A Comparative Study of Optical Anisotropies of BC₃ and B₃C Systems by Density Functional Theory

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The optical properties of (8,0) BC₃ and B₃C single-wall carbon nanotubes (SWCNTs) are computed using ab initio density functional theory (DFT). The electronic band structure reveals that the Fermi energy of B₃C system is reduced compared to BC₃. The static dielectric constant in the long wavelength limit for B₃C system is 9 times larger than that of BC₃ in unpolarized electromagnetic field. Within 10 eV frequency (energy) range, the absorption coefficient of B₃C is higher compared to BC₃, while, above 10 eV, it is less than that of BC₃. In parallel polarization, the peak of the loss function for B₃C is shifted to higher frequency (energy) region with significantly six orders of magnitude compared to BC₃ system. The analysis of this study indicates that the optical anisotropies can be gained easily in these boron-doped systems by appropriately choosing the direction of the polarization of the electromagnetic field. Besides, the results of the loss functions may throw some light on the nature of collective excitations of these two systems.

1. Introduction

From its very discovery in 1991, carbon nanotubes (CNTs), both single wall as well as multiwall, have attracted the attention of theoretical and experimental research groups [1, 2]. Due to their unique one-dimensional structure and unusual electronic properties, they can be regarded as one of the natural building blocks of molecular electronics. Single-wall carbon nanotubes (SWCNTs) consist of a single graphene layer rolled on a cylinder with diameters between 1 and 2 nm having lengths of the order of few hundred micrometers. The calculations reveal that their electronic properties can be semiconducting, metallic, or quasimetallic depending on their geometrical structure dictated by a quantity known as the chirality. The optical properties of 4 Å diameter pure SWCNT have been investigated [3–5] recently by first principles calculation to explain the experimental results. Most recently, ab initio calculations of the linear and nonlinear optical properties of pure CNTs have shown that the dielectric function depends essentially on chirality, diameter and the nature of polarizations of incident electromagnetic field [6].

The electronic properties of single-wall carbon nanotubes (SWCNTs) can be tailored [7, 8] by substituting carbon atom(s) by heteroatom (s) such as boron or nitrogen. It is well known that pure CNTs are unable to detect highly toxic gases, water molecules, and biomolecules [9]. To improve the nanosensor reliability and quality, the importance of substitution alloying of impurity atoms such as boron and nitrogen has been discussed [10]. In fact, a calculation on the chemical interaction reveals that the boron doped CNT can act as a novel sensor [11] for formaldehyde. The synthesis of composite BₓCᵧNₐ tubes has been performed and their energy loss spectroscopy have been reported [12, 13]. In general, through the reaction of B₂O₃ with CNTs under an Ar atmosphere [14], B atom(s) can be substituted for the carbon atom(s) of SWNT. In the literature, the synthesis and electronic properties of B-substituted SWCNT have been discussed [15, 16]. A quantum chemical calculation [17] has been employed to
investigate the larger mobility (i.e., electronic conductivity) of B- and N-doped CNTs. Recently, the electronic structure and optical properties of B-doped single-wall carbon nanotubes (SWCNTs) have been studied in detail, and it is found that boron is in sp$^2$ configuration [18]. It has also been shown recently that even a small amount dopant can significantly change the mesoscopic conductivity [19] of chemically B-doped CNTs. The electron current distribution in B- and N-doped armchair CNTs has been investigated [20] using Density Functional Theory (DFT) and Green’s function to show a chiral flow of current. All the above examples eventually indicate the importance of the study of B-doped CNTs and invite further investigation about the optical properties of the doped system as a function of B concentration. Since this doping can alter the band structure and optical properties of the doped system as a function of B concentration, we would naturally invoke for the optical calculation. Because of using of the self-consistent Kohn Sham (KS) equation has been employed here to compute the eigenstates. To determine the wave functions in (1), we perform the first-principles spin unpolarized density functional theory using plane wave pseudopotential methods [30, 31]. Like any ab initio calculation, the self-consistent Kohn Sham equation has been employed here to compute the eigen function. For the exchange and correlation term, the generalized gradient approximation (GGA) as proposed by Perdew-Berke-Ernzerhof [32] is adopted. The standard norm-conserving pseudo-potential in reciprocal space is invoked for the optical calculation. Because of using of nonlocal potentials in this software, the matrix elements are modified as

$$
\langle \psi_k^p | \vec{r} | \psi_k^s \rangle = \frac{1}{im_{\omega}} \langle \psi_k^p | \vec{p} | \psi_k^s \rangle + \frac{1}{h_{\omega}} \langle \psi_k^p | V_{\alpha}(\vec{r}), \vec{r} | \psi_k^s \rangle.
$$

(2)

In comparison with the standard local density approximation (LDA) (with appropriate modifications) used mostly in electronic band structure calculation, the optical properties of the system are normally standardized by spin unpolarized GGA.

