Theoretical investigation of the deformation stability and thermostability of carbon diamond-like phases

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Abstract. In this work, first-principle calculations of the mechanical and thermal stability of diamond-like LA3 and LA5 phases with equivalent atomic positions were carried out. It was established that these phases can be stable under uniaxial deformations in the pressure range from -62 to 85 GPa. The calculations also showed that LA3 and LA5 phases should be stable at a temperature of 500 K and normal pressure.

1. Introduction
To date, numerous theoretical studies of the structures and properties of new polymorphic modifications of diamond, called diamond-like nanostructures and phases, have been performed [1-8]. These diamond-like polymorphs can find wide practical application as anti-corrosion coatings, abrasive materials, and they can also be used in optics, electronics and medicine [9-11]. Diamond-like LA3 (bct C4) and LA5 (Y-carbon) phases the crystal structures of which are characterized by one Wyckoff position attract the greatest interest of researchers [12]. This is due to the fact that these phases must be superhard wide-gap semiconductors [1, 5, 12], and a large number of other diamond-like structures can be obtained on their basis. However, to date, detailed studies of the mechanical and thermal stability of LA3 and LA5 phases have not been carried out. Thus, the present work is devoted to a theoretical study the stability of these hypothetical diamond-like phases at high uniaxial stresses and high temperatures.

2. Methods
To solve the problem, the density functional theory (DFT) method implemented in the Quantum ESPRESSO software package [13] was applied. In the DFT method, the generalized gradient approximation (GGA) with the exchange-correlation energy functional in the formulation of Perdew-Burke-Ernzerhof [14] was used. The influence of the ion cores was taken into account through the norm-conserving pseudopotentials. The calculations were carried out for the following k-point grids: 14 × 14 × 14. The wave functions were decomposed by a truncated basis set of plane waves. The cutoff energy was 60 Rydberg.

The geometrical optimization of graphite and diamond-like phase unit cells was carried out until the values of atomic forces and stresses were less than 1 meV/Å and 0.1 GPa, respectively. The study of the mechanical stability of diamond-like phases was carried out using the technique from [15, 16]. The thermal stability of their structures was investigated by the method of molecular dynamics [17] at a temperature of 500 K.
3. Results

At the first stage of this work, the extended unit cells of diamond-like phases were geometrically optimized. It was found that diamond-like LA3 phase has a tetragonal unit cell with the parameters $a = b = 4.402$ Å, $c = 5.054$ Å and $Z = 16$, while LA5 phase has an orthorhombic unit cell with the parameters $a = 4.385$ Å, $b = 5.079$ Å, $c = 4.395$ Å and $Z = 16$. The calculated total energies ($E_{\text{total}}$) of LA3 and LA5 phases are $-154.58$ and $-154.57$ eV/atom, respectively. An analysis of the structures of these phases showed that the diamond-like LA3 and LA5 phases have the same Wells ring parameter [18] equal to $4^16^38^2$; therefore, the precursors of these phases are graphene layers $L_6$ and $L_{4-8}$ [19] with the ring parameters $6^3$ and $4^18^2$, respectively.

At the second stage of the work, the deformation stability of LA3 and LA5 phases was studied. The stability of diamond-like LA3 phase was studied in the process of uniaxial compression or stretching of the structure along the crystallographic [100]-, [010]- and [001]-axes. It was established that the phase is stable under compression along these directions at least up to 95 GPa (figure 1). When the structure of LA3 phase is stretched along the [100]- or [010]-axes, its destruction with further transformation to P6/mmm graphite occurs at 75 GPa, when the atomic volume ($V$) reaches 6.58 Å$^3$/atom (figure 1a). As the pressure decreases to zero, the expanded unit cell of the obtained graphite has the following parameters: $a = 4.9750$ Å, $b = 4.3076$ Å and $c = 7.7083$ Å. The stretching of LA3 phase along the [001]-axis leads to its transition to an intermediate diamond-like structure which immediately splits into $L_{4-8}$ tetragonal graphite P4/mmm at 88 GPa ($V = 6.70$ Å$^3$/atom) (figure 1b). The crystal lattice of $L_{4-8}$ graphite is characterized by the parameters $a = b = 4.9051$ Å and $c = 7.2448$ Å at 0 GPa.

