

Ultimate Metastable Solubility of Boron in Diamond: Synthesis of Superhard Diamondlike BC₅

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Here, we report the synthesis of cubic BC₅ (c-BC₅), the diamondlike B-C phase with the highest boron content ever achieved, at 24 GPa and about 2200 K, using both a laser-heated diamond anvil cell and large-volume multianvil apparatus. The synthesized phase is low compressible (bulk modulus of 335 GPa), conductive, and exhibits extreme Vickers hardness (71 GPa), unusually high for superhard materials fracture toughness (9.5 MPa m^{0.5}), and high thermal stability (up to 1900 K); this makes it an exceptional superabrasive and promising material for high-temperature electronics.

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Diamond has found a wide variety of applications in modern science and technology due to its unique properties, such as extreme hardness, high thermal conductivity, wide band gap, high electron and hole mobility [1]. At the same time, it is nonresistant to oxidation and reactive with ferrous metals. The growing demand for advanced superhard materials in cutting and shaping hard metals and ceramics [2], as well as in electronic [3] and electrochemical [4] applications, has stimulated the search for novel diamondlike phases that are more thermally and chemically stable than pure diamond.

The traces of boron impurities change the electrical properties of diamond from an insulator into a semiconductor [3,4]. Moreover, boron-doped diamond was reported to be a type-II superconductor with transition temperature $T_c \approx 5$ K [5], while heavily boron-doped diamond (≥ 20 at% B) is predicted to be a superconductor with very high, up to 55 K, T_c [6]. However, only very limited amount of boron (~ 2 at%) can be introduced into diamond lattice by common methods of thermal chemical vapor deposition and high-pressure synthesis. The limiting concentration of boron that can be incorporated into diamond structure has not been established yet, although under extreme pressure-temperature conditions, this content could be significantly increased. Since all B-C materials show higher resistance to oxygen and ferrous metals than similar carbon materials [7], the diamondlike B-C phases with high boron content are expected to combine the best properties of the elements including advanced electrical and optical properties, very high hardness, and high thermal and chemical stability.

A number of graphitelike B-C phases of different stoichiometry (so called boron-substituted graphites with boron content up to 50 at%) have been synthesized by thermal chemical vapor deposition [8]. These materials should be perfect precursors for diamondlike B-C phases; however, their high-pressure, high-temperature behavior has not been well understood so far. Recent experiments on graphitelike BC₃ showed that at 20 GPa and 2200 K in a multianvil press, the phase decomposes into the mixture of boron-doped diamond (~ 1.8 at% of boron) and boron carbide [9]. Very recently, phase segregation of graphitelike BC_{1.6} into a mixture of diamond, boron carbide, and elemental boron was observed in a diamond anvil cell at 45 GPa and 2230 K [10]. Hence, all previous attempts to synthesize diamondlike B-C phases with boron concentration higher than ~ 2 at% have failed.

In the present study, we have performed a systematic investigation of phase transformations of turbostratic graphitelike BC_x phases (t-BC_x) at pressures up to 25 GPa and temperatures up to 2500 K with the aim to establish the ultimate boron solubility in diamond and synthesize diamondlike B-C phase(s) with a high boron content.

Our *in situ* studies of t-BC and t-BC₃ in the 3–7 GPa pressure range using multianvil system MAX80 and energy-dispersive x-ray diffraction with synchrotron radiation at HASYLAB-DESY have shown that neither phase undergoes any transformation up to 2000 K.

In situ experiments at higher pressures and temperatures have been conducted at ID30 and ID27 beam lines of the European Synchrotron Radiation Facility using laser-

heated diamond anvil cell (DAC) and angle-dispersive x-ray diffraction. At pressures above 20 GPa in the 2000–2500 K range, $t\text{-BC}_x$ phases ($1 \leq x \leq 4$) decompose into boron-doped diamond (1–2 at% of boron) and boron carbides (B_4C and B_{50}C_2) that are accompanied by the formation of cubic B-C phases ($c\text{-BC}_z$) with lattice parameters up to 2% higher than that of diamond [Fig. 1(a)]. The decrease of the maximal temperature in an experiment from 2500 down to 2000 K leads to a higher amount of forming $c\text{-BC}_z$. At the same time, the higher is the pressure, the lower is the starting temperature of $t\text{-BC}_x$ decomposition, especially in the case of the phases with high boron content. Thus, at 41 GPa, phase segregation of $t\text{-BC}$ and $t\text{-BC}_{1.5}$ was observed already at 1750 K. Based on these results, one can conclude that synthesis of a pure cubic B-C phase corresponding to the ultimate solubility of boron in diamond may be expected only in the case of $t\text{-BC}_x$ precursors with relatively low boron content ($x \geq 5$).

