



Evidence for a low-compressibility carbon nitride polymorph elaborated at ambient pressure and mild temperature

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ABSTRACT

Superhard materials like diamond are essential for abrasive or cutting tool applications. In this way, carbon nitrides are of relevant interest because they are expected to exhibit exceptional mechanical properties, high values of bulk modulus being predicted. A smart and simple method was used to synthesize carbon nitrides and allowed elaborating a low-compressibility polymorph. The processing consists in the decomposition of commercial thiosemicarbazide ($\text{H}_2\text{NC}(\text{S})\text{N}_2\text{H}_3$) powder at ambient pressure and 600 °C under nitrogen flow. Besides the presence of a graphitic C_3N_4 phase, a nanocrystalline material is obtained and is identified as a cubic carbon nitride with a cell parameter of 3.163 Å. Its impressive bulk modulus of 355 GPa propels it as a challenger for cubic boron nitride among low-compressibility materials. Thus, we prove that, in accordance with previous numerous theoretical predictions, crystalline carbon nitrides exhibit exceptional compressibility behaviour. Moreover, our synthesis strategy evidences that, despite usual admitted considerations, severe and expensive pressure and temperature conditions are not mandatory to elaborate low-compressibility covalent materials, which could give new insights for their development.

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1. Introduction

Considering that the nature of the bonding and arrangement of atoms in a solid determine its mechanical properties, dense covalent materials are expected to exhibit the highest superhardnesses, especially those consisting of elements from the B–C–N triangle. Then, because it is the hardest material of all known solids, diamond appears fascinating and is currently used for cutting, drilling, grinding, or polishing tools in industry [1]. Cubic boron nitride (c-BN) ranks second among superhard materials and is widely used as abrasive [2]. Recently, BC_2N heterodiamond was synthesized and found to exhibit an unusual combination of mechanical parameters as its bulk modulus is lower than that of c-BN while its Vickers hardness ranks second only after that of diamond [3]. Since 1989, the C–N binary system also aroused deep interest because exceptional mechanical properties were theoretically predicted for three-dimensional (3D) C_3N_4 by Liu and Cohen [4]. Consequently many efforts were devoted to the experimental and theoretical studies of highly incompressible carbon nitrides (CN_x). *Ab initio* calculations first proposed several crystal-

lographic networks (either hexagonal or cubic) for dense CN_x with C_3N_4 composition where carbon and nitrogen are in tetrahedral (C sp^3) and trigonal (N sp^2 or sp^3) coordinations, respectively [4–8]. According to calculations, bulk moduli B of 3D C_3N_4 polymorphs are expected to reach and even exceed (when nitrogen adopts sp^3 hybridization) diamond value. Further calculations also suggested that the 3 to 4 stoichiometric C/N ratio (C_3N_4) may not be necessary to obtain very low compressibility in these 3D networks [9–12]. For example, dense carbon nitrides with CN composition where C and N both adopt sp^2 hybridization could exhibit bulk moduli in the range 345–375 GPa [9]. These values are comparable with those predicted for their pure carbon homologues similar in structure, while higher than for the BN ones where bond is less covalent. Then, because C–N distance is particularly short and C–N chemical bond is strongly covalent, 3D carbon nitrides are expected to exhibit superhardness properties.

For this reason, many attempts were carried out to synthesize these materials [13,14]. Because, until now, the most superhard materials such as diamond, c-BN or even BC_2N require severe pressure and temperature conditions to be elaborated, high-pressure high-temperature processes were widely used in the case of carbon nitrides. Many other techniques including solvothermal reactions, mechanosynthesis, use of shockwaves, thermal decomposition of triazines, thin films elaboration were also performed for crystalline CN_x synthesis attempts [13,14]. Experimental evidences for hexagonal

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structures of C_3N_4 (most of the results concerning crystalline carbon nitride nanoclusters embedded in amorphous matrix) as well as other unpredicted 3D structures with unknown compositions were reported. These works underlined the great difficulty to retain nitrogen in the material, to obtain crystallized carbon nitrides and to stabilize 3D networks [13].

Nevertheless, despite some dense CN_x have been claimed (mainly with β - C_3N_4 structure or unidentified networks [13,15]), their compressibility features and bulk modulus have not been established until now. Recently, a bulk modulus of 277 GPa was measured in a carbon nitride imide $C_2N_2(NH)$ elaborated under severe conditions [16]. Although high, this value was suspected to be lower than those predicted for dense C_3N_4 polymorphs because of the presence of N–H groups that do not contribute to the solid-state network. So the high mechanical performances of carbon nitrides remain an opened and fascinating question.

We report here the elaboration and discovery of an unpredicted low-compressibility carbon nitride. It has been synthesized in very soft experimental conditions (ambient pressure and mild temperature) far from those usually required for low-compressibility covalent materials. Moreover, its high incompressibility propels it as a direct rival for cubic boron nitride.

2. Experimental section

In the typical procedure, 2 g of thiosemicarbazide ($H_2NC(S)N_2H_3$, Aldrich, 99%) were placed in a Pyrex boat, this manipulation being performed in a glove-box with flowing nitrogen gas because the organic reagent is hygroscopic. The tube was maintained during any transport under N_2 atmosphere and was introduced in a tubular furnace under nitrogen flow. Temperature was slowly increased (1 °C/min) up to several consecutive intermediate 1 h steps at 180, 250, 350 and 480 °C and then finally maintained at 600 °C during 10 h. Then the sample was cooled down to room temperature under nitrogen flow (1 °C/min). The measured mass loss was about 68%.

