1)	0.96(8)	91.0(8)	1.2(1)	0.83(8)	2.7(7)	0.8(1)	0.60(9)	1.1

Table S4. Parameters obtained from four-layer model for *in situ* XRR fits of LSC_{113/214}/GDC/YSZ, where ρ is experimental and ρ_i (i = Y, G, L1 or L2) is the bulk or theoretical electron density of the corresponding material, t is the thickness with unit nm and σ is the roughness in unit nm. The number in the bracket of each parameter is the last digit error.

T (°C)	Interfacial Layer			GDC			LSC ₁₁₃			LSC ₂₁₄			χ^2
	t	σ	ρ/ρ_Y	t	σ	ρ/ρ_G	t	σ	ρ/ρ_{L1}	t	σ	ρ/ρ_{L1}	
25	0.6(4)	0.3(1)	0.9(1)	5.6(2)	0.1(1)	0.99(3)	90.0(2)	0.1(2)	0.87(3)	4.2(8)	1.7(2)	0.81(4)	8.6
220	0.4(5)	0.3(1)	0.9(2)	5.7(1)	0.2(1)	0.97(2)	89.6(3)	0.5(4)	0.87(2)	4.1(5)	1.6(1)	0.79(4)	7.0
350	0.6(8)	0.4(4)	0.9(2)	5.8(7)	0.3(1)	0.93(3)	89.8(7)	0.5(2)	0.84(3)	4.9(5)	1.7(1)	0.73(2)	5.9

Table S5: Parameters obtained from five-layer model for *in situ* XRR fits of 90 nm LSC_{113/214}/GDC/YSZ, where ρ is experimental and ρ_i is the bulk or theoretical electron density of the corresponding material, t is the thickness with unit nm and σ is the roughness in nm. The number in the bracket of each parameter is the last digit error^a.

T (°C)	Interfacial Layer			GDC			LSC ₁₁₃			LSC _{113/214} Interfacial Layer			LSC ₂₁₄			χ^2
	t	σ	ρ/ρ_Y	t	σ	ρ/ρ_G	t	σ	ρ/ρ_{L1}	t	σ	ρ/ρ_{L1}	t	σ	ρ/ρ_{L1}	
25	0.6(1)	0.3(1)	0.90(1)	5.6(1)	0.2(1)	0.99(1)	90.1(1)	0.2(2)	0.78(7)	1.7(5)	0.2(2)	0.75(4)	2.2(1)	1.5(2)	0.77(3)	3.5
220	0.6(3)	0.3(1)	0.92(3)	5.6(1)	0.2(1)	0.93(3)	89.8(5)	0.3(2)	0.78(3)	1.3(1)	0.9(1)	0.73(3)	2.6(6)	1.6(3)	0.72(3)	8.4
350	0.6(5)	0.6(2)	0.91(6)	5.8(5)	0.3(1)	0.93(4)	89.5(7)	0.8(3)	0.81(3)	1.2(7)	0.2(1)	0.69(2)	3.2(8)	1.8(2)	0.73(2)	7.1

^aBoth four- and five-layer model give the same thickness, electron density and roughness for GDC, bulk LSC₁₁₃, and total film, in the error ranges. However, five-layer model separates the interface layer between LSC₁₁₃ and LSC₂₁₄ and better represents the change of the interface region, mostly notably the electron density. In particular, the five-layer model can fit the LSC oscillation much better than four-layer model. The difference of interface electron density becomes obvious in five-layer model as temperature was increased.

Table S6a: 90 nm LSC₁₁₃ single temperature cycle detailed XPS peak positions and information on the fitting parameters.

Condition	Name	BE (eV)	FWHM (eV)	Area
LSC ₁₁₃ , <i>T</i> = 220 °C, increase	O 1s - Surface	531.3	1.7	814.2
	O 1s - Surface (M-O)	529.8	1.3	140.0
	O 1s - Lattice	528.6	1.3	788.6
	Sr 3d 3/2 - Surface	135.3	1.9	2057.7
	Sr 3d 5/2 - Surface	133.5	1.9	3086.5
	Sr 3d 3/2 - Lattice	133.8	1.5	696.0
	Sr 3d 5/2 - Lattice	132.0	1.5	1045.0
	La 4d	-	-	7362.6
	Co 3p	-	-	1579.3
LSC ₁₁₃ , <i>T</i> = 370 °C, increase	O 1s - Surface	531.5	1.7	1076.4
	O 1s - Surface (M-O)	529.8	1.0	113.4
	O 1s - Lattice	528.6	1.4	769.8
	Sr 3d 3/2 - Surface	135.2	1.8	957.4
	Sr 3d 5/2 - Surface	133.4	1.8	1436.1
	Sr 3d 3/2 - Lattice	134.2	1.6	1063.3
	Sr 3d 5/2 - Lattice	132.4	1.6	1596.5
	La 4d	-	-	6505.9
	Co 3p	-	-	1353.0
LSC ₁₁₃ , <i>T</i> = 520 °C	O 1s - Surface	531.6	1.7	918.6
	O 1s - Surface (M-O)	529.8	1.5	248.7
	O 1s - Lattice	528.6	1.4	765.1
	Sr 3d 3/2 - Surface	135.6	2.0	1496.8
	Sr 3d 5/2 - Surface	133.8	2.0	2245.2
	Sr 3d 3/2 - Lattice	134.4	1.6	1688.7
	Sr 3d 5/2 - Lattice	132.6	1.6	2535.7
	La 4d	-	-	6910.6
	Co 3p	-	-	1384.1
LSC ₁₁₃ , <i>T</i> = 370 °C, decrease	O 1s - Surface	531.5	1.6	518.8
	O 1s - Surface (M-O)	529.8	1.5	286.0
	O 1s - Lattice	528.6	1.3	658.6
	Sr 3d 3/2 - Surface	135.6	2.0	1140.9
	Sr 3d 5/2 - Surface	133.8	2.0	1711.3
	Sr 3d 3/2 - Lattice	134.5	1.6	1524.4
	Sr 3d 5/2 - Lattice	132.7	1.6	2288.9
	La 4d	-	-	5461.0
	Co 3p	-	-	1179.7
LSC ₁₁₃ , <i>T</i> = 220 °C, decrease	O 1s - Surface	531.4	1.7	679.9
	O 1s - Surface (M-O)	529.8	1.1	168.3
	O 1s - Lattice	528.7	1.3	668.5
	Sr 3d 3/2 - Surface	135.6	1.9	1026.1
	Sr 3d 5/2 - Surface	133.8	1.9	1539.1
	Sr 3d 3/2 - Lattice	134.5	1.5	1525.3
	Sr 3d 5/2 - Lattice	132.7	1.5	2290.2
	La 4d	-	-	5616.1
	Co 3p	-	-	1222.5

Table S6b: 90 nm LSC₁₁₃ multiple temperature cycled detailed XPS peak positions and information on the fitting parameters.

