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Structural stability, mechanical and electronic properties of cubic BC_xN crystals within a random solid solution model

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Abstract

We propose a random solution model for cubic BC_xN ($0.21 < x < 19.28$) crystals and compute the formation energies, elastic moduli and bandgaps for different compositions. Significant deviations of the elastic moduli and lattice parameters from the predictions of Vegard's law reveal that the BC_xN solid solutions are not a simple mixing of diamond and cubic-BN. The computed bandgaps are substantially lower than those of diamond and BN. Compared to BC_2N , the BC_xN solids with higher carbon content ($x > 2$) exhibit better structural stability and higher elastic moduli, making them more attractive as potential superhard materials.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The structural similarity [1] of diamond and cubic-BN (c-BN) has stimulated research of the alloys of these two components. It was expected that such B–C–N alloys may be thermally and chemically more stable than diamond and have potential applications as superhard and electronic materials [2]. On the B–C–N ternary phase diagram, the isoelectronic cubic- BC_xN (c- BC_xN) compounds emerge as a natural choice as a mixture of the diamond and c-BN, among which the BC_2N composition has attracted most attention and has been extensively investigated experimentally [3–6] and theoretically [1, 2, 7–11]. In previous experiments, crystalline BC_xN ($x = 1, 2, 2.5$) of cubic phase have been prepared using different techniques such as ball milling [5] and shock compression [6]. These synthesized cubic- BC_xN solids usually possess high hardness that is comparable to

cubic-BN [3]. So far, little is known about those compositions with higher carbon contents ($x > 2$) on the isoelectronic line of BC_xN . Intuitively, incorporating a small amount of boron and nitrogen into the diamond lattice can tune its electronic properties without downgrading its superior mechanical properties remarkably [12]. Therefore, it would be interesting to study BC_xN crystals with all different compositions, in particular those carbon-rich ones with $x > 2$.

For a ternary alloy mixed from two component crystals, it is often assumed that Vegard's law [13] holds for the lattice parameters and maybe also the physical properties. The small lattice mismatch [14] of diamond and c-BN ($\approx 1\%$) implies that the lattice parameters of c- BC_xN would satisfy Vegard's law. However, the measured lattice parameters for $x = 1, 2$ and 2.5 clearly deviate from the ideal mixing of diamond and c-BN [3, 4, 6]. Furthermore, bulk moduli of the BC_2N and BCN crystals measured by Tkachev [15] and Knittle [3] also show distinct deviation from Vegard's predictions. These

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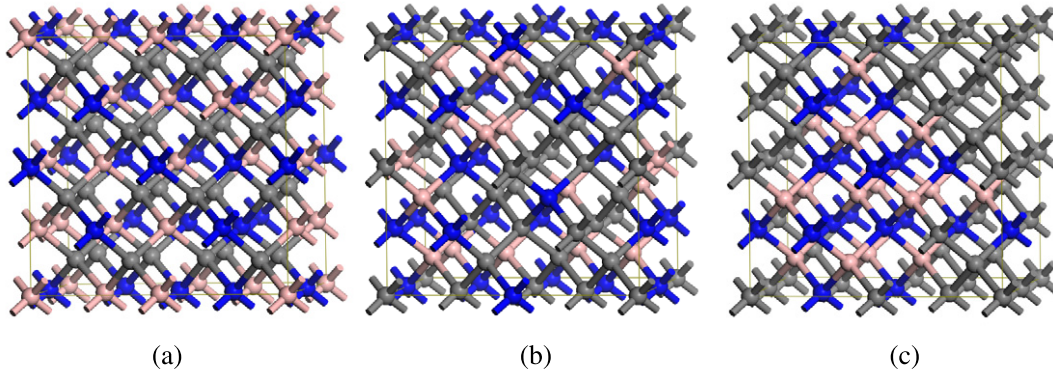


