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Synthesis of dense forms of B-C-N system using chemical-vapor-deposition/high-pressure process

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Composites made up of boron, carbon, and nitrogen were studied using a combination of chemical vapor deposition (CVD) and high pressure (HP) techniques. The CVD/HP process comprised deposition of $C_x(BN)_{1-x}$ composites where $x = 0.03$ or 0.8, followed by heat treatment of the deposited samples under pressures from 6 to 10 GPa using an octahedral-anvil apparatus. Also a sample prepared by nitriding of boron and carbon to compose $x = 0.5$ was studied up to 16 GPa. A diamond-type solid solution was obtained after the $C_{0.8}(BN)_{0.2}$ sample was treated at 10 GPa and 1600°C or at 8 GPa and 1700°C whereas the $C_{0.03}(BN)_{0.97}$ and $C_{0.5}(BN)_{0.5}$ samples exhibited decomposition into carbon and BN under all the P, T conditions studied. Sintered compacts consisting primarily of the cubic BN and carrying hardness with a maximum value of 54 GPa were obtained from $C_{0.03}(BN)_{0.97}$. © *2001 Kluwer Academic Publishers*

1. Introduction

Carbon and boron nitride are both very intriguing materials, being similar to each other in the physical and mechanical properties as well as the phase relations. In particular, the cubic forms, diamond and zincblende-type BN (*z*-BN), are known to be the hardest materials ever known. Also, they have the highest thermal conductivities. For such excellent properties, there occurred interest in synthesizing alloys, or solid solutions, of diamond and *z*-BN. The basic idea to obtain such materials is to apply high pressure to the graphitic form, similar to the synthesis of diamond and *z*-BN.

In 1981 Badzian first reported high-pressure synthesis of cubic C-BN at 14 GPa and 3300 K [1]. About a decade was needed before the relevant studies were made extensively [2–8]. The experimental results have been rather controversial, however. Some of the studies have reported synthesis of ternary compounds [1, 3, 4, 6] or solid solution of carbon and BN [5], while decomposition into a mixture of diamond (or graphite) and *z*-BN has also been observed [2, 3, 7, 8]. These experiments have employed BC_2N (i.e., $C_{0.67}(BN)_{0.33}$) as the starting material in many cases [2–4], eventually similar to all the theoretical calculations [9–15].

In this regard, the amounts of boron and nitrogen incorporated into diamond as substitutional atoms do not exceed an order of 10^3 ppm and, hence, simultaneous addition of boron and nitrogen to diamond may be basically difficult [16]. Thus, it would be practical to deal with low BN concentration. Along this line, we have studied a sample with a composition $C_{0.8}(BN)_{0.2}$ in this work. Another issues to be noted are that most of the previous experiments have dealt with a single composition in $C_x(BN)_{1-x}$ (actually $C_{2x}(BN)_{1-x}$ [2–4, 6]) system and that only a single pressure has been studied in each experiment [1–4, 6–8]. Here in this work, $C_{0.03}(BN)_{0.97}$ and $C_{0.5}(BN)_{0.5}$ were also studied and the pressure covered has been wide, ranging from 6 to 16 GPa. Two of the three starting materials were prepared by chemical vapor deposition (CVD) and all were subjected to high pressure-high temperature (HP-HT) conditions. The combination of CVD and HP techniques (CVD/HP process) has been shown to be feasible for inventing novel ceramic composites [17, 18], and the process has also been applied to open a new route for synthesizing *z*-BN [19, 20].

2. Experimental procedure

The CVD technique was employed to prepare two of the C-BN starting materials, $C_{0.8}(BN)_{0.2}$ and $C_{0.03}(BN)_{0.97}$. A mixture of BCl_3 and CH_4 was introduced into a reaction chamber with aid of carrier gases NH_3 and H_2. The samples were deposited on a graphite plate which was heated to 1200–1900°C. Preparation of $C_{0.5}(BN)_{0.5}$ sample was done by nitriding of a mixture of amorphous

