Investigation of a new $C_{24}$ cluster for obtaining diamond-like phases: first-principle calculations

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Abstract. In this work, first-principle calculations of the structure of a new fullerene-like $C_{24}$ cluster are carried out. The surface of this cluster is formed of four- and six-membered atomic rings. It is established that these clusters should be stable under normal conditions. A simple cubic fullerite based on the $C_{24}$ clusters can be used to synthesize the diamond-like CA4 phase under bulk compression up to 4.8 GPa. In addition, X-ray diffraction patterns of the «fullerite $C_{24} \rightarrow$ CA4 phase» structural transition are calculated.

1. Introduction
Carbon nanostructures are used as catalysts, adsorbents, structural elements of nanoelectronic devices and nanocomposites. They can also be used as precursors for new diamond-like and hybrid materials. Such precursors include graphene [1-3], carbon nanotubes [4-6], fullerenes [7-9], and a large number of hypothetical graphite-like nanostructures [10, 11]. One of the promising hypothetical nanostructures is a cubic cluster $C_{24}$ similar to a truncated octahedron [11-13]. Various porous diamond-like phases with equivalent atomic positions can be obtained from these clusters [12-14]. The theoretical analysis, which was carried out in [11], showed that the most likely to obtain the porous diamond-like CA4 phase from a fullerite $C_{24}$. Therefore, first-principle calculations of the thermal stability of the $C_{24}$ cluster and the process of obtaining the diamond-like CA4 phase from the fullerite $C_{24}$ are performed in this work.

2. Methods
Geometric optimization of the structures and calculations of the total energy of carbon clusters and phases are carried out in the Quantum ESPRESSO program package [15] using the density functional theory (DFT) method [16] in the generalized gradient approximation (GGA) [17]. Modelling of the direct structural transitions of graphite-like $C_{24}$ phase into diamond-like CA4 phase under uniform bulk compression of fullerite was performed using the technique described in [18, 19]. The norm-conserving pseudopotentials and the $10 \times 10 \times 10$ grids of $k$-points were used for the calculations. The cutoff energy for the basis of plane waves was 60 Rydberg.

The thermal stability of the $C_{24}$ cluster was investigated using the molecular dynamics method with the time step of 0.5 fs and the $6 \times 6 \times 6$ $k$-point grid. The X-ray diffraction patterns of the «fullerite $C_{24} \rightarrow$ diamond-like CA4 phase » structural transition were calculated by the standard technique for the characteristic $K_{\alpha1}$ copper radiation.
3. Results
As a result of DFT calculations, it is found that the optimized structure of the $C_{24}$ cluster has the shape of a truncated octahedron (the point symmetry group is $m3m$) (figure 1a). The Cartesian coordinates of the atomic positions of this cluster are given in table 1. Each atomic position is characterized by three lengths of interatomic bonds ($L_1 = 1.395 \text{ Å}, L_2 = L_3 = 1.505 \text{ Å}$) and three angles between bonds ($\beta_{12} = \beta_{13} = 120^\circ, \beta_{23} = 90^\circ$).

![Figure 1](image1.png)

Figure 1. The structures of carbon compounds: (a) simple cubic fullerite $C_{24}$; (b) diamond-like CA4 phase.

| Atomic number | $X$ (Å) | $Y$ (Å) | $Z$ (Å) | Atomic number | $X$ (Å) | $Y$ (Å) | $Z$ (Å) |
|---------------|---------|---------|---------|---------------|---------|---------|---------|
| 1             | 0.987   | 2.051   | 0.000   | 13            | 0.000   | 2.051   | 0.987   |
| 2             | 3.116   | 0.000   | 2.051   | 14            | 2.051   | 0.000   | 3.116   |
| 3             | 0.987   | 2.051   | 4.102   | 15            | 4.103   | 2.051   | 0.986   |
| 4             | 3.116   | 4.102   | 2.051   | 16            | 2.051   | 4.102   | 3.115   |
| 5             | 2.051   | 0.987   | 0.000   | 17            | 0.987   | 0.000   | 2.051   |
| 6             | 0.000   | 3.116   | 2.051   | 18            | 3.116   | 2.051   | 0.000   |
| 7             | 2.051   | 0.987   | 4.102   | 19            | 0.987   | 4.103   | 2.051   |
| 8             | 4.102   | 3.116   | 2.051   | 20            | 3.116   | 2.051   | 4.102   |
| 9             | 0.000   | 0.987   | 2.051   | 21            | 2.051   | 0.000   | 0.987   |
| 10            | 2.051   | 3.116   | 0.000   | 22            | 0.000   | 2.051   | 3.116   |
| 11            | 4.103   | 0.987   | 2.051   | 23            | 2.051   | 4.103   | 0.986   |
| 12            | 2.051   | 3.116   | 4.102   | 24            | 4.102   | 2.051   | 3.115   |

The calculated cohesive energy of the $C_{24}$ cluster is 6.70 eV/atom, which is 14.8 % less than the corresponding value for cubic diamond calculated in [11, 19]. To assess the thermal stability of the new fullerene-like cluster, its structure was annealed at 300 K using the molecular dynamics method. The graph of the total energy change ($E_{\text{total}}$) versus the annealing time is shown in figure 2. As a result of the annealing over 7 ps, neither destruction nor strong deformation of the structure is observed, which indicates the stability of the $C_{24}$ cluster under normal conditions. Only the $C_{24}$ cluster rotation
relative to the equilibrium position in the simple cubic lattice is observed; therefore, the graph characterizing this process differs significantly from the standard relaxation graph.

![Figure 2. Dependence of the total energy on the annealing time for the cluster C_{24} at 300 K.](image2)

At the next stage of the study, the simulation of the direct phase transition of a simple cubic (sc) fullerite C_{24} (figure 1a) to the low-density diamond-like CA4 (figure 1b) phase is performed. The crystal lattices of the initial fullerite C_{24} and final CA4 phase belong to the space group Pm3m. In the process of bulk compression of the fullerite C_{24}, the formation of the CA4 phase occurs when the energy barrier of 0.36 eV/atom is overcome and the pressure reaches 4.8 GPa (figure 3). For this phase transition, X-ray diffraction patterns were calculated during compressing the fullerite and decompression of the formed CA4 phase. This first-order phase transition is accompanied by a significant change in the diffraction pattern, in which many of the original low-intensity maxima disappear, and many new maxima appear (figure 4). The theoretical X-ray diffraction pattern of the new diamond-like CA4 phase can be used for its experimental identification.

![Figure 3. Dependence of the total energy difference on the atomic volume for the simple cubic fullerite C_{24} and diamond-like CA4 phase.](image3)
4. Conclusions

Thus, theoretical calculations of the stability and the possible method of applying the new fullerene-like C_{24} cluster, the surface of which is formed from four- and six-membered atomic rings, are carried out. The DFT calculations showed that these clusters should be stable at room temperature. It is also found that the simple cubic fullerite from C_{24} clusters can be used to synthesize the porous diamond-like CA4 phase during bulk compression up to 4.8 GPa. For experimental identification of the sc fullerite C_{24} and CA4 phase, the calculated X-ray diffraction patterns can be used.

Acknowledgments

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Figure 4. Theoretical powder X-ray diffraction patterns for the «simple cubic fullerite C_{24} → diamond-like CA4 phase» structural transition.
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