Figure 1. (Color online) Atomic structures of the representative composition BC_2N with different degree of mixture: (a) $\chi = 1$; (b) $\chi = 0.469$; (c) $\chi = 0.203$. Carbon: gray, nitrogen: blue, boron: light pink.

results suggest that the structures and physical properties of $c\text{-}BC_xN$ cannot simply be understood by an ideal mixing of diamond and $c\text{-}BN$. Obviously, the chemical compositions and the detailed atomic arrangements [6] play a vital role. However, direct experimental determination of the atomic occupation within the crystal lattice is very difficult [6, 16]. Thus, first-principles calculations [1, 7, 17] are crucial to elucidate the structural and physical properties of the $c\text{-}BC_xN$ crystals synthesized in experiments.

Previous theoretical efforts focused on searching the energetically preferred structural models for the cubic BC_2N crystal. For example, layered [1, 7, 8, 18, 19] and superlattice [11] structures have been constructed. Most of these proposed crystal structures possess a certain space-group symmetry with B, C and N atoms orderly distributed on the lattice sites. Under extremely non-equilibrium conditions in experiments, however, it is hard to form highly symmetric phases. Indeed, XRD data [4, 6, 20, 21] revealed the absence of the (200) diffraction peak, implying that the B, C and N atoms were randomly distributed over the lattice sites. Meanwhile, Hubble *et al* [22] observed a wide peak at 1325.7 cm^{-1} in the Raman spectrum of $c\text{-}BC_2N$, and they speculated that the C atoms were substituted randomly by B and N atoms in the diamond lattice. All these experimental facts strongly suggest a random distribution of B, C and N atoms on the diamond crystal lattice in the ternary B–C–N alloys.

In this paper, we proposed a random solid solution model for $c\text{-}BC_xN$ crystals. Extended from the BC_2N composition to those with higher and lower carbon contents, we have systematically investigated the BC_xN crystals with different compositions ($0.21 < x < 19.28$) along the C–BN isoelectronic line on the ternary phase diagram. The structural stabilities, elastic and electronic properties of $c\text{-}BC_xN$ within this random solid solution model have been discussed. Our computational results show that the lattice parameters and physical properties of $c\text{-}BC_xN$ are not a linear interpolation between those of diamond and $c\text{-}BN$, in agreement with previous experimental [3, 4, 6] and theoretical findings [23, 24].

2. Structural models and computational details

Our random solid solution model for $c\text{-}BC_xN$ crystals was based on the following considerations. Firstly, the structural similarities [1] and small lattice mismatch [14] between diamond and $c\text{-}BN$ indicate the possibility of forming a $(BN)_C$ solid solution in the B–C–N systems. Secondly, the model was proposed according to experimental evidence that B, C and N atoms are distributed evenly on the diamond lattice [4, 6, 20]. Thirdly, no B–B or N–N bond, which is highly energetically unfavorable, is allowed [1, 6, 7].

In this work, we constructed a series of 64-atom supercell models for the random solid solutions by randomly substituting the boron and nitrogen atoms for carbon in the diamond lattice to meet the BC_xN stoichiometry and the basic bonding rule (no B–B and N–N bonds) [23]. For each composition, a number of random configurations can be obtained, in which the BN and C crystals are mixed in different fashions. Here we defined a degree of mixture χ in terms of the ratio of different bond contents (C–C, B–C, N–C, B–N), that is,

$$\chi = \frac{N_{B-C} + N_{N-C}}{N_{C-C} + N_{B-C} + N_{N-C} + N_{B-N}}, \quad (1)$$

where N_{C-C} , N_{B-C} , N_{N-C} and N_{B-N} are the numbers of C–C, B–C, N–C and B–N bonds within the supercell, respectively. Taking the BC_2N crystal as an example, in figure 1 we depict several representative structures within the random solid solution model of different χ values. It is clear that small χ means severe separation of the two component C and BN phases, whereas $\chi = 1$ corresponds to a complete mixture of BN and C sublattices. In principle, there are many possible choices of χ . For each composition, we have counted the statistical distribution of χ from a large number of random configurations (2.5×10^6) and determined the most probable χ value (see figure 2 for the most probable χ value of different compositions).

