ESRF	**Experiment title:** Determination of nitrogen's phase diagram up to 400 GPa	**Experiment number**: HC-5273
Beamline: ID27	**Date of experiment**: from: July 14th 2023 to: July 17th 2023	**Date of report**: 16.08.2023
Shifts: 9	**Local contact(s)**: Tomasz Poreba and Mohamed Mezouar	*Received at ESRF:*

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Report:

Objectives

This proposal's goals were to uncover nitrogen's phase diagram between 220 and 400 GPa, form novel polymeric phases through laser-heating and solve their structure with single-crystal X-ray diffraction (SC-XRD). These experiments provide a rare, but crucial, example of the behavior of simple homoatomic systems at ultrahigh pressures and challenge current theoretical models. It must be emphasized that given the targetted pressures and the need for laser-heating, the planned experiments were very ambitious, though realistic.

Results

To accomplish the objectives of this proposal, two toroidal diamond anvil cells (DAC), each with a culet size of 25x350 μm (DAC1), 25x350 μm (DAC2), as well as a DAC equipped with regular bevelled diamond anvils of 30x350 μm (DAC3), were carefully prepared. All were loaded with molecular nitrogen at high pressure (~1300 bars) in a gas loader, and a small aggregate of Au, used as a pressure calibrant and, if necessary, as a laser absorber. DAC1, DAC2 and DAC3 were precompressed to pressures of 210, 70 and 130 GPa. Unfortunately, the anvils of DAC1 broke moments before our departure to the ESRF. Moreover, the geometry of DAC2 was non-optimal, with a sample cavity of about 6 μm at 15 GPa. DAC3, however, appeared as a very promising sample with an experimental cavity of about 12 μm at 130 GPa (see Figure 1).

It must be noted that this beamtime was also the impetus for an ID27-led development: an on-axis and offline YAG laser-heating system. The system, designed by CEA and ESRF staff, was assembled before the beamtime. The system presents advantages over an off-axis online setup, *i.e.* a very straightforward and fast sample alignment procedure, an adjustable, smaller beam size (down to 1 micron) thanks to the use of Mitutoyo

objectives coupled with a variable beam expander, and the fact that it frees the beamline for X-ray measurements on other samples while another is being heated. Given its very new nature, the system does not yet allow for temperature measurements.

Upon arriving at the ID27 beamline, the CeO_2 and vanadinite calibrants were ran. After screening DAC2 and DAC3, a change of strategy was decided in order to maximize the beamtime's scientific output. Indeed, it was decided to laser-heat DAC3 at the pressure of 150 GPa to try to form either cg-N or bp-N, both synthesizable at this pressure.[1,2] The unit cell of the formed allotrope would then be followed upon its compression to about 250 GPa, giving first insight on its behavior at multimegabar pressures and potentially observing a phase transition into another polymeric solid. At 250 GPa, the sample was planned to be reheated in the hope to either form HLP-N[3] or a phase predicted from theoretical calculations.[4] Given the poor condition of the sample in DAC2, we decided against compressing it to higher pressures.

According to the above-described strategy, DAC3 was laser-heated at 150 GPa using the new offline setup, and a large single-crystal of cg-N formed. The DAC sample was successfully pressurized to 250 GPa in seven pressure steps and, as shown in Figure 1, the unit cell volume of cg-N was obtained up to that pressure. Besides the two last points, the unit cell volume of cg-N closely follows the volume previously predicted from density functional theory (DFT) calculations. It is worth noting this is the first time cg-N was compressed above the 160 GPa mark.[1]