Condition	Name	BE (eV)	FWHM (eV)	Area
LSC ₁₁₃ , <i>T</i> = 520 °C	O 1s - Surface	531.6	1.9	1767.7
	O 1s - Surface (M-O)	529.8	1.0	141.0
	O 1s - Lattice	528.6	1.4	1018.8
	Sr 3d 3/2 - Surface	135.5	1.8	1272.5
	Sr 3d 5/2 - Surface	133.7	1.8	1908.7
	Sr 3d 3/2 - Lattice	134.5	1.6	2471.2
	Sr 3d 5/2 - Lattice	132.7	1.6	3710.5
	La 4d	-	-	8780.2
	Co 3p	-	-	2092.6
LSC ₁₁₃ , <i>T</i> = 220 °C, 1 st – 2 nd cycle	O 1s - Surface	531.5	1.7	1253.7
	O 1s - Surface (M-O)	529.8	1.0	122.1
	O 1s - Lattice	528.7	1.2	707.5
	Sr 3d 3/2 - Surface	135.5	1.8	951.9
	Sr 3d 5/2 - Surface	133.7	1.8	1427.9
	Sr 3d 3/2 - Lattice	134.5	1.5	2577.0
	Sr 3d 5/2 - Lattice	132.7	1.5	3869.4
	La 4d	-	-	6218.2
	Co 3p	-	-	1239.8
LSC ₁₁₃ , <i>T</i> = 520 °C, 2 nd cycle	O 1s - Surface	531.6	1.8	1722.1
	O 1s - Surface (M-O)	529.8	1.1	176.6
	O 1s - Lattice	528.7	1.4	1179.8
	Sr 3d 3/2 - Surface	135.5	1.8	1482.8
	Sr 3d 5/2 - Surface	133.7	1.8	2224.3
	Sr 3d 3/2 - Lattice	134.5	1.6	3218.4
	Sr 3d 5/2 - Lattice	132.7	1.6	4832.4
	La 4d	-	-	9256.8
	Co 3p	-	-	1976.9
LSC ₁₁₃ , <i>T</i> = 220 °C, 2 nd – 3 rd cycle	O 1s - Surface	531.5	1.7	1329.5
	O 1s - Surface (M-O)	529.8	1.0	132.3
	O 1s - Lattice	528.7	1.3	869.9
	Sr 3d 3/2 - Surface	135.5	1.8	833.7
	Sr 3d 5/2 - Surface	133.7	1.8	1250.5
	Sr 3d 3/2 - Lattice	134.5	1.5	2809.4
	Sr 3d 5/2 - Lattice	132.7	1.5	4218.3
	La 4d	-	-	6210.8
	Co 3p	-	-	1402.4
LSC ₁₁₃ , <i>T</i> = 520 °C, 3 rd cycle	O 1s - Surface	531.7	1.7	1416.8
	O 1s - Surface (M-O)	529.8	1.3	278.4
	O 1s - Lattice	528.7	1.3	1047.4
	Sr 3d 3/2 - Surface	135.4	1.8	1701.5
	Sr 3d 5/2 - Surface	133.6	1.8	2552.2
	Sr 3d 3/2 - Lattice	134.5	1.6	3122.1
	Sr 3d 5/2 - Lattice	132.7	1.6	4687.8
	La 4d	-	-	9789.0
	Co 3p	-	-	2087.4
LSC ₁₁₃ , <i>T</i> = 220 °C, 3 rd – 4 th cycle	O 1s - Surface	531.5	1.6	1235.3
	O 1s - Surface (M-O)	529.8	1.0	140.9
	O 1s - Lattice	528.7	1.3	790.5
	Sr 3d 3/2 - Surface	135.6	1.8	629.8
	Sr 3d 5/2 - Surface	133.8	1.8	944.7
	Sr 3d 3/2 - Lattice	134.5	1.5	2847.0
	Sr 3d 5/2 - Lattice	132.7	1.5	4274.8
	La 4d	-	-	5958.0
	Co 3p	-	-	1284.8
LSC ₁₁₃ , <i>T</i> = 520 °C, 4 th cycle	O 1s - Surface	531.7	1.8	1531.9
	O 1s - Surface (M-O)	529.8	1.0	220.3
	O 1s - Lattice	528.7	1.4	1221.5
	Sr 3d 3/2 - Surface	135.4	1.9	1910.4
	Sr 3d 5/2 - Surface	133.6	1.9	2865.7
	Sr 3d 3/2 - Lattice	134.5	1.6	3212.4
	Sr 3d 5/2 - Lattice	132.7	1.6	4823.4
	La 4d	-	-	9336.0
	Co 3p	-	-	2029.0
LSC ₁₁₃ , <i>T</i> = 220 °C, 4 th cycle	O 1s - Surface	531.5	1.6	965.1
	O 1s - Surface (M-O)	529.8	1.2	242.2
	O 1s - Lattice	528.7	1.2	976.0
	Sr 3d 3/2 - Surface	135.5	1.8	799.1
	Sr 3d 5/2 - Surface	133.7	1.8	1198.6
	Sr 3d 3/2 - Lattice	134.5	1.5	3060.4
	Sr 3d 5/2 - Lattice	132.7	1.5	4595.2
	La 4d	-	-	6414.6
	Co 3p	-	-	1249.5

Table S6c: 400-pulse LSC₂₁₄ decorated LSC_{113/214} increase in temperature detailed XPS peak positions and information on the fitting parameters.

Condition	Name	BE (eV)	FWHM (eV)	Area
LSC _{113/214} <i>T</i> = 220 °C	O 1s - Surface	531.2	1.6	774.8
	O 1s - Surface (M-O)	529.8	1.5	214.4
	O 1s - Lattice	528.4	1.2	789.7
	Sr 3d 3/2 - Surface	135.2	2.0	1023.7
	Sr 3d 5/2 - Surface	133.4	2.0	1535.6
	Sr 3d 3/2 - Lattice	133.7	1.3	817.1
	Sr 3d 5/2 - Lattice	131.9	1.3	1226.9
	La 4d	-	-	6130.9
	Co 3p	-	-	977.2
LSC _{113/214} <i>T</i> = 370 °C	O 1s - Surface	531.4	1.7	1607.8
	O 1s - Surface (M-O)	529.8	1.0	182.3
	O 1s - Lattice	528.6	1.3	1313.0
	Sr 3d 3/2 - Surface	135.5	2.0	2648.4
	Sr 3d 5/2 - Surface	133.7	2.0	3972.6
	Sr 3d 3/2 - Lattice	133.7	1.3	873.0
	Sr 3d 5/2 - Lattice	131.9	1.3	1310.8
	La 4d	-	-	10025.7
	Co 3p	-	-	1742.9
LSC _{113/214} <i>T</i> = 520 °C	O 1s - Surface	531.6	1.8	939.4
	O 1s - Surface (M-O)	529.8	1.4	380.6
	O 1s - Lattice	528.7	1.4	1202.4
	Sr 3d 3/2 - Surface	135.5	2.0	3031.5
	Sr 3d 5/2 - Surface	133.7	2.0	4547.3
	Sr 3d 3/2 - Lattice	134.4	1.6	1665.0
	Sr 3d 5/2 - Lattice	132.6	1.6	2500.0
	La 4d	-	-	7061.7
	Co 3p	-	-	986.6

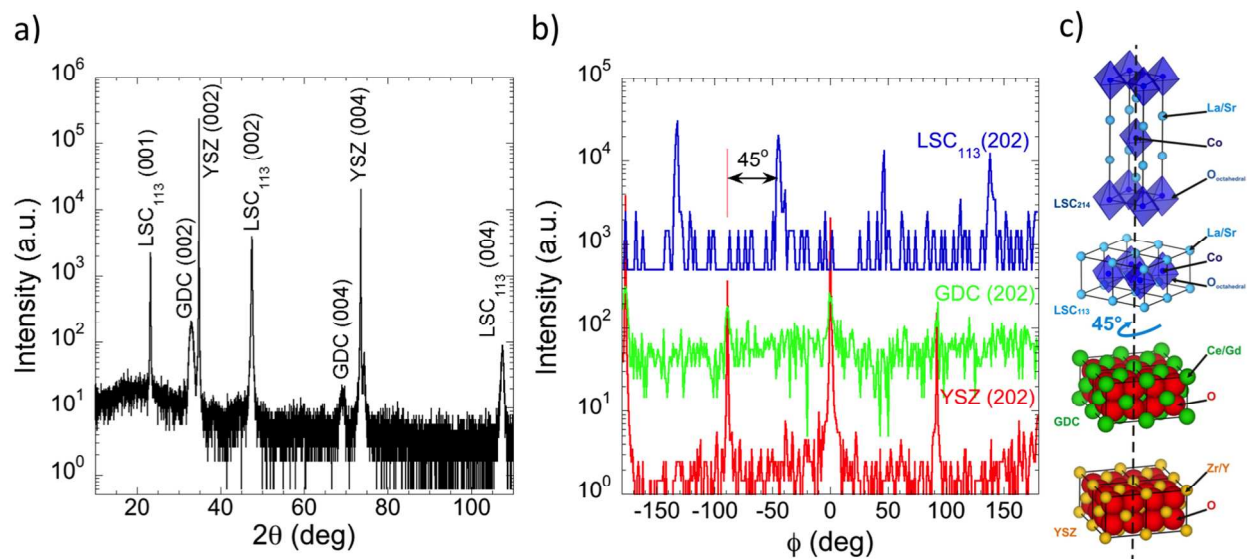


Figure S1. (a) Representative normal XRD data of 90 nm LSC₁₁₃ or 90 nm LSC_{113/214} films, (b) representative off-normal XRD phi scan. (c) Schematic of the crystallographic rotational relationships among the LSC₂₁₄(001)_{tetragonal}, LSC₁₁₃(001)_{pc}, GDC(001)_{cubic}, and YSZ(001)_{cubic}. These samples were used for XRR, EIS and AES measurements, too. 90 nm LSC₁₁₃ was also used for APXPS measurements.