The typical computational supercell used here is the 3D triclinic crystal ($a = 18.801$ Å, $b = 19.004$ Å, $c = 4.219$ Å, and angles $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$) having symmetry P1. The supercells are built by taking four units of CNT. The energy cut-off, k-point sampling, geometry, GGA/norm-conserving pseudopotential are the same in these two systems as well...
as the pristine one. The anisotropic behavior in the optical properties can be investigated by taking into account the polarization vector $\mathbf{u}$ of the electromagnetic field in (1). Thus, the dielectric constant can be evaluated for three separate cases: one can choose in the direction of $\mathbf{u}$ (i) of electric field vector for the light at normal incidence (polarized); (ii) choosing $\mathbf{u}$ in the direction of propagation of incident light at the normal incidence but the electric field vector is considered as an average over the plane perpendicular to this direction (unpolarized); (iii) choosing $\mathbf{u}$ not in specified direction while the electric field vectors are taken as full isotropic average (polycrystalline). The directions of the field ($\mathbf{k}$ wave vector) have been chosen with respect to axis of the B-doped carbon nanotubes.

The parallel polarization refers to $k(0,0,1)$ while perpendicular one $k(1,0,0)$.

### 3. Numerical Results and Discussions

#### 3.1. Study of Band Structure of $B_3C$ and $BC_3$ Systems

Before we discuss the optical properties, we show in Figure 1 the typical ball and stick model of $(8,0)$ BC$_3$ and B$_3$C systems.

All the results presented in this paper have the same set of parameters as indicated in earlier section. For pure $(8,0)$ we find the Fermi energy $6.028$ eV with band gap at $\Gamma$ point (most symmetric point in the BZ) as $0.48$ eV. However, alloying with boron atoms in $(8,0)$ nanotubes such as in BC$_3$ system, the Fermi energy reduces to $4.256$ eV. With increasing
B3C nanotubes, a further reduction of the Fermi energy to more number of boron atoms in SWNTs, we find, for (8,0) (Un: unpolarized, Perp: perpendicular, Para: parallel).

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0.58 eV at $\Gamma$ point, which is larger than the pure one. This is understood simply from the fact that the electronic configuration of B atom is $1s^2\,2s^2\,2p^1$.

Therefore, doping by B atom always reduces the total number of electrons $N_0$ in the system which on the other hand implies the decrease of Fermi energy with B doping. This has also been observed in boron doped multiwalled carbon nanotubes [33, 34]. In Figure 2, we show the typical number of self-consistent field (SCF) iterations and the convergence of the typical energy per atom of B3C system.

In Figure 3, we schematically show the band structure of B3C system, respectively. All the energies shown in the diagram have been measured with respect to the Fermi energy (shown as the dashed line in the band diagram). The most symmetric point ($k_x = k_y = k_z = 0$) is known as $\Gamma$ point and is denoted by G in the energy band diagram. The band gap in B3C system turns out as 0.43 eV at $\Gamma$ point, which is smaller than the pure one.

However, for B3C system, the band gap turns out as 0.58 eV at $\Gamma$ point, which is larger than the pure one. This is expected as the Fermi energy of B3C is higher compared to its counterpart s electrons. However, the contribution of s electrons in both of the cases in the conduction band is meagre. In B3C case, the contribution of p electrons at the Fermi level have been increased substantially compared to pure case. In fact, the higher value of DOS at the Fermi level signifies the metallicity character of B3C. The DOS at the Fermi level is a measure of available free charge carriers. Thus, the increase of the DOS at the Fermi levels is a signature of more metallic character of B3C system compared to B3C one.

The direction with relatively flat dispersionless bands at various $k$-points seems to contribute significantly to the optical absorption and hence allows one to explain the anisotropy of the optical properties. This is due to the fact that at those $k$ values the group velocity of the electronic states vanishes with increase of DOS. Hence, an increase of the value of $\varepsilon_2$ is expected.

