Preparation of Amorphous Boron Nitride from the Reaction of Haloborazines with Alkali Metals and Formation of a Novel Tubular Morphology by Thermal Annealing

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Amorphous boron nitride is obtained by a new, relatively low-temperature (120–210 °C) procedure that involves the reaction of B-trihaloborazines, $B_3X_3N_3H_3$ (X = Cl, Br) with alkali metals (Cs, Rb, K) in the absence of a solvent. The amorphous product after removal of alkali metal halide and unreacted $B_3X_3N_3H_3$ may be converted to the partially ordered turbostratic form of boron nitride by heating to 1100 °C. The material was characterized by IR spectroscopy, X-ray powder diffraction, and electron energy loss spectroscopy (EELS). Detailed studies of the morphology of the product from the reaction of *B,B′,B″*-trichloroborazine with cesium were carried out using scanning electron microscopy and transmission electron microscopy. These revealed a new, hollow tubular morphology for BN and also gave insight into possible reasons for its unexpected formation.

Introduction

Boron nitride is a well-known non-oxide ceramic, possessing a number of useful properties[1] and articles composed (wholly or in part) of BN are finding an increasing number of applications. There is consequently great interest in finding new and improved methods for its production.[2]

Traditionally,[2–4] routes to boron nitride have involved classical high-temperature syntheses. These usually involve reaction of ammonia or other cheap nitrogen-bearing compounds such as urea, guanidine, or biuret with borates or boric acid at elevated temperatures, with involved workup procedures necessary to obtain a product of high purity. Often, in addition to the high temperature, these reactions are required to be carried out under inert or reducing atmospheres.

Other typical high-temperature reaction types[2] include reaction of boron with nitrogen, metal borides with ammonia and nitrogen, and metal borohydrides with ammonium chloride (under N_2).

The most common current method for commercial BN production, however, is via carbothermal reduction of, for example, boric acid.[2] These reactions are carried out at temperatures in excess of 1500 °C, under an atmosphere of N_2, and are driven by classical high-temperature principles, viz., the thermodynamic stability of the BN product and the entropic driving force of formation of gaseous (carbon- and oxygen-containing) side products.

For production of BN thin films of exceptionally high purity, chemical vapor deposition (CVD) may be employed.[1a,2,5] In practice, the most widely used precursors are BCl_3/NH_3 and $BCl_3/NH_3/H_2$ mixtures, with resultant film quality strongly dependent on the temperature at which the CVD was carried out. Very high quality BN films are normally obtained at temperatures above 1000 °C.[2]

In addition to the methods outlined above, much recent interest has been paid to polymeric preceramic compounds,[2,6] where the boron- and nitrogen-containing polymer may then undergo thermolysis to yield BN. This approach may be particularly useful in pursuit of, for example, boron nitride coatings and fibers.

Given that there are many known molecules containing both boron and nitrogen, the lack of reported examples of attempted BN formation as a result of their direct thermal decomposition may appear surprising. Perhaps an explanation for this may lie in the fact that many of the potential molecular precursors to BN contain organic groups, possible sources of highly undesireable carbon contamination in the ultimate product. However, considerable interest[2,7] is currently being shown in the pyrolysis chemistry of borazine ($B_3N_3H_6$) and its derivatives as potential molecular precursors to BN.

A previous report from this laboratory[8] described a new tubular morphology for BN obtained from the thermal treatment of the product of the reaction be-

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1994.

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tween *B,B′,B″*-trichloroborazine and cesium. Here, not only do we describe more fully the method used to prepare the BN and illustrate the utility of other starting materials, but we also describe further electron microscopy studies of the BN produced by this method. These provide further insight into the possible causes for adoption of the unusual tubular morphology described in the previous paper.[8] In particular, high-resolution TEM study of the amorphous product, prior to the 1100 °C heating step, provides clues as to the causes for tube formation upon thermal annealing.

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the handling and manipulation of all reagents.[9] Cesium, rubidium, potassium, and *B,B′,B″*-tribromoborazine were purchased from Strem Chemical and were used as received. *B,B′,B″*-Trichloroborazine was prepared according to the method of Brown and Laubengayer[10] and was triply sublimed before use. Diffuse reflectance infrared spectra were recorded using a Mattson Polaris FT-IR spectrometer equipped with diffuse reflectance apparatus. X-ray powder patterns were obtained on a Rigaku Geigerflex powder diffractometer with a Cu target. Scanning electron microscopy was carried out using JEOL JSM-840 and Hitachi S-510 instruments. Transmission electron microscopy (TEM) and selected area electron diffraction (ED) were carried out using a JEOL 200CX analytical transmission electron microscope. High-resolution TEM was performed using a Hitachi H9000NAR transmission electron microscope. Electron energy loss spectroscopy (EELS) was performed using a Gatan 666 PEELS. Energy-dispersive X-ray spectroscopy (EDS) was carried out using a JEOL JSM-820 SEM with a Link Analytical Oxford Instruments eXL EDS and a Hitachi H9000NAR TEM with a NORAN Voyager light-element EDS detector.

