	Experiment title: Polymeric nitrogen polymorphism at multi-megabar pressures	Experiment number: HC-4084
Beamline: ID11	**Date of experiment**: from: 12.03.2021 to: 16.03.2021	**Date of report**: 04.09.2021
Shifts: 12	**Local contact(s)**: Eleanor Lawrence Bright and Carlotta Giacobbe	*Received at ESRF:*

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Report:

Objectives

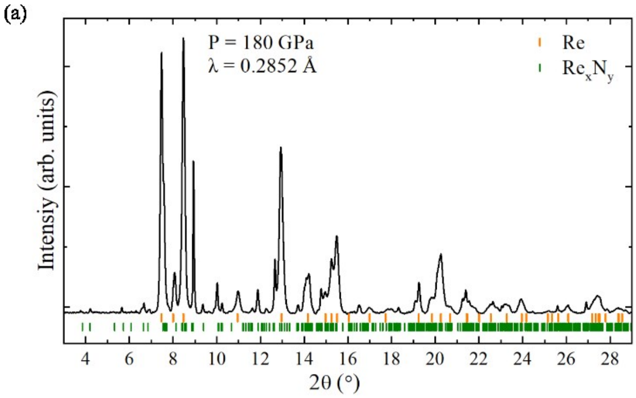
The aim of this proposal was to cross for the first time the 250 GPa pressure threshold on nitrogen and largely exceed that pressure, reaching up to 600 GPa. Novel polymeric nitrogen polymorphs were expected to be discovered and fully structurally solved by combining the tremendously powerful single-crystal X-ray diffraction of polycrystalline samples (SC-XRDp) approach with the intense and submicron beamsize of ID11.

Results

A grand total of four BX90 diamond anvil cells (DACs) were prepared, two equipped with 40 µm culets (40-DACs) and two with double-stage anvils (ds-DACs). All were loaded with molecular nitrogen. While the preparation of toroidal DACs was also attempted, these were not successful in reaching the desired pressures. Despite the technical difficulties related to readying ds-DACs, the two prepared reached unprecedented pressures of approximately 550 and 850 GPa while pressures of 180 and 185 GPa were attained with the 40-DACs. Because of the sanitary conditions, we could not travel to the ESRF and, therefore, the planned on-site laser-heating could not be done. As a result, all samples were thoroughly laser-heated to temperatures above 2000 K at our home laboratory in Bayreuth before being sent by postal mail to the ESRF. Laser-heating blindly—*i.e.* without immediate access to X-ray diffraction—changes the usual procedure where the samples are heated at progressively higher temperatures until new diffraction lines can be observed. While Raman spectroscopy measurements substituted X-ray diffraction for direct characterization after laser-heating, this method is not as reliable due to the much lower spatial resolution (~ 5 µm laser beam size vs ~ 0.5 µm at ID11), and poorer signal-to-noise ratio on account of the stressed diamonds. No new Raman modes could be observed before sending the DACs to the ESRF.

Remarkably, sample mapping by X-ray diffraction at ID11 revealed new diffraction lines in one 40-DAC as well as in the two ds-DACs (see Figure 1). Single-crystal X-ray diffraction data could be collected on all phases. While the analysis of these datasets is still ongoing, unit cells of two new phases have been unambiguously determined: one at 180 GPa in the 40-DAC and another one found in both ds-DACs. Based on the intensity of the diffraction lines and the preliminary assessment of the unit cells' content, it is strongly suspected that the novel solids are in fact rhenium nitrides. While the formation and characterization of any solid under these extreme conditions is in itself a great success, the formation of rhenium nitrides is hypothesized to be due to the combination of the very small sample sizes and the "blind" laser-heating procedure that was necessary on account of the sanitary situation. When heating, even though the detected thermoemission was undoubtedly observed to come from the nitrogen sample, it is likely that the tails of the tightly-focused YAG laser (~ 5 µm FWHM) sufficiently heated the rhenium to allow small quantities to diffuse throughout the sample chamber and react with nitrogen.

Nonetheless, the beamtime is deemed a resounding success. Indeed, it was demonstrated that we could compress nitrogen to unprecedented multi-megabar pressures and laser-heated. Moreover, the formation of new phases and the collection of good quality single-crystal data were also obtained, which will undoubtedly result in a high-impact publication. The opening of the ID27 beamline, allowing for both online YAG laser-heating and single-crystal X-ray diffraction with a submicron beam, provides us with the ideal setting to further pursue these experiments. Moreover, an even greater focus on the preparation of toroidal DACs—for example through a collaboration with scientists from the CEA (Paris, France), who developed them—should enable reaching pressures of up to 400 GPa on significantly larger sample volumes, thus drastically decreasing the risk of unintentionally heating the rhenium gasket. We strongly believe that these first experiments are extremely promising for the synthesis and complete characterization of novel nitrogen polymorphs and thus warrant further experiments to be performed.



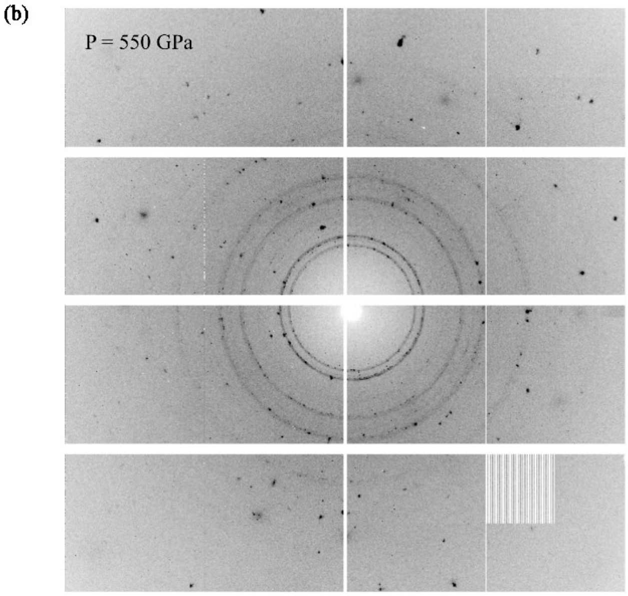


Figure 1: (a) Integrated X-ray diffraction pattern collected on a N_2 sample at 180 GPa. New diffraction lines belong to a previously unidentified phase. (b) X-ray diffraction pattern collected at about 550 GPa on a N_2 sample. Sharp and intense diffraction spots are clearly visible, and belong to an unknown phase.