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Modeling of synthesis pathways for diamond-like polycyclobutane phases

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In this paper, the investigation of possible methods for obtaining two diamond-like polycyclobutane LA3 and LA5 phases was carried out using the density functional theory method. The calculations were performed in the local density approximation and the generalized gradient approximation. It was established that the structures of the polycyclobutane phases can be formed on the basis of layer precursors made of hexagonal L_6 graphene and tetragonal L_{4-8} graphene. Tetragonal LA3 phase can be obtained from hexagonal L_6 graphite with AA packing at pressures from 59 to 67 GPa. Another way to obtain this phase is compression of tetragonal L_{4-8} graphite AB in the pressure range from 50 to 52 GPa. Orthorhombic LA5 phase can be obtained from orthorhombic L_6 graphite AB and hexagonal L_6 graphite AA in the pressure ranges from 64 to 71 GPa and from 59 to 67 GPa, respectively. Also, this phase can be formed under compression of tetragonal L_{4-8} graphite AB when the pressure reaches 46 – 50 GPa. The minimum values of the energy barriers separating the structural states corresponding to diamond LA3 and LA5 polymorphs from the states corresponding to different types of graphite are in the range from 0.09 to 0.29 eV/atom, which indicates the stability of these phases under normal conditions. For the experimental identification of diamond-like LA5 phase formed during the compression of orthorhombic graphite along the crystallographic axis [001], a series of the X-ray diffraction patterns of the carbon material in which this phase transition takes place was calculated.

Keywords: graphene, diamond, diamond-like phase, phase transition, *ab initio* calculations.

1. Introduction

Diamond-like compounds have superior strength and optical properties and exhibit high corrosion resistance [1, 2]. Monocrystalline, thin-film, and nanocrystalline diamond-like materials are used in the production, which, as a rule, have structures of cubic diamond and its polytypes, as well as amorphous sp^3-carbon [1 – 3]. As shown by numerous theoretical studies, materials based on new structural modifications of diamond called diamond-like phases [4 – 7] can be very promising for practical application. Currently, more than a hundred of such phases are predicted that can be obtained from various graphite-like precursors [5, 8 – 10]. Among these diamond-like phases, the most interesting for researchers are the superhard phases LA3 (polycyclobutane) and LA5 (*Y*-carbon), crystal structures of which are formed by polymerized cyclobutane rings [5, 8, 11 – 14]. However, to date, detailed studies of possible methods for obtaining the structures of phases LA3 and LA5 have not been carried out. Therefore, in this work, the first principle modeling of the formation of two polycyclobutane diamond-like phases LA3 and LA5 based on hexagonal and tetragonal graphene layers is performed.