Condensation of Haloborazines with Alkali Metals. *Preparation of BN from B,B′,B″-Trichloroborazine and Cesium.* Under a dry nitrogen atmosphere, a heavy-walled glass bomb (Fischer & Porter) of 160 mL volume was loaded with *B,B′,B″*-trichloroborazine (1.72 g, 9.36 mmol), a lump of metallic cesium (0.99 g, 7.5 mmol) and a glass-coated stirbar. The bomb was evacuated and immersed in a 125 °C oil bath behind a safety shield. The top of the bomb was also heated using a heat gun, to prevent excessive sublimation of the $[BClNH]_3$. Once both reactants had melted and the *B,B′,B″*-trichloroborazine began to reflux, the bomb was raised from the oil bath and the mixture was stirred with a magnet, resulting in a virtually instantaneous orange flash with the production of a very finely divided white powder and a concomitant rapid rise in pressure in the bomb to 40–60 psi, sufficient to shatter the glass-coated stirbar. **N.B. Care should be taken to shield the vessel whenever possible, as the reaction is extremely rapid and highly exothermic and produces gaseous side products under significant pressure.**

Evolved gas measurements typically indicated that more H_2 than HCl was produced by the reaction, although the exact mole ratio varied considerably. This is consistent with initially produced HCl becoming involved in a competitive reaction with the Cs metal.

The white powder was transferred to a sublimation apparatus, and unreacted *B,B′,B″*-trichloroborazine (0.59 g) was sublimed away in vacuo at 70 °C. As a safety precaution, the product was transferred to a quartz tube while still under nitrogen and heated to 450 °C under vacuum for 2 h, to ensure no Cs or water-reactive materials remained. IR spectrum: 3433 cm^{-1} (w, residual N–H), 1393 cm^{-1} (vs, br), 808 cm^{-1} (m).

The product was exposed to air and washed with 3 × 15 mL portions of water, filtering through a medium-fritted funnel. The remaining pieces of glass from the stir bar were removed at this stage. The product was then dried overnight under vacuum.

X-ray powder data indicated the sample to be essentially amorphous for Cu Kα: very broad band at 3.56 Å. The powder was then transferred to a quartz tube and heated to 1100 °C for 24 h, yielding turbostratic BN (0.29 g, 64% based on B and N content of consumed starting material). X-ray powder data for turbostratic BN: *d* Å(I) for Cu Kα: 3.56(vs), 2.13(w). IR data: 1387 cm^{-1} (vs, br), 807 cm^{-1} (m).

Preparation of BN from B,B′B″-Trichloroborazine and Rubidium. In a reaction essentially similar to that with Cs, Rb (0.471 g, 5.50 mmol) and *B,B′,B″*-trichloroborazine (1.10 g, 6.00 mmol) were placed in a glass bomb and, after evacuation, heated to 160 °C. A surface coating of purple material was observed on the Rb. The bomb was raised from the oil bath, and the contents were stirred with a magnet. After 5–10 s, a flash was observed and a colorless powder was produced. Workup was carried out as above. Yield of amorphous BN, after washing with water, was 48%. The IR spectrum was identical to that given above.

Preparation of BN from B,B′,B″-Tribromoborazine and Potassium. In a reaction similar to that described above, *B,B′,B″*-tribromoborazine (1.586 g, 5.00 mmol) and K (0.391 g, 10.0 mmol) were heated to 210 °C in a sand bath. The *B,B′,B″*-tribromoborazine began to reflux, and a dark coating formed on the K. The bomb was raised from the bath, and the contents were stirred, resulting in an orange-red flash of light and production of a finely divided colorless powder. The workup was conducted essentially as above. The amorphous BN yield, after washing with water, was 51%. The IR spectrum was identical to that given above.

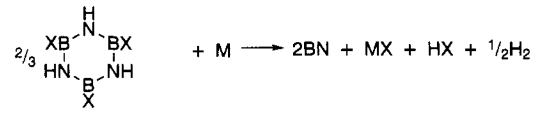
Attempted Reaction of B,B′,B″-Trichloroborazine with Sodium Peroxide. In a controlled-atmosphere drybox, a heavy-walled glass bomb of 160 mL volume was charged with *B,B′,B″*-trichloroborazine (0.733 g, 3.99 mol) and Na_2O_2 (0.078 g, 1.0 mmol). The bomb was evacuated, sealed, and placed in an oil bath, behind a safety shield, at 190 °C. The *B,B′,B″*-trichloroborazine melted and began boiling, but no reaction was observed, even after 45 min at 190 °C. The *B,B′,B″*-trichloroborazine was recovered quantitatively.

Attempted Reaction of B,B′,B″-Trichloroborazine with Benzoyl Peroxide. In a controlled-atmosphere drybox, a heavy-walled glass bomb of 160 mL volume was loaded with *B,B′,B″*-trichloroborazine (0.550 g, 2.99 mmol) and benzoyl peroxide (0.022 g, 0.091 mmol). The vessel was evacuated, sealed, placed in an oil bath behind a safety shield, and very slowly heated to 105 °C, the melting point of benzoyl peroxide. The *B,B′,B″*-trichloroborazine melted around 80–85 °C and the initiator melted around 104 °C, but no reaction was observed. The *B,B′,B″*-trichloroborazine was recovered quantitatively.

