# Structural studies of perovskite $La_{1-x}Sr_xCoO_{3-\delta}$ during chemical looping with methane

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## Electronic Supplementary Information

### Material Synthesis.

Citric acid was first dissolved in stirring DI water, and stoichiometric amounts of $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, and $Co(NO_3)_2 \cdot 6H_2O$ were dissolved into the same solution, with a 1:3 molar ratio of metal ion to citric acid. Five milliliters of ethylene glycol were added, and the solution was stirred while gently heating for several hours until a thick gel formed. The gel was heated at 300 °C overnight (~12 h). The resulting brown powder was ground in an agate mortar and pestle before being heated at 1200 °C for 48 h, which led to dark gray powders.

### *In situ* Diffraction Experiments Setup

*In situ* synchrotron X-ray powder diffraction (SXRD) experiments were performed in transmission geometry on the 17 BM beamline at the APS (Advanced Photon Source) at Argonne National Laboratory, Lemont, IL, United States. A 2D PerkinElmer a-Si flat panel detector was used with an average wavelength of 0.75009 Å and 0.72768 Å. Fused quartz powder was used to dilute the sample to minimize beam absorption.

Each sample was first characterized with SXRD at room temperature under the air. As for the *in situ* diffraction experiments, two kinds of gas flow experiments were carried out as a function of temperature and atmosphere. A quartz capillary sample holder was used with a gas of choice flowing through at a rate of 15 mL/min. The diffraction patterns were collected every 6.5 seconds. In the first experiment, the samples were heated under air (20 % $O_2$ in He) from RT to 800 °C with 40 °C/min. In the second experiment, after reaching the target temperature, then held at that temperature while the atmosphere was cycled between 100% He (1min), 15% $CH_4$/He (5 min) and 20% Air/He (2 min). Six complete cycles were performed.

$La_{1-x}Sr_xCoO_{3-\delta}$ for $x$ = 0.5 and 0.75. Also, two complete cycles (reduction then reoxidation) were performed for each material at 500, 600, and 700 °C. The atmosphere was cycled between 100% He (2 min), 15% $CH_4$/He (12 min), 100% He (1 min) and 20% Air/He (6 min).

All the resulted 2D images were integrated using GSAS II. [1] And Rietveld refinement was performed using TOPAS 4. [2] .In the refinement, the position of each atoms is fixed. Only lattice parameters are refined. For the initial sample at room temperature, occupancy of La, Sr, Co are also refined to check the element ratio. Though the oxygen occupancy changes across the whole process, we did not refine it mainly because X-ray is not as sensitive to the electron cloud of oxygen atoms as it is for metal cations. In addition, we performed the refinement in order to get unit cell volume information, which is only determined by the diffraction peak position.

For the x = 0.25 and 0.5 samples, we found an impurity that we could index with the phase $LaSrCoO_4$. We estimate it to be in the samples at near 5 to 8 wt.%. For the x =0 sample, we found an impurity phase with very weak reflections near $2\theta$ = 14.4° and 14.7°. We could not index this phase although it may be decomposition products such as $SrCO_3$ and $Co_3O_4$. Based on similar peak intensity of the known impurity $LaSrCoO_4$ in the x=0.25 and 0.5 samples, this unidentified phase may be estimated between 5 to 10 wt. %. Interestingly, after cycling the x = 0.25 and 0.5 samples, the same impurity appears in the diffraction pattern as in $LaCoO_{3-\delta}$. Since the intensity of the new reflections of the unidentified phase are of similar intensity to those of the identified phase $LaSrCoO_4$, we estimate that this new impurity arising from cycling may be between 5 to 10 wt. %.

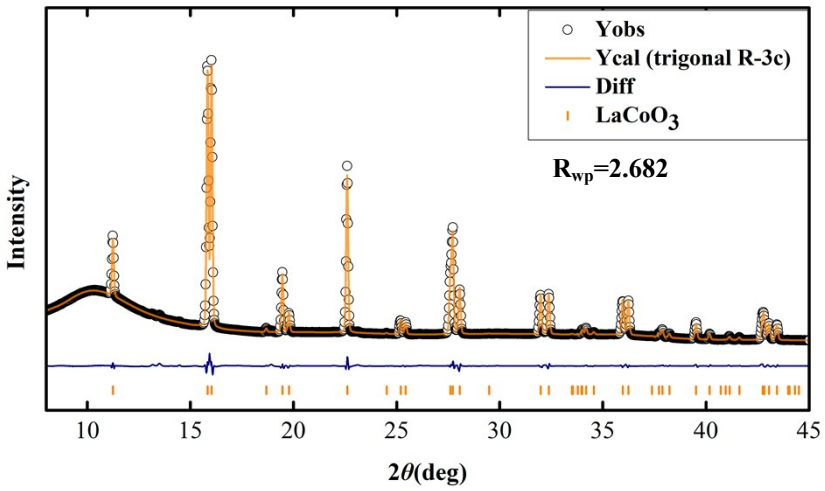


**Figure S1.** SXRD (λ=0.75009 Å) data of synthesized perovskite $LaCoO_3$ at room temperature. Rietveld refinement was performed.

| **$LaCoO_{3-\delta}$** | | | |
|---|---|---|---|
| **Space Group** | *R*-3*c* | | |
| **a (Å)** | 5.44508(7) | | |
| **b (Å)** | | | |
| **c (Å)** | 13.103(2) | | |
| **volume (Å3)** | 336.44(1) | | |
| **$R_{wp}$** | 2.682 | | |
| **Atom** | **Beq (Å²)** | **coordination** | **occupancy** |
| La | 1.643 | x 0.00000<br>y 0.00000<br>z 0.25000 | 1.000(1) |
| Co | 1.262 | x 0.00000<br>y 0.00000<br>z 0.00000 | 1.003(3) |
| O | 2.404 | x 0.45370<br>y 0.00000<br>z 0.25000 | 1 |

**Table S1.** Structural parameters from Rietveld refinement with *in situ* (17-BM) synchrotron X-ray powder diffraction data for the $LaCoO_3$ at room temperature.

