ESRF	**Experiment title:** **High-pressure high-temperature study of fcc and hcp Ir-Re and Ir-Os solid solutions**	**Experiment number**: **CH-3991**
Beamline: ID09A	**Date of experiment**: from: 30.10.2013 to: 04.11.2013	**Date of report**: 17.02.2014
Shifts: 15	**Local contact(s)**: Michael Hanfland	*Received at ESRF:*

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Report:

In order to improve gain knowledge about phase stability and compressibility of platinum group metals alloys and compounds we launched systematic investigation of Ir—Os alloys under high-pressure high-temperature conditions. Their high-pressure behaviour has relevance for materials chemistry while Ir and Os are the less compressible metals as well as for geology of platinum group metals metallic minerals such as iridoosmine and related minerals which associated with crystal rocks formed under high-pressure high-temperature conditions form the melt.

Ir_xOs_{1-x} samples were prepared by thermal decomposition of single-source precursors $(NH_4)_2[Ir_xOs_{1-x}Cl_6]$ in 10-%-H_2/90-%N_2 stream during 0.5 h at 600 °C with further natural cooling to the room temperature during 10 h. 7 samples in the whole range of concentrations were prepared. 4 samples with Os concentration greater than 45 at.% appeared with hcp structure. hcp-$Ir_{0.55}Os_{0.45}$ and hcp-$Ir_{0.40}Os_{0.60}$ have compositions close to limiting stability regions of fcc and hcp phases correspondently. hcp-$Ir_{0.50}Os_{0.50}$ was in the middle of miscibility gap between fcc and hcp phases on the experimental phase diagram. Two compositions ($Ir_{0.60}Os_{0.40}$ and $Ir_{0.65}Os_{0.35}$) appeared to be two-phase (fcc+hcp), only a single sample ($Ir_{0.80}Os_{0.20}$) was fcc single-phase solid solution.

We investigated compressibility of synthetic fcc-$Ir_{0.80}Os_{0.20}$, hcp-$Ir_{0.20}Os_{0.80}$, and hcp-$Ir_{0.55}Os_{0.45}$ solid solutions at pressures up to 55 GPa, and hcp-$Ir_{0.40}Os_{0.60}$ up to 145 GPa. High-pressure powder X-ray diffraction data on fcc-$Ir_{0.80}Os_{0.20}$, hcp-$Ir_{0.20}Os_{0.80}$, and hcp-$Ir_{0.40}Os_{0.60}$ were collected at room temperature at

ID-09a beam-line at ESRF (wavelength 0.4145 Å, MAR 555 flat panel detector, beam size 10x15 μm^2). Diamond anvil cells with culet sizes 250 μm (in experiments to 55 GPa) and bevelled with culets 120 μm (in experiment with maximum pressure 145 GPa) were employed. Rhenium gaskets were pre-indent to thickness of about 20 μm and holes with diameter of about ½ of culet size were drilled in the centre of the indentation. Mineral oil was used as pressure transmitting medium in experiments at ESRF. Pressure was determined from Au loaded in the pressure chamber as small piece of wire of 5 μm diameter and about 10 μm length, or as flake of compressed fine powder.

In the frame of the experiment a set of experimental data was obtained which gives promising results, which allow us the better understanding the nature of incompressible metals. Nevertheless, there are several issues, which should be further investigated including high-temperature compressibility (which was proposed but due to the technical issues did not completely measured) and more detail investigation of region close to 30 GPa where we obtained unusual behaviour characteristic for electronic topological transition. Based on the experimental data bellow 30 GPa we fitted compressibility curves using Birch-Murnaghan equation of state (B-M EoS; 3rd order) with the bulk moduli (pressure derivatives were fixed as 4) summarized in the table below. Experimental data in a graphical form are summarized in Figure below. It should be noted that compressibility data below and above 25-30 GPa cannot be fitted as a single function which is a sign for electronic topological transition known for pure hcp-Os. Compressibility data for all samples were collected in mineral oil and to address all possible technical issues at least one sample should be compressed in neon or helium as a pressure transmitting medium, as well as pure iridium should be investigated while experimental data known from the literature should be improved.

Table. Bulk moduli for Ir-Os solid solutions.