Starting from the random solid solution structures with the most likely χ constructed for each BC_xN crystal ($0.21 < x < 19.28$), first-principles calculations have been performed using density functional theory (DFT) and

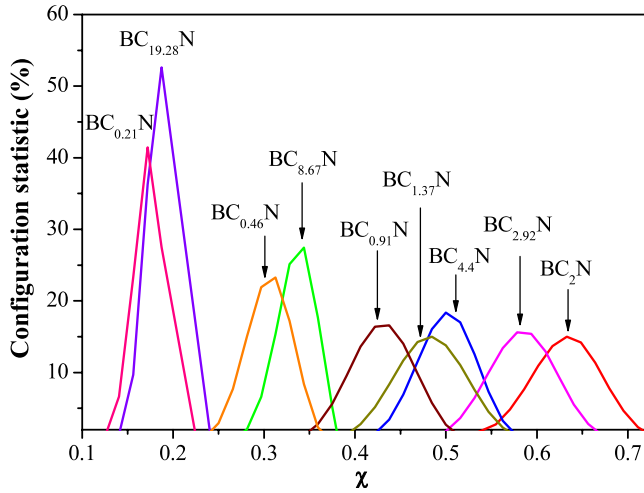


Figure 2. Distribution of degree of mixture (χ) for $c\text{-BC}_x\text{N}$ of different compositions ($x = 0.21, 0.46, 0.91, 1.37, 2, 2.92, 4.4, 8.67$ and 19.28).

Table 1. The lattice constants, bulk and shear moduli, and bandgaps of diamond and c-BN from previous experiments [3, 23, 36] and present theoretical calculations.

		Lattice constant a_0 (Å)	Bulk modulus B_0 (GPa)	Shear modulus G (GPa)	Bandgap (eV)
Diamond	Theo.	3.531	444	544	4.68
	Expt.	3.567 ^a	443 ^a	534 ^b	5.5 ^c
c-BN	Theo.	3.596	378	399	4.86
	Expt.	3.617 ^a	368 ^a	405 ^b	6.1 ^c

^a Reference [3]. ^b Reference [36]. ^c Reference [23].

the plane-wave pseudopotential technique implemented in the CASTEP program [25, 26]. The ion–electron interaction was described by norm-conserving pseudopotentials [27]. A cutoff of 1000 eV was used for the plane-wave basis to ensure convergence of total energy and stress. The exchange–correlation interaction was described by the PW91 functional in the generalized gradient approximation (GGA) [28]. During the geometry optimization and elastic constant calculations, the Brillouin zone of the reciprocal space was sampled by a $2 \times 2 \times 2$ \mathbf{k} -point mesh, and the \mathbf{k} -point mesh was increased to $4 \times 4 \times 4$ to compute the electronic structures and bandgaps. The lattice parameters, bulk moduli, shear moduli and electronic bandgaps for diamond and c-BN crystals from our calculations are compared with the experimental data in table 1, which shows that our theoretical calculations underestimate the lattice constants by about 0.5%–1% and the deviation between theory and experiment is within 3% for the elastic moduli. For each composition of $c\text{-BC}_x\text{N}$, three representative structures (with the most probable χ) were studied and the average results for the three systems are used to avoid the fluctuations due to the arbitrary choice of random configurations.