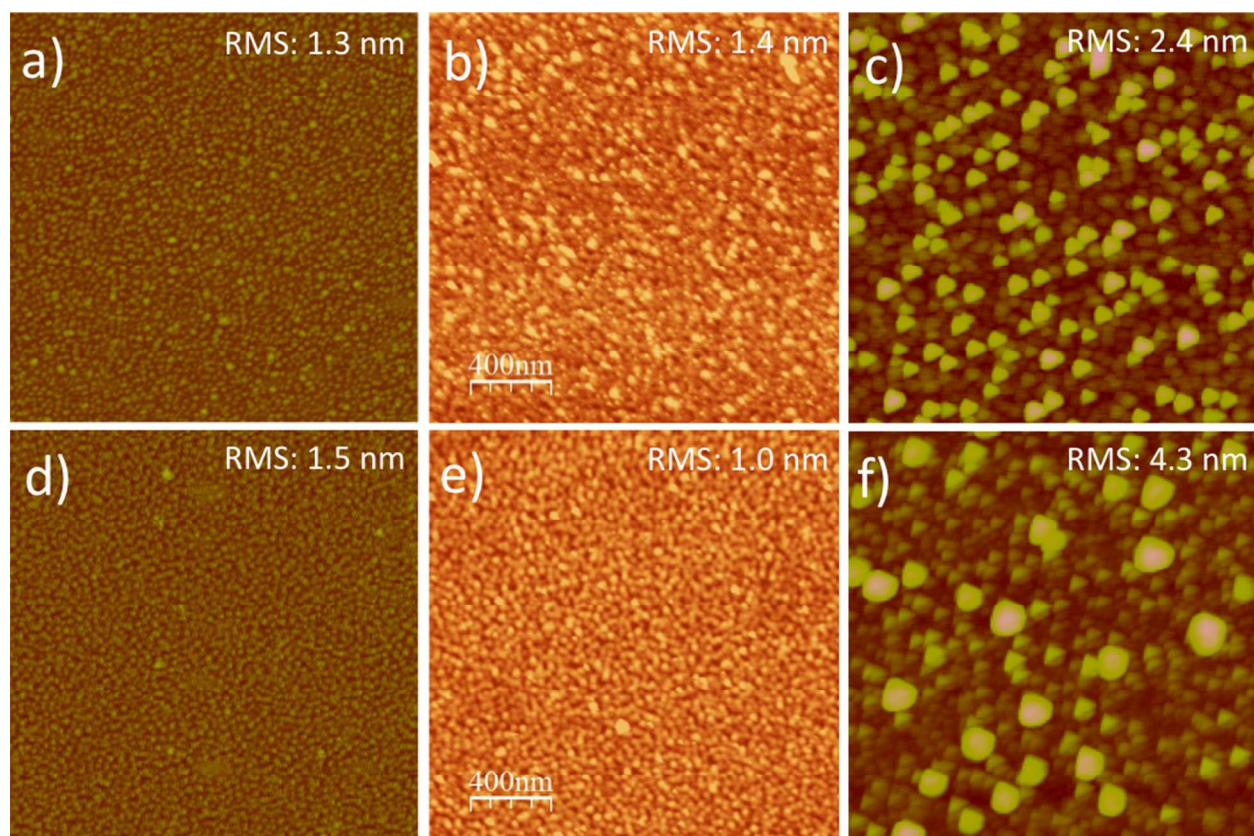


Figure S2. AFM images ($2 \times 2 \mu\text{m}^2$) of 90 nm LSC_{113} at (a) as-deposited (AD), (b) after *in situ* XRR measurements, (c) after annealing (AN) at 550 °C in 1 atm O_2 for 6 hours; and 90 nm $\text{LSC}_{113/214}$ at (d) AD, (e) after *in situ* XRR measurements, and (f) AN. The universal scale bar is shown in (b) and (e). These samples were also used for XRD, XRR, EIS and AES measurements. 90 nm LSC_{113} was also used for APXPS measurements.

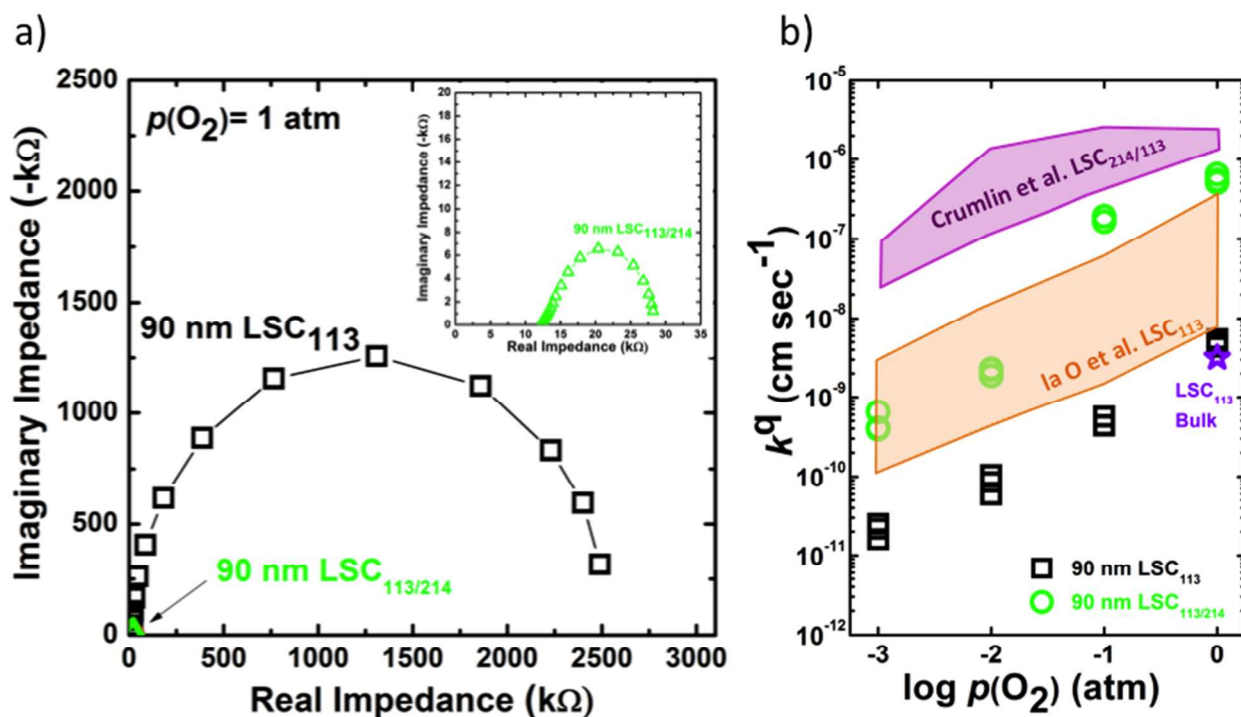


Figure S3. Electrochemical impedance spectroscopy (EIS) results of microelectrodes ($\sim 200 \mu\text{m}$) for the 90 nm LSC_{113} and 90 nm $\text{LSC}_{113/214}$ films (a) Nyquist plots at 1 atm $p(\text{O}_2)$; (b) k^q from 90 nm LSC_{113} (black) and 90 nm $\text{LSC}_{113/214}$ (green) microelectrodes calculated from EIS spectra. k^q value from bulk LSC_{113} (purple star) is obtained from previous studies of De Souza, et al.¹². For comparison, k^q values from la O' et al.² (LSC_{113}) and Crumlin, et al.¹ ($\text{LSC}_{113/214}$) were plotted. These samples were used for XRD, XRR and AES measurements. 90 nm LSC_{113} was also used for APXPS.

