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First-principles study of wurtzite BC_2N

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The structural, electronic, and mechanical properties have been calculated by using first-principles pseudopotential density functional method for three possible configurations of wurtzite BC_2N, which are deduced from four-atom wurtzite boron nitride unit cell. Our results show that the BC_2N-w3 with the maximum C-C and B-N bonds has the lowest total energy among all the reported sp^3-bonded BC_2N structures. Energetically, the wurtzite structure is more stable than the zinc-blende structure for the sp^3-bonded BC_2N, which is different from sp^3-bonded carbon and boron nitride. The present BC_2N-w3 has the highest density, the largest bulk and shear moduli, the largest band gap, and the largest Vickers hardness among all the investigated sp^3-bonded BC_2N structures. The phase stability of BC_2N-w3 indicates that it should be experimentally synthesized more easily than the zinc-blende-structured BC_2N.

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Recently, ternary boron-carbon-nitride (B-C-N) compounds have attracted much attention due to their potential physical and chemical properties. Considerable efforts have been devoted to the synthesis of the B-C-N compounds with different stoichiometric compositions such as BC_2N, BC_4N, and BC_6N, and with different structures such as the hexagonal and cubic structures.[1–6] Up to now, superhard cubic BC_2N with zinc-blende (ZB) structure has been synthesized by using laser heated diamond-anvil cell.[4] However, due to the very similar atomic masses of boron, carbon, and nitrogen atoms (10.81, 12.01, and 14.01, respectively) and the difficulty in growing a larger single crystal, it is still an open question to experimentally determine the refinement crystal structures of these B-C-N compounds. Therefore, first-principles method becomes an important route to explore the crystal structures and properties of the B-C-N compounds.

The previous studies were based on the assumption that the B-C-N compounds should have crystal structures similar to carbon and boron nitride (BN). As known, both carbon and BN have several crystal structures: sp^2 hybridized hexagonal structure such as graphite and hexagonal BN (*h*-BN), sp^3 hybridized ZB structure such as diamond and cubic BN (*c*-BN), and sp^3 hybridized wurtzite (WZ) structure such as lonsdaleite and wurtzite BN (*w*-BN).[7,8] Usually, the stable sequence for the above-mentioned three structures can be ordered as hexagonal, ZB, and then WZ structures. In the possible B-C-N compounds, theoretically, the hypothetical sp^2-bonded hexagonal BC_2N compounds with different interlayer stackings and intralayer distributions,[9–12] and the hypothetical sp^3-bonded zinc-blende BC_2N (ZB-BC_2N) compounds including structural, electrical, mechanical, and optical properties[13–17] have been studied in detail. However, only one paper concerning the one configuration of the hypothetical sp^3-bonded wurtzite BC_2N (WZ-BC_2N) compounds has appeared in literature up to now.[14] Therefore, the systematic investigations of all the possible configurations, and their corresponding properties, of the hypothetical WZ-BC_2N became interesting and necessary. The detailed comparisons among the dense BC_2N phases of WZ, ZB, and recently investigated chalcopyrite structures[18] should be helpful for the deeper understanding of the dense BC_2N compounds. Furthermore, it is necessary to confirm whether WZ-BC_2N is a superhard material, since both lonsdaleite and *w*-BN are superhard materials.[19] As the bulk and shear moduli are not always good indicators of the hardness of a material, the exact estimation of Vickers hardness with microscopic model of hardness[20,21] is necessary for the possible superhard structures of WZ-BC_2N.

In this Brief Report, we have determined the atomic configurations, electronic structures, and elastic properties of the hypothetical WZ-BC_2N crystals by using first-principles calculations, and their Vickers hardness has been estimated by using the microscopic model of hardness. It was found that the WZ-BC_2N has a higher stability and larger Vickers hardness than the cubic BC_2N in the BC_2N system, indicating another possibility to seek novel superhard materials besides cubic BC_2N.

