

Computational prediction of body-centered cubic carbon in an all- sp^3 six-member ring configuration

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Recent shock compression experiments produced clear evidence of a new carbon phase, but a full structural identification has remained elusive. Here we establish by *ab initio* calculations a body-centered cubic carbon phase in $Ia\bar{3}d$ (O_h^{10}) symmetry, which contains twelve atoms in its primitive cell, thus termed BC12, and comprises all- sp^3 six-membered rings. This structural configuration places BC12 carbon in the same bonding type as cubic diamond, and its stability is verified by phonon mode analysis. Simulated x-ray diffraction patterns provide an excellent match to the previously unexplained distinct diffraction peak found in shock compression experiments. Electronic band and density of states calculations reveal that BC12 is a semiconductor with a direct band gap of ~ 2.97 eV. These results provide a solid foundation for further exploration of this new carbon allotrope.

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I. INTRODUCTION

Carbon is one of the most versatile elements in its ability to assemble diverse structural types. In pure elemental form, there are three naturally occurring carbon allotropes, graphite, diamond, and amorphous carbon, which contain sp^2 , sp^3 , and mixed sp^2/sp^3 bonding types, respectively. A rich variety of carbon phases also have been synthesized under laboratory conditions, including, most notably, carbon nanotubes (CNTs) [1], fullerenes [2], and graphene [3]. These discoveries have stimulated great interest in search of more carbon allotropes [4–8]. A particularly appealing approach is to explore new carbon phases under extreme conditions, such as high pressure or shock compression, which can induce new bonding modifications. A prominent example is the recent discovery of cold-compressed graphite [9] that has led to the identification of several new carbon forms [10–18]. In addition, cubic modifications of carbon have been produced during the heating of carbon soot or shock compression of polycrystalline graphite [19–21], which led to a proposed simple cubic carbon phase termed SC24 in $Pa\bar{3}$ symmetry [22]. Moreover, a body-centered cubic carbon denoted BC8 is suggested to be the high-pressure modification of carbon derived from cubic diamond under pressure of ~ 1100 GPa [23–25]. Among all these carbon structures, only BC8 carbon comprises entirely a diamond-like six-membered ring bonding structure, while other reported sp^3 hybridized carbon structures contain mixed bonding configurations, such as the (5+6+7)-membered ring in *M* carbon [10], (4+6+8)-membered ring in *Z* carbon [13], or (3+6+7)-membered ring in SC24 carbon [22].

In this paper, we report by *ab initio* calculations a body-centered cubic carbon phase with a 24-atom unit cell in $Ia\bar{3}d$ symmetry with all- sp^3 six-membered rings, which is the same bonding type as cubic diamond (8-atom unit cell in $Fd\bar{3}m$ symmetry) and BC8 carbon (16-atom unit cell in $Ia\bar{3}$ symmetry). This new carbon phase has a twelve-atom primitive cell (thus termed BC12 carbon hereafter) with a single bond

length (1.566 Å) but two distinct bond angles (99.59° and 131.81°), placing it between cubic diamond, which has a single bond length and a single bond angle, and BC8, which has two distinct bond lengths and two bond angles. Electronic band and density-of-states calculations reveal that BC12 carbon is a semiconductor with a direct band gap of 2.97 eV, and its dynamic stability is verified by phonon mode analysis. Simulated x-ray diffraction (XRD) patterns suggest the presence of BC12 carbon in shock compressed soot carbon [20], and this finding resolves previously unexplained experimental data and lays the foundation for further exploration of this new carbon form.

II. COMPUTATIONAL METHOD

We performed calculations using the density functional theory as implemented in the Vienna *ab initio* simulation package (VASP) [26]. Both the local density approximation (LDA) in the form of Ceperley-Alder [27] and the generalized gradient approximation (GGA) developed by Perdew, Burke, and Ernzerhof (PBE) [28] are adopted for the exchange-correlation potential. The all-electron projector augmented wave (PAW) [29] method is adopted with $2s^2 2p^2$ treated as valence electrons. We used a plane-wave basis set with an energy cutoff of 800 eV and sampled the Brillouin zone with an $8 \times 8 \times 8$ *k*-point grid. The geometries are optimized with symmetry constraints until the remaining atomic forces are less than 10^{-6} eV/Å and the energy convergence criterion is set at 10^{-8} eV. Electronic band structures are calculated using the Heyd-Scuseria-Ernzerhof hybrid functional (HSE06) [30]. Phonon calculations are performed using the PHONOPY package [31,32] with the forces calculated from VASP.