Results and Discussion

In the search for alternative methods of BN production, the method of alkali-metal-assisted polycondensation of haloborazines has a number of positive aspects. The temperatures required by this method are relatively low, in contrast to the forcing conditions traditionally employed in syntheses of BN powders,[2-4] and the boron nitride produced need never come in contact with carbon-containing materials, as no solvent is required for the reaction to occur.

The reaction is thought to proceed by eq 1.



(1)

X = Cl, Br; M = Cs, Rb, K

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[8] Hamilton, E. J. M.; Dolan, S. E.; Mann, C. M.; Colijn, H. O.; McDonald, C. E.; Shore, S. G. *Science* **1993**, *260*, 659. Figures 6–9 are reproduced with permission from *Science*.

[9] Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; John Wiley and Sons: New York, 1986.

[10] Brown, C. A.; Laubengayer, A. W. *J. Am. Chem. Soc.* **1955**, *77*, 3699.

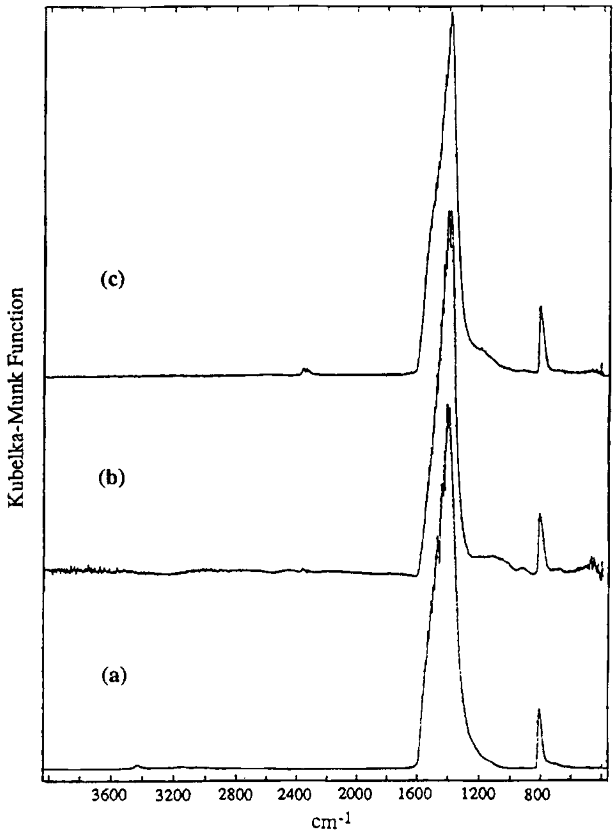

Figure 1. Diffuse reflectance infrared spectra of (a) amorphous, unwashed, (b) amorphous, washed, and (c) turbostratic boron nitride.

In practice, more H_2 than HX is typically collected. This may be attributed to the competing reaction of liberated hydrogen halide with the alkali metal (eq 2).

$$M + HX \rightarrow MX + {}^{1}/{}_{2}H_2 \qquad (2)$$

Presumably, this is at least in part responsible for the practical limitation of the yield of the synthesis to around 65%.

Impurities formed in the reaction may be removed by heating and/or washing with water. The main impurity to be removed is the alkali metal halide byproduct. This is removed by washing with water. It might also be removed by vacuum sublimation at the appropriate temperature, enabling BN to be prepared which has not been exposed to either water or oxygen. However, the geometry of the apparatus used does not allow this separation method to be fully investigated. It was also suggested by a reviewer that the washing step should be postponed until after the final (1100 °C) heating stage. However, alkali metal halides have significant vapor pressures at elevated temperatures and will rapidly sublime out of the hot zone of the furnace, entraining the boron nitride as they do so. Thus, leaving the washing step until after the thermal treatment has practical limitations in our laboratory.

A weak absorbance in the IR spectrum at 3433 cm^{-1} due to residual N–H disappears upon washing with water and drying in vacuo, as illustrated in Figure 1a,b. It should be noted that residual N–H is seen in some commercial BN samples. Samples were heated to 1100 °C for 24 h and converted to the turbostratic form of BN. Samples prepared in this manner showed no water in their infrared spectra (see Figure 1c), which are in accord with reported spectra.[11] Additionally, any appreciable attack upon the BN product by water would presumably result in O–H stretching vibrations in the IR spectrum, as observed even in dried samples of B_2O_3.[12] As indicated in Figure 1, no such absorptions were observed for our materials before or after the H_2O washing step. However, samples exposed to the atmosphere for significant periods of time produce IR bands that are attributable to adsorbed H_2O.

Figure 1 also clearly shows that there are no changes in the infrared absorption frequencies of boron nitride on going from the amorphous form (Figure 1a,b) to the turbostratic form (Figure 1c).

Samples were heated at 450 °C under vacuum prior to washing away the halide salt with water. This ensures the removal of any water-reactive contaminants, including tiny pieces of unreacted metal. Skipping this step resulted in a slight fuming of the product, and on occasion several tiny sparks were observed on addition of water.

