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A new superhard carbon allotrope: Orthorhombic C20

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ABSTRACT

A new superhard carbon orthorhombic allotrope *o*C20 is proposed, which exhibits distinct topologies including C4, C3 and two types of C6 carbon rings. The calculated elastic constants and phonon spectra reveal that *o*C20 is mechanically and dynamically stable at ambient pressure. The calculated electronic band structure of *o*C20 shows that it is an indirect band gap semiconductor with a band gap of 4.46 eV. The Vickers hardness of *o*C20 is 75 GPa. The calculated tensile and shear strength indicate that the weakest tensile strength is 64 GPa and the weakest shear strength is 48 GPa, which means *o*C20 is a potential superhard material.

1. Introduction

Superhard materials are widely used because of their unique properties, they generally have high compressive strength and high hardness. Their chemical properties are stable, and they are not easy to react with other substances. The most typical and well-known superhard material is diamond, as known, there are scarce diamonds in the world, and synthetic diamonds require complex conditions, thus, searching for new superhard materials has attracted much attention of researchers [1–10]. Carbon is one of the most important elements of the formation of superhard materials. Many superhard carbon allotropes have been reported, such as the cubic phase (*bct*-C_4 [11]), the monoclinic carbon phase (*M*-carbon [12], *F*-carbon [13], *C*2/*m*-carbon [14], and *X*-carbon [15]), and the orthorhombic phase (*W*-carbon [16], *Cco*-C_8 [17], *O*-carbon [18], *o*C32 [19], and *Imma*-carbon [20]), etc. Among them, *o*C32 was proposed as a new ultra-incompressible and superhard sp^3 carbon polymorph, it was proved that it has a $4 + 8 + 6$ topology and it is more stable than graphite above 4.7 GPa. More importantly, *oC*32 possesses a high hardness (96.2 GPa) and bulk modulus (457.4 GPa), which are comparable to those of diamond, and *oC*32 may be experimentally synthesizable by carefully chosen experimental conditions. In addition, *Cco*-C_8 was also a sp^3-hybridized crystalline carbon allotrope. *Cco*-C_8 can be obtained from direct compression on periodic CNTs [21], it has a high bulk modulus of 444.1 GPa and a high hardness of 95.1 GPa. The search for a similar superhard carbon allotrope has always been a target for researchers. In the present paper, a new superhard sp^3-hybridized crystalline carbon allotrope with an orthorhombic phase (*o*C20) is reported. The structural, mechanical and electronic properties of *o*C20 were also studied.

2. Computational methods

The crystal structure searching is based on a global minimization of energy surfaces merging ab initio total-energy calculations as implemented in CALYPSO code [22]. We performed variable cell structure searches containing 1–4 formula units (5 carbon atom per formula units) in the simulation cell at 0 GPa. The structural relaxations and electronic calculations were performed within the density functional theory, carried out within the Vienna ab initio simulation package (VASP) [23], with the projector-augmented wave method [24]. In the case of the well-converged cut-off energy of 900 eV, the electronic wave functions were expanded in a plane-wave basis. To ensure that the total energies converged to be better than 1 meV/atom, Monkhorst–Pack *k*-point meshes were set as $14 \times 6 \times 10$ for Brillouin zone sampling. The phonon frequencies were calculated by a supercell approach as implemented in PHONOPY code [25], with the forces calculated from VASP. The elastic constants were calculated by the stress–strain method, and

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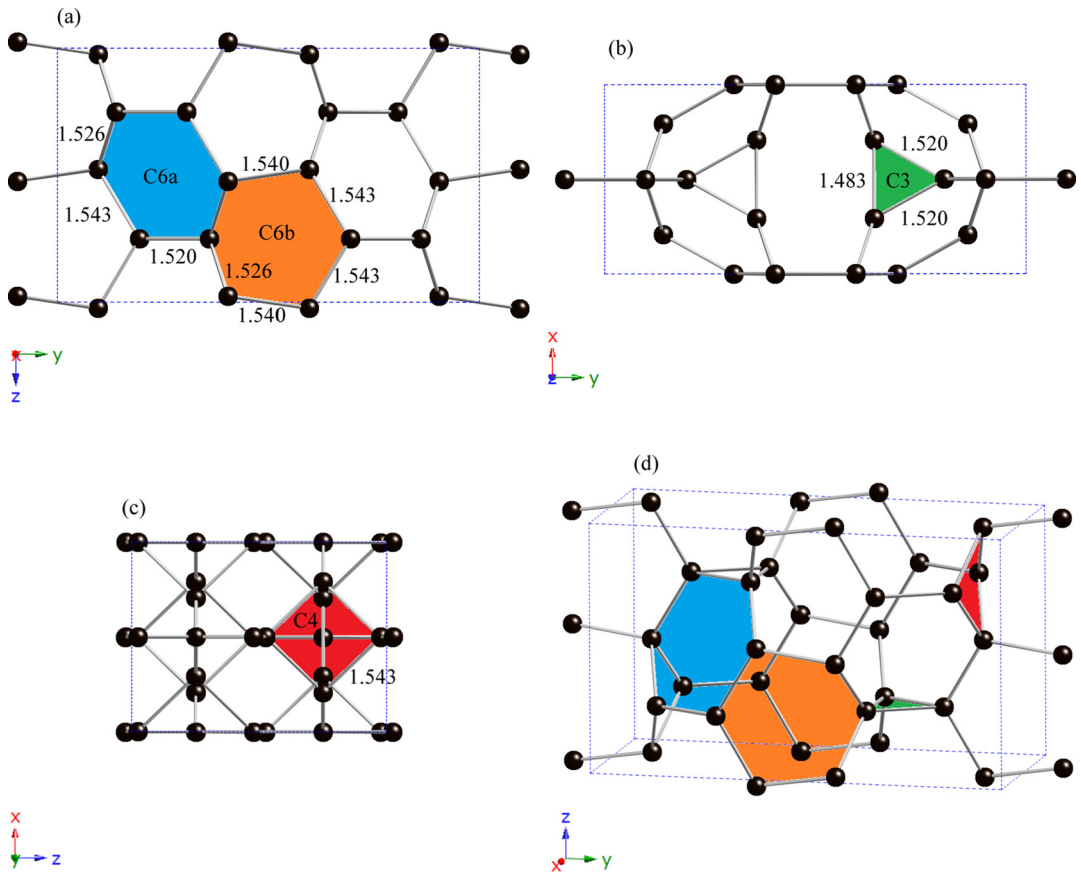

