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Mechanical and electronic properties of diamondlike BC_5*

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Abstract: The structural properties, mechanical behavior, and electronic structure of the newly developed diamondlike BC_5 (d-BC_5) was investigated using density functional theory (DFT) calculations. The results indicate that d-BC_5 has great bulk modulus of 393 GPa, large shear modulus of 398 GPa, and high hardness of 62 Pa, and thus support the fact that d-BC_5 is an ultra-incompressible and superhard material. Remarkably, the superhard d-BC_5 exhibits metallic features. Furthermore, the trend that the mechanical behavior falls with the increase of boron content was revealed. The combination of huge stiffness, high hardness, and good metallicity makes series of diamondlike BC_x (d-BC_x) valid for wider applications in comparison with pure diamond.

Key words: Mechanical properties, Metallicity, Diamondlike BC_5
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1 Introduction

Diamond is well known for its mechanical, electrical, and chemical properties, including exceptional hardness, high hole and electron mobility, good thermal conductivity, wide band gap, and a large energy barrier. These properties arise from the strongly directional covalent bonds of the four sp^3 hybrids of carbon (Rivadulla *et al*., 2009). However, it cannot resist oxidation and reacts with ferrous metals, which largely limits its practical applications. Two ways are adopted to overcome this limitation. On the one hand, some new hard compounds such as B_{28}, C_4, and Ta_2N_3 (Jiang *et al*., 2009a; 2009c; Umemoto *et al*., 2010), have been proposed to replace diamond. On the other hand, all materials composed of boron (B) and carbon (C) appear to have better resistance to ferrous metals and oxygen than similar materials of C, since B has one less electron than C and is relatively easily incorporated into diamond due to its small atomic radius (Ekimov *et al*., 2004). Therefore, one expects the diamondlike BC_x (d-BC_x) materials to combine the best properties of the elements such as high hardness, good electrical properties, and high chemical and thermal stability (Jones and Thrower, 1991; Isberg *et al*., 2002).

Very recently, d-BC_5 with superior capabilities has successfully been synthesized by a laser-heated diamond anvil cell at 24 GPa and approximately 2200 K (Solozhenko *et al*., 2009). The experimental characterizations of d-BC_5 indicate that it not only has large bulk modulus of 335 GPa, high Vickers hardness of 71 GPa, and great fracture toughness of 9.5 MPa·$m^{0.5}$, but also exhibits conductive character and thermal stability of above 1900 K. The combination of these distinguished properties has stimulated many theoretical studies (Lazar and Podloucky, 2009;

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Wang and Wang, 2009; Zhang *et al*., 2009; Nkambule and Lowther, 2010). Nevertheless, the exact crystal structure has not been experimentally definitively determined due to the similar atomic numbers between B and C, which has led to different and even contradictory reports on d-BC_5 crystal structure and mechanical properties (Calandra and Mauri, 2008; Yao *et al*., 2009; Zhang *et al*., 2009; Nkambule and Lowther, 2010). To fully explore the physical properties of d-BC_5, systematic accurate calculations that can provide further details about structural properties, mechanical behavior, and electronic structure therefore are highly desired.

In this work, based on our previous works (Liang *et al*., 2009c), first-principles plane-wave pseudopotential method is further performed to systematically study the structural properties, mechanical behavior, and electronic structure of d-BC_5 along with diamond and d-BC_7. Our calculated results not only support d-BC_5 to be an ultra-incompressible and superhard material, but also indicate that it is mechanically stable and metallic. Moreover, it is found that the mechanical behavior of diamond, d-BC_7, and d-BC_5 drop slightly with the increase of B composition.

2 Calculation methods

Our calculations on d-BC_5, d-BC_7, and diamond are performed using Beijing simulation tool of atom technology code (Fang and Terakura, 2002) based on the plane-wave basis sets and Vanderbilt ultrasoft pseudopotentials (Vanderbilt, 1990). We use both local density approximation (LDA-PW91) (Perdew and Wang, 1992) and generalized gradient approximation (GGA-PBE96) (Perdew *et al*., 1996) for the exchange correlation functional.

After carefully checking the convergences of total energy and force with respect to the cutoff energy and the number of *k*-points, we employ 490 eV as a cutoff energy of plane-wave basis for all the systems and the dense 12×12×12, 12×12×12, and 12×12×6 Monkhorst-Pack *k*-points meshes for diamond, d-BC_7, and d-BC_5, respectively. For the three systems, the converged absolute total energy and atom force are less than 10^{-4} eV and 10^{-3} eV/Å, respectively. The tetrahedron method has been performed for the Brillouin zone integration.