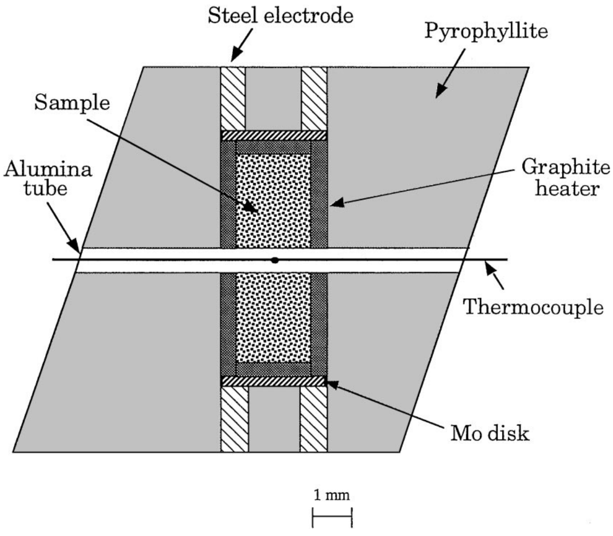

Figure 1 Cross-sectional view of octahedral sample cell.

boron and carbon in NH_3 atmosphere [21]. All the samples were turbostratic [22] in structure as judged from x-ray diffraction profiles. The compositions were estimated from elementary analysis.

Each sample was encapsuled in a graphite tube which in turn was placed in a hole provided in an octahedral sample cell made of pyrophyllite, Fig. 1. The sample cell was pressurized with an octahedral anvil apparatus [23]. The pressure generated was estimated from a calibrated relation obtained from separate experiments using resistance-related fixed points [24, 25]. At each pressure, the sample was heated to a targeted temperature by passing an alternating current through the graphite tube. The temperature was known by a Pt-Pt/Rh(10%) thermocouple reading. After prolongation of 10 min at the targeted temperature, the sample was rapidly cooled (at a rate of 10^2–10^3 °C/S) to room temperature and the pressure was released in order to retrieve the sample to the ambient conditions. The retrieved samples were subjected to x-ray diffraction with reference to commercially obtained synthetic diamond and *z*-BN powders. A limited number of samples were analysed with soft x-ray emission spectroscopy. For samples retrieved as sintered compacts, hardness measurements were undertaken with an applied load of 300 gr.

3. Results and discussion

3.1. $C_{0.8}(BN)_{0.2}$ sample

Fig. 2 shows evolution of x-ray-diffraction patterns of the $C_{0.8}(BN)_{0.2}$ sample after heat treatment at 1600°C at different pressures. The starting sample gives two strong lines at angles 26.0° and 53.8° which are respectively lower than the (002) and (004) lines of graphite or graphite-type BN (*g*-BN). The unsplitting of the two lines suggests that these are attributed to the (002) and (004) lines of turbostratic form of composited C-BN. At 6 and 7 GPa, there appears an asymmetric peak at 42.4°, which is assignable to the (10) band of the composite, suggesting that two-dimensional ordering is achieved. Elevation of pressure to 8 GPa causes an appearance of the graphite (100) line at 41.8° and *z*-BN (111) line at 43.3°, indicating that the composite has undergone decomposition. The formation of *z*-BN upon decomposition can be interpreted by the fact that, above about 6 GPa, *z*-BN is readily formed from amorphous [26] or from turbostratic [18] state without catalyst. On the other hand, the appearance of turbostratic carbon, instead of diamond, is attributed to the large excess pressure required to obtain diamond without presence of catalyst [27]. This should be compared with the experiment of Sasaki *et al.* who, with the presence of Co, obtained from BC_2N a mechanical mixture of diamond and *z*-BN at a pressure as low as 5.5 GPa [2].