3.2. Study of Dielectric Constant of BC3 and B3C Systems. We compute the imaginary part of the dielectric constant within the specified frequency range. The polarizations of the electromagnetic field play an important role in computing the imaginary part of the dielectric constant. We

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>BC3</th>
<th>B3C</th>
<th>Pristine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fermi energy</td>
<td>4.25 eV</td>
<td>3.61 eV</td>
<td>6.03 eV</td>
</tr>
<tr>
<td>(Un)</td>
<td>38.45 eV</td>
<td>346.58 eV</td>
<td>19.82 eV</td>
</tr>
<tr>
<td>Static real dielectric constant</td>
<td>21.71 eV</td>
<td>76.80 eV</td>
<td>11.66 eV</td>
</tr>
<tr>
<td>(Perp)</td>
<td>33.26 eV</td>
<td>396.71 eV</td>
<td>30.98 eV</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>Lower</td>
<td>Higher</td>
<td>Highest</td>
</tr>
<tr>
<td>Loss function</td>
<td>Lower (7–12 eV) (Un)</td>
<td>Higher in the same Range (Un)</td>
<td>Higher than BC3 but lower than B3C (Un)</td>
</tr>
<tr>
<td>Reflectivity</td>
<td>Smaller (Para)</td>
<td>Larger (Para)</td>
<td>Higher than BC3 but very close to B3C (Para)</td>
</tr>
</tbody>
</table>

(Un: unpolarized, Perp: perpendicular, Para: parallel).

**Table 1: Comparison of electronic and optical properties of BC3 and B3C systems.**

![Figure 4: Typical band structure of BC3 system.](image-url)
compute the dielectric constant for parallel, perpendicular polarization and unpolarized one with normal incidence (1,0,0). The parallel polarization refers here to the direction of light parallel to the axis of respective SWCNTs. In Figure 5, we schematically show the dielectric constant (real) for both pure (8,0), BC$_3$- and B$_3$C-doped systems as a function of frequency for unpolarized scheme. It is seen in the numerical computation (not shown in the figure) that, in both cases, the imaginary part of the dielectric constant is always positive throughout the range of frequency. This can be understood...
very simply from (1) used for the numerical simulation study. The square of the matrix element and the even functional nature of the energy conserving delta function ensure the positivity of $\varepsilon_2$. This property of $\varepsilon_2$ serves as one of the crosschecks in our numerical computation.

However, as evident from the figure itself, such a restriction is not obeyed by the real part of the dielectric constant $\varepsilon_1$. We also note that the static value (strictly speaking $\omega \to 0$ but in our numerical computation $\omega = 0.0150 \text{ Hz}$) of the dielectric constants for both pure and doped systems is always positive. This observation is further satisfied by a theorem in continuous media stating that the static electric dielectric constant is always positive [35] for any material in thermal equilibrium. The variation of static
dielectric constant with concentration of B has been reported recently [36] to show that a small concentration is enough to change the value drastically from the pure (8,0) SWCNT. It is evident from Figure 6 that the static value of the dielectric constant (real as well as imaginary) of BC₃ system is higher compared to pure one. It has been observed that the static dielectric constant of B₃C is higher than that of BC₃ for any type of polarizations (see Table 1).

In case of semiconducting SWCNT, an ab initio tight-binding calculation [37–39] relates the static value of the dielectric constant with the energy band gap as

\[ \varepsilon_1 (0) = 1 + \frac{(\hbar \omega_p)^2}{(5.4 E_g^2)^2}. \]  

(3)

Here \( \omega_p \) is the plasma frequency and \( E_g \) is the energy band gap. Our numerical calculations are in qualitative agreement with the higher value of the dielectric constant B₃C compared to BC₃ one. In particular, the static dielectric constant in the long wave length limit for B₃C system is 9 times larger than that of BC₃ in unpolarized electromagnetic field with normal incidence (1,0,0).

### 3.3. Study of the Absorption Spectra of the Doped System

The absorption coefficient \( \alpha \) is related to the imaginary part of the dielectric constant as

\[ \alpha = \frac{\varepsilon_2 \omega}{nc}, \]  

(4)

where \( n \) and \( c \) are the refractive index and the speed of light, respectively. The absorption spectra depend critically on the nature of CNT as well as the direction of polarization. The absorption spectra are limited to UV region only.

