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Stability and mechanical properties of BC_x crystals: the role of B–B bonds and boron concentration

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Abstract

Based on a random solid solution model, first-principles calculations were performed to investigate the structural stabilities and mechanical properties of cubic BC_x ($1 < x < 63$) crystals. Judging by the formation energy, hardness and ductility, a boron concentration between 2.8×10^{21} and $8.4 \times 10^{21} \text{ cm}^{-3}$ (1.56–4.69 at.%) is a compromise choice to balance the structural stabilities and mechanical properties of BC_x crystals. The ratio of B–B bonds has an evident effect on the structural stability of the cubic BC_x crystals. Controlling the ratio of B–B bonds in the precursor materials might be a practicable route for synthesizing BC_x crystals with higher boron concentrations.

1. Introduction

The applications of diamond are limited by its poor oxidation resistance and reaction with ferrous metals [1]. Doping a small amount of boron content into diamond can improve the oxidation resistance [2], reduce the energy bandgap [3] and increase the superconducting transition temperature (T_c) [4–9] of the original diamond crystals. Therefore, diamond-based BC_x crystals with typically boron concentrations between 2.4×10^{20} and $1.4 \times 10^{22} \text{ cm}^{-3}$ (0.16–7.1 at.%) have attracted significant attention over the past few years [1–11]. Under high pressure and high temperature (HPHT) conditions, Solozhenko *et al* [12] recently synthesized cubic BC_5 crystals, which have indeed the highest boron concentration in BC_x crystals achieved so far. The BC_5 crystals exhibit an superior hardness of 71 GPa [12] and a high T_c of 45 K [9].

Since the atomic numbers and sizes of B and C are very close, it is very difficult to analyze the detailed atomic arrangement in the BC_5 crystals [13]. Hence the

crystal structure of BC_5 has not been well determined yet. Theoretically, different models [1, 13–17] have been suggested as the possible crystal structures of BC_5 . For example, superlattice-like heterostructures with one B layer and five C layers arranged alternately along different crystal orientations were proposed [13, 14, 16]. However, within these heterostructure models, significant weakening of the B–C bonds adjacent to the boron layers would result in low intrinsic shear strength, in contrast to the high value of hardness measured in experiment [12]. Therefore, Zhang *et al* [18] concluded that the heterostructure models are not suitable for the c- BC_5 crystal. Although there is no perfect model for the crystal structure of BC_5 yet, it is generally considered that theoretical results are close to the experiment when B atoms are distributed randomly in the diamond lattice [13, 15]. Furthermore, according to the experimental NMR data for B-doped diamond with a boron concentration of about 2.8 at.%, Ekimov *et al* [11] found that B atoms are distributed evenly in the diamond lattice. Raman scattering analysis by Zinin *et al* [19] also suggested a random distribution of B atoms in the diamond-based BC_x crystals.

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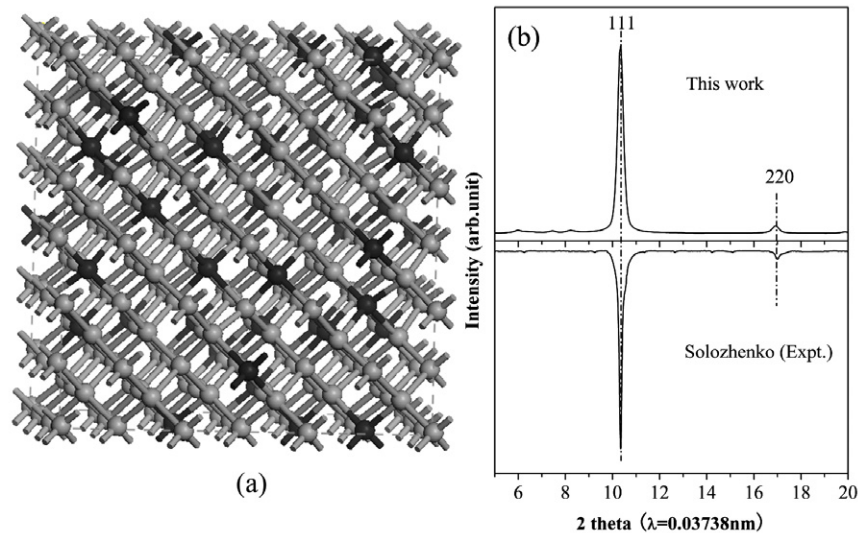


Figure 1. (a) Random solid solution model for cubic BC_5 crystal within a 216-atom supercell. Carbon: light gray, boron: dark gray. (b) Simulated XRD pattern (upper plot) compared with experimental one (lower plot) [12].

