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

Pure and Zr-doped $YMnO_{3+\delta}$ as YSZ-compatible SOFC cathode

Supplementary Materials

1. Structural parameters of $P6_3cm$ $Y_{1-x}Zr_xMnO_3$ (x= 0, 0.05 and 0.10) after synthesis using solid state route, as obtained from Rietveld refinement using XRD data.

a). Refined cell parameters and volumes and reliability factors.

Sample	a (Å)	c(Å)	V(Å^3)	Reliability factors	
x=0	6.1403(3)	11.3952(5)	372.08(3)	R_p(%)=2.37	GOF=1.45
				R_{wp}(%)=3.20	R_B=5.20
x=0.05	6.1398(3)	11.3637(6)	370.084(3)	R_p(%)= 3.12	GOF=1.56
				R_{wp}(%)=4.35	R_B=4.74
x=0.10	6.1405(4)	11.3171(8)	369.55(4)	R_p(%)=3.16	GOF=1.74
				R_{wp}(%)=4.49	R_B=9.46

R_p: profile factor R_{wp}: weighted-profile factor GOF: goodness of fit R_B: Bragg factor

b). Refined atomic positions for $YMnO_3$ (space group: *P*6_3*cm*)

Atom	Wyckoff position	x	y	z	U_{eq}
Y_1	2[a]	0	0	0.2729(5)	0.01481(26)
Y_2	4b	1/3	2/3	0.2323(3)	0.1452(15)
Mn	6c	0.3263	0	0.0005(20)	0.01715(48)
O_1	6c	0.3136	0	0.1604(40)	0.0096(20)
O_2	6c	0.6328	0	0.3389(43)	0.0096
O_3	2[a]	0	0	0.4700(45)	0.0096
O_4	4b	1/3	2/3	0.0150(29)	0.0096

c). Refined atomic positions for $Y_{0.9}Zr_{0.1}MnO_3$ (space group: *P*6_3*cm*)

Atom	Wyckoff position	x	y	z	U_{eq}
Y_1	2[a]	0	0	0.2663(8)	0.0093(42)
Zr_1	2[a]	0	0	0.2663	0.0093
Y_2	4b	1/3	2/3	0.2404(7)	0.0381(44)
Zr_2	4b	1/3	2/3	0.2404	0.0381
Mn	6c	0.3359(99)	0	-0.0086(23)	0.0187(13)
O_1	6c	0.3085(18)	0	0.1531(10)	0.0404(57)
O_2	6c	0.6566(21)	0	0.3300(90)	0.04040
O_3	2[a]	0	0	0.4919(68)	0.04040
O_4	4b	1/3	2/3	0.0269(41)	0.04040

2. Structural parameters of $YMnO_3$ and $Y_{0.9}Zr_{0.1}MnO_3$ synthesized by the Pechini method, as obtained from LeBail refinement using XRD data.

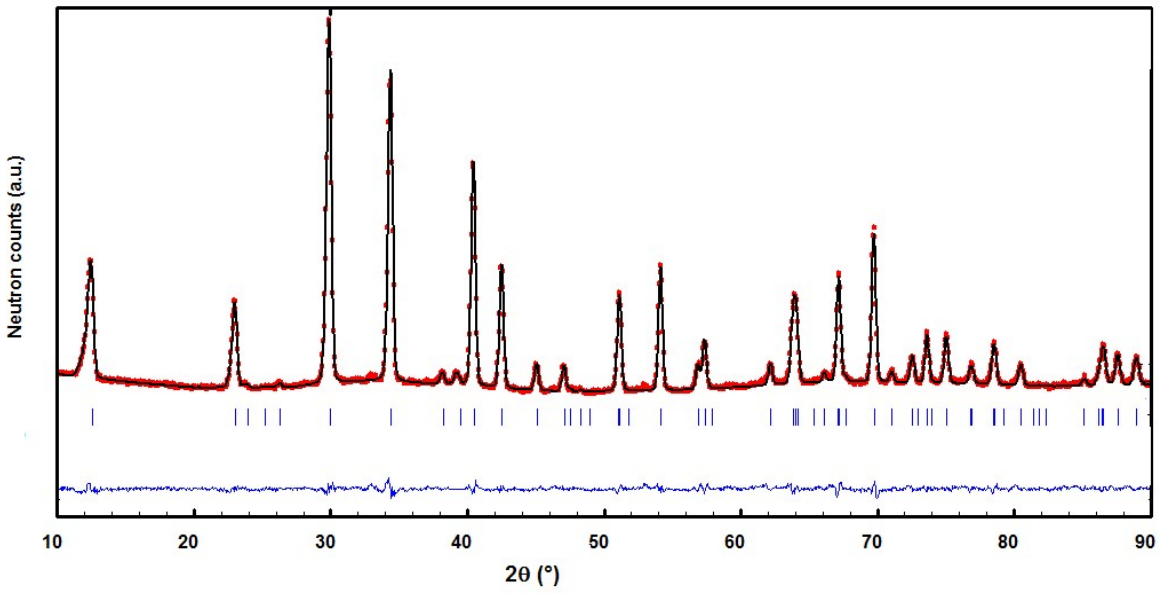
Space group	*a* (Å)	*c*(Å)	*V*(Å^3)	Reliability factors	
			$YMnO_3$		
*P*6$_3$*cm*	6.1446(3)	11.3843(6)	372.23(3)	R_p(%)=2.67	GOF=1.51
				R_{wp}(%)=3.59	
			$Y_{0.9}Zr_{0.1}MnO_3$		
*P*6$_3$*/mmc*	3.5503(3)	11.2513(9)	122.82(2)		
				R_p(%)=2.68	GOF=1.56
*P*6$_3$*cm*	6.1491(5)	11.2513(9)	368.46(6)	R_{wp}(%)=3.66	