3 Results and discussion

3.1 Equation of states

Since X-ray diffraction cannot differentiate B from C due to their similar atomic numbers, a definitive identification of the exact positions of B atoms has not been experimentally obtained for d-BC_5. Solozhenko *et al.* (2009) have interpreted their experiment in terms of a pseudocubic structure (a= 0.3635 nm). Implicit in such a structure is an assumption that the formation has B atoms arranged regularly within the diamond lattice and B is thought to be randomly substituting for C. The conclusion of the disordered d-BC_5 phase is supported by the theoretical work of Jiang *et al*. (2009b). However, the disordered position of B atoms does not affect the mechanical properties (Lazar and Podloucky, 2009). Based on the concept of Calandra and Mauri (2008), we have substituted B for C and performed a structural optimization. The obtained structure of d-BC_5 is a hexagonal symmetry, which in fact comes from 2.3% elongation of a cubic structure along the (1, 1, 1) direction. For d-BC_7, the unit cell of diamond with one B atom replacing one C atom has been adopted. Fig. 1 schematically shows the geometric structures of diamond, d-BC_7, and d-BC_5.

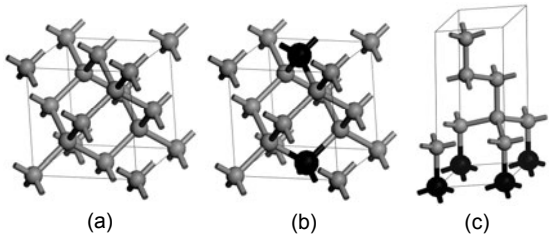

Fig. 1 Unit cell structures for diamond (a), d-BC_7 (b), and d-BC_5 (c)

Total-energy calculations on d-BC_5, d-BC_7, and diamond have been performed over a wide range of primitive cell volumes. The three-order Birch Murnaghan equation of state (EOS) (Liang *et al*., 2009a) is used as a fitting curve to the calculated values of total energy and volume. The obtained results of equilibrium lattice constants, volume, bulk modulus, and pressure derivative for d-BC_5, d-BC_7, and diamond are listed in Table 1. In general, LDA usually overestimates the elastic properties but underestimates the lattice constants, whereas the reverse holds for GGA, so the averages of the GGA and LDA

results have been used in our following discussion. From this table, it can be seen that the equilibrium volume increases but the bulk modulus steadily decreases with the increase of B composition. The bulk moduli of diamond and d-BC_7 have been predicted to be 452 and 402 GPa, respectively, which agree well with the respective experimental result of 446 GPa (Occelli *et al*., 2003) and the theoretical result of 403 GPa (Lowther, 2005), suggesting the validity of our results. Our calculated equilibrium volume of d-BC_5 (5.906×10^{-3} nm^3/atom) is within 1.6% deviation from the experimental data (6.004×10^{-3} nm^3/atom), and the experimental bulk modulus (335 GPa) is 15% smaller than our prediction (393 GPa). Hence, d-BC_5, d-BC_7, and diamond are all ultra-incompressible materials.

Table 1 Equilibrium lattice constants *a* and *c*, volume V_0, bulk modulus B_0, and pressure derivative B_0' for d-BC_5, d-BC_7, and diamond at zero pressure

Material	Method	*a* (nm)	*c* (nm)	V_0 (10^{-3} nm^3/atom)	B_0 (GPa)	B_0' (GPa)
Diamond	LDA	0.353	0.353	5.508	469	3.59
	GGA	0.357	0.357	5.693	435	3.66
	Average	0.355	0.355	5.601	452	3.63
BC_7	LDA	0.358	0.358	5.733	417	3.58
	GGA	0.362	0.362	5.933	387	3.66
	Average	0.360	0.360	5.833	402	3.62
BC_5	LDA	0.252	0.632	5.805	407	3.58
	GGA	0.255	0.639	6.006	379	3.62
	Average	0.254	0.636	5.906	393	3.60

LDA: local density approximation; GGA: generalized gradient approximation

In order to compare the volume compressibility of d-BC_5, d-BC_7, and diamond under pressure, the pressure dependence of the relative volume are plotted in Fig. 2. Cubic boron nitride (c-BN) is calculated for comparison (Liang and Zhang, 2007). As can be seen from Fig. 2, diamond is still the lowest compressible material. The trend among the curves indicates the compressibility increases in the order of diamond→d-BC_7→d-BC_5→c-BN, and verifies again that d-BC_5 is an ultra-incompressible material.

