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

In situ exsolution of Ni particles on the $PrBaMn_2O_5$ SOFC electrode material monitored by high temperature neutron powder diffraction under hydrogen

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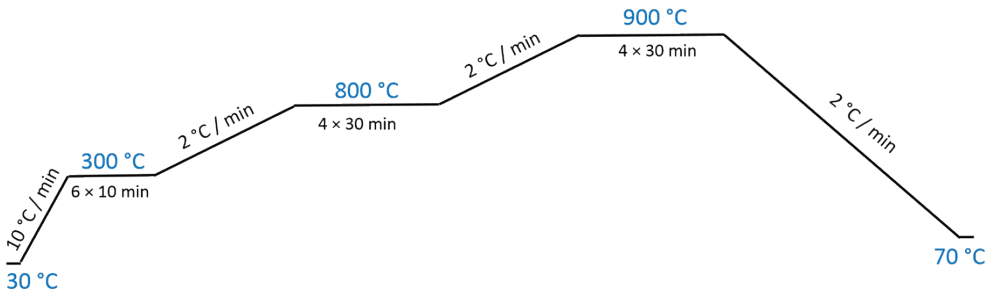

Fig. S.I. 1. Temperature profile used in the neutron experiment.

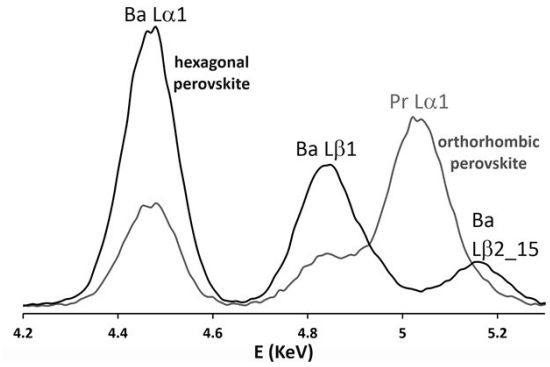

Fig. S.I. 2. TEM-EDS spectra for (grey) orthorhombic and (black) hexagonal perovskites resulting in the $Pr_{0.65(3)}Ba_{0.35(3)}Mn_{0.97(1)}Ni_{0.03(1)}O_3$ and $BaMnO_3$ compositions, respectively.

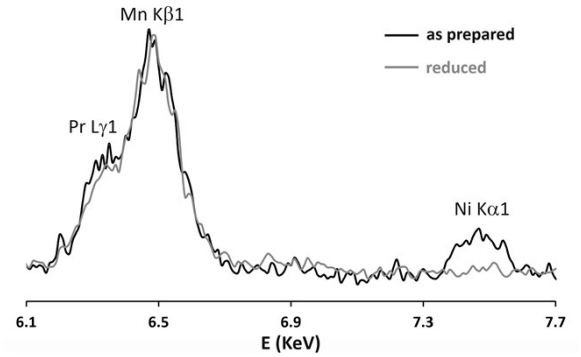

Fig. S.I. 3. Representative TEM-EDS spectra of PBMN (black) before and (grey) after reduction in 5% H_2/Ar. The analyses of few tens of particles show that all the Ni introduced in the parent material has been pulled outside the structure.

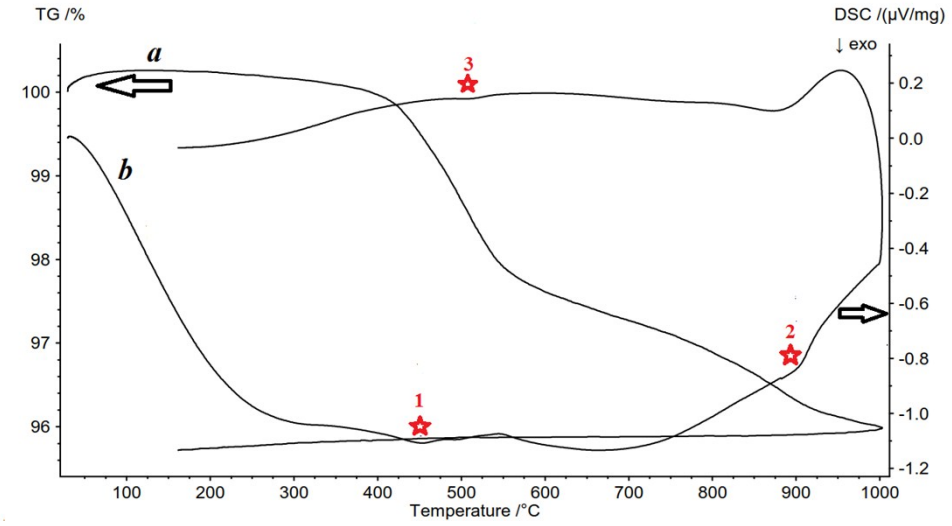

Fig. S.I. 4. Simultaneous TGA-DSC for as-prepared PBMN carried out under dry 5% H_2/N_2. Markers (1 and 2) on the DSC curve are concomitant with oxygen loss; marker 2 points at the formation of the layered perovskite. Marker (3) on cooling corresponds to the Mn^{3+}/Mn^{2+} charge ordering transition.

