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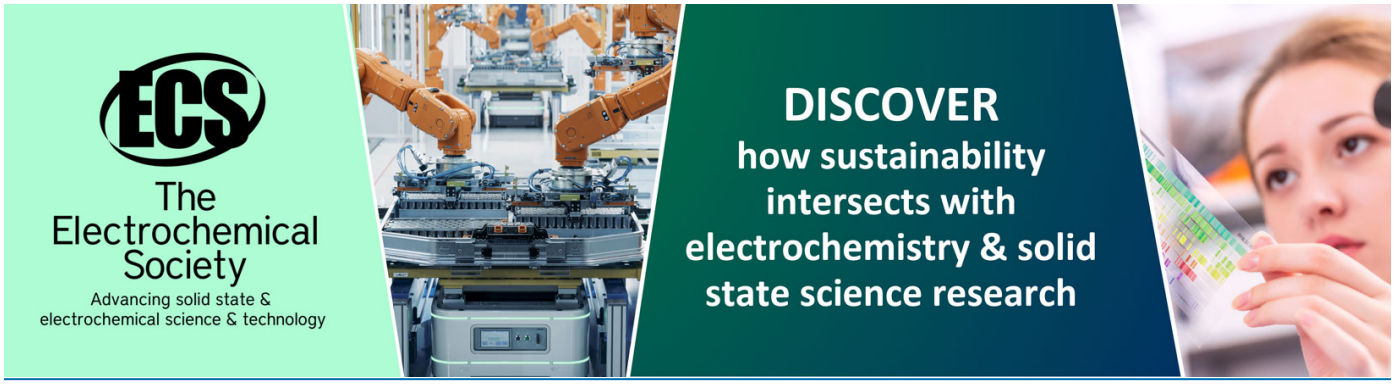

New diamond-like phases boron nitride TA-type

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Abstract. A theoretical study of the structure and electronic properties of three new polymorphic varieties of diamond-like phases of boron nitride, the atoms of which are in equivalent crystallographic positions, was carried out by the density functional theory (DFT) method in the generalized gradient approximation (GGA). The primary structures of these phases were built modelically from the corresponding carbon diamond-like phases by replacing carbon atoms with alternating boron and nitrogen atoms, so that an atom of one kind was surrounded by atoms of another kind. As a result of the calculations, the possibility of stable existence of new structural varieties of boron nitride was established: BN-TA1, BN-TA2, BN-TA3. The sublimation energy of new BN phases varies from 17.08 to 17.59 eV(BN)$^{-1}$. The new BN polymorphs are wide-gap semiconductors with a band gap at the Fermi energy level from 3.6925 to 5.4565 eV.

1. Introduction

Boron nitride compounds can have different crystal structures like carbon compounds, diamond and graphene [1-4]. The allotropic variety of carbon in the form of diamond can have many ploymorphic varieties [5]. In this regard, the existence of similar analogues of structural varieties for boron nitride is possible. Previously, the DFT-GGA method proved the possibility of stable existence of a number of new BN polymorphs with a diamond-like structure, such as BN-s; BN-r and BN-LA4 – BN-LA7 [6,7]. Modeling BN-TA-phases can be obtained as a result of "cross-linking" of single-walled nanotubes. The properties of polymorphic varieties can vary over a wide range, which is important for obtaining practical materials for the synthesis of compounds with a variety of properties required for specific applications. In this connection, it is necessary to study new polymorphs of boron nitride and calculate their expected properties. This paper presents the results of a model study of diamond-like phases that can be obtained from single-walled BN nanotubes.

2. Methods

Theoretical studies of boron nitride compounds with a diamond-like structure, studied in [6, 7], established the possibility of the stable existence of diamond-like phases with equivalent structural positions of atoms. In addition, the analysis of carbon compounds from four-coordinated atoms with tubular nanoprecursors (TA-phases) obtained as a result of cross-linking of chair-shaped and zigzag single-walled CNTs also showed the thermodynamic stability of these compounds [8–10]. However, the possibility of the existence of boron nitride analogs for diamond-like TA phases has not been investigated. The construction of the primary structure of new BN-TA phases was carried out as a result of “cross-linking” of zigzag or armchair-shaped BNNTs according to the method used in [11]. After that, carbon atoms were replaced by boron and nitrogen atoms. Atomic substitution was carried out in such a way that each nitrogen atom in the structure formed three covalent bonds with neighboring boron

atoms. The geometric optimization of the structures of the boron nitride phases and the calculation of the energy characteristics and electronic properties were performed as a result of ab initio calculations by the density functional theory (DFT) [12] in the generalized gradient approximation (GGA) [13]. The calculations were carried out using the Quantum ESPRESSO software package [14] for k-point grids 12x12x12 in the Brillouin zone. The temperature in the calculations was taken close to the temperature of absolute zero (0.01 K). To calculate the sublimation energy and densities of electronic states, a basis set of plane waves with a cutoff energy (E_{cutoff}) of 70 Rydbergs was used. The sublimation energy (E_{sub}) was calculated as the difference between the total energy (E_{total}) per BN molecular group and the energy of isolated nitrogen and boron atoms.

