



Exploration of the structural, optoelectronic and vibrational behavior of Sb_2S_3 through the first principles approach for phenomenal applications in solar cells

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Abstract

In order to study any material the first principles approach has been considered an appropriate forum and deemed the best remedy to ensure the validity of the achievements/results obtained either theoretically or experimentally. We are, therefore, motivated to use this approach to explore the structural, optoelectronic and vibrational properties of Sb_2S_3 while utilizing the plane-wave pseudopotential technique and conjugate gradient method employed through the CASTEP simulation code. The crystal structure of Sb_2S_3 is optimized in orthorhombic phase having space group $Pnma$ with lattice parameters $a = 11.31 \text{ \AA}$, $b = 3.84 \text{ \AA}$ and $c = 11.23 \text{ \AA}$. It is noticed that magnitude of these lattice parameters approximately replicate the formerly reported theoretical as well as experimental results. The energy band gap is found to be 1.012 eV, which is utter evidence that the studied compound belongs to semiconductor category of the materials. The optical parameters unveil that Sb_2S_3 is capable to absorb wide range of radiations from the ultraviolet (UV) portion of the spectrum. The dynamical analysis through density functional perturbation theory (DFPT) shows that there is no soft mode which further ensures dynamical stability of Sb_2S_3 . The optical analysis of the studied compound are enough to declare it a potential material for applications in solar cells.

Keywords Ultra violet · Solar cell · DFPT · Band gap · Stretching

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1 Introduction

So far as the population has been increased tremendously in the whole world, the reason being there is an acute shortage of energy resources. It is further suspected that resources of oil, gasoline as well as coal are being extinct gradually. To overcome such limitations, researchers are motivated to cultivate such devices which could utilize sunlight for producing useful electrical energy, eventually establishing solar cell industries (Khalil et al. 2021; Wang et al. 2019). Sb_2S_3 is an important V–VI main group semiconductor compound, and recently has gained significant attention in the fabrication of numerous photonic, and optoelectronics devices, and in the industry of nanotechnology (Nwofe 2015). In the literature, it has been extensively reported that the antimony trisulphide (Sb_2S_3) compound can be widely used in thermoelectric cooling devices and also effectively utilized in the solar cells as window layers/absorbers due to its outstanding optoelectronic properties (Nezu et al. 2010; Messina et al. 2009; Maghraoui-Meherzi et al. 2010) in IR region. Among various metal sulfides, Sb_2S_3 has numerous applications in electronic devices as a target material in television camera tubes, optoelectronic applications (Godel et al. 2015) and microwave devices as well as in various switching devices (Nwofe 2015; Koc et al. 2012; Killedar et al. 1997). For clinical applications, Sb_2S_3 has been vested its services for labeling of the radio (Billinghurst 2001). Solar cells constructed by Sb_2S_3 thin films have also been reported in literature (Meng et al. 2013). Savadogo and Mandal (1992) have reported the photoconductivity of the Sb_2S_3 thin films. Sb_2S_3 thin films are more abundant and environmentally friendly as compared to other Cd-based chalcogenides, commonly used in the manufacturing of some photonic and optoelectronic devices such as in solar cells. Antimony trisulfide thin films have good electrical properties, an optimum band gap and good optical transmittance suitable for their solar cells (Aousgi et al. 2015) applications. Although metal chalcogenides materials are highly efficient, but they are very expensive, as well as high toxicity, which limit their applications (Candelise et al. 2012; Razykov et al. 2011).

