Supporting information

A-site order in rhombohedral perovskite-like oxides

$La_{2-x}Sr_xCoTiO_6$ ($0.6 \leq x \leq 1.0$)

Alejandro Gómez-Pérez[ab]*, Clemens Ritter[c], Khalid Boulahya[d], Alvaro Muñoz-Noval[ef], Flaviano García-Alvarado[a] and Ulises Amador[a]*

[a]Quimica Facultad de Farmacia, Universidad CEU-San Pablo, Carretera de Boadilla km 5.300, Boadilla del Monte, Madrid, 28668, Spain
[b]Quimica Facultad de Farmacia, Universidad CEU-San Pablo, Carretera de Boadilla km 5.300, Boadilla del Monte, Madrid/Spain, 28668, Spain
[c] Institut Laue-Langevin, 6 Rue J. Horowitz, Grenoble, Isere/Rhone-Alpes, 38042, France
[d]Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda. Complutense s/n, Madrid, Madrid, 28040, Spain
[e]SpLine Spanish CRG Beamline, ESRF, 6 Rue J. Horowitz, Grenoble, Isere/Rhone-Alpes, 38042, France
[f] Instituto de Ciencia de Materiales de Madrid-ICMM/CSIC, Sor Juana Inés de la Cruz, 3, Madrid, Madrid, 28049, Spain

Correspondence email: a.gomez126@usp.ceu.es; uamador@ceu.es

Table S1 Structural parameters for as prepared $La_{2-x}Sr_xCoTiO_6$ compounds obtained from SXRD/XRD and NPD data (no A-ions order); agreement factors are given for NPD data.

	[b]$La_{1.4}Sr_{0.6}CoTiO_6$	[c]$La_{1.30}Sr_{0.70}CoTiO_6$	[d]$La_{1.20}Sr_{0.80}CoTiO_6$	[e]$La_{1.10}Sr_{0.90}CoTiO_6$	[f]$La_{1.00}Sr_{0.00}CoTiO_6$
X-ray Source	Synchrotron	Conventional diffractometer	Synchrotron	Conventional diffractometer	Synchrotron
Space Group[a]	R-3c	R-3c	R-3c	R-3c	R-3c
***a* (Å)**	5.5090 (1)	5.4951 (2)	5.4854 (1)	5.4767 (1)	5.4713 (2)
***b* (Å)**	5.5090 (1)	5.4951 (2)	5.4854 (1)	5.4767 (1)	5.4713 (2)
c (Å)	13.3648(3)	13.3529(6)	13.3492(3)	13.3463 (3)	13.3472 (8)
Volume (Å^3)	351.18 (3)	349.19 (3)	347.86 (1)	346.68 (2)	346.02 (3)
La/Sr position	6a	6a	6a	6a	6a
Occ La/Sr	0.1166(4)/0.0499(4)	0.116(3)/0.051(3)	0.1017(6)/0.0647(6)	0.097(3)/0.068(3)	0.089(1) /0.077(1)
U*100 (Å^2)	0.63(3)	0.75(9)	0.73(2)	0.68(4)	0.55 (4)
B' position	6b	6b	6b	6b	6b
Occ Co/Ti	0.08333 /0.08333	0.08333 /0.08333	0.08333 /0.08333	0.08333 /0.08333	0.08333 /0.08333
U*100 (Å^2)	0.40(8)	0.78(9)	0.45(7)	1.2(1)	1.45(7)
O(1) position	18e	18e	18e	18e	18e
X	0.5443(1)	0.5405(2)	0.5365(2)	0.5324(3)	0.5298(3)
Occ	0.500	0.500	0.500	0.500	0.500
U*100 (Å^2)	0.80(3)	0.83(3)	0.85(2)	0.72(3)	0.71(3)

[a] R-3c: 18e (x 0 ¼), 6a (0 0 ¼), 6b (0 0 0);

[b] χ^2= 4.05, R_{wp}= 5.46%, R_{exp}= 2.71%, R_B= 2.32%,

[c] χ^2= 2.21, R_{wp}= 4.41%, R_{exp}= 2.96%, R_B= 2.24%,

[d] χ^2= 3.41, R_{wp}= 5.09%, R_{exp}= 2.76%, R_B= 2.01%,

[e] χ^2= 3.55, R_{wp}= 5.19%, R_{exp}= 2.75%, R_B= 2.02%,

[f] χ^2= 2.15, R_{wp}= 4.85%, R_{exp}= 3.31%, R_B= 1.48%,

Table S2 Selected structural information for La2-xSrxCoTiO6 (0.6≤x≤1.0) oxides (no A-ions order) obtained from XRD and NPD data. Angles are given in degrees and distances in Å.

