A study ab-initio of relative stability and electronic properties of substitutions of C by B and N atoms in the w-BN compound

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Abstract. In this work we study relative stability, structural and electronic properties of pure BN and with substitutions of carbon by boron and nitrogen atoms, e.i. for B0.9375C0.0625N and BC0.0625N0.9375, respectively. Using first-principles calculations in the Density Functional Theory (DFT), we found that it is more energetically favourable that the carbon atoms occupy the positions of the boron atoms (C by B). It was found that the new compounds BC0.0625N0.9375 (C by N) and B0.9375C0.0625N (C by B) have high bulk modulus, so they are very rigid. This property makes them good candidates for applications in hard coatings or devices for high power and temperatures. The density of state calculations shows that compound has metallic behaviour due to the hybridization of the orbitals C-2p and N-2p that cross the Fermi level.

1. Introduction
The boron nitride (BN) is a semiconductor material. Due to different modifications in structure, zincblende (cubic) boron nitride (c-BN), wurtzite boron nitride (w-BN), hexagonal boron nitride (h-BN) and rhombohedral boron nitride (r-BN), it exhibits some very fascinating physical properties such as high temperature stability, chemical inertia, high hardness, low coefficient of thermal expansion and high thermal conductivity [1-4]. BN has a broad range of potential applications, in high temperature devices, radio frequency and high-frequency, high-power laser diodes, light emitting diodes operating in the ultraviolet region, solar detectors, field effect transistors and high electron mobility transistors [4-8]. In this paper, we present first-principles total energy calculations of the structural and electronic properties of pure BN and BN:C system. First, we calculated the structural parameters of pure BN and the two ternary compounds considered in this study (C by B and C by N). Finally, we made a detailed analysis of the density states of BN:C most favourable system. We found that the ternary compounds exhibit metallic behaviour and have a high bulk modulus, therefore can be used in hard coatings.

2. Computational method
The calculations are performed in the DFT framework using the Quantum Espresso package [9]. The correlation and exchange effects of the electrons are treated using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [10]. Electron–ion interactions were treated with the pseudopotential method [11,12]. The electron wave functions were expanded into plane waves with a kinetic-energy cutoff of 40 Ry. For the charge density, a kinetic energy cutoff of 400 Ry was used. A 6x6x6 Monkhorst-Pack mesh [13] was used to generate the k-points in the unit cell. The calculations are performed taking into account the spin polarization. To calculate the
structural, electronic, and magnetic properties of pure BN, a 32-atom $2a \times 2b \times 2c$ wurtzite supercell was considered. First, we study a carbon located in the N-substitutional site (C by N), i.e. the concentration BC$_{0.0625}$N$_{0.9375}$ and finally, we analyse a carbon located in the B-substitutional site (C by B), the B$_{0.9375}$C$_{0.0625}$N. In order to calculate the lattice constant, the bulk modulus and the total energy of boron nitride BN and the substitutions C by N and C by B, the calculated data are fitted with the Murnaghan equation of state \[14\], Equation (1).

\[
E(V) = E_0 + \frac{B_0}{B'_0} \left( \frac{V}{V_0} \right)^{1/B'_0} - \frac{B_0 V_0}{B'_0 - 1} + \frac{B_0 V_0}{B'_0 - 1}
\]

(1)

3. Results and discussions

3.1. Structural properties

The Figure 1 shows the wurtzite supercell of pure BN, the concentrations BC$_{0.0625}$N$_{0.9375}$ (C by N) and B$_{0.9375}$C$_{0.0625}$N (C by B) respectively, after of structural relaxation. In three cases, the space group obtained is the same, the tetragonal structure p3m1 (#156). The structural properties in the ground state, such as lattice constant ($a_0$), a/c ratio, bulk modulus ($B_0$) and total energy ($E_0$) of BN and BN:C (C by B and C by N). The structural properties were obtained adjusting the results of isotropic variation of the volume to the Murnaghan equation of state, Equation (1). Figure 2 shows the energy-volume curves for BN and with substitutions C by B and C by N.

![Figure 1. Unit cell of the ternary compound: (a) pure BN, (b) BC$_{0.0625}$N$_{0.9375}$ and (c) B$_{0.9375}$C$_{0.0625}$N after structural relaxation.](image)

In the Figure 2 we can observe that, with respect to pure-BN, the BC$_{0.0625}$N$_{0.9375}$ (C by N) is energetically unfavourable because, in the ground state the total energy difference between pure-BN and BC$_{0.0625}$N$_{0.9375}$ ($\Delta E=E_{BN:C}–E_{BN}$) is 232.07 eV, difference is positive because the minimum of energy of pure-BN is lower than the BC$_{0.0625}$N$_{0.9375}$ compound, while that B$_{0.9375}$C$_{0.0625}$N (C by B) is energetically most favourable, because the difference between pure-BN and B$_{0.9375}$C$_{0.0625}$N ($\Delta E=E_{BN:C}–E_{BN}$) is -112.94 eV. These results indicate that the B$_{0.9375}$C$_{0.0625}$N compound is energetically most stable, because it has the lowest energy. Additionally, table 1 shows the main structural parameters of pure-BN and BC$_{0.0625}$N$_{0.9375}$ and B$_{0.9375}$C$_{0.0625}$N concentrations.

As we can see in Table 1, the calculated lattice constant of the binary BN compound accords well with both experimentally \[2\] and theoretical \[3\] values, since it differs by less than one percent. Bulk modulus of w-BN agrees with theory work \[3\], with an error of about 1.0%. Calculated bulk modulus for w-BN is close with the diamond (442GPa). This may be due to the strong sp3 B-N bonding.
(similar structure to diamond). We note that values of the bulk modules of the pure BN, BC0.0625N0.9375 (C by N) and B0.9375C0.0625N (C by B) concentrations are higher, which confirms that they are quite rigid, making them good candidates for possible application in devices operated at high temperature and high power, as well as in hard coatings.

![Energy versus volume BN, C by B and C by N substitutions.](image)

**Figure 2.** Energy versus volume BN, C by B and C by N substitutions.

|           | \(a_0\) (Å) | c/a  | \(V_0\) (Å³) | \(B_0\) (GPa) | \(E_0\) (eV) |
|-----------|--------------|------|--------------|---------------|-------------|
| BN        | 2.550        | 1.640| 189.80       | 398.95        | -5717.36    |
|           | 2.530\(^a\) | -    | -            | -             | -           |
|           | 2.556\(^b\) | 1.650| -            | 403\(^b\)     | -           |
| C by B    | 2.540        | 1.649| 189.80       | 389.78        | -5852.30    |
| C by N    | 2.550        | 1.648| 192.14       | 395.80        | -5485.29    |

a: Experimental reference [2], b: Theoretical reference [3].

3.2. **Electronics properties**

The Figure 3 shows the total density of states (TDOS) and partial density of states (PDOS) of the orbitals that more contribute near the Fermi level for most energetically favourable substitution, namely, B0.9375C0.0625N (C by B). We note that the compound exhibit a metallic behaviour due to that valence orbitals (the two spin states, spin up and down) cross the Fermi level. This metallic behaviour it is determined by the states C-2p in greater proportion and the states N-2p and B-2p in minor proportion. Moreover, the partial density of states belonging to the C-2p orbital exhibits a high peak near of Fermi level, about -0.3eV, thus indicating localized states in that region. Additionally, we can see (Figure 3) that in the valence band around the Fermi level, the C-2p states overlap with another two peaks of smaller amplitude belonging N-2p and B-2p. Therefore, there is strong hybridization between the C-2p, N-2p, and B-2p orbitals that cross the Fermi level resulting in a strong covalent
bond that is responsible for the high rigidity of the ternary compounds. A similar result was obtained by Murillo et al [15] in their first-principles study of the C-doped AlN.

Figure 3. Density of states for substitution C by B (B_{0.9375}C_{0.0625}N) w-BN compound

4. Conclusions
We found energetically more favourable that C atoms occupy the atomic positions of B in the w-BN supercell. Additionally, we found that the compounds are rigid quite due to that the bulk modulus are high, therefore are ultra-hard and can be potentially used in hard coatings. The calculations of the density of states, show that compound has metallic behaviour due to the hybridization C-2p, B-2p and N-2p orbitals that cross the Fermi level.

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