Experimental report

06/05/2019

Proposal: 5-23-703 **Council:** 4/2017

Title: Complex Ruthenium-Containing Oxideand Oxide-Hydride Phases

Research area: Chemistry

This proposal is a new proposal

Main proposer: Michael HAYWARD

Experimental team: Lun JIN
Michael HAYWARD
Jacob PAGE

Local contacts: Emmanuelle SUARD

Samples: LaSr3NiRuO4H4
LaSr3NiRuO6
LaSr3CoruO4H4
LaSr3CoRuO6

Instrument	Requested days	Allocated days	From	To
D2B	3	3	20/04/2018	23/04/2018

Abstract:

Transition metal oxides have been of enduring interest due to the wide variety of complex electronic behaviour they can exhibit. Topochemical reduction offers the opportunity to prepare novel transition metal oxide systems containing transition metal cations in novel oxidation states and/or coordination geometries.
Using this approach we have prepared a series of novel reduced oxides and oxide-hydride phases containing ruthenium and cobalt or nickel in extremely low oxidation states.
Specifically we have reduced LaSr3NiRuO8, first to the Ni1+, Ru2+ oxide LaSr3NiRuO6 and then to the iso-valent oxide-hydride LaSr3NiRuO4H4. X-ray diffraction data suggest a structure which contains infinite Ni/RuH2 sheets, analogous to the CuO2 sheets present in high Tc superconductors. Following this we have also prepared the analogous cobalt phases LaSr3CoRuO8, LaSr3CoRuO6 and LaSr3CoRuO4H4.
We propose to collect neutron powder diffraction data from all of these phases to accurately characterise the anion lattices of these systems, and low temperature neutron diffraction data to determine the ordered magnetic states they adopt.

Experimental Report for Experiment 5-23-703:
Complex Ruthenium-Containing Oxide and Oxide-Hydride Phases

Neutron powder diffraction data were collected from $LaSr_3NiRuO_8$ and $LaSr_3CoRuO_8$ confirming both phases have anion-disordered n = 1 Ruddlesden-Popper structures.

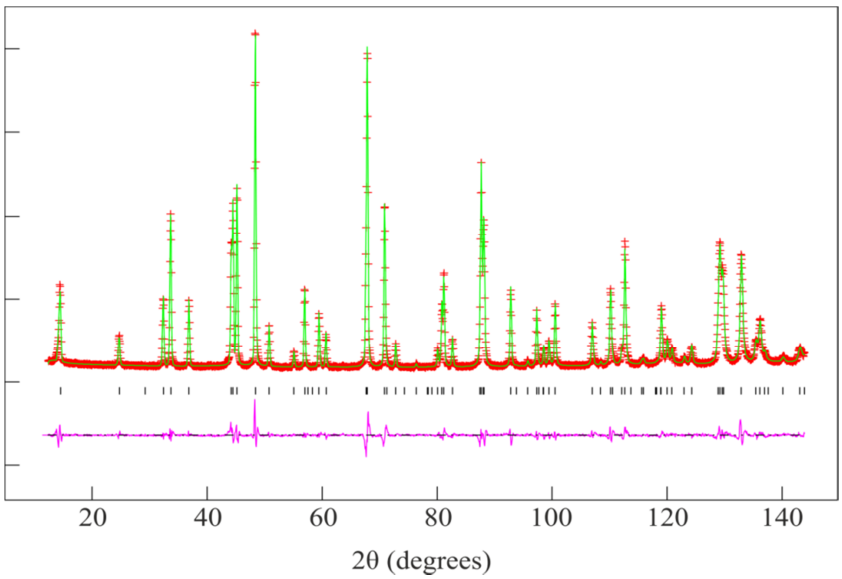

Figure 1: Observed, calculated and difference plots from the structural refinement of $LaSr_3NiRuO_8$ (space group *I*4/*mmm*) against neutron powder diffraction data collected at 300 K.

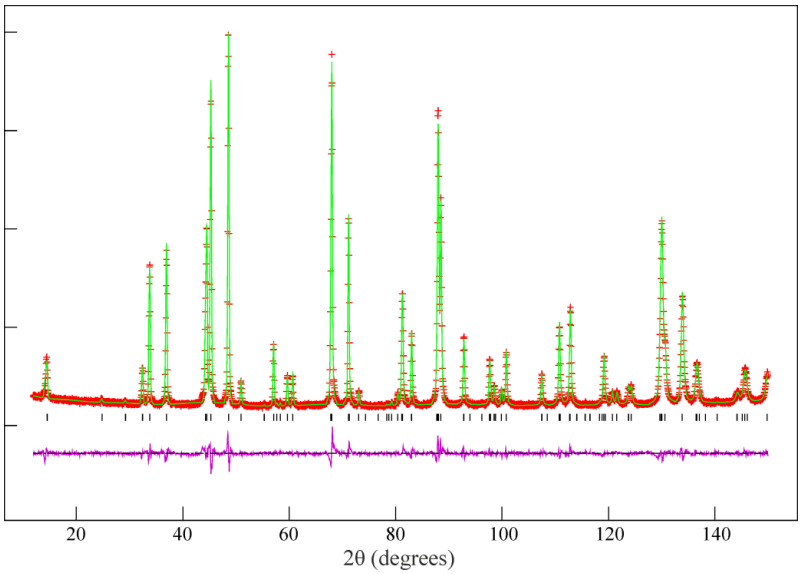

Figure 2: Observed, calculated and difference plots from the structural refinement of $LaSr_3CoRuO_8$ (space group *I*4/*mmm*) against neutron powder diffraction data collected at 300 K.

