Four superhard carbon allotropes: a first-principles study

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Using a generalized genetic algorithm, we propose four new sp³ carbon allotropes of 5-6-7 (5-6-7-type Z-ACA and Z-CACB) or 4-6-8 (4-6-8-type Z4-A3B1 and A4-A3B2) carbon rings. Their stability, mechanical and electronic properties are systematically studied using a first-principles method. We find that the four new carbon allotropes show amazing stability in comparison with the carbon phases proposed recently. Both 5-6-7-type Z-ACA and Z-CACB are direct band-gap semiconductors with band gaps of 2.261 eV and 4.196 eV, respectively. However, the 4-6-8-type Z4-A3B1 and A4-A3B2 are indirect band-gap semiconductors with band gaps of 3.105 eV and 3.271 eV, respectively. Their mechanical properties reveal that all the four carbon allotropes proposed in present work are superhard materials, which are comparable to diamond.

1 Introduction

Carbon is considered to be the most active element in the periodic table due to its broad sp, sp² and sp³ hybridizing ability. Besides the four best known carbon allotropes—graphite, cubic diamond (C-diamond), hexagonal diamond (H-diamond) and amorphous carbon—an unknown superhard phase of carbon has been reported experimentally along with a structural phase transition in cold compressing graphite. Several structures have been proposed theoretically as being a candidate for this superhard phase, such as the monoclinic M-carbon, cubic body center C4 carbon (bct-C4) and the orthorhombic W-carbon. Although the monoclinic form, named M-carbon, has been preliminarily identified by an experimental process that compresses graphite, bct-C4 and orthorhombic W-carbon also fit the experimental XRD data to some extent. These discoveries attract great interest in theoretical prediction and experimental research on such superhard carbon allotropes. Very recently, another new carbon allotrope, named Z-carbon, was proposed and investigated simultaneously by three independent research groups (this structure was also named cC16H1 in ref. 8 and Cco-C8 in ref. 10). Z-carbon is more stable (its cohesive energy is about 129 meV per atom more than diamond) and harder than bct-C4, M-carbon and W-carbon. Moreover, its transition pressure is around 10 Gpa, which is lower than those of bct-C4, M-carbon and W-carbon. Thus, it is believed that cold compressing graphite would preferentially result in the formation of Z-carbon. Although none of the above allotropes solely fit the experimental results satisfactorily, these theoretically proposed intermediate phases are significant for the understanding of the experimental process of cold compressing graphite and the cold compressing of carbon nanotubes. Moreover, these theoretical studies also arouse great interest in superhard carbon materials and analogous superhard BN phases.

All of the above new carbon phases can be designed using the recently developed particle-swarm optimization method, graph theoretical methods and the evolutionary algorithm USPEX, which was developed by Oganov. All of them can be divided into two groups: the 5-6-7-type (M-carbon and W-carbon containing 5-, 6- and 7-carbon rings) and the 4-6-8-type (bct-C4 and Z-carbon containing 4-, 6- and 8-carbon rings). We notice that, from the point of view of the structure, they all can be constructed through mutating H-diamonds or combing the segments of H-diamond and C-diamond. H-diamond and C-diamond are the most favorable sp³ carbon allotropes in nature and can be used as excellent starting materials for the development of new carbon allotropes through the hybridization of their stable segments. For example, bct-C4 and Z-carbon can be looked upon as the hybridization of H-diamond and mutated H-diamond. M-carbon and W-carbon can be taken as the hybridization of distorted H-diamond and C-diamond segments. The 4H, 6H and 12R carbon allotropes can be regarded as the superlattice of C-diamond (along the [111] direction) and H-diamond (along the [001] direction). By hybridizing C-diamond and H-diamond in different manners, almost all previously proposed carbon structures can be obtained. Such a structural construction process is compatible with the essence of the genetic algorithm (GA). The genetic algorithm is widely used in the search for zero-dimensional (0D) element clusters, such as carbon fullerenes. Moreover, it is an effective method
for the prediction of three-dimensional (3D) superhard carbon phases. In this paper, using a generalized GA, we chose H-diamond and C-diamond as the starting materials to hybridize new carbon allotropes. Four new carbon allotropes with 5-6-7 (Z-ACA and Z-CACB) or 4-6-8 (Z4-A3B1 and A4-A3B2) carbon rings are proposed in our present work and their stability, electronic and mechanical properties are systematically studied using first-principles calculations based on density functional theory. All the four carbon allotropes in our present work are more favorable than bct-C4. Our results indicate that all of them are superhard insulators with direct or indirect band gaps. Because the four new allotropes are more stable than graphite under certain pressures, all of them are expected to be obtained from cold compressing graphite.