R_p: profile factor R_{wp}: weighted-profile factor GOF: goodness of fit

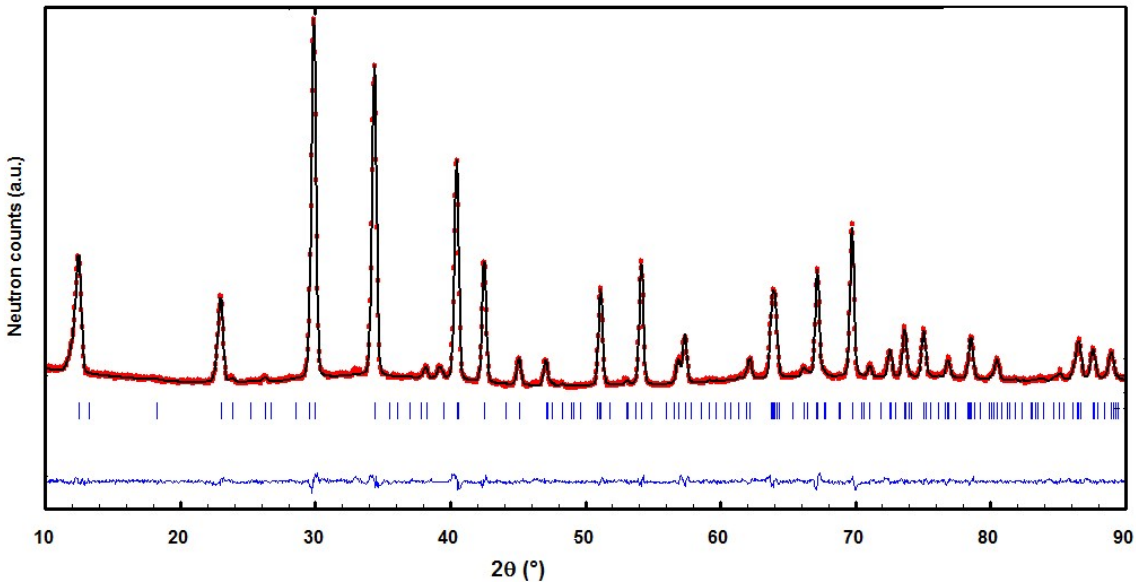
3. Results of Rietveld refinement using neutron diffraction data for $Y_{0.9}Zr_{0.1}MnO_3$ prepared by Pechini method

Neutron diffraction (ND) analysis was carried out for as-synthesized Zr-doped $YMnO_3$. Using only FPM refinement, *i.e.* without including the cell content, the neutron diffraction pattern can be indifferently indexed using either $P6_3cm$ or $P6_3/mmc$ space groups, with quite good R-factors, as shown in (a) and (b):

a). Space group: $P6_3/mmc$; **lattice parameters:** a=3.5517 Å, c=11.2611 Å, **Reliability factors:** GOF=1.55, R_p=2.24, R_{wp}=2.86.

