Experimental report

16/08/2022

Proposal: 5-23-761 **Council:** 10/2020

Title: Disproportionation of Rh(II) in Reduced Perovskite Oxides.

Research area: Chemistry

This proposal is a new proposal

Main proposer: Michael HAYWARD

Experimental team: Ines PUENTE ORENCH

Local contacts: Emmanuelle SUARD
Ines PUENTE ORENCH
Vivian NASSIF
Claire COLIN

Samples: LaCo0.5Rh0.5O2.25
LaMn0.5Rh0.5O2.25
LaNi0.5Rh0.5O2.25

Instrument	Requested days	Allocated days	From	To
D2B	2	1	06/06/2021	07/06/2021
D1B	0	1	14/06/2021	15/06/2021

Abstract:

We propose to measure high-resolution neutron powder diffraction data from LaMn0.5Rh0.5O2.25, LaCo0.5Rh0.5O2.25 and LaNi0.5Rh0.5O2.25 at room temperature and 5 K to establish their crystal and magnetic structures.
These phases are prepared by topochemical reduction from the corresponding LaM0.5Rh0.5O3 perovskite oxides. Their compositions suggest oxidation state combinations M(I), Rh(II). However, a previous study of an analogous Ruddlesden-Popper phase, LaSrCo¬0.5Rh0.5O3.25, revealed that the rhodium cations had ‘disproportionated’ to a 1:1 mixture of Rh(I), Rh(III) driven by the presence of both square-planar and square-based pyramidal coordination sites for Rh. Our main motivation for studying these new LaM0.5Rh0.5O2.25 phases is to see if a similar Rh disproportionation occurs in the LaM0.5Rh0.5O2.25 phases.
Magnetisation data collected from the LaM0.5Rh0.5O2.25 phases indicates these phases adopt magnetically ordered states at low temperature. So we wish to also measure data sets at low temperature to establish the magnetic structures of the phases and their ordering temperatures.

Experimental report for Experiment 5-23-761

Disproportionation of Rh(II) in Reduced Perovskite Oxides

Neutron powder diffraction data were collected from $LaCo_{0.5}Rh_{0.5}O_{2.25}$, $LaNi_{0.5}Rh_{0.5}O_{2.25}$ and $LaSrMn_{0.5}Rh_{0.5}O_{2.25}$ at room temperature using the D2B instrument and then at low temperature using D1B.

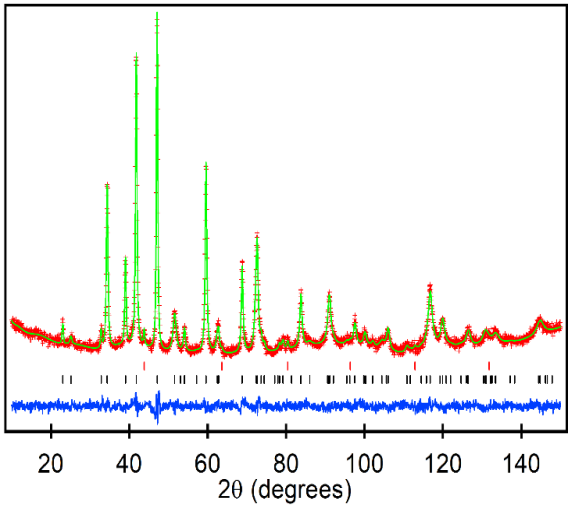

Figure 1. Observed, calculated and difference plots from the structural refinement of $LaCo_{0.5}Rh_{0.5}O_{2.25}$ against NPD data collected at room temperature using instrument D2B. Black and red tick marks indicated peak positions for the majority phase and contributions from the vanadium sample holder, respectively.

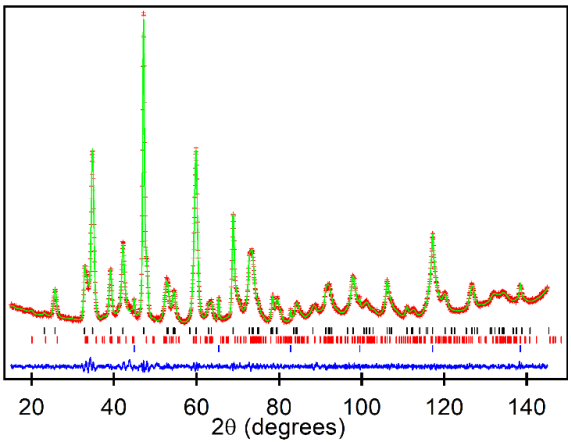

Figure 2. Observed, calculated and difference plots from the structural refinement of $LaNi_{0.5}Rh_{0.5}O_{2.25}$ against NPD data collected at room temperature using instrument D2B. Black and red and blue tick marks indicated peak positions for the majority phase, a $LaNi_{0.5}Rh_{0.5}O_3$ secondary phase and contributions from the vanadium sample holder, respectively.