At room temperature, compression of turbostratic BC_5 is accompanied by a pronounced decrease of intensities of the $00l$ lines similar to that observed for turbostratic CBN solid solutions [11,12]. Upon compression to 24 GPa, these lines almost disappear [Fig. 1(b)]. Also, with increasing pressure, the profile of the two-dimensional 10 reflection becomes more symmetric, and the intensity of this line increases. These features, observed independently on the diffraction geometry in relation to the compression axis [12,13], point to the reconstruction of the turbostratic graphitelike sp^2 -layers into the disordered sp^3 -structure,

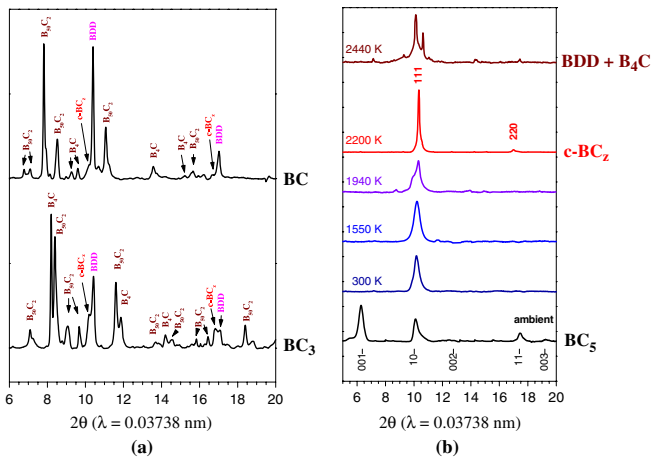


FIG. 1 (color online). (a) Representative diffraction patterns of the BC_3 and BC samples quenched from 26 GPa and 2400 K. Both phases decompose into boron-doped diamond with ~ 1.8 at % of B (BDD), cubic BC_z phase (according to lattice parameters, BC_9 and BC_5 for starting $t\text{-BC}_3$ and $t\text{-BC}$, respectively), and boron carbides B_4C and B_{50}C_2 . (b) Typical laser-heating sequence of diffraction patterns of BC_5 sample taken *in situ* at 24 GPa and several temperatures. The bottom pattern corresponds to $t\text{-BC}_5$ at ambient conditions.

previously reported for other graphitic phases of the B-C-N system [12,14].

At 24.0 GPa, no change in the diffraction patterns of $t\text{-BC}_5$ has been observed below 1550 K [Fig. 1(b)]. At higher temperatures, the profile of the only broad line of the pattern that is located in the region of 111 reflection of diamond shows the appearance of a fine structure. Finally, at 2200 K, the formation of the cubic BC_z phase has been observed, and the diffraction pattern exhibits only 111, 220, and 311 lines of the cubic (or, to be precise, pseudo-cubic) lattice, which indicates that the sample contains a single crystalline phase. Since no amorphous phase has been observed in the quenched samples by both transmission electron microscopy and Raman spectroscopy, one can assume that the composition of the cubic phase is the same as that of the precursor, namely, BC_5 . The 1:5 boron-to-carbon ratio has been additionally confirmed by electron energy loss spectroscopy (GIF2000, Gatan) and by electron microprobe analysis (Cameca SX-50, Camebax).

Being instantly heated up to 2440 K at the same pressure, the as-synthesized cubic phase undergoes the decomposition into boron-doped diamond (~ 2 at% of boron according to the lattice parameter) and boron carbide B_4C [Fig. 1(b)]. The relatively narrow temperature range (~ 200 K) of the $c\text{-BC}_5$ formation clearly indicates the metastable character of this phase; e.g., its slight overheating leads to the phase segregation into more thermodynamically stable boron-doped diamond and boron carbides. Thus, the value of 16 at% of boron may be considered as a concentration limit of existence of metastable diamondlike B-C phases. These metastable phases do not participate in the phase equilibria in the B-C system at high pressures and temperatures, while the p - T - x domain of their formation is determined by the boron concentration dependencies of the activation barriers for $t\text{-BC}_x$ and $c\text{-BC}_x$ decomposition, and $t\text{-BC}_x$ into $c\text{-BC}_x$ transformation.

