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Abstract

An assumed B$_2$CN crystal system containing seven possible diamond-structured configurations in boron-carbonitride B–C–N compounds has been studied by using an *ab initio* pseudopotential density functional method. After structural relaxation, the lattice constant, bulk modulus and shear modulus, and electronic band structures as well as the electron density of states are calculated for the derived B$_2$CN structures. A unique type t-B$_2$CN phase deduced from the diamond structure contains only B–N and B–C bonds in a tetragonal cell, and it has the lowest total energy and an electron-deficiency structure with non-vanishing density of states at the Fermi energy. Unlike diamond and c-BN, the t-B$_2$CN phase may show metallicity.

1. Introduction

In recent years, ternary diamond-structured B–C–N compounds have received considerable attention. Diamond and cubic boron nitride (c-BN) are the hardest of all known solids. They share a number of similar physical properties including hardness, wide band gap and high melting points. The phase diagrams of C and B–N are similar, including a hexagonal structure as their stable form at ambient conditions, and a high-pressure and high-temperature hexagonal (wurtzite) structure as well as a cubic (zinc-blende) form. Therefore, a solid solution between C and BN is anticipated to exist in the ternary B–C–N system according to their atom size [1].

Early theoretical calculations of the bulk modulus B and shear modulus G have suggested that the diamond-structured B–C–N compounds should possess an intermediate hardness between diamond and c-BN and have some interesting properties found in diamond and c-BN [2, 3]. Diamond can only be used at around 600 °C in air, while c-BN avoids oxidation

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up to 1100 °C [4, 5]. Based on this idea, many researchers devoted their effort to modify the graphite-like B–C–N phases into denser covalently bonded materials. Badzian [6] carried out pioneering work in which the graphitic material $B_x C_y N_x$ was compressed under high pressure (14 GPa) and high temperature (3300 K). The product was claimed to be a hybrid of diamond and c-BN. Nakano *et al* [7] observed the formation of diamond-structured cubic boron carbonitrides (c-BC_2N) from graphitic BC_2N under 7.7 GPa and ∼2000–2400 K. However, the c-BC_2N segregates into diamond and c-BN-like structures at higher temperature. Knittle *et al* [1] reported the synthesis of cubic BC_xN ($x = 0.9$–3.0) solid solutions from microcrystalline B–C–N compounds or a mixture of graphitic carbon and boron nitride, using static pressure (30 GPa) and a laser-heated diamond cell (∼2000–2500 K). A similar technique was also used by Solozhenko *et al* [8] to synthesize c-BC_2N from graphitic BC_2N. They indicated that the hardness of the synthesized c-BC_2N is higher than that of c-BN single crystals and slightly lower than that of diamond. As mentioned above, ultrahigh pressure and temperature were needed in the transformation from hexagonal to cubic form in the B–C–N system. Sasaki and co-workers [9] tried to find some catalyst such as Co to synthesize diamond-structured B–C–N compounds. They observed simultaneous crystallization of diamond and c-BN from a melt of cobalt–boron–carbon–nitrogen at 5.5 GPa and 1400–1600 °C. In order to reveal the possible electronic structures and elastic properties, several first-principles studies on the structure of diamond-structured B–C–N compounds have been carried out [10–13]. Recently, Sun *et al* [10] studied seven possible diamond-structured BC_2N structures by using an *ab initio* pseudopotential density functional method. The bulk and shear moduli of the hardest structures they studied [10] are comparable to or slightly higher than those of c-BN, which is similar to the c-BC_2N synthesized by Knittle *et al* [1]. Theoretical calculation revealed only metastable phases for diamond-structured BC_2N structures which energetically favour separation into superlattices of alternating diamond and c-BN layers [10, 13]. Experimental research has also indicated the occurrence of phase separation in the c-BC_2N system [7, 8].

Up to now, almost all the zinc-blende structures such as diamond, c-BN and c-BC_2N that have been studied are isoelectronic, and are either insulators or semiconductors, whereas a electron-deficient system would show some complicated but interesting electronic transport properties [14]. An orthorhombic-structured B_2CN in B–C–N systems has recently been synthesized from the turbostratic B_2CN by high pressure and high temperature [15]. Though the B_2CN crystal has a low density in comparison with that of diamond, phase separation has not been observed. So far there has been no report on theoretical or experimental research on the possible diamond-structured B_2CN crystal. By replacing C with B atoms in the unit cell of BC_2N, electron deficiency would be introduced into the B–C–N system. It is not clear that a diamond-structured B_2CN crystal could exist either in stable or metastable form and if it could be superhard with characteristic electronic properties. Therefore we focus our attention on the stoichiometry B_2CN in the present work. The structural stabilities, elastic modulus and electronic properties of the diamond-structured B_2CN crystal were studied by first principles and discussed according to their structural forms.