![Figure 1](image1.png)

Figure 1. Dependences of the total energy difference ($\Delta E_{\text{total}}$) on the volume ($V$) during the deformation of LA3 phase along the following crystallographic axes: (a) [001]; (b) [100]. The geometrically optimized unit cells of LA3 phase, graphites and intermediate phases are given at normal pressure.

To study the destruction of orthorhombic LA5 phase, three main deformation directions were also chosen. The calculations showed that LA5 phase is stable under compression along the [100]-, [010]- and [001]-axes at least up to 85 GPa (figure 2). In the process of stretching the structure of LA5 phase along the [100]-axis, its transformation into P6/mmm graphite occurs at a tensile stress of 72 GPa ($V = 6.57$ Å$^3$/atom). The structural parameters of this graphite are the same as for $L_6$ graphite obtained from LA3 phase. Upon reaching the ultimate stress of 62 GPa along the [010]-axis, the first-order phase transition of this phase to Cmmm graphite occurs at $V = 6.45$ Å$^3$/atom. The orthorhombic unit cell of $L_6$ graphite Cmmm has the parameters $a = 4.3081$ Å, $b = 4.9766$ Å and $c = 7.3613$ Å. The stretching of
the LA5 phase structure along the [001]-direction leads to its gradual transition to an intermediate diamond-like phase ($V = 6.72 \text{ Å}^3/\text{atom}$), which is converted to tetragonal L$_{4.8}$ graphite $I4/mmm$ at 93 GPa. The crystal lattice of tetragonal L$_{4.8}$ graphite can be characterized by the following parameters: $a = b = 4.9051 \text{ Å}$ and $c = 7.2448 \text{ Å}$.

![Dependences of the total energy difference (ΔE$_{\text{total}}$) on the volume (V) during the deformation of orthorhombic LA5 phase along the following crystallographic axes: (a) [001]; (b) [010]; (c) [100]. The geometrically optimized unit cells of LA5 phase, graphites and intermediate phases are given at normal pressure.](figure_2)

As a result of the geometrical optimization of the crystal structures, it is found that the sublimation energies of diamond-like LA3 and LA5 phases are less than those for cubic diamond by $\sim 0.21$ eV/atom. This value significantly exceeds the corresponding calculated value for hexagonal diamond (also called LA2) [8], which was observed experimentally [20]. Therefore, at the final stage of the work, the thermal stability estimation of these phases is performed in the process of annealing their structures at 500 K and normal pressure. The figures 3a and 3b show the relaxation dependences characterizing the change in the total energy ($E_{\text{total}}$) on the annealing time ($t$) for LA3 and LA5 phases. The structures of tetragonal LA3 phase and orthorhombic LA5 phase at different stages of the annealing are shown in figures 3c–3h. As a result of the annealing over 8 ps, neither destruction nor strong deformation of the structure is observed, which indicates the stability of diamond-like LA3 and LA5 phases under high temperature and normal pressure.
Figure 3. Dependences of the total energy fluctuation ($E_{\text{total}}$) on the annealing time ($t$) for the unit cells of diamond-like LA3 (a) and LA5 (b) phases at 500 K. The diamond-like phase structures in the annealing process: LA3 at 0.15 (c), 4 (d) and 8 ps (e), respectively; LA5 at 0.15 (f), 3.8 (g) and 7.5 ps (h), respectively.
4. Conclusions

Thus, the first-principle calculations of the mechanical and thermal stability of diamond-like LA3 and LA5 phases were performed. It was found that tetragonal LA3 phase can withstand static compressive and tensile loads up to ~ 90 and 70 GPa, respectively. Orthorhombic LA5 phase should be stable at pressures in the value range from -62 to 85 GPa. The molecular dynamics calculations showed that the structures of LA3 and LA5 phases should be stable at elevated temperature (500 K) and normal pressure.

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