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A-site order-disorder in the NdBaMn₂O_{5+ δ} SOFC electrode material monitored *insitu* by neutron diffraction under hydrogen flow

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ABSTRACT

The *A*-site cation disordered perovskite oxide, Nd_{0.5}Ba_{0.5}MnO₃, a precursor of promising electrode materials for Solid Oxide Fuel Cells (SOFCs), has been prepared by heating the *A*site-ordered and vacancy ordered layered perovskite, NdBaMn₂O₅, in air at 1300 °C for 5 h. Both neutron powder diffraction (NPD) and transmission electron microscopy (TEM) showed that Nd_{0.5}Ba_{0.5}MnO₃ has a pseudotetragonal unit cell with orthorhombic symmetry (space group *Imma*, $\sqrt{2} a_p \times 2 a_p \times \sqrt{2} a_p$) at 20 °C due to antiphase tilting distortion of the MnO₆ octahedra, with the cell dimensions a = 5.503(1) Å, b = 7.7962(4) Å, c = 5.502(1) Å. *In-situ* NPD showed that the oxygen content of Nd_{0.5}Ba_{0.5}MnO₃ decreases on heating under 5 vol. % H₂/He flow to ~ 2.50/f.u. at 600 °C while the symmetry becomes cubic. On further heating, the oxygen stoichiometry remains unchanged up to $T \sim 800$ °C at which point localisation of the oxygen vacancies in the lanthanide layer as well as ordering of the Nd and Ba cations proceeds converting Nd_{0.5}Ba_{0.5}MnO_{2.5} to a layered NdBaMn₂O₅ double perovskite. Impedance spectroscopy measurements for the electrode material, NdBaMn₂O₆, screen printed on a Ce_{0.9}Gd_{0.1}O_{2.6} (CGO) electrolyte showed promising electrochemical performance with polarization resistance of 1.09 Ω cm² at 700 °C in air without any optimization. **Keywords:** *In-situ* neutron diffraction, *A*-site cation ordering, double perovskite manganites, cation order-disorder phase transition, SOFC electrodes, electrochemical impedance spectroscopy (EIS).

1. Introduction

Owing to their excellent mixed-ionic and electronic conductivity and fast oxygen kinetics, layered double perovskite cobaltites, $LnBaCo_2O_5$ (Ln = lanthanide), exhibit excellent properties as air electrodes for solid oxide cells (SOCs)¹⁻⁴. The related layered manganites, such as $PrBaMn_2O_5$ and $NdBaMn_2O_5$ were shown to exhibit high performance as a fuel electrode with good redox stability and tolerance to coking and sulphur contamination from hydrocarbon fuels^{5, 6}. A noteworthy feature of these manganites is the flexibility of the manganese environment which can vary from 5- to 6-fold coordination. These layered manganites are stable to redox cycling between air and diluted hydrogen atmosphere up to at least 850°C. In air, the phase is oxidised to A-site ordered NdBaMn₂O₆ (P4/mmm) whereas it is reduced back to NdBaMn₂O₅ in anode operating conditions within the formation of the intermediate metastable ordered orthorhombic phase, NdBaMn₂O_{5.5}⁷. Therefore, the $LnBaMn_2O_{5+\delta}$ materials are suitable as both fuel and oxygen electrodes in symmetrical SOCs⁵. This novel concept has significant advantages compared to traditional configurations, regarding both fabrication and maintenance/operation The reduced phase, LnBaMn₂O₅, can be fabricated by annealing the A-site cation disordered materials, Ln0.5Ba0.5MnO3-8 under a hydrogen atmosphere at $T \sim 800-900$ °C⁵. Cation order plays a critical role in mediating the stability and physical properties of these oxides, such as high electrical conductivity and mechanical compatibility. Indeed, fast anion mobility in $LnBaM_2O_5$ (M = Co, Mn) is mediated by *Ln*/Ba ordering^{8, 9}. Considering the use of these materials in electrochemical devices, cell manufacture which involves co-sintering of the electrode and electrolyte in air⁶ can alter *A*-site ordering resulting in formation of the disordered phase, $Ln_{0.5}Ba_{0.5}MnO_{3.6}^{8, 9}$. In order to mimic this thermal treatment, a NdBaMn₂O₅ layered perovskite was sintered in air at 1300 °C for 5 hours and the *A*-site cation disordered phase so obtained was subsequently heated under hydrogen flow to monitor by *in-situ* neutron powder diffraction the disorder/order structural transition that proceeds under anode SOFC working conditions. Since the NdBaMn₂O₆ electrode material is thermally and mechanically stable with ceria electrolytes^{6, 10, 11}, impedance spectroscopy measurements for a thin layer screen printed on a Ce_{0.9}Gd_{0.1}O_{2-δ} (CGO) electrolyte were performed in the temperature range of 500-800 °C to evaluate its electrochemical performance as an oxygen electrode for SOCs.

