Formation of a nanostructured diamond-like phase from $C_{48}$ clusters: Ab initio calculations

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Abstract. A new fullerene-like cluster $C_{48}$ and a nanostructured cubic diamond-like phase formed from an ordered condensate of these clusters were theoretically investigated. Calculations of structures, properties and stability were performed using the density functional theory method. It was found that the new cluster should be stable under normal conditions. As a result of the hydrostatic compression of the $C_{48}$ clusters, a high-strength semiconducting diamond-like phase, called CA7, can be obtained at 26.5 GPa. The CA7 phase can be unambiguously identified experimentally using a calculated powder X-ray diffraction pattern.

1. Introduction
Nanostructures consisting of carbon atoms are used in the manufacture of lithium-ion batteries, hydrogen storage systems, supercapacitors, catalysts, sensors, and composite materials [1]. Such carbon nanostructures as graphene layers, nanotubes, and fullerenes are also used for the experimental production of superhard diamond-like materials at high pressures [2]. However, there are a number of hypothetical nanostructures of three-coordinated carbon atoms predicted in [3], which are more promising precursors for the formation of new nanostructured diamond-like phases [2]. These precursors include fullerene-like clusters, on the surface of which there are quadrangular or octagonal faces, but there are no pentagonal faces [3-5]. The most promising fullerene-like cluster is $C_{48}$, the shape of which is similar to that for the synthesized $B_{24}N_{24}$ nanostructure [6]. Therefore, this study is devoted to ab initio calculations of the structure and thermal stability of the new fullerene-like $C_{48}$ cluster, as well as to the study of the crystal structure, properties, and the synthesis process of a nanostructured diamond-like phase formed from these clusters.

2. Methods
Calculations of the crystal structures and electronic properties of diamond, fullerene-like $C_{48}$ clusters and nanostructured diamond-like phase were carried out by the density functional theory (DFT) method in the generalized gradient approximation (GGA) [7] using the Quantum ESPRESSO software package [8]. The norm-preserving Troullier-Martins pseudopotentials [9] and $8 \times 8 \times 8$ $k$-point grids were used for the calculations. The cutoff energy ($E_{\text{cutoff}}$) in the plane wave basis was 800 eV. The study of the thermal stability of the $C_{48}$ cluster was carried out using the DFT-GGA and molecular dynamics methods.

The bulk modulus of the diamond-like phase was calculated using the modified Kumar-Sharma equation of state [10]. The Vickers hardness was calculated according to the method proposed by Gao et al. [11]. A theoretical study of the structural transformation of the $C_{48}$ cluster condensate into the...
nanostructured diamond-like phase was carried out under the hydrostatic compression of the initial condensate according to the method described in [12, 13]. Also, X-ray diffraction patterns of carbon compounds were calculated for the Cu-Kα1 characteristic radiation according to the standard procedure [14].

3. Results
The optimized structure of the new C_{48} cluster, which has the shape of a truncated cuboctahedron and belongs to the m3m point symmetry group, is shown in figure 1. The surface of this cluster consists of 4-, 6-, and 8-sided faces and differs from the C_{48} fullerene, on the surface of which there are only 5- and 6-sided faces. The DFT-GGA calculations showed that all atoms on the surface of the fullerene-like C_{48} cluster are in equivalent crystallographic positions. Three different lengths of interatomic bonds (0.1397, 0.1478, and 0.1488 nm) and three angles between these bonds (90.0, 120.0, and 135.0°) correspond to each atomic position. The diameter and the Wells ring parameter (Rng [16]) of this cluster are 0.6710 nm and 4.618, respectively.

Figure 1. Model transformation of the structure of the fullerene-like C_{48} cluster condensate (a) into the structure of the diamond-like CA7 compound (b).

