# Experimental report

06/05/2019

**Proposal:** **5-23-704**

**Council:** 4/2017

**Title:** Topochemically Reduced Iridium Oxides

**Research area:** Chemistry

**This proposal is a new proposal**


**Main proposer:** **Michael HAYWARD**

**Experimental team:** Lun JIN
Jacob PAGE
Michael HAYWARD

**Local contacts:** Emmanuelle SUARD


**Samples:** LaSr3CoIrO8
LaSr3CoIrO6
CaMn0.5Ir0.5O3
CaMn0.5Ir0.5O2.12

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D2B | 4 | 2 | 13/06/2018 | 15/06/2018 |


**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 two novel iridium-containing oxide phases containing iridium in extremely low oxidation states; specifically the Ir2+ phase LaSr3CoIrO6 (prepared by the reduction of the novel phase LaSr3CoIrO8)and the Ir2+/3+ phase CaMn0.5Ir0.5O2.125 (via the reduction CaMn0.5Ir0.5O3).

We propose to collect neutron powder diffraction data from these reduced phases, and the novel unreduced starting materials, to accurately determine their structures. In the case of the reduced phases we wish to determine if these novel compounds are vacant oxides (e.g. LaSr3CoIrO6) or oxide-hydrides (e.g. LaSr3CoIrO6H2).

In addition we wish to collect low temperature neutron diffraction data to determine the nature of the ordered magnetic states these phases adopt.

# Experimental Report for Experiment 5-23-704:

# Topochemically Reduced Iridium Oxides

Neutron powder diffraction data were collected from samples of

$Sr_2Fe_{0.5}Ir_{0.5}O_4$, $Sr_2Co_{0.5}Ir_{0.5}O_4$, $La_{0.5}Sr_{1.5}Co_{0.5}Ir_{0.5}O_4$, $Sr_2Fe_{0.5}Ir_{0.5}O_3$, $Sr_2Co_{0.5}Ir_{0.5}O_3$, $La_{0.5}Sr_{1.5}Co_{0.5}Ir_{0.5}O_3$ and $CaMn_{0.5}Ir_{0.5}O_{2.5}$ using the D2b diffractometer.

Cation-disordered Ruddlesden-Popper structural models were refined against the data collected from the $A_2M_{0.5}Ir_{0.5}O_4$ phases, as shown in Figure 1.