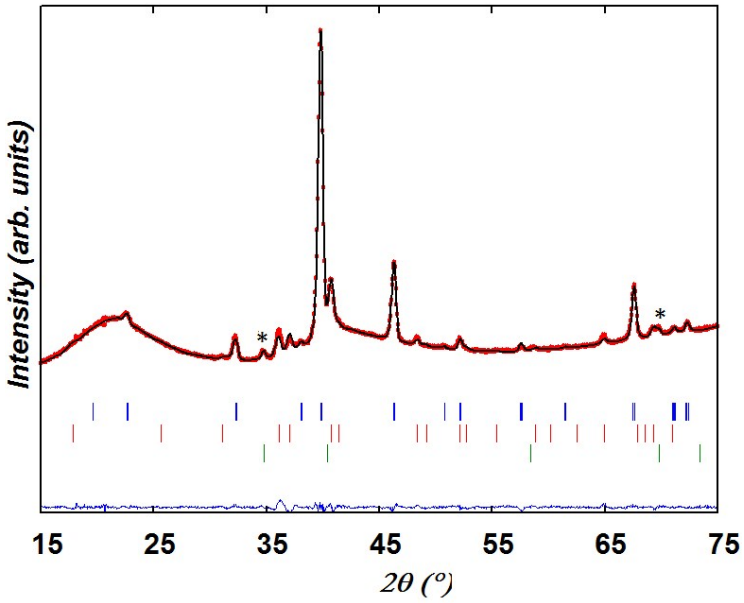

Fig. S.I. 5. Part of the NPD pattern of PBMN collected at T ~ 510 °C under 5% H_2/He; upper: (Pr,Ba)$MnO_{3-\delta}$ (S.G. *Ibmm*), middle: 2H-$BaMnO_{3-\delta}$ (S.G. $P6_3/mmc$), lower: MnO (S.G. Fm-3m). Main peaks from MnO are labelled (*).

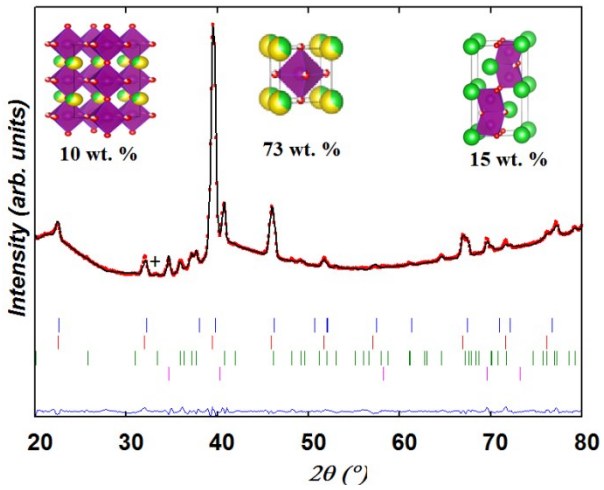

Fig. S.I. 6. Rietveld fit of the first dataset at T ~ 800 °C. Bragg ticks refer to (blue) tetragonal perovskite, (red) cubic perovskite, (green) hexagonal perovskite, (pink) MnO.

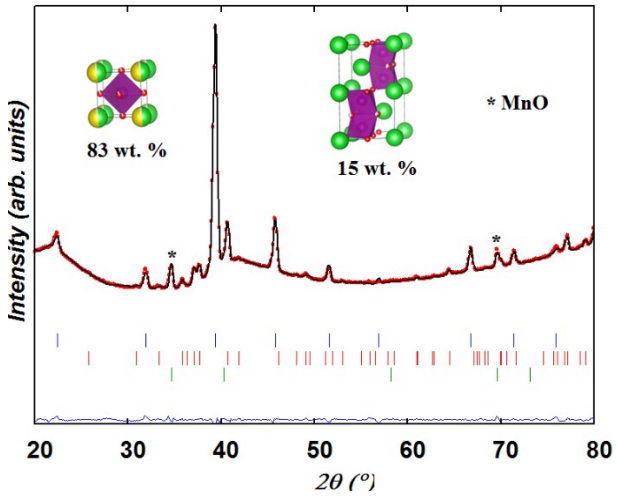

Fig. S.I. 7. Rietveld fit of the fourth (last) dataset at T ~ 800 °C. Bragg ticks refer to (blue) cubic perovskite, (red) hexagonal perovskite and (green) MnO. Peaks from MnO are labelled (*).