Despite the above efforts on the structural properties of the BC_x crystals, much less is known about the effect of boron concentration on their structural stability and mechanical properties. In particular, from the materials design point of view, it is desirable to find out an appropriate range of boron concentration that is able to balance the stability, hardness and ductile/brittle properties of cubic BC_x crystals. In this work, we introduced a random solid solution model for cubic BC_5 crystals and assessed its validity by comparing the simulated XRD pattern and lattice parameter with the experimental data. Within this model, the effects of boron concentration and ratio of B–B bonds on the structural stability and mechanical properties of BC_x ($1 < x < 63$) crystals were investigated using first-principles methods.

2. Computational methods

First-principles calculations were performed using density functional theory (DFT) and the plane-wave pseudopotential technique as implemented in the CASTEP program [20]. The ion–electron interaction was modeled by norm-conserving pseudopotentials [21]. An energy cutoff of 1000 eV was used for the plane-wave basis to ensure convergence of total energy and stress. The generalized gradient approximation (GGA) with the PW91 parameterization was adopted to describe the exchange–correlation interaction [22]. Most calculations were performed on 64-atom supercells. The Brillouin zone of the corresponding reciprocal space was sampled by a $2 \times 2 \times 2$ grid of \mathbf{k} -points. Further increasing to a $4 \times 4 \times 4$ grid only leads to very little change of the theoretical results; for example, the change of total energy is less than 0.19 meV/atom and the change of the computed bulk modulus and shear modulus are both less than 0.1 GPa. A previous theoretical study also demonstrated that the $2 \times 2 \times 2$ \mathbf{k} -point mesh was suitable for the 64-atom supercell with diamond-like structures [23]. For each composition, three structures were used and the average

results were presented to avoid fluctuations due to the random choice of configurations.

The elastic constants of the cubic BC_x crystals were computed using the finite strain technique based on homogeneous deformation of the unit cell, as implemented in the CASTEP program. With the computed elastic constants, the bulk modulus and (isotropic) shear modulus of each crystal were then evaluated using the Voigt–Reuss–Hill average scheme [24]. The geometry optimizations and the consequent elastic constant calculations on the crystalline BC_x systems were performed using a series of 64-atom cubic supercells. The computed bulk modulus and shear modulus of the diamond crystal are $B = 443.8$ GPa and $G = 544.1$ GPa, respectively, in good agreement with the experimental values of $B = 443$ GPa and $G = 534$ GPa [25].

3. Results and discussion

3.1. Crystal structures

The structure of cubic BC_x crystal was described by a random solid solution model recently proposed by us [25], in which a certain number of boron atoms randomly substitute the carbon atoms in the diamond lattice to meet the BC_x stoichiometry. A typical 216-atom supercell structure of cubic BC_5 crystal from fully DFT relaxation is shown in figure 1(a). The validity of our structural model can be assessed by comparing the simulated XRD pattern using this 216-atom supercell with the measured data [12], as shown in figure 1(b). The (111) and (220) diffraction peak positions from our simulations agree well with experiments, with a discrepancy less than 0.05%. Previous studies also used the simulated XRD pattern to evaluate their models [13, 15]. Their simulated 111 and 220 peak positions show deviations from the experiment of approximately 1.43% and 1%, respectively. Comparing with their simulated patterns, our results show better agreement with the experimental one [12]. In this work, we have

Table 1. Theoretical formation energy (E_f), bulk modulus (B), isotropic shear modulus (G), Young's modulus (E), ratio of bulk modulus and shear modulus (B/G), Cauchy pressure ($C_{12}-C_{44}$) and Poisson ratio (ν) for BC_x crystals with different boron concentrations. C_B denotes the number of B atoms per unit volume. The theoretical values of diamond are also shown for comparison.

