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Most likely phase of superhard BC_2N by *ab initio* calculations

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We predict a most likely structure of superhard BC_2N, named z-BC_2N, which is constructed from the sixteen-atom supercell of diamond by using first-principles calculations. z-BC_2N is a more stable metastable phase with respect to other structures and has the tetragonal symmetry belonging to the space group P-$42M$. z-BC_2N obeys the bond-counting rule that the chemical bonds in the unit cell consist of B-C, B-N, C-C, and C-N bonds, and C-C and B-N bonds are as many as possible. The calculated x-ray diffraction spectrum of z-BC_2N agrees with the reported experimental result more well than the previously-predicted structures. Our results indicate that z-BC_2N is perhaps the most likely structure of BC_2N. Theoretical Vickers hardness and bulk modulus of z-BC_2N are calculated to be 75.9 and 402.7 GPa exceeding those of cubic BN.

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Much theoretical and experimental effort has been devoted to finding the possibility of new low-compressibility materials with bulk modulus and hardness comparable with diamond.[1–3] In particular, ternary boron carbon nitrogen (B-C-N) compounds have attracted special attention, because of not only the extremely high hardness but also the greatly thermal stability and exciting electronic property for potential applications on mechanical tools and electronic devices. Despite the fact that some cubic (strictly speaking, should be pseudocubic) B-C-N materials have been successfully synthesized,[4–7] the crystal structure of superhard BC_2N has still not been conclusively determined. Possible pseudocubic BC_2N phases have been predicted by first-principles calculations starting from zinc-blende boron nitride (BN) and diamond in an eight-atom unit cell. The predicted BC_2N phase with the $Pmm2$ space group (while this structure has different appellations in the literature such as β-BC_2N,[8] II-BC_2N,[9] and struc-1 of BC_2N (Ref. 10), they are, in fact, identical) was supposed to be the most possible structure fitted for the experimental results. Several first-principles studies have explored the ideal strength and Vickers hardness of β-BC_2N.[11–14] However, all predicted structures do not match the experimental x-ray diffraction (XRD) data of the so-called cubic BC_2N (c-BC_2N) synthesized in Ref. 7. Therefore, the determination of the refined crystal structure of c-BC_2N is still a huge challenge.

Here we predicted a most likely phase of superhard BC_2N, with tetragonal structure and the P-$42M$ space group, which is named z-BC_2N. A great number of calculations we made (including some unpublished) have proved that the bond-counting rule proposed by Tateyama *et al.* in the layered structures[15] is also valid for the polymorph of BC_2N; especially, the BC_2N phases composed of B-C, C-N, B-N, and C-C bonds should be more stable than those containing B-C and C-N bonds only. The idea that the existence of B-N and C-C bonds will certainly reduce the total energy of the system is easily understood because diamond and cubic BN (c-BN) are the most stable phases. Consequently, we need to choose as many B-N and C-C bonds as possible to construct the structural model of BC_2N. In the reported results in the literature, the BC_2N structures were almost built by substituting C atoms by B and N atoms in an eight-atom unit cell. In this case, the ratio of the chemical bonds (B-N:C-C:B-C:C-N) is 1:1:1:1. It is, in fact, very difficult to further increase the number of the B-N and C-C bonds in the BC_2N structures constructed only from the eight-atom unit cell, so we must seek new ways to construct the structure model of BC_2N. It must be emphasized that the measured XRD spectrum of the experimentally synthesized BC_2N sample in Ref. 7 is very similar that of diamond, with the three strong peaks only, implying that the synthesized BC_2N sample should be very crystalline and has high space symmetry. In addition, in the BC_2N system the formation energy E_f, defined as $E_f = E_{BC_2N} - (E_{\mathrm{diamond}} + E_{c-\mathrm{BN}})/2$,[10] is also an important factor for evaluating the stability of BC_2N. Therefore, for constructing the BC_2N structure model, we should simultaneously consider four important factors as follows: bond-countering rule, high space symmetry, low total energy, and low formation energy. Here we configure the BC_2N structure model starting from the sixteen-atom supercell of diamond, which is possible to yield the desired structure. We use the *ab initio* pseudopotential density functional method for our investigations. Ultrasoft pseudopotentials are expanded within a plane wave basis set with the cutoff energy of 400 eV. The k-point samplings are $8 \times 8 \times 4$ in the Brillouin zone. Exchange and correlation effects are described by Perdew-Burke-Ernzerhof (PBE) in generalized gradient approximation (GGA). The elastic constants C_{ij} and bulk modulus B_0 can be straightforwardly calculated by the CASTEP code.[16] The powder XRD spectrum is simulated by the REFLEX software.

