

Synthesis of nitrogen-rich B–C–N materials from melamine and boron trichloride

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Nitrogen-rich B–C–N materials have been prepared by the reaction between melamine and boron trichloride at different temperatures. The composition of the materials was dependent on the synthesis and annealing temperatures: $C_6N_{10.8-11}H_{9.4}B_{1.5-1.7}$ (for products synthesized and annealed at 673 K), $C_6N_{9.3-9.4}H_{3.8-3.9}B_{2.2-2.5}$ (for those synthesized at 673 K and annealed at 873 K) and $C_6N_{9.2}H_{3.6}B_{1.2-1.3}$ (for those synthesized and annealed at 873 K). Fourier transform infrared spectroscopy and ^{13}C nuclear magnetic resonance showed that the s-triazine rings from the melamine molecules were preserved in materials synthesized and annealed at 673 and 873 K. The sample obtained at 873 K had a graphite-like structure as suggested by X-ray and electron diffraction studies. The s-triazine rings were decomposed in the materials synthesized or annealed at 1223 K and the main product obtained was turbostratic boron nitride. © 1998 Chapman & Hall

1. Introduction

Recently interest in the materials of the ternary system containing boron, carbon and nitrogen (B–C–N materials) has increased [1–16] since the properties of graphite-like B–C–N materials are expected to be hybrids of those of graphite and hexagonal boron nitride (BN). For example, several types of semiconductor can be expected for these materials, depending on their composition and structure [1]. On the other hand, boron carbonitrides could be used as starting materials for the preparation of heterodiamond [2].

B–C–N materials have been synthesized by various techniques: nitriding a mixture of amorphous boron and carbon black [3]; chemical vapour deposition (CVD) using boron trichloride and ammonia as boron and nitrogen precursors, respectively, the tetrachloromethane [4], methane [5, 6], acetylene [6–8] or propane [6] as carbon precursors; CVD from BCl_3 and acetonitrile [9–11] or acrylonitrile [12]; synthesis by condensation of polyacrylonitrile-based polymer with BCl_3 [12] and pyrolysis of appropriate precursors [13–16]. These materials had different compositions, but none of them was in the nitrogen-rich part of the B–C–N phase diagram.

In this paper, the synthesis of B–C–N materials from melamine and boron trichloride is reported. The goal of the present work is the preparation of nitrogen-rich B–C–N materials, and melamine is chosen as a starting material owing to its high nitrogen content. The s-triazine ring in melamine is rather stable (up to 893 K) [17] and the formation of layered materials, in

which the s-triazine rings were preserved, has been reported [18, 19]. Melamine itself undergoes condensation with release of ammonia when heated above its melting point of around 623 K. Products with an increasing degree of condensation were obtained in the temperature range 623–893 K and they were called melam, melem and melon [20, 21]. Two different schemes have been proposed for the condensation process [21]. The first leads to the formation of cyameluric triamide which further reacts as a trifunctional monomer to obtain the final product of the condensation. The other assumes that melamine progressively condenses and the products are composed of s-triazine rings bridged by NH groups. Although the structure of the melamine condensates is not clear, the melam, melem and melon obtained by thermal condensation can be identified by their infrared (IR) spectra since there are some differences between them. Boron atoms are expected to bind with nitrogen atoms of melamine condensates, producing in this way nitrogen-rich B–C–N materials, i.e., materials in the nitrogen-rich part of the B–C–N phase diagram. These materials could be used as targets for deposition of thin B–C–N films by laser ablation or as starting materials for preparation of cubic phases under high-pressure high-temperature conditions.

2. Experimental procedure

B–C–N materials were synthesized in a quartz tube reactor heated by an electric furnace. Melamine

(C₃H₆N₆) (Kanto Chemicals; purity, 99.5%) was placed in a platinum boat in the central part of the reaction tube. After the reactor was flushed with nitrogen (purity, 99.9999%) at 500 sccm for 60 min with melamine charged inside, the N₂ flow was reduced to 100 sccm and boron trichloride (BCl₃) (Nihon Sanso; purity, 99.999%) was introduced into the reactor at a flow rate of 15 sccm. These two flows were continued while heating the furnace at a rate of 5 K min⁻¹. When the synthesis temperature was reached, it was maintained for 30 min. The flows were then stopped and the synthesized product was annealed sequentially in vacuum at the same or higher temperature for 60 min. The temperatures for synthesis and annealing of different samples are given in Table I. The choice of these temperatures was determined in accordance with already known data from the literature for melamine behaviour upon heating [20]; its sublimation starts at around 623 K and it undergoes complete degradation at 923 K.