The synthesis proceeds best when a single solid lump of alkali metal is used and when the metal is not allowed to touch the sides of the bomb. When both reactants become molten, magnetic stirring produces a virtually instantaneous orange flash. When the reaction was conducted as above, the highest yields of boron nitride were obtained, with little or no unreacted metal remaining. It appears that a fresh surface of alkali metal is required for the reaction to proceed, and this is produced by the agitation of the reaction mixture. The rapid nature of the reaction precludes identification of any intermediate product. It is difficult to visualize a mechanism for the polycondensation. Indeed, it is unknown whether the structural integrity of the B_3N_3 ring is conserved during the reaction or if scrambling occurs. Ring opening at relatively low temperatures has been invoked in proposed mechanisms of BN formation from borazine-based polymeric precursors.[13]

Evidence for the requirement for a highly electropositive metal in the initiation of the reaction may be taken from the fact that there is no apparent reaction between *B,B′,B″*-trichloroborazine and Na or K even at temperatures higher than that required for the reaction with Cs. The reactions of Rb with *B,B′,B″*-trichloroborazine and K with *B,B′,B″*-tribromoborazine occurred at higher temperatures than that of Cs with *B,B′,B″*-trichloroborazine. It should also be noted that the yields of BN obtained were higher in reactions involving Cs than those using Rb or K. Additionally, attempts to polymerize the haloborazines using the radical initiators benzoyl peroxide and sodium peroxide proved fruitless, suggesting that a possible mechanism for the polycondensation is via initial halide abstraction from the haloborazine. Presumably, a highly reactive unsaturated boron center results, which leads to the extremely rapid reactions observed.

The X-ray powder patterns obtained show that the BN product, as initially prepared, is essentially amor-

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(12) Dachille, F.; Roy, R. *J. Am. Ceram. Soc.* **1959**, *42*, 78.

(13) (a) Rye, R. R.; Tallant, D. R.; Borek, T. T.; Lindquist, D. A.; Paine, R. T. *Chem. Mater.* **1991**, *3*, 286. (b) Paciorek, K. J. L.; Harris, D. H.; Kratzer, R. H. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 173. (c) Toeniskoetter, R. H.; Hall, F. R. *Inorg. Chem.* **1963**, *2*, 29.

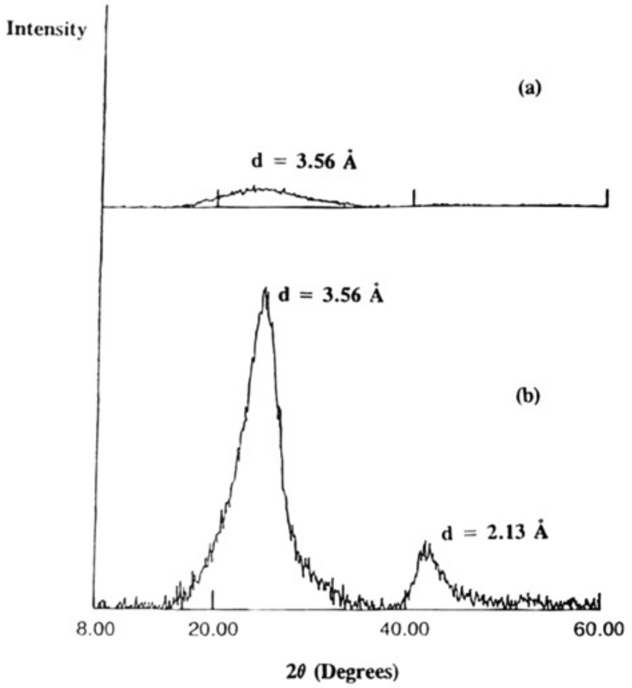

Figure 2. X-ray powder diffraction analyses of (a) amorphous and (b) turbostratic boron nitride.

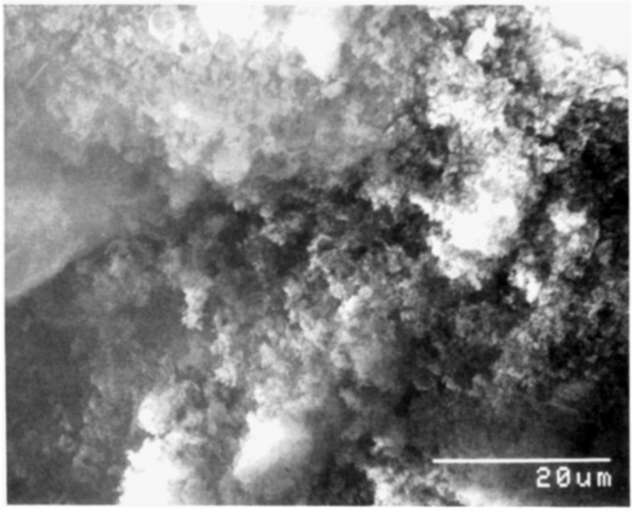

Figure 3. Scanning electron micrograph of amorphous boron nitride.

phous, with only a broad peak of low intensity centered around the location of the 002 plane reflection, $d = 3.56$ Å (Figure 2a). While it is difficult to precisely measure the position of the intensity maximum in Figure 2a, it is consistent with the accepted value for turbostratic BN[14] and so was ascribed the appropriate d spacing.

