The optoelectronic properties of boron nitride nanotubes of armchair (7, 7) and zigzag (12, 0) types: A theoretical study

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Abstract. In this article, the electronic and optical properties of single-walled boron nitride nanotubes (SWBNNTs) in zigzag (12, 0) and armchair (7, 7) configurations were examined using density functional theory (DFT) with the Vienna Ab initio Simulation Package (VASP). The analysis shows that SWBNNTs exhibit electronic characteristics with a density of states and an electronic band gap around 4 eV. Regarding optical properties, the calculations reveal key features such as absorption, reflection, and dielectric constant, with a notably strong absorption peak in the ultraviolet region. These results highlight the potential of SWBNNTs for applications in optoelectronic devices.

1 Introduction

Carbon nanotubes have been widely studied. Their diameters and chiralities give them both semiconducting and metallic properties, making them attractive for applications in nanoscale devices such as single-electron transistors, gas storage materials, and magnetic refrigerators [1]. Additionally, several studies have focused on boron nitride (BN) nanomaterials, including BN nanotubes, BN nanocapsules, BN nanoparticles, and BN clusters. BN nanotubes, structurally similar to carbon nanotubes, consist of alternating boron and nitrogen atoms that entirely replace carbon atoms in a graphite-like sheet, with minimal variations in atomic spacing. In 1981, Ishii et al. reported the discovery of one-dimensional boron nitride (BN) nanostructures with a bamboo-like structure, which they termed BN whiskers [2]. However, it was not until 1994 that the existence of BN nanostructures with flawless tubular structure was first proposed by theoretical studies [3], before being synthesized by arc discharge in 1995. In the following years, much of the research has focused on synthesizing boron nitride nanotubes (BNNTs) and characterizing their structures. In recent years, there has been a growing interest in boron nitride nanotubes (BNNTs) due to their semiconductor properties across all configurations, featuring a wide band gap. These characteristics make them particularly suitable for the development of ultraviolet light-emitting devices and various applications in solar cells. Furthermore, their ability to maintain stable optoelectronic properties under extreme conditions opens up new

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possibilities for applications in harsh environments and for the advancement of sophisticated sensors [4]. In this study, we undertook a theoretical investigation of the optoelectronic properties of boron nitride nanotubes (BNNTs) with dimensions (12, 0) and (7, 7) for the first time, using density functional theory (DFT). We examined electronic properties such as electronic band gap and density of states, as well as optical properties such as absorption, reflection, and real and imaginary parts. This research is of particular importance for future applications in nanotechnology and in the field of solar cells, offering adjustable properties.

2 Models and computational method

In this study, we used computational methods based on density functional theory (DFT) to explore the electronic and optical properties of boron nitride nanotubes (BNNTs) in armchair (7, 7) and zigzag (12, 0) configurations. The calculations were performed using the Vienna Ab initio Simulation Package (VASP), with an energy cutoff of 520 eV and a k-mesh of 1x1x5 to ensure sufficient accuracy. PAW-PBE pseudopotentials were employed to model the interactions between electrons and atomic nuclei, focusing only on valence electrons. Prior to analyzing the electronic properties, a geometric relaxation of the nanotube structures was carried out to minimize the forces acting on the atoms and the system's total energy, reaching a convergence threshold of 10^{-6} eV. For the optical properties, absorption coefficients were calculated from the complex dielectric function $\varepsilon(\omega)$, using the Kramers-Kronig transformation to relate its real and imaginary parts. The results show that the nanotubes exhibit a strong absorption peak in the ultraviolet region, highlighting their potential for applications in optoelectronic devices.

3 Results and discussion

3.1 Density of states

Figure1 present the density of states (DOS) of single-walled boron nitride nanotubes (SWBNNTs) of zigzag (12,0) and armchair (7,7) types, plotted as a function of the energy difference ($E - E_f$) in electronvolts (eV). For the armchair (7,7) structure, the density of states shows a significant concentration of electronic states at high energy levels, indicating the presence of numerous states available for electronic transitions. The DOS curve also exhibits several fluctuations, revealing electronic transitions occurring within the conduction band. Regarding the zigzag (12, 0) structure, it displays a different density of states distribution, characterized by less pronounced peaks at higher energy levels. The DOS features a broader distribution of states in the conduction band indicating a reduced density of states compared to the armchair configuration. This supports the notion that the zigzag structure behaves as an insulator. A comparative analysis of the DOS indicates that the armchair structure (7, 7) exhibits a higher density of states at higher energy levels, suggesting semiconductor behavior, while the zigzag structure (12,0) shows a lower density of states, consistent with its insulating characteristics. The differences in density of states between these two configurations highlight the influence of the chirality of the nanotubes on their electronic properties. The presence of a greater number of available electronic states in the armchair structure suggests it could have improved conductivity compared to the zigzag structure [10]. In parallel, the electronic properties of zigzag single-walled boron nitride nanotubes (ZSWBNNTs) (12, 0) and armchair single-walled boron nitride nanotubes

