C_{20} - T carbon: a novel superhard sp³ carbon allotrope with large cavities

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C$_{20}$ – T carbon: a novel superhard $sp^3$ carbon allotrope with large cavities

Jia-Qi Wang$^1$, Chun-Xiang Zhao$^1$, Chun-Yao Niu$^1$, Qiang Sun$^1$ and Yu Jia$^{1,2}$

1. Introduction

Carbon is one of the most fascinating elements in the periodic table. It exists in many forms across dimensions that possess a wide range of properties with vast applications in many areas of science and technology, due to its ability to form $sp$, $sp^2$, and $sp^3$ hybridized chemical bonds. Carbon can also bind itself with other elements to generate innumerable organic compounds with chemical and biological diversity, giving us a colorful world. As we all know, there exist three carbon allotropes in natural materials, graphite, diamond, and amorphous carbon, containing the $sp^2$, $sp^3$, and mixed $sp^2/sp^3$ hybridized carbon atoms [1], respectively. So far, many new carbon allotropes have been theoretically predicted and experimentally synthesized, and exhibit intriguing properties. Among them, the zero-dimensional (0D) fullerenes [2], one-dimensional (1D) carbon nanotubes [3], and two-dimensional (2D) graphene [4] are the three most typical examples. It is worth noting that some three-dimensional (3D) metallic carbon allotropes with fascinating properties have also been predicted, for example, T6 carbon [5], $K_6$ carbon [6], $Tri – C_9$ [7], and $H_{18}$ carbon [8], and several others. These prototypical examples have significant impacts in material and information sciences, and have attracted considerable experimental and theoretical attention focusing on carbon allotropes [9–25].

In the field of synthesizing and predicting new carbon allotropes, superhard carbon allotropes have attracted special attention from researchers. Superhard materials are of particular importance in industrial applications, such as cutting, polishing, and drilling tools, and surface-protecting coatings, due to their superior mechanical properties [26–28]. Over recent decades, extensive experimental and theoretical efforts have been devoted to discovering new superhard carbon allotropes. Recently, some superhard carbon allotropes, e.g. the monoclinic M-carbon [29], bct-C$_4$ carbon [30], W-carbon [31], O-carbon [32], and Z-carbon [33] have been proposed, simulating a high-pressure phase with hardness even higher than diamond, which are obtained by compressing graphite with a very high pressure [34]. Besides, the solid C$_{20}$, Amm2-carbon, Imma-carbon, C2/m-carbon, C48 carbon, etc have...
Interestingly, the indirect band gap of 5.44 eV. Assuredly, these results could be validated using the GGA developed by Perdew, Burke, and Ernzerhof (PBE) as implemented in the Vienna \textit{ab initio} simulation package (VASP). The all-electron projector augmented wave (PAW) method is adopted with 2s2p3 treated as valence electrons. A plane-wave basis set with an energy cutoff of 800 eV is used and gives well converged total energies. The Brillouin zone (BZ) is sampled with a 15×15×15 Monkhorst-Pack (MP) special k-point grid including Γ-point. The geometries are optimized with no symmetry constraints. The convergence criteria employed, for both electronic self-consistent relaxation and ionic relaxation, are set to 10^{-7} eV and 10^{-3} eV Å^{-1} for energy and force, respectively. Phonon dispersion curves are calculated using the package phonopy \cite{52, 53} with the forces calculated from VASP. The first-principles molecular dynamics simulations are performed in the canonical (NVT) ensemble with the Nosé thermostat with a time step of 1 fs at 1500 K and lasting for 6 ps. The x-ray diffraction is simulated using the Cambridge Sequential Total Energy Package (CASTEP). All the calculations in this work are performed at zero pressure.

2. Computational method

The calculations are carried out using density functional theory within both the local density approximation (LDA) in the form of Ceperley–Alder and the generalized gradient approximation (GGA) developed by Perdew, Burke, and Alder \cite{46} and the generalized gradient approximation (GGA) developed by Perdew, Burke, and Alder. This new carbon allotrope is structurally analogous to c-BN \cite{45}. The calculated ideal density of 3.298 g cm$^{-3}$ is even higher than that of c-BN \cite{45}. The calculated ideal density of 3.298 g cm$^{-3}$ is even higher than that of c-BN \cite{45}. These results broaden our understanding of superhard carbon allotropes, promoting the development of superhard materials.