The existence of peaks in the spectra indicates the maximum absorption at that particular energy. With doping by B atom(s), both the magnitude of the peaks and its position change significantly. We depict, in Figure 7, a comparative study of the absorption coefficient of BC₃ and B₃C systems as a function of frequency in the unpolarized case with normal incidence (1,0,0). We notice that in contrast to B₃C, there exist several peaks in the absorption spectra. The existence of these rich absorption peaks in the overall frequency range is consistent with the theoretical tight-binding calculations made on (3,3) and (6,0) BC₃ nanotubes [40]. It is also evident from the figure that up to 10 eV or so (frequency measured in units of energy), the absorption coefficient of B₃C is always higher than that of BC₃. However, above 10 eV, the reverse is true.

### 3.4. Study of the Reflectivity at Normal Incidence of the Doped System

The reflectivity \( R(\omega) \) of any media at normal incidence is calculated from the refractive indexes via the relations (as implemented in CASTEP [25]) given by

\[ R(\omega) = \left( \frac{1 - \sqrt{\varepsilon(\omega)}}{1 + \sqrt{\varepsilon(\omega)}} \right)^2, \quad \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega). \]  

(5)

It is clearly evident from the definition that the reflectivity is always positive in the scheduled range of the frequency and is dimensionless. \( R \) is sometimes regarded as the index of refraction as a function of wavelength of light used. In Figure 8, we show the variation of reflectivity of BC₃ and B₃C systems for parallel polarization as a function of frequency. It is clear from the figure that the reflectivity of B₃C system is always higher than that of BC₃ in the whole range of frequency. This could be helpful in designing optical devices involving B-doped SWCNT.

### 3.5. Study of the Loss Function of the Doped System

In this time-dependent calculation of the ground state electronic states, the interaction is between the photon and electrons. The transitions between the occupied and unoccupied states are caused by the electric field of the photon. When these excitations are collective in nature, they are termed as plasmons. The loss function, which is a direct measure of the collective excitations of the systems, is defined as \( \text{Im}[-1/\varepsilon(q, \omega)] \). Since we are taking \( q \to 0 \) limit in our calculation, therefore, we are considering the loss function behavior under the long wavelength limit. The peak position of this loss function determines the typical energy of the plasmons in the system. High-resolution transmission electron microscopy (HRTEM) and nanoelectron energy loss spectroscopy (nano-EELS) can provide information about the systematic and atomic structural defects of B-doped SWCNTs [41–43]. The spectra resulting from these collective excitations can be alternatively understood as a joint DOS between VB and CB weighted by appropriate matrix elements. In terms of the real and imaginary dielectric constants, a straightforward algebra reveals that \( \text{Im}[-1/\varepsilon(q, \omega)] = (\varepsilon_2(\omega)/\varepsilon_1^2(\omega) + \varepsilon_1^2(\omega)). \) At the plasma frequency, the above expression attains the higher value when \( \varepsilon_1 \to 0 \) and \( \varepsilon_2 < 1 \).

In Figures 9 and 10, we depict the anisotropic signature of BC₃ and B₃C systems for unpolarized case and parallel polarization, respectively. For unpolarized case, we notice that within the range of frequency (7–12 eV), the loss function of BC₃ is smaller than that of B₃C. However, above 12 eV, the loss function of BC₃ is higher than that of B₃C. Besides, the main peak of BC₃ at 7.24 eV is seen to shift to 9.89 eV with significantly higher magnitude. While in parallel polarization as evident from Figure 10, the single peak of B₃C at 8.39 eV is shifted to 8.81 eV for BC₃ system with significantly six orders of magnitude. In Table 1, we summarize the main results of the two systems.

### 4. Conclusions and Perspectives

From the first-principles relaxed C–C bond length DFT calculation of the optical property of BC₃ and B₃C (8,0) SWNT systems, we have observed significant changes in the optical behavior for different polarizations. The behavior of the static dielectric constant of B-doped system depends on the flavor (nature) of the nanotubes. The anisotropy signatures of the dielectric constants noticed in these systems are due to the confined geometry of the CNTs. The electronic band structure reveals that the Fermi energy of B₃C system is reduced compared to BC₃. The static dielectric constant in
the long wavelength limit for B$_3$C system is 9 times larger than that of BC$_3$ in unpolarized electromagnetic field with normal incidence (1,0,0). Within 10 eV frequency (energy) range, the absorption coefficient of B$_3$C is higher compared to BC$_3$, while, above 10 eV, it is less than that of BC$_3$. In parallel polarization, the peak of the loss function for B$_3$C is shifted to higher-frequency (energy) region with significantly six orders of magnitude compared to BC$_3$ system. All these facts about these two systems may throw some light on the nature of collective excitations and nanoscale optical devices.

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