



# **Structural, Electronic and Optical Properties of Stanene Doped Beryllium: A First Principle Study**

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## **Authors' contributions**

*This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.*

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## **ABSTRACT**

Stanene is a 2D hexagonal layer of tin with exceptional electronic and optical properties. However, the semiconductor applications of stanene are limited due to its zero band-gap. However, doping stanene could lead to a band gap opening, which could be a promising material for electronic and optical applications. In this work, optimized structure, electronic band structure, real and imaginary parts of the frequency-dependent dielectric function, electron loss function, and refractive index of stanene substitutionally doped with alkaline earth metal (beryllium) were analyzed using density functional theory (DFT) calculations as implemented in the quantum espresso and yambo suites. A pure stanene has a zero band gap energy, but with the inclusion of spin-orbit coupling in the electronic calculation of pure stanene, the band-gap is observed to open up by 0.1eV. Doping stanene with beryllium opens the band-gap and shifts the Dirac cone from the Fermi level, the band gap opens by 0.25eV, 0.55eV, and 0.8eV when the concentration of Beryllium is 12.5%, 25%, and 37.5% respectively. The Dirac cone vanished when the concentration of the dopant was increased to 50%. The Fermi level is shifted towards the valence band edge indicating a p-type material. The material absorption shows that SnBe absorption ranges in the visible to the ultraviolet region. The refractive index in stanene doped beryllium (SnBe) was found to be higher than that of pristine stanene, the highest refractive index was 9.2 at SnBe25%. In a nutshell, the results indicate that stanene can be a good material for electronic and optical applications if doped with beryllium.

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## 1. INTRODUCTION

Recently, a lot of attention has been drawn to study two-dimensional materials due to their exceptional electronic and optical properties. After the discovery of graphene, the heavy group-IV elements silicon (Si), Germanium (Ge), and Tin (Sn) are receiving a lot of interest owing to their almost identical electronic properties. For example, charge carriers act like massless Dirac Fermions resulting from linear band dispersion at the Fermi energy [1]. Recently, various experimental methods have been used to obtain 2d materials. Molecular beam epitaxy was used to synthesis honeycomb-like structures of silicene and germanene[2]. Being one of the most salient honeycomb-like structures, stanene also shows interesting properties like Dirac-cone shaped energy band structure with Dirac-cone-shape, topological superconductivity, a near room temperature and the ultra-high carrier mobility [3]. However, the zero band-gap in stanene which shows the semiconductor nature of stanene restricts its semiconductors application [4]. Thus, doped stanene could be a promising material for various electronic applications. Therefore, the thought of a band-gap opening in stanene has raised a lot of scientific interest. Various attempts have been taken to tune the electronic properties of stanene. Ghezali et al showed that when external strain and electric field is applied there is an effect in the electronic band gap, while the Dirac cone-like shape is still present at the Fermi level. They concluded that in tuning the band gap, the external electric field is effective [5]. Abbasi & Sardroodi illustrated that the band-gap in stanene can be opened up by functionalization. Also, in modulating the electronic properties of stanene the substrate plays a key function due to the strong interaction [6]. In the bonding and anti-bonding states of stanene, substrate induces band inversion which results in a band-gap opening, thus substrates affect the electronic properties of stanene [7]. Recently, Liu et al. showed that a tunable gap is induced in stanene when a stanene hetero-structure is made with an h-BN sheet [8]. However, another effective way of modulating the electronic properties of 2D materials is by doping, thereby altering the symmetry of the sub-lattice.

