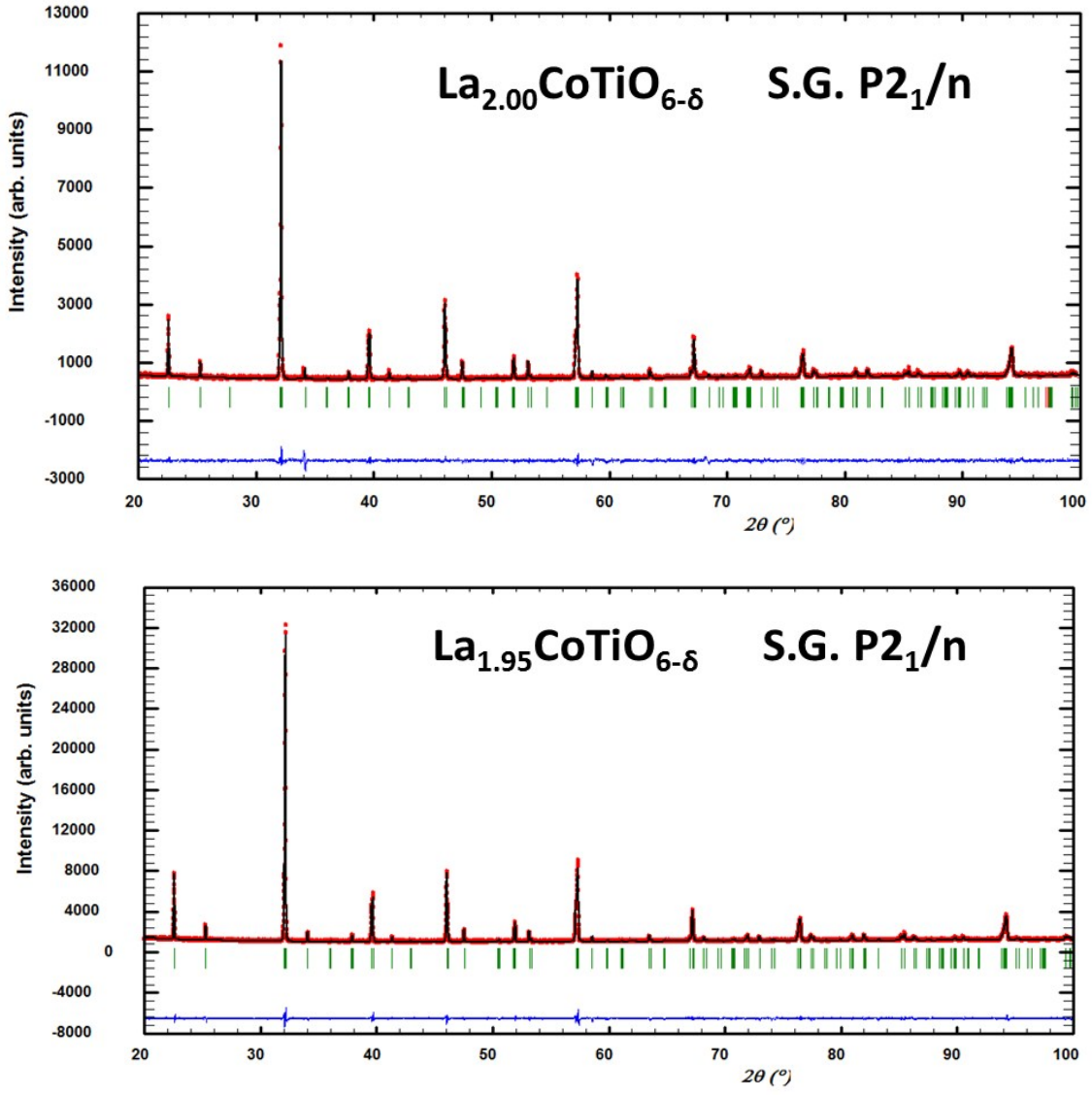
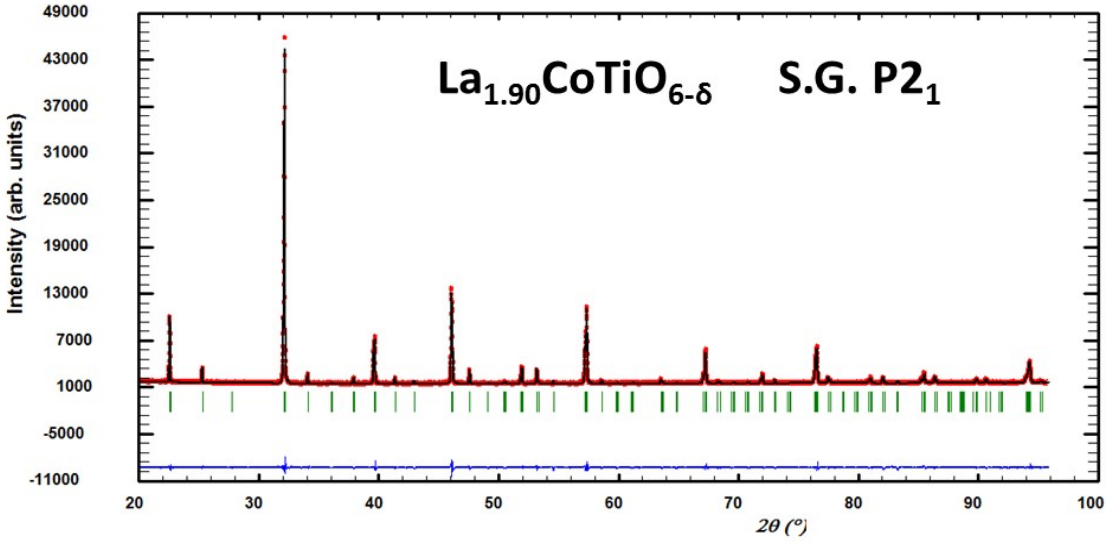
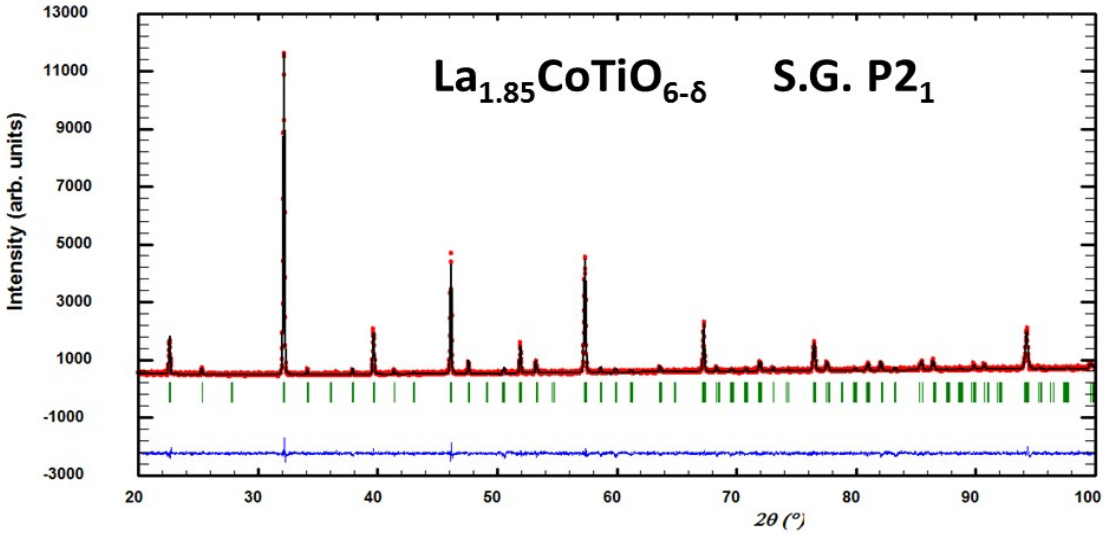
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

