Simultaneous Crystallization of Diamond and Cubic Boron Nitride from the Graphite Relative BC_2N under High Pressure/High Temperature Conditions

Takayoshi Sasaki,*,† Minoru Akaishi,† Shinobu Yamaoka,† Yoshinori Fujiki,† and Tetsuo Oikawa‡

National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305, Japan, and JEOL, Ltd., 1418 Nakagami, Akishima, Tokyo 196, Japan

Received December 4, 1992. Revised Manuscript Received February 25, 1993

Graphitic BC_2N has been compressed with Co metal at a pressure of 5.5 GPa and temperatures of 1400–1600 °C. The principal resulting products were crystals (average dimension 3 μm) with cubiclike facets. The powder X-ray diffraction pattern revealed two kinds of cubic phase, in approximately equal amounts, which were identified as diamond and cBN on the basis of their lattice parameters. Microelemental analyses on individual crystal fragments by K-edge electron energy-loss spectroscopy confirmed this disproportionating crystallization scheme: half of the grains were composed of carbon-only signals of which gave fine-structure characteristic of sp^3 bonding and the other half gave spectra characteristic of sp^3 boron and nitrogen. The crystallization of cBN as well as diamond in the catalytic solvent of pure Co metal is observed here for the first time and is of relevance to the mechanism of the accepted catalytic action of cobalt on the hexagonal/cubic transformation.

Introduction

Carbon and its isoelectronic III–V compound, boron nitride, ordinarily occur in hexagonal (graphite and hBN) and cubic (diamond and cBN) polymorphs. Due to their extreme importance both in fundamental and practical aspects, they have been studied extensively. Close similarities in cell dimensions as well as crystal structural types between each pair of the two compounds[1] have stimulated the exploration of hybrid relatives of boron, carbon, and nitrogen, with the expectation of novel properties in them.

Several groups[2-9] have claimed syntheses of a so-called "BCN" graphite (formulated as $B_xC_yN_x$) by reacting three starting reactants or more, typically BCl_3, hydrocarbons, and NH_3. However, these synthetic strategies were inevitably complicated by the statistical probability of the resulting material containing graphite and hBN as well as the desired hybrids. An associated difficulty is that of distinguishing a genuine "BCN" material from an intimate mixture of graphite and hBN. Their diffraction patterns are substantially superimposable with each other, especially for the materials of low crystallinity which is generally the case in such preparations.

Recently a low-temperature process has been described[10] for the preparation of a graphitic material of composition BC_2N by the vapor-phase interaction of BCl_3 and CH_3CN. The product from the two reactants should be free from graphite and hBN contaminants provided the reaction is carried out at modest temperatures, where the skeleton of CH_3CN is never cleaved. The electric conductivity, thermal diffusivity, and intercalation capability of BC_2N have been studied.[10,11] Liu et al.[12] have discussed the electronic structure on the basis of pseudopotential local orbital calculations.

Although it is well-known that graphite and hBN are transformed into their denser forms in cubic structure by high pressure/high temperature (HP/HT) treatments,[13-18] there have been few reports aimed at syntheses of a "BCN" diamond from a "BCN" graphite. Badzian[19] carried out pioneer work in which the graphitic material $B_xC_yN_x$ (x/y

† National Institute for Research in Inorganic Materials.
‡ JEOL, Ltd.

(1) Grphite and hBN have hexagonal layer structures: Two-dimensional sheets, infinite arrays of contiguous hexagon rings, are stacked along the c axis. Only difference is the mode of sheet stacking: All atoms are eclipsed along c in hBN while the half are staggered in graphite. Graphite: hexagonal, $P6_3/mmc$, a = 2.463 Å, c = 6.714 Å (JCPDS No. 23-65). hBN: hexagonal, $P6_3/mmc$, a = 2.5044 Å, c = 6.656 Å (JCPDS No. 34-42). Diamond and cBN have virtually the identical structure, characterized by zinc blende type, except for the heteroatomicity for the latter. Diamond: cubic, $Fd3m$, a = 3.5667 Å (JCPDS No. 6-0675). cBN: cubic, $F43m$, a = 3.6158 Å (JCPDS No. 35-1365).

(2) Kosolapova, T. Ya.; Makarenko, G. N.; Serebryakova, T. I.; Prilutskii, É. V.; Khorpyakov, O. T.; Chernysheva, O. I. *Poroshk. Metall.* **1971**, *1*, 27.

