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Structures and elastic properties of crystalline and amorphous BC_2N solids

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Abstract. Crystalline and amorphous BC_2N supercells with 216 atoms have been constructed by random distributions of B, C, and N atoms in the diamond lattice and amorphous sp^3 carbon structure, respectively. The atomic structures of these two systems were relaxed using density functional theory, and their mechanical properties including the bulk modulus, shear modulus, and Young's modulus were computed. Crystalline BC_2N possess higher elastic moduli than those of cubic BN. Amorphous BC_2N exhibit reasonable elastic moduli and appreciable ductility with a large ratio between the bulk modulus and shear modulus. Both crystalline and amorphous BC_2N are superior candidates as superhard materials.

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Key words: BC_2N, structure, elastic properties, superhard material

1 Introduction

C_2 and BN are isoelectronic with eight valence electrons, which can lead to isoelectronic compound of BC_2N. It is expected that the BC_2N crystals of cubic phase can combine the excellent properties of diamond (high hardness) [1, 2] and cubic-BN (c-BN) (higher chemical inertness) [3] in the field of superhard materials [1, 4]. Therefore, both crystalline [1,4–9] and amorphous BC_2N [10–13] solids have received considerable attentions. However, neither their atomic structures nor physical properties have been well understood [1, 2, 14].

For crystalline BC_2N, previous experiments showed evidences for both diamond-like solid solutions [1, 6, 9] and phase separation into diamond and c-BN [15, 16]. According

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to the absence of (200) peaks in X-ray diffraction (XRD), Knittle *et al*. [9] reported that several cubic B-C-N solid solutions have been synthesized. Solozheko *et al*. [1] employed high-brilliance synchrotron radiation to study in situ the process of phase formation. The presence of 111, 220, and 311 lines and the absence of 200 lines suggested a diamond-like cubic B-C-N phase with BC_2N composition. Under similar high-pressure and high-temperature conditions, however, Sasaki [16] and Nakano [15] observed the simultaneous crystallization of diamond and c-BN. Due to the poor resolution of X-ray detection systems [17], it was unclear whether the synthesized products are B-C-N ternary alloys or just mechanical mixtures of highly dispersed diamond and c-BN [1,17].

Meanwhile, various theoretical models have been proposed to describe the most probable structure of crystalline BC_2N [4,5,7,14]. Typically, in these models, B, C, and N atoms are orderly distributed within the diamond lattice with certain space-group symmetry. However, both XRD data [1, 6, 9, 18] and Raman analysis [19] in previous experiments strongly suggested random distributions of B, C, and N atoms in the diamond lattice. In addition to the unclear crystal structure, there are also some controversies on the physical properties (particularly the mechanical properties) of the BC_2N solids. For example, using shock compression methods, Komatsu *et al*. [8] synthesized the cubic $BC_{2.5}N$ with a bulk modulus of 401 GPa, which is larger than that of c-BN (369 GPa) [20]. However, Solozhenko *et al*. [1] reported a rather small bulk modulus (282 GPa) for cubic BC_2N synthesized under the high pressure and high temperature conditions.

Parallel to the study of crystalline BC_2N, amorphous BC_2N solids have been prepared by chemical vapor deposition (CVD) [13], magnetron sputtering [11, 21, 22] and other techniques [10, 12, 23, 24], and their structures and composition were characterized by means of Fourier Transform-Infrared Spectroscopy (FTIR) and X-ray photoelectron spectroscopic (XPS). Most of these works were focused on structural characterization to verify whether the synthesized films are atomic-level hybridizations [11,13,21] or simple phase separations [10, 23], while the detailed atomic structure of the amorphous BC_2N solid was still unclear. Moreover, the mechanical properties of the BC_2N films were not well understood due to the great influences of the substrates.

To the best of our knowledge, there was no theoretical investigation on the amorphous BC_2N solids yet. In this paper, we carried out a comparative first-principles study on the crystalline and amorphous BC_2N solids within a random solid solution model, in which boron and nitrogen atoms randomly replace the carbon atoms in the diamond lattice and the amorphous sp^3 network structure, respectively. From our theoretical calculations, both crystalline and amorphous BC_2N solids exhibit appreciable mechanical properties with regard to those of c-BN and amorphous carbon, making them good candidates for superhard materials.