	$La_{1.4}Sr_{0.6}CoTiO_6$	**$La_{1.30}Sr_{0.70}CoTiO_6$**	**$La_{1.20}Sr_{0.80}CoTiO_6$**	**$La_{1.10}Sr_{0.90}CoTiO_6$**	**$La_{1.00}Sr_{0.00}CoTiO_6$**
Tilt angle	10.12 (1)	9.27(2)	8.35(1)	7.42(1)	6.82(2)
B'-O(1) x 6	1.9567(2)	1.9504 (2)	1.9455(2)	1.9411(2)	1.9386(2)
A-O(1) x 6	2.74783 (6)	2.7421 (8)	2.7382 (3)	2.7348 (3)	2.7331(4)
A-O(1) x 3	2.5107 (4)	2.5248 (4)	2.5425 (5)	2.5607 (5)	2.5720 (6)
A-O(1) x 3	2.9982 (4)	2.9704 (4)	2.9430 (3)	2.9161(4)	2.8988(6)
Average A-O	2.7511 (4)	2.7448 (1)	2.7405 (1)	2.7366 (1)	2.7344 (1)
Coordination A-site	12	12	12	12	12
A-B' x 2	3.3412	3.3382	3.3373	3.3366	3.3368
A-B'' x 6	3.3700	3.3621	3.3567	3.3519	3.3490

Table S3 Structural parameters for as prepared $La_{1.60}Sr_{0.40}CoTiO_6$ compound obtained from SXRD/XRD and NPD data (A-ions ordered); agreement factors are given for NPD data.

	[b] $La_{1.4}Sr_{0.6}CoTiO_6$
X-ray Source	Synchrotron
Space Group[a]	R32
***a* (Å)**	5.5090 (1)
***b* (Å)**	5.5090 (1)
c (Å)	13.3648(3)
Volume (Å^3)	351.18 (3)
La/Sr position	3a
Occ La/Sr	0.120 (9)/0.047(9)
U*100 (Å^2)	0.831
La/Sr position	3b
Occ La/Sr	0.114(9)/0.053(9)
U*100 (Å^2)	0.402
B' position	6c
Z	0.2458 (11)
Occ Co/Ti	0.16667 /0.16667
U*100 (Å^2)	0.424
O(1) position	9d

X	0.5443(2)
Occ	0.500
U*100 (Å^2)	0.599
O(2) position	9e
X	0.4544(1)
Occ	0.500
U*100 (Å^2)	1.049

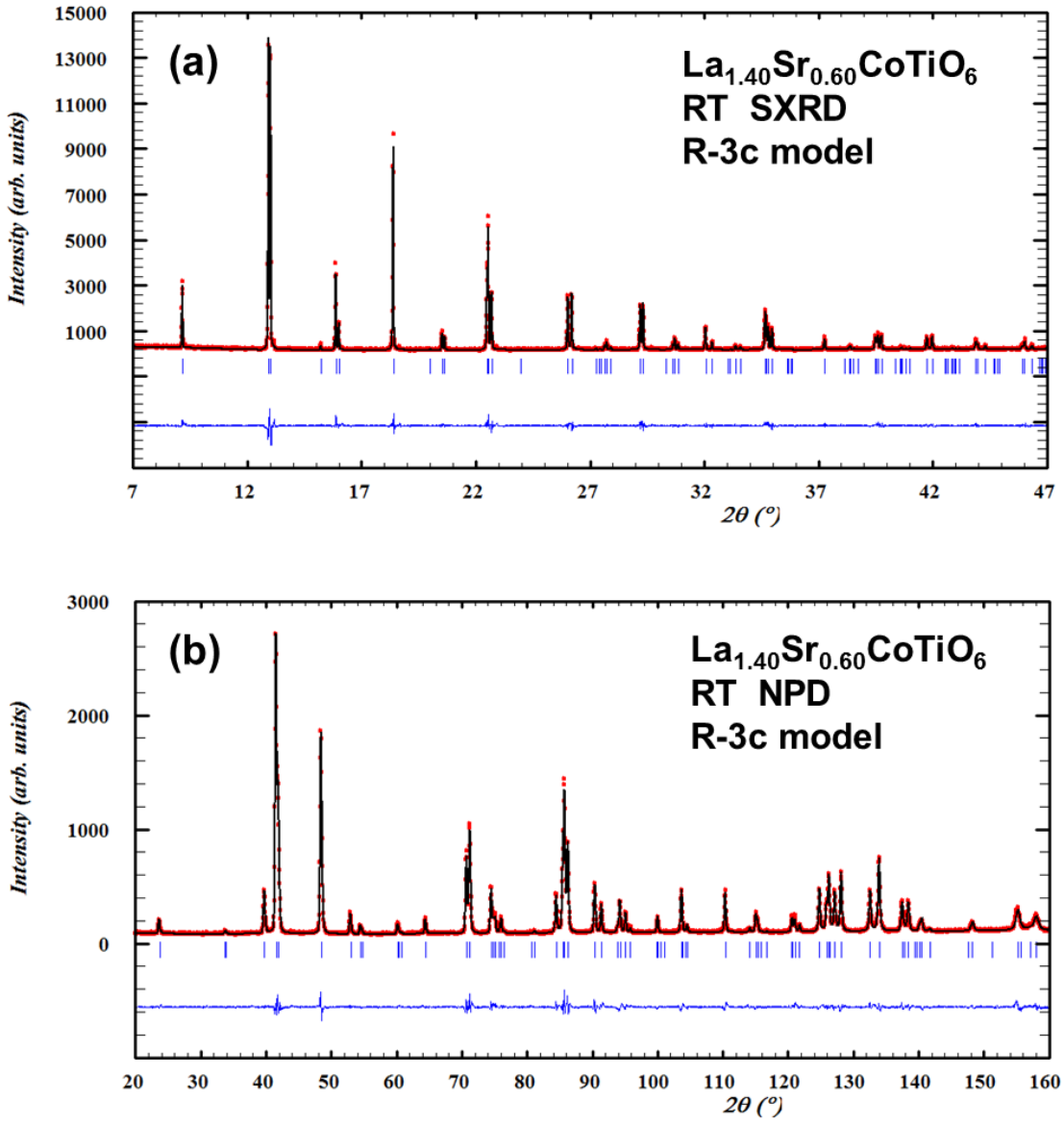
[a] R32: 9e (0 x ½), 9d (0 x 0), 6c (0 0 z); 3a (0 0 0); 3b (0 0 ½)