The present calculations were performed with CASTEP code based on the density functional theory.[22] The exchange-correlation functional was treated by the local density approximation (LDA-CAPZ).[23,24] The norm-conserving pseudopotential[25] with cutoff energy of 770 eV was used. According to the Monkhorst-Pack scheme,[26] the *k* points of $12\times12\times6$ for the WZ structures were used. All the structures were relaxed by the Broyden-Fletcher-Goldfarb-Shanno methods.[27] The Mulliken overlap populations were integrated by a distance cutoff of 3 Å. The phonon calculation was carried out using the linear-response method with *k* points of $12\times12\times6$ and *q* vector of $9\times9\times6$.

Figure 1 shows the three possible atomic configurations for the WZ-BC_2N constructed from the four-atom unit cell of *w*-BN. The structural data of relaxed WZ-BC_2N are summarized in Table I. For comparison, the corresponding data of two selected configurations of ZB-BC_2N are listed also in Table I. After structural relaxation, the lattice parameters *a* and *c* of BC_2N-w1 and BC_2N-w2 become larger than the corresponding values of both *w*-BN and lonsdaleite, but the

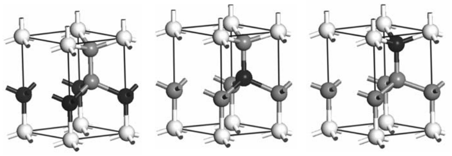
(a) BC_2N-w1 (b) BC_2N-w2 (c) BC_2N-w3

FIG. 1. Three possible configurations of wurtzite BC_2N (after structural relaxation) starting from the four-atom wurtzite BN unit cell. Boron, carbon, and nitrogen are depicted in white, gray, and black, respectively.

lattice constant $a=2.501$ Å of BC_2N-w3 is between $a=2.530$ Å of *w*-BN and $a=2.479$ Å of lonsdaleite. Another change is the bond length along the *c* axis. For lonsdaleite or *w*-BN, the bond length of C-C or B-N along the *c* axis is longer than that in the buckled *a*-*b* plane. In relaxed BC_2N-w3 (see Fig. 1), the bond length of B-C (1.629 Å) is still larger than that of C-C (1.527 Å) or B-N (1.544 Å), but the C-N bond length (1.531 Å) lies between the C-C and B-N bond lengths. Similarly, this change can be found also in BC_2N-w1 and BC_2N-w2. For WZ structure, it is obvious that the chemical bonds in ternary crystals are more complicated than those in binary crystals. Therefore, the refinement structure of ternary WZ-structured crystal cannot be described completely just by the parameters of *a*, *c*, and *u* as in the binary WZ-structured crystal.

The calculated total energy shows that BC_2N-w3 has a lower total energy than the other two structures, which is in accordance with the bond counting rule.[17,28] From Table I, the total energy of BC_2N-w3 is the lowest among the three WZ-BC_2N structures, two selected ZB-BC_2N structures, and one chalcopyrite BC_2N (cp-BC_2N) structure. The previous theoretical studies have shown that the two selected ZB-BC_2N structures have the lowest total energy among all the seven possible ZB-BC_2N configurations.[15,16] Therefore, it can be concluded that BC_2N-w3 is energetically favorable in all the above known sp^3-bonded BC_2N structures. Interestingly, the phase stability sequence of the sp^3-bonded ternary BC_2N is not the same as that of sp^3-bonded carbon or binary BN. The results from our calculations and another group[29] indicate that the ZB structures are more stable than the corresponding WZ structures for both carbon and BN. For a given binary A^NB^{8-N} compound, the phase stability of WZ structure relative to the corresponding ZB structure can be determined by the critical parameter of $\Delta(c/a)$, which is defined as $\Delta(c/a)=c/a-\sqrt{8/3}$.[30] The positive value of $\Delta(c/a)$ indicates that the ZB structure is more stable than the corresponding WZ structure. We also obtain the positive $\Delta(c/a)$ of 0.048 for BC_2N-w3 as well as for lonsdaleite (0.033) and *w*-BN (0.022), indicating that the critical parameter $\Delta(c/a)$ developed from the binary WZ compounds is not valid for the ternary WZ compounds. In fact, the phase stability of sp^3-bonded BC_2N is similar to those of AlN, GaN, BeO, and ZnO to some extent, in which the WZ structure is more stable than the corresponding ZB structure.[30,31] The lower total energy of BC_2N-w3 and the anomalous phase stability of WZ-BC_2N indicate that we should pay more attention to the experimental synthesis of dense WZ-BC_2N crystal, since the previous efforts in searching for dense BC_2N compounds were focused on synthesizing ZB-BC_2N crystal.