(ASWBNNTs) (7, 7) were also examined. The results indicate that ZSWBNNTs exhibit semiconductor behavior, while ASWBNNTs display insulating behavior. Additionally, ZSWBNNTs possess direct band gaps, whereas ASWBNNTs have indirect band gaps. These findings are consistent with previous studies, as indicated in the figures and summarized in Table 1. The values of the electronic band gaps align with experimental results reporting a gap of approximately 4 eV for SWBNNTs [9]. The analysis of electronic properties confirms the value of the band gap for SWBNNTs, which falls within the same range as previously studied BNNTs. Furthermore, a higher density of states is observed in the valence band compared to the conduction band, which is consistent with earlier observations. These results align with the previously mentioned values of electronic gaps and reinforce the interpretation that SWBNNTs with different chirality exhibit distinct electronic behaviors. In summary, the analysis of the density of states reveals essential information about the electronic properties of SWBNNTs, highlighting the behavioral differences between zigzag and armchair structures, which are crucial for potential applications in electronic devices.

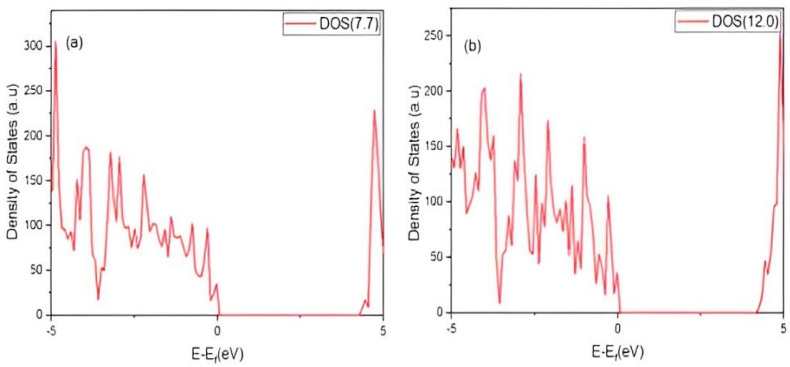

Fig. 1. Density of states for SWBNNT (a) armchair (7.7) and (b) zigzag (12.0).

Table 1. The electronic properties, including HOMO, LUMO, Fermi Energy, and HOMO-LUMO gaps, for SWBNNT armchair (7.7) and zigzag (12.0).

	Homo	Lumo	E_f	Eg
(12.0)	−4.8031	−0.5530	−4.794949	4.2501
(7.7)	−4.7944	−0.3833	−4.742320	4.4111

3.2 Dielectric Constant

Simulation analyses were conducted on the real and imaginary parts of the dielectric function of single-walled boron nitride nanotubes (SWBNNT) (7, 7) and (12, 0) in both low and high energy ranges. The studies were performed in the parallel and perpendicular directions to the nanotube axis for both systems studied, as illustrated in Figures 2 and 3.

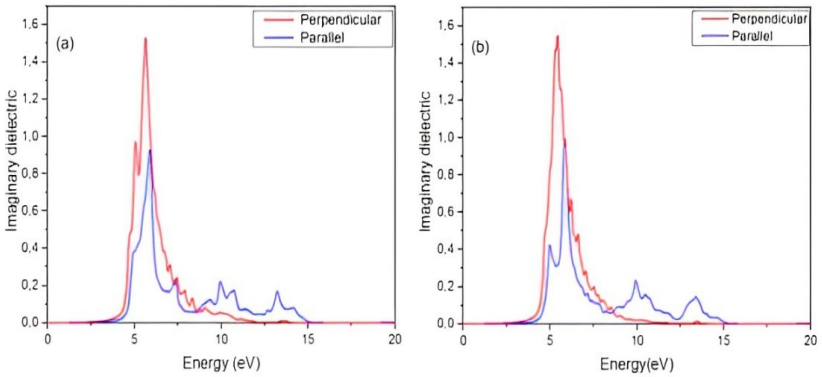

Fig. 2. Imaginary dielectric for SWBNNT (a) armchair (7.7) and (b) zigzag (12.0).

