Spin–orbit coupling effect on electronic, linear and nonlinear optical properties of Bi\(_2\)S\(_3\) and the ternary bismuth sulfide Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\): Ab-initio calculations

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Abstract

Although the relevant properties of the bismuthinite Bi\(_2\)S\(_3\), it was recently approved that the substitution of Se atoms in the Bi\(_2\)S\(_3\) lattice can significantly enhance its electro-optical properties. In the present work, a detailed study on the structural, electronic and optical properties of Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\) has been carried out based on first principle calculations. The simultaneous effect of Se-doping and spin–orbit coupling (SOC) on bismuth sulfide Bi\(_2\)S\(_3\) was investigated. Our calculations show that Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\) exhibits a narrow direct band gap of 1.062 eV after inclusion of the (SOC). The calculation of the carrier effective masses indicates that Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\) may possess a high electron mobility material which is in accordance with experimental studies. The linear absorption optical spectra for both Bi\(_2\)S\(_3\) and Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\) show that doping bismuthinite with (Se) increases the optical absorption coefficient in the visible range and takes a value up to 10\(^{10}\)\(^5\) cm\(^{-1}\). In addition, the dielectric function, optical conductivity and the energy loss function of Bi\(_2\)S\(_3\) and Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\) were also derived. The addition of the (Se) content induces a red shift in agreement with experimental studies. A noticeable effect of the (SOC) on the linear optical parameters was observed. The stability of the excitons was also studied by the estimation of the binding energy value. The dispersion energy parameters of Bi\(_2\)S\(_3\) and Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\) were estimated using a single oscillator model. Some nonlinearities have been computed with and without inclusion of (SOC) showing that Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\) with large nonlinear optical parameters is promising candidate in photonic switching applications.

Keywords Electronic structure · Optical properties · Spin–orbit coupling · Bismuth sulfide