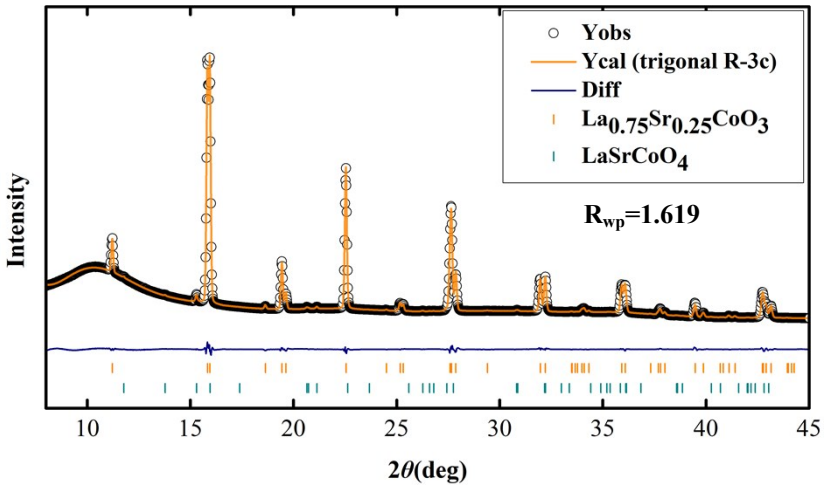


**Figure S2.** SXRD (λ=0.75009 Å) data of synthesized perovskite $La_{0.75}Sr_{0.25}CoO_{3-\delta}$ at room temperature. Very small amount of $LaSrCoO_4$ exists in the samples. Rietveld refinement was performed.

| **$La_{0.75}Sr_{0.25}CoO_{3-\delta}$** | | | |
|---|---|---|---|
| **Space Group** | *R*-3*c* | | |
| **a (Å)** | 5.44672(7) | | |
| **b (Å)** | | | |
| **c (Å)** | 13.1959(1) | | |
| **volume (Å$^3$)** | 339.03(1) | | |
| **weight percent** | 94(3) % | | |
| **$R_{wp}$** | 1.619 | | |
| **Atom** | **Beq (Å$^2$)** | **coordination** | **occupancy** |
| La | 1.11 | x 0.00000<br>y 0.00000<br>z 0.25000 | 0.7450(2) |
| Sr | 6.301 | x 0.00000<br>y 0.00000<br>z 0.25000 | 0.249(4) |
| Co | 1.358 | x 0.00000<br>y 0.00000<br>z 0.00000 | 1.004(3) |
| O | 1.97 | x 0.45370<br>y 0.00000<br>z 0.25000 | 1 |

**Table S2.** Structural parameters from Rietveld refinement with in situ (17-BM) synchrotron X-ray powder diffraction data for the $La_{0.75}Sr_{0.25}CoO_3$ at room temperature.

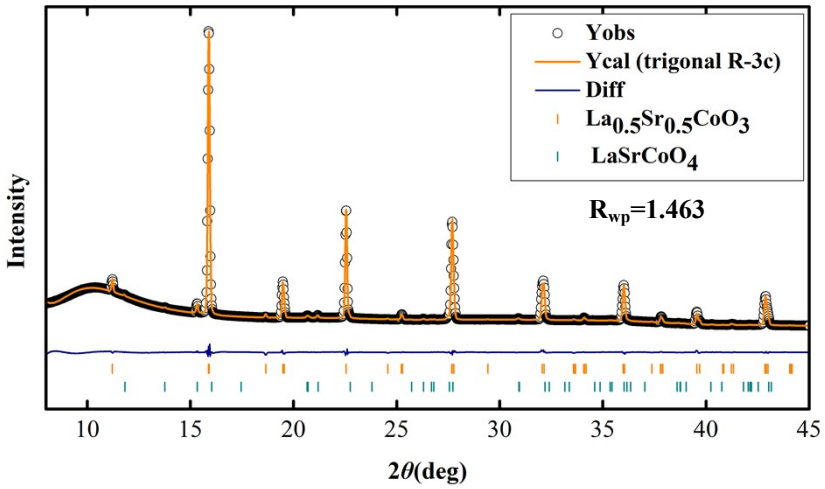


**Figure S3.** SXRD (λ=0.75009 Å) data of synthesized perovskite $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ at room temperature. Very small amount of $LaSrCoO_4$ exists in the samples. Rietveld refinement was performed.

| **$La_{0.5}Sr_{0.5}CoO_{3-\delta}$** | | | |
|---|---|---|---|
| **Space Group** | *R*-3*c* | | |
| **a (Å)** | 5.43110(6) | | |
| **b (Å)** | | | |
| **c (Å)** | 13.2526(2) | | |
| **volume (Å$^3$)** | 338.54(1) | | |
| **weight percent** | 94.6(2) % | | |
| **$R_{wp}$** | 1.463 | | |
| **Atom** | **Beq (Å2)** | **coordination** | **occupancy** |
| La | 0.962 | x 0.00000<br>y 0.00000<br>z 0.25000 | 0.496(2) |
| Sr | 1.302 | x 0.00000<br>y 0.00000<br>z 0.25000 | 0.500(3) |
| Co | 1.183 | x 0.00000<br>y 0.00000<br>z 0.00000 | 1.008(2) |
| O | 0.8313 | x 0.45370<br>y 0.00000<br>z 0.25000 | 1 |

**Table S3.** Structural parameters from Rietveld refinement with in situ (17-BM) synchrotron X-ray powder diffraction data for the $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ at room temperature.