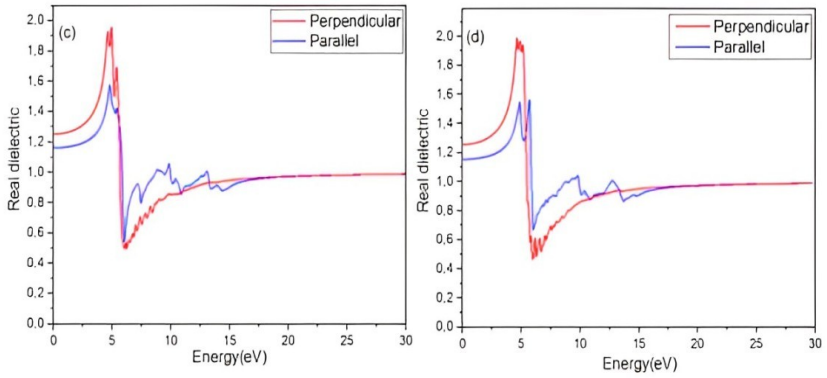

Fig. 3. Real dielectric for SWBNNT (c) armchair (7.7) and (d) zigzag (12.0).

The peaks in the imaginary parts of the dielectric constants for SWBNNTs (12, 0) and (7, 7) clearly reveal their optical band gaps. For both systems, results were calculated for the directions parallel and perpendicular to the tube axis. For SWBNNT (7, 7), optical gap values of 5.63 eV and 5.88 eV were obtained, while for SWBNNT (12, 0), the values were 5.41 eV and 5.85 eV, respectively, in the parallel and perpendicular directions. The results show that the optical gap is larger for SWBNNT (7, 7), confirming that armchair-type structures tend to exhibit wider band gaps compared to zigzag-type structures. As shown in the figures 2, the optical band gap of SWBNNT (12, 0) and (7, 7) in the imaginary part of the dielectric function is larger in the perpendicular direction than in the parallel direction, indicating clear anisotropy in the dielectric function of SWBNNTs [10,11]. Furthermore, the dielectric function in the z-direction is generally higher than in the x-direction across most energy ranges. Peaks observed in the imaginary part of the dielectric function correspond to inter-band transitions [12], where electrons transition from the valence band to the conduction band upon absorbing photons. These findings underscore the critical role that the directionality and structure of boron nitride nanotubes play in determining their optical and electronic properties.

3.3 Reflection

Our study shows the reflectivity properties of boron nitride nanotubes (BNNTs) in two orientations (Figure4): perpendicular and parallel to the nanotube axis. It is clear that reflectivity is significantly higher for short wavelengths, around 200 nm, when the light is perpendicular to the nanotube axis. This phenomenon is explained by transverse electronic transitions, such as π-π* excitations, which are more intense in this configuration [13]. Conversely, when the light is parallel to the nanotube axis, the reflectivity is significantly lower, indicating a more limited interaction between the light and the nanotube in this direction. This optical anisotropy, where the response varies depending on the light's orientation, highlights the directional nature of BNNTs' properties, typical of nanostructured materials. Additionally, differences in the intensity of reflectivity peaks between the two graphs can be observed, which may be linked to structural differences between the nanotubes studied, such as the zigzag (12,0) and armchair (7,7) configurations. These variations demonstrate the importance of nanotube chirality on their optical properties, offering the possibility of tailoring these materials for specific applications. The strong reflectivity observed in the UV region could, for example, be used in detection devices or UV reflectors, while the low reflectivity in the parallel direction could be utilized in applications requiring directional transparency. In summary, understanding this optical anisotropy in BNNTs opens interesting perspectives for their use in optoelectronic or photovoltaic devices, where the orientation and structure of the nanotubes could be adjusted to optimize performance.

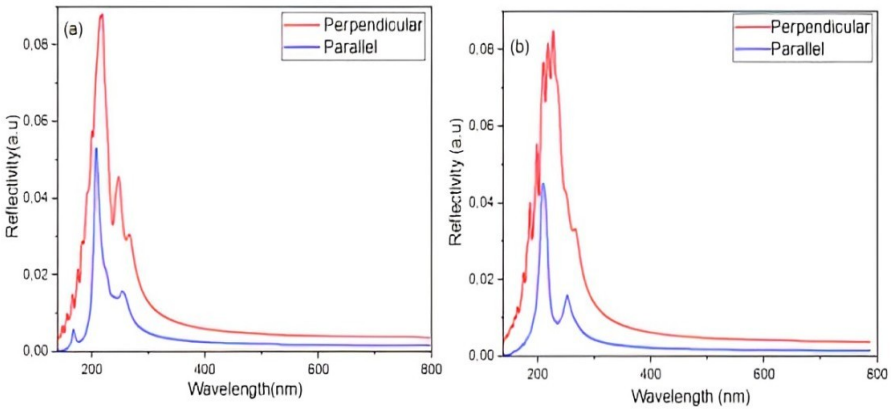

Fig. 4. Optical reflection for SWBNNT (a) armchair (7, 7) and (b) zigzag (12.0).

