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Report:

A great deal of theoretical and experimental activity has been directed toward the possibility of developing new carbon nitride materials with a hardness that may rival or even exceed that of diamond. Several hypothetical high density high compressibility carbon nitrides with stoichiometry C_3N_4 have been at the focus of this search for superhard materials : a β-C_3N_4 phase isostructural to β-Si_3N_4, an α-form of C_3N_4 isostructural to α-Si_3N_4, model structures with a cubic I-43d symmetry and a pseudocubic defective zinc blende symmetry. All of these dense forms are based on 4,3 networks where the carbon atoms are in tetrahedral coordination with nitrogen and nitrogen atoms in trigonal coordination with carbon. While many authors tend to elaborate these dense forms via direct solvothermal synthesis (some of them succeeded to evidence α and β phases), we have chosen to work in analogy with the high-pressure synthesis of diamond from graphite : a carbon nitride graphitic phase could then be an ideal precursor for the formation of bulk three dimensional carbon nitrides through high pressure treatment. At the present time literture reports several graphitic carbon nitride phases obtained through solvothermal processes either with hexagonal or orthorhombic unit cell, samples being systematically hydrogenated. Moreover no experimental evidence for the 2D to 3D C_3N_4 transition is at present reported.

Our strategy was first based on the elaboration of reactive graphitic carbon nitrides in order to favor the 2D to 3D C_3N_4 structural transition. In this sense, we have performed the synthesis in highly soft conditions of a poorly cristallized hydrogenated carbon-defective graphitic material which chemical composition is $C_6N_9H_3$. The local structure is strongly related to the hexagonal graphitic C_3N_4 expected structure : 1,3,5 substituted aromatic C_3N_3 rings are linked one to another with sp^3 nitrogen atom, the non stoichiometry being accommodated by an ordered arrangement of C_3N_3 voids and protonation of nitrogen atoms in the graphene sheets.

This material has then been submitted to high pressure – high temperature treatment (diamond anvil cell, laser heating, synchrotron radiation) in order to evidence phase transitions. We have then observed the progressive amorphization of this layered material under pressure, the whole removal of the graphitic peak being effective above 35 GPa. When the graphitic carbon nitride is submitted to high pressure and high temperature, it decomposes into diamond and nitrogen (20 GPa, 1500 K). Other layered precursors have been tested : they have been obtained by soft solvothermal treatment of graphitic $C_6N_9H_3$ which mainly induce a modulation of the chemical composition (hydrogen content). No significant change has been observed. These experiments have allowed us to evaluate the stability under pressure and temperature of the starting layered carbon nitride. We assume that this behaviour can be due either to poor starting cristallization state or to the non-stoichiometry of the material which is too far from chemical composition of the expected superhard 3D- C_3N_4.

When studying the behaviour of the 2D carbon nitride with synchrotron radiation, we have evidenced another phase, embedded into the graphitic matrix and which is present in the starting material. This cubic phase is highly stable under pressure (no structural transition has been evidenced during compression until 60 GPa) and still remains after decompression. On the basis of the Birch-Murnaghan equation, the bulk modulus of this phase was estimated at 390 +/- 20 GPa which is slightly higher to that of cubic boron nitride, second hardest material after diamond (Fig. 1). Combined Auger, XPS and microprobe analysis have evidenced that this material only contains carbon and nitrogen both in significant amount (the crystallographic data and chemical characterization allow us to affirm that this phase can not be considered as nitrogen-doped diamond). Further characterizations (mainly structural and mechanical) are at the moment in progress. This result is really important at the international scale because a new carbon nitride which can be expected harder than cubic boron nitride has been evidenced. These results will be submitted for publication before may 2006.

In near future, we are willing to understand the criteria which favor the high pressure-high temperature 2D 3D phase transition. In this sense, we should evaluate the influence of hydrogen content, C/N molar ratio and cristallinity of the graphitic starting material.
Moreover it will be of significant interest to determine the pressure and temperature stability of the three-dimensional phase evidenced during HS2772 experiment.

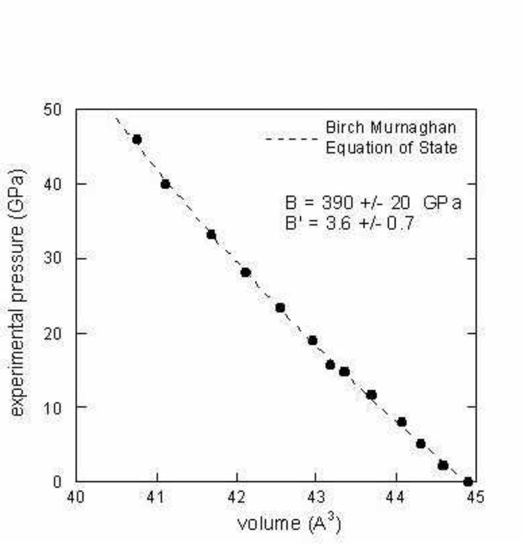

Figure 1- Birch-Murnaghan Equation of State of the novel dense carbon nitride