III. RESULTS AND DISCUSSION

We first characterize the structural property of BC12 carbon, which is in $Ia\bar{3}d$ (O_h^{10}) symmetry, as shown in Fig. 1(a), and has an sp^3 bonding network purely consisting of connected zigzag C_6 benzene rings. In cubic representation, the equilibrium lattice parameter is estimated to be $a = 5.116$ Å

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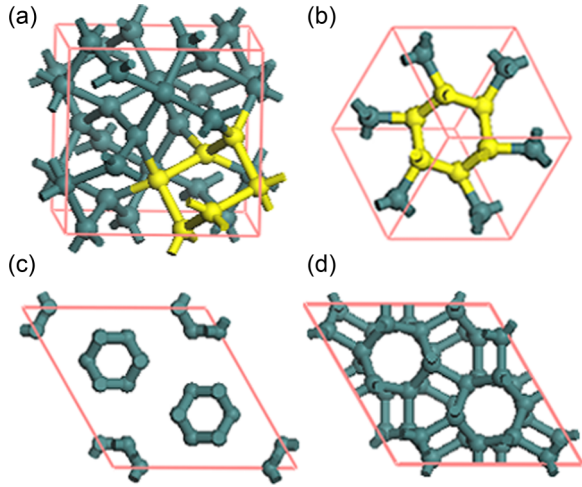


FIG. 1. (Color online) Schematic depiction of the bonding structure of BC12 carbon. (a) The cubic crystalline structure of BC12 carbon in $Ia\bar{3}d$ (O_h^{10}) symmetry with the lattice parameter of 5.116 Å. All the carbon atoms are equivalent and occupy the $24d$ (0.375, 0, 0.25) Wyckoff position. (b) The primitive cell of BC12 carbon containing twelve carbon atoms, consisting of zigzag C_6 rings (C_6 unit is marked in yellow). (c) The view along the c axis of the (3,0)-CNT structure. (d) A hexagonal representation of BC12 carbon, corresponding to the (3,0)-CNT.

with only one inequivalent crystallographic site, occupying the $24d$ (0.375, 0, 0.25) Wyckoff position. In the primitive unit cell, it has twelve atoms with lattice parameters $a = 4.430$ Å, $\alpha = \beta = \gamma = 109.47^\circ$ [Fig. 1(b)]. All the C-C bonds in BC12 carbon are of equal length of 1.566 Å, which is only slightly larger than 1.544 Å for diamond. Meanwhile there are two different bond angles of 99.59° and 131.81° in BC12 carbon, which also occurs in BC8 carbon where the two bond angles are 101.22° and 116.31° [23–25], and in SC24 carbon where the two bond angles are 60° and 102.71° [22].

It is interesting to note that BC12 carbon can be viewed as a polymerized form of (3,0)-CNT, which is similar to the case of bct- C_4 carbon that can be viewed as a polymerized form of (2,2)-CNT [16]. When each six-membered ring of (3,0)-CNT [see Fig. 1(c)] is twisted around the c axis, a hexagonal

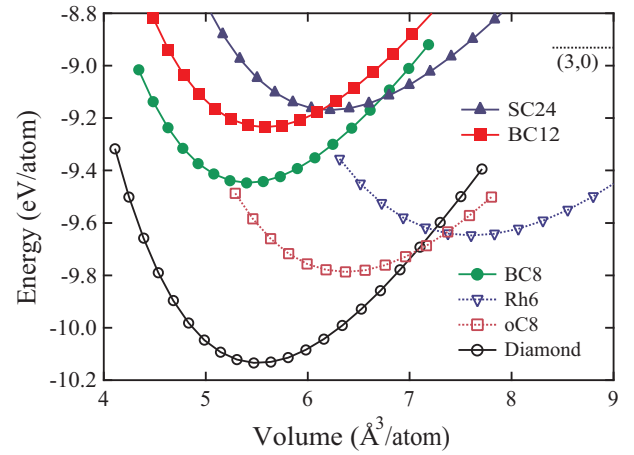


FIG. 2. (Color online) The total energy as a function of volume per atom for BC12 carbon in comparison with diamond, BC8 [24], SC24 [22], Rh6 [5], oC8 carbon [18], and (3,0)-CNT.

structure [Fig. 1(d)] can be obtained. The view along the [111] direction BC12 carbon resembles the view along the c axis of this hexagonal structure. This structural relation suggests that BC12 carbon may be synthesized by the polymerization of properly selected CNTs as starting materials. In fact, the (3,0) CNT bundle has a higher energy of -8.93 eV per atom (see Fig. 2) and can easily convert to BC12 carbon with an energy gain of 0.29 eV per carbon atom.