The chemical analysis of the synthesized materials was carried out by combustion in oxygen followed by gas chromatography for nitrogen, carbon and hydrogen, and by titration for chlorine. The chemical states were studied by X-ray photoelectron spectroscopy (XPS) on a Perkin–Elmer PHI 5600 spectrometer. IR spectra were obtained in KBr pellets on a Biorad FTS-60A/896 spectrometer. X-ray diffraction (XRD) data were collected on a Philips PW 1800 diffractometer using CuK_α radiation. Transmission electron micrographs and electron diffraction (ED) data were obtained using a Karl Zeiss EM 902A transmission electron microscope. ¹³C nuclear magnetic resonance (NMR) spectra were recorded at 50 MHz on a JEOL GSH-200 NMR spectrometer.

3. Results and discussion

The products obtained in the boat had different colours for each experiment: pale yellow for H19, yellow for H20 and H21, greyish white for H25 and grey for H26. The samples synthesized at temperatures below the destruction temperature of s-triazine rings had the following compositions, determined by chemical analysis: C₆N_{10.8–11}H_{9.4}B_{1.5–1.7} (for H19, see Table I), C₆N_{9.3–9.4}H_{3.8–3.9}B_{2.2–2.5} (for H20) and C₆N_{9.2}H_{3.6}B_{1.2–1.3} (for H21). The boron, nitrogen and hydrogen contents in the samples decreased with increasing synthesis temperature from 673 to 873 K. Similar results for the loss of nitrogen and hydrogen due to the

elimination of ammonia have been reported for the condensation process of melamine [20, 21]. The products were composed of s-triazine rings linked by NH bridges and the nitrogen-to-carbon ratio in the condensates was 1.83 for melam (C₆N₁₁H₉), 1.67 for melem (C₆N₁₀H₆) and 1.50 for melon (C₆N₉H₃). For our samples, this ratio was close to that in melam for H19 (1.82) and to that in melon for H20 (1.57) and H21 (1.53). We suppose that similar condensation, as described above, has proceeded also in the presence of BCl₃. The reduced number of –NH₂ groups resulted in a lower boron content for H21, because boron atoms were mainly attached to them. Chlorine content in the synthesized materials was 2 at% for H19 and 0.5 at% for H20 and H21 which showed that the release of chlorine as HCl was close to completion at higher temperature. Besides these two main processes, the condensation of melamine and its interaction with BCl₃, and also the partial depolymerization of melamine to cyanamide [20] should not be excluded, especially for samples treated at 873 K. The formation of NHCN groups has been suggested in case of laser-induced decomposition of s-triazine rings [22].

For samples H25 and H26, both obtained at 1223 K, the boron-to-nitrogen ratio was almost 1 and the carbon content was about 10 at%. The destruction of s-triazine rings at this high temperature led to formation of boron nitride as a main product. Similar results were obtained by Kawaguchi and Nozaki [19] for the interaction of nitrogen-rich polymer with AlCl₃ at 1273 K, where the final product was AlN.

IR spectra of the obtained products showed rather different patterns for the experiments up to and above 873 K (Fig. 1). The spectrum of H19 showed that the condensation of melamine had started. Absence of the band at 1560 cm⁻¹ (typical for the triazine ring) suggested that triazine rings were probably modified and rearranged. Some authors explain this by the formation of cyameluric rings (with typical bands at 1600, 1435 and 798 cm⁻¹), one of the proposed structures of melem, the condensation product of melamine when heated to 673 K [23]. However, this structure has not been completely elucidated. In our case the process was carried out in BCl₃ flow and, as a result, B–N bonds were newly formed (bands at 1390 and 788 cm⁻¹). The N–H stretching bands in the initial material at 3138, 3336, 3420 and 3470 cm⁻¹ coalesced into broad bands at 3181 and 3340 cm⁻¹.

