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C_3N_4: Dream or reality? Solvothermal synthesis as macroscopic samples of the C_3N_4 graphitic form

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In order to prepare C_3N_4 as macroscopic sample, two synthesis attempts of the graphitic variety were carried out. The first consists on the condensation of melamine and cyanuric chloride ($P = 130$ MPa, $T = 250°C$) with triethylamine acting as solvent in supercritical conditions. The second one consists on the pyrolysis of melamine ($P = 2.5$ GPa, $T = 800°C$) in presence of hydrazine. The two routes led to a graphite-like carbon nitride, nevertheless, the first product is poorly crystallized and contains a larger amount of hydrogen as NH_x due to a partial condensation. Several analysis (XRD, SEM, TEM, FTIR, XPS, EELS) reveal that the brown black solid issued from the route 2 presents a bidimensional honey-type structure close to those expected for the theoretical g-C_3N_4. This synthesis represents a first step in the C_3N_4 synthesis and its study as macroscopic sample. *© 2000 Kluwer Academic Publishers*

1. Introduction

Since the Cohen's relation concerning the bulk modulus of tetrahedral C_3N_4 [1], many works were published. Some ones treat of calculations trying to verify the Cohen's prediction and leading to the proposition of five different structures for C_3N_4 [2]. The major part of these papers exposes the attemps of synthesis of this covalent material, mainly through deposition processes [3]. If some cristallites with structure close to those predicted have been isolated, the obtained materials are usually nitrogen deficient. The works including high pressure treatments also lead to poor nitrogen products close to diamond [4, 5]. This nitrogen loss results to the N_2 molecule stability. Then, it seems inescapable that synthesis methods must involved nitriding species. One route to succeed in the elaboration of three-dimensional phases of C_3N_4 could be directly inspired by processes developped in the case of diamond and c-BN synthesis [6]. These synthesis are based on flux-assisted conversion processes, e.g.: dissolution of the low-density form (graphite, h-BN) in an appropriated solvent and recristallization of the cubic one (thermodynamically stable in the selected P, T conditions). However, these routes need a low-density (bi-dimensional) variety as starting material, but any C_3N_4 forms (and *a fortiori* g-C_3N_4) have ever been prepared as macroscopic sample. The aim of the present work was to prepare the graphitic form of C_3N_4. Two different routes have been selected with two common features: (i) the presence of a solvent in supercritical conditions and (ii) the use of organic precursors containing carbon and nitrogen prefigurating the honey-comb graphitic structure.

- The first is based on the condensation at medium pressure (130 MPa) of melamine with cyanuric chloride in presence of triethylamine.
- The second consists on the reaction of melamine with hydrazine at high pressure (2.5 GPa).

2. Experimental procedure

2.1. Route 1: condensation of melamine and cyanuric chloride

Melamine a (2.4.6 triamino-1.3.5 triazine) and cyanuric chloride b (2.4.6 trichloro-1.3.5 triazine) have been selected because their structure can easily induce the expected lacunar graphitic form through condensation (Fig. 1). The reaction of a with b produces HCl molecules, trapped by triethylamine Et_3N ($Et = C_2H_5$) that is a weakly nucleophilic base. The experimental conditions have been chosen in order that this base, also acting as the solvent, was in supercritical conditions ($P_c < 5$ MPa, $T_c = 250$–$300°C$).

The organic precursors as a solid phase (melamine and cyanuric chloride intimely mixed) and the liquid non-nucleophilic base in a mass ratio close to 1 are introduced in a gold tube with a thickness close to 0.2 mm and a diameter of 6 mm. After sealing carefully at low temperature to avoid the decomposition of the starting materials, this tube is placed in a high pressure vessel with a glove-finger shape, containing water as the transmitting pressure medium [7]. The pressure vessel is closed and then heated in a furnace. The percentage of water filling leads to control the pressure value versus the temperature after calibration. The

