# Superhard BC<sub>2</sub>N in cubic diamondlike structure

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Cubic  $BC_2N$ , a superhard material with a slightly lower hardness than diamond, has been synthesized but the determination of its crystal structure has long been elusive, impeding the further understanding of pertinent physics. Here, by employing a first-principles electronic structure framework, we predicted a cubic  $BC_2N$  crystal structure (*dia*-BC<sub>2</sub>N), marking it as the hitherto cubic phase among all previously proposed structures. Our simulated x-ray diffraction patterns of diamondlike BC<sub>2</sub>N agree with the experimental data, implying that our predicted structure is likely to be the high-symmetry BC<sub>2</sub>N structure synthesized in experiment. Furthermore, the estimated Vicker's hardness of this structure is 77 GPa, demonstrating its intrinsic superhard nature. Our current findings may begin to clarify the long-term unsolved crystal structure of cubic BC<sub>2</sub>N, and they may pave the way for further design and discovery of superhard materials.

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## I. INTRODUCTION

Superhard materials, which have a hardness value above 40 GPa, are known as some of the most important functional materials. They have attracted considerable attention due to their excellent physical properties and mechanical applications [1–11]. To date, diamond [12–21] and cubic boron nitride (*c*-BN) [22–24], which are widely used in numerous industries, are the most well-known superhard materials. However, they have limitations for practical use. For example, diamond is neither stable in the presence of oxygen (even at moderate temperatures), nor is it a suitable abrasive for machining ferrous alloys. In addition, the hardness of cubic boron nitride is lower than that of diamond [25,26]. Dense phases of boron carbonitrides (B-C-N) can also be considered as potential superhard materials [27].

There is a great deal of interest in pursuing new superhard materials. As an alternative candidate, B-C-N ternary phases are not only expected to be thermally and chemically more stable than diamond, but also harder than *c*-BN. They would therefore be an ideal candidate for applications such as high-speed cutting and polishing of ferrous alloys [28–30].

In an attempt to synthesize high-density B-C-N phase, several seminal experimental studies were conducted in which the precursor of graphitelike BC<sub>2</sub>N was used under high pressure [27,31]. In 2001, Solozhenko *et al.* successfully synthesized a cubic phase BC<sub>2</sub>N with a high hardness of 55–76 GPa from graphitelike BC<sub>2</sub>N at pressures above 18 GPa and temperatures above 2200 K. This cubic BC<sub>2</sub>N phase has

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been synthesized in a ternary B-C-N system using a laserheated diamond-anvil cell (DAC) as well as a multi-anvil press. For the c-BC<sub>2</sub>N phase, with increasing pressure, the experiment observed the presence of 111, 220, and 311 Bragg lines, which point to the reconstruction of the graphitelike  $sp^2$ structure into the cubic diamondlike  $sp^3$  structure [27]. However, given similar x-ray cross sections of B, C, and N atoms, the crystalline structure of the synthesized c-BC<sub>2</sub>N has not been unambiguously determined experimentally thus far. As a result, there is great interest in carrying out further theoretical investigation of crystal structures [30,32-40] of c-BC<sub>2</sub>N. For example, based on the substitution of diamond cells, there are several proposed structures for the experimental phase [30]. Among these, a chalcopyrite structured cp-BC<sub>2</sub>N with tetragonal symmetry (space group  $I-4_2D$ ) was identified with a simulated hardness of 72 GPa, which is close to that measured by Solozhenko et al [32]. A survey of the literature has shown that previously proposed structures do not have cubic symmetry, as pointed out in experiment. Therefore, it is highly desirable to search for a diamondlike cubic structure for the BC<sub>2</sub>N system. In our previous work, we correctly identified the first boron carbide of BC<sub>3</sub> in a cubic diamond structure with remarkable hardness. This greatly motivated us to shift our focus to a search for the cubic structure of BC<sub>2</sub>N with a slightly higher hardness of c-BN [41]. A determination of the crystal structure for cubic BC2N remains necessary for the further understanding of the pertinent physical mechanism of these light-element superhard materials.