Therefore, more abundant, low cost, and less-toxic materials are required (Todorov et al. 2011). A recent study revealed that Sb_2S_3 compound have efficient charge extraction which makes it suitable candidate for photovoltaic (Nasr et al. 2011) applications, due to its reasonable band gap and high absorption coefficient in the visible region (Chang et al. 2010). Therefore, detailed knowledge of optical and electronic properties is important for understanding its optoelectronic behavior such as light absorption and band gap. Due to these types of candid problems, nowadays, two compounds that is Sb_2Se_3 and Sb_2S_3 have attained the concentric attention of the researchers (Wang et al. 2017; Choi et al. 2014). Amongst, antimony tri selenide, having low energy gap (1.2 eV), is very efficient material for light absorption. While Sb_2S_3 compound offers an energy gap ranging from 1.5 to 1.7 eV, which is a more appropriate one to be considered for absorption of electromagnetic radiations upto the extent of $1.8 \times 10^5 \text{cm}^{-1}$, leading it to be a more desirous compound for utilizing in solar cell applications (Lan et al. 2018; Chang et al. 2012). This potential material is much capable to absorb photons even in cloudy weather as well as in weak light illumination conditions (Lojpur et al. 2018). In addition, by using Sb_2S_3 in solar applications one can overwhelm many hurdles (high cost, toxicity and rare materials etc.) that are facing our industrialists while manufacturing solar cells implementing theoretical as well as experimental outcomes. It is less toxic, plentiful and cheap absorber of sun rays. And that its band gap is very suitable for solar cell applications. Besides, Cd and Te based solar cells can't serve greatly owing to be toxic and rare materials (Asim et al. 2012). Recently,

researchers have recommended As_2S_3 , Sb_2S_3 and Bi_2S_3 like compounds rather than silicon for solar applications because these materials have shown more absorptions with a high value of refractive index (Green 2007; Yesugade et al. 1995).

Before this work, few studies have been done on the structural and electronic properties of this compound due to their applications in solar cells (Kondrotas et al. 2018; Validzic et al. 2014; Tang et al. 2018). The present study has excellent correspondence with previous available theoretical and experimental work. However, no theoretical comprehensive work has been done on the vibrational properties of Sb_2S_3 compound before this work. Moreover, no theoretical work has been done on the optical properties of this compound using PBE-GGA functional within the CASTEP simulation code.

2 Research methodology

The simulation of the Sb_2S_3 compound is conducted here by using DFT formalism and GGA approach as parameterized by Perdew, Burke and Ernzerhof (Perdew et al. 1996) for the xc-energy through CASTEP code (Clark et al. 2005; Hohenberg and Kohn 1964) by using the conjugate gradient method. The atomic pseudopotentials are produced individually for S atom and Sb atom using the $3s^23p^4$ and $5s^25p^3$ configurations, respectively. The norm-conserving pseudopotential along with the conjugate gradient method has been applied for Sb and S atoms (Troullier and Martins 1991). The optimization is carried out with an energy cut-off value of 400 eV and k-point sampling (Monkhorst and Pack 1976) of $2 \times 6 \times 2$ is used for the Brillouin zone. Here the optical analysis is performed by solving Kramer-Kronig (Kronig 1926) relations. Using the DFPT approach (Baroni et al. 2001), vibrational behavior has been discussed here to determine the various mode of dynamics.

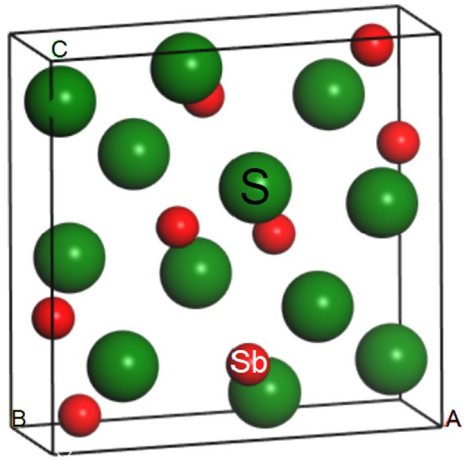
3 Results and discussions

3.1 Structural properties

The crystal structure of Sb_2S_3 compound is shown in Fig. 1, where the green color represents Sulfur atoms, while red color designates atoms of the Antimony. This Sb_2S_3 structure consists on 8 atoms of Sb and 12 S atoms. It is stable in the orthorhombic phase having space group Pnma (No. 62), point group D_{2h} and lattice parameters $a = 11.31 \text{ \AA}$, $b = 3.84 \text{ \AA}$, $c = 11.23 \text{ \AA}$. Whereas the experimentally reported lattice parameters by Micke and co-workers (Micke and McMullan 1975) are $a = 11.30 \text{ \AA}$, $b = 3.83 \text{ \AA}$ and $c = 11.22 \text{ \AA}$. It has been noticed that our results of lattice parameters are approximately equal to the formerly reported experimental results with only 0.4% deviation. Our results regarding lattice parameters are compared with formerly reported theoretical as well as experimental values as summarized in Table 1.