	B (at.%)	C_B ($\times 10^{21}$ cm $^{-3}$)	E_f (eV)	B (GPa)	G (GPa)	E (GPa)	$C_{12}-C_{44}$ (GPa)	B/G	ν
BC	50.0	76.0	0.51	287.8	295.3	660.1	-282.7	0.975	0.118
BC $_{4.8}$	17.19	29.4	0.32	375.1	358.8	816.2	-253.8	1.045	0.137
BC $_{6.1}$	14.06	24.4	0.30	386.6	382.9	863.6	-261.2	1.010	0.128
BC $_{8.1}$	10.94	19.2	0.28	404.5	445.0	976.8	-361.9	0.909	0.098
BC $_{11.8}$	7.81	13.8	0.26	414.0	465.9	1016.4	-391.7	0.889	0.091
BC $_{20.3}$	4.69	8.4	0.23	426.6	485.2	1055.5	-325.4	0.879	0.088
BC $_{63}$	1.56	2.8	0.21	440.4	485.3	1064.8	-282.3	0.907	0.097
Diam.	—	—	—	443.8	544.1	1158.8	-466.0	0.816	0.064

generated six random solid solution structures (within a 216-atom supercell) for BC_5 crystals. The simulated XRD patterns for all of them are nearly identical, suggesting that B atoms distribute randomly within the diamond lattice. Moreover, the theoretical lattice constant of the BC_5 crystal (3.598 Å) is also very close to the experimental value of 3.597 Å measured by SAED or 3.635 Å from angle-dispersive x-ray diffraction [12]. Such excellent agreement clearly shows that the random solid solution model is appropriate for describing the cubic BC_5 and maybe the other BC_x crystals.

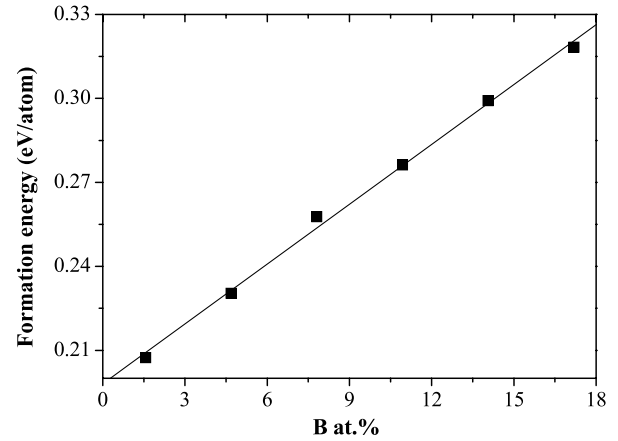
3.2. Structural stability

Within the random solid solution model, the structural stabilities of the BC_x crystals of different compositions (i.e. $1 < x < 63$) can be characterized by the formation energy (E_f) defined as

$$E_f = E_{B_m C_n} - (m E_{(\alpha-B_{12})} + n E_{\text{graphite}}) / (m + n), \quad (1)$$

where $E_{B_m C_n}$, $E_{(\alpha-B_{12})}$ and E_{graphite} represent the total energy per atom of cubic $B_m C_n$, α - B_{12} and graphite crystals, respectively. All theoretical results are summarized in table 1. The computed formation energy is plotted as a function of boron concentration in figure 2. One can see that the formation energy of BC_x crystals increases as the boron concentration increases. In other words, doping diamond crystals with boron content is endothermic and the doped system becomes less stable as boron concentration increases. As the boron concentration in BC_x crystals approaches 4.69 at.% (about 8.4×10^{21} cm $^{-3}$), the corresponding formation energy is as high as 0.23 eV/atom. In fact, the boron concentration in most synthesized BC_x crystals is lower than 8.4×10^{21} cm $^{-3}$ [10, 11, 26, 27]. Until recently, a high boron concentration of up to 16.7 at.% ($\sim 2.8 \times 10^{22}$ cm $^{-3}$) has been achieved [12]. However, such a boron concentration is still far away from the ultimate boron concentration (50 at.%) of the cubic BC crystal, in which the B and C atomic layers are arranged alternately and there is still no B-B bond.

