	Experiment title: High Pressure Synthesis of Conductive Hydrocarbon-Derived Carbon Nanothreads	**Experiment number**: CH-6138
Beamline: ID06-LVP	**Date of experiment**: from: 24-Nov-2021 to: 28-Nov-2021	**Date of report**: 14-Dic-2021
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Report:

Carbon nanothreads are novel 1D nanomaterials synthesized by compression of aromatic compounds, whose mechanical properties are very similar to those of diamond (stiffness, strength) combined with an extraordinary flexibility [1-9]. Providing also electrical conductivity is one important missing tile. The main purpose of this proposal was to synthesize low bandgap semiconductive C nanothreads from diphenylacetylene (DPhA), at 30 GPa and room T, using large volume high pressure assemblies, in order to easily access in situ electrical conductivity measurements and to provide large samples available for standard ex-situ characterization methods of physiochemical properties: NMR, optical spectroscopy, etc.

We performed 3 distinct high pressure runs (samples):

i) run1 and run2 (6 shifts in total). These runs were performed by using the Drickamer type high pressure assembly, based on two opposite truncated anvils with 3 mm culet diameter. The sample (pure DPhA powder) diameter and thickness were equal to 0.8 mm and 0.5 mm, respectively. The coaxial configuration of the gasket/sample materials was, from outside to inside: pyrophyllite, diamond epoxy, MgO (pressure sensor), and sample. This set-up provided uniaxial stress, which facilitates the synthesis of the nanothreads along the stress axis. The P-T path was 0-16-0 GPa for

run1 (too low to observe polymerization of DPhA) and 0-33-0 GPa for run2, at room T. The XRD data were collected continuously, at azimuth ~56º for true pressure readings and with 1-2 GPa pressure steps for estimation of stress via full 2D collections. Incident and collected, diffracted X-rays went through the gasket made of materials that gave reasonably low background signal. We attempted electrical resistance measurements using a high sensitivity ohmmeter: Keithley 6430, for continuous in situ resistance acquisitions along the compression runs. The electrical wires were connected at the bases of the two anvils. The ohmmeter can measure resistance (R) values up to 20 TeraOhm, and our samples were indeed expected to exhibit R values within this range, before compression. On the other hand, we expected a drop of the resistance by several orders of magnitude along the high pressure polymerization. Unfortunately, parasitic electric currents flowing around the sample environment entirely dominated measurements of the true sample resistance. Anyway, through XRD, we observed a phase transition of the sample to a new, dense molecular phase at around 8-9 GPa, already found with diamond anvil cells (DACs). The new phase seems to have a very important role for the polymerization process in DACs, where indeed polymerization has been observed to start from this very phase, above 15-16 GPa. Run2 also achieved the polymerization of DPhA ending up in a dark brown, hence low bandgap recovered sample.

ii) Run3 (6 shifts). This run was performed by using the "standard" 6/8 HP assembly with hard cubes having 3 mm truncations and enclosing a 7 mm octahedrally shaped sample region. The sample chamber, inside the Cr:MgO octahedron, was a hBN (pressure sensor) cylindrical cavity with 2.2 mm outer diameter, 1.4 mm internal diameter and 2.0 mm length, filled entirely with the pre-compressed DPhA powder sample. At variance with the DAC and the Drickamer type LVP set-ups, this set-up provided substantially isotropic compression, which led us to the extremely interesting opportunity of investigating the effect of the intrinsic anisotropy of the starting molecular phase on the formation of carbon nano-threads, as opposed to the extrinsic, uniaxial stress related anisotropy typical of the two opposed anvils systems. The P-T path was 0-29-0 GPa, at room T, and the sample has been compressed with continuous XRD data collection in order to characterize the degree of conversion. We also attempted in situ electrical resistance measurements using the Keithley 6430, similarly to run1 and run2, and here too measurements were entirely dominated by parasitic currents, which prevented us to observe the true sample resistance. Then, at variance with what we found with DACs and Drickamer type apparatuses, we did not observe the phase transition at around 8-9 GPa (figure 1). In fact, the observed Bragg angles continuously and monotonically increase vs. pressure. Nevertheless, we achieved the polymerization of DPhA and recovered a dark brown sample, similarly to DACs (figure 2), although the present sample looks denser (Bragg peaks at higher Qs). This is a very important results, which highlights that, at least for DPhA, the intrinsic anisotropy of the starting monomeric crystal is the main driving force for the formation of the C-nanothreads. Also important, while the recovered nano-thread form is similar to those found in DACs, the starting monomeric phase seems to differ, since we did not observe the monomer-monomer high pressure phase transition at 8-9 GPa. The nanothreads being always the high pressure synthesis product, whatever the starting monomeric phase and the compression methods (either isotropic or anisotropic) are, suggests that these nano-structured materials are "nearly" thermodynamically stable at their HP synthesis conditions. The adjective "nearly" is here used since nano-threads are not entirely ordered as a solid thermodynamic phase should be. We can then infer that a fully ordered version of DPhA derived C nano-threads should exist. Based on a structural description which we obtained from measurements in DACs [10], we can also say here that the present extended structure of high pressure reacted DPhA is mainly made of double-core, hydrogenated C-nanothreads, with C in sp^3 hybridization, where the two cores are linked by a conjugated sp^2 C, polyacetylene-like backbone. Therefore, the materials is a C nanothread form with also delocalized electronic charge, that is to say an organic semiconductor. Indeed, our optical spectroscopy measurements for these materials report a low bandgap energy of about 1.7 eV. Importantly, the sample volume for run3 is ~ 4.4 mm^3. This large amount of sample will make post-synthesis standard characterization measurements (ex. XPS, NMR, among others etc.) possible. Indeed, we are currently planning NMR measurements.

