

Study of the products of melamine ($C_3N_6H_6$) treated at high pressure and high temperature

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A black-brown powder was synthesized from melamine ($C_3N_6H_6$) at 850 °C and 4.5 GPa. There are two possibilities for the sample phase components based on the analyses of C/N/H elements and X-ray diffraction patterns. One is that the powder is composed of 2H-type g- C_3N_4 and some intermediate phases, while the other is that it consists of some undecomposed raw material, graphite and intermediate phases. The existence of the intermediate phase with long periodicity along one direction is confirmed through transmission electron microscopy observations. Scanning electron microscopy images show many block regions, in which a few holes exist. The atomic fraction of carbon and nitrogen was checked with energy dispersive X-ray analysis, and the chemical bond states were investigated by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. Based on the general analysis of the experimental results, the second possibility is favoured.

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1 Introduction

Ever since a new material of a covalent carbon–nitrogen alloy (β - C_3N_4) was predicted by Liu and Cohen [1–3] to have bulk moduli and hardness nearly as high as those of diamond, generally known as the hardest material, intense theoretical and experimental studies have been focused on this material. Teter and Hemley [4] proposed that, besides the known β -phase, several prototypes of C_3N_4 , such as α , cubic, pseudo-cubic and 2H-type graphitic, exist. Up to now, more than ten different structures of this carbon nitride have been predicted. At the same time, motivated by these predictions, many research groups have made great efforts to synthesize carbon nitride compounds. Recently, the growth of C–N films has become a hot topic in synthesizing the stoichiometric structure of C_3N_4 using various deposition techniques and methods [5], such as rf sputtering, ion beam sputtering, pulsed-laser ablation, and arc-plasma jet. It is very difficult, however, to measure some of the physical properties, such as hardness, of the C–N films for a comparison with calculations. Hence the main goal in experiments is to synthesize large carbon nitride crystals for measuring accurately composition, structure and physical properties. A recent review by Kroke and Schwarz [6] systematically summarized the theoretical work as well as the attempts to prepare carbon nitride by chemical and physical vapour deposition, and covered, in particular, the concepts and results of bulk synthesis routes. Teter and Hemley [4] and Malkow [7] suggested that high-pressure synthesis methods would play an important role in the search for new carbon nitrides. Hence several groups have carried out tentative experiments on carbon nitrides using high-pressure and high-temperature (HPHT) techniques [8–11], which confirmed the availability and feasibility of using HPHT in synthesizing carbon nitrides.

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Although many structural models for carbon nitride have been proposed, Malkow [7] emphasized the fact that C_3N_4 phases with sp^3 hybridization for both C and N are less stable than graphitic C_3N_4 with its sp^2 C and N. Actually, there are several different graphitic C_3N_4 phases, as described in Refs. [6, 12]. To obtain one of the graphitic forms of C_3N_4 (g- C_3N_4), besides using HPHT techniques, an appropriate precursor material should be chosen. Melamine ($C_3N_6H_6$), with a honeycomb structure very close to that of the expected one for C_3N_4 , was previously considered as a suitable molecular precursor compound for the synthesis of graphitic C_3N_4 phases, and its behaviour under high pressure has also been investigated [13]. Ideally, melamine can change into g- C_3N_4 by complete reaction of de-ammonation. However, it is very difficult to obtain g- C_3N_4 because of its weak basicity, so polycondensation of melamine often produces some intermediate phases such as melam, melem and melon [14–17]. As the derivatives of melamine, these phases with carbon nitride networks can also be considered as precursors for synthesizing g- C_3N_4 . In the present paper melamine is used as the starting material for the synthesis of stoichiometric phase of C_3N_4 . We mainly study the products of $C_3N_6H_6$ when treated by HPHT.

2 Experimental

Synthesis experiments were carried out with a six-anvil 600-ton high-pressure apparatus. The $C_3N_6H_6$ (white powder; Sigma-Aldrich; purity ≥ 99 at%) powders were wrapped in an Au thin film and sealed into a BN sample cell (\varnothing 5 mm, length 4 mm). Experiments were carried out at 4.5 GPa and 750–850 °C for 5 min. After quenching, the pressure was reduced to ambient pressure and the sample was uncovered. Three samples, A, B and C, were prepared at 750, 800 and 850 °C, respectively.