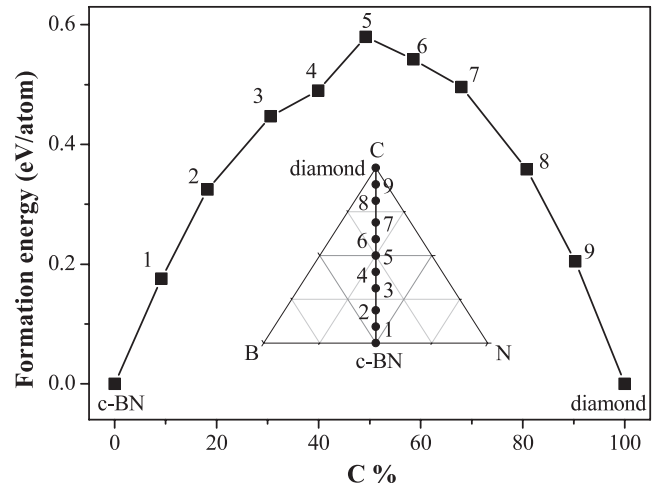


Figure 3. Formation energies of $c\text{-BC}_x\text{N}$ crystals as a function of the $C\%$. The numbers 1–9 represents the compositions of $c\text{-BC}_{0.21}\text{N}$, $c\text{-BC}_{0.46}\text{N}$, $c\text{-BC}_{0.91}\text{N}$, $c\text{-BC}_{1.37}\text{N}$, $c\text{-BC}_2\text{N}$, $c\text{-BC}_{2.92}\text{N}$, $c\text{-BC}_{4.4}\text{N}$, $c\text{-BC}_{8.67}\text{N}$ and $c\text{-BC}_{19.28}\text{N}$, respectively. Inset plot: location of the nine compositions along the C–BN isoelectronic line on the B–C–N ternary phase diagram.

3. Results and discussion

3.1. Crystal structure and stability

In each BC_xN crystal, the carbon content $C\%$ can be related to the stoichiometry x as follows:

$$C\% = \frac{xM_C}{M_B + xM_C + M_N} \times 100\%, \quad (2)$$

where M_B , M_C and M_N is the mole mass of boron, carbon and nitrogen atoms, respectively. Figure 3 shows the computed formation energy as a function of $C\%$. One can see that all $c\text{-BC}_x\text{N}$ crystals have positive formation energy. In other words, they are all metastable structures with regard to the diamond and c-BN crystals and can be separated into two phases of diamond and c-BN [7, 23, 29, 30]. Starting from the c-BN, the formation energy first increases with $C\%$ and approaches a maximum value of 0.58 eV/atom at the middle composition of BC_2N . Then, it gradually drops towards zero at the diamond limit in the carbon-rich region ($x > 2$). Hence, the formation of $c\text{-BC}_2\text{N}$ crystals is most difficult from a thermodynamic point of view. Comparing the formation energy of the carbon-poor compositions with those carbon-rich ones, i.e. $c\text{-BC}_{0.21}\text{N}$ versus $c\text{-BC}_{19.28}\text{N}$, $c\text{-BC}_{0.46}\text{N}$ versus $c\text{-BC}_{8.67}\text{N}$, $c\text{-BC}_{0.91}\text{N}$ versus $c\text{-BC}_{4.4}\text{N}$ and $c\text{-BC}_{1.37}\text{N}$ versus $c\text{-BC}_{2.92}\text{N}$, the former ones are slightly more stable because of lower formation energies, suggesting that incorporating a small amount of carbon into a BN crystal is easier than the inverse process.

The relationship between the lattice parameters and the carbon content $C\%$ is shown in figure 4. For the BC_xN crystals with $x \leq 2$, the theoretical lattice parameters are larger than those of c-BN. This lattice expansion effect can be related to the weakening of ionicity of the original BN crystal. From the Mulliken analysis of our calculations, the amount of charge

Table 2. Carbon contents ($C\%$), most probable degree of mixture (χ), lattice parameters, formation energies, bulk moduli (B_0) and shear moduli (G) for cubic BC_xN crystals with $x = 0.21, 0.46, 0.91, 1.37, 2, 2.92, 4.4, 8.67$ and 19.28 .