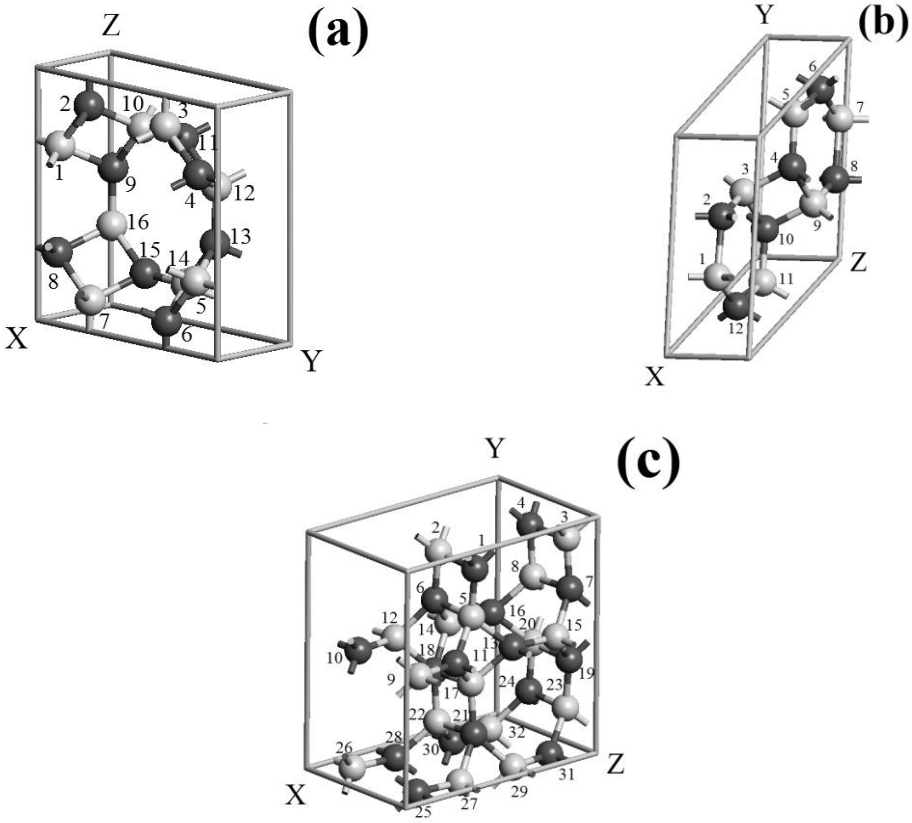

Figure 1. Unit cells of diamond-like TA phases of boron nitride with atomic numbering: (a) BN-TA1; (b) BN-TA2; (c) BN-TA3 (boron atoms are shown in beige, nitrogen - in blue).

3. Results and discussion

Theoretical analysis and model calculations performed by the DFT-GGA method made it possible to find the optimal structures of BN-TA phases corresponding to the minimum total bond energy for crystal lattices of polymorphic varieties of boron nitride: BN-TA1; BN-TA2 and BN-TA3. Images of unit cells of geometrically optimized structures are shown in figure 1. In BN-TA phases, all atoms are in a four-coordinated state (sp^3 is the hybridization of the electronic orbitals of atoms), that is, in crystallographically equivalent positions, which corresponds to the structure of diamond-like compounds. The crystal lattice of the new BN-TA1 and BN-TA3 polymorphs is tetragonal, while for the BN-TA2 polymorph it is hexagonal. The unit cell of the BN-TA1 phase contains 16 atoms; the unit cells of BN-TA2 and BN-TA3 contain 12 and 32 atoms, respectively (figure 1, table 1). The numerical values of the vectors of elementary translations are given in table 1.

Table 1. Values of structural parameters and physical quantities characterizing the properties of BN-TA phases (a,b,c - are elementary translation vectors; N - is the number of atoms in a unit cell; ρ - is bulk density; E_{total} - is total energy; E_{sub} - is sublimation energy; Δ - band gap, E_F - is the Fermi energy).