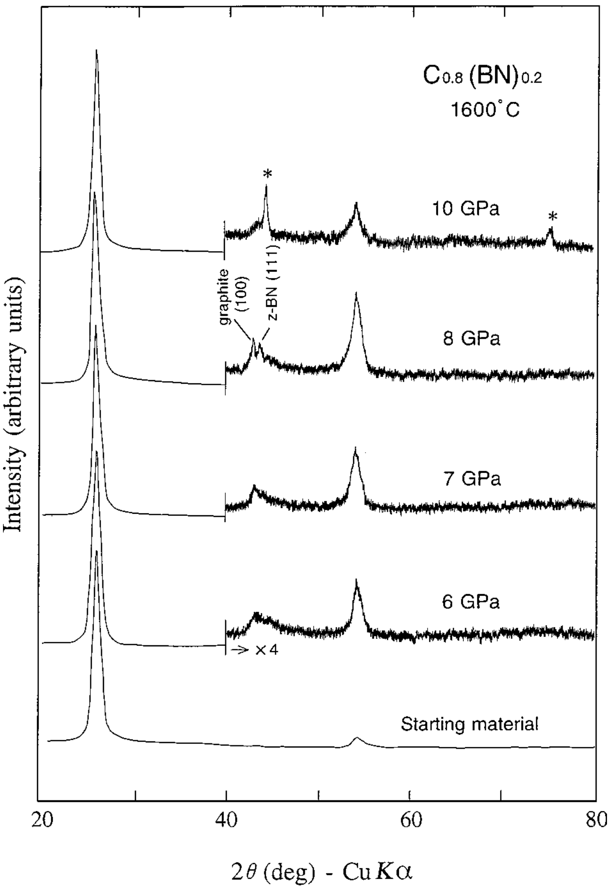

Figure 2 X-ray-diffraction patterns of the $C_{0.8}(BN)_{0.2}$ sample. See text for the asterisk.

At 10 GPa in Fig. 2, two new lines appear at angles labeled by asterisk whereas the graphite (100) and *z*-BN (111) lines have almost disappeared. The *d* spacings of the new lines, 2.064 Å and 1.265 Å, are respectively between the (111) and (220) lines of *z*-BN and diamond, indicating that a solid solution of C-BN system in the cubic diamond-like form was synthesized at 10 GPa and 1600°C. A similar result was obtained from the sample treated at 8 GPa and 1700°C. The disappearance of graphite and *z*-BN suggests that the cubic solid solution was formed by recombination of the two species, although our separate experiment indicated that simply subjecting a mixture of graphite and *z*-BN (and also a mixture of diamond and *z*-BN or a mixture of diamond and *g*-BN) under the same conditions did not yield the solid solution. The disappearance of *z*-BN could not be owing to a phase transition, for instance to *g*-BN or

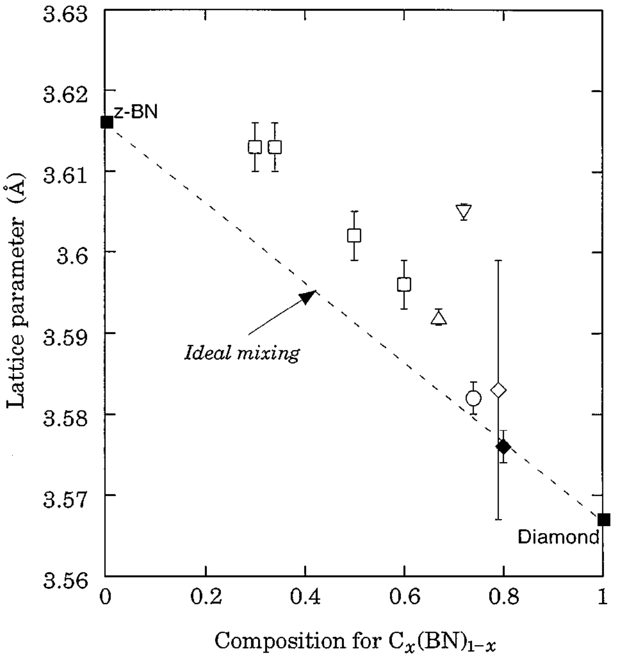

Figure 3 Lattice parameters of the cubic B-C-N system. ♦:This study, ○ : Ref. 1, ▽:Ref. 3, △:Ref. 4, □:Ref. 5, ◇:Ref. 6.

other polymorphs, because this form is thermodynamically stable under the pertinent conditions.

From the *d* spacings of the two solid solution products, a lattice parameter of 3.576 ± 0.002 Å was deduced for the cubic diamond-like structure. This is plotted in Fig. 3 against the composition for $C_x(BN)_{1-x}$ together with other experiments [1, 3–6]. Within the experimental uncertainty, our data virtually falls on the line of ideal mixing, hence following Vegard's law [28]. In other experiments [3–6], a significant expansion of the lattice from the ideal mixing occurs and this has been interpreted by local stress arising from the difference between the B-N and C-C bond lengths [4] or by nonideal volume model [5]. No interpretation in terms of possible change in the composition or of imperfection in the diamond-type structure has been made although such can be readily caused by the HP-HT treatment.

Fig. 4 shows x-ray boron *K*- and carbon *K*-emission band spectra from the 10 GPa-1600°C sample. The spectrum of Fig. 4a can be interpreted on the basis of *z*-BN owing primarily to the absence of a shoulder on the higher-energy side of main peak [29, 30], although the energy of the main peak located at 181.4 eV is lower than that of *z*-BN (182.5 eV) but is close to that of *g*-BN (181.5 eV) [29, 30]. Also, the absence of the high-energy satellite which should appear at ~191 eV [29, 30] is in favor of this interpretation because this satellite is only prominent when boron is three-fold coordinated [31]. The carbon *K* spectrum, Fig. 4b, is similar to that of turbostratic carbon with a peak located at about 276 eV [32, 33] and is differnt from that of diamond [32–34]. This is not surprizing because the turbostratic form remains abundantly in the sample, as demonstrated by the persistence of the strong line at about 26° in the x-ray diffraction pattern (Fig. 2).

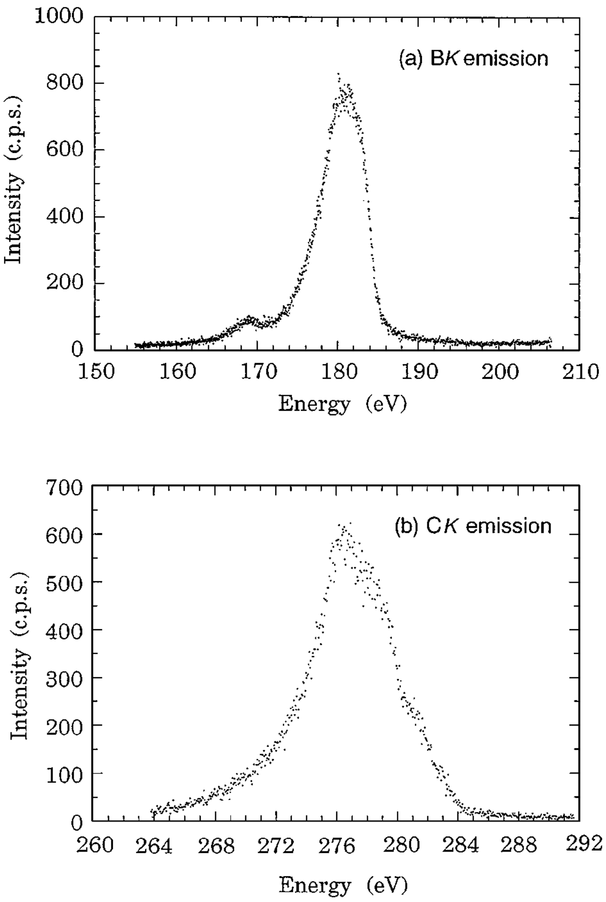

Figure 4 Soft x-ray-emission spectra from the $C_{0.8}(BN)_{0.2}$ sample treated at 10 GPa and 1600°C. (a) Boron *K*, (b) carbon *K*.

3.2. $C_{0.5}(BN)_{0.5}$ sample

This sample was studied up to 16 GPa while the temperature was held at 1600°C. Decomposition into carbon and BN almost in equal amounts was observed under all the conditions studied. The structure of the carbon upon decomposition was turbostratic throughout while the structure of the BN differed according to the pressure regime. It was the graphite-type below about 8 GPa and the zincblende-type at pressures greater than 10 GPa.

The appearance of *z*-BN in coexistence with turbostratic carbon above 10 GPa is similar to the behavior of the $C_{0.8}(BN)_{0.2}$ sample exhibited at 8 GPa at the same temperature. A different point is that no solid solution was formed from this $C_{0.5}(BN)_{0.5}$ sample under the same condition (10 GPa, 1600°C) as the $C_{0.8}(BN)_{0.2}$ sample was studied. Another point in difference was the appearance of *g*-BN from the $C_{0.5}(BN)_{0.5}$ sample at lower pressures, whereas it was skipped in the $C_{0.8}(BN)_{0.2}$ sample. These differences may be ascribed to the greater interaction between the carbon and BN, arising from the larger content in BN.

3.3. $C_{0.03}(BN)_{0.97}$ sample

X-ray-diffraction patterns of the $C_{0.03}(BN)_{0.97}$ sample after heat treatment at 1600°C at various pressures are shown in Fig. 5. The diffraction pattern of the starting material is somewhat different from that of the $C_{0.8}(BN)_{0.2}$ sample in that the (002) line is accompanied by a shoulder and that there appears an asymmetric

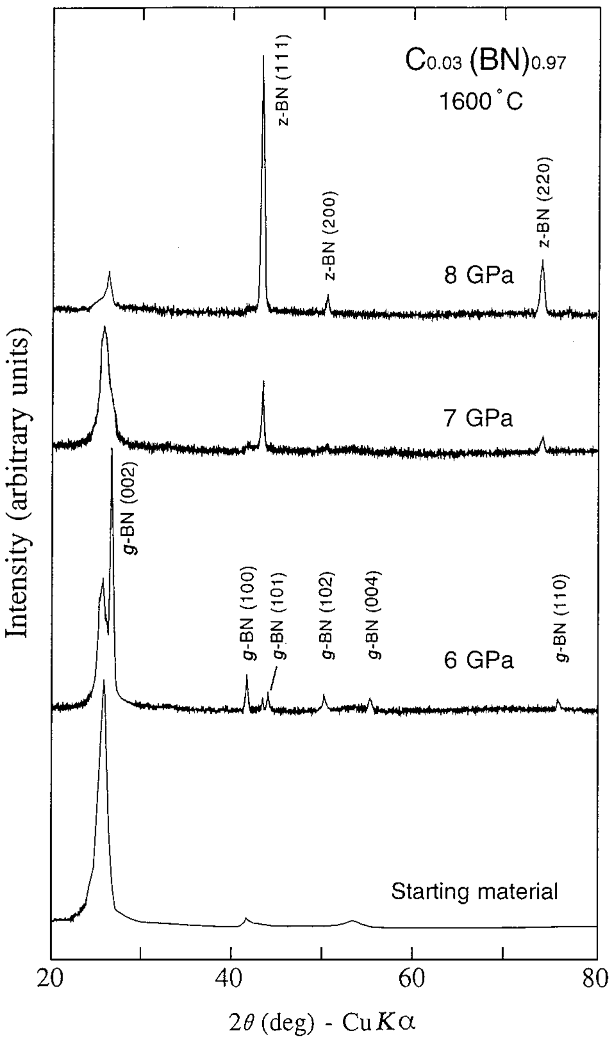

Figure 5 X-ray-diffraction patterns of the $C_{0.03}(BN)_{0.97}$ sample.

peak at ~42°. At 6 GPa the (002) line of *g*-BN appears, together with some other lines of *g*-BN, indicating that BN is decomposed from the starting sample. Although the state of carbon at this pressure is difficult to know owing to the small content in the starting sample, it is likely that the separation of the BN is associated with separation of carbon from the composite. At 6 GPa, in addition, the (111) line of *z*-BN is perceivable between the (100) and (101) lines of *g*-BN. Upon increasing the pressure to 7 GPa, the (002) line of *g*-BN merges into the turbostratic (002) line and other *g*-BN lines loose their intensities, whereas the (111) line of *z*-BN grows. The (200) and (220) lines of *z*-BN are also clearly observed. These suggest that the transition of *g*-BN into *z*-BN takes place at this pressure. At 8 GPa, the *z*-BN (111) line becomes predominant. No graphite or diamond is observed in any of these patterns. This is because the small content of carbon does not allow to detect such lines if they were formed.

By joining results from other series of experiments to the 1600°C series, the lowest bound for the formation of *z*-BN from the $C_{0.03}(BN)_{0.97}$ sample was delineated as shown by the solid line on a pressure-temperature diagram in Fig. 6. This line is shifted by about 600°C from the case of turbostratic BN being free of carbon (dotted line) [18]. The upward shift of the boundary may be ascribed to an extra energy required to break the C-B and C-N bonds in the $C_{0.03}(BN)_{0.97}$ composite, in addition to the energy needed for formation of *z*-BN. The absence of catalyst in these systems places the two lines apart from the thermodynamic equilibrium between *g*-BN and *z*-BN (dash-dotted line in Fig. 6) [35].