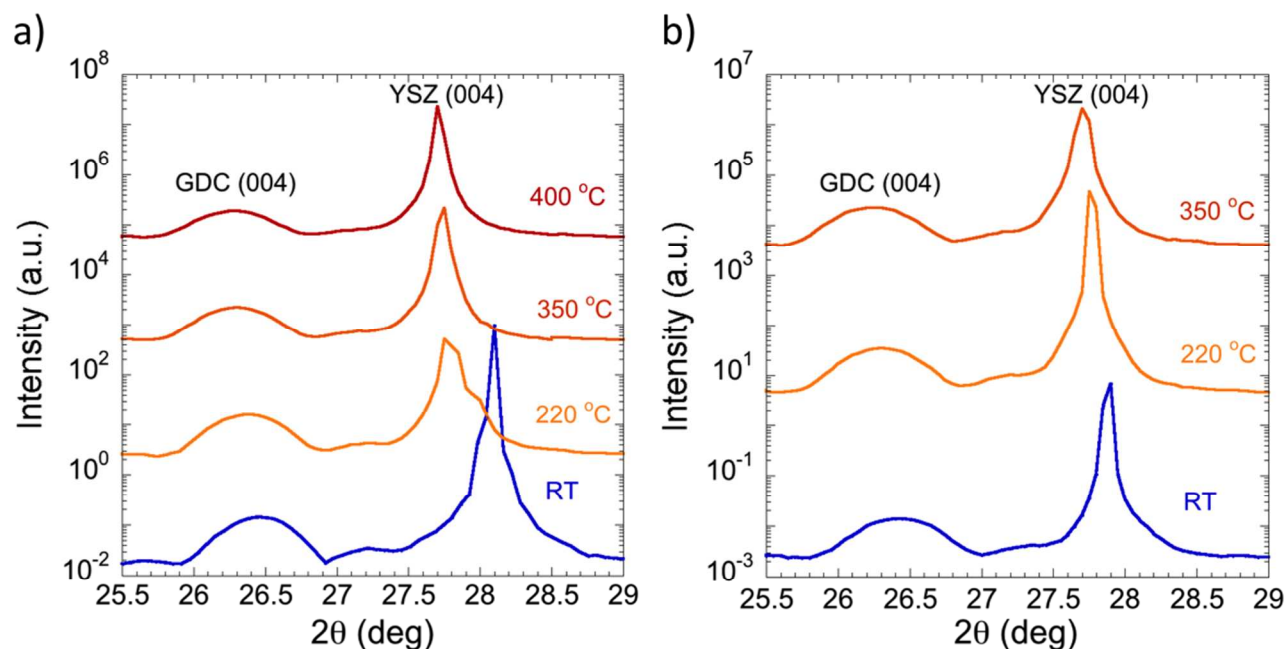


Figure S4. *In situ* XRD of YSZ (004) and GDC (004) for (a) 90 nm LSC₁₁₃ and (b) 90 nm LSC_{113/214} at different temperatures. For LSC₁₁₃ case, there is an abrupt thermal expansion change of YSZ (004) from room temperature (RT) to 220 °C. The incident X-ray energy is 20 keV. These samples were also used for XRR, EIS and AES measurements. 90 nm LSC₁₁₃ was also used for APXPS.

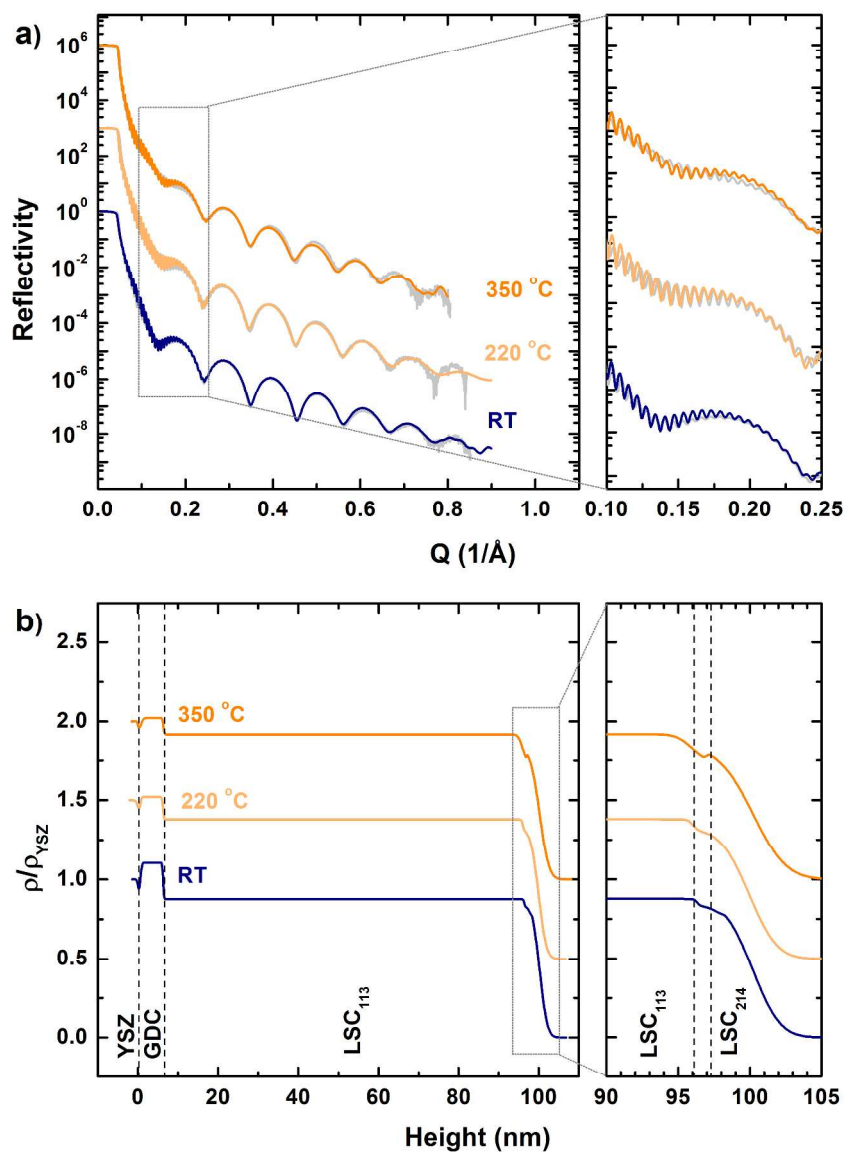


Figure S5. (a) *In situ* XRR data and five-layer model fits of 4 nm LSC₂₁₄ decorated 90 nm LSC₁₁₃/GDC/YSZ at different temperatures: room temperature (RT), 200 °C, and 350 °C in ambient air. (b) The EDY obtained from the fits of the XRR data. Interfacial EDY became smaller as temperature increased, compared to LSC₁₁₃ and LSC₂₁₄ layers. The sample was used for XRD, EIS, and AES measurements.