Parameters	**BN-TA1**	**BN-TA2**	**BN-TA3**
Crystal family	Tetragonal	Hexagonal	Tetragonal
a (Å)	6.6062	6.1794	7.2357
b (Å)	6.6062	6.1794	7.2357
c (Å)	2.5891	2.5846	4.3655
Rng	$4^2 6^3 8^1$	$4^2 6^4$	$4^2 6^2 8^2$
N (atom)	16	12	32
ρ (g $(cm)^{-3}$)	2.9178	2.8880	2.8850
E_{total} (eV $(u.c.)^{-1}$)	-2821.40	-2117.13	-5637.58
E_{total} (eV $(BN)^{-1}$)	-352.68	-352.86	-352.58
E_{subl} (eV $(BN)^{-1}$)	17.41	17.59	17.08
Δ (eV)	3.6925	5.4565	4.9195
E_F (eV)	-4.1226	-3.8944	-4.0727

The new diamond-like phases of boron nitride differ from each other by the value of the Welsh ring parameter (Rng), which symbolically indicates the minimum number of bonds in the trajectories of all possible round trips from one bond for a selected atom to another. For BN-TA1 phase, the parameter value is $4^2 6^3 8^1$, and for BN-TA2 and BN-TA3 - $4^2 6^4$ and $4^2 6^2 8^2$, respectively. The bulk density of the new polymorphs varies in the range from 2.8850 g $(cm)^{-3}$ observed for the BN-TA3 structure to 2.9178 g $(cm)^{-3}$ for the BN-TA1 structure, which is less than the density of diamond-like boron nitride (3.438 g $(cm)^{-3}$).

The results of measuring the lengths of interatomic bonds, as well as the angles between them in the BN-TA phases, are shown in table 2. Due to the fact that the boron and nitrogen atoms in BN polymorphs are in crystallographically equivalent positions, the bonds will be characterized by four different lengths and a set of six corners between them. The lengths of covalent bonds vary from 1.4997 to 1.7109 Å (BN-TA2). The angles between atoms differ depending on the type of atom: at a boron atom, from 86.16˚ (BN-TA3) to 129.41˚ (BN-TA1).

The parameter Def is a characteristic of the stress of the structure of diamond-like phases relative to the structure of cubic diamond, which was calculated as the sum of the modules of deviations from the equilibrium value of the angle between bonds and 109.47°, characteristic of cubic diamond. The minimum value of the deformation parameters for boron and nitrogen is observed for the BN-TA2 phase, which indicates that this phase should have the least deformed structure compared to the structure of an ideal diamond crystal lattice, and this phase should be the most stable. DFT-GGA calculations of the energies characterizing the diamond-like phases of boron nitride showed that the maximum sublimation energy (17.59 eV $(BN)^{-1}$) is also observed for the BN-TA2 structure, which also indicates that this phase should be the most stable. However, the sublimation energies of the remaining phases are also high, so these phases (BN-TA1 and BN-TA3) can exist stably under normal conditions.

Table 2. Interatomic bond lengths (L_i, Å) and angles between them (φ_i, ˚) in crystal structures of boron nitride diamond-like phases.

Atomic type	Interatomic bond lengths	Diamond-like phases			The angle between the bonds	Diamond-like phases		
		BN-TA1	BN-TA2	BN-TA3		BN-TA1	BN-TA2	BN-TA3
B	L_1 (Å)	1.5846	1.4997	1.5225	φ_1 (˚)	113.62	116.19	126.90
	L_2 (Å)	1.5157	1.7097	1.5920	φ_2 (˚)	129.41	117.33	126.90
	L_3 (Å)	1.5846	1.5481	1.6158	φ_3 (˚)	113.62	117.33	92.84

	L_4 (Å)	1.6196	1.5481	1.5920	φ_4 (˚)	109.56	113.18	112.68
					φ_5 (˚)	93.80	94.016	112.68
					φ_6 (˚)	93.80	94.016	86.16
					Def (˚)	59.67	57.058	81.22
	L_1 (Å)	1.5846	1.4997	1.5225	φ_1 (˚)	114.51	119.51	135.56
	L_2 (Å)	1.5157	1.5479	1.5922	φ_2 (˚)	140.59	123.82	135.56
	L_3 (Å)	1.5846	1.7109	1.5922	φ_3 (˚)	114.51	119.51	87.172
N	L_4 (Å)	1.6196	1.5479	1.6160	φ_4 (˚)	109.56	113.20	109.00
					φ_5 (˚)	86.21	85.99	109.00
					φ_6 (˚)	86.21	85.99	79.14
					Def (˚)	87.81	85.12	105.748

DFT-GGA calculations of the electronic density of states and band structure were performed to evaluate the electronic properties of the BN-TA phases, the results of which are shown in figure 2. The maximum band gap at the Fermi energy level is observed for the BN-TA2 diamond-like phase and is 5.4565 eV. For the BN-TA1 and BN-TA3 phases, the band gaps are 3.6925 and 4.9195 eV, respectively; therefore, all BN-TA diamond-like phases are wide-gap semiconductors.

