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Prediction of a sandwichlike conducting superhard boron carbide: First-principles calculations

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Our first principles calculations predict a tetragonal BC_3 (t-BC_3) phase originating from the cubic diamond structure. The t-BC_3 structure is formed by alternately stacking sequence of metallic CBC and insulating CCC blocks, exhibiting a sandwichlike metal and/or insulator layered structure with the anisotropic conductivity on the basal planes formed by the metallic CBC blocks. Its stability has been confirmed by our calculations of the total energy, elastic constants, and phonon frequencies. A low critical pressure of ~4 GPa for a synthesis of the t-BC_3 from the graphitelike BC_3 (g-BC_3) is expected.

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Superhard materials have very important applications in mechanical machining and semiconductor industries. Both synthetic and hypothetical superhard materials belong to covalent and polar-covalent compounds composed of light elements in periods 2 and 3 of the Periodic Table.[1] In the past couple of decades, a lot of interests have focused on the theoretical predictions[2–5] and experimental syntheses[6–8] of C_3N_4 and cubic BC_2N. One important focus has been the search for novel superhard materials with conductivity.[9,10] First-principles calculation is one strong and useful tool to predict the crystal structure and its properties related to the electron configuration of a material before its synthesis. Bond density, bondlength and a degree of covalency are three determinant factors for the hardness estimation. These three parameters can be determined by first-principles calculations and used in a microscopic model of hardness to successfully estimate the hardness of a covalent crystal material,[11] making the design of a new superhard material before its synthesis possible. Experimentally, a graphitic BC_3 material has been synthesized by the chemical reaction of benzene and boron trichloride.[12] The calculated electronic structure[13] suggested that the B atoms in the graphitic BC_3 lead to a small perturbation on the charge density and structure of the carbon ring, resulting in a slight difference between the C-C bond (1.42 Å) and B-C bond (1.55 Å). It is well known that graphite and hexagonal BN can be transformed into a denser cubic structure in high pressure and high-temperature conditions.[14] It may be possible that a new high-pressure BC_3 phase could be synthesized from the graphitic BC_3 phase with high temperature and high pressure, and it may be the one new candidate of superhard materials. The superhard diamond and cubic BN are insulators with energy gaps of 5.45 eV (Ref. 15) and 6.0 eV,[16] respectively. Theoretically predicted superhard materials such as C_3N_4 (Ref. 2) and cubic BC_2N (Ref. 5) with isoelectronic structure are insulators or semiconductors. The boron-doped diamond is a very interesting material due to its hopping conductivity and unusual behavior of the Hall coefficient in a wide temperature region.[17] Because of the electronic deficiency in a hypothetic tetragonal B_2CN crystal, first-principles calculations revealed certain metallicity in it.[18] Therefore, a diamondlike BC_3 compound with the electronic structure similar to the tetragonal B_2CN crystal is likely to be a conductive and superhard material. In this Brief Report, first-principles calculations have been performed to investigate the stability and conductivity of a tetragonal BC_3 (t-BC_3) phase derived from the diamond structure. We found that this phase, which is metastable at zero pressure, has a metallicity and hardness of over 40 GPa.

Our calculations were performed using the *ab initio* plane-wave pseudopotential approach within the framework of the density-functional theory implemented in the CASTEP software.[19] The ultrasoft pseudopotentials[20] were used in the calculations, and the plane-wave cutoff energy was 310 eV. The exchange-correlation terms were considered by the Perdew-Berke-Ernzerhof form of the generalized gradient approximation.[21] The k-points samplings were $7\times7\times7$ and $6\times6\times4$ in the Brillouin zone for the t-BC_3 and the graphitelike BC_3 (g-BC_3), respectively, according to the Monkhorst-Pack scheme.[22] The elastic constants C_{ij} and bulk modulus B were directly calculated by the CASTEP code. The phonon frequencies of the structure were calculated with a linear response theory[23] using the ABINIT code.

For the cubic diamond and the typical intermetallic structures of $B2$, $B11$, $B33$, $C11b$, $D0_{15}$, $D0_{19}$, $D0_{22}$, $D0_{23}$, $L1_0$, $L1_1$, $L1_2$, $L2_1$, $D0_3$, the number of atoms in the unit cell or the super unit cell composed of two unit cells (for only the B_2 and $L1_0$) is $4n$ with n being an integer. Based on the above structures, we have constructed a series of different hypothetic configurations of BC_3 crystals. After the full geometrical optimization, we have found that except for three hypothetic BC_3 structures derived from $L1_2$, $L2_1$, and diamond, all the other configurations are not able to keep their original structures, indicative of their instability. Among these three probable structures, the one derived from diamond is found to have the lowest total energy per atom. For this structure, only two possible configurations have been found, which are constructed by the boron substitution of two carbon atoms either within or between the two fcc sublattices of the eight carbon atoms in the diamond unit cell.