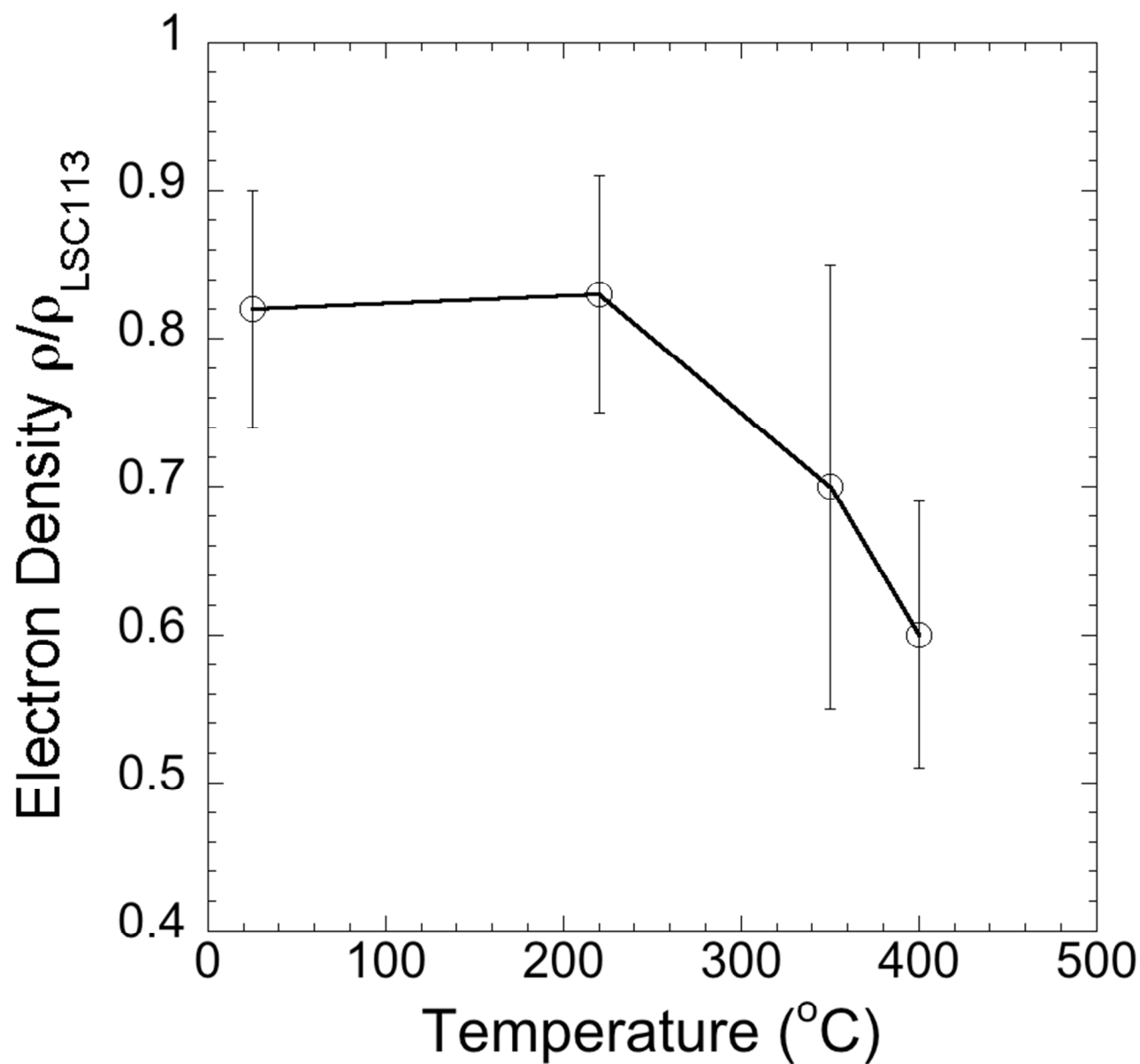


Figure S6. The surface layer electron density ($\rho/\rho_{\text{LSC113}}$) of 90 nm LSC_{113} as the function of temperature in ambient air. The decreasing trend indicates the surface went through a structural change as the temperature was increased. Values are taken from Table S3.

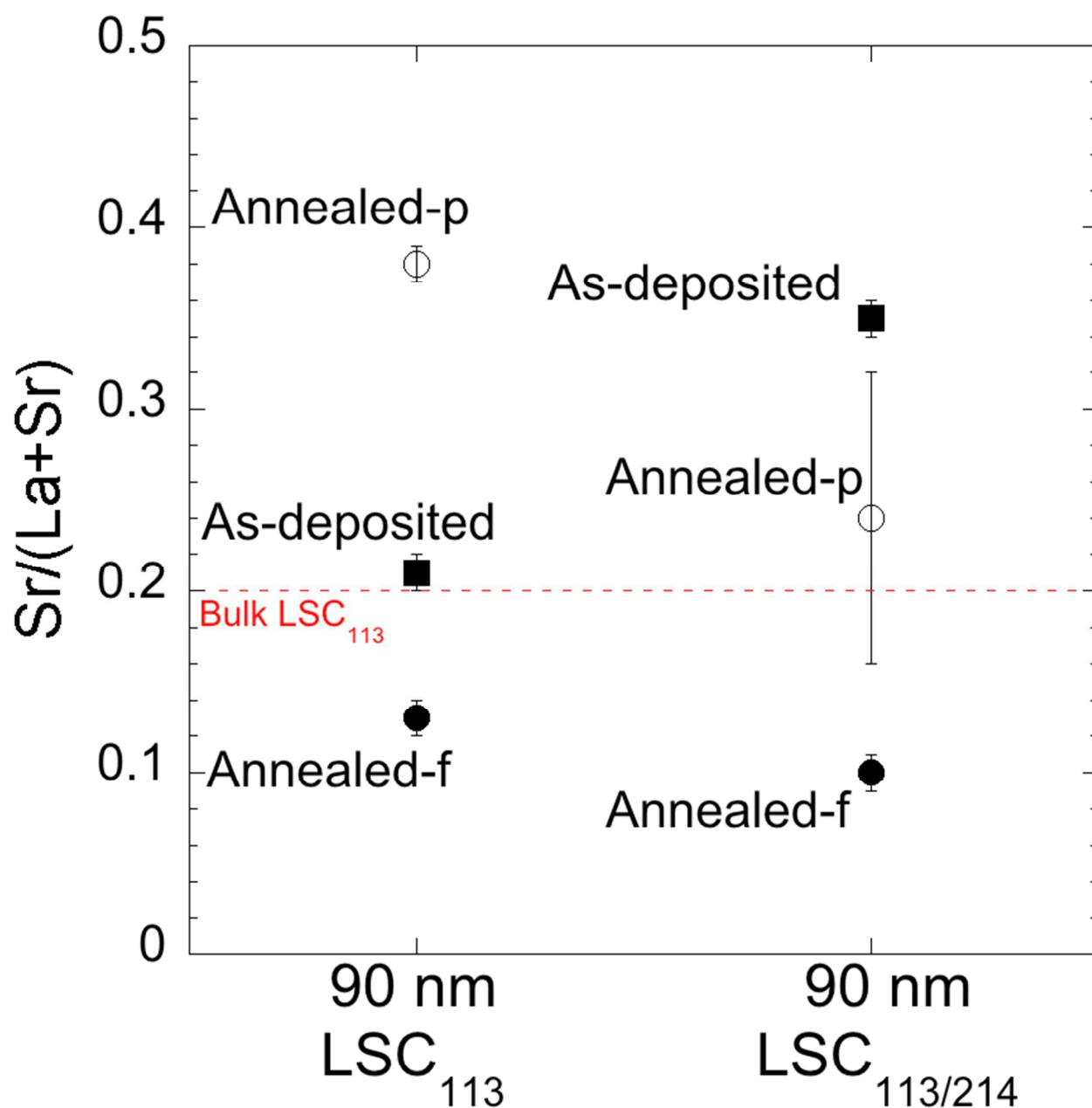


Figure S7. Normalized Sr concentrations for 90 nm LSC₁₁₃ and 90 nm LSC_{113/214} films at as-deposited and annealed conditions. The bulk LSC₁₁₃ Sr nominal value, 0.2 (red dashed line), is used as the reference. Three $10 \times 10 \mu\text{m}^2$ area analysis were performed on as-deposited and annealed films (denoted as “f”). Two $0.4 \times 0.4 \mu\text{m}^2$ “point” analysis (denoted as “p”) were performed for particles on annealed films. Representative points can be found in Fig. 3. These samples were used for XRD, XRR and EIS measurements, too. 90 nm LSC₁₁₃ was also used for APXPS.