3.2 Electronic properties

To determine the electronic behavior of Sb_2S_3 compound, the electronic band structure elongated the density of states within Brillouin zone (BZ) across the high symmetry is shown in Fig. 2a, b. From the band structure plot, the energy gap is found to be 1.012 eV, leading to a narrative that the studied compound falls in semiconducting

Fig. 1 Crystal structure of Sb_2S_3 compound**Table 1** Lattice parameters reported for Sb_2S_3

Reference	Lattice constant (Å)		
	<i>a</i>	<i>b</i>	<i>c</i>
Present work	11.31	3.84	11.23
Previously reported experimental works (Micke and McMullan 1975)	11.30	3.83	11.22
	11.31	3.84	11.22
Previously reported theoretical work (Nasr et al. 2011)	11.30	3.84	11.22

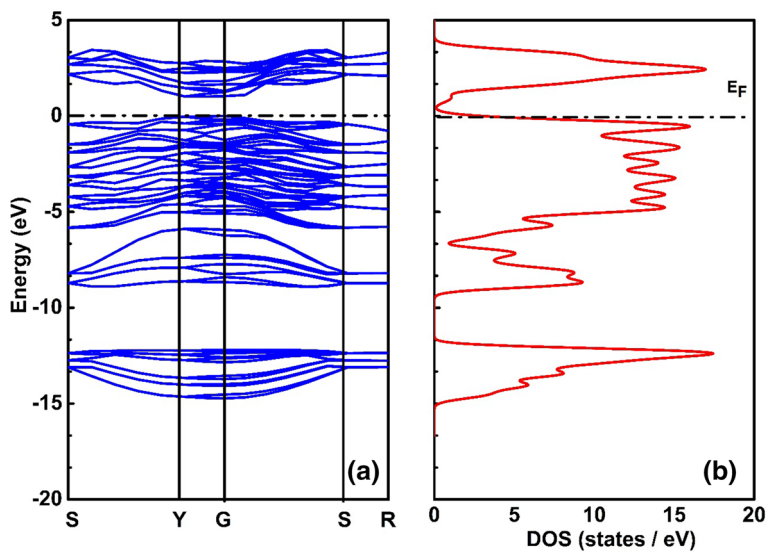
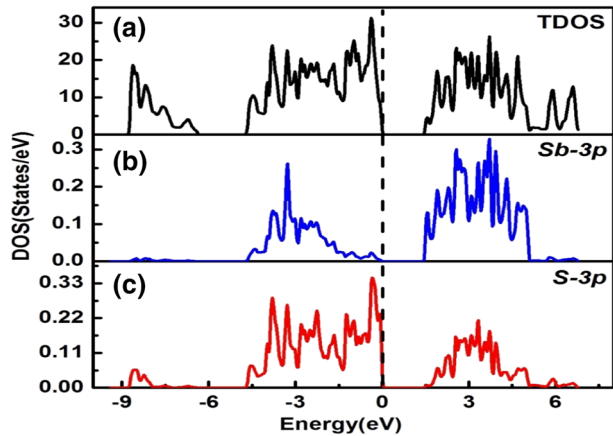
**Fig. 2** Calculated **a** electronic band structure, **b** density of states for Sb_2S_3

Table 2 The calculated energy band gap and formerly reported for Sb_2S_3 compound

Reference	Band gap energy E_g (eV)
Present work	1.012
Previously reported theoretical work (Koc et al. 1205)	1.18
Previously reported experimental work (Chen et al. 2008)	1.56