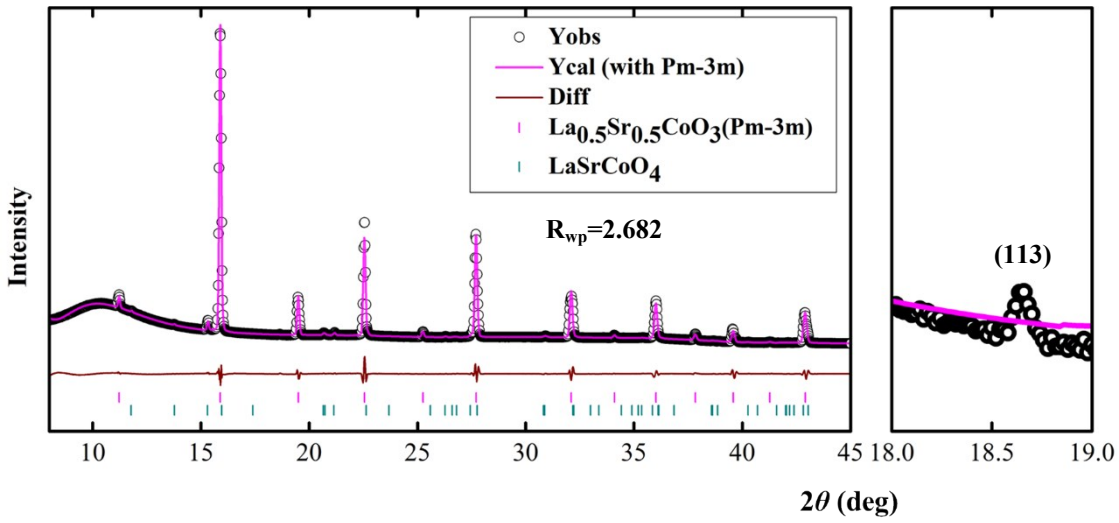


**Figure S4.** SXRD patterns (λ=0.75009 Å) of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$, as well as its Rietveld refined patterns which is refined with cubic $Pm\bar{3}m$ symmetry. The mismatch at 113 plane (2θ ~18.7°) indicates the phase is not $Pm\bar{3}m$. instead, the phase is $R\bar{3}c$.

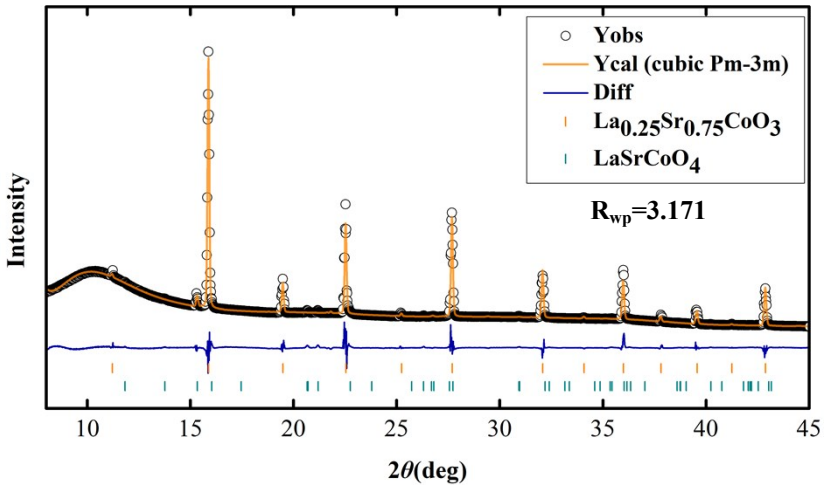


**Figure S5.** SXRD (λ=0.75009 Å) data of synthesized perovskite $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ at room temperature. Very small amount of $LaSrCoO_4$ exists in the samples. Rietveld refinement was performed.

| **$La_{0.25}Sr_{0.75}CoO_{3-\delta}$** | | | |
|---|---|---|---|
| **Space Group** | *Pm*-3*m* | | |
| **a (Å)** | 3.8383(1) | | |
| **b (Å)** | | | |
| **c (Å)** | | | |
| **volume (Å$^3$)** | 56.546(5) | | |
| **weight percent** | 93(5)% | | |
| **$R_{wp}$** | 3.171 | | |
| **Atom** | **Beq (Å2)** | **coordination** | **occupancy** |
| La occ=0.25 | 1.118 | x 0.50000<br>y 0.50000<br>z 0.50000 | 0.253(8) |
| Sr occ=0.75 | 0.9274 | x 0.50000<br>y 0.50000<br>z 0.50000 | 0.75(1) |
| Co | 0.9539 | x 0.00000<br>y 0.00000<br>z 0.00000 | 1.012(3) |
| O | 2.865 | x 0.00000<br>y 0.00000<br>z 0.50000 | 1 |

**Table S4.** Structural parameters from Rietveld refinement with in situ (17-BM) synchrotron X-ray powder diffraction data for the $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ at room temperature.