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1 Introduction

Bismuth chalcogenide materials $\text{Bi}_2\text{X}_3$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$) are considered as the second generation topological insulators as they have insulating bulk band gap and conducting states on their surface (Koc et al. 2014). Their bulk band gaps are generated because of the inherent spin–orbit coupling in these systems. The cation $\text{Bi}^{3+}$ has a large relativistic effect and a strong $\text{sp}$ hybridization in the valence band (Ganose et al. 2016). As a result, the Bi based materials may possess low carrier effective masses and therefore high carrier mobility leading them to be very useful in photovoltaic applications as a solar cell. Particularly, VI- bismuth materials $\text{Bi}_2\text{X}_3$ are functional compounds (Deng and Zhao 2018) and they are very attractive materials for several applications including: photovoltaics (Konstantatos et al. 2008), thermoelectrics (Harman et al. 2002), photo-electrochemicals (Kim et al. 2019), photocatalytic activity (Wu et al. 2010), micro- and optoelectronic devices (Hu et al. 2020) and infrared detectors (Grigas et al. 2002). Among $\text{Bi}_2\text{X}_3$ materials, the bismuth sulfide $\text{Bi}_2\text{S}_3$-bismuthinite- is a metal chalcogenide with a very attractive and intriguing properties: a large optical absorption coefficient ($> 10^5 \text{ cm}^{-1}$ for $\lambda < 500$ nm), high electron mobility ($> 500 \text{ cm V}^{-1} \text{ s}^{-1}$) (Rahman et al. 2016) and so on. The band gap of $\text{Bi}_2\text{S}_3$ is around 1.3–1.7 eV (Bernechea et al. 2015) and therefore lies in the visible light spectrum allowing it to be a light-absorber material in solar cells (Song et al. 2016). These relevant properties have allowed $\text{Bi}_2\text{S}_3$ to be a potential candidate for diverse domains such as photovoltaics (Whittaker-Brooks et al. 2015), thermoelectrics (Liu et al. 2007), electrochemical hydrogen storage (Zhang et al. 2006), lithium and sodium batteries (Ellis et al. 2014), electrochemical sensors (Andzane et al. 2015), X-ray computed tomography (Rabin et al. 2006), and so on. Despite its interesting and relevant properties, the use of $\text{Bi}_2\text{S}_3$ in the various fields mentioned above is hampered by its large electrical resistivity (Zhang et al. 2013) in the case that it will be used as an electron acceptor and also by its short life of minority carriers when it will be used in the manufacture of solar cells To improve the efficiency of $\text{Bi}_2\text{S}_3$ in solar cells development and to enhance its electrical transport properties, a systematic study on the intrinsic and extrinsic defects it is crucial to optimize performances of bismuth sulfide $\text{Bi}_2\text{S}_3$. Several researches have carried out a comprehensive study on intrinsic defects and doping in $\text{Bi}_2\text{S}_3$. For example, Mizoguchi et al. (1995) found that S vacancies in the lattice of bismuthinite can reduced its electrical resistivity by 2–3 orders of magnitude. Similarly, doping $\text{Bi}_2\text{S}_3$ by substitutional extrinsic elements such as Cl (Du et al. 2014), Sb (Kawamoto and Iwasaki 2014), Cu (Ge et al. 2012), Ag (Yu et al. 2011), Eu (Zhang et al. 2017) and Mn (Anasane and Ameta 2017) has been found to optimizing its carrier concentration so improving its electrical properties. Recently, much experimental reports have shown that the introducing selenium atoms to $\text{Bi}_2\text{S}_3$ can be considered as a very efficient way to increase its electrical and optoelectronic properties. It has shown that Se alloying bismuthinite in S sites ($\text{Bi}_2\text{S}_3\text{Se}_{x}$) could increase a figure of merit (ZT) and enhance the thermal conductivity upon Se incorporation (Zhang et al. 2013). Ajara et al. (Rahman et al. 2016) have found that ($\text{Bi}_2\text{S}_3_{-x}\text{Se}_x$) solid solutions possess interesting and attractive electrical properties than $\text{Bi}_2\text{S}_3$. Recently, experimental investigations conducted by Ye Chen et al. (2019) show that the power factor in the case of Se alloying at S sites in $\text{Bi}_2\text{S}_3$ is about 100 times larger than that of undoped $\text{Bi}_2\text{S}_3$. $\text{Bi}_2\text{S}_3_{-x}\text{Se}_x$ can be also an all-optical phonons switching device due to its interesting non-linear optical properties (Shubar et al. 2020). Photocatalytic activity can be highly increased when doping selenium into $\text{Bi}_2\text{S}_3$ photocatalyst (Song et al. 2011). It has also been proved that Se-doped $\text{Bi}_2\text{S}_3$ can be used as anodes for sodium-ion batteries (Chen et al. 2020). In contrast, to our
knowledge no theoretical study has been reported to date to investigate changes in electro-optical properties caused by the substitution of Se atoms into Bi2S3. For this purpose, our study is focused on predicting the structural, electronic and optical properties of Bi2S3−xSex (x = 0 and 0.25). The calculations were carried out using ab initio density functional theory (DFT) employing the Full-Potential Linearized Plane Wave (FP-LAPW) method. In the present paper we also discussed the effect of the spin–orbit coupling (SOC) on the electro-optical properties for Bi2S3 and the ternary bismuth sulfide Bi2S2.75Se0.25.

2 Computational details

In the present study, the full potential linearized plane wave (FP-LAPW) method (Nordström et al. 2001) as implemented in the Ab-initio simulation Wien2k (Blaha et al. 2020) package based on the density functional theory (DFT) (Chu and Leung 2001), is used to carried out all of the calculations. Perdew-Burke-Ernzerhof (PBE-GGA) scheme was used to describe the exchange–correlation interaction (Perdew et al. 1996) in addition of spin–orbit coupling (SOC) (Bala et al. 2008). In this study, the valence electrons are: [6s2 6p3], [3s2 3p4] and [4s2 4p4] for Bi, S and Se atoms respectively. The potential and charge density inside the atomic spheres are taken as lmax = 10. The plane wave cut-off was set at RMT*Kmax = 8, where RMT denotes the smallest muffin-tin radii of all atomic spheres and Kmax is the largest k-vector of the reciprocal lattice. Gmax = 12 (Ryd)1/2 is truncated to develop charge density and the plane wave potential. The energy cut-off for separation core and valence electrons is set to −10 Ry. A 500 k-point are used in the irreducible Brillouin zone. A denser k-mesh are used for calculation of the optical properties. The calculations are self-consistently converged when the total energy convergence was stable within 10−4 Ry.

