Computational Discovery of A New Rhombohedral Diamond Phase

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Computational discovery of a new rhombohedral diamond phase

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We identify by first-principles calculations a new diamond phase in $R\bar{3}c\ (D_{6h}^6)$ symmetry, which has a 16-atom rhombohedral primitive cell, thus termed R16 carbon. This rhombohedral diamond comprises a characteristic all-$sp^3$ six-membered-ring bonding network, and it is energetically more stable than previously identified diamondlike six-membered-ring bonded BC8 and BC12 carbon phases. A phonon mode analysis verifies the dynamic structural stability of R16 carbon, and electronic band calculations reveal that it is an insulator with a direct band gap of 4.45 eV. Simulated x-ray diffraction patterns provide an excellent match to recently reported distinct diffraction peaks found in milled fullerene soot, suggesting a viable experimental synthesis route. These findings pave the way for further exploration of this new diamond phase and its outstanding properties.

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I. INTRODUCTION

Carbon exhibits extremely versatile bonding abilities that produce a rich variety of crystalline forms with novel properties. There exist three naturally occurring carbon allotropes, namely, graphite, diamond, and amorphous carbon, formed by $sp^2$, $sp^3$, and mixed $sp^2/sp^3$-hybridized chemical bonds [1], respectively. A rich variety of carbon phases also have been synthesized under laboratory conditions, among which graphene [2], carbon nanotubes [3], and fullerenes [4] are among the most notable examples, which have stimulated efforts to search for more carbon phases [5–16]. Recent years have seen the exploration of new carbon phases under extreme conditions, such as high pressure or shock compression, which can induce new bonding modifications. At high-pressure and high-temperature conditions, graphite can convert to cubic diamond or (113) twinned cubic diamond with (111) hexagonal-diamond-like stacking faults [17]. Meanwhile, the discovery of cold-compressed graphite [18] has led to the identification of several new carbon forms [19–27] such as monoclinic $M$-carbon [19], bust-C4 carbon [20], orthorhombic $W$-carbon [21], $O$-carbon [22], and $Z$-carbon [24]. In addition, cubic modifications of carbon have been produced during the heating of carbon soot or shock compression of polycrystalline graphite [28–30], which led to a proposed simple cubic carbon phase termed SC24 in $P\bar{a}3$ symmetry [31]. Very recently, a new cubic modification of carbon denoted as BC12 in $Ia\bar{3}d$ symmetry [32] is proposed to be a likely candidate structure found in the shock-compressed tetracyanoethylene powder [29]. Moreover, carbon crystals share many of the structures adopted by silicon and germanium [33–35], including the denser R8, BT8, BC8, and ST12 carbon. The body-centered-cubic BC8 carbon, adopted by the high-pressure $\gamma$-Si allotrope [36], is suggested to be the high-pressure modification of carbon derived from cubic diamond under a pressure of $\sim 1100$ GPa [37–40]. Among all these carbon structures, only BC8 and BC12carbon comprise entirely diamondlike six-membered ring bonding networks.

In this paper, we identify by first-principles calculations a new carbon phase that comprises entirely diamondlike six-membered rings in $R\bar{3}c\ (D_{6h}^6)$ symmetry. It has a 16-atom rhombohedral primitive cell in an all-$sp^3$ bonding network, thus termed R16 carbon. This rhombohedral diamond phase is identified through a systematic structure search process, and the obtained structure is energetically more stable than the previously predicted and synthesized BC8 and BC12 carbon phases. Its dynamical stability has been verified by phonon mode analysis and molecular dynamics simulations. Electronic band calculations reveal that it is an insulator with a direct band gap of 4.45 eV. The stimulated x-ray diffraction spectrum provides an excellent match to distinct diffraction peaks found in the milled fullerene soot [41]. These findings lay a foundation for further exploration of this new diamond phase.

