Supporting Information

for

A-site order-disorder in the $NdBaMn_2O_{5+\delta}$ SOFC electrode material monitored *in-situ* by neutron diffraction under hydrogen flow

Florent Tonus[1], Mona Bahout[2], Vincent Dorcet[2], Rakesh K. Sharma[3], Elisabeth Djurado[3] Serge Paofai[2], Ronald I. Smith[4], and Stephen J. Skinner[1*]*

[1] Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom.

[2]Institut des Sciences Chimiques de Rennes, UMR CNRS 6226, Université de Rennes 1, 263 Avenue du Général Leclerc, 35042 Rennes, France.

[3] Univ. Grenoble Alpes, CNRS, G-INP, LEPMI, F-38000, Grenoble, France.

[4]The ISIS Facility, STFC Rutherford Appleton Laboratory, Harwell Campus, Didcot, OX11 0QX, UK.

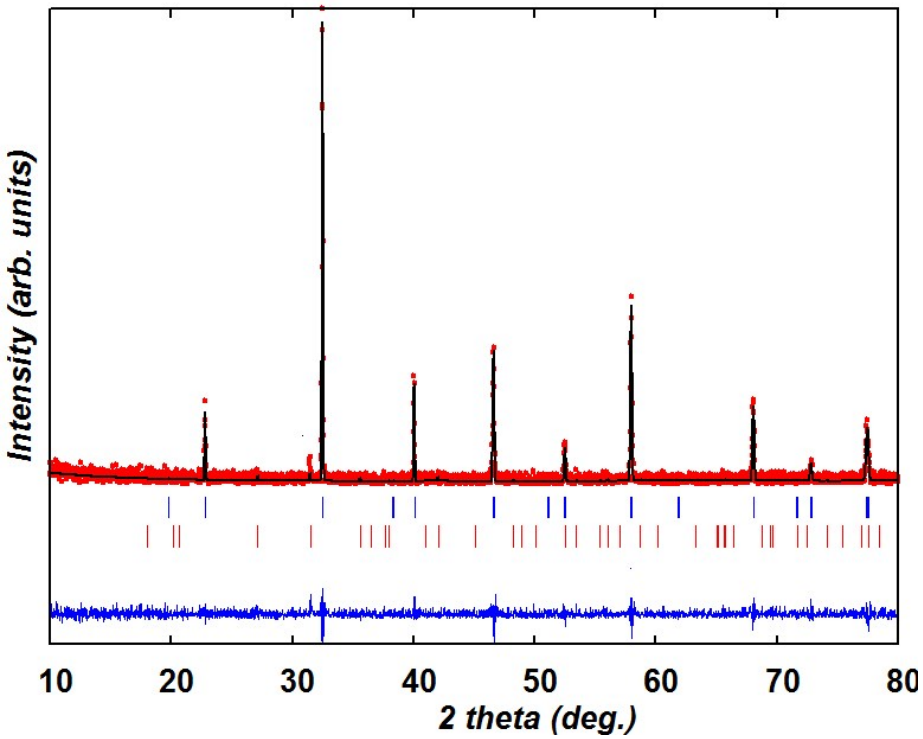

Fig. S.I. 1. Fitted room temperature X-ray diffraction pattern of $Nd_{0.5}Ba_{0.5}MnO_{3-\delta}$ phase indexed in *Imma* (upper markers); lower markers correspond to $BaMnO_3$ secondary phase (~ 8 wt %) indexed in $P6_3/mmc$.