3 Results and discussion

3.1 Structural properties

Bismuthinite Bi2S3 crystallizes in orthorhombic structure with the space group pbnm (62) (Caracas and Gonze 2005). There are four formula units per unit cell giving rise to 20 atoms in the primitive cell. The crystal structure of Bi2S3 consists of five non-equivalent atoms: two non-equivalent Bi sites and three non-equivalent S sites. Each Bi atom is linked to seven atoms of S. Three atoms of S are linked to Bi atom by short distances and the other four atoms of S are linked to Bi by long distances. The Bi–S short-bonds formed a strongly bonded ribbons while the Bi–S long-bonds formed a Van der Waals force introducing a weak interaction between the aligned ribbons (Li et al. 2016). To model the Bi2S3−xSex structure, a 221 supercell was constructed generating eight Bi atoms and twelve S atoms in unit cell with formula Bi8S12 in which three S atoms were replaced by three Se atoms to get Bi2S2.75Se0.25. The crystal structures of Bi2S3 and Bi2S2.75Se0.25 are shown in Fig. 1.

To find the ground state properties of Bi2S3 and Bi2S2.75Se0.25, the variation in the total energies with volume is computed using the GGA-PBE method for different volumes about the equilibrium cell volume V0, using the Murnaghan’s equation of state (Ouerghui and Alkhalifah 2019) as demonstrated in Fig. 2. The calculated equilibrium lattice constants, the bulk modulus (B) and its derivative of pressure (B’),...
both compounds are given in Table 1, with other previous theoretical and experimental results. From Table 1, we see that the optimized lattice parameters for bismuthinite $\text{Bi}_2\text{S}_3$ are in good agreement with theoretical results and slightly higher than the experimental data since the GGA approximation overestimates the lattice constants. In addition, the lattice constants increase with adding Se in the $\text{Bi}_2\text{S}_3$ lattice which can be explained by ionic radii difference between $\text{S}^{2-}$ (1.81 Å) and $\text{Se}^{2-}$ (1.98 Å).
### 3.2 Electronic properties