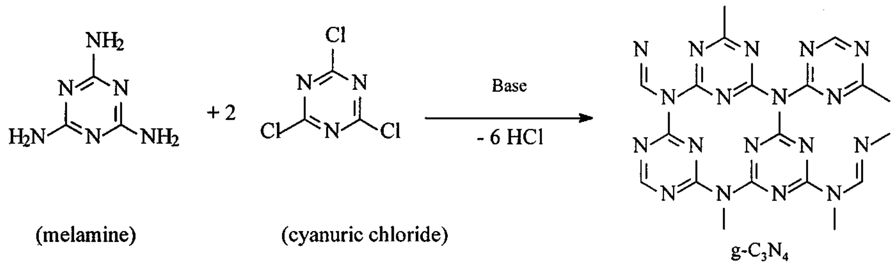


Figure 1 Condensation of melamine with cyanuric chloride.

selected conditions were $P = 140$ MPa, $T = 250°C$. When the reaction is completed, the high pressure vessel is cooled, depressurized, opened and the gold tube is extracted. The tube is weighed before and after reaction in order to control its tightness. It is then opened and the resulting brown-orange solid phase (sample no. 1) is extracted.

2.2. Route 2: solvothermal treatment of melamine with hydrazine

Melamine (2.4.6 triamino-1.3.5 triazine) has been selected for the same reasons that in case of route 1. The selected nitriding solvent was hydrazine (N_2H_4, $P_c = 14.7$ MPa, $T_c = 380°C$) due to its liquid state in normal P, T conditions and also its specific properties in the solvothermal conversion of h-BN into c-BN [8]. The experiments have been conducted by means of a “Belt type apparatus.” Melamine and hydrazine were encapsulated in an hermetic copper capsule which was put inside the high pressure cell. The optimized P, T conditions (in order to obtain a material with a graphitic structure and a C/N ratio close to 0.75 were $P = 2.5$ GPa, and $T = 800–850°C$). For higher temperatures, the ratio C/N increases drastically (carbon-rich product). At lower temperatures melamine is not decomposed. The obtained solid (sample no. 2) is brown-black color.

2.3. Treatment before characterization

In order to eliminate the by-products, the samples are washed in KOH then in permutted water before to be dry at reduce pressure.

3. Physico-chemical characterisations

The morphology of the synthesized powders was observed by scanning electron microscope (SEM, Jeol JSM 840A). The crystallinity of the sample was characterized by X-ray diffraction (XRD, Phillips PW 1730/10 K_α Cu) and electron diffraction (TEM, JEOL FX 2000). The chemical composition was defined by two different methods: electron probe microanalysis (EPMA, Cameca SX100) and chemical titration whose advantage lies in the evaluation of the hydrogen amount. The vibration spectra were obtained by FTIR spectrometer (Perking Elmer Paragon 1000). The thermogravimetric analysis (TGA) were carried out by a thermogravimeter (Setaram B54) that the resulting species were followed by mass spectrometry (Balzers Thermocube Mass 300). X-ray photoelectron spectroscopy (XPS, Escalab 220i-XL, Mg K_α: 1853.6eV) permits to study the nitrogen site.