Figure 1(a) shows the z-BC_2N structure (with the sixteen-atom unit cell) we predicted, which has the tetragonal symmetry and belongs to the space group of P-$42M$. There are three kinds of nonidentical C atoms (C1, C2, and C3) and two kinds of nonidentical N atoms (N1 and N2), while all the B atoms are identical in the supercell of z-BC_2N, with the atom positions of C1 (0.5,0,0.255), C2 (1,0,0.5), C3

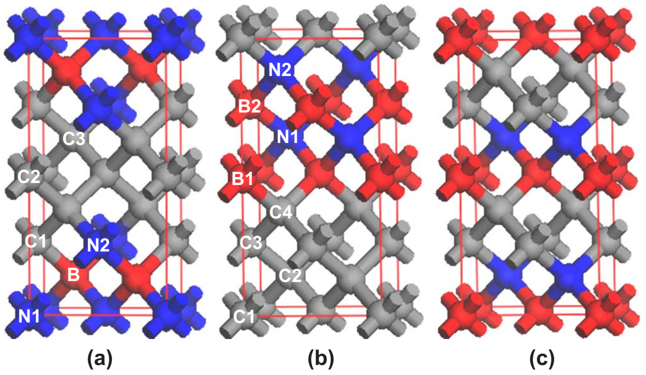

FIG. 1. (Color online) Crystal structures of z-BC$_2$N (a), β^*-BC$_2$N (b), and β-BC$_2$N (c), in the sixteen-atom unit cell.

(0.252,0.248,0.623), N1 (1,0,0), N2 (1,0.5,0.255), and B (0.252,0.248,0.125). Figure 1(b) displays another BC$_2$N structure we found, which is named as β^*-BC$_2$N, due to the same symmetry of Pmm2 as β-BC$_2$N. The difference from z-BC$_2$N is that they have four kinds of nonidentical C atoms (C1, C2, C3, and C4), two kinds of nonidentical N atoms (N1 and N2) and two kinds of nonidentical B atoms in one supercell of β^*-BC$_2$N, with the atom positions of C1 (1,0,0), C2 (0.25,0.25,0.124), C3 (0.5,0,0.248), C4 (0.75,0.25,0.37), N1 (0.25,0.25,0.631), N2 (0.75,0.25,0.879), B1 (1,0,0.497), and B2 (0.5,0,0.746). For comparison, the β-BC$_2$N structure is also shown as Fig. 1(c). It should be pointed out that in order to easily find the difference of z-BC$_2$N from β^*-BC$_2$N and β-BC$_2$N, here the structures of β^*-BC$_2$N and β-BC$_2$N are also described by the sixteen-atom unit cell.

Figure 2(a) plots the calculated band structure of z-BC$_2$N, with a direct gap of ~2.7 eV wider than ~1.2 eV of β^*-BC$_2$N and ~2.1 eV of β-BC$_2$N.[17] The exact band gap of z-BC$_2$N should be in fact wider, due to the well-known fact that the density functional method underestimates usually the band gap. Figure 2(b) displays the total and partial DOS (density of states) spectra, including the local DOS spectra of s electrons (solid lines) and p electrons (dot lines) of different elements in the unit cell of z-BC$_2$N. It can be seen from Fig. 2 that the deep valence bands below −17.5 eV originate mainly from the contributions of the s orbitals of N1, N2, C2, and C3 atoms, the valence bands between −17.5 and −12.5 eV are from the dominant contributions of the s orbitals of N1, N2, C1, C2, and C3 atoms, between −12.5 and 0 eV from the p orbitals of N1, N2, C1, C2, C3, and B atoms. For the conduction bands, the contributions of the p orbitals of N2, C1, C2, C3, and B atoms are dominant, while the s orbitals of N2, C1, C2, C3, and B atoms as well as the s and p orbitals of N1 atoms have a little contribution.