Composition	$BC_{0.21}N$	$BC_{0.46}N$	$BC_{0.91}N$	$BC_{1.37}N$	BC_2N	$BC_{2.92}N$	$BC_{4.4}N$	$BC_{8.67}N$	$BC_{19.28}N$
$C\%$	9.2	18.2	30.6	39.9	49.2	58.6	68.0	80.8	90.3
χ	0.172	0.313	0.438	0.484	0.625	0.578	0.5	0.344	0.188
\bar{a} (Å)	3.600	3.603	3.604	3.600	3.599	3.589	3.579	3.561	3.547
E_f (eV/atom)	0.18	0.32	0.45	0.49	0.58	0.54	0.5	0.36	0.2
B_0 (GPa)	374.4	369.5	370.1	369.8	372.7	379.4	386.4	409.4	425
G (GPa)	399.1	394.6	397.3	399.2	431.6	440	454.1	487.4	515.5

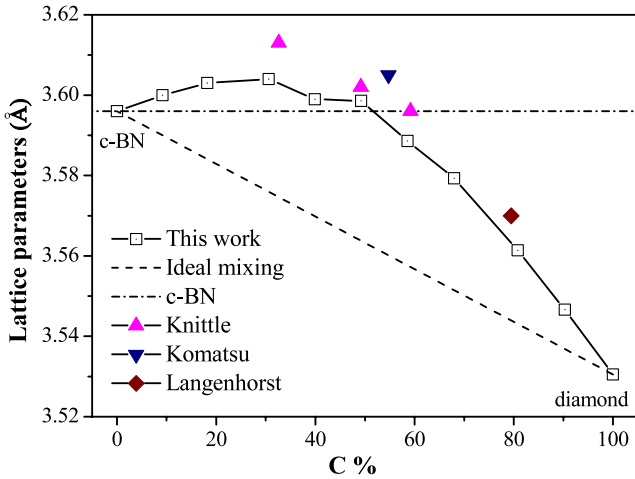


Figure 4. Lattice parameters for $c-BC_xN$ with $x = 0.21, 0.46, 0.91, 1.37, 2, 2.92, 4.4, 8.67$ and 19.28 as a function of the $C\%$. The dashed line represents the ideal mixing by Vegard's law. The dotted line represents the lattice constant of $c-BN$. Some previous experimental values by Knittle [3], Komatsu [6] and Langenhorst [31] are also shown for comparison.

transfer between boron and nitrogen is 0.64 electrons for the pure $c-BN$ crystal, while the amount of charge transfer reduces with increasing carbon content and is about 0.44 electrons for BC_2N .

Obviously, the lattice parameters for all of the BC_xN compositions are away from Vegard's line for ideal mixing of diamond and $c-BN$, but in excellent agreement with experimental observations. For example, the measured lattice parameters [3] for the composition of $C_{0.6}(BN)_{0.4}$, $C_{0.5}(BN)_{0.5}$ and $C_{0.33}(BN)_{0.67}$ were 3.596 ± 0.003 Å, 3.602 ± 0.003 Å and 3.613 ± 0.003 Å, respectively; the corresponding theoretical values from linear interpolation of the data in table 2 or figure 4 are 3.588 Å, 3.599 Å and 3.604 Å, having discrepancies with experiment of only 0.22%, 0.08% and 0.25%, respectively. For the $BC_{2.5}N$ and BC_3N crystals, the theoretical lattice constants are 3.593 Å and 3.563 Å, respectively, which are slightly lower than the experimental values [6, 31] of 3.605 Å and 3.57 Å by only 0.33% and 0.2%, respectively.