(3) Badzian, A. R.; Niemyski, T.; Oppenheimer, S.; Olkusnik, E. *Khim. Svyaz. Poluprov. Polumetall.* **1972**, 362.

(4) Chen, S. H.; Diefendorf, R. J. *Proc., 3rd Int. Carbon Conf., Baden-Baden* **1980**, 44.

(5) Kaner, R. B.; Kouvetakis, J.; Warble, C. E.; Sattler, M. L.; Bartlett, N. *Mater. Res. Bull.* **1987**, *22*, 399.

(6) Moore, A. W.; Strong, S. L.; Doll, G. L.; Dresselhaus, M. S.; Spain, I. L.; Bowers, C. W.; Issi, J. P.; Piraux, L. *J. Appl. Phys.* **1989**, *65*, 5109.

(7) Saugnac, F.; Marchand, A. *C. R. Acad. Sci., Ser. 2* **1990**, *310*, 187.

(8) Saugnac, F.; Teyssandier, F.; Marchand, A. *J. Phys. IV* **1991**, *1*, C2-673.

(9) Besmann, T. M. *J. Am. Ceram. Soc.* **1990**, *73*, 2498.

(10) Kouvetakis, J.; Sasaki, T.; Shen, C.; Hagiwara, R.; Lerner, M.; Krishnan, K. M.; Bartlett, N. *Synth. Met.* **1989**, *34*, 1.

(11) Mitsuhashi, T.; Sasaki, T.; Arii, T.; Haneda, H.; Fujiki, Y. *Proc. JSTP* **1990**, *11*, 433.

(12) Liu, A. Y.; Wentzcovitch, R. M.; Cohen, M. L. *Phys. Rev. B* **1989**, *39*, 1760.

(13) Bovenkerk, H. P.; Bundy, F. P.; Hall, H. T.; Strong, H. M.; Wentorf, R. H., Jr. *Nature* **1959**, *184*, 1094.

(14) Wentorf, R. H., Jr. *J. Chem. Phys.* **1957**, *26*, 956.

(15) Wentorf, R. H., Jr. *J. Chem. Phys.* **1961**, *34*, 809.

(16) Nakano, S.; Ikawa, H.; Fukunaga, O. *J. Am. Ceram. Soc.* **1992**, *75*, 240.

(17) Flom, D. G.; DeVries, R. C.; Rees, W. G. *GE R and D Rep.* **1989**, 89CRD90.

(18) Hirano, S.; Yamaguchi, T.; Naka, S. *J. Am. Ceram. Soc.* **1981**, *64*, 734.

(19) Badzian, A. R. *Mater. Res. Bull.* **1981**, *16*, 1385.

0897-4756/93/2805-0695$04.00/0

= 15/85, 26/74, 40/60) was compressed under the conditions of 14.0 GPa and 3300 K. The direct transformation was chosen due to the failure of catalyzed conversion. The cubic nature of the product was based on diffraction rings diagnostic of microcrystalline material. The cubic substance was claimed to be a hybrid of diamond and cBN on the ground that its lattice parameter was intermediate and composition-dependent between those of diamond and cBN, following the Vegard's law.

The hexagonal-to-cubic transformation with the help of appropriate catalysts can proceed under relatively mild conditions (e.g., ~6 GPa and ~1500 °C) and can grow crystals of considerable size. For graphite to diamond, it has been established[13] that metals such as Co and Ni catalyze the conversion. On the other hand, the transformation from hBN to cBN is driven by alkali metals, alkaline-earth metals, and their nitrides, e.g., Ca_3N_2, Mg_3N_2, and Li_3N.[14-16] It has has been reported that cBN is also precipitated in metal alloys including Co–Al and Ni–Al.[17]

In this paper, we describe the Co-catalyzed phase transformation of the graphitic BC_2N mentioned above under the HP/HT conditions. Co metal was chosen as the catalyst because of the physical similarities of BC_2N and graphite. From this system, however, "BCN" diamond is not obtained. Instead, well-crystallized diamond and cBN are simultaneously produced.