The condensation of melamine went further for sample H20. The s-triazine rings were restored (a band at 1560 cm⁻¹ could be seen) as in the case of melamine pyrolysis [21]. The B–N stretching was distinguishable (at 1409 cm⁻¹) although it was overlapped by the s-triazine ring stretching (at 1417 cm⁻¹). Probably the condensation of melamine went to completion for sample H21, which had a similar spectrum to H20, but it showed enhancement of the bands at 1640, 1574 and 1461 cm⁻¹ indicative of the higher degree of polymerization of the synthesized material.

The rise of the temperature above 893 K resulted in changes in the IR spectra of samples H25 and H26, which showed the same patterns due to the destruction of the s-triazine rings and new predominant

TABLE I Temperatures of synthesis and annealing for different samples

Sample	Temperature of synthesis (with BCl ₃ and N ₂ flows) (K)	Temperature of annealing (in vacuum) (K)
H19	673	673
H20	673	873
H21	873	873
H25	873	1223
H26	1223	1223

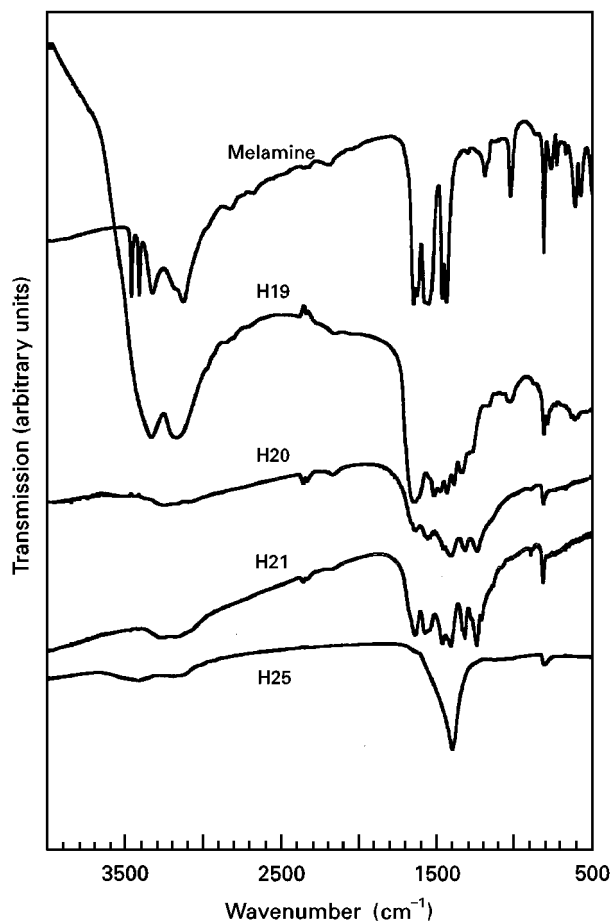


Figure 1 IR spectra of melamine and products of its interaction with BCl_3 at different temperatures.

bonding. The two sharp bands at 1400 and 810 cm^{-1} could be assigned to B–N stretching and bending, respectively, although they were slightly shifted compared with the spectrum of BN [24]. The broad bands at around 3418 and 3157 cm^{-1} were attributed to residual N–H bonding.

The chemical states of the elements in the synthesized materials were studied by XPS and the data entirely supported the results obtained by Fourier transform infrared (FTIR) spectroscopy. Peak shapes and positions were compared with those of melamine (for N 1s and C 1s) and with those of BN (for B 1s). The N 1s spectra of samples H19 and H20 were very close and broader than that of melamine (Fig. 2). The broadening suggested that the nitrogen atoms were in a wide variety of atomic environments. While the shoulder on the high-energy side of the peak was observed also for melamine (attributed to N–H), the shoulder on the low-energy side indicated interaction with less electronegative atoms than carbon, i.e., interaction with boron. A slight asymmetry appeared for sample H21 (Fig. 3) and the absence of a shoulder on the high-energy side was the result of the reduction in negatively charged nitrogen atoms (the process was accompanied by the release of NH_3). The higher degree of polymerization of the material resulted in sharpening of the peak. The N 1s peak of sample H26 was shifted (-0.7 eV) owing to the new predominant N–B bonding (Fig. 4). In Fig. 5, XPS indicated that the C 1s peak became sharper with rising temperature.

