Experimental Report

29/11/2013

Proposal:	**5-31-2268**	**Council:**	10/2012

Title: Crystal and magnetic structures ofnew double perovskites containing iridium and ruthenium

This proposal is a new proposal

Researh Area: Materials

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Samples: R2NiIrO6 (R= La, Nd, Pr, Ho, Y)
R2NiRuO6 (R= Nd, Ho, Y, Er, Tm, Yb)

Instrument	Req. Days	All. Days	From	To
D2B	2	3	03/05/2013	06/05/2013

Abstract:

We propose the study of novel oxides of stoichiometry R2NiRuO6 (R= La, Nd, Pr, Ho, Y, Er, Tm, Yb) and R2NiIrO6 (R= Nd, Pr, Ho, Y). The ability of Ru and Ir to exist in different oxidation states and the spatially more extended 4d and 5d orbitals result in a rich variety of interactions with Ni in the mentioned double perovskites. The actual oxidation states of Ni and Ru/Ir (e.g. Ni2+ + Ir6+ vs Ni3+ + Ir5+) are also an unknown, since these compounds are reported here for the first time. For all the compounds the ZFC susceptibilities show anomalies plausibly corresponding to the long-range magnetic ordering of Ni and Ru/Ir magnetic sublattices. For instance, for Ho2NiRuO6 TN= 110 K. In this experiment we expect to make a comprehensive and detailed structural description, unveiling the influence of the covalency of Ru-O and Ir-O bonds on the tilting and deformation of the RuO6 and IrO6 octahedra, as well as to understand the microscopic origin of the observed magnetism from the study of the magnetic structures.

The ruthenates perovskites have attracted immense attention in material science over the past few years, since they show a rich variety of electronic and magnetic properties. Since the discovery of ferromagnetism in $SrRuO_3$ perovskite, considerable efforts have been done to improve its properties and enhance its Curie temperature by doping in A- and B-sites.[i] Compounds with general formula R_2BRuO_6 (R= rare-earths and B= Mn, Ni) have particularly attracted our interest. The combinations of these transition-metal elements with ruthenium at the B position is a promising path to find new materials with intriguing properties, since the manganites ($RMnO_3$) and nickelates ($RNiO_3$) are extremely interesting and rich systems.

The study of iridium-based oxides is the second part of this experiment. The ability of Ir to exist in different oxidation states and the more extended 5*d* orbitals, together with the spin-orbit coupling, result in a rich variety of possibilities. Introducing other transition metal (Ni) into the Ir-site appears extremely appealing to develop new materials.

The purpose of the NPD experiment was to make a comprehensive and detailed structural description and to examine the interplay of the cationic order, charge balance, transport and magnetic interactions between both cations, placed in a perovskite network. In the present experiment, high-resolution NPD data at room temperature were collected at D2B instrument in order to determine the crystal structure. The neutron patterns were collected using a wavelength of ~ 1.594 Å. For the R_2MnRuO_6 perovskites, the charge difference is not large enough to establish an ordered structure and the cations are located randomly over the B-site, resulting in a orthorhombic symmetry (*Pbnm*). On the other side, the structural refinement of the series of iridium based compounds with general formulae R_2NiIrO_6 (R= La, Pr and Nd) allowed us to define all of the members of this family with monoclinic symmetry in the $P2_1/n$ space group. The structure consists of a tridimensional network of NiO_6 and IrO_6 alternating octahedra with 1:1 rock-salt ordering Fig. 1 shows, as an example, satisfactory agreement between the observed and calculated profiles of some of the measured oxides.