Results

Figures 1 and 2 summarize scanning electron micrographs and powder X-ray diffraction (XRD) patterns for the material before and after the HP/HT treatment, respectively. The graphitic BC_2N of well-defined layerlike texture was transformed into cubiclike crystals of dimension <5 μm under all the conditions studied: 5.5 GPa, 1400 °C, 1500 °C, and 1600 °C.

The XRD pattern for the graphitic BC_2N gave broad lines indexable to $00l$ and hk reflections. This profile is very similar to that of turbostratic graphite; a sheet-stacking regularity was not developed even for the material annealed at 1800 °C. The compression changed the pattern drastically in which two kinds of cubic phases, comparable in yield, were detected. The refined cell parameters, listed in Table I, strongly suggest that one cubic substance is diamond and the other cBN. Although the different extinction rules appropriate for their space groups ought to distinguish between the diamond and cBN phases,[20] the electron diffraction photographs, as exemplified by the reciprocal lattice section of hhl^*, did not do so [compare Figure 3A(b) with 3B(b)]. This may be ascribed to plural reflection effect. On the other hand, the powder XRD pattern did support the distinction since the (200) line for diamond was absent.

An analytical electron microscopic study provided a straightforward support for the heterogeneous crystallization scheme. The parallel electron energy-loss spectra (PEELS) in the energy region attributable to K-edge loss can be classified into two groups. One exhibited only one signal, assignable to C, and the other gave two peaks for B and N as depicted in Figures 3A(c) and 3B(c). Each pattern was encountered approximately in equal possibility. This is consistent with the similar intensities of the corresponding XRD lines for the cubic phases. Simultaneous detection of all three elements in one grain was not observed although over 20 specimens were surveyed.

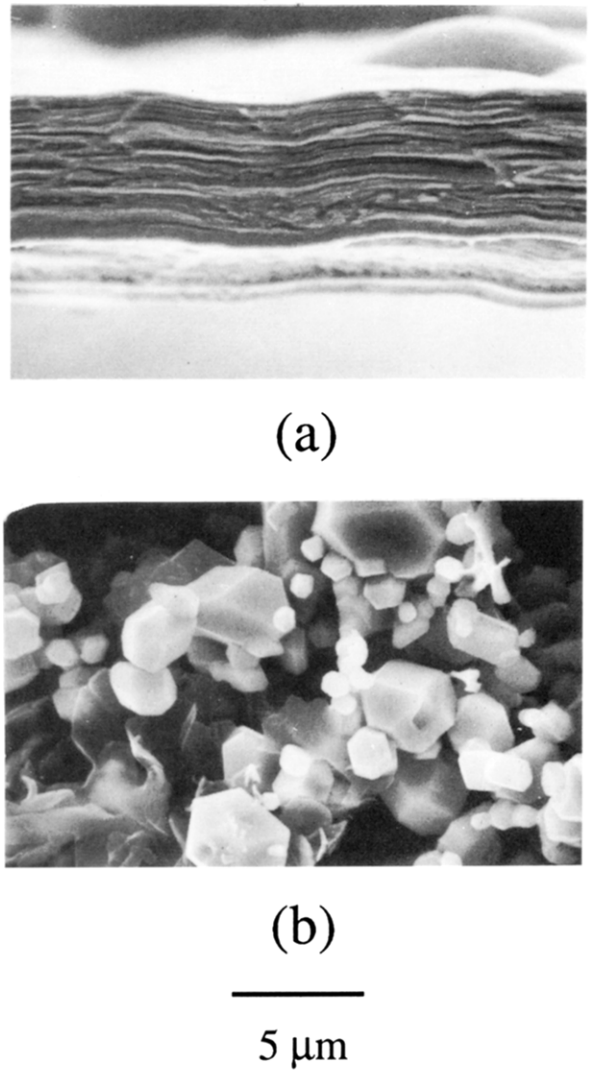

Figure 1. Scanning electron micrographs for the graphitic BC_2N (a) before and (b) after the HP/HT treatment. Pressure 5.5 GPa; temperature 1500 °C; duration 20 min.

The fine structures for the signals were very similar to those for diamond and cBN reported previously.[21] A prominent peak close to the K-edge onset for each element, designated by the symbol σ^* in Figures 3A(c) and 3B(c) (inset), is attributable to the excitation of a K-shell electron to the σ^* antibonding level. This, along with an absence of a π^* feature, supports the representation that all three elements are in adamantanic bonding, i.e., sp^3 hybridization, consistent with C in diamond and B and N in cBN.

