Superhard Superstrong Carbon Clathrate

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Abstract

Carbon clathrate is a kind of typical carbon allotrope that has an open framework composed of various types of cages, displaying intriguing electronic and mechanical properties. This paper proposes a superhard superstrong carbon clathrate via first-principle calculations. This carbon clathrate, called C₆₀ clathrate, contains 60 carbon atoms buckled through sp^3 -hybridized bonds in a cubic unit cell with symmetry of $Im-3m$, and possesses the network topology of commonly called binodal net. C₆₀ clathrate is energetically more stable than fullerene C₆₀ at ambient pressure, and it is more favorable than graphite at a pressure above 50.1 GPa. C₆₀ clathrate can be constructed by small C₂₄ cage and flat C₁₈ drum. It shows a high density of 3.34 g/cm³, which is the densest carbon clathrate to date. ~~The estimated Vickers hardness and tensile strength of C₆₀ clathrate are comparable with those of diamond, reaching remarkably high values of 91.6 and 90.7 GPa, respectively.~~ The estimated Vickers hardness, tensile strength, and shear strength of C₆₀ clathrate reach remarkably high values of 82.8, 90.7, and 76.4 GPa, respectively, indicating its superhard and superstrong characteristic. Band structure calculations indicate that C₆₀ clathrate is semiconductive with a direct band gap of 2.26 eV. C₆₀ clathrate can be potentially used in photovoltaic devices.

1. Introduction

Carbon can form a large number of allotropes with distinct electronic and mechanical properties, such as superhard insulators (diamond and lonsdaleite), ultrasoft semimetals (graphite), and superconductors (doped diamond), because of its unique capability to form sp -, sp^2 -, and sp^3 -hybridized bonds [1-5]. In recent years, carbon clathrates with 3D sp^3 -bonded networks constructed by coplanar polyhedral cages have attracted considerable interest. Benedek *et al.* [6] first proposed three basic series of periodic lattices of carbon clathrates, which are denoted as *fcc*-C₁₃₆, *sc*-C₄₆, and *hex*-C₄₀. Experimentally, these clathrates have been synthesized in pure or guest atom-modified Si and Ge structures [7-13]. However, similar carbon clathrates have not been synthesized so far. Some pioneer theoretical works demonstrate that these carbon clathrates possess numerous attractive properties, such as good thermoelectric properties, promising mechanical properties, and wide band gap, for potential optoelectronic applications [14-27]. Carbon clathrates generally have low densities and hardness because of their porous structures. For example, the synthesized 3D C₆₀ polymers have a density of 2.4–2.6 g/cm³ and hardness of 35–45 GPa, which are much lower than those of diamond. By regulating the size, shape, and structure of basic cage units, diverse carbon clathrates can be designed. In particular, carbon clathrates with high hardness, high strength, and certain porosity are expected.

In this study, we proposed ~~predicted~~ a cubic carbon clathrate with novel electronic and mechanical properties through first-principle calculations. This clathrate structure is constructed by C₂₄ cage and flat C₁₈ drum with 60 carbon atoms in a unit cell, and it is named C₆₀ clathrate. C₆₀ clathrate has a structural topology of called binodal net with the systematic name of sdt. C₆₀ clathrate is dynamically and mechanically stable with energy lower than that of fullerene C₆₀ at ambient pressure. Under hydrostatic compression, C₆₀ clathrate is energetically more stable than graphite above 50.1 GPa. The density of C₆₀ clathrate is 3.34 g/cm³, which is slightly lower than that of diamond but higher

than that of other known carbon clathrates. Electronic band structure calculations reveal that C₆₀ clathrate is a semiconductor with a direct band gap of 2.26 eV. C₆₀ clathrate is a novel superhard carbon with the estimated Vickers hardness of 82.8 GPa. ~~Compared with diamond, C₆₀ clathrate is a novel superhard material with Vickers hardness of 91.6 GPa.~~ Furthermore, we systematically investigated the ideal tensile and shear strength of C₆₀ clathrate, and the results revealed that the C₆₀ clathrate has a tensile strength similar with that of diamond, but its shear strength is lower than diamond. ~~Furthermore, we systematically investigated the uniaxial stress-strain relations of C₆₀ clathrate in three principal symmetry directions.~~