In 2016, using first-principles calculations within density functional theory (DFT) alkaline and alkaline earth metals were doped into stanene

with the contingency of creating superconductivity. They found that superconductivity is achieved when stanene is doped with calcium and Lithium, at a very low superconducting transition temperatures  $T_c$  of 1.3K and 1.4K respectively. These values, when compared with the case of grapheme doped lithium are smaller [9]. In early 2017, while maintaining the linear dispersion at Dirac points, stanene (Sn) on graphene (C) substrate was synthesized. Also, the tunable band-gap is excited at stanene's Dirac points resulting from the sub-lattice interaction between stanene and grapheme heterostructure. The band-gap created due to spin-orbit coupling corresponded to the band-gap created due to the substrate effect in Sn on C, the Sn on C system displayed semiconductor material properties [10]. Evazzade et al. used first-principles calculations to investigate the electronic properties of two-layer molecules of stanene and fluorine. They found that the band structure indicates a minor overlap between valence band maxima and conduction band minima at the Dirac, this indicates properties of semimetal in the two-layer SnF system. Their results suggest that the bilayer SnF is not a potential material for topological insulators [11]. Abbasi & Sardroodi carried out calculations on the band-gap variations in stanene via density functional theory, and the effects of elemental doping were taken into account. They found that, for the pure stanene sheet, Sn 5p orbitals contributed most in the valence and conduction bands. The pure stanene has an energy band gap  $E_g = 0$ , with a Dirac cone shape like at the Fermi level ( $E_f$ ). The doped systems (Al, B, N, and P) exhibit metallic properties. In the Al and B-doped stanene, the ( $E_f$ ) shifts towards the valence band maxima, while in the N- doped and P-doped systems, the ( $E_f$ ) shifts towards the conduction band minima. These doped materials exhibit characteristics of degenerate semiconductors, these characteristics result from the shifts in( $E_f$ ). Silicon and Germanium were also investigated in their work. Due to the similar properties of Silicon, Germanium, and Tin atoms, both Silicon and Germanium-doped stanene exhibit similar properties to pure stanene. The Dirac cone exists around the ( $E_f$ ) level in all the doped systems except for nitrogen-doped stanene in which the Dirac cone vanishes. Their results thus suggest a theoretical basis for the potential application of such doped systems in

electronic and optoelectronic devices [12]. Abbasi carried out DFT calculations to observe the changes in the electronic properties of stanene when co-doped with metal and nonmetal. There is a band-gap opening of about 0.07eV when stanene is co-doped with AIP whereas pure stanene has a zero band gap. Also, the band-gap opening in individual doping of Al and P into stanene is smaller compared with the co-doped AIP system. In SnAl system the Fermi level shifts towards the valence band, they suggest that SnAl shows metallic properties. In SnP system, the Fermi level shifts towards the conduction band edge. Mulliken's charges show that the Aluminium atoms were positively charged, while Phosphorus atoms were negatively charged. They found that AIP- co-doped stanene shows semiconductor material characteristics, while individual doping of Al or P atoms gives a metallic system. They suggest a theory basis for AIP-co-doped stanene monolayer for application in future nanoelectronic devices [13].

In this work, we analyzed the optimized structure, electronic band structure, real and imaginary part of the dielectric function, electron energy loss function, and refractive index of stanene doped beryllium (SnBe) by using first-principles density functional theory (DFT) calculations. A similar approach had been used by Ullah et al on graphene [14].

## 2. THEORETICAL BACKGROUND

Density functional theory (DFT) is a computational quantum mechanical modeling method, used in finding solutions to the fundamental equation that describes the behavior of atoms and molecules. It is used in material science to investigate the electronic structure of many-body systems, ionic states, neutral states, surface defects, in particular atoms, molecules, and condensed phases. Besides its simplicity, it is highly successful in describing structural and electronic properties in quite many materials [15]. DFT focus on the electron density, rather than the many-body wave function. The fundamental rule of DFT is that the total energy of the system is a unique functional of the electron density, therefore, it is not required to calculate the full many-body wave function of the system. Nevertheless, the accurate value of the functional dependence of the energy on the density is unknown[16].