According to the transmission electron microscopy (JEM 2010HR, JEOL), cubic BC_5 quenched down to ambient conditions occurs as nanocrystalline aggregates with clearly visible but very small (average size: 10–15 nm) grains. The three strongest diffraction rings of the selected area electron diffraction (SAED) patterns, i.e., 111, 220, and 311, allowed us to evaluate the lattice parameter of cubic BC_5 as $a = 0.359(7)$ nm. The more precise value of lattice parameter was established by angle-dispersive x-ray diffraction with synchrotron radiation and was found to be $a = 0.3635 \pm 0.0006$ nm, which is larger than those of both diamond (0.35667 nm for single crystal diamond according to JCPDS No. 6-0675, and 0.35688 nm for nanodiamond [15]) and cubic boron nitride (0.36158 nm, JCPDS No. 35-1365). This is consistent with the fact that the B-C bond is longer than C-C and B-N bonds [16] due to the weakened bonding caused by the electron-deficit character of the B atoms.

The a -value for cubic BC_5 expected from ideal mixing (Vegard's law) between diamond and "diamondlike boron" ($a = 0.404$ nm corresponding to the B-B bond length of 0.175 nm [16]) is 0.3646 nm that is in good agreement with the experimental value [Fig. 2(a)]. The theoretical simulations performed by Lowther for hypothetical diamondlike boron-carbon structures [17] have also shown a satisfactory correspondence between calculated lattice parameters of cubic BC and BC_3 and the Vegard law [see Fig. 2(a)]. The ideal mixing approach has allowed us to evaluate the compositions of quenched $c\text{-}BC_z$ phases formed during phase segregation of $t\text{-}BC_x$ ($x = 1\text{--}5$) at pressures above 20 GPa and various temperatures [inset of Fig. 2(a)]. Thus, one can conclude that there exists a continuous series of $c\text{-}BC_z$ solid solutions (between 0 and 16 at% of B), and $c\text{-}BC_5$ corresponds to the metastable ultimate solubility of boron in diamond.

The Raman spectrum (Dilor XY system, 514.5 nm Ar^+ ion laser) of cubic BC_5 [Fig. 2(b)] is different from that of pure diamond (one prominent Γ'_{25} band at ~ 1332 cm^{-1}), but is very similar to the spectrum of boron-doped diamond (~ 2 at% B) [18]. To date, the Raman spectra of such phases are not well understood. The comparison of the Raman data with the dispersion curves for phonons in diamond [19] shows that all observed band frequencies are very close to that of diamond. The appearance of new active modes may be attributed to a translation disordering in diamondlike structure due to the boron incorporation in the structure, when the Raman selection rules fail and we observe a phonon density of state. In addition to diamond modes, some local vibrations corresponding to the B-C and B-B (due to boron coupling in structure) bondings may

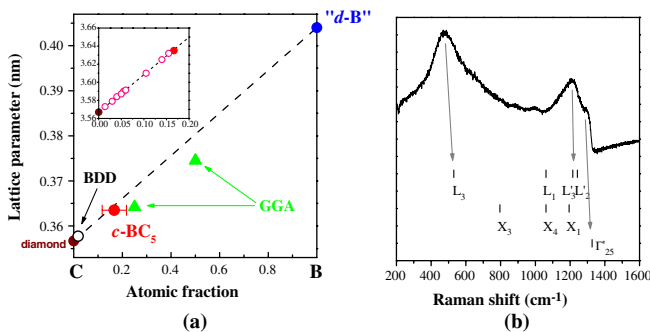


FIG. 2 (color online). (a) Lattice parameters of boron-substituted diamonds versus boron content. The dashed line represents Vegard's law, while the symbols show the result of present work (circle with error bar) in comparison with other experimental (circles) [9] and theoretical (triangles) [17] data. The open circles in the inset show the lattice parameters and ideal mixing estimate for compositions of quenched $c\text{-}BC_z$ phases formed during phase segregation of $t\text{-}BC_x$ ($x = 1\text{--}5$) at p - T conditions under study. (b) Raman spectrum of cubic BC_5 at ambient conditions (514.5 nm excitation wavelength). The vertical bars represent the phonon frequencies observed by inelastic neutron scattering in pure diamond [19].