The XRD pattern obtained after heating the material at 1100 °C for 24 h is like that described in the literature for turbostratic BN,[14] with increased resolution of the 002 reflection at 3.56 Å and the appearance of a less intense, broad peak corresponding to the [10] reflection (unresolved 100 and 101 reflections for hexagonal BN) at 2.13 Å (Figure 2b).

Using the Scherrer formula,[15] values for the average crystallite size were 20 and 30 Å from the 002 and [10] reflections, respectively. The larger value from the [10] reflection may be due to uncertainty arising from the asymmetry observed in this peak, as the peak width at

Figure 4. TEM image of amorphous BN, showing hollow shelllike structures. Note the partial collapse of the shell at the left of the image.

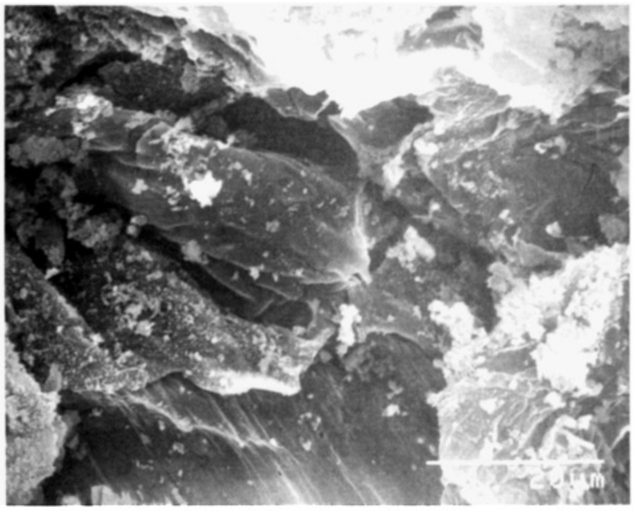

Figure 5. SEM image of turbostratic BN showing a distorted lamellar morphology.

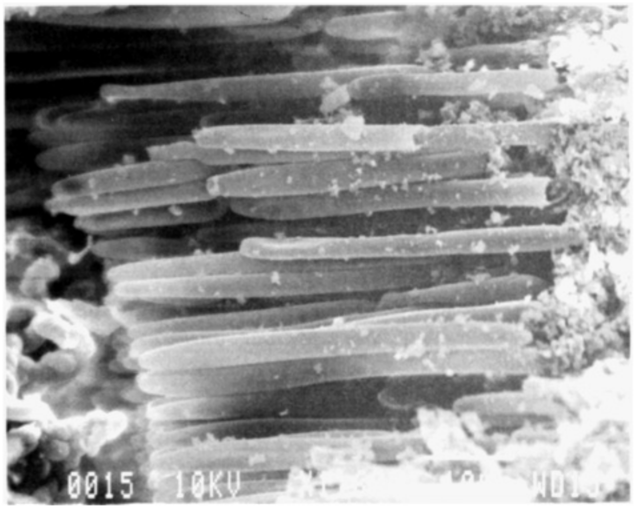

Figure 6. Scanning electron micrograph of a typical group of parallel, hollow tubular structures.[8]

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(14) Thomas, J.; Weston, N. W.; O'Connor, T. E. *J. Chem. Soc.* **1963**, *84*, 4619.

(15) Cullity, B. D. *Elements of X-Ray Diffraction*; Addison-Wesley: Reading, PA, 1978; p 102.