Along with the cubic phases, some graphitic material was also detected both from X-ray and electron diffraction patterns. This is likely to be the filmlike material which is seen with the cubic crystals in Figure 1b. Its electron diffraction pattern consisted of hexagonal sharp spots, not rings of a diffuse nature as observed for the starting BC_2N. The PEELS analyses demonstrated a perfect

(20) The reflections of $0kl$ for $k + l \neq 4n$ and hhl for h (or l) $\neq 2n$ are absent for diamond besides the general extinction for the face-centered cubic lattice.

(21) Hosoi, J.; Oikawa, T.; Inoue, M.; Matsui, Y.; Endo, T. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *27*, 243.

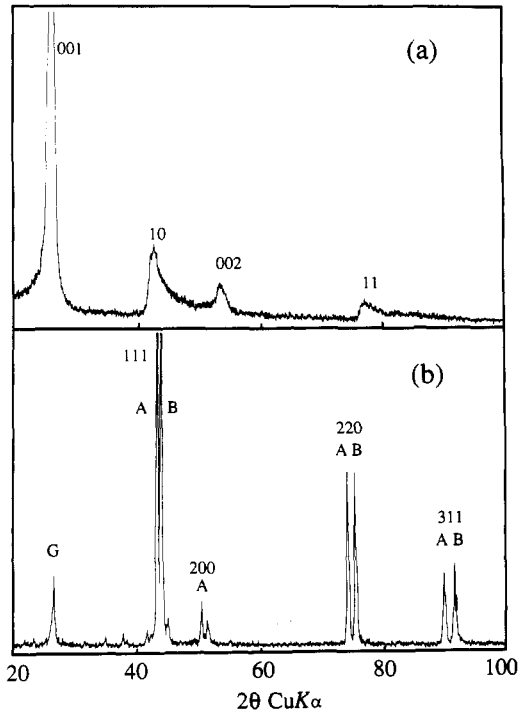

Figure 2. Powder XRD pattern for the graphitic BC_2N (a) before and (b) after the HP/HT treatment. Pressure 5.5 GPa; temperature 1500 °C; duration 20 min. The pattern in (a) is for the material deposited on a Ni metal chip at 850 °C and then annealed at 1800 °C under a N_2 gas flow. The symbols A, B, and G denote two kinds of cubic phase and a graphitic residue, respectively.

Table I. Lattice Constant (Å) for the Cubic Phases Obtained by the HP/HT Treatments[a,b]

	temp (°C)		
phase	1400	1500	1600
A	3.6162(3)	3.6169(4)	3.6162(3)
B	3.5656(5)	3.5660(3)	3.5662(5)

[a] Pressure 5.5 GPa; duration 20 min. [b] a = 3.5667 Å for diamond and a = 3.6158 Å for cBN.[1]

element separation (C and B/N) for every fragment, similar to the case for the cubic counterparts. This means that the graphitic BC_2N was entirely differentiated into the separate phases, graphite and hBN, by this HP/HT treatment.

In conclusion, the phase transformation caused by the compression may be formulated as

$$BC_2N(\text{graphitic}) \xrightarrow[\text{Co}]{\text{5.5 GPa, 1400–1600 °C}} \text{diamond} + \text{cBN} + (\text{graphite} + \text{hBN})$$

Discussion

It is of interest that cBN was crystallized in the Co metal solvent. The crystallization of cBN via Co itself has not been reported so far. Flom et al.[17] have reported that the phase transformation from hBN to cBN is facilitated in the metal alloy of Co–Al. However, the additive of Al is essential in this system, and this may be explained by the involvement of AlN in the nucleation of cBN.[18]

It has been believed that the diamond catalysts such as pure Ni and Co are not effective for the conversion from hBN to cBN. This implies that graphite is soluble in Co metal solvent while hBN is not. To confirm this, a 1/1 mechanical mixture of graphite and hBN was placed in the no. 4 position of the pressure vessel (see Figure 4) and was brought to the HP/HT conditions (5.5 GPa, 1500 °C). (Note that the nominal composition of this mixture is "BC_2N".) Powder XRD did not reveal cBN in the resulting product, which was identified as a mixture of diamond and a graphitic material, most likely unreacted hBN. The graphitic BC_2N, subject to the HP/HT treatment simultaneously in the same pressure vessel (no. 2 position), was crystallized into diamond and cBN. This difference suggests that the mingling of constituent elements (B, C, N) at an atomic level in the starting materials is essential to the growth of cBN crystals under the conditions applied here. Presumably the graphitic BC_2N exhibits some solubility in the Co metal. When the dissolved BC_2N crystallizes from the solvent, it evidently does so as to separate C and B/N phases, forming diamond and cBN together with their corresponding hexagonal relatives. These probably are thermodynamically preferred to their "BCN" hybrid forms. The comparable yields for diamond and cBN imply that some cooperative action operates in the crystallization.