The progress of the DFT was determined by Hohenberg, Kohn and Sham, which certified the

model instinctively developed by Thomas, Fermi, and Dirac. For practical reasons, they replace the term  $U_{ei}$  with  $V_{ext}$  to identify that the electrons move in an arbitrary external potential including the Coulomb energy due to point nuclei, so that the Schrödinger equation for N electrons reads:

$$[T + U_{ee} + V_{ext}]\psi_{el} = E_{el}\psi_{el} \quad (1)$$

and the electronic energy is a functional of the electron density  $n(r)$

$$E_{el}[n] = \langle \psi_{el} | H | \psi_{el} \rangle = F[n] + \int V_{ext}(r)n(r)dr \quad (2)$$

where

$$F[n] = \langle \psi_{el} | H | \psi_{el} \rangle + \langle \psi_{el} | U_{ee} | \psi_{el} \rangle = T[n] + U_{ee}[n] \quad (3)$$

is called universal energy functional, implying that it does not contain the external potential  $V_{ext}(r)$  and can be determined independently of  $\int V_{ext}(r)n(r)dr$ . The effects of electron-electron interactions are expressed by Local Density Approximation (LDA) or Generalized Gradient Approximation (GGA)[17].

## 2.1 Computational Method

In this paper, the electronic properties of SnBe were performed based on the first principles density functional theory calculations as implemented in the Quantum Espresso code. The electronic calculations were performed within the Generalized Gradient Approximation (GGA) and the Perdew-Burke- Ernzerhof exchange (GGA-PBE) correlation was adopted. For describing the electronic wave function (GGA-PBE), the projected augmented wave (PAW) method was employed. To obtain accurate results, the energy of the system convergence was achieved with respect to effective parameters of self-consistent calculations, such as energy cut-off and the number of k points. The structural model of the 2d nano sheets of stanene and doped stanene was viewed with XcrysDen. The k-point path for band structure calculations was done according to the high symmetry path Brillion zone for hexagonal lattices, as  $\Gamma$ -K- M- $\Gamma$ . The required k-points for this path is generated using the XcrysDen package. The density of states (DOS) was computed with higher k-points. After the structure, band structure, DOS, and PDOS of pure stanene were calculated. Beryllium (dopant) was embedded substitutionally by removing one Tin atom from a super-cell of eight atoms and filling the vacancy by an atom of beryllium

(dopant), the same process was repeated while increasing the number of atoms that were replaced thereby increasing the concentration of the dopant. The real and imaginary parts of the dielectric function and electron energy loss function of photon energy were obtained from the Yambo simulation package via the DFT+RPA method. From the real and imaginary parts of the dielectric function, optical properties like absorption coefficient, refractive indices, etc can be derived.

The refractive index  $\eta(\omega)$  was obtained from the equation[18].

$$\eta(\omega) = \sqrt{\frac{\epsilon_1(\omega) + \sqrt{Y}}{2}} \quad (3)$$

and

$$Y = \epsilon_2^2(\omega) + \epsilon_2^2(\omega) \quad (4)$$

Where

$\epsilon_1$ = Real parts of frequency dependent dielectric function,

$\epsilon_2$ = Imaginary parts of frequency dependent dielectric function

### 3. RESULTS AND DISCUSSION

#### 3.1 Pristine Stanene

##### 3.1.1 Structural and electronic properties

A 2-d hexagonal unit cell is considered for the stanene structure, the computed lattice parameter in stanene is  $a=b=9.36$ , and the Sn-Sn bond length is  $2.8258 \text{ \AA}$ , which is in line with a previously reported value of  $2.82 \text{ \AA}$ [13], and the buckling height of is  $0.87$ , this is in good agreement with a previous investigation [12].

Fig. 1(a) Optimized structure of stanene which indicates Sn-Sn bond length of  $2.8258 \text{ \AA}$ . (b) band structure of stanene where the Fermi level is set to zero, the figure shows that stanene is a zero band-gap material with Dirac cones at k points. (c) Band structure of stanene with spin orbit coupling inclusion, the band gap opens when we include spin orbit coupling in our electronic structural calculations, it gives a band-gap of  $0.08 \text{ eV}$  after inclusion of SOC, which is close to a previous reports  $0.07$  on stanene with the inclusion of SOC[5].