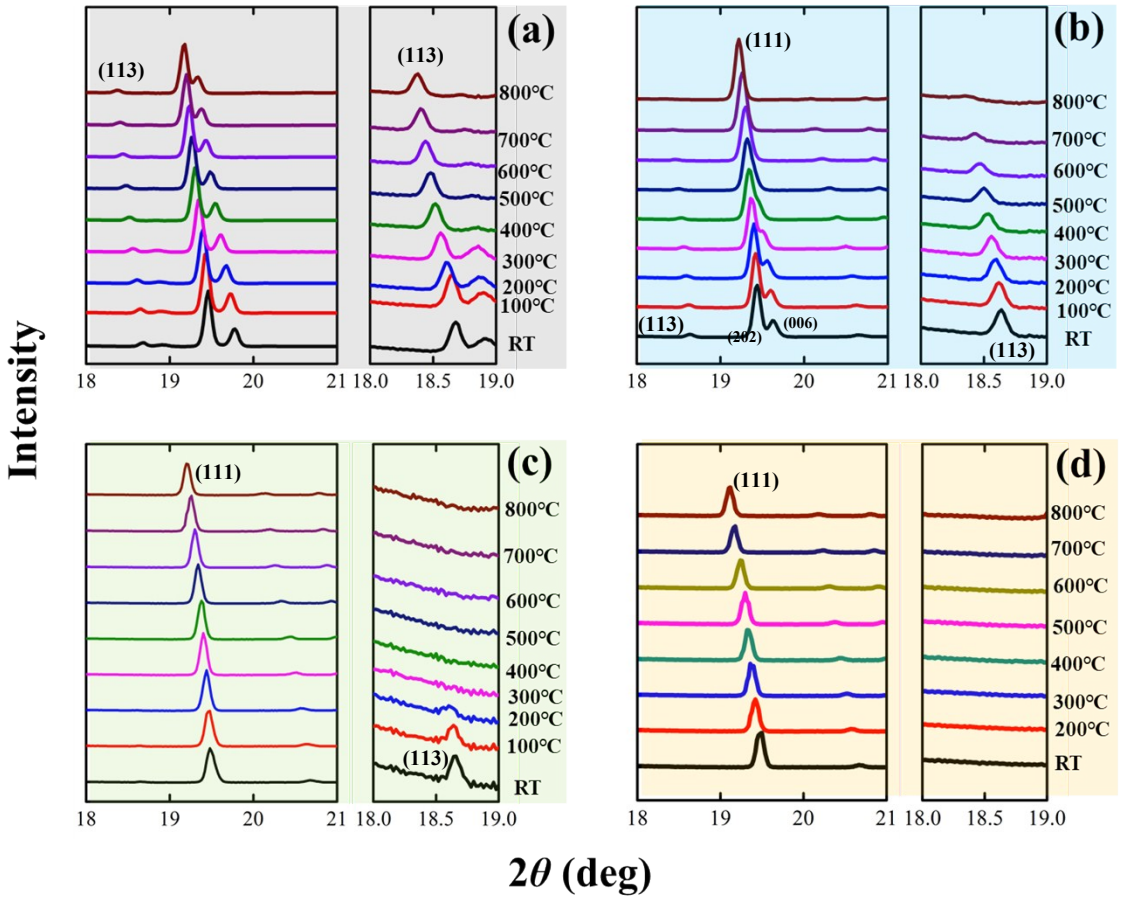


**Figure S6.** SXRD (λ=0.75009 Å) patterns evolution of $La_{1-x}Sr_xCoO_{3-\delta}$ (x=0, 0.25, 0.5, 0.75) under air from room temperature to 800 °C. (a) x=0, (b) x=0.25, (c) x=0.5, (d) x=0.75. $La_{1-x}Sr_xCoO_{3-\delta}$ (x=0.25, 0.5) experienced a phase transition from $R\bar{3}c$ to $Pm\bar{3}m$ upon heating. RT stands for room temperature.

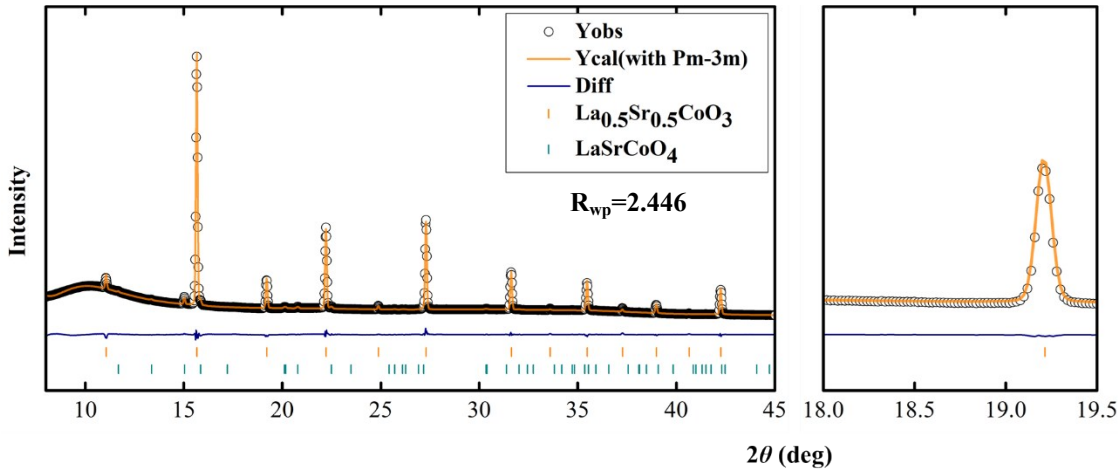


**Figure S7.** SXRD (λ=0.75009 Å) patterns of $La_{0.75}Sr_{0.25}O_{3-\delta}$ at 800 °C under air. The pattern is refined with $Pm\bar{3}m$ symmetry.

| **$La_{0.75}Sr_{0.25}CoO_{3-\delta}$** | **800°C in Air** | | |
|---|---|---|---|
| **Space Group** | *Pm*-3*m* | | |
| **a (Å)** | 3.89081(2) | | |
| **b (Å)** | | | |
| **c (Å)** | | | |
| **weight percent** | 98.3(3) % | | |
| **$R_{wp}$** | 2.446 | | |
| **volume (Å$^3$)** | 58.9008(9) | | |
| | **Atom** | **Beq (Å$^2$)** | **coordination** |
| | La occ=0.75 | 1.509 | x 0.50000<br>y 0.50000<br>z 0.50000 |
| | Sr occ=0.25 | 1.291 | x 0.50000<br>y 0.50000<br>z 0.50000 |
| | Co | 1.49 | x 0.00000<br>y 0.00000<br>z 0.00000 |
| | O | 2.345 | x 0.00000<br>y 0.00000<br>z 0.50000 |

**Table S5.** Structural parameters from Rietveld refinement with in situ (17-BM) synchrotron X-ray powder diffraction data for the $La_{0.75}Sr_{0.25}CoO_3$ at 800°C.

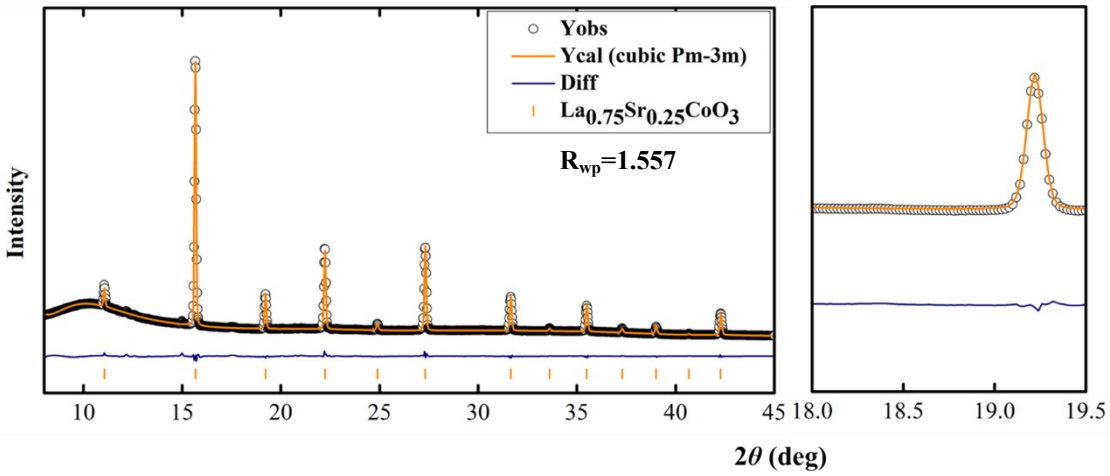


**Figure S8.** SXRD (λ=0.75009 Å) patterns of $La_{0.5}Sr_{0.5}O_{3-\delta}$ at 800 °C under air. The pattern is refined with *Pm* $\bar{3}m$ symmetry.

