Experimental Report

Proposal: **5-31-2229** **Council:** 4/2012

Title: Crystal and magnetic structures ofiridium-containing double perovskites Sr2IrMO6 (M= Ca, Ni, Cu, Zn)

This proposal is a new proposal

Researh Area: Chemistry

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Samples: Sr2MIrO6 (M= Ca,Ni,Cu,Zn)

Instrument	Req. Days	All. Days	From	To
D2B	2	2	23/11/2012	25/11/2012

Abstract:

We propose the study of novel oxides of stoichiometry Sr2MIrO6 (M= Ca, Zn, Ni and Cu). The ability of Ir to exist in different oxidation states and the spatially more extended 5d orbitals result in a rich variety of interactions with the first-row transition metal partner in the mentioned double perovskites. Here we have been able to stabilize Ir(VI) at 200 bar O2 pressure. The Ca material was previously described in the pioneering work by Demazeau, who studied the crystal structure by XRD (TN= 80 K). For Sr2NiIrO6, the ZFC susceptibility shows a maximum at TN=58 K, plausibly corresponding to the long-range magnetic ordering of Ni and Ir magnetic sublattices. The actual oxidation states of Ni and Ir (Ni2++Ir6+ vs Ni3+ + Ir5+) are also an unknown, since this compound is reported here for the first time. In this experiment we expect to make a comprehensive and detailed structural description, unveiling the influence of the covalency of Ir-O bonds on the tilting and deformation of the IrO6 octahedra, as well as to understand the microscopic origin of the observed magnetism from the study of the magnetic structures.

The study of iridium-based oxides is attracting a lot of interest during the last years, since elements with 4*d* and particularly 5*d* electrons are expected to present unusual electronic structures due to their characteristic spin-orbit coupling[i]. The ability of Ir to exist in different oxidation states and the more extended 5*d* orbital, together with the spin-orbit coupling, result in a rich variety of possibilities. Although Ir^{4+} is the most common oxidation state, Ir^{3+} in the octahedral site of a perovskite structure has been described in double perovskites and also Ir^{5+} and Ir^{6+}, can be obtained under high oxygen pressure conditions.[ii,iii] The stabilization of Ir^{5+} and Ir^{6+} is especially interesting since the Ir^{5+}-O and Ir^{6+}-O bonds should be among the strongest chemical bonds in an oxygen lattice.

The purpose of the NPD experiment was to make a comprehensive and detailed structural description of different Ir double perovskites of composition Sr2MIrO6 (M= Ni, Zn, Mg, Ca). In the present experiment, high-resolution NPD data were collected at D2B instrument in order to determine the crystal structure. The neutron patterns were collected using a wavelength of ~ 1.594 Å. The Rietveld refinement of the structure confirms that these oxides present an ordered arrangement of the B-site cations at room temperature, and that its structure at RT can be described with the $P2_1/n$ space group and unit-cell parameters related with ideal perovskite as $a\approx\sqrt{2}a_0$, $b\approx\sqrt{2}a_0$ and $c\approx2a_0$ and $\beta\approx90^o$. Fig. 1 shows satisfactory agreement between the observed and calculated profiles.

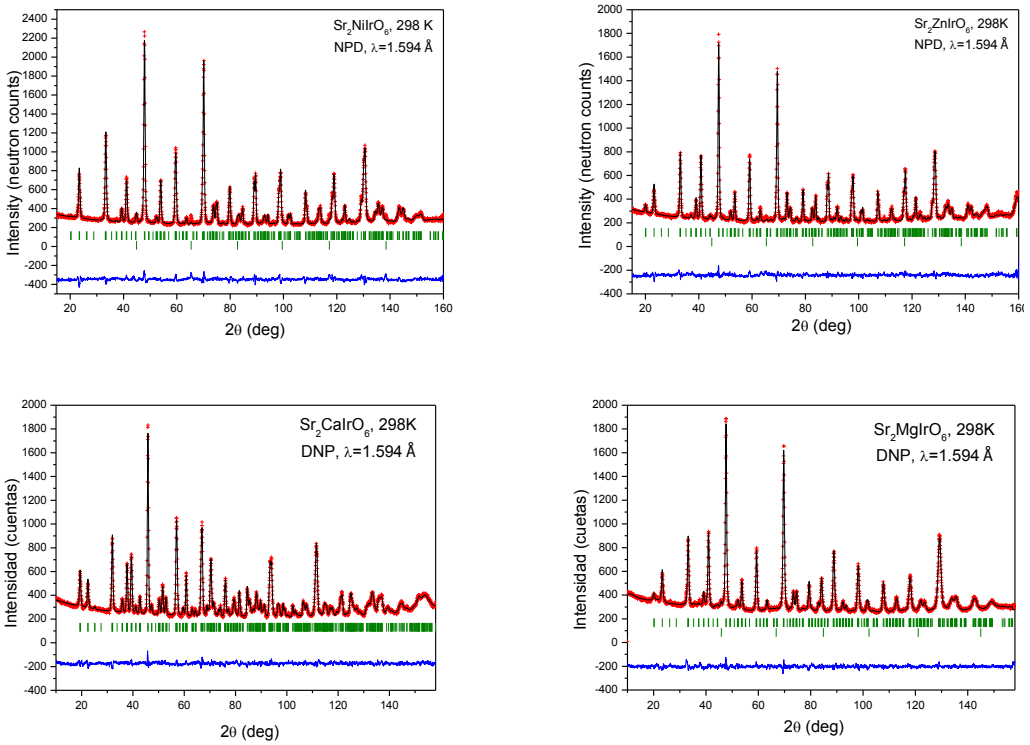

Fig. 1. Observed (crosses), calculated (solid line) and difference (bottom) NPD Rietveld profiles for Sr_2MIrO_6 (M= Ni, Zn, Ca and Mg) at RT, collected at the high flux D2B-ILL diffractometer.

Moreover, NPD experiments in the D2B diffractometer, equipped with a furnace, allowed us to study the temperature dependence of the crystal structure. The thermal evolution of the structure of the Ni-containing compound shows the presence of two phase transition in the 373-673 K interval following the sequence $P2_1/n \rightarrow I4/m \rightarrow Fm3\text{-}m$. Also, in previous measurements in D1B instrument we determined the magnetic structure, and the analysis of all of the NPD data, complemented with magnetic measured has resulted in two publications:

P. Kayser, M.J. Martinez-Lope, J.A. Alonso, M. Retuerto, M. Croft, A. Ignatov, M.T. Fernández-Díaz, " Crystal structure, phase transitions, and magnetic properties of iridium perovskites Sr_2MIrO_6 (M = Ni, Zn)" **Inorganic Chemistry** 52, 11013-11022, (2013)

P. Kayser, M.J. Martínez-Lope, J.A. Alonso, M. Retuerto, M. Croft, A. Ignatov, M.T. Fernández-Díaz "Crystal and magnetic structure of Sr_2MIrO_6 (M= Ca, Mg) double perovskites: a neutron diffraction study". **Eur. J. Inorg. Chem**. DOI: 10.1002/ejic.201301080

[i] J.P. Clancy, N. Chen, C.Y. Kim, W.F. Chen, K.W. Plumb, B.C. Jeon, T.W. Noh and Young-June Kim **Phys. Rev. B** 86, 195131 (2012)

[ii] D.Y. Jung and G. Demazeau **J. Solid State Chemistry** 115,447 (1995)

[iii] . P.D. Battle, G.R. Blake, T.C. Gibb and J.F. Vente **J. Solid State Chemistry** 145,541 (1999)