	Experiment title: Single-crystal X-ray diffraction studies of novel metal nitrides with polymeric nitrogen chains at pressures up to 300 GPa	**Experiment number**: MA-3911
Beamline: ID11	**Date of experiment**: from: 09.07.2018 to: 12.07.2018	**Date of report**:
Shifts: 15	**Local contact(s)**: Pavel Sedmak	*Received at ESRF:*

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Report:

During the allocated beamtime we studied high-pressure high-temperature reactions between transition metals Fe, Os, Re and nitrogen. In each experiment, a piece of metal was placed inside a sample chamber of a BX90 diamond anvil cell equipped with BoehlerAlmax-type diamonds (40 μm culet diameter). Nitrogen was used as a pressure-transmitting medium and as a reagent. The samples were compressed up to ~170 GPa and laser-heated. Single-crystal X-ray diffraction experiments were performed at the beamline ID11. All studied metals react with nitrogen with the formation of compounds containing polymeric nitrogen units: FeN_4, Os_5N_{34} and ReN_{12}.

The results of this experiment are used in three publications (1 published, 1 under review and 1 in the final stage of preparation):

1. M. Bykov, S. Khandarkhaeva, T. Fedotenko, P. Sedmak, N. Dubrovinskaia, and L. Dubrovinsky, Acta Crystallogr. Sect. E Crystallogr. Commun. **74**, 1392 (2018).

Abstract:

Iron tetranitride, FeN_4, was synthesized from the elements in a laser-heated diamond anvil cell at 180 (5) GPa and 2700 (200) K. Its crystal structure was determined based on single-crystal X-ray diffraction data collected from a submicron-sized grain at the synchrotron beamline ID11 of ESRF. The compound crystallizes in the triclinic space group P-1. In the asymmetric unit, the Fe atom occupies an inversion centre (Wyckoff position 1d), while two N atoms occupy general positions (2i). The structure is made up from edge-sharing [FeN_6] octahedra forming chains along [100] and being interconnected through N-N bridges. N atoms form catena-poly[tetraz-1-ene-1,4-diyl] anions $[–N–N–N=N–]_\infty^{2-}$ running along [001]. In comparison with the previously reported structure of FeN_4 at 135 GPa [Bykov et al. (2018). Nat. Commun. 9, 2756], the crystal structure of FeN_4 at 180 GPa is similar but the structural model is significantly improved in terms of the precision of the bond lengths and angles

2. Maxim Bykov, Stella Chariton, Elena Bykova, Saiana Khandarkhaeva, Timofey Fedotenko, Alena V. Ponomareva, Johan Tidholm, Ferenc Tasnádi, Igor A. Abrikosov, Pavel Sedmak, Vitali Prakapenka, Michael Hanfland, Hanns-Peter Liermann, Mohammad Mahmood, Alexander Goncharov, Natalia Dubrovinskaia, Leonid Dubrovinsky. *High-pressure synthesis of metal-inorganic frameworks $Hf_4N_{20}·N_2$, $WN_8·N_2$, and $Os_5N_{28}·3N_2$ with polymeric nitrogen linkers.*

   Under review in Angewandte Chemie

   Abstract: The synthesis of various polynitrogen compounds have been actively pursued for the past hundred years due to their potential as high energy density materials. Polynitrides are intrinsically thermodynamically unstable at ambient conditions and require peculiar synthetic approaches. Here we report one-step synthesis of metal-inorganic frameworks $Hf_4N_{20}·N_2$, $WN_8·N_2$, and $Os_5N_{28}·3N_2$ *via* direct reactions between elements in a diamond anvil cell at pressures exceeding 100 GPa. The porous frameworks - Hf_4N_{20}, WN_8 and Os_5N_{28} - are built from transition metal atoms linked either by polymeric polydiazenediyl (polyacetylene-like) nitrogen chains or through dinitrogen units. Triply bound dinitrogen molecules occupy channels of these frameworks. Due to conjugated polydiazenediyl chains these compounds exhibit metallic properties. The high-pressure reaction between Hf and N2 also leads to a non-centrosymmetric polynitride Hf_2N_{11} that features double-helix catena-poly[tetraz-1-ene-1,4-diyl] nitrogen chains $[\text{-N-N-N=N-}]_\infty$.

3. Synthesis of layered polymeric compound ReN_{12}

   Despite very high synthetic pressure Re and nitrogen form a layered compound ReN_{12}, shown on the figure below. Unlike metal-inorganic frameworks $Hf_4N_{20}·N_2$, $WN_8·N_2$, and $Os_5N_{28}·3N_2$, it doesn't have channels in its structure. All nitrogen atoms have sp^2 hybridization and form infinite polyacetylene-like chains along the crystallographic *c*-axis. Due to the delocalized pi-systems of these chains, this compound is expected to be a metal. Moreover, due to the lathe layered structure of ReN12, it is expected to possess quasi-low-dimensional propeties. We plan new experiments at the beamline ID12 to study the electronic states of Re in this unique compound.