Diamond-like phase formed of carbon $C_{24}$ clusters

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Abstract. The crystalline structure and some properties of the cubic diamond-like CA6 phase have been calculated by the density-functional theory method in the generalized gradient approximation. As a result of calculations, it was found that the density, cohesive energy, bulk modulus, hardness and band gap width of this phase are 2.824 g/cm$^3$, 7.59 eV/atom, 351 GPa, and 71 GPa, respectively. The phase structure of CA6 should be stable at room temperature.

1. Introduction

Compounds with diamond-like structures are widely used as anticorrosive coatings, abrasive and structural materials. A number of new diamond-like phases that can be formed on the basis of fullerene-like molecules, carbon nanotubes, graphene layers, and 3D covalently bonded graphite-like compounds are theoretically predicted [1-4]. These phases can be close to cubic diamond by mechanical characteristics [1-10]. The diamond-like CA6 phase formed on the basis of fullerene-like $C_{24}$ molecules may be the most stable among other diamond-like carbon C-phases [4]. Therefore, this paper is devoted to theoretical calculations of the structure, properties, and stability of cubic diamond-like CA6 phase.

2. Methods

Calculations of the structural and energy characteristics of the CA6 phase were performed in the software package Quantum ESPRESSO [11] using the density functional theory method in the generalized gradient approximation. The Perdew-Burke-Ernzerhof exchange-correlation energy functional was used for the calculations [12]. The effect of ion cores was taken into account using norm-conserving pseudopotentials. We used a $10 \times 10 \times 10$ grid of $k$-points in our calculations. The wave functions were decomposed in terms of a truncated basis set of plane waves with the cut-off energy of 60 Ry. The unit cell of the CA6 phase was optimized until the magnitudes of the stresses and forces acting on the atom became less than 1 mRy/Å and 0.50 GPa, respectively. The hardness and the bulk modulus were calculated using the methods described in [13,14].

3. Results

The crystalline structure of the diamond-like CA6 phase was modelled as a result of the linking of $C_{24}$ carbon clusters according to the procedure described in [1,4]. The geometrical optimized structure of the new phase is shown in figure 1a. The CA6 phase unit cell is body-centred cubic ($Im\bar{3}m$ – № 229) with the parameter $a = 4.3927$ Å (figure 1b). The unit cell contains 16 atoms, the coordinates of which are given in table 1. All atoms in the CA6 phase are in symmetrically equivalent positions. As in the cubic diamond, all covalent bond lengths in the structure of CA6 are the same and equal to 1.5531 Å. However, there are two non-equivalent bond angles, the values of which are 90 and 120°.
Figure 1. Fragment of the structure (a) and unit cell (b) of the diamond-like CA6 phase.

Table 1. Atomic coordinates in the CA6 phase unit cell.

| Atomic number | X (Å)  | Y (Å)  | Z (Å)  | Atomic number | X (Å)  | Y (Å)  | Z (Å)  |
|---------------|--------|--------|--------|---------------|--------|--------|--------|
| 1             | 0.0000 | 1.0982 | 2.1963 | 7             | 2.1963 | 0.0000 | 3.2945 |
| 2             | 0.0000 | 2.1963 | 1.0982 | 8             | 3.2945 | 0.0000 | 2.1963 |
| 3             | 0.0000 | 2.1963 | 3.2945 | 9             | 1.0982 | 2.1963 | 0.0000 |
| 4             | 0.0000 | 3.2945 | 2.1963 | 10            | 2.1963 | 1.0982 | 0.0000 |
| 5             | 1.0982 | 0.0000 | 2.1963 | 11            | 2.1963 | 3.2945 | 0.0000 |
| 6             | 2.1963 | 0.0000 | 1.0982 |               | 3.2945 | 2.1963 | 0.0000 |

Further, the following properties of the cubic diamond-like CA6 phase were determined: density, cohesive energy, bulk modulus and Vickers hardness. The cohesive energy, density, hardness and bulk modulus of a new structural modification of diamond are lower than these properties of 3C diamond polytype by 5.3, 17.5, 18.1 and 21.1%, respectively.

The electronic properties of cubic diamond-like CA6 phase were studied using the band structure and the density of electronic states (DOS) calculations. Figure 2a shows the band structure of this phase. The electron energy was calculated with six intervals between four points of high symmetry in the Brillouin zone: ΓN, NH, HΓ, ΓP, PN, and PH. The minimum difference in the electron energies between the bottom of the conduction band and the top values of the valence band is 4.72 eV and is observed at 1/3 of the length of the HΓ vector. As a result of the DOS calculation (figure 2b), the magnitude of the indirect band gap of the diamond-like CA6 phase is determined, and its value is 3.96 eV. Therefore, the studied structural variety of diamond is a wide-gap semiconductor with an indirect band gap, which is 27% less than the corresponding value for 3C diamond polytype.

The thermal stability of the cubic diamond-like CA6 phase was studied by the molecular dynamics method. The structure was annealed for 8 ps at a constant temperature of 400 K. The graph of the total energy change from the annealing time is shown in figure 3. As a result of the calculation it was established that the CA6 phase crystal lattice is stable when the temperature is above room temperature.
To enable experimental identification of the theoretically predicted phase, the calculation of its X-ray diffraction pattern was performed. The calculated powder X-ray diffraction patterns of the cubic diamond and the diamond-like CA6 phase are shown in figure 4. The positions of the most intense diffraction lines of the CA6 phase differs significantly from the positions of the diffraction maxima of the cubic diamond, which should allow its uncomplicated identification in the synthesized carbon materials.

**Figure 2.** Band structure (a) and DOS (b) of diamond-like CA6 phase.

**Figure 3.** Dependence of the total energy on annealing time for diamond-like CA6 phase.
Figure 4. Powder X-ray patterns of the cubic diamond (a) and the CA6 phase (b).

4. Conclusions
As a result of the calculations performed by the density functional theory method, a geometrically optimized structure and some properties of the cubic diamond-like CA6 phase are determined. The structure of this polymorph can be formed by linking carbon fullerene-like C$_{24}$ clusters in the form of truncated octahedra. The calculated properties of the CA6 phase are close in values to the properties of the 3C diamond polytype. Thus, the density, cohesion energy, Vickers hardness, and bulk modulus of this phase are 5-20 % lower than the corresponding properties of the cubic diamond. The CA6 phase should be a wide-gap semiconductor with a direct band width of ~ 4.7 eV. The energy and mechanical characteristics of the cubic CA6 phase, studied in detail in this paper, exceed the corresponding properties of most diamond-like phases with equivalent atomic positions [1-6,9]. It was also found that the structure of this phase is stable at a temperature of 400 K which indicates a high probability of its experimental production.

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