

## Synthesis of superhard cubic BC<sub>2</sub>N

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Cubic BC<sub>2</sub>N was synthesized from graphite-like BC<sub>2</sub>N at pressures above 18 GPa and temperatures higher than 2200 K. The lattice parameter of *c*-BC<sub>2</sub>N at ambient conditions is 3.642(2) Å, which is larger by 1.48% than would be expected based on ideal mixing between diamond and cubic boron nitride. The bulk modulus of *c*-BC<sub>2</sub>N is 282 GPa which is one of the highest bulk moduli known for any solid, and is exceeded only by the bulk moduli of diamond and *c*-BN. The hardness of *c*-BC<sub>2</sub>N is higher than that of *c*-BN single crystals which indicates that the synthesized phase is only slightly less hard than diamond. © 2001 American Institute of Physics.

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In the last few years, a great interest has been aroused in studying a possibility to synthesize dense ternary phases in the B–C–N system. In addition to diamond and cubic boron nitride (*c*-BN) existent in the B–C–N composition triangle, dense phases of boron carbonitrides can also be considered as potential superhard materials. While diamond exhibits extreme hardness, its actual performance as a superabrasive is somewhat limited. It is neither stable in the presence of oxygen even at moderate temperatures, nor is it a suitable abrasive for machining ferrous alloys. *c*-BN exhibits greater thermal stability and is the superabrasive of choice for machining steel, but is only half the hardness of diamond. Dense B–C–N ternary phases are expected to be thermally and chemically more stable than diamond, and harder than *c*-BN, and would therefore be excellent materials for high-speed cutting and polishing of ferrous alloys.

The data on attempted synthesis of dense B–C–N phases reported by different authors<sup>1–7</sup> are contradictory and to date it is unclear whether the synthesis products are solid solutions between carbon and cubic boron nitride or just mechanical mixtures of highly dispersed diamond and *c*-BN. In addition, the results from these previous studies have been obtained from quench experiments, without any *in situ* control of the process of phase formation.

In the present study, a cubic BC<sub>2</sub>N phase has been synthesized in the ternary B–C–N system under well controlled pressure-temperature conditions using a laser heated diamond-anvil cell (DAC) and a multi-anvil press.

The starting materials consisted of graphite-like BC<sub>2</sub>N and BC<sub>4</sub>N(*g*-BC<sub>x</sub>N) synthesized according to the method

described in Ref. 8 by simultaneous nitridation of boric acid and carbonization of saccharose in molten urea followed by annealing in nitrogen at 1770 K. Diffraction patterns of *g*-BC<sub>x</sub>N have broad x-ray diffraction lines (002), (10), and (004) for *g*-BC<sub>2</sub>N and (003), (10), and (006) for *g*-BC<sub>4</sub>N that are typical for turbostratic layered structures. At ambient conditions the *c* parameters for BC<sub>2</sub>N and BC<sub>4</sub>N were found to be 7.27(5) Å and 10.9(2) Å, respectively, while the *a* parameters have the same value of 2.47(2) Å.

The majority of experiments were performed using a large-aperture membrane-type diamond anvil cell<sup>9</sup> with anvil tips 300 μm in diameter. The samples were loaded, without pressure medium, in the 100 μm diameter hole drilled in a rhenium gasket of thickness 250 μm preindented down to 55 μm. Pressure was determined *in situ* from the calibrated shift of the ruby *R*<sub>1</sub> fluorescent line.<sup>10</sup> After compression, the samples were heated with a multimode YAG laser (with an output of 240 W at λ = 1.064 μm) focused on the sample through the front diamond with a plano-convex infrared lens (*f* = 75 mm).<sup>11</sup> Average temperatures in the laser heated spot were measured with an optical system designed for on-line measurements with an accuracy of 70 and 150 K at 1500 and 3000 K, respectively.

Angle-dispersive x-ray diffraction patterns were recorded using an on-line image-plate FastScan detector<sup>12</sup> at the ID30 beamline of the European Synchrotron Radiation Facility. High-brilliance synchrotron radiation from a two-phased undulator was set to a wavelength of 0.3738(1) Å using a channel-cut Si (111) monochromator. Correction of the two-dimensional diffraction images for spatial distortions and integration of the Debye–Scherrer rings were performed using the FIT2D software.<sup>13</sup> Lattice parameters were obtained

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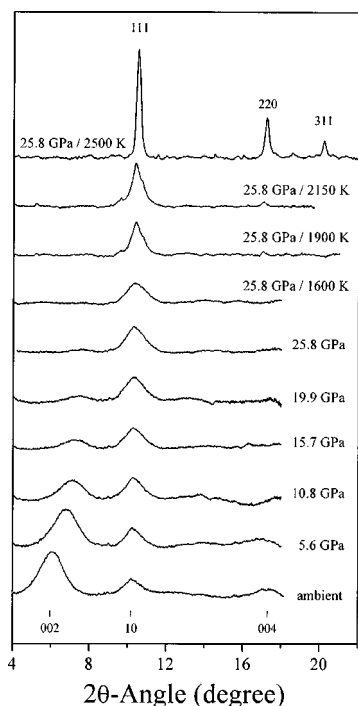