3.2 Mechanical properties

Elastic constants describe the linear response to external strain in a solid crystal, and are indispensable in catching the mechanical behavior of crystals and in designing superhard materials. The complete sets of elastic constants for diamond, d-BC_7, and d-BC_5 at

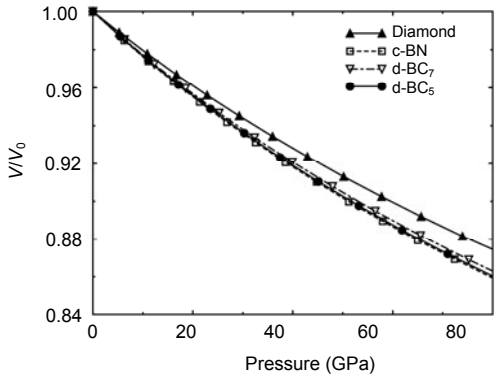

Fig. 2 Calculated pressure-volume relations for diamond, d-BC_7, d-BC_5, and c-BN

zero pressure have been accurately evaluated by the first-principles methods developed by us (Liang *et al*. 2009a), which have been demonstrated to provide reliable predictions of mechanical properties of various systems (Liang *et al*., 2008a; 2008b; 2009b). At the same time, their Young's modulus, shear modulus, and Poisson's ratio can be calculated by the Voight-Reuss-Hill method (Liang *et al*., 2009a).

The obtained results of elastic constants, shear moduli, Young's moduli, and Poisson's ratios for d-BC_5, d-BC_7, and diamond are summarized in Table 2. Firstly, we have checked the mechanical stability of the three crystals according to the Born-Huang criterion (Born and Huang, 1956). Our results satisfy the criteria of cubic or hexagonal crystals, and it follows that d-BC_5, d-BC_7, and diamond are stable, which theoretically supports the experimental conclusion that there exists a continuous series of d-BC_x ($x\geq5$) solid solution (Solozhenko *et al*., 2009). Secondly, we can note that Young's modulus (shear modulus) decreases from 1153 GPa (536 GPa) for diamond to 918 GPa (410 GPa) for d-BC_7, and to 894 GPa (389 GPa) for d-BC_5. Nevertheless, the values of Poisson's ratio increase from 0.076 for diamond to 0.119 for d-BC_7 and to 0.123 for d-BC_5. These trends indicate the mechanical properties of d-BC_x drop with the increase of B content. Finally, we clearly notice that the shear modulus and the elastic constant C_{44} of d-BC_5, indirectly controlling its hardness, are estimated to be 398 and 392 GPa, respectively. Compared with the hardest diamond, the two values of d-BC_5 are smaller by 26% and 32%, respectively, but they still match the second hard material c-BN (G=403 GPa, C_{44}=479 GPa) (Liang and Zhang, 2007).

Table 2 Elastic constants C_{ij}, shear modulus G, Young's modulus E, Poisson's ratio v, and hardness H_V for d-BC_5, d-BC_7, and diamond

Material	Method	Elastic constant (GPa)					G (GPa)	E (GPa)	v	H_V (GPa)
		C_{11}	C_{12}	C_{13}	C_{33}	C_{44}				
Diamond	LDA	1106	151	151	1106	604	550	1186	0.079	94
	GGA	1053	127	127	1053	565	522	1119	0.072	90
	Average	1080	139	139	1080	585	536	1153	0.076	92
BC_7	LDA	807	222	222	807	537	421	945	0.122	64
	GGA	769	196	196	769	498	399	891	0.116	61
	Average	788	209	209	788	518	410	918	0.119	63
BC_5	LDA	931	194	69	1164	401	410	922	0.125	63
	GGA	865	177	64	1086	382	386	865	0.121	60
	Average	898	186	67	1125	392	398	894	0.123	62