2. Calculation methods

Crystal structure ~~prediction~~ search is based on global minimization of free energy surfaces merging *ab initio* total-energy calculations via the particle swarm optimization (PSO) technique as implemented in the CALYPSO code [28]. First-principle calculations were carried out using the CASTEP [29] code based on density functional theory (DFT) [30, 31]. The exchange and correlation effects were described by the local density approximation (LDA) exchange-correlation functional of Ceperley and Alder, as parameterized by Perdew and Zunger (CA-PZ) [32]. Ultrasoft pseudopotentials were expanded using a plane-wave basis set with a cutoff energy of 310 eV, and a k-point spacing ($2\pi \times 0.04 \text{ \AA}^{-1}$) was assigned to generate Monkhorst-Pack k-point grids for Brillouin zone sampling [33]. Structural optimization using the BFGS minimization method was performed until the energy change of each atom was less than 5×10^{-6} eV, the forces on atoms were less than $0.01 \text{ eV \AA}^{-1}$, and all stress components were less than 0.02 GPa [34]. The phonon modes of the equilibrium crystal structure obtained after structural relaxation were calculated using linear response theory [35]. The coordinates of the high symmetry points in reciprocal space for calculated phonon dispersion are G (0, 0, 0), H (0.5,

$-0.5, 0.5)$, N $(0, 0, 0.5)$, and P $(0.25, 0.25, 0.25)$. The fixed strain method was used to assess the tensile and shear strength [36, 37].

3. Results and discussion

The crystal structure searches through the CALYPSO code were performed with cell size up to 30 carbon atoms at a pressure range of 0–100 GPa. Besides diamond, lonsdaleite, and previously predicted *M*-carbon, *Z*-carbon, and *W*-carbon etc. [38-43], our search ~~structure—simulations~~ discovered ~~predict~~ a new cubic clathrate phase with *Im-3m* symmetry, which contains 60 carbon atoms in a unit cell and is named as C₆₀ clathrate. This clathrate structure has been known in metal-organic framework (MOF) compounds with the topology of binodal net and systematic name of sdt [44]. Recently, the application of network topology approach to search for new allotropes of group 14 elements has been emphasized by Lars Öhrström and Michael O'Keeffe [45]. Nevertheless, the structure of sdt has not been considered for carbon so far, and C₆₀ clathrate indeed presents a novel carbon allotrope.

We firstly study the structural feature of C₆₀ clathrate. At zero pressure, the equilibrium lattice constant of ~~a C₆₀ clathrate~~ unit cell of C₆₀ clathrate is 7.1 Å with two inequivalent atoms occupying the crystallographic 48j $(0, 0.15296, 0.69205)$ and 12d $(1/2, 1/4, 0)$ sites. C₆₀ clathrate ~~carbon~~ can be derived by stacking two kinds of cage-like structures (A and B), as shown in Fig. 1. Cage A (blue) contains 24 carbon atoms, and it is also the building block of previous proposed *bcc*-C₆ and *fcc*-C₃₂ [18, 20]. Cage B (yellow) is a drum-shaped structure with 18 atoms and composed of six hexagonal carbon rings. Each C₂₄ cage is buckled with surrounding eight C₁₈ cages through shared hexagonal faces.

Figure 1. Crystal structure of C₆₀ clathrate along [100] direction (a) and the basic building blocks: cage A and cage B (b).

In comparison with other carbon clathrates, C₆₀ clathrate has the highest density and relatively low energy (Fig. 2a). The high density is originated from the dense flat C₁₈ drum with a much smaller volume than fullerene-like cages, such as C₂₀, C₂₄, C₂₆, C₂₈, and C₆₀, which are the basic building blocks for the typical carbon clathrates such as *fcc*-C₁₃₆, *sc*-C₄₆, *hex*-C₄₀, and 3D C₆₀ polymers (Fig. 1). As a result, this superdense carbon clathrate is expected to have high hardness and strength.

The thermodynamic stability of C₆₀ clathrate is further examined by a direct enthalpy comparison with known experimental and theoretical carbon allotropes (Fig. 2b). C₆₀ clathrate is metastable relative to diamond and graphite at ambient pressure, and it has the enthalpy higher than diamond and other carbon clathrates of *fcc*-C₁₃₆, *sc*-C₄₆, and *hex*-C₄₀ [6] at pressure from 0 to 60 GPa. However, the C₆₀ clathrate is more stable than fullerene C₆₀, the experimentally synthesized 3D C₆₀ [26, 27], and other theoretical clathrate structures of *bcc*-C₆, *sc*-C₂₀, *fcc*-C₃₂, and C₉₆ [18-20], indicating its viability. Above 50.1 GPa, C₆₀ clathrate is energetically more stable than graphite, indicating its possible synthesis from graphite under compression. ~~C₆₀ clathrate also has lower enthalpy than the experimentally synthesized 3D C₆₀ polymer~~

[26] from ambient to high pressures, which further confirms its thermodynamic stability.