2 Structural models and computational details

Our random solid solution models [25] were based on the following considerations: (i) the structural similarities [4] and small lattice mismatch [26] between diamond and c-

BN indicate the possibility of forming (BN)C_x solid solution; (ii) there are some indirect experimental evidences that B, C, and N atoms are distributed evenly on the diamond lattice [1,8,9]; (iii) no B-B or N-N bond is allowed [4,7,8], since they are highly energetically unfavorable.

Our structural models contain 216 atoms in a cubic (crystalline) or quasi-cubic (amorphous) supercell. For the BC_2N crystal, we substituted boron and nitrogen atoms for carbon in the diamond lattice to meet the BC_2N stoichiometry and the basic bonding rule (no B-B or N-N bond). For the amorphous BC_2N solid, we first generated a 216-atom supercell for the tetrahedral amorphous carbon (ta-C) as the template for B/N substitution, which was obtained by quenching the system from 4000 K to 300 K using constant-temperature molecular dynamics and an empirical Tersoff potential [27] with a total simulation time of 38 ns. Afterwards, we randomly replaced C atoms by B and N atoms in the ta-C network, similar to the case of BC_2N crystal.

In principle, a large number of random configurations can be obtained from different ways of mixing B, C, and N atoms. Here we defined a degree of mixture χ in terms of the ratio of bond contents (C-C, B-C, N-C, B-N),

$$\chi = \frac{N_{B-C}+N_{N-C}}{N_{C-C}+N_{B-C}+N_{N-C}+N_{B-N}}, \tag{1}$$

where N_{C-C}, N_{B-C}, N_{N-C}, N_{B-N} are the numbers of C-C, B-C, N-C, B-N bonds within the supercell, respectively. Taking the crystalline BC_2N for an example, Fig. 1 depicts several representative structures with different χ values. By definition, small χ denotes severe separation of diamond and c-BN phases, whereas χ=1 corresponds to a complete mixture of the BN and diamond sublattices. Obviously, there are many possible choices of χ. Here 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. Fig. 2 shows the distribution of χ for crystalline and amorphous BC_2N and the corresponding supercell structures for the most probable χ values are displayed in Fig. 3.

Starting from the structural models constructed for crystalline and amorphous BC_2N, first-principles calculations have been performed using density functional theory (DFT) and the plane-wave pseudopotential technique implemented in the VASP program [28]. The ion-electron interaction was described by ultra-soft pseudopotentials [29]. A cutoff of 650 eV was used for the plane-wave basis to ensure converge of total energy and stress. The exchange-correlation interaction was described by the PW91 functional in the generalized gradient approximation (GGA) [30]. Brillouin zone of the reciprocal space was sampled by the Γ point. As shown in Table 1, the lattice parameters and elastic moduli for diamond and c-BN crystals from our DFT-PW91 calculations compare satisfactorily with the experimental data. For either crystalline or amorphous BC_2N, three representative supercell structures (with the most probable χ) were considered and the average results for the three systems were used to reduce the fluctuations due to the arbitrary choice of random configurations.

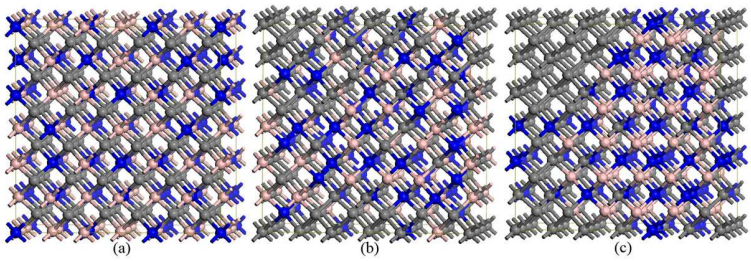

Figure 1: (Color online) Representative atomic structures of the BC_2N crystals with different degrees of mixture: (a) χ=1; (b) χ=0.579; (c) χ=0.347. Carbon: grey, nitrogen: blue, boron: light pink.

