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Strength and bonding nature of superhard Z-carbon from first-principle study

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Z-carbon is a candidate structure proposed recently for the cold-compressed phase of carbon. We have studied the mechanical properties of Z-carbon by performing the first-principles density functional calculations. The single-crystal elastic constants calculations show that Z-carbon is mechanically stable. The predicted bulk and shear moduli of Z-carbon are comparable to diamond and cubic BN, suggesting that Z-carbon can be a superhard material. We also obtained the ideal tensile and shear strengths for Z-carbon through deformation from the elastic regime to structural instability. The failure modes under tensile deformation were explored carefully based on the calculated charge density distribution and bonding evolution. Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4732136]

Carbon is an interesting element. Due to its ability to form $sp^-, sp^2-$, and $sp^3$-hybridized bonds, it exists in a large number of structures such as graphite, hexagonal diamond, diamond, nanotubes, fullerenes, and amorphous carbon.1–8 It is well known that at high temperature (>1300 °C) and high pressures (>15 GPa), graphite can be suitably transformed into hexagonal or cubic diamond.9–14 Also, it has been reported that by cold-compression at room temperature, graphite can be transformed into a transparent and superhard phase.15 However, the atomic structure of this cold-compressed phase of carbon is yet unresolved in experiment. In order to understand the structure, some possible candidates (monoclinic $C_{2/m}$ phase M-carbon,15 body-centered tetragonal $C_4$-carbon,16 orthorhombic phase W-carbon,17 and R and P carbon,18 have been proposed by first-principles calculations. These candidate phases of carbon possess high hardness, which are very close to that of diamond.19–22 Very recently, using a combination of minima hopping method (MHM) and Raman spectroscopy at high pressure (diamond anvil cell (DAC)), Amsler et al.23 predicted a Cmmm symmetry cold-compressed carbon, Z-carbon, which could be a transparent wide band-gap semiconductor with hardness comparable to diamond.

To understand the mechanical properties and bonding nature of this cold-compressed phase of carbon, we report in this letter a theoretical investigation using first-principles calculations based on density functional theory. Our calculations were performed with the local density approximation (LDA), as implemented in the VASP code.24 The projector augmented wave (PAW) method25 was employed to account for the electron–ion core interaction. The plane-wave cutoff energy is set to 600 eV and a $3\times6\times12\Gamma$-centered $k$-point grid in the Monkhorst-Pack scheme is employed to sample the Brillouin zone (BZ) of Z-carbon. Our convergence tests show the above computational setup is sufficient to provide a converged result in the present study. The conjugate gradient method was used in the geometry optimization. The structural parameters ($a = 8.672$ Å, $b = 4.208$ Å, and $c = 2.486$ Å)

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When the uniaxial stress or to slip systems for shear deformation. The calculated procedure is basically
for the materials strength at larger strains, where significant changes are expected in bonding
characteristics. Thus, we next discuss the ideal strength from the elastic regime to the limit of its
structural stability.

To verify the accuracy of our calculated $c_{ij}$, the bulk modulus of Z-carbon was estimated by fitting
the total energies of Z-carbon at 11 different volumes to third-order Birch-Murnaghan equation of
state (EOS). The bulk modulus $B_0$ and its pressure derivative $B'_0$ of Z-carbon are 450.9 GPa and 3.7,
respectively. The bulk modulus obtained from the Birch-Murnaghan EOS fit is in good agreement
with that estimated from independent elastic constants. Figure 1 shows the pressure dependence of
the normalized lattice constants ($a/a_0$, $b/b_0$ and $c/c_0$) and primitive cell volume $V/V_0$, where $a_0$, $b_0$, $c_0$ and $V_0$ are the equilibrium structural parameters at zero pressure. It can be seen that the $c$ axis is the most uncompressible crystallographic direction.

