Experimental report

16/08/2022

Proposal: 5-23-774 **Council:** 4/2021

Title: Ruthenium-containing topochemically reduced oxides and oxyhydrides

Research area: Chemistry

This proposal is a new proposal

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Experimental team:

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Samples: LaSrCoRuO4
LaSrNiRuO3H3
LaSrCoRuO4H2
LaSrCoRuO5

Instrument	Requested days	Allocated days	From	To
D2B	2	2	17/09/2021	19/09/2021

Abstract:

Topochemical reduction reactions allow the preparation of novel anion-deficient and anion-exchanged phases containing transition metal cations in unusual oxidation states and coordination geometries, which cannot be prepared by conventional high-temperature routes.
Using these techniques we have prepared LaSrCoRuO5, LaSrCoRuO4 and LaSrCoRuO4H2 from LaSrCoRuO6 and LaSrNiRuO3H3 from LaSrNiRuO6.
We propose to collected high-resolution neutron powder diffraction data to determine their crystal and magnetic structures. Neutron diffraction data are essential to this study due to the low X-ray scattering powder of oxide and hydride anions, which means characterization by X-ray powder diffraction is not possible.

Experimental report for Experiment 5-23-774

Topochemically Reduced Ruthenium-containing Perovskites

Neutron powder diffraction data were collected for samples of $LaSrNiRuO_3H_3$, $LaSrCoRuO_4H_2$, $LaSrCoRuO_5$ at room temperature and 5 K and from $LaSrCoRuO_4$ and $Ba_3CoRu_2O_6H_3$ at room temperature only, using the D2B diffractometer.

Initial analysis reveals that $LaSrNiRuO_3H_3$ and $LaSrCoRuO_5$ exhibit a complex superstructure consistent with anion ordering and anion-vacancy ordering respectively. Data from both phases can be fit by Pawley type refinements, as shown in Figure 1. Complete structure solution is still in progress.