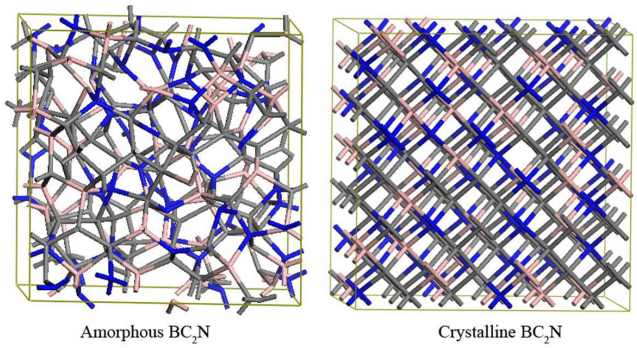

Figure 2: (Color online) Structural models for amorphous (left) and crystalline (right) BC_2N solids with the most probable degree of mixture. Carbon: grey, nitrogen: blue, boron: light pink.

3 Results and discussion

The stability of crystalline BC_2N with respect to the diamond and c-BN can be evaluated by the formation energy E_f, which is defined as

$$E_f = [E_{BC_2N} - (E_{diamond} + E_{c-BN})/2], \tag{2}$$

where E_{BC_2N}, $E_{diamond}$, E_{c-BN} and are the total energies per atom for c-BC_2N, diamond, and c-BN crystals, respectively. From the present calculation, the formation energy of BC_2N crystal is 0.58 eV/atom, indicating that the crystalline BC_2N is a metastable phase and tends to separate into diamond and c-BN phases.

However, under the high-temperature conditions in experiments, the positive formation energy of BC_2N crystal can be compensated by the contribution of configurational entropy to free energy, which is described by

$$\Delta U = -Tk_B \ln W, \tag{3}$$

where U and k_B is the free energy and Boltzmann constant, respectively, T is temperature, and W represents the configurational possibility. As shown in Fig. 2, at the most

probable degree of mixture (χ=0.8125) for crystalline BC_2N, $W \cong 8\%$; whereas the configuration possibility for severe phase separation ($\chi < 0.5$) drops to $W \cong 0$. Since the typical synthesis temperature for BC_2N crystal is as high as 2500 K [1,9], the contribution of configuration entropy to the free energy is about 0.55 eV for $W \cong 8\%$ and 1.99 eV for $W \cong 0.01\%$. The difference of these free energies ($\geq$1.5 eV) is big enough for compensating the formation energy of crystalline BC_2N (0.58 eV).

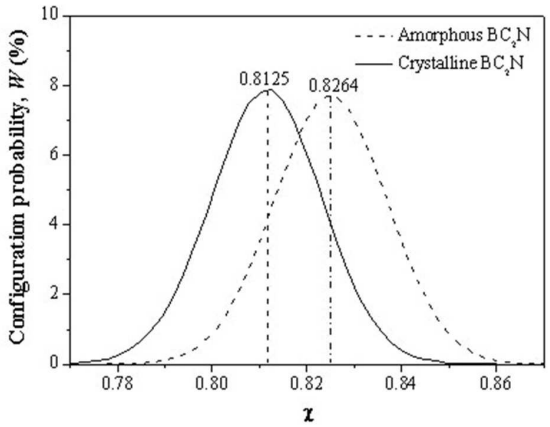

Figure 3: Statistic distribution of degree of mixture (χ) for crystalline and amorphous BC_2N.

For BC_2N crystal, the lattice constants from our theoretical calculations is 3.646 Å, which is comparable to previous experimental values, i.e., 3.642 Å by Solozhenko *et al*. [1], 3.602 Å by Knittle *et al*. [9], and 3.605 Å Komtsu *et al*. [8]. For comparison, previous theoretical calculations typically underestimated the lattice constant, for example, a=3.579 Å by Zhang *et al*. [7], and a=3.565 Å by Zhou *et al*. [5].