The chemical composition was analysed by combustion chemical analyses for C, N, H using an Elementar Vario EL elemental analyser. Powder X-ray diffraction measurements were carried out using a Rigaku rotating anode powder X-ray diffractometer (RINT 2000). The HPHT-treated sample was observed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Vibration spectra were investigated using Fourier transform infrared spectroscopy (FTIR; Bio-RAD, FTS-60v) and the carbon and nitrogen sites were investigated by X-ray photoelectron spectroscopy (XPS; VG KGII, MgK $_{\alpha}$, 1253.6 eV).

3 Results and discussion

3.1 Compositional analysis, structure and morphology of the products

The prepared samples had a brown colour and gave off an ammonia odour when taken out from the pressure cell. Table 1 gives the chemical compositions of the products. From Table 1 it can be seen that with increasing temperature the C/N ratio increases, and the concentration of nitrogen and hydrogen decreases. Melamine decomposes only partly at lower temperature (750 °C), whereas the carbon content increases drastically at higher temperature (850 °C). This indicates that most of the starting material is carbonized at higher temperatures. However, some of the nitrogen and hydrogen may still remain, indicating that a small amount of NH_x exists. For sample B (prepared at 4.5 GPa, 800 °C), the nitrogen content is higher than that in sample C. However, the atomic C/N ratio is larger than 3/4. Certainly, compared with sample C, more NH_x and carbon nitrides may exist in sample B. Further evidence can be provided from powder X-ray diffraction (XRD), which is discussed below.

Table 1 Element analysis for C, N, H of the products synthesized at 4.5 GPa and different temperatures.

sample	C (wt%)	N (wt%)	H (wt%)	C/N	T (°C)
A	47.54	44.28	2.74	1.25	750
B	62.04	24.59	2.50	2.94	800
C	76.11	13.72	1.99	6.47	850

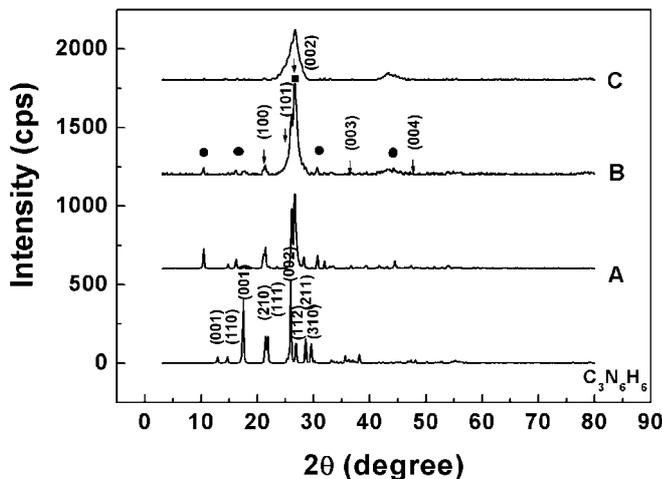


Fig. 1 XRD patterns ($\text{CuK}\alpha$) of the raw material and the samples (A, B, C) produced under different synthesis conditions.

Figure 1 shows the XRD patterns of melamine and the three treated samples. The XRD pattern of melamine shown in Fig. 1 is consistent with that given in the standard card (24-1923). The XRD patterns of the three samples show remarkably different diffraction peaks and relative intensities, indicating they are products with compositions different from melamine. Furthermore, compared with melamine, it is clear that sample A is composed of imperfectly decomposed melamine, while sample C is carbonized due to a higher temperature treatment. Although the elemental analysis for sample C shows a small quantity of nitrogen and hydrogen, it is likely to consist of some NH_x groups, while the related well-crystallized phases cannot be detected. Hence sample B, synthesized at $800\text{ }^\circ\text{C}$, is considered to be the main sample suitable for study. Actually, it is found in the experiments that carbonization of melamine also occurs if the treat time is long even at $800\text{ }^\circ\text{C}$, e.g. more than 5 min. Hence both the temperature and treat time are of great importance.

