High-pressure pyrolysis study of $C_3N_6H_6$: a route to preparing bulk C_3N_4

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Abstract
In order to prepare bulk C_3N_4, high-pressure pyrolysis of melamine ($C_3N_6H_6$) at different temperatures was carried out. The products were characterized by C, N, H element analysis, Fourier transform infrared spectroscopy, x-ray photoelectron spectroscopy, and x-ray diffractometry. The results of the analysis reveal that graphitic phase C_3N_4 has been synthesized. It provides a novel route to synthesis of the theoretical superhard cubic C_3N_4 and other C_3N_4 phases from organic compounds by a high-pressure and high-temperature method.

1. Introduction

Much attention has been paid to the synthesis of C_3N_4 since β-C_3N_4 was predicted to be a superhard material theoretically by Liu and Cohen [1, 2]. Techniques of all kinds, including vapour deposition [3, 4], laser ablation [5, 6], arc discharging [7], and high-pressure and high-temperature (HPHT) methods [8, 9] have been used to synthesize this superhard material. Much progress has been made in synthesizing C_3N_4. It has been reported that β-C_3N_4, α-C_3N_4, and other C_3N_4 microcrystalline phases exist in the synthesized samples [3–9]. Nevertheless, up to now, a single-crystalline phase of stoichiometric C_3N_4 has not been synthesized.

Further theoretical studies of C_3N_4 compounds were also motivated by the early work. Systematic first-principles calculations of the relative stability, structure, and physical properties of carbon nitride polymorphs including α-, β-, cubic, pseudocubic and graphitic C_3N_4 (g-C_3N_4) were given by Teter and Hemley [10]. The calculated bulk modulus of cubic C_3N_4 is 4.96 Mbar, which is greater than that of diamond (4.62 Mbar). The pressures of the phase transitions from α-C_3N_4 and g-C_3N_4 to cubic C_3N_4 are 68 and 12 GPa respectively. These results suggest that application of HPHT may be a more effective method for synthesizing this superhard material. However, this procedure needs a low-density phase of C_3N_4 as the starting material. At HPHT, many organic chemical reactions will occur, which are different from that at ambient pressure. The bond and molecular structure types will be modified and rearranged.
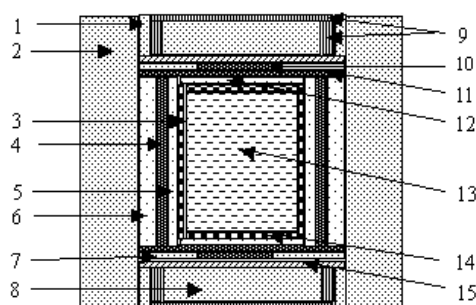
Figure 1. The sample assembly for the HPHT treatments. 1, 2, 7, 8: pyrophyllite; 3, 14: Mo foil; 4: graphite heater; 5, 6, 12: NaCl + ZrO$_2$ (20 wt%); 10, 11: graphite sheet; 9: steel ring; 13: sample (melamine); 15: metal plate.

New material will be synthesized. In this paper, the high-pressure pyrolysis behaviour of melamine was studied. Brown graphitic phase C$_3$N$_4$ (g-C$_3$N$_4$) crystal has been synthesized. It provides a novel route to the synthesis of the theoretical superhard cubic C$_3$N$_4$ and other C$_3$N$_4$ phases from organic compounds by HPHT methods.

2. Experimental details

The experiments were performed in a cubic anvil high-pressure apparatus (SPD-6X800). Melamine was selected as the starting material because of its graphitic-like CN ring structure. The melamine white powder was pre-pressed and sealed in a molybdenum capsule. Figure 1 shows the sample assembly. The experiments were carried out at the conditions of 5 GPa pressure and 400–900 °C temperature for 15 min. After quenching, the pressure was reduced and the sample was recovered. Six samples, 'sam 1–6', were prepared at 400, 500, 650, 700, 800, and 900 °C respectively. The synthesis pressure was estimated by the calibrated relation curve that was established based on the phase transitions of bismuth, thallium, and barium. The synthesis temperature was determined from a relation between the temperature and input power, which had been calibrated using a Pt6% Rh–Pt30% Rh thermocouple.

3. Results and discussion

The chemical composition was analysed by combustion analysis for C, N, H on a Perkin-Elmer 240C Elemental Analyzer. IR spectra were obtained for KBr pellets on an AVATAR 360 FT-IR ESP spectrometer. The chemical states were studied by x-ray photoelectron spectroscopy (XPS) on a VG ESCALAB MARK II spectrometer. X-ray diffraction (XRD) data were collected on a D/max-rA diffractometer using Cu Kα radiation.

The synthesized samples are observed by optical microscopy (OM). Sam 1 and 2 are still white powder, revealing that only a little of each sample decomposes. Some brown crystallites appear in sam 3, while sam 4 and 5 have transformed into black powder.

Table 1 gives the chemical compositions of the products. From table 1, it can be seen that with the rise of temperature, the C/N ratio increases, and the content of H decreases. At lower temperature (400 °C), melamine decomposes only slightly. At higher temperatures (900 °C), the C/N ratio increases drastically. In sam 3 (5 GPa and 650 °C), the atomic C/N ratio is close to 3/4; however, some of the elemental H still remains, indicating that the decomposition of melamine in sam 3 is insufficient and some NH$_x$ groups may remain in sam 3.
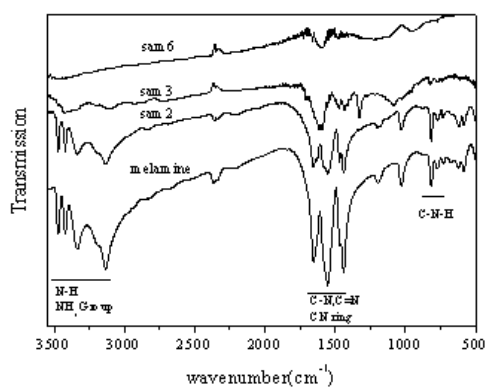
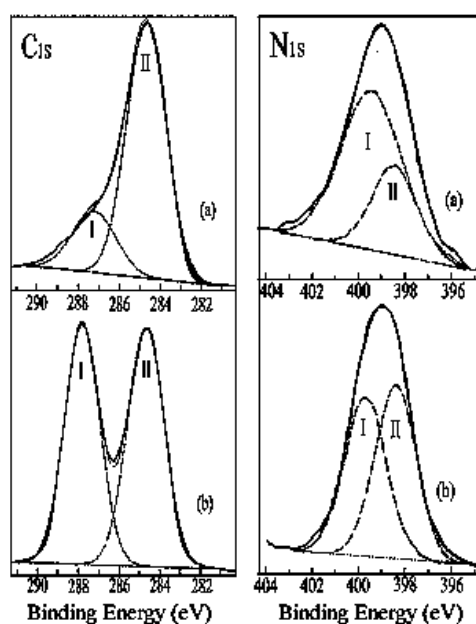**Figure 2.** FTIR spectra of melamine and sam 2, 3, 6.

Figure 3. XPS spectra of (a) sam 3 and (b) melamine.

Table 1. Element analysis for C, N, H of the products synthesized at 5 GPa and different temperatures.

Sample	C (wt%)	N (wt%)	H (wt%)	C/N	T (°C)
Sam 1	28.51	63.42	4.97	1:1.91	400
Sam 2	28.52	63.58	4.54	1:1.91	500
Sam 3	33.41	52.24	4.05	1:1.34	650
Sam 4	44.06	42.92	2.95	1:0.84	700
Sam 5	66.12	21.63	1.39	1:0.28	800
Sam 6	70.72	14.23	1.03	1:0.17	900
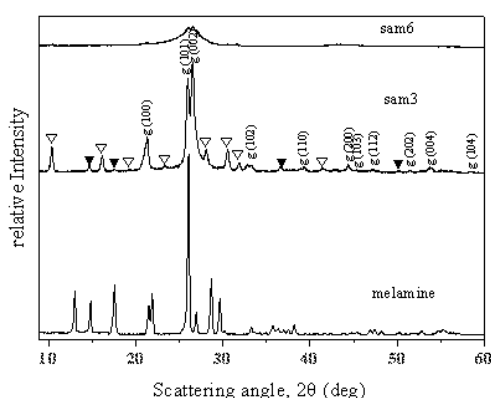
Figure 4. Powder XRD patterns of melamine, sam 3, and sam 6. g: g-C_3N_4; ▽: $C_3N_4H_x$; ▼: $C_3N_6H_6$.

Table 2. XPS data for figure 3.

	Peak		Position (eV)	Width (eV)	Height (CPS)	Area (CPS eV)
C 1s	(b)	I	287.8	2.02	13 658.9	29 371.2
		II	284.7	2.11	13 571.9	30 416.3
	(a)	I	287.2	2.50	6 939.5	18 451.0
		II	284.7	2.27	28 942.2	69 807.8
N 1s	(b)	I	399.7	2.12	15 285.1	34 478.74
		II	398.4	2.08	16 538.1	36 601.0
	(a)	I	399.5	3.16	5 421.24	18 232.1
		II	398.4	2.30	2 994.0	7 307.5

The transmission infrared spectra of melamine and the synthesized products are shown in figure 2. Three absorption bands (3100–3500, 1300–1650, and 810–830 cm^{-1}) are observed in the spectra. The absorption peak at 2350 cm^{-1} is attributed to the environmental CO_2 background inside the spectrometer. The absorption spectra of melamine are in good agreement with the data [13]. The 3100–3500 cm^{-1} bands are identified with the N–H stretching vibration, and are associated with $-NH_x$ groups. The 1300–1650 cm^{-1} band is shown to contain some absorption modes such as double-bonded C=N stretching and N–H bending modes. The peak of 1025 cm^{-1} is associated with the C–N mode, and the 810–830 cm^{-1} band is linked to the C–NH_2 group. With temperature increasing, the absorption intensities of the 3100–3500 cm^{-1} bands decrease, which indicates that the amine-type bonds break, resulting in a decrease in the contents of N and H. For sam 3, the spectra clearly indicate the presence of the CN ring. In addition, the presence of a new peak at 1333 cm^{-1} shows the condensation of decompounded melamine. At higher temperature (sam 6), these absorption peaks disappear, indicating that the sample had decomposed completely.

The C 1s and N 1s spectra of melamine and sam 3 are given in figure 3. Table 2 gives the XPS data for figure 3. The peak position of sam 3 is consistent with that of melamine. C 1s II and N 1s I are identified with the sp^2 CN bond, which corresponds to the CN heterocircles. N 1s II corresponds to amine-type nitrogen. Compared with the spectra of melamine, the intensities of C 1s II and N 1s I are stronger for sam 3. This shows that in sam 3, the amino bond has broken, and the sp^2 CN heterocircle has formed.

Table 3. XRD data for synthesized and calculated g-C_3N_4.

Experimental data		Calculated data [12]				
d (nm)	I (au)	h	k	l	d (nm)	I/I_0
0.4153	10 260	1	0	0	0.4107	2.64
0.3416	28 392	1	0	1	0.3504	10.17
0.3350	33 575	0	0	2	0.3360	100.00
0.2689	1 759	1	0	2	0.2601	1.18
0.2367	825	1	1	0	0.2371	1.29
0.2039	2 312	2	0	0	0.2053	3.78
0.1997	748	1	0	3	0.1967	1.22
0.1943	682	1	1	2	0.1937	1.14
0.1772	830	2	0	2	0.1752	3.87
0.1702	1 681	0	0	4	0.1680	7.24
0.1579	590	1	0	4	0.1555	0.15

Figure 4 shows the powder XRD patterns of melamine, sam 3, and sam 6. The results for melamine are in good agreement with the literature data [11]. The formation of graphitic phase C_3N_4 g-C_3N_4 in sam 3 is confirmed. The diffraction pattern is consistent with the result calculated using the structure of g-C_3N_4 proposed by Teter and Hemley [10] (see table 3). According to the observation by OM and the above analysis, the starting melamine did not translate into g-C_3N_4 completely. Although it is mainly composed of g-C_3N_4, sam 3 contains small quantities of an unknown intermediate product ($C_3H_4H_x$) and the starting melamine. The pattern for sam 6 shows disordered amorphous carbon formed at 900 °C.

4. Conclusions

At appropriate temperature and pressure (5 GPa and 650 °C), the high-pressure pyrolysis of melamine induces the formation of g-C_3N_4. This provides a novel route to the further synthesis of superhard cubic carbon nitride and other carbon nitride phases from g-C_3N_4 by HPHT methods.

Acknowledgments

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