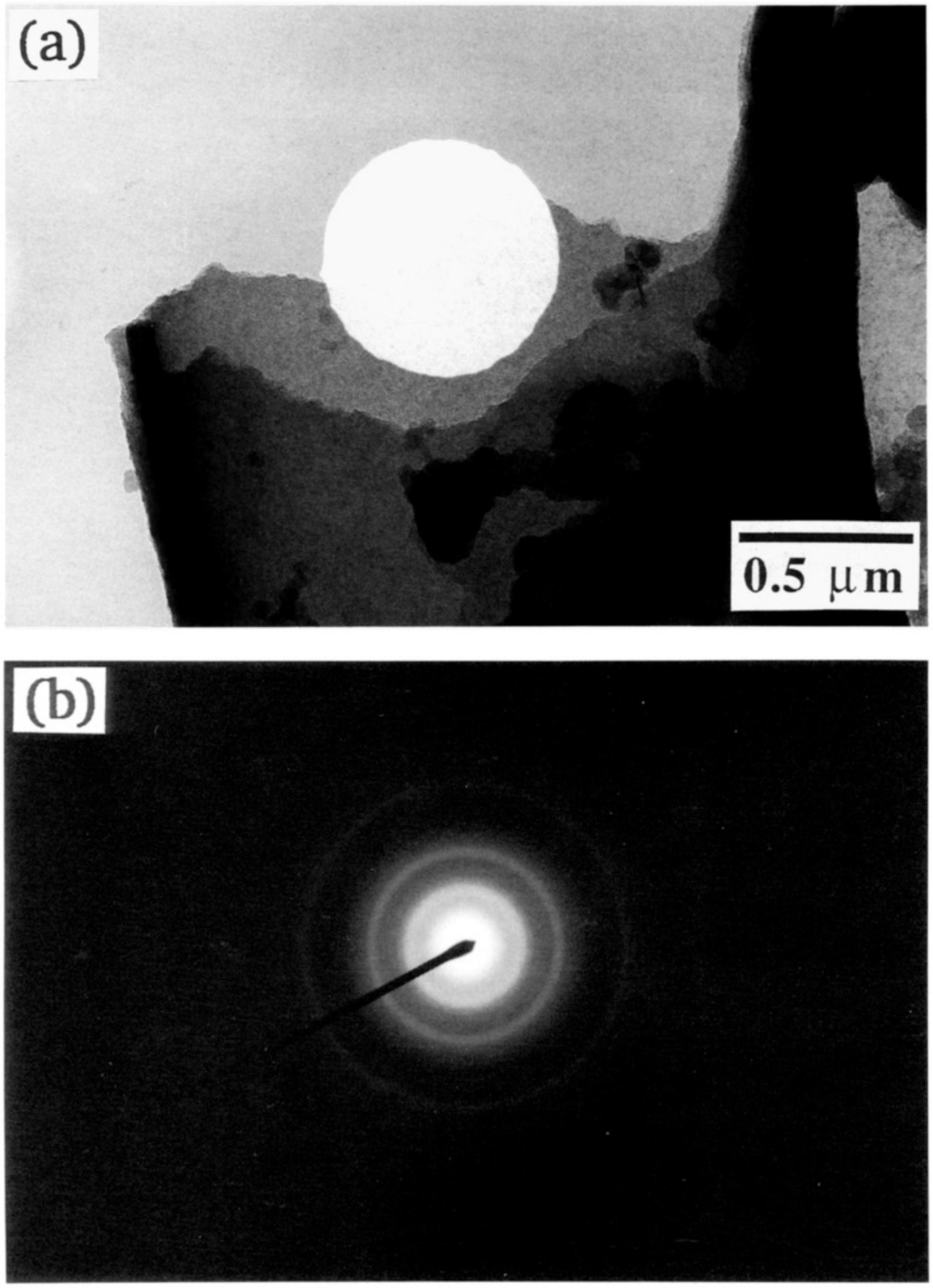

Figure 7. (a) Transmission electron micrograph of tube opening, the highlighted circle corresponding to the area illuminated to produce the electron diffraction (ED) pattern shown in (b).[8]

half-height may not be a reliable measurement. These values are consistent, however, with the order of magnitude of the ordered regions in the tubular material observed by high resolution TEM studies (see below).

Density measurements carried out on the turbostratic boron nitride produced after the 1100 °C heating step gave a value of 1.7 g/mL, in reasonable accord with previously published figures.[6a]

EELS revealed a boron:nitrogen ratio of 1.00 (48.4 ± 0.3% atomic concentration) to 1.065 (51.6 ± 0.8%) B:N respectively. This technique has previously been used for microanalysis of boron nitride.[16] Additionally, no residual chlorine could be detected by EELS on the material heated to 1100 °C.

Electron Microscopy. Detailed scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies of the morphology of BN produced by the reaction of Cs with *B,B′,B″*-trichloroborazine have been carried out, some of which are the subject of an earlier report from this laboratory.[8] The earlier work described a hollow tubular morphology previously unreported for boron nitride. While apparent sites of growth of the hollow BN tubes were detected by transmission electron microscopy (TEM), the mechanism of or reasons for the tube formation were unclear. It was suggested that the novel method of preparation for amorphous BN described here may be crucial to the ultimate formation of the tubular morphology. To shed further light on this possibility, detailed electron microscopy studies of the

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[16] (a) See ref 1, p 330. (b) Matsui, Y.; Sekikawa, Y.; Ishii, T.; Isakosawa, S.; Shii, K. *J. Mater. Sci.* **1981**, *16*, 1114.

[17] Powder Diffraction File: Inorganic Phases, JCPDS–International Center for Diffraction Data, 1989.