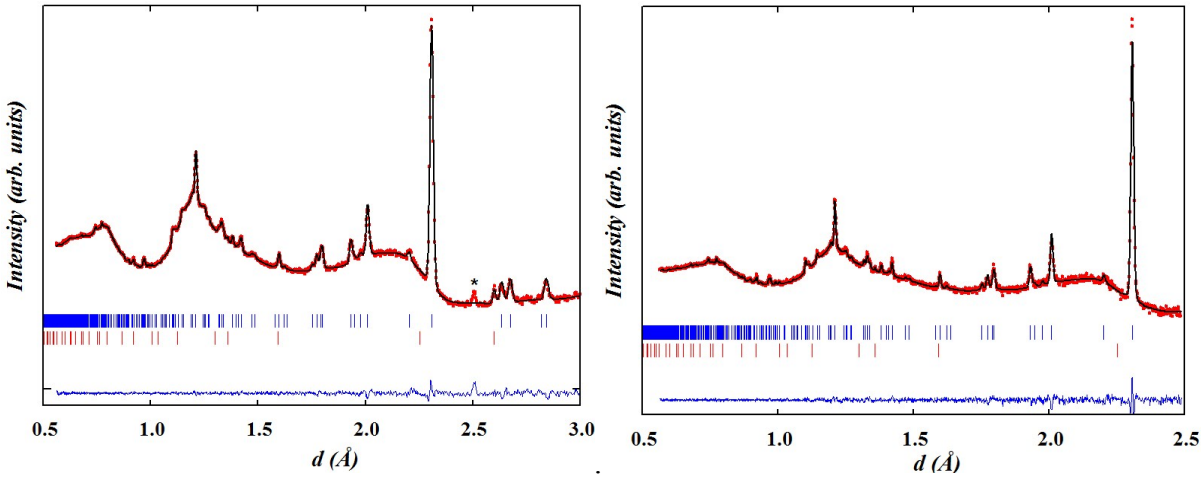

Fig. S.I. 2. Rietveld fits to data collected at 900 °C for 2 hours from the (left) 90 ° detector bank and (right) backscattering-bank. Bragg peaks correspond to $NdBaMn_2O_5$ *P*4/*mmm* (upper markers) and MnO $Fd\bar{3}m$ (lower markers). The unindexed peak at $d \sim 2.5$ Å is labelled (*).

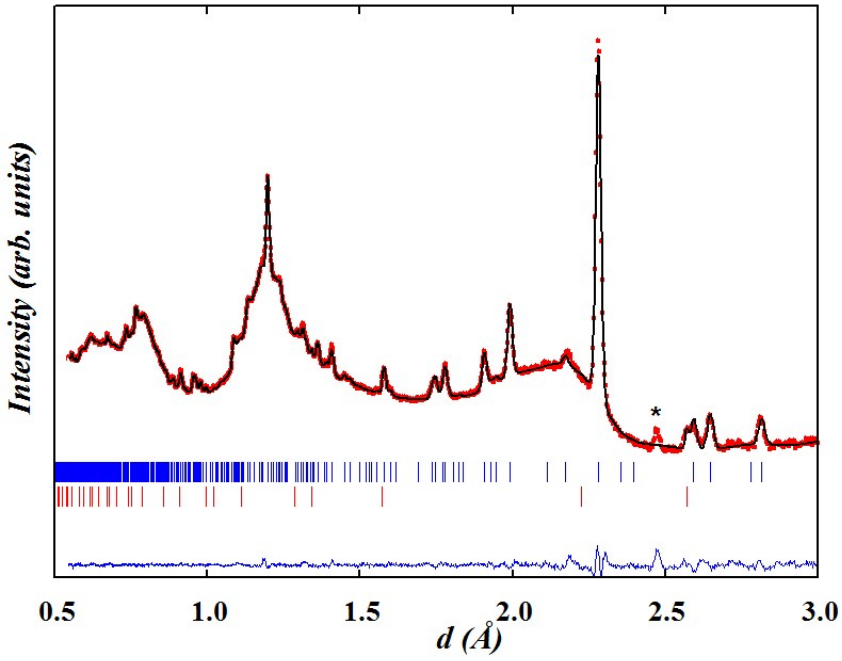

Fig. **S.I. 3**. Rietveld fit to the data collected for 2 h in the 90° detectors after cooling to 65 °C. Bragg peaks correspond to $NdBaMn_2O_5$, S.G. *P*4/*nmm* (upper markers) and MnO, S.G. $Fd\bar{3}m$ (lower markers). The additional peak likely to arise from crystallization of SiO_2 from the quartz tube is labelled (*).