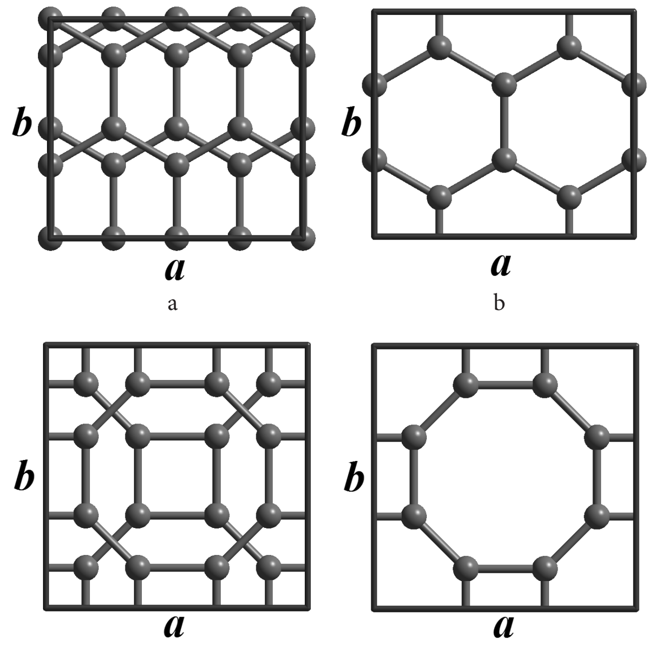
2. Calculation methodology

The crystal structures and energy parameters of carbon compounds were calculated in the Quantum ESPRESSO software package [15] by the density functional theory (DFT) method using the exchange-correlation energy functionals in the formulations of Perdew-Zunger (PZ) [16] and Perdew-Burke-Ernzerhof (PBE) [17]. For integration in the Brillouin zones, sets of k-points 12 × 12 × 12 were used. To limit the dimension of the set of basis functions, the cutoff energy was taken equal to 60 Rydberg. Theoretical calculations of phase transitions of various structural modifications of graphites to diamond-like phases under uniaxial deformations were performed according to the method from [10, 18]. Theoretical powder X-ray diffraction patterns of carbon compounds were calculated by compression and decompression for the characteristic radiation of Cu-$K_{\alpha 1}$.

3. Results and discussion

As a result of the analysis of possible methods for producing diamond-like compounds, it was found that the phases LA3 and LA5 can be formed from graphites L_6 AB (Cmmm) and AA (P6/mmm), as well as from tetragonal graphites L4–8 AB (I4/mmm) and AA (P4/mmm). To study the structural transformations of graphites (Fig. 1) into diamond-like phases LA3 and LA5 (Fig. 2), orthorhombic unit cells containing 16 atoms were used. Table 1 shows the equilibrium parameters of the unit cells of graphite and diamond-like phases, calculated in the absence of external stresses.

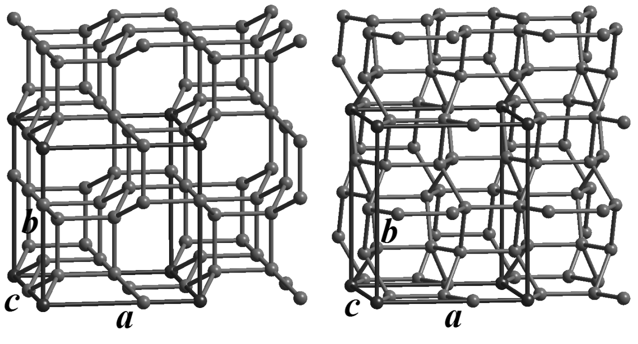
Structural transformations between graphites and diamond-like phases were simulated by compressing all



a b

c d

Fig. 1. Unit cell projections of L_6 graphite with layer packing AB (a) and AA (b), and also $L_{4\text{–}8}$ graphite with packing AB (c) and AA (d) on the (001) plane.



a b

Fig. 2. Crystalline structure fragments and unit cells of LA3 (a) and LA5 (b) diamond-like phases.

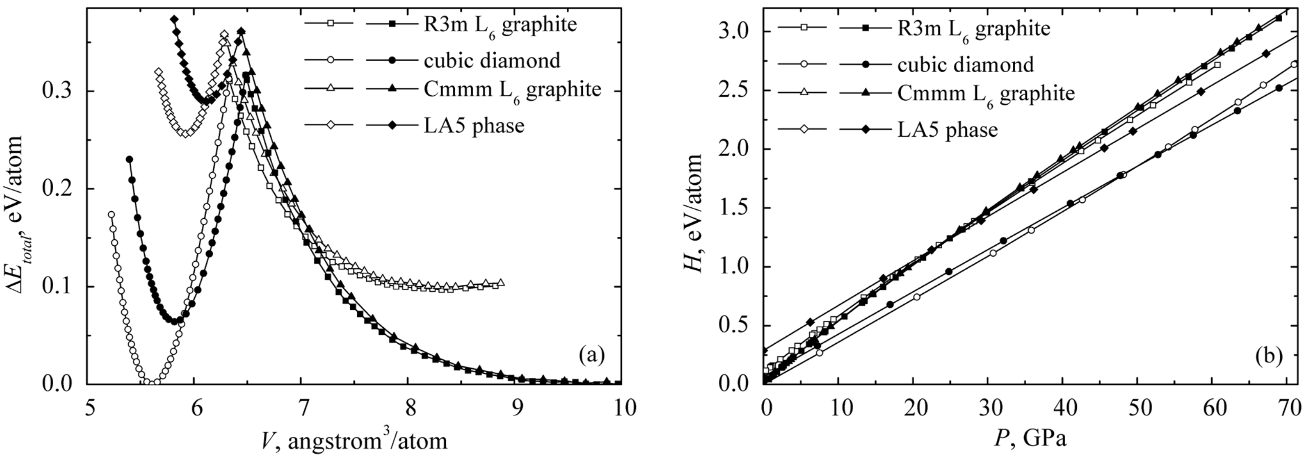
Table 1. The parameters of orthorhombic unit cells for carbon compounds calculated by the DFT-PZ and DFT-PBE methods (the values obtained by the DFT-BPE method are indicated in parentheses).