Fig. 1. View of *o*C20 along the [100] direction (a), view of *o*C20 along the [001] direction (b), view of *o*C20 along the [010] direction (c), and global view of *o*C20 (d). (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

Table 1
Calculated elastic constants C_{ij} (GPa), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio ν and Vickers hardness H_V (GPa).

	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	B	G	E	ν	B/G	H_V
*o*C20	794	760	979	405	251	261	112	61	75	335	327	742	0.13	1.02	75
Diamond[a]	1053			563			120			431	522	1116	0.07	0.83	90
C_{64}[b]	598		677	254		107	43	108		264	217	510	0.18	1.21	60

[a] Ref. [27].
[b] Ref. [30].

the Young's modulus, shear modulus, bulk modulus and Poisson's ratio were derived from the Voigt–Reuss–Hill approximation [26].

3. Results and discussions

The crystal structure of *o*C20 is orthorhombic symmetry with the space group of *Cmcm* (No. 63). The lattice parameters are optimized and the results are $a = 3.5695$ Å, $b = 7.9515$ Å and $c = 4.7898$ Å in an orthorhombic unit cell with carbon atoms occupying 8f (0.0, 0.404250, 0.52380), 8g (0.79230, 0.139280, 0.250) and 4c (0.0, 0.306130, 0.250) Wyckoff positions. There are 20 carbon atoms in a unit cell. The density of *o*C20 is 2.934 g/cm^3, which is smaller than that of diamond (3.517 g/cm^3) [27]. By comparing this *o*C20 phase with the known phases collected by Hoffman et al. [28], it is confirmed that this *o*C20 phase is a new phase. Fig. 1 (a)–(c) show the top and side view of the structure of *o*C20, and Fig. 1 (d) shows the global view. All of the atoms are four-coordinated, and there are four kinds of carbon rings in the structure: C6a (marked blue), C6b (marked orange), C4 (marked red) and C3 (marked green). As Fig. 1 (a) shows, in the C6a carbon rings, the opposite bond length is equal, and the adjacent C–C bonds have a bond length of 1.520, 1.543 and 1.526 Å, respectively. There are three kinds of C–C bonds in the C6b carbon rings, the bond length are 1.540, 1.543 and 1.526 Å. As Fig. 1 (b) shows, in the C3 carbon rings, we can see that there are two C–C bonds with a length of 1.520 Å and a C–C bond with a length of 1.483 Å. In the C4 carbon rings (see Fig. 1 (c)), all the bond length of C–C bonds are equal, the bond length is 1.543 Å. Fig. 1 (d) shows the global view of *o*C20 and the positions of the carbon rings in the structure of the carbon rings marked in Fig. 1 (a)–(c).

Elastic properties play a very important role in the mechanical stability of materials. To examine the mechanical stability of *o*C20, the elastic constants are calculated and listed in Table 1. For orthorhombic symmetry crystal, there are nine independent components: C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13} and C_{23}. As known, the criteria for mechanical stability of an orthorhombic structure are [29]: $C_{11} > 0$, $C_{11}C_{22} > C_{12}^2$, $C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 > 0$, $C_{44} > 0$, $C_{55} > 0$, and $C_{66} > 0$. According to the results of the elastic constants listed in Table 1, the elastic constants of carbon are completely consistent with the criterion, so we can conclude that the *o*C20 is mechanical stable. Furthermore, to ensure the dynamical stability of *o*C20, we also calculated the phonon spectra, as shown in Fig. 2 (a), the phonon spectra at ambient pressure have no imaginary frequency in the