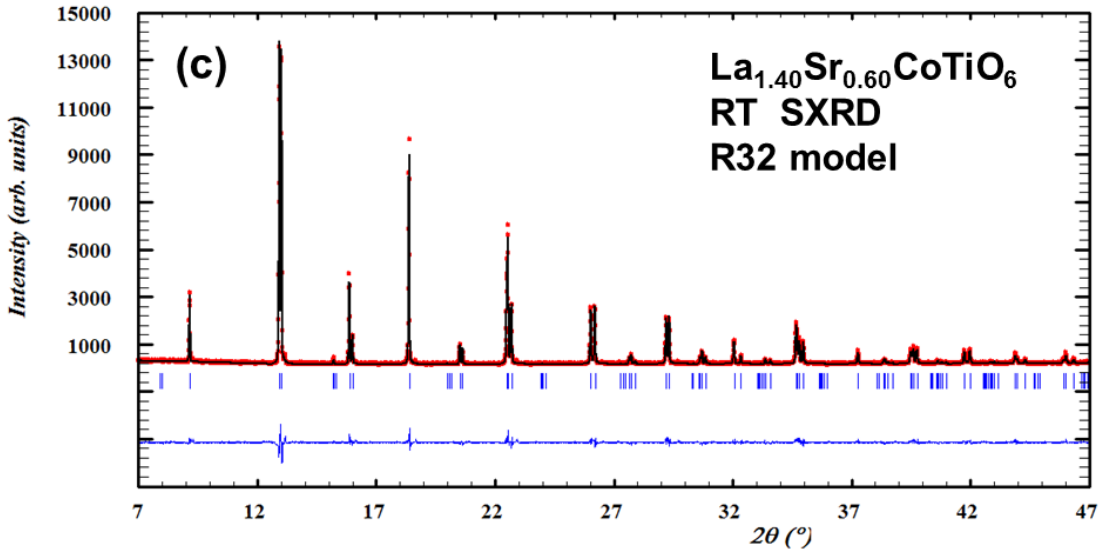
[b] χ^2= 4.09 R_{wp}= 5.49%, R_{exp}= 2.71%, R_B= 2.60%