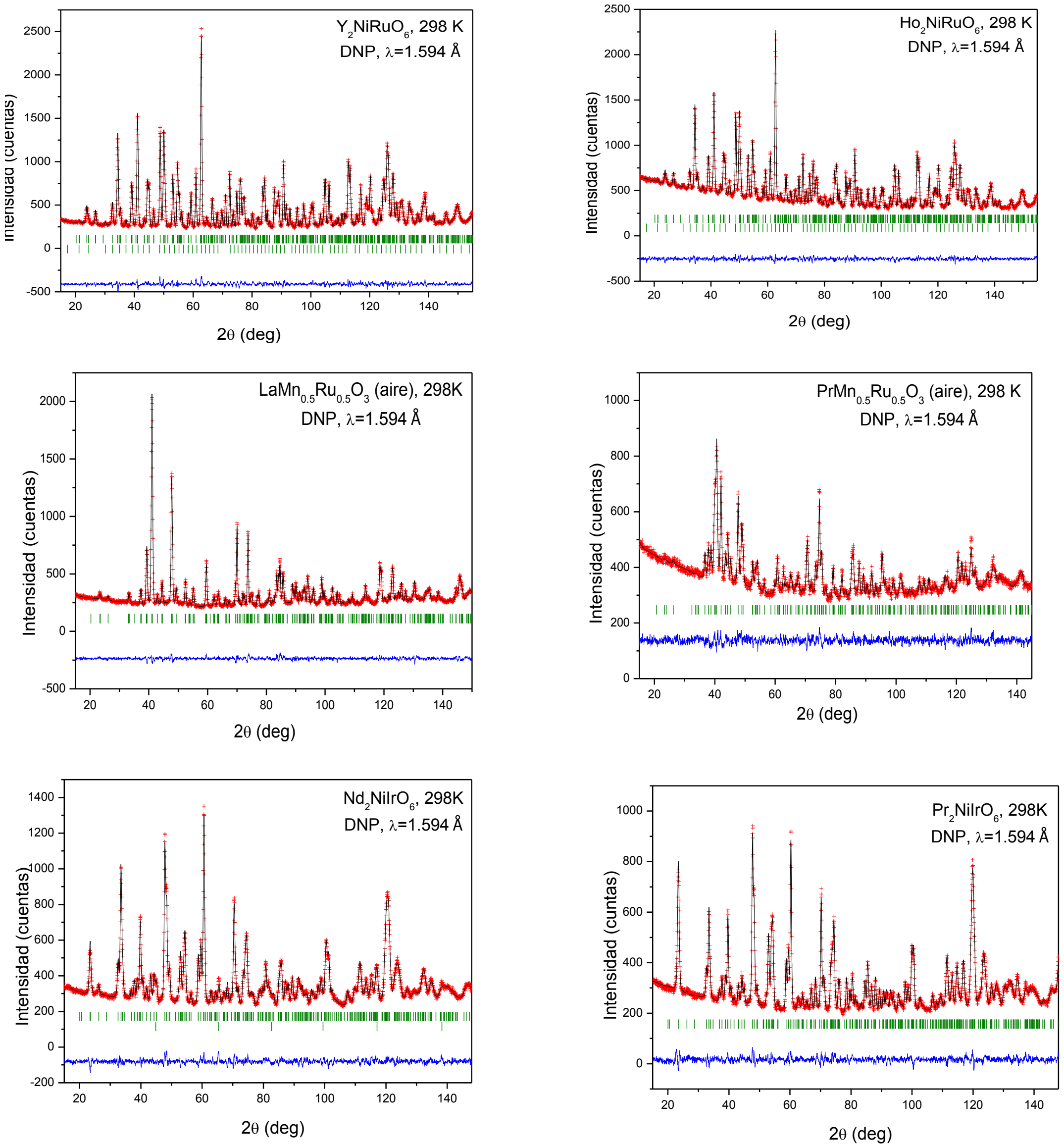

Fig. 1. Observed (crosses), calculated (solid line) and difference (bottom) NPD Rietveld profiles for R_2MRuO_6 and R_2MIrO_6 at RT, collected at the high flux D2B-ILL diffractometer.

For the magnetic structure determination we performed experiments at 2 K, at the D2B instrument equipped with a displex unit. Fig. 2 shows the NPD pattern at 2 K and a schematic view of the magnetic structure.

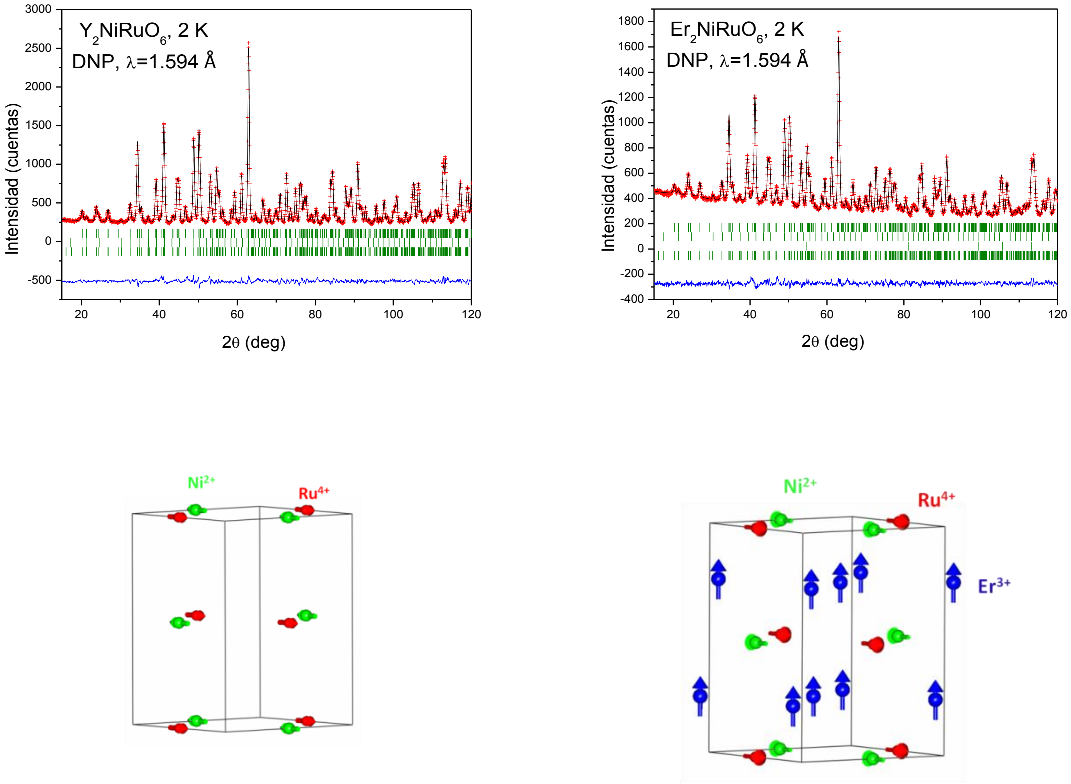

Fig. 2. Observed (crosses), calculated (solid line) and difference (bottom) NPD Rietveld profiles for R_2MRuO_6 at 2 K, collected at the high flux D2B-ILL diffractometer. Schematic view of the magnetic structure for R_2NiRuO_6 (R= Y and Er)

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[i] A. Callaghan, C. W. Moeller and R. Ward, "Magnetic *Interactions in Ternary Ruthenium Oxides"* **Inorganic Chemistry**, 5, 1572 (1966)