Computational Materials Science 150 (2018) 259–264

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Theoretical exploring the mechanical and electrical properties of $tI12$-$B_6C_4O_2$

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ARTICLE INFO

Keywords:
B—C—O
Anisotropy
Mechanical property
Electronic property
First principles

ABSTRACT

Utilizing the crystal structure prediction method (CALYPSO), a tetragonal B—C—O compound ($tI12$-$B_6C_4O_2$ with $I\bar{4}m2$ symmetric structure) was predicted. Computed formation enthalpies, elastic constants and phonon dispersion spectra certify that $tI12$-$B_6C_4O_2$ is thermodynamically, dynamically and mechanically stable. Our results indicate that $tI12$-$B_6C_4O_2$ has large mechanical moduli and high hardness (21.9 GPa). The directional dependences of the Young's modulus, shear modulus and Poisson's ratio have been visualized to analysis the mechanical anisotropy. The calculated band structure and partial density of state revealed that $tI12$-$B_6C_4O_2$ is a typical for conductor with sp^3 hybrid B—C and B—O covalent bonds.

1. Introduction

Since the B—C—O compounds ($B_6C_{1.1}O_{0.33}$ and $B_6C_{1.28}O_{0.31}$) have been synthesized for the first time via the high-pressure technology in the year 1997 [1,2], B—C—O compounds have walked into the field of scientific research. In 2001, boron suboxycarbide $B(C,O)_{0.1555}$ has first prepared by the reaction between B_4C and B_2O_3 compounds with 1:1 ratio at 5.5 GPa and 1400 K [3]. All the B—C—O compounds that have been synthesized are all non-stoichiometric ratio compounds, however, the research of the stoichiometric ratio B—C—O compounds has never been given up.

With the increasing perfection of computational materials science, the research of B—C—O compounds has been turned into theoretical aspects. As the simplest ternary compound in the B—C—O compounds and is isoelectronic with diamond, the potential structures of B_2CO were explored by Li et al. [4]. Two B_2CO polycrystalline structures ($tP4$-, and $tI16$-B_2CO) with superhard and semi-conduction nature were presented. Li suggested that in B—C—O compounds, such as B_2C_XO (X = 2, 3…), the increased C content will lead to more sp^3 C-C bonds, the compounds will be more harder [4], which has been verified by Zhang et al. [5]. Zhang et al. have introduced three diamond-like B_2C_XO (X ≥ 2) phases ($I4_1/amd$-B_2C_2O, $I\bar{4}m2$-B_2C_3O, and $P\bar{4}m2$-B_2C_5O). By evaluating the trends of mechanical property as a function of the C content, Zhang also discovered that the large C content is benefit to improve mechanical property of B_2C_XO compounds including elastic moduli and ideal strengths [5]. After explored the B—C—O system, Wang et al. first proposed a superhard B_4CO_4 phase, unlike the presented B—C—O compounds, which is nonisoelectronic with diamond [6]. The mechanical and electronic properties of B_4CO_4 have been systematically explored [7,8], and the domination strength is found as 27.5 GPa along the (0 0 1)⟨1 0 0⟩ slip system, demonstrating that B_4CO_4 is not intrinsically superhard, but is indeed a hard material [7]. Inspired by all superhard B_2C_XO (X ≥ 1) have the crystal structures similar to the allotropes of carbon, such as diamond and lonsdaleite, Liu et al. proposed two superhard B_2CO phases which derived from Cco-C8 and Bct-C4 [9]. Although all the proposed superhard B_2C_XO (X ≥ 1) phases and pseudo superhard B_4CO_4 are tetragonal structures, a lonsdaleite-like superhard B_2CO with nontetragonal structure was proposed [10], which broadened the structural system of B—C—O compounds. Up to this day, B—C—O compounds attracted increasing attention on not only three dimensional (3D) materials but also 2D materials. Zhou and Zhao discovered that the 2D B—C—O compounds are promising electronic devices [11]. The 2D B—C—O systems can be either metals or semiconductors depending on the B:O ratio (1:1 and 3:1, metallic; 2:1, semiconductive with a band gap range of 1.0 eV–3.9 eV [11].