Phase	*a*, Å	*b*, Å	*c*, Å	*Z*, at.
L_6 AB	4.265 (4.308)	4.931 (4.977)	6.428 (7.214)	16
L_6 AA	4.927 (4.975)	4.265 (4.308)	6.745 (7.708)	16
$L_{4\text{-}8}$ AB	4.867 (4.905)	4.867 (4.905)	6.006 (7.244)	16
$L_{4\text{-}8}$ AA	4.866 (4.905)	4.866 (4.905)	6.008 (7.245)	16
LA3	4.353 (4.401)	4.353 (4.401)	5.002 (5.055)	16
LA5	4.337 (4.386)	5.025 (5.080)	4.349 (4.393)	16

graphites along the crystallographic direction [001], while the structures of the phases LA3 and LA5 were deformed along the directions [100], [010] and [001]. The dependences of the difference total energy (ΔE_{total}) on the volume (V) for Cmmm of graphite L_6 and the orthorhombic phase LA5 (deformation along the [010] axis), characterizing phase transitions between these compounds, are shown in Fig. 3a. Also Fig. 3a shows the ΔE_{total} and V values for the structural transition of rhombohedral graphite L6 ABC ($R\bar{3}m$) into cubic diamond, which are necessary for a comparative analysis of the conditions for the formation of polycyclobutane phases. The structural transformation of graphite into the LA5 phase can occur at pressures (P) from 64.0 to 71.4 GPa as a result of overcoming the potential barrier, which exceeds the $\Delta E_{G\text{-}D}$ of diamond formation by 14 – 20%. The direct phase transition will be accompanied by an increase in the system density by 9% with a change in the enthalpy from –0.29 to –0.25 eV/atom (Fig. 3b), which indicates the exothermic nature of the first-order phase transition. For reverse structural transformation into graphite, the stress should exceed 75 GPa. In this case, the barrier $\Delta E_{D\text{-}G} = 0.07 – 0.10$ eV/atom and can correspond to the structural transformation temperature (T_{trans}) of ~ 560 – 790 K.

The results of calculations of the structural and energy parameters for P6/mmm of graphite L6, diamond-like phases LA3 and LA5, as well as intermediate states of these compounds are shown in Fig. 4. The deformation of the structures of the phases LA3 and LA5 was carried out along the [100] axes. The minimum pressure of the direct phase transition is characteristic for the formation of the tetragonal phase LA3 (58.8 – 66.8 GPa) and corresponds to $\Delta E_{G\text{-}D} = 0.292 – 0.400$ eV/atom, whereas the rhombic phase LA5 can be formed at a higher pressure (59.0 – 67.2 GPa), corresponding to $\Delta E_{G\text{-}D} = 0.294 – 0.404$ eV/atom (Fig. 4a). All direct phase transitions will be exothermic, since $\Delta H_{G\text{-}D}$ is in the range from –0.46 to –0.34 eV/atom (Fig. 4b). The reverse structural transformation of the phases LA3 and LA5 to graphite will occur in the process of overcoming the energy barriers of 0.128 – 0.164 and 0.120 – 0.154 eV/atom, respectively (Fig. 4a), which can occur at T_{trans} ~ 930 –1260 K.