Based on the XRD analysis for sample B, there are two possibilities for the sample phase components. One is that the powder is composed of 2H-type $\text{g-C}_3\text{N}_4$ (indexed in Fig. 1, sample B) in agreement with a previous report [18] and some intermediate phases, while the other is that it is composed of some undecomposed raw material, carbon (labelled with a filled square in Fig. 1) and intermediate phases (unknown peaks marked with filled circles). However, the 2H-type $\text{g-C}_3\text{N}_4$ phase cannot be definitely determined in sample B since its strong (100) and (002) peaks [19] are very close to the (210) and (002) peaks of melamine, respectively. In fact, as mentioned above, some research groups have found that a few intermediate phases can be produced during polycondensation processes of melamine [14, 15, 17].

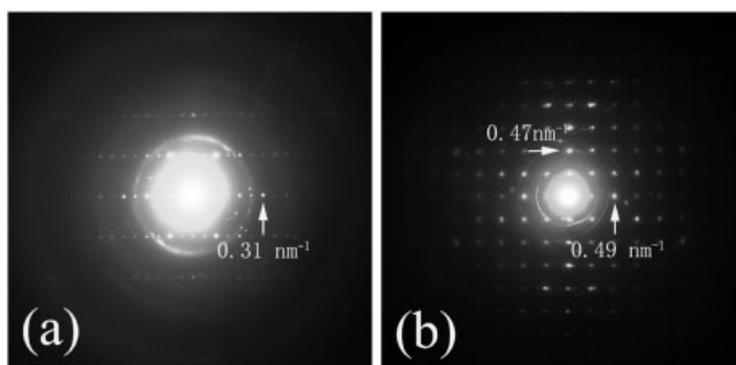


Fig. 2 Electron diffraction patterns of sample B.

Table 2 Comparison of diffraction data for sample B, melamine and 2H-type g-C₃N₄.

sample B		melamine		2H-type g-C ₃ N ₄			
<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>hkl</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>hkl</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀
8.4182 ^{a)}	17	001	6.71	100			
5.4401 ^{a)}	16	110	5.91	10			
4.9951 ^{b)}	15	011	5.01	65			
4.1373 ^{b)}	30	210	4.10	25	100	4.1067	2.6
		111	4.04	20	101	3.5042	9.9
3.4088 ^{b)}	77	202	3.47	70			
3.3360 ^{b, c)}	100	002	3.36	90	002	3.3602	100.0
		112	3.30	15	200	2.0533	3.8
		211	3.10	40	201	1.9637	19.1
		310	2.998	10	202	1.7521	3.9
2.9117 ^{b)}	24	121	2.940	5	004	1.6801	7.2
		112	2.683	5	203	1.5137	6.1
2.4506 ^{b)}	14	402	2.455	10	220	1.1855	4.8
2.2795 ^{a)}	13	412	2.344	5	222	1.1180	8.0
2.0404 ^{c)}	17		2.243	5			

^{a)} The interplanar spacing of intermediate phases.

^{b)} The interplanar spacing of the raw material.

^{c)} The interplanar spacing of carbon.

By comparing the diffraction data of sample B with those of melam, melon, etc., the unknown phases in sample B do not belong to any of them. However, we cannot rule out completely the existence of melam and/or melon the amounts of which are/is too small and cannot be detected by the XRD measurements due to detector limitations. In Table 2, diffraction data for sample B, melamine and 2H-type g-C₃N₄ [19] are listed. Figure 2 shows electron diffraction patterns obtained from sample B. A long periodicity of approximately 1.86 nm along one direction is determined from Fig. 2a, and approximate *d* values of 0.98 nm and 0.94 nm are calculated from Fig. 2b. These *d* values belong to neither 2H-type g-C₃N₄ nor melamine. Hence they should be related to the intermediate phases formed during the decomposition of melamine. Here it should be pointed out that no *d* values were observed in the TEM experiments related to g-C₃N₄. Hence we favour the second possibility mentioned above for the phase components of sample B.