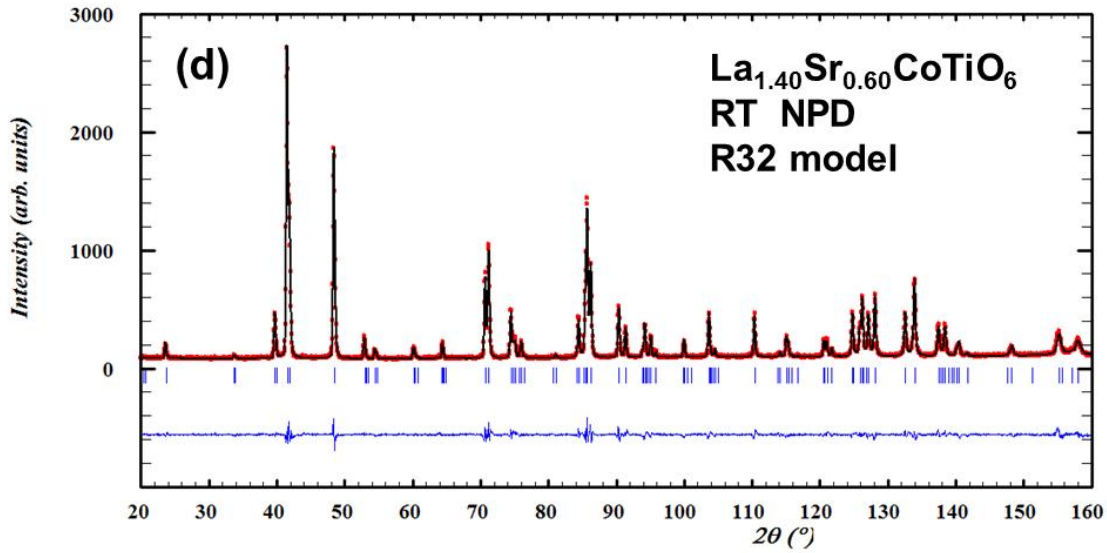
Table S4 Selected structural information for $La_{2-x}Sr_xCoTiO_6$ oxide (A-ions ordered) obtained from XRD and NPD data. Angles are given in degrees and distances in Å.

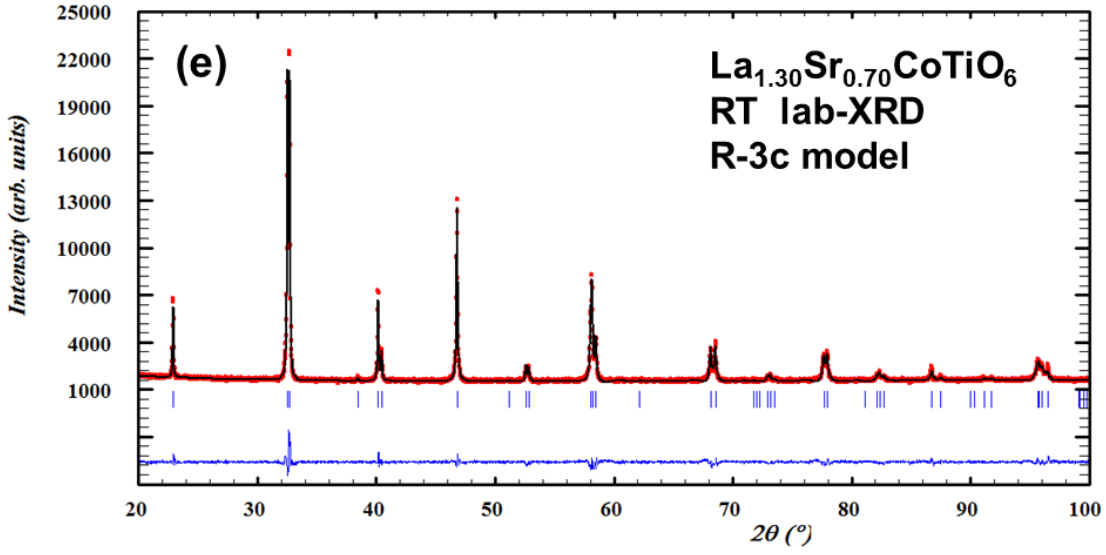
	$La_{1.4}Sr_{0.6}CoTiO_6$
Tilt angle	10.12 (1)
B'-O(1) x 6	1.9567(2)
A-O(1) x 6	2.74783 (6)
A-O(1) x 3	2.5107 (4)
A-O(1) x 3	2.9982 (4)
Average A-O	2.7511 (4)
Coordination A-site	12
A-B' x 2	3.3412
A-B'' x 6	3.3700