Table I lists the calculated related parameters of z-BC$_2$N and β^*-BC$_2$N, and those of β-BC$_2$N, c-BN, and diamond are also given for comparison. Here z-BC$_2$N, β^*-BC$_2$N, and β-BC$_2$N are described by the sixteen-atom unit cell as in Fig. 1, while c-BN and diamond use the eight-atom unit cell. Evidently, the total energy of z-BC$_2$N is lowest among z-BC$_2$N, β^*-BC$_2$N, and β-BC$_2$N, and lower than those of all the structures proposed in Ref. 10. In the BC$_2$N system, from the point of view of the formation energy, although E_f of z-BC$_2$N is also positive, but lower than that of β^*-BC$_2$N, β-BC$_2$N and all the structures proposed by Sun *et al.*[10] Based on the facts mentioned above, z-BC$_2$N is indeed a more stable metastable-phase compared with all the structures presented in the literature. Since z-BC$_2$N has the tetragonal symmetry and the space group of P-42M, all the calculated

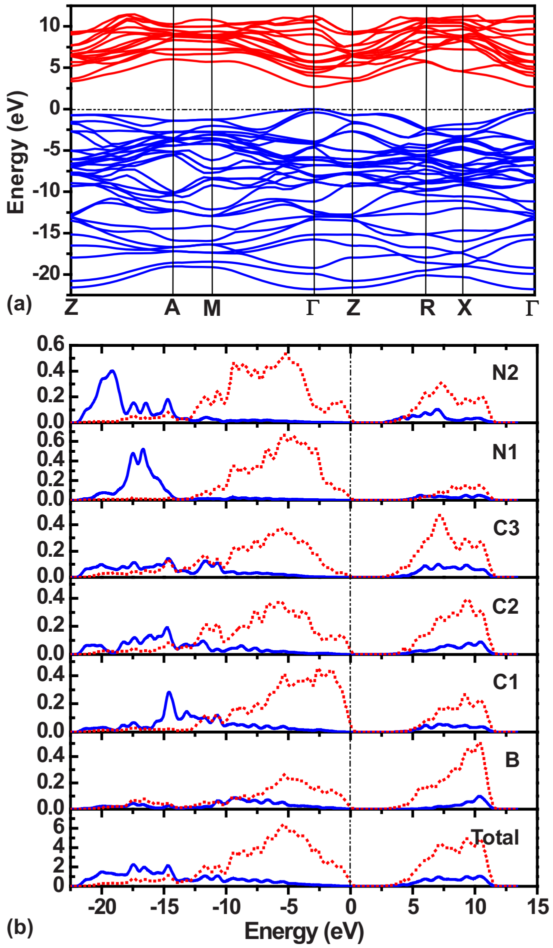

FIG. 2. (Color online) Band structure (a) and DOS spectra (b) of z-BC$_2$N.

TABLE I. Parameters of z-BC$_2$N, β^*-BC$_2$N, and β-BC$_2$N compared with c-BN and diamond.

Parameter	z-BC$_2$N	β^*-BC$_2$N	β-BC$_2$N	c-BN	Diamond
Symmetry	P-42M	$Pmm2$	$Pmm2$	F-43M	FD-3M
a(Å)	3.565	3.571	3.568	3.594	3.533
b(Å)	3.565	3.571	3.568	3.594	3.533
c(Å)	7.168	7.169	7.210	3.594	3.533
ρ (g/cm^3)	3.561	3.548	3.534	3.551	3.619
G (GPa)	447.4	443.2	482.3	393.3	539.4
B_0(GPa)	402.7	405.5	383.2	373.0	442.7
H_v^{calc}(GPa)	75.9	70.8	71.1	69.9	97.6
E_{total} (eV/atom)	−165.80	−165.74	−165.59	−176.20	−155.83
E_f (eV/formula)	0.86	1.10	1.73	×	×

