



	Experiment title: HP-HT transformation of alkaline graphite intercalated compounds	Experiment number: HS2995
Beamline: ID27	Date of experiment: from: 17/05/2006 to: 23/05/06	Date of report: 07/09/06
Shifts: 12	Local contact(s): Nicolas Guignot	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

- *Denis Machon
- *Sylvie Le Floch
- *Pierre Toulemonde
- *Alfonso San Miguel
- *Nicolas Rey

Report:

The goal of this study was to investigate the phase diagram of alkaline graphite intercalated compounds "GICs" (CsC_8 and LiC_6) at high pressures and high temperatures and to probe the size effect of the intercalates on the host structure, *i.e.* graphite. We have made 4 HP-HT cycles (2 per sample) in a diamond anvil cell (Le Toullec DAC) provided by the ESRF high pressure lab using the double sided laser heating facility available on the ID27 beamline.

- CsC₈ at HP-HT:

- a) CsC₈ at high pressure:

X-ray diffraction patterns have been collected up to 12 GPa in the DAC. This pressure was limited by the systematic opening of the rhenium or the stainless steel gaskets. For each cycle, fine grain of sample was "sandwiched" between two NaCl flakes in the hole of the gasket in order to keep thermal isolation and to avoid any contact with the diamonds of the cell. From the experimental point of view, the major inconvenient of layered compounds such GICs or graphite is their strong anisotropy. Indeed, it is well-known that pressure induces preferential orientation along the axis of compression, leading to the alignment of the compression axis with the c-axis. Since the high pressure set-up on ID27 is in the axial configuration where the beam goes through the diamonds, *i.e.* along the compression axis, we are supposed to collect weak (001) planes and strong (hk0) planes. X-ray patterns up to 12 GPa are

presented in Fig.1. Starting pressure is quite elevated due to the small size of the diamonds' culet. Indeed, each loading of the sample was done in the glove box of the chemistry lab at the ESRF and the cell was immediately pressurized outside to prevent any contamination of the highly reactive samples. High pressure patterns of the samples were not successfully indexed related to their strong preferential orientation effects as we can see and also because we supposed that a transition might occur at low pressures (Fig.2). Figure 3 shows evolution of the d-spacing attributed to the sample with the pressure in comparison with graphite. Most of these points seem to follow the “a” lattice parameter of graphite (opened symbols), indicating that they might correspond to the basal plane, while filled symbols show a linear compressibility smaller than the compressibility of the graphite c-axis. A striking change for a couple of data (filled lozenge and circles) happens between 6-8 GPa with a behaviour very close of the graphite c-axis. This transition has already been seen in our recent XANES experiment at the Cs L-edges, involving its electronic character which tends to localize Cs atoms. These results are confirmed with our recent Raman study.

b) CsC₈ at high pressure and high temperature:

The double-sided Laser heating technique (YAG Laser) was performed. Inhomogeneous sample due to extremely difficult glove box loading of the DAC made the acquisition of data during the Laser heating treatment “LHT” harder (strong flashes). Several areas of the sample were annealed and then we mapped it. A new phase has been obtained at 12 GPa/1500K which structure analysis is currently in progress. This phase remains up to 19.7 GPa with peaks attributed to the starting material. LHT at 1800 K provided a partially transformation to cubic-diamond while the new structure is unchanged. These two HP-HT phases remain when pressure is released to 3.1 GPa.

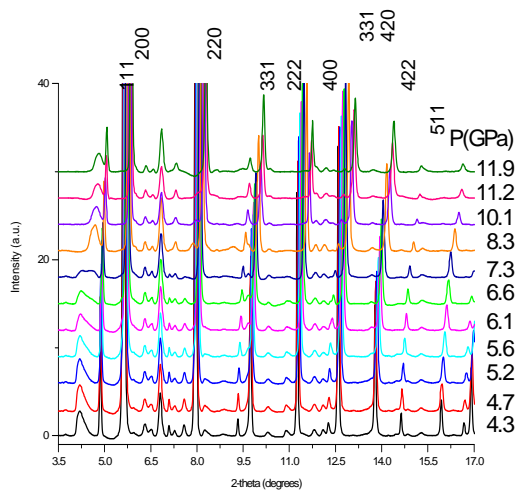


Figure 1 XRD patterns of CsC₈ from 4.3 to 11.9 GPa. Indexed peaks correspond to NaCl. A transition occurs between 6.6 and 8.3 GPa.

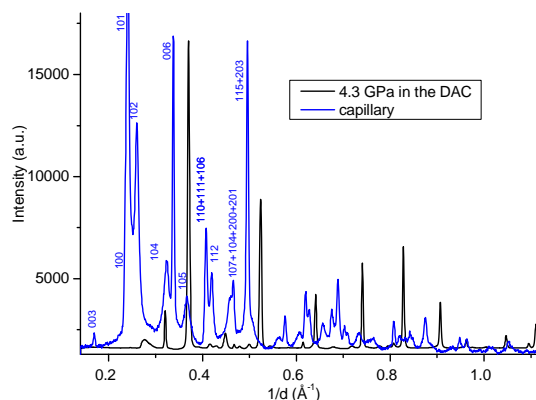


Figure 2 Comparison of CsC₈ XRD patterns between ambient (capillary) where peaks can be indexed and the first high pressure point in the DAC.