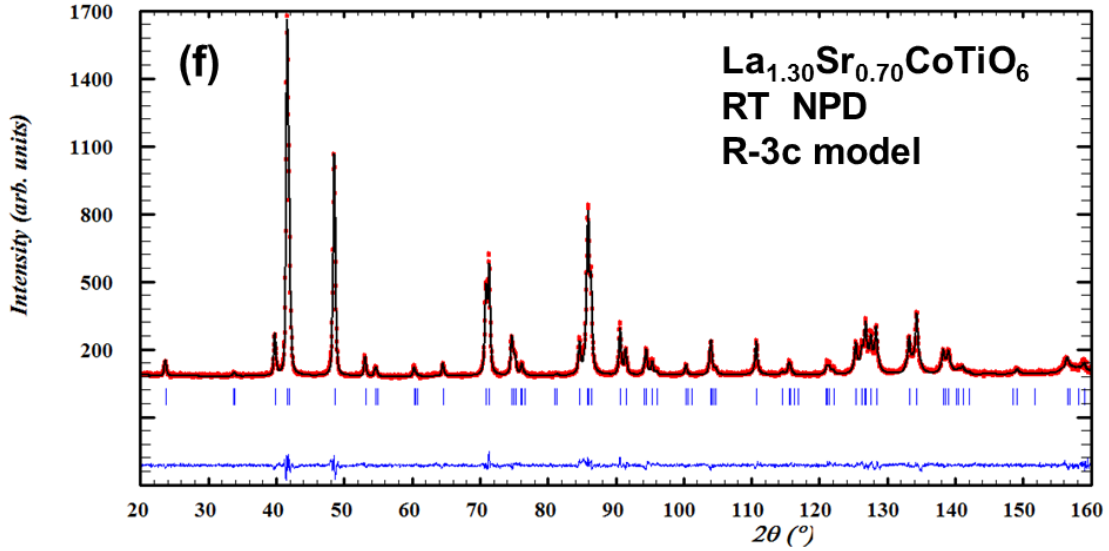
Figure S1 Experimental (points), calculated (continuous line) SXRD, XRD and NPD patterns and their difference (bottom) for $La_{2-x}Sr_xCoTiO_6$ ($0.6 \leq x \leq 1.0$) oxides. The rows of vertical bars indicate the positions of Bragg peaks. For x=0.6 and 0.7 R-3c (no A-site oder) and R32 (A-ions ordered) models have been tried. For x=1.0 a small amount of CoO is detected (second row bars in the corresponding plots).

