New polymorphic varieties of boron nitride with structure similar to graphyne

D S Ryashentsev and E A Belenkov

1Chelyabinsk State University, 129, Bratiev Kashirinykh Str., Chelyabinsk, 454001, Russia

E-mail: ryashentsev_dmitry@mail.ru

Abstract. Seven new layer polymorphic varieties of boron nitride, with a structure similar to the structure of the α, β and γ types of graphyne layers, were theoretically studied. The calculation of the structure and electronic properties was carried out by the ab initio method of the density functional theory. The sublimation energy varies from 16.29 eV (BN)\textsuperscript{-1} (minimum for the BN\textsuperscript{-α-L\textsubscript{6}} layer) to 17.00 eV (BN)\textsuperscript{-1} (maximum for the BN\textsuperscript{-γ-L\textsubscript{6}} layer). The structure of BN polymorphs differs in the values of the Def parameters characterizing the relative degree of deformation of their structure. The band gap of the boron nitride layers varies from 2.14 to 4.02 eV.

1. Introduction

Boron nitride compounds can exist in the form of various polymorphic varieties whose structure is similar to the structure of carbon compounds [1-6]. Boron and nitrogen atoms in BN as well as carbon atoms in carbon materials can be in different hybridized states sp, sp\textsuperscript{2} or sp\textsuperscript{3}. Therefore, it is theoretically possible the existence of hybrid sp+sp\textsuperscript{2} compounds of boron nitride like graphyne compounds of carbon atoms [7,8]. Some of these BN structures were studied theoretically in a number of works [9, 10]. Polymorphic varieties of hybrid compounds differ in the ratio of atoms in different states and the degree of deformation of their structure, as a result of which their properties may vary. In this article, new polymorphic layered varieties of BN with a structure similar to that of graphyne carbon compounds are theoretically investigated.

2. Methods

The structure of the new BN polymorphs was theoretically built using the method [7,8,11] used earlier to build graphyne layers from various graphene layers. The construction was performed on the basis of a layer of hexagonal boron nitride. Like graphyne layers, sp+sp\textsuperscript{2} polymorphs of boron nitride formed on the basis of the BN-L\textsubscript{6} layer can be of the α-, β-, and γ-types. Theoretical analysis showed that there is one type of α layer and three types of β and γ layers. Geometric optimization of the structure, as well as calculations of the energies and electronic properties were performed by the density functional theory (DFT) method in the generalized gradient approximation (GGA). Optimization was performed for three-dimensional crystals, which are stacks of layers of different types. The distance between the layers in the stack was chosen equal to 10 Å, so that the layers in the stacks did not distort the structure of neighboring layers. The calculations were performed for k-point networks: 12 × 12 × 12. The sublimation energy was calculated as the difference between the total energy per molecular group BN in the layers of boron nitride and the energy of isolated boron and nitrogen atoms. The deformation
parameter (Def) characterizes the distortion of the angles between bonds for atoms in sp$^2$ states, compared with the angles between bonds in hexagonal boron nitride.

3. Results and discussion

Theoretical analysis of the structure for boron nitride graphyne analogs has shown that there are seven basic polymorphic $\alpha$-, $\beta$1-, $\beta$2-, $\beta$3-, $\gamma$1-, $\gamma$2 and $\gamma$3-types. As a result of the DFT-GGA calculations, it was found that the seventh of the main structural varieties - the $\gamma$3-type turned out to be unstable and from geometric optimization turned into a layer of hexagonal boron nitride. Figure 1 shows the images of the geometrically optimized structure of six BN layers with a structure similar to the structure of graphyne layers of $\alpha$, $\beta$, and $\gamma$ types. The crystal lattices of the nitride-borne layers belong to the hexagonal, oblique, or rectangular Bravais lattices. The unit cell layers contain from 4 to 18 atoms. In all layers, with the exception of the BN-$L_6$-$\beta$3 layer, fragments of linear BN chains turned out to be straight. In the BN-$L_6$-$\beta$3 layer, the chains are bent.

**Figure 1.** The structure of polymorphic varieties of graphyne-like layers of boron nitride, geometrically optimized as a result of DFT-GGA calculations: (a) BN-$L_6$-$\alpha$1, (b) BN-$L_6$-$\beta$1, (c) BN-$L_6$-$\beta$2, (d) BN-$L_6$-$\beta$3, (e) BN-$L_6$-$\gamma$1, (f) BN-$L_6$-$\gamma$2.
The calculated values of interatomic distances (Rₙ) in the structures of the BN layers are shown in table 1. The interatomic bond R₄ characterizes the distance between atoms in a fragment of a linear chain. This relationship is the shortest and its values range from 1.241 to 1.274 Å. The other three bonds R₁, R₂ and R₃ correspond to the distance from the initial three-coordinated atom to neighboring atoms. The lengths of these bonds are much longer — their lengths vary from 1.389 to 1.532 Å. Different lengths of interatomic bonds are due to different electron densities in the interatomic space. The maximum electron density is observed in the gap between the atoms of a fragment of a linear chain.

