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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 C_{60} 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. C_{60} clathrate is energetically more stable than fullerene C_{60} at ambient pressure, and it is more favorable than graphite at a pressure above 50.1 GPa C_{60} clathrate can be constructed by small C_{24} cage and flat C_{18} drum. It shows a high density of 3.34 g/cm^3, which is the densest carbon clathrate to date. The estimated Vickers hardness, tensile strength, and shear strength of C_{60} 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 C_{60} clathrate is semiconductive with a direct band gap of 2.26 eV. C_{60} 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*-C_{136}, *sc*-C_{46}, and *hex*-C_{40}. 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 C_{60} polymers have a density of 2.4–2.6 g/cm^3 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 a cubic carbon clathrate with novel electronic and mechanical properties through first-principle calculations. This clathrate structure is constructed by C_{24} cage and flat C_{18} drum with 60 carbon atoms in a unit cell, and it is named C_{60} clathrate. C_{60} clathrate has a structural topology of called binodal net with the systematic name of sdt. C_{60} clathrate is dynamically and mechanically stable with energy lower than that of fullerene C_{60} at ambient pressure. Under hydrostatic compression, C_{60} clathrate is energetically more stable than graphite above 50.1 GPa. The density of C_{60} clathrate is 3.34 g/cm^3, which is slightly lower than that of diamond but higher than that of other known carbon clathrates. Electronic band structure calculations reveal that C_{60} clathrate is a semiconductor with a direct band gap of 2.26 eV. C_{60} clathrate is a novel superhard carbon with the estimated Vickers hardness of 82.8 GPa. Furthermore, we systematically investigated the ideal tensile and shear strength of C_{60} clathrate, and the results revealed that the C_{60} clathrate has a tensile strength similar with that of diamond, but its shear strength is lower than diamond.

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2. Calculation methods

Crystal structure 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 ($2\pi \times 0.04$ Å^{-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 eV Å^{-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 discovered a cubic clathrate phase with *Im-3m* symmetry, which contains 60 carbon atoms in a unit cell and is named as C_{60} 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 C_{60} clathrate indeed presents a novel carbon allotrope.

We firstly study the structural feature of C_{60} clathrate. At zero pressure, the equilibrium lattice constant unit cell of C_{60} clathrate is 7.1 Å with two inequivalent atoms occupying the crystallographic 48*j* (0, 0.15296, 0.69205) and 12*d* (1/2, 1/4, 0) sites. C_{60} clathrate 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*-C_6 and *fcc*-C_{32} [18,20]. Cage B (yellow) is a drum-shaped structure with 18 atoms and composed of six hexagonal carbon rings. Each C_{24} cage is buckled with surrounding eight C_{18} cages through shared hexagonal faces.

In comparison with other carbon clathrates, C_{60} clathrate has the highest density and relatively low energy (Fig. 2a). The high density is originated from the dense flat C_{18} drum with a much smaller volume than fullerene-like cages, such as C_{20}, C_{24}, C_{26}, C_{28}, and C_{60}, which are the basic building blocks for the typical carbon clathrates such as *fcc*-C_{136}, *sc*-C_{46}, *hex*-C_{40}, and 3D C_{60} polymers (Fig. 1). As a result, this superdense carbon clathrate is expected to have high hardness and strength.

The thermodynamic stability of C_{60} clathrate is further examined by a direct enthalpy comparison with known experimental and theoretical carbon allotropes (Fig. 2b). C_{60} clathrate is metastable relative to graphite at ambient pressure, and it has the enthalpy higher than diamond and other carbon clathrates of *fcc*-C_{136}, *sc*-C_{46}, and *hex*-C_{40} [6] at pressure from 0 to 60 GPa. However, the C_{60} clathrate is more stable than fullerene C_{60}, the experimentally synthesized 3D C_{60} [26,27], and other theoretical clathrate structures of *bcc*-C_6, *sc*-C_{20}, *fcc*-C_{32}, and C_{96} [18–20], indicating its viability. Above 50.1 GPa, C_{60} clathrate is energetically more stable than graphite, indicating its possible synthesis from graphite under compression.

We have calculated the phonon dispersion of C_{60} clathrate at ambient pressure, as shown in Fig. 3a. No imaginary frequencies are observed throughout the whole Brillouin zone, suggesting the dynamic stability of C_{60} clathrate. The calculated highest phonon frequency of C–C bond stretching mode in C_{60} clathrate is ~38 THz, which is close to that of diamond (40 THz), indicating relatively strong C–C bonding in C_{60} clathrate. The electronic band structure is calculated to clarify the electronic properties (Fig. 3b). C_{60} 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.

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

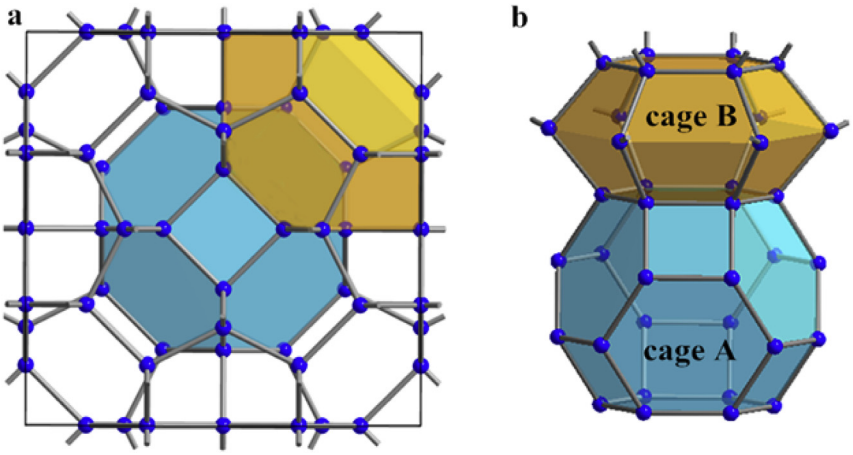

Fig. 1. Crystal structure of C_{60} clathrate along [100] direction (a) and the basic building blocks: cage A and cage B (b). (A colour version of this figure can be viewed online.)