Theoretical hardness of the cubic BC$_2$N

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Abstract

Vickers hardness of the cubic BC$_2$N has been investigated using the microscopic hardness model, in which the parameters have been obtained using first principles calculations. Ionicities of the chemical bonds in the cubic BC$_2$N depend on their surrounding chemical environments, which are included in the hardness calculations of the cubic BC$_2$N using the population ionicity scale. For the four selected configurations of the cubic BC$_2$N, the theoretical Vickers hardness has been found to lie between 70 and 72 GPa, consistent with the experimental value of 76 GPa. According to our calculations, it should be the cubic BC$_2$N that ranks second among the superhard materials instead of the cubic BN.
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Diamond and cubic boron nitride (*c*-BN) are considered to rank first and second among the known superhard materials, respectively, because their crystal structures have the common features such as the short bond length, the same coordination number, and the similar lattice parameters. This fact has motivated interests in searching for novel superhard materials from the ternary B–C–N system due to its structural similarity to those of diamond and cubic boron nitride. It is expected that for the cubic BC$_x$N compound, its hardness should lie between diamond and *c*-BN because of its thermal and chemical stabilities comparable to those of *c*-BN [1,2]. Recently, much effort has been devoted to the theoretical design and experimental synthesis of this kind of superhard ternary compound.

Isoelectronic cubic C$_x$BN solids [3–10], especially the cubic BC$_2$N [7–10], are the primary objects which have been studied experimentally. The Vickers hardness of the cubic BC$_2$N (*c*-BC$_2$N) synthesized by Solozhenko et al. was reported to be 76 GPa [8], lying between the hardness values of diamond (96 GPa) and *c*-BN (66 GPa) [11]. Unexpectedly, the lattice parameters *a* of the synthesized *c*-BC$_2$N is 3.642 Å [8], larger than those of diamond and *c*-BN. Several theoretical studies on the *c*-BCN compounds have been reported [1,12–16]. Sun et al. gave a systematic study

on the *c*-BC$_2$N originating from the eight-atom zinc-blende structure [14]. Among the 420 investigated configurations for the *c*-BC$_2$N, only seven have been found to be possible, and their unit cells were named as BC$_2$N-1 to BC$_2$N-7, corresponding to struc-1 to struc-7 in Ref. [14]. All of the average lattice constants achieved in their first principles calculations are close to the experimental values, thus it is difficult to determine the fine structure of the *c*-BC$_2$N synthesized by Solozhenko et al.

Recently, Zhang et al. performed detailed calculations to study the ideal strengths of all the seven structures [16]. Based on the lower shear and tensile strengths of the *c*-BC$_2$N relative to the *c*-BN, they thought that the hardness of any *c*-BC$_2$N phase is lower than that of the *c*-BN, and the nanocrystalline size effect and the bonding with the amorphous carbon matrix should be responsible for the measured high hardness of the *c*-BC$_2$N [16]. For the lowest-energy configuration of *c*-BC$_2$N, its Vickers hardness has been estimated to be 78 GPa using our microscopic model of hardness [17], which is a useful tool to predict the theoretical hardness of a covalent solid. The estimated hardness of 78 GPa is consistent with the experimental result obtained by Solozhenko et al. [8]. It should be pointed out that in our previous calculations of the hardness of *c*-BC$_2$N [17], the ionicity of the B–C bond was taken approximately as zero because no data on the Phillips ionicity of the B–C bond was available at that time, and the ionicities of the C–C and B–N

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Table 1
Lattice parameters, total energies and bulk moduli calculated for the seven configurations of c-BC_2N, where V is the volume of the BC_2N unit cell, E is the total energy per atom, and B is the bulk modulus

Structure	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)	E (eV/atom)	B (GPa)
BC_2N-1	3.570	3.570	3.607	90	90	90	45.976	−165.58	402.1
BC_2N-2	3.565	3.568	3.608	90	90	90	45.900	−165.58	380.7
BC_2N-3	3.590	3.590	3.635	90	90	90	46.843	−165.12	362.9
BC_2N-4	3.595	3.597	3.595	90.45	89.79	90.21	46.483	−165.23	355.9
BC_2N-5	3.653	3.679	3.653	86.91	93.67	93.09	48.862	−165.32	263.5
BC_2N-6	3.661	3.661	3.668	86.73	93.27	93.39	48.923	−165.20	249.5
BC_2N-7	3.603	3.603	4.072	100.66	79.35	90.31	51.031	−165.46	302.8

bonds were calculated by using the dielectric theory. The calculations by using the dielectric theory give the same ionicity for a type of chemical bond in all materials, which is not able to reflect the variation of ionicity with the chemical environment around the chemical bond. The ionicity of the B–C bond in c-BC_2N should be small, but it is not zero, depending on the surrounding chemical environment of the bond. Therefore, a large error may arise in the hardness calculation if the dielectric theory is used to get the ionicity.

