Experimental report

24/10/2016

Proposal: 5-31-2372 **Council:** 10/2014

Title: Topochemically reduced ruthenium double perovskites

Research area: Chemistry

This proposal is a new proposal

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Samples: LaSrNiRuO4
LaSrCoRuO4
Sr2CoRuO4

Instrument	Requested days	Allocated days	From	To
D2B	3	2	30/04/2015	02/05/2015

Abstract:

Topochemical reduction of the ruthenium containing double perovskite phases LaSrNiRuO6, LaSrCoRuO6 and SrCo0.5Ru0.5O3 yields phases of composition LaSrNiRuO4, LaSrCoRuO4 and SrCo0.5Ru0.5O2 respectively. X-ray powder diffraction data indicate that the first two reduced phases adopt cation-ordered infinite-layer structures, while SrCo0.5Ru0.5O2 has an infinite-layer structure with Co/Ru disorder. We propose to collect room temperature neutron powder diffraction data to accurately determine the structures of these phases, with a particular emphasis on the oxide anion framework.

Magnetization data indicate that LaSrNiRuO4 undergoes a transition at 250K to a state with a spontaneous magnetization, although it is unclear if this arises from ferrimagnetic or ferromagnetic couplings between nickel and ruthenium centers. We propose to collect low temperature neutron diffraction data in an applied magnetic field to resolve this issue.

Magnetization data from LaSrCoRuO4 and SrCo0.5Ru0.5O2 suggest antiferromagnetically ordered states are adopted at low temperature. We propose to collect low-temperature data sets to determine the magnetically ordered structures of these materials.

Neutron powder diffraction data were collected from $LaSrNiIrO_6$ at room temperature and 5K. Analysis of the data collected at room temperature (Figure 1) confirmed that $LaSrNiIrO_6$ has a pseudo-cubic monoclinic structure. A model with space symmetry $P2_1/n$ and B-site cation order was refined against the data collected and gave an excellent statistical fit. The crystallographic unit cell obtained from this analysis is shown in Figure 2.

Neutron powder diffraction data collected at 5K had addition peaks compared to the room temperature data. These extra peaks could be attributed to long range magnetic order. A series of models were constructed with highs spin Ni^{2+} (d^8 s=1) and diamagnetic Ir^{5+} (d^4 J_{eff}= 0) were constructed. The best fit was obtained with a unit cell related to the crystallographic unit cell by a 2x1x2 expansion with G-type antiferromagnetic ordering. In this model the spin vectors are aligned parallel to the crystallographic *c*-axis. The refinement of this model against the data gave an excellent fit and is shown in Figure 3.

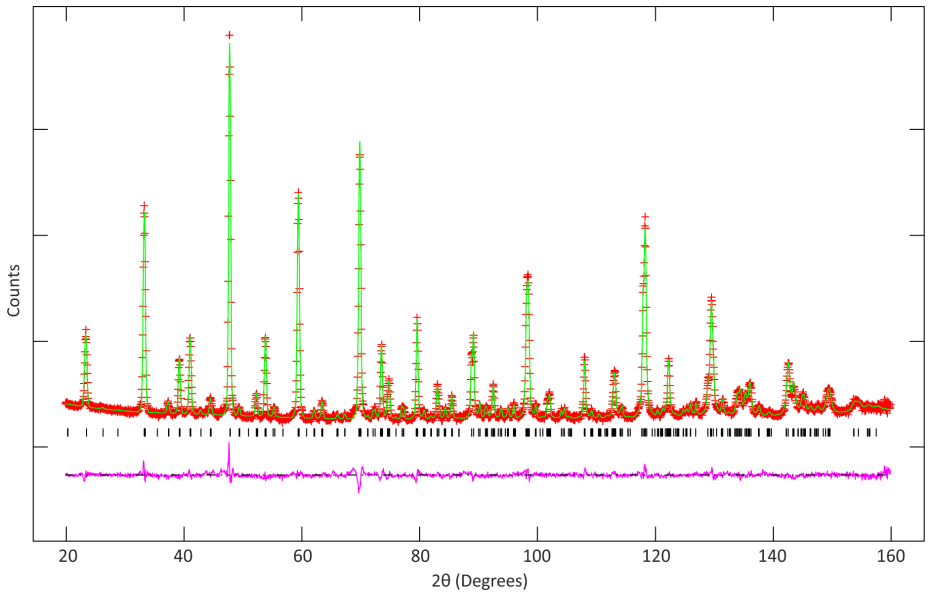

Figure 1. Observed, calculated and difference plots from the refinement of a $P2_1/n$ model against neutron data collected from $LaSrNiIrO_6$ at room temperature