The A-cation Deficient Perovskite Series $La_{2-x}CoTiO_{6-\delta}$ ($0 \leq x \leq 0.20$): New Components for Potential SOFC Composite Cathodes

Alejandro Gómez-Pérez[*,a], M.Teresa Azcondo[a], Mercedes Yuste[a], Juan Carlos Pérez-Flores[a], Nikolaos Bonanos[b], Florence Porcher[c], Alvaro Muñoz-Noval[d], Markus Hoelzel[e], Flaviano García-Alvarado[*,a] and Ulises Amador[a].




La1.90CoTiO6-δ S.G. P21
Intensity (arb. units)
49000
43000
37000
31000
25000
19000
13000
7000
1000
-5000
-11000
20
30
40
50
60
70
80
90
100
2θ (°)


La1.85CoTiO6-δ S.G. P21
Intensity (arb. units)
13000
11000
9000
7000
5000
3000
1000
-1000
-3000
20
30
40
50
60
70
80
90
100
2θ (°)

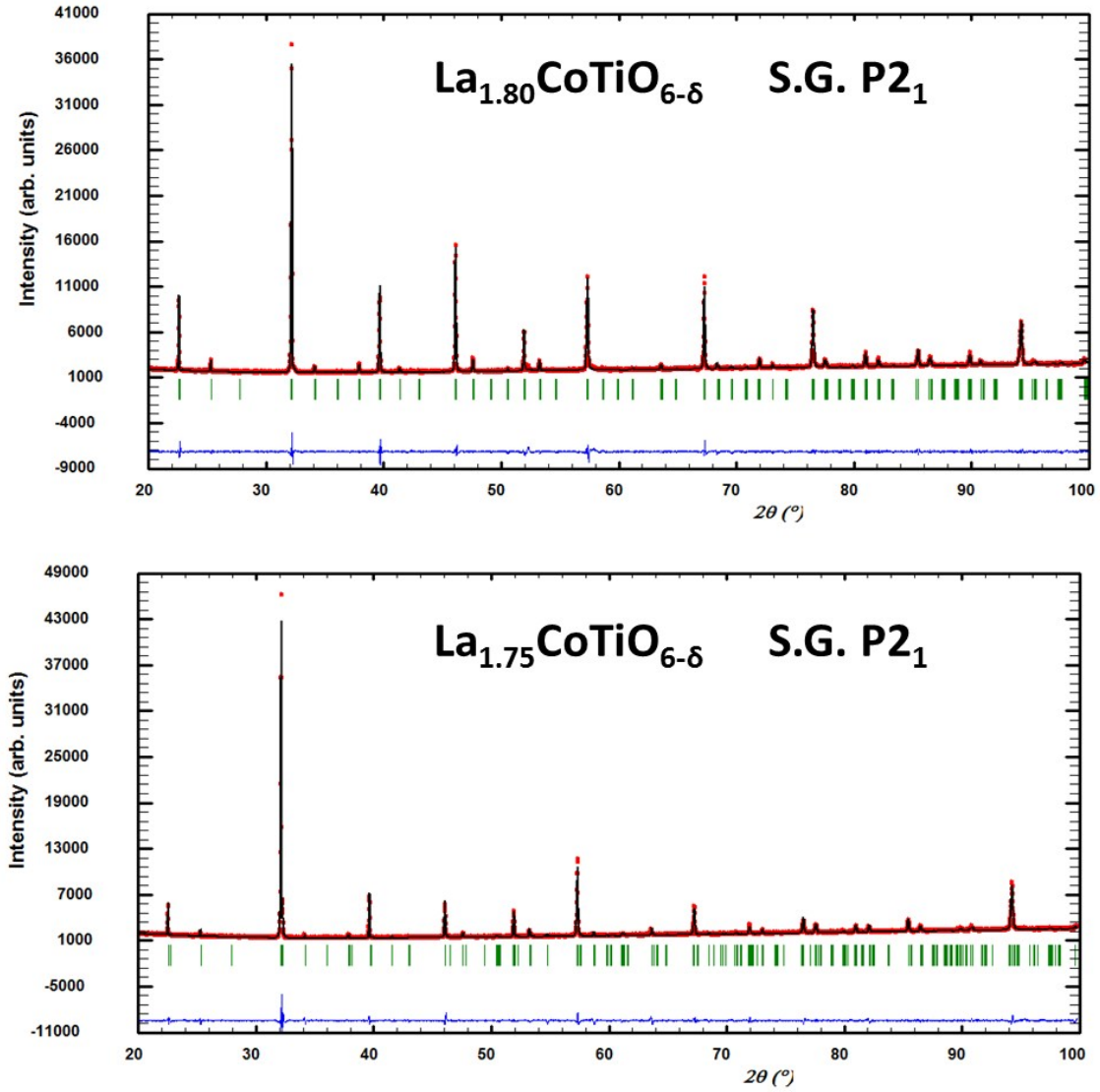


Figure SI 1: Experimental (red circles) and calculated (black continuous line) XRD patterns at RT (and their difference, blue line at the bottom) for $La_{2-x}CoTiO_{6-\delta}$ ($0 \leq x \leq 0.25$) series. Green vertical bars indicate the positions of the Bragg peaks of the phases.