Here, a new superhard cubic carbon allotrope with full sp$^3$ bonding network is predicted using first-principles calculations. The structure of this new carbon allotrope has a cubic $T$ symmetry with space group No.198 (P2$_13$) and its primitive unit cell contains twenty atoms (thus termed C$_{20}$–T carbon hereafter). This new carbon phase is structurally analogous to Si$_{20}$–T \cite{44}. C$_{20}$–T carbon has a smaller atom density of 3.298 g cm$^{-3}$ compared to 3.501 g cm$^{-3}$ of diamond. Interestingly, C$_{20}$–T carbon has a large cavity with a diameter of approximately 3 Å in its structure. Its structural stability is verified by analyses of total energy, phonon mode, elastic constants and molecular dynamic simulations. The calculated bulk modulus and shear modulus show that C$_{20}$–T carbon is a highly brittle material. In addition, we found that C$_{20}$–T carbon has a high Vickers hardness value of 72.76 GPa, which is even higher than that of c-BN \cite{45}. The calculated ideal density of 3.298 g cm$^{-3}$ is even higher than that of c-BN \cite{45}. These results broaden our understanding of superhard carbon allotropes, and attract more attention in this field.

3. Results and discussion

We first characterize the structural properties of this new carbon allotrope. The C$_{20}$–T carbon is a 3D all sp$^3$ hybridized bonding network with a 20-atom cubic primitive cell as shown in figure 1. It has the cubic T symmetry with space group No. 198 (P2$_13$). The equilibrium lattice parameter of C$_{20}$–T carbon is 4.945 Å at zero pressure. The C$_{20}$–T carbon has three chemically nonequivalent atomic Wyckoff positions: 12h(0.4274, 0.7301, 0.8103), 4a(0.2694, 0.2307, 0.7694) and 4a(0.0894, 0.4106, 0.5894), which are indicated by C$_1$, C$_2$ and C$_3$ respectively. In C$_{20}$–T carbon, the bond lengths between C$_1$–C$_4$, C$_2$–C$_3$, C$_1$–C$_2$ and C$_1$–C$_3$ atoms are 1.541 Å, 1.541 Å, 1.548 Å and 1.550 Å, respectively. The average bond length is quite similar to that of diamond. There exists a large cavity with a diameter of about 3 Å inside the C$_{20}$–T carbon structure, implying that this new carbon phase may have great potential in hydrogen storage.

Figure 1. Schematic depiction of the structure of C$_{20}$–T carbon. C$_{20}$–T carbon has P2$_13$ symmetry with a lattice constant of 4.945 Å. The carbon atoms occupy the 12h(0.4274, 0.7301, 0.8103), 4a(0.2694, 0.2307, 0.7694) and 4a(0.0894, 0.4106, 0.5894) Wyckoff positions, which are denoted by C$_1$(blue), C$_2$(red) and C$_3$(green) respectively.