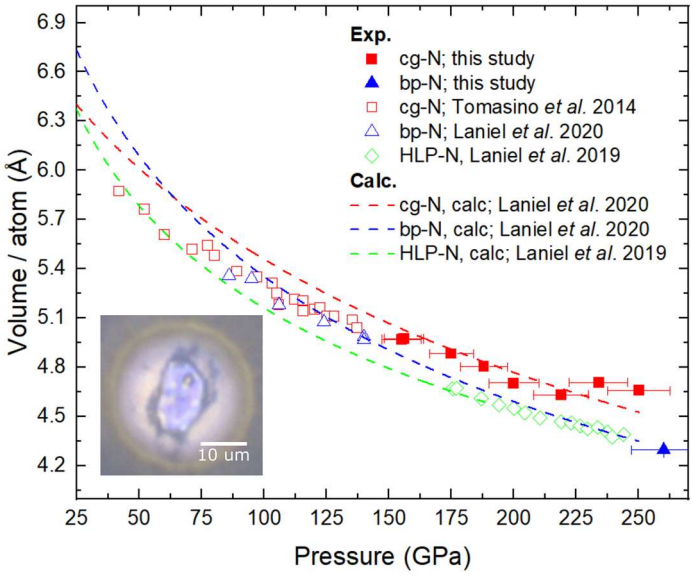

Figure 1: Evolution of the volume per atom of all three polynitrogen allotropes with respect to pressure. The points collected during these experiments are represented by filled red squares and a filled blue triangle. As as inset, in the bottom left, is a microphotograph of the sample in DAC3 at 80 GPa.

The sample was then laser-heated and the experimental chamber mapped by X-ray diffraction. Pressure was found to have increased to 260 GPa and previously unobserved diffraction lines that did not match those of cg-N were detected. Single-crystal data were collected on the most promising sample positions. Surprisingly, the obtained unit cell did not match that of the expected HLP-N phase, but rather that of bp-N. This is at odds with theoretical calculations,[4] which report bp-N to have the fourth lowest enthalpy value at that pressure, preceeded by LP-N, diamondoid N_{10} and HLP-N. This result also seemingly contrasts with our previous measurements, which had shown the formation of HLP-N at 244 GPa. This suggests either the re-entrant phase transition of bp-N, or that temperature plays an important role in determining which polymeric nitrogen is stabilized. While the latter seems more likely, it cannot be directly verified as we could not measure the temperature attained when laser-heating DAC3 with the offline setup. Figure 2 shows the phase diagram of nitrogen with the addition of the bp-N point at 260 GPa. After the synthesis of bp-N, DAC3 was further compressed to 267 GPa with to goal to reheat the sample at 275 GPa. Unfortunately, the diamond anvils broke before reaching that pressure value.

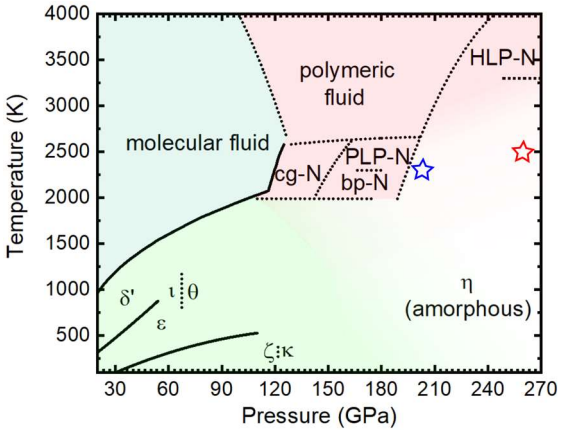

Figure 2: Known phase diagram of nitrogen before the experiments performed during HC-5273. The blue star represents the synthesis of bp-N near 200 GPa and above 2000 K, previously demonstrated during HC-4881. The second red star, positioned at 260 GPa and 2500 K, represents the datapoint obtained during this proposal. The latter datapoint extends the phase stability region of the bp-N phase from the previous known limit of 160 GPa to 260 GPa.

With this beamtime, we demonstrated our capability to reach multi-megabar pressures on pure nitrogen, successfully laser-heat tiny samples using a new on-axis YAG system and collect single-crystal X-ray diffraction on these polycrystalline samples. Importantly, we extended the pressure-volume data on cg-N up to 250 GPa, with the obtainted unit cell volume matching very well with theoretical calculcations. Moreover, the demonstrated formation of bp-N at 260 GPa—as opposed to the previously observed HLP-N—underlines the complexity of nitrogen's phase diagram, and suggests the produced phases to heavily depend on the reached temperature. We emphasize the very difficult nature of these experiments, and are confident that despite not having attainted the maximum desired pressures, we have the necessary expertise to lead these experiments to a success.

References

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