#### 3.2.1 Electronic band structure

Based on the optimized lattice parameters, the electronic band structures of Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ were evaluated using GGA-PBE approach with and without spin–orbit coupling (SOC). Figure 3a–d show the electronic band structures plotted along the high symmetry directions for the two structures Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$. For Bi$_2$S$_3$, Fig. 3a shows an indirect band gap with the valence band maxima (VBM) occurs at the $\bar{X}$-point whereas the conduction band minima (CBM) is located along the $G-Z$ direction. The calculated band gap of bismuthinite Bi$_2$S$_3$ at the PBE level is $E_{\text{g}}^\text{PBE} = 1.492$ eV which is in accordance with other theoretical and experimental results suggesting that Bi$_2$S$_3$ is an indirect band gap semiconductor ranging from 1.3–1.7 eV (Bernechea et al. 2015). It is well-known that the inclusion of the SOC effect modify the electronic properties of the materials which contain heavy elements. In our case, with the spin–orbit effect consideration, the band gap of Bi$_2$S$_3$ decreases from $E_{\text{g}}^\text{PBE} = 1.492$ eV to $E_{\text{g}}^{\text{PBE+SOC}} = 1.208$ eV. $E_{\text{g}}^{\text{PBE+SOC}}$ is also an indirect band gap with (VBM) and (CBM) are located at $Z$-point and $GY$- path respectively, which is very close to the experimental value of 1.26 eV (Chen et al. 2019). The computed energy band gaps of Bi$_2$S$_3$ at PBE and PBE + SOC levels are summarized in Table 2 within previously theoretical and experimental studies. Figure 3c, d shows the electronic band structures of Bi$_2$S$_{2.75}$Se$_{0.25}$ with and without (SOC). Both band structures present a direct band gaps of $E_{\text{g}}^{\text{PBE}} = 1.34$ eV and $E_{\text{g}}^{\text{PBE+SOC}} = 1.062$ eV at PBE and PBE + SOC level respectively at $Z$ point. The incorporation of Se atoms in the Bi$_2$S$_3$ lattice allowed to obtain a narrow band gap leading to activate the intrinsic conduction electrons and subsequently to enhance the electrical transport properties of the undoped Bi$_2$S$_3$ material. The reduction of the band gap by introducing the Se atoms in Bi$_2$S$_3$ has been observed experimentally by studying the Bi$_2$S$_3$–$x$Se$_x$ ($x=0.06–0.75$) materials (Biswas et al. 2012) in which the band gap passes from 1.35 to 1.12 eV. Due to the fact that the obtained gap is direct, the Bi$_2$S$_{2.75}$Se$_{0.25}$ is satisfactory in optoelectronics and also it can be considered as a light-absorber compound in solar cells due to its value that is close to the optimal value of this kind of materials (Zhu et al. 2017). The calculated band gaps $E_{\text{g}}^{\text{PBE+SOC}}$ for Bi$_2$S$_3$ and the ternary Bi$_2$S$_{2.75}$Se$_{0.25}$ indicate that the (SOC) induces a considerable reduction compared to the $E_{\text{g}}^{\text{PBE}}$ which can be explained by the splitting states near the Fermi level.

#### 3.2.2 Density of states

The total density of states (TDOS) and the partial density (PDOS) for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ were calculated to unveil the atom orbital contribution to the band structure.
(TDOS) and (PDOS) are calculated with and without (SOC) and are presented in Figs. 4 and 5. In these figures, the zero energy level is attributed to the Fermi level ($E_F$). It emerges from Fig. 4 that the lower part of the valence band is dominated by the Bi-6s and S-3s states. The 3p orbitals of S atoms have highly contribution to the upper valence band showing hybridization with Bi-6sp orbitals with a weak presence of Bi-5d states. The conduction band minimum is composed principally of the Bi-6p and S-3p characters. The same orbital contributions to the energy bands of Bi$_2$S$_{2.75}$Se$_{0.25}$ are observed with the addition of the p states of Se atoms which has a considerable contribution in the valence band.
maximum giving rise to the hybridization with Bi-6p orbitals. The Se 4p states contribute also in the conduction band minimum besides the p states of Bi and S atoms. After the inclusion of the (SOC), the contribution of the different states in the valence and the conduction bands remains unchanged but a remarkable reduction in their densities is observed as shown in the Figs. 4d and 5d for the two materials. We find also that the bandwidth has increased by 0.112 eV for Bi₂S₃ and by 0.086 eV for Bi₂S₂.₇₅Se₀.₂₅ in the presence of (SOC). The obtained results from the electronic band structures as well as the density of

### Table 2

The calculated energy band gaps of Bi₂S₃ and Bi₂S₂.₇₅Se₀.₂₅ with PBE and PBE+SOC methods with their corresponding theoretical and experimental data

| Compound          | Method                          | $E_g$ (eV) |
|-------------------|---------------------------------|------------|
| Bi₂S₃             | Present (GGA-PBE)               | 1.492      |
|                   | Present (PBE-SOC)               | 1.208      |
|                   | Theory (DFT-GGA and PAW) (Guo et al. 2013) | 1.220      |
|                   | Theory (LDA-PBE) (Chen et al. 2019) | 1.380      |
|                   | Theory (PBE-SOC) (Chen et al. 2019) | 1.030      |
|                   | Experimental (Chen et al. 2019)  | 1.260      |
|                   | Experimental (Cheng et al. 2010) | 1.360      |
| Bi₂S₂.₇₅Se₀.₂₅     | Present (GGA-PBE)               | 1.340      |
|                   | Present (PBE-SOC)               | 1.062      |

**Fig. 4** Calculated total (TDOS) and partial density of states (PDOS) of Bi₂S₃ with PBE and PBE+SOC methods
states show the influence of the introduction of the (SOC) on the electronic structure of the undoped and doped bismutinite Bi$_2$S$_3$.