2. Method of calculation and structural model

CASTEP employs the density functional theory (DFT) plane-wave pseudopotential method to perform first-principles quantum mechanics calculations that explore the structural stability and properties of crystals [16]. One of the main features of the CASTEP code is that the internal coordinates can be automatically relaxed so that the structure with the minimum total energy is obtained. A gradient-corrected form of the exchange–correlation functional (generalized gradient approximation (GGA-PBE)) was used [17]. Ultrasoft pseudopotentials

(USP) were introduced by Vanderbilt in order to allow calculations to be performed with the lowest possible cut-off energy for the plane-wave basis set [18]. The calculations were made using a plane-wave cut-off of 310 eV. This cut-off yields well-converged properties of the fully relaxed structure. The Brillouin zone (BZ) sampling was performed using special k-points generated by the Monkhorst–Pack scheme with parameters $7 \times 7 \times 7$ [19].

The average shear modulus G can be expressed by means of elastic constants. The elastic constants are calculated by the finite strain technique implemented in CASTEP [20]. For an orthorhombic crystal the value of G is given by the following formula [11]:

$$G = \{(C_{11} + C_{22} + C_{33} - C_{12} - C_{31} - C_{23}) + 3(C_{44} + C_{55} + C_{66})\}/15.$$
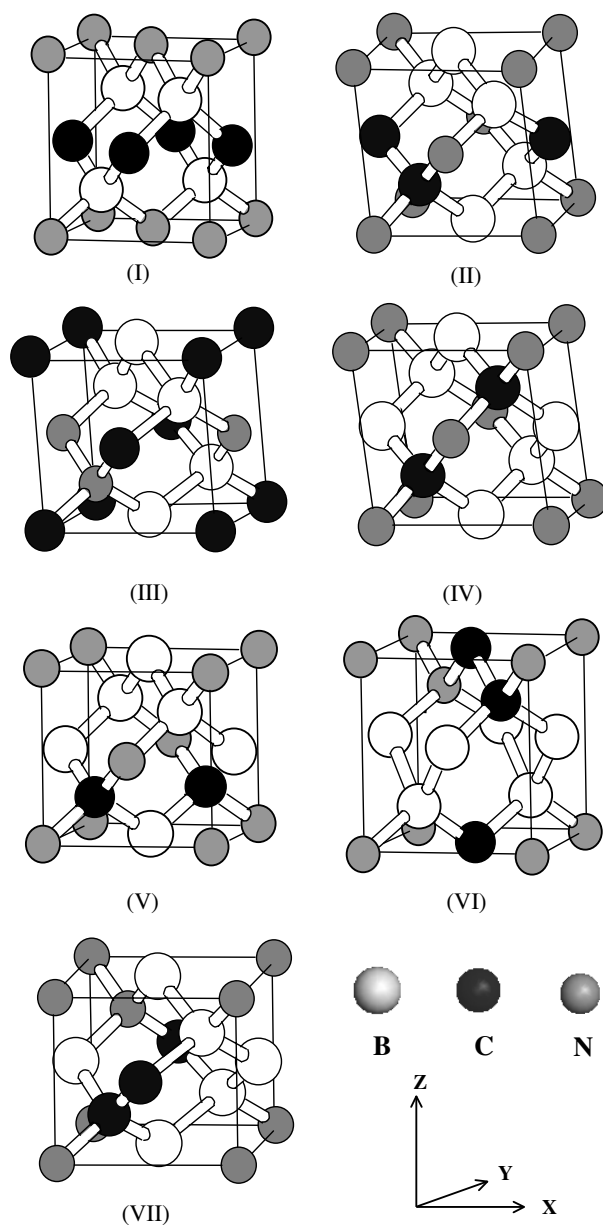
Starting from a diamond structure, six of the eight carbon positions were replaced by two nitrogen and four boron atoms in an eight-atom cubic unit cell. However, for the diamond-structured B$_2$CN in general, according to Sun et al [10] there are only seven topologically different B$_2$CN configurations out of totally 420 possible configurations in an eight-atom zinc-blende-structured cubic unit cell (see figure 1, after structural relaxation). The seven B$_2$CN configurations are numbered according to increasing numbers of B–B and N–N bonds in the unit cell. The I-B$_2$CN is B–B, C–C and N–N bonds free, and only contains B–N and B–C bonds. Besides three B–B bonds, the second (II-B$_2$CN) configuration has a C–C bond, whereas the third (III-B$_2$CN) configuration has an N–N bond. The fourth (IV-B$_2$CN) and fifth (V-B$_2$CN) configurations are both constructed by avoiding C–C and N–N bonds, but differ in whether the four B–B bonds form layers separating the N–C layers. The sixth (VI-B$_2$CN) and seventh (VII-B$_2$CN) configurations both have a C–C and an N–N bond, but have different atomic layer arrangements similar to that between IV-B$_2$CN and V-B$_2$CN. We performed the first-principles calculations for the seven B$_2$CN configurations, and preliminarily assigned the lowest symmetry P1 to the crystals so that no symmetry conditions are imposed and all atoms in the cells are free to optimize independently. The optimization of the lattice parameters and the ions' relaxation were performed iteratively until the minimum on the total energy was met.