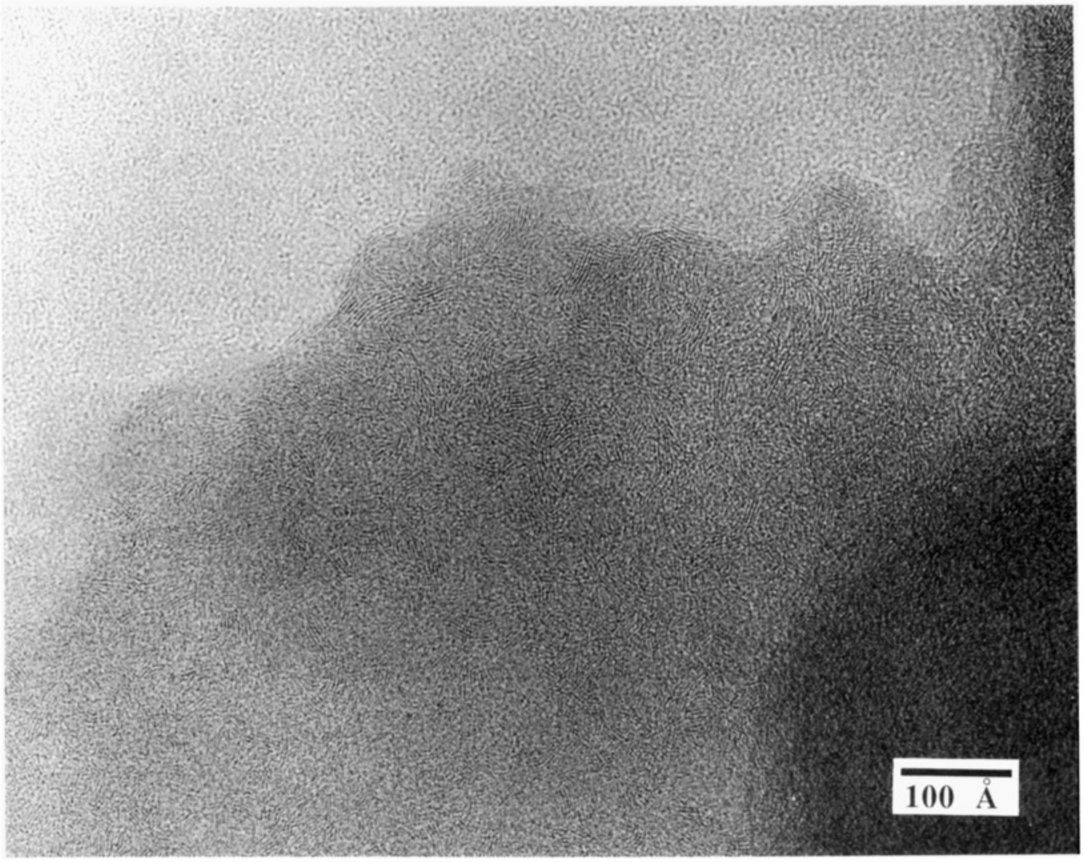

Figure 8. High-resolution TEM image of an area of a single-tube wall.[8]

amorphous material have been performed. These results are presented here and give a possible explanation for the unusual tube growth from the initially obtained amorphous product.

Electron Microscopy of Amorphous BN. SEM images of the BN product after the removal of byproducts and prior to heat treatment at 1100 °C indicate the product to be largely unstructured, as shown in Figure 3. However, TEM work on this material at higher powers of resolution reveals the presence of shelllike pseudospherical structures which would appear to be hollow in nature (see Figure 4). These hollow shells are typically a fraction of a micrometer in diameter and are very thin walled, with a typical wall thickness of around 100 Å. Note, in Figure 4, that the structure at the left of the image appears to be undergoing collapse, the importance of which will become apparent as further studies are discussed.

Given that the reaction of Cs with $[BClNH]_3$ results in the formation of a poorly ordered solid from molten precursors, it might be possible that these shells are actually bubbles caused by rapid expulsion of gaseous side products (HCl, H_2) from the reaction mixture, which then rapidly solidify as the BN is formed.

Energy-dispersive X-ray spectroscopy coupled with transmission electron microscopy revealed traces of cesium and chlorine to be present in the amorphous material. Neither of these elements were detected by EDS on the turbostratic BN obtained after the final heat treatment step.[8] While the EDS studies were only qualitative in nature, owing to the difficulty in observing light elements such as boron and nitrogen, the quantities of Cs and Cl present in the amorphous sample are estimated to be very small.

Electron Microscopy of Turbostratic BN. After the final heating step (1100 °C/24 h), significant changes are observed in the morphology of the BN product. While residual unstructured material, such as that shown in Figure 3 is observed, there also coexist two distinct, more ordered morphologies in the turbostratic samples. At this stage however, relative proportions of each of the morphologies vary widely between individual trials.

Figure 5 shows a region of distorted lamellar material, which might be thought to be consistent with the partially ordered layer structure found in turbostratic BN.

However, in addition to this lamellar BN, SEM also reveals a morphology composed of hollow, tubular structures. This is, to our knowledge, a previously unknown morphology for boron nitride, more traditional methods of production normally leading to unstructured or lamellar, platelike manifestations. The largest of these new tubular structures appear to be on the order of 3–4 μm in external diameter and approximately 50–100 μm in length. The tube walls appear to be of the order of a few hundred angstroms thick, with relatively smooth surfaces. There is no evidence of seams along the length of the tubes, nor does it appear that they are the result of "rolling up" of thin sheets, akin to the rolling of a cigar. Figure 6 shows a typical group of these tubular structures. It is of interest that the tubes appear to grow in a parallel orientation and possess at least one closed end. Indeed, most appear to have both ends closed. Where openings are seen in the tubes, the open ends appear to be relatively ragged, suggesting that the openings may be the result of fracture.