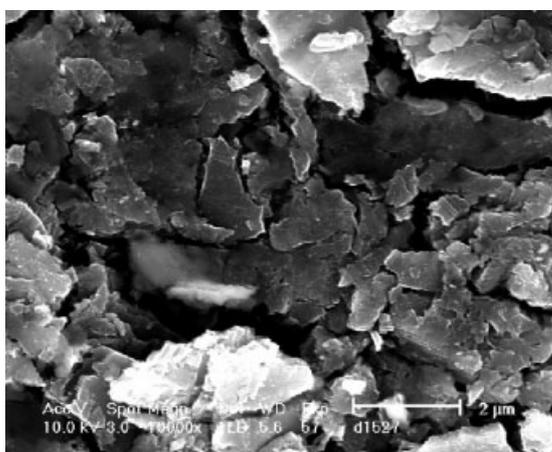


Fig. 3 SEM image of sample B.

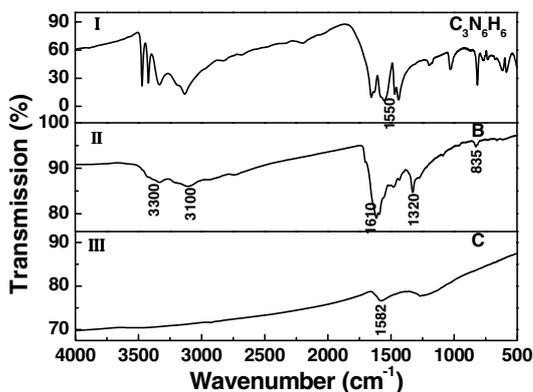


Fig. 4 FTIR patterns of the raw material and samples B and C.

An SEM image of sample B is shown in Fig. 3, where there are a lot of block regions combined loosely with one another because of the existence of interspaces between grains. There are also a few holes left as a result of a large amount of ammonia not given off immediately in the chemical reaction. In order to examine the chemical composition of the product, the sample was examined with energy dispersive X-ray analysis *in situ* with the SEM observations and an atomic ratio of 3.27:1 for carbon and nitrogen was obtained. The result is close to that of combustion chemical analyses discussed above. Referring to the results of XRD, the higher carbon content is caused by the existence of carbon in the sample. We also carried out TEM observations, but it is difficult to distinguish different phases from the morphology, since the morphology is affected by many factors.

3.2 Analysis of bonding configurations

3.2.1 FTIR spectra

Figure 4 shows the FTIR spectra for the raw material, sample B and sample C. The spectra of melamine, coincident with that of the standard in Ref. [20], has a distinctive, strong and broad band in the 1550 cm^{-1} region due to the in-plane ring vibrations of heterocyclic aromatic rings [21]. Compared with the melamine spectrum, that of sample B shows the absence of a strong absorption peak located at 1550 cm^{-1} , indicating that the heterocyclic rings are broken up during chemical reaction, but it cannot provide enough evidence of the complete disappearance of the rings in view of a much broader band between 1300 and 1630 cm^{-1} . The spectrum has a broad absorption band around 3200 cm^{-1} , a strong one at 1300 – 1630 cm^{-1} and another one at 835 cm^{-1} . The first reduced region for sample B is associated with

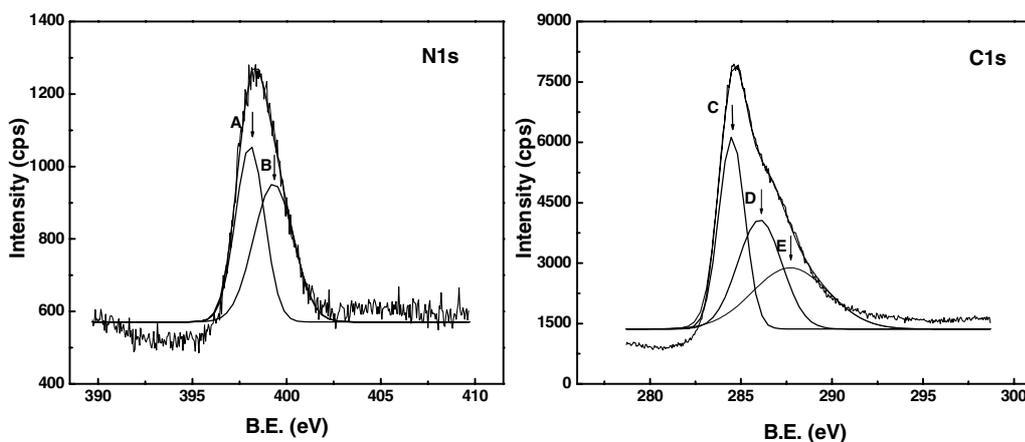


Fig. 5 XPS N 1s and C 1s core-level spectra of sample B.