FIG. 1. Laser heating sequence of diffraction patterns taken at several pressures and temperatures. Bottom and top patterns correspond to *g*-BC<sub>2</sub>N and *c*-BC<sub>2</sub>N, respectively.

by LeBail full profile refinement of integrated patterns using the GSAS program package.<sup>14</sup>

An increase in pressure at room temperature is accompanied by a pronounced decrease in the line intensities of the turbostratic *g*-BC<sub>2</sub>N (Fig. 1). Upon compression to 19.9 GPa, the intensity of the strongest 002 line decreases by a factor of 6, and at 25.8 GPa this line almost disappears. Also, with increasing pressure, a variation in the 10 asymmetric line of the turbostratic structure is observed. The intensity of scattering in this region increases, the profile of the line becomes increasingly symmetric, and its peak shifts towards a value of 2.07 Å which is close to those observed for the 111 reflections of diamond-like phases. These effects point to the reconstruction of the graphite-like *sp*<sup>2</sup> structure into the diamond-like *sp*<sup>3</sup> structure, which starts at about 5 GPa and ends at about 25 GPa.

At 25.8 GPa, the heating of *g*-BC<sub>2</sub>N up to 1600 K is not accompanied by any change in the diffraction patterns which exhibit only a broad line in the region of 111 reflections of diamond-like phases (Fig. 1). At higher temperatures, the profile of this broad line changes to a rather complicated fine structure, and two new weak lines with  $d_{hkl} = 1.26$  and 1.09 Å (at ambient temperature) also appear. Finally, above 2200 K a drastic change in the spectrum is observed (Fig. 1, top pattern) which clearly points to the formation of a new phase. The diffraction pattern of the quenched sample exhibits only 111, 220, and 311 lines of the cubic lattice, which indicates that the sample is single phase. We therefore assume that the composition of the high-pressure cubic phase is the same as that of the graphite-like starting material, namely, BC<sub>2</sub>N.

The lattice parameter of the as synthesized cubic phase at ambient conditions is  $a = 3.642 \pm 0.002$  Å, which is larger than those of both diamond (3.5667 Å) and *c*-BN (3.6158 Å)

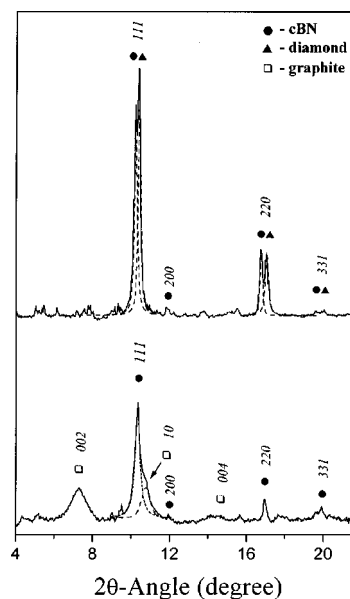


FIG. 2. Diffraction patterns of *g*-BC<sub>2</sub>N decomposition products taken at 11.0 GPa (bottom pattern) and 14.5 GPa (top pattern) after laser heating at about 2000 K.

(JCPDS NN. 6-0675 and 35-1365, respectively). The large deviation of the lattice parameter of cubic BC<sub>2</sub>N (*c*-BC<sub>2</sub>N) from the value that would be expected from ideal mixing (Vegard's law) between diamond and *c*-BN (3.583 Å) testifies that the synthesized phase is distinct the diamond-*c*-BN solid solutions reported earlier.<sup>3-7</sup> Re-analysis of the earlier results by Kurdyumov and Solozhenko<sup>15</sup> shows that, because of the poor resolution of the x-ray detection systems, the reported products can also be interpreted as mechanical mixtures of dispersed (Bragg scattering area less than 50 Å) diamond and *c*-BN. The positive deviations of the lattice parameter from Vegard's law (0.25–0.68%) observed in Refs. 3–7 are evidently caused by a high concentration of structural defects as has been reported for ultradispersed powders of cubic BN<sup>16</sup> and diamond.<sup>17</sup> In our case, it is clear that a ternary phase was synthesized, as ID30 provides adequate resolution for distinguishing a mixture of *c*-BN and diamond (see Figs. 1 and 2).

For the *c*-BC<sub>2</sub>N phase, we observe the presence of 111, 220, and 311 Bragg lines, which correspond to the *Fd*-3*m* space group. The apparent lack of the 200 line is a significant, as it would indicate a space group between *Fd*-3*m* and *F*-43*m*, as found for diamond and *c*BN, respectively. Indeed, for a B-C-N diamond-like phase, the lines that are most sensitive to the atomic distribution are those for which  $h + k + l = 2n$ , where  $n$  is an odd number (the 200 line is the strongest). The intensities of these lines are defined by the  $F = 4(f_1 - f_2)$  structure amplitude, where  $f_1$  and  $f_2$  are the atomic scattering factors of two face centered cubic (fcc) sublattices of the zinc-blende lattice. The absence of the 200 line for *c*-BC<sub>2</sub>N indicates that  $\langle f_1 \rangle = \langle f_2 \rangle$ , which is possible if B, C, and N atoms are uniformly distributed over both sublattices.