2. Experimental

A polycrystalline oxygen-deficient perovskite sample (~ 5 g) with layered ordering of Nd and Ba referred to as NdBaMn₂O_{5+ δ} hereafter, was prepared *via* the citrate-nitrate synthesis route as described elsewhere¹². Part of the NdBaMn₂O_{5+ δ} sample was heated in air at 1300 °C for 5 h to obtain the *A*-site disordered phase, referred to as Nd_{0.5}Ba_{0.5}MnO₃ hereafter. Phase purity of both disordered and ordered samples was assessed from powder X-ray diffraction measurements (XRD) at room temperature over the range $10 \le 2\theta \le 120^\circ$, $\Delta 2\theta = 0.02^\circ$ using a Bruker AXS D8 Advance diffractometer in Bragg-Brentano geometry equipped with Ge (1 1 1) Johansson-Guinier focusing primary monochromator (Cu-K α_1 radiation) and a silicon strip Lynxeye detector. The XRD patterns were analysed using the Rietveld method with the FullProf software¹³. The microstructure of the Nd_{0.5}Ba_{0.5}MnO₃ phase was probed by means of transmission electron microscopy (TEM) using a JEOL 2100 LaB₆ instrument operating at 200 kV double tilt (±20°) (point resolution 0.17 nm), fitted with a XEDS microanalysis system (OXFORD INCA) and ENFINA spectrometer with an energy resolution of 1.3 eV. The sample was crushed in dry ethanol and a few drops of the suspension were deposited on a carbon-coated film (copper grid). Diffraction patterns were collected with a GATAN Orius 200D Charge Coupled Device (CCD) camera. *In-situ* neutron powder diffraction data were collected on the high-flux medium resolution POLARIS diffractometer at ISIS, the UK spallation source at the Rutherford Appleton Laboratory. Approximately 4 g of Nd_{0.5}Ba_{0.5}MnO_{3.6} powder was loaded to a depth of 4 cm (corresponding to the height of the incident neutron beam) in a double-walled quartz glass cell built to enable gas to flow through the sample. The cell was mounted in a furnace designed for neutron diffraction measurements and connected to an external gas-handling system to control the oxygen content and flow as the sample was heated to 900 °C in 5% H₂/He gas, allowing the structural stability under anode SOFC operation conditions to be probed directly. The temperature profile used is illustrated schematically in Fig. 1.



Fig.1. Thermal profile used in the neutron diffraction experiment under 5% H₂/He flow to convert the *A*-site disordered Nd_{0.5}Ba_{0.5}MnO_{3- δ} phase to A-site ordered NdBaMn₂O_{5+ δ} phase. Heating and cooling rates are 10 °C min⁻¹.

Two thermocouples were attached on opposite sides of the wall of the (inner) quartz tube approx. 5 mm above the sample to control the furnace temperature and monitor the sample temperature. Data normalization and file output was undertaken using the Mantid software package¹⁴. The patterns from two banks of detectors; the backscattering bank (average $2\theta = 146.7^{\circ}$) which covers a range in 2θ from 135 to 167° with a *d*-spacing range of 0.2-2.65 Å and the 90° bank (average $2\theta = 92.6^{\circ}$) which covers a 2θ range of 75 to 113° with a maximum *d*-spacing of 4.1 Å were used together for structure refinement by the Rietveld method, using the FullProf Suite ¹³. Peak shapes were modeled by a convolution of two back-to-back exponentials with a pseudo-Voigt function. The background arising from the amorphous quartz glass cell was fitted by the Fourier filtering technique. In addition to the profile parameter (σ_1) describing the Gaussian contribution to the Bragg peak profiles, lattice parameters, fractional occupancy of oxygen sites, atomic positions and isotropic atomic displacement parameters (ADP) were refined. Any additional constraints are noted when describing specific models.

The electrochemical properties of an oxidised NdBaMn₂O₆ phase were measured by electrochemical impedance spectroscopy (EIS) in air. The NdBaMn₂O₆ phase was obtained by topotactic oxidation of NdBaMn₂O₅ in air at $T \sim 500$ °C for 5 hours, as described previously¹². This temperature is low enough to avoid any changes in the *A*-site distribution. The ink was prepared by mixing the polycrystalline NdBaMn₂O₆ powder with a commercial dispersant (KD2921, Zschimmer and Schwarz). The film was deposited on a Ce_{0.9}Gd_{0.1}O_{2.6} (CGO) electrolyte, 19.6 mm in diameter and 1.4 mm thick, by the screen printing technique (SP) then annealed at 700 °C for 3 h in air to increase overall crystallinity and improve interface bonding with the electrolyte. The EIS measurements were carried out using an Autolab potentiostat-galvanostat (PGSTAT 302N) in the temperature range 500 °C - 700 °C at 50 °C intervals and with a frequency range of 0.05 Hz - 100 kHz. The measurements were performed with a signal amplitude of 0.02 V at open circuit potential (OCP), using gold grids (Heraeus, woven gauzes, 1024 meshes per cm² and a wire diameter of 0.06 mm) as the current collectors. The EIS data were normalized to the electrode surface area (A = 1.54 cm²) and

fitted using equivalent circuits with the ZView[®] software (Scribner Associates). The polarization resistance, R_{pol} , values were calculated by subtracting the high frequency (HF) intercept from the low frequency (LF) intercept on the real axis of the electrode impedance on the Nyquist plane. Since the measurements were performed on symmetrical cells, the obtained R_{pol} values were calculated as follows; $(R_1+R_2) \times A / 2$, where R_1 and R_2 are the HF and LF contributions, respectively.

3. Results and discussion

The initial characterisation of the NdBaMn₂O_{5+δ} sample heated in air at $T \sim 1300$ °C was carried out by X-ray diffraction recorded at 20 °C. The diffraction pattern shows the presence of the main *A*-site disordered manganite phase, Nd_{0.5}Ba_{0.5}MnO₃, and a minor hexagonal perovskite impurity, BaMnO_{3-δ}^{2, 15} (Fig. 2). Although the pattern of Nd_{0.5}Ba_{0.5}MnO₃ can be indexed using a cubic unit cell, as reported previously², lower symmetry was suggested from transmission electron microscopy (TEM) and neutron powder diffraction (NPD). Therefore, indexing was performed in the orthorhombic *Imma* space group on the basis of NPD analysis and in agreement with the symmetry of the related compounds, $Ln_{0.7}Ba_{0.3}MnO_3$ (Ln = Pr, Nd)¹⁶, giving the cell parameters, a = 5.503 (1) Å, b = 7.7962 (4) Å, c = 5.502 (1) Å and V = 236.1 (3) Å³.



Fig. 2. Fitted room temperature X-ray diffraction pattern of Nd_{0.5}Ba_{0.5}MnO₃₋₈ phase indexed in *Imma* (upper markers); lower markers correspond to BaMnO₃ secondary phase (~ 8 wt %) indexed in $P6_3/mmc$.

3.1 Electron diffraction at room temperature

Fig. 3 shows selected area electron diffraction (SAED) pattern of the NdBaMn₂O_{5+ δ} sample treated in air at 1300 °C. The strong reflections can be indexed on the single perovskite cubic phase and no extra reflections related to the cation ordering along the *c*-lattice parameter were observed.





However, $\frac{1}{2}(ooo)_p$ superlattice reflections (*o* refers to odd Miller indices of the cubic cell), as indicated by an arrow in Fig. 3b, are observed and result from anti-phase tilting of the MnO₆ octahedra network according Glazer¹⁷ and Woodward ¹⁸. Moreover, no $\frac{1}{2}(ooe)_p$ superlattice reflections (*e* refers to even Miller indexes) are observed in Fig. 3a and 3b suggesting no evidence of in-phase tilting. As a result, the $\frac{1}{2}(ooo)_p$ reflections can be described in six space groups (S.G.) ^{17, 19}: I4/mcm ($a^0a^0c^-$), Imma ($a^0b^-b^-$), R $\overline{3}c$ ($a^-a^-a^-$), C2/m ($a^0b^-c^-$), C2/c ($a^-b^-b^-$) and P-1 ($a^-b^-c^-$)¹⁸. Since barium perovskite manganites usually crystallise in I4/mcm or Imma¹⁶, both groups have been evaluated on the basis of NPD patterns collected in this study.

3.2 Neutron diffraction on heating/cooling under dry 5% H₂/He

The neutron diffraction patterns collected at 20 °C from the sample treated in air at 1300 °C reveal the presence of a main perovskite phase, Nd_{0.5}Ba_{0.5}MnO_{3.6} whose pattern could be indexed either in a tetragonal *I4/mcm* ($\sqrt{2} a_p \times \sqrt{2} a_p \times 2 a_p$) or orthorhombic *Imma* ($\sqrt{2} a_p \times 2 a_p \times \sqrt{2} a_p \times \sqrt{2} a_p$) cell where a_p refers to the lattice parameter of the primitive cubic perovskite structure. Both space groups (S.G.) comprise two oxygen sites; O1 within the Nd/Ba layer and O2 within the Mn layer. Quite similar fits to the NPD data were obtained in both *I4/mcm* ($\chi^2 \sim 1.56$) and *Imma* ($\chi^2 \sim 1.50$) space groups but the latter reproduced the patterns better (Fig. 4) and was consistent with that reported for the $Ln_{0.7}Ba_{0.3}MnO_3$ and $Ln_{0.9}Ba_{0.1}MnO_3$ (Ln = Pr, Nd) manganites¹⁶. However, we stress that unambiguous determination of the S.G. of Nd_{0.5}Ba_{0.5}MnO₃ is complicated since the detection of superlattice peaks or resolution of the splitting of the fundamental reflections is impossible due to the resolution limits of Polaris ($\Delta d/d = 10^{-3}$) combined with poor statistics and the background originating from the quartz cell.



Fig. 4 Part of the NPD data collected at 20 °C for Nd_{0.5}Ba_{0.5}MnO₃₋₈ comparing the fits at $d \sim 2.35$ Å (left) S.G. *I4/mcm* and (right) S.G. *Imma*; lower markers relate to the hexagonal BaMnO₃ phase (S.G. *P*6₃/*mmc*).

The site occupation factor at the O1 and O2 sites in Nd_{0.5}Ba_{0.5}MnO_{3- δ} refined to ~ 1.00 and ~ 0.97(1), respectively, resulting in an overall calculated oxygen content of ~ 2.94(2). Bond angle and distance calculations show octahedral tilting angles Mn-O1-Mn = 170.2(5) °, Mn-O2-M =175.3(5) ° and similar Mn-O bond lengths; Mn-O1 = 1.9562 (9) Å, Mn-O2 = 1.9477 (5) Å. The crystal structure of Nd_{0.5}Ba_{0.5}MnO_{3- δ} and the full Rietveld fit are displayed in Fig. 5 while the structural parameters and agreement factors are listed in Table 1.



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Fig. 5 (left) orthorhombic *Imma* Nd_{0.5}Ba_{0.5}MnO₃₋₈ structure with two independent oxygen sites with (red) O1 (0, 0.25, *z*) and (pink) O2 (0.25, *y*, 0.25); (right) NPD patterns recorded at 20 °C from the 90° bank for the air treated sample; Nd_{0.5}Ba_{0.5}MnO₃₋₈ ~ 92 wt % (upper markers) and BaMnO₃ ~ 8 wt % (lower markers). The peak labelled (*) is a superlattice reflection not indexed in cubic $Pm\bar{3}m$.

Table 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	$B_{\rm iso}({\rm \AA}^2)$
Nd, Ba	0.0	0.56(2)
Mn		0.62(3)
01	0.470(2)	2.1(2)
02	0.512(1)	2.5(1)

Besides Nd_{0.5}Ba_{0.5}MnO_{3.8} (~ 92 wt %), the sample contains a minor $P6_3/mmc$ hexagonal BaMnO₃ phase (~ 8 wt. %) with lattice parameters, a = 5.6268 (7) Å and c = 9.241(2) Å. This phase commonly forms readily in air during the synthesis of barium manganite perovskites. Fig. 6 shows representative NPD patterns collected isothermally for 1 hour throughout the heating cycle under a 5% H₂/He gas flow and reveal clearly two successive phase changes; from pseudotetragonal Nd_{0.5}Ba_{0.5}MnO₃, to cubic Nd_{0.5}Ba_{0.5}MnO_{2.5} and tetragonal. NdBaMn₂O₅. At $T \sim 600^{\circ}$ C, the structure of the majority phase has clearly transformed to cubic $Pm\overline{3}m$ and the oxygen content refined to ~ 2.54(4)/f.u. The ratio of the hexagonal phase remained unchanged (~ 6 wt %) while a MnO impurity (< 1 wt %) is also included in the refinement.



Fig. 6 A section of the observed neutron diffraction patterns of Nd_{0.5}Ba_{0.5}MnO₃₋₈ recorded in the 90° detector bank at selected temperatures throughout the heating and cooling cycle under 5% H₂/He flow. The disorder-order phase transition proceeds at $T \sim 800$ °C. The peak labelled (*) arises from SiO₂ of the quartz tube.

Additional data were recorded at $T \sim 700$ °C with no changes occurring at this temperature, as

revealed by the Rietveld plots displayed in Fig. 7 and structural parameters listed in Table 2.



Fig. 7. Rietveld fits to the data collected at $T \sim 700$ °C for 2 h from (left) 90 ° bank and (right) backscattering-bank. Bragg peaks correspond to Nd_{0.5}Ba_{0.5}MnO_{2.50}, S.G. *Pm* $\overline{3}m$ (upper markers), BaMnO₃₋₈, S.G. *P* 6_3 /*mmc* (middle markers) and MnO, S.G. *F* $d\overline{3}m$ (lower markers).

Table 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)
0	39(2), 154(2), 154(2)

The large anisotropy of thermal vibrations for the oxygen atoms originates principally from the dynamic disorder suggesting large mobility and lability. The cubic structure of Nd_{0.5}Ba_{0.5}MnO_{2.5} is unstable as oxygen-vacancy ordering proceeds at ~ 800 °C causing a phase transformation to tetragonal NdBaMn₂O₅ (Fig. 8) while the hexagonal BaMnO₃ phase has completely disappeared. Ordering of anion vacancies reduces the coordination of the A sites producing two different A-site coordination geometries; 12 and 8 occupied by the Ba and Nd ions respectively. The first dataset recorded for 1 hour at 800 °C can be modelled assuming the coexistence of three phases NdBaMn₂O₅, P4/mmm (~ 68 wt %), $Nd_{0.5}Ba_{0.5}MnO_{2.5}$, $Pm\bar{3}m$ (~ 30 wt %) and MnO (~ 2 wt %) whose ratios are difficult to estimate accurately because of peak overlay and background approximations. An extra peak labelled (*) emerges at $d \sim 2.50$ Å (Fig. 9) whose intensity increases on further heating and likely arises from crystallization of SiO₂ from the quartz tube. The conversion of $Nd_{0.5}Ba_{0.5}MnO_{2.5} \rightarrow NdBaMn_2O_5$ is slow because it involves phase separation into two distinct forms and requires nucleation and growth of a different crystal structure. The effect is illustrated by the presence of a significant amount of cubic perovskite (~ 20 wt %) in the second dataset collected at 800 °C. The unit cell volume of the A-site ordered phase normalized to the primitive perovskite, $V \sim 63.0 \text{ Å}^3$, is similar to that of the oxygen deficient disordered phase, $V \sim 63.5$ Å³. The structural parameters of NdBaMn₂O₅ at 800 °C are displayed in Table 3 and are consistent with those reported previously¹².



Fig. 8. Rietveld fits to the dataset collected at 800 °C in the 90 °detector bank. Bragg peaks correspond to NdBaMn₂O₅, *P*4/*mmm* (upper markers), Nd_{0.5}Ba_{0.5}MnO_{2.50}, S.G. *Pm* $\overline{3}m$ (middle markers) and MnO, S.G. *Fd* $\overline{3}m$ (lower markers). The extra peak at $d \sim 2.5$ Å labeled (*) likely arises from crystallised SiO₂ of the quartz tube.

Table 3. Refined structural parameters and anisotropic thermal vibration parameters B_{ii} at 800 °C for NdBaMn₂O₅ 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* ~ 4.0066(5) Å, *c* ~ 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)
01	106(6), 106(6), 4(1)
O2	41(3), 31(2), 27(1)

At $T \sim 900$ °C, the kinetics increase and the cubic phase has completely transformed into the *A*-site ordered phase (Fig. 9) while the MnO content remains constant at ~ 2 wt %. The phase transformation may proceed with nucleation and subsequent growth of the generated phase rather than by a diffusion-controlled process.



Fig. 9. 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 NdBaMn₂O₅ *P*4/*mmm* (upper markers) and MnO $Fd\bar{3}m$ (lower markers). The unindexed peak at $d \sim 2.5$ Å is labelled (*).

Although the *P4/mmm* and *P4/mmm* models gave equivalent fits ($\chi^2 \sim 2.0$) to the neutron data collected at 65 °C for 2.5 h after cooling, the charge ordered model was adopted in agreement with our previous study. The large width of the diffraction peaks reflects a substantial decrease in the crystallite size of the polycrystalline ordered compound that is consistent with ordering of the Nd³⁺/Ba²⁺ cations and oxygen vacancies. The normalized unit cell volume of NdBaMn₂O₅, $V \sim 61.5$ Å³, is larger than that of Nd_{0.5}Ba_{0.5}MnO_{3.0}, $V \sim 59.0$ Å³ as expected when oxygen is removed from the structure. The Rietveld fit to the data collected after cooing to 65°C using space group *P4/nmm* is displayed in Fig. 10 and the structural parameters and agreement factors are listed in Table 4. The oxygen content was fixed at the value refined from the 900 °C data set. The additional peak that originates from SiO₂ is still present and was not observed in our previous experiment¹² in which heating was limited to a temperature of 800 °C.



Fig. 10. Rietveld fit to the data collected for 2 h in the 90° detectors after cooling to 65 °C. Bragg peaks correspond to NdBaMn₂O₅, S.G. *P4/nmm* (upper markers) and MnO, S.G. *Fd* $\overline{3}m$ (lower markers). The additional peak likely to arise from crystallization of SiO₂ from the quartz tube is labelled (*).

Table 4. Refined structural parameters and isotropic thermal vibration parameters B_{iso} at 65 °C for NdBaMn₂O₅ in space group *P4/nmm* with atoms in the following positions: Nd, 2b (3/4, 1/4, 1/2); Ba, 2a (3/4, 1/4, 0); Mn1(Mn²⁺), 2c (1/4, 1/4, z); Mn2(Mn³⁺), 2c (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	<i>a</i> (Å)	5.6251(4)
	<i>c</i> (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)
01	z	0.002(3)
O2	x	0.500(2)
	Z	0.3077(2)
	$B_{\rm iso}$ (Å ²)	1.38(4)
	χ^2	2.11
	<i>R</i> _B %	5.42

3.3 Electrochemical properties

In this section, the electrochemical properties of screen-printed NdBaMn₂O₆ electrodes studied by EIS are presented. The impedance diagrams were analyzed using the ZView[®] software with an equivalent circuit, consisting of a combination of two resistance (R)-constant phase element (CPE) parallel circuits, connected in series with an inductance (L1) and a series resistance including the ohmic losses originating from electrolyte (Rs), as shown in Fig. 11. This electrical element (L1), appearing as a high frequency tail below the real axis, represents the contribution of the connecting leads, measuring device and connecting wires to the measured total impedance²⁰. CGO conductivity of 0.018 S cm⁻¹ has been calculated from the data obtained at 600 °C from the R_s value and was found to be in good agreement with the literature²¹.



Fig. 11. Equivalent circuit used for the fitting of the electrochemical impedance diagrams.

According to the selected analysis, the electrode response is composed of two main elementary contributions located at high frequency (HF) and low frequency (LF), as shown in Fig. 12a for data recorded at 600 °C. The high frequency contribution (HF) is attributed to charge transfer at the electrode/electrolyte interface whereas the low frequency contribution (LF) can be associated with various electrode processes such as adsorption of gaseous oxygen





Fig. 12. Electrochemical performance of NdBa Mn_2O_6 symmetrical cell on CGO electrolyte: Nyquist impedance diagrams at 600 °C in air at OCV (numbers indicate the logarithm of the measuring frequency), (b) Arrhenius plot.

The thermal variations of Polarization resistance, R_{pol} , values are shown in Fig. 12b. R_{pol} decreases with increasing temperature, as expected. The R_{pol} value was found to be 7.29 Ω cm² at 600 °C (1.09 Ω cm² at 700 °C). Activation energy has been found to be 1.46 eV. The R₂ values are always larger than the R₁ ones (as shown in Fig. 12a at 600 °C), suggesting that the oxygen desorption or adsorption process is the rate-limiting step for the oxygen reduction reaction (ORR)^{24, 25, 26}. Indeed, NdBaMn₂O₆ oxygen electrodes shows similar performance as La₃Ni₂O_{7+δ} and La₄Ni₃O_{10-δ} electrodes²⁷. However, cathode composition, microstructure and architecture for a given composition plays a very important role in improving the cathode performance²⁷⁻³⁴. For example R. Sayers *et al.* reported R_{pol} values of 1.0 Ω cm² at 700 °C, screen printed (SP) after the addition of a thin and dense La₂NiO_{4+δ} layer in between SP La₂NiO_{4+δ} and CGO electrolyte³⁰. Sharma *et al.* have recently reported a R_{pol} value of 0.08 Ω cm² at 700 °C for a double layer La₂NiO_{4+δ} electrode prepared by electrostatic spray deposition technique followed by screen-printing a layer of La₂NiO_{4+δ} on a CGO electrolyte, which is the reference in the literature at the moment for the pure La₂NiO_{4+δ}²⁸. Further

improvement in the cathode performance has been recently reported (R_{pol} value equal to 0.04 Ω cm² was found at 700 °C) by Sharma *et al.* when a La₂NiO_{4+δ}/CGO composite layer was inserted in between a CGO electrolyte and La₂NiO_{4+δ} cathode³³. Nicollet *et al.* have also reported similar performance (R_{pol} value equal to 0.05 Ω cm² was found at 700 °C) when La₂NiO_{4+δ} was infiltrated inside a CGO backbone³⁴. Therefore, our future goal is to improve the cathode performance by improving the cathode microstructure, architecture and composition as well as to study the effect of sintering temperature on its performance.

Conclusions

Crystal evolution of the *A*-site disordered manganite, Nd_{0.5}Ba_{0.5}MnO₃, has been studied under hydrogen flow as a function of temperature up to 900 °C. Nd_{0.5}Ba_{0.5}MnO₃ crystallises in a pseudo-tetragonal orthorhombic cell at room temperature due to tilting of the MnO₆ octahedra. Heating in a dilute hydrogen atmosphere induces oxygen loss leading to the oxygen vacant cubic phase, Nd_{0.5}Ba_{0.5}MnO_{2.50}, which retains *A*-site cation disorder up to *T* ~ 700 °C. On further heating, a structural rearrangement consisting of oxygen vacancy ordering proceeds at *T* ~ 800 °C along with *A*-site cation ordering resulting in the NdBaMn₂O₅ layered perovskite. NdBaMn₂O₆ screen printed onto a Ce_{0.9}Gd_{0.1}O_{2-δ} (CGO) substrate shows promising performance as an oxygen electrode in a solid oxide fuel cell, with polarisation resistance down of 1.09 Ω cm² at 700 °C in air.

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References

- 1. M. Burriel, J. Peña-Martínez, R. J. Chater, S. Fearn, A. V. Berenov, S. J. Skinner and J. A. Kilner, *Chemistry of Materials*, 2012, **24**, 613-621.
- 2. T. Broux, M. Bahout, J. M. Hanlon, O. Hernandez, S. Paofai, A. Berenov and S. J. Skinner, *Journal of Materials Chemistry A*, 2014, **2**, 17015-17023.
- 3. Y. Hu, O. Hernandez, T. Broux, M. Bahout, J. Hermet, A. Ottochian, C. Ritter, G. Geneste and G. Dezanneau, *Journal of Materials Chemistry*, 2012, **22**, 18744-18747.
- 4. M. Bahout, S. S. Pramana, J. M. Hanlon, V. Dorcet, R. I. Smith, S. Paofai and S. J. Skinner, *Journal of Materials Chemistry A*, 2015, **3**, 15420-15431.
- 5. S. Sengodan, S. Choi, A. Jun, T. H. Shin, Y.-W. Ju, H. Y. Jeong, J. Shin, J. T. S. Irvine and G. Kim, *Nat Mater*, 2015, **14**, 205-209.
- 6. O. L. Pineda, Z. L. Moreno, P. Roussel, K. Świerczek and G. H. Gauthier, *Solid State Ionics*, 2016, **288**, 61-67.
- 7. F. Tonus, M. Bahout, V. Dorcet, G. H. Gauthier, S. Paofai, R. I. Smith and S. J. Skinner, *Journal of Materials Chemistry A*, 2016, **4**, 11635-11647.
- 8. A. A. Taskin, A. N. Lavrov and Y. Ando, *Progress in Solid State Chemistry*, 2007, **35**, 481-490.
- 9. A. A. Taskin, A. N. Lavrov and Y. Ando, *Applied Physics Letters*, 2005, **86**, 091910-091913.
- 10. H. Hayashi, M. Kanoh, C. J. Quan, H. Inaba, S. Wang, M. Dokiya and H. Tagawa, *Solid State Ionics*, 2000, **132**, 227-233.
- 11. M. S. Kaluzhskikh, S. M. Kazakov, G. N. Mazo, S. Y. Istomin, E. V. Antipov, A. A. Gippius, Y. Fedotov, S. I. Bredikhin, Y. Liu, G. Svensson and Z. Shen, *Journal of Solid State Chemistry*, 2011, **184**, 698-704.
- 12. F. Tonus, M. Bahout, V. Dorcet, G. H. Gauthier, S. Paofai, R. I. Smith and S. J. Skinner, *Journal of Materials Chemistry A*, 2016, DOI: 10.1039/C6TA03224A.
- 13. J. Rodríguez-Carvajal, *Physica B: Condensed Matter*, 1993, **192**, 55-69.
- 14. Mantid, Manipulation and Analysis Toolkit for Instrument Data. Mantid Project, 2013.
- 15. T. Nakajima, H. Kageyama and Y. Ueda, *Journal of Physics and Chemistry of Solids*, 2002, **63**, 913-916.
- 16. S. Trukhanov, V. Khomchenko, L. Lobanovski, M. Bushinsky, D. Karpinsky, V. Fedotova, I. Troyanchuk, A. Trukhanov, S. Stepin, R. Szymczak, C. Botez and A. Adair, *Journal of Experimental and Theoretical Physics*, 2006, **103**, 398-410.
- 17. A. M. Glazer, *Acta Crystallographica B* 1972, **28**, 3384-3392.
- 18. I. M. Reaney and D. I. Woodward, *Acta Crystallographica Section B*, 2005, **61**, 387-399.
- 19. A. M. Glazer, *Acta Crystallographica Section A*, 1975, **31**, 756-762.
- 20. C. Fu, K. Sun, N. Zhang, X. Chen and D. Zhou, *Electrochimica Acta*, 2007, **52**, 4589-4594.

- 21. B. C. H. Steele, *Solid State Ionics*, 2000, **129**, 95-110.
- 22. S. B. Adler, *Solid State Ionics*, 2000, **135**, 603-612.
- 23. M. J. Escudero, A. Aguadero, J. A. Alonso and L. Daza, *Journal of Electroanalytical Chemistry*, 2007, **611**, 107-116.
- 24. Z. Lou, J. Qiao, Y. Yan, J. Peng, Z. Wang, T. Jiang and K. Sun, *International Journal of Hydrogen Energy*, 2012, **37**, 11345-11350.
- 25. S. Huang, Q. Lu, S. Feng, G. Li and C. Wang, *Advanced Energy Materials*, 2011, **1**, 1094-1096.
- 26. H. Gu, H. Chen, L. Gao, Y. Zheng, X. Zhu and L. Guo, *International Journal of Hydrogen Energy*, 2009, **34**, 2416-2420.
- 27. R. K. Sharma, M. Burriel, L. Dessemond, J.-M. Bassat and E. Djurado, *Journal of Power Sources*, 2016, **325**, 337-345.
- 28. R. K. Sharma, M. Burriel, L. Dessemond, V. Martin, J.-M. Bassat and E. Djurado, *Journal of Power Sources*, 2016, **316**, 17-28.
- 29. R. K. Sharma, S.-K. Cheah, M. Burriel, L. Dessemond, J.-M. Bassat and E. Djurado, *Journal of Materials Chemistry A*, 2017, DOI: 10.1039/C6TA08011A.
- 30. R. Sayers, M. Rieu, P. Lenormand, F. Ansart, J. A. Kilner and S. J. Skinner, *Solid State Ionics*, 2011, **192**, 531-534.
- 31. V. Vibhu, A. Rougier, C. Nicollet, A. Flura, J.-C. Grenier and J.-M. Bassat, *Solid State Ionics*, 2015, **278**, 32-37.
- 32. R. K. Sharma, M. Burriel and E. Djurado, *Journal of Materials Chemistry A*, 2015, **3**, 23833-23843.
- 33. R. K. Sharma, M. Burriel, L. Dessemond, J. M. Bassat and E. Djurado, *Journal of Materials Chemistry A*, 2016, **4**, 12451-12462.
- 34. C. Nicollet, A. Flura, V. Vibhu, A. Rougier, J. M. Bassat and J. C. Grenier, *Journal of Power Sources*, 2015, **294**, 473-482.