EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

	Experiment title:	Experiment number:
	Synthesis and characterization of mixed valence doped $NaOsO_3$	CH-4530
Beamline: ID06LVP	**Date of experiment:** from: 25.11.2015 to: 01.12.2015	**Date of report:** 28.02.2016
Shifts: 18	**Local contact(s):** Wilson Crichton	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Serena Margadonna * (Swansea University)

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Report:

The purpose of the study was to identify suitable protocol to produce mixed valence osmate perovskites (pv) and postperovskites (ppv). We have successfully produced large single crystals of Ca- and Ir-doped $NaOsO_3$-pv and $NaOsO_3$-ppv by a traditional metastable pv to ppv route (figure 1). That is, we have grown only the second known pentavalent ppv.

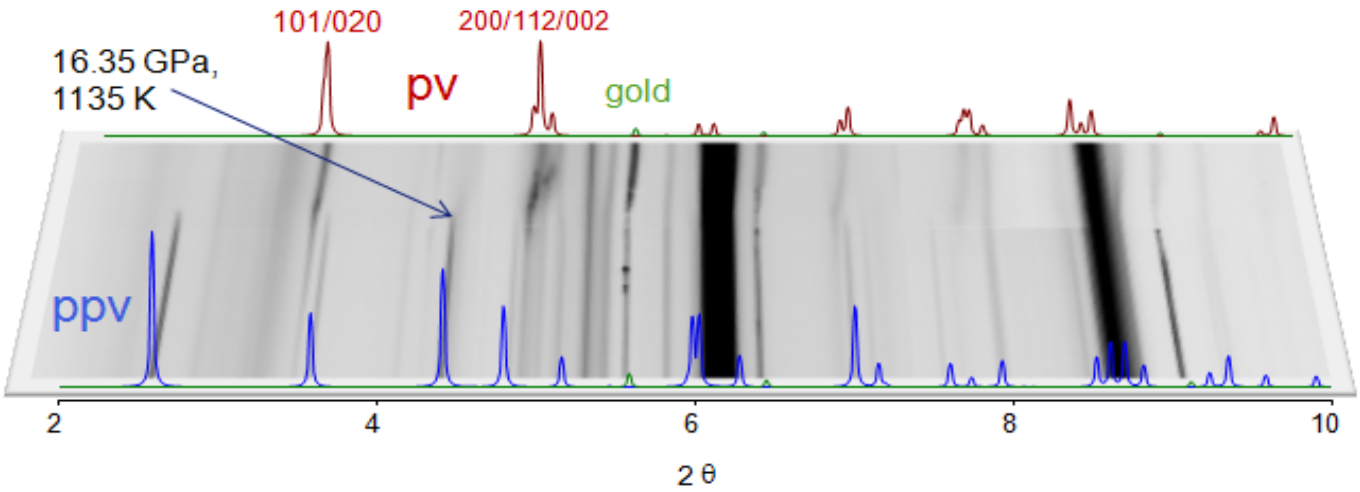

Figure 1. The transition from pv to ppv takes place above 1100 K and 16 GPa with rapid onset. The ppv phase is quenchable and recoverable. The initial sample was crushed, hand-picked pv single crystals and loaded in a thin-walled gold capsule. The same transformation has also been observed with pv loaded directly in *h*-BN.

In addition, we have produced $Na_4CaOs_3(OH)_{24}$, the largest ordered protonated hydroxide phase

yet encountered and a number of higher valence osmates: hexavalent Na_2OsO_4 and heptavalent Na_3OsO_5. More importantly, we have repeated the synthesis of Sleight of $KSbO_3$-type $NaOsO_3$ and shown that it also exists in a rhombohedral distortion, distinct from the rhombohedral ilmenite form that occurs in other $KSbO_3$-bearing systems. We show that the rhombohedral form is stabilised by pressure and the cubic by temperature. The highlight is that ppv-type $NaOsO_3$ grows directly from the $KSbO_3$-type, Figure 2.