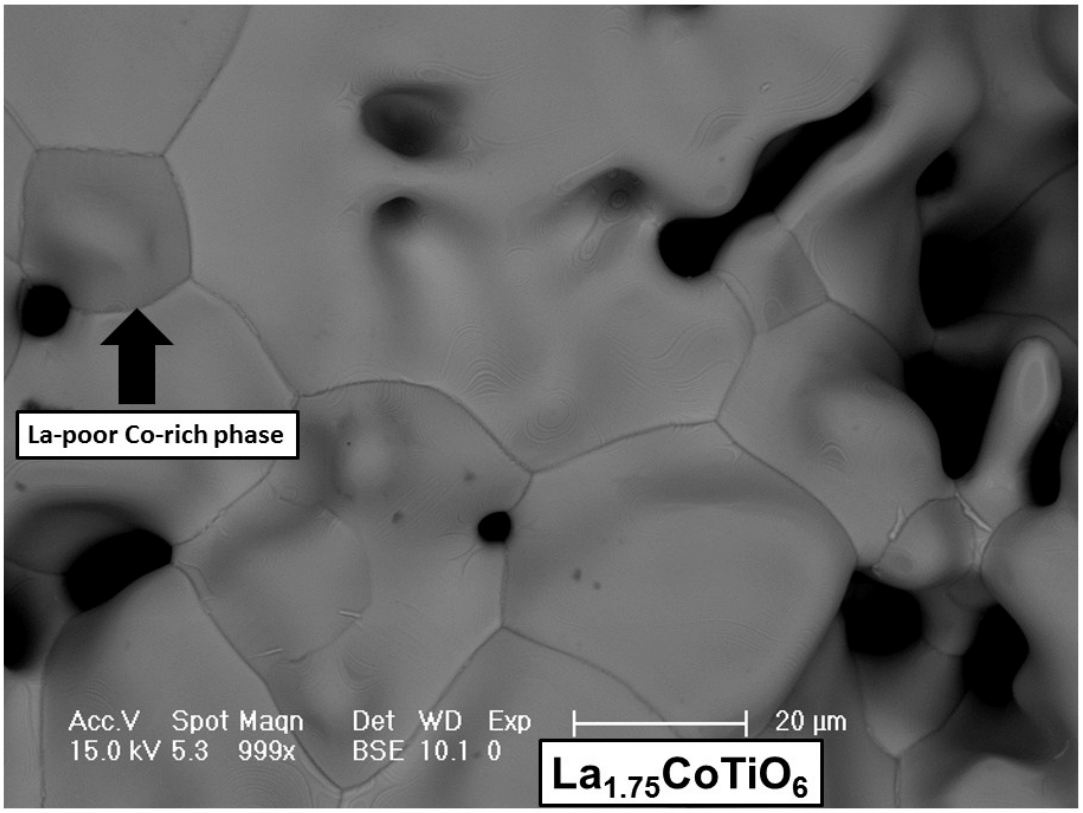


Figure SI 2: Back-scattered electron scanning image of a pellet of $La_{1.75}CoTiO_6$ showing a La-poor Co-rich segregated particle.

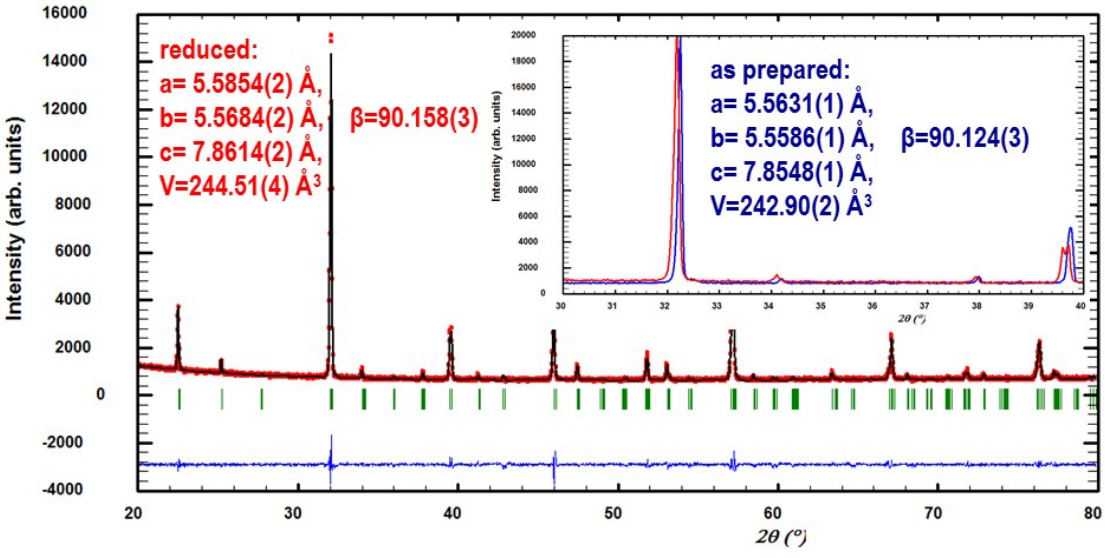


Figure SI 3: Experimental (red circles) and calculated (black continuous line) XRD patterns at RT (and their difference, blue line at the bottom) of a sample of composition $La_{1.80}CoTiO_{6-\delta}$ reduced at pO_2 10^{-25} atm. for a week. Green vertical bars indicate the positions of the Bragg peaks of the phases. In the inset a comparison with as-prepared sample (blue line) of the same batch is depicted.