| $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ | **800°C in Air** | | |
|---|---|---|---|
| **Space Group** | *Pm*-3*m* | | |
| **a (Å)** | 3.89219(3) | | |
| **b (Å)** | | | |
| **c (Å)** | | | |
| **volume (Å³)** | 58.964(2) | | |
| **weight percent** | 94.9(2) % | | |
| **$R_{wp}$** | 1.557 | | |
| | **Atom** | **Beq (Å²)** | **coordination** |
| | La occ=0.5 | 2.771 | x 0.50000<br>y 0.50000<br>z 0.50000 |
| | Sr occ=0.5 | 2.722 | x 0.50000<br>y 0.50000<br>z 0.50000 |
| | Co | 0.3642 | x 0.00000<br>y 0.00000<br>z 0.00000 |
| | O | 2.972 | x 0.00000<br>y 0.00000<br>z 0.50000 |

**Table S6.** Structural parameters from Rietveld refinement with in situ (17-BM) synchrotron X-ray powder diffraction data for the $La_{0.5}Sr_{0.5}CoO_3$ at 800°C.

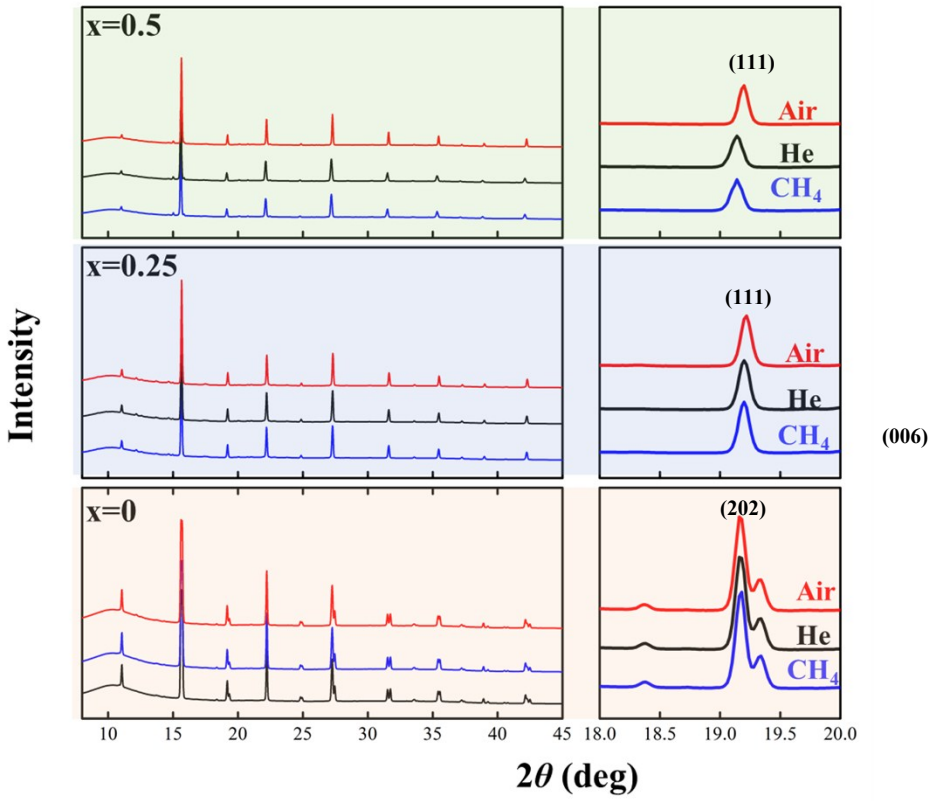


**Figure S9.** SXRD (λ=0.75009 Å) data of $La_{1-x}Sr_xCoO_{3-\delta}$ (x=0, 0.25, 0.5) under He/$CH_4$/air atmosphere at 800 °C within one chemical looping cycle. No phase transition was observed. Each pattern was collected just before switching the gas flow.

