

# Semiconducting to metallic transition in $C_x(BN)_y$ nanotubes: effects of C stripes in BN basis

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## Abstract

In this work, we study the structural and electronic properties of  $C_x(BN)_y$  nanotubes, varying the  $C_x$  concentration in the BN base structure. The developed work was done combining semiempirical, density functional theory (DFT) and Green's function calculation methods. In the first part, we shown by structure energies that the distribution of B – C, C – N, C – C, and B – C chemical bonds greatly influence the structural stabilization of the nanotubes and the integration of the carbon (C) atoms within the  $C_x(BN)_y$  systems has a strong dependence on the atomic distribution of B, C, and N atoms, independently of increasing of carbon atoms concentration in the tubular structure. In the second part, we shown that atomic distribution of B, C, and N atoms has also a strong impact on the electronic band gap, transforming the electronic structure of initial BN electronic configurations.

**Keywords:** Boron carbonitride nanostructures, DFT, electronic properties, energy band gap, Green's function.

## 1. Introduction

Tubular nanostructures composed of carbon (C), boron (B), and nitrogen (N) atoms were proposed theoretically in 1994 [11, 13, 14, 44, 14, 47] and obtained experimentally in 1995 [6, 27, 35, 45, 58, 66, 71, 72, 76, 79, 80, 83, 84, 85]. These nanostructures are known as boron carbonitride ( $B_xC_yN_z$ ) nanotubes [44]. Carbon nanotubes can be metallic or semiconductor materials, depending on their diameter and chirality [62]. On the other hand, BN nanotubes present insulator behavior, with an energy band gap value from ~3.0 to ~6.0 eV [10, 15, 19, 23, 34, 70]. However, the B – C – N ternary tubular structures are semiconducting with band gaps lower than that of BN nanotubes and, furthermore, the value of the gap opening is dependent

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on the chemical composition [13, 14, 18, 35, 37, 44]. Consequently, the electronic properties of  $B_xC_yN_z$  tubes can be engineered to the desired level by controlling their chemical composition.

An important member of the  $B_xC_yN_z$  family is the  $BC_2N$  nanotube [2, 6, 3, 39, 55, 77]. Experimental and theoretical results have shown that this nanotube is the most energetically favorable structure [3], with semiconducting character, the gap being lower than that of BN nanotube. Since the  $BC_2N$  nanotube is a ternary composite, so a number of possibilities exist to form the hexagonal structure with different patterns. Liu et al [37] proposed several structures depending on the linkage of B, C, and N bonding including two different geometric structures of a (4,4)  $BC_2N$  nanotube. Among these, one (type I) showed metallic characteristics, whereas another (type II) was a semiconductor. In addition to this, other possible atomic arrangements and chemical compositions ( $BCN$ ,  $B_3C_2N_3$ ,  $BC_4N$ , and  $B_5C_2N_5$ ) of B – C – N tubular structures can also be found in the literature [9, 18, 20, 26, 37, 42, 43, 60, 68, 75, 77, 86]. By virtue of these flexible electronic properties (from metallic to semiconducting), these materials have several potential applications such as electrical conductors [6, 30, 36, 81], capacitors, light-emitting diodes, optical devices [6, 18, 29, 30, 55], and gas adsorption devices [7, 33].

Considering the different stoichiometries proposed in the literature, and their relationship with the electronic properties, there is a discussion about the roles played by four important parameters in determining the electronic characteristics of  $B_xC_yN_z$  nanotubes. These are: (i) stoichiometry, (ii) diameter, (iii) chirality, and (iv) atomic distribution of B, C, and N atoms in the hexagonal network. In light of the theoretical results for the same stoichiometry,  $B_xC_yN_z$  nanotubes can show different diameters, chiralities, and atomic arrangements [22, 26, 52, 56, 77, 78]. That being said, some studies have indicated that the electronic band gap values can be altered according to nanotube chirality and diameter [26, 55, 56]. Besides, Miyamoto [44] and Liu [37] suggested that the more symmetric  $BC_2N$  nanotubes have lower band gap values and are independent of the chirality and diameter of the tube. Additionally, Azevedo et al [2, 3] showed that in the case of  $BC_2N$  and  $BCN$  nanotubes, the band gap values depend on the B, C, and N atomic arrangement in the hexagonal network. Moreover, theoretical studies suggested that in the case of B – C – N ternary tubular structures, it is the C atoms (rather than B and N) which act as dopant atoms in BN nanotubes. Therefore, the electronic properties of BN nanotubes [1, 33, 39, 41, 56, 82, 86] can be modified by the concentration of C atoms along with their atomic distribution. Carvalho et al [68] demonstrated that  $B_3C_2N_3$ ,  $BCN$ , and  $B_5C_2N_5$  nanotubes could be as stable as  $BC_2N$  tubes, depending on the atomic distribution. In addition, the minimum number of B – C bonds led to the most favorable structures.