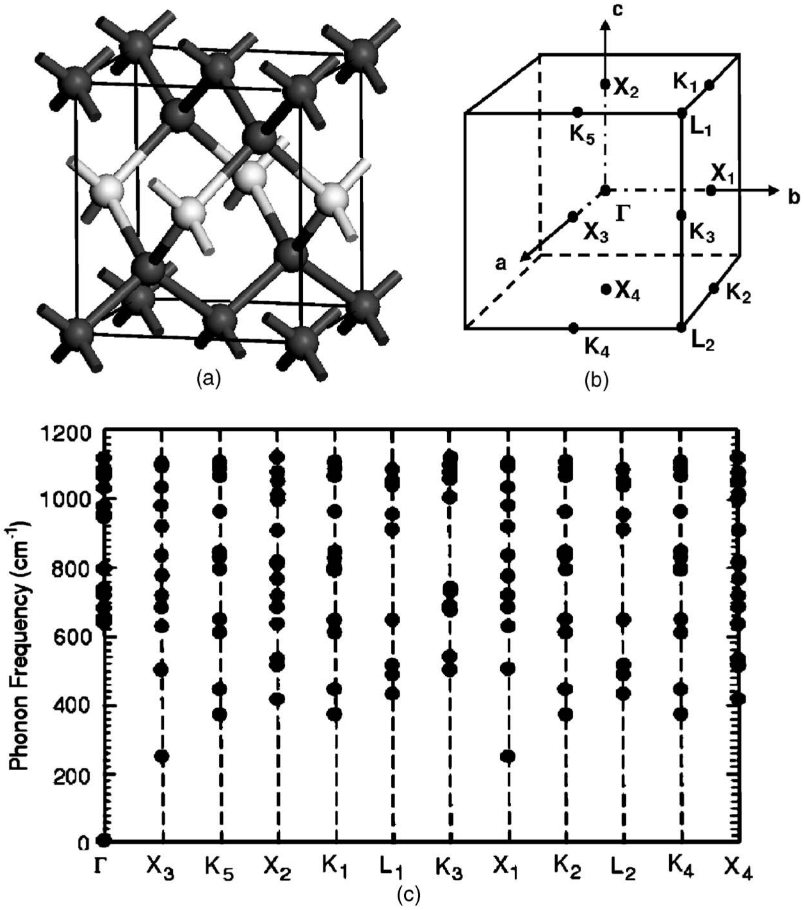

FIG. 1. (a) The unit cell for the t-BC$_3$ structure with the boron (white) substitution of two carbon (black) atoms within the same fcc sublattice of the eight-atom diamond unit cell; (b) high **q** symmetry points indicated in the Brillouin zone of the t-BC$_3$ phase; (c) the phonon frequencies calculated at the high **q** symmetry points shown in (b).

The t-BC$_3$ structure derived from the first case has been shown to have the lower energy. Hence, the t-BC$_3$ phase is energetically the most stable one among our investigated hypothetic structures. Its unit cell as shown in Fig. 1(a) contains eight atoms with the density of 3.26 g/cm^3 and the $P\bar{4}2m$ symmetry. Both carbon and boron are fourfold-coordinated. Different stacking arrangements of the g-BC$_3$ crystals have been investigated by Sun *et al.* using the *ab initio* pseudopotential density-functional method at an equilibrium of zero pressure.[24] Only two possible g-BC$_3$ structures were found among them, one has the ABAB,…, stacking sequence, and the other has the ABCABC,…, stacking sequence. The ABAB,…, stacking sequence has the lower energy, so it is energetically favorable. For comparison, the g-BC$_3$ with the ABAB,…, stacking sequence has been chosen in our studies to explore the possible synthesis of the t-BC$_3$ from the g-BC$_3$ in high-pressure condition. Its unit cell has 32 atoms with the *Cmmcm* symmetry and the density of 1.95 g/cm^3.