#### 3.2 Optical Properties

To understand the optical applications of a material, it is crucial to investigate the optical properties of the material. The optical properties were calculated by evaluating microscopic dielectric function  $\epsilon(\omega)$  via random phase approximation (RPA) based on PBE (DFT+RPA) without taking into account the electron-electron and electron-hole interaction. The real part of the dielectric function indicates the amount of material polarized as a result of induced electric dipole creation when an electric field is applied while imaginary part of the dielectric function indicates the quantity of material absorption photon energy. Fig.2 (a) and (b) show the real and imaginary parts of the dielectric function of pure stanene. The peak of the material absorption of photon energy was found to be at  $0.15 \text{ eV}$ . The electron energy loss function  $L(\omega)$  describes the loss in energy of a fast-moving electron traversing the material, the peaks in  $L(\omega)$  spectra reveals the point of transition from the metallic to dielectric property of the material called Plasma frequency. Fig.2 (c) shows the electron energy loss function of pure stanene. The peak was found to be at  $3.5 \text{ eV}$ , the sharp maxima peak of the energy loss function indicates the existence of plasma resonance which corresponds to the results of John 2017[19]. The refractive index is a quantity that describes how much light is refracted after entering the material, the refractive index was found to be  $3.4$ . Fig.2 (d) shows the plot of the refractive index.

#### 3.3 Stanene Doped Beryllium

##### 3.3.1 Structural and electronic properties

The Beryllium doped system has been investigated and found to be promising for electronic applications. Here, we have considered 12.5%, 25%, 37.5% and 50% of beryllium doping i.e. for 12.5% one Be atom was doped in 8 atomic unit cells of stanene. The SnBe buckles like stanene, though the buckling of SnBe is higher than that of pristine stanene. Furthermore, the structure distorts more due to the difference in atomic radius.

To understand the change in electronic properties due to Be-doping, the electronic structure in Fig.3 (a), (b), (c), (d), (e), (f), (g) and (h) show that the Fermi level is shifted towards the valence band edge compared to in pristine stanene and this indicates that stanene doped

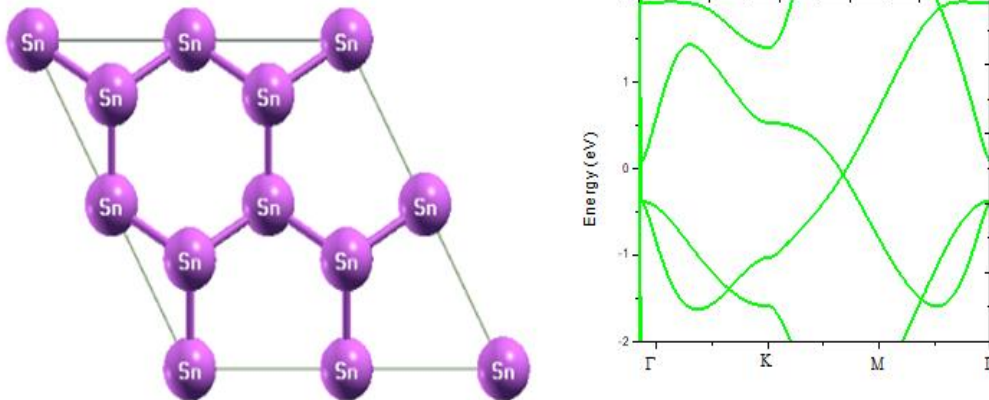
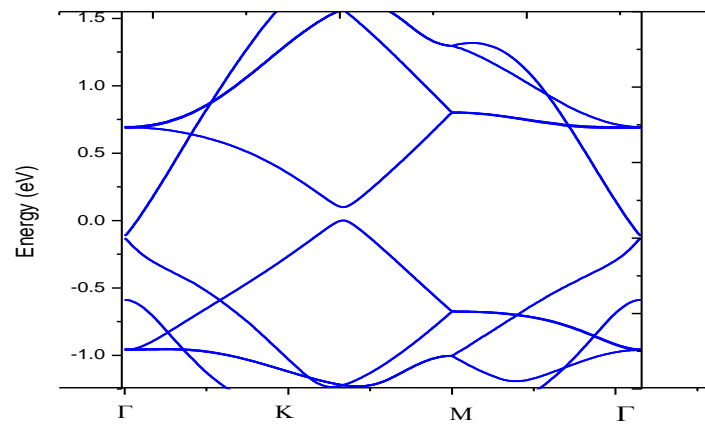


Fig. 1. a) Optimized structure of stanene (b) Electronic Band structure of stanene



c) Electronic Band structure of stanene with spin-orbit coupling inclusion

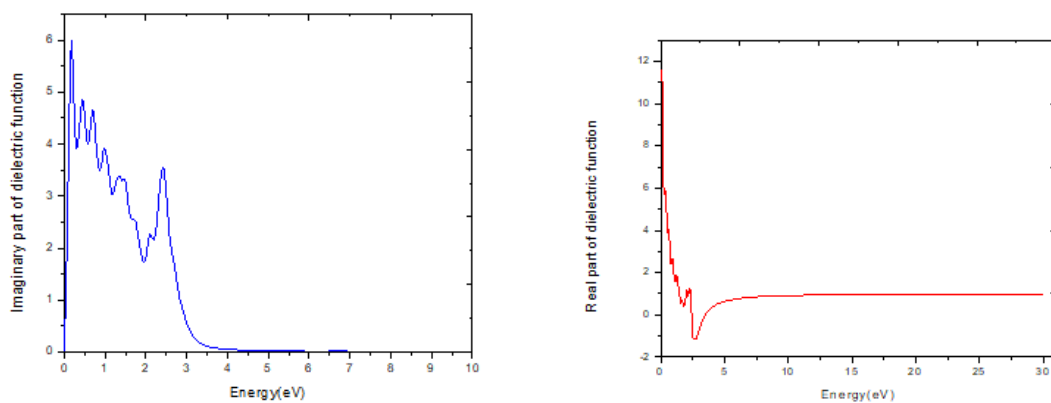
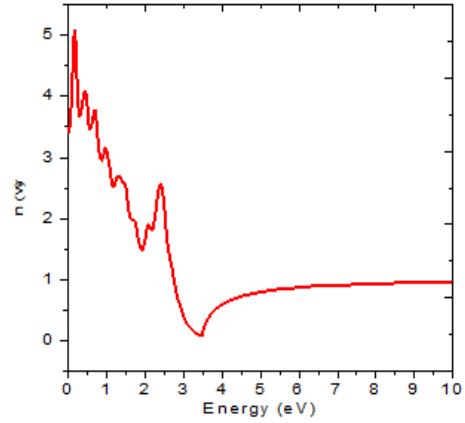
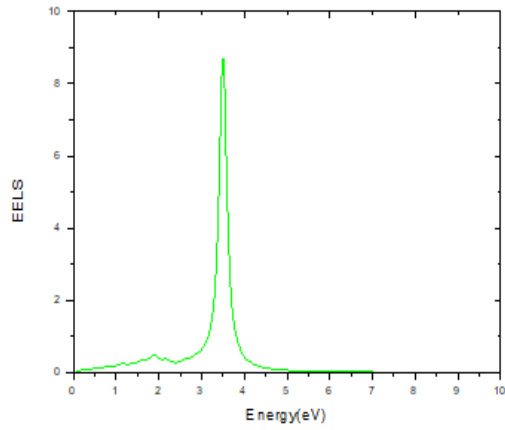


Fig.2 (a) Imaginary part of dielectric function (b) Real part of the dielectric function of pure stanene