In this work, we attempted to design cubic structure using density-functional theory (DFT) simulations. As a result, our simulations successfully uncovered a hitherto unknown cubic  $BC_2N$  structure under high pressure. The further simulations on its formation enthalpies, phonon spectra, and elastic

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FIG. 1. Predicted crystal structure of metastable *dia*-BC<sub>2</sub>N. (a) A side view along the *a* axis and (b) a polyhedral view of *dia*-BC<sub>2</sub>N. Its B atoms sit at 1a (0, 0, 0), 3d (0.5, 0, 0), and <math>12i (0.250, 0.250, 0); C atoms occupy at 12i (0.252, 0.252, 0.499), 12i (0.377, 0.377, 0.127), 3c (0.5, 0.5, 0), 12i (0.373, 0.626, 0.373), and 1b (0.5, 0.5, 0.5); and N atoms occupy at <math>4e (0.123, 0.123, 0.123) and 12i (0.622, 0.127, 0.127).

constants showed that the structure could become stable at ambient pressure similar to diamond and c-BN. Our simulations also indicated that the structure is a superhard material with hardness values of 77 GPa. Our in-depth analysis revealed the semiconducting feature of this structure with a band gap of 3.8 eV. These results provide insights into further exploring superhard materials with superior properties.

## **II. METHODS**

In this work, we designed a cubic diamond structure (dia-BC<sub>2</sub>N) for superhard BC<sub>2</sub>N crystal structure. First-principles

calculations were performed using density functional theory within the Perdew-Burke-Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA) [42,43] as implemented in the Vienna ab initio simulation package VASP code [44]. We used projector augmented wave (PAW) [45] potentials in which the valence electrons for the B, C, and N atoms were represented as  $2s^22p^1$ ,  $2s^22p^2$ , and  $2s^22p^3$ . An energy cutoff of 800 eV and dense Monkhorst-Pack k-meshes were used to ensure that the total energies were converged to within around 1 meV/at in the structural optimizations [46]. Integrations in the Brillouin zone were performed using special k points generated with a  $4 \times 4 \times 4$  mesh parameters grid. To verify the dynamical stability of the predicted structure, phonon calculations are carried out by using the finite displacement approach as performed in the PHONOPY code [47]. The bulk modulus and shear modulus are estimated within the Voigt-Reuss-Hill approximation [48]. The Vickers hardness is estimated by using the microscopic hardness model [49–53].

#### **III. RESULTS AND DISCUSSION**

Based on a 2 × 2 × 2 supercell of the cubic diamond structure, we performed extensive simulations and predicted a great number (108) of cubic BC<sub>2</sub>N structures. The details for our design strategy are described in the supplemental material [54]. We found that the most energetically favorable structure, as shown in Fig. 1, can also be viewed as the space group of *P*-43*m* and 64 atoms/cell, where we marked this phase as *dia*-BC<sub>2</sub>N. The lattice constants of predicted *dia*-BC<sub>2</sub>N take a = 7.216 Å and  $\alpha = 90.0^{\circ}$  at ambient pressure. The bonding containing boron, carbon, and nitrogen atoms could be viewed



FIG. 2. (a) Calculated enthalpy vs pressure for various  $BC_2N$  structures relative to that of *bc*6-BC<sub>2</sub>N. (b)–(d) Calculated phonon dispersion, electronic band structure, and electronic density of states of *dia*-BC<sub>2</sub>N at 0 GPa.



FIG. 3. Simulated XRD of *dia*-BC<sub>2</sub>N compared to experimental data. The x-ray wavelength we adopted for simulation is 0.3738 Å.

as  $sp^3$  hybridization characterization, which plays a critical role in determining the high hardness of cubic BC<sub>2</sub>N.

Notably, as shown in Fig. 2(a), our further simulations suggest that the predicted dia-BC2N phase is energetically more favorable than the previously proposed bc6-BC<sub>2</sub>N [33], BC<sub>2</sub>N-1 [30], *t*-BC<sub>2</sub>N [35], and *R*3*m*-BC<sub>2</sub>N [36] in the whole considered pressure region. The phase stability of dia-BC2N was investigated by calculating the enthalpy of formation, which is given via  $\Delta H = H$  (*dia*-BC<sub>2</sub>N)-*H* (*g*-BC<sub>2</sub>N), where H (dia-BC<sub>2</sub>N) is the enthalpy of BC<sub>2</sub>N in cubic diamond structure, and H (g-BC<sub>2</sub>N) is the enthalpy of BC<sub>2</sub>N in the graphite structure. As shown in Fig. S4a [54], upon compression we found that *dia*-BC<sub>2</sub>N becomes more stable than g-BC<sub>2</sub>N [55] at  $\sim$  1.8 GPa, indicating that it is a pressureinduced stable phase. Compared to diamond and c-BN, we found that the *dia*-BC<sub>2</sub>N structure has positive formation enthalpies of 0.171 and 0.183 eV/atom at ambient pressure and 50 GPa, respectively. The phonon simulations show that there is no imaginary frequency in the phonon dispersion of this structure throughout the entire Brillouin zone, indicating its dynamical stability. The electronic band structures [Fig. 2(c)] of dia-BC2N were calculated at ambient pressure, which revealed that *dia*-BC<sub>2</sub>N is a semiconductor with a direct band gap of 3.8 eV. To provide further insights into the electronic structure of *dia*-BC<sub>2</sub>N, the projected density of states (PDOS) at ambient pressure has been calculated. It can be clearly seen that the obvious overlap between B 2p, C 2p, and N 2p orbitals was found near the Fermi level, suggesting the existence of a strong interaction between B 2p, C 2p, and N 2p orbitals. This is in agreement with the fact that there is a charge transfer from 2s to 2p due to the  $sp^3$  hybridization.