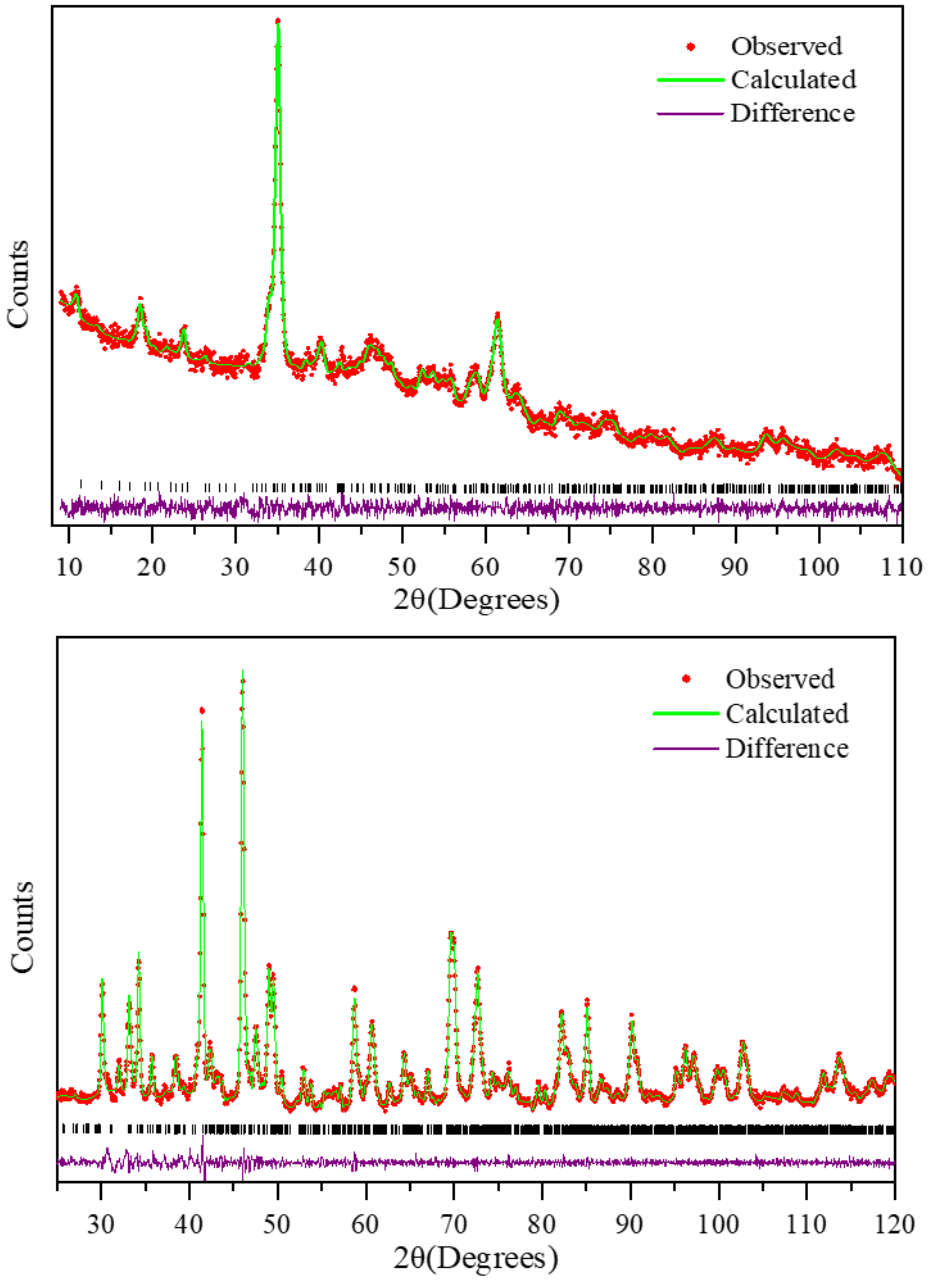

Figure 1. Observed, calculated and difference plots from the Pawley refinement of $LaSrNiRuO_3H_3$ (top) and $LaSrCoRuO_5$ (bottom).

Diffraction data collected from $LaSrCoRuO_4H_2$ can be refined with a body-centred monoclinic cell (S.G. *I*11*m*) with oxide and hydride anions adopting a disordered arrangement at the equatorial sites.

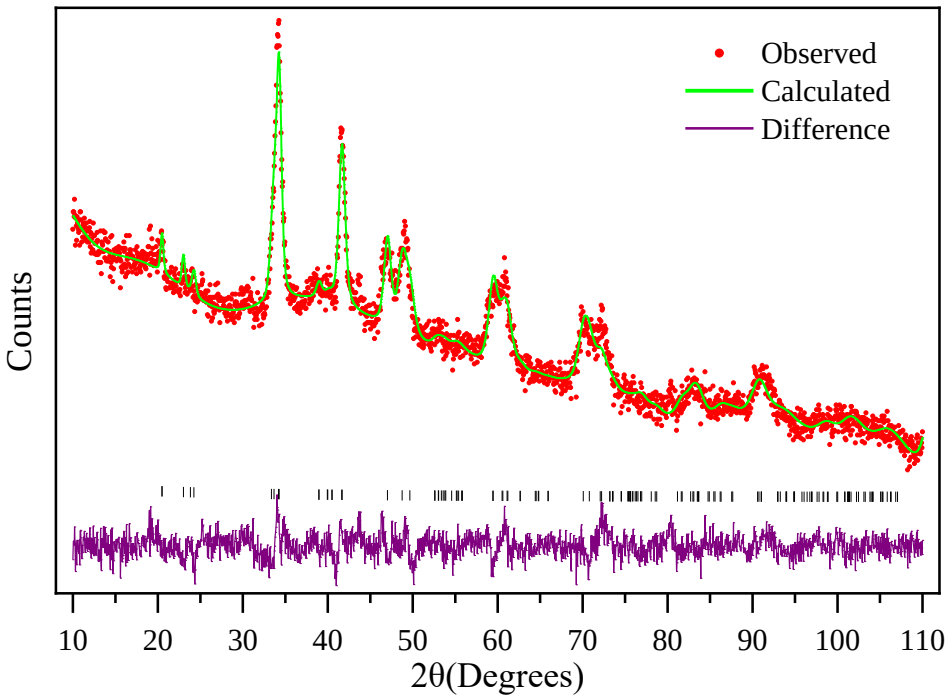

Figure 2. Observed, calculated and difference plots from the refinement of *I*11*m* structure model against neutron powder diffraction data collected from $LaSrCoRuO_4H_2$.

Neutron powder diffraction data collected from $Ba_3CoRu_2O_6H_3$ can be fit with an ortho-hexagonal model (S.G. *Cmcm*), with oxide and hydride anions distributed in a disordered manner throughout the structure.