Because no experimental data is available for the fine crystal structure of c-BC_2N so far, the assignment of the seven configurations is still difficult. Moreover, it is still open whether c-BC_2N is harder than c-BN or not. Therefore, the systematic hardness calculations for the different configurations of c-BC_2N are of crucial importance. Now the accurate prediction of the hardness becomes possible for c-BC_2N since the recent appearances of the generalized population ionicity scale [18] and the microscopic model of hardness [17] for the covalent
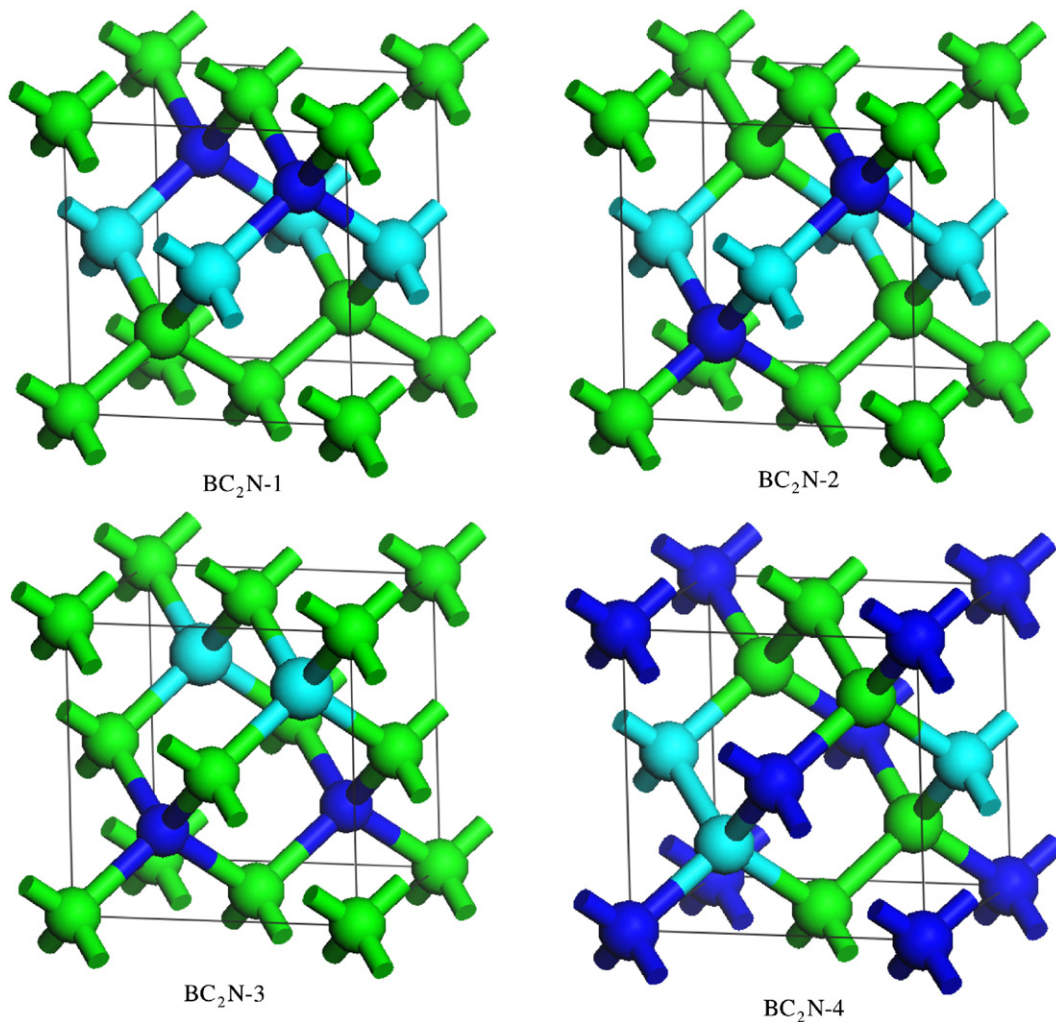

Fig. 1. Four selected configurations of c-BC_2N after geometry optimization. The sky-blue spheres are B atoms, the green ones are C atoms, and the blue ones are N atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

solids. Because c-BC_2N is a typical polar covalent solid, the microscopic model of hardness is valid for its hardness calculation. Our previous hardness calculations have shown that the accuracy of the calculated hardness is within 5% for superhard materials, while for usual covalent and polar covalent materials, the accuracy is within 10% [17].