Table S.I. 1. Refined lattice parameters and isotropic atomic displacement parameter (B_{iso}) for $Nd_{0.5}Ba_{0.5}MnO_{3.00}$ (S.G. *Imma*) at 20 °C with atoms in the following positions: (Nd,Ba), 4*e* (0, 1/4, *z*); Mn, 4*b*(0, 0, 1/2); O1, 4*e*(0, 1/4, *z*); O2, 8*g* (1/4, *y*, 01/4), a = 5.503(1) Å, b = 7.7962(4) Å, c = 5.502(1) Å, V_p = 59.01(2) Å^3, $\chi^2 \sim 1.92$, $R_B \sim 1.98$ %, $R_f \sim 4.45$%.

Atom	***z* or *y***	B_{iso} **(Å²)**
Nd, Ba	0.0	0.56(2)
Mn		0.62(3)
O1	0.470(2)	2.1(2)
O2	0.512(1)	2.5(1)

Table S.I. 2. Refined structural parameters and anisotropic thermal vibration parameters B_{ii} for $Nd_{0.5}Ba_{0.5}MnO_{2.5}$ (S.G. $Pm\bar{3}m$) at $T \sim 700$ °C 700 °C with atoms in the following positions: Nd,Ba, 1*a* (0, 0, 0); Mn, 1*b* (1/2, 1/2, 1/2); O, 3*c* (0, 1/2, 1/2).

Atom	B_{11}, B_{22}, B_{33} ($\times 10^3$)
Nd, Ba	44(1), 44(1) 44(1)
Mn	29(1), 29(1), 29(1)
O	39(2), 154(2), 154(2)

Table S.I. 3. Refined structural parameters ~and anisotropic thermal vibration parameters B_{ii} at 800 °C for $NdBaMn_2O_5$ in space group *P*4/*mmm* with atoms in the following positions: Nd, 1*a* (0, 0, 0); Ba, 1*b* (0, 0, 1/2); Mn, 2*h* (1/2, 1/2, z); O1, 1*d* (1/2, 1/2, 1/2); O2, 4*i* (1/2, 0, *z*); $a \sim 4.0066(5)$ Å, $c \sim 7.889(1)$ Å, $\chi^2 \sim 1.0$, $R_B \sim 4$ %, $R_F \sim 8$ %.

Atom	B_{11}, B_{22}, B_{33} ($\times 10^3$)
Nd	22(2), 22(2) 5(1)
Ba	27(3), 27(2), 4(1)
Mn	25(2), 25(2), 8(1)
O1	106(6), 106(6), 4(1)
O2	41(3), 31(2), 27(1)

Table S.I. 4. Refined structural parameters and isotropic thermal vibration parameters B_{iso} at 65 °C for $NdBaMn_2O_5$ in space group *P*4/*nmm* with atoms in the following positions: Nd, 2b (3/4, 1/4, 1/2); Ba, 2a (3/4, 1/4, 0); Mn1(Mn^{2+}), 2*c* (1/4, 1/4, *z*); Mn2(Mn^{3+}), 2*c* (1/4, 1/4, *z*); O1, 2c (1/4, 1/4, *z*); O3, 8*j* (*x*, *x*, *z*); O3, 2*c* (1/4, 1/4, 1/2). B_{iso} for Mn1 and Mn2 were constrained to be equal.

Atom	*a* (Å)	5.6251(4)
	c (Å)	7.7717(7)
Nd	B_{iso} (Å^2)	0.47(4)
Ba	B_{iso} (Å^2)	0.56(7)
Mn1	*z*	0.258(2)
	B_{iso} (Å^2)	0.31(6)
Mn2	*z*	0.756(1)
O1	*z*	0.002(3)
O2	*x*	0.500(2)
	z	0.3077(2)
	B_{iso} (Å^2)	1.38(4)
	χ^2	2.11
	R_B %	5.42