

Superdense *t*12 carbon: Unexpectedly high elastic moduli but low ideal strength

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ABSTRACT

The basic physical and chemical properties of new carbon allotropes are important to explore their further technique and industrial applications. Here, a systematic theoretical investigation on the electronic, dynamical, and elastic properties for the superdense carbon (*t*12) are performed, especially the ideal tensile and shear strength and the corresponding bond-breaking modes are explored to uncover its intrinsic mechanical nature and the corresponding bond-breaking modes. Our results show that the bulk, shear and Young's modulus of *t*12 carbon are ultrahigh, close to those of diamond, reflecting its excellent performance of the substance's resistance to be deformed elastically at small strains. However, the calculated tensile and pure shear strengths are remarkably lower than that of diamond, which is attributed to its original structural anisotropy by analyzing the atomic structural deformation under different strains. The current results highlighted the need to carefully examine the stress response at large strains, which provide crucial insights for the bond-breaking modes and deformation mechanisms that may lead to conclusions different from those obtained from equilibrium structures.

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1. Introduction

Carbon materials are of great importance in the field of both fundamental scientific investigations and industrial applications [1]. It is well known that carbon has various allotropes that adopt dramatic different physical properties due to its flexibility of chemical bond hybridization [2,3]. For example, graphite is the ground state phase of carbon with ultrasoft and semimetal character with hexagonal sp^2 planes bound together by weak *van der Waals* forces. For the other extreme, diamond is the naturally existing hardest crystalline material, which stemming from its three-dimensional high-strength sp^3 hybridized C–C bonds. Besides the superhard trait, diamond also kept superior optical and electrical properties which make it possesses many potential technological applications. Moreover, various other forms of carbon materials, such as carbon fullerenes, nanotubes, graphene, graphyne, and graphdiyne had been synthesized experimentally [4–7] and were reported to possess many fascinating electronic, thermal and mechanical properties.

The searching for new carbon allotropes that may have higher hardness, superior mechanical strength, and semiconducting prop-

erties are of great interests. Under high-pressure conditions, new three-dimensional carbon phases formed by sp^3 hybridized C–C bonds exist and are expected to be potential superhard and superdense materials. Experimentally, an amorphous carbon material produced from fullerene and a superhard carbon phase was obtained by cold compression of graphite [8]. Subsequently, several new superhard carbon structures (i.e., M-carbon, Z-carbon, bct4 carbon, W-carbon, Cco-8 carbon, bc8 carbon, oC32 carbon and so on) [9–22] were proposed theoretically. In the process, it was believed and proved that the crystal structure prediction methods and functional material design methods that based on particle swarm optimization [23–28], evolutionary [29,30], random sampling [31] and other intelligence techniques [32–37] are highly effective to predict new carbon phases and other high pressure structures. Recently, a metastable carbon phase (denoted as *t*12 carbon) with tetragonal $I-42d$ symmetry and 12 atoms per unit cell has been predicted [17], which is the densest allotrope of carbon. The high strength and hardness for covalent compounds are contributed by the strong and dense chemical bonds [38–41]. Thus, a covalent compound with high density may possess high strength and other excellent mechanical properties. Therefore, it is critical to understand the ideal strength and the bond-breaking modes for *t*12 carbon, which are the critical information for its further industrial applications as superhard material. In the current

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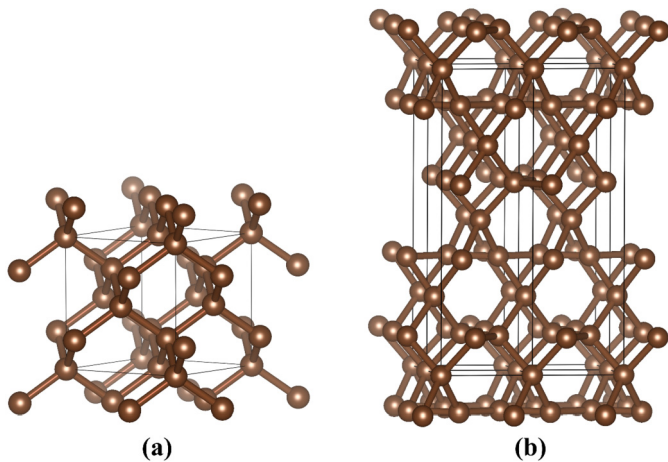


Fig. 1. Crystal structures of diamond (a) and *t112* carbon (b).

work, we have systematically investigated the basic physical properties of *t112* carbon including structural, electronic, ideal strength and mechanical properties by the first-principles calculations. Our theoretical results show that *t112* carbon possesses unexpectedly high elastic moduli but low ideal strength, reflecting its excellent performance of the substance's resistance to being deformed elastically but relative poor performance of resistance at large strain. The lowest compressive strength of *t112* carbon is comparable with that of diamond which indicates *t112* carbon can be used as anvil under compressive conditions. The theoretical stress responses at large strains of *t112* carbon provide crucial insights for the bond-breaking modes and deformation mechanisms.