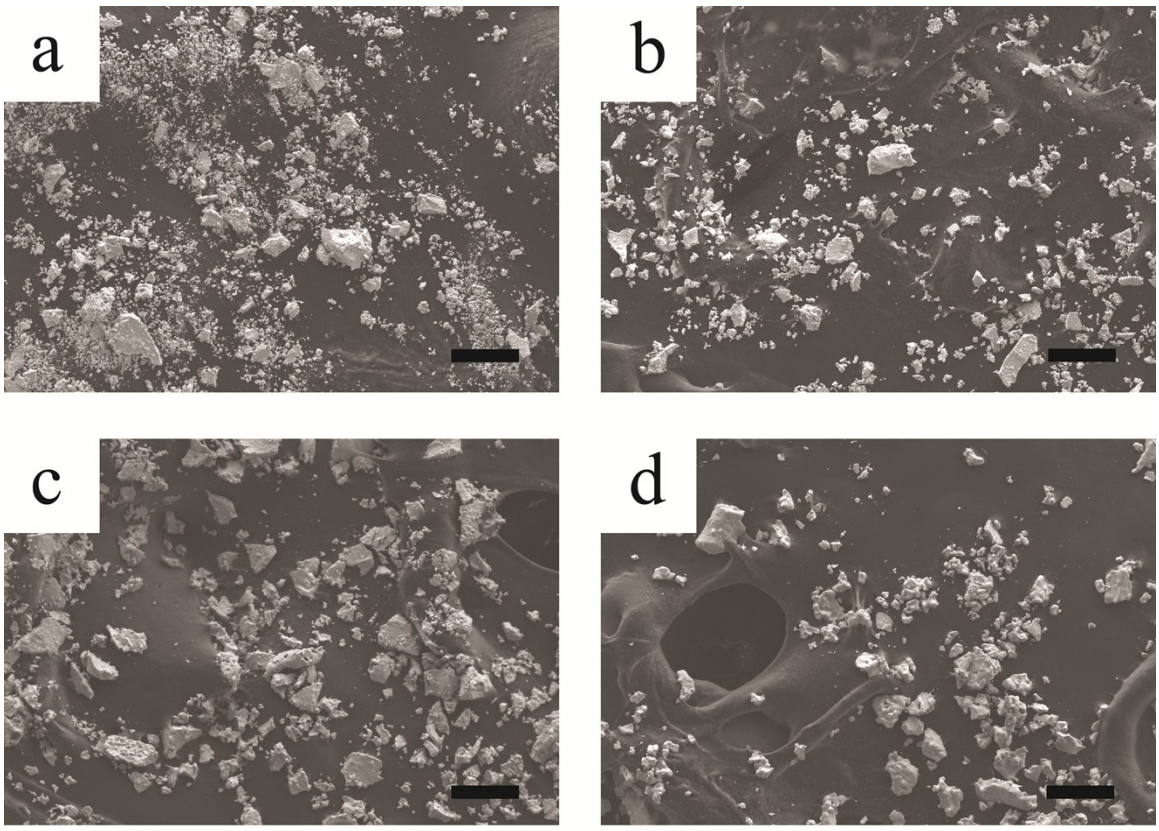


**Figure S10.** SEM image of $La_{1-x}Sr_xCoO_{3-\delta}$ samples: (a) x=0; (b) x=0.25; (c) x=0.5; (d) x=0.75. Scale bar as 50 μm.

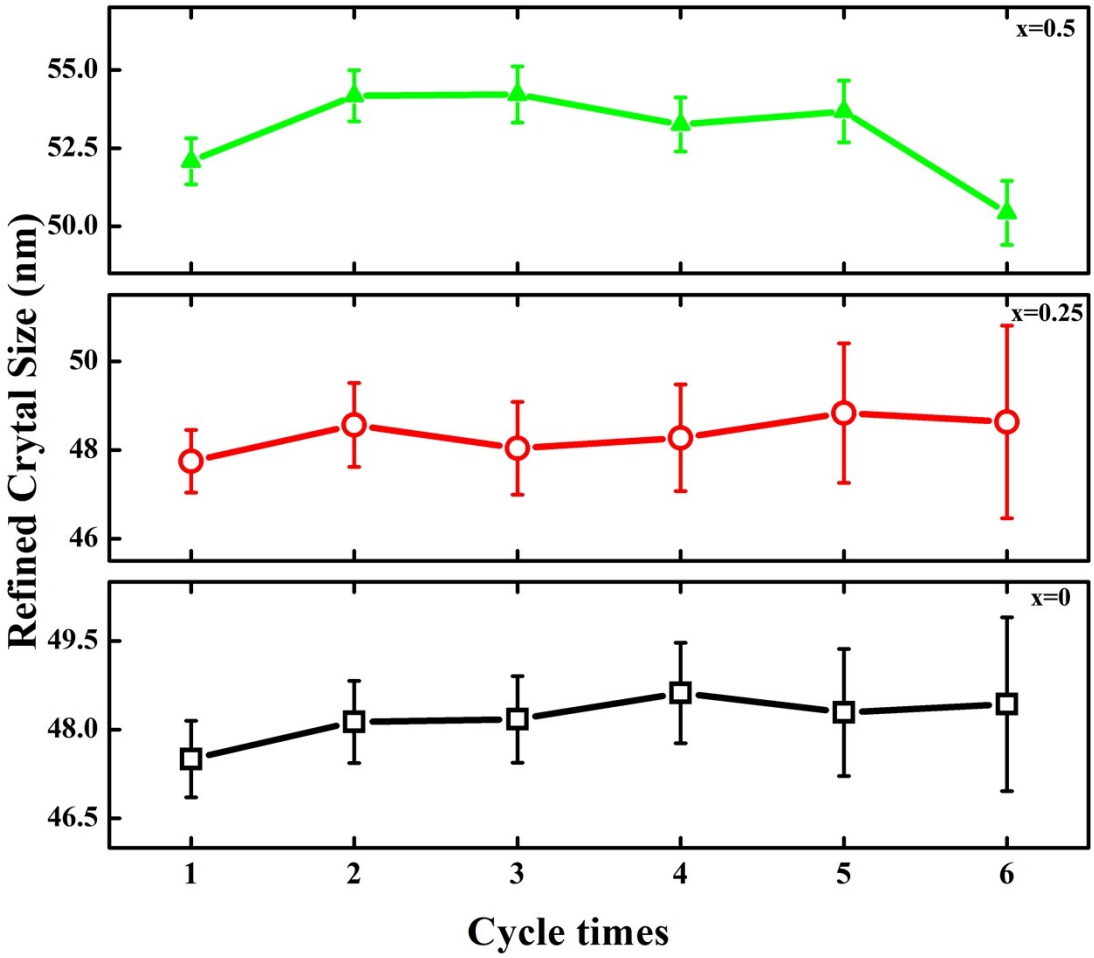


**Figure S11.** Refined Crystal grain size at end of each chemical looping cycles on $La_{1-x}Sr_xCoO_{3-\delta}$ for $x$ = 0, 0.25, and 0.5. The refinement results are based on peak shape of *in situ* SXRD patterns (λ=0.75009Å).