II. COMPUTATIONAL METHOD

We performed a structure search using a technique based on a Monte Carlo algorithm [42]. The energetics were first screened by highly efficient Tersoff potential calculations [43] and then refined by more accurate first-principles methods. Our search identified R16 carbon in a 16-atom simulation cell. Density functional theory calculations are performed using the Vienna ab initio simulation package (VASP) [44]. Both the local density approximation (LDA) in the form of Ceperley-Alder [45] and generalized gradient approximation (GGA) developed by Perdew, Burke, and Ernzerhof (PBE) [46] are used for the exchange-correlation potential. The all-electron projector augmented-wave (PAW) [47] method is adopted...
with equilibrium lattice parameters $a = 4.492$ Å and $\alpha = 90.87^\circ$. There are two inequivalent crystallographic sites, occupying the 4$c$ (0.4049, 0.4049, 0.4049) and 12$f$ (0.5929, 0.0558, 0.8809) positions, denoted by $C_1$ (black) and $C_2$ (red), respectively. (b) Structure of R16 carbon viewed along the [111] direction. (c), (d) Polyhedral views of BC8 carbon. (e), (f) Polyhedral views of the crystal structure of supercubane [38].

FIG. 1. (a) The primitive rhombohedral crystalline structure of R16 carbon in $R\bar{3}c$ ($D^{6}_d$) symmetry with the lattice parameters $a = 4.492$ Å and $\alpha = 90.87^\circ$. There are two inequivalent crystallographic sites, occupying the 4$c$ (0.4049, 0.4049, 0.4049) and 12$f$ (0.5929, 0.0558, 0.8809) positions, denoted by $C_1$ (black) and $C_2$ (red), respectively. (b) Structure of R16 carbon viewed along the [111] direction. (c), (d) Polyhedral views of BC8 carbon. (e), (f) Polyhedral views of the crystal structure of supercubane [38].

with $2\alpha^2 2p^2$ treated as valence electrons. Wave functions of the valence electrons are expanded in plane waves up to a kinetic energy cutoff of 800 eV and the Brillouin zone (BZ) is sampled with a $9 \times 9 \times 9$ Monkhorst-Pack special $k$-point grid including the $\Gamma$ point. 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 $10^{-6}$ eV. Electronic band structures are calculated using the Heyd-Scuseria-Ernzerhof hybrid functional (HSE06) [48]. Phonon calculations are performed using the PHONOPY package [49].

III. RESULTS AND DISCUSSION

We first present the structural characterization of R16 carbon, which is in $R\bar{3}c$ ($D^{6}_d$) symmetry, as shown in Fig. 1(a). It has a 16-atom rhombohedral primitive unit cell with equilibrium lattice parameters $a = 4.492$ Å and $\alpha = 90.87^\circ$, occupying the 4$c$ (0.4049, 0.4049, 0.4049) and 12$f$ (0.5929, 0.0558, 0.8809) Wyckoff positions, denoted by $C_1$ and $C_2$, respectively. When viewed along the [111] direction, two $C_1$ atoms (black) and six $C_2$ atoms (red) take the same positions as in BC8 carbon, while the other six $C_2$ atoms (blue) rotate relative to their positions in BC8 carbon [see Figs. 1(b) and 1(d)]. In the hexagonal representation, R16 carbon has a 48-atom hexagonal unit cell with the lattice parameters $a = 6.401$ Å and $c = 7.661$ Å occupying the 12$c$ (0.6667, 0.3333, 0.9284) and 36$f$ (0.7497, 0.9623, 0.8432) positions, respectively. This new phase has an all-$sp^3$ bonding network consisting of six-membered rings, which are characteristic of the diamond structure. However, in contrast to the uniform bond length of 1.544 Å in diamond, R16 carbon contains four distinct bond lengths, 1.457, 1.488, 1.569, and 1.748 Å, and it also has varying bond angles ranging from 100.13$^\circ$ to 120.68$^\circ$. These structural arrangements are different from those in BC8 carbon that contain two distinct bond angles of 101.22$^\circ$ and 116.31$^\circ$ and two distinct bond lengths of 1.446 and 1.611 Å [32]. Note that although R16 and BC8 have similar crystalline structures, they hardly convert to each other due to the relatively large kinetic barrier; meanwhile, our kinetic calculations show that R16 carbon can be easily transformed from supercubane [see Figs. 1(e) and 1(f)] via local bond rotation (see Fig. S1 in the Supplemental Material [50]). The nanocrystals of supercubane have been synthesized from amorphous carbon films by using a pulsed-laser-induced liquid-solid interface reaction (PLIIIR) [51].