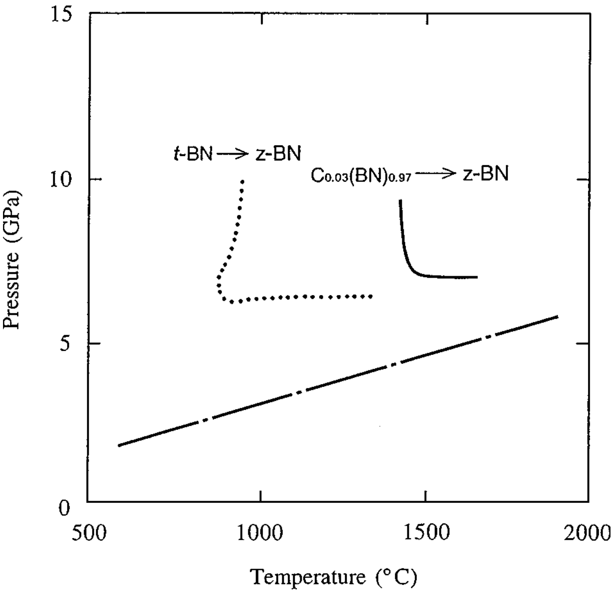

Figure 6 Reaction boundary (solid line) for the $C_{0.03}(BN)_{0.97}$ sample in comparison to turbostratic BN (dotted line, Ref. 18). *z*-BN can be formed at the top-right sides of the boundaries. The straight dash-dotted line is the thermodynamic equilibrium between *g*-BN and *z*-BN (after Ref. 35).

Many of the $C_{0.03}(BN)_{0.97}$ samples after being treated under HP-HT conditions were retrieved as sintered compacts, carrying micro Vicker's hardness as shown in Fig. 7. A general trend is that the hardness increases with an increase in either the pressure or temperature under which the sample was treated. The hardness of the 7 GPa sample is close to those of *z*-BN compacts sintered with addition of metallic or ceramic binders [36]. The sintered compacts obtained at 8 GPa exhibit

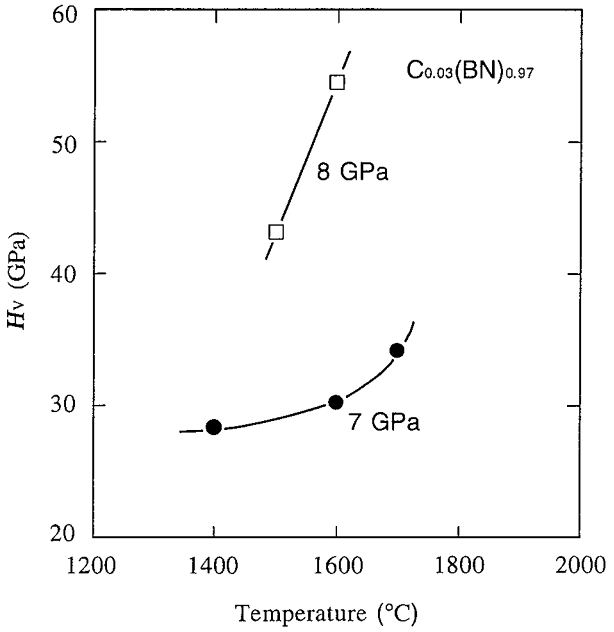

Figure 7 Micro Vicker's hardness of the $C_{0.03}(BN)_{0.97}$ sample with respect to the treated pressure and temperature.

higher hardness comparable to that of sintered *z*-BN without using binder [36], suggesting that direct bonding is achieved among the *z*-BN grains.

3.4. Stability of C-BN or B-C-N

The present study on three different samples in the $C_x(BN)_{1-x}$ system has shown that decomposition into carbon and BN can occur in each sample at HP-HT. The structure of the carbon after the decomposition is turbostratic or graphite, while either the low-pressure graphite-type or the high-pressure zincblende-type appears as the BN species, depending on the P, T conditions. Such a decomposition has been also observed when BC_4N (the same composition as the $C_{0.8}(BN)_{0.2}$ sample in the present study) was heated at 6.6 GPa [7, 8]. In the BC_2N system, decomposition into diamond and *z*-BN was observed with [2] and without [3] catalyst. These observations show that a mixture of decomposed phases is thermodynamically stabler than the B-C-N ternary compounds or C-BN solid solutions. The observed decomposition is in harmony with the theory of Lambrecht and Segall showing that alloys of diamond and *z*-BN are in principle metastable towards phase separation [11].

