ESRF	**Experiment title:** High pressure synthesis of xenon nitride	**Experiment number**: hc-2182
Beamline: ID27	**Date of experiment**: from: October 3rd 2015 to: October 6th 2015 from: December 13th 2015 to: December 16th 2015	**Date of report**: 28/02/2016
Shifts: 9	**Local contact(s)**: Gaston Garbarino	*Received at ESRF:*
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Objectives

Both N_2 and Xe are inert under ambient conditions and hardly interact with other elements. The properties of xenon change drastically under pressure and its chemistry becomes richer. XeF_2 [1] and Xe_3O_2 [2] compounds with covalent bonding have recently been formed at high pressure. The aim of this proposal is to synthesize the first xenon nitride under compression. This novel compound is predicted to have the peculiar XeN_6 stoichiometry, with the formation of N_6 rings and weak Xe-N covalent bonds [3]. Pressure in the range 130 GPa – 200 GPa will be generated in a laser-heated diamond anvil cell so as to enter the predicted stability domain of XeN_6. The reaction products are to be characterized by X-ray diffraction.

October 3rd to October 6th 2015

Experimental method

Three membrane diamond anvil cells were equipped with anvils of 50, 70 and 100 µm in culet size, respectively. All cells were loaded with a Xe-N_2 mixture, with xenon concentrations of 25 (2x) and 33 mol %. A gold particle was loaded along with the sample, and its equation of state was used to determine the pressure inside the cavity. A thin LiF layer thermally insulated the sample from the diamond anvils. Laser-heating was performed with the on-line setup of ID27. Each sample was laser-heated above 2500 K for over 15 minutes at ~ 140 GPa, and then every 5 GPa up to the maximum pressure. Between each pressure step, angular dispersive powder X-ray diffraction was performed with a monochromatic beam of energy E = 33 keV at the ID27 beamline. The X-ray diffraction images were collected with an on-line image plate detector (MARCCD). The beam was focussed down to ~ 3x3 μm^2.

Results

Three xenon-nitrogen samples with concentrations of 33, 25 and 25 mol % were studied up to maximum pressure of 154, 184 and 169 GPa, respectively. The van der Waals compound previously characterized at beamline ID09A of the ESRF (see experimental report hc-1890) was observed at both concentrations up to the maximum measured pressure. For both samples at 25 mol % of Xe, a new phase was observed after laser heating at ~ 150 GPa (see Fig. 1). Due to the poor crystalline quality of the synthesized product, structure solving could not be performed. Further laser-heating (both at synthesized and higher pressures) did not yield better powder quality nor promoted conversion of the van der Waals phase to the new one.

Taking into account the results of this first run, cell preparation and sample concentrations were optimized for the second campaign.

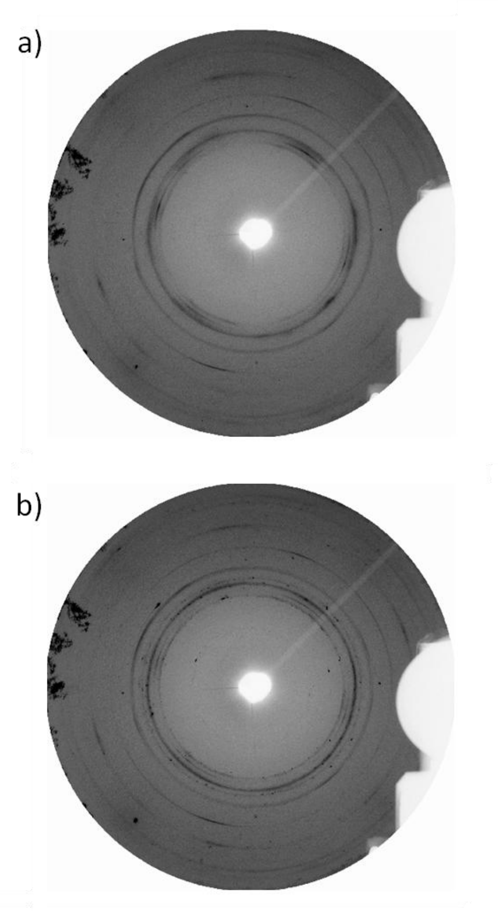

Figure 1: a) and b) Image plates of a Xe-N_2 sample at 154 GPa before and after laser heating above 2500 K. New diffraction rings and spots characterize the high-pressure high - temperature synthesized solid.