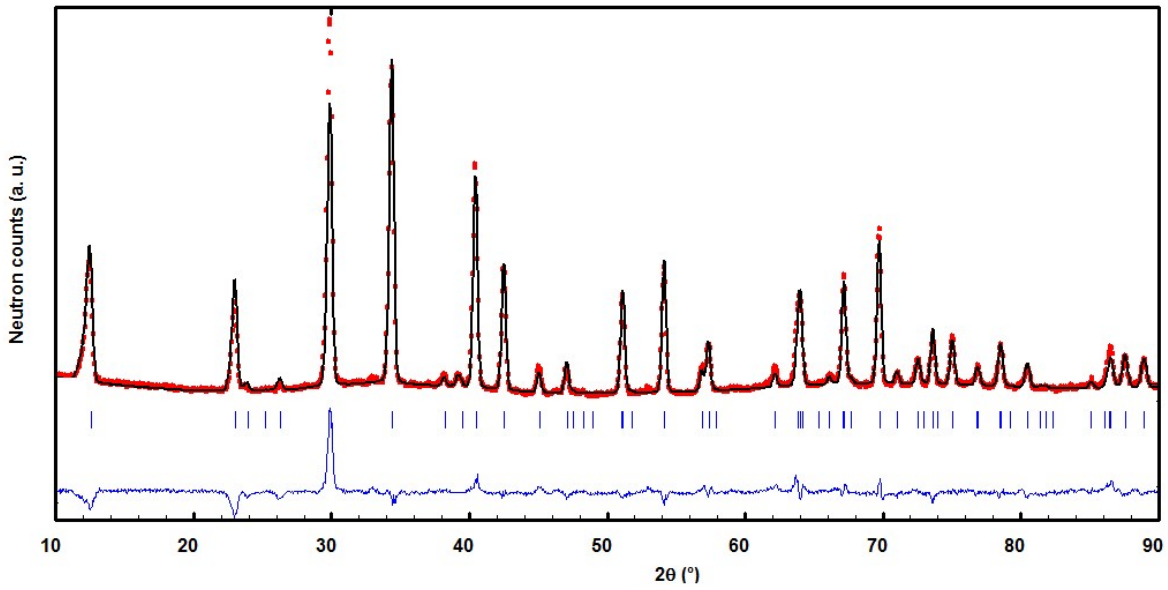


b). Space group: $P6_3cm$; **lattice parameters:** a=6.1518 Å, c=11.2582 Å, **Reliability factors:** GOF=1.43, R_p=2.05, R_{wp}=2.61.



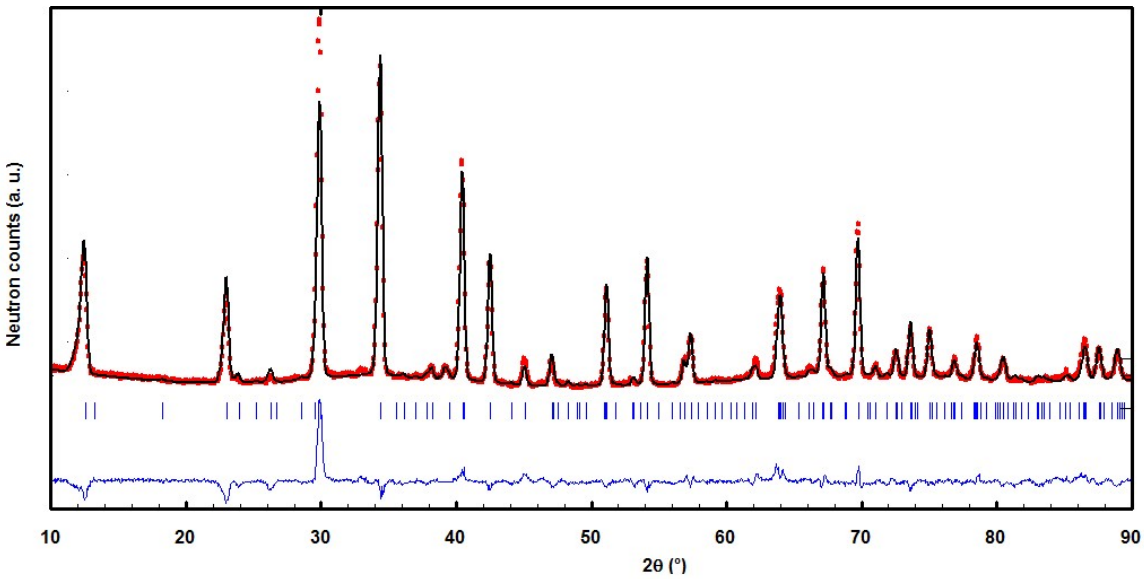
However, the corresponding Rietveld refinements yield high values of reliability factors in both cases (c) and (d):

c). Space group: $P6_3/mmc$; **lattice parameters:** a=3.5517 Å, c=11.2611 Å, **Reliability factors:** GOF=1.72, R_p=3.93, R_{wp}=5.44, R_B=11.98.



Atom	Wyckoff position	x	y	z	U_{iso}
Y	4e	0	0	-0.0223(2)	0.0122(6)
Zr	4e	0	0	-0.0223	0.0122
Mn	2c	1/3	2/3	1/4	0.0155(4)
O_1	4f	1(3	2/3	0.0850(7)	0.0134(2)
O_2	2b	0	0	1/4	0.0530(5)