appear [18]. The electron-deficit character of these bondings should give rise to the interaction of phonons with a continuum of charge carriers; that could lead to the appearance of additional modes. Thus, the Raman spectrum is consistent with a diamondlike structure of the synthesized phase, and one may suggest that the boron distribution in $c\text{-}BC_5$ is similar to that of known B-doped diamonds with lower (1–2 at%) boron concentration.

The 300-K equation of state of cubic BC_5 has been measured up to 40 GPa in three independent runs. Nitrogen and 4:1 methanol-ethanol mixture have been used as a pressure medium to maintain quasihydrostatic conditions. The fit of the two-parameter Birch equation of state to the experimental data have given the values of bulk modulus $B_0 = 335 \pm 8$ GPa and its first pressure derivative $B_0' = 4.5 \pm 0.6$, with the zero-pressure cell volume $V_0 = 0.04802 \pm 0.00005$ nm^3 . The bulk modulus of cubic BC_5 is smaller than those of diamond (446 GPa [20]) and cBN (377 GPa [21]), that is expected from a weaker bonding between B and C atoms in comparison to the C-C and B-N bondings.

To synthesize a bulk sample of $c\text{-}BC_5$ for hardness measurements, etc., we have performed a number of quenching experiments in a large-volume V7 Paris-Edinburgh press combined with a "T-cup" multianvil stage [22] under the same p , T -conditions as for the DAC synthesis. We have succeeded to obtain two single-phase millimeter-sized bulk samples in the experiments when the precursor was not overheated. X-ray powder diffraction analysis, transmission electron microscopy, and electron energy loss spectroscopy have revealed that the synthesized phase is identical to the cubic BC_5 observed in the DAC experiments.

The Vickers hardness measurements of bulk cubic BC_5 under loads from 1 to 20 N have shown that the calculated microhardness decreases with the load and reaches its asymptotic value at 2–3 N. As recommended for hard and brittle materials [23], the sample hardness was estimated in the asymptotic-hardness region as $H_V = 71(8)$ GPa. This value is close to the Vickers hardness of nanostructured bulk cubic BC_2N , the second-hardest known phase [11], and is in excellent agreement with the value predicted in the framework of the thermodynamic model of hardness, i.e., 70.6 GPa [24]. Under the 10 and 20-N loads, we have observed the cracks that allowed us to calculate the reliable load-independent value of fracture toughness, $K_{Ic} = 9.5(2.5)$ $MPa m^{1/2}$, by the method described in Ref. [25]. Nanoindentation measurements have also shown the extremely high value of $c\text{-}BC_5$ nanohardness, i.e., 73(7) GPa. In Table I, we compare $c\text{-}BC_5$ with diamond, cBN, and boron carbide in terms of mechanical properties [25–28].

The thermal stability of cubic BC_5 at ambient pressure in a nonoxidizing environment has been *in situ* studied by x-ray diffraction with synchrotron radiation using MAX80

TABLE I. Mechanical properties of superhard phases of the B-C-N system.

Phase	Vickers hardness [GPa]	Nanohardness [GPa]	Fracture toughness [MPa m ^{0.5}]
c-BC ₅	71	73	9.5
B ₄ C ^a	38 ^b		3–4 ^b
cBN ^c	62 ^b	55 ^b	2.8 ^b ; 6.8 ^d
c-BC ₂ N ^e	76 ^d	75 ^d	4.5 ^d
diamond ^f	115 ^b		5.3 ^{b,d}

^aRefs. [26,27].^bSingle crystal, (111) face. Polycrystalline material.^cRef. [25].^dPolycrystalline material.^eRefs. [11,25].^fRef. [28].

system at HASYLAB-DESY. The sequence of the powder diffraction patterns taken in the course of c-BC₅ heating has shown that the phase is stable up to 1890 K, while at higher temperatures, it decomposes into disordered graphite and amorphous boron and/or boron carbides. Hence, c-BC₅ is about 500 K more thermally stable than nanocrystalline diamond with the same grain size [15]; that can be attributed to the increase of decomposition activation barrier due to the presence of boron in the diamondlike lattice.