Fits to the NPD data collected from $LaCo_{0.5}Rh_{0.5}O_{2.25}$, $LaNi_{0.5}Rh_{0.5}O_{2.25}$ indicated that they adopt the anion-vacancy ordered perovskite structure shown in Figure 3.

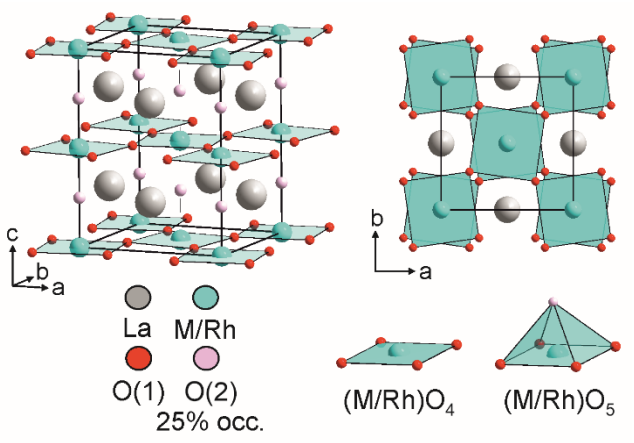

Figure 3. The structure of $LaM_{0.5}Rh_{0.5}O_{2.25}$ (M = Co, Ni) and the local $(M/Rh)O_x$ coordination polyhedra.

Low temperature NPD data collected from $LaCo_{0.5}Rh_{0.5}O_{2.25}$ show this phase adopts a complex magnetic structure which can be described as the sum of two irreducible modes, mM_5^+ and $m\Gamma_1^+$ as shown in Figure 4.

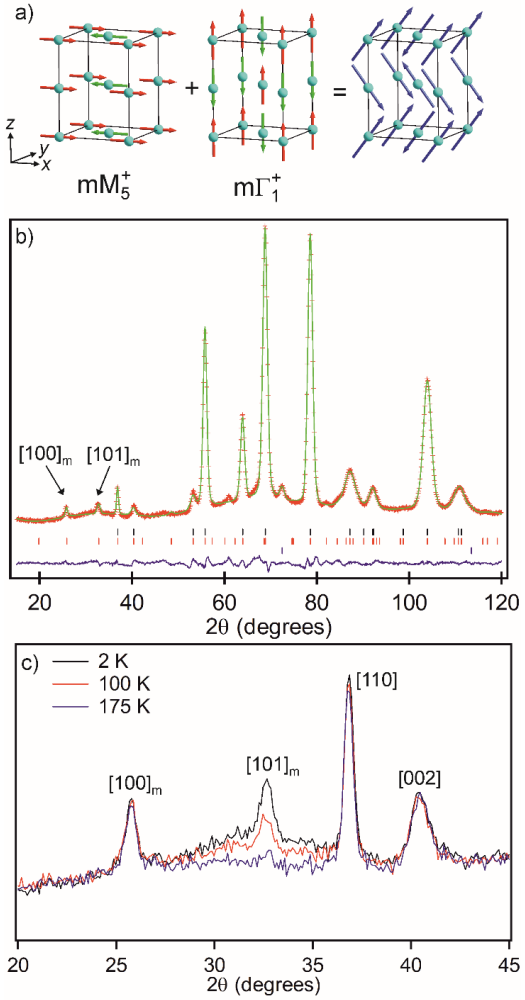

Figure 4. a) The mM_5^+ and $m\Gamma_1^+$ symmetry magnetic orderings on $LaCo_{0.5}Rh_{0.5}O_{2.25}$. b) Observed calculated and difference plot from a combined magnetic and structural refinement of $LaCo_{0.5}Rh_{0.5}O_{2.25}$ against NPD data collected at 2K using instrument D1B. Black ticks indicate peak positions for the crystallographic cell, red ticks the magnetic cell, and blue ticks contributions from the vanadium sample holder. c) A selected region of NPD data collected from $LaCo_{0.5}Rh_{0.5}O_{2.25}$ at 2, 100 and 175 K.