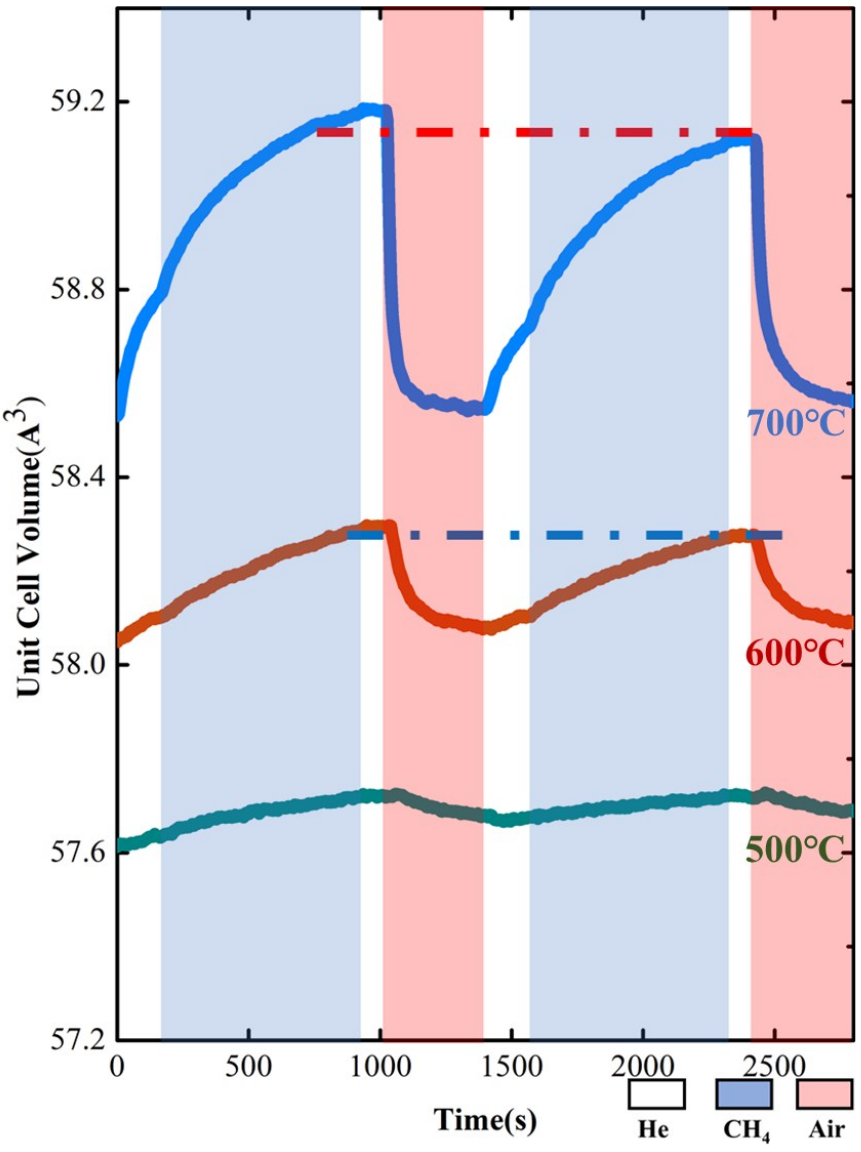


**Figure S12.** Refined unit cell volume, from in situ SXRD experiment (λ=0.72768Å) for $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ for two chemical looping cycles at 500 °C, 600 °C and 700 °C. The patterns are refined with $Pm\bar{3}m$ symmetry.

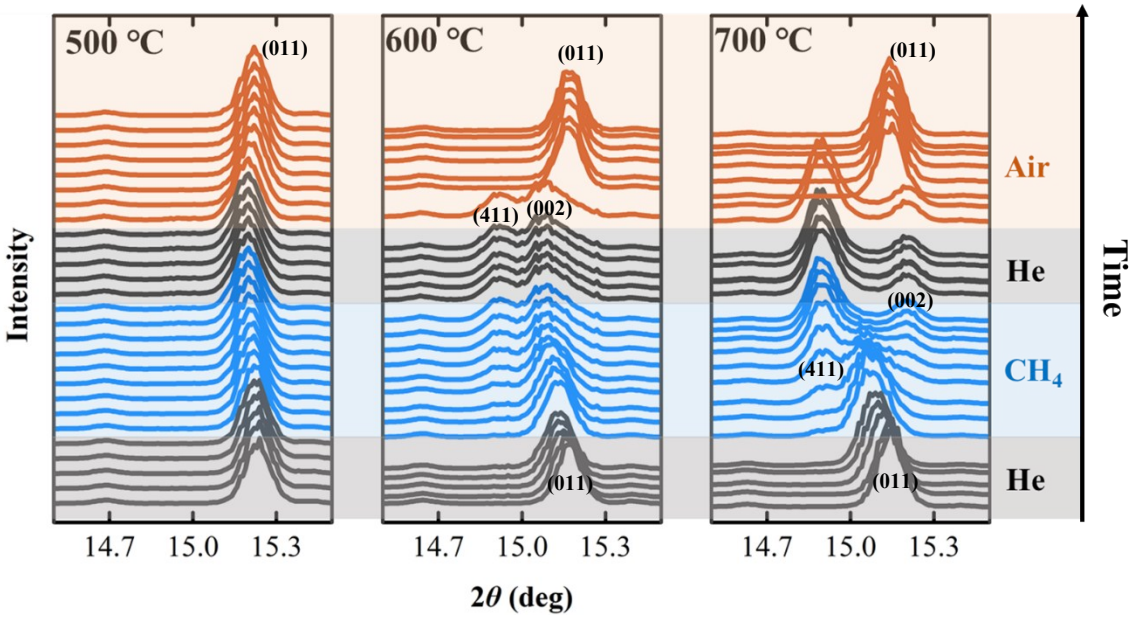


**Figure S13.** SXRD (λ=0.72768 Å) data of $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ under He/$CH_4$/air atmosphere at 500 °C, 600 °C and 700 °C within one chemical looping cycle.