Figure 2 shows the calculated total energy versus the volume per atom for diamond, BC8, BC12, and SC24 carbon. It is clearly seen that BC12 carbon is less stable than diamond and BC8 carbon, but more stable than SC24 carbon. These energetic results strongly suggest that bond-angle deviation from that of cubic diamond has a significant influence on the total energy of cubic carbon allotropes in all sp^3 bonding networks. The larger bond angle deviation of BC12 carbon from the cubic diamond values compared to BC8 pushes its equilibrium energy to a higher level. The equilibrium volume per atom of BC12 carbon is comparable to that of cubic diamond, but it is smaller than that of SC24 carbon [22]. By fitting the calculated total energy as a function of volume to Murnaghan’s equation of state [33], we obtain the

TABLE I. Calculated equilibrium structural parameters (space group, lattice parameter a , volume per atom V_0 , density ρ , bond lengths d_{C-C} , bond angles $\angle C-C-C$), total energy per atom E_{tot} , electronic band gap E_g , and bulk modulus B_0 for diamond, BC8, BC12, and SC24 carbon at zero pressure, compared to available experimental data [20,35].

Structure	Space group	Method	a (Å)	V_0 (Å ³)	ρ (g/cm ³)	d_{C-C} (Å)	$\angle C-C-C$ (deg)	E_{tot} (eV)	E_g (eV)	B_0 (GPa)
Diamond	$Fd\bar{3}m$	LDA	3.534	5.52	3.616	1.530	109.47	-10.134	5.43	452
		PBE	3.572	5.70	3.502	1.547	109.47	-9.094	5.34	418
		Expt. [35]	3.567	5.67	3.520	1.544	109.47		5.47	442
BC8	$Ia\bar{3}$	LDA	4.425	5.41	3.684	1.611,1.446	101.22, 116.31	-9.447	3.58	409
		PBE	4.477	5.61	3.556	1.631,1.456	101.37, 116.21	-8.399	3.58	372
BC12	$Ia\bar{3}d$	LDA	5.116	5.58	3.576	1.566	99.59, 131.81	-9.235	2.97	428
		PBE	5.172	5.76	3.461	1.583	99.59, 131.81	-8.205	2.98	393
		Expt. [20]	5.140							
SC24	$Pa\bar{3}$	LDA	5.304	6.22	3.192	1.523,1.525	60, 102.71	-9.169	3.05	323
		PBE	5.368	6.45	3.094	1.539,1.542	60, 102.75	-8.168	2.96	299

bulk modulus (B_0) of BC12 as 428 GPa, which is lower than the value for diamond (452 GPa), but larger than the value for BC8 (409 GPa) and *c*-BN (396 GPa) [34]. The calculated equilibrium structural parameters and bulk modulus for diamond, BC8, BC12, and SC24 carbon at zero pressure are summarized in Table I, compared to available experimental data [20,35].

As listed in Table I, our calculated lattice parameter is 5.116 Å from LDA and 5.172 Å from GGA. Considering LDA tends to underestimate and GGA tends to overestimate the lattice parameter, the actual value should be somewhere in between, which very well matches the experimental value of 5.14 Å found in shock-compressed tetracyanoethylene (TCE) powder [20]. To further establish the presence of BC12 carbon