Figure 2. Total energy as a function of volume per atom for C$_{20}$–T carbon in comparison with several other carbon allotropes.
Table 1. Calculated lattice parameters \(a\) and \(c\) (in Å), equilibrium density (\(\rho\) in g cm\(^{-3}\)), bond length (\(d\) in Å), and cohesive energy (\(E_{coh}\) in eV) for C\(_{20} - T\) carbon in comparison with diamond, graphite, BC8 carbon, BC12 carbon, W carbon and T-carbon.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Space group</th>
<th>Method</th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
<th>(\rho) (g cm(^{-3}))</th>
<th>(d) (Å)</th>
<th>(E_{coh}) (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>(F\bar{d}3m)</td>
<td>LDA</td>
<td>3.535</td>
<td>3.611</td>
<td>1.531</td>
<td>1.578</td>
<td>8.927</td>
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<tr>
<td></td>
<td></td>
<td>PBE</td>
<td>3.572</td>
<td>3.501</td>
<td>1.578</td>
<td>7.780</td>
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<tr>
<td></td>
<td></td>
<td>Exp. [20]</td>
<td>3.567</td>
<td>3.520</td>
<td>1.544</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>(P6_3/mmc)</td>
<td>LDA</td>
<td>2.446</td>
<td>6.594</td>
<td>2.335</td>
<td>1.412</td>
<td>8.918</td>
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<td>2.467</td>
<td>8.145</td>
<td>1.859</td>
<td>1.424</td>
<td>7.900</td>
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<td></td>
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<td>Exp. [19]</td>
<td>2.460</td>
<td>6.704</td>
<td>2.280</td>
<td>1.420</td>
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<td>BC8</td>
<td>(I\bar{a}3)</td>
<td>LDA</td>
<td>4.426</td>
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<td>1.446</td>
<td>1.611</td>
<td>8.239</td>
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<td>1.456</td>
<td>1.631</td>
<td>7.082</td>
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<tr>
<td>BC12</td>
<td>(I\bar{a}3d)</td>
<td>LDA [22]</td>
<td>5.116</td>
<td>3.576</td>
<td>1.566</td>
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<tr>
<td></td>
<td></td>
<td>PBE</td>
<td>5.172</td>
<td>3.461</td>
<td>1.583</td>
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<td></td>
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<tr>
<td>W carbon</td>
<td>(Pnma)</td>
<td>LDA</td>
<td>8.979</td>
<td>4.114</td>
<td>3.461</td>
<td>1.491–1.579</td>
<td>8.759</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PBE</td>
<td>9.081</td>
<td>4.154</td>
<td>3.352</td>
<td>1.505–1.598</td>
<td>7.625</td>
</tr>
<tr>
<td>T-carbon</td>
<td></td>
<td>LDA</td>
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<td></td>
<td>1.546</td>
<td>1.403, 1.487</td>
<td>7.577</td>
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<tr>
<td></td>
<td></td>
<td>PBE</td>
<td>7.512</td>
<td></td>
<td>1.506</td>
<td>1.416, 1.500</td>
<td>6.607</td>
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<tr>
<td>C(_{20} - T)</td>
<td></td>
<td>LDA</td>
<td>4.892</td>
<td></td>
<td>3.407</td>
<td>1.524, 1.526, 1.533</td>
<td>8.321</td>
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<td></td>
<td></td>
<td>PBE</td>
<td>4.945</td>
<td></td>
<td>3.298</td>
<td>1.541, 1.548, 1.550</td>
<td>7.191</td>
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</table>

In figure 2, we show total energy against volume for graphite, diamond, BC8, BC12, W-carbon, T-carbon, and C\(_{20} - T\) carbon. We can see that the C\(_{20} - T\) carbon is energetically more favorable than BC8 carbon, which has been suggested to be the derivative of cubic diamond under pressure of \(\sim 1100\) GPa [54–56]. The C\(_{20} - T\) carbon is also more stable than BC12 carbon and T-carbon, but less stable than W-carbon, graphite, and diamond due to the large distortions among the C–C bonds. The calculated lattice parameters, equilibrium density, bond length, and total energy per atom for diamond, graphite, BC8 carbon, BC12 carbon, W-carbon, T-carbon and C\(_{20} - T\) carbon are summarized in table 1.

The phonon band structure and density of states (DOS) of C\(_{20} - T\) carbon have been calculated and shown in figure 3 to study its dynamical stability. Throughout the entire Brillouin zone, there exist no imaginary frequencies, confirming the dynamical stability of the C\(_{20} - T\) carbon. The predicted highest vibrational frequency for C\(_{20} - T\) carbon is \(\sim 1329\) cm\(^{-1}\), lower than both \(\sim 1400\) cm\(^{-1}\) for the perfectly \(sp^3\) bonded diamond [57] and \(\sim 1600\) cm\(^{-1}\) for the \(\sigma\)-conjugated graphite [58]. The distortions of the C–C bonds weaken the bond strength and result in the decrease of the vibrational frequency compared to that of diamond. It can be seen that there exists a band gap (50 cm\(^{-1}\)) in the phonon spectra of C\(_{20} - T\) carbon. The atom-resolved phonon DOS indicate that the high frequency modes are mainly contributed by the C\(_1\) atoms. We think that the bond strength difference between C\(_1\)–C\(_1\) bonds and other C–C bonds lead to the appearance of the small band gap. These features could be useful in characterizing this new carbon allotrope.