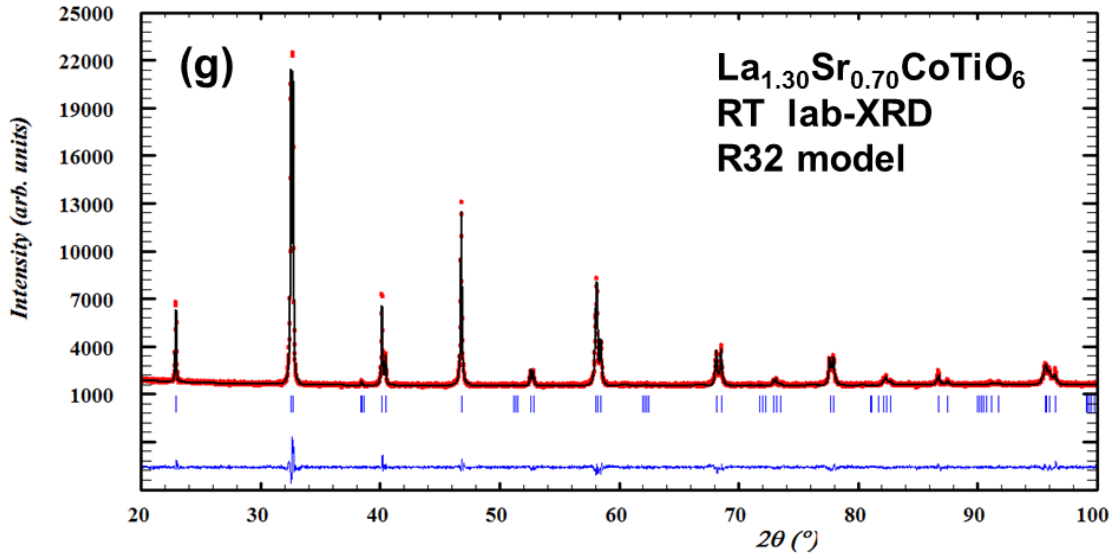


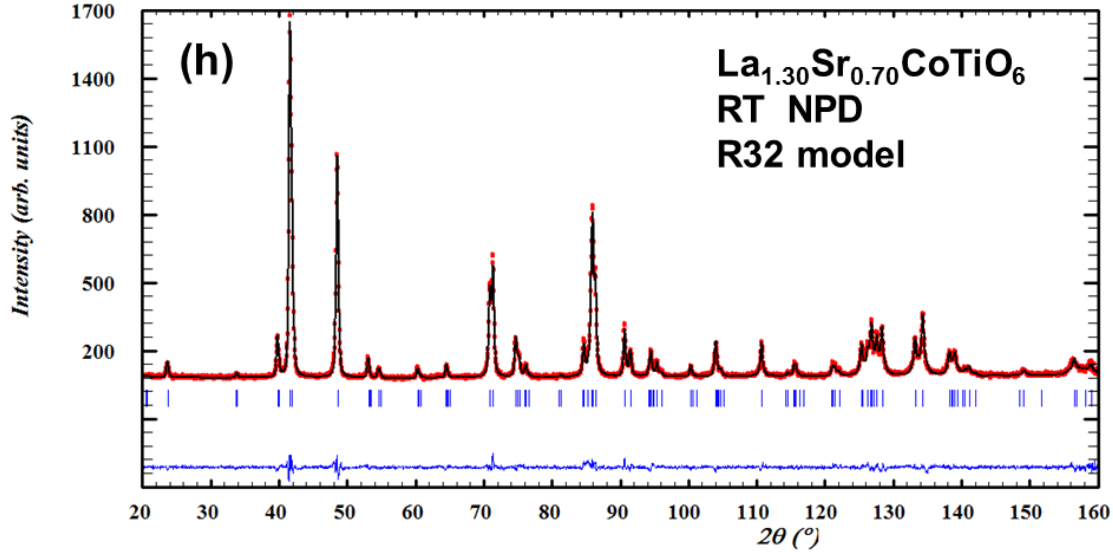

(c)
La1.40Sr0.60CoTiO6
RT SXRD
R32 model
Intensity (arb. units)
2θ (°)

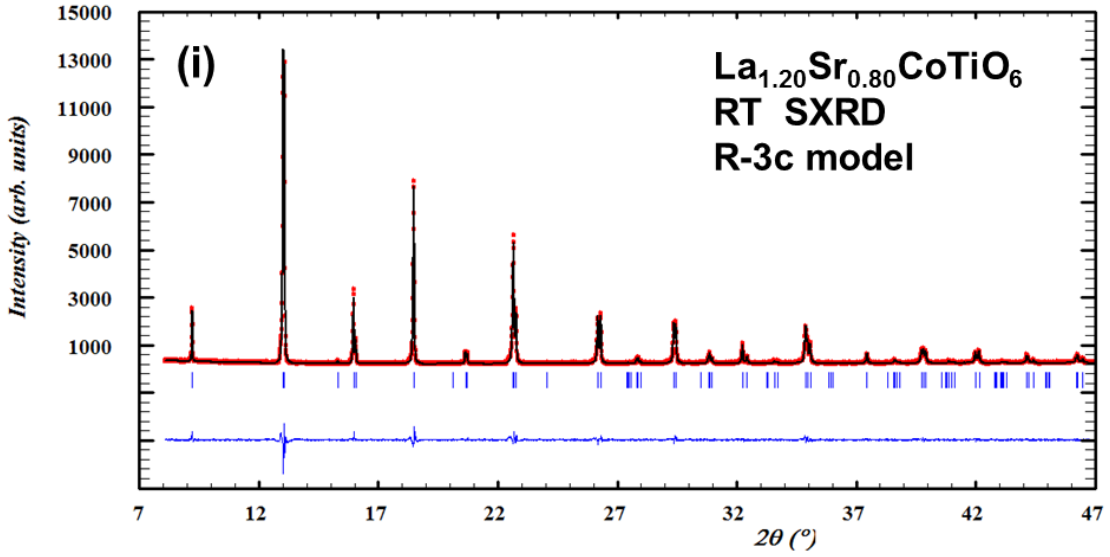

(d)
La1.40Sr0.60CoTiO6
RT NPD
R32 model
Intensity (arb. units)
2θ (°)

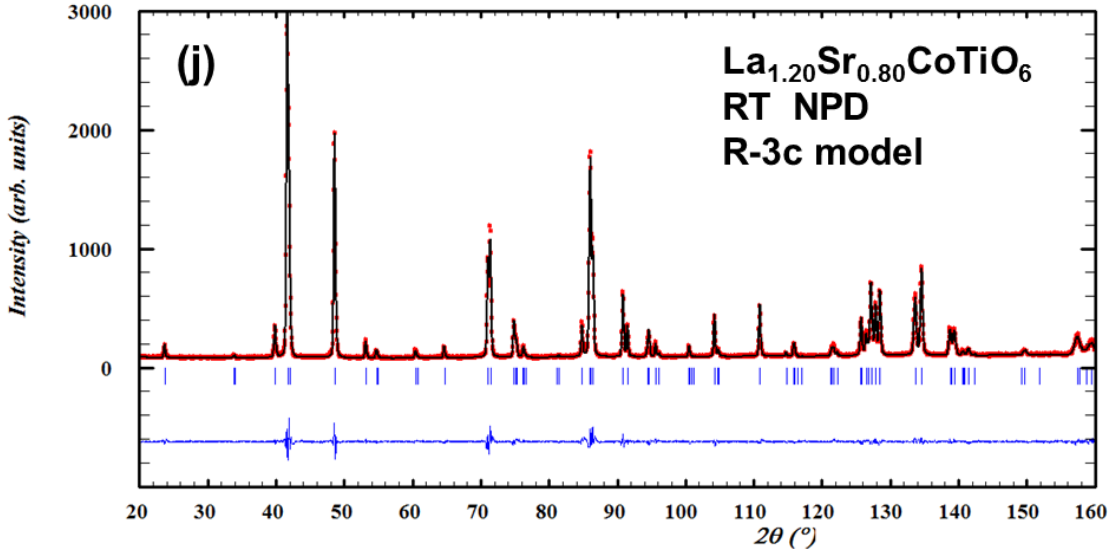

(e)
La1.30Sr0.70CoTiO6
RT lab-XRD
R-3c model
Intensity (arb. units)
2θ (°)

