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Cubic diamondlike BC_7 predicted from first principles as a superhard material

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ABSTRACT

A cubic diamondlike BC_7 structure with *I*-43*m* space group and 64 atoms per cell is theoretically designed from first-principles calculations. Our calculated phonon spectra and elastic constants confirmed that BC_7 is both dynamically and mechanically stable. Based on the calculated electronic band structure and density of states, a hole-conducting behavior is predicted in BC_7. The simulated high elastic constants, modulus, hardness and ideal strength reveal that BC_7 exhibits excellent mechanical characters and belongs to a superhard material with prospects for potential multi-functional material in electronic and mechanical application.

1. Introduction

Diamond possesses superlative physical qualities (e.g., the highest hardness, highest thermal conductivity and excellent electrical properties [1]), and plays an important role in various industrial fields, such as abrasives, coating, grinding and cutting tools [2], and as important device for high-pressure experiments. However, the shortcomings of weak chemical and thermal stabilities of diamond [3] leads to the inapplicability for machining iron based alloys that at high speeds. These failings motivate researchers to synthesize and design novel superhard materials with better thermal and chemical stability than these of diamond. It is generally accepted that the covalent compounds formed by light elements (B, C, N, O), such as *c*-BN [4], BC_2N [5–9], C_3N_4 [10], B_3NO [3], BC_5 [11] and BC_3 [12], exhibit potential superhard phases with strong covalent bonds to resist structural deformation. Among them, boron carbides are considered as suited candidates with a broad application prospect in the industrial field since they possess better chemical and thermal stabilities and amusing electronic properties. It is reported that diamond-like BC_5 synthesized by Solozhenko et al. at 24 GPa and 2200 K [13], and its measured hardness reaches 71 GPa, which is harder than *c*-BN. Meanwhile, the theoretical calculations about BC_2 [14], BC_3 [15] and BC_5 [11] suggest their captivating electronic natures. In recent study, the accurate structure with 64 atoms/cell and *I*-43*m* space group for BC_3 is proposed using an unbiased swarm structure search, and the calculated results of the BC_3 are excellent agreement with previous experimental data [12]. Due to relative lower B content (~12.5%) in BC_7 than that of BC_5 (~16.7%), BC_7 could be synthesized by the appropriate experimental conditions and precursor. Several structural models [16–19] are presented to understand the structural stability and mechanical properties of these boron carbides, however, none of BC_7 in the cubic diamond structure has been established.

In the current study, a novel structure for BC_7 is designed using the substitution method by replacing B atoms to C atoms within the previous cubic BC_3 structure. It is found that the optimized BC_7 possesses the identical space group with that of cubic BC_3, suggesting the introduction of more C atoms does not cause lattice distortion of BC_3. The calculated phonon spectrum reveals that the designed BC_7 phase is dynamically stable due to no imaginary in the whole Brillouin zone. Moreover, the theoretical bulk modulus, shear modulus and hardness indicate that cubic BC_7 has excellent mechanical properties. In especial, the current designed cubic BC_7 possesses a simulated Vickers hardness above 71.5 GPa, exceeding the criterion (40 GPa) of superhard materials. We then carry out a series of calculations on the stress-strain relations of BC_7 in the main symmetry directions at atmospheric pressure and large tensile as well as shear deformation.

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2. Computational methods

The structural optimization, energetic and electronic calculations are performed using the density functional theory with the Perdew-Burke-Ernzerh generalized gradient approximation exchange-correlation potential [21] as implemented in the Vienna ab initio simulation package (VASP) code [22]. The projector augmented wave (PAW) [20] was used to describe electron-ion interaction with $2s^2 2p^1$ and $2s^2 2p^2$ for B and C, respectively. The plane wave cutoff energy of 800 eV and Monkhorst-Pack k point meshes with $8 \times 8 \times 8$ are taken to ensure the total energy converged to be about 1 meV per atom. The direct supercell method is used to calculate the dynamical vibration for BC_7 with an 128-atoms ($2 \times 2 \times 2$ primitive) cell, as implemented in phonopy software with the forces obtained by the Hellmann-Feynman (H-F) theorem [23,24]. Elastic properties were calculated by the theoretical strain-stress relationship, and the bulk, and shear modulus were then derived from the Voigt–Reuss–Hill averaging scheme [25]. The quasistatic ideal strength and relaxed loading path in the various directions was determined using strain-stress method [26–29]. The lattice vectors were incrementally deformed in the direction of the applied strains. At each step, the atomic basis and all the atoms in the unit cell were optimized unit all the H-F stress tensor orthogonal to the applied strains were less than 0.1 GPa. To explore the easy-slip plane, we performed a number of calculations of strain-stress relationship along several tensile directions. The shear calculations are then performed by applying shear along various directions in the cleavage plane.

