DFT investigation on electronic and optical properties of $Sn_2Sb_2S_5$ compound

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The electronic structure and optical properties of the ternary compound $Sn_2Sb_2S_5$ have been investigated by using the full-potential linear augmented plane wave (FP-LAPW) method based on the density functional theory (DFT). From this study, it is found that the compound $Sn_2Sb_2S_5$ has direct band gap which is calculated with the GGA and mBJ potentials as 1.22 and 1.51 eV, respectively. $Sn_2Sb_2S_5$ crystallizes in an orthorhombic structure, with the Pnma space group, the lattice parameters are a = 19.590 Å, b = 3.938 Å and c = 11.426 Å. Optical parameters, such as dielectric constant, refractive index and reflectivity are investigated and analyzed for the first quantitative theoretical prediction of $Sn_2Sb_2S_5$. The results demonstrated that the compound $Sn_2Sb_2S_5$ has the potential to be used for photovoltaic and optoelectronic applications.

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1. Introduction

The Sn-Sb-S systems have attracted great interest in theoretical and experimental investigations, systematic study of the potential of many sulfosalts exhibit suitable optical band gaps and electrical behaviors for photovoltaic applications [1-3]. They include thermoelectric energy conversion and phase change memory. The Sn-Sb-S systems have wide range of applications in solar cells, cryoelectronics and optoelectronic devices [4-6]. However, the sulfosalt $Sn_2Sb_2S_5$ compound contain abundant and toxic elements like Sn and S. The $Sn_2Sb_2S_5$ compound is suitable to photovoltaic applications [7].

As far as we know, there are no theoretical studies using mBJ approach on the optical response and electronic properties of the $Sn_2Sb_2S_5$ compound.

Furthermore, ab-initio calculations within the DFT based on LDA or GGA frequently underestimates the band gap as seen in Refs. [8,9]. Therefore, we are motivated to determine these properties using the recently proposed mBJ approach. This technique is highly suitable to describe the accurate electronic structure and optical properties of [10].

$Sn_2Sb_2S_5$ has an orthorhombic structure, the lattice parameters a = 19.590 Å, b = 3.938 Å and c = 11.426 Å and with the Pnma space group as shown in Ref. [11]. In this work, we present the investigation of electronic structure and optical response for $Sn_2Sb_2S_5$ compound within mBJ potential. We think that the obtained results may improve the optoelectronic applications of $Sn_2Sb_2S_5$compound.

2. Computational methods

In this study, all the calculations for $Sn_2Sb_2S_5$ have been realized within the density functional theory (DFT)[12,13], by using the full potential linear augmented plane wave (FP-LAPW) method[14] as implemented inWien2k code [15]. We have employed GGA approach for electronic structure and mBJ approach for electronic properties and optical response. Convergence parameter $R_{MT}*K_{max}$ is about 8 and the I_{max} is arround to 10. Charge density was found up to G_{max}=12 (a.u.)$^{-1}$. Lower than 0.10 mRy of self consistency computation of total energy were employed in order to ensure the convergence of the present results.

3. Results and discussion

3.1. Electronic properties

To understand the electronic properties of $Sn_2Sb_2S_5$ compound, band structure and the DOS are studied with mBJ approach. In Fig. 1, we can see the band structure for $Sn_2Sb_2S_5$. The direct band gaps energies of $Sn_2Sb_2S_5$ calculated with GGA and mBJ approaches are 1.22 and 1.51 eV, respectively. Moreover, mBJ gives more rigorous values of energy band gaps than GGA [8-10]. The calculate band gap is in accord with experimental results reported in our previous work [11]. The density of states (DOS) were calculated with the mBJ approach. Furthermore, the optical properties are calculated from the interband transitions. In Fig.2, we can see the total density of states TDOS and the partial density of states PDOS for the $Sn_2Sb_2S_5$ compound. The valence band below the Fermi level (EF) consists of different regions: the lower region which is between -10.0 and -8.0 eV is principally

due to the Sb-s states. The valence states between -6.0 eV and Fermi level are dominated by the Sn-s/p, Sb-p and S-p states. In addition, the opening of band gap energy is due to the pd- hybridization of the constituent atoms. Above the Fermi level (EF), the conduction band with positive energies is composed of Sn/Sb/S-p states.

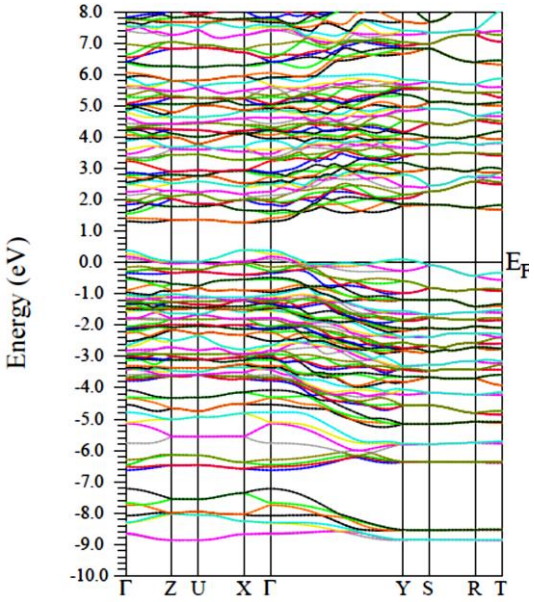

Fig. 1. Band structure for $Sn_2Sb_2S_5$ (color online).

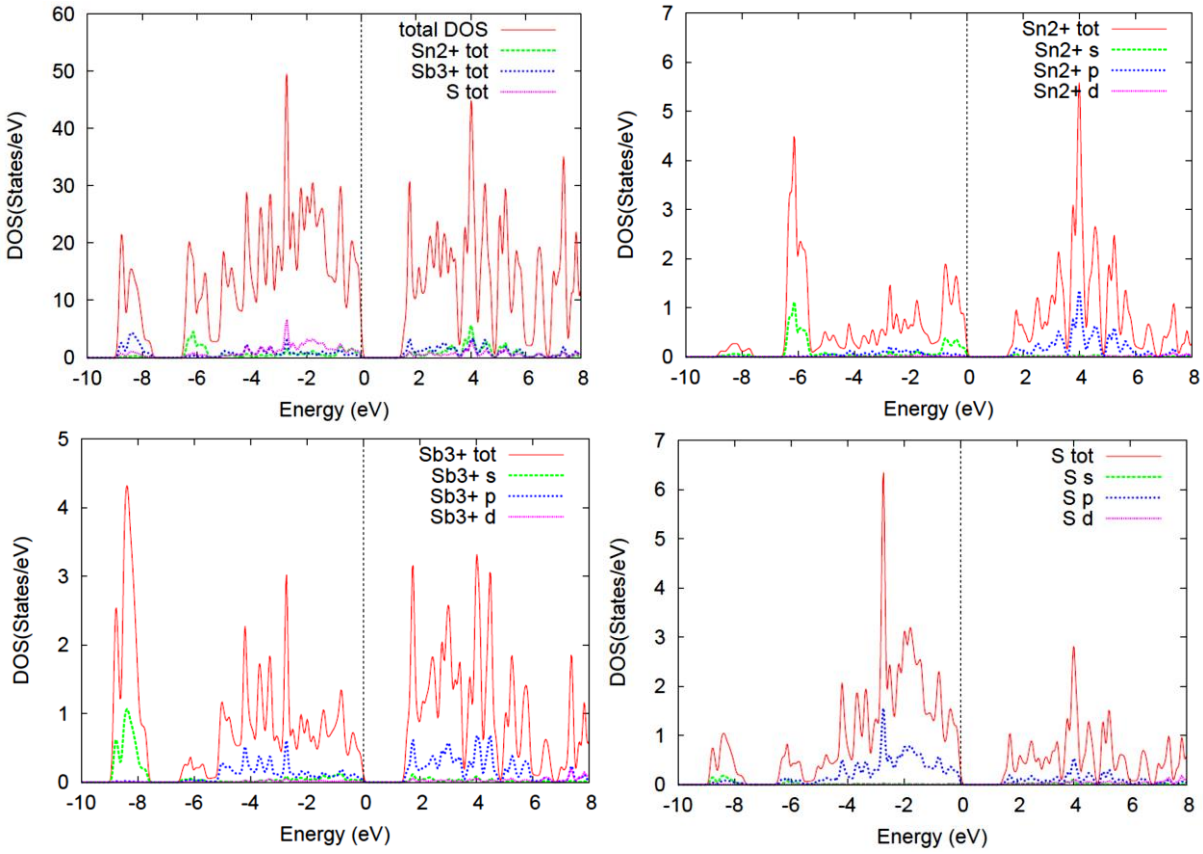

Fig. 2. Calculated total and partial density of states (DOS) for $Sn_2Sb_2S_5$ (color online)