The room temperature electrical resistivity of cubic BC₅ was measured by the standard four-point probe dc technique combined with van der Pauw method, and was found to be $\sim 0.6 \Omega \cdot \text{m}$, which is the typical value for semiconductors.

Thus, diamondlike BC₅ phase that corresponds to the ultimate solubility of boron in diamond has been synthesized under well-controlled pressure-temperature conditions using a laser-heated diamond anvil cell. Well-sintered millimeter-sized bulks of nanostructured c-BC₅ have been produced in a large-volume multianvil press. The material exhibits extreme hardness and fracture toughness, and very high thermal stability, which makes cubic BC₅ an exceptional superabrasive overcoming diamond. The fortunate combination of the electrical conductivity, band structure that is unusual for diamondlike phases due to electron deficiency of boron atoms, and high thermal stability will eventually allow the expansion of the boundaries of high-temperature electronics and electrochemistry at extreme conditions.

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- [1] *The Nature of Diamonds*, edited by E. G. Harlow (Cambridge University Press, New York, 1998).
- [2] N. V. Novikov, *J. Mater. Proc. Tech.* **161**, 169 (2005).
- [3] J. Isberg *et al.*, *Science* **297**, 1670 (2002).
- [4] T. Yano *et al.*, *J. Electrochem. Soc.* **146**, 1081 (1999).
- [5] E. A. Ekimov *et al.*, *Nature (London)* **428**, 542 (2004).
- [6] J. E. Moussa and M. L. Cohen, *Phys. Rev. B* **77**, 064518 (2008).
- [7] L. E. Jones and P. A. Thrower, *Carbon* **29**, 251 (1991).
- [8] T. Shirasaki *et al.*, *Carbon* **38**, 1461 (2000).
- [9] V. L. Solozhenko, N. A. Dubrovinskaia, and L. S. Dubrovinsky, *Appl. Phys. Lett.* **85**, 1508 (2004).
- [10] P. V. Zinin *et al.*, *J. Appl. Phys.* **100**, 013516 (2006).
- [11] V. L. Solozhenko *et al.*, *Appl. Phys. Lett.* **78**, 1385 (2001).
- [12] V. L. Solozhenko and O. O. Kurakevych, *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **61**, 498 (2005).
- [13] V. L. Solozhenko *et al.*, *Solid State Commun.* **137**, 268 (2006).
- [14] V. L. Solozhenko, O. O. Kurakevych, and A. Yu. Kuznetsov, *J. Appl. Phys.* **102**, 063509 (2007).
- [15] The nanodiamond with grain size of 10–20 nm has been synthesized by shockwave compression of highly ordered graphite.
- [16] J. Emsley, *The Elements* (Clarendon Press, Oxford, 1991).
- [17] J. E. Lowther, *J. Phys. Condens. Matter* **17**, 3221 (2005).
- [18] M. Bernard, C. Baron, and A. Deneuve, *Diam. Relat. Mater.* **13**, 896 (2004).
- [19] J. L. Warren, J. L. Yarnell, G. Dolling, and R. A. Cowley, *Phys. Rev.* **158**, 805 (1967).
- [20] Ph. Gillet *et al.*, *Phys. Rev. B* **60**, 14660 (1999).
- [21] V. L. Solozhenko *et al.*, *Appl. Phys. Lett.* **72**, 1691 (1998).
- [22] Y. LeGodec *et al.*, *High Press. Res.* **25**, 243 (2005).
- [23] V. Brazhkin *et al.*, *Nature Mater.* **3**, 576 (2004).
- [24] V. A. Mukhanov, O. O. Kurakevych, and V. L. Solozhenko, *High Press. Res.*, **28**, 531 (2008).
- [25] V. L. Solozhenko, S. N. Dub, and N. V. Novikov, *Diam. Relat. Mater.* **10**, 2228 (2001).
- [26] F. Thevenot, *J. Eur. Ceram. Soc.* **6**, 205 (1990).
- [27] G. DeWith, *J. Mater. Sci.* **19**, 457 (1984).
- [28] N. V. Novikov and S. N. Dub, *J. Hard Mater.* **2**, 3 (1991).