



	<b>Experiment title:</b> High pressure behaviour of the graphitic form of C <sub>3</sub> N <sub>4</sub> : a challenge to new superhard materials	<b>Experiment number:</b> HS 491
<b>Beamline:</b> <b>ID 09</b>	<b>Date of experiment:</b> from: 22 April 98                      to: 23 April 98	<b>Date of report:</b> 20 August 98
shifts: 6	<b>Local contact(s):</b> Dr; Michael Hanfland	<i>Received at ESRF:</i> <b>2 4 AOUT 1998</b>

Names **and affiliations of applicants** (\* indicates experimentalists):

Prof. Gerard Demazeau, Institut de Chimie la **Matière Condensée** de Bordeaux (ICMCB), UPR-CNRS 9048,87 Avenue du Docteur Albert Schweitzer, 33608 **Pessac Cedex**, France  
Miss Isabelle Alves, PhD student (experimentalist), same address,  
Dr. Christian Cros (experimentalist), same address,  
Dr Alain Largeteau (experimentalist), same address,  
Dr. **Hervé** Montigaud, same address,  
Prof. Bernard Tanguy, same address

---

## Report:

The pressure evolution of the crystal structure of the graphitic form of C<sub>3</sub>N<sub>4</sub> has been studied at room temperature in a diamond anvil cell, in order to try to obtain one or several of the possible high pressure forms of this material, which is (are) expected to exhibit a value of the bulk modulus comparable to that of diamond.

Given the composition of the material, and to avoid any loss of nitrogen, a first sample of C<sub>3</sub>N<sub>4</sub> was loaded with nitrogen as pressure transmitting medium, which ensures hydrostatic conditions in the studied pressure range. The pressure was increased from 6 GPa up to 32.4 GPa, and then decreased to atmospheric pressure in steps of about 2 GPa. Due to the graphite like structure of the material and the conditions of its synthesis from organic precursors, the observed X-ray diffraction patterns consisted of mainly the characteristic (002) line and a few very weak ones, difficult to observe and superimposed with those of solid nitrogen. On increasing pressure, an important shift of the (002) line was observed, but no extra lines appeared in the patterns up to 32.4 GPa, except those of solid nitrogen. On decreasing pressure, only the reversible shift of the (002) line position was observed.

In order to avoid the presence of the intense lines of nitrogen which screen most of the time the weak lines of C<sub>3</sub>N<sub>4</sub>, a second sample was loaded with silicone oil as pressure transmitting medium in a nother cell with a larger gasket hole. The pressure was in that case increased

from 1 atm. to 14.7 GPa. This second series of experiments enabled us to detect more clearly the few extra weak peaks attributable to graphitic  $C_3N_4$ , and from the position of these lines and their relative intensity, a new structural model based on a different distribution of the carbon vacancies in the graphitic form of this material has been determined. A complementary study by high resolution transmission electronic microscopy is in progress.

A third sample, also prepared by decomposition of melamine ( $C_3N_6H_6$ ), but in slightly modified experimental conditions (addition of another solvent), was studied in the same cell as in the first series of experiments and with silicone oil as pressure transmitting medium. The aim of this study was to test the influence of this other solvent on the final structure and crystallinity of the resulting  $C_3N_4$ . No detectable difference with the second series of experiments was observed.

All these experiments, carried out at room temperature, have clearly established that pressure by itself is not enough to induce the conversion from the graphitic form of  $C_3N_4$  into one of its possible high pressure 3-D forms, except maybe at much higher pressure. It seems necessary, therefore, to combine the effect of high pressure and high temperature to obtain the expected results.