However, a solid solution of diamond and *z*-BN was eventually formed in the $C_{0.8}(BN)_{0.2}$ in this study and, as shown in Fig. 3, there have appeared a number of experiments reporting the formation of cubic ternary compounds [1, 3, 4, 6] or solid solutions [5]. It appears from Fig. 3 that getting the dense phases of B-C-N system is easier when samples with higher carbon concentration are employed. We also note that the samples in some of these studies were instantaneously heated by flash or laser [1, 5, 6]. Such techniques can achieve nonequilibrium process, permitting the rise of temperature very rapid, the duration of high temperature short, and the cooling speed high. Similar conditions can be met by the shock wave technique [4]. Besides, one of the flash heating experiments is believed to have melted the sample under study [6], presumably reaching temperatures beyond the miscibility gap between diamond and *z*-BN [11]. Exceptions to these are our study and the experiment of Nakano *et al.* [3], showing that synthesis of cubic B-C-N system without employing the nonequilibrium process is also possible.

Not shown in Fig. 3 but of importance is the pressure studied. Again except for the studies of ours and Nakano *et al.* [3], pressures applied have been greater than 15 GPa. In this regard, a first-principles calculation has suggested that, at a pressure of 11 GPa, graphite-type BC_2N would transform into a denser form which is γ-form possessing a rhombohedral configuration [15]. Application of pressure greater than 10 GPa may provide a greater chance for the formation of ternary compounds or solid solutions, irrespective of the mode of heating the sample.

The present findings and considerations, in conjunction with the earlier studies [1–8], suggest that the dense forms of B-C-N system can be obtained from samples with high carbon centent, at pressures beyond 10 GPa, preferably employing nonequilibrium processes and beyond the melting points of carbon and BN. Although the latter two issues were not filled in this study, the synthesis of the solid solution was achieved. The approach of the solid solution to ideal mixing could be ascribed to the equilibrated solid state process employed here. The quenching of the synthesized product in spite of the significantly lower speed of cooling (see the experimental section) than that of nonequilibrium processes appears to be enabled by the large kinetic barriers hindering the solid solutions from decomposition [11].

4. Conclusions

The study of three $C_x(BN)_{1-x}$ samples under a wide range of pressure and temperature conditions has revealed that the products can be governed by the composition of the starting samples, by the pressure, and by the temperature as well, as detailed below.

(1) Diamond-like form of C-BN solid solution was obtained from $C_{0.8}(BN)_{0.2}$ after being treated at 10 GPa and 1600°C or at 8 GPa and 1700°C. The lattice parameter (3.576 ± 0.002 Å), when plotted against the composition, falls on the ideal mixing of diamond and *z*-BN. Under some other P, T conditions, this sample decomposed into a mixture of graphite (or turbostratic carbon) and *z*-BN.

(2) From $C_{0.5}(BN)_{0.5}$, turbostratic carbon and BN were formed under pressures up to 16 GPa and at a temperature of 1600°C. The structure of BN was graphite-type (*g*-BN) below 8 GPa and zincblende type (*z*-BN) above 10 GPa.

(3) Decomposition was also observed in $C_{0.03}(BN)_{0.97}$, resulting in formation of either *g*-BN or *z*-BN. The formation of *z*-BN that occurred under combined conditions of pressure greater than 7 GPa and temperature higher than 1400°C was accompanied by sintering to yield compacts with micro Vicker's hardness of 28–54 GPa.

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References

1. A. R. BADZIAN, *Mater. Res. Bull.* **16** (1981) 1385.
2. T. SASAKI, M. AKAISHI, S. YAMAOKA, Y. FUJIKI and T. OOSAWA, *Chem. Mater.* **5** (1993) 695.
3. S. NAKANO, M. AKAISHI, T. SASAKI and S. YAMAOKA, *ibid.* **6** (1994) 2246.
4. Y. KAKUDATE, M. YOSHIDA, S. USUBA, H. YOKOI, S. FUJIWARA, M. KAWAGUCHI, K. SAKO and T. SAWAI, *Trans. Mater. Res. Soc. Jpn.* **14** (1994) 1447.
5. E. KNITTLE, R. B. KANAR, R. JEANLOZ and M. L. COHEN, *Phys. Rev. B* **51** (1995) 12149.
6. H. KAGI, I. TSUCHIDA, Y. MASUDA, M. OKUDA, K. KATSURA and M. WAKATSUKI, in Proc. XVth AIRAPT Int'l Conference, edited by W. A. Trzeciakowski (World Scientific, Singapore, 1996) p. 258.
7. V. L. SOLOZHENKO, V. Z. TURKEVICH and T. SATO, *J. Amer. Ceram. Soc.* **32** (1997) 3239.