3. Results and discussion

The calculated lattice parameters, total energies and cohesive energies of the seven B$_2$CN structures are listed in table 1. The calculated and experimental values of diamond and c-BN as well as the calculated values of I-BC$_2$N proposed by Sun et al [10] are also provided in table 1 for comparison. The agreements between calculated and experimental values are satisfactory. The errors are less than 1% for lattice parameters and 5% for bulk modulus and shear modulus.

Of all the optimized B$_2$CN structures, I-B$_2$CN structure has the lowest total energy (-146.3 eV/atom), the lowest unit-cell volume (48.83 Å^3) and the highest crystal symmetry (tetragonal $P\bar{4}2m$ (No. 111)) due to the lack of bonds of the same type of atoms in the structure. We thus name I-B$_2$CN as t-B$_2$CN hereafter. All other structures from II-B$_2$CN to VII-B$_2$CN have their total energy between -145.7 and -146.0 eV/atom, unit-cell volume between 49.23 and 50.04 Å^3, and triclinic P1 crystal symmetries.

The increase of B content and decrease of C content are the essential facts for differentiating B$_2$CN from BC$_2$N structures. It has been predicted that the more stable BC$_2$N structures would have no B–B or N–N bonds and maximize the number of C–C and B–N connections, with C–B disfavoured [11]. However, though B–B and N–N bonds have been avoided in the most stable BC$_2$N structures of the eight-atom zinc-blende-structured unit cell, the structures still contain equal numbers of C–C, B–N, C–N and C–B bonds [10]. Whereas for the B$_2$CN structures, the formation of lower energy C–C bonds would not help, since there are only two C atoms in

Figure 1. The seven possible topologically different B_2CN structures starting from an eight-atom diamond-structured unit cell after structural relaxation. Figure 1 in [10] is referred to for these structures.

the unit cell, adding a C–C bond will unavoidably introduce at least three higher energy B–B bonds to the system. As seen in figure 1, the high stability of the t-B_2CN structure relies on the formation of a unique high symmetry structure in which the B–B and N–N bonds are avoided, but equal numbers of B–N and C–B bonds can be retained.

In comparison with that of the c-BN structure, the optimized t-B_2CN phase becomes tetragonal due to lattice expansion of the z axis caused by sequentially replacing one of the two layers of N by C on the basal planes. Therefore a sandwich-like ordered structure in the

Table 1. The calculated total energies (E_{tot}), cohesive energies (E_{coh}), structural parameters and elastic moduli of seven B$_2$CN structures after structural relaxation. As a comparison, the corresponding values for diamond, c-BN and I-BC$_2$N proposed by Sun *et al* [10] are also listed.

Structures	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	Cell volume (Å^3)	E_{tot} (eV/atom)	E_{coh} (eV/atom)	B (GPa)	G (GPa)
I-B$_2$CN	3.544	3.544	3.893	90.00	90.00	90.00	48.83	−146.3	−8.8	332.1	269.3
II-B$_2$CN	3.567	3.887	3.567	90.60	94.27	89.39	49.30	−146.0	−8.5	319.2	272.7
III-B$_2$CN	3.754	3.557	3.756	92.51	91.04	87.46	50.04	−145.7	−8.2	304.6	285.2
IV-B$_2$CN	3.560	4.024	3.560	90.00	96.58	90.00	49.23	−145.9	−8.4	298.1	357.9
V-B$_2$CN	3.498	3.978	3.547	90.00	90.00	90.00	49.37	−145.8	−8.3	315.1	291.5
VI-B$_2$CN	3.516	3.516	4.034	89.90	90.01	83.56	49.56	−145.9	−8.4	323.2	351.2
VII-B$_2$CN	3.780	3.775	3.512	92.30	87.76	90.71	50.04	−145.6	−8.1	304.2	257.4
Diamond	3.538	3.538	3.538	90.00	90.00	90.00	44.23	−155.6	−9.3	439.8	530.5
(Exp.)	(3.567[a])									(443[b])	(535[b])
c-BN	3.611	3.611	3.611	90.00	90.00	90.00	46.41	−176.0	−9.8	374.7	392.8
(Exp.)	(3.615[a])									(400[b])	(409[b])
I-BC$_2$N	3.570	3.606	3.570	90.00	90.56	90.00	45.97	−165.6	−9.0	363.7	423.6