In the present work, we report a quantum chemical study of  $C_x(BN)_y$  zigzag and armchair nanotubes with different stoichiometries and atomic distributions. The domain formation in the  $B_xC_yN_z$  nanostructures, and the dependence of the electronic properties on the distribution of B, N, and C atoms are well documented in the literature. However, our results provide new insight into the relationship between the electronic properties of  $C_x(BN)_y$  nanotubes, their chemical composition and atomic arrangement of B, C, and N atoms in the tubular structure. We also examine the role played by C doping in the energetic and structural stabilization of these systems, together with the C domain formation in the BN network.

## 2. Methodology and Computational details

We optimized the geometries of tubular structures composed of BN and B – C – N atoms using the semiempirical Austin Method 1 (AM1) quantum chemical technique [59], which is based on Hartree-Fock theory as implemented in GAMESS package [65]. The energy associated with the incorporation of C was calculated as the difference between the formation enthalpies of C-doped and pure BN systems, divided by the number of carbons. In the case of the electronic properties, the  $C_x(BN)_y$  nanotubes were described within the framework of the  $\pi$ -band tight-binding model. The density of states (DOS) and energy band gaps were then numerically calculated by Green's function formalism, employing the Rubio-Sancho technique (TB/GF) [64]. The physical parameters used for the numerical calculations were taken from the literature [46]. The on-site energies for B and N atoms were  $\varepsilon_B = +2.33\text{eV}$  and  $\varepsilon_N = -2.50\text{eV}$ , respectively, relative to the C on-site energy ( $\varepsilon_C = 0.0\text{eV}$ ); the values for the hopping integrals were  $t_{C-C} = -3.0\text{eV}$ ,  $t_{C-N} = -3.14\text{eV}$ ,  $t_{B-C} = -2.7\text{eV}$ , and  $t_{B-N} = -2.81\text{eV}$ .

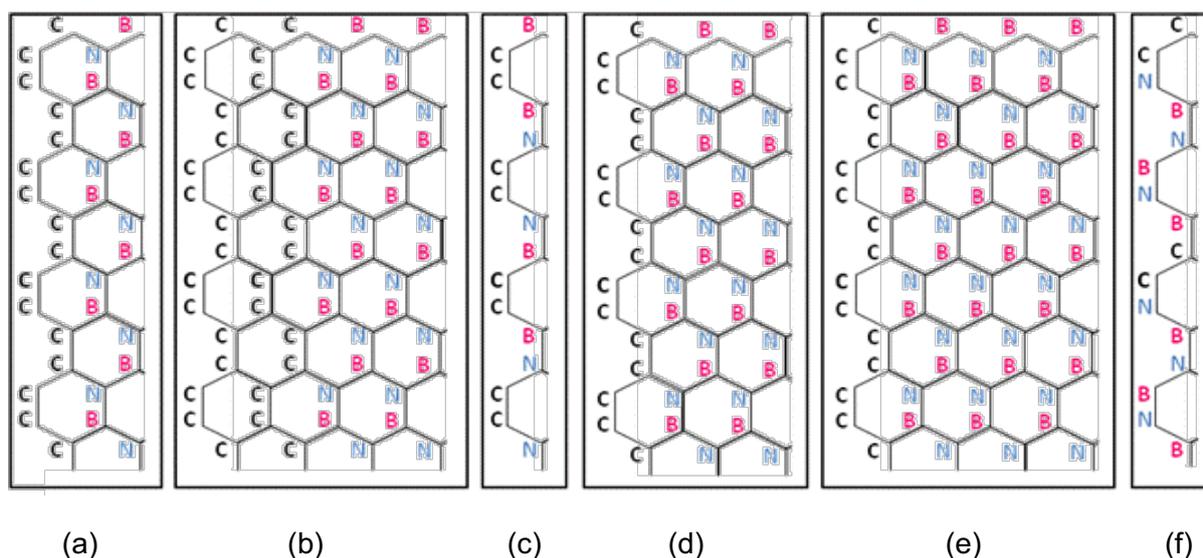
Electronic band structures were calculated using cited TB/GF and Density Functional Theory (DFT) implemented in SIESTA code (version 2.0) [54, 63, 67] in the framework of local density approximation (LDA/CA) [57], employing periodic boundary conditions (PBC). The longitudinal, periodic, tube axis was set in the z direction and the radial directions was set in the xy-plane. The lattice parameter in x and y directions was set twenty times greater than z direction to mimic the vacuum space, avoiding any interactions between replicated images. In order to guarantee high precision results, we have used double-basis set functions (DZ). The norm-conserving pseudopotentials built on Troullier-Martins scheme [73] were used. The mesh cutoff is set to 250 Ry. We relaxing both cell lattice vectors and atomic positions until atomic forces below to 0.01 eV/ang.