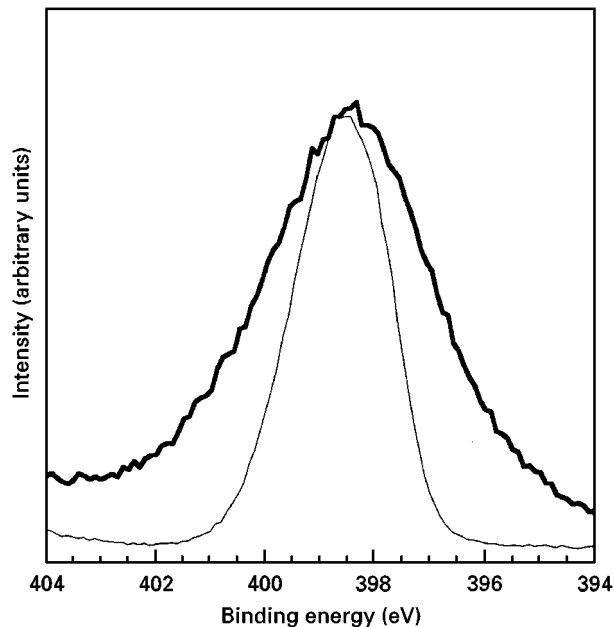


Figure 2 X-ray photoelectron N 1s spectra of sample H20 (—) and melamine (—).

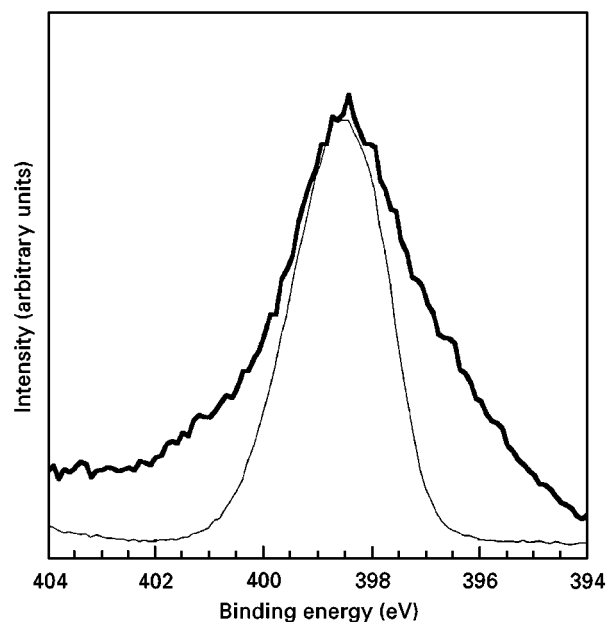


Figure 3 X-ray photoelectron N 1s spectrum of sample H21 (—) and melamine (—).

In this case the shoulder on the low-energy side of the peak was probably due to establishment of bonds with boron atoms. The shift in the C 1s peak position for H26 towards lower binding energy suggested that the predominant bonding was C–B [25]. The formation of B_4C together with BN and graphite has been observed as a result of annealing the B–C–N material at a high temperature in an argon atmosphere [15]. The weak peak at 287.6 eV was due to residual phase containing C–N bonds. The position of the B 1s peak (190.4 eV) indicated that boron was bonded mainly to nitrogen in all samples (Fig. 6). The shoulder on the low-energy side of the peaks indicated the formation of B–C bonds.