Figure 2 presents the total energy as a function of volume per atom for R16 carbon in comparison with graphite, diamond, bct-C4, BC8, supercubane, and BC12 carbon. The dashed line indicates the energy level of the linear carbyne chain.

![Figure 2](https://example.com/figure2.png)
fit [52] of the total energy curves, we obtain the bulk modulus ($B_0$) of R16 as 351 GPa, which is smaller than the value of diamond (452 GPa), BC8 (409 GPa), and BC12 (428 GPa), consistent with its lower density. The calculated equilibrium structural parameters, total energy, and bulk modulus for graphite, diamond, BC8, BC12, R16, bct-C4, and supercubane are listed in Table I, compared to available experimental data [29,53,54].

For comparison, we have also calculated the total energy for Si phases. It is shown that R16 silicon is less stable than the diamond phase, showing as a dense form of Fd̄3m [29,53,54]. Among these structures, however, diamondlike carbon allotropes in all-hybridized bonds registered to the Samara Carbon Allotrope Database (SACADA) [55,56]. These structures, however, diamondlike carbon allotropes in all-sp$^3$ six-membered ring network are rarely reported. In fact, R16 carbon is only the fourth such structure, along with cubic diamond, BC8, and BC12 carbon, which all of which are metastable carbon phases that have been experimentally synthesized. While R16 carbon is about 0.5 eV per atom less stable than cubic diamond, it is more stable than the BC8 and BC12 carbon phases. It is therefore feasible to synthesize R16 carbon under laboratory conditions that produced both the more stable cubic diamond and the less stable BC8 and BC12 carbon phases. Recently, T-carbon has been produced from pseudopotopatic conversion of a multiwalled carbon nanotube suspension in methanol by picosecond pulsed-laser irradiation [57], despite its rather high energy of about 1.2 eV per atom above that of graphite and diamond [12].

To further characterize R16 carbon and make a connection to its experimental synthesis, we have simulated its x-ray diffraction (XRD) spectra as well as those for graphite, diamond, BC8, and BC12 carbon and compared the results with recent experimental XRD data of morphed graphene nanostructures obtained from mild fullerene soot [41]. Results in Fig. 3 show that the XRD of R16 carbon produces a more complicated pattern than those of similarly bonded diamond, BC8, and BC12, reflecting its structural complexity stemming from its multiple bond lengths and angles as discussed above. The experimental XRD diffraction data contain peaks arising from unreacted and amorphized graphite and other unidentified carbon phases [41]. The broad peak on the lower-angle side is attributed to the dominant crystalline graphite (002) diffraction around 26° and the contribution from the amorphized graphite structure. The peaks at 40° and 44.7° match well with the main (202) and (211) peaks in the R16 carbon spectra, respectively. The peak around 49.3° may be assigned to the weaker and closely spaced (300) and (104) peaks of R16. This good match between the simulated and measured XRD peaks makes a strong case for assigning R16 carbon as the experimentally observed new carbon phase. Experimental advances in phase purification should further improve the XRD matching, and provide a viable route for sample synthesis of better quality and quantity.

To assess the mechanical stability of R16 carbon, we have calculated its elastic constants $C_{11}$, $C_{33}$, $C_{44}$, $C_{12}$, and $C_{13}$, and obtained the values 970, 901, 499, 41, and 110 GPa, respectively. These results satisfy the mechanical stability criteria $C_{44} > 0$, $C_{11} > |C_{12}|$, and $(C_{11} + 2C_{12})C_{13} > 2C_{44}^2$ for the hexagonal structure [58]. To examine the thermal stability, we have also performed $ab$ initio molecular dynamics (AIMD) simulations with the canonical (NVT) ensemble at temperatures of 1000, 1500, 2000, and 2500 K, by the

<table>
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<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
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<th>$V_0$ (Å³)</th>
<th>$\rho$ (g/cm³)</th>
<th>$d_{CC}$ (Å)</th>
<th>$E_{tot}$ (eV)</th>
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Nosé thermostat [59] with a step of 1 fs. The systems are modeled by a $2 \times 2 \times 2$ supercell with 128 carbon atoms. The energy fluctuations at 2000 K are presented in Fig. 4. The structures around steps 1000 and 4000 are also given in Fig. 4. It is seen that after heating up to 2000 K for 5 ps, no structural changes occur. Some carbon atoms deviate from the equilibrium positions appreciably with some bond breaking, but they can be relaxed back to the R16 structure. Therefore, R16 carbon has robust thermal stability well around room temperature.