December 13th to December 16th 2015

Experimental method

Two membrane diamond anvil cells were equipped with anvils of 100 µm in culet size. These were loaded with different Xe-N_2 mixtures, one with a concentration of 25 mol% Xe and the other one 11 mol% Xe. The equation of state of gold was used as a pressure calibrant. This time, samples were thermally insulated from the diamond anvils by a thin Al_2O_3 layer instead of LiF. Testing with different assemblies allows to prove that no parasitic chemical reaction with the insulating media or the diamond anvils occurred. One sample was laser-heated with our in-house laser-heating setup before the experiments at the ESRF while the other was laser-heated with the on-line setup of ID27. Angular dispersive X-ray diffraction with a monochromatic beam of energy E = 33 keV was performed with the beam focussed down to ~ 3x3 µm^2. The X-ray diffraction images were collected with an on-line image plate detector (MARCCD).

Results

After laser-heating, new crystalline phases were observed, one as a powder and the other as a single crystal (see Fig. 2). Due to temperature and pressure gradients inside the cavity as well as what appears to be a quite complex Xe-N_2 phase diagram, the resulting samples were highly spatially heterogeneous. One of the samples was brought down from 161 GPa to 76 GPa while characterizing it by X-ray diffraction at regular pressure intervals. The synthesized phases were still observed at 76 GPa.

Preliminary data analysis of the high-pressure high-temperature solids revealed that none of these novel phases match the predicted XeN_6 phase or any phase of the pure compounds (hcp-Xe, cg-N, LP-N, ζ-N_2). Further characterization of the reaction products by Raman spectroscopy in our laboratory revealed several new Raman modes between 400 and 1000 cm^{-1}.

These experiments strongly suggest that a xenon nitride was synthesized from a mixture of xenon and nitrogen but its structure does not correspond to the nitride proposed in ref. [3].

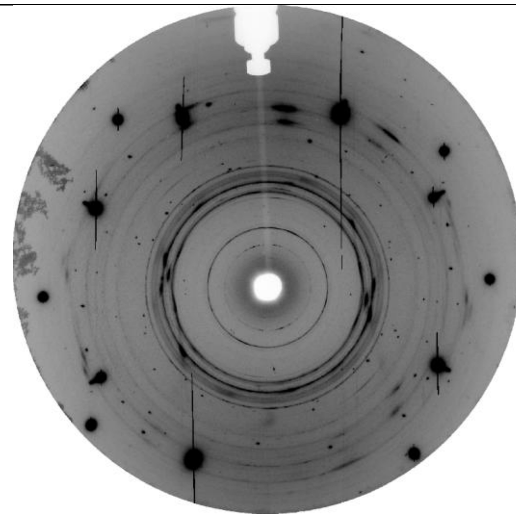

Figure 2: Image plate of Xe-N_2 sample at 146 GPa after laser heating. High-quality diffraction rings and spots of new crystalline phases are visible.

XAS experiments will soon be performed on BM23 to confirm xenon-nitrogen bonding. Furthermore, new, experimentally-guided numerical simulations will be performed and are expected to solve the crystalline structure and determine the properties of the synthesized compounds.

References:

[1] M. Kim, M. Debessai and C.-S. Yoo, Nat. Chem. **2**, 784 (2010).
[2] A. Dewaele et al. Submitted Nature Chemistry and ERSF Experimental Report HC 767.
[3] F. Peng, Y. Wang, H. Wang, Y. Zhang and Y. Ma, arXiv:1501.03891 (2015).