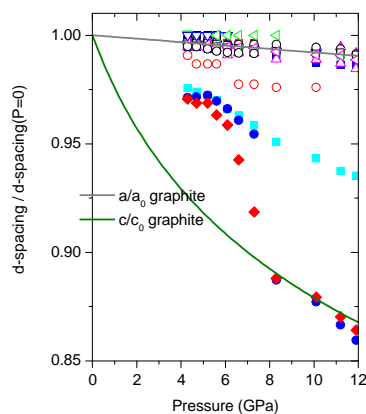


Figure 3 Evolution of the relative d-spacing of eight peaks attributed to the sample (dashed points) compared to a/a₀ and c/c₀ ratio for the graphite (lines). Ambient d-spacing (P=0) was extrapolated with linear fit from each data set.

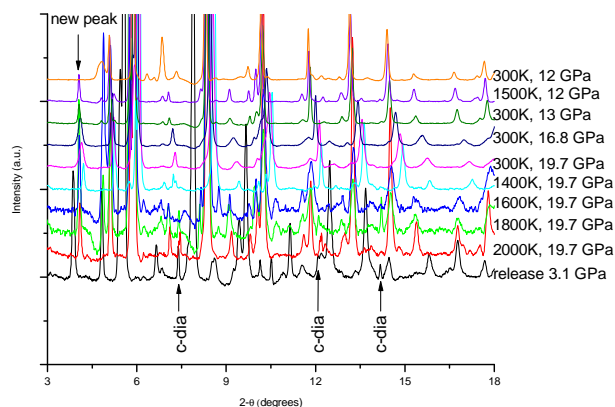


Figure 4 New peaks appear at 12 GPa/1500 K. At 19.7 GPa and 1800 K, formation of c-diamond. The HP-HT phases remain until 3.1 GPa (release).

- LiC₆ at HP-HT:

- a) LiC₆ at high pressure:

In fact the starting material was not pure and contained residues of LiC₁₂, indicating that the intercalation process during the synthesis was not complete. We have studied this compound in the pressure range 3-17 GPa for reasons given previously. Difficulties to identify precisely the peaks impeded to plot the lattice parameters, instead d-spacing are shown in Fig.5. No drastic changes were found excepted a change in the slope starts at 8 GPa (opened squares). Besides, weakening of some peaks was found above 7 GPa.

- b) LiC₆ at HP-HT:

LHT on this compound at nearly 10 GPa led to the synthesis of c-diamond. This transformation was not complete and some residual peaks remained. The c-diamond phase is still present when pressure is released to 1.2 GPa (Fig.5). Poor intensity of the c-diamond peaks made harder to determine the corresponding d_{hkl}.

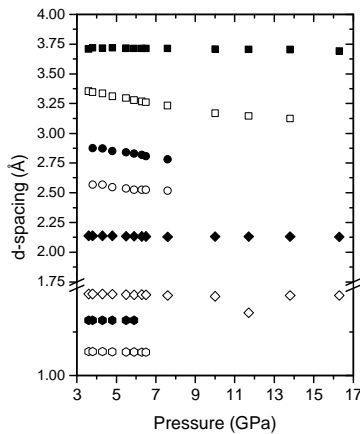


Figure 5 High pressure evolution of the d-spacing of LiC₆/LiC₁₂.

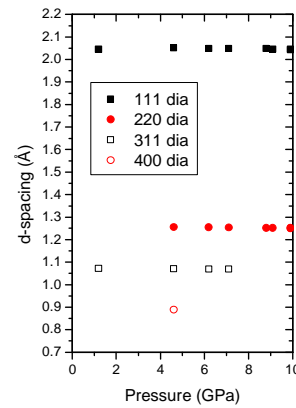


Figure 6 c-diamond d-spacing released from 9.9 to 1.9 GPa. Weak intensity of the 400 peak did not allow to determine its position.

- Preliminary conclusions:

Both CsC₈ and LiC₆ have driven to the synthesis of c-diamond under HP-HT conditions. More precisely, in the case of cesium intercalated graphite these conditions 19.7 GPa/1800 K (+/- 1 GPa and +/- 100 K) are higher than those of lithium intercalated graphite 9.9 GPa/1600K. Heavier size of Cs atoms seems to delay the bridging of the graphite layers, thus making harder to move carbon atoms in order to rearrange in the c-diamond structure. No traces of hexagonal-diamond were found which frequently appear during the HP-HT synthesis of c-diamond. Lattice parameters of the c-diamond synthesized indicate that any alkali atoms either are trapped inside. We foresee to study these recovered samples so that we could determine where the guest atoms have moved. Also, we could not determine (00l) peaks in these layered compounds with the axial configuration because pressure induces preferential orientations. An alternative way is to use a radial configuration, which makes the object of our next accepted proposal. We also point out the lack of information between ambient and 3 GPa for the two compounds.