The difficulty in synthesizing BC_x crystals with higher boron concentrations (> 16.7 at.%) is probably related to the B-B bonds introduced in the starting materials (or precursors) as the boron concentration exceeds a certain value. Typically, the precursors for preparing cubic BC_x crystals are synthesized by chemical vapor deposition using different gas sources and they have graphite or turbostratic structures [12, 19]. Previous

**Figure 2.** Formation energy of cubic BC_x crystals as a function of boron concentration.

experiments [28] revealed that a number of B-B bonds will be introduced and become dominant in such precursors as the boron concentration increases up to 23 at.% or more.

Based on the reported value of boron concentration (23 at.%) [28], we constructed several structural models for the cubic BC_x crystal with the composition $BC_{3.3}$ (23.3 at.%), in which B-B bonds of different ratios (0%, 2.3%, 4.7% and 7%) were introduced. After geometry optimization, the formation energies of all these structures were calculated to characterize their relative structural stabilities. Taking the system without B-B bonds (0% ratio) as reference, the cubic $BC_{3.3}$ crystals with a B-B bond ratio of 2.3% and 4.7% are only slightly higher in energy by 0.005 and 0.008 eV/atom, respectively. However, increasing the B-B bond ratio up to 7% would greatly increase the energy difference to 0.83 eV/atom, implying substantial structural instability. The corresponding formation energy (as high as 1.17 eV/atom) of this system also clearly demonstrates that a B-B bond ratio up to 7% evidently aggravates the structural stability of cubic $BC_{3.3}$.

According to the experimental observation [28], we infer that more B-B bonds will be introduced when the boron concentration in the starting materials is higher. Hence, the B-B bonds will further increase the formation energies and deteriorate the structural stabilities of BC_x crystals. Since B-B bonds are unstable with high energies, they would probably be broken during the structural transformation under HPHT conditions. Consequently, these very unstable structures

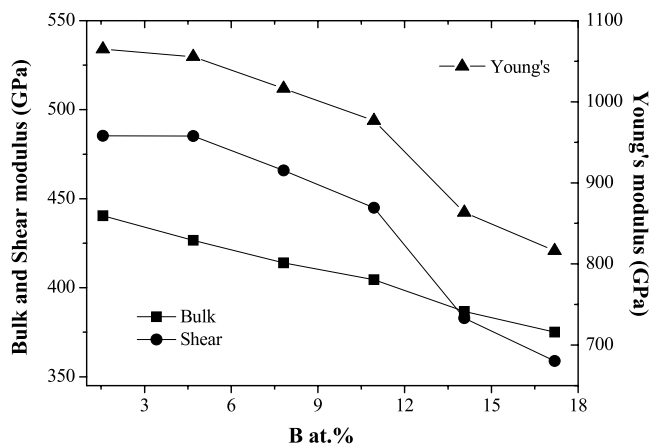


Figure 3. Bulk modulus, shear modulus and Young's modulus as functions of boron concentration for BC_x crystals.

would be decomposed into other compositions with low boron concentration. Indeed, a previous experiment observed that graphite-like BC_3 (with 25 at.% boron content) was decomposed into BC_x crystals with low boron concentration of about 1.8 at.% and other boron carbides under high pressure (20 GPa) and high temperature (2200 K) conditions [29]. In fact, the graphite-like BC_3 precursor was prepared using similar methods as described in the previous work [28]. With such a high boron concentration (25 at.%), B–B bonds are very likely present in their precursors. During the transformation under HPHT conditions, graphite-like $BC_{1.6}$ (B%: 38.5 at.%) materials were also segregated into a mixture of diamond, boron carbide and boron [30]. The present results indicate the crucial role of B–B bonds in deteriorating the structural stability of cubic BC_x crystals with high boron concentration. The B–B bond ratio in precursors may be responsible for the difficulty in synthesizing BC_x crystals with high boron concentrations. Therefore, we suggest that controlling the B–B bond ratio in the precursor materials to be as low as possible is a practicable route to synthesize BC_x with high boron concentrations.