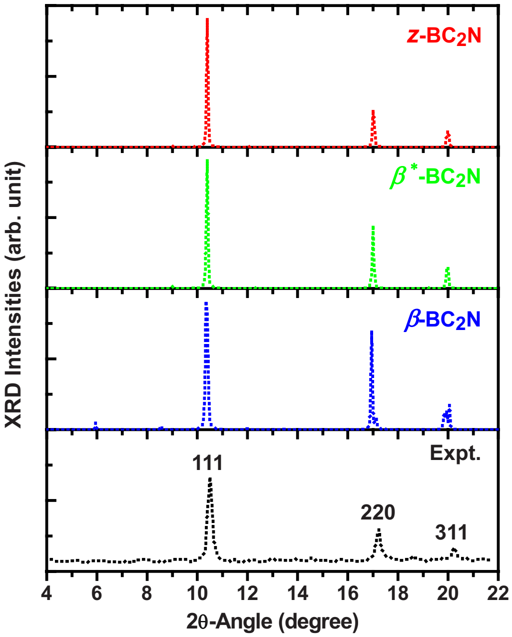

FIG. 3. (Color online) Calculated powder XRD spectra of z-BC$_2$N, β^*-BC$_2$N, and β-BC$_2$N compared with the measured XRD spectrum of the experimentally synthesized c-BC$_2$N.

nine nonzero elastic constant elements are $C_{11}=C_{22}=919.8$, $C_{33}=979.3$, $C_{44}=C_{55}=503.6$, $C_{66}=507.3$, $C_{12}=137.3$, and $C_{13}=C_{23}=133.4$ GPa. It is clear that the elastic constants of z-BC$_2$N satisfy simultaneously the four mechanical stability criteria as follows: $C_{11}(C_{22}+C_{33})\geqslant 2C_{12}^2$, $C_{22}\geqslant C_{23}$, $C_{44}>0$, and $C_{55}>0$, implying that z-BC$_2$N is mechanically stable. The calculated bulk modulus B_0 of z-BC$_2$N is 402.7 GPa, which is one of the largest values in the proposed polymorphs of BC$_2$N. As an evidence, the calculated B_0 of diamond is 442.8 GPa, in good agreement with the measured value of 442 GPa.[18] The shear modulus G is calculated by $G=[C_{44}+(C_{11}-C_{12})/2]/2$.[19,20] It can be seen from Table I that the theoretically predicted shear and bulk moduli of z-BC$_2$N, β^*-BC$_2$N and β-BC$_2$N are much higher than the measured values of $G=238$ GPa (Ref. 21) and $B_0=282$ GPa (Ref. 7) and $B_0=259$ GPa,[21] for the synthesized c-BC$_2$N samples. The reason is very easily understood that the experimentally synthesized c-BC$_2$N is a mixture of crystalline and amorphous phases, which results certainly in the remarkable decrease of the experimental values of the shear and bulk moduli.

We now focus on the simulated powder angle-dispersive XRD spectra of z-BC$_2$N, β^*-BC$_2$N, and β-BC$_2$N at a 0.3738-Å wavelength being the same as the synchrotron radiation used in the XRD experiment of c-BC$_2$N,[7] as shown in Fig. 3. There exist only three strong 111, 220, and 311 peaks (the apparent lack of 200 peak) in the experimentally measured XRD spectrum,[7] implying that the c-BC$_2$N synthesized in Ref. 7 should be a high-symmetry single-crystal phase. Inasmuch as, for low-symmetry structures, the XRD peaks experimentally detectable are more than three, apart from the layered structure. If two single-crystal phases coexist in the c-BC$_2$N sample, we should observe more than six marked XRD peaks in the experimental XRD spectrum in the general case. Hence we can assert that the three XRD peaks conclusively come only from one single-crystal phase, in particular, which should be close to the cubic phase. Of course, we cannot exclude the existence of amorphous phases in this sample, because the presence of amorphous phases has only contributions to the background of diffractions or results in a broadened peak. It should be pointed out that, in principle, the 200 peak of a high density phase for the BC$_2$N system should exist similar to binary c-BN, but should be so weak that it is very difficult for experimental detection. We find from Fig. 3 that although z-BC$_2$N, β^*-BC$_2$N, and β-BC$_2$N have three strong peaks of 111, 220, and 311, some differences can be still found. For β-BC$_2$N, the calculated 220 and 311 peaks are the overlapped peaks of two and three diffraction peaks, respectively. This means that the so-called c-BC$_2$N obtained experimentally cannot be reasonably assigned to be β-BC$_2$N. From the relative intensities of the three peaks for both β^*-BC$_2$N and β-BC$_2$N, the 220 peaks are too strong, compared with the experimental measurement of c-BC$_2$N. Most importantly, the 111, 220, and 311 peaks of z-BC$_2$N match the experimental observation very well, and the calculated relative intensity of 200 peak is very weak (is only 0.7% of the strongest 111 peak). It is evident that from the analysis of the XRD spectra, z-BC$_2$N is a well-matched structure with the experimentally synthesized c-BC$_2$N so far.