The cohesion energy (E_{coh}) of the C_{48} cluster was calculated as the difference between the total energies of isolated atoms and atoms in bound states. The calculated E_{coh} value is 7.00 eV/atom and is 10.9 % less than the corresponding value for 3C diamond, which was calculated by the DFT-GGA method in [15, 16]. In addition, the cohesion energy of the C_{48} cluster is lower than those for almost all diamond-like T- and S-phases (with the exception of SA2 and SA4); therefore, the molecular dynamics study of the stability of this cluster was carried out at room temperature. The isothermal annealing was simulated for 8.5 ps with a time step of 1 fs. The graph of the change in the total energy (E_{total}) versus the time of heat treatment is shown in figure 2. As a result of the annealing, the fullerene-like C_{48} cluster turned out to be stable at normal temperature. However, a slight deformation of the structure and a significant rotation of the C_{48} cluster with respect to the equilibrium position at the center of a simple cubic unit cell are observed during the annealing process.

An analysis of the C_{48} cluster structure showed that a porous material with a diamond-like structure of the CA7 phase described in [2] can be obtained on its basis (figure 1b). To obtain the CA7 phase, a condensate from the C_{48} clusters is required having a simple cubic (sc) lattice belongs to the Pm3m space symmetry group (figure 1a). Figure 3 contains graphs of the dependences of the difference total energy ΔE_{total} (relative to the total energy of the C_{48} condensate at zero pressure) on the atomic volume V_{at} under
bulk uniform deformations. It was found that the formation of the diamond-like CA7 phase is possible upon hydrostatic compression of the sc C_{48} condensate, when the pressure reaches 26.5 GPa. The formation pressure value of the CA7 phase is much less than the corresponding values for the formation of diamond-like compounds from graphite [12, 13, 17-21]. During the direct phase transition, it is necessary to overcome the energy barrier of 0.22 eV/atom.

Figure 2. Calculated dependence of the total energy change on the time of annealing for the C_{48} cluster at room temperature.

Figure 3. Dependences of the difference total energy on the atomic volume, characterizing the structural transformation "sc C_{48} condensate → CA7 phase".

At the next stage of the work, the mechanical and electronic properties of the new nanostructured phase from the polymerized C_{48} clusters were investigated. The bulk modulus ($B_0$) was defined in the range of relative volume change from 0 to 5.8 %. The $B_0$ value was 270 GPa, which is 39 % less than
the corresponding value for diamond. The calculated Vickers hardness for the CA7 phase is 66.4 GPa. This value is only 26.2% less than the calculated value for cubic diamond. The band structure of this phase, calculated by the DFT-GGA method, is shown in figure 4. The electron energies were calculated over six intervals (ΓN, NP, PN, NH, HP, and PΓ) between four high symmetry points (Γ, N, P, and H) in the Brillouin zone. The minimum direct band gap of the diamond-like CA7 phase, calculated as the difference between the electron energy of the conduction band bottom and the electron energy of the valence band top, is observed at the Γ point (i.e., at the center of the Brillouin zone) and is equal to 3.75 eV. This value is less than those for cubic diamond by 36.6%. The electronic density of states (DOS) of the diamond-like CA7 phase was also calculated (figure 4). Using the calculated DOS-pattern, the minimum band gap value of the nanostructured CA7 phase was determined to be 3.34 eV. Therefore, this cubic diamond-like phase should be a wide-gap semiconductor with an indirect band gap.

![Figure 4](image_url)

*Figure 4.* The band structure and the density of electronic states of the CA7 phase, calculated using the DFT-GGA method (zero on the energy scale corresponds to the Fermi energy).

For the experimental identification of the studied nanostructured CA7 phase in synthesized carbon materials, the calculation of its powder X-ray diffraction pattern was performed. Figure 5 shows the calculated X-ray diffraction patterns of cubic diamond, initial condensate from the fullerene-like C₄₈ clusters, and diamond-like CA7 phase. It was found that the X-ray diffraction pattern of the CA7 phase contains only three most intense diffraction maxima corresponding to the following interplanar distances: 0.3083, 0.3776, and 0.5340 nm. The positions of these diffraction maxima differ significantly from the positions of the diffraction maxima of cubic diamond and the initial condensate from the C₄₈ clusters; therefore, the new nanostructured CA7 phase can be unambiguously identified in experimentally obtained carbon materials.
Figure 5. Calculated powder X-ray diffraction patterns of the following carbon compounds: (a) cubic diamond; (b) C_{48} cluster condensate; (c) nanostructured CA7 phase.