2. Computational details

The current first-principles calculations were carried out by using the plane-wave basis Vienna *Ab-initio* Simulation Package (VASP) [42], which is based on the density functional theory. Local density approximation (LDA) exchange-correlation potential [43] was implemented and the valence configuration of $2s^2 2p^2$ [44] were used for carbon atom. Before the calculations of electronic, dynamical and elastic properties, the structures have been fully optimized. The kinetic energy cutoff of 550 eV was adopted for plane-wave expansion and Monkhorst-Pack *k* point meshes [45] with a grid of 0.179 \AA^{-1} was employed to generate Brillouin zone integration for all cases to ensure the total energies converged to be better than about 10^{-3} eV/atom. The phonon frequencies were calculated by the direct supercell method with combined PHONOPY [46] and VASP codes. The single elastic constants were determined from strain–stress method [47], by which a set of given strains with a finite variation were applied on the optimized structure and the atomic positions were fully optimized. The bulk modulus, shear modulus, Young's modulus and Poisson's ratio were estimated by the Voigt–Reuss–Hill averaging scheme [48]. The quasistatic ideal strengths were calculated by incrementally imposing the strain in a particular direction or a shear plane and simultaneously relaxing the other strain components and the atomic positions in the unit cell.

3. Results and discussions

T112 carbon, with space group of *I-42d* and 12 atoms per unit cell, is a metastable phase of carbon which can be transformed from graphite at high pressure conditions. The currently optimized equilibrium lattices are $a = b = 2.674 \text{ \AA}$, $c = 8.896 \text{ \AA}$ at ambient conditions, which is slight lower than the previously reported GGA results. This structure is closely related to the high-pressure SiS₂

polymorph with the carbon atoms occupied two different Wyckoff positions: C1 at $4a$ (0.0, 0.0, 0.0) and C2 at $8d$ (0.8333, 0.25, 0.625) positions, respectively. All the carbon atoms form sp^3 hybridizing tetrahedral bonds, as shown in Fig. 1(b). There are two kinds of C–C bonds with length 1.575 Å for C1–C2 bond and 1.606 Å for C2–C2 bond. Although these bonds are longer than that of diamond (1.54 Å, the crystal structure of diamond is shown in Fig. 1(a)), it is fascinating to note that the *t112* carbon is 3.2% denser than diamond and 2.2% denser than bc8 due to its effective way of bond packing.

It is well known that a stable structure needs to possess all positive phonon frequencies in the entire Brillouin zone. The phonon spectra of *t112* structure at zero temperature and pressure conditions have been calculated to examine its dynamical stability. For comparison, we have calculated the phonon spectra of diamond and *t112* at ambient condition as shown in Fig. 2(a) and Fig. 2(b). No imaginary frequency was found in the whole Brillouin zone for *t112* structure, which confirms its dynamical stability. The primitive cells of diamond and *t112* contain 2 and 6 atoms, giving 6 and 18 phonon branches, respectively. The phonon bands of the both phases have very large dispersion in the entire Brillouin zone, indicating that the corresponding interactions and the chemical bonds are strong.

We calculated the electronic band structure of *t112* carbon and compared with that of diamond by using LDA approximation and the results are shown in Fig. 3. It is obvious that the *t112* carbon has an indirect band gap since the conduction band minimum and the valence band maximum dose not occurs at the same point. The current calculated band gap of *t112* carbon is about 4.693 eV that is comparable to that of diamond (4.315 eV), but lower than the previously reported GW results (5.5 eV). It is reasonable since the traditional DFT calculations usually underestimates band gap by about $\sim 30\%$. As predicted previously, *t112* carbon also has higher dielectric constants and significantly greater dispersion of light. If this phase can be obtained by experimental techniques such as chemical-vapor-deposition or shock compression of amorphous carbon, it might have wide applications as superior optical device.

The mechanical properties of *t112* carbon are important for its industrial applications. Here we calculated the elastic constants by using the strain–stress method. The obtained average bulk modulus, shear modulus, Young's modulus and the Poisson's ratio are 464.4 GPa, 580.9 GPa, 1230 GPa and 0.06, respectively. It should be emphasized that all the calculated single elastic constants satisfy the generalized elastic stability criteria for a tetragonal structure [49] ($C_{11} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{66} > 0$, $C_{11} - C_{12} > 0$, $C_{11} + C_{33} - 2C_{13} > 0$ and $2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0$) suggesting the elastically stability. It should be emphasized that the bulk modulus of *t112* carbon (464 GPa) is comparable to that of diamond (468 GPa calculated in this work) and slightly higher than other carbon polymorphs, such as M-carbon (434 GPa), Cco-C₈ carbon (449 GPa), bct4 carbon (437 GPa), *Imma*-carbon (440 GPa) and C-carbon (444 GPa) [50,51]. While the shear modulus and Young's modulus are slightly lower than that of diamond indicating the strong resistance to the shear compression at constant volume and higher stiffness. Furthermore, the Pugh's ratio (G/B) [52] of *t112* carbon is 1.25, which is higher than that of diamond (1.17) indicating that this phase might be more ductile than diamond. To examine the elastic anisotropy intuitively, the three-dimensional Young's modulus, shear modulus, Poisson's ratio and compressibility are calculated and shown in Fig. 4. Only Poisson's ratio shows highly directional dependence, the shear modulus, Young's modulus and compressibility exhibit small deviation from spherical shape indicating weak anisotropy effect.

The Vickers hardness of *t112* carbon was calculated to be 87.2 GPa [17] by using Gao's theoretical hardness model [53]. But the ideal strength under specified loading compressive, tensile

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