Fig. 3 The calculated **a** total density of states, **b**, **c** partial density of states for Sb_2S_3 compound

category of the materials. Additionally, bottom of the conduction band and top of the valence band are positioned at same point G of the BZ, so Sb_2S_3 compound has a direct energy gap (1.012 eV). The magnitude of the energy gap reported in this study (Fig. 2a), as well as the density of states shown in Fig. 2b, is approximately analogous to that reported previously (Koc et al. 2012). Moreover, in the valence band many peaks are seen while in the conduction band only one peak is dominant. The maximum peak occurred in the valence band at the energy of -12.38 eV, whereas in the conduction band the maximum states are noticed at 2.44 eV energy. It is predicted from Table 2 that the energy band gap presented in our work is approximately 14% less than earlier theoretical value reported by Koc et al. (2012).

In this study, WIEN2K (Blaha et al. 2001) code is also utilized to calculate the total and partial electronic density of states for the considered compound are displayed in Fig. 3. The total density of states as shown in Fig. 3a clearly endorse value of the energy gap extracted from the electronic band structure (Fig. 2a), which on the other hand can also be envisioned from partial density states (Fig. 3b, c). These figures also illustrate that S-3p states in the valence band exist near the Fermi level, while in the higher energy range (conduction band) the contribution of Sb-3p states is away from the Fermi level. These states have contributed dominantly in the conduction region, however its significant share has been seen in the valence band as well. The origin of these anisotropic effects is associated with lone pair formation of stereochemically cation Sb 5s orbitals which distorts the Sb coordination environment. The asymmetric electronic density of states that appear at the top of the valence band corresponds to a bonding interaction

between Sb 5s and S3p states due to stereochemically lone of antibonding states (Wang et al. 2022; Ganose et al. 2016; Walsh et al. 2011).

3.3 Optical properties

As depicted in Fig. 4a, we firstly discuss the reflection phenomenon of Sb₂S₃ in the frequency ranging 0–20 eV where single peak has been noticed in the plot. It ascends gradually on increasing energy, which however rises briskly on the further escalation of energy upto 9.64 eV and maximum value of the reflectivity is found to be 0.91 at 9.72 eV. Afterwards it decreases on increasing frequency. After the frequency range of 19.62 eV, the reflection remains constant. High reflectance in the ultraviolet region ~ 9.16 eV indicates that it is a promising reflecting compound.

As regard the absorption coefficient, it can be reported as under:

$$\alpha = \ln(1/T) = \ln(I_0/I) \quad (1)$$

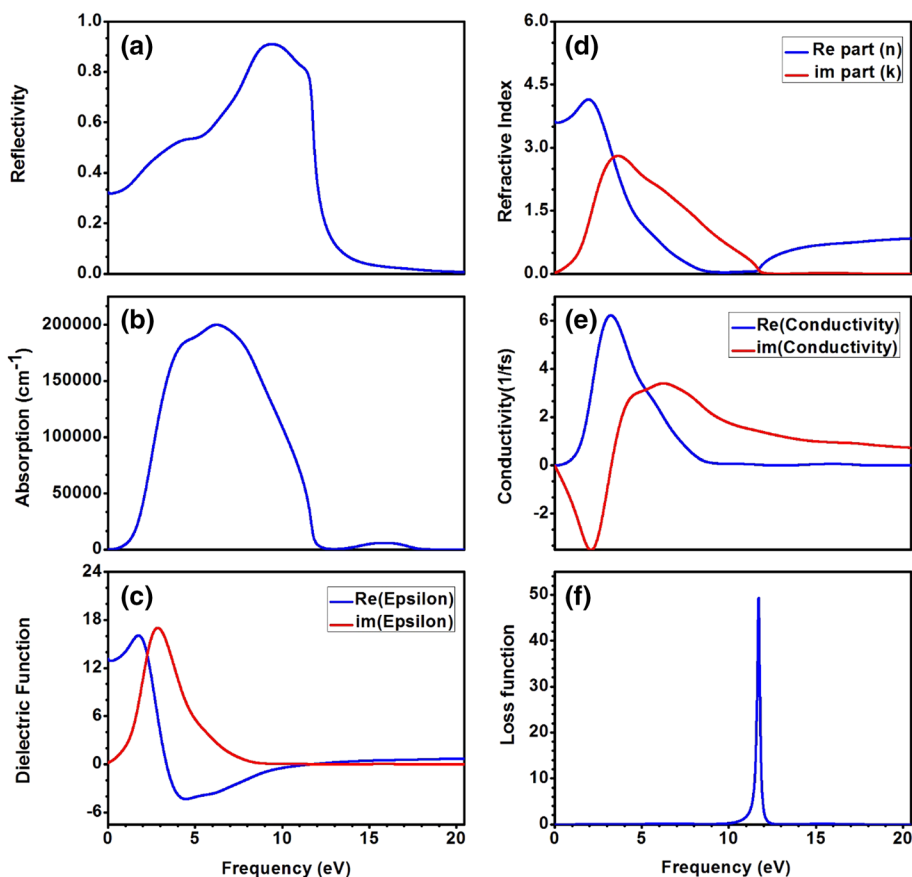


Fig. 4 a Reflectivity, b absorption coefficient, c real and imaginary parts of the dielectric function, d refractive index and extinction coefficient, e conductivity and f optical loss function for Sb₂S₃ compound

The absorption spectra of Antimony tri Sulfide is indicated in Fig. 4b which exhibits semiconducting nature of this compound. The absorption coefficient specifies how far light can pass through the material before absorption (Rahman et al. 2016). The absorption rises from zero energy and after various transition rates the absorption reaches to a maximum value in an energy region where the reflection is minimum (Fig. 4a). Sb_2S_3 have high absorption coefficients which could absorb photons more effectively and generate electron–hole pairs for photovoltaic applications (Zeng et al. 2016).

The dielectric constant as a function of energy is presented in Fig. 4c. The static value of the dielectric function $\epsilon_1(0)$ is noted to be 12.98, which is very close to the experimentally (Ghosh and Varma 1979) reported value such as 12.0. This value of the dielectric function demonstrates that the studied compound is good dielectric material. The dielectric constant of Sb_2S_3 is anisotropic and its static value is relatively large, which is common in lone-pair containing crystals. Large dielectric constants indicate the potential for strong screening of charged defects and low recombination losses (Kavanagh et al. 2021). $\epsilon_1(\omega)$ rises from critical values to a maximum polarization at photonic energy of 1.73 eV. It becomes negative at 4.49 eV due to reflection of the light striking on surface of the material where the materials behaves like metallic. It is seen that real dielectric function becomes zero at energy value of 13 eV expressing that antimony tri Sulfide compound is transparent above 13 eV.

The extinction coefficient (k) and Absorption coefficient (α) can be interlinked with each other as given below (Soliman 1998; Wooten 1972).

$$k = \alpha c / 2\omega = \alpha \lambda / 4\pi \quad (2)$$

The refractive index (n) is interconnected with the extinction coefficient (k) by the following relation (Ziang et al. 2015).

$$n_c = n + ik \quad (3)$$

The refractive index (real part) $n(\omega)$ and the extinction coefficient (imaginary part) $k(\omega)$ of Sb_2S_3 compound is depicted in Fig. 4d. The value of the static refractive index reported for Sb_2S_3 compound is 3.60 which is higher as compared to former studies such as 3.29 (Radzwan et al. 2017) and 2.089 (Wypych 2016). We note two peaks in this spectrum, one for real refractive index and the other for extinction coefficient. The value of the real refractive index starts to increase from the critical value and its first sharp peak appears at the energy of 2.023 eV, showing its excitonic nature. This means that Sb_2S_3 compound show maximum transparency at 2.023 eV. Thereafter the transparency decreases up to 9.82 eV. Whereas the highest peak for its imaginary part is noticed at the energy of value 3.62 eV. From Fig. 4d, it can also be seen that the refractive index is high in the visible region. The reported spectra of $n(\omega)$ and $k(\omega)$ have alike trends as $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ since these can be connected through the following relations:

$$n^2 - k^2 = \epsilon_1(\omega) \quad (4)$$

$$2nk = \epsilon_2(\omega) \quad (5)$$

Moreover, the static values $n(0)$ and $\epsilon_1(0)$ are linked with each other through a relation:

$$n_0^2 = \epsilon_1(0) \quad (6)$$

Figure 4e depicts a typical conductivity versus frequency plot for the Sb_2S_3 compound. It rise because of the absorbing photons. The real conductivity increases and attains

maximum value at 3.26 eV. The conductivity spectrum indicates that imaginary conductivity is maximum at 6.39 eV. In accordance with Fig. 4e, the conductivity is maximum in ultraviolet region. As the absorption is small in energy range from 13 to 18 eV, so the conductivity is also small in this region. The relation between absorption coefficient (α) and optical conductivity (σ) is given below (Soliman 1998; Wooten 1972).

$$\alpha = 4\pi\sigma/\hbar c \quad (7)$$

The energy loss spectra shown in Fig. 4f is the key parameter to express loss of energy of fast moving electrons whenever pass over the material and that maximum energy is lost at a plasma frequency (Hossain et al. 2012). The sharp maxima ~11.71 eV indicated in the plot can be related to the presence of plasma oscillations. The optical loss function indicates the loss of energy either by heating, dispersion, or scattering. It is revealed that absorption and transmission is minimum at 11.71 eV where loss of energy is maximum. It can be seen that the plasma response condition is fulfilled at the energy level where real dielectric function crosses zero level. The loss of energy is minimum at low frequency but it is noted maximum when frequency is increased to 12 eV. It is thus noted that the studied material has shown minimum energy losses in the visible region where absorption is maximum, so, it might a promising material for optoelectronic applications.

3.4 Vibrational properties

This theoretical study gives accurate predictions for some quantities which are not easy to calculate experimentally, like vibrational eigenvectors and silent mode frequencies. Moreover, phonon dispersion analysis assumed to be useful for examining thermal properties and structural stability. Usually it is explored by using various experimental techniques, like Raman spectroscopy which encounters phonons interaction with the wave or particles (Dove 1993) and neutron scattering. However, in the present study, IR and Raman spectroscopies are used for exploring phonons dispersion. In this regard DFPT (Baroni et al. 1987; Giannozzi et al. 1991) approach is considered an accurate and very energetic theory to calculate the vibrational properties of materials and compounds. It is reported that DFPT is mainly used for semiconductors in which phonon spectrum requires few wave vectors (k) (Giannozzi et al. 1991). We have investigated vibrational properties of Sb_2S_3 via DFPT approach by using PBE-GGA functional in the CASTEP program (Segall et al. 2002).

The phonon dispersion curve and phonon DOS are shown in Fig. 5a, b. There is no imaginary frequency in the phonon dispersion curve which reveal that the structure is dynamically stable. The first panel in Fig. 5a indicates different dispersion branches along symmetry direction in first BZ. For all directions, there are optical and acoustic branches which can be splitted into transverse and longitudinal modes. Both these modes are further divided into transverse optical (TO) and transverse acoustic (TA) as well as longitudinal optical (LO) and longitudinal acoustic (LA), respectively.

As the unit cell of Sb_2S_3 has twenty atoms, so, it has sixty modes of vibrations. The dispersion curve depicts (Fig. 5a) three acoustic modes, out of which two are transverse acoustic (TA and ZA) and the third one is longitudinal acoustic (LA) vibrational mode. In acoustic mode, atoms vibrate in phase in the unit cell. Therefore, at point G the acoustic phonon's frequency reaches to zero rather showing polarization. For each wave vector (k) there may be (3S-3) optical branches. Thus our crystal structure has fifty seven optical branches. In optical phonons, the vibration of atoms is out of phase in each unit cell. Here frequency is not zero at point G but it has a finite value. In contradiction to linear dispersion