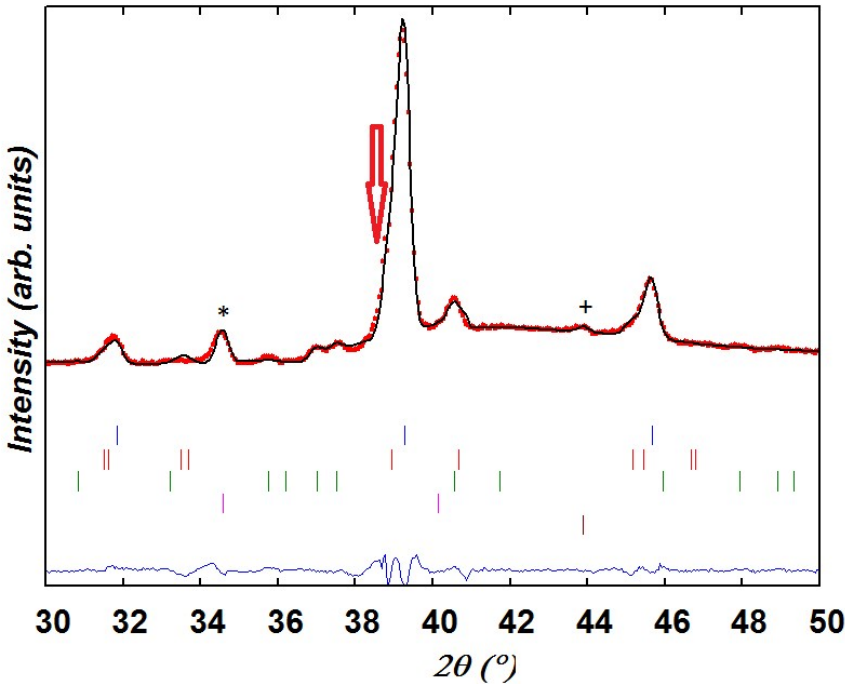

Fig. S.I. 8. Rietveld fit of the first neutron dataset collected at T ~ 900 °C. The arrow points at the growth of a layered perovskite. Bragg marks refer to (upper) cubic perovskite, (second) layered perovskite $PrBaMn_2O_5$, (third) hexagonal perovskite; (fourth) MnO, (fifth) Ni. Peaks from MnO (*) and Ni (+) are labelled.

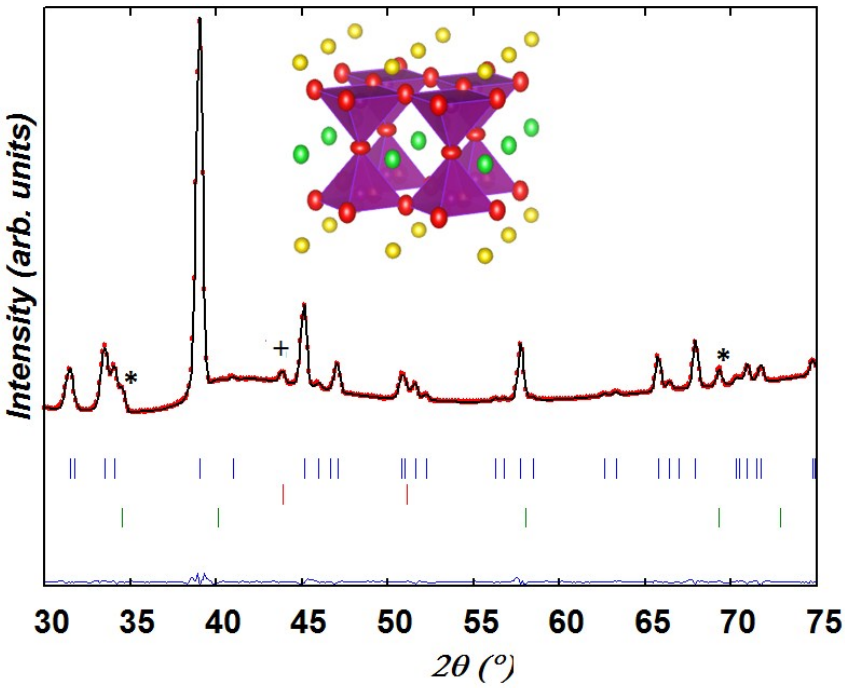

Fig. S.I. 9. Rietveld fit of the last NPD dataset collected at 900 °C. Bragg marks refer to (upper) $PrBaMn_2O_5$, (middle) MnO and (lower). Peaks from MnO (*) and Ni (+) are labelled.