4. Results and discussion

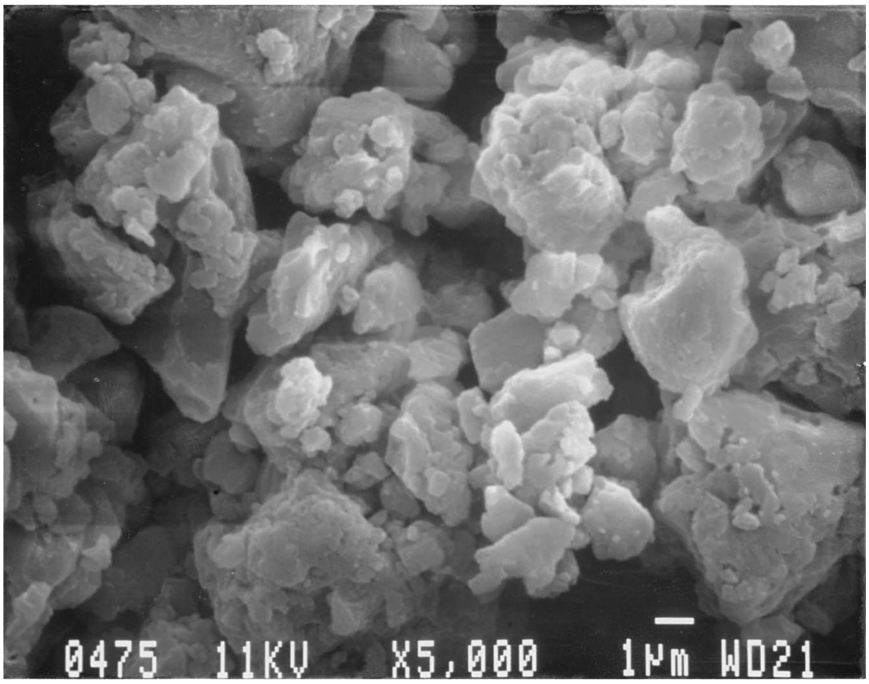
The two synthesized products have been characterized by different techniques in order to precise its structure and its physico-chemical properties.

The SEM analysis reveals strong differences between the morphology of the two synthesized samples. In the first case (Fig. 2a), the particules dimension is from 1 μm to 5 μm, but the second route leads to a relatively homogenous powder with 1 μm microcrystallites (Fig. 2b). Table I gives a comparison of the chemical composition through two different methods (EPMA, chemical titration) of the two samples. In every cases, the C/N ratio is higher than the theoretical one according to the C_3N_4 stoichiometry. Nevertheless, chemical titration underlines the presence of a larger amount, of hydrogen in the product from route 1. This result indicates that the condensation of melamine with cyanuric chloride is partial.

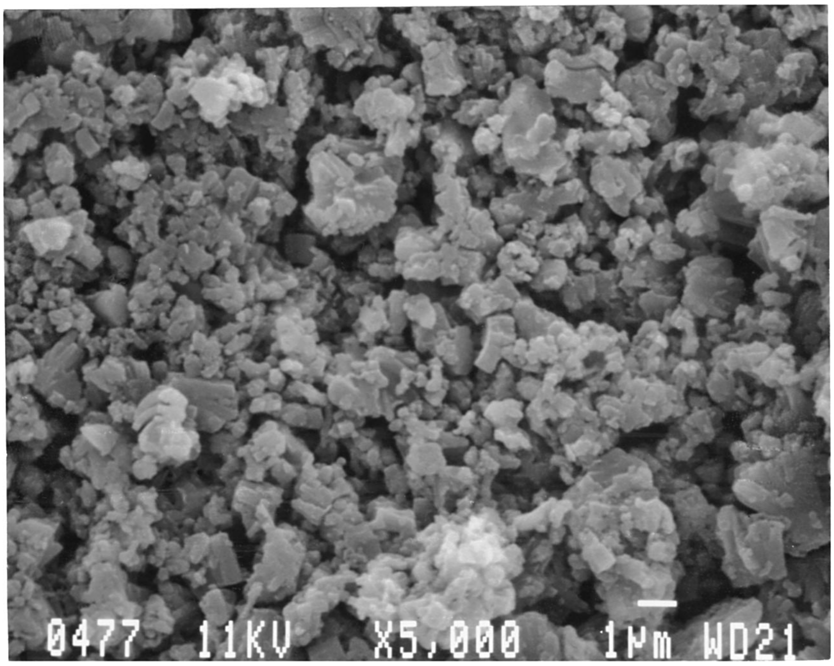
The XRD analysis pointed out the formation of a bidimensional phase (Fig. 3). The two diagrams present a single peak for 3.27 Å. This interplanar distance is smaller than the graphite one (3.33 Å) [9] and the