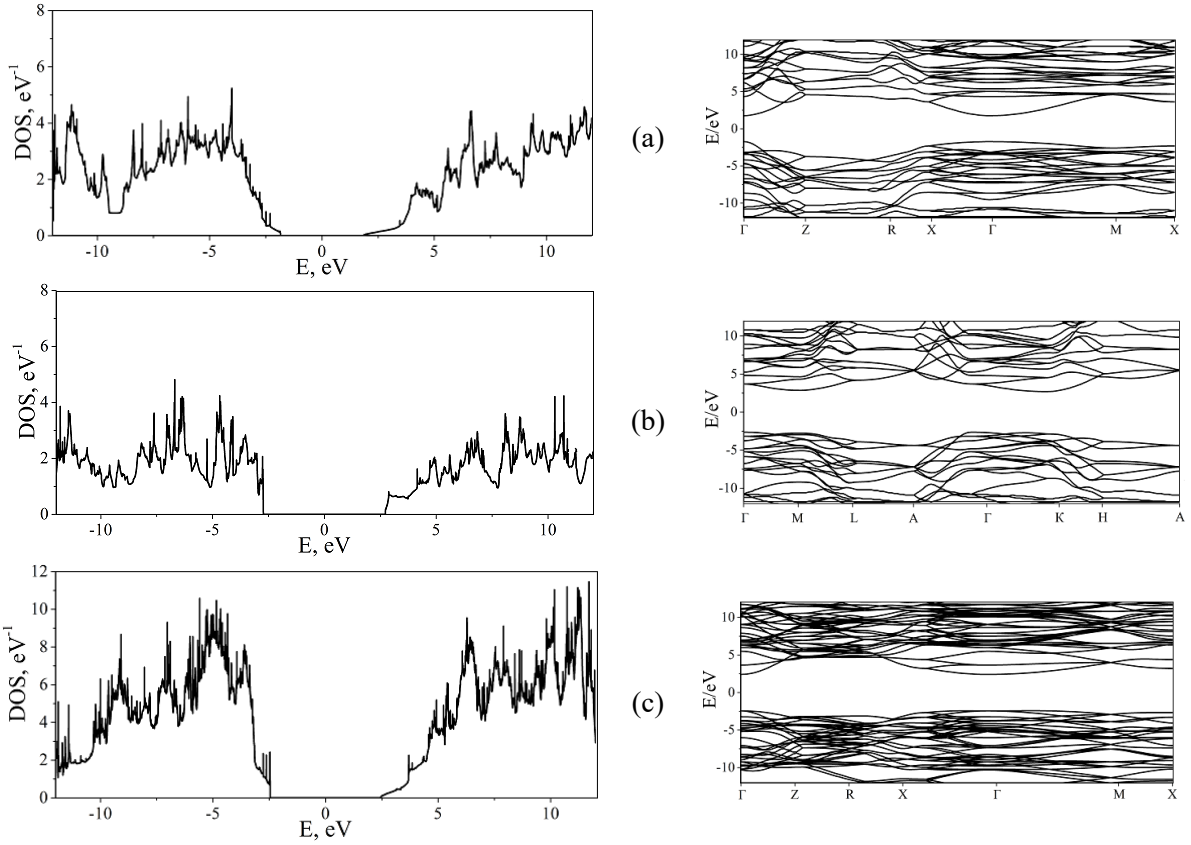

Figure 2. Density of electronic states and band structure of new diamond-like phases of boron nitride: (a) BN-TA1; (b) BN-TA2; (c) BN-TA3

4. Conclusion

In this work, the possibility of stable existence of three boron nitride phases: BN-TA1, BN-TA2, and BN-TA3, having structures similar to the structure of the corresponding carbon diamond-like phases,

was established by the DFT-GGA method. In addition, the structural parameters and the electronic and energy characteristics of the BN-TA phases were theoretically studied. The relatively high sublimation energy of 17.59 eV $(BN)^{-1}$ for the BN-TA2 phase indicates that this phase should have a stable structure under normal conditions. This is also indicated by the minimum value of the Def parameter. In the course of the study, it turned out that the band gap of new diamond-like phases varies in a fairly wide range: from 3.6925 eV to 5.4565 eV, which makes it possible to vary the electronic properties due to the formation of the structure of various polymorphic varieties with an unchanged chemical composition of the phases. In this regard, these BN-TA phases can be widely used in nanoelectronics.

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