## 3. Results and Discussion

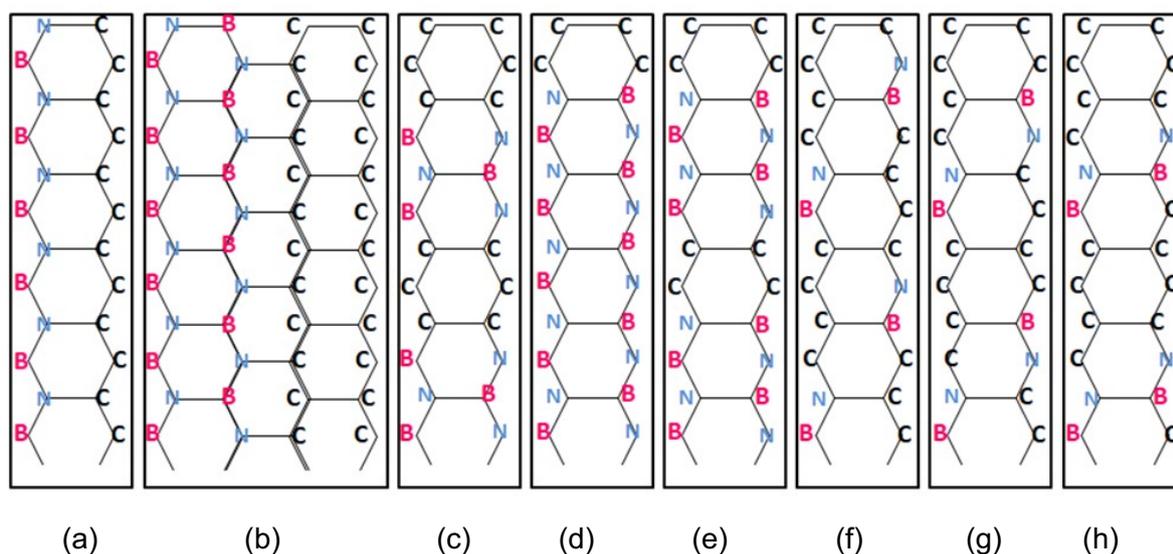
### 3.1 Structural and Energetic Stabilization

We consider armchair (8,8) and zigzag (12,0) nanotubes to examine the role played by atomic distribution on the structural and energetic stabilization. This choice enables us to investigate the parameters (chirality or atomic distribution of C atoms) influencing more on the structural and energetic stabilization of the nanotubes. The number of atoms in (8,8) and (12,0) chiralities does not forbid the geometry calculations in the case of semiempirical methods. On the other hand, the radius size of these nanotubes prevents the hybridization effects in the electronic structure that can occur in the case of small diameters tubes [12, 28, 31, 49, 53].

Figures 1 and 2 show some of the atomic configurations of unit cells considered in this work. It can be noted that for the same chirality, there can be different stoichiometries and atomic distribution of B, N, and C atoms. We consider the atomic distribution of C atoms in the axial (A) and transversal (T) directions, assuming the axial direction of tubes as the main parameter.



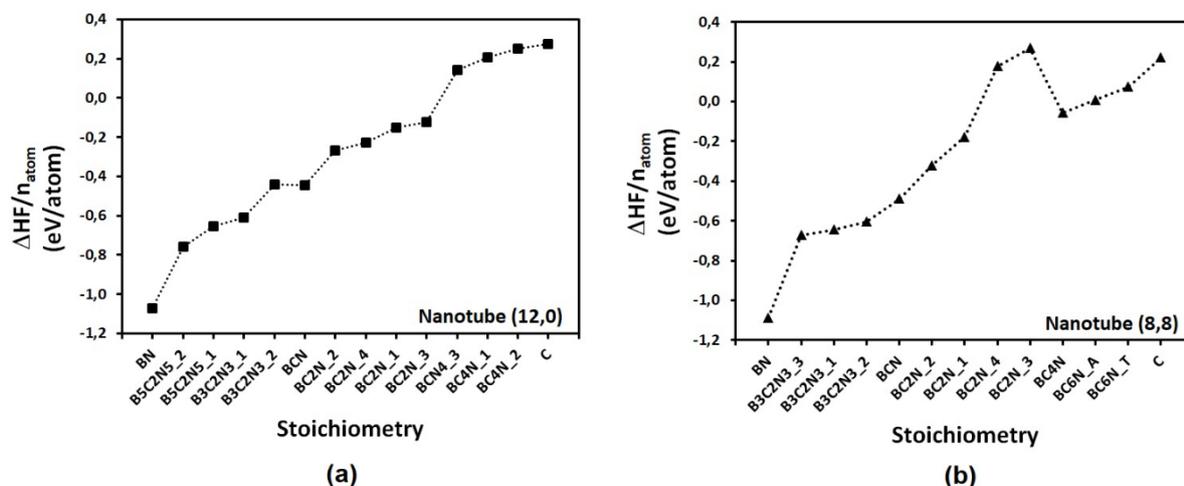
**Figure 1:** Some atomic distributions and stoichiometries analyzed in this work for  $C_x(BN)_y$  armchair (8,8) nanotubes (from left to right): (a)  $BC_2N_1(T)$ , (b)  $BC_2N_2(T)$ , (c)  $BC_2N_3(A)$ , (d)  $BCN(T)$ , (e)  $B_3C_2N_3_1(T)$ , and (f)  $B_3C_2N_3_2(A)$ . The letters A and T in parentheses indicate that the carbon-carbon bonds are distributed in the axial or transversal direction, respectively, relative to the tube axes.



**Figure 2:** Some atomic distributions and stoichiometries analyzed in this work for  $C_x(BN)_y$  zigzag (12,0) nanotubes (from left to right): (a)  $BC_2N_1(T)$ , (b)  $BC_2N_2(T)$ , (c)  $BC_2N_4(A)$ , (d)  $B_5C_2N_5_2(A)$ , (e)  $BCN(A)$ , (f)  $BC_4N_1(A)$ , (g)  $BC_4N_2(A)$ , and (h)  $BC_4N_3(A)$ . The letters A and T in parentheses indicate that the carbon-carbon bonds are distributed in the axial or transversal direction, respectively, relative to the tube axes.

Figure 3 shows the numerical results for the heat of formation ( $\Delta H_f$ ) per atom (eV/atom), for the (8,8) and (12,0)  $C_x(BN)_y$  nanotubes considered in this work. Comparing the results for the armchair (8,8) nanotubes with stoichiometries  $BC_4N$ ,  $BC_2N$ ,  $BCN$ , and  $B_3C_2N_3$ , it can be seen that as the increasing concentration of C atoms has a direct impact on the enthalpy of formation. This can be understood by the introduction of planar  $sp^2$  bonds between C atoms

which are replaced with B and N. These planar bonds increase the structural stress in the walls of tubular systems, due to the curvature. In the case of  $CN_x$  nanotubes, the N substitution influences the curvature resulting in a lower structural stress [16, 17]. However, for the (8,8)  $BC_2N$  group, different  $\Delta HF/n_{atom}$  values were calculated even for the same stoichiometry as shown in Fig. 3. Similar results were also obtained for (12,0) nanotubes.



**Figure 3:** The heat of formation numerical results for nanotubes with (a) (12,0), and (b) (8,8) chiralities. It can be seen that for the same chirality (armchair or zigzag), the energy of formation increased with the increasing number of carbon atoms. This can be explained by the greater structural stress due to the carbon domain generated by the carbons introduced into the BN network.

Machado et al. [39], in a study of the distribution of BN and C stripes in  $BC_2N$  nanotubes, showed that the differences in stability of different  $BC_2N$  structures could be explained by the relationship between the numbers of regular chemical bonds (C – C and B – N) and wrong bonds (C – B and C – N). One recent study about BCN heterocycle rings [69] demonstrated that  $BC_2N$  and  $BC_4N$  molecules which have more C – C and B – N bonds are energetically more favorable if compared with their isomers. In the case of BCN graphene nanosheets, the increasing B – N bonds and their interactions with the graphene matrix influences the stability and electronic properties of these nanostructures [25, 51].

The total number of atoms ( $N_{Total}$ ), including hydrogens, in the (12,0) and (8,8) nanotubes considered in this study, with the total number of bonds ( $T_b$ ), the number of regular chemical bonds ( $R_b$ ), and de number of wrong chemical bonds ( $W_b$ ) for the group of molecules are shown in Table 1. As in the work of Machado et al. [39], the ratio between the total number of chemical bonds ( $T_b$ ) and the number of wrong bonds ( $W_b$ ) was calculated for the  $B_5C_2N_5$ ,  $B_3C_2N_3$ , BCN,  $BC_2N$ ,  $BC_4N$ , and  $BC_6N$  nanotubes. Considering molecules with the same stoichiometry, an increase in  $T_b/W_b$  has an influence on the  $\Delta HF/n_{atom}$  as it can increase/decrease the structural stabilization of the nanotubes (see Table 1 and Fig. 3).

Theoretical studies about domains formation, with different shapes, in  $B_xC_yN_z$  nanostructures have been reported [4, 5, 8, 24, 38, 40, 41, 50, 74, 87]. Annealing process simulations [4, 41] indicate that ordered patterns are more favorable than disordered patterns of BN and C domains. According to Martins [41], carbon atoms form isolated islands in BN network. In order to analyze the energy of incorporation of C atoms and the formation of C

domains in the BN network, the relative enthalpy of formation ( $E_{rel}$ ) was calculated from the heat of formation.  $E_{rel}$  is defined as the relative enthalpy of formation per carbon atom:

$$E_{rel} = \frac{\Delta HF(C_x(BN)_y) - \Delta HF(BN)}{n_c}$$

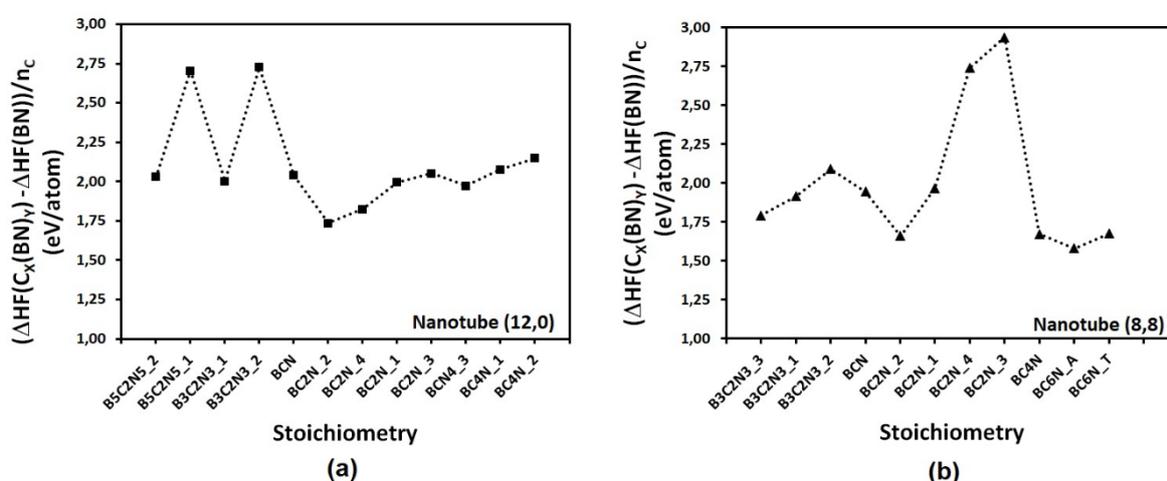
where  $\Delta HF(C_x(BN)_y)$  is the enthalpy of formation of the  $C_x(BN)_y$  nanotube calculated using AM1 semiempirical methods,  $\Delta HF(BN)$  is the enthalpy of formation of a pristine BN nanotube obtained by the same method, and  $n_c$  is the total number of carbon atoms.

**Table 1:** The total number of atoms ( $N_{Total}$ ), total bonds (Tb), regular bonds (Rb), wrong bonds (Wb), and Tb/Wb ratios for the nanotubes considered in this work. A decrease in wrong bonds resulted in lower heats of formation of the molecules, reflecting structural stabilization of the nanotubes.

Nanotube (12,0)	$N_{Total}$	Tb	Rb	Wb	Tb/Wb
B <sub>5</sub> C <sub>2</sub> N <sub>5</sub> _2	312	420	372	48	8.8
B <sub>5</sub> C <sub>2</sub> N <sub>5</sub> _1	312	420	324	96	4.4
B <sub>3</sub> C <sub>2</sub> N <sub>3</sub> _1	312	420	360	60	7.0
B <sub>3</sub> C <sub>2</sub> N <sub>3</sub> _2	312	420	276	144	2.9
BCN	312	420	324	96	4.4
BC <sub>2</sub> N_2	312	420	360	60	7.0
BC <sub>2</sub> N_4	312	420	308	112	3.8
BC <sub>2</sub> N_1	312	420	288	132	3.2
BC <sub>2</sub> N_3	312	420	276	144	2.9
BC <sub>4</sub> N_3	312	420	284	136	3.1
BC <sub>4</sub> N_1	312	420	236	184	2.3
BC <sub>4</sub> N_2	312	420	236	184	2.3

Nanotube (8,8)	$N_{Total}$	Tb	Rb	Wb	Tb/Wb
B <sub>3</sub> C <sub>2</sub> N <sub>3</sub> _2	416	576	464	112	1.2
B <sub>3</sub> C <sub>2</sub> N <sub>3</sub> _1	416	576	528	96	1.1
B <sub>3</sub> C <sub>2</sub> N <sub>3</sub> _3	416	576	528	48	1.1
BCN	416	576	448	128	1.3
BC <sub>2</sub> N_4	416	576	192	384	3.0
BC <sub>2</sub> N_3	416	576	192	384	3.0
BC <sub>2</sub> N_1	416	576	384	192	1.5
BC <sub>2</sub> N_2	416	576	528	48	1.1
BC <sub>4</sub> N	416	576	464	112	1.2
BC <sub>6</sub> N_T	416	576	336	240	1.7
BC <sub>6</sub> N_A	416	576	480	96	1.2



**Figure 4:** Relative heat of formation divided by the total number of carbon atoms for nanotubes with (a) (12,0) chirality and (b) (8,8) chirality. For the same chirality and stoichiometry, the energy of carbon incorporation is related to the atomic distribution of carbon, nitrogen, and boron atoms in the tube walls.

As the total number of atoms is different for tubes with different chiralities, this fact can be used to compare the enthalpies of formation of model molecules with a different number of

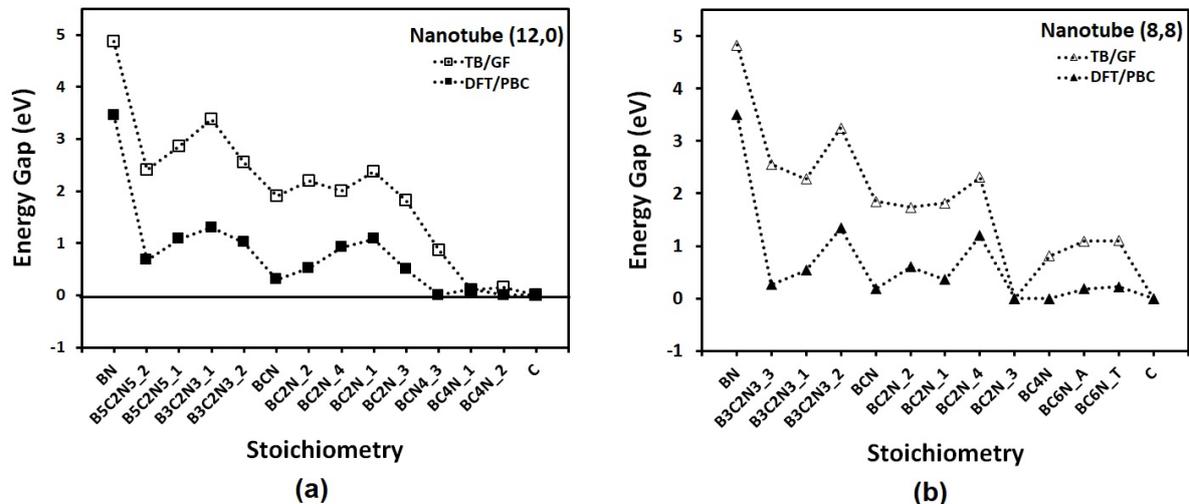
atoms. From the results shown in Figure 4, comparison of the energy of incorporation for molecules with the same chirality, but different numbers of carbon atoms, suggests that the energy of incorporation should increase with the increasing numbers of carbon atoms. However, comparison of the results for the (8,8) nanotube with  $B_3C_2N_3_1$ , BCN, and  $BC_2N_1$  stoichiometries revealed no notable differences between the carbon atoms incorporation energies. Comparison of the  $\Delta HF/atom$  values for the  $BC_2N_1$  and  $BC_2N_2$  nanotubes can indicate that the introduction of carbon atoms into the BN network could facilitate the introduction of new carbon atoms. These findings provide an explanation for the experimental observation of the creation of carbon and BN domains in the case of the  $B_xC_yN_z$  structures [21, 32, 48]. Moreover, in the case of the  $BC_2N$  group, the carbon incorporation energy changed with the atomic distribution. It could therefore be concluded that the atomic distribution influenced the structural stabilization of the nanotubes.

### 3.2 Electronic Properties

Previous studies of boron nitride nanotubes using tight-binding (TB) and local density approximation (LDA) approaches have shown that TB results agree with experimental measurements for large radius tubes. For small tubes, however, there are discrepancies. Strong hybridization effects of the antibonding  $\pi^*$  and  $\sigma^*$  can occur because of the curvature of small radius tubes [12, 28, 31, 49, 53]. For (n,0) tubes with diameter larger than 9.0Å, the hybrid state does not play any role in determination of the band gap of the BN tubes using a simple TB model [15, 61]. As can be notice the chiralities that were chosen in this study - (8,8) and (12,0) - avoid the hybridization effects. We calculate the electronic properties of C doped BN nanotubes (both armchair and zigzag) by TB/GF and DFT/PBC methods. Figure 5 shows the numerical results of tight-binding calculations (TB/GF), and periodic boundary conditions calculations (DFT/PBC) for the electronic band gaps of (8,8) and (12,0)  $C_x(BN)_y$  nanotubes shown in Figure 4. Theoretical values of energy band gap calculated in this work are in good agreement with experimental measurements (2.03 eV and 3.43 eV) for two-dimensional BN nanostructures doped with low carbon concentration [74].