For many of the high-strength covalent solids, it is known that the strength and elastic modulus
are not necessarily linearly corrected. This is because elastic constants are obtained strictly within
the linear elasticity regime of materials (i.e., near the equilibrium state), they cannot give an accurate
account for the materials strength at larger strains, where significant changes are expected in bonding
characteristics. Thus, we next discuss the ideal strength from the elastic regime to the limit of its
structural stability and understand the underlying bond-responding processes. To examine the ideal
strength of Z-carbon from the elastic regime to the limit of its structural stability, we calculated
the uniaxial stress or to slip systems for shear deformation. The calculated procedure is basically
similar to the one proposed in Ref. 33 The $<100>$, $<010>$, and $<001>$ crystallographic directions
were selected for tensile deformation. Three typical slip systems (010)$<001>$, (100)$<001>$, and
(100)$<010>$ were selected for shear deformation. Figures 2(a) and 2(b) show the results of tensile
and shear deformation of Z-carbon, respectively. It can be seen that the tensile strength of Z-carbon
in $<100>$, $<010>$, and $<001>$ directions are 102.2, 80.4, and 139.9 GPa at the critical strain of
about 0.15, 0.12, and 0.27, respectively. Therefore, the ideal tensile strength of Z-carbon is
80.4 GPa, which is lower than that of diamond ($\sim$90 GPa), but higher than cBN (64.8 GPa).

The Z-carbon has an orthorhombic symmetry with a $Cmmm$ space group and thus it has nine
independent single-crystal elastic constants. The elastic constants ($c_{ij}$) of Z-carbon were calculated
using an efficient strain-stress approach, i.e., through a linear least-squares fit of the first-principles
calculated stresses as a function of strain. All internal atomic coordinates were optimized for
every given strain state. The calculated results of $c_{ij}$ of Z-carbon are summarized in Table I along a
comparison with the results of diamond and cubic BN (cBN). It can be seen that the elastic
constants of Z-carbon obey the elastic stability criteria for an orthorhombic structure, and thus
Z-carbon can be mechanically stable under the ambient condition.

Once the single-crystal elastic constants $c_{ij}$ are obtained, one can estimate the polycrystalline
elastic moduli by means of the Voigt-Reuss-Hill approximation. The results for Z-carbon are presented
in Table I. Z-carbon has the very large elastic constants and elastic modulus between those
of diamond and cBN. As point out by Teter,32 the polycrystalline shear modulus could be a better predictor of hardness. Because diamond and cBN are well-known superhard materials, it is conceivable that Z-carbon could be a superhard material considering its shear modulus between those of diamond and cBN.

| $c_{ij}$ | $c_{11}$ | $c_{22}$ | $c_{33}$ | $c_{44}$ | $c_{55}$ | $c_{66}$ | $c_{12}$ | $c_{13}$ | $c_{23}$ |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Z-Carbon | 1135 | 1183 | 1255 | 477 | 531 | 370 | 76 | 100 | 27 | 441 | 494 |
| Diamond | 1079 | 578 | 124 | 443 | 538 |
| cBN | 798 | 469 | 172 | 381 | 398 |
| 844 |

*Experimental data from Ref. 27.
*Theoretical (LDA) data from Ref. 28.
*Theoretical (LDA) data from Ref. 29.
*Theoretical data (LDA) from Ref. 30.

TABLE I. The calculated $c_{ij}$ for Z-carbon along a comparison with those of diamond and cBN.

For many of the high-strength covalent solids, it is known that the strength and elastic modulus
are not necessarily linearly corrected. This is because elastic constants are obtained strictly within
the linear elasticity regime of materials (i.e., near the equilibrium state), they cannot give an accurate
account for the materials strength at larger strains, where significant changes are expected in bonding
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80.4 GPa, which is lower than that of diamond ($\sim$90 GPa), but higher than cBN (64.8 GPa).
FIG. 1. The pressure dependence of the normalized lattice constants $a/a_0$, $b/b_0$ and $c/c_0$ as well as the normalized primitive cell volume $V/V_0$ (where $a_0$, $b_0$, $c_0$ and $V_0$ are the zero pressure equilibrium structural parameters).

FIG. 2. The stress-strain relationships of Z-carbon calculated by the first-principles method for (a) tensile deformation, and (b) shear deformation.