From a viewpoint of synthesizing a "BCN" diamond, the catalytic solvents need to be avoided else disproportionation will occur, as evidently observed in this study. A direct transformation including shock-wave compression may be promising as demonstrated by Badzian,[19] although much more severe HP/HT conditions are required.

We also treated the graphitic BC_2N with one of cBN producing catalysts, Mg_3BN_3,[16] under the conditions of 6 GPa and 1600 °C. No change was observed. This indicates that BC_2N is the genuine "BCN" graphite, not simply a microcrystalline mixture of graphite and hBN, since the latter ought to have yielded cBN. Another noteworthy fact to be deduced from the observations above is that BC_2N is more like graphite rather than hBN with respect to the hexagonal/cubic transformation. This may be in line with similarities between BC_2N and graphite in electric conductivity and intercalation behavior: BC_2N exhibits a specific electric conductivity of 10–100 Ω^{-1} cm^{-1} at an ambient temperature.[10,11] (10^3–10^4 Ω^{-1} cm^{-1} for graphite while $<10^{-14}$ Ω^{-1} cm^{-1} for hBN). BC_2N undergoes reductive and oxidative intercalation.[10] (A similar reactivity or higher is shown for graphite,[22] while only the most powerful oxidizers such as $SO_3F^{\bullet}$ radical bring about intercalation of hBN.[23])

It is anticipated that "BCN" graphites form a diverse family of compounds, the properties of which will depend on their composition and the particular atomic arrangement of B, C, and N. Therefore, the findings for BC_2N may not be general for all "BCN" graphites. Perhaps each material will behave in a unique way under the HP/HT conditions. Such studies as these for other members of the B–C–N system may shed light upon the HP/HT-induced formation of diamond from graphite and cBN from hBN themselves.

Experimental Section

Reagents. BCl_3 of 99.999% purity or higher (Ube Industires, Ltd.) was used as supplied. CH_3CN of analytical grade was dried

(22) Dresselhaus, M. S.; Dresselhaus, G. *Adv. Phys.* **1981**, *30*, 139.
(23) Bartlett, N.; Biagioni, R. N.; McQuillan, B. W.; Robertson, A. S.; Thompson, A. C. *J. Chem. Soc., Chem. Commun.* **1978**, 200.
(24) Kobayashi, M.; Ichinose, A.; Einaga, H. *Yogyo Kyokaishi* **1976**, *84*, 513.
(25) Ichinose, A.; Einaga, H. *Yogyo Kyokaishi* **1975**, *83*, 465.