Now, we examine the mechanical stability of C\(_{20} - T\) carbon. As we already know, in the linear elastic range, the elastic constant tensor forms a symmetric \(6 \times 6\) matrix with 21 independent components. For the cubic lattice, only C\(_{11}\), C\(_{12}\), and C\(_{44}\) are independent [59]. According to Born stability conditions [59], the elastic constants of a cubic crystal should satisfy \(C_{11} - C_{12} > 0\), \(C_{11} + 2C_{12} > 0\) and \(C_{44} > 0\). The calculated elastic constants of C\(_{20} - T\) carbon, diamond, and BC12 are listed in table 2. These calculated elastic constants \(C_{ij}\) of C\(_{20} - T\) carbon obey all of the conditions listed above very well, verifying the mechanical stability of C\(_{20} - T\) carbon. It is well known that a low (high) ratio of bulk modulus (B) to shear modulus (G) often suggests brittleness (ductility) of materials—the critical value being about 1.75 [60]. With the Voigt–Reuss–Hill approximation [61], we obtained the bulk and shear modulus of C\(_{20} - T\) carbon: 395 GPa and 427 GPa respectively. The B/G value of C\(_{20} - T\) carbon is 0.93, revealing its brittle character. In addition, according to the Frantsevich rule [62], we can also judge the brittleness/ductility of a material by a low (high) Poisson’s ratio, with a critical value about 1/3. The Poisson’s ratio of C\(_{20} - T\) carbon is 0.11, which also indicates that C\(_{20} - T\) carbon is a brittle material.

We have also performed first-principles molecular dynamics simulations with the canonical (NVT) ensemble...
at temperature of 1500 K to examine the thermal stability of $C_{20}^{-T}$ carbon at high temperatures. To do this, we built a $2 \times 2 \times 2$ supercell containing 160 carbon atoms and set the time step to be 1 fs. Figure 4 shows the fluctuations of potential energy as a function of simulation time. We find the geometry of $C_{20}^{-T}$ carbon remains intact after 6000 steps, strongly suggesting that the $C_{20}^{-T}$ carbon is stable even at high temperatures.

To explore the hardness of $C_{20}^{-T}$ carbon, we adopt the empirical scheme [63] to evaluate the Vickers hardness ($H_v$) of $C_{20}^{-T}$ carbon and some other carbon phases. The Vickers hardness ($H_v$) is determined by the bulk modulus ($B$) and shear modulus ($G$), where $H_v = 2G^2/B^2 - 0.585 - 3$. The values of Vickers hardness for diamond, BC12 carbon, and $C_{20}^{-T}$ carbon are 93.27, 65.65, and 72.76 GPa respectively (see table 2). The Vickers hardness value of $C_{20}^{-T}$ carbon is even higher than BC12 carbon and the famous superhard material c-BN [45]. Therefore, $C_{20}^{-T}$ carbon is a potential superhard material candidate.

In order to assess the strength of $C_{20}^{-T}$ carbon, we have calculated its ideal strengths within the GGA-PBE scheme. The ideal strength is defined as the maximum of stress in the stress–strain curve of the weakest tensile stretch or shear slip direction [64, 65]. The calculations of ideal strengths for $C_{20}^{-T}$ carbon were performed along (100), (110), and (111) for tension and (100)(010), (100)(011), (110)(110), (110)(110), (111)(112), and (111)(110) on

<table>
<thead>
<tr>
<th>structure</th>
<th>Method</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>$B$ (GPa)</th>
<th>$G$ (GPa)</th>
<th>$B/G$</th>
<th>$\nu$</th>
<th>$H_v$ (GPa)</th>
</tr>
</thead>
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<tr>
<td>diamond</td>
<td>LDA</td>
<td>1107</td>
<td>149</td>
<td>594</td>
<td>468</td>
<td>545</td>
<td>0.86</td>
<td>0.08</td>
<td>92.33</td>
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<tr>
<td></td>
<td>PBE</td>
<td>1055</td>
<td>126</td>
<td>565</td>
<td>435</td>
<td>522</td>
<td>0.83</td>
<td>0.08</td>
<td>93.27</td>
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<tr>
<td></td>
<td>Exp [21]</td>
<td>1076</td>
<td>125</td>
<td>577</td>
<td>442</td>
<td>534</td>
<td>0.83</td>
<td>0.07</td>
<td>93.27</td>
</tr>
<tr>
<td>BC12</td>
<td>LDA</td>
<td>1123</td>
<td>103</td>
<td>455</td>
<td>443</td>
<td>477</td>
<td>0.93</td>
<td>0.10</td>
<td>61.80</td>
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<tr>
<td></td>
<td>PBE</td>
<td>1056</td>
<td>88</td>
<td>433</td>
<td>441</td>
<td>451</td>
<td>0.98</td>
<td>0.10</td>
<td>65.65</td>
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<tr>
<td>$C_{20}^{-T}$</td>
<td>LDA</td>
<td>1064</td>
<td>108</td>
<td>434</td>
<td>427</td>
<td>452</td>
<td>0.94</td>
<td>0.11</td>
<td>73.42</td>
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<tr>
<td></td>
<td>PBE</td>
<td>994</td>
<td>95</td>
<td>412</td>
<td>395</td>
<td>427</td>
<td>0.93</td>
<td>0.11</td>
<td>72.76</td>
</tr>
</tbody>
</table>