3.2. Optical properties

The study within mBJ approach of optical response of the $Sn_2Sb_2S_5$ compound is so important for optoelectronic applications. Due to the orthorhombic structure of $Sn_2Sb_2S_5$compound, the optical constants should be

separated into three diagonal components, xx, yy, and zz.

The optical parameters, like reflectivity, extinction coefficient were calculated from the dielectric function.

The dielectric function $\varepsilon(\omega)$ represents the collective excitations of the Fermi sea like the volume and surface plasmons[16].The dielectric function is composed of a real and an imaginary parts [17]:

$$\varepsilon(\omega)=\varepsilon_1(\omega)+ i\varepsilon_2(\omega) \tag{1}$$

We obtain imaginary part $\varepsilon_2(\omega)$ of the dielectric function [18]:

$$\varepsilon_2(\omega)=\left(\frac{4\pi^2e^2}{m^2\omega^2}\right)\sum_{i,j}\int\left|\langle i|M|j\rangle\right|^2 f_i\left(1-f_j\right)$$

$$\delta\left(E_f-E_i-\hbar\omega\right)d^3k \tag{2}$$

where i and j are the initial and final states, M is the dipole matrix, f_i is the Fermi distribution function for the i^{th} state and E_i is the energy of the electron at the i^{th} state. The real part $\varepsilon_1(\omega)$ is obtained by the Kramers–Kroning relation [19]:

$$\varepsilon_1(\omega)=1+\frac{2}{\pi}P\int_0^\infty\frac{\omega'\varepsilon_2(\omega')}{\left(\omega'^2-\omega^2\right)}d\omega' \tag{3}$$

where P is the principal value of the integral.

The refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$ are obtained from the real and imaginary part of the dielectric function [20]:

$$n(\omega)=\left\{\frac{\varepsilon_1(\omega)}{2}+\frac{\sqrt{\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)}}{2}\right\}^{\frac{1}{2}} \tag{4}$$

$$k(\omega)=\left\{\frac{\sqrt{\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)}}{2}-\frac{\varepsilon_1(\omega)}{2}\right\}^{\frac{1}{2}} \tag{5}$$

The reflectivity $R(\omega)$ is given by the relation:

$$R(\omega)=\frac{(n-1)^2+k^2}{(n+1)^2+k^2} \tag{6}$$

The maximum values of $\varepsilon_1(\omega)$ are $\varepsilon_{1\,xx}$= 13.86 at 1.64 eV, ε_{1yy} = 18.08 at 1.77 eV and $\varepsilon_{1\,zz}$ = 18.16 at 2.38 eV for $Sn_2Sb_2S_5$ (Fig.3).

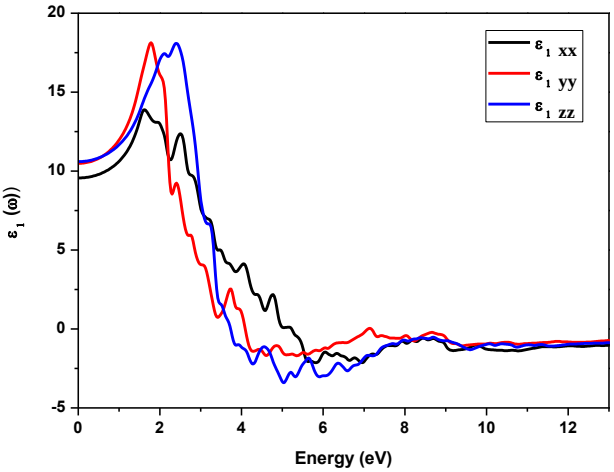

Fig. 3. Real part $\varepsilon_1(\omega)$ of the theoretical dielectric function for $Sn_2Sb_2S_5$ (color online)

We see a decrease of $\varepsilon_1(\omega)$ then it becomes negative,in this photon energy range; the compound has a metallic behavior. Refractive index $n(\omega)$ of the $Sn_2Sb_2S_5$ compound has been given (Fig. 7), which has similar profile of $\varepsilon_1(\omega)$. From Fig. 4, we obtain main peaks at 3.29 eV, 2.17 eV and 3.32 eV along the components, xx, yy, and zz, respectively. The imaginary part ε_2 was calculated from the electronic structure.