The computed bulk modulus (B) and the isotropic (Voigt-Reuss-Hill average) shear modulus (G) for BC_2N crystal are 384.4 GPa and 455.5 GPa, respectively, lying between those of diamond (B=445 GPa, G=534 GPa) [31] and c-BN (B=369 GPa, G=405 GPa) [20]. The theoretical Young's modulus for crystalline BC_2N is 980 GPa, which is higher than that of c-BN but lower than that of diamond (see Table 1). Similarly, the Vickers hardness of the crystalline BC_2N estimated using a semi-empirical microscopic model [32] is about 69 GPa, which also lies between those of diamond (96 GPa) and c-BN (65 GPa). Previous theoretical studies based on the ordered crystal structures of cubic BC_2N predicted a hardness value of 76 GPa [5] or 70 GPa [33], comparable to the present value from random solid solution model. All together, the present theoretical results indicate that the crystalline BC_2N possesses excellent mechanical properties that are superior to c-BN; thus it can be considered as a superhard material.

For amorphous BC_2N, the computed formation energy is 0.88 eV per atom, which is higher than that of the crystalline counterpart by 0.3 eV/atom. Again, the positive value indicates that the structure is metastable. The calculated bulk and shear modulus

Table 1: Lattice constants, mass densities, formation energies, Young's modulus, bulk modulus, and shear modulus for cubic BN (c-BN), crystalline BC_2N (c-BC_2N), amorphous BC_2N (a-BC_2N), and tetrahedral amorphous carbon (ta-C) from our calculations and previous theoretical [3, 9, 20, 31, 36] and experimental works [32].

	Lattice constant (Å)	Density (g/cm^3)	E_f (eV/atom)	Young's modulus (GPa)	Bulk modulus (GPa)	Shear modulus (GPa)
Diamond	3.586	3.46	0	1154	439	544
Expt. [a,d]	3.567	3.52	-	1145	445	534
c-BN	3.634	3.44	0	876	364	399
Expt. [a,b,c]	3.617	3.49	-	909	369	405
c-BC_2N	3.646	3.34	0.58	980	384	456
a-BC_2N	-	3.17	0.037	669	323	290
ta-C [e]	-	3.23	-	823	366	365
Expt. [d]	-	3.26	-	758	334	338
Expt. [f]	-	3.37	-	800	-	-

[a] Ref. [9]; [b] Ref. [3]; [c] Ref. [20]; [d] Ref. [31]; [d] Ref. [37]; [f] Ref. [36]

is 323 GPa and 290 GPa, respectively. Accordingly, the Young's modulus for amorphous BC_2N is 669 GPa. As shown in Table 1, even though the amplitudes of these elastic parameters for amorphous BC_2N are less than those for the crystalline BC_2N, c-BN, and ta-C, they are rather appreciable (about 72-82% of c-BN). More importantly, amorphous BC_2N possesses a large B/G ratio of 1.12, higher than those of crystalline BC_2N (0.84) [34], c-BN (0.92) [3, 9, 20], diamond (0.81) [31], and ta-C ($\sim$1.0) [35]. Generally speaking, the bulk modulus and shear modulus represent the resistance to bond rupture and plastic deformation, respectively. The B/G ratio usually describes the ductility/brittleness of a material, that is, higher B/G corresponds to good ductility (the ability to change shape without fracture). Thus, with appreciable elastic moduli, the amorphous BC_2N exhibit good performance of resistance to stress cracking (ductility) that prevails the crystalline BC_2N, c-BN, diamond, and ta-C, thus broadening its applications in materials science.

4 Conclusions

In summary, random solid solution structural models have been constructed for crystalline and amorphous BC_2N solids and DFT calculations have been performed to investigate their atomic structures, formation energies, and elastic properties. Both crystalline and amorphous BC_2N solids are metastable with an intermediate formation energy (0.58 and 0.88 eV/atom, respectively), which can be compensated by the contribution of configurational entropy to free energy. Crystalline BC_2N as a random solution of diamond lattice has higher elastic moduli than those of c-BN. With relatively lower elastic moduli, amorphous BC_2N exhibits certain ductility that is superior to the crystalline counterparts (diamond, c-BN, and BC_2N) and the amorphous (ta-C) solids. Therefore, both crystalline and amorphous BC_2N are potential candidates for the superhard materials.

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