The formation energy of WZ-BC_2N can be defined as $E_f=E_{BC_2N}-(E_{w\text{-BN}}+E_{\text{lonsdaleite}})/2$. All the three WZ-$BC_2N$ structures are found to have positive formation energy, indicating that they are metastable. The tendency of phase separation in WZ-BC_2N is quite similar to that in ZB-BC_2N, indicative of the difficulty in the experimental synthesis of WZ-BC_2N. For the trigonal crystal with the classes of $3m$, 32, and $-3m$,[32] its six independent elastic stiffness constants are given as c_{11}, c_{12}, c_{13}, c_{14}, c_{33}, and c_{44}. The complete set of these elastic constants for BC_2N-w3 is listed as follows: $c_{11}=1093.0$ GPa, $c_{12}=113.4$ GPa, $c_{13}=26.4$ GPa, $c_{14}=0$ GPa, $c_{33}=1149.4$ GPa, and $c_{44}=393.2$ GPa. Clearly, the calculated elastic constants c_{ij} of BC_2N-w3 satisfy the mechanical stability restrictions of $c_{11}-|c_{12}|>0$, $(c_{11}+c_{12})c_{13}-2(c_{13})^2>0$, and $(c_{11}-c_{12})c_{44}-2(c_{14})^2>0$ for the trigonal structures,[33] suggesting that BC_2N-w3 structure should be

TABLE I. Calculated lattice parameters, density ρ, total energy E_t, formation energy E_f, energy gap E_g, bulk modulus B, and shear modulus G for three configurations of WZ-BC_2N, two configurations of ZB-BC_2N, and one configuration of cp-BC_2N.

	BC_2N-w1	BC_2N-w2	BC_2N-w3	BC_2N-1	BC_2N-2	cp-BC_2N	cp-BC_2N (Expt.)
Symmetry	$P3m1$	$P3m1$	$P3m1$	$Pmm2$	$P2221$	I-$42d$	
a (Å)	2.545	2.542	2.501	3.565	3.564	3.613	3.642[a]
b (Å)	2.545	2.542	2.501	3.604	3.560	3.613	
c (Å)	4.193	4.238	4.205	3.565	3.607	7.146	
c/a	1.648	1.667	1.681				
ρ (g/cm^3)	3.449	3.419	3.561	3.541	3.544	3.477	3.358[a]
E_t (eV/atom)	−164.68	−164.42	−165.38	−165.14	−165.14	−164.72	
E_f (eV/atom)	0.883	1.138	0.180	0.442	0.447	0.863	
E_g (eV)	0.63		3.99	1.65	2.08	3.10	
B (GPa)	353.2	344.4	407.5	399.2	391.4	367.4	282,[a] 259±22[b]
G (GPa)	312.9	252.7	466.5	440.0	444.4	432.0	238±8[b]

[a] Reference 4.

[b] Reference 34.

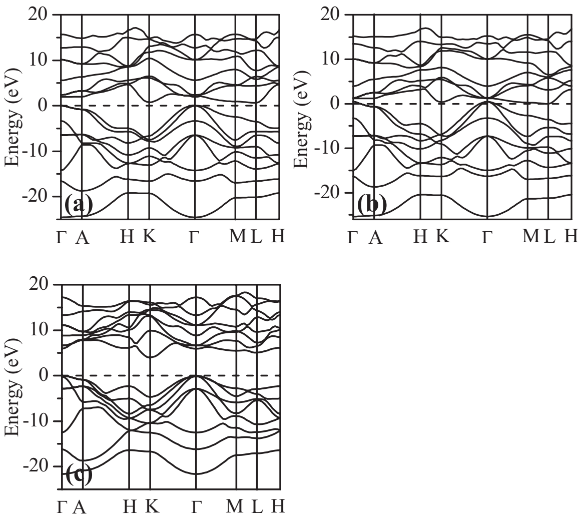

FIG. 2. Calculated electronic band structures of (a) BC_2N-w1, (b) BC_2N-w2, and (c) BC_2N-w3. The Fermi level is indicated by the horizontal dashed line.