### 3.2.3 Effective masses

To understand the physical mechanism of the thermoelectric property of bismuthinite and the Se-doped bismuthinite (Bi$_2$S$_3$), carrier effective masses were calculated at G-point along G-Z (0, 0, 1/2) and G-X (1/2, 0, 0) directions in the first Brillouin zone of the pbnm orthorhombic structure. For the calculation of the effective masses we use the approximation model given by Ben Abdallah and Ouerghui (2020) based on the calculated band structures with PBE + SOC model. The results are depicted in Table 3. As it is presented in Table 3, the electron effective masses $m^*_e$ for both Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ are smaller than the effective hole masses $m^*_h$, which is in accordance with the experimental and theoretical studies (Chen et al. 2019; Guo et al. 2013). For Bi$_2$S$_3$, our calculated average value of $m^*_e$ is 1.85 $m_0$ consistent with the previous experimental data (Pejova and Grozdanov 2006) showing that $m^*_e$ is ranging from 0.6 to 2.2 $m_0$. The carrier effective mass anisotropy can be attributed to the anisotropic ratio $\frac{m^*_c}{m^*_a}$ where $m^*_c$ and $m^*_a$ are the carrier effective masses along the (G-Z) and (G-X) directions respectively. The calculated electron effective mass anisotropy is 1.30 for Bi$_2$S$_3$ and 2.42 for Bi$_2$S$_{2.75}$Se$_{0.25}$. The obtained higher anisotropy is related to the chemical bonds in the two crystals. The anisotropy increased when selenium atoms were substituted in Bi$_2$S$_3$ crystal resulting in a more covalent bonds along c-axis and a weaker ionic bonds along the a and b directions. In addition, the introduction of the Se

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Fig. 5 Calculated total (TDOS) and partial density of states (PDOS) of Bi$_2$S$_{2.75}$Se$_{0.25}$ with PBE and PBE+SOC methods.
atoms in bismuthinite crystal has the effect of reducing the electron and hole effective masses and thus an increase in the carrier mobility. This has been observed experimentally by Ajara et al. (Shubar et al. 2020).

### 3.3 Optical properties

#### 3.3.1 Linear optical properties

The linear optical properties of Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ are calculated with and without (SOC) for radiation up to 12 eV as shown in Figs. 6, 7, 8, 9 and 10. All optical parameters are derived from the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ which define the optical response of a medium at all photon energy. $\varepsilon_1(\omega)$ is the real part of $\varepsilon(\omega)$ corresponds to the dispersive behavior of the material while $\varepsilon_2(\omega)$ is the imaginary part of $\varepsilon(\omega)$ describing the absorptive behavior of the medium (Ben Abdallah and Bennaceur 2009).

As Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ crystallize in orthorhombic structure, the dielectric tensor $\varepsilon(\omega)$ have three diagonal independent components ($\varepsilon_{xx}$, $\varepsilon_{yy}$, $\varepsilon_{zz}$). In this paper, we have restricted our study of the optical properties for polarization parallel to the z direction (E||z) which is considered as a preferential direction for enhancing electro-optical properties of Bi$_2$S$_3$ (Miller and Bernechea 2018). $\varepsilon_1(\omega)$ spectra calculated with and without (SOC) for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ for (E||z) are given by Fig. 6.

All $\varepsilon_1(\omega)$ curves start from the static dielectric constant $\varepsilon_1(0)$ which corresponds to the dielectric response at zero frequency. The static dielectric constants for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ are listed in Table 4. It can be seen from Table 4 that $\varepsilon_1(0)$ increased with the

| System         | Direction | $m_e^* