Experimental report

19/02/2018

Proposal:	**5-25-250**	**Council:**	4/2016

Title: High temperature neutron diffraction study under flowing 5%H2 and O2 of the cation and charge ordered SOFC electrode material, NdBaMn2O5+d

Research area: Chemistry

This proposal is a new proposal

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Samples: NdBaMn2O5

Instrument	Requested days	Allocated days	From	To
D20	3	3	13/02/2017	16/02/2017

Abstract:

The aim of the in situ high temperature experiment using D20 concerns the potential SOFC electrode material, the A-site and charge ordered double perovskite, NdBaMn2O5. On heating under 5%H2 up to 900 °C, we want to (i) monitor the charge order/disorder phase transition, (ii) monitor the growth of the new tetragonal phase that forms under hydrogen at T > 800 °C and characterize its structure and oxygen content/oxygen positions and (iii) investigate the structural evolution between NdBaMn2O5 and NdBaMn2O6 to check whether the transformation is topoelectronic and characterize accurately the structure of NdBaMn2O6 which is a subject of controversy since different space groups such as P4/mmm, Pmmm as well as P-1 and have been suggested. D20 will be used in its high take-off geometry; it is ideally suited due to the in situ nature of the experiment and the timescales of the kinetics of oxygen intercalation (seconds to minutes). No other instruments at ILL fulfil the requirement of fast data collection times while retaining good resolution and very high flux for full pattern refinement.

Experimental report for the experiment N° 5-25-250 (D20)

“High temperature neutron diffraction study under flowing 5% H_2 and O_2 of the cation and charge ordered SOFC electrode material, $(Nd,Ce)BaMn_2O_{5+\delta}$”

The neutron experiment focused on the potential SOFC electrode, $Nd_{0.97}Ce_{0.03}BaMn_2O_5$, whose layered perovskite structure exhibits *A*-site ordering and Mn^{3+}/Mn^{2+} charge ordering (Fig. 1). Cerium was introduced at the *A*-site to improve the electrocatalytic properties through the Ce^{3+}/Ce^{4+} redox couple. The experiment was carried out on D20 using $\lambda = 1.54$ Ã.

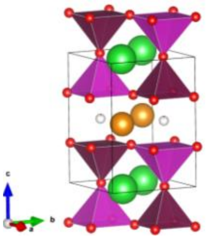

Fig. 1 Crystal structure of $(Nd,Ce)BaMn_2O_5$ (S.G. P4/nmm) with $Mn^{3+}O_5$ and $Mn^{2+}O_5$ polyhedra.

The powder sample (4 g) was placed in a quartz tube of 8 mm diameter, opened at the top and bottom to allow the gas flow cross the sample. Two thermocouples were set to measure and control the temperature of the sample. The setup used is shown in Fig. 2

The sample was heated under air at 10° C min^{-1} up to 800 °C and then cooled quickly to 25 °C. Data were collected every minute on ramping and four isothermal data sets were collected: at 25 °C before heating, 500 °C, 800 °C and 25 °C after cooling. A phase change from *P*4/*nmm* to *P*4/*mmm* due to the oxidation of $Nd_{0.97}Ce_{0.03}BaMn_2O_5$ to $Nd_{0.97}Ce_{0.03}BaMn_2O_6$ happened on heating (Fig. 3). During oxidation which proceeds in the temperature range 160 - 200 °C, the data were analyzed by sequential two-phase Rietveld refinements involving the reduced and oxidized phases. A further look at the data shows a spike in the sample temperature which does not match with the set temperature, but matches in the interval where oxidation occurs. This overshot was due to the exothermicity of the oxidation reaction (Fig. 4).

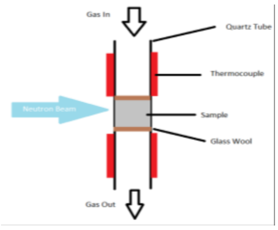

Fig. 2 set-up used

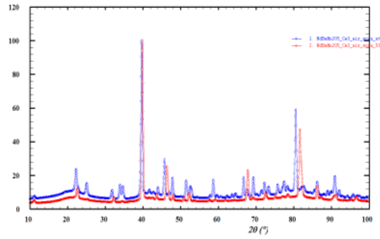

Fig. 3 (blue) T = 25°C data and (red) T = 500°C data showing

The oxidation completed at *T* = 200 °C consistent with the $Nd_{0.97}Ce_{0.03}BaMn_2O_{6.04(6)}$ composition. On further heating to *T* = 800 °C and subsequent cooling the oxygen stoichiometry did not vary significantly. $Mn^{2+/3+}$ oxidise to $Mn^{3+/4+}$ in air along with oxygen uptake to fill the oxygen site in the lanthanide layer along with disappearance of the charge ordering resulting in the change to the *P*4/*mmm* S.G. The low amount of Ce prevents us from detecting possible oxidation of Ce^{3+} to Ce^{4+} within $Nd_{0.97}Ce_{0.03}BaMn_2O_{5+\delta}$ or exsolution of Ce to form CeO_2 secondary phase. Refinement for $Nd_{0.97}Ce_{0.03}BaMn_2O_{6.04(6)}$ at *T* = 800 °C is shown in Fig. 5. The results of the neutron experiment will be submitted to J. Mater. Chem. A in Feb. 2018.

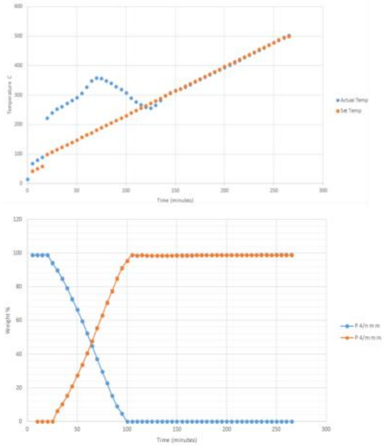

Fig. 4 (Top) variation of the sample temperature versus the set temperature, (bottom) phase change $Nd_{0.97}Ce_{0.03}BaMn_2O_5$ (*P4/nmm*)→$Nd_{0.97}Ce_{0.03}BaMn_2O_6$ (*P4/mmm*) during oxidation.

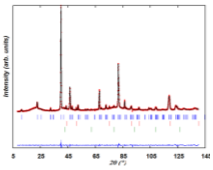

Fig. 5 Fitting of the P4/mmm model to the T= 800 °C data