In present work, through the analysis of the elastic constants and phonon spectra, a new B—C—O compound with chemical formula $B_6C_4O_2$ and space group $I\bar{4}m2$ was proposed. Then its mechanical and

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https://doi.org/10.1016/j.commatsci.2018.04.020
Received 21 December 2017; Received in revised form 12 March 2018; Accepted 8 April 2018

electronic properties are researched, and the mechanical anisotropy has been explored systematically.

2. Computational methods

Adopting the CALYPSO code [12–14], the potential B—C—O polymorphs' structures with unfixed stoichiometric ratio were explored at ambient pressure. Once the structures were generated from the CALYPSO, geometric optimization, elastic constants and phonon frequency calculation, and physical properties research were implemented in CASTEP code [15]. The local density approximation was employed as the exchange correlation potential, which was calculated by the CA-PZ functional [16,17]. Geometric optimization was performed by BFGS minimization algorithm [18] with the following criteria were satisfied: (1) the force on atom is less than 0.01 eV/Å; (2) the atoms' displacement is below 5×10^{-4} Å; (3) the energy change does not go beyond 5×10^{-6} eV/atom; (4) the stress component does not exceed 0.02 GPa. The atomic electronic configuration was described by the norm conserving pseudopotential [19] with an energy cutoff of 960 eV. To ensure calculation precision at 1 meV, the k-points for Monkhorst − Pack grid was generated by a k-point separation ($2\pi \times 0.04$ Å^{-1}).

To ensure that the obtained structures were mechanically and dynamically stable, the elastic constants and phonon frequency throughout the Brillouin zone are calculated. For the elastic constants, we applied the efficient stress–strain method within CASTEP code and adopted the maximum strain amplitude 0.003 and 9 steps for each strain. For the phonon frequency, we employed the ultrasoft pseudopotential [18] and finite displacement method [20] with the primitive cells.

3. Results and discussion

3.1. Optimization of crystal structures

A wide selection of candidate structures of B—C—O compounds with variable stoichiometric ratios was calculated. In addition to the studied structures within compounds as B_2C_XO (X = 1, 2, 3, 5) and B_4CO_4, a new B—C—O compound were emerged from the thousands of candidate structures. It is a body-centered (1/2, 1/2, 1/2) tetragonal crystal structure with two formula units (f.u.) in unit cell, and possess the Laue class 4/*mmm* and point group $\bar{4}2m$. This one we proposed is $B_6C_4O_2$ with space group $I\bar{4}m2$ with 12 atoms per unit cell, denoted as *t*I12-$B_6C_4O_2$ (Fig. 1). All C atoms in *t*I12-$B_6C_4O_2$ are combined with four B atoms and formed [CB_4] tetrahedra, all O atoms are combined with four B atoms to form [OB_4] tetrahedra, indicating that there no C-O bonds in *t*I12-$B_6C_4O_2$. At ambient pressure, the optimized lattice parameters of *t*I12-$B_6C_4O_2$ are $a = 2.617$ Å, $c = 11.226$ Å with boron occupying 4*f* (0, 0.5, 0.587) and 2*c* (0, 0.5, 0.25) Wyckoff positions, carbon taking up 4*e* (0, 0, 0.341) Wyckoff position and oxygen occupying 2*a* (0, 0, 0) Wyckoff position.

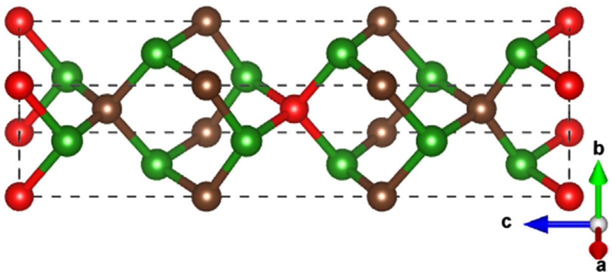

Fig. 1. Structure graphs for *t*I12-$B_6C_4O_2$. The balls in green, gray and red represent the B, C and O atoms, respectively.