mechanically stable. No imaginary phonon frequency observed in the whole Brillouin zone in the calculated phonon dispersion curve and phonon density of states of BC_2N-w3 indicates also that BC_2N-w3 structure is dynamically stable.

The electronic band structures of three WZ-BC_2N configurations are shown in Fig. 2. BC_2N-w1 is a semiconductor with its valence band (VB) at the Γ point, while the bottom of its conduction band (CB) is at K point and L point, respectively. Therefore, there are two distinct indirect band gaps of 0.74 eV at K point and 0.63 eV at L point. For the BC_2N-w2, it seems to be metallic because the top of the VB at the Γ point is above the Fermi level. The band structure of BC_2N-w3 is similar to that of BC_2N-w1. We get the indirect band gaps of 3.99 eV from K point and 5.05 eV from L point for BC_2N-w3, respectively. Besides the difference in band gap values between BC_2N-w1 and BC_2N-w3, the bottom of the CB is on the L point for BC_2N-w1, while it is on the K point for BC_2N-w3.

The calculated indirect band gap of BC_2N-w3 is 3.99 eV, between 3.01 eV of lonsdaleite and 5.01 eV of *w*-BN, which is much larger than the previously reported value of 1.976 eV calculated by using full potential linearized augmented plane wave method.[14] Our results also indicate that BC_2N-w3 has the largest band gap among all the investigated sp^3-bonded BC_2N structures. The band gap of BC_2N-w3 is close to that of diamond (4.15 eV) and less than that of *c*-BN (4.49 eV) obviously. Because of the general underestimation of the band gap in the LDA calculations, BC_2N-w3 should belong to the class of larger gap insulators.

As shown in Table I, the theoretical density ($3.561\ \text{g/cm}^3$) of BC_2N-w3 is the highest among all the reported configurations for the sp^3-bonded BC_2N. This value is also higher than the experimental density ($3.358\ \text{g/cm}^3$) of the synthesized cubic BC_2N.[4,34] Generally speaking, BC_2N-w3 in density is lower than diamond and lonsdaleite, larger than *w*-BN, and close to *c*-BN. The calculated bulk and shear moduli of different WZ-BC_2N configurations are listed in Table I. The bulk and shear moduli of BC_2N-w3 are 407.5 and 466.5 GPa, respectively, larger than those of the other configurations of WZ-BC_2N. In comparison to those of the other dense BC_2N structures, both bulk and shear moduli of BC_2N-w3 are also the largest, respectively.

At last, we will estimate the Vickers hardness of different configurations for WZ-BC_2N. Because the metallic component in the chemical bonds of BC_2N-w2 will severely decrease hardness,[35] here we consider only BC_2N-w1 and BC_2N-w3. According to our microscopic model[20] of hardness, their Vickers hardness can be calculated as follows:

$$H_V=[(H_V^{\text{C-C}})^{n_1}(H_V^{\text{B-N}})^{n_2}(H_V^{\text{B-C}})^{n_3}(H_V^{\text{C-N}})^{n_4}]^{1/(n_1+n_2+n_3+n_4)}, \qquad (1)$$

where $H_V^{X-Y}=350(N_e^{X-Y})^{2/3}e^{-1.191f_i^{X-Y}}/(d^{X-Y})^{2.5}$ is the hardness of the hypothetical binary compound composed of $X-Y$ bond, n_j $(j=1-4)$ is the number of corresponding chemical bond in the unit cell, d^{X-Y} is the length of the $X-Y$ bond, N_e^{X-Y} is the valence electron densities of the hypothetical compounds composed of $X-Y$ bond, and f_i^{X-Y} is Phillips ionicity of $X-Y$ bond. According to our generalized ionicity scale,[21] the Phillips ionicity f_i^{X-Y} of $X-Y$ bond can be calculated as

