

## Shock synthesis of a hybrid of diamond and cubic boron nitride<sup>†</sup>

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A hybrid of diamond and cubic boron nitride has been synthesized with a shock compression technique. The X-ray powder diffraction measurements of recovered specimens show that the shock compression makes a graphitic compound composed of B, C and N transform to a cubic phase, while a mechanical mixture of graphite and hexagonal boron nitride transforms to three phases, diamond, cubic and wurtzite forms of boron nitrides, under the same condition. The lattice constant of the cubic phase is  $0.3605 \pm 0.0001$  nm which is between those of diamond and cubic boron nitride. There is no evidence of long range order of atomic arrangement in the lattice of diamond structure.

### 1. INTRODUCTION

For the mechanical and the electronic applications, much concern has been given to diamond and cubic boron nitride because of their promising properties: large bulk moduli and hardnesses, high melting temperatures, high thermal conductivities, chemical inactivities, and moreover, wide band gaps. Carbon and boron nitride (BN) systems have very similar phase diagrams to each other[1,2]; graphitic hexagonal BN(hBN), wurtzite BN (wBN) and cubic BN (cBN, zinc-blende type) corresponds to graphite, hexagonal and cubic diamonds, respectively. In addition to this similarity, small difference of lattice constants between diamond and cBN makes us anticipate that solid solutions of diamond and cBN should exist even though they might be thermodynamically unstable at ambient conditions. Properties

of such solid solutions may be similar to diamond and cBN, and may be able to be tailored by varying their compositions, as shown in a recent theoretical study[3].

Difficulty to prepare the hybrids of diamond and cBN lies in the fact that both diamond and cBN are stable only at high pressures and high temperatures[1,4]. Indeed in 1981, Badzian[5] reported the synthesis of the hybrids of diamond and cBN by using a static high pressure and high temperature technique (14 GPa, 3600 °C) starting from graphitic layered compounds composed of B, C and N. On the other hand a recent report[6] shows that graphitic  $BC_2N$  transforms into two kinds of cubic phases, diamond and cBN, by using a similar static technique, but at lower temperatures (1400–1600 °C).

Shock compression techniques with which we can easily obtain higher pressures and higher temperatures than those with static methods are often employed to quench high pressure and high temperature phases, such as diamond[7] and cBN

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[8,9]. In this report results of experiments on phase transition of a graphitic BN-C compound to the hybrids of diamond and cBN with a shock compression technique are presented.

## 2. EXPERIMENTAL

Graphitic BN-C employed as a starting material in this study was prepared as follows [6,10]. Acetonitrile( $\text{CH}_3\text{CN}$ ) vapor carried by nitrogen gas and boron trichloride( $\text{BCl}_3$ ) gas were introduced into a fused quartz tube the central zone of which was heated at  $1000^\circ\text{C}$ . Black powder of BN-C was produced on the wall of the tube in the downstream side of the hot zone as a result of thermal decomposition of a product from the interaction of  $\text{CH}_3\text{CN}$  with  $\text{BCl}_3$ . The powder was further heat-treated at  $1000$  to  $1500^\circ\text{C}$  in an atmosphere of nitrogen. Chemical analysis showed that the composition of the obtained material is  $x = 0.44$  for  $(\text{BN})_x\text{C}_{2(1-x)}$ .

Mixtures of small copper balls of diameter  $0.1$  mm and the BN-C powder were pressed into steel capsules to form disks  $5$  mm in thickness and  $30$  mm in diameter[11]. The disks contain  $4$ – $6$  % BN-C by weight and their densities are about  $70$  % of the theoretical one. Shock compression experiments were performed using copper flyer plates accelerated by explosives and momentum trapping recovery systems. Incident shock pressures to the specimens were estimated to be  $30$ – $40$  GPa. The recovered specimens were immersed into strong acids to remove the copper matrices and unreacted BN-C.

For comparison, a mechanical mixture of graphite and hBN powder was also shock loaded with the same apparatus and treated with the same procedures.

Crystal structures of the specimens were examined by using an X-ray powder diffractometer ( $\text{CuK}\alpha$ ) equipped with a monochromator on the detector (Philips PW1800). A transmission electron microscope(TEM) was used to observe micro structures of the recovered specimens.