The solid-state (^{13}C) NMR spectrum of H21 exhibited four signals: two sharp peaks with maximum at

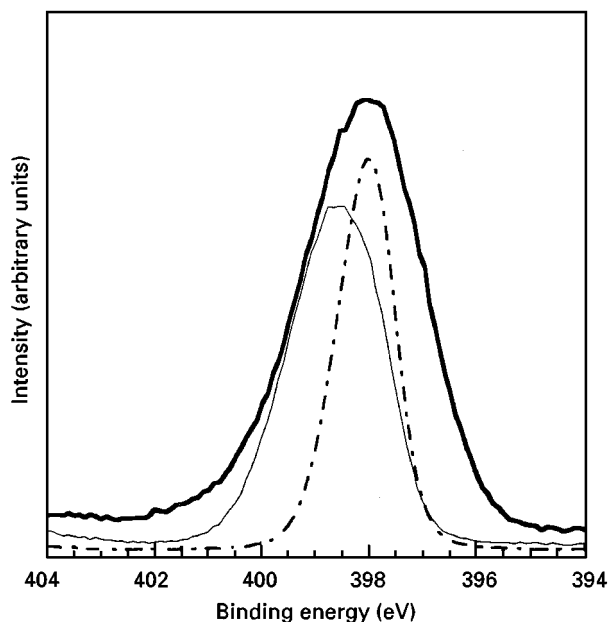


Figure 4 X-ray photoelectron spectra N 1s of sample H26 (—), melamine (---) and hexagonal BN (-.-).

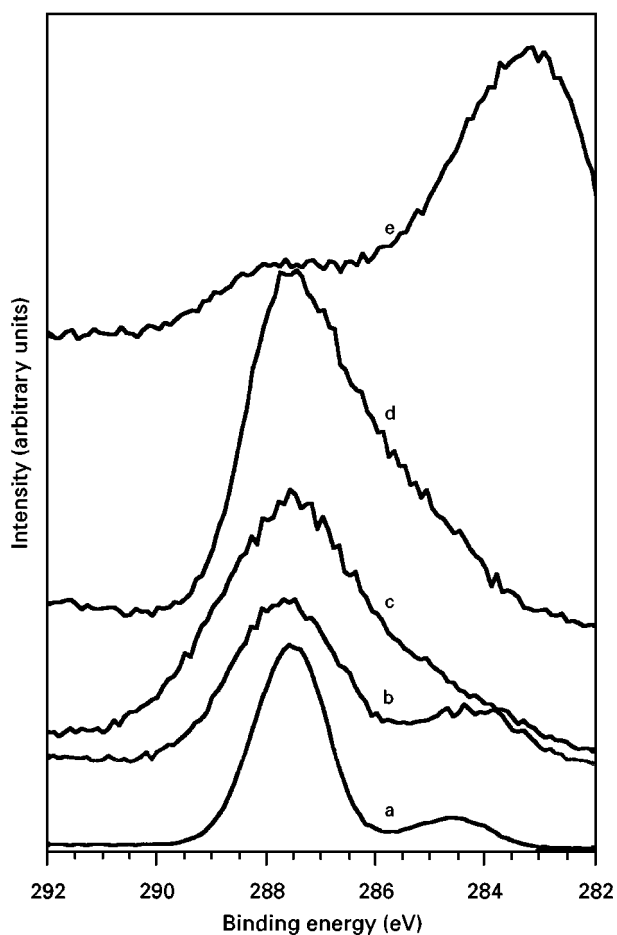


Figure 5 X-ray photoelectron C 1s spectra. Curve a, melamine; curve b, H19; curve c, H20; curve d, H21; curve e, H26.

164 and 157 ppm corresponding to sp^2 -hybridized carbon atoms from the s-triazine rings and two broad peaks at 73 and 41 ppm for carbon atoms probably from bridges originating from the partial depolymerization of melamine to cyanamide.