From Fig. 2(b), it can be found that the ideal shear strengths are found to be 115.3, 119.5, and 104.9 GPa for (010)<001>, (100)<001>, and (100)<010> systems, respectively. Therefore, the weakest shear strength in the Z-carbon is much higher than the tensile strength by above 20% and it is even higher than those of diamond (86.8 GPa\textsuperscript{21} and 92.5 GPa\textsuperscript{22}) and cBN (58 GPa\textsuperscript{34}). In other words, the failure mode in Z-carbon is dominated by tensile type, which is same with the cases of diamond and cBN.\textsuperscript{21,22,28} It is known that plastic deformation occurs in shear and the shear strength is the
FIG. 3. (a) The crystal structure of Z-carbon used in the present calculations, (b-d) the projection of charge density into the (001) plane of Z-carbon under equilibrium conditions (b), and at large strains corresponding to the critical points for structural instability under $<100>$ (c), and $<010>$ (d) uniaxial deformation, respectively.

stress where a defect-free crystal becomes unstable and undergoes spontaneous plastic deformation. The measurement of hardness has to first encounter the elastic deformation and then experience permanent plastic deformation. Therefore, our results suggest that Z-carbon would be intrinsically harder than cBN and be close to diamond.

In order to obtain deeper understanding of the mechanical properties of Z-carbon, the charge density distribution was analyzed. Figure 3(a) shows the crystal structures used in the present calculations. For simplicity, we denoted the inequivalent carbon atoms as C1, C2, C3, and C4 [see Fig. 3(a)] according to their position in the unit cell, and the C-C bond lengths at equilibrium state are $d_{C1-C1} = 1.55206 \text{ Å}$, $d_{C1-C2} = 1.51261 \text{ Å}$, $d_{C2-C3} = 1.5421 \text{ Å}$, $d_{C3-C3} = 1.553 \text{ Å}$, $d_{C3-C4} = 1.51261 \text{ Å}$ and $d_{C4-C4} = 1.54466 \text{ Å}$, which are very close to the C-C bond length in diamond (1.547 Å). According to the bond strength and contribution to the direction (C4-C4, most partially C2-C3, and little partially C1-C2 and C3-C4 contribute to $a$ direction, C1-C1, C3-C3, little partially C1-C2, C2-C3, and C3-C4 contribute to $b$ direction, and mainly C1-C2 and C3-C4 contribute to $c$ direction), it may explain why $c$ axis is the strongest crystallographic direction in Z-carbon.

Figures 3(b)–3(d) show that the projection of charge density in the (001) plane of Z-carbon under equilibrium conditions, large strains corresponding to the critical points for structural instability under $<100>$, and $<010>$ uniaxial deformation, respectively. Clearly, the breaking of C4-C4 and C2-C3 bonds are responsible for the structural instability of Z-carbon upon tensile deformation along the $<100>$ direction [see Fig. 3(c)]. Under $<010>$ uniaxial tension, the softening and breaking of C3-C3 bonds is responsible for the failure of Z-carbon [see Fig. 3(d)]. Such a bond-breaking event can also be clearly seen from Fig. 4, which shows the changes of bond lengths as a function of applied strain under $<010>$ uniaxial tension. As shown in Fig. 4, it can be seen that C3-C3 bonds increase slowly after the critical strain of about 0.12, and then increase abruptly at the strain of about 0.15. The results indicate that the C3-C3 bonds soften before bond breaking. We have analyzed the projection of charge density in the (001) plane of Z-carbon under $<010>$ uniaxial deformation before and after bond breaking, respectively (see inset picture of Fig. 4). The softening and breaking of C3-C3 bonds are clearly driven with increasing strain.

In summary, using first-principles calculations, we have investigated the mechanical properties of Z-carbon. Our results show that the bulk and shear modulus of Z-carbon are extremely high and they are very close to (even higher than) those of diamond (and cBN), indicating that Z-carbon should be intrinsically weaker (and harder) than diamond (and cBN). We also obtained the ideal tensile and
shear strengths for Z-carbon through deformation from the elastic regime to structural instability. Additionally, the failure modes were explored carefully based on calculated the charge density distribution and bonding evolution. The present calculations provide fundamental information for better understanding of mechanical performance of this interesting material.

Note added. Recently, predictions of the elastic constants and ideal strength of Z-carbon were made via the generalized gradient approximation (GGA) in Ref. 35. It is well known that the LDA (GGA) typically overestimates (underestimates) the elastic constants and bulk modulus. Therefore, the elastic constants of Z-carbon in the present LDA calculations are larger than the GGA results in Ref. 35 by 80 GPa at most. In particular, the $c_{23}$ of Z-carbon was predicted by the GGA calculations in Ref. 35 to be negative (i.e., $-2.3$ GPa). The LDA calculations in the present study and the GGA in Ref. 35 both predict that the tensile mode of Z-carbon along the [010] direction has the smallest ideal strength.

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