Figure 2. Enthalpy-density relationship of C₆₀ clathrates compared with other theoretical proposed carbon clathrates and two different 3D C₆₀ [26, 27] at ambient pressure (a), and enthalpy-pressure relationship of various carbon clathrates with respect to graphite (b). The dashed line is the enthalpy of experimentally synthesized 3D C₆₀ polymers, presenting a partition of thermodynamic stability for carbon clathrates.

We have calculated the phonon dispersion of C₆₀ clathrate at ambient pressure, as shown in Fig. 3a. No imaginary frequencies are observed throughout the whole Brillouin zone, suggesting the dynamic stability of C₆₀ clathrate. The calculated highest phonon frequency of C–C bond stretching mode in C₆₀ clathrate is ~38 THz, which is close to that of diamond (40 THz), indicating relatively strong C–C bonding in C₆₀ clathrate. The electronic band structure is calculated to clarify the electronic properties (Fig. 3b). C₆₀ clathrate is a semiconductor with a direct band gap of 2.26 eV, which is about half that of indirect band gap diamond (4.1 eV). The valence band maximum and conduction band minimum are both located at the H point. The direct band gap

feature suggests it is a promising material for the solar cell or photography industry, and it can be potentially applied in light-emitting devices.

Figure 3. Electronic band structure (a) and phonon dispersion curves of C_{60} clathrate at ambient pressure (b).

To evaluate the mechanical stability of a crystal structure, the elastic constants of a crystal should satisfy the generalized elastic stability criteria. For a cubic crystal, the three independent elastic constants C_{11} , C_{12} , and C_{44} should obey the following generalized Born mechanical stability criteria: $C_{11} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$, and $C_{11} + 2C_{12} > 0$ [46]. The calculated elastic constant values of C_{60} clathrate at ambient pressure are $C_{11} = 929$ GPa, $C_{44} = 443$ GPa, and $C_{12} = 123$ GPa. The calculated elastic constants of C_{60} clathrate are positive and satisfy the Born stability criteria, indicating that C_{60} clathrate is mechanically stable at ambient pressure. Given that C_{60} clathrate possesses cubic crystal symmetry, the stiffness constant C_{11} can be directly related to the linear Young's modulus along crystallographic a, b, and c axes. An extremely large C_{11} (929 GPa) of C_{60} clathrate is observed, indicating its high incompressibility along the principal axis in the cubic C_{60} clathrate.

Although bulk modulus (B) and shear modulus (G) represent the resistance to material elastic deformations, they may also be associated with the fracture

and plastic deformation of a material. Hence, the B/G ratio can be used as a quantitative index to assess the brittle or ductile behavior of crystals. Paugh [47] proposed that a high (low) B/G ratio is often associated with ductility (brittleness), and the critical value that differentiates ductile and brittle material is 1.75. With the Voigt–Reuss–Hill approximation [48], the bulk and shear modulus of C₆₀ clathrate are 392 and 427 GPa, respectively. The calculated B/G ratio of C₆₀ clathrate is 0.92, which is bigger than that of diamond (0.82) and suggests its higher ductility than diamond. The brittleness/ductility can also be estimated by the Frantsevich rule adopting the Poisson’s ratio of a material [49]. A high (low) Poisson’s ratio usually suggests ductility (brittleness), and the critical value is 1/3. The Poisson’s ratio of C₆₀ clathrate (0.12) indicates that it is brittle, which agrees well with the estimation from the B/G ratio.