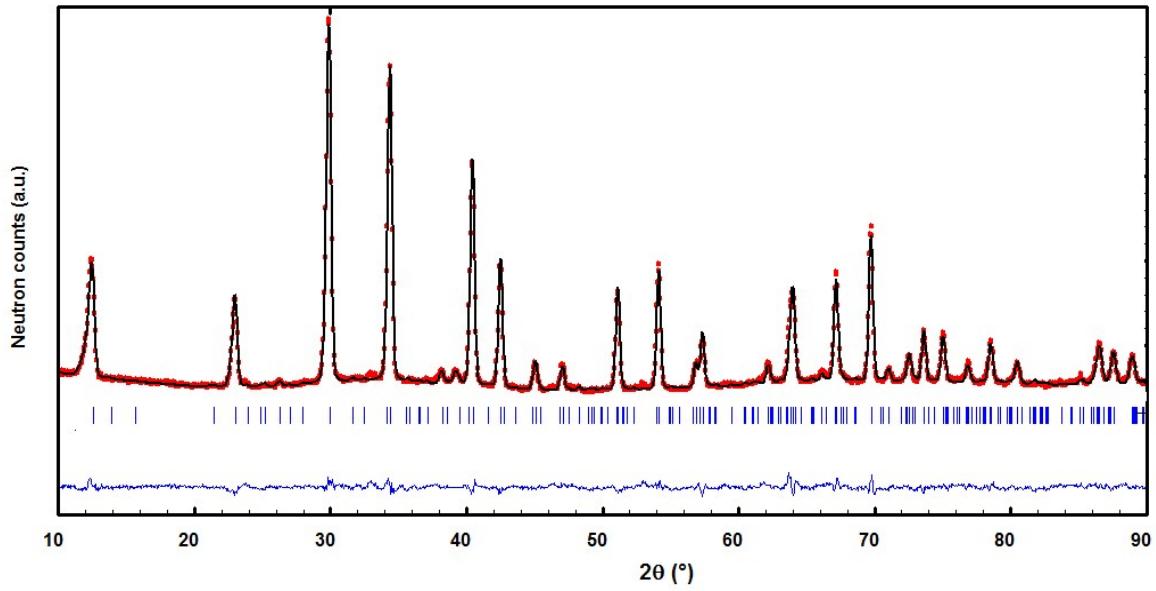
d). Space group: $P6_3cm$; **lattice parameters:** a=6.1520 Å, c=11.2605 Å, **Reliability factors:** GOF=1.73, R_p=4.03, R_{wp}=5.50, R_B=12.24.



Atom	Wyckoff position	x	y	z	U_{iso}
Y_1	2a	0	0	0.2489(6)	0.0378(2)
Zr_1	2a	0	0	0.2489	0.0378
Y_2	4b	1/3	2/3	0.2377(3)	0.0273(8)
Zr_2	4b	1/3	2/3	0.2377	0.0273
Mn	6c	0.3091(8)	0	0.0020(5)	0.0078(7)
O_1	6c	0.3156(6)	0	0.1679(3)	0.0110(7)
O_2	6c	0.6611(6)	0	0.3400(4)	0.0142(7)
O_3	2a	0	0	0.4869(5)	0.0118(8)
O_4	4b	1/3	2/3	0.0156(5)	0.0687(2)

In addition, we tried to carry out Rietveld refinements using other two models that have been described in literature for oxygen overstoichiometric compounds, *i.e.* with space groups *R*3*c* (e) and *P*ca2$_1$ (f), respectively [16] [30]. These models had better results than the before space groups, and the difference between them is the additional oxygen atoms positions.

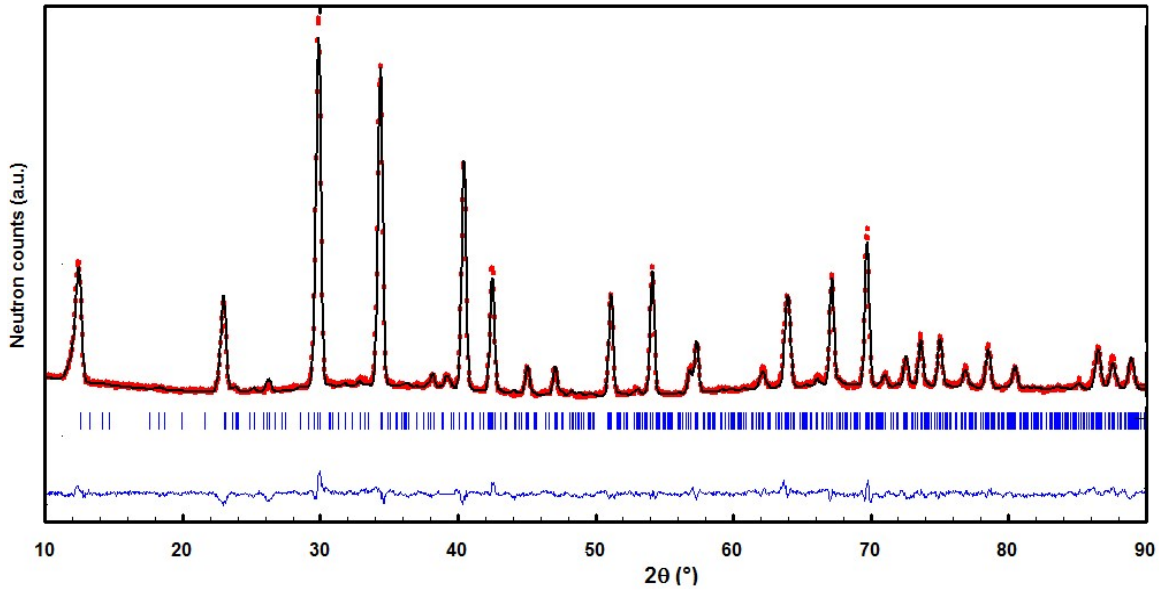
e). Space group: *R*3*c*; **lattice parameters:** *a*=6.1319 Å, *c*=33.6723 Å, **Reliability factors:** GOF=1.36, R_p=2.69, R_{wp}=3.34, R_B=6.92