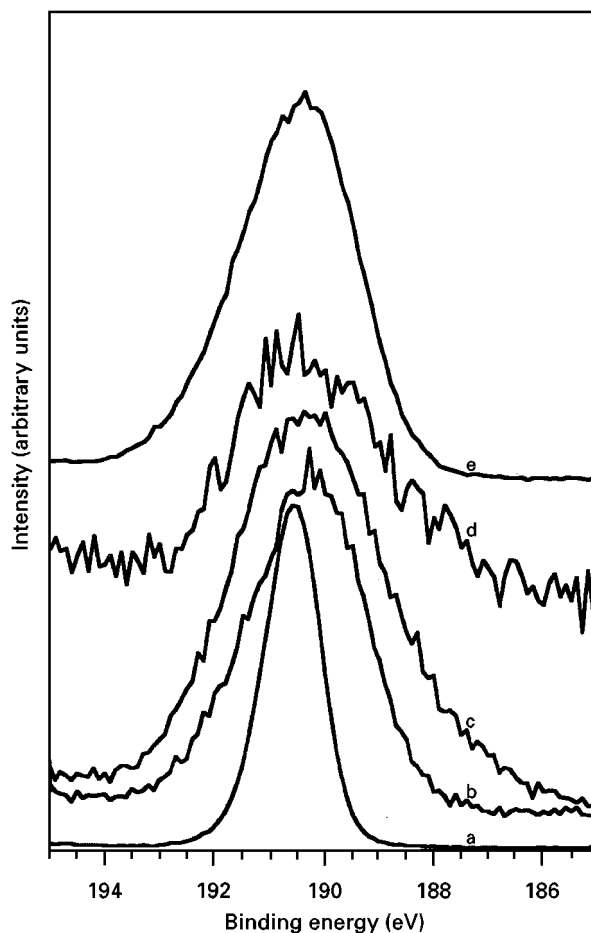


Figure 6 X-ray photoelectron B 1s spectra. Curve a, hexagonal BN; curve b, H19; curve c, H20; curve d, H21; curve e, H26.

Fig. 7 shows a series of XRD patterns for melamine and different samples. The results for melamine were in good agreement with literature data [26]. The formation of a new structure was observed for sample H21 owing to the higher temperature (873 K) of synthesis and annealing. The interlayer spacing was determined from the peak with maximum intensity ($2\theta = 27.7^\circ$), and corresponded to 0.322 nm. This value was slightly smaller than that of graphite (0.336 nm). The diffraction peak could be indexed as (002) corresponding to the similar peak in the diffraction pattern of graphite. Other weak and broad peaks were observed at around 44.5° and 57.2° , and they were similar to the (101) and (004) diffraction peaks of graphite. The weak peak at $2\theta = 13.1^\circ$ corresponds to an interlayer spacing of 0.679 nm in the c -axis direction. We assume as a probable explanation for its appearance the stacking model given by Kawaguchi and Nozaki [19] for the nitrogen-rich polymer which they synthesized; alternatively stacking of C-N planes with hydrogen atoms from bridges outside the planes. These hydrogen atoms from two different planes faced each other, thus changing the electronic density of the layered spaces and forming hydrogen bonds with nitrogen atoms from the other plane. The inclusion of boron atoms resulted in a smaller d spacing between stacked planes (0.322 nm) and a larger d spacing between stacked "pairs" (0.679 nm). The reason for this