3.2. Mechanical and electronic properties

Figure 5 shows the theoretical bulk moduli and shear moduli as functions of $C\%$. Again, both curves deviate from those of ideal mixing, indicating that the bulk and shear moduli of $c-BC_xN$ are not simple interpolations of those of the diamond

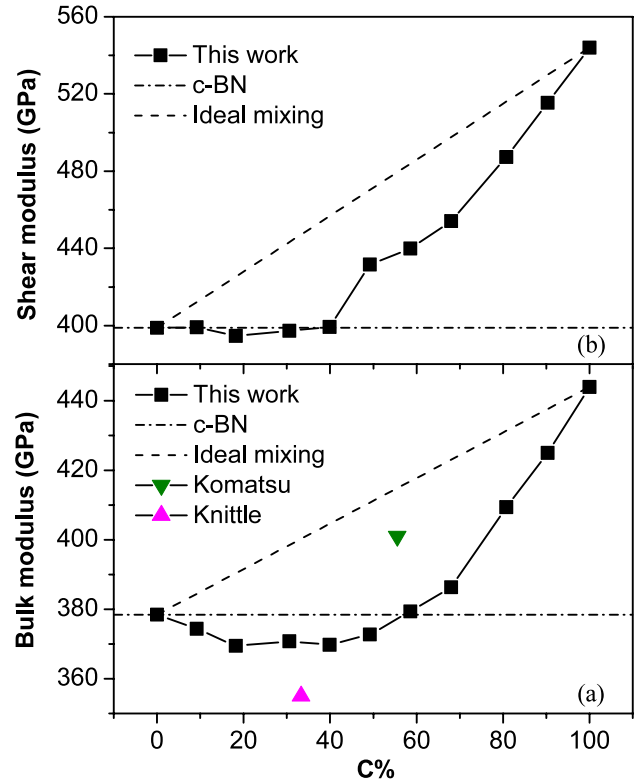


Figure 5. (a) Bulk modulus and (b) shear modulus of $c-BC_xN$ crystals ($x = 0.21, 0.46, 0.91, 1.37, 2, 2.92, 4.4, 8.67$ and 19.28) as functions of $C\%$. The dashed lines represent the ideal mixing of diamond and $c-BN$ by Vegard's law; the dotted lines represent that of $c-BN$. Some previous experimental values by Knittle [3] and Komatsu [6] are also shown for comparison.

and $c-BN$. The computed bulk/shear modulus for BC_xN crystals first decreases with $C\%$ monotonically from diamond to $BC_{1.37}N$ ($C\% = 39.9\%$); then it drops rather slowly (with some weak oscillations) to BCN ($C\% = 32.6\%$); finally, it rises to the value of $c-BN$. Along the $C-BN$ isoelectronic line in the ternary phase diagram, there is no local maximum of either bulk or shear modulus. In other words, no superhard composition was found from our calculations.

In a previous experiment by Knittle *et al* [3], the bulk modulus of the BCN was 355 ± 19 GPa, which is close to our theoretical value of $B = 370.1$ GPa for $BC_{0.91}N$. For BC_2N , our theoretical bulk modulus is 372.7 GPa, lower than that of $c-BN$ ($B = 378.4$ GPa). For comparison, Solozhenko *et al* [4] obtained an even lower bulk modulus of 259 ± 22 GPa in experiments. As shown in figure 5, incorporating

a little amount of carbon (boron/nitrogen) atoms into the c-BN (diamond) lattice effectively reduces the hardness of the host lattice. Compared to the BC_2N crystal, our present theoretical results suggest that the carbon-rich BC_xN materials ($x > 2$) possess better mechanical properties and are easier to form. In contrast, even with lower formation energies, the compositions on the carbon-poor side are less attractive due to the lower elastic moduli (see table 2 and figure 3). In the experiment, synthesis of a cubic BC_8N phase has been reported under high-temperature and long-annealing conditions [31]. According to the present theoretical results, we anticipate the experimental preparation of other BC_xN compositions with higher carbon contents, which are promising as candidate superhard materials with greater chemical stability with regard to diamond.

Compared with the experimental value of c-BN (6.1 eV) and diamond (5.5 eV), [23] the calculated bandgap for c-BN (4.86 eV) and diamond (4.68 eV) is lower by about 20% and 15%, respectively. The underestimation of the bandgap is a well-known deficiency of the standard DFT method. However, this systematic error would not affect the variation behavior of the bandgap due to the effects of crystal structure and composition.