The detailed data analysis on the whole set of XRD patterns for runs 1-3 (several thousands) is now in progress.

References

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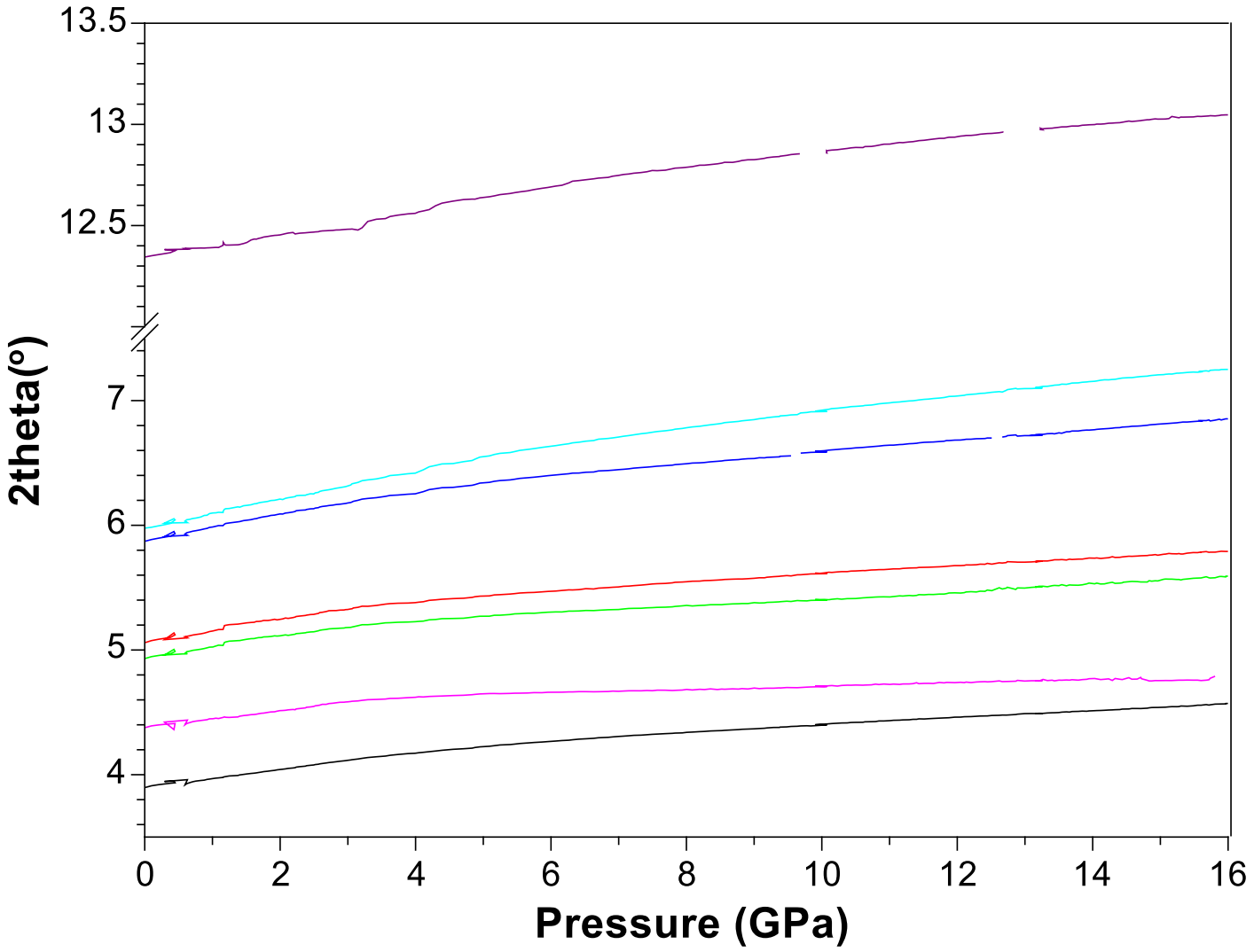