Figure 4. Fluctuations of potential energy of the $C_{20}^{-T}$ carbon supercell as a function of the molecular dynamic simulation step at 1500 K. The inset shows the snapshot of the simulated system.

Figure 5. Stress–strain relationships calculated by the first-principles method for $C_{20}^{-T}$ carbon: (a) tension and (b) shear.

Figure 6. Simulated XRD spectrum of $C_{20}^{-T}$ carbon in comparison with diamond and graphite. The x-ray wavelength we adopted is 1.54059 Å.
respectively. In addition to these main peaks, there also exist several other small peaks for C20 carbon. (b) Projected density of states (PDOS) for C1, C2 and C3 atoms within HSE06 hybrid functional. The overall VBM and CBM are denoted by a red dashed line and a blue dashed line, respectively. The Fermi level is set at 0 eV.

Figure 7. (a) Electronic band structures of C20 – T carbon obtained by HSE06 potential. (b) Projected density of states (PDOS) for C1, C2 and C3 atoms within HSE06 hybrid functional. The overall VBM and CBM are denoted by a red dashed line and a blue dashed line, respectively. The Fermi level is set at 0 eV.

The overall VBM and CBM are denoted by a red dashed line and a blue dashed line, respectively. The band gap of C20 – T carbon is much larger than the fundamental band gap of 1.61 eV for Si20 – T [44]—being, however, very close to that of 5.47 eV for diamond [20]. The PDOS show that there is strong hybridization between 2s and 2p states, verifying the sp3 hybridized character of the C20 – T carbon. Different from C2 and C3 atoms, where the 2pₓ, 2pᵧ, and 2pᶻ orbitals are almost degenerate, the 2pₓ orbitals contribute most electronic states around Fermi level for C1 atoms.

4. Conclusion

In summary, we have predicted a new superhard carbon allotrope (C20 – T carbon) with P2₁3 symmetry and porous structure by first-principles calculations. The structural stability of C20 – T carbon is verified by analyses of total energy, phonon mode, elastic constants and molecular dynamic (MD) simulations. Our calculations show that the C20 – T carbon is a brittle material with a high Vickers hardness value of 72.76 GPa. The calculated ideal tensile and shear strength of C20 – T carbon are 71.1 and 54.5 GPa, comparable to that of c-BN [67]. Accordingly, the C20 – T carbon should exhibit similar strength to C-BN.

Finally, we discuss the electronic properties of C20 – T carbon. We show in figure 7 the electronic band structures of C20 – T carbon and the projected density of states (PDOS) for C1, C2 and C3 atoms, which are calculated using a hybrid density functional method based on the Heyd–Scuseria–Ernzerhof scheme (HSE06) [68, 69]. As shown in figure 7(a), C20 – T carbon exhibits an insulating character with a wide indirect band gap of 5.44 eV. The conduction band bottom and valence band top are located along the M-Γ and Γ-X directions respectively. The band gap of C20 – T carbon is much larger than the fundamental band gap of 1.61 eV for Si20 – T [44]—being, however, very close to that of 5.47 eV for diamond [20]. The PDOS show that there is strong hybridization between 2s and 2p states, verifying the sp3 hybridized character of the C20 – T carbon. Different from C2 and C3 atoms, where the 2pₓ, 2pᵧ, and 2pᶻ orbitals are almost degenerate, the 2pₓ orbitals contribute most electronic states around Fermi level for C1 atoms.

Acknowledgment

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