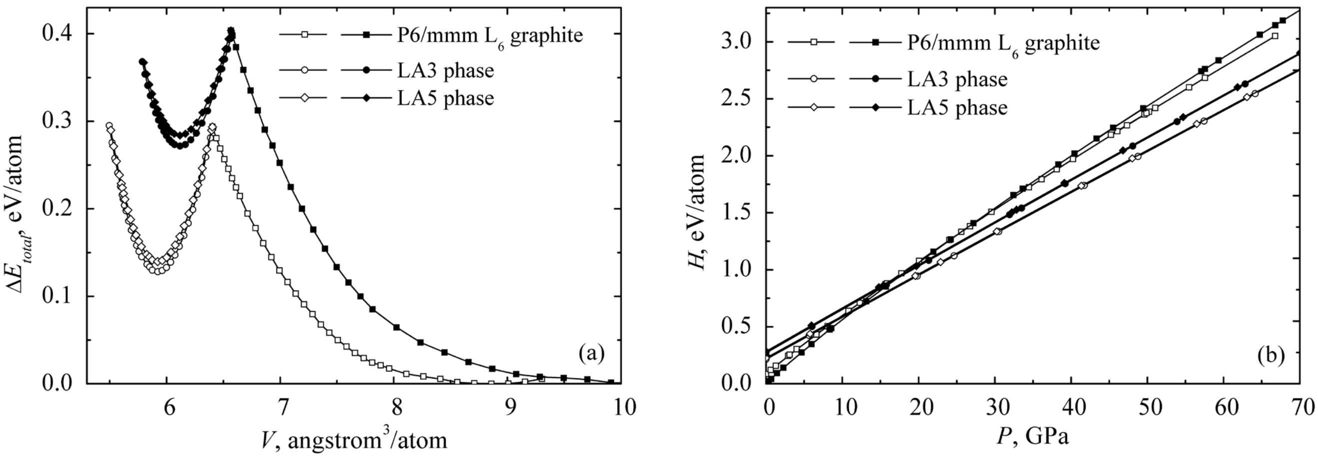
Graphs characterizing the structural transformations of tetragonal graphites $L_{4\text{–}8}$ into phases LA3 and LA5 are shown in Fig. 5. To evaluate the $\Delta E_{D\text{-}G}$ phases of LA3 and LA5, orthorhombic diamond-like phases LA6 and LA7, whose unit cells contained 16 atoms, were also considered. The structures of the phases LA3, LA5, LA6, and LA7 were deformed in the directions [001], [001], [010], and [100], respectively. Direct structural transitions of graphite $L_{4\text{–}8}$ AB to phases LA5 and LA7 occur at 45.5 – 49.9 and 42.5 – 46.4 GPa, respectively. Modification of graphite $L_{4\text{–}8}$ with AA packing is converted to phases LA3 and LA6, respectively, at pressures of 49.8 – 51.9 and 43.9 – 44.2 GPa. $\Delta E_{G\text{-}D}$ energy barriers take the following values: 0.207 – 0.295 (LA3), 0.195 – 0.283 (LA5), 0.158 – 0.230 (LA6), and 0.176 – 0.253 (LA7) eV/atom (Fig. 5a). The formation of phases LA3 and LA5 from graphites $L_{4\text{–}8}$ AB and AA is less likely, since the pressures required to obtain them are 7 –18% higher than the corresponding values for phases