The calculated Vickers hardness of diamond is 98.2 GPa (in comparison with the experimental value of 96±5 GPa) based on the empirical formula $H_v(\text{GPa}) = 350N_e^{2/3}e^{-1.191f_i}/d^{2.5}$ [50], where N_e is the valence electron density in units of 1/Å³, d is the bond length (Å), and f_i is the Phillips ionicity of the chemical bond in a crystal [51]. ~~The Vickers hardness H_v of C₆₀ clathrate is estimated to be 91.6 GPa and comparable with that of diamond.~~ After the overlap populations of carbon-carbon bonds were calculated, we discovered that they are not equivalent, indicating the present of ionicity in C₆₀ clathrate. The overlap populations of three different kinds of carbon-carbon bonds are 0.85, 0.74 and 0.84, respectively. Therefore, we calculated the Phillips ionicity f_i of carbon bonds in C₆₀ clathrate by our previously established formula: $f_i = (f_h)^{0.735} = [1 - \exp(-|P_c - P|/P)]^{0.735}$, where f_h is the population ionicity scale, P is the overlap population of a bond, and P_c is the overlap population of the bond in a pure covalent crystal. Here, P_c is the overlap population of diamond, and equal to 0.75. Then, the estimated hardness of C₆₀ clathrate is 82.8 GPa. Fig. 4a shows the relationship between hardness and density of C₆₀ clathrate, 3D C₆₀ polymer [27], and some other carbon allotropes. As a result, the hardness increases with density in the carbon allotropes. This finding may provide us a

direction to find superdense superhard carbon clathrates or other carbon allotropes. To carry out a fair consideration, we also use the macroscopic hardness model proposed by Chen *et al.* to estimate the hardness of carbon clathrates [52-54]. The result also shows that the four clathrates of *fcc*-C₁₃₆, *sc*-C₄₆, *hex*-C₄₀, and C₆₀ clathrate are all superhard with hardness above 70 GPa (Fig. 4a).

Ideal strength calculations can provide valuable information on the mechanical properties of materials under stress [37,38,55-57]. In the current study, the uniaxial tensile strengths of C₆₀ clathrate are investigated. The three primary crystal orientations, namely, [100], [110], and [111], are chosen to calculate the ideal tensile strength. The calculated tensile strengths along the [100], [110], and [111] directions are 112.4 GPa with a strain of 0.2, 90.7 GPa with a strain of 0.21, and 92.3 GPa with a strain of 0.16, respectively (Fig. 4b); these values indicate the strength anisotropy of C₆₀ clathrate. Obviously, the lowest tensile strength is along the [110] direction, that is, the crystal will be cleaved along the [110] direction when the external stress exceeds 90.7 GPa. By contrast, the [100], [110], and [111] tensile strengths of diamond are 225, 130, and 90 GPa, respectively [57]. The lowest tensile strengths of C₆₀ clathrate and diamond are quite close.

Slippage usually occurs in the crystal plane perpendicular to the weakest tensile direction, hence we calculated the shear strengths of C₆₀ clathrate along the (110)[001], (110)[1-10] and (110)[1-11] slip systems. Furthermore, the (100)[001] and (111)[11-2] slip systems were also considered. We obtained the critical shear strengths of 90.3, 76.4, 89.2, 91.8, and 93.3 GPa for (110)[001], (110)[1-10], (110)[1-11], (100)[001], and (111)[11-2] slip systems, respectively (Fig. 4c). Consequently, the lowest shear strength of C₆₀ clathrate is 76.4 GPa, less than its tensile strength, suggesting that the crystal is more sensitive to the shear deformation. The close value of shear strength and hardness of C₆₀ clathrate is due to the lowest shear strength that almost reflects the real hardness of the material.

Figure 4. Hardness and densities of C_{60} clathrate and other carbon allotropes (a), the ideal tensile strengths of C_{60} clathrate along [100], [110] and [111] directions (b), and the ideal shear strengths of C_{60} clathrate along various directions (c). In Fig.4a, the hardness values estimated from *Gao's* and *Chen's* models are marked as blue and red color, respectively. The experimental data of 3D C_{60} is labeled as the black symbol. In Fig. 4b and 4c, the D[111] and D(111)[11-2] represent the weakest crystal orientations of diamond during tension and shear deformation [55, 57].

4. Conclusions

In summary, we have proposed ~~predicted~~ a novel sp^3 -hybridized carbon clathrate, namely, C_{60} clathrate. C_{60} clathrate is a superdense, superhard, superstrong carbon clathrate with mechanical performance comparable with that of diamond. C_{60} clathrate is also a direct band gap semiconductor, potentially showing efficient light absorption and emission. Despite its high density, C_{60} clathrate can still adopt some small guest atoms, such as Li and Na, in the C_{24} cages; it may become a superconductor like the recently discovered alkali metal-doped fullerene cages with high superconducting transition temperatures [58]. Our current research can stimulate the further exploration of novel carbon clathrates with attractive mechanical and electronic properties.

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