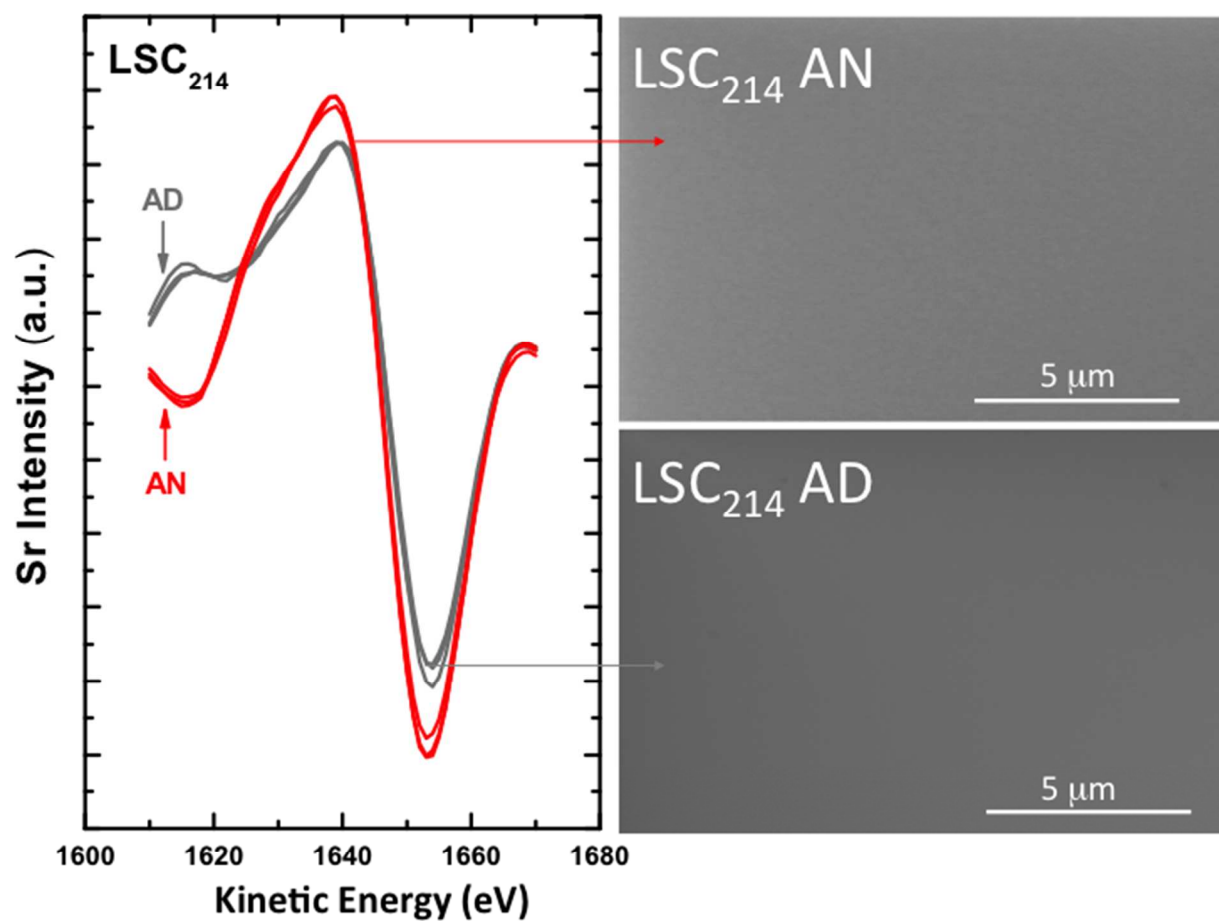


Figure S8. Sr Auger spectra (left) and SEM images (right) for 160 nm LSC₂₁₄ film grown on GDC/YSZ(001) at as-deposited (AD) and annealed (AN) conditions. Minimal morphological and Sr concentration changes were found, indicating a very stable surface.

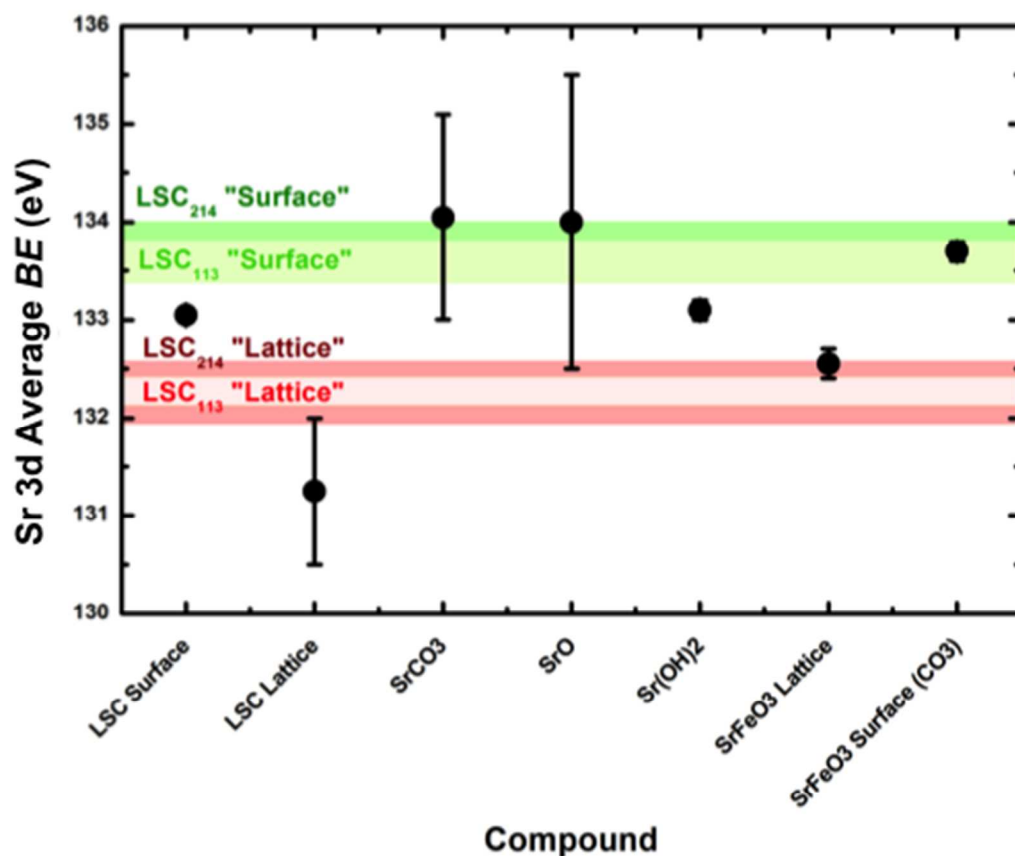


Figure S9. Average Sr 3d_{5/2} binding energies for various Sr compounds from literature.¹³⁻¹⁸ The red bars designate the range of binding energies observed for the “lattice” component in LSC₁₁₃ and LSC₂₁₄ films in this work, while the green bars designate the range of binding energies observed for the “surface” component. A ~50 nm LSC₂₁₄ thin film was also used as a reference for LSC₂₁₄ binding energies in our experiments.