Table S.I. 1. Structure parameters of as-prepared PBMN obtained from Neutron Powder Diffraction (NPD) from the data collected at $T \sim 60$ °C at the beginning of the reducing cycle.

Atom	*x*	*y*	*z*	B_{iso} (Å²)	*Occupancy*
Pr/Ba	-0.002(5)	0	0.25	0.3(1)	0.65/0.35
Mn/Ni	0.5	0	0	0.3(1)	0.975/0.025
O1	0.043(3)	0.5	0.25	1.0(5)	0.93(7)
O2	- 0.25	0.25	0.020(1)	2.1(3)	1.05(5)

S.G. *Ibmm* # 74, $a = 5.5079$ (3) Å, $b = 5.4893(2)$ Å, $c = 7.7539(4)$ Å, $V = 234.44(2)$ Å³, $Z = 4$.

Atom	*x*	*y*	*z*	B_{iso} (Å²)	*Occupancy*
Ba	1/3	2/3	0.75	0.3(1)	0.5/0.5
Mn	0.0	0	0	0.3(1)	1
O	0.152(3)	0.303(5)	0.25	0.5(2)	0.81(5)

S.G. $P6_3/mmc$ # 194, $a = 5.6869(2)$ Å, $c = 4.7916(3)$ Å), $V = 134.21(1)$ Å³, $Z = 2$.

Table S.I.2. Structural parameters of $PrBaMn_2O_{5.08(9)}$ at $T \sim 900$ °C (last isotherm)

Atom	site	*x*	y	z	B_{iso} (A^2)	Occupancy
Pr	1*a*	0	0	0	2.3(2)	1
Ba	1*b*	0	0	0.5	2.8(2)	1
Mn	2*h*	0.5	0.5	0.1944(4)	2.1 (1)	1
O1	1*c*	0.5	0.5	0	3.4 (2)*	0.03(1)
O2	1*d*	0.5	0.5	0.5	3.4 (2)*	1.02(2)
O3	4*i*	0.5	0	0.19	3.38(9)	1.01(2)

S.G. *P*4/*mmm* # 123, $a = 4.0123(2)$ Å, $c = 7.8836(4)$ Å, $V = 126.91(1)$ Å^3, $R_{wp} \sim 11$ %, $R_p \sim 9$%, $\chi^2 \sim 5.5$.

Table S.I. 3 Evolution of phase fraction (wt. %) on heating from 800 to 900 °C .

	800	**810**	**830**	**850**	**870**	**890**	**895**	**900**	**900**
$(Pr,Ba)MnO_{3-\delta}$ S.G. *Pm*-3*m*	83(2)	82(2)	82(2)	82(2)	50(1)	42(1)	32(1)	12(1)	0
$BaMnO_{3-\delta}$ S.G. $P6_3/mmc$	15(1)	15(1)	15(1)	14(1)	9(1)	8(1)	6(1)	2(1)	0
$PrBaMn_2O_S$ S.G. *P*4/*mmm*	0	0	0	0	38(1)	47(1)	59(1)	83(1)	97(1)
MnO	1.71(1)	1.7(1)	1.7(1)	1.7(1)	1.7(1)	1.7(1)	1.7(1)	1.7(1)	1.7(1)
Ni	0	0	0	0	0.11(3)	0.19(3)	0.24(3)	0.31(3)	0.57(3)

Table S.I. 4. Structure parameters of $PrBaMn_2O_{5.04(3)}$ at $T \sim 60$ °C (end of the reducing cycle).

Atom	site	*x*	y	z	β_{11} (A^2)	B_{33}	B_{12}, B_{13}	*SOF*
Pr	2b	0.75	0.25	0.5	90(5)	62(5)	0, 0	1
Ba	2a	0.75	0.25	0	81(5)	55(5)	0, 0	1
Mn1	2c	0.25	0.25	0.250(2)	67(4)	39(5)	0, 0	1
Mn2	2c	0.25	0.25	0.734(2)	67(4)	39(5)	0, 0	1
O1	2c	0.25	0.25	0.5				0.03(1)
O2	2c	0.25	0.25	0	123(7)	58(4)	0 ,0	1.01(2)
O3	8j	0.5099(5)	0.5099(5)	0.3063(3)	88(2)	71(2)	-15(4), 5(3)	1

S.G. *P*4/*nmm* #193: $a = 5.6127(1)$ Å, $c = 7.7510(3)$ Å, $R_{wp} = 6.72$ %, $R_p = 7.63$ %, $\chi^2 = 5.55$. B_{iso} for O1 was set at 0.