TABLE I EPMA and Chemical titration of the two synthesized samples

	C (%at.)	N (%at.)	O (%at.)	H (%at.)	C/N ($C_3N_4 \Leftrightarrow 0.75$)
Sample no. 1 (EPMA)	44.0 ± 4.3	52.0 ± 4.0	4.0 ± 1.0		0.85
Sample no. 1 (titration)	27.0 ± 0.3	32.9 ± 0.3	2.1 ± 0.3	37.5 ± 5.0	0.82
Sample no. 2 (EPMA)	45.6 ± 4.3	52.2 ± 4.0	2.2 ± 1.0		0.87
Sample no. 2 (titration)	38.1 ± 0.3	41.5 ± 0.3	1.2 ± 0.3	19.3 ± 5.0	0.92



(a)



(b)

Figure 2 Scanning electron micrograph of (a) sample no. 1 obtained from the condensation of melamine and cyanuric chloride at 130MPa and 250°C; (b) sample no. 2 obtained from the reaction of melamine with hydrazine at 2.5GPa and 800°C.

h-BN one (3.35 Å) [10]. Their full widths at half maximum (FWHM) are very different. The sample no. 2 is much better crystallized than the first one (FWHM $(1) = 2.0^\circ > \text{FWHM}\ (2) = 0.4^\circ$).

In the case of the sample no. 2, the TEM analysis confirms the playered structure of the microcrystallites with the presence of same amorphous particles. It was difficult to analyse these particles because of their unstability under the electron beam. Microcrystallites of the sample no. 1 are so unstable under electron beam that the result is characteristic to an amorphous phase. Such a behaviour could be attributed to the presence of hydrogen.

The transmission infrared spectra shown in Fig. 4 are similar. Both present a large absorption band around 3200 cm^{-1}, a strong one between 1300 cm^{-1} and 1650 cm^{-1} and another one centered at 830–810 cm^{-1}. The first one, more intense in the case of sample no. 1, is attributed to the N-H stretching modes [11]. This remark can be linked with the fact that sample no. 1 allows more hydrogen atoms. The second domain corresponds to $C(sp^2)$-N (1310 cm^{-1}) and $C(sp^2) = N$ (1610 cm^{-1}) stretching modes in a graphite-type structure (such a band is IR forbidden with pure graphite single crystal [11]). The better definition of these two absorptions in the case of sample no. 2 seems to indicate a better

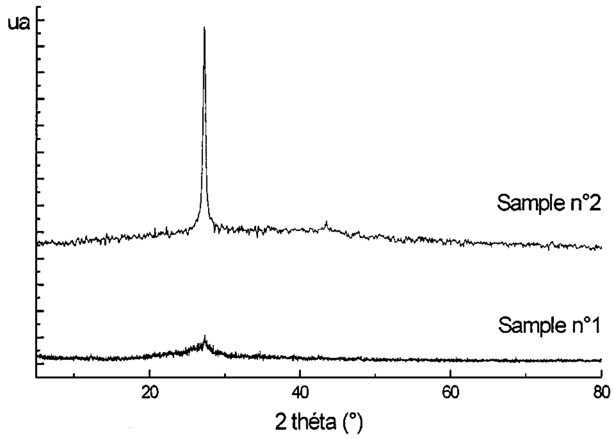


Figure 3 XRD diagrams of sample no. 1 and sample no. 2.

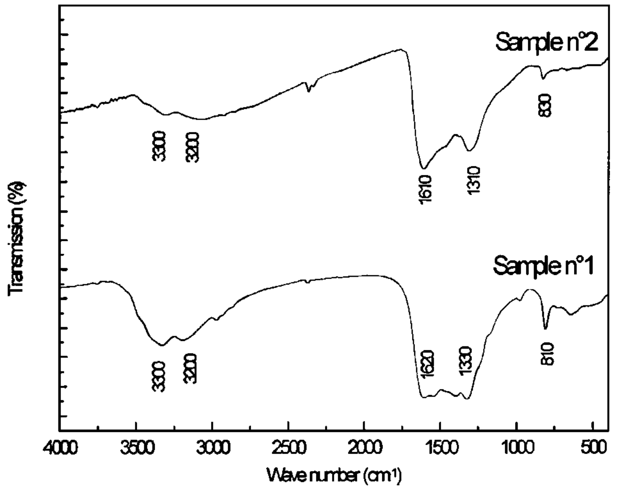
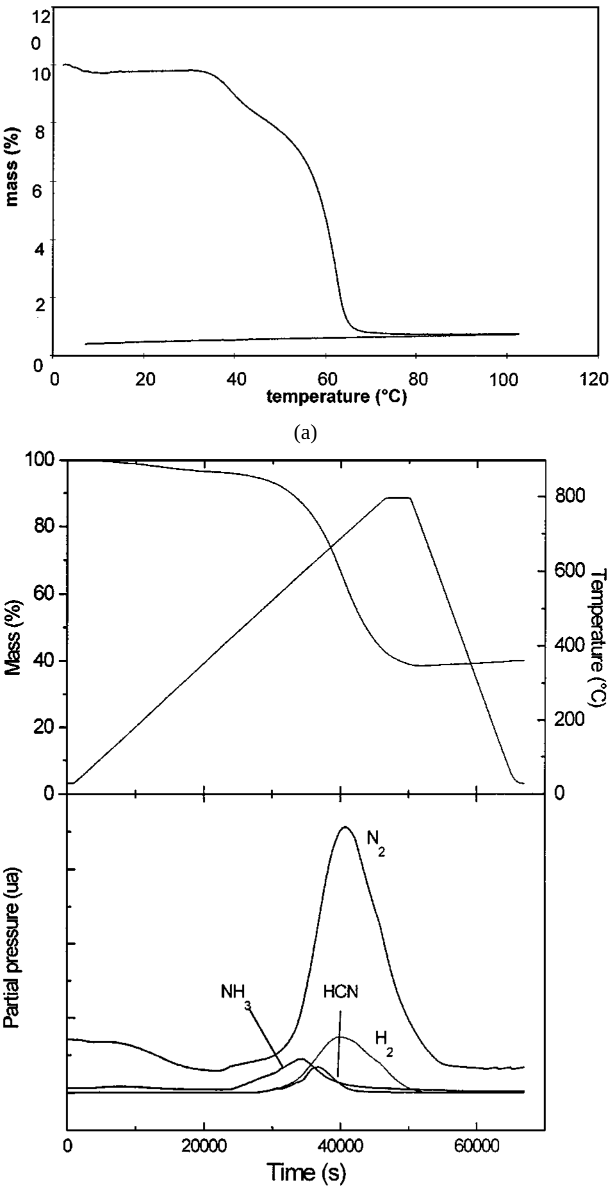


Figure 4 FTIR spectra of Sample no. 1 and Sample no. 2.

arrangement of the holey-type structure. Finally, the absorption at 830 cm^{-1} is characteristic of out-of-plane bending modes of the rings [12]. The lack of absorption at 2200 cm^{-1} indicates that the samples do not allow C≡N triple bonds.

The thermogravimetric analysis (TGA) was carried out under an argon flux (Air Liquide N56 pure). In the case of the sample no. 2, the resulting species were simultaneous analysed by mass spectrometry. The results are given at Fig. 5a (sample no. 1) and Fig. 5b (sample no. 2). The mass-loss curve obtained for sample no. 1 presents two inflexion points: the first at 380°C and the second at 610°C. According to FTIR analysis (carried out after treatment at different temperatures), the first decomposition consists on elimination of NH_x entities probably as NH_3 molecules (analogous study of melamine $C_3N_3(NH_2)_3$ reveals the departure of ammonia in the same temperature range: 350°C). In the case of sample no. 2, the mass-loss curve presents an unique inflexion point at 680°C, that approximately corresponds to the maximum departure of N_2, the main decomposition product. The formation of N_2 is observed between 570°C and 800°C. The total mass loss is close to 58% that is 3% less than the theoretical one according to the reaction:

$$C_3N_4 \longrightarrow 3C + 2N_2\,(\Delta m = -61\%).$$



(a)

(b)

Figure 5 (a) Thermogravimetric analysis with FTIR spectra of sample no. 1; (b) the results of thermogravimetric analysis and simultaneous mass spectrometry in the case of sample no. 2.

This difference is probably due to the presence of hydrogen that is involved in the formation of small quantity of NH_3 between 450°C and 700°C and the loss of carbon with the formation of HCN between 570°C and 720°C. We also observed the formation of molecular hydrogen H_2.

XPS was used to study the nitrogen site (the study of the carbon atoms is very difficult due to the importance of the absorbed carbaceous species in the case of fine powder). Since melamine is the C, N precursor and its aromatic nitrogen site are analogous with those expected in g-C_3N_4 (see Part I), it has been used as reference (Fig. 6). The N1s spectra of melamine and that of the two synthesized carbon nitrides are given in Fig. 6. The peak A (401.8 eV) and B (400.8 eV) correspond to nitrogen bonded with oxygen [13]. This type of surrounding is due to the O_2 and H_2O adsorption from air but mainly to the different cleaning steps (KOH-H_2O). This last oxygen source is only available in the case of

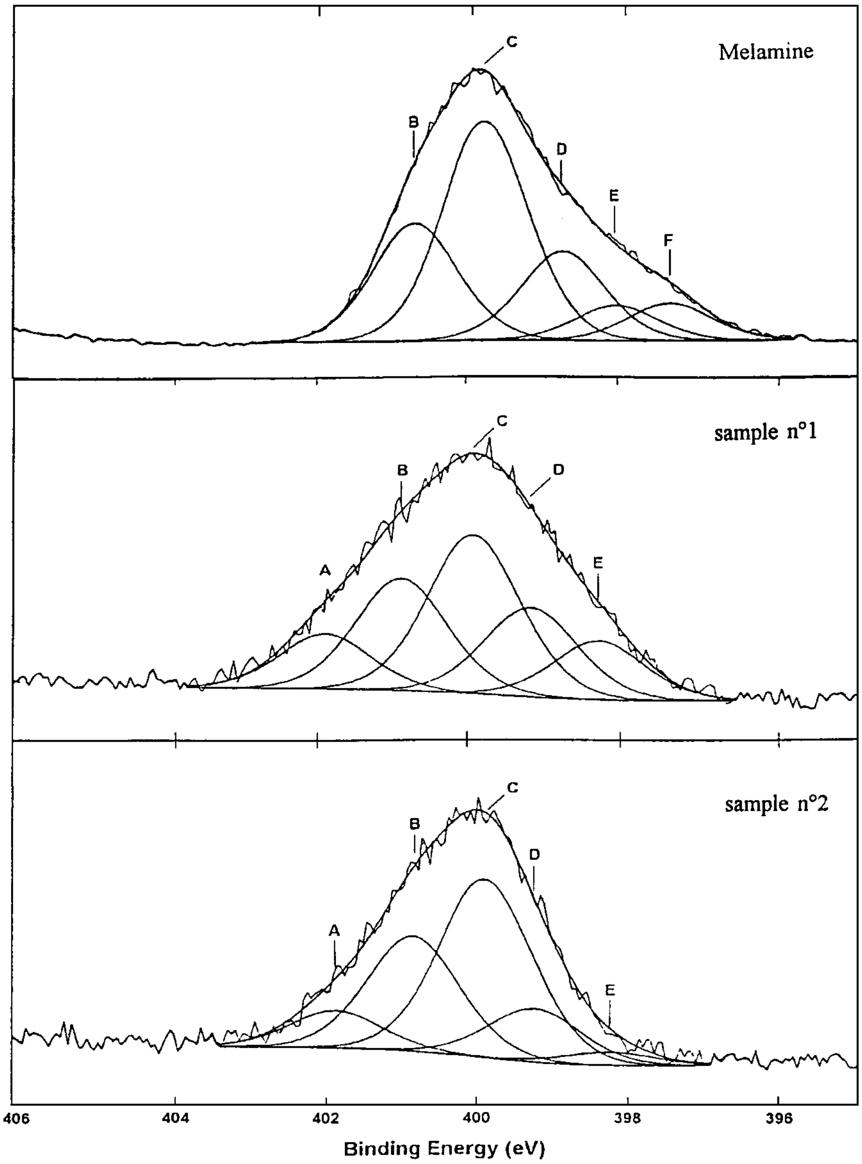


Figure 6 XPS N1s spectra of melamine sample no. 1 and sample no. 2.

the two samples, therefore the signal relative to oxygen pollution is exhausted than in the case of melamine (melamine was not cleaned). What's more, we noted that this difference is correlated with the O1s signal at 532 eV that confirms the attribution of the peaks A and B. In the case of the melamine, the major peak at 400,0 eV has been identified to nitrogen inside aromatic heterocycles according to litterature: the N1s binding energy for pyridine is 399.8 eV [14, 15]. The three other peaks at lower energies D, E, F (399.2 eV, 398.3 eV and 397.5 eV) correspond to the amine-type nitrogen NH_2. FWHM being fixed at 1.45 eV, three peaks were required to represent this type of nitrogen whose the signal is broadened because of the hydrogen bonds between molecules. The N1s signal of the two samples also presents a major peak at 400.0 eV which confirms the presence of C_3N_3 heterocycles. However the main difference between the three spectra concerns the lower energies region. The intensity of E and F decreases until to disappear for F in the case of the sample no. 2. The intensity of D also decreases but remains approximatively one-third that of C (sample no. 2) as would be expected for C_3N_4 ($n_{Nb}/n_{Na} = 1/3$). XPS confirms the presence of two kinds of nitrogen atoms (exepted the oxide forms) and the smaller amount of hydrogen in the case of the sample no. 2 than the sample no. 1.

In order to study into more detail the structure of the two samples, EELS analysis have been carried out. The spectrum given at Fig. 7 presents the background-substracted carbon and nitrogen K-edges for the sample

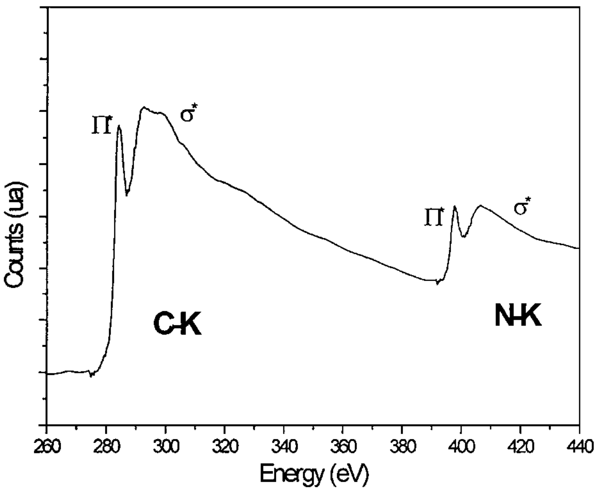


Figure 7 EELS spectrum of sample no. 2.

no. 2. These carbon and nitrogen K-edge features allow a sharp peak (at 284 eV for C and 399 eV for N) that corresponds to 1s-Π^* transitions in the case of sp^2 bonded atoms within a graphitic network. The similarity of the carbon and nitrogen K-edge and their evolution if we study a more carbon richer microcrystallite, underlines that carbon and nitrogen belong to the same network.

5. Conclusion

From the results of the different physico-chemical analysis, it appears that the high pressure pyrolysis ($P = 2.5$ GPa, $T = 850°$C) of melamine in the presence of hydrazine induces the formation of a material with a graphite-like structure and a stoichiometry close to that of C_3N_4. The structural analysis (XRD, TEM) present a bidimensional structure and FTIR, EELS confirm that the honey-type structure allows C-N bonds. XPS analysis shows the presence of nitrogen inside the rings composing this graphite-type material, stable until 680°C and close to g-C_3N_4. The solid obtained through the route no. 1 (melamine and cyanuric chloride) also presents a graphite-type structure but it is less defined (less crystallized, less stable), and allows a larger amount of hydrogen than sample no. 2. Sample no. 2 can represent a first step in the race to reach β-C_3N_4 or other exceptional carbon-nitrides.

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