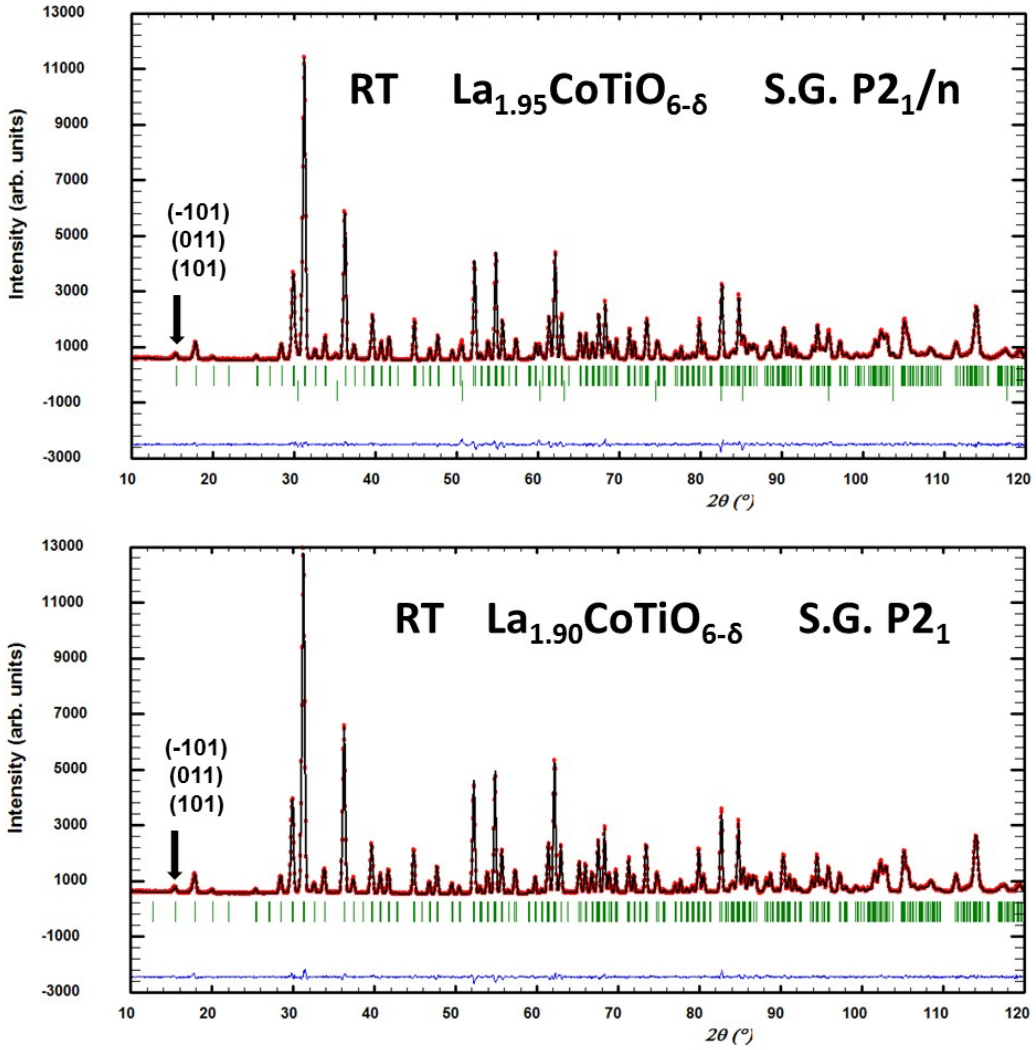


Figure SI 4: Experimental (red circles) and calculated (black continuous line) NPD patterns at RT (and their difference, blue line at the bottom) for $La_{2-x}CoTiO_{6-\delta}$ (x= 0.05 and 0.1). Green vertical bars indicate the positions of the Bragg peaks of the phase; in some cases very weak peaks due to Al of the experimental setup are observed (second row of bars).

