ESRF	**Experiment title:** Phase relations of pentavalent post-perovskites	**Experiment number**: CH-4264
Beamline: ID06	**Date of experiment**: from: 10/09/2014 to: 14/09/2014	**Date of report**: 08/09/2016
Shifts: 12	**Local contact(s)**: Wilson Crichton	*Received at ESRF:*

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Report:

The aim of this beamtime was to study the structural P-T phase relations in the pentavalent compounds, $NaIrO_3$ and $KIrO_3$, using *in-situ* X-ray powder diffraction at the Large Volume Press at ID06. In a previous study, we found that $NaIrO_3$ can be stabilized in the post-perovskite (PPV) structure at 4.5 GPa and 800°C [1], and we have also identified a polymorph at lower pressure. In addition to study the transformation, we also wanted to explore whether a PPV phase of $KIrO_3$ can be stabilized by pressure, since at low pressure $KIrO_3$ is isostructural to the low-pressure polymorph of $NaIrO_3$.

During the preparation of the experiments at ID06 we encountered several obstacles and as a consequence we did not get the expected data and results during. The precursors for the syntheses are highly air-sensitive, and they have to be handled in a glove-box. However, at the time of the experiment, the chemistry lab and the glove-box were not available to users due to renovation. Instead, we had to use a small portable Argon glove-bag, which complicated the preparation significantly. The precursors have to be encapsulated in gold foil before assembling the octahedral assemblies, but with limited visual access through the glove-bag it was difficult to ensure the capsules were properly sealed. Furthermore, the data quality were greatly affecting by the strong diffraction from the gold capsules, despite optimizing this to the thinnest practical thickness (~50 micron). Several runs were conducted (see Table 1) and the *in-situ* diffraction data from one of the more successful experiments is shown in Figure 1. The figure shows the diffraction from the $NaIrO_3$ precursors (Na_2O_2, Ir and $NaClO_3$) during heating from room temperature to 1000°C. Between scan number 129 and 151 a gradual shift of the peaks are observed indicating an on-going reaction. A sudden shift in peak positions are observed at scan 152 (T~800°C), caused by movement of the rams and a pressure drop. Between scan 153 and 668 the temperature was increased further to 1000°C, no significant amount of PPV-$NaIrO_3$ formed, but changes in the powder pattern are observed. The intensity of the Ir precursor show only

small variation showing that no oxidation occurred, either because the Na_2O_2 reagent and oxidizing agent had degraded during the preparation or because the gold capsule were not properly sealed. Both explanations can be ascribed to the technical problems with the use of a glove-bag. After similar results for $KIrO_3$ and $NaOsO_3$, we decided to study two systems that did not involve air-sensitive precursors, to generate some useful results during this first beamtime. The studies of $SrIrO_3$ and BiS_2 both lead to useful insights that contributed to the two independent publications/manuscripts [2,3].

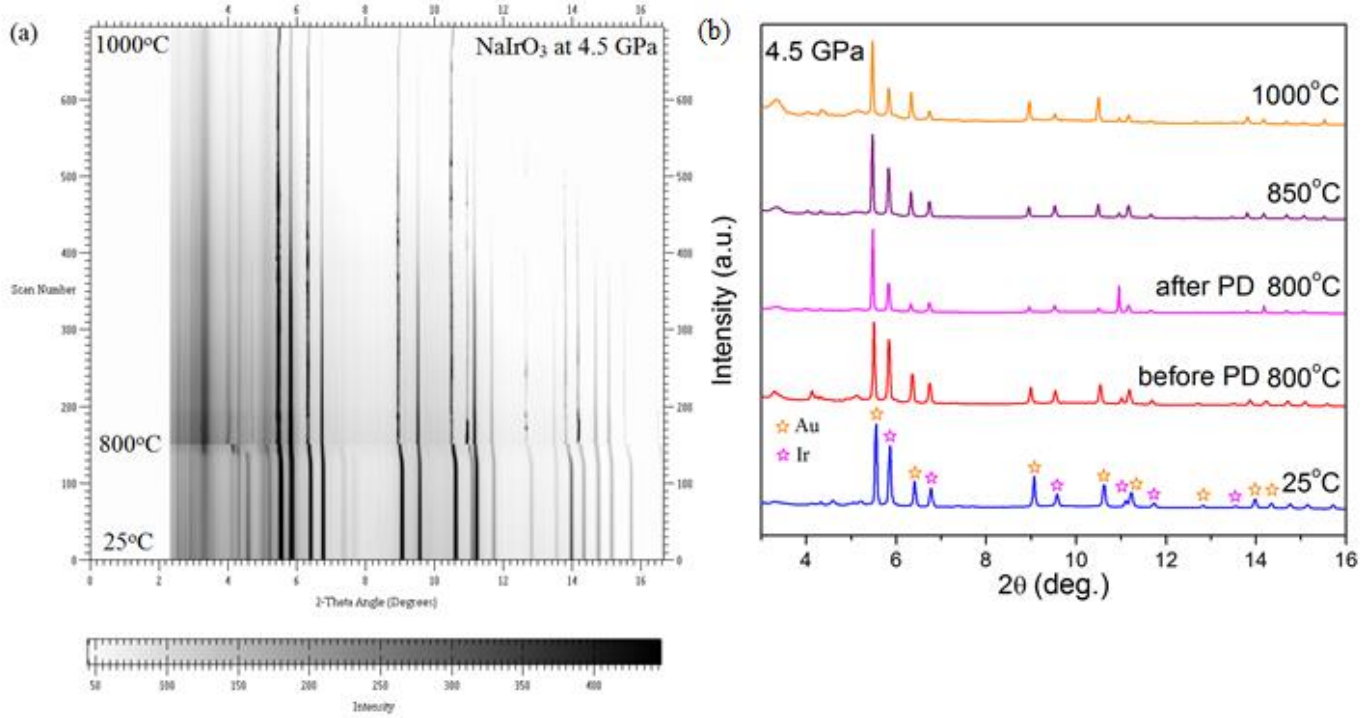

Figure 1: (a) Powder X-ray diffraction of $NaIrO_3$ precursor during heating from room temperature to 1000°C at 4.5 GPa. (b) Selected powder diffraction patterns for Experiment 1. The wavelength is 0.225 Å (55 keV).

Table 1. Summary of the experiments performed during the beamtime.

Experiment	Precursor	Target phase	Max. Pressure (GPa)	Max. Temperature (°C)
Run 1	**Na_2O_2, $NaClO_3$, Ir**	**$NaIrO_3$**	**4.5**	**1000**
Run 2*	**KO_2, $KClO_3$, Ir**	**$KIrO_3$**	**-**	**-**
Run 3	**$NaOsO_3$**	**$NaOsO_3$**	**12**	**1200**
Run 4	**6H-$SrIrO_3$**	**$SrIrO_3$**	**8.1**	**1000**
Run 5	**Bi, S**	**BiS_2**	**5.5**	**1300**

* Visual expection and ambient PXRD measurement of the gold capsule showed that it was not proberly.

The problems experienced during the first beamtime are related to the air-sensitivity of the precursors and the need for very thin gold capsules that at least to some extent allow sufficient X-ray transmission. The fact that we only had a small glove-bag available meant that we could not stabilize the targeted compounds.

References

1. M.Bremholm, et al., J. Solid State Chem., 2011, 184(3), 601-607.
2. C.H. Kronbo, et al., J. Solid State Chem., 2016. 238, 74-82.
3. S.M. Kevy, et al., *In preparation*.