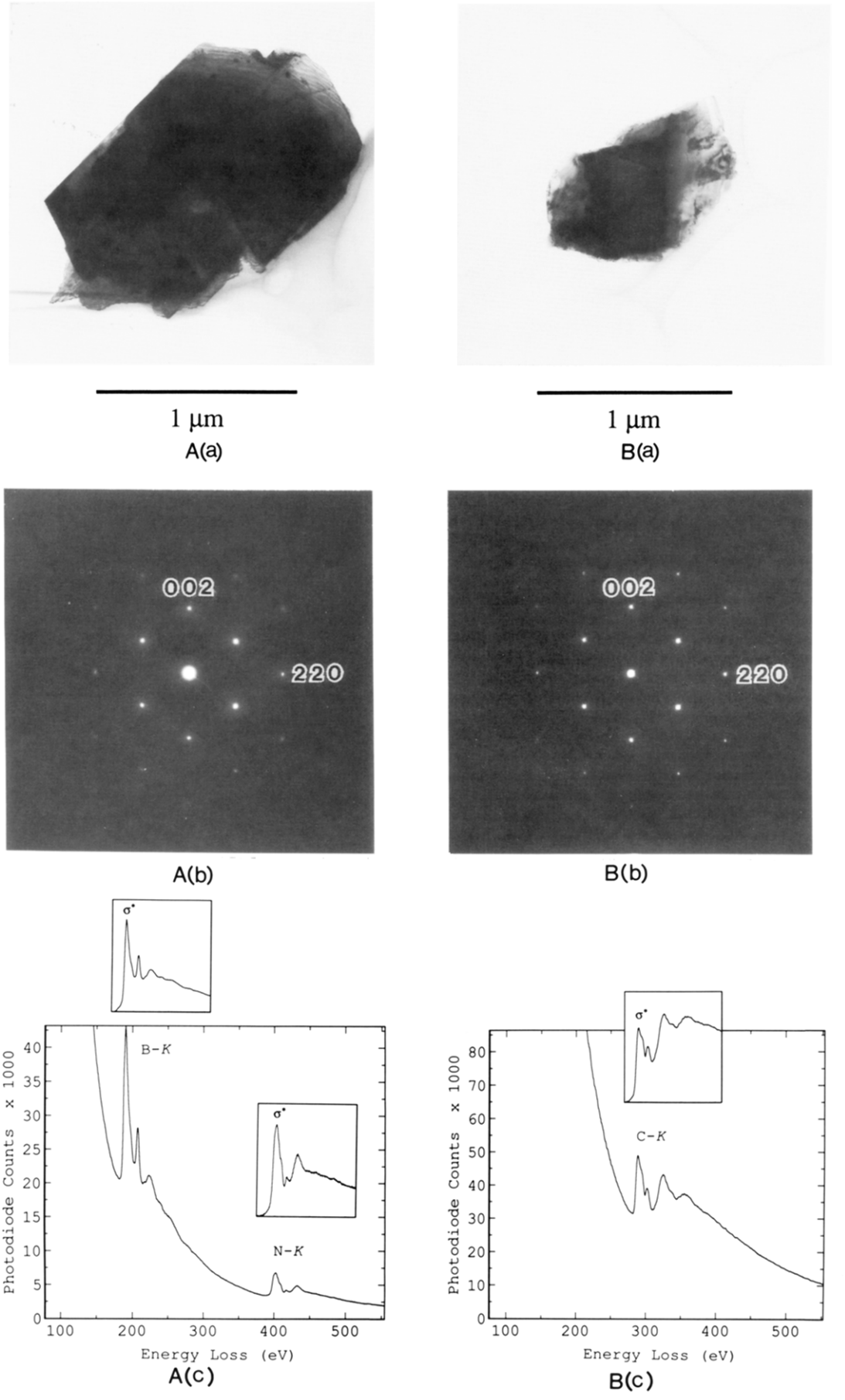

Figure 3. Two typical results of microanalyses on individual grains in the sample compressed at 5.5 GPa and 1500 °C. The labels A and B give (a) TEM image, (b) electron diffraction pattern of *hhl**, (c) K-edge electron energy-loss spectrum for the crystal fragments identified as cBN and diamond, respectively. The 002 and 00$\bar{2}$ spots in B(b) are to be absent according to the extinction rule.[20]

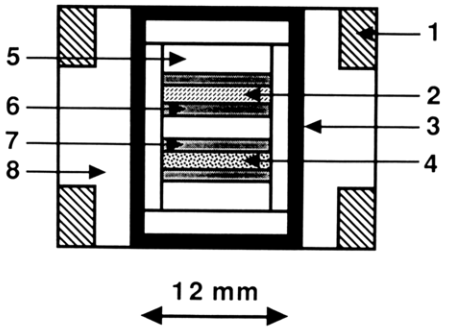

Figure 4. Sample assembly for the HP/HT treatments. 1, steel ring; 2, sample (ground BC_2N); 3, graphite heater; 4, reference material (graphite powder or graphite + hBN); 5, 8, NaCl + ZrO_2(10 wt %) as a pressure medium; 6, 7, pressed disk of Co metal powder.