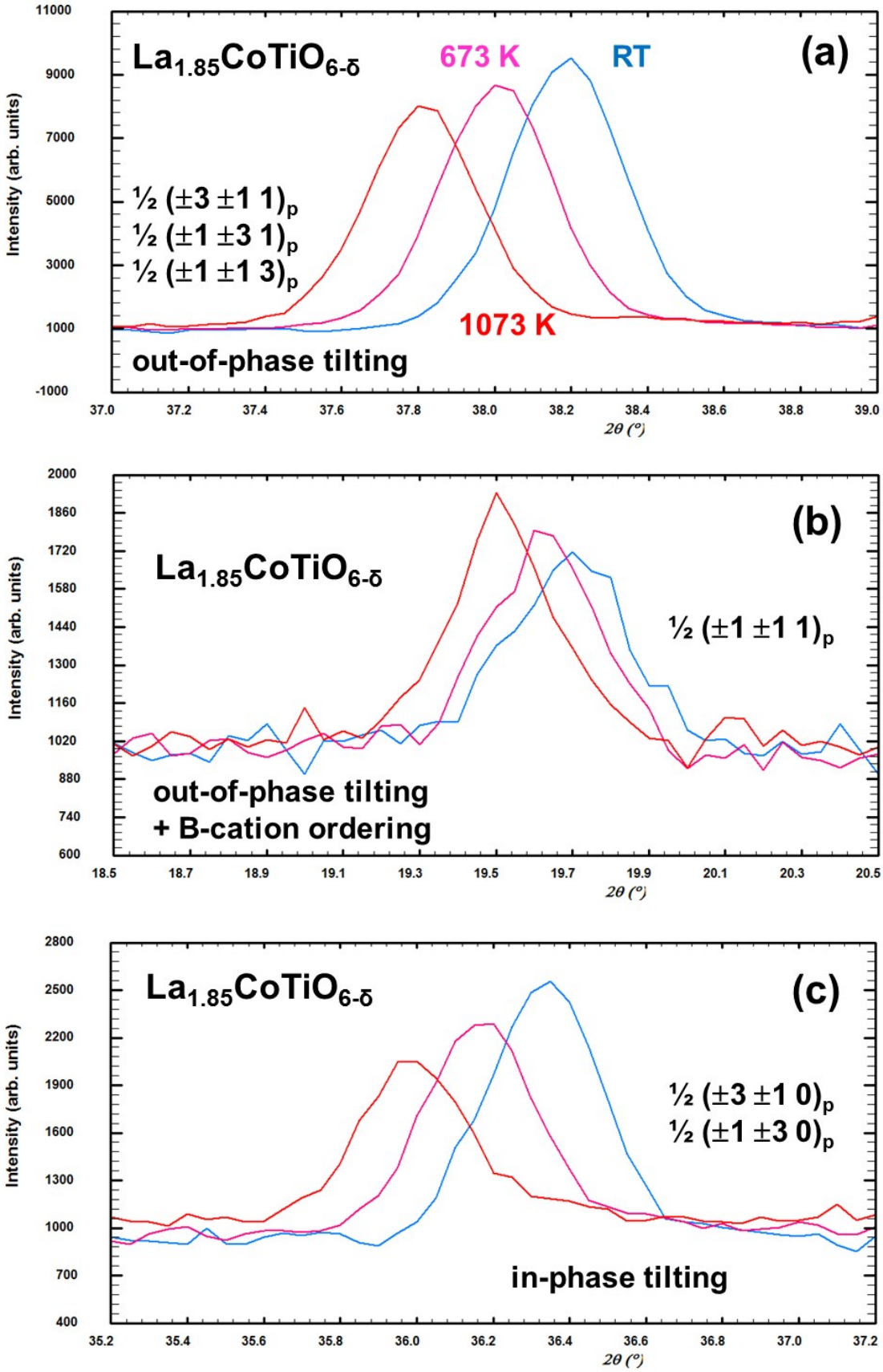


Figure SI 5: Thermal evolution of NPD super-structure peaks of $La_{1.85}CoTiO_{6-\delta}$ related to (a) out-of-phase octahedral tilting, (b) B-cation ordering and (c) in-phase tilting.

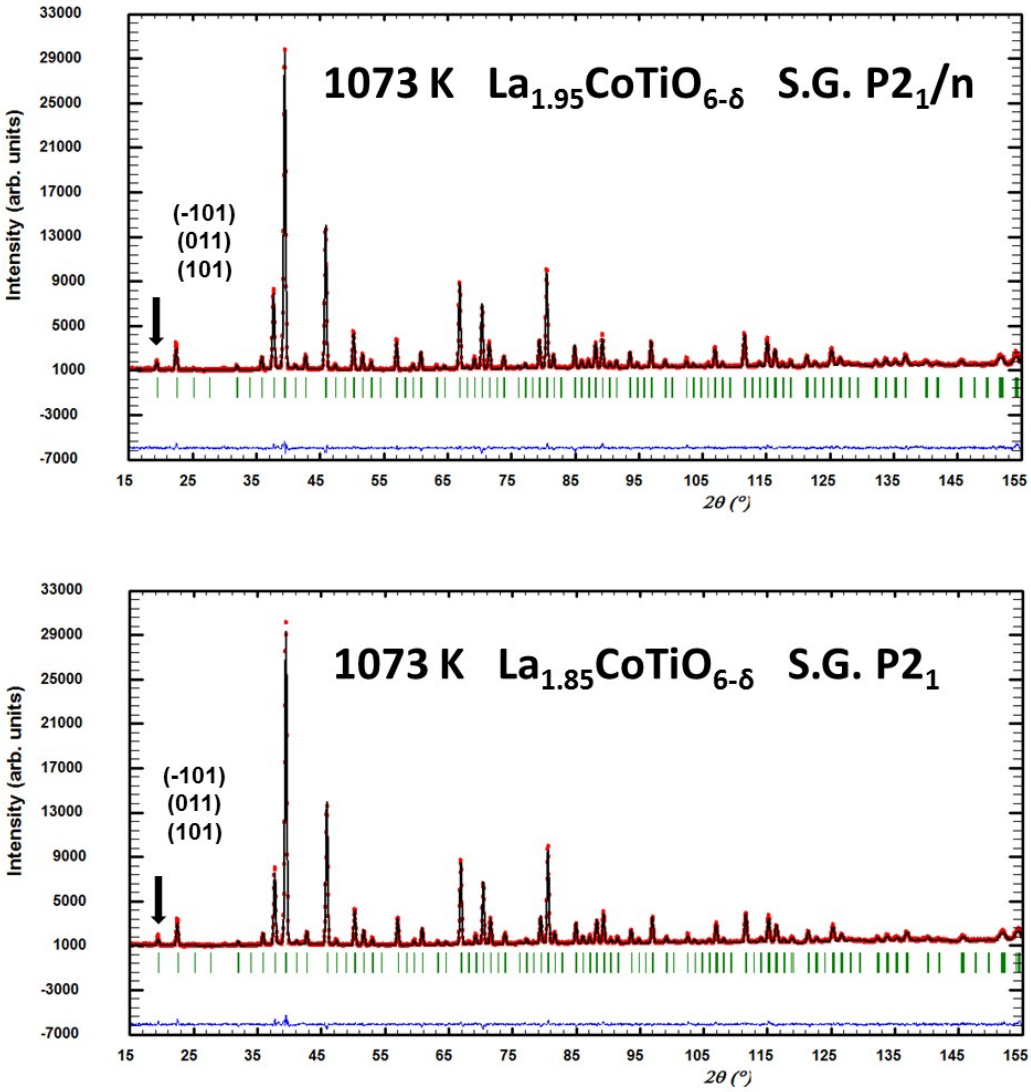


Figure SI 6: Experimental (red circles) and calculated (black continuous line) NPD patterns at 1073 K (and their difference, blue line at the bottom) for $La_{2-x}CoTiO_{6-\delta}$ (x= 0.05 and 0.15). Green vertical bars indicate the positions of the Bragg peaks of the phases.