## 3. RESULTS AND DISCUSSION

Fine powder of purified product was obtained at above  $50$  % of the shock loaded graphitic BN-C

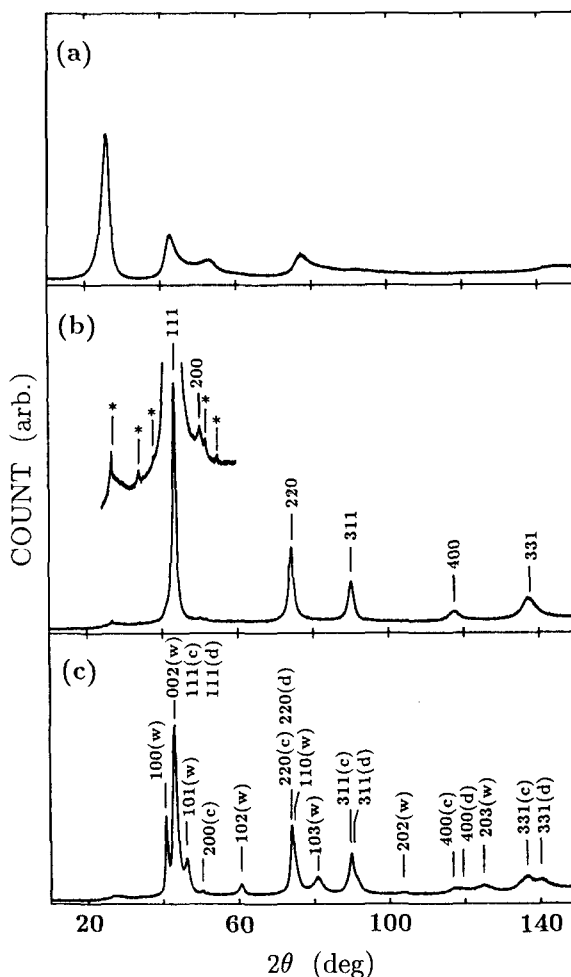


Figure 1. X-ray powder diffraction patterns ( $\text{CuK}\alpha$ ) of (a) unshocked graphitic BN-C, (b) shock loaded BN-C, and (c) shock loaded mechanical mixture of graphite and hBN powder. An enlarged pattern in the vicinity of  $111$  is also shown in (b), where marked (\*) lines are from  $\text{SnO}_2$  included in the specimen. In (c) diffraction line from diamond, cBN and wBN is denoted by d, c and w, respectively.

compound in weight.

Results of the X-ray diffraction measurements of the graphitic BN-C, the shock loaded BN-C, and the shock loaded mechanical mixture of graphite and hBN powder are shown in Figure 1, and parameters for the shock loaded BN-C are summarized in Table 1. The X-ray diffraction pattern for the graphitic BN-C is almost the same

Table 1  
Observed and calculated lattice parameters for cubic BN-C.

<i>hkl</i>	$a = 0.3605 \pm 0.0001$ nm		<i>I<sub>obs</sub></i>
	<i>d<sub>obs</sub></i> (nm)	<i>d<sub>calc</sub></i> (nm)	
111	0.2083	0.2081	100
200 <sup>a</sup>	0.1809	0.1803	0.5
220	0.1276	0.1275	24
311	0.1088	0.1087	13
222 <sup>a</sup>	—	0.1041	—
400	0.09015	0.09013	5
331	0.08272	0.08270	12
420 <sup>a</sup>	—	0.08061	—

<sup>a</sup>These lines are inhibited for the diamond structure due to the extinction rule.

with the result previously reported[6]; it gives a layered hexagonal structure, but its broad lines show a poor stacking regularity.

The diffraction pattern for shock loaded BN-C can be indexed by the fcc lattice except for lines from a very small amount of impurities and unreacted graphitic BN-C. Although the line widths are very broad, it is easy to confirm that the specimen is a single phase, because the diffraction pattern of the shock loaded mechanical mixture of graphite and hBN reveals the phase separation into three phases, diamond, cubic and wurtzite forms of BN [8,13], and the reflection of 331 from the cubic BN-C phase can be clearly distinguished from those of diamond and cBN. It is, however, difficult to determine the atomic arrangement in the cubic BN-C phase due to very close atomic scattering factors of B, C, and N. If B, C, and N atoms are completely disordered in the cubic phase, that is, if the phase has the diamond structure, the reflections of 200, 222, 420 etc. are absent because of the extinction rule. Very weak 200, of the order of 1 % of 111, was observed for cubic BN-C, and its width is almost the same with that of 111, as shown in Figure 1(b). Badzian[5] reported the existence of 420 as well as 200. We also made precise measurements, but could not detect the reflections of 222 and 420 within an error of 0.1 % of 111 intensity. It is concluded that cubic BN-C has the diamond structure without long range order of atomic arrangement, but short range order may exist. Preference for formation of B-N and C-C pairs, which has advantages to

