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Research paper

A new orthorhombic ground-state phase and mechanical strengths of ternary B_2CO compound

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ABSTRACT

A novel orthorhombic *oI*16 structure, formed by strong covalent sp^2-sp^3 B—C and B—O bonds, was identified as to be the thermodynamic ground-state phase for B_2CO compound by using an unbiased structure searching method. The energy of this new *oI*16 phase is considerably lower than all those of previously proposed candidates, and it is dynamically stable at atmosphere pressure through the phonon calculations. The evidences of the indirect semiconducting and chemical bonding nature are manifested by the electronic structure calculations and AIM analyses. The pronounced elastic anisotropy of *oI*16 structure has been revealed by the calculated distributions of elastic moduli along different crystal orientations. The calculated stress-strain relations of *oI*16 structure disclose its common hard nature but with an extended ductility.

1. Introduction

To conquer the limitations on the practicality and applicability of traditional superhard materials like diamond and *c*-BN, a rational strategy to improve important properties is to produce strong covalent compounds formed by the light elements (B, C, N, and O) with the aim that these materials might be more chemically and thermally stable than diamond, and harder than *c*-BN, and thus should be promising materials for high-speed cutting and polishing of different materials including ferrous alloys [1–3]. So far, considerable attempts have been performed and many successes have been achieved in synthesizing potential superhard materials in B—C—N [2,4,5], B—C [6–8], B—N [9,10], and B—O [11,12] systems. For example, a cubic phase of BC_2N with the measured Vickers hardness of 76 GPa was successfully synthesized by Solozhenko et al [2]. In addition, recently developed crystal structure searching methods combined with accurate first-principles energetic approach have been successfully applied to seek and design the global energy minimum ground-state and (super) hard structures to complement experiments, and this gives the theory predictive power that can be used to guide experimental studies.

Currently, the ternary B—C—O compounds have been the focus of intense recent research due to their excellent mechanical properties as like those of reported B—C—N compounds. Experimentally, various single crystal interstitial phases $B(C,O)_x$ (such as $B_6C_{1.1}O_{0.33}$, $B_6C_{1.28}O_{0.31}$, etc.) were produced and characterized under high temperature and high pressure since the last decade [13,14]. However, the precise crystal structures and internal atomic positions of these compounds were not well determined due to the poor quality of the sample in the actual experiments. Theoretically, two diamond-like tetragonal phases (*tI*16 and *tP*4) with calculated Vickers hardness of 50 GPa were first proposed for ternary B_2CO compound in B—C—O system by Li et al [15]. In the subsequent works, using different crystal structure searching methods based on first-principles energetic calculations [16,17], several novel potential superhard phases were discovered for C-rich (B_2C_2O, B_2C_3O, and B_2C_5O) and O-rich (B_4CO_4) compounds in B—C—O system, which are all stabilized with tetragonal crystal system. It is found that these C-rich compounds can be derived from the *tP*4-B_2CO crystal lattice and the O-rich B_4CO_4 phase is stable than the proposed *tP*4- and *tI*16-B_2CO through the enthalpy of the reaction calculations [17]. More recently, for ternary B_2CO compound, three orthorhombic superhard structures (denoted as *oP*8, *oC*16, and *oP*16) were reported by Liu et al [18,19] and they all possess larger band gaps than those of suggested tetragonal B_2CO phases (*tP*4 and *tI*16). Although several structures have been proposed for B_2CO which is a simple stoichiometric ternary compound in B-C-O system, the hunt for new unsuspected energetically stable phases is still fascinating in view of the flexibility of

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the light elements in chemical junctions and the reported wide stable pressure range. For this purpose, we have explored the thermodynamic stable structure of B_2CO at ambient conditions by means of the prevalent Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) code [20,21], a high-efficient structure searching method. Indeed, a new orthorhombic *Ima*2 structure (Z = 4, denoted as *oI*16) for B_2CO was discovered, which is energetically more stable than all those earlier proposed candidates. The structural character and electronic structure as well as mechanical properties of the *oI*16 phase were thus systematically studied.

2. Computational details

The crystal structures searching of B_2CO was executed by the CALYPSO methodology combined with first-principles calculations. The effectiveness of this method has been validated by different successes in predicting structures of materials systems, ranging from elements to binary and ternary compounds [22–27]. Here, the structure searches were performed at ambient pressure using models consisting of one to six formula units (f.u.). The underlying structure optimizing and electronic structure calculations were executed in the framework of the density functional theory with the Perdew-Burke-Ernzerhof generalized gradient approximation [28] and a plane-wave basis set as implemented in the VASP code [29]. Meanwhile, the local density approximation potentials [30] were also considered in our partly calculations to avoid a possible artifact for the choice of potentials. The frozen-core all-electron projector augmented wave (PAW) method [31] was adopted to describe the electron-ion interactions. Energy cutoff of 600 eV and Monkhorst-Pack *k* point meshes [32] with grid spacing of $2\pi \times 0.032$ Å^{-1} were employed in the Brillouin zone integrations. The energy convergence is about 1 meV per atom, with residual stresses and forces in the fully relaxed structures less than 0.1 GPa and 0.001 eV/Å, respectively. The Phonon curves and crystal-orbital Hamilton population (COHP) for *oI*16-B_2CO phase were calculated by PHONOPY [33] and LOBSTER code [34], respectively. The single-crystal elastic constants were calculated by the stress tensor produced by small strain, and the corresponding derived elastic moduli were thus estimated from the Voigt-Reuss-Hill averaging scheme [35]. The quasistatic ideal strength is calculated by incrementally deforming the modeled cell in the direction of the applied strain and controlling the specific strain components, and simultaneously relaxing both the other strain components, as well as the atoms inside the unit cell, at each step.