In this letter, the seven possible configurations of c-BC_2N proposed by Sun et al. [14] have been selected for further investigations. To calculate the theoretical Vickers hardness of c-BC_2N by using the microscopic model of hardness, the equilibrium structural parameters, bond lengths, and the overlap populations of chemical bonds used in this model were obtained first by using first-principles calculations within the framework of density functional theory implemented in CASTEP code. The calculation of the total energy was based on Perdew–Berke–Ernzerhof form of the generalized gradient approximation (GGA-PBE) [19] and ultra-soft Vanderbilt potentials [20]. The Brillouin zone sampling was performed according to Monkhorst–Pack grid [21]. The plane-wave cut-off E_{cut} was 310 eV and the k-point mesh parameters were $7 \times 7 \times 7$ for all configurations of c-BC_2N.

According to Sun's work [14], only seven configurations are possible for c-BC_2N. The calculated total energies, the lattice parameters, and the bulk muduli of the seven c-BC_2N are listed in Table 1. From the viewpoint of energy, the stability of these seven configurations can be in the order of BC_2N-1, BC_2N-2, BC_2N-7, BC_2N-5, BC_2N-4, BC_2N-6, and BC_2N-3. However, BC_2N-7 has been shown to be unstable because of the existence of complex phonons as demonstrated in the further phonon calculations, and as to BC_2N-5 and BC_2N-6, it has not been determined up to now if they are semimetals or semiconductors [14,15]. Therefore, only four configurations of BC_2N-1, BC_2N-2, BC_2N-3 and BC_2N-4 have been considered in our calculations of hardness.

The four configurations of the eight-atom zinc-blende-structured c-BC_2N are shown in Fig. 1. There are four C atoms,

two B atoms, and two N atoms in the unit cell, and all the three kinds of atoms are four-coordinated. The 16 chemical bonds present in the four configurations are listed in Table 2. In BC_2N-1 and BC_2N-2, four types of chemical bonds of C–C, B–C, C–N and B–N are formed. In BC_2N-3, each C atom is bonded with two B atoms and two N atoms, resulting in two types of chemical bonds of B–C and C–N. The types of chemical bonds are abundant in BC_2N-4 compared with the other three configurations. There are two kinds of C atoms, two kinds of B atoms and one kind of N atoms in one unit cell, and sixteen bonds are formed. The sixteen bonds in the unit cell can be separated into ten kinds, and the atoms are then denoted by the kind of bond formed by them as shown in Fig. 2. First, the bonds in stru-4 can be divided into four groups with each group containing four bonds. The four bonds are formed between one of the atoms (B2, C2, C3 and C4) and four other atoms, forming one tetrahedron with the atom (B2, C2, C3, or C4) locating in the center and the other four atoms locating at the apexes of the tetrahedron, respectively. It can be found that for the tetrahedron with B2 in the center, its volume is a little larger than those of the other tetrahedra with the C atom (C2, C3, or C4) in the center, and the bond lengths are dependent upon the radii of the four atoms bonding with B2. In general, the larger radius implies the longer bond length. Hence, the B1–B2 bond is the longest one, the B2–C1 bond is the second, and the B2–N1 and B2–N2 bonds have the same length and are the shortest ones. For the bonds in the same eight-atom zinc-blende unit cell, the B1–B2, N1–C2, C1–C3 and C4–N2 bonds are longer to some extent than the other bonds formed by the same atoms. For instance, the length of the C1–C3 bond is longer than those of the C1–C2 and C1–C4 bonds. It should be noted that these four bonds are parallel to each other, and by taking the bond lengths in the tetrahedron with B2 in the center as a basis for comparison, for the bonds composed by the same elements, it can be distinguished precisely which group they belong to. The