Transmission electron microscopy, coupled with electron diffraction proved an invaluable tool in illustrating the nature of the tube walls. Figure 7a shows a typical BN tube, with the highlighted area corresponding to the region illuminated by the electron beam to produce the diffraction pattern shown in Figure 7b. The diffraction rings can be indexed as the [002], [10], [004], and [110] reflections by reference to the XRD pattern of hexagonal boron nitride (*h*-BN)[17] and thus illustrate that both the bulk sample and a small area of a single tube wall possess similar diffraction characteristics. Selected area diffraction gave essentially identical results independent of morphology. (Indeed, SAD also indicated a greater degree of order in material prior to the final heating step than did XRD.)

It is noteworthy that only poor and very local ordering is observed by high-resolution TEM studies of the tube walls, as shown in Figure 8. This is entirely consistent with the diffraction phenomena observed. The interlayer (pseudographitic) spacing of approximately 3.5 Å may be clearly seen, as may grain boundaries between apparently randomly oriented ordered regions of tens of angstroms in diameter. TEM also revealed the presence of smaller tubular structures, with a typical diameter of around 0.15 μm. However, the wall thickness of these smaller tubes, around 300 Å, is similar to that found in the larger tubes found earlier by SEM. Most interestingly, in the vicinity of some of the smaller tubes were observed flatter, pseudocircular structures, or "corpuscles", shown in Figure 9. These corpuscular structures were of comparable diameter and wall thickness to tubes found nearby, and it is suggested that these may be starting points for the growth of the tubular structures.

Possible Mechanism for Tube Formation. It is possible that the corpuscular structures shown in Figure 9 are themselves a result of collapse at elevated temperatures of the shells observed in the amorphous material. Figure 4 shows a hollow particle (bubble) undergoing the type of collapse necessary to give the corpuscular structures. We might then imagine the corpuscles to the sites of tube growth, as suggested previously.[8] Thus it might appear that the formation of the hollow shells in the initial reaction is central to the ultimate formation of the novel tubular morphology, in that upon collapse, they might provide convenient nucleation centers for aggregation or sintering of small particles, thus facilitating an effective reduction of surface energy.

The formation of tubular structures from amorphous material by a type of sintering mechanism would necessarily require some mobility of the amorphous precursor at the requisite temperature, in this case 1100 °C. This might suggest that tube formation may require a relatively "local" supply of amorphous BN in the vicinity of the nucleation centers (or corpuscles), as BN might not be thought to be highly mobile at 1100 °C. This might also help explain the observation by SEM of domains of tubular structures coexisting with other morphologies in the turbostratic samples.[8]

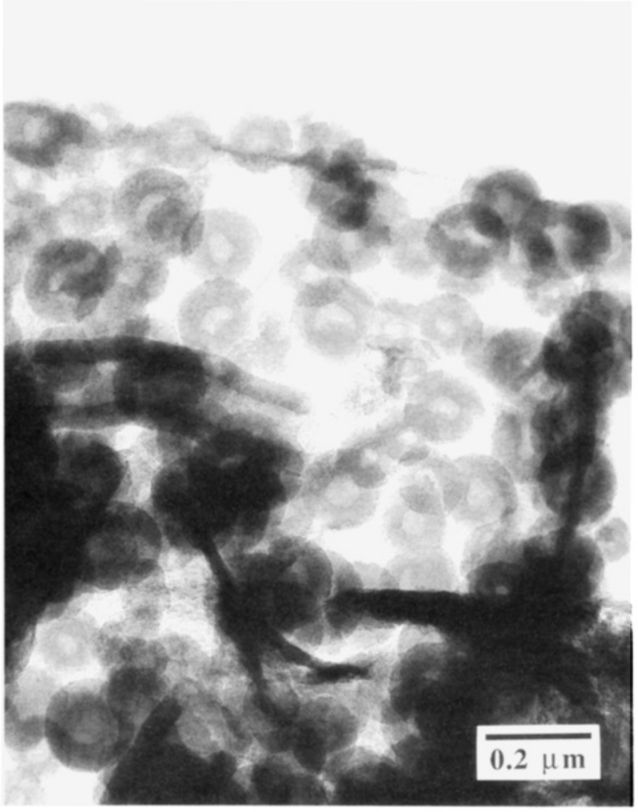

Figure 9. TEM image of corpuscular structures, suggested starting points for the growth of the hollow tubular morphology.[8]

As noted above, the largest of the tubes observed by SEM appeared to be of the order of 3–4 μm in diameter. No hollow shells or corpuscles of comparable diameter to these larger structures have been observed. However, tubes have been observed where the external diameter appears to change markedly along the tube's length. It is therefore possible that tubes of both most commonly observed diameters (ca. 0.15 μm and ca. 3 μm) are derived from the same source. Growth orthogonal to the corpuscle surface would lead to a tube of diameter comparable to that of the corpuscle. Alternatively, initial growth outward from the corpuscle edge, thereby increasing its diameter, followed by onset of orthogonal growth at some favorable point would lead to a tubular structure with larger diameter than that of the initially formed shell and corpuscle. In this regard, it is particularly interesting that a typical wall thickness of around 300 Å is common to both the larger and smaller tubes. It may be that this wall thickness is optimal for both surface energy reduction and heat transfer phenomena.

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