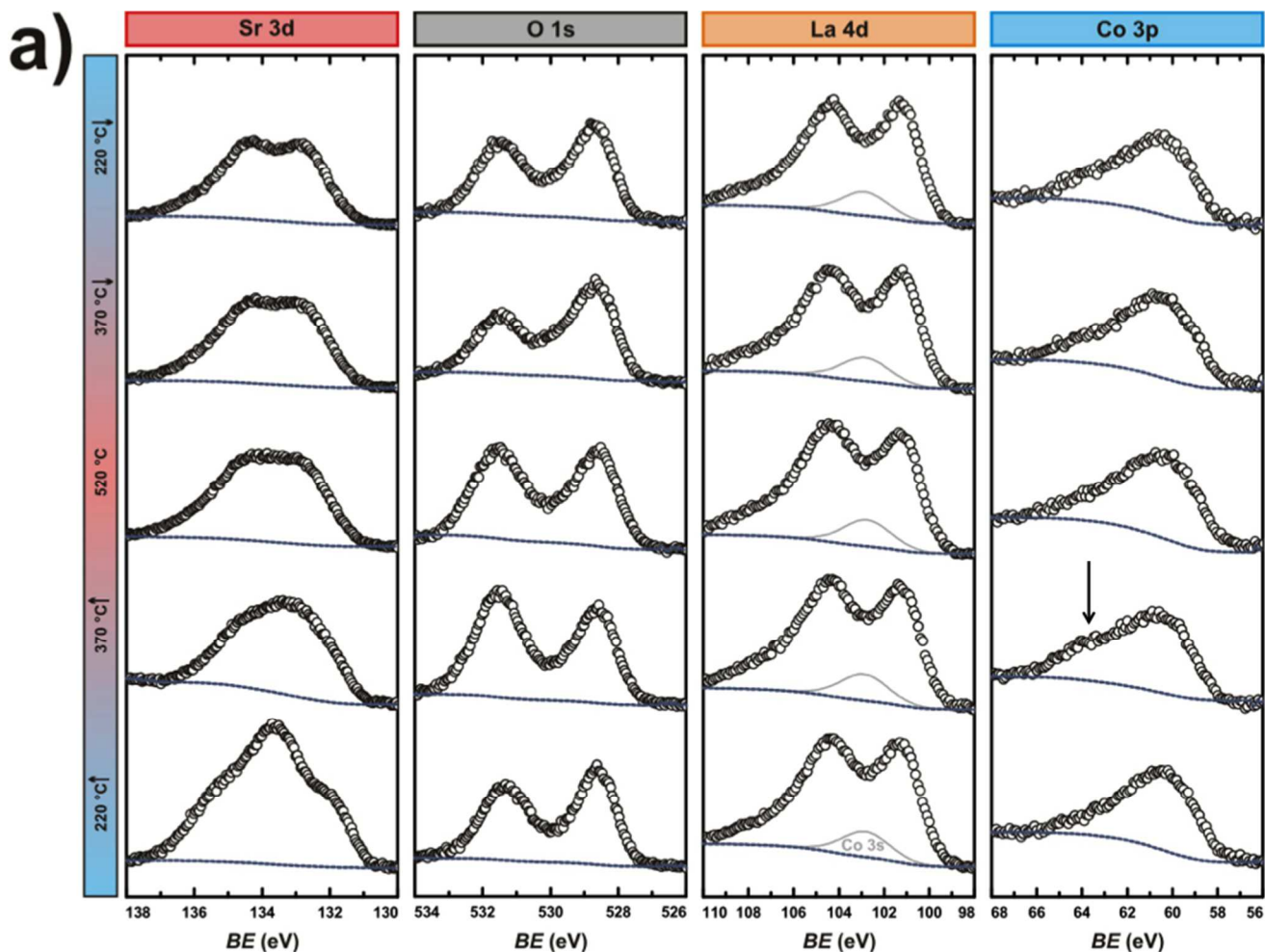


Figure S10a. *In situ* APXPS data of a 90 nm LSC_{113} film as a function of temperature upon the first heating. Sr 3d ($E_{\text{photon}} = 390$ eV), O 1s ($E_{\text{photon}} = 690$ eV), La 4d ($E_{\text{photon}} = 390$ eV) and Co 3p ($E_{\text{photon}} = 390$ eV) spectra at 220 °C, 370 °C, 520 °C then decreased to 370 °C and 220 °C at a $p(\text{O}_2)$ of 1×10^{-3} atm. White circles are for the measured data and grey dotted lines correspond to the background, spectra are normalized to raw spectra max height or ‘lattice’ component when applicable. This sample was used for XRD, XRR, EIS and AES measurements, too.

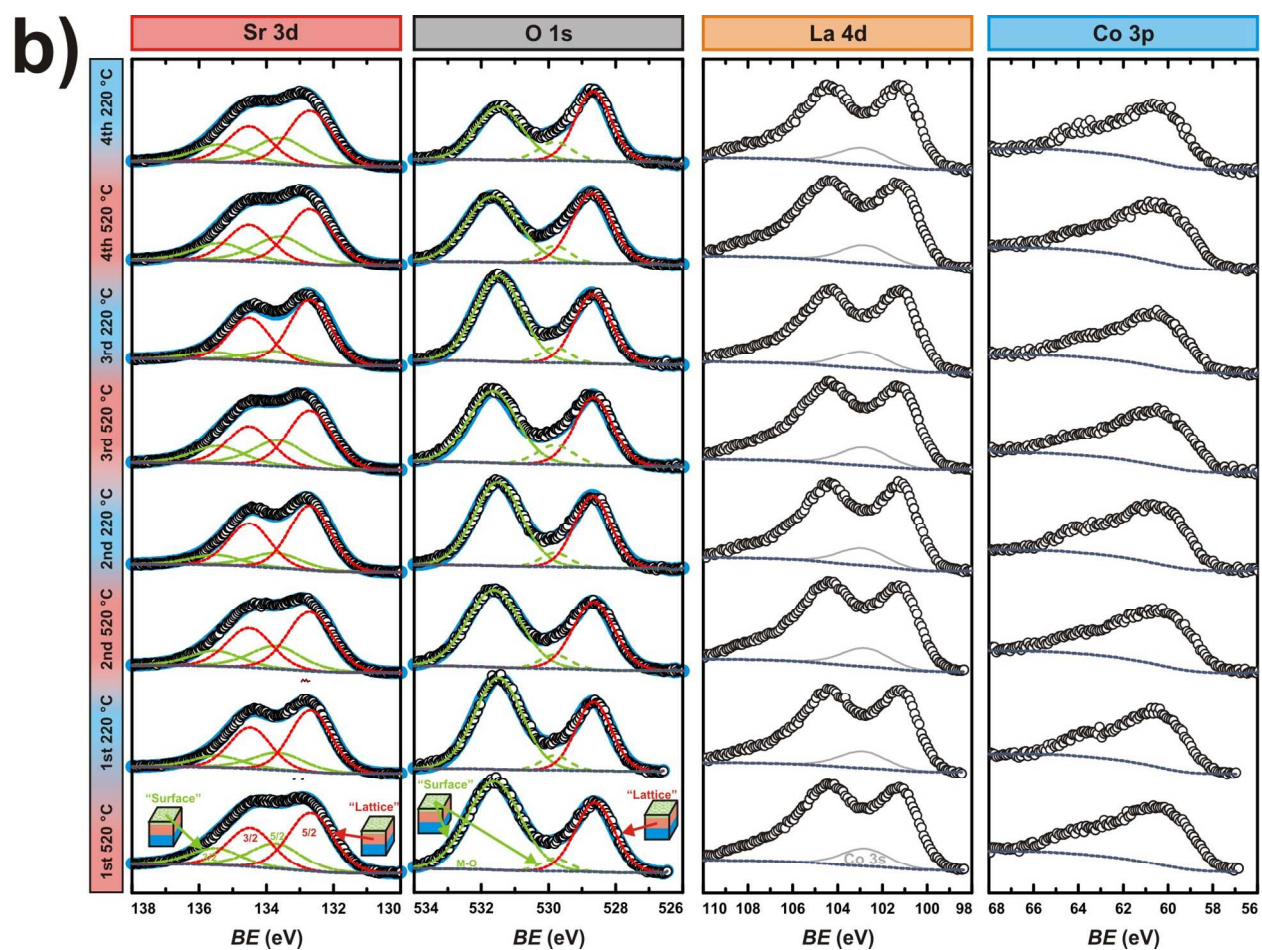


Figure S10b. *In situ* APXPS data of a second piece of 90 nm LSC₁₁₃ film as a function of temperature over multiple temperature cycles. Sr 3d ($E_{\text{photon}} = 390$ eV), O 1s ($E_{\text{photon}} = 690$ eV), La 4d ($E_{\text{photon}} = 390$ eV) and Co 3p ($E_{\text{photon}} = 390$ eV) spectra at 520 °C decreased to 220 °C and subsequent temperature cycles at a $p(\text{O}_2)$ of 1×10^{-3} atm. The “lattice” component of the perovskite structure in the near-surface region is shown in red while the “surface” component for the secondary phases (including both surface components) is shown in green. White circles are for the measured data, blue lines indicate the sum of fits, and grey dotted lines correspond to the background, spectra are normalized to raw spectra max height or ‘lattice’ component when applicable. This sample was used for XRD, XRR, EIS and AES measurements, too.