As the atomic configuration has a strong impact on the structural stability and, it is interesting to verify if the electronic properties respond in the same fashion or not. Starting by how carbon concentration in BN structure could change the electronic properties, we can analyze the TB/GF and DFT/PBC results for (12,0) nanotubes with  $B_5C_2N_5$ ,  $B_3C_2N_3$ , and  $BC_4N$  stoichiometries. Comparing the number of carbon atoms in the case of the  $B_5C_2N_5$ ,  $B_3C_2N_3$ , and  $BC_4N$  (12,0) nanotubes, it can be seen that the first nanotube has fewer C atoms than the second one, and the second tube has fewer C atoms than the last one. As the (12,0) carbon nanotube shows metallic behavior, it is expected that the increase of carbon atoms in the  $C_x(BN)_y$  nanostructure should decrease the band gap value. The results shown in Figure 5 for  $B_5C_2N_5_1$  ( $E_g = 2.86\text{eV}$ ),  $B_3C_2N_3_2$  ( $E_g = 2.98\text{eV}$ ), and  $BC_4N_1$  ( $E_g = 0.10\text{eV}$ ) revealed the expected behavior for the  $BC_4N_1$  nanotube. Nevertheless, the numerical results of the TB/GF and DFT/PBC methods applied on  $BC_6N_T$  and BCN (8,8) nanotubes showed less evidence of dependence on the increasing of carbon concentration and decreasing energy band gap.  $BC_6N_T$  (8,8) has a higher number of carbon atoms if compared with BCN (8,8) nanotube. In both cases the carbon atoms are distributed in the transversal direction of the tubular axes. As can be seen at Figure 5, the difference between the number of C atoms in the tubes is not sufficient to generate any significant modification in the semiconductor characteristics of these

$C_x(BN)_y$  nanostructures. In agreement with our results, Gonçalves and co-workers in their theoretical studies of  $B_xC_yN_z$  nanoribbons have concluded the band gap value is independent of the carbon concentration [24].



**Figure 5:** Energy band gap values ( $E_g$ ) calculated using the Green's function and PBC methods for (12,0) and (8,8) nanotubes with different stoichiometries. Note that for the same chirality, diameter, and stoichiometry, the energy band gap can vary depending on the carbon, nitrogen, and boron atomic distribution in the hexagonal network.

To analyze if the electronic structure is related with stoichiometry, diameter, and chirality we can make a comparison of the energy band gap values for the (8,8) nanotubes with the same  $BC_2N$  stoichiometry ( $BC_2N_1$ ,  $BC_2N_2$ ,  $BC_2N_3$ ,  $BC_2N_4$ ). As can be seen, a variation of 1.0 eV is observed in band gap, showing that the behavior changed from semiconductor to metallic. If we share the structures in groups with the same chirality, diameter and stoichiometry, despite the numerical differences (as expected), a similar profile of the gaps is observed. In other words, the atomic distribution of B, C, and N greatly affect the band gap opening (see Figures 1, 2, and 5). This is an indication of the importance of the atomic distribution of C, B, and N atoms in comparison with the stoichiometry, chirality, and diameter in determining the electronic properties of  $C_x(BN)_y$  nanotubes. However, the influence of transversal and axial atomic distributions on the electronic properties of armchair and zigzag  $C_x(BN)_y$  nanotubes remains an open question.

The results obtained can be summarized as follows: i) for the same stoichiometry, the relative stability of the tubes depends on the atomic distribution of B, N, and C atoms; (ii) the stability of the structure is defined by the number of C – C and B – N bonds (inducing C and BN domains in the hexagonal structure); (iii) the relative atomic distributions of C, B, and N atoms can have a greater influence on the electronic properties compared to stoichiometry, diameter, and chirality.

## 4. Conclusions

In conclusion, we examine that the atomic distribution of B, C, and N atoms has a great impact on the stability of the tubes. The results obtained for enthalpy of formation showed that the number of B – C, C – N, C – C, and B – C bonds influence the structural stabilization of  $C_x(BN)_y$  nanotubes. In electronic structure calculations, we report that the relative position of C, B, and N atoms is critical for determining the band gap opening. Consequently, the electronic properties can efficiently be engineered by controlling the atomic distribution of C, B, and N. These results provide the possibility of using these nanotubes (consisting of B, C, and N) in nanoelectronics.

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