In Table I, we list the calculated total energies and structural parameters for t-BC$_3$ and g-BC$_3$ phases. Clearly, the t-BC$_3$ phase has a relatively high symmetry but low isotropy. It is constructed by two types of building blocks of CBC and CCC, forming a sandwich-like layered structure with the alternately stacking sequence of atomic planes C-C-B-C-C-C-B-C-C,…, along the c axis. The CBC block is composed of one boron sheet and one carbon sheet, while the CCC block is composed of two carbon sheets. The bond lengths are 1.627 and 1.522 Å for the B-C and C-C bonds, respectively, leading to a longer c axis and the formation of the tetragonal phase. In the t-BC$_3$ cell, there exist three types of bond angles: C-C-C, C-B-C, and B-C-C. Because of the difference between the B-C and C-C bondlengths, the formation of the ideal diamond-type tetrahedral bond angle of 109.4° becomes impossible. The C-B-C bond angles in the

TABLE I. Equilibrium structural parameters, total energies, volumes of unit cells, bulk moduli, and densities calculated for the t-BC$_3$ and g-BC$_3$ structures.

	t-BC$_3$	g-BC$_3$
Space group	$P\bar{4}2m$ (No. 111)	*Cmcm* (No. 63)
a (Å)	3.513	8.834
b (Å)	3.513	5.104
c (Å)	3.871	7.071
Atomic positions	*B* (0.5,0,0.5)	*B* (0.167,0.823,0.25)
	*C*1 (0,0,0)	*C*1 (0.159,0.323,0.25)
	*C*2 (0.25,0.25,0.229)	*C*2 (0.792,0.562,0.25)
	*C*3 (0.5,0.5,0)	*C*3 (0.421,0.585,0.25)
E_{tot} (eV/atom)	−136.11	−136.18
V (Å^3)	47.8	318.8
B (GPa)	360.6	
ρ (g/cm^3)	3.26	1.95

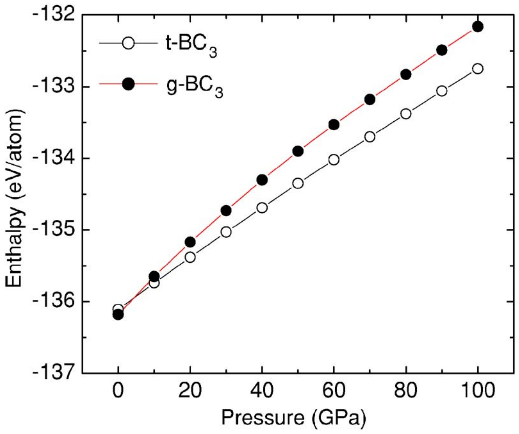

FIG. 2. (Color online) Enthalpy vs pressure curves.

(110) and $(0\bar{1}1)$ planes are altered to 99.7° and 114.5°, respectively, the B-C-C bond angles are increased up to 111.7°, and the C-C-C bond angles change just slightly in the range $109.3°-109.7°$.

The elastic constants of t-BC$_3$ have been calculated, which are listed as follows: $C_{11}=C_{22}=660.1$ GPa, $C_{33}=724.4$ GPa, $C_{44}=C_{55}=459.7$ GPa, $C_{66}=285.1$ GPa, $C_{12}=168.0$ GPa, and $C_{13}=C_{23}=221.2$ GPa. Obviously, they satisfy the Morris mechanical stability criteria for a tetragonal crystal, i.e., $C_{11}(C_{12}+C_{33})\geq C_{12}^2$, $C_{22}\geq C_{23}$, $C_{44}\geq 0$, and $C_{55}\geq 0$.[25] In Fig. 1(c), we give the calculated phonon frequencies for the t-BC$_3$ structure at high symmetry points. No imaginary frequency is observed, indicative of the dynamical stability of the structure. In comparison to diamond, the existence of B atoms in the t-BC$_3$ crystal is favorable to the thermal stability. The bulk modulus of t-BC$_3$ is 360.6 GPa, close to the experimental value of the cubic BN.[1] Its shear modulus calculated with the formula in Ref. 18 is 336.5 GPa, lying between the spinel Si$_3$N$_4$ (Ref. 26) and cubic BN.[1] The hardness of t-BC$_3$ (~41 GPa) has been calculated using our microscopic model of hardness with some further modification,[11] indicative of the superhard property.