4. Conclusions
An \textit{ab initio} study of a new fullerene-like C_{48} cluster and a nanostructured diamond-like CA7 phase based on polymerized C_{48} fullerite was carried out in this work. The DFT calculations showed that the C_{48} cluster, consisting of 4-, 6-, and 8-membered structural units, should be stable at room temperature. It was also found that the transformation of the condensate from these fullerene-like clusters into the porous cubic diamond-like phase CA7 can occur at a pressure of 27 GPa. This diamond-like phase must have high mechanical characteristics and can exhibit the properties of a wide-gap semiconductor. The calculated X-ray diffraction pattern of the nanostructured CA7 phase can be used for its experimental identification in carbon materials.

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References
[1] Morandi V and Ottaviano L 2017 GraphITA: Selected Papers from the Workshop on Synthesis, Characterization and Technological Exploitation of Graphene and 2D Materials Beyond Graphene. Carbon Nanostructures (Cham: Springer International Publishing AG) 221 p
[2] Belenkov E A and Greshnyakov V A 2016 Phys. Solid State \textbf{58} 2145
[3] Belenkov E A and Greshnyakov V A 2013 Phys. Solid State \textbf{55} 1754
[4] Krylova K A, Baimova Y A, Dmitriev S V and Mulyukov R R 2016 Phys. Solid State \textbf{58} 394
[5] Kang S, Xiang Z, Mu H and Cai Y 2020 Phys. Lett. A \textbf{384} 126035
[6] Pokropivny V V, Smolyar A S, Ovsianikova L I, Pokropivny A V, Kuts V A, Lyashenko V I and Nesterenko Y V 2013 Phys. Solid State \textbf{55} 878
[7] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. \textbf{77} 3865
[8] Giannozzi P \textit{et al.} 2017 \textit{J. Phys.: Condens. Matter.} \textbf{29} 465901
[9] Troullier N and Martins J L 1991 Phys. Rev. B \textbf{43} 1993
[10] Greshnyakov V A and Belenkov E A 2014 Russ. Phys. J. \textbf{57} 731
[11] Gao F, He J, Wu E, Liu S, Yu D, Li D, Zhang S and Tian Y 2003 Phys. Rev. Lett. \textbf{91} 015502
[12] Belenkov E A and Greshnyakov V A 2018 Phys. Solid State \textbf{60} 1294
[13] Greshnyakov V A, Belenkov E A and Brzhezinskaya M M 2019 Phys. Status Solidi B \textbf{256} 1800575
[14] Guinier A 1964 *Theorie et technique de la radiocristallographie. 3rd edition* (Paris: A. Dunod) 740 p
[15] Belenkov E A and Greshnyakov V A 2015 *J. Mater. Sci.* **50** 7627
[16] Belenkov E A and Greshnyakov V A 2015 *Phys. Solid State* **57** 1253
[17] Baimova J A and Rysaeva L K 2018 *J. Struct. Chem.* **59** 884
[18] Rysaeva L K, Baimova J A, Lisovenko D S, Gorodtsov V A and Dmitriev S V 2019 *Phys. Status Solidi B* **256** 1800049
[19] Baimova J A, Galiakhmetova L K and Mulyukov R R 2021 *Comput. Mater. Sci.* **192** 110301
[20] Fan D, Lu S, Golov A A, Kabanov A A and Hu X 2018 *J. Chem. Phys.* **149** 114702
[21] Zhou Y, Chen X, Liu S-Li and Gan Li-H. 2021 *Solid State Commun.* **323** 114095