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The electronic and mechanical properties of tetragonal YB_2C as explored by first-principles methods

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ABSTRACT

By means of the first-principles calculations, the lattice parameters, electronic structures, phonon dispersions, and mechanical properties of the rare earth metal borocarbide YB_2C have been theoretically investigated. The dynamically stability of the layered tetragonal YB_2C has been evidenced based on the frozen phonon method. We have found that the covalent bonding between B-2*p*, C-2*p* and Y-5*d* orbitals are responsible for the strong interlayer interactions based on the calculated electronic structures and ELF images. The estimated hardness of $P4_2/mbc$-YB_2C is around 23.46 GPa which is comparable with the well-known ultra-incompressible *oP*6-OsB_2. Additionally, the analysis of the ideal shear and tensile strength of YB_2C reveals the importance of covalent bonds between Y and B/C layer which help to enhance the resistance under deformation.

1. Introduction

The solid-state rare earth (RE) metal borocarbide materials have attracted extensive interest over the past decades due to their rich and unique mechanical and electronic properties [1–7]. For instance, the class of RE transition-metal borocarbides with the general formula of RNi_2B_2C (R = Y and Lu) exhibit fairly high superconducting transition temperatures with T_C about 15–16 K [8–10]. Furthermore, a series of interesting electronic and magnetic properties [11,12] have been found in the RB_2C_2 (R = Y, La-Lu) indicating they are promising magnetic materials [13]. Thus, the exploration of novel electronic and mechanical properties of RE metal borocarbides is hotspot for materials discovery.

The ternary rare earth metal borocarbides solid-state compounds of general formula $M_xB_yC_z$ can be classified into three kinds based on the bonding styles of B and C atoms: i), 2D planar networks [1,14], such as LaB_2C_2 [15], ScB_2C_2 [16], YB_2C [17,18] and UB_2C [19]; ii), 1D atomic chains or zigzag B/C ribbons [3,20,21], like YBC [17,18], ThBC [22], UBC [17] and $Th_3B_2C_3$ [23]; iii), B/C clusters isolated into cavities formed by the metal atoms [24–26], including $Ce_{10}B_9C_{12}$ [27], $Ce_5B_4C_5$ [27], Sc_2BC_2 [28] Lu_3BC_3 [29]and $La_{15}B_{14}C_{19}$ [27]. According to the way of designing superhard materials proposed by Kanar et al. [30], the incorporated transition metal can simultaneously optimize the covalent bonding and the valence-electron density of borides and carbides producing superhard or ultra-incompressible materials [30,31]. Therefore, it is possible to find materials with high hardness or distinct mechanical properties in the RE metal borocarbides. In our present work, we have paid our attention to the layered YB_2C, in order to explore its undiscovered electronic and mechanical properties.

2. Computational method

The Vienna *ab-initio* Simulation Package (VASP) [32–34] was employed in this work. All the calculations were carried out by utilizing the projector augmented wave (PAW) [35,36] method

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within the framework of density functional theory(DFT) [37,38]. The generalized gradient approximation (GGA) [39] of Perdew-Burke-Ernzerhof (PBE) [40,41] was applied for the description of exchange-correlation. The structure optimizations were achieved by minimizing forces and total energies and the convergence criteria of the total energy and force were set to be 0.001 meV and 0.01 meV/Å, respectively. The quasi-Newton algorithm as implemented in the VASP code is used in all structural relaxations. In this work, both the cell volume and the atomic positions are all allowed to relax to minimize the internal forces. The plane wave cut-off energy is set at 400 eV which was tested to be sufficient for the accurate calculation of all these elements considered in this work. The tetrahedron method with Blöchl corrections was utilized in the integrations. The valence electrons of atoms are $2s^2{}_2p^2$ (C), $2s^2 2p^1$ (B) and $4s^2 4p^6 5s^2 4d^1$ (Y). For the bulk properties of the tetragonal YB_2C, a $9 \times 9 \times 7$ ***k***-mesh sampling was applied in the Brillouin Zone according to the Monkhorst-Pack scheme. Note that, YB_2C is found to be non-magnetic based on our spin-polarized calculation. In terms of the elastic constants, the elastic tensors were obtained by performing finite distortions of the lattice and deriving the elastic constants from the strain-stress relationship [42,43]. The polycrystalline elastic moduli were computed by applying the Voigt-Reuss-Hill [44–46] approximation [43]. The phonon spectra of YB_2C were derived with the frozen phonon method by constructing the $2 \times 2 \times 1$ supercell with a finite displacement method within the code of Phonopy [47]. The force constants were obtained by the Parlinski-Li-Kawazoe method [48] and the phonon frequencies were calculated from the force constants [49]. The stress-strain relations of a perfect YB_2C crystal in various tensile and shear deformation directions were carried out within the VASP using the method in Ref. [50].