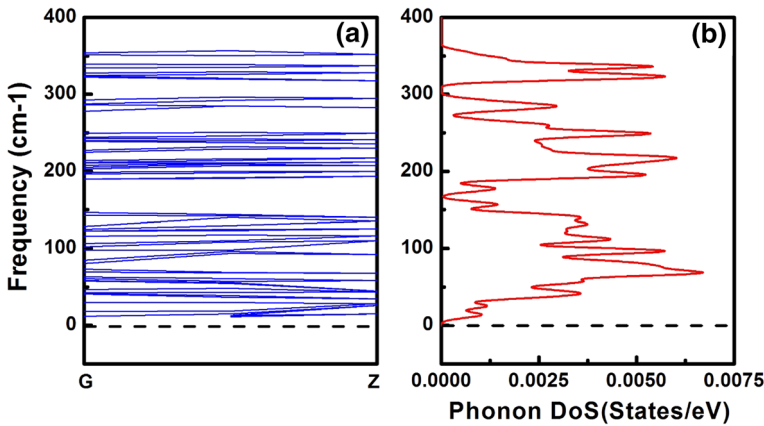


Fig. 5 **a** Phonon dispersion curve and **b** phonon DOS for Sb_2S_3 compound

Table 3 Vibration frequencies of Raman and IR active modes of polycrystalline Sb_2S_3 compound

Nos	Frequency (cm^{-1})	IR active	Raman active	Irreducible representation
1.	97.90	No	Yes	A_g
2.	128.58	Yes	No	B_{3u}
3.	213.87	No	No	A_u
4.	249.47	No	Yes	A_g
5.	354.20	Yes	No	B_{1u}

near point G, the transverse acoustic and longitudinal acoustic vibration modes (in-plane) and the ZA mode (out of plane) indicate a q^2 dispersion in the crystal. The few modes of vibration determined by Infrared and Raman spectroscopy for Sb_2S_3 are displayed in Table 3. It is interesting to mention here that heretofore none of the researchers has made any effort to study such infrared and Raman spectroscopy of the studied compound.

As reported in former studies, any change of polarizability during the phonon vibration leads that vibrational modes (Atkins and Paula 2009) are Raman active only. Where it might be possible that Asymmetric stretching modes and bending modes are not Raman active vibrational modes but symmetric stretching vibration mode may be Raman active mode. Hence, it is reported that vibrational modes of atoms are either Raman active or IR active but not both. Literature reveals that the strong phonon anharmonicity effect is induced due to the coupling of the lone pair electrons with lattice vibration. A theoretical study by the harmonic approach of the vibrations spectrum of crystal revealed B_{1u} -mode (354.20 cm^{-1}) active in the IR region. These results show the high anharmonicity of some atoms in semiconducting Sb_2S_3 material and the polar distortion of the B_{1u} -mode with temperature leading to the appearance of weak ferroelectricity (Zigas et al. 2017).

In Fig. 6, the arrow's length depicts eigenvector amplitude. At low frequencies contribution of heavy atoms of antimony is more as compared to sulfur atoms. Further Jmol analysis unveils that sulfur atoms have in-plane stretching vibrations at frequencies 324.59 cm^{-1} and 354.20 cm^{-1} nevertheless out of the plane stretching is noticed at