[a] Reference [1].
[b] Reference [3].

sequence of N–B–C–B along the z axis can be observed. The t-B$_2$CN structure, shown in figure 1(a), has both N and C atoms coordinated with four B atoms, whilst the B atoms are surrounded by two C and two N atoms. Only two types of chemical bonds appear in the t-B$_2$CN crystal. All the B–C bond lengths are 1.63 Å, substantially larger than that of 1.57 Å for c-BN, whereas the B–N bond lengths are 1.54 Å, leading to a high density of 3.46 g cm^{-3} for the crystal. Owing to the different bond lengths, the formation of ideal diamond-type tetrahedral bond angles of 109.4° is impossible. The C–B–C bond angles are decreased to 99.8°, and the C–B–N bond angles are increased to 112.0°, while the N–B–N bond angles are transformed to 108.4°. These characterizations have formed a contrast to those in the BC$_2$N system. In the BC$_2$N system [10], the optimized low-energy pseudo-cubic structure (i.e. struc-1 in Sun *et al* [10]) has four types of bonds forming five bond angle configurations, but the corresponding bond lengths and angles are spread within a narrow region (1.51–1.57 Å and 107.2°–112.3°) and result in relatively smaller lattice distortion.

All the calculated elastic constants C_{ij} ($C_{11} = C_{22} = 598.8$, $C_{33} = 686.3$, $C_{44} = C_{55} = 419.5$, $C_{66} = 69.9$, $C_{12} = 145.8$, $C_{13} = C_{23} = 212.6$, others $= 0$ in GPa) of the t-B$_2$CN phase are positive. For a crystal with tetragonal symmetry, the mechanical stability is governed by the following conditions: $C_{11}(C_{22} + C_{33}) \geqslant 2C_{12}^2$, $C_{22} \geqslant C_{23}$, $C_{44} \geqslant 0$ and $C_{55} \geqslant 0$ [21]. The calculated C_{ij} for t-B$_2$CN appears to meet the above conditions. Material scientists have aimed at finding materials with high values of bulk modulus B and shear modulus G. In fact, the bulk modulus measures the resistance to volume change, which has little direct connection with hardness. A better correlation has been observed between hardness and G for the covalent compounds with the zinc-blende structure [3]. Although the bulk modulus of t-B$_2$CN is close to that of c-BN, its isotropic shear modulus is only 269.3 GPa, much lower than the 409 GPa of c-BN. As mentioned above, unlike BC$_2$N, B$_2$CN is an electron-deficient system. The eight atoms (4B–2C–2N) in a unit cell lack two electrons for standard sp^3 hybrid bonds. The electron deficiency is likely to be the fundamental cause of the weaker B–C bonds, which results in remarkable bond angle distortion and elongation of the unit cell along the c axis, and subsequently leads to the lower shear modulus of the t-B$_2$CN phase. Here, we only discuss the shear modulus of B$_2$CN phase in a supercell containing eight atoms. For supercells containing
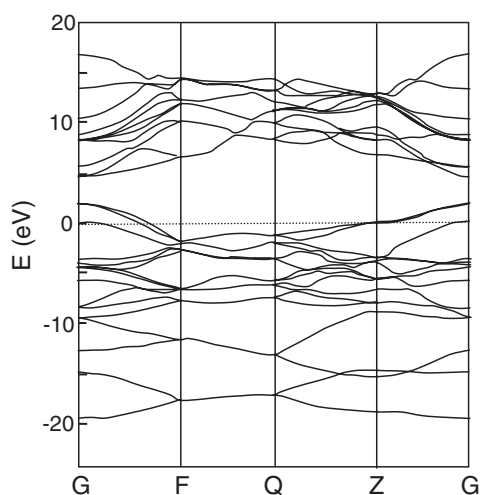
Figure 2. The electronic band structures of the t-B_2CN crystal shown in figure 1.

more atoms, the shear modulus could be different due to different arrangements of the atoms in the crystal structure. However, the shear modulus of the ternary system is not likely to reach that of c-BN, due to the weaker B–C bond introduced by the substitutional C atoms.