Table II. Chemical Analysis Results for the Material Deposited at Different Temperatures[a]

preparation temp (°C)	B (wt %)	C (wt %)	N (wt %)
800	22.4	48.7	26.9
850	21.4	49.7	27.2
900	20.9	52.7	25.4
950	20.8	53.3	25.5
1000	20.1	53.9	24.9
calcd for BC_2N	22.13	49.19	28.68

[a] Analytical Procedures: Boron:[24] A weighed amount (~20 mg) of the material was decomposed by NaOH fusion at 400–500 °C, followed by aqueous decomposition of the melt. A weak acid $B(OH)_3$ formed by this procedure was changed into a strong acidic species of mannitol complex, which was then titrated by a standard NaOH solution. Carbon: The material (~10 mg) was inductively heated, using a LECO WR-12 analyzer, under O_2 gas flow with Cu and Fe metal powders as susceptors. The evolved CO_2 was determined by gas chromatography. Nitrogen:[25] The constituent nitrogen was converted into NH_3 by fusing the material (~20 mg) with NaOH pellets (~3 g) under a moist air flow. The NH_3 gas was absorbed into an acidic solution, which was volumetrically titrated.

with CaH_2 and then distilled before each use. It was transferred into the line of the reaction apparatus without being exposed to air. Graphite powder (325 mesh) was of spectroscopic grade (Nippon Carbon, Co.). Cobalt metal powder was of 99.99% purity. All the other chemicals used were of reagent grade.

Preparation of the Graphitic BC_2N. The vapors of BCl_3 (~60 Torr) and CH_3CN (~20 Torr) were carried separately by He gas and mixed in the reaction chamber inside a furnace (800–1000 °C). The former was controlled by diluting BCl_3 gas (1 atm) with He. The latter was set by bubbling He gas through CH_3CN(l) cooled with ice. The overall flow rate was regulated at 100 cm^3 min^{-1} by a STEC mass flow meters. The 12-h interaction resulted in a black monolithic deposit of 10–50-μm thickness, which was easily peeled off from a substrate of Ni metal chips.

X-ray and electron diffraction patterns revealed graphitelike turbostratic structure. Pseudohexagonal lattice parameters for the material prepared at 850 °C were a = 2.44 Å, c = 3.4 Å. These values are comparable to the unit cell dimensions of graphite and of hBN.[1] The absence of sheet-to-sheet registry makes the c dimension for BC_2N approximately half of those for graphite and hBN which have ABA stacking.

Chemical analyses (Table II) confirmed that the composition was approximately BC_2N although the samples produced at higher temperatures were slightly carbon-rich. The material deposited at 850 °C was used in the HP/HT experiments after annealing it at 1800 °C under a N_2 gas flow to eliminate any volatiles. No compositional change was observed by annealing up to this temperature.

HP/HT Treatments on the Graphitic BC_2N. Two sets of the sample (~200 mg), ground and embedded with pressed pellets of Co metal powder (~500 mg), were put in a pressure vessel whose assembly is illustrated in Figure 4. The system was subject to the HP/HT treatments (5.5 GPa, 1400, 1500, and 1600 °C) using a belt-type high-pressure-generating apparatus. After being held at those conditions for 20 min, it was quenched to the ambient environment.

In most of the experiments, one of the two sets of sample was BC_2N (no. 2 in Figure 4) and the other was graphite (no. 4). The latter was readily converted into diamond under the conditions above, confirming the effectiveness of the pressure and temperature.

The obtained product was immersed in a HCl solution to remove the Co metal. Some sample was further heated with a mixed acid of cH_2SO_4 and $cHNO_3$ to decompose graphitic residues.

Instruments. Powder XRD data were collected by a Rigaku Denki RAD-2B diffractometer with a monochromatized Cu Kα radiation (λ = 1.5405 Å). The lattice constant was refined by a least-squares analysis[26] for the data corrected by an internal Si standard.

Electron diffraction patterns were recorded by a JEM-2010 electron microscope operated at 200 kV. The energy-loss spectra (resolution 2 eV) were acquired using a Gatan 666-2K parallel energy analyzer attached to the JEM-2010.

An Akashi α-30 scanning electron microscope was employed to observe microscopic textures.

Acknowledgment. The authors are very grateful to Professor N. Bartlett, University of California, Berkeley, for his continuing interest and valuable suggestions for this study. We also thank Mr. Y. Yajima, National Institute for Research in Inorganic Materials, for his assistance with chemical analyses on the graphitic BC_2N.

(26) Appleman, D. E.; Evans, H. T., Jr. Report No. PB216188, U.S. Dept. of Commerce, National Technical Information Service: Springfield, VA, 1973.