3.4 Absorption

To gain a deeper understanding of the fraction of incident photons absorbed, we investigated the light absorbed per unit distance in a medium, referred to as the absorption coefficient. This study simulated the variation of this coefficient for the (7,7) and (12,0) structures of single-walled boron nitride nanotubes (SWBNNTs), analyzing both parallel and perpendicular orientations relative to the nanotube axis. We examined the absorption coefficient α (ω) for the incident light with frequency ω, employing the well-known expression:

$$P(\omega) = \chi(\omega)\, E(\omega) \tag{1}$$

where *P(ω)* represents the macroscopic polarization and E(ω) the electric field[15].

$$\alpha(\omega) \sim \omega\, \mathrm{Im}\, \chi(\omega) = \mathrm{Im}[\ ] \tag{2}$$

The spectrum of single-walled boron nitride nanotubes (SWBNNTs) shows notable differences between the zigzag and armchair configurations (Figure5), reflecting the impact of structural chirality on optical properties. In both configurations, the nanotubes exhibit distinct absorption behaviors depending on the polarization of light relative to the nanotube axis. For armchair-type SWBNNTs, such as the (7, 7) configuration, the absorption peaks are generally more intense, particularly in the UV region around 200 nm, when the light is polarized perpendicular to the nanotube axis. This can be attributed to more efficient electronic transitions, such as $\pi - \pi^*$ excitations [15]. Conversely, in the parallel direction, absorption is significantly weaker, illustrating the anisotropic nature of these materials. On the other hand, zigzag-type SWBNNTs, like the (12, 0) configuration, follow a similar trend, although the intensity of the absorption peaks is generally weaker compared to armchair configurations . The optical gap tends to be smaller in zigzag structures, leading to less pronounced absorption in the UV region. However, as with the armchair structures, absorption is also much weaker in the parallel direction, confirming the strong directional dependence of the optical properties of SWBNNTs. In conclusion, both zigzag and armchair SWBNNTs exhibit marked anisotropy in their absorption spectra, with armchair nanotubes generally displaying stronger absorption in the perpendicular direction. These differences are critical for tailoring SWBNNTs for specific optoelectronic applications, where their optical response can be optimized based on the structural configuration [4].

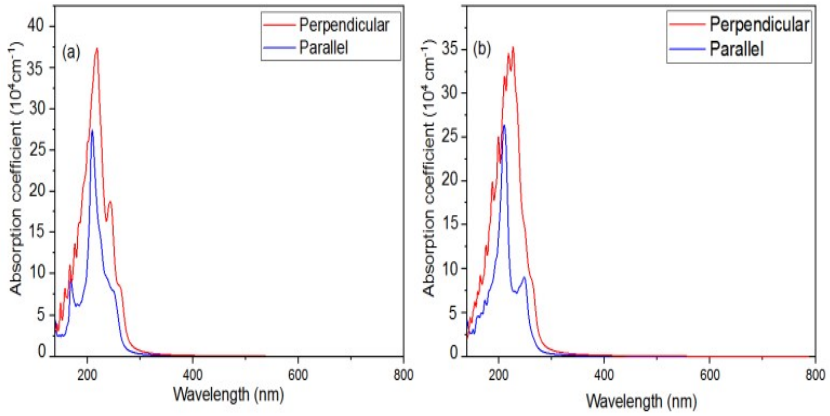

Fig. 5. Optical absorptivity for SWBNNT (a) armchair (7, 7) and (b) zigzag (12.0).

4 Conclusion

Our study explored the electronic properties of single-walled boron nitride nanotubes (SWBNNTs) in the zigzag (12,0) and armchair (7,7) configurations. We observed an electronic band gap of around 4 eV, confirming the potential of these nanotubes as semiconductors for applications in transistors and

other electronic devices. Their density of states exhibits behavior typical of materials with a wide bandgap, which could be utilized in various electronic systems. Regarding optical properties, our calculations revealed significant absorption in the ultraviolet region, paving the way for applications in UV detectors, solar cells, and other optoelectronic devices. The chemical and mechanical stability of SWBNNTs, combined with their unique electronic and optical properties, makes them promising materials for cutting-edge technologies in photonics and electronics.

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