a

b

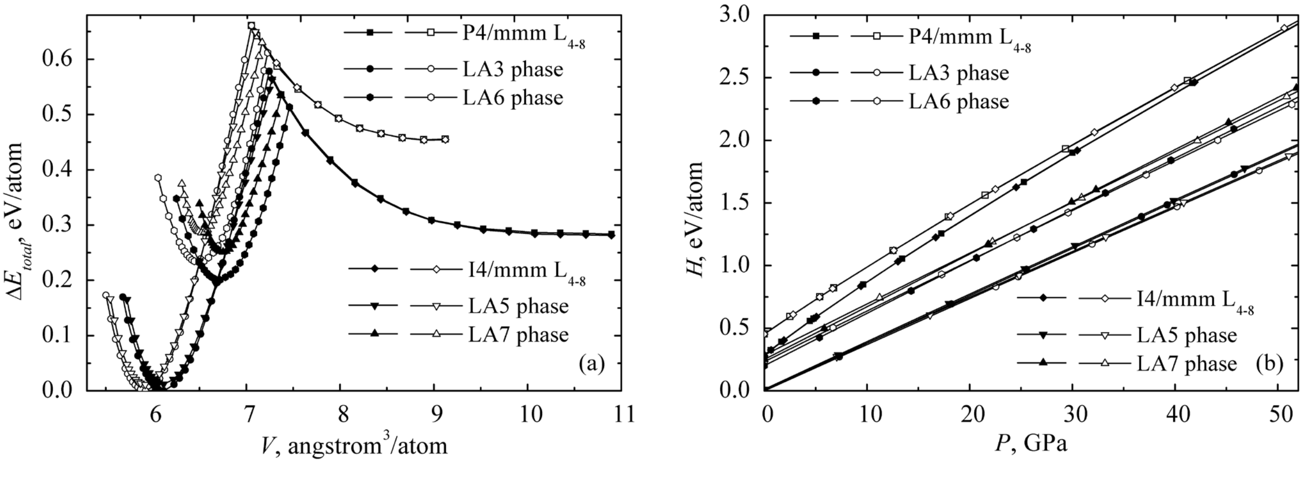
Fig. 3. Dependences of the difference total energy on the atomic volume (a) and the enthalpy on the pressure (b) for phase transitions of L_6 graphite AB into LA5 phase, as well as L_6 graphite ABC into cubic diamond (white and black fill of markers correspond to the DFT-PZ and DFT-PBE methods).



a

b

Fig. 4. Dependency graphs of $E_{total}=f(V)$ (a) and $H=f(P)$ (b) for structural transitions of P6/mmm L_6 graphite into LA3 and LA5 phases (black markers are DFT-PZ, white markers are DFT-PBE).



a

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Fig. 5. Dependences of $E_{total} = f(V)$ (a) and $H = f(P)$ (b) for structural transitions of L_{4-8} graphites into LA3 and LA5 phases (black markers are DFT-PZ, white markers are DFT-PBE).