Table 3 XPS analysis results for sample B.

XPS	binding energy (eV)	FWHM (eV)	intensity (cps)	bonding states
C 1s	284.4	1.43	4760.1	C–C
	286.0	2.42	2695.5	C(sp ²)–N
	287.7	4.15	1517.2	C(sp ³)–N
N 1s	398.1	1.52	482.1	C–N=C
	399.3	2.11	378.9	C(sp ²)–N

the N–H stretching modes. This remark can be linked with the fact that sample B contains a certain amount of hydrogen (2.50 wt%). The two absorption peaks at 1300–1330 cm⁻¹ and 1600–1630 cm⁻¹ involved in the second region are assigned, respectively, to C(sp²)–N (1320 cm⁻¹) and C(sp²)=N (1610 cm⁻¹) stretching modes in a graphite-type structure (such a band is forbidden in the FTIR spectrum of pure graphite single crystals). These are in agreement with those reported previously [10]. The absorption peak at 835 cm⁻¹ is characteristic of the out-of-plane bending modes of heterocyclic rings [22]. In the melamine spectrum, the peak at 1582 cm⁻¹ is related to the E_{1u} mode of graphite [23], confirming the results of XRD analyses.

3.2.2 XPS spectra

In order to investigate in more detail the chemical bonding states, we carried out XPS measurements for sample B. The N 1s and C 1s peaks for the sample are illustrated in Fig. 5. Judging by the complex N 1s and C 1s signals, a number of chemical states are involved in the bonding between the constituent elements. The most relevant C–N XPS bonding peaks are found at 284–288 eV for carbon and 398–401 eV for nitrogen. In the case of our sample, considering the possibilities of phase components, the XPS data of some relevant materials [24], especially melamine [12, 25], melon-based CN_x [26] and CN_{4+x} [27] were referred to in the process of assigning peaks. Applying the method of Gaussian fitting with multi-peaks, the N 1s and C 1s peaks are decomposed into A, B and C, D, E peaks, respectively. The corresponding results of decomposition of the N 1s and C 1s peaks are given in Table 3. The low-energy N 1s component A, positioned at 398.1 eV, is assigned to C–N=C type bonds, while peak B (399.3 eV) corresponds to nitrogen bonded with carbon (C(sp³)–N). The C 1s peak shape is usually considered to be more complex, containing a number of components with less defined energy positions. The lowest energy peak C at 284.5 eV can be assigned to the C–C bonds of carbon, and according to the analysis of Boyd et al. [28], the two peaks at higher energies, D and E (286.0 and 287.7 eV), are associated with C(sp²)–N and C(sp³)–N bonding states, respectively. It should be pointed out that, with regard to energy positions of N 1s and C 1s peaks, many researchers have not reached concurring views. In this paper, the mainstream parlance in the literature is adopted for chemical states analysis.

Based on the analyses, we favour that sample B has the second possibility of the phase components mentioned above. The observed bonds between carbon and nitrogen in FTIR and XPS experiments are considered to be caused by the undecomposed raw material and the intermediate phases in the sample. It should be pointed out that although we got negative results in synthesizing C₃N₄, we think these results are useful in identifying components in the sample.

4 Conclusions

The decomposition of melamine at high pressure and high temperature (4.5 GPa, 800 °C, 5 min) induces the formation of a brown-black powder (sample B). There are two possibilities for the sample phase components. One is that it is composed of 2H-type g-C₃N₄ and some intermediate phases, while the other is that it consists of some undecomposed raw material, graphite and intermediate phases. The TEM observations confirmed the existence of an intermediate phase with long periodicity along one direction. Based on the general analyses of the experimental data, we favour the second of these possibilities. In addition, our experiments suggest that very rigorous conditions are needed to synthesize stoichiometric phase of C₃N₄. Hence further research is expected to obtain better samples.