3.3. Mechanical properties

Within the present structural model, we further discuss the mechanical properties of the BC_x crystals. The bulk modulus, shear modulus and Young's modulus were plotted as a function of boron concentration in figure 3. All of them decrease as boron concentration increases, indicating that more boron content will degrade the hardness of BC_x crystals.

In addition to the hardness, the ductility/brittleness also plays a key role in determining the mechanical performance of a material, which can be evaluated by the ratio of bulk and shear modulus (B/G) and the Cauchy pressure ($C_{12}-C_{44}$) [31, 32]. For instance, Pugh [31] proposed an approximate critical value of B/G for the ductile–brittle transition: a material behaves in a ductile manner when its ratio of B/G is greater than 2.0; otherwise, it is brittle. In addition, a lower B/G value denotes worse ductility properties.

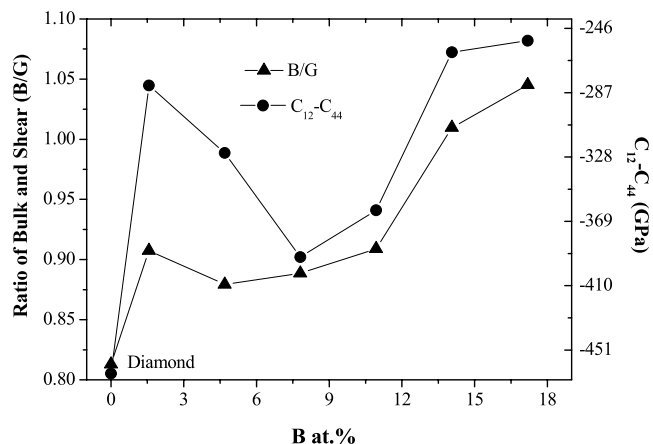


Figure 4. Ratio of bulk modulus and shear modulus (B/G) and Cauchy pressure ($C_{12}-C_{44}$) as a function of boron concentration. The theoretical values of diamond are also shown for comparison.

The relationship between the characteristic ductility parameters and the boron concentration is shown in figure 4. All the B/G values are lower than 2, indicating that the current cubic BC_x crystals are mainly brittle. With regard to the pristine diamond, doping a small amount of boron atoms would significantly improve the ductility of the crystal. However, further increasing the boron concentration does not continuously enhance the crystal ductility. As shown in figure 4, at a boron concentration of about 4.7 at.%, a local minimum of the B/G curve is found; a similar trend can be seen from the curve of Cauchy pressure ($C_{12}-C_{44}$), in which a local minimum of $C_{12}-C_{44}$ is found at about 7.8 at.%. In other words, the BC_x crystals with boron concentrations below 4.7 at.% or above 7.8 at.% possess better ductility. However, BC_x crystals with boron concentrations $>7.8\%$ have higher formation energies and lower hardness, compared with those with boron concentrations $<4.7\%$. Therefore, the boron concentration between 1.6 and 4.7 at.% (2.8×10^{21} – $8.4 \times 10^{21} \text{ cm}^{-3}$) in BC_x crystals is an optimal choice for mechanical properties from the perspectives of hardness, ductility and formation energy.

4. Conclusions

A random solid solution model was presented for the cubic BC_x crystals. The simulated lattice constant and XRD pattern for BC_5 reproduce experimental data satisfactorily. The effects of boron concentration and B–B bonds on the structural stabilities and mechanical properties of BC_x crystals with different boron concentrations have been systematically investigated using first-principles methods. For precursor materials with sufficiently high boron concentrations, the existence of a large number of B–B bonds would hamper the formation of cubic BC_x crystals with higher boron concentrations under HPHT conditions. In other words, controlling B–B bonds in the precursor materials as low as possible might be a practicable route for the synthesis of boron-rich BC_x materials. Generally speaking, doping diamond with boron would reduce the hardness but improve the ductility

of the diamond crystal. From the theoretical formation energy, hardness and ductility, cubic BC_x crystals with boron concentrations between 2.8×10^{21} and $8.4 \times 10^{21} \text{ cm}^{-3}$ (1.6–4.7 at.%) have optimal overall performance in structural stability and mechanical properties.

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