Laser heating experiments at different pressures have shown that the formation of *c*-BC<sub>2</sub>N is observed only at pressures above 18 GPa. At 14.5 GPa and temperatures above 2000 K *g*-BC<sub>2</sub>N decomposes to form a mixture of

*c*-BN and diamond (Fig. 2, top pattern). On further decrease in pressure down to 11.0 GPa (Fig. 2, bottom pattern), thermal decomposition of *g*-BC<sub>2</sub>N proceeds to form *c*-BN and disordered graphite, as reported earlier by Solozhenko and co-workers.<sup>18,19</sup>

For compressibility measurements, a sample of cubic BC<sub>2</sub>N synthesized at 25.8 GPa and 3000 K was compressed at room temperature in the DAC using 4:1 methanol–ethanol pressure medium to maintain quasihydrostatic conditions. High-pressure x-ray patterns were collected to 30 GPa with exposure times of 4 min. The two-parameter Birch equation of state was fitted to the data. The fitted parameters are  $B_0 = 282 \pm 15$  GPa and  $B'_0 = 4.3 \pm 1.1$ , with the zero-pressure cell volume  $V_0 = 48.49 \pm 0.08 \text{ \AA}^3$ . The bulk modulus ( $B_0$ ) of cubic BC<sub>2</sub>N is smaller than the 420 GPa value expected for ideal mixing between diamond<sup>20</sup> and *c*-BN.<sup>21</sup>

To synthesize *c*-BC<sub>2</sub>N using a different technique and produce this phase in an amount sufficient for hardness measurements, we used a large-volume multi-anvil system at the Bayerisches Geoinstitut in Bayreuth, Germany. The pressure cell, consisting of a 10 mm MgO octahedron and cylindrical LaCrO<sub>3</sub> heater, was compressed using WC cubes with 4 mm truncations.<sup>22</sup> The sample was graphite-like BC<sub>4</sub>N contained in a MgO capsule. The experimental conditions were 25 ( $\pm 2$ ) GPa and 2100 ( $\pm 100$ ) K and the run duration was 30 min. The recovered sample was investigated using x-ray powder diffraction with synchrotron radiation at the F2.1 station of DORIS-III at HASYLAB-DESY in Hamburg. The diffraction patterns of different regions of the sample showed the presence of a cubic phase with the lattice parameter of 3.640(4) Å (i.e., identical within error to that reported above for *c*-BC<sub>2</sub>N) and MgCO<sub>3</sub> that resulted from chemical reaction between *g*-BC<sub>4</sub>N, oxygen and the MgO capsule. Electron microprobe analysis (Cameca SX50) was carried out to examine the chemical composition of the synthesized sample. From the full x-ray emission spectra of B, C, and N for three different Mg-free regions of the sample, the stoichiometry of the cubic B–C–N phase is determined to be B<sub>0.4±0.1</sub>C<sub>1.1±0.1</sub>N<sub>0.5±0.1</sub>. Taking into account large errors when analyzing light elements, the stoichiometry of this phase can be assumed to be BC<sub>2</sub>N. The observed change in the carbon content of the B–C–N phase is evidently caused by the chemical reaction between *g*-BC<sub>4</sub>N and oxygen due to the much higher fugacity of oxygen in the high-pressure cell as compared to that in the DAC.

Vickers and Knoop hardness measurements of *c*-BC<sub>2</sub>N have been performed with a microhardness tester (type MXT70, Matsuzawa Seiki, Inc.) under a 2 to 5 N load. Nanohardness tests have been carried out with a Berkovich indenter under a 50 mN load at a penetration rate of 15 nm/s using a Nano Indenter II mechanical properties microprobe (Nano Instruments, Inc.). A single crystal of *c*-BN grown in the Li<sub>3</sub>N–BN system was used as a standard. The results obtained by different methods (Table I) are in good agreement and clearly show that the hardness of *c*-BC<sub>2</sub>N is higher than that of the {111} plane of a *c*-BN single crystal.

In conclusion, cubic BC<sub>2</sub>N with diamond-like structure can be synthesized at pressures higher than 18 GPa and temperatures above 2100 K. The lattice parameter of *c*-BC<sub>2</sub>N

TABLE I. Hardness of superhard cubic phases of the B–C–N system at room temperature.

	Vickers hardness (GPa)	Knoop hardness (GPa)	Nanohardness (GPa)
<i>c</i> -BC <sub>2</sub> N	76	55	75
Cubic BN	62	44	55
Diamond	115	63 <sup>a</sup>	

<sup>a</sup>See Ref. 23.

determined at ambient conditions is 3.642(2) Å, which is larger than those of diamond and *c*-BN. The bulk modulus of *c*-BC<sub>2</sub>N is 282 GPa, which is lower than those of diamond and *c*-BN, but is still one of the largest bulk moduli known for any solid. Hardness of *c*-BC<sub>2</sub>N measured by different methods is higher than that of *c*-BN single crystal, which indicates that the synthesized phase is a superhard material which ranks next to diamond.

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