$$f_i^{X-Y}=(f_h^{X-Y})^{0.735}=[1-\exp(-|P_c-P^{X-Y}|/P^{X-Y})]^{0.735}, \qquad (2)$$

where f_h^{X-Y} is the new ionicity scale of an $X-Y$ bond based on bond overlap population, P^{X-Y} is the overlap population of an $X-Y$ bond, and P_c is the overlap population of the bond in a pure covalent crystal containing the same type of chemical bond. From the calculation results of the population in pure covalent lonsdaleite, we obtain two P_c values of 0.41 and 0.86 for the bonds along the c axis and in the buckled *a*-*b* plane in the wurtzite structure, respectively. The bond number n_j, the bond length d^{X-Y}, the bond population P^{X-Y}, the valence electron density N_e^{X-Y}, the ionicities f_h^{X-Y} and f_i^{X-Y}, and H_V^{X-Y} for each type of chemical bond are listed in Table II. Based on the above data, the theoretical Vickers hardness of BC_2N-w1 and BC_2N-w3 are found to be 62.0 and 76.8 GPa, respectively, indicating that they are superhard materials. In comparison to the theoretical Vickers hardness of ZB-BC_2N (70–72 GPa),[36] the Vickers hardness of BC_2N-w3 is slightly higher, which is consistent with the above results of the calculated higher density and higher bulk and shear moduli. It should be noted that the same type of chemical bonds, such as C-C and B-N bonds, exhibit very large difference of ionicities in different configurations. When the bond length in WZ-BC_2N is close to the length of the corresponding C-C bond in lonsdaleite, this bond shows small ionicity. For the WZ-BC_2N, it seems that the decrease of the C-N and B-C bond numbers benefits the hardness.

In summary, we have presented a complete first-principles investigation on the structural, electronic, and mechanical properties of the three possible configurations of wurtzite BC_2N deduced from the four-atom *w*-BN unit cell. The BC_2N-w3 is more energetically stable than the other reported sp^3-bonded BC_2N structures at zero pressure. The BC_2N-w3 also has the highest density, the largest bulk and shear moduli, the largest energy band gap, and the highest Vickers hardness among all the previously considered sp^3-bonded BC_2N structures. It is interesting that the wurtz-

TABLE II. Bond type, bond number n_j, bond length d^{X-Y}, bond population P^{X-Y}, valence electron density N_e^{X-Y}, ionicities f_h^{X-Y} and f_i^{X-Y}, H_V^{X-Y} for each type of chemical bond in BC_2N-w1 and BC_2N-w3, and their theoretical Vickers hardness H_V.

	Bond type	n_j	d^{X-Y} (Å)	P^{X-Y}	N_e^{X-Y}	f_h^{X-Y}	f_i^{X-Y}	H_V^{X-Y}	H_V (GPa)
BC_2N-w1	C-C	1	1.435	0.68	0.885	0.328	0.440	77.4	62.0
	B-N	1	1.615	0.26	0.662	0.438	0.545	41.9	
	B-C	3	1.557	0.80	0.808	0.072	0.145	84.5	
	C-N	3	1.598	0.66	0.577	0.261	0.373	48.2	
BC_2N-w3	C-N	1	1.531	0.37	0.653	0.102	0.187	72.7	76.8
	B-C	1	1.629	0.36	0.703	0.130	0.223	62.7	
	C-C	3	1.527	0.88	0.731	0.022	0.061	91.6	
	B-N	3	1.544	0.72	0.754	0.177	0.280	70.1	

ite structure is more stable than the zinc-blende structure for the sp^3-bonded ternary BC_2N phase, which is different from the sp^3-bonded carbon and BN. Considering the phase stability and Vickers hardness of BC_2N-w3, more attention should be paid to the experimental synthesis of wurtzite BC_2N crystal.

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