Table 2
Bond parameters and theoretical Vickers hardness values of c-BC_2N, where d^{X-Y} is the X–Y bond length, P is the Mulliken overlap population, n is the number of X–Y bond in the unit cell, N_e^{X-Y} is the electron density, f_h is the overlap population ionicity, f_i is the Phillips ionicity, H_V^{X-Y} is the hardness of the hypothetical binary compound composed of the X–Y bond, H_v is the hardness of the BC_2N compound

| Structure	Bond	d^{X-Y} (Å)	p	n	N_e^{X-Y} (Å^{-3})	f_h	f_i	H_V^{X-Y} (GPA)	H_v (GPA)
BC_2N-1	C–C	1.512	0.83	4	0.753	0.092	0.173	84.0	70
	B–C	1.573	0.71	4	0.585	0.055	0.118	68.6	
	C–N	1.561	0.6	4	0.770	0.221	0.330	65.3	
	B–N	1.561	0.61	4	0.684	0.205	0.312	61.6	
BC_2N-2	C–C	1.525	0.8	4	0.734	0.061	0.127	85.3	72
	B–C	1.562	0.74	4	0.598	0.013	0.042	77.6	
	C–N	1.544	0.64	4	0.796	0.158	0.257	74.8	
	B–N	1.575	0.58	4	0.667	0.254	0.365	55.6	
BC_2N-3	B–C	1.566	0.74	8	0.591	0.013	0.042	76.5	72
	C–N	1.555	0.61	8	0.777	0.205	0.312	67.7	
BC_2N-4	B–B	1.598	0.67	1	0.479	0.113	0.201	52.3	70
	C–C	1.522	0.8	2	0.739	0.061	0.127	86.1	
	C–C*	1.557	0.73	1	0.690	0.027	0.070	83.2	
	B–C	1.547	0.78	2	0.615	0.038	0.090	76.5	
	B–C*	1.562	0.75	1	0.598	0	0	81.5	
	B–C**	1.571	0.73	1	0.588	0.027	0.070	73.1	
	C–N	1.538	0.64	2	0.805	0.158	0.257	76.1	
	C–N*	1.544	0.62	2	0.796	0.189	0.294	71.6	
	C–N**	1.598	0.55	2	0.718	0.305	0.418	52.9	
	B–N	1.569	0.59	2	0.674	0.238	0.348	57.8	
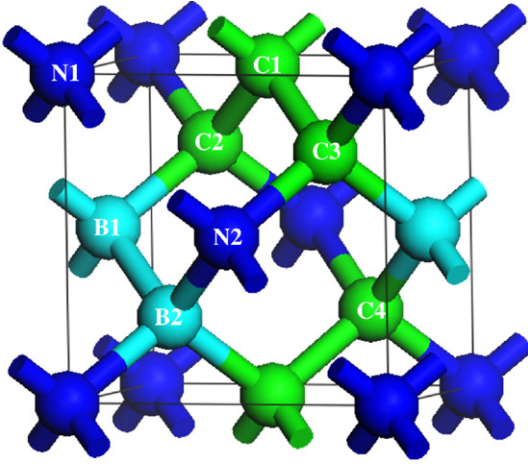
Fig. 2. Detailed representation of bond types in cubic BC$_2$N stru-4. The sky-blue spheres are B atoms, the green ones are C atoms, and the blue ones are N atoms. The three C–C bonds are divided into two types: (C1–C2, C1–C4) and C1–C3, The four B–C bonds are divided into three types: (B1–C2, B1–C4), B1–C3, and B2–C1, the six C–N bonds are divided into three types: (C3–N1, C3–N2), (C2–N2, C4–N1), and (C2–N1, C4–N2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

C2–N2 and C4–N1 bonds, which are parallel to the B2–C1 bond, are longer than the C3–N1 (or C3–N2) bond, which is parallel to B2–N2 (or B2–N1) bond, because the B2–C1 bond is longer than the B2–N2 bond. The B1–C2 and B1–C4 bonds are parallel to the B2–N1 bond, so they are shorter than the B1–C3 bond, which is parallel to the B2–C1 bond. So far, all the sixteen bonds in stru-4 have been sorted to ten types: the first type of 2 B–B bonds, the second type of 2 B–N bonds, the third type of C1–C2 and C1–C4 bonds, the fourth type of C1–C3, the fifth type of B1–C2 and B1–C4, the sixth type of B1–C3, the seventh type of B2–C1, the eighth type of C2–N1 and C4–N2, the ninth type of C2–N2 and C4–N1, and the tenth type of C3–N1 and C3–N2.