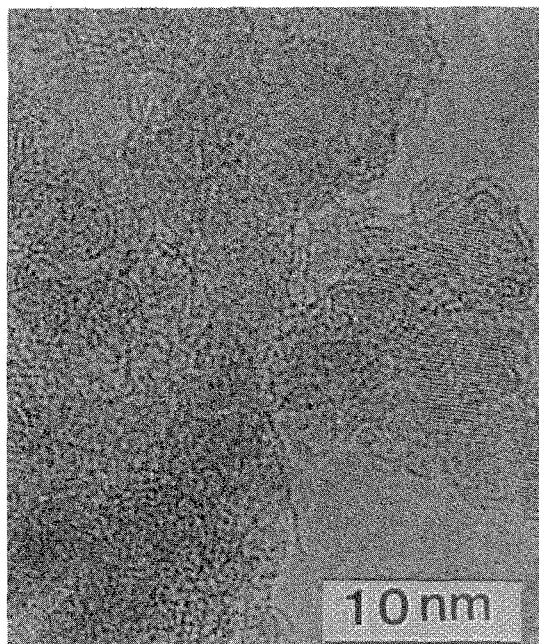


Figure 2. TEM image of cubic BN-C.

bonding energies and to holding local charge neutrality, does not cause only the nearest neighbor correlation of charge, but also local strain due to bond length difference among B-N, C-C etc.

The diffraction line widths for cubic BN-C increase monotonically with increasing scattering angle. The Scherrer relationship gives a crystallite size of around 10 nm which agrees with observations with TEM, as shown in Figure 2. Stackings of (111) planes were observed in TEM images, and their spacing, 0.208 nm, agrees with the X-ray diffraction data in Table 1.

A lattice constant obtained from the X-ray diffraction measurements is  $0.3605 \pm 0.0001$  nm which is between those of diamond and cBN[4,13]. Chemical analysis, however, for the composition of cubic BN-C is very difficult because of its chemical stability and the necessity of a large amount of specimen. Preliminary measurements of composition show that  $x$  is within the range from 0.42 to 0.50 on the assumption that the chemical formula is expressed as  $(\text{BN})_x\text{C}_{2(1-x)}$ . Dependence of the lattice constants on  $x$  is indicated in Figure 3. Apparent deviation from Vegard's law is observed, while Badzian's results[5] obey Vegard's law, where it is assumed that the com-

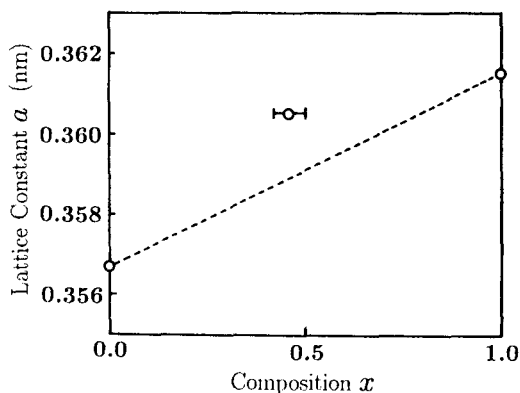


Figure 3. Composition dependence of lattice constant for cubic  $(\text{BN})_x\text{C}_{2(1-x)}$ . Dotted line shows Vegard's law between diamond ( $x = 0$ ) and cBN ( $x = 1$ ).

positions do not change by high pressure and high temperature treatments. Disagreements in the lattice constants as well as in the reflection of 420 mentioned above might be ascribed to difference of order parameters which should strongly depend on the compositions and on temperatures where the specimens were quenched.

It is of great interest that recovered cubic BN-C exhibits black in contrast to the shock synthesized diamond or BN compounds which are grey or white. Band gap of diamond and cBN is in the ultraviolet region, 6.4 eV and 5.5 eV, respectively. The optical absorption measurements of GaAs-Ge alloys show that the direct gap exhibits a large negative bowing as a function of the composition[14,15]. The reduction of the band gap in the cubic BN-C system is very plausible, because the GaAs-Ge solid solution system has the very similarities to BN-C system; they both consist of group-IV elements and III-V compounds, and can have diamond and zinc-blende crystal structures composed of tetrahedral coordination of atoms. Recent theoretical study[3] expects the large band gap bowing in relation to the staggered band offset at the corresponding heterojunction.

#### 4. CONCLUSIONS

A hybrid of diamond and cBN, a cubic phase of B, C and N, was synthesized with a shock com-

pression technique starting with a graphitic BN-C compound. A lattice constant of the cubic phase is  $0.3605 \pm 0.0001$  nm which is between those of diamond and cBN, but deviates from Vegard's law. There is no evidence of long range order of atomic arrangement in the lattice of diamond structure.

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Using copper balls as a matrix should be effective for getting higher temperatures. This method makes it possible to convert hBN to cBN directly, although only wBN is obtained by using usual methods with fine copper powder. See Ref. [8,12].
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