The data from $LaSr_3NiRuO_8$ are included the publication:

$LaSr_3NiRuO_4H_4$: A 4d transition-metal oxide-hydride containing metal hydride sheets, L. Jin, M. Lane, D. Zeng, F. K. K. Kirschner, F. Lang, P. Manuel, S. J. Blundell, J. E. McGrady and M. A. Hayward , *Angewandte Chemie*, **57** (2018) 5025.

Neutron powder diffraction data were also collected from $LaSr_3NiRuO_6$ and $LaSr_3CoRuO_6$.

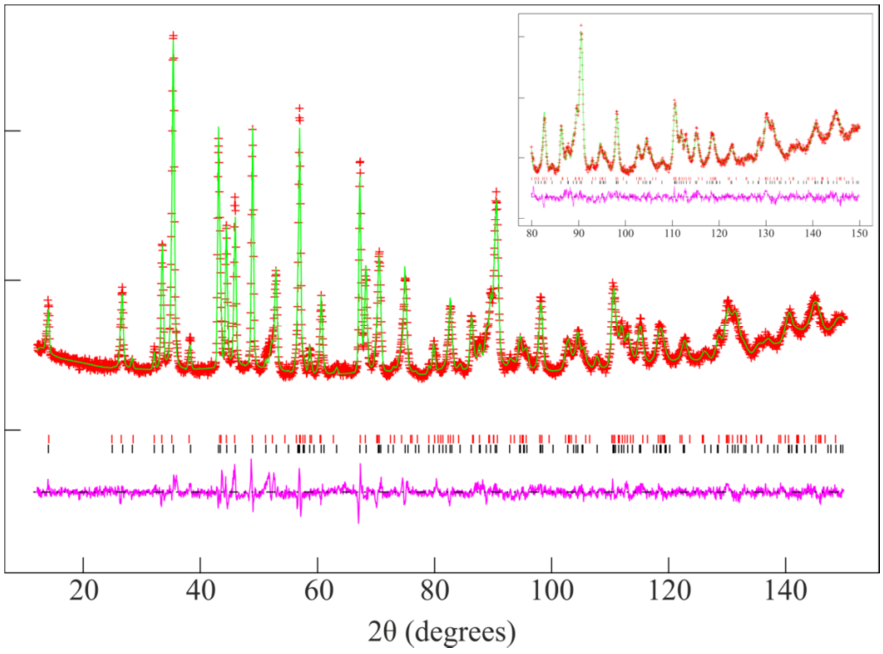

Figure 3: Observed, calculated and difference plots from the two-phase refinement of neutron powder diffraction data (space group *Immm*) collected from $LaSr_3NiRuO_6$ at 298 K.

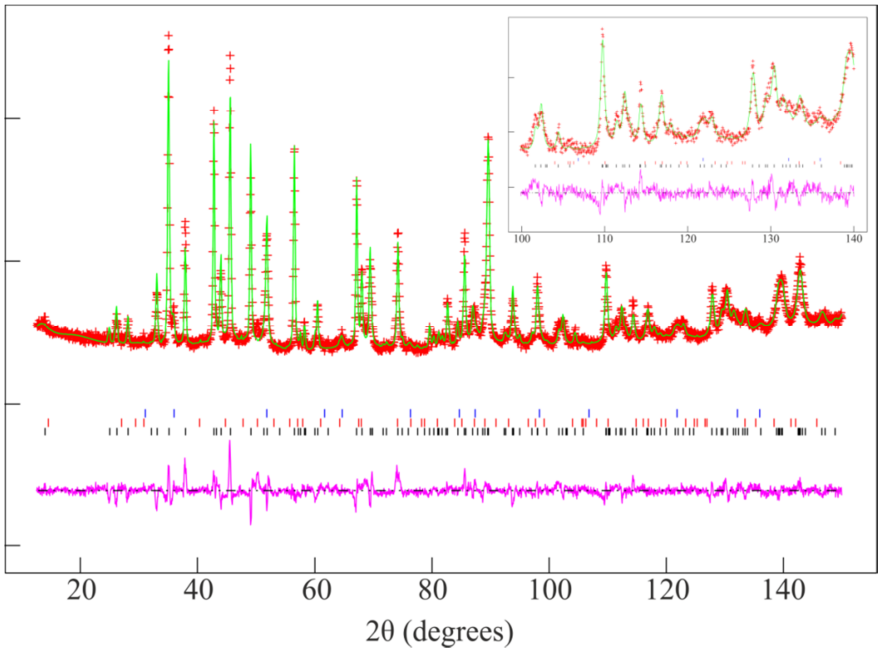

Figure 4: Observed, calculated and difference plots from the refinement of neutron powder diffraction data collected from $LaSr_3CoRuO_6$ (space group *Immm*) at 298 K

The data show they adopt anion-deficient orthorhombic structures, in which all the transition metal cations are in square-planar coordination sites.