Figure 2 shows the enthalpies for g-BC$_3$ and t-BC$_3$ calculated in the presence of pressure. At zero pressure, g-BC$_3$ has a lower enthalpy than t-BC$_3$, indicative of its higher stability. With the increase of pressure, the enthalpies of both g-BC$_3$ and t-BC$_3$ increase. At ~4 GPa, they become equal to each other, while above ~4 GPa, the enthalpy of t-BC$_3$ becomes lower than that of g-BC$_3$, implying that at high pressure t-BC$_3$ becomes more stable than g-BC$_3$. The critical pressure for the synthesis of t-BC$_3$ from g-BC$_3$ can be as low as just ~4 GPa, lower than that of diamond (7.2 GPa) and the hypothetical cubic C$_3$N$_4$ (12 GPa).[4] It should be stressed that the t-BC$_3$ phase cannot be achieved by a direct compression of the stable g-BC$_3$ phase due to the lack of consistence in their structures. Even at the pressure as high as 500 GPa, our calculations show that the g-BC$_3$ phase still keeps its layered structure. However, with a proper catalyst developed, the synthesis of the t-BC$_3$ phase from the g-BC$_3$ phase would be possible. With g-BC$_3$ being solved in the liquid catalyst at high temperature and high pressure, after the supersaturation is reached, a BC$_3$ phase will precipitate. Because the enthalpy of the t-BC$_3$ is lower than that of the g-BC$_3$ with the given pressure higher than 4 GPa, the precipitating BC$_3$ phase will favor the t-BC$_3$ phase. The electronic band structure of the t-BC$_3$ phase at equilibrium shows that the top of its valence band is ~2.7 eV above Fermi level, suggesting that the t-BC$_3$ phase should have a metallicity as expected. Generally, all covalent isoelectronic compounds with the zinc-blende structure are semiconducting, i.e., the tops of their valence bands are tangential to the Fermi level. Due to the electron deficiency of boron atoms in the system, the charges are not balanced and the electrons do not fill up the sp^3-hybridized orbits with the appearance of some empty orbits above the Fermi level. In fact, the t-BC$_3$ crystal is similar in the band structure to the electron-deficient B$_2$CN, which has been predicted to have the conducting property.[18] The question here is whether all of the boron and carbon atoms in t-BC$_3$ contribute to the formation of the empty orbits. As shown in Fig. 3, the s and p local density of states for each atom as well as the total density of states in the t-BC$_3$ unit cell have been calculated. The valence bands beneath the Fermi level are mainly from the 2p orbits of the carbon and boron atoms, while the empty bands above the Fermi level come almost equally from the 2p orbits of boron and carbon atoms in the CBC block with just a small contribution from 2p orbits of carbon atoms in the CCC block. Therefore, these empty orbits are focused to the sp^3-hybridized B-C bonds in the CBC block, indicating that the CBC block is metallic, while the CCC block is almost insulating. In other words, the t-BC$_3$ crystal may be able to conduct anisotropically on its basal planes formed by the CBC blocks instead of the CCC blocks.

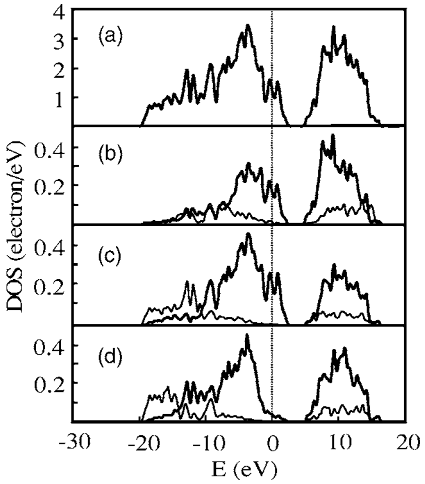

FIG. 3. The total density of states for t-BC$_3$ (a) and the s (thin line) and p (thick line) local density of states for the boron atom (b), the carbon atom coordinated with the boron atom in the CBC block (c), and the carbon atom in the CCC block (d).

In summary, a superhard t-BC$_3$ phase originating from the cubic diamond structure has been predicted according to our first-principles calculations. The t-BC$_3$ phase is constructed by an alternately stacking sequence of metallic CBC and insulating CCC blocks along the c axis, forming an ideal sandwichlike metal-insulator lattice at the atomic level with relatively high symmetry but low isotropy, suggestive of the anisotropically conducting property on the basal planes formed by the CBC blocks. The structural stability has been unambiguously confirmed by our calculations of total energy, elastic constants, and phonon frequencies. A critical pressure of ~4 GPa is predicted for the synthesis of the *t*-BC_3 phase from the *g*-BC_3 phase in a high-pressure condition if the proper catalyst is found, much lower than those of diamond and hypothetical cubic C_3N_4. This unique crystallographic feature of *t*-BC_3 is expected to have some potential applications in electronic devices such as the metal-insulator junction and metal-insulator "multiple quantum well" devices and photonic devices based on the surface plasmon polaritons.

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