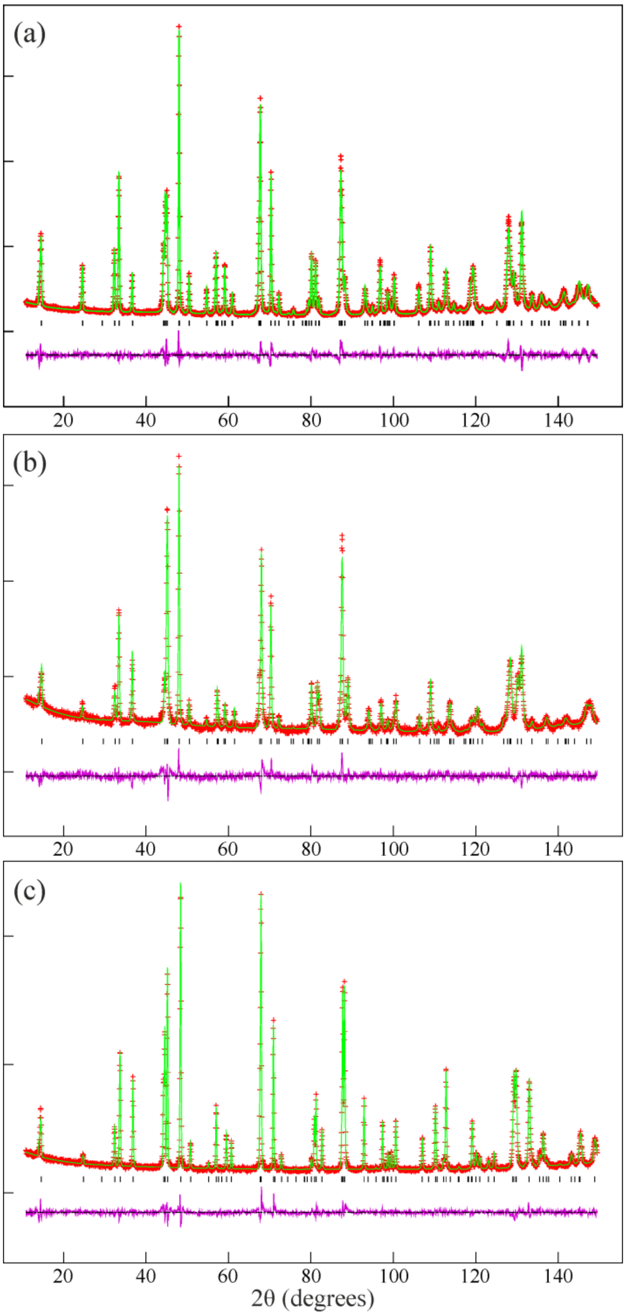


**Figure 1:** Observed, calculated and difference plots from the structural refinement of a) $Sr_2Fe_{0.5}Ir_{0.5}O_4$, b) $Sr_2Co_{0.5}Ir_{0.5}O_4$ and c) $La_{0.5}Sr_{1.5}Co_{0.5}Ir_{0.5}O_4$ against neutron powder diffraction data collected at 298 K.

Cation-deficient orthorhombic structural models were refined against the data collected from the $A_2M_{0.5}Ir_{0.5}O_3$ phases as shown in Figure 2.

These data have now been published as part of a study of these iridium phases :

Structure and magnetism of $(La/Sr)_2M_{0.5}Ir^{V}_{0.5}O_4$ and topochemically reduced $(La/Sr)_2M_{0.5}Ir^{II}_{0.5}O_3$ (M = Fe, Co) complex oxides.
J. E. Page and M. A. Hayward.
*Inorganic Chemistry*, **58** (2019) 6336.

