	Experiment title: Search for the diamondoid form of polymeric nitrogen	Experiment number: HC 4238
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Report:

Objectives

The triple N_2 bond has been observed to rupture under pressure and various polymeric extended single bonded solids have already been characterized over the past 10 years. First, the cubic cg-N phase around 100 GPa, then the layer polymeric phase, LP-N, above 160 GPa and recently the hexagonal layered polymeric nitrogen, HLP-N, above 240 GPa. Above 300 GPa, a new cagelike diamondoid structure has been predicted to be much more stable than all other polymeric forms of nitrogen Hence, it should be observed experimentally but pressures in excess of 300 GPa must be generated. The aim of this proposal was to investigate the structural transformation of solid nitrogen in the pressure range 250 – 350 GPa under laser heating using toroidal anvils.

Experimental method and results

Two membrane diamond anvil cells (MDAC) were successfully prepared for the X-ray diffraction experiment. The MDACs were equipped with Boehler-Almax anvils with large X-ray aperture (+/- 35°). A toroidal shape was FIB machined on the anvils culet (of 30 µm diameter) to reach/exceed 300 GPa. The MDACs were loaded with pure nitrogen at 1400 bar and ambient temperature. Since nitrogen becomes opaque above 150 GPa in the infrared, there was no additional laser absorbing material, hence preventing the risk of a chemical reaction. The X-ray measurements were performed on the ID15 beamline. A 30 keV x-ray beam was focussed down to 2 microns with Beryllium lenses. Data were collected on an Eiger 2 detector that offers a large dynamic range and a very weak electronic noise. Because of the sanitary conditions, we didn't know if we could travel to the ESRF. Moreover, it was also not certain that we would have access to a laser heating system on site. We therefore chose to perform the preparation of the nitrogen polymeric sample in our laboratory at the CEA. A first sample was compressed to 350 GPa using the shift of the first-order Raman spectra of the diamond anvils as a pressure gauge. Since the optical gap of diamond closes progressively with pressure, measurements were performed with a laser of wavelength λ=660 nm to prevent risk of anvil breakage. The sample was then laser heated to 2500 K and Raman measurements were performed. They revealed the presence of a weak vibron peak at around 1100 cm^{-1}, signature of single bonds in polymeric nitrogen. The MDAC was then sent by mail to ESRF before the beam time to check for the presence of diffraction peaks. Unfortunately, it did not survive the trip. The second sample was laser heated at 260 GPa during several minutes in order to ensure a complete transformation of the sample. The Raman characterization of the laser-heated sample also showed the presence of polymeric nitrogen vibron peaks. After transformation, the sample had a diameter of 10 microns and was brought to ESRF. An X-ray mapping of the sample cavity showed the presence of single crystals of HLP-N with observed diffraction peaks at characteristic d-spacings of 3.98, 2.08, 1.84, 1.44, 1.124 Angstrom. In addition, we observed no signs of chemical reaction with the gasket or the anvils. We then attempted to increase pressure but the diamond anvils rapidly failed. It is very likely that this is because we blind heated the sample for long minutes, which weakened the sample assembly.

Experiment HC 4238 was certainly hampered by sanitary condition but it allowed demonstrating that it is possible to laser heat samples in toroidal anvils at pressures (above 300 GPa) where diamondoid nitrogen is predicted stable. Thanks to the new source combined with the use of the highly sensitive Eiger 2 detectors, now present on both ID27 and ID15 high-pressure beamlines, we could also confirm that the weak diffraction signal of a light element such as nitrogen is now easily measurable in the multi-megabar regime. Already the single crystal X-ray diffraction signal from HLP-N solid synthesized at 260 GPa was collected. The full success of this project now requires the ability to manage the entire experimentation on site. This will be possible on the ID27 beamline where samples can be laser heated online and single crystal x-ray diffraction will be performed with a submicron beam. Moreover, an ongoing collaboration with the scientists from Bayreuth who developed the technics of single crystal diffraction on laser heated samples will certainly help to improve our chance of success.