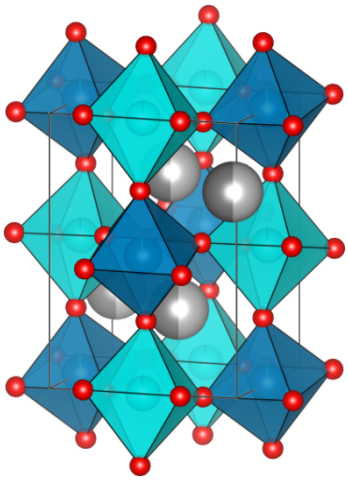

Figure 2. Crystallographic unit cell of $LaSrNiIrO_6$

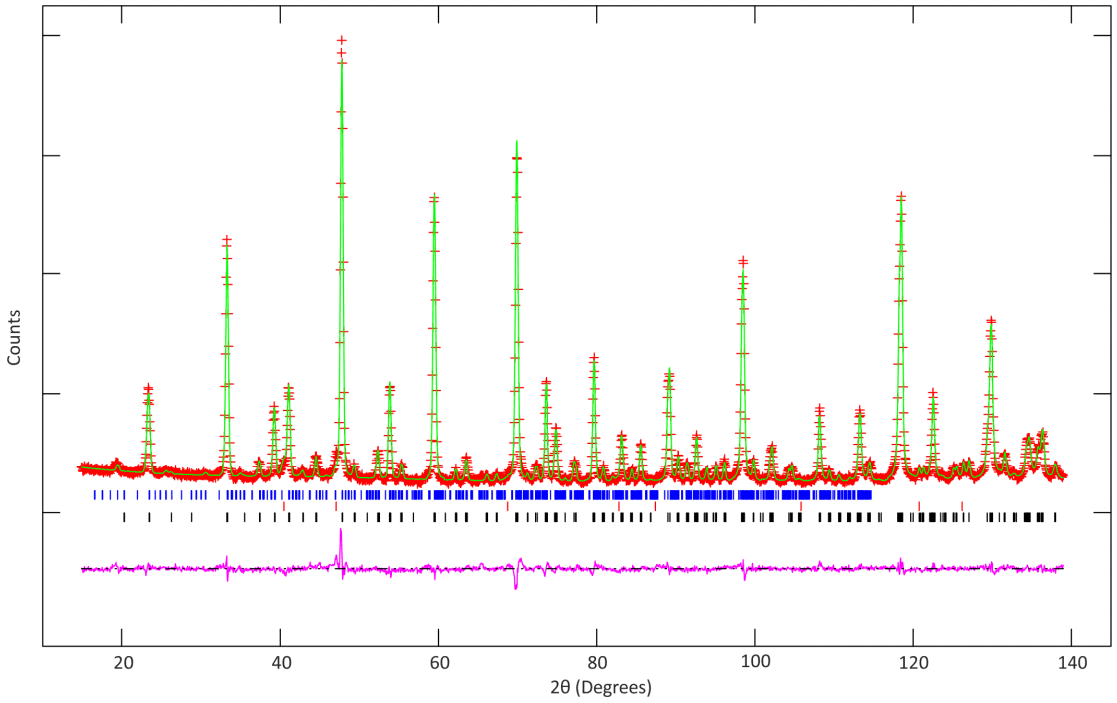

Figure 3. Observed, calculated and difference plots from the refinement of a $P2_1/n$ model against neutron data collected from $LaSrNiIrO_6$ at 5K. Black tick marks are structural peaks, blue tick marks are magnetic peaks and red tick marks are the unknown cubic phase.

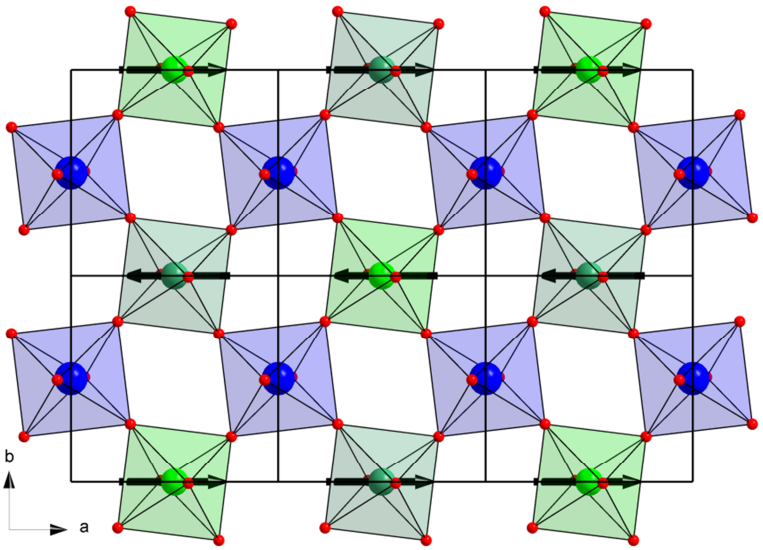

Figure 4. The refined magnetic structure of LaSrNiIrO6. Green octahedra represent Ni^{2+}, blue octahedra represent Ir^{5+}