3.2. Stability analysis

For tetragonal crystal system with Laue class 4/*mmm*, the necessary and sufficient conditions for elastic stability [21] are listed as Eq. (1).

$$C_{44} > 0,\ C_{66} > 0,\ C_{11} > |C_{12}|,\ (C_{11} + C_{12})C_{33} > 2C_{13}^2; \tag{1}$$

Here, the calculated independent elastic constants C_{ij}s at ambient pressure are $C_{11} = 538.3$ GPa, $C_{33} = 557.0$ GPa, $C_{44} = 219.1$ GPa, $C_{66} = 120.3$ GPa, $C_{12} = 152.8$ GPa and $C_{13} = 164.8$ GPa. The C_{ij}s satisfy the criteria above, declaring that *t*I12-$B_6C_4O_2$ possesses mechanical stability.

The existence of imaginary frequency denotes the dynamical instability and will cause distortion of crystal. Phonon dispersion of *t*I12-$B_6C_4O_2$ at ambient pressure is calculated and plotted in Fig. 2a. There are no soft phonon modes in entire Brillouin zone, suggesting it's dynamically stable.

For further experimental synthesis, there is necessity to explore the thermodynamic stability of *t*I12-$B_6C_4O_2$, which with respect to the separate phases as a function of pressure and can be quantified in the form of the formation enthalpies (ΔH):

$$\Delta\ \mathrm{H} = \mathrm{H}(B_6C_4O_2) - 6\mathrm{H}(B) - 4\mathrm{H}(C) - 2\mathrm{H}(O); \tag{2}$$

The α-B, graphite, and α-O_2 [22] are selected as the reference reactants. As exhibited Fig. 2b, the formation enthalpy decreases with the pressure increase and is always negative, which indicates the thermodynamic stability of *t*I12-$B_6C_4O_2$ and increasing pressure is be beneficial to synthesize *t*I12-$B_6C_4O_2$ through the path mentioned above.

3.3. Mechanical properties

The pressure-volume curves of *t*I12-$B_6C_4O_2$ are fitted by Birch-Murnaghan equation of state (BM-EOS) [23].

$$P(V) = 1.5B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}]\{1 + 0.75(B_0' - 4)[((V/V_0)^{-2/3} - 1]\}; \tag{3}$$

Herein, V_0 and V represent the volume per formula unit at zero pressure and given pressure; B_0 and B_0' represent the isothermal bulk modulus and its first pressure derivative. The fitting results and a series value of pressure versus volume are presented in Fig. 3. The obtained values of B_0 (GPa), B_0' and V_0 (Å^3) are listed as an interpolation table in Fig. 3.

Based on the elastic constants, the bulk modulus (B) and shear modulus (G) are calculated (288.6 GPa and 183.9 GPa, respectively). The value of B agrees well with the fitted value B_0 derived from the BM-EOS, declaring the calculation is correct and accurate. And then via Eq. (4), Young's modulus (E) and Poisson's ratio (ν) are obtained (455.1 GPa and 0.237, respectively). The results reveal that *t*I12-$B_6C_4O_2$ has high mechanical moduli, suggesting *t*I12-$B_6C_4O_2$ maybe a hard material. As one basic physical property of solid material, the hardness of *t*I12-$B_6C_4O_2$ is calculated based on Chen's empirical scheme [24] in accordance with Eq. (5).

$$\mathrm{E} = 9\mathrm{BG}/(3B + G); \nu = (3B - 2G)/(6B + 2G); \tag{4}$$

$$H_V = 2(\kappa^2 G)^{0.585} - 3; \kappa = G/B; \tag{5}$$

The calculation of mechanical properties demonstrates that *t*I12-$B_6C_4O_2$ is indeed a hard material with hardness 21.9 GPa.

Elasticity anisotropy is important for understanding the microcracks produced in ceramic materials and significantly influences materials' engineering application [25]. As a widely used criterion, the degree of anisotropy in the bonding between atoms in different planes can be measured by the shear anisotropy. The shear anisotropic factors [26] A_1, A_2 and A_3 are described for shear planes {1 0 0} between ⟨0 1 1⟩ and ⟨0 1 0⟩ directions, {0 1 0} between ⟨1 0 1⟩ and ⟨0 0 1⟩, {0 0 1} between ⟨1 1 0⟩ and ⟨0 1 0⟩, respectively.

For a tetragonal structure,

$$A_1 = A_2 = 4C_{44}/(C_{11} + C_{33} - 2C_{13}); A_3 = 2C_{66}/(C_{11} - C_{12}); \tag{6}$$