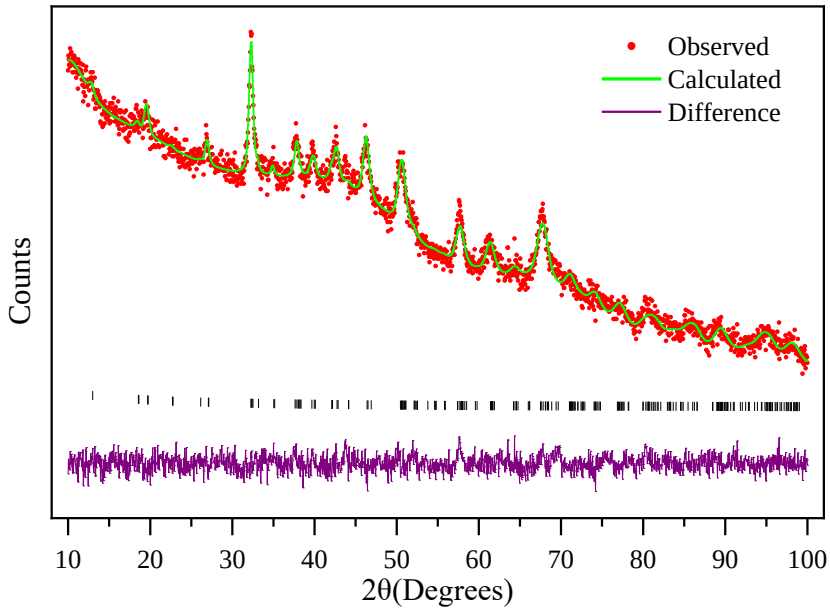

Figure 3. Observed, calculated and difference plots from refinement of *Cmcm* structural model against neutron powder diffraction data collected from $Ba_3CoRu_2O_6H_3$

$LaSrCoRuO_4$ can be refined with an infinite-layer structure (S.G. *I*4/*m*). analogous to that reported for Sr_2FeIrO_4 at high temperature.

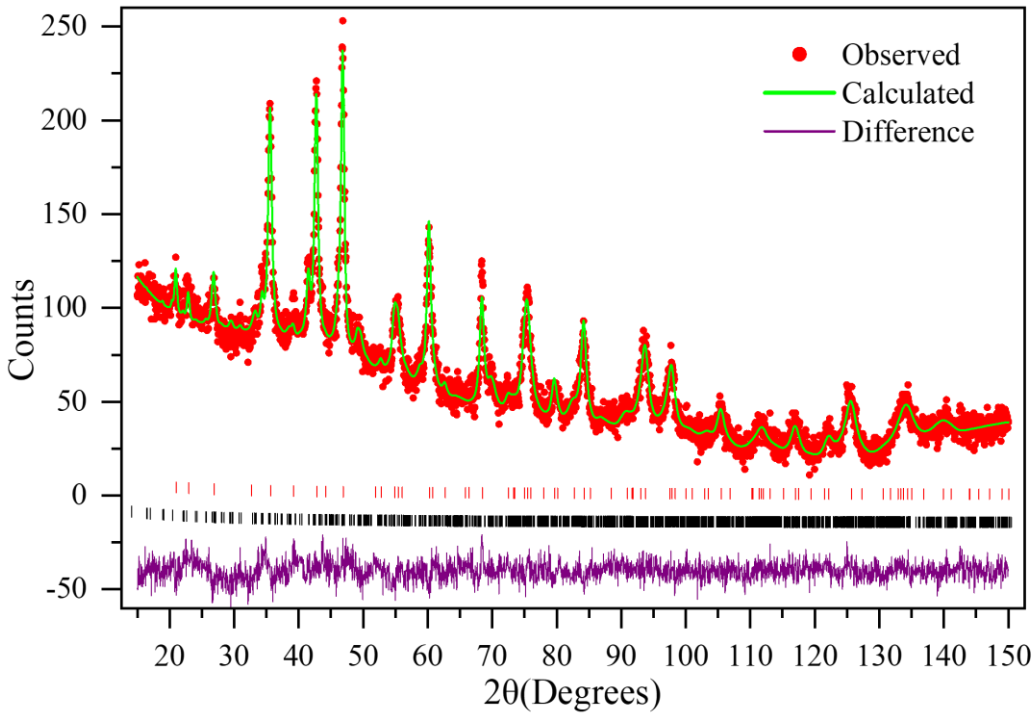

Figure 4. Observed, calculated and difference plot from refinement of I4/*m* structural model against neutron powder diffraction from $LaSrCoRuO_4$