Atom	Wyckoff position	x	y	z	U_{iso}
Y_1	6a	0	0	-0.0835(1)	0.0347(1)
Zr_1	6a	0	0	-0.0835	0.0347
Y_2	6a	0	0	0.0836(2)	0.0297(9)

Atom	Wyckoff position	x	y	z	U_{iso}
Zr_2	6a	0	0	0.0836	0.0297
Y_3	6a	0	0	0.2508(2)	0.0323(1)
Zr_3	6a	0	0	0.2508	0.0323
Mn_1	18b	0.3412(9)	0.0054(1)	0.0031(1)	0.0258(1)
O_1	6a	0	0	0.1688(2)	0.0285(2)
O_2	6a	0	0	1.0045(2)	0.0326(1)
O_3	6a	0	0	0.3437(5)	0.2872(5)
O_4	18b	0.3370(5)	0.0005(6)	0.0592(1)	0.0262(1)
O_5	18b	0.0006(6)	0.3355(5)	0.2828(9)	0.0217(9)
O_6	18b	0.6413(2)	0.0315(4)	0.0013(2)	0.0618(5)

f). Space group: *Pca2*$_1$; **lattice parameters:** *a*=6.1447 Å, *b*=10.6489 Å, *c*=11.2503 Å, **Reliability factors:** GOF=1.43, R_p=2.96, R_{wp}=3.70, R_B=7.73