Considering that each of the four configurations for c-BC$_2$N consists of at least two types of chemical bonds in the unit cell, they belong to the complex crystals. According to the microscopic model of hardness [17], the Vickers hardness for the complex crystals of BC$_2$N-1 and BC$_2$N-2 can be calculated as follows

$$H_v = [H_v^{C-C} H_v^{B-C} H_v^{C-N} H_v^{B-N}]^{1/4}, \qquad (1)$$

For BC$_2$N-3, the Eq. (1) can be simplified as

$$H_v = [H_v^{B-C} H_v^{C-N}]^{1/2}, \qquad (2)$$

and the hardness equation for BC$_2$N-4 should be written as follows

$$H_v = [H_v^{B-B}(H_v^{C-C})^2 H_v^{C-C^*}(H_v^{B-C})^2 H_v^{B-C^*} H_v^{B-C^{**}}$$
$$(H_v^{C-N})^2 (H_v^{C-N^*})^2 (H_v^{C-N^{**}})^2 (H_v^{B-N})^2]^{1/16}, \qquad (3)$$

In the Eqs. (1), (2), and (3), H_V^{X-Y} are the hardness of the hypothetical binary compound composed of the X–Y bond, and can be calculated as

$$H_V^{X-Y} = 350(N_e^{X-Y})^{2/3} e^{-1.191 f_i^{X-Y}} / (d^{X-Y})^{2.5}, \qquad (4)$$

where d^{X-Y} is the length of the X–Y bond, N_e^{X-Y} is the valence electron density, and can be calculated by

$$N_e^{X-Y} = [Z_X/N_X + Z_Y/N_Y]\left[\sum_j N^j (d^j)^3\right]/[V(d^{X-Y})^3], \qquad (5)$$

where Z_X and Z_Y are the valence electron numbers of the X and Y atoms, N_X and N_Y are the nearest coordination numbers of the X and Y atoms, V is the volume of the unit cell, N^j is the number of j bond in the unit cell, and f_i^{X-Y} is the Phillips ionicity of the X–Y bond. According to our generalized ionicity scale [18], the Phillips ionicity f_i (or f_i^{X-Y}) can be calculated as

$$f_i = (f_h)^{0.735} = [1 - \exp(-|P_c - P|/P)]^{0.735}, \qquad (6)$$

where f_h is the population ionicity scale of a bond, P is the overlap population of the X–Y bond, P_c is the overlap population of a pure covalent bond in the zinc-blende structure, which is equal to 0.75 [18]. The calculated Vickers hardness of c-BC$_2$N is listed in Table 2.

Our calculations indicate that the ideal BC$_2$N-2 and BC$_2$N-3 crystals should have the same theoretical Vickers hardness of 72 GPa, and the ideal BC$_2$N-1 and BC$_2$N-4 crystals should have 70 GPa. In other words, all of them are superhard materials, even harder than c-BN. The hardness difference among the four configurations is less than 3%, indistinguishable in the practical hardness measurements. On the assumption that BC$_2$N-5 and BC$_2$N-6 are semiconductors, their calculated hardness is 69 GPa. The hardness values calculated for cubic BC$_2$N structures are within 10% accuracy compared with the experimental results data of c-BC$_2$N, indicating that for c-BC$_2$N, its hardness has little dependence on its fine crystal structure. From the above-mentioned calculations, it can be found that for a chemical bond such as the C–C, B–C, C–N, and B–N bonds, its ionicity value depends on the surrounding chemical environment of the bond. In the four configurations, for example, the ionicity value of the C–C bond can be different in the range from 0.070 to 0.173, and the ionicity of the C–N bond can be different in the range from 0.257 to 0.418, depending on their surrounding chemical environments. One more stress is that the chemical bonds consisting of identical atoms in complex crystals also have ionicities, such as the C–C bonds in BC$_2$N-1 and BC$_2$N-2 and the B–B bonds in BC$_2$N-4, while the chemical bonds consisting of different atoms in complex crystals such as the B–C* bonds in BC$_2$N-4 do not exhibit ionicities. From the calculated hardness and bulk modulus for the different configurations of c-BC$_2$N, there is no monotonic dependence of hardness on bulk modulus as predicted in our previous studies [22,23]. Similarly, strength is not an indicator of hardness for the covalent solids. In the strength calculation of Si, the ideal shear strength of Si is half of its hardness while the tensile strength is 62% higher than its hardness [24,17]. Therefore, it is not proper to estimate the hardness of a material by using its strength.

In summary, we have calculated the Vickers hardness of c-BC$_2$N by using the microscopic model of hardness. Our results show that the c-BC$_2$N is a superhard material, ranking second to diamond, and its hardness depends little on the atomic arrangements in the crystal structure. Both bulk

modulus and strength are not good indicators of hardness for the covalent solids.

Acknowledgements

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