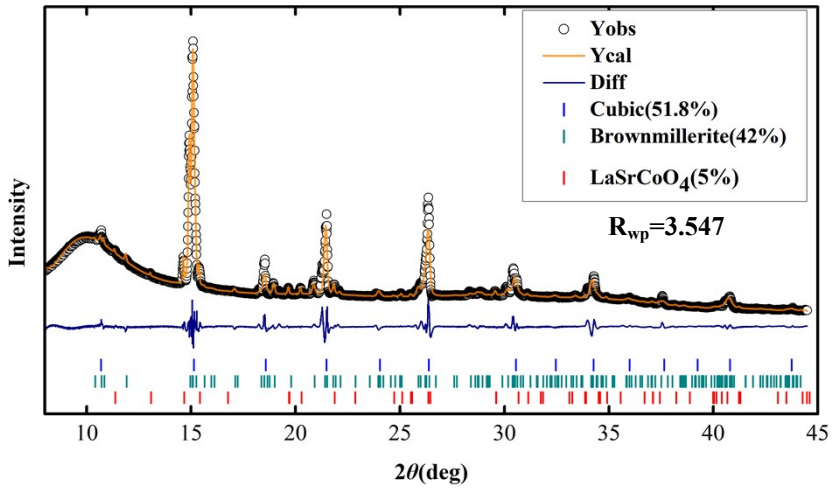


**Figure S14.** SXRD (λ=0.72768 Å) data of $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ under $CH_4$ flow at 600 °C. Both cubic $Pm\bar{3}m$ and brownmillerite *Ima*2 phase exist. Rietveld refinement was performed.

| $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ | 600°C in Methane | | | | | |
|---|---|---|---|---|---|---|
| **Space Group** | *Pm*-3*m* | | | *Ima*2 | | |
| **a (Å)** | 3.9027(3) | | | 16.538(2) | | |
| **b (Å)** | | | | 5.712(1) | | |
| **c (Å)** | | | | 5.6523(8) | | |
| **volume (Å$^3$)** | 59.44(2) | | | 534.0(1) | | |
| **weight percent** | 52(2) % | | | 43(2)% | | |
| **Rwp** | 3.547 | | | | | |
| | **Atom** | **Beq (Å$^2$)** | **coordination** | **Atom** | **Beq (Å$^2$)** | **coordination** |
| | La occ=0.25 | 2.643 | x 0.50000 | La occ=0.25 | 2.831 | x 0.11040 |
| | | | y 0.50000 | | | y 0.01110 |
| | | | z 0.50000 | | | z 0.51700 |
| | Sr occ=0.75 | 2.477 | x 0.50000 | Sr occ=0.75 | 2.724 | x 0.11040 |
| | | | y 0.50000 | | | y 0.01110 |
| | | | z 0.50000 | | | z 0.51700 |
| | Co | 2.931 | x 0.00000 | Co1 | 1.962 | x 0.00000 |
| | | | y 0.00000 | | | y 0.00000 |
| | | | z 0.00000 | | | z 0.00000 |
| | O | 10.7 | x 0.00000 | Co2 | 6.075 | x 0.25000 |
| | | | y 0.00000 | | | y 0.94200 |
| | | | z 0.50000 | | | z 0.04500 |
| | | | | O1 | 1.571 | x 0.99510 |
| | | | | | | y 0.24390 |
| | | | | | | z 0.25300 |
| | | | | O2 | 20 | x 0.14070 |
| | | | | | | y 0.04080 |
| | | | | | | z 0.01800 |
| | | | | O3 | 20 | x 0.25000 |
| | | | | | | y 0.87050 |
| | | | | | | z 0.06410 |

**Table S7.** Structural parameters from Rietveld refinement with in situ (17-BM) synchrotron X-ray powder diffraction data for the $La_{0.25}Sr_{0.75}CoO_3$ at 600°C.

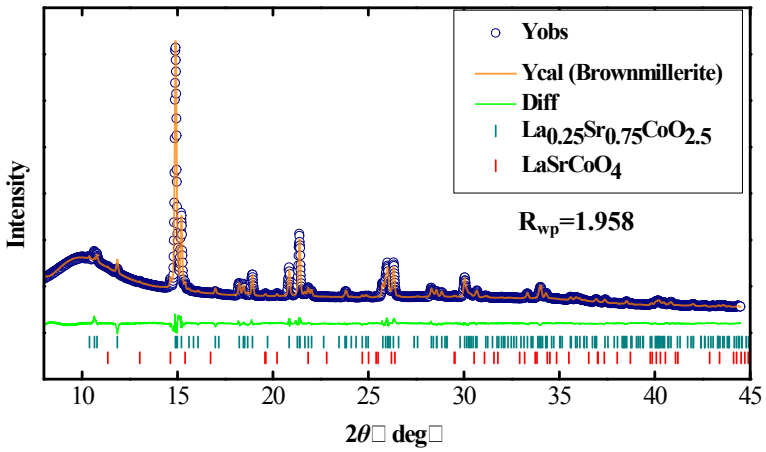


**Figure S15.** SXRD (λ=0.72768 Å) data of $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ under $CH_4$ flow 700 °C. The sample completely transformed to brownmillerite Ima2 phase. Rietveld refinement was performed.

| **$La_{0.25}Sr_{0.75}CoO_{3-\delta}$** | **700°C in Methane** | | |
|---|---|---|---|
| **Space Group** | *Ima*2 | | |
| **a (Å)** | 16.0868(7) | | |
| **b (Å)** | 5.5949(2) | | |
| **c (Å)** | 5.4986(2) | | |
| **volume (Å$^3$)** | 494.90(3) | | |
| **weight percent** | 88(2) % | | |
| **$R_{wp}$** | 1.958 | | |
| | **Atom** | **Beq (Å$^2$)** | **coordination** |
| | La occ=0.25 | 2.525 | x 0.11040<br>y 0.01110<br>z 0.51700 |
| | Sr occ=0.75 | 2.305 | x 0.11040<br>y 0.01110<br>z 0.51700 |
| | Co1 | 1.804 | x 0.00000<br>y 0.00000<br>z 0.00000 |
| | Co2 | 3.014 | x 0.25000<br>y 0.94200<br>z 0.04500 |
| | O1 | 2.3 | x 0.99510<br>y 0.24390<br>z 0.25300 |
| | O2 | 5.096 | x 0.14070<br>y 0.04080<br>z 0.01800 |
| | O3 | 20 | x 0.25000<br>y 0.87050<br>z 0.06410 |

**Table S8.** Structural parameters from Rietveld refinement with in situ (17-BM) synchrotron X-ray powder diffraction data for the $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ at 700°C.

## References


(1) B. H. Toby and R. B. Von Dreele, *J. Appl. Crystallogr.* 2013, **46**, 544–549.

(2) B. Y. R. W. Cheary and A. Coelho, *J. Appl. Cryst.*, 1992, **25**, 109–121.