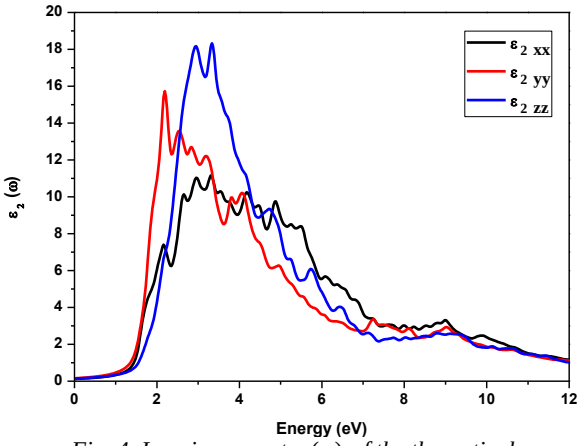

Fig. 4. Imaginary part $\varepsilon_2(\omega)$ of the theoretical dielectric function for $Sn_2Sb_2S_5$(color online)

The energy loss $L(\omega)$ is so important in the description of microscopic properties of any material. The major peak in the $L(\omega)$ spectrum is identified as the plasmon peak. The energy-loss function $L(\omega)$ is obtained by the relation[21]:

$$L(\omega)=\varepsilon_2(\omega)/\left[\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)\right] \tag{7}$$

In Fig. 5, we can see the energy loss $L(\omega)$ for $Sn_2Sb_2S_5$. The major peaks occur at 12.72 eV, 12.96 eV and 12.93 eV; along the directions, x, y and z , respectively. This major peak is related to the bulk plasmon[22]. The bulk plasmon peak in L(ω) can be used to give information about the strain in solids [23].

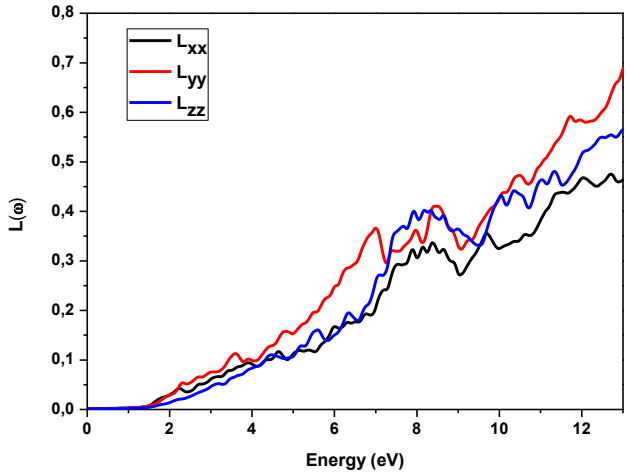

Fig. 5. Energy loss function L(ω) of $Sn_2Sb_2S_5$(color online)

In Fig. 6, we show an abrupt reduction in the reflectivity spectra $R(\omega)$ at $\approx$7.0 eV and 8.5 eV which is due to the occurrence of a collective plasma resonance [24]. The refractive index $n(\omega)$ is seen in Fig. 7, the values of the static refractive index n(0), are $n_{xx}(o)$= 3.12, $n_{yy}(o)$= 3.24 and $n_{zz}(o)$=3.26. A refractive index $n(\omega)$ smaller than unity ($v_g = \frac{c}{n}$) indicated that the group velocity of the incident radiation is superior to the speed of light [25]. The refractive index $n(\omega)$ is related to the density and the local polarizability of this compound[26-31]. From Fig. 8, we see local maxima of the extinction coefficient $k(\omega)$ at the energies 5.61 eV, 4.15 eV and 3.37eV for $Sn_2Sb_2S_5$ along the components, xx, yy, and zz, respectively.