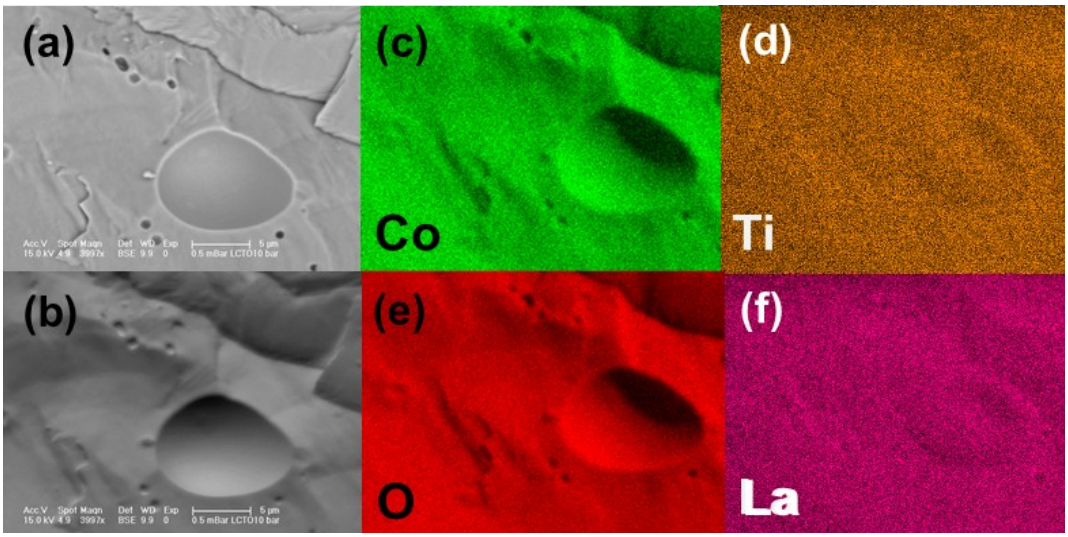


Figure SI 7: Backscattered electron micrograph (a), topographic image (b) and elemental distribution (c-f) inside a bar of a sample with composition $La_{1.80}CoTiO_{6-\delta}$ after electrical measurements under reducing conditions.

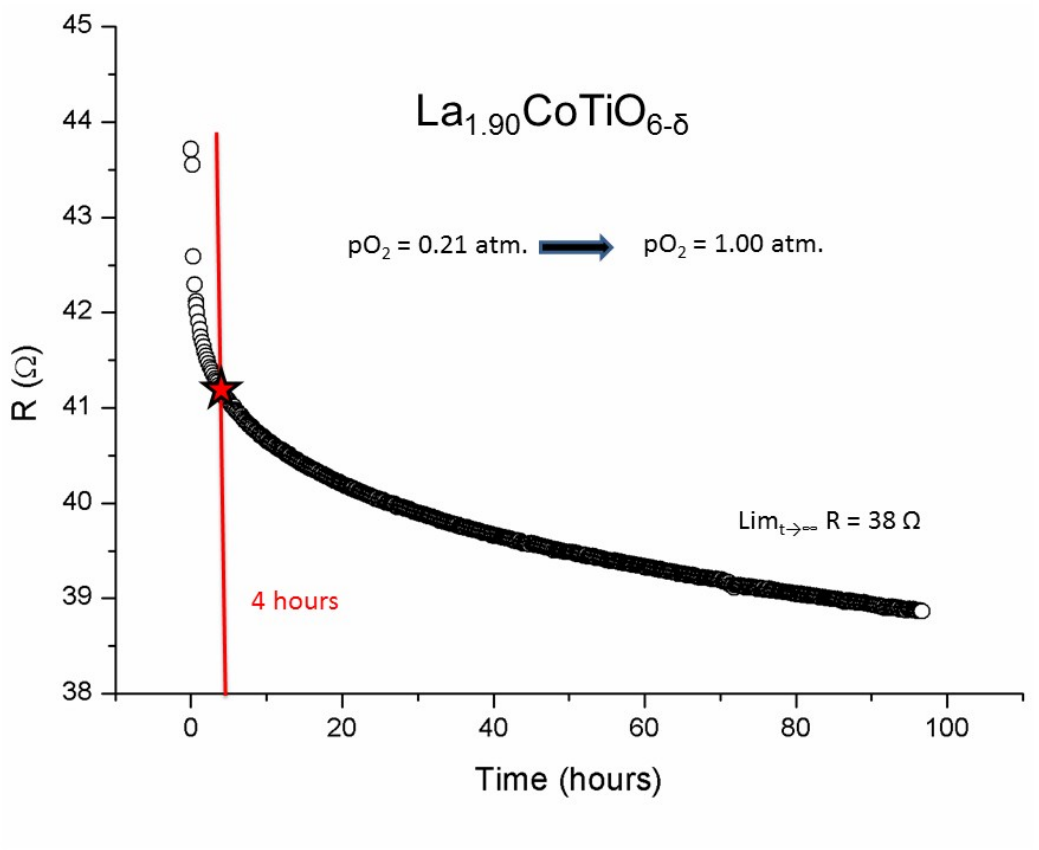


Figure SI 8: Variation of the resistance with time upon a change of pO_2 from 0.21 atm to 1.00 atm for a sample of composition $La_{1.90}CoTiO_{6-\delta}$.

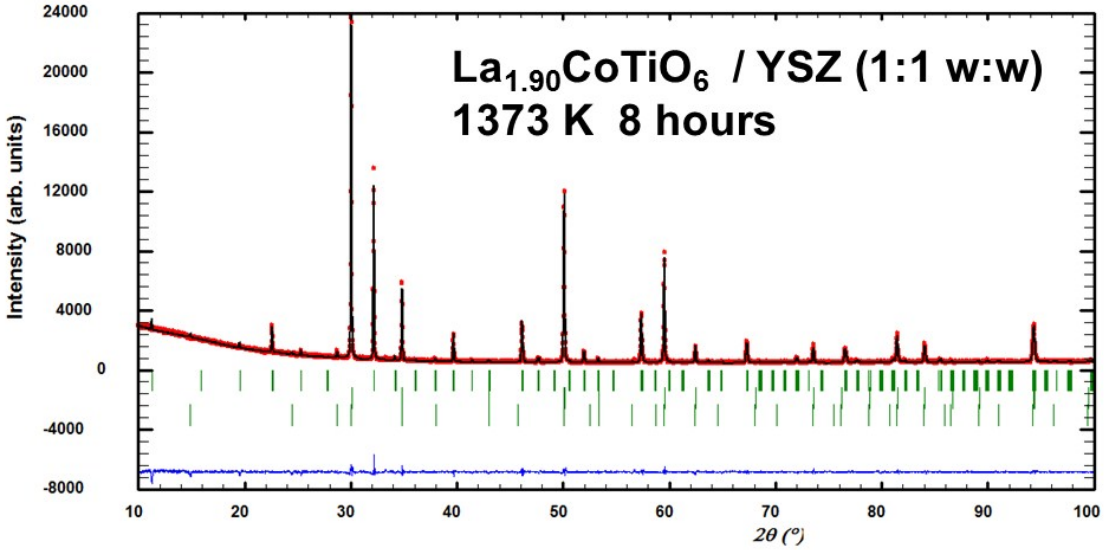


Figure SI 9: XRD-pattern of $La_{1.90}CoTIO_{6-\delta}$:YSZ (1:1 w:w) composite after fired at high temperature for eight hours.