TABLE II. Calculated bond parameters and Vickers hardness of z-BC$_2$N ($H_v^{\rm calc}$) compared with the measured value ($H_v^{\rm expt}$) of c-BC$_2$N.

Bond	n^{μ}	d^{μ} (Å)	N_e^{μ}	P	f_i^{μ}	H_v^{μ} (GPa)	$H_v^{\rm calc}$ (GPa)	$H_v^{\rm expt}$ (GPa)
B-C	4	1.559	0.600	0.860	0.231	62.30	75.9	76±4
C-C(I)	4	1.527	0.730	0.830	0.186	78.91		
C-C(II)	8	1.537	0.716	0.830	0.186	76.64		
B-N(I)	8	1.546	0.704	0.720	0.092	83.53		
B-N(II)	4	1.579	0.660	0.650	0.217	65.40		
C-N	4	1.542	0.798	0.680	0.169	83.39		

Finally, we would like to discuss the hardness of z-BC$_2$N. On the basis of microscopic model,[13] the Vickers hardness of z-BC$_2$N can be calculated by

$$H_v = \left[\prod^{\mu} (H_v^{\mu})^{n^{\mu}}\right]^{1/\sum n^{\mu}},$$

where

$$H_v^{\mu} = 350 (N_e^{\mu})^{2/3} e^{-1.191 f_i^{\mu}} / (d^{\mu})^{2.5}.$$

Here H_v^{μ}, n^{μ}, d^{μ}, and f_i^{μ} are the hardness, bond number, bond length, and Phillips ionicity of a crystal composed of pure μ-type bonds, respectively. N_e^{μ} is the number of valence electrons of μ-type bond per cubic Å. We use the new ionicity scale of $f_h = 1 - e^{-|P_c - P|/P}$ and the relationship of $f_h = f_i^{1.36}$ to calculate the Phillips ionicity, where P is the overlap population of a bond and P_c is the overlap population of bonds in a specified pure covalent crystal[22] ($P_c=0.75$ for zinc blende structure here). As listed in Table II and shown in Fig. 1(a), there are six subtypes of bonds for *z*-BC_2N, including four B-C, four C-C(I) eight C-C(II), eight B-N(I), four B-N(II), and four C-N bonds. All the six subtypes of bonds have different values of n^μ, d^μ, N_e^μ, P, f_i^μ, and H_v^μ, as listed in Table II. The calculated Vickers hardness is 75.9, 70.8, 71.1, and 69.9 GPa for *z*-BC_2N, β^*-BC_2N, β-BC_2N, and *c*-BN, respectively. The hardness of *z*-BC_2N is more close to the experimental value of 76±4 GPa of *c*-BC_2N (Ref. 7) and exceeds that of *c*-BN, indicating that *z*-BC_2N is a second superhard material to diamond.

The *z*-BC_2N structure we constructed from the sixteen-atom unit cell obey indeed the bond-counting rule. The ratio of (B-N+C-C bonds):(B-C+C-N bonds) for *z*-BC_2N is 3:1, which is much larger than the ratio of 1:1 for the hypothetical high density BC_2N phases reported in the literature. *z*-BC_2N has not only the lowest total energy and formation energy but also the highest structural symmetry (belonging to the space group of *P*-42*M* and the tetragonal symmetry) among all the previously predicted *z*-BC_2N structures (including the β^*-BC_2N phase we found here). In particular, the calculated XRD spectrum of *z*-BC_2N matches very well to that of the BC_2N sample synthesized in Ref. 7 and should be the second superhard material to diamond at present. All the results indicate that *z*-BC_2N we predicted is a most likely phase of the so-called *c*-BC_2N synthesized in experiment. This goes an important step in the determination of crystal structure for *c*-BC_2N so far.

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