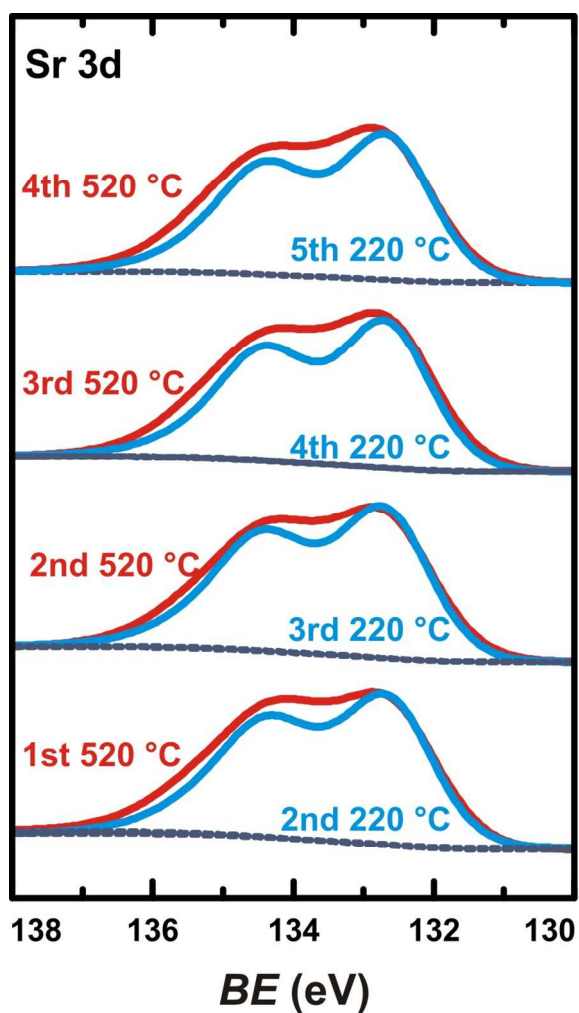


Figure S11. Overlay of *in situ* APXPS Sr 3d ($E_{\text{photon}} = 390$ eV) data of a second piece of 90 nm LSC_{113} film as a function of temperature over multiple temperature cycles at 520 °C decreased to 220 °C and subsequent temperature cycles at a $p(\text{O}_2)$ of 1×10^{-3} atm. This sample was used for XRD, XRR, EIS and AES measurements, too.

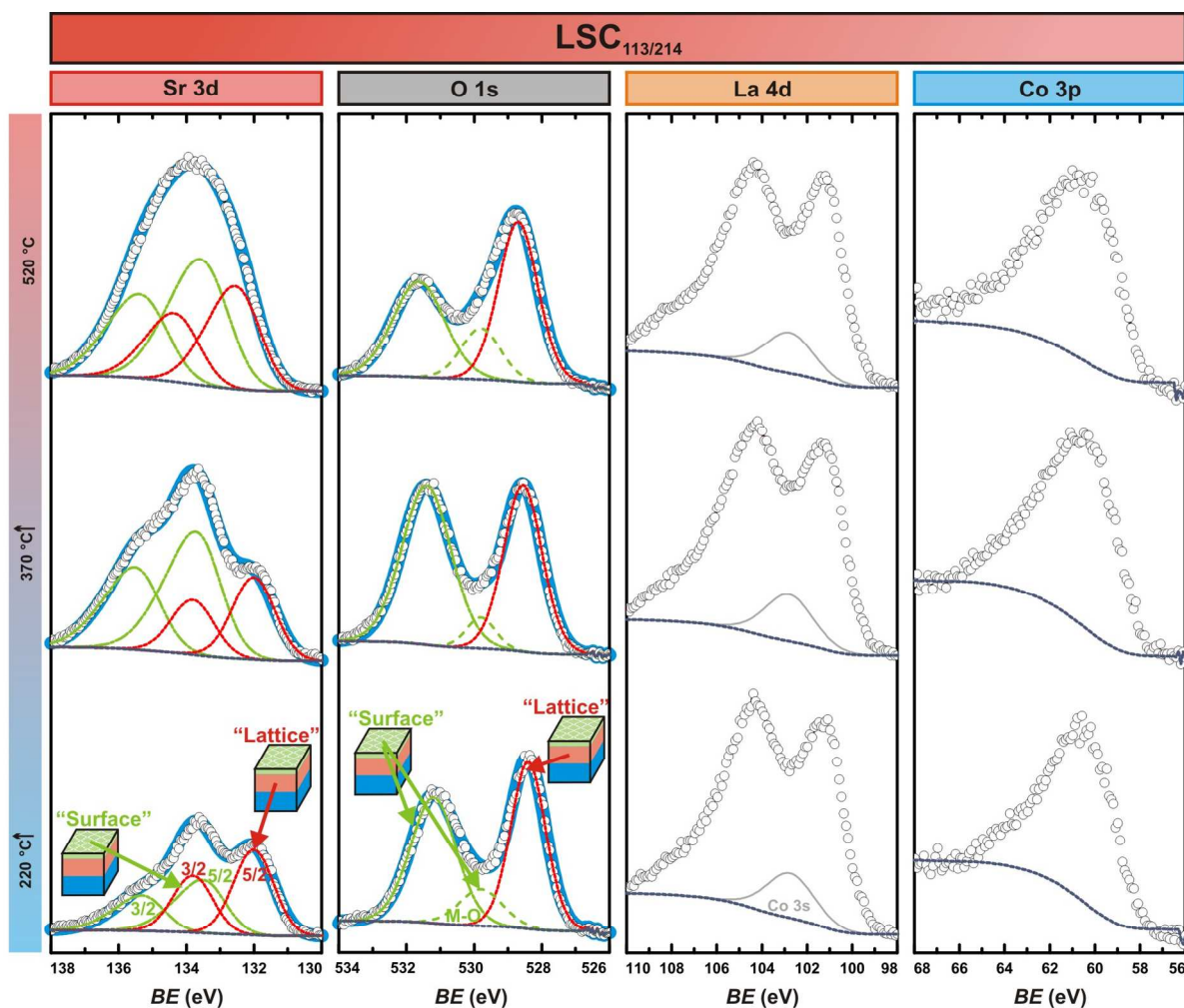


Figure S12. *In situ* APXPS data of a 400-pulse LSC₂₁₄ decorated LSC₁₁₃ film as a function of temperature. Sr 3d ($E_{\text{photon}} = 390$ eV), O 1s ($E_{\text{photon}} = 690$ eV), La 4d ($E_{\text{photon}} = 390$ eV) and Co 3p ($E_{\text{photon}} = 390$ eV) spectra at 220 °C, 370 °C, and 520 °C at $p(\text{O}_2)$ of 1×10^{-3} atm. The “lattice” component of the perovskite structure in the near-surface region is shown in red while the “surface” component for the secondary phases (including both surface components) is shown in green. White circles are for the measured data, blue lines indicate the sum of fits, and grey dotted lines correspond to the background, spectra are normalized to raw spectra max height or ‘lattice’ component when applicable.

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