Table SI 1: Structural parameters for $La_{2-x}CoTiO_{6-\delta}$ obtained from XRD and NPD data; agreement factors are given for NPD data.

	[a,b]$La_{1.95}CoTiO_{6-\delta}$	[c,d]$La_{1.90}CoTiO_{6-\delta}$	[c,e]$La_{1.80}CoTiO_{6-\delta}$
a (Å)	5.5601(1)	5.5567(1)	5.5562(1)
b (Å)	5.5808(1)	5.5753(1)	5.5693(1)
c (Å)	7.8646(1)	7.8612(1)	7.8605(2)
β (deg)	90.012(2)	90.011(3)	90.014(4)
V(Å^3)	244.035(2)	243.544(3)	243.239(6)
La1 position			
Occ La1	0.978(2)	0.969(2)	0.880(4)
X	0.0053(4)	0.2422(9)	0.249(2)
Y	0.0334(2)	0.241(2)	0.248(1)
Z	0.7482(6)	0.000(1)	0.000(1)
U*100 (Å^2)	0.56(2)	0.67(2)	0.66(2)
La2 position			
Occ La2		0.953(2)	0.941(4)
X		0.253(1)	0.257(1)
Y		0.303(2)	0.307(1)
Z		0.500(1)	0.499(1)
U*100 (Å^2)		0.73(2)	0.66(2)
B’ position			
Occ Ti/Co	0.074(2)/0.926(2)	0.097(3)/0.903(3)	0.146(4)/0.854(4)
X	½	0.747(7)	0.758(9)
Y	0	0.287(4)	0.269(8)
Z	0	0.245(3)	0.251(9)
U*100 (Å^2)	0.43(2)	0.52(3)	0.46(3)
B’’ position			
Occ Ti/Co	0.926(2)/0.074(2)	0.903(3)/0.097(3)	0.854(4)/0.146(4)
X	0	0.753(4)	0.745(5)
Y	½	0.276(4)	0.285(4)
Z	0	0.746(3)	0.752(3)
U*100 (Å^2)	0.36(3)	0.56(2)	0.46(3)
O(1) position			
X	0.2757(7)	0.543(1)	0.535(3)
Y	0.2917(7)	0.554(1)	0.546(2)
Z	0.9602(6)	0.711(1)	0.705(2)
Occ	0.991(3)	0.950(8)	0.856(5)
U*100 (Å^2)	0.58(4)	0.76(2)	0.81(2)
O(2) position			
X	0.2942(6)	0.532(1)	0.522(3)
Y	0.2805(7)	0.573(2)	0.557(3)
Z	0.5379(6)	0.287(1)	0.288(2)
Occ	1.00	1.00	1.00
U*100 (Å^2)	0.58(4)	0.76(2)	0.81(2)
O(3) position			
X	0.9255(4)	-0.019(1)	-0.026(2)

Y	0.4854(3)	-0.008(2)	-0.018(2)
Z	0.7567(6)	0.207(1)	0.209(2)
Occ	1.00	1.00	1.00
U*100 (Å^2)	0.58(4)	0.76(2)	0.81(2)
O(4) position			
X		-0.043(2)	-0.047(2)
Y		-0.005(2)	-0.013(2)
Z		0.787(2)	0.782(1)
Occ		1.00	1.00
U*100 (Å^2)		0.76(2)	0.81(2)
O(5) position			
X		0.826(1)	0.820(1)
Y		0.266(2)	0.251(2)
Z		0.506(2)	0.507(2)
Occ		1.00	1.00
U*100 (Å^2)		0.76(2)	0.81(2)
O(6) position			
X		0.678(1)	0.675(2)
Y		0.296(2)	0.278(2)
Z		-0.007(2)	-0.006(2)
Occ		0.923(3)	0.925(8)
U*100 (Å^2)		0.76(2)	0.81(2)

[a] $P2_1/n$: 4e (xyz), 2d (½ 0 0), 2c (0 ½ 0)

[b] χ^2= 4.01, R_{wp}= 3.13%, R_{exp}= 1.61%, R_B= 2.61%, Composition: $La_{1.956(6)}Co_{1.000(1)}Ti_{1.000(1)}O_{5.982(2)}$

[c] Space Group $P2_1$: 2a (xyz)

[d] χ^2= 2.69, R_{wp}= 2.57%, R_{exp}= 1.57%, R_B= 2.04%, Composition: $La_{1.922(5)}Co_{1.000(2)}Ti_{1.000(2)}O_{5.914(3)}$

[e] χ^2= 5.28, R_{wp}= 3.63%, R_{exp}= 1.58%, R_B= 3.22%, Composition:$La_{1.821(5)}Co_{1.000(2)}Ti_{1.000(2)}O_{5.781(5)}$

Table SI 2: Selected structural information for $La_{2-x}CoTiO_{6-\delta}$ obtained from XRD and NPD data. Angles are given in degrees and distances in Å, distortion (Δ) of the BO_n polyhedra and Bond Valence Sums [Zachariasen, W.H., *ActaCryst.*,**(1963)**, 16, 385,] are reported. $\Delta=1/n\ \Sigma_{j=1,n}\ \{(d_n - <d>)/<d>\}^2$ where <d> is the average B-O distance.