in the experimental specimen, we plot in Fig. 3(a) the simulated XRD spectrum of graphite, diamond, SC24, BC8, BC12, Rh6, and oC8 [18] carbon, compared to the experimental data [20]. The experimental XRD of shock-compressed TCE powder [see Fig. 3(b)] reveals the superposition of diffraction lines from two major phases: graphite and this new cubic modification of carbon with a unit cell parameter of 5.14 Å. The strongest peak around 26° is consistent with the graphite (002) diffraction. Meanwhile, the peaks at 43° and 50.7° match well with the (211) and (220) spectrum for BC12 carbon, respectively. Here the (220) peak of BC12 maybe overlaps with the (102) peak of graphite. Also, in the original experimental paper, a peak was observed at 73.9°, which may be assigned as the (400) peak of BC12, while the (321) peak of BC12 is missed in the experimental XRD patterns, which may be due to the local disorder in the shock-compressed samples. These results suggest that BC12 carbon is a likely candidate structure for the unidentified carbon phases found in the shock-compressed TCE [20]. Such BC12 carbon framework was also found in silicon dioxide as a Si (24d) network [36].

Meanwhile, some new XRD peaks are found in a different shock-compressed carbon-black/tetracyanoethylene (CB/TCE) powder mixture [see Fig. 3(b)]. The peak at 43.74° is attributed to the diamond (111) diffraction; the peak at 30° may be associated with an all- sp^2 rh6 carbon found in detonation carbon nanoparticles and chimney soot [5,37]. Also, the peaks at 35° and 62.3° may be assigned as the (110) and (311) peaks for a mixed sp^2 - sp^3 oC8 carbon in *cmmm* symmetry [18] found in the graphite-to-diamond phase conversion process. The rh6 and oC8 are less stable than diamond but more stable than SC24, BC12, and BC8 carbon as shown in Fig. 2. The remaining diffraction patterns are likely to have originated from some unknown forms of carbon. Such complicated mixture of a rich variety of carbon structures is commonly found in detonation soot [37].

We also calculated the phonon spectra of BC12 carbon, as presented in Fig. 4. The highest phonon frequency of BC12 carbon is located at the Γ point with a value of $\sim 1150 \text{ cm}^{-1}$, which is lower than $\sim 1350 \text{ cm}^{-1}$ for perfectly sp^3 bonded diamond [38]. Throughout the entire Brillouin

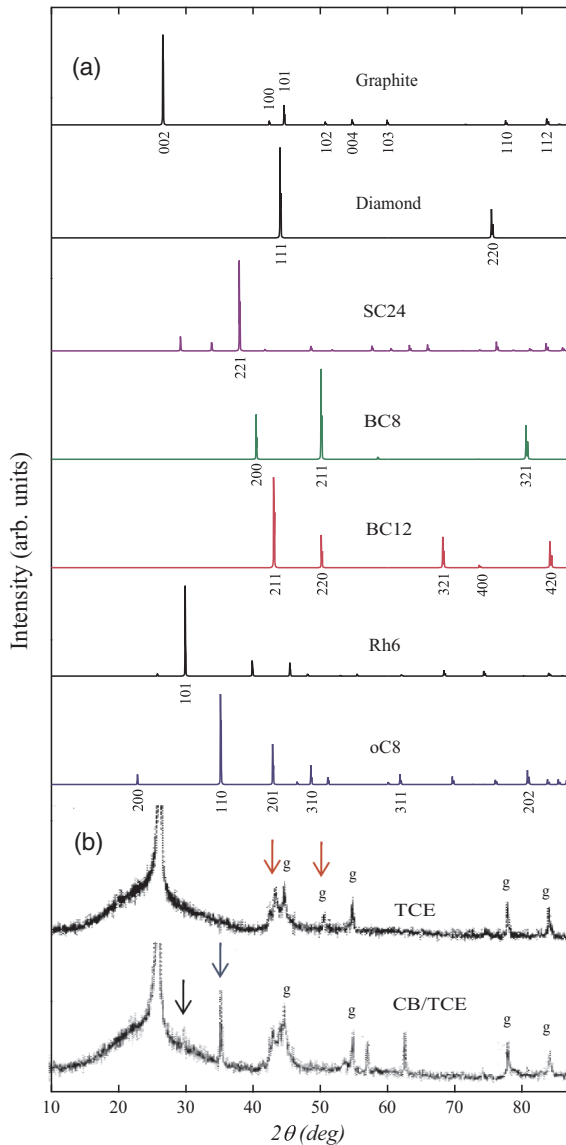


FIG. 3. (Color online) X-ray diffraction (XRD) patterns. (a) Simulated XRD patterns for graphite, diamond, SC24, BC8, BC12, Rh6, and oC8 carbon. (b) Experimental XRD patterns for shock-compressed tetracyanoethylene (TCE) powder and shock-compressed carbon-black/tetracyanoethylene (CB/TCE) powder mixture [20]. X-ray wavelength is 1.5406 Å with a copper source.