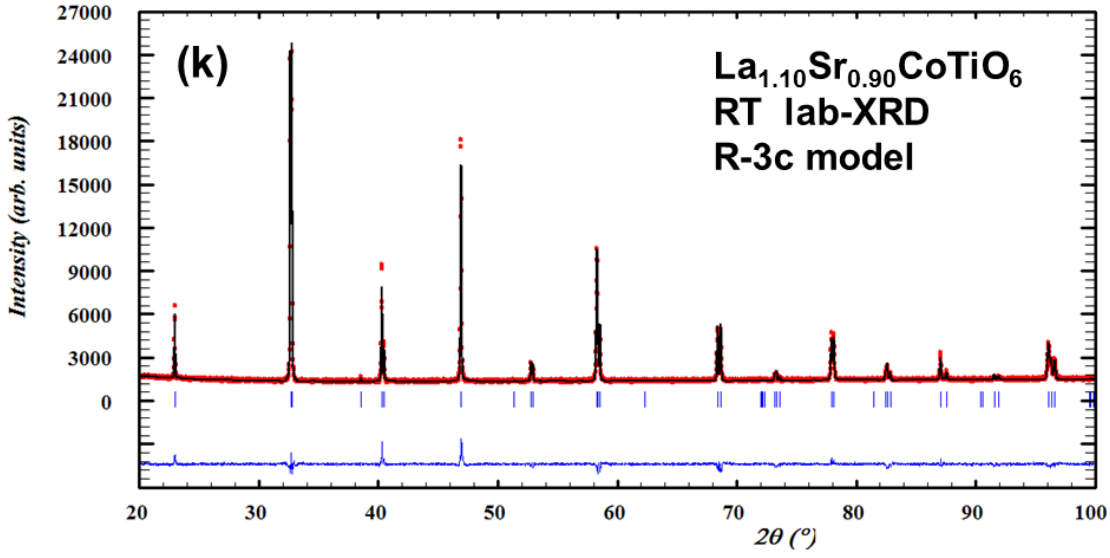

(f)
La1.30Sr0.70CoTiO6
RT NPD
R-3c model
Intensity (arb. units)
2θ (°)

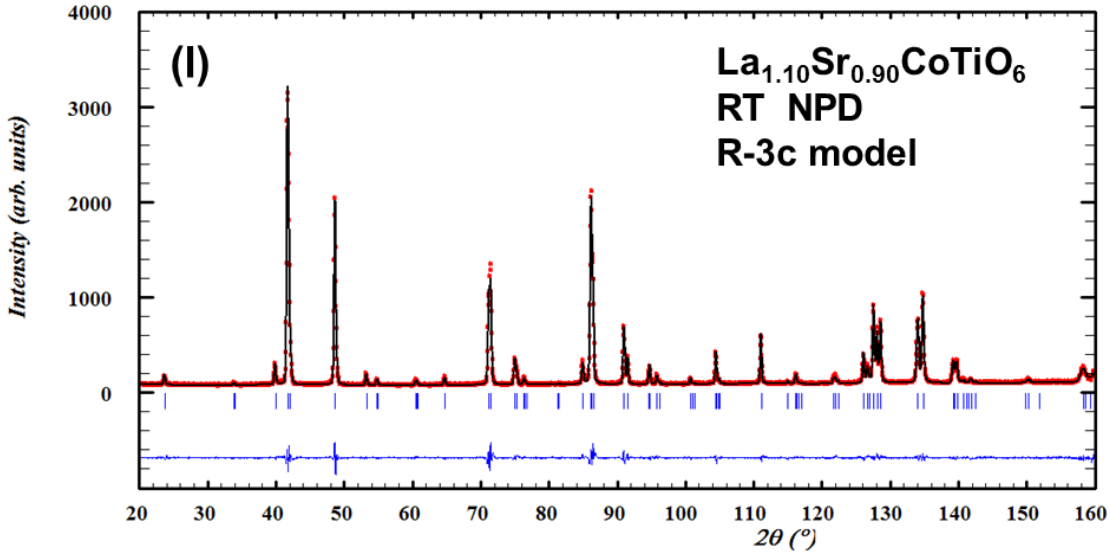

(g)
La1.30Sr0.70CoTiO6
RT lab-XRD
R32 model
Intensity (arb. units)
2θ (°)

