



A possible superhard orthorhombic carbon

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ABSTRACT

Carbon is a versatile element in the periodic table because of its ability to form various stable and metastable allotropes. In the present work, an orthorhombic carbon allotrope with ‘4-membered rectangles’ is predicated by Particle Swarm Optimization method at 0 GPa. Calculations indicate that this new phase is dynamically and mechanically stable although it has a high enthalpy. Its electronic and mechanical properties such as elastic constants, hardness, ideal tensile strength and shear strength are systematically studied. The results show that it is an indirect band gap crystal with a gap of 2.68 eV; in spite of its elastic anisotropy, the theoretical hardness of 76.2 GPa still makes it a potential superhard material; the obtained ideal tensile strength and shear strength are 69.0 GPa and 75.6 GPa, respectively, confirming its superhard character. The related microscopic deformation mechanisms are also detailedly analyzed through investigating the corresponding charge density, which reveals that the bonds arranged parallel to the *b*-axis are responsible for the breakdown of the crystal under the critical tension and shear deformations. These studies provide important information for the potential applications of the crystal once it is synthesized.

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1. Introduction

Unquestionably, carbon is the most versatile element of the periodic table. Owing to its ability to form sp -, sp^2 -, and sp^3 -hybridized bonds, carbon has many polymorphs, such as graphite, diamond, hexagonal diamond, fullerenes, nanotubes, etc. [1–4]. Due to their large differences in both electronic and mechanical properties, for example, the softer mineral of graphite can be transformed to the hardest material of diamond under certain conditions [5,6], and the phase transition mechanism between these allotropes has been a hot subject of research. Recently, an experiment of cold compression of graphite [7] has indicated the existence of a new carbon allotrope owning exceptional indentation strength, which even has the ability to indent diamond anvils. This phase is transparent, dynamically stable at zero pressure, and more stable than graphite beyond 13.4 GPa [7]. A monoclinic $C2/m$ structure carbon (*M*-carbon) was first predicted to be a candidate by ab initio evolutionary algorithm [8]. A tetragonal I/mmm carbon (bct C4) was also recommended by Umemoto et al. [9]. They found that the coexistence of the bct C4 with *M*-carbon can explain better the X-ray diffraction pattern of the unrevealed hard phase of carbon. But later, an orthorhombic carbon (*W*-carbon) was put forward being more favorable than the *M*-carbon and bct C4, in terms of the enthalpy and enthalpy barrier [10]. However, soon after, a new carbon allotrope: Cco-C8 was claimed to be the crystal searched by using Particle Swarm Optimization (CALYPSO) code and the mechanism underlying the transition from carbon

nanotube to Cco-C8 was also identified [11]. The same structure was also found by the minima hopping method (MHM) for crystal structure prediction [12]. Meanwhile, *H*-carbon and *S*-carbon were also proposed to be possible candidates [13].

Thus it is evident that crystal-structure predication plays a significant role in the field of the material science, which constructs a bridge between the pertinent experimental and theoretical fields. CALYPSO [14], a code designed to search stable or metastable crystal structures using only the chemical compositions of a given compound at given pressures, is a powerful tool for crystal structure predication. In the past days, it has successfully predicated a series of new crystal phases on elemental, binary, or ternary compounds with metallic, ionic, or covalent bondings [15–19]. Here we employed this code to further search the potential carbon allotropes in order to enrich its family member. Predictions ultimately successfully revealed a new high-enthalpy orthorhombic carbon crystal. We then systematically studied the electronic and mechanical properties of this new carbon allotrope.

The remainder of this work is organized as follows: In Section 2, the computational details were described, then in Section 3, the crystal structure, electronic properties, and mechanical properties including its elastic properties, its ideal strengths and microscopic deformation mechanisms were studied and analyzed. Finally, the conclusions were presented in Section 4.

2. Computational details

In structural predication, random structures of every generation were produced by CALYPSO code [14] with the cells containing up to

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12 carbon atoms, then these structures were relaxed by the interfaced first-principles code, VASP [20], to find the possible carbon crystals. During our calculations, the local density approximation (LDA) and (PAW) pseudopotentials were employed as implemented in VASP. For convenience, the subsequent property calculations of the predicated carbon phases were carried out by CASTEP [21], using the density functional theory within the LDA scheme and ultrasoft pseudopotentials. The electron–electron exchange interaction was described by the exchange–correlation function of Ceperley and Alder [22], as parameterized by Perdew and Zunger (CA-PZ) [23]. The cutoff energy of 310 eV was used for the plane wave basis set, and a k -point spacing of $2\pi \times 0.04 \text{ \AA}^{-1}$ was selected to generate the Monkhorst–Pack grids [24].

The tensile and shear stresses were computed by the method introduced in Ref. [25–27]. The stress–strain dependence was calculated by incrementally deforming the modeled cell in the direction of the exerted strain. Both the atomic basis vectors orthogonal to the applied strain and the atoms were simultaneously relaxed at each step until the Hellmann–Feynman stresses converged to within 0.02 GPa. For the shear strain, the strained cell was optimized until all of the stress components, except for the imposed shear stress, were reduced to less than 0.02 GPa. The starting structure at each strain step was taken from the relaxed cell of the previous strain step to ensure the continuity of the strain path.