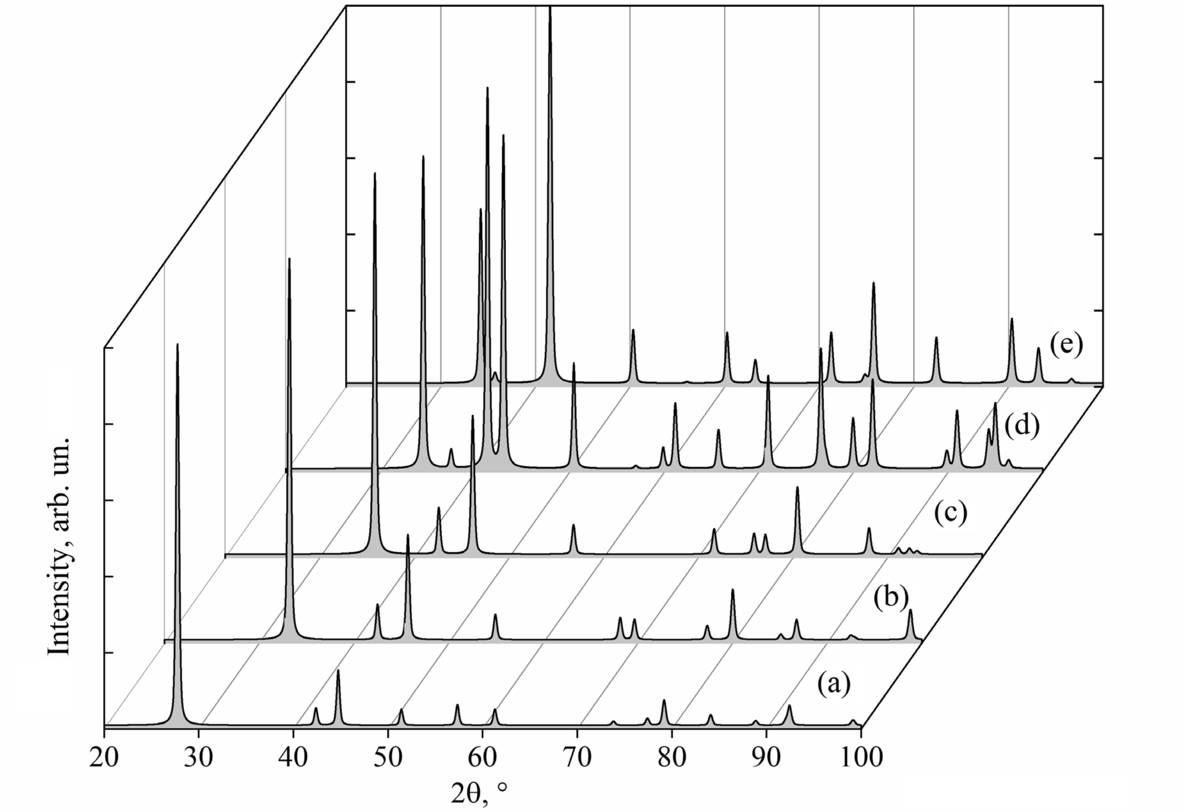

Fig. 6. Powder X-ray patterns of carbon compounds under strong compression and decompression: (a), (b) and (c) are I4/mmm L_6 graphite at 0, 20 and 44 GPa, respectively; (d) and (e) are LA5 phase at 64 and 0 GPa, respectively.

LA6 and LA7. For the reverse structural transformation of diamond polymorphs into graphite under tension, the total energy of the phases LA3, LA5, LA6, and LA7 should be increased by 0.233 – 0.251, 0.201 – 0.292, 0.313 – 0.379, and 0.113 – 0.283 eV/atom (Fig. 5 a), respectively. Direct phase transitions of L_{4-8} graphites to diamond polymorphs are exothermic phase transitions of the first kind, which will result in a jump decrease in the system volume by 9.9 – 18.7% with the release of energy in the form of heat ~ 0.52 – 1.04 eV/atom (Fig. 5 b).

The results of estimating the temperatures of the reverse phase transitions of the polycyclobutane phases LA3 ($T \sim 990 - 1260$ K) and LA5 ($T \sim 560 - 790$ K) to graphite are also in good agreement with experimental data on the thermal stability of saturated hydrocarbons. So, for example, tetraasterane, which is a structural unit of LA3, can stably exist up to a temperature of 770 K [19]. The underestimated value of T_{trans} for the LA5 phase, obtained by the DFT-PBE method, can be explained by the fact that the vibrations of all atoms during the transition will take place not only along the crystallographic directions along which the tension occurs.

Since hexagonal graphite with packing of layers AB is the most stable precursor of the considered diamond-like phases, X-ray diffraction patterns of the "L_6 AB → LA5 graphite" phase transition were calculated for experimental identification of the LA5 phase formed during compression of this graphite. When graphite is compressed along the [001] axis to a pressure of 64 GPa, its most intense maximum 002 shifts strongly toward large angles (from 27.8 to 37.6°) (Fig. 6 a – c). As a result of the phase transition, the diffraction pattern changes significantly, since the initial low-intensity maxima disappear and a number of new maxima appear (Fig. 6 d). During decompression of the formed LA5 phase, a significant change in the intensities and angular positions of most of the maxima is also observed (Fig. 6 e).

4. Conclusion

Thus, the first principle modeling of possible methods for producing the polycyclobutane LA3 and LA5 phases was performed. It was established that these diamond-like phases can be obtained as a result of strong compression of varieties of ordinary graphite along the [001] axis in the pressure range from 59 to 71 GPa. Another possible synthesis method is uniaxial compression of tetragonal graphite crystals at a pressure of ~ 46 – 52 GPa. The studied structural transformations of graphites into polycyclobutane phases are first-order phase transitions and should be accompanied by heat evolution of ~ 0.3 – 1.0 eV/atom. The calculations also showed that the LA3 and LA5 phases can stably exist under normal conditions.

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