8. V. L. SOLOZHENKO, *Eur. J. Solid State Inorg. Chem.* **34** (1997) 797.
9. A. Y. LIU, R. M. WENTZKOVITCH and M. L. COHEN, *Phys. Rev. B* **39** (1989) 1760.
10. J. P. LAFEMINA, *J. Phys. Chem.* **94** (1990) 4346.
11. W. R. L. LAMBRECHT and B. SEGALL, *Phys. Rev. B* **47** (1993) 9289.
12. Y. MIYAMOTO, M. L. COHEN and S. G. LOUIE, *ibid.* **52** (1995) 14971.
13. H. NOZAKI and S. ITOH, *J. Phys. Chem. Solids* **57** (1996) 41.
14. *Idem*., *Phys. Rev. B* **53** (1996) 14161.
15. Y. TATEYAMA, T. OGITSU, K. KUSAKABE, S. TSUNEYUKI and S. ITOH, *ibid.* **55** (1996) R10161.
16. R. C. DEVRIES, in "Diamond and Diamond-Like Films and Coatings," edited by R. E. Clausing, L. L. Horton, J. C. Angus and P. Koidl (Plenum, New York, 1991) p. 151.
17. A. ONODERA, N. TAKAHASHI, H. YOSHIHARA, H. NAKAE, Y. MATSUNAMI and T. HIRAI, *J. Mater. Sci.* **25** (1990) 4157.
18. H. YOSHIHARA, A. ONODERA, K. SUITO, H. NAKAE, Y. MATSUNAMI and T. HIRAI, *ibid.* **25** (1990) 4595.
19. A. ONODERA, K. INOUE, H. YOSHIHARA, H. NAKAE, T. MATSUDA and T. HIRAI, *ibid.* **25** (1990) 4279.
20. M. UENO, K. HASEGAWA, R. OSHIMA, A. ONODERA, O. SHIMOMURA, K. TAKEMURA, H. NAKAE, T. MATSUDA and T. HIRAI, *Phys. Rev. B* **45** (1992) 10226.
21. T. YA. KOSOLAPOVA, G. N. MAKARENKO, T. I. SEREBRYAKOVA, É. V. PRILLUTSUKI, O. T. KHORPYAKOV and O. I. CHERNYSHEVA, *Porosh. Metall.* **97** (1971) 27.
22. J. THOMAS, JR., N. E. WESTON and T. E. O'CONNER, *J. Am. Chem. Soc.* **84** (1963) 4691.
23. A. ONODERA, *High Temp. High Press.* **19** (1987) 579.
24. A. OHTANI, S. MIZUKAMI, M. KATAYAMA, A. ONODERA and N. KAWAI, *Jpn. J. Appl. Phys.* **16** (1977) 1843.
25. A. ONODERA and A. OHTANI, *J. Appl. Phys.* **51** (1980) 2581.
26. H. SUMIYA, K. ISEKI and A. ONODERA, *Mat. Res. Bull.* **18** (1983) 1203.
27. F. P. BUNDY, *Carbon* **34** (1996) 141.
28. L. VEGARD, *Z. Phys.* **5** (1921) 17.
29. V. A. FOMICHEV and M. A. RUMSH, *J. Phys. Chem. Solids* **29** (1968) 1015.
30. G. HANKE, M. KRAMER and K. MÜLLER, in "Synthesis and Preparation of Boron Nitride," edited by J. J. Pouch and S. A. Alterovitz (Trans Technical Publications, Zürich, 1990) p. 207.
31. S. LUCK and D. S. URCH, *Phys. Scr.* **41** (1990) 970.
32. D. W. FISCHER and W. L. BAUN, *J. Chem. Phys.* **43** (1965) 2075.
33. E. Z. KURMAEV, S. N. SHAMIN, K. M. KOLOBOVA and S. V. SHULEPOV, *Carbon* **24** (1986) 249.
34. J. E. HOLLIDAY, *J. Appl. Phys.* **38** (1967) 4720.
35. N. SIROTA and N. A. KOFMAN, *Sov. Phys. Dokl.* **24** (1979) 1001.
36. H. SUMIYA, S. UESAKA and S. SATOH, in Proc. 6th NIRIM Int'l Symp. Advanced Materials (NIRIM, Tsukuba, 1999) p. 13.

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