The as-obtained powder was dispersed in alcohol by ultrasonication and a drop of the suspension was deposited on a copper grid covered with a carbon film or on an aluminium pin for TEM or SEM experiments, respectively. The preparation was finally air-dried. It should be noticed that the use of a carbon membrane was necessary to retain the nanoparticles on the copper grid.

High resolution transmission electron microscopy (HRTEM) and energy filtered transmission electron microscopy (EFTEM) observations were performed using a field emission gun JEOL 2200 FS operating at 200 kV, equipped with an in-column filter (Omega Filter). The spatial resolution is 0.23 nm. High resolution images were acquired with a Gatan Ultrascan CCD 2 k × 2 k. Digital Diffractograms were calculated using the Gatan Digital Micrograph program. The EFTEM maps were obtained by the three window method on the K edge (401 eV) of Nitrogen.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDXS) experiments were performed on a JEOL 840A and a JEOL 6700 S (field emission gun) operating both at 10 kV, and with energy resolutions of 136 eV (Mn) and 131 eV (Mn), respectively.

Bulk elemental combustion analysis of C, H, N, O, S elements was performed on a Thermofisher Flash EA 112 analyzer.

Powder X-ray diffraction (XRD) experiments were performed at 1 bar and at high pressure at the ID27 beamline at ESRF. A gas-driven membrane diamond anvil cell (DAC) was used for the in-situ measurements from atmospheric pressure up to 40 GPa. For compressibility measurements, the sample was loaded between two NaCl pellets in a cavity drilled in a rhenium gasket. NaCl acted as both pressure transmitting medium and pressure calibrant. To measure pressure into the DAC, we used the equations of state (EOS) of the NaCl B1 [17] or B2 [18] forms above or below ~30 GPa. To validate this pressure scale, pure diamond grains (0.3 μ m grain size) were inserted

simultaneously with c - CN_x and NaCl into the DAC in order to determine diamond's EOS and compare it with currently admitted values [1,19]. This simultaneous determination of diamond's EOS also allowed a quantitative comparison with our superhard carbon nitride phase. Some samples were laser-heated at high pressure in the DAC using a YAG infrared laser [20,21]. For experiments at atmospheric pressure, the DAC was opened to allow collecting some of the high-angle diffraction peaks, the sample being simply placed into the cavity drilled in the rhenium gasket. Angle dispersive ($\lambda=0.3738$ Å) diffraction images were captured on a Mar345 plate detector and integrated using the FIT2D software [22]. The whole pattern profile analysis of the powder diffraction data was performed using the Fullprof program [23].

3. Results and discussion

To prevent nitrogen departure during carbon nitride elaboration, we performed the synthesis at moderate temperature using precursors of high reactivity, the thermal decomposition of an organic reagent (thiosemicarbazide) being chosen as the synthesis route. After thermal treatment completed, chemical analysis by elemental combustion of the as-obtained orange powder leads to 35 wt.% carbon, 56.8 wt.% nitrogen, 1.9 wt.% hydrogen and 6.3 wt.% oxygen. No sulfur is present in the obtained material (thermal analysis coupled with mass spectrometry has evidenced that its departure from the chemical system during decomposition is mainly due to the formation of H_2S [26]), sulfur can then be totally excluded as a potential contaminant.

The structural characterization of the synthesized material under synchrotron radiation allows to observe two types of XRD patterns when probing different sample portions. The first one mainly consists of a broad reflection at 3.24 Å characteristic of a highly hydrogenated graphitic carbon nitride that we previously characterized combining EELS [25], XRD, IR, TGA-MS, XPS and NMR analysis [26]. In this graphitic material, we evidenced the presence of water molecules either adsorbed on the surface or trapped into the voids of the graphene planes, which fully explains a part of hydrogen amount and the presence of oxygen (which is not bonded neither to carbon nor to nitrogen) in the system [26]. The second type of XRD pattern appears more complex and can be fully indexed on the basis of a cubic unit cell with $a=3.163\pm 0.002$ Å (see Le bail fit in Fig. 1). This diffraction pattern

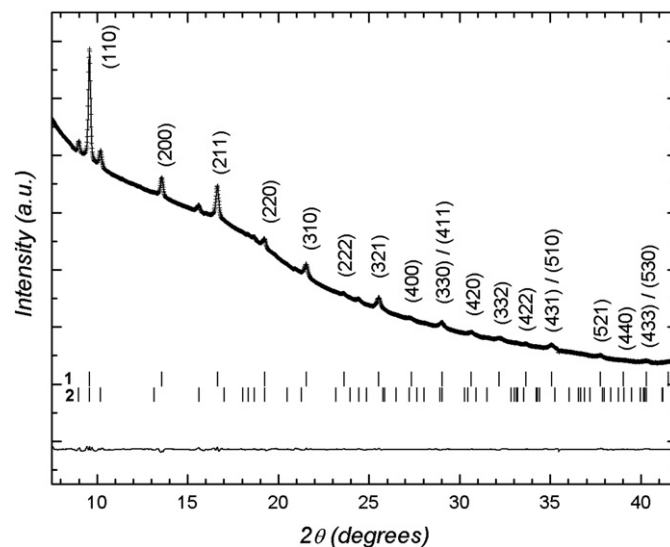


Fig. 1. Experimental X-ray diffraction pattern (+) compared to calculated one (solid line) using a Le Bail model for a phase mixture of cubic (I-Mode) carbon nitride (upper ticks) and Re originating from the gasket of the open DAC (lower ticks). The residual is also shown (lower solid line).

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