3. Results and discussion

Several BC_7 structures are designed by replacing part of B atoms with C atoms based on previously proposed cubic crystal structure for BC_3 [12] with 64 atoms/cell and I-43m space group along the body diagonals. These crystal structures have been fully optimized using the first principles calculation, and the most thermodynamically stable structure at ambient pressure has high cubic symmetry with the identical space group with cubic BC_3, as shown in Fig. 1 from the polyhedral and front view. The calculated lattice parameters for I-43m BC_7 are determined to be $a = b = c = 7.239$ Å with B atoms possessing 8c (0.1206, 0.8794, 0.8794) Wyckoff positions and C atoms possessing 8c (0.2433, 0.2433, 0.7567), 12e (0.5, 0.2400, 0.5), 12d (0.5, 0.0, 0.75) and 24g (0.3372, 0.1255, 0.8745) Wyckoff positions, respectively. The structural stability is the primary prerequisite for material design. In a solid, the phonon frequency is important to determine whether the atoms in crystal structure maintain the oscillation around each equilibrium position. The appearance of imaginary frequencies in the calculated phonon spectrum is a sign that the solid is dynamically instable [30]. The phonon spectra for designed BC_7 are thus calculated. As shown the Fig. 2(a) and (b), no imaginary frequency curves are observed in the whole Brillouin zone for BC_7 with I-43m space group at 0 GPa and 100 GPa, indicating it is dynamically stable. By comparing Fig. 2(a) with (b), it is clearly found that the highest phonon frequency for I-43m BC_7 reaches about 36 THz and 43 THz, respectively, which illustrates the phonon vibrations shift to higher frequency and the chemical bonds are shorter at higher compression conditions.

The electronic properties play an important role in potential technological and industrial applications. In order to investigate the electronic characters of designed I-43m BC_7, the electronic band structure and electronic density of states were simulated employing first-principles calculation, as shown in Fig. 3(a) and (b), respectively. Interestingly, the top bond state of BC_7 with I-43m space group is about 1.6 eV above the Fermi level, indicating cubic BC_7 phase exits a hole-conductive behavior at ambient pressure which is different from diamond, but similar to heavy boron-doped diamond. We shown the total and partial electronic density of stats of cubic BC_7 phase in Fig. 3(b) to reveal the contributions of orbital electronics for valence bands and energy. Our results shown that the low valence bands are mainly from 2s orbital electrons of B atoms and C atoms, while, the 2p orbital electrons of B atoms and C atoms contribute to high valence bands, with tiny contributions of 2s orbital electrons. The physical mechanism for hole-conductive behavior of BC_7 phase is that the boron atoms with three valence electrons cannot form a complete sp^3 bonding network with C atoms due to the lack of electrons, which leads to the empty orbital arise above the Fermi level in the calculated band structures.

The elastic properties that defines the stresses undergoes different types of strains for a given material within elastic limit, provides the structural stability and mechanical information. For the cubic BC_7, three independent elastic constants C_{ij} ($C_{11} = 801$ GPa, $C_{44} = 495$ GPa, and $C_{12} = 187$ GPa), have been obtained by introducing small finite strains to the equilibrium structure. According to the mechanical stability criteria for a cubic crystal, i.e., ($C_{44} > 0$, $C_{11} > C_{12}$, and $C_{11} + 2C_{12} > 0$), the designed cubic structure satisfies

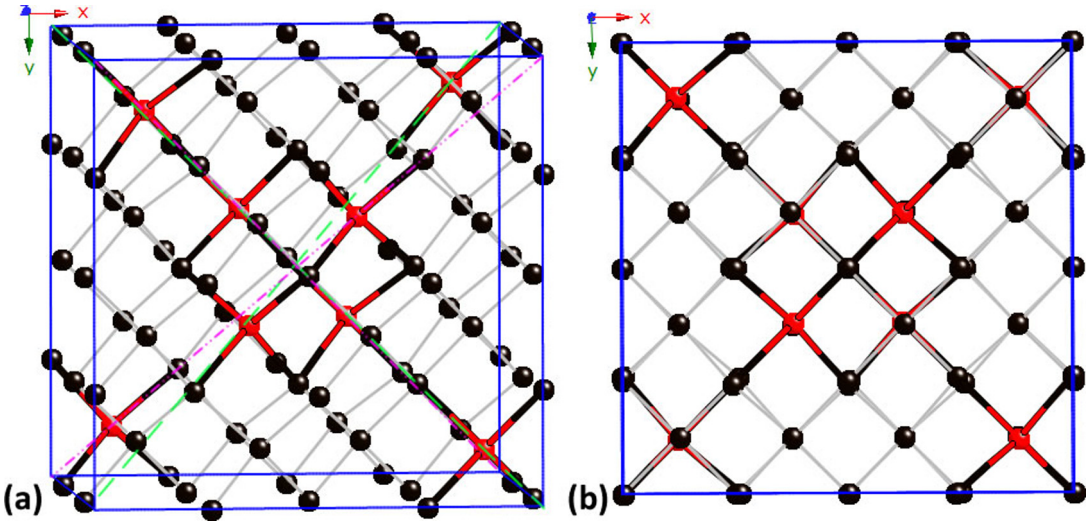

Fig. 1. The crystal structure of designed BC_7 with I-43m symmetry. The polyhedral and front view along x axis of unit cell are shown in (a) and (b), respectively.