LDA: local density approximation; GGA: generalized gradient approximation

It has now been well recognized that the bulk modulus and shear modulus of a crystal are not always directly correlated with its hardness, and it therefore is vital to calculate the hardness of d-BC_5, d-BC_7, and diamond. According to the recent theory of hardness estimation (Gao *et al*., 2003; Šimůnek and Vackář, 2006), the hardness may be mainly determined by the electron concentration, bond length, and degree of covalent bonding. Our calculated hardness values of d-BC_5, d-BC_7, and diamond are obtained from the following equations:

$$H=\frac{C}{\Omega}n(\prod_{i,j=1}^{n}N_{ij}S_{ij})^{1/n}\mathrm{e}^{-\sigma f_e}, \tag{1}$$

$$f_e=1-\left[k(\prod_{i=1}^{k}e_i)^{1/k}\Big/\sum_{i=1}^{k}e_i\right]^2, \tag{2}$$

where all parameters refer to the original paper (Šimůnek and Vackář, 2006). All data of hardness are also listed in Table 2. The hardness of diamond is 92 GPa, which is consistent with the other theoretical and experimental data of 93.6, 96, and 90 GPa (Gao *et al*., 2003), suggesting the accuracy of our predictions. For d-BC_5, the theoretical hardness is approximately 62 GPa. The hardness of d-BC_7 (63 GPa) is slightly larger than that of d-BC_5. The present calculations of hardness therefore support d-BC_5 an ultrahard material (>40 GPa).

3.3 Microscopic mechanisms

It is very helpful to understand the mechanical properties that we have studied, i.e., the crystal and electronic structures of d-BC_5, d-BC_7, and diamond. Diamond has widely been viewed as the hardest material (92GPa) and also has the highest bulk modulus (452 GPa) and shear modulus (536 GPa). High valence electron concentration (715 electrons/nm^3), short bond length (0.154 nm), pure covalent bond, and 3D network of high symmetry are responsible for its high hardness and ultra stiffness. As the B content gradually increases, the valence electron concentration falls and the bond lengths increase, which results in the drop in hardness and incompressibility. For d-BC_5, its valence electron concentration decreases to 677 electrons/nm^3 and the bond length splits into non-equivalent distances: a long one of 0.162 nm and a short one of 0.160 nm.

The density of states (DOS) for the d-BC_5, d-BC_7, and diamond crystals have been calculated using first-principle calculations and presented in Fig. 3. It is well known that most superhard materials with strongly covalent bonds are semiconductors or insulators. As expected in Fig. 3, diamond shows insulator properties. Surprisingly, the d-BC_5 and d-BC_7 crystals show the metallic feature, as the band gap around the Fermi level could not be observed. The fortunate combination of excellent mechanical properties and the electrical conductivity make this series of d-BC_x an extreme superabrasive and promising functional material for electronics in high-temperature and high-pressure conditions. From Fig. 3, we can see that sp^3 hybridizations of C or B split into bonding states and anti-bonding states. In the case of diamond, its bonding states (−14 to −1 eV) have fully been occupied whereas its anti-bonding states (>3 eV) have been empty. Since the valence electron number decreases from C to B, the bonding

states of d-BC_5 and d-BC_7 have been partially occupied, and thus their mechanical properties gradually fall with the increase of B content.

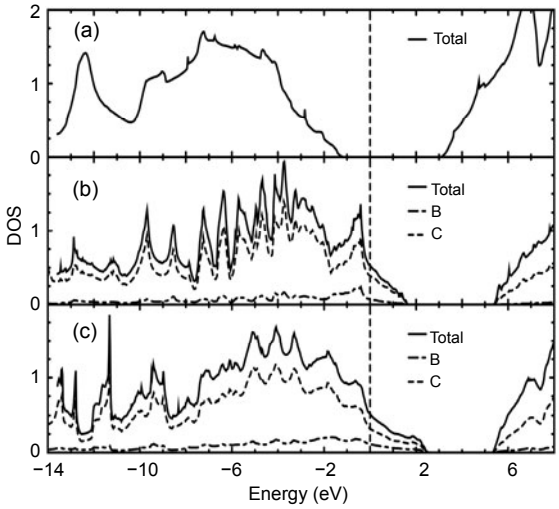

Fig. 3 Total and partial density of states (DOS) of diamond (a), d-BC_7 (b), and d-BC_5 (c)

4 Conclusions

In summary, the structural properties, mechanical behavior, and electronic structures of d-BC_5, d-BC_7, and diamond have been systematically studied by performing first-principles calculations. Our predicted bulk modulus, elastic constant C_{44}, shear modulus, and theoretical hardness of d-BC_5 are in the ranges of 379–407, 382–401, 386–410, and 60–63 GPa, respectively. Our theoretical investigations not only support that d-BC_5 is an ultra-incompressible and superhard material, but also show that it is mechanically stable and metallic. In addition, the trend of mechanical behavior for d-BC_5, d-BC_7, and diamond has been qualitatively clarified from the crystal structures and electronic mechanisms. This class of metallic and superhard materials may allow us to replace pure diamond in some applications at extreme conditions of high temperatures and high pressures.

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