Figure 2 shows the calculated band structure of t-B_2CN phase at the equilibrium geometries. In figure 3, we plot the s and p local density of states (LDOS) of each atom as well as the total DOS in the unit cell in t-B_2CN. The valence band (VB) of t-B_2CN is dominated by the states of N and C atoms with some mixing of B states. The peaks at the bottom of the VB are mainly derived from the 2s orbitals of N, while the peaks at higher energy are mainly from C 2s, C 2p, N 2p and B 2p states. It is obvious that the conduction bands (CB) come mainly from the p states of the atoms in t-B_2CN. There is about 1/4 of the area of the C 2p peak below the gap in every carbon atom surpassing the Fermi level. The small sections of CB of B and N below the gap are also from the participation of the 2p orbitals. However, for the CB above the gap, besides the distributions from the 2p orbitals there are also some admixtures from the 2s orbitals. As an electron-deficient system, the charges are not balanced in t-B_2CN crystal and there is an absence of a gap at the Fermi level as shown in figure 2. When B atoms and the neighbouring C and N atoms are sp^3 hybridized and reassembled to form t-B_2CN crystal, the electrons in the orbitals of these atoms are redistributed. The calculation of LDOS indicates that, after redistribution, the electron deficiency is mainly transferred into the C atoms of the B–C bonds, which results in a large section of empty 2p orbitals of C atoms above the Fermi level ($\sim$0.48 max LDOS e/eV). Some proportion of unfilled orbitals above the Fermi level from B atoms still remains ($\sim$0.12 max LDOS e/eV). Since the C atoms are connected to B atoms and there is an LDOS above the Fermi level for the B and C atoms, the excited electrons could be delocalized through the empty 2p orbitals of B and C atoms. This means that the t-B_2CN crystal would show metallicity because of the features of the states near the Fermi level. The weaker B–C bond of the crystal may also be attributed to such unique electron structure.

4. Conclusions

We predicted a new denser electron-deficient B_2CN material. A total of seven configurations of diamond-structured B_2CN crystals were optimized using an *ab initio* pseudopotential density
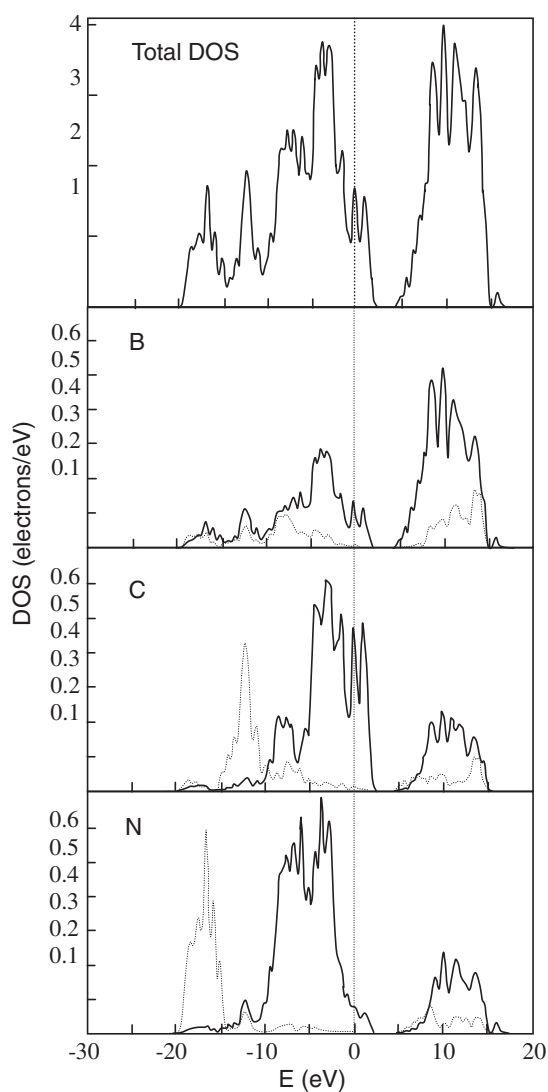
Figure 3. The s (dashed curves) and p (solid curves) local density of states of B, C and N atoms in t-B$_2$CN crystal.

functional method. Among them, the t-B$_2$CN phase deduced from diamond structure contains only B–N and B–C bonds, and has the highest symmetry, the lowest energy and the lowest cell volume. The t-B$_2$CN phase has certain conductivity that may show metallicity. Its bulk modulus is close to that of c-BN, while its isotropic shear modulus is about 2/3 that of c-BN.

Acknowledgments

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