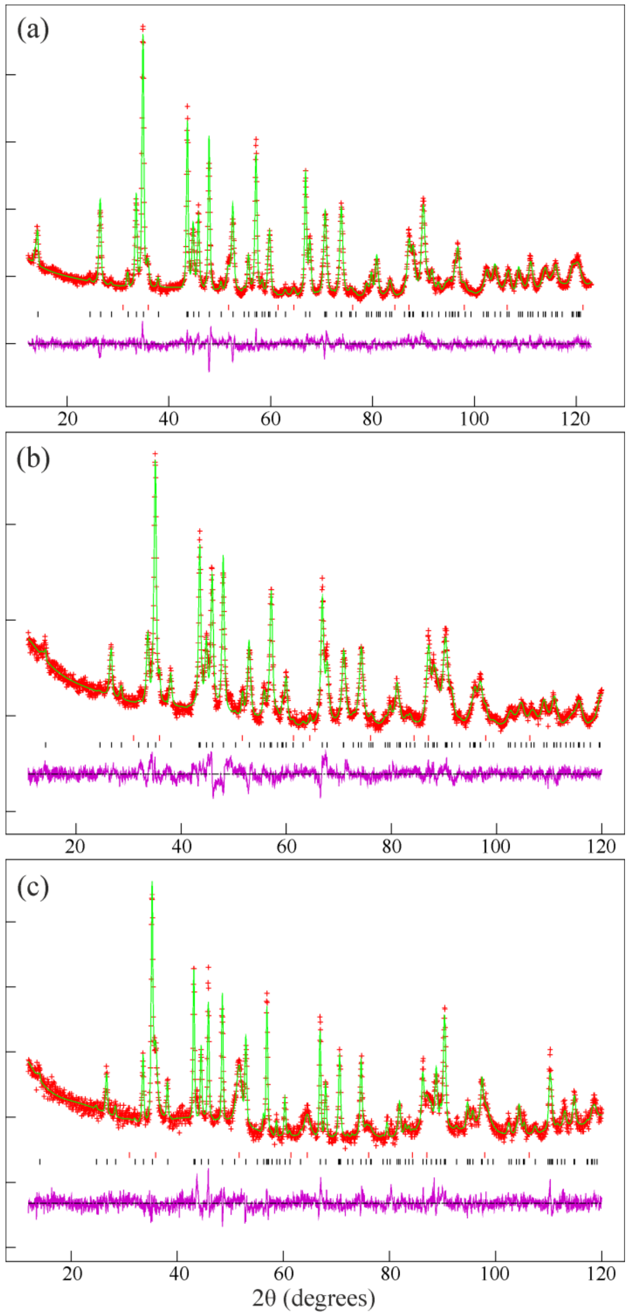


**Figure 2:** Observed, calculated and difference plots from the structural refinement of a)$Sr_2Fe_{0.5}Ir_{0.5}O_3$, b) $Sr_2Co_{0.5}Ir_{0.5}O_3$ and c) $La_{0.5}Sr_{1.5}Co_{0.5}Ir_{0.5}O_3$ against neutron powder diffraction data collected at 298 K. Lower tick marks indicate peak positions form the majority phase, upper tick marks for an SrO secondary phase. The unindexed peaks at $2\theta \sim 45°$ come from the vanadium sample holder.

A structural model based on a anion-vacancy ordered perovskite phase was refined against the diffraction data collected from $CaMn_{0.5}Ir_{0.5}O_{2.5}$ (space group *Pnma*).

Figure 3 shows data from the simultaneous strucutral refinement against both the neutron powder diffraction data and synchrotron X-ray powder diffraction data (I11, DLS).

These data are included in a publication:

$CaMn_{0.5}Ir_{0.5}O_{2.5}$ – an anion-deficient perovskite oxide containing $Ir^{3+}$.
J. E. Page and M. A. Hayward

Which is currently in review.

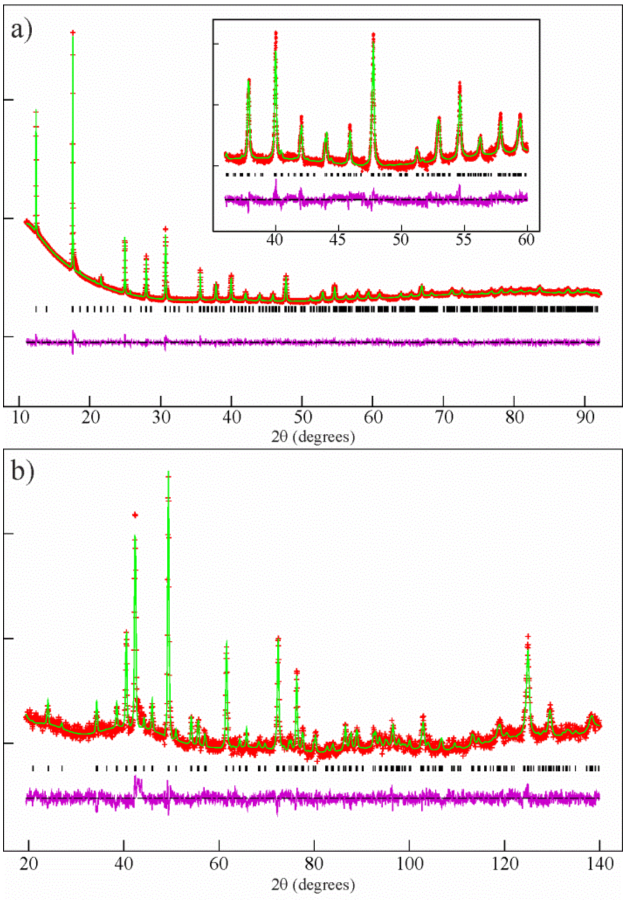


Figure 3. Observed calculated and difference plots from the combined structural refinement of $CaMn_{0.5}Ir_{0.5}O_{2.5}$ against a) synchrotron X-ray and b) neutron powder diffraction data.