Figure 1. *Pressure shift for some of the most intense Bragg angles of DPhA, compressed in the "standard" 6/8 HP assembly with hard cubes having 3 mm truncations and enclosing a 7 mm octahedrally shaped sample region. X-ray wavelength: 0.389887 Å.*

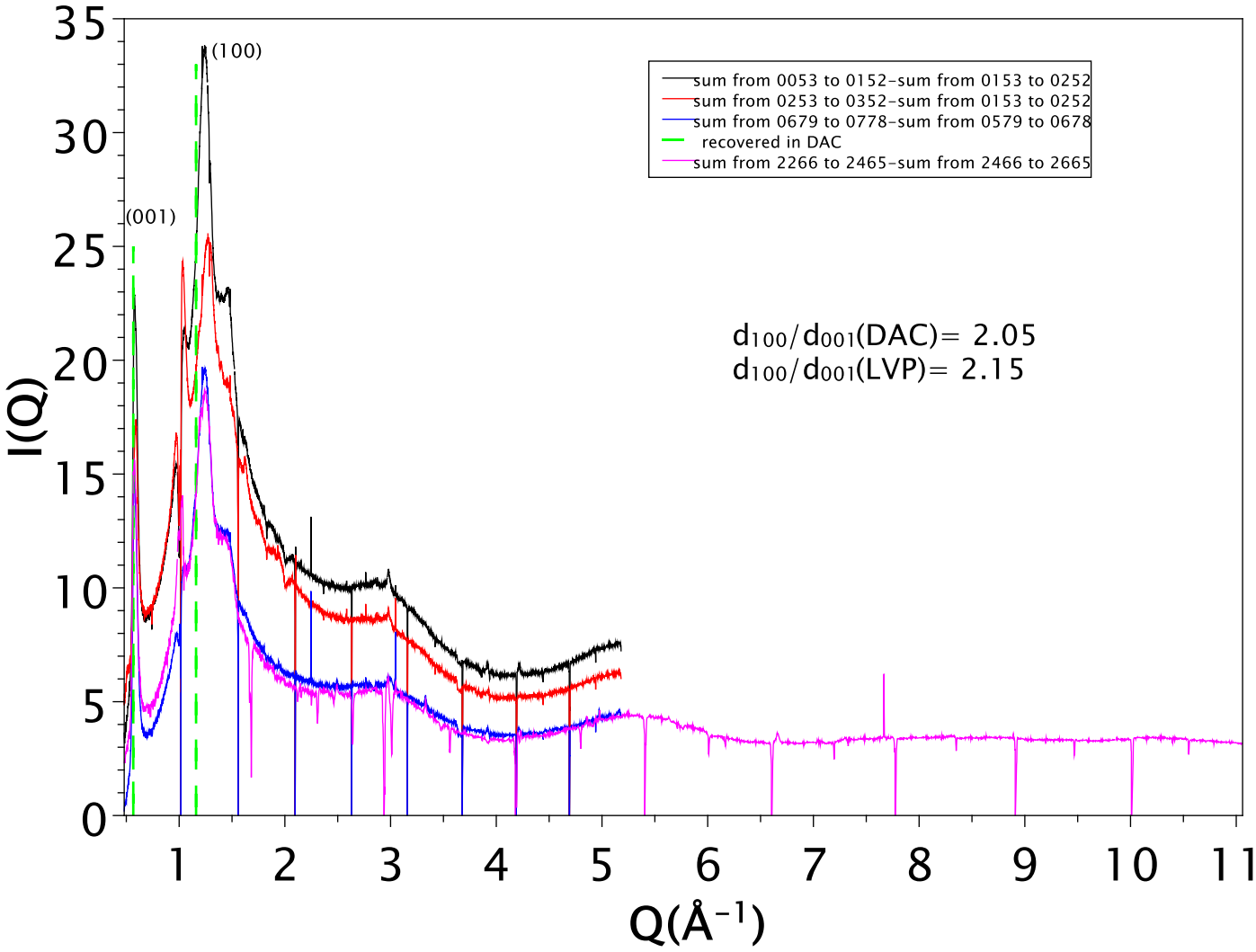

Figure 2. *XRD patterns of recovered samples after run3. The smooth Compton background from air has been subtracted. Black, red and blue (magenta): patterns measured at different points with incident energy of 32 KeV (53 KeV). Green, dashed lines: Q positions for samples synthesized in DACs. Peaks at 1.0 and 1.49 Å^{-1} are from the sample holder (tape). Negative peaks: gaps of the 2D detector.*