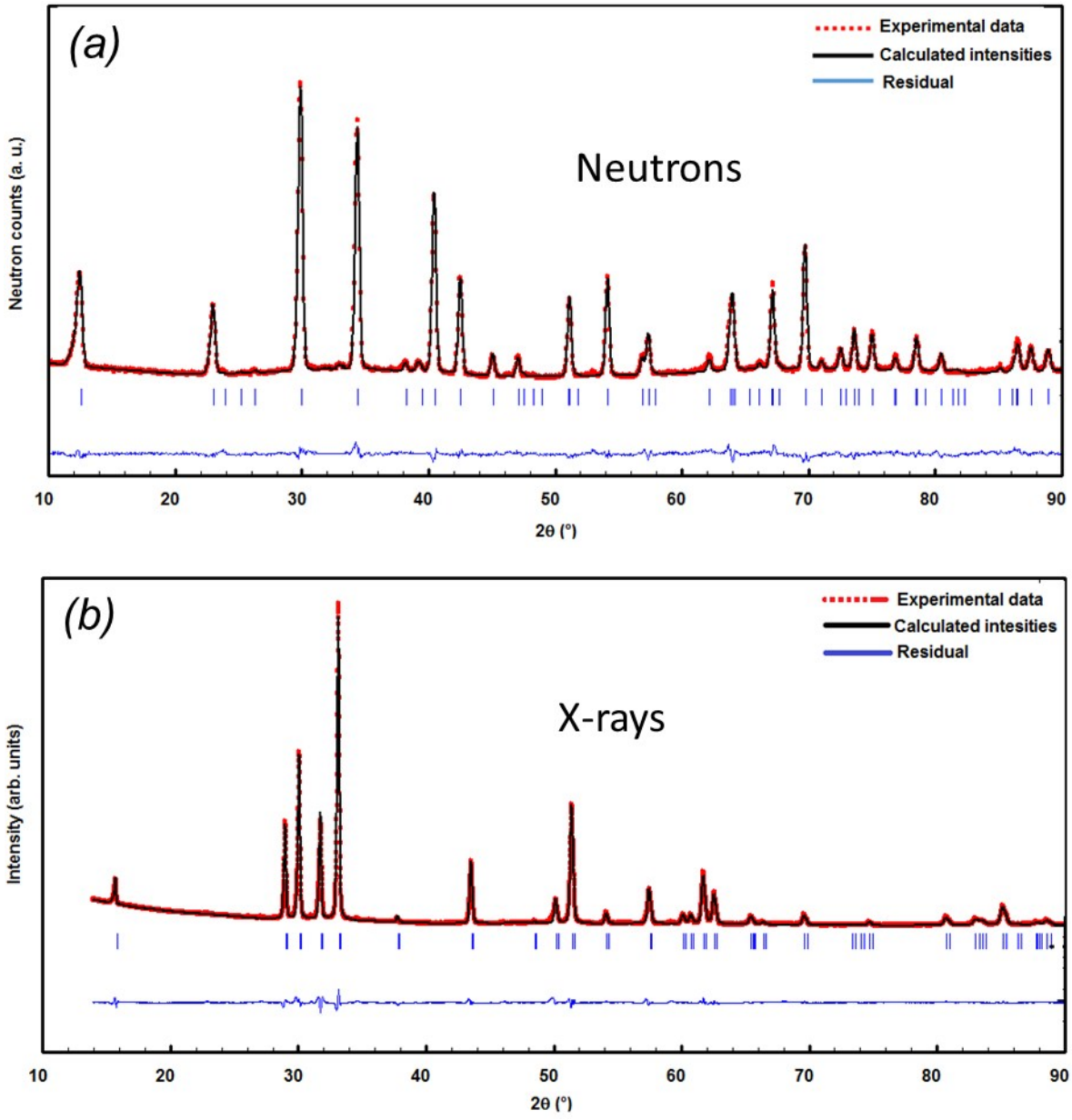


Atom	x	y	z	U_{iso}
Y_1	0.7523(2)	0.7505(4)	0.2408(2)	0.0376(1)
Zr_1	0.7523	0.7505	0.2408	0.0376
Y_2	0.2483(1)	0.9173(4)	0.2494(2)	0.0351(2)
Zr_2	0.2483	0.9173	0.2494	0.0351
Y_3	0.7566(2)	0.4166(6)	0.2444(2)	0.0702(2)
Zr_3	0.7566	0.4166	0.2444	0.0702
Mn_1	0.8954(8)	0.9146(6)	-0.0021(6)	-0.0080(8)
Mn_2	0.4057(1)	0.4121(1)	0.0019(9)	0.0177(2)

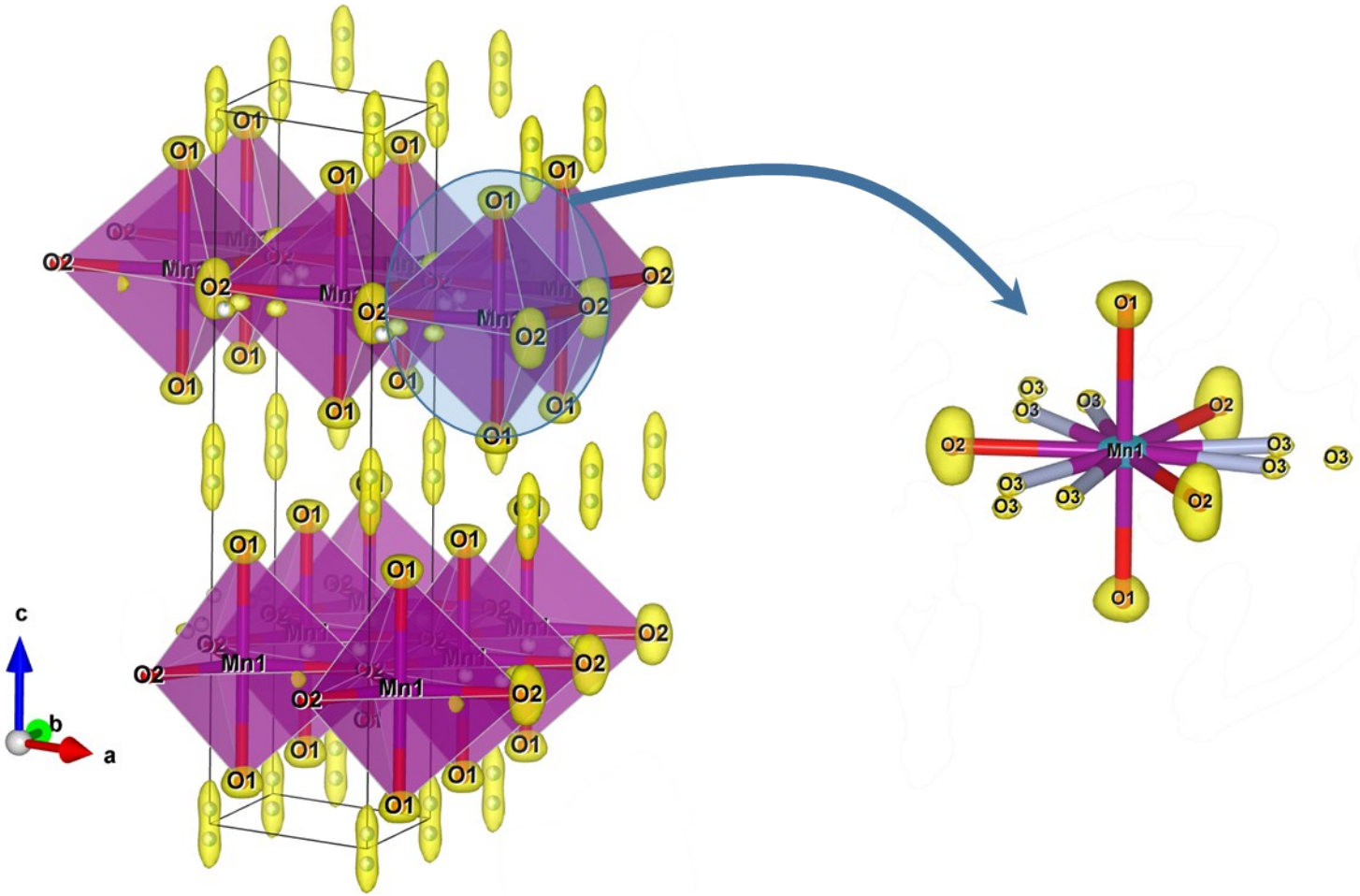
Atom	x	y	z	U_{iso}
Mn_3	0.3903(9)	0.7364(4)	0.0009(7)	-0.0148(8)
O_1	0.9307(1)	0.9181(9)	0.1671(5)	0.0257(2)
O_2	0.4272(1)	0.4135(8)	0.704(5)	0.0256
O_3	0.4147(2)	0.7435(8)	0.1699(9)	0.0257
O_4	0.5728(2)	0.5905(8)	0.3348(5)	0.0257
O_5	0.0879(1)	0.0834(8)	0.3394(5)	0.0257
O_6	0.0805(2)	0.7585(7)	0.3386(5)	0.0257
O_7	0.7758(1)	0.7744(5)	0.5378(3)	0.0257
O_8	0.2512(9)	0.9169(9)	0.1348(5)	0.0257
O_9	0.7568(9)	0.4221(9)	0.0140(5)	0.0257
O_{10}	0.6162(2)	0.5792(1)	0.0856(4)	0.0257
O_{11}	0.1408(4)	0.1395(1)	0.0134(8)	0.0257
O_{12}	0.0866(2)	0.7229(8)	0.0105(7)	0.0257