2 Models and methods

2.1 Models

To compare with previously proposed carbon allotropes, we restrict the atoms to a primitive unit cell no larger than 16 carbon atoms. The primitive cells and the side and top views of Z-carbon, Z4-A3B1, A4-A3B2, Z-ACA and Z-CACB are shown in Fig. 1. Here Z and A denote that the framework of the systems are constructed with zigzag and armchair carbon chains along the [100] direction, respectively. From the side view, we can see that Z-carbon (Z4-A3B2) as shown in Fig. 1(a) is composed of two A segments derived from H-diamond and two B segments derived from mutated H-diamond (the mutation is a c/2 translation along the [001] orientation). At the AA-BB interface, a series of 4 and 8 carbon rings appear. According to such denomination, previously proposed bct-C4 is Z2-A3B1 (Z4-A3B1-A3B1) due to the fact that there is one A segment and one B segment in its crystal cell. Z4-A3B1, as shown in Fig. 1(b), is hybridized by a triple A segment derived from H-diamond and one B segment derived from mutated H-diamond. The primitive cell of A4-A3B2 contains 16 carbon atoms and its crystal cell contains one double A segment and one double B segment of H-diamond, as shown in Fig. 1(c). Z3-systems are restricted according to their topological requirement. Systems of A3-, A4-A3B1, Zn- and An- (where n is larger than 4) containing more than 16 atoms in their primitive cells are not included in the present work. The A2-A3B1 and A4-A3B1-A3B1 systems are energetically unstable in comparison to bct-C4. In Fig. 1(d) and (e), we show the outcome of hybridizing H-diamond and C-diamond in the zigzag direction with 5-7 carbon rings at the C/A or C/B interface. The system obtained by hybridizing H-diamond and C-diamond in the armchair direction is unstable because it contains carbon atoms deflecting the stable four-bonds configuration. In fact, by hybridizing H-diamond and C-diamond segments, many new allotropes can also be constructed. In the present work, two low energy allotropes, named Z-ACA and Z-CACB containing 16 and 12 atoms in their primitive cell, respectively, are taken as examples. Here, A, B and C denote the H-diamond, mutated H-diamond and C-diamond segments, respectively.

2.2 Methods

To investigate the stability, electronic and mechanical properties of these new carbon allotropes, first-principles calculations based on density functional theory were employed. All calculations were performed within the general gradient approximation (GGA) as implemented in the Vienna ab initio simulation package (VASP). The interactions between the nucleus and the 2s2p2 valence electrons of carbon were described by the projector augmented wave (PAW) method. A plane-wave basis with a cutoff energy of 500 eV was used to expand the wave functions. The Brillouin Zone (BZ) sample meshes were set to be dense enough (less than 0.21 Å−1) to ensure the accuracy of our calculations. Crystal lattices and atom positions of graphite, diamond, bct-C4, M-carbon, W-carbon, Z-carbon, Z4-A3B1, A4-A3B2, Z-ACA and Z-CACB were fully optimized up to the residual force on every atom less than 0.005 eV Å−1 through the conjugate-gradient algorithm. Vibration properties were calculated using the phonon package with the forces calculated from VASP. To evaluate the transition pressure from graphite to the superhard phase, the exchange–correlation functional was described by LDA as it was considered that LDA can give reasonable interlayer distances and mechanical properties of graphite sheets due to the delicate error cancellation of the exchange and correlation interactions in comparison with that of the semi-local generalized gradient approximation (GGA).