To determine whether our newly predicted structure is the experimentally synthesized structure, we have also compared the powder angle-dispersive XRD spectra of *dia*-BC<sub>2</sub>N at 0.3738 Å wavelength with the XRD spectra of the experimentally synthesized *c*-BC<sub>2</sub>N [27], as shown in Fig. 3. Remarkably, the three main peaks of *dia*-BC<sub>2</sub>N match the experimental data almost perfectly, which greatly supports the idea that the structural assignment of the *dia*-BC<sub>2</sub>N phase is the experimentally synthesized *c*-BC<sub>2</sub>N.

The mechanical properties of this structure were examined by calculating their elastic modulus. The estimated Vickers hardness of *dia*-BC<sub>2</sub>N is 77 GPa, which is slightly higher than *c*-BN (63 GPa). Table I lists the calculated hardness values for *dia*-BC<sub>2</sub>N and for diamond and *c*-BN under the same calculated conditions. The comparison clearly shows that this structure is superhard material ( $H_v > 40$  GPa) with hardness between that of diamond and *c*-BN, which is completely consistent with the experiment. Moreover, we also calculated the elastic constants of *dia*-BC<sub>2</sub>N and obtained  $C_{11} = 889$  GPa,  $C_{44} = 491$  GPa, and  $C_{12} = 144$  GPa of *dia*-BC<sub>2</sub>N, which satisfy the mechanical stability criteria for a cubic crystal, i.e.,  $C_{44} > 0$ ,  $C_{11} > C_{12}$ , and  $C_{11} + 2C_{12} > 0$ .

In addition, ductility and brittleness are also important for the mechanical behaviors, which could describe the ability to change shape without the fracture of a material. Low ductility/high brittleness may affect their potential applications, even though they possess extreme hardness. The brittleness and ductility can be estimated by the B/G value from Frantsevich's rule [58], and the approximate criterion for the ductile-brittle transition is 1.75. It is clearly seen from Table I that *dia*-BC<sub>2</sub>N with a ratio of B/G is close to *c*-BN and higher than diamond. This suggests that *dia*-BC<sub>2</sub>N adopts better ductility than that of diamond.

## **IV. CONCLUSIONS**

In summary, we designed a cubic diamond structure for the superhard c-BC<sub>2</sub>N compound. The formation enthalpies, elastic constants, and phonon spectra showed that this structure is the experimentally synthesized phase of BC<sub>2</sub>N. The results showed that this structure is a superhard material with a hardness of 77 GPa, which is slightly harder than c-BN.

TABLE I. Calculated elastic constants  $C_{ij}$  (in GPa), bulk modulus *B* (GPa), shear modulus *G* (GPa), ratio of *B/G*, and Vickers hardness  $H_v$  (GPa) of diamond, *c*-BN, and *dia*-BC<sub>2</sub>N. The values in parentheses are the experimental data of diamond [56], *c*-BN [57], and *c*-BC<sub>2</sub>N [27].

		<i>C</i> <sub>11</sub>	<i>C</i> <sub>12</sub>	C 44	В	G	B/G	$H_v^{ m Chen}$	$H_v^{\mathrm{Tian}}$
diamond	Theor.	1046	128	564	434	519	0.84	92.6	94.3
	$Expt.^{a}$	(1079)	(124)	(578)	(443)	(537)	(0.82)		(98.0)
c-BN	Theor.	776	171	445	373	381	0.98	63.3	63.3
	$Expt.^{b}$				(400)	(409)	(0.98)		(63±5)
dia-BC <sub>2</sub> N	Theor.	889	144	491	392	439	0.89	77.3	77.8
	Expt. <sup>c</sup>								(55-76)

<sup>a</sup>Reference [56]

<sup>b</sup>Reference [57]

<sup>c</sup>Reference [27]

Our in-depth analysis revealed the semiconducting feature of this newly predicted phase with a direct band gap of 3.8 eV. Once graphitelike structured  $BC_2N$  was used as the precursor, the analysis of the phase transition process revealed that pressurization technology significantly affects the phase transition results. This work provides key insights for the experimental synthesis of the cubic  $BC_2N$  structure.

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