ESRF	**Pressure Synthesis of Ultrahard Carbon Nitrides**	**Experiment number**: HC-5082
Beamline:	**Date of experiment**: from: November 18 2022 to: November 21 2022	**Date of report**: 29.01.2023
Shifts:	**Local contact(s)**: Tomasz Poreba and Mohamed Mezouar	*Received at ESRF:*

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Report:

Objectives

For these experiments, we proposed to employ the extremely powerful method of single-crystal Xray diffraction of a polycrystalline sample (SC-XRDp) to characterize the reaction products of a laser-heated carbon-nitrogen precursor, tetracyanoethylene (TCNE, C_6N_4), between 20 and 130 GPa. These experiments were expected to result in i) the synthesis of novel C_xN_y solids, ii) the determination of their crystal structure and iii) obtaining their equation of state and establishing if they are recoverable to atmospheric pressure. These experiments were previously impossible to do without the ESRF incredibly intense beam combined with the SC-XRDp technique and were hoped to finally provide answers regarding the feasibility of synthesizing ultrahard C_xN_y compounds.

Results

BX90-type diamond anvil cells with culets of 120 to 80 μm were prepared. TCNE was loaded along with molecular nitrogen, acting as a reagent as well as a pressure transmitting medium. Pressures were measured based on the equation of state of the Re gasket and verified using the Raman signal of diamond and nitrogen.[1,2] The samples were precompressed to pressures between 60 and 140 GPa and laser-heated to temperatures above 2000 K at our laboratory in Bayreuth. These samples were brought to ID27 for single-crystal X-ray diffraction measurements of the synthesized phases.

The experiments were a huge success. A new phase was synthesized as well as solved and refined using the obtained single-crystal data. An unwarp of the data collected at the pressure of synthesis of shown in Figure 1. The phase was decompressed in seven steps from its pressure of synthesis down to ambient conditions. At each pressure, data were collected allowed for a full structure refinement. Most impressively, the phase was found fully recoverable down to ambient conditions, as demonstrated by single-crystal data. As such, a full

equation of state was obtained is and very well constrained both due to the number of datapoints as well as having its volume at 1 bar. Remarkably, the obtained phase has a compressibility a bit lower, but not too far, from that of diamond.

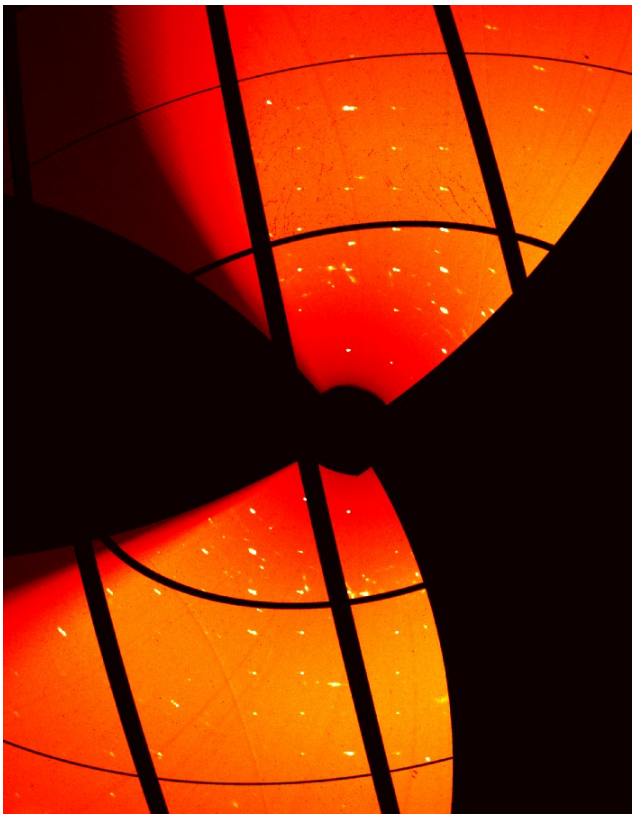

Figure 1: Reciprocal space unwarp of the newly synthesized C-N compound.

We must note that there are small issues related to the data conversion from h5 files to esperanto files (i.e. the files used for single-crystal data analysis). As uncovered after discussing with the ID27 staff, the mask automatically generated to block bad pixels and empty regions of the detector is not up-to-date following corrections that were made. This results in some reflections having an incorrect intensity. The very helpful ID27 staff said they would fix this issue as soon as possible—and have even taken initial steps for this to be addressed by the support IT group.

With the synthesis of this phase, and its recoverability to ambient conditions our objectives were accomplished. However, further investigation of the C-N phase diagram, for example employing different precursors, is of great relevance to try and produce other novel C-N phases with different stoichiometry than the one here obtained. Unexpectedly, this system appears to have a rich chemistry and the potentially available phases having great application prospects.

References

1. Anzellini, S., Dewaele, A., Occelli, F., Loubeyre, P. & Mezouar, M. Equation of state of rhenium and application for ultra high pressure calibration. *J. Appl. Phys.* **115**, 043511 (2014).
2. Akahama, Y. & Kawamura, H. Pressure calibration of diamond anvil Raman gauge to 410 GPa. *J. Phys. Conf. Ser.* **215**, 012195 (2010).