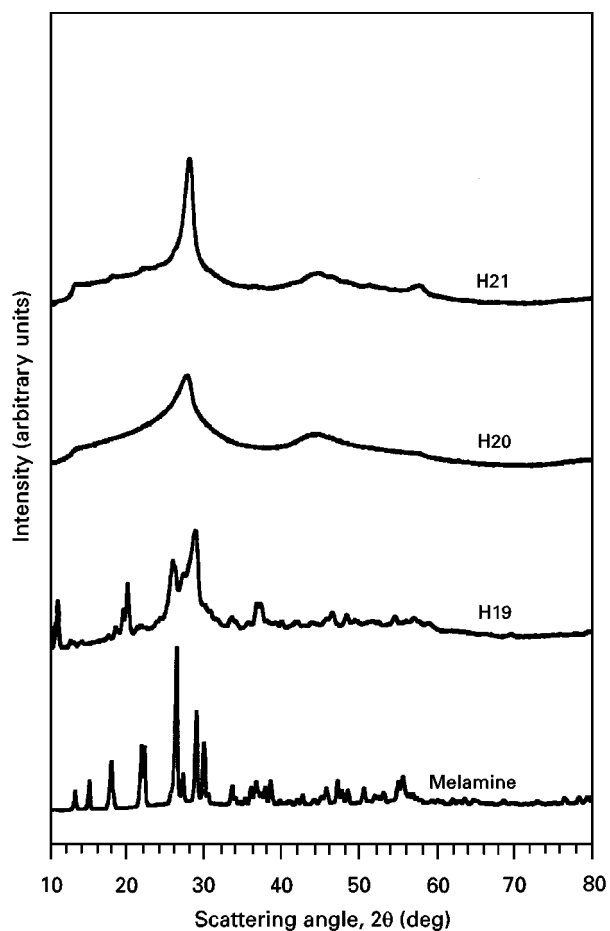


Figure 7 Powder XRD patterns of melamine and products of its interaction with BCl_3 at different temperatures.

was probably the additional interaction between two planes due to the affinity between boron and nitrogen.

The electron diffraction pattern taken using transmission electron microscopy from sample H21 yielded fully developed rings (Fig. 8). The d -spacing values calculated from the ED pattern coincided with those obtained by XRD.

The results from XRD and ED showed that the material synthesized at 873 K had an ordered structure. Unfortunately a definite structure could not be given and the main difficulty came from the complex character of the process. In the literature there is uncertainty about the structure of melamine condensates, especially melem and melon [20, 21, 23, 27]. When boron was included in the materials, the problem became more complicated. On the basis of the results obtained by XRD, ED, FTIR spectroscopy and XPS we propose the formation of a material with a graphite-like structure. The layers were composed of s-triazine rings bridged by NH groups, carbon-containing groups originating from partial depolymerization of melamine, boron atoms and nitrogen atoms.

XRD patterns of the samples obtained at 1223 K exhibited only broad lines at the same positions as (002) and (100) or (101) diffraction lines of hexagonal or turbostratic BN. These results indicated that the materials synthesized had a turbostratic structure, whose orientational correlation between the planes was disordered.

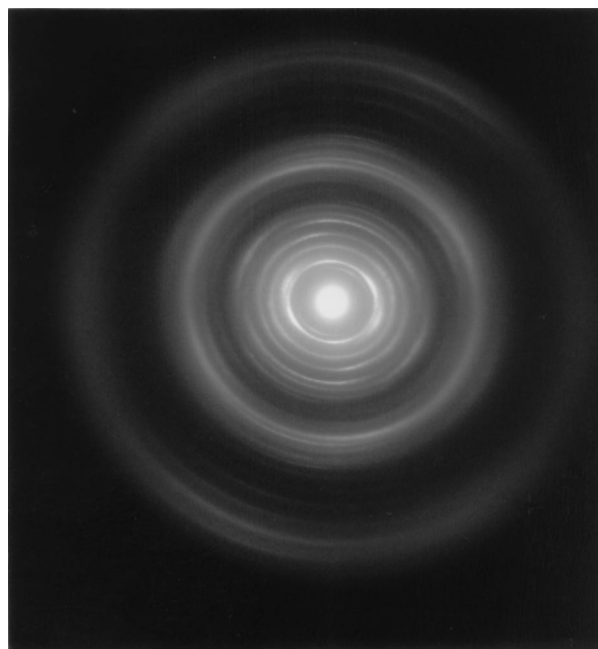


Figure 8 ED pattern of sample H21 synthesized from melamine and BCl_3 at 873 K.

4. Conclusions

Nitrogen-rich B–C–N materials have been synthesized by the reaction between melamine and boron trichloride at different temperatures. The s-triazine rings were preserved in the materials obtained at temperatures up to 873 K, as revealed by FTIR and ^{13}C NMR techniques. The nitrogen-to-carbon ratio was in the range 1.82–1.53, dependent on the synthesis and annealing temperatures, and the presence of bonds between boron, nitrogen and carbon atoms in the prepared materials was confirmed by XPS and FTIR spectroscopy. The sample obtained at 873 K had a structure similar to that of graphite as suggested by XRD and ED studies and the layers were composed of bridged s-triazine rings. Increasing the temperature to 1223 K resulted in the destruction of the s-triazine rings and turbostratic BN was obtained as a main product.

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