(c) EEIS

(d) Refractive Index

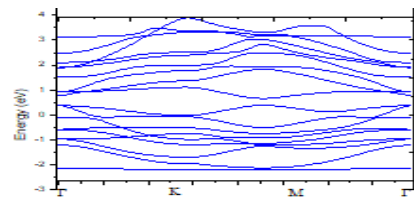
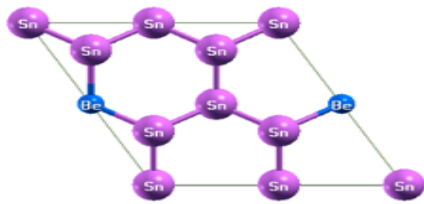
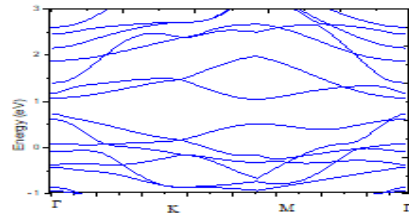
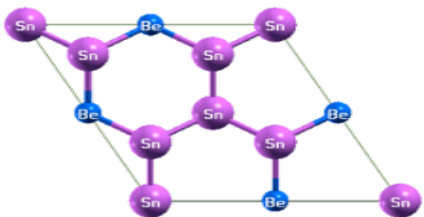


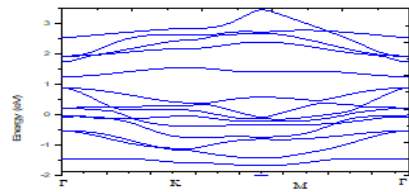
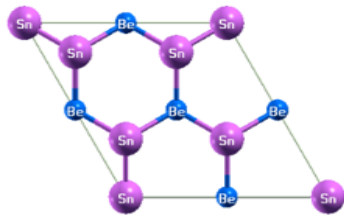
Fig.3 (a) Optimized Structure of SnBe12.5%

(b) Electronic band structure of SnBe12.5



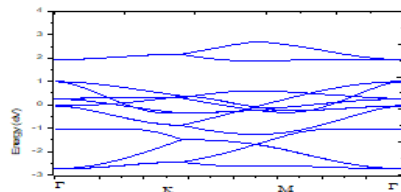
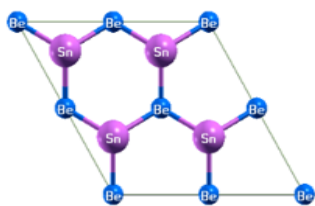
(c) Optimized Structure of SnBe25%

(d) Electronic Band structure of SnBe25%



(e) Optimized structure of SnBe37.5%

(f) Electronic Band structure of SnBe37.5%



(g) Optimized Structure of SnBe50%

(h) Electronic Band structure of SnBe50%

Fig. 3.

beryllium is a p-type material. Doping stanene with 12.5% beryllium shifts the Dirac cone 0.4eV from the Fermi level, the Fermi level is set to zero, there is a band-gap of 0.25eV above the Fermi level. In 25% and 37.5% concentration of beryllium doping the band-gap above the Fermi level are 0.55eV and 0.8eV, respectively. this indicates that stanene doped beryllium is a p-type material. the Dirac cone disappears when the concentration of beryllium is increased to 50% as shown in Figure .

### 3.4 Optical Properties

The optical properties were calculated by evaluating the microscopic dielectric function  $\epsilon(\omega)$  via random phase approximation (RPA) based on PBE (DFT+RPA) without taking into account the electron-electron and electron-hole interaction. Fig.4 (a) and (b) show the real and the imaginary parts of the dielectric function of stanene doped beryllium. The material absorption for SnBe12.5%, SnBe25%, SnBe37.5% and SnBe50% were found to be 0.11eV, 0.22eV, 0.28eV and 0.14eV respectively. Although the material can absorb photon energy up to 3.5eV as the imaginary line approaches zero. The relatively strong absorption of the

0.11-3.5eV energy range shows that SnBe has the potential to be used for detecting light within the visible and the ultraviolet regions. An added advantage is that the peak is obtained in the visible region which would find applications in optoelectronic devices.