### Table 1. Structural parameters and some properties of BN layers with a graphyne-like structure.

| Layer | BN-L₆-α1 | BN-L₆-β1 | BN-L₆-β2 | BN-L₆-β3 | BN-L₆-γ1 | BN-L₆-γ2 |
|-------|----------|----------|----------|----------|----------|----------|
| R₁ (Å) | 1.420   | 1.406   | 1.395   | 1.493   | 1.466   | 1.532   |
| R₂ (Å) | 1.420   | 1.509   | 1.490   | 1.408   | 1.466   | 1.508   |
| R₃ (Å) | 1.420   | 1.406   | 1.395   | 1.409   | 1.404   | 1.389   |
| R₄ (Å) | 1.263   | 1.270   | 1.241   | 1.272   | 1.274   | 1.267   |
| φ₁:₂ (°) | 120.01 | 119.77 | 117.42 | 121.16 | 122.73 | 122.46 |
| φ₁:₃ (°) | 120.00 | 120.41 | 125.18 | 124.05 | 118.55 | 118.23 |
| φ₂:₃ (°) | 119.99 | 119.82 | 117.40 | 114.78 | 118.73 | 119.32 |
| φ₃:₄ (°) | 179.99 | 179.00 | 174.35 | 173.22 | 179.89 | 178.92 |
| Def (°) | 0.013 | 0.700 | 8.627 | 6.950 | 4.603 | 4.457 |
| Crystal family | Hex | Hex | Mon | Orth | Hex | Mon |
| a (Å) | 7.120 | 9.671 | 5.010 | 1.012 | 7.011 | 4.983 |
| b (Å) | 4.936 | 5.024 | 1.489 | 1.493 |
| φ (°) | 120 | 120 | 90 | 90 | 120 | 148.9 |
| Nₐ (atom) | 8 | 18 | 6 | 12 | 12 | 4 |
| E_{total} (eV) | -351.58 | -351.87 | -351.88 | -351.84 | -352.30 | -351.99 |
| E_{sub} (eV) | 16.29 | 16.58 | 16.58 | 16.55 | 17.00 | 16.69 |
| Δ (eV) | 3.927 | 3.885 | 3.904 | 3.892 | 4.016 | 2.135 |
| ρ (mg m⁻²) | 0.375 | 0.458 | 0.500 | 0.486 | 0.581 | 0.333 |

The angles between covalent bonds formed by sp²-hybridized atoms vary in the range from 114.78 to 125.18 ° (table 1). These values differ from the angle of 120 °, which is characteristic of the structure of hexagonal BN, and the structure of graphyne-like layers of boron nitride can be considered as deformed compared to the BN₆ layer. The magnitude of the deformation can be characterized by the deformation parameter Def, which was calculated as the sum of the difference in the angles between the bonds in the new BN polymorphs and the angle of 120 °. The deformation parameters of the BN layers vary from 0.013 to 8.627 ° (table 1). The BN₆-β2 layer has the most deformed structure. Minimum deformation for the BN₆-α1 layer.

Based on the calculated values of the total energy (E_{total}) per molecular BN group, the sublimation energies of the BN layers were calculated. The specific sublimation energy (E_{sub}) calculated for BN-grapynes layers is minimum for the BN₆-α1 layer and is 16.29 eV (BN)⁻¹, and the maximum for the BN₆-γ1 layer is 17.00 eV (BN)⁻¹. Therefore, the BN₆-γ1 layer should be the most stable structural variety. However, the sublimation energies of the new polymorphic modifications of BN are quite high, so that these layers can stably exist under normal conditions.

The layered density (ρ) of the structural varieties of boron nitride varies from 0.333 mg m⁻² for the BN₆-γ2 layer to 0.581 mg m⁻² for the BN₆-γ2 layer. The band structure and density of electronic states of polymorphic varieties of graphyne-like boron nitride were also calculated - their images are shown in figures 2 and 3.
Figure 2. Band structure of graphyne-like layers of boron nitride: (a) BN-L₆-α₁, (b) BN-L₆-β₁, (c) BN-L₆-β₂, (d) BN-L₆-β₃, (e) BN-L₆-γ₁, (f) BN-L₆-γ₂.

The maximum band gap (Δ) at the Fermi energy level is characteristic of the BN-L₆-γ₁ layer and is 4.02 eV, and the minimum for the BN-L₆-γ₂ layer is 2.14 eV. Thus, the electronic properties of polymorphic varieties of boron nitride can be varied over a fairly wide range, synthesizing various polymorphic varieties of graphyne-like boron nitride. New layered varieties of BN, with a structure similar to graphyne layers, can find practical application in the creation of nanoelectronic devices.
Figure 3. Density of electronic states of graphyne-like layers of boron nitride: (a) BN-L6-α1, (b) BN-L6-β1, (c) BN-L6-β2, (d) BN-L6-β3, (e) BN-L6-γ1, (f) BN-L6-γ2.

4. Conclusion
New structural species of boron nitride, with a structure similar to the structure of graphyne polymorphs, have been theoretically investigated using DFT-GGA methods. The possibility of the sustainable existence of six polymorphic varieties of boron nitride with a layered structure of α-, β1-, β2-, β3-, γ1- and γ2 has been established. The structure of the seventh polymorph BN-L6-γ3 during geometrical optimization turned out to be unstable and transformed into the structure of a layer of hexagonal boron nitride. The maximum sublimation energy is observed for the BN-γ1-L6. Layers of boron nitride with a graphyne-like structure should have semiconductor properties, since the width of their band gaps varies in the range from 2.14 to 4.02 eV.

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