THEORETICAL STUDY OF STRUCTURAL, ELECTRONICS AND THERMOELECTRIC PROPERTIES OF h-BN NANOTUBE ACTIVATED BY Fe IONS

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Abstract

Actually, Boron Nitride nanotubes (BNNT) have received great interest as material dedicated to many applications such as electronic and thermoelectrical devices. This work is a theoretical study of the structural, electronic and thermic transport properties of pure and iron (Fe) doped Boron Nitride nanotubes (BNNT) in its hexagonal phase (h-BN). This theoretical study was performed with the CRYSTAL program (www.crystal.unito.it) providing crystalline orbitals built on localized orbitals at the DFT (B3LYP hybrid hamiltonian) level of approximation. We have shown that Fe-doping nanotubes could behave as narrow bandgap semiconductors, the presence of Fe atoms modifying the gap value because of the presence of states participating to the thermoelectrical transport.

Our calculations show that the undoped nanotubes are ceramic materials with a large band gap around 6 eV while this latter value can be divided by 2 when the nanotube is doped by Fe. The related Seebeck coefficient, and electrical and thermal conductivity properties allow to deduce the values of the figure of merit ZT. Obtained results indicate that BNNT can be considered promising as thermoelectrical materials.

Keywords: BN-Fe nanotubes, DFT, electronic, thermoelectric

1. INTRODUCTION

Based on the similarities between carbon-based materials and boron nitride (BN)-based materials, the existence of boron nitride nanotubes (BNNTs) has been proposed [1,2]. These novel nanomaterials have shown great promise across various fields, including medicine, biology, and the nanotechnology industry. Electronic structure calculations reveal that, unlike carbon nanotubes, BNNTs are consistent bandgap materials, opening intriguing possibilities for potential device applications. Their unique properties make BNNTs appealing for a range of applications, such as optoelectronic nanodevices, functional composites, hydrogen storage, and electrically insulating substrates, including nanotube and nanosheet forms [3, 4].

Additionally, BNNTs exhibit exceptional thermal and mechanical stability, making them ideal candidates for use in nanoelectromechanical systems (NEMS) actuators. Theoretical and experimental studies indicate that BNNTs possess a high crystalline structure with minimal defects, enhancing their utility in ceramics and alloys to reduce friction on solid surfaces. The measured axial Young's modulus is approximately (1.22 ± 0.24), [5]. Consequently, BNNTs find applications in corrosion-resistant materials, transistor heat sinks, nuclear reactor control rods, crucibles for metal evaporation, and neutron absorbers [4]. Furthermore, they show potential for solar cell device applications and are recognized for their superior thermal shock resistance due to their high electrical resistance and low dielectric constant.

Various studies have demonstrated that defects in boron nitride nanotubes (BNNTs) can significantly impact their electronic, optical, mechanical, and thermoelectrical properties [6,7]. These defects are crucial for introducing new properties and applications to BNNT materials. Among these defects are vacancies and the

attachment of metal nanoparticles (such as Ag, Au, Pt, and Fe) onto BNNTs [4,13]. Additionally, edge-functionalization through hydroxylation of BNNTs presents a significant method for modifying band gaps. Through ab-initio calculations, it has shown that the energy band gap is dependent on the diameter of the nanotubes, with band gaps decreasing as tube size diminishes [8].

Currently, the pursuit of suitable thermoelectric materials is one of the most active areas of research. These materials can generate voltage from temperature differences or create temperature gradients from applied potential differences, making them applicable in two advanced industries: power generation and cooling. Modern solid-state thermoelectric devices offer effective solutions for managing heat dissipation on both large and small scales. In these devices, solid-state materials are employed for heat management, where electrons and holes behave similarly to liquids in semiconductor materials. The engineering goal for these materials in energy conversion applications is to maximize electrical power output [9-12].

In this context, our study aims to investigate the effects of iron (Fe) doping on the properties of boron nitride nanotubes (BNNTs), specifically examining how the introduction of Fe atoms influences their electronic and thermoelectric properties. A key objective is to analyze how Fe doping can modify the energy band gaps of BNNTs, potentially enhancing their performance in various applications. Additionally, the research seeks to establish the relationship between the concentration of Fe dopants and the resulting changes in the structural and functional properties of BNNTs. By optimizing Fe doping strategies, the study aims to develop advanced thermoelectric materials that leverage the unique properties of doped BNNTs for improved efficiency in power generation and cooling applications. Ultimately, the goal is to engineer these materials for maximum electrical power conversion in thermoelectric devices through effective iron doping techniques.

2. THEORETICAL AND COMPUTATIONAL DETAILS

Our study is began from a perfect one-dimensional (1D) boron nitride (h-BN) nanotubes obtained by rolling a (2D) hexagonal sheet of the BN (modelized by SLAB model), (n,m)=(10,0) giving a BNNT of radius of 3.98Å. To study the effect of iron on BNNTs, two cases are considered, the substitution of one and two atoms of Fe with one and two atoms of N, respectively **Figure 1**. Positions of Fe atoms are selected with respecting of symmetry and to ensure to the conditions of convergence of calculations.

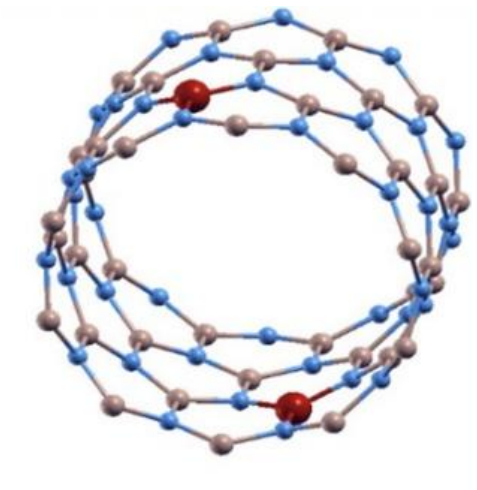


Figure1 Non relaxed BNNT 3x1x1 supercell doped Fe atoms. Blue, purple and red circles represent, respectively; B, N and Fe atoms

First-principles calculations were all carried out using CRYSTAL 17 software package [14] within the framework of the density functional theory (DFT) at the level of B3LYP hybrid hamiltonian [15]. Consistent Gaussian basis-sets of triple-zeta (TZVP) and double-zeta (DZVP_rev2) valence with polarization quality are used for B and N atoms, respectively, and all electrons (86-411d41G) for Fe atom [14] are used. To define a reasonable orbital occupancy in presence of Fe atoms, a spinlock option is used and optimized. These forces a given (n_α-n_β) electrons value to obtain a correct atomic spin density to start SCF process. Calculations are released for BNNT (10, 0) doped with one and two Fe atoms, for this a supercell of 3 times the primary cell along the principle tube axis is used (3x1x1)p. undoped BNNT structures are studied and used as references. A set of 12 × 1 × 1 Monkhorst-Pack corresponding to 7 special *k* points is used to sample the Brillouin zone of the system. Before starting the actual calculations and to obtain minimal value of energy, the geometry of the structures was optimized by consideration of all atoms of our structure including Fe atoms. All atoms were free to move in all directions. As default, the model of optimization adopted in the Crystal code is of Hessian [14].

3. RESULTS AND DISCUSSION

3.1. Structural and Electonic properties

Relaxed structure obtained after optimization of the supercell (3x1x1)p containing 120 atoms of (10,0) is used to simulate BNNT doped Fe materials. Our calculations show that non doped structure is not relaxed.

The substitution on a single Fe atom by N atoms has an important effect on the relaxation of the structure. For this, full structural relaxation is performed and obtained structure is represented in the **Figure2**.

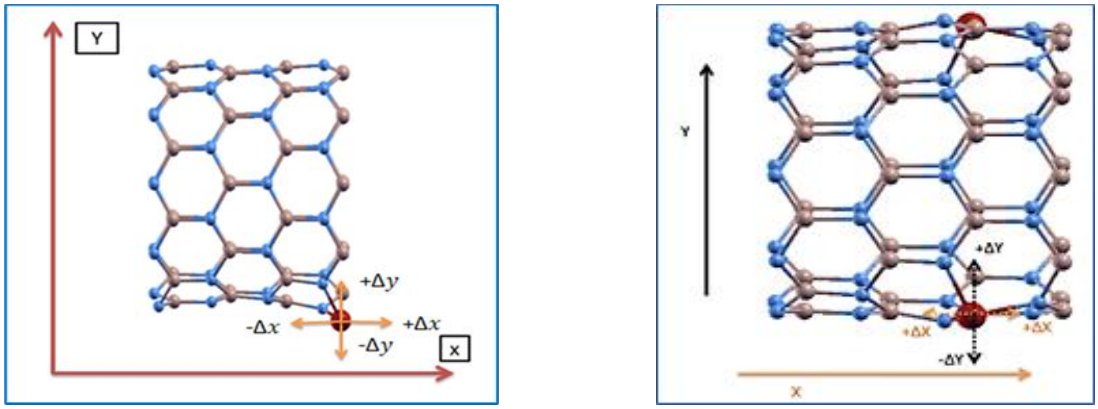
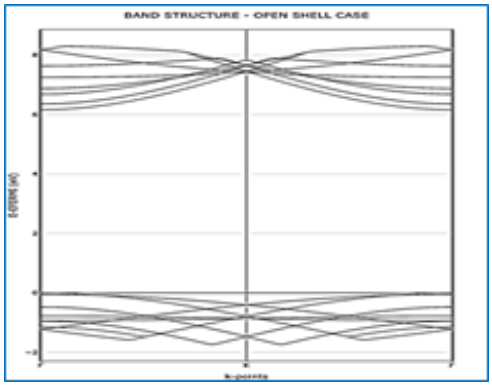


Figure2 relaxation parameters Δx and Δy for BNNT (a) doped with single Fe atoms and (b) doped with two Fe atoms

An important displacement of Fe atoms and her neighboring is presented by the structures. How inner and outer variations of relaxation parameters (Δx and Δy) varied between 0.3Å to 1Å for the BNNT:1Fe and between 0.6Å to 1Å to BNNT:2Fe are measured as mentioned at the **Figure 2**. We notice that there is no reconstruction of all structures.

The nanotube deformation confirms the formation of a strong chemical bonding between Fe atoms and B ones.

a)



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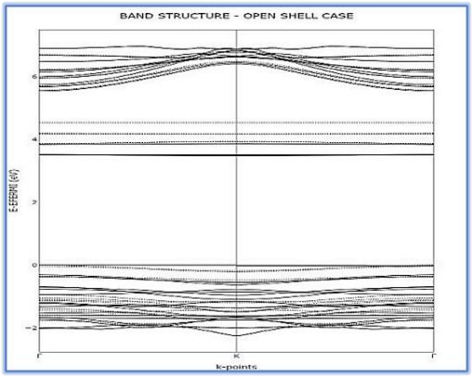

c)

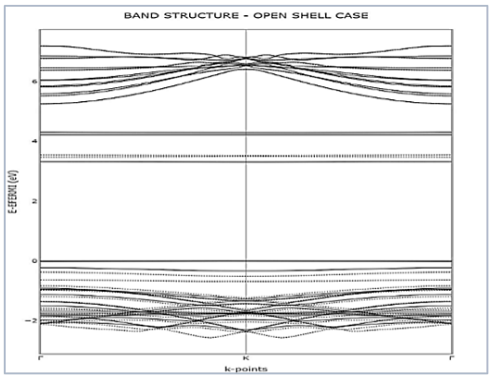

Figure3 band structures of BNNT structures (a) undoped, (b) doped with 1Fe and (c) 2Fe

Band structures and density of states (DOS) from Γ (0, 0, 0) to K (1, 1,0) points corresponding to the direction Σ of the Brillouin zone are computed for non-doped and doped BNNTs **Figure3**.

The band gap calculated value of non-doped BNNTs is 6.16 eV. The presence of Fe atoms caused a diminution of this value to 3.5 eV for BNNT:1Fe and to 3.31 eV for BNNT:2Fe. From **Figure3**, we find that this diminution is caused by presence of impurities states. Knowledge of the nature of these contributions is release by calculating of the projected density of state (PDOS) represented in the **Figure 4**. It is apparent that this is the result of participation of (3d) AOs of Fe atoms in the band gap. In addition, the asymmetry of the PDOS in the range of 0 to -0.4 eV and from 3 to 4 eV caused by the spin state difference caused by the presence of the Fe atoms. We can conclude the increases of the magnetic characteristics in this compound.

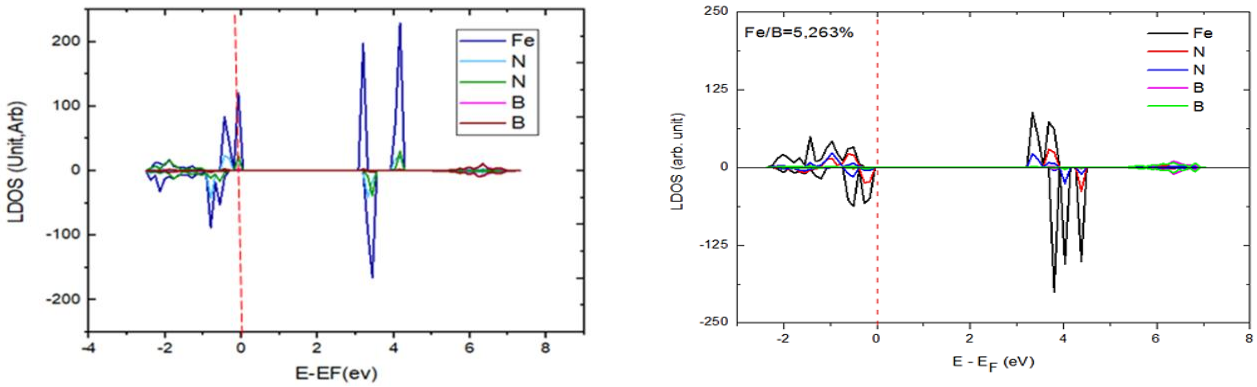

Figure4 projected density of state (PDOS) on the AOs of the Fe atoms for BNNT:1Fe and BNNT:2Fe.

The comparison with another works (table1), we see that our results are slightly different from those obtained in the literature.

Table 1 energy band gap values comparison

	BNNT	BNNT:Fe
Our results	6.16	3.31 / 3.50
References	5.5 [16] - 5.8 [6]	3.16 [7]

3.2. TRANSPORT PROPERTIES

The Seebeck coefficient, Electrical and thermal conductivity, can be estimated by calculating the three transport coefficients. These expressions are obtained by solving Boltzmann's transport equation within the relaxation time approximation [9]. We note that, using Crystal code, the thermal conductivity is derived from only the electronic thermal conductivity k_{el}.

The effect of doping with Fe atoms on the thermoelectric properties of BNNT is represented here. In **Figure 5**, the variation of Seebeck coefficient (S) of the different BN nanotubes are shown as a function of the, where μ is the chemical potential at different values of temperature: 900 K, 1200 K and 1500 K. Here, (μ-E_F) is positive for n-type doping and negative for p-type doping.

The Seebeck coefficient displays a symmetric behavior with respect to the charge neutrality point (μ = 0.0 eV) and its maximum value varies from 0.003V/K for 900K to 0.002V/K for 1500V/K for undoped BNNT. The positive and negative values at Fermi energy level confirm the existence of band gap and our materials are a semiconductor. Now, introducing Fe atoms has decreased the value of Seebeck coefficient to 0.002V/K at the temperatures 900 K and to 0.001 V/K at 500 K for different concentrations of Fe atoms **Figure 5(b-c)**. which is comparable to the other suitable thermoelectric compounds, as 110 μ V/K for BN-Be (8.0) [18] and 0.06 x 10^{-3} eV/K for (pristine (6,6)-CNT) up to 4.0 x 10^{-3} eV/K (pristine (6,6)-BNNT) upon increasing the BN concentration [17].

The corresponding μ values of S_{max} for doped BNNTs move far from the charge neutrality point more and more according to the doping rates. This displacement is due because of decreasing of the electronic bandgap caused by presence of "3d" states of Fe atoms. In addition, we notice in the interval of the 1 to 3 eV, appearance of new states participating to the thermal transport. The significant Seebeck coefficient demonstrates that a small temperature difference creates a large voltage on both sides of the material, so a large Seebeck coefficient is essential for a thermoelectric material.

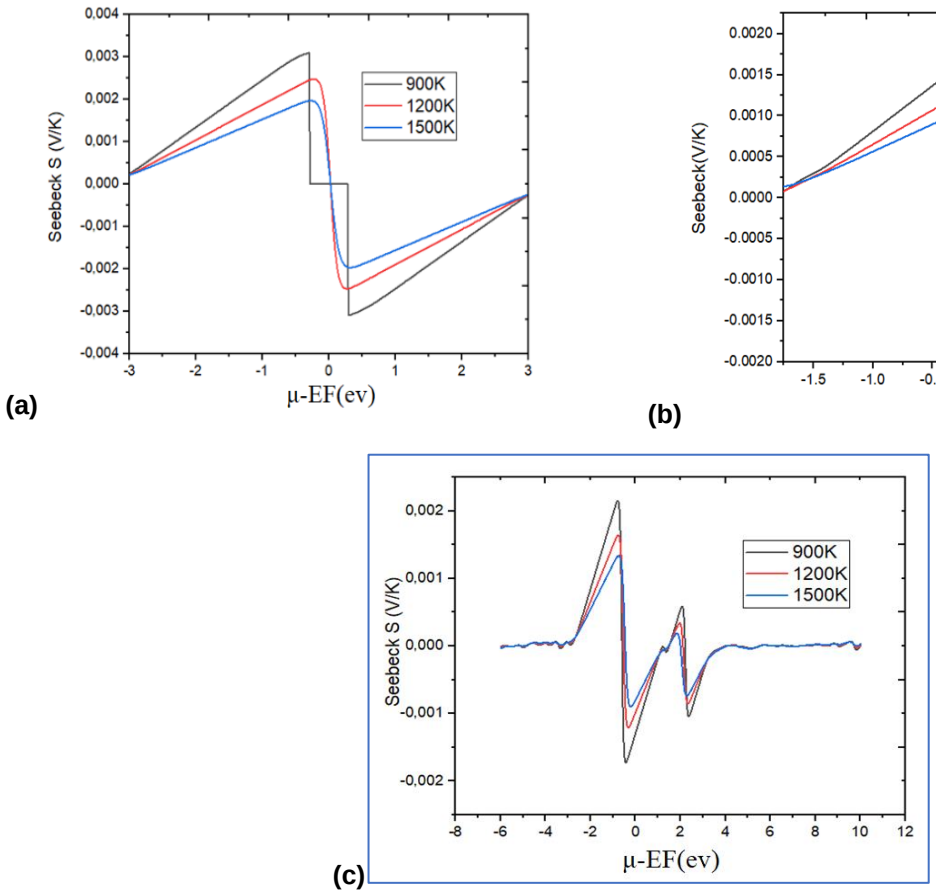

Figure 5 Seebeck coefficient at various temperatures; (a) pure BNNTs, (b) BNNT:1Fe and (c) BNNT:2Fe

It is well known that good thermoelectric materials must have high electrical conductivity. This is the case of our material. As mentioned in the **Figure 6-a**, electrical conductivity (σ) and electronic thermal conductivity (K) presents an important value for different structures. Thus, values of electrical conductivity varied for 900 K from $40x10^{+6}$ $\Omega^{-1}.m^{-1}$ for undoped BNNT to $6x10^{+8}$ $\Omega^{-1}.m^{-1}$ for BNNT:2Fe. In addition, the electronic thermal conductivity oscillates 2500 W/mK for undoped BNNT to 11000 W/mK for BNNT:2Fe. Comparing to the CNT, how it's characterized by a thermal conductivity superior as 3000 W/mK. Our results have verified the high thermal conductivity how reflect a good choice of conditions of calculation as compared with other works [11,17,18].

The thermoelectric efficiency of materials, important to know if the materials are good thermoelectrically or not, can be measured by calculating the dimensionless figure of merit, ZT, and the power factor, which can be calculated using the following formula. $ZT = S^2\sigma T\ K$, where T is the absolute temperature, S is the Seebeck coefficient or thermopower, σ is the electrical conductivity, and K is the thermal conductivity, including the electron contribution only ($K=K_{el}$) see **Figures 6-b**. For all cases we observe that the (ZT) is at his maximum values (~0.98) near to the value "1" and we noticed the appearance of the of "d" states intensively in the case of 2Fe doping **Figures 6-c**. Moreover, ZT values increase strongly with chemical potential and its maximum

value is observed for a range of -3.3 to 3 eV for both cases of doping. These results proves that BNNTs materials are promising to thermoelectrical applications.

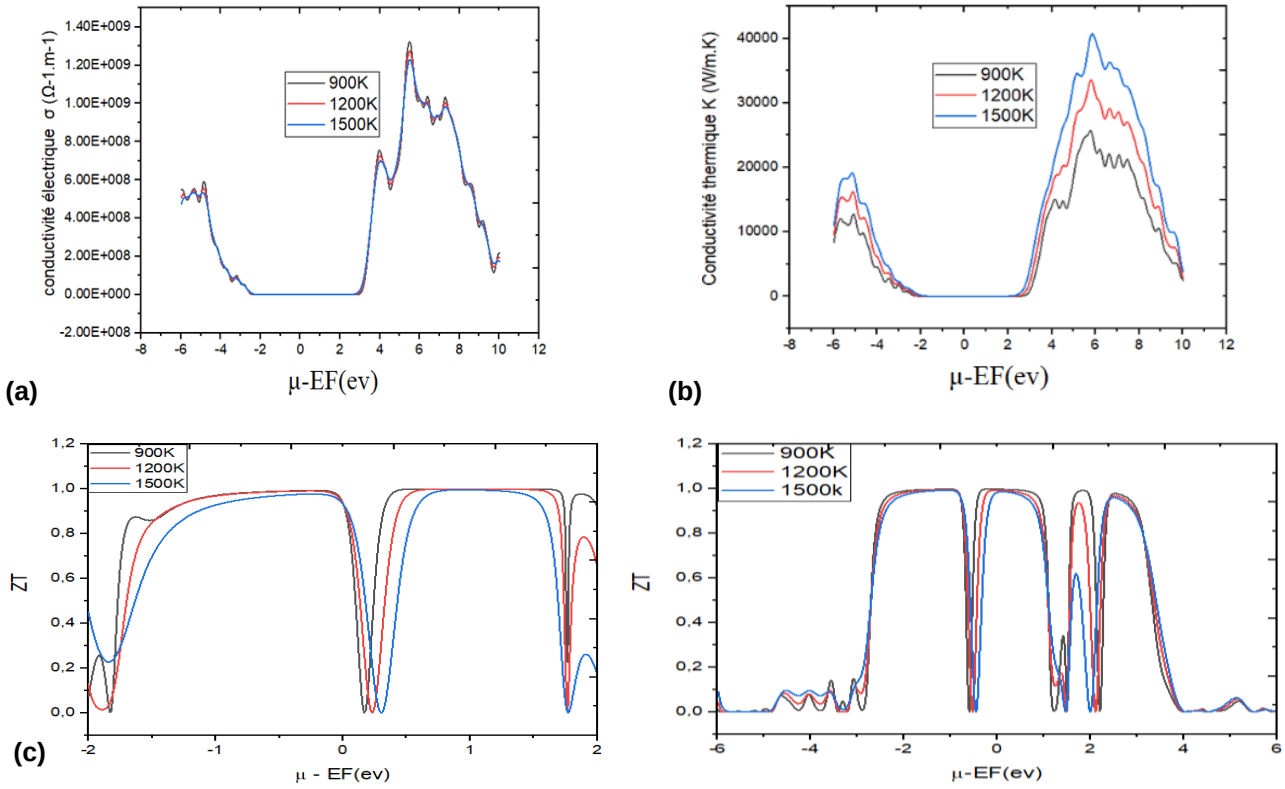

Figure 6 (a) electrical conductivity, (b) electronic thermal conductivity (Ke) for BNNT:2Fe and (c) figure of merit for BNNT:1Fe and BNNT:2Fe for different temperatures

4. CONCLUSION

This work presents an *ab-initio* calculation of the structural, electronic, and thermoelectric properties of BNNT activated by Fe atoms. Doping with metallic species significantly contributes to thermal transport due to the appearance of new impurity states. The substantial Seebeck coefficient indicates that a small temperature difference generates a large voltage across the material, making a high Seebeck coefficient crucial for thermoelectric materials. The results show that the presence of Fe atoms reduces the band gap due to the involvement of "d" states, which contribute to the thermal transport in BNNT:Fe.

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