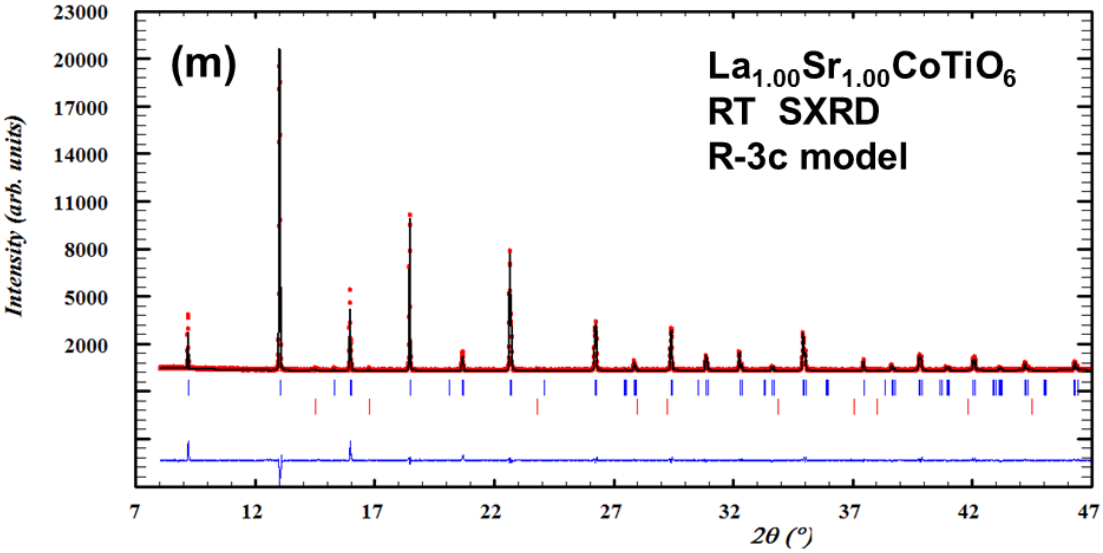

(h)
La1.30Sr0.70CoTiO6
RT NPD
R32 model
Intensity (arb. units)
2θ (°)

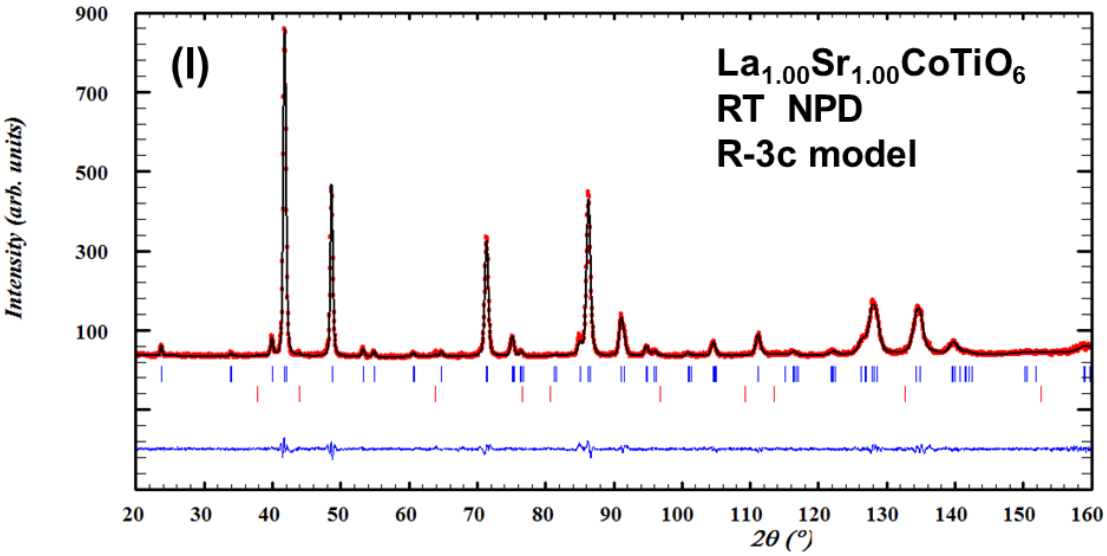

(i)
La1.20Sr0.80CoTiO6
RT SXRD
R-3c model
Intensity (arb. units)
2θ (°)


(j)
La1.20Sr0.80CoTiO6
RT NPD
R-3c model
Intensity (arb. units)
2θ (°)


(k)
La1.10Sr0.90CoTiO6
RT lab-XRD
R-3c model
Intensity (arb. units)
2θ (°)


(l)
La1.10Sr0.90CoTiO6
RT NPD
R-3c model
Intensity (arb. units)
2θ (°)


(m)
La1.00Sr1.00CoTiO6
RT SXRD
R-3c model
Intensity (arb. units)
2θ (°)


(l)
La1.00Sr1.00CoTiO6
RT NPD
R-3c model
Intensity (arb. units)
2θ (°)