3 Results and discussion

3.1 Structures

Similar to bct-C4 and Z-carbon, Z4-A3B1 and A4-A3B2 belong to the 4-6-8-type. The crystal structure of Z4-A3B1 belongs to the Pnaa space group. At zero pressure, its equilibrium lattice constants calculated from GGA are a = 8.762 Å, b = 4.263 Å
and $c = 2.514 \text{ Å}$. Four inequivalent atoms (16 atoms per primitive cell) in its unit cell occupy positions at (0.041, 0.312, 0.5), (0.208, 0.185, 0.5), (0.285, 0.316, 1.0) and (0.464, 0.318, 1.0). A4-A3B2 belongs to the $Cmca$ space group and its equilibrium lattice constants obtained from GGA are $a = 4.257 \text{ Å}$, $b = 10.114 \text{ Å}$ and $c = 4.363 \text{ Å}$. There are only two inequivalent atoms (16 atoms per primitive cell) in A4-A3B2, which are located at the positions of (0.317, 0.067, 0.088) and (0.314, 0.188, 0.584). Recently proposed Z-carbon holds $Cmnn$ symmetry with equilibrium lattice parameters of $a = 8.772 \text{ Å}$, $b = 4.256 \text{ Å}$ and $c = 2.514 \text{ Å}$. There are only two inequivalent atoms in the Z-carbon unit cell located at $0.089, 0.316, 0.5$ and $(0.167, 0.185, 1.0)$. Z-ACA and Z-CACB belong to the 5-6-7-type, similar to M-carbon and W-carbon containing 5-, 6- and 7-carbon rings. Z-ACA belongs to the $Pmnn$ space group and contains five inequivalent atoms (16 atoms per primitive cell) in its orthorhombic lattice with constants of $a = 4.760 \text{ Å}$, $b = 2.521 \text{ Å}$ and $c = 7.930 \text{ Å}$. The five inequivalent atom positions are listed in Table 1. Z-CACB, with an orthorhombic lattice $(a = 4.876 \text{ Å}, b = 2.529 \text{ Å}, c = 11.535 \text{ Å})$, belongs to the $Imma$ space group containing only 12 carbon atoms per primitive cell with four inequivalent atoms located at $(0.500, 0.750, 0.542), (0.237, 0.750, 0.618), (0.177, 0.250, 0.691)$ and $(0.500, 0.750, 0.965)$. The structural information of Z-carbon, Z4-A3B1, A4-A3B2, Z-ACA and Z-CACB derived from the GGA calculations is listed in Table 1. All these new carbon allotropes can be constructed by hybridizing C-diamond and H-diamond as depicted in Fig. 1(a)-(e). Moreover, similar to the previously proposed bct-C4, Z-carbon, M-carbon and W-carbon, all of them can be considered as potential products in the process of cold compressing graphite.

### 3.2 Stability

The relative stability of diamond, bct-C4, M-carbon, W-carbon, Z-carbon, Z4-A3B1, A4-A3B2, Z-ACA and Z-CACB was evaluated through a comparison of their cohesive energies per atom. All these new allotropes are more energetically stable than bct-C4. At zero pressure, the cohesive energy of Z-ACA is about 30 meV lower than bct-C4 and only 5 meV higher than that of M-carbon. Z-CACB is more favorable than both M-carbon and W-carbon. Its cohesive energy is $-7.556 \text{ eV per atom}$, which is about 17 meV lower than that of W-carbon ($-7.539 \text{ eV per atom}$) and 8 meV larger than that of Z-carbon ($7.564 \text{ eV per atom}$). The two most stable allotropes are Z4-A3B1 and A4-A3B2 and their cohesive energies are $-7.568 \text{ eV}$ and $-7.565 \text{ eV per atom}$, respectively. Both of them are more stable than Z-carbon and they are the most stable new carbon phases theoretically predicted so far. The enthalpies per atom for diamond, H-diamond, bct-C4, M-carbon, W-carbon, Z-carbon, Z4-A3B1, A4-A3B2, Z-ACA and Z-CACB as a function of pressure relative to graphite and derived from the LDA calculations are shown in Fig. 2. The results indicate that Z-ACA is more stable than M-carbon under external pressure and becomes more stable than W-carbon when the pressure is above 35 GPa. The transition pressures for M-carbon, W-carbon and Z-ACA are very close to each other (located at around $12.1 \pm 1.3 \text{ GPa}$). Z-CACB is always more favorable than bct-C4, M-carbon, W-carbon and Z-ACA and is more stable than graphite when the external pressure is larger than 10 GPa. Z-carbon, Z4-A3B1 and A4-A3B2 have almost the same relative stabilities and transition pressures.

Table 1  The GGA calculated structural information for Z-carbon, Z4-A3B1, A4-A3B2, Z-ACA and Z-CACB at 0 GPa

<table>
<thead>
<tr>
<th>System</th>
<th>Space group and cell</th>
<th>Inequivalent atoms position</th>
<th>Ring type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-carbon</td>
<td>$Cmnn$ (No. 65)</td>
<td>(0.089, 0.316, 0.500)</td>
<td>4-6-8</td>
</tr>
<tr>
<td>Z-A3B1</td>
<td>$Pmnn$ (No. 59)</td>
<td>(0.041, 0.312, 0.500)</td>
<td>4-6-8</td>
</tr>
<tr>
<td>A4-A3B2</td>
<td>$Cmca$ (No. 64)</td>
<td>(0.317, 0.067, 0.088)</td>
<td>4-6-8</td>
</tr>
<tr>
<td>Z-ACA</td>
<td>$Pmnn$ (No. 59)</td>
<td>(0.090, 0.500, -0.069)</td>
<td>5-6-7</td>
</tr>
<tr>
<td>Z-CACB</td>
<td>$Imma$ (No. 74)</td>
<td>(0.500, 0.750, 0.542)</td>
<td>5-6-7</td>
</tr>
</tbody>
</table>