The calculated band structures for all the c- BC_xN crystals show a direct bandgap with both the conduction-band minimum and the valence-band maximum at the Γ point. Figure 6 displays variation of bandgap for BC_xN crystals of different compositions. The gaps for all BC_xN crystals are significantly lower than those of diamond and c-BN. Except for $\text{BC}_{0.21}\text{N}$ (whose gap is 3.72 eV), the bandgaps for most of the BC_xN crystals lie between 2 and 3 eV, with some composition-dependent variations. This is obviously away from the prediction of Vegard's law, which was found to be valid for many other ternary alloys like Cd–Zn–Te [32, 33], Ga–As–N [34] and In–Ga–As [35]. The present results are in accordance with a previous calculation of the cubic $(\text{BN})_x\text{C}_{2(1-x)}$ by Lambrecht *et al* [23]. They argued that the contribution of the C component to the valence-band maximum and the B component to the conduction-band minimum results in gap reduction. Pasva and Azevedo [10] also observed a similar effect of gap narrowing in the ordered $(\text{BN})_x\text{C}_{2(1-x)}$ alloys. Further analysis of the electronic density of state revealed that the valence-band maximum and conduction-band minimum are mainly contributed by the carbon and boron atoms, in agreement with previous studies [10, 23]. Such a significant narrowing of bandgap implies a tunable bandgap via controlling composition, which makes these BC_xN alloys useful for optoelectronic applications.

4. Conclusions

Inspired by the experimental information on the structure of the c- BC_2N crystal, we proposed a random solid solution model for BC_xN alloys and systematically studied the structural stabilities, mechanical and electronic properties of the c- BC_xN ($0.21 < x < 19.28$) crystals along the C–BN isoelectronic line. The computed lattice parameters and bulk modulus are consistent with the available experimental data. Significant deviations of the structural and physical parameters from

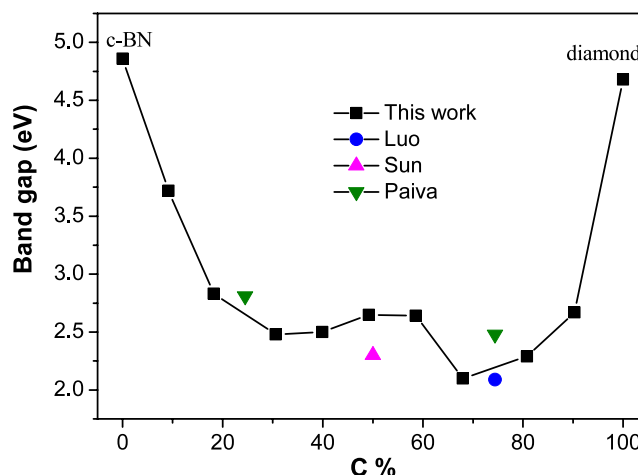


Figure 6. Bandgap as a function of the $C\%$ for c- BC_xN crystals ($x = 0.21, 0.46, 0.91, 1.37, 2, 2.92, 4.4, 8.67$ and 19.28). Previous theoretical values by Sun *et al* [1], de Paiva *et al* [10] and Luo *et al* [17] are also shown for comparison.

Vegard's law indicate that the BC_xN alloys are not simply the linear interpolation of diamond and c-BN via ideal mixing. The bulk and shear moduli of c- BC_xN are evidently lower than those of diamond, revealing that the superhard phase does not exist on the C–BN isoelectronic line. However, the carbon-rich BC_xN crystals may still be attractive due to their better structural stability and mechanical properties with regard to the intensive investigated c- BC_2N . Outside the C–BN isoelectronic line, we propose the ternary alloys along the BN– C_3N_4 line may also lead to new superhard materials.

Acknowledgments

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