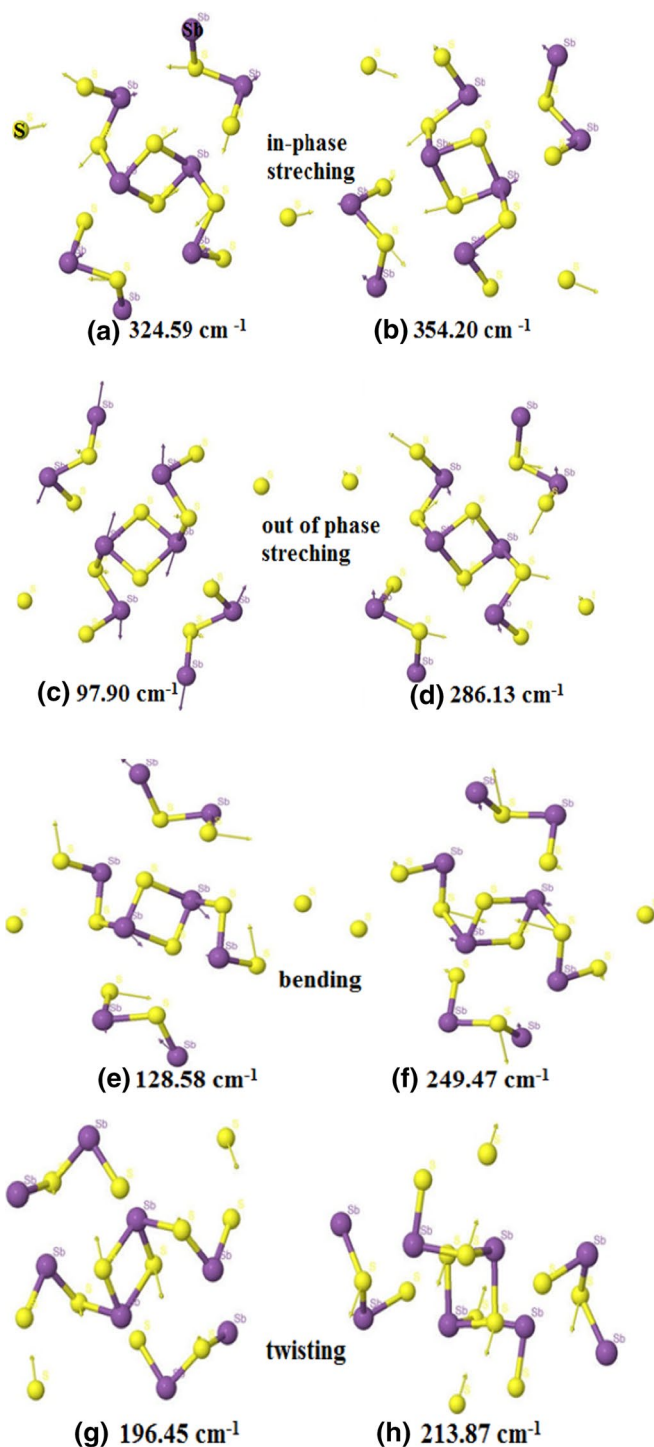


Fig. 6 Analysis of vibrational modes at relative frequencies (cm^{-1}) of Sb_2S_3 compound

97.90 cm^{-1} and 286.13 cm^{-1} (Fig. 6a–d). The highest optical phonon mode is found at a frequency 354.20 cm^{-1} . It has also been noticed that bond angle changes between antimony and sulfur atoms if and when atoms vibrate. So, antimony and sulfur atoms have shown bending motion at frequency 128.58 cm^{-1} and 249.47 cm^{-1} (Fig. 6e, f). Whereas Sb_2S_3 has reflected twisting modes of vibration at frequency 196.45 cm^{-1} and 213.87 cm^{-1} (Fig. 6g, h).

4 Conclusions

DFT based present study about the structural, optoelectronic and vibrational properties of Sb_2S_3 has been performed by using PBE-GGA functional via CASTEP code. The calculated lattice parameters such as $a=11.31$ Å, $b=3.84$ Å and $c=11.23$ Å are found approximately equal to the formerly reported theoretical as well as experimental results with merely 0.4% deviation. It is declared a semiconducting material having direct energy gap of 1.012 eV. The studied material has shown minimum energy losses in the visible region where absorption is maximum, so, it might a promising material for optoelectronic applications. Owing to high magnitude (12.98) of the static dielectric function, it can be utilized as dielectric material. It is noted to be dynamically stable since there are no negative frequencies. In this compound symmetrical and asymmetrical stretching modes, twisting and bending vibrational modes are observed at different frequencies. Based on the results summarized in the manuscript, Sb_2S_3 be declared a potential material for optoelectronic applications.

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Data availability The data that supports findings of this study are available from the corresponding authors upon reasonable request.

Declarations

Conflict of interest Authors declare no conflict of interest to publish this manuscript.

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