# Experimental Report



**Proposal:** **5-25-199** **Council:** 10/2010

**Title:** In situ structural studies of the reduction of the Ruddlesden-Popper phase,La1.2Sr0.8MnO4-x in flowingH2-gas and O2-gas

**This proposal is a new proposal**

**Researh Area:** Chemistry

**Main proposer:** **BAHOUT Mona**

**Experimental Team:** PAOFAI SERGE
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**Local Contact:** HANSEN Thomas

**Samples:** La1.2Sr0.8MnO4

| Instrument | Req. Days | All. Days | From | To |
|---|---|---|---|---|
| D20 He3 Spin Filter | 4 | 3 | 27/05/2011 | 30/05/2011 |

**Abstract:**

This application is concerned with the defect chemistry of metal oxides having relevance to fuel-cell technology. More specifically, it focuses on the oxidized form La1.2Sr0.8MnO4.27 of the n = 1 Ruddlesden-Popper phase that forms under oxygen gas with retention of the I4/mmm symmetry despite the highest amount of interstitial oxygen inserted, ever found in a K2NiF4-like oxide material. We wish to study the oxidation of La1.2Sr0.8MnO3.92 in situ under oxygen flow using NPD on D20 as function of the temperature in order to understand the dynamics of the interstitial oxygen incorporation paying particular attention to the structure relationship that might exist between La1.2Sr0.8MnO3.92 and its connection with the unpredicted behaviour of the lattice parameters on oxidation.

Experimental report for the experiment N° 5-25-199 (D20)
*"In situ structural studies of the reduction and oxidation of the Ruddlesden- Popper phase, $La_{1.2}Sr_{0.8}MnO_{4-\delta}$ in flowing $H_2$-gas and $O_2$-gas"*

This experiment was conducted at the Institute Laue-Langevin (ILL) on the high flux neutron powder diffractometer D20 (wavelength 1.3594 Å) in real time. The *in situ* thermal treatment was as follows: with 5% $H_2$ gas flowing, the as-prepared sample was heated to ~ 950°C at 2°C $min^{-1}$ then held at 950 °C for 80 min before cooling to 64 °C. The reduced sample was subsequently heated to ~ 550ºC under $O_2$ flow at 1 °C $min^{-1}$ and held at 550 °C for ~ 3h45 before cooling to 64 °C. A schematic representation of the experimental set-up and the heating/cooling cycles is displayed in Figure 1.

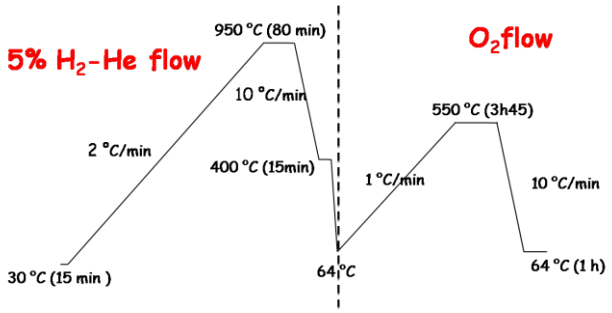


**Figure 1: Schematic representation of the cycle used in the *in situ* NPD experiment**

Diffraction patterns were collected every 5 minutes throughout the aforementioned thermal cycles and analyzed sequentially by the Rietveld method using FullProf.

Rietveld refinements show that $La_{1.2}Sr_{0.8}MnO_{4-\delta}$ crystallizes in the tetragonal *I*4/*mmm* space-group and retains its structure throughout a heating/cooling cycle under 5% $H_2$, as shown on Figure 2.

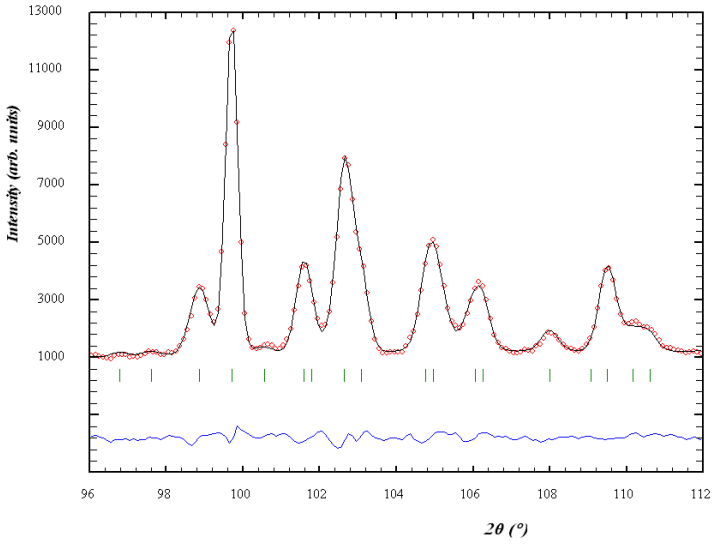


**Figure 2: Rietveld refinement of NPD pattern of $La_{1.2}Sr_{0.8}MnO_{3.94}$ at 64°C after a heating/cooling under 5% $H_2$-He flow, *a* = 3.83181(6) Å and *c* = 13.0862(3) Å.**

Investigation of the behaviour of the *in situ* reduced material $La_{1.2}Sr_{0.8}MnO_{3.94}$ under $O_2$ flow reveals oxygen intercalation up to 300 °C at the equatorial positions first then at the interstitial positions up to 400 °C, the latter is accompanied by expansion in the *ab* plane and large contraction along the *c* axis, resulting in a first order phase transition (see Figure 3) induced by the transformation of Jahn-Teller $Mn^{3+}$ into a spherical $Mn^{4+}$ ion.