The electron energy loss function peak for SnBe were found to be 3.1eV, 2eV, 1.8eV and 1.5eV for SnBe12.5%, SnBe25%, SnBe37.5% and SnBe50% respectively. The highest peak was at 3.1eV which is lower than that of pristine stanene, The cause of several peaks in the electron loss function is as a result of collective excitations at various photon energies. A peak in the loss function corresponds to a dip in the dielectric function. Fig.4 (d) shows the refractive index for SnBe. The refractive index of SnBe was found to be higher than that of pristine stanene, having the highest refractive index of 9.2 for SnBe at SnBe25%. this infers that the velocity of light decreases as it polarizes through the doped system when compared with pure stanene. From the refractive index plot, we noted that the material possesses a high refractive index within the infrared region and decreases at higher energy in the visible to UV region.

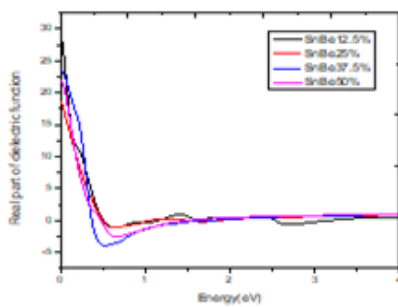
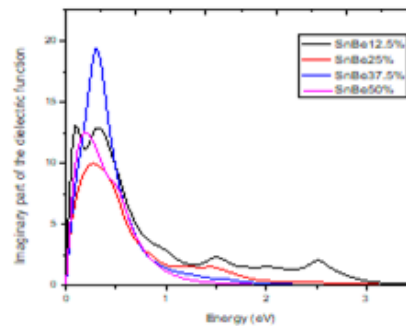
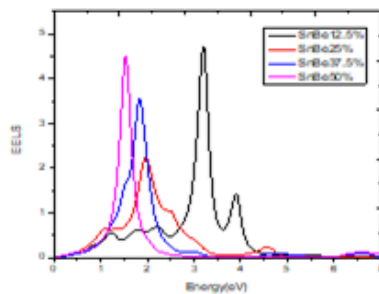


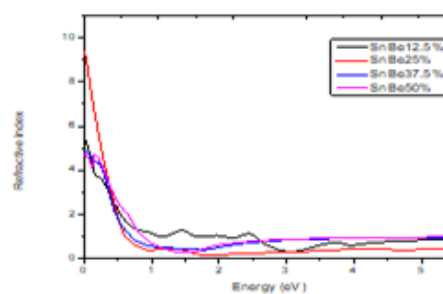
Fig.5(a) Real part of dielectric function of SnBe



(b) Imaginary part of dielectric function of SnBe



(c) EELS



(D) Refractive Index

Fig. 4.

#### 4. CONCLUSION

In this work, the structural, electronic, and optical properties of pristine stanene and stanene doped beryllium (SnBe) were investigated using density functional theory as implemented in quantum espresso and yambo simulation package. In pristine stanene, the electronic band-gap was found to be zero, which is in agreement with experimental results. With the inclusion of spin-orbit coupling (SOC), the band-gap was observed to open up by 0.1eV which is in agreement with previous theoretical results. SnBe was observed to have an opening in the band gap, SnBe exhibits p-type material electronic properties. Optical properties like Real and the imaginary parts of the dielectric function, electron energy loss spectroscopy (EELS), and refractive index of pristine stanene and doped stanene (SnBe) were investigated. SnBe showed a material absorption response in the infrared, visible, and ultraviolet light regions. The refractive index in the doped system (SnBe) was found to be higher than the refractive index of pristine stanene. Thus, stanene doped beryllium could be a promising material for the optoelectronic devices.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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