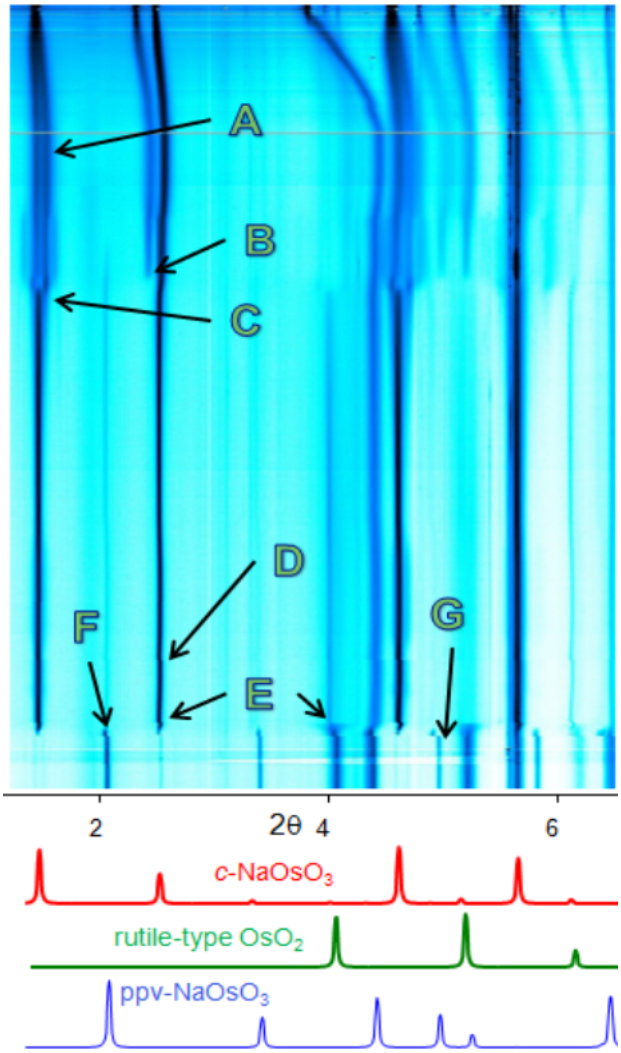

Figure 2. A series of semi-continuous x-ray diffraction patterns collected upon pressurizing and during two heating-cooling cycles. Shown is the lower angle part only. Of note: **A**. Increased splitting of the (110/1-10) pair; **B.** Loss of Na_2OsO_4 **C.** *rR* to *c*-$NaOsO_3$ transformation. **D**. Quench, end heating cycle 1. **E.** 's'-shaped-kink, onset of OsO_2 and crystallization of ppv (**F**). **G**. Quench end of heating cycle 2, followed by reheat. Simulated diffraction patterns for *c*-$NaOsO_3$, OsO_2 and ppv-$NaOsO_3$ are shown as key. Other peaks are due to *h*-BN (the fast-moving peak at ~4° is the 002) and the 111 of MgO, at about 5.4°.

This is an entirely new and unique demonstration of this method, which foregoes any pv intermediate. It also occurs at 10 GPa less pressure than the pv to ppv transformation, probably driven by the large competing densities. At 1bar pv is denser than ppv, at transformation it is 1-2% less dense. At 6 GPa, ppv is 10-12% denser than the $KSbO_3$ type, so clearly the pressure effect can be considerable. At intermediate pressures pv is only encountered at highest temperatures.

Our syntheses made use of presynthetic mixes of $KSbO_3$+Na_2OsO_4 (= Na_2O_2 + OsO_2 + 10mol% excess peroxide) and pv, providing a new way to overcome the drawbacks of using Pt or Au capsules for in situ measurements. It may be that the capsules themselves promote synthesis, of pv in Pt, in particular, though we have no evidence from EMPA for any Pt or Au incorporation in the pv (etc) phase synthesised.

Of particular note, estimation of the likelihood of pv transforming to ppv by any usual methods (pseudocubic tilt, volumetric ratios, etc) fails for this composition. Therefore, as also demonstrated by the synthesis of $CaIrO_3$, the only other known pentavelent ppv, these rules must be reestimated for the production of other new ppv stoichiometries with pentavalent cations, which may also forego any pv precursor or intermediate.