	[a]La_2CoTiO_6	$La_{1.95}CoTiO_6$	$La_{1.90}CoTiO_6$	$La_{1.80}CoTiO_6$
[b]Tilt angle θ	11.9(1)	11.7(2)	11.4(4)/12.2(4)	12.4(4)/11.4(4)
[c]Tilt angle φ	12.0(1)	12.1(2)	11.5(4)/12.1(4)	9.9(4)/13.0(4)
[d]Tilt angle μ	12.0(1)	12.1(2)	12.6(3)/11.4(3)	11.7(4)/12.3(4)
Tolerance factor	0.953	0.941	0.930	0.910
B'-O(1)	2.085(5)	2.075(4)	2.09(3)	2.08(6)
B'-O(2)	2.082(5)	2.067(4)	2.02(3)	2.09(5)
B'-O(3)	2.029(6)	2.062(5)	2.12(3)	2.03(5)
B'-O(4)	-	-	2.03(3)	2.03(6)
B'-O(5)	-	-	2.10(3)	2.04(9)
B'-O(6)	-	-	2.02(3)	2.07(9)
Average B'-O	2.065(2)	2.068(2)	2.06(1)	2.06(3)
Distortion B'-O_6 x 10^4	1.345	0.066	4.007	1.451
B' BVS	2.2(1)	2.14(1)	2.17(7)	2.63(3)
B''-O(1)	1.938(5)	1.947(4)	1.94(2)	1.90(3)
B''-O(2)	1.943(5)	1.961(4)	1.94(2)	1.98(3)
B''-O(3)	1.988(6)	1.959(5)	1.96(2)	1.93(3)
B''-O(4)	-	-	1.98(2)	2.04(3)
B''-O(5)	-	-	1.94(3)	1.98(3)
B''-O(6)	-	-	1.98(3)	1.94(3)
Average B''-O	1.957(3)	1.956(2)	1.957(10)	1.961(12)
Distortion B''-O_6 x 10^4	1.085	0.100	0.849	4.809
B'' BVS	4.1(1)	4.04(2)	4.03(11)	3.89(12)

[a]Data from ref. [A.Gómez-Pérez, J.C.Pérez-Flores, C.Ritter, K.Boulahya, G.R.Castro, F.García-Alvarado, U. Amador,*J. Appl. Cryst.*(2014). 47, 745–754];
For S.G. $P2_1/n$ the B' and B'' ions are co-ordinated to O(1) x 2, O(2) x 2 and O(3) x 2.
[b] With [110]: for $P2_1/n$; θ = ½ [180-angle<B'-O(1)-B">];
for $P2_1$; θ = ½ [180-angle<B'-O(1)-B">] or θ = ½ [180-angle<B'-O(4)-B">]
[c] With [1-10]: for $P2_1/n$; φ = ½ [180-angle<B'-O(2)-B">];
for $P2_1$; φ = ½ [180-angle<B'-O(2)-B">] or φ = ½ [180-angle<B'-O(3)-B">]
[d] With [001:] for $P2_1/n$; μ = ½ [180-angle<B'-O(3)-B">];
for $P2_1$; μ = ½ [180-angle<B'-O(5)-B">] or μ = ½ [180-angle<B'-O(6)-B">]

Table SI 3: Structural parameters for $La_{2-x}CoTiO_{6-\delta}$ (x=0.05 and 0.15) at 1073 K obtained from SXRD and NPD data; agreement factors are given for NPD data.

	[a,b]$La_{1.95}CoTiO_{6-\delta}$	[d,e]$La_{1.85}CoTiO_{6-\delta}$
***a* (Å)**	5.6186(3)	5.6171(7)
***b* (Å)**	5.6133(2)	5.6114(5)
c (Å)	7.9401(3)	7.9361(9)
β (deg)	89.990(13)	90.040(11)
V(Å³)	250.42(2)	250.16(5)
La1 position		
Occ La1	0.966* (fixed from RT refinement)	0.879(8)
X	0.0037(8)	0.2501(41)
Y	0.0206(2)	0.2693 (61)
Z	0.7477(8)	-0.0030(24)
U*100 (Å²)	1.72(2)	1.77(6)
La2 position		
Occ La2		1.000(8)
X		0.2521 (23)
Y		0.3013 (64)
Z		0.5022 (21)
U*100 (Å²)		1.77(6)
B' position		
Occ Ti/Co	0.128(8)/0.872(8)	0.087(9)/0.913(9)
X	½	0.7315(45)
Y	0	0.3118(75)
Z	0	0.2464(41)
U*100 (Å²)	0.94(7)	0.70(7)
B'' position		
Occ Ti/Co	0.872(8)/0.128(8)	0.913(9)/0.087(9)
X	0	0.7562(52)
Y	½	0.2986(80)
Z	0	0.7497(48)
U*100 (Å²)	0.98(6)	0.70(7)
O(1) position		
X	0.2690(17)	0.5481(60)
Y	0.2811(23)	0.5368(56)
Z	0.9570(10)	0.7149(51)
Occ	1.00	0.845(9)
U*100 (Å²)	2.26(22)	2.38(9)
O(2) position		
X	0.2886(19)	0.5045(43)
Y	0.2804(24)	0.5423(57)
Z	0.5340(11)	0.2918(43)
Occ	0.980 (2)	1.00
U*100 (Å²)	2.45(24)	2.38(9)

O(3) position		
X	0.9336(10)	-0.0374(56)
Y	0.4889(7)	-0.0108(62)
Z	0.7557(26)	0.2063(40)
Occ	1.00	1.00
U*100 (Å^2)	2.21(7)	2.38(9)
O(4) position		
X		-0.0320(42)
Y		0.0074(45)
Z		0.7894(40)
Occ		1.00
U*100 (Å^2)		2.38(9)
O(5) position		
X		0.8071 (42)
Y		0.2658 (32)
Z		0.5035 (42)
Occ		1.00
U*100 (Å^2)		2.38(9)
O(6) position		
X		0.6910(45)
Y		0.2776(34)
Z		-0.0047(40)
Occ		0.976 (8)
U*100 (Å^2)		2.38(9)

[a] $P2_1/n$: 4e (xyz), 2d (½ 0 0), 2c (0 ½ 0)

[b] χ^2= 1.96, R_{wp}= 3.81%, R_{exp}= 2.72%, R_B= 4.45%, Composition: $La_{1.966(6)}Co_{1.000(1)}Ti_{1.000(1)}O_{5.960(2)}$

[d] Space Group $P2_1$: 2a (xyz)

[e] χ^2= 5.28, R_{wp}= 5.22%, R_{exp}= 2.89%, R_B= 8.76%, Composition: $La_{1.879(8)}Co_{1.000(2)}Ti_{1.000(2)}O_{5.821(16)}$