Composition	V_0/Z, Å^3*	V_0/Z, Å^3**	B_0, GPa
fcc–Ir (up to 65 GPa)***	14.1556	14.1556	354(6)
fcc–$Ir_{0.80}Os_{0.20}$ (up to 20 GPa)	14.112(2)	14.09(1)	368(4)
hcp–$Ir_{0.55}Os_{0.45}$ (up to 32 GPa)	14.092(2)	14.07(1)	393(7)
hcp–$Ir_{0.40}Os_{0.60}$ (up to 20 GPa)	14.069(2)	14.06(2)	403(32)
hcp–$Ir_{0.20}Os_{0.80}$ (up to 15 GPa)	13.982(4)	14.00(1)	420(5)
hcp–Os (up to 75 GPa)***	13.982(5)	13.971(4)	411(6)

*according to ambient PXRD; ** according to B-M EoS; *** literature data

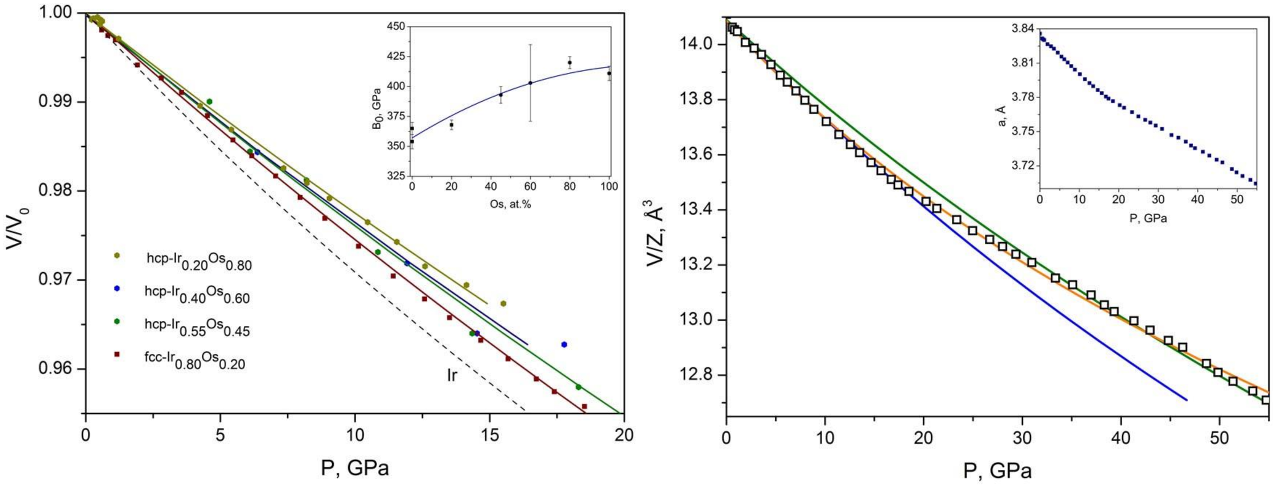

Figure. *Left*: Compressibility curves for Ir-Os solid solutions. Insert shows the composition dependence of bulk moduli. *Right*: Compressibility curve for fcc–$Ir_{0.80}Os_{0.20}$. Lines show B-M EoS fits below 20 GPa (blue), above (green) and whole region (orange). Insert shows pressure dependence of cell parameter.

The data obtained below 35 GPa have been summarized as paper which was submitted to PhysRevB: KV Yusenko, EA Bykova, MA Bykov, SA Gromilov, VB Prakapenka, AV Kurnosov, S Margadonna1, and LS Dubrovinsky, Compressibility of Ir_xOs_{1-x} solid solutions under high-pressure, Phys. Rev. B, 2014, submitted. With the following abstract:

"Several fcc and hcp Ir-Os solid solitions were prepared from single source precursors in hydrogen stream at 600 °C. Their atomic volumes measured at ambient conditions using powder X-ray diffrac- tion follow nearly linear dependence with a slight positiv deviation. Compressibility curves for fcc and hcp Ir-Os solid solutions were measured in diamon-anvil cells at room temperature up to 30 GPa. The corresponding bulk moduli depend on the composition and growing with increasing os- mium content. Bulk moduli fitted using the third order Birch-Murnaghanequition of state are higher in comparison with pure Ir (B_0=306 GPa) and maximal value is characteristic for hcp-$Ir_{0.20}Os_{0.80}$ which is slightly higher than B_0 for pure Os (B_0=411 GPa) and still smaller the diamond value (B_0=446(1) GPa, B'=3.0(1)). Concentration dependence of bulk moduli for Ir-Os solid solutions shows a positive deviation from linearity. Compressibility curve for fcc-$Ir_{0.80}Os_{0.20}$ measure up to 55 GPa cannot be fitted with a single EoS function and splits into two regions below and above 20 GPa, which can be interpreted as electronic topological transition."