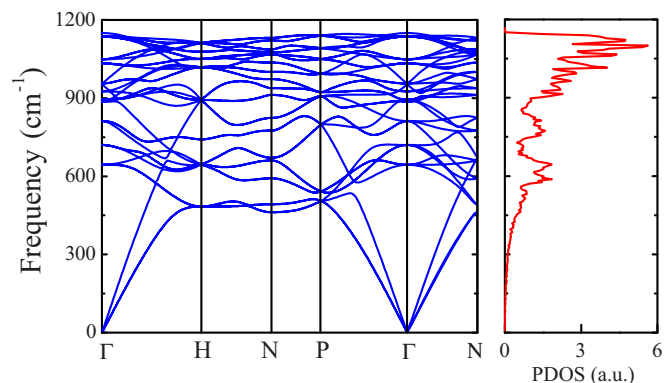


FIG. 4. (Color online) Calculated phonon band structures and phonon density of states (PDOS) for BC12 carbon at zero pressure. The highest vibrational frequency is located at the Γ point with a value of $\sim 1150 \text{ cm}^{-1}$.

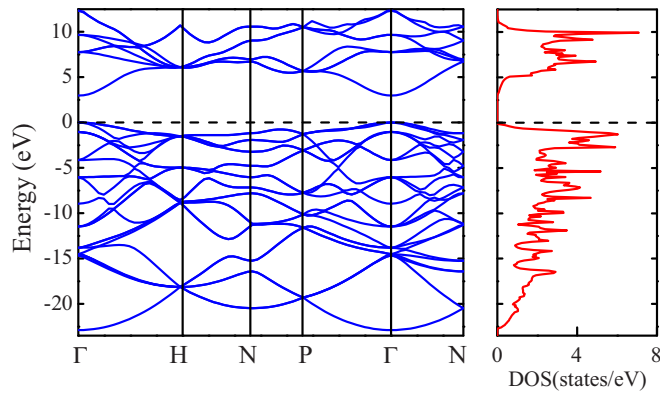


FIG. 5. (Color online) Calculated electronic band structures and density of states (DOS) for BC12 carbon. The valence band maximum and conduction band minimum are at the Γ point with a direct band gap of 2.97 eV.

zone, no imaginary frequencies are observed, confirming the dynamical stability of BC12 carbon.

We finally discuss the electronic properties of BC12 carbon. The band structure and density of states are calculated using the hybrid functionals (HSE06) [30]. The calculated band gap for diamond is about 5.43 eV, which is closed to the experimental data of 5.47 eV [35], suggesting the validity of the HSE06 method in predicting band gaps for diamond and related sp^3 bonded carbon structures. For BC12 carbon, as shown in Fig. 5, the band gap is estimated to be 2.97 eV, which is smaller than the value 5.43 eV for diamond and 3.58 eV for BC8 carbon. Moreover, both the valence band maximum and conduction band minimum are at the Γ point, showing a direct band gap

semiconductor character. These results are essential for further study and application of this new carbon phase.

IV. SUMMARY

In summary, we have identified by means of *ab initio* calculations a new cubic carbon structure in $Ia\bar{3}d$ (O_h^{10}) symmetry comprising fully sp^3 hybridized six-membered rings. The structural stability is verified by phonon mode analysis. Electronic band structure calculations reveal that it is a semiconductor with a direct band gap of about 2.97 eV. Simulated lattice parameter and x-ray diffraction patterns provide an excellent match to the previously unexplained new carbon allotrope found in recent shock-compressed experiments. These results strongly suggest the presence of the BC12 carbon phase, which belongs to the same bonding type as diamond and BC8 carbon with an all- sp^3 six-membered ring configuration. Shock compression only produced a minute amount of BC12 carbon mixed with other carbon phases, and the next challenge is to find a route toward more effective synthesis. Similar challenges have been encountered and overcome in the study of other novel carbon phases, such as nanotubes and fullerenes. The full structural identification and characterization reported in the present work may stimulate further exploration for fundamental understanding and practical application of BC12 carbon.

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