3. Results and discussions

3.1. Crystal structure and phonon

The tetragonal YB_2C crystallizes in a tetragonal lattice with $a = 6.800$ Å and $c = 7.498$ Å (ICSD41761, space group of $P4_2/mbc$, $Z = 8$). Its structure is consisted of four- and seven-membered B–C layers and the alternative rare-earth element Y layers, as presented in Fig. 1. The optimized lattice parameters are in accordance with the experimental value (Table 1). There are two kinds of B atoms in YB_2C, B1: 8*h* (0.0344, 0.1517, 0.0000) and B2: 8*h* (0.0948, 0.4030, 0.0000), the C and Y atoms lies at 8*h* (0.3227, 0.4593, 0.0000) and 8*g* (0.1906, 0.6906, 0.2500), respectively. From Fig. 1(a), the crystal structure of YB_2C is composed of stacked … Y-(B/C)–Y triple-layer groups and each B/C atomic layer is made up of jointly connected seven-membered and four-membered B–C rings. The length of B1–B2 bond in the seven-membered B–C rings is 1.758 Å which is comparable to the B1– B1 (1.670 Å), B1– B2 (1.807 Å) and B2– B2 (1.785 Å) bonding length in α-B. The fact that the atomic distances of B–C in the seven-membered B–C rings (1.596 Å) are slightly shorter than those in the four-membered B–C rings indicates the existence of stronger chemical bonding. As there are no imaginary frequencies in the phonon dispersion curves (Fig. 1(b)), the dynamically stability of $P4_2/mbc$-YB_2C can be demonstrated. Besides, Babizhetskyy et al. [51] re-characterized the crystal structure of YB_2C to be a new *Pbam* phase. We have compared the thermal stability of these two phases of YB_2C. The optimized crystallographic data are listed in Table 1. Although the newly characterized *Pbam* structure was found energetically more stable (about 0.678 meV/atom) than the previous reported $P4_2/mbc$ phase, such small energy difference indicates that both phases can present at low temperature, especially under the circumstance with stresses or defects. In our present paper, the electronic and mechanical properties of $P4_2/mbc$ phase is emphasized, while the detailed investigation of the new *Pbam* phase would be carried out in our following work.

3.2. Electronic properties

The electronic band structure along the selected high symmetry directions in the Brillouin zone (BZ) and partial density of states (PDOS) of $P4_2/mbc$-YB_2C are presented in Fig. 2. Note that the Fermi level is set at zero. It is clear that tetragonal YB_2C is metallic as there exist no energy gap and the total DOS at the Fermi level ($N(E_F)$) is about 4.376 states/eV. As shown in Fig. 2(b), the DOS at Fermi level is mainly contributed by B-2*p*, C-2*p* and Y-5*d* orbitals. From the energy range of −1 eV to Fermi level, strong hybridization of the B-$2p_z$, C-$2p_z$ and Y-d_{x2}(Y-d_{xy}) orbitals can be noticed (Fig. 2(b–d)). The formation of covalent bonding between transition metal and light elements (B, C, N, O, etc) usually leads to robust interlayer interactions, which can be found in a series of superhard or incompressible materials, such as MnB_3 [54], WB_{3+x} [55], CrB_4 [56], Ir_4B_5

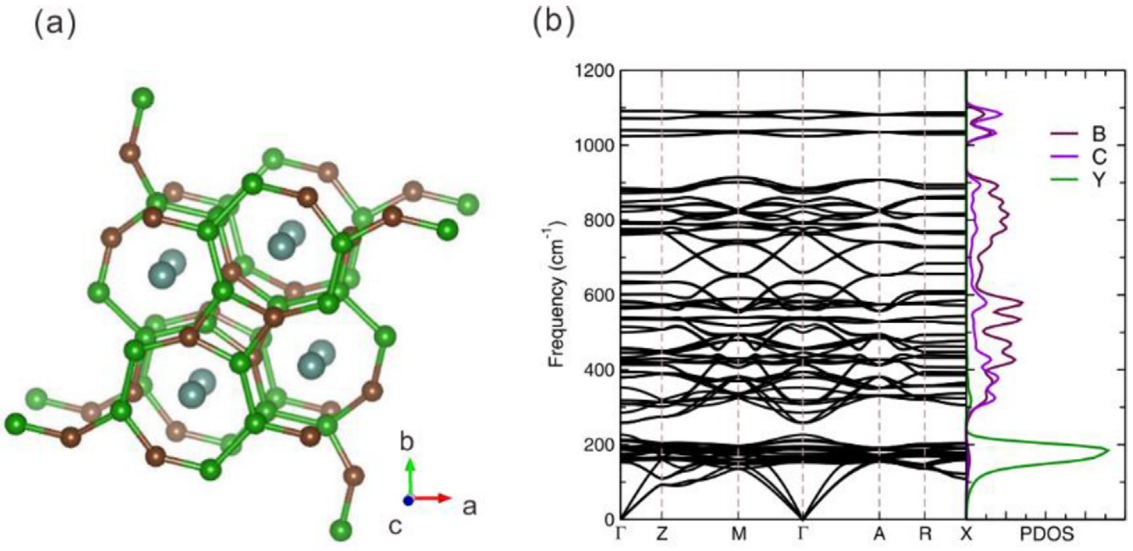

Fig. 1. (a) Crystal structure of YB_2C ($P4_2/mbc$) and (b) its phonon dispersion curves together with the phonon partial density of states (PDOS).