![Fig. 2](image_url)  
Fig. 2  Enthalpy per atom for C-diamond, H-diamond, bct-C4, M-carbon, W-carbon, Z-carbon, Z4-A3B1, carbon, A4-A3B2, Z-ACA and Z-CACB as a function of pressure relative to graphite derived from the LDA calculations.
They are more stable than graphite when the external pressure is larger than 9.16 GPa. To further confirm the dynamic stability of Z4-A,B1, A4-A,B2, Z-ACA and Z-CACB, their phonon band structures and phonon density of states were calculated. The phonon band structures and phonon density of states at zero pressure are shown in Fig. 3. There is no negative frequency for all of the four new carbon allotropes up to 40 GPa, confirming that these allotropes are dynamic stable phases of carbon.

3.3 Mechanical and electronic properties

The mass density, band gaps, cohesive energies, bulk moduli and hardness values of diamond, bct-C4, M-carbon, W-carbon, Z-carbon, Z4-A,B1, A4-A,B2, Z-ACA and Z-CACB are summarized in Table 2. The results indicate that all the above carbon allotropes are superhard intermediate phases between graphite and diamond due to their considerable bulk moduli and hardness values. The bulk modulus (B0) was obtained by fitting the total energy as a function of the volume to the third-order Birch–Murnaghan equation of state. Further hardness evaluation was considered according to the recently introduced empirical scheme,13 which correlates the Vickers hardness to the bulk modulus (B0) and shear modulus (G) through the formula:

\[ H_v = 2(G/B_0)^{3/5} - 3. \]

From Table 2 we can see that Z-carbon, Z4-A,B1 and A4-A,B2 have almost the same stabilities, band gaps, mass densities, bulk moduli and hardness. The values of the bulk modulus are 415.83 Gpa, 415.49 Gpa and 413.62 Gpa for Z-carbon, Z4-A,B1 and A4-A,B2, respectively. The values of the Vickers hardness are 81.09 Gpa, 80.54 Gpa and 83.18 Gpa for Z-carbon, Z4-A,B1 and A4-A,B2, respectively, which are comparable to that of diamond (88.51 Gpa). M-carbon, W-carbon, Z-ACA and Z-CACB have similar stabilities, densities, bulk moduli and Vickers hardness. Their calculated values of Vickers hardness (79.24 Gpa, 79.08 Gpa, 78.74 Gpa and 82.01 Gpa, respectively) are also comparable to that of diamond. The results indicate that the four new carbon allotropes proposed in present work are superhard materials comparable to diamond.

The electronic properties of diamond, bct-C4, M-carbon, W-carbon, Z-carbon, Z4-A,B1, A4-A,B2, Z-ACA and Z-CACB were investigated and the band structures of Z4-A,B1, A4-A,B2, Z-ACA and Z-CACB are shown in Fig. 4. The results indicate that all these superhard carbon allotropes are indirect wide-band-gap semiconductors, except for Z-ACA and Z-CACB. From the results of Fig. 4, we can see that Z4-A,B1 is an indirect wide-band-gap semiconductor and its band gap (3.105 eV) is larger than that of bct-C4 (2.491 eV) and close to that of Z-carbon (3.273 eV). A4-A,B2 is also an indirect band-gap semiconductor and its band gap (3.271 eV) is close to those of Z-carbon and Z4-A,B1. In contrast to diamond, bct-C4, M-carbon, W-carbon, Z-carbon, Z4-A,B1 and A4-A,B2, both Z-ACA and Z-CACB are direct band-gap semiconductors with gaps of 2.261 eV and 4.196 eV, respectively. The wide band gaps of all these four new carbon allotropes indicate that all of them are transparent carbon phases.

4 Conclusion

In summary, using a generalized genetic algorithm, we proposed four new carbon allotropes. The stability, electronic and mechanical
properties of the four new carbon allotropes are investigated using a first-principles method. The dynamic stability of all these new carbon phases is confirmed from the phonon band calculations. Under proper external pressure, these four new allotropes of carbon are expected to be obtained from cold compressing graphite. Z4-A1B1 and A4-A2B2 are the most stable new carbon phases theoretically predicted so far. All these four new carbon allotropes are transparent superhard carbon phases with bulk moduli and hardness values comparable to that of diamond.

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