3. Results and discussion

3.1. Crystal structure and stability

The present simulations reproduced the already known structures such as diamond, graphite, etc. Meanwhile, a new orthorhombic carbon (space group *Imma*, named *Imma* C hereafter) was discovered. The related lattice constants are $a = 2.515 \text{ \AA}$, $b = 4.885 \text{ \AA}$, $c = 4.154 \text{ \AA}$, and $V = 51.04 \text{ \AA}^3$; all the carbon atoms are symmetrically equivalent and their Wyckoff position is $8h (0, -0.5869, 0.3541)$. As shown in Fig. 1, the structure of *Imma* C can be seen as being formed by ‘4-membered rectangles (see the atoms 0–1–8–2, etc.)’ sharing one d_2 bond (see atoms 0–2, etc.), which are then connected by two d_3 bonds (see atoms 0–3 and 6–5) forming the ‘6-membered rings (see atoms 0–3–4–5–6–1)’. Its unit cell has eight atoms, and each of them is four-fold

coordinated with two d_1 bonds (1.527 \AA , see atoms 0–1; 0–9; etc., where the atom 9 in the adjacent cell is not shown for clarity), one d_2 bond (1.593 \AA), and one d_3 bond (1.479 \AA), constituting a tetrahedron as that formed by the atoms 1, 2, 3 and 9 with the central atom 0.

It is known that the structure of a crystal often has a significant influence on its physical properties, thence it is meaningful to make some comparison between these of *Imma* C and some familiar carbon allotropes: all the bond lengths of *Imma* C are longer than that of the C–C covalent bonds in graphite (1.42 \AA); d_1 is nearly equal to the value of 1.54 \AA in diamond [28], while the other two behave opposite: d_2 is 0.053 \AA longer than that of diamond, whereas d_3 is 0.061 \AA shorter, which shows that the differences of the bond lengths between the *Imma* C and diamond are very small. There are four types of angles in tetrahedrons of *Imma* C: they are that $\angle 901 = 110.8^\circ$, $\angle 902 = \angle 102 = 90.0^\circ$, $\angle 903 = \angle 301 = 117.7^\circ$ and $\angle 203 = 125.1^\circ$, where the notation $\angle 901$ represents the angle formed by the central atom 0 and the two terminal atoms 9 and 1, other notations above have a similar meaning as this definition. Except the angle $\angle 901$, other five angles have a large deviation compared with these values (about 109.5° , from our calculation) in diamond (the ideal sp^3 hybridized carbon crystal), especially the angles $\angle 902$ and $\angle 102$, which have the largest deviation of 19.5° . For the torsion, the representative ones are that $\angle 1034 = 43.2^\circ$, $\angle 2034 = -68.4^\circ$, $\angle 9034 = 180.0^\circ$, $\angle 2016 = 90.0^\circ$, $\angle 3016 = -40.5^\circ$, $\angle 9016 = 180.0^\circ$, $\angle 1028 = 0^\circ$, $\angle 3028 = 124.6^\circ$ and $\angle 9028 = -110.8^\circ$, where $\angle 1034$ represents the torsion formed by atoms 1, 0, 3 and 4 along the d_3 bond, other notations above have a similar meaning as this. Also these values deviate significantly from the corresponding value of 60.0° in diamond. Other values such as the atomic volume and density are listed in Table 1. It can be seen from it that these values of *Imma* C can't compare to those of diamond, or even bct C4, revealing that *Imma* C is not as closely packed as diamond and bct C4, which will lower its bulk modulus and hardness as will be seen in the following section.

In order to investigate the relative stability, we compared the enthalpy differences of diamond, bct C4 and *Imma* C with respect to graphite as a function of pressure, as displayed in Fig. 2. The calculation gives a pressure of 18.7 GPa for the phase transition from graphite to bct C4, which agrees well with other theoretical prediction (18.6 GPa) [9]. Clearly, *Imma* C has a much higher enthalpy compared with diamond and bct C4, about 0.40 eV/atom and 0.19 eV/atom higher, respectively.

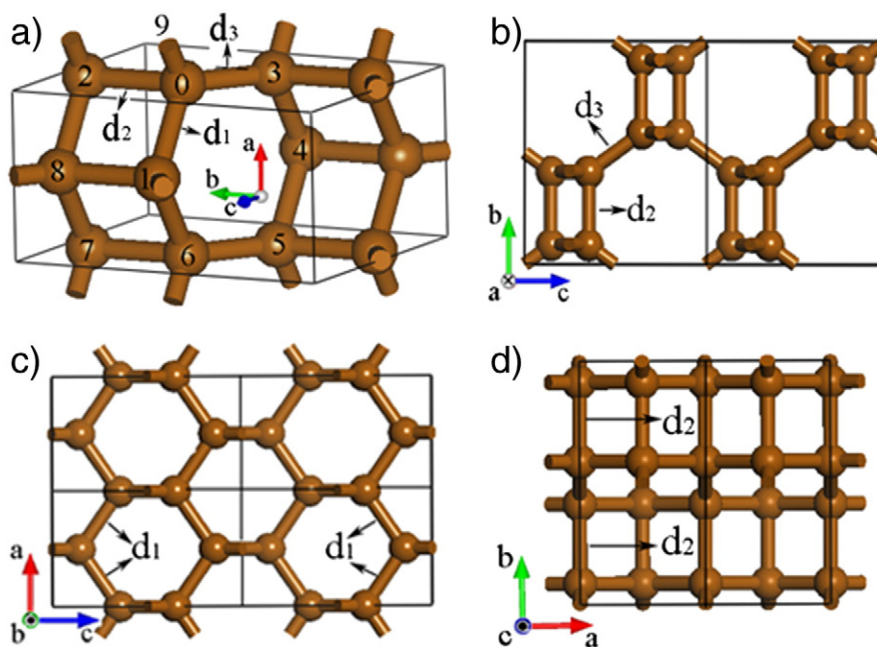


Fig. 1. Crystal structure of the new orthorhombic carbon (*Imma* C): (a) three-dimensional view of the unit cell; (b) view along the a axis, (c) view along the b axis, and (d) view along the c axis of the $2 \times 1 \times 2$ supercell.

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