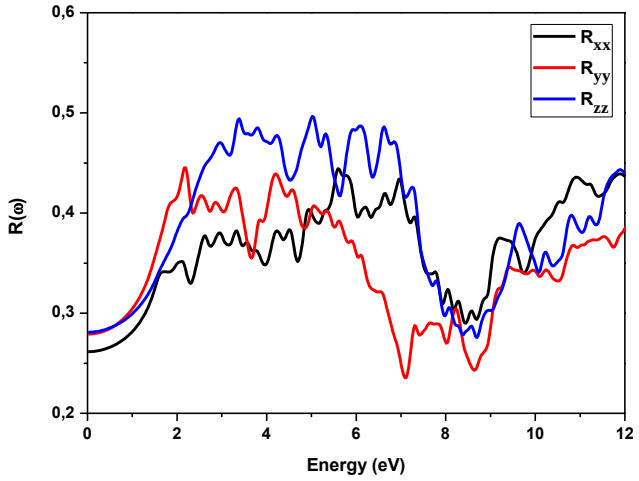

Fig. 6. Reflectivity spectra R(ω) of $Sn_2Sb_2S_5$ (color online)

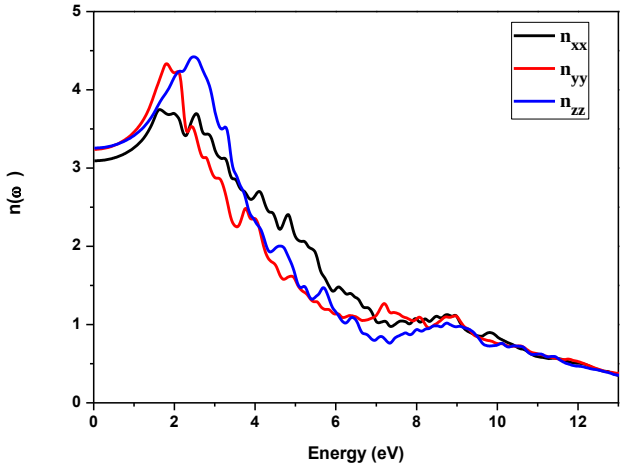

Fig. 7. Refractive index n(ω) of $Sn_2Sb_2S_5$(color online)

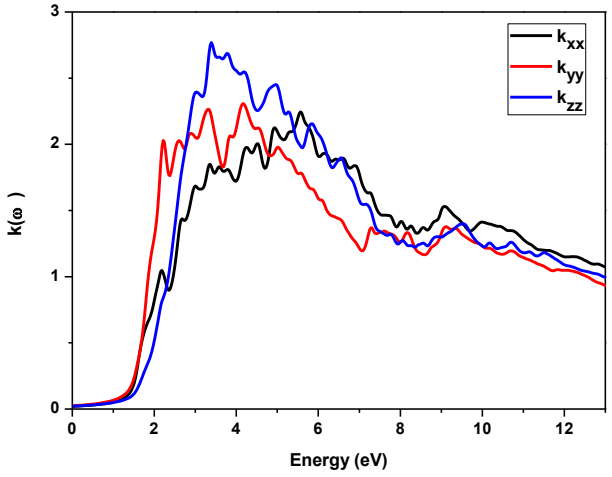

Fig. 8. Extinction coefficient k(ω) of $Sn_2Sb_2S_5$(color online)

4. Conclusion

We have investigated the electronic structures and optical properties of $Sn_2Sb_2S_5$ compound using the FP-LAPW method. Band gap dependent optical constants like the dielectric function, the refractive and reflectivity were investigated based on the mBJ approach. Moreover, we found that this material has direct band gap. We calculated the real $\varepsilon_1(\omega)$ and the imaginary $\varepsilon_2(\omega)$ parts of dielectric function. The maximum values of $\varepsilon_1(\omega)$ are $\varepsilon_{1\,xx}$= 13.86 at 1.64 eV, ε_{1yy} = 18.08 at 1.77 eV and $\varepsilon_{1\,zz}$ = 18.16 at 2.38 eV. We have also calculated the refractive index $n(\omega)$, the extinction coefficient $k(\omega)$, the energy-loss $L(\omega)$ and the reflectivity $R(\omega)$. The values of the static refractive index $n_{xx}(o)$= 3.12, $n_{yy}(o)$= 3.24 and $n_{zz}(o)$=3.26. The electronic structure and optical results in our investigation demonstrate promising applications of $Sn_2Sb_2S_5$ compound for photovoltaic and optoelectronic applications.

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