Simulation of the formation of polymorphic varieties of nanodiamonds

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Abstract. Structural stability and the possible pathways to experimental formation of lonsdaleite and other polymorphic modifications of diamond have been studied in the framework of the density functional theory. It was established that the structural transformation of orthorhombic Cmmm graphite to lonsdaleite must take place at a pressure of 61 GPa, while the formation of lonsdaleite from hexagonal P6\textit{mmm} graphite must take place at 56 GPa.

1. Introduction

Cubic diamond is a reference material setting the upper limit of hardness on the Mohs scale. However, according to the theoretical research, performing in [1], hardness of hexagonal polytype of diamond (as called as lonsdaleite) exceeds hardness of cubic diamond twice. How lonsdaleite can be synthesized till now remains insufficiently clear. Therefore in this work, formation conditions of lonsdaleite have been theoretically studied at the strong compression of graphite.

2. Methods

The model investigation of the structural stability and possible pathways of formation of lonsdaleite and other polymorphs of diamond was based on calculations of the «graphite ↔ lonsdaleite (hexagonal diamond)» and «graphite ↔ diamond-like phases» phase transitions using the method described in [2, 3]. Calculations of the crystalline structures and energy characteristics of carbon phases were performed by methods of the density functional theory (DFT) [4]. These calculations employed the Perdew-Zunger density functional for the exchange-correlation energy in the local density approximation (LDA) [5]. Figures 1 and 2 show unit cells of structural modifications of graphite and diamond used for the DFT-LDA calculations.

![Figure 1](image1.png)  
**Figure 1.** Unit cells of orthorhombic (a) and hexagonal (b) graphites used for DFT-LDA calculations.
The heats of structural transitions of graphite to diamond polymorphs under isothermal compression conditions were determined by calculating the difference of enthalpies at the point of transition. The enthalpy was calculated using the standard relation $H = E_{\text{total}} + P \cdot V_{at}$, where $E_{\text{total}}$ is the total energy, $P$ is the pressure, and $V_{at}$ is the volume per atom.

![Orthorhombic unit cells](image)

Figure 2. Orthorhombic unit cells of hexagonal diamond (a), LA3 (b), LA5 (c), $Pmna$ (d), $P2_1/m$ (e), and $C2/m$ (f) diamond-like phases, respectively.

3. Results

As a result of the first stage of DFT calculations, we determined the values of equilibrium unit cell parameters for the initial and final structures. At the second stage of calculations, we simulated the direct and reverse phase transitions from three- to four-coordinated carbon compounds under uniaxial deformation conditions.

Figures 3 and 4 show dependences of the total energy difference ($\Delta E_{\text{total}}$) on the atomic volume ($V_{at}$) characterizing direct and reverse phase transitions between polymorphic modifications of carbon. Investigations of the possible synthesis pathways to lonsdaleite (hexagonal diamond) showed that this carbon structure can be formed from two metastable graphite phases, $Cmmm$ and $P6/mmm$. The structural transition from $Cmmm$ graphite to hexagonal diamond (with the [100] strain direction) requires surmounting an energy barrier of 0.241 eV per atom (Figure 3) at an atomic volume of 6.332 Å$^3$ per atom, when the pressure reaches 61.0 GPa. In the case of initial $P6/mmm$ graphite, the potential barrier height slightly increases to 0.275 eV per atom (Figure 4), whereas the phase transition pressure decreases to 56.3 GPa. Since the pressure required for the structural transition from graphite to hexagonal diamond is lower that the values calculated for the formation of diamond-like LA3, LA5, $Pmna$, $P2_1/m$, and $C2/m$ phases, the formation of lonsdaleite from $P6/mmm$ graphite must take place before the formation of other polymorphic modifications of diamond.

For estimating the stability of hexagonal diamond in comparison to other diamond polymorphs, we have studied the reverse phase transitions caused by the uniaxial tensile deformation of this diamond until complete transformation to graphite. The calculations were performed for the stress applied along axes parallel to the [001], [100], and [110] crystallographic directions. The values of potential barriers for the destruction of hexagonal diamond by tension along the [001] and [110] axes amounted to 0.361 and 0.383 eV per atom, respectively (Figure 3). The value of energy barrier to be surmounted for the
transition from hexagonal diamond to orthorhombic graphite under applied stress of 112 GPa was 0.310 eV per atom (Figure 4). The minimum barrier value for hexagonal diamond significantly exceeds the corresponding values of energy barriers for diamond-like LA3, LA5, Pnma, P2_1/m, and C2/m phases (Figures 3 and 4), which is indicative of a higher thermodynamic stability of lonsdaleite in comparison to all diamond-like phases with equivalent and non-equivalent atomic positions. It should be noted that a potential barrier for the transition from hexagonal diamond to graphite is only 0.003 eV per atom smaller than the corresponding value for cubic diamond [3]. Since the phase transition from diamond to graphite under normal pressure takes place at temperatures above 1500 Kelvin and taking into account the theoretically calculated value of «cubic diamond→graphite» barrier, the temperature of phase transition from hexagonal diamond to graphite can be estimated at approximately 1470 Kelvin.

Figure 3. The relationship between total energy difference (ΔE_{total}) and atomic volume (V_{at}) for orthorhombic graphite, hexagonal diamond, and LA5.

Figure 4. The relationship between total energy difference and atomic volume for P6/mmm graphite, hexagonal diamond, and diamond-like LA3, LA5, Pnma, P2_1/m, and C2/m phases.

The calculated enthalpy of the carbon phases is shown in Figures 5 and 6. The structural transition of P6/mmm graphite into hexagonal diamond is accompanied by a heat evolution of 0.43 eV per atom (Figure 5). The difference of enthalpies of the initial and final carbon phases for the formation of hexagonal diamond from Cmmm graphite amounts to ΔH = -0.69 eV per atom (Figure 6).
4. Conclusions

It was established that lonsdaleite (hexagonal diamond) is stable at temperatures up to about 1470 Kelvin and can be synthesized from graphite as a result of compression at pressures of 56–61 GPa, which are close to those necessary for the formation of cubic diamond. It has been also found that the lonsdaleite can be obtained from other structural varieties of graphite at lower pressures necessary for the formation of most stable diamond-like phases [6].

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