3. Results and discussion

At atmosphere pressure, the variable-cell structure simulations with the given chemical composition of B:C:O=2:1:1 uncovered the ground-state phase to be the orthorhombic *oI*16 phase, as displayed in Fig. 1a. The *oI*16-B_2CO phase has four f.u. per unit cell (a = 4.866 Å, b = 5.924 Å, and c = 4.374 Å at 0 GPa) in which four inequivalent atom B1, B2, C, and O occupies the Wyckoff 4*b* (0.25, 0.375, 0.312), 4*a* (0.0, 0.0, 0.294), 4*b* (0.25, 0.112, 0.450), and 4*a* (0.0, 0.0, 0.966) sites, respectively. In contrast to the previous reports that all the nonequivalent atoms are tetrahedrally bonded with sp^3 bonding environment in the *tP*4, *tI*16, *oP*8, *oC*16, and *oP*16 phases [15,18,19], only B1 and C atoms are tetrahedrally coordinated in this predicted *oI*16 phase (see Fig. 1b), resulting a mixed sp^2-sp^3 bonded environment. The *oI*16 phase thus possesses a lower calculated density of 2.616 g/cm^3 than those of reported dense structures (*tP*4: 3.332 g/cm^3, *tI*16: 3.337 g/cm^3, *oP*8: 3.320 g/cm^3, *oC*16: 3.214 g/cm^3, and *oP*16: 3.280 g/cm^3) [18,19]. In more detail, the calculated B—O (1.434 Å and 1.577 Å) and B—C (1.545 Å, 1.585 Å, and 1.669 Å) bond lengths in *oI*16 phase are shorter and longer than those in *tP*4, *tI*16, *oP*8, *oC*16, and *oP*16 phase [15,18,19], respectively. Total energy as a function of volume for B_2CO within these six structures were displayed in Fig. 2a, in which the *oI*16 phase is energetically far more stable than all those earlier proposed phases, verifying the reliability of the structure predictions conducted here. The third-order Birch-Murnaghan equation of state (EOS) [36] fitting to the *oI*16-B_2CO data gives an ambient bulk modulus of B_0 = 217 GPa (B_0' = 2.022), which are much lower those of five candidates in previous theoretical results [15,18,19]. Fig. 2b shows the calculated phonon dispersion curves and no imaginary phonon frequencies were found to confirm the dynamic stability of the *oI*16 phase at 0 GPa.

The enthalpy difference curves of the predicted *oI*16 phase relative to these five competitive candidates under high pressure were shown in Fig. 2c. One can see that the *oI*16 phase is much more stable at pressure range of 0–19 GPa and previous proposed tetragonal *tI*16 phase stabilizes above 19 GPa. At ambient and high pressures, the exothermic character of the *tP*4, *tI*16, *oP*8, *oC*16, and *oP*16 phases have been demonstrated in previous studies [16,18,19] according to two possible reaction routes: $\Delta H_{f1} = H(B_2CO) - 2H(B) - 1/2H(O_2) - H(C)$ and $\Delta H_{f2} = H(B_2CO) - H(B_2O) - H(C)$. The synthesis of this new predicted *oI*16 phase is thus highly desirable, considering that it is energetically far more stable than these five proposed phases presented in Fig. 2a. However, a tetragonal O-rich B_4CO_4 phase recently discovered by Wang et al [17] is suggested to be more stable than the *tP*4- and *tI*16-B_2CO

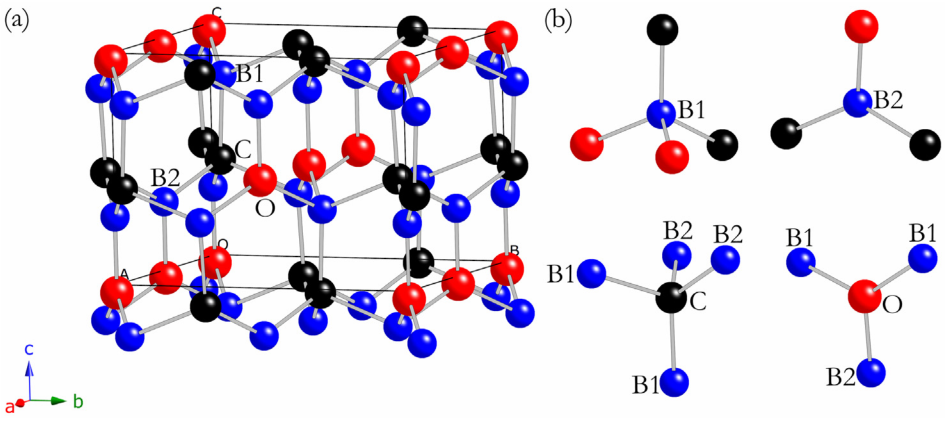

Fig. 1. Crystal structure of *oI*16-B_2CO (a) and arrangements B, C, and O and their neighbors in *oI*16-B_2CO (b).