We further examined the dynamic stability of R16 carbon by calculating the phonon dispersion curves [see Fig. 5(a)]. The highest phonon frequency of R16 is about 1400 cm$^{-1}$, which is higher than $\sim$1370 cm$^{-1}$ for BC8 carbon, $\sim$1150 cm$^{-1}$ for BC12 carbon, and $\sim$1350 cm$^{-1}$ for perfectly $sp^3$ bonded diamond [60]. Throughout the entire Brillouin zone, no imaginary frequencies are observed, confirming the dynamic stability of R16 carbon.

We also have calculated the electronic band structure and density of states of R16 carbon using the hybrid functionals (HSE06) [48]. The obtained band gap for R16 carbon is 4.45 eV [see Fig. 5(b)], which is smaller than 5.43 eV for diamond, but larger than the calculated value of 3.58 eV for BC8 carbon and 2.97 eV for BC12 carbon. The valence band top and the conduction band bottom are both located at the $\Gamma$ point, showing a direct insulator behavior, which is the same as that of BC8 carbon at the $H$ point [38]. These results provide essential information for further experiments and applications of this new carbon allotrope.
IV. SUMMARY

In summary, our first-principles calculations combined with an XRD spectra analysis have identified a new rhombohedral diamond in $R\bar{3}c$ ($D_{3d}^6$) symmetry with an all-$sp^3$ six-membered-ring bonding network. This new diamond phase is energetically more stable than previously known diamondlike BC8 and BC12 carbon phases, and is mechanically and dynamically stable as well. Electronic band structure calculations reveal that it is an insulator with a direct band gap of 4.45 eV. Its simulated XRD patterns match well with the measured XRD data of a recently reported unidentified carbon phase found in milled fullerene soot [41]. These findings establish a computational discovery of a new rhombohedral diamond, which expands our understanding of the prominent class of diamondlike materials. The metastability of R16 carbon inside the energy range set by previously identified and synthesized cubic diamond, BC8, and BC12 carbon not only makes the synthesis of R16 carbon feasible but, more importantly, also offers new insights for understanding the formation and coexistence of multiple diamond phases synthesized in laboratory [17].

ACKNOWLEDGMENTS

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In the crystal structure search and prediction procedure used in the present study, we first prepare a random configuration of carbon atoms in a specific unit cell and determine the energy of the structure using Tersoff potential calculations \[43\]. The ensuing structural relaxation is carried out by a Monte Carlo (MC) method. The displacement of carbon atoms at each MC step is set to 0.01 Å at the initial steps and 0.0001 Å at the final steps. The lowest-energy structures from the initial screening process are then refined by further first-principles calculations based on density functional theory as implemented in the VASP code. Our search is performed using simulation cells containing eight to 32 atoms. This targeted search resulted in the identification of \( \text{R16} \) carbon in the 16-atom cell. Our search also found many widely known carbon structures, including cubic diamond, hexagonal diamond, supercubane, bct-C4, BC8 carbon, R6h carbon, BC12 carbon, as well as many other more complicated lower-symmetry structures, which are not of direct interest to the present work and are, therefore, omitted.

\[50\] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.98.094107 for the pathways from BC8 toward R16 and graphite [Figs. S1(a) and S1(b)], pathway from supercubane toward R16 [Fig. S1(c)], pathways from R16 toward graphite and bct-C4 [Figs. S1(d) and S1(e)], the relative energy changes versus pathways [Figs. S1(f) and S1(g)], the enthalpy per atom for R16 carbon as a function of pressure compared to BC8 carbon [Fig. S1(h)], and the calculated total energy for Si phases (Fig. S2).
\[52\] F. D. Murnaghan, Proc. Natl. Acad. Sci. USA 30, 244 (1944).