The good results obtained with *R*3*c* (e) and *P*ca2_1 (f) space groups incited us to try a model with the *P*6_3*cm* and *P*6_3*/mmc* space groups but adding one extra oxygen position, and it worked very good as well.

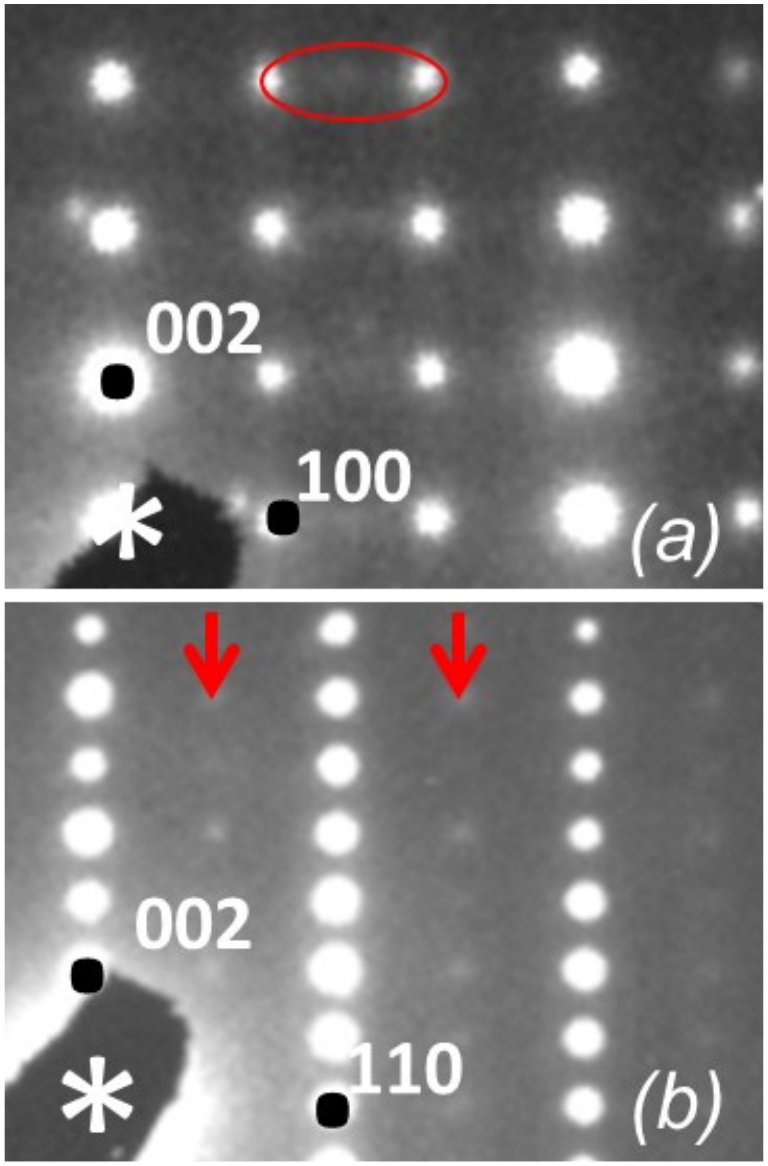
g). Graphical result of coupled Rietveld refinement for $Y_{0.9}Zr_{0.1}MnO_{3+\delta}$ (a) Neutron Diffraction and (b) X-Ray powder diffraction.



4. Distribution of nuclear densities obtained at room temperature for $Y_{0.9}Zr_{0.1}MnO_3$ by MEM from neutron powder diffraction data. O3 refers to interstitial sites. Isosurface levels are set at 0.02 fm/Å^3.



5. Transmission Electron Microscopy of $Y_{0.9}Zr_{0.1}MnO_3$ (a) [010] Electron Diffraction Pattern. The oval highlight weak streak (b) [$\bar{1}$10] EDP. Red arrows indicate line of additional spots.



6. Calculated crystal structure parameters with respect to Zr concentration, x, and oxygen hyperstoichiometry, δ, in $Y_{1-x}Zr_xMnO_{3+\delta}$. The reported values are the average between adding Zr on the two inequivalent Y-sites in the $P6_3cm$ crystal structure.

Stoichiometry	a (Å)	c (Å)	V (Å^3)
x in $Y_{1-x}Zr_xMnO_3$			
0	6.0997	11.4204	368.00
0.042	6.0981	11.4110	367.48
0.167	6.0903	11.3981	366.15
δ in $YMnO_{3+\delta}$			
0	6.0997	11.4204	368.00
0.042	6.1056	11.4207	368.41
0.167	6.1027	11.4129	368.68
x=δ in $Y_{1-x}Zr_xMnO_{3+\delta}$			
0	6.0997	11.4204	368.00
0.042	6.1039	11.3955	367.74
0.167	6.1127	11.3233	366.62

7. Results of Impedance data fit measured in air:

a). Impedance response of $YMnO_3$ at 600 °C

L (Ωcm^2)	R1 (Ωcm^2)	R_{CPE1} (Ωcm^2)	t	p	Capa R_{CPE1} (Fcm^2)	R_G (Ωcm^2)	t	p	Capa R_G (Fcm^2)	R_{CPE2} (Ωcm^2)	t	p	Capa R_{CPE2} (Fcm^2)
1.556E-07	5.641	0.036	6.174E-04	0.792	3.711E-05	0.487	0.024	0.476	0.049	4.471	0.049	0.950	0.045

b). Impedance response of $YMnO_3$ at 700 °C

L (Ωcm^2)	R1 (Ωcm^2)	R_G (Ωcm^2)	t	p	Capa R_G (Fcm^2)	R_{CPE2} (Ωcm^2)	t	p	Capa R_{CPE2} (Fcm^2)
3.186E-07	2.276	0.148	0.005	0.423	0.034	1.185	0.035	0.949	0.033

c). Impedance response of $YMnO_3$ at 800 °C

L (Ωcm^2)	R1 (Ωcm^2)	R_G (Ωcm^2)	t	p	Capa R_G (Fcm^2)
4.526E-07	1.352	0.328	0.010	0.500	32.077

d). Impedance response of $Y_{0.9}Zr_{0.1}MnO_3$ at 600 °C

L (Ωcm^2)	R1 (Ωcm^2)	R_{CPE1} (Ωcm^2)	t	p	Capa R_{CPE1} (Fcm^2)	R_G (Ωcm^2)	t	p	Capa R_G (Fcm^2)
2.816E-07	26.13	0.997	5.673E-06	0.851	6.848E-07	10.105	0.875	0.350	0.087

e). Impedance response of $Y_{0.9}Zr_{0.1}MnO_3$ at 700 °C

L (Ωcm^2)	R1 (Ωcm^2)	R_G (Ωcm^2)	t	p	Capa R_G (Fcm^2)
3.214E-07	10.99	2.83	0.124	0.350	0.044

f). Impedance response of $Y_{0.9}Zr_{0.1}MnO_3$ at 800 °C

L (Ωcm^2)	R1 (Ωcm^2)	R_G (Ωcm^2)	t	p	Capa R_G (Fcm^2)
1.167E-07	6.469	0.881	0.013	0.350	0.0149