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References

- [1] M. L. Cohen, *Phys. Rev. B* **32**, 7988 (1985).
- [2] A. Y. Liu and M. L. Cohen, *Science* **245**, 841 (1989).
- [3] A. Y. Liu and R. M. Wentzcovitch, *Phys. Rev. B* **50**, 10362 (1994).
- [4] D. M. Teter and R. J. Hemley, *Science* **271**, 53 (1996).
- [5] S. Muhl and J. M. Mendez, *Diam. Relat. Mater.* **8**, 1809 (1999).
- [6] E. Kroke and M. Schwarz, *Coord. Chem. Rev.* **248**, 493 (2004).
- [7] T. Malkow, *Mater. Sci. Eng. A* **292**, 112 (2001).
- [8] R. C. Yu, L. C. Chen, Z. C. Qin, T. N. Yu, X. F. Duan, Z. Zhang, and C. Q. Jin, *Mater. Sci. Eng. A* **328**, 104 (2002).
- [9] D. W. He, F. X. Zhang, X. Y. Zhang, Z. C. Qin, M. Zhang, R. P. Liu, Y. F. Xu, and W. K. Wang, *J. Mater. Res.* **13**, 3458 (1998).
- [10] H. Montigaud, B. Tanguy, G. Demazeau, I. Alves, and S. Courjault, *J. Mater. Sci.* **35**, 2547 (2000).
- [11] L. Maya, D. R. Cole, and E. W. Hagaman, *J. Am. Ceram. Soc.* **74**, 1686 (1991).
- [12] I. Alves, G. Demazeau, B. Tanguy, and F. Weill, *Solid State Commun.* **109**, 697 (1999).
- [13] H. A. Ma, X. Jia, Q. L. Cui, Y. W. Pan, P. W. Zhu, B. B. Liu, H. J. Liu, X. C. Wang, J. Liu and G. T. Zou, *Chem. Phys. Lett.* **368**, 668 (2003).
- [14] B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Müller, and W. Schnick, *J. Am. Chem. Soc.* **125**, 10288 (2003).
- [15] H. May, *J. Appl. Chem.* **9**, 340 (1959).
- [16] L. Costa and G. Camino, *J. Therm. Anal.* **34**, 423 (1988).
- [17] T. Komatsu, *J. Mater. Chem.* **11**, 802 (2001).
- [18] H. A. Ma, X. P. Jia, and L. X. Chen, *J. Phys.: Condens. Matter* **14**, 11269 (2002).
- [19] J. B. Wang, J. L. Lei, and R. H. Wang, *Phys. Rev. B* **58**, 11890 (1998).
- [20] C. J. Pouchert, *The Aldrich Library of Infrared Spectra*, 2nd edition (Aldrich Chemical Co., Milwaukee, 1975), p. M1203H.
- [21] J. M. Chalmers and P. R. Griffiths, *Handbook of Vibrational Spectroscopy* (Wiley, Chichester, UK/New York, 2002), p. 2918.
- [22] H. X. Han and B. J. Feldman, *Solid State Commun.* **65**, 921 (1998).
- [23] R. J. Nemanich and G. Lucovsky, *Solid State Commun.* **23**, 117 (1977).
- [24] S. Souto, M. Pickholz, M. C. dos Santos, and F. Alvarez, *Phys. Rev. B* **57**, 2536 (1998).
- [25] C. Popov, K. Saito, K. Yamamoto, A. Ouchi, T. Nakamura, Y. Ohana, and Y. Koga, *J. Mater. Sci.* **33**, 1281 (1998).
- [26] T. Komatsu and T. Nakamura, *J. Mater. Chem.* **11**, 474 (2001).
- [27] D. R. Miller, J. J. Wang, and E. G. Gillan, *J. Mater. Chem.* **12**, 2463 (2002).
- [28] K. J. Boyd, D. Marton, S. S. Todorov, A. H. Al-Bayati, J. Kulik, R. A. Zuhr, and J. W. Rabalais, *J. Vac. Sci. Technol. A* **13**, 2110 (1995).