Magnetisation data indicate that these phases are ferromagnetically ordered at low temperature, but this could not be observed in neutron powder diffraction data collected at 5K. A manuscript is in preparation.

Data were also collected from $LaSr_3MnRhO_8$, $La_2Sr_2CoRhO_8$ and $La_2Sr_2CoRhO_6H_2$.

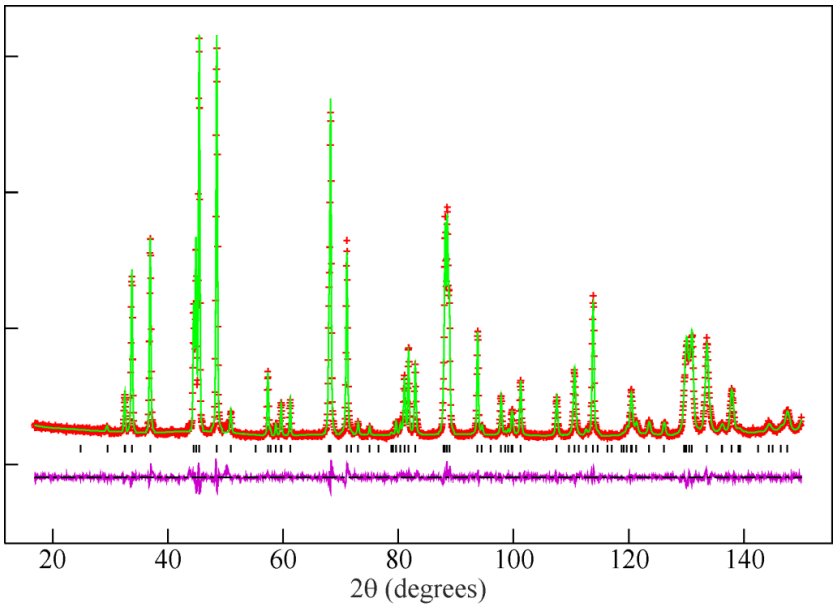

Figure 5. Observed, calculated and difference plots from the structural refinement of $La_2Sr_2CoRhO_8$ against neutron powder diffraction data collected at room temperature.

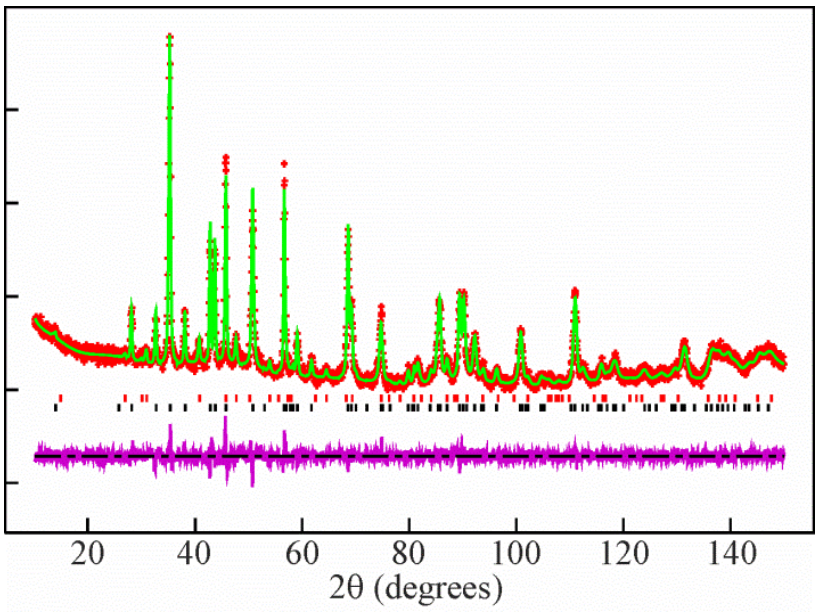

Figure 6. Observed calculated and difference plots from the structural refinement of $LaSrCo_{0.5}Rh_{0.5}O_3H$ against neutron powder diffraction data collected at room temperature. Lower tick marks indicate peak positions of $LaSrCo_{0.5}Rh_{0.5}O_3H$, upper tick marks indicate peak positions of the La_2O_3 secondary phase.

These data confirm that $LaSr_3MnRhO_8$ and $La_2Sr_2CoRhO_8$ adopt cation disordered structures, while $La_2Sr_2CoRhO_6H_2$ is an anion-disordered oxide-hydride, as described in :

Rhodium-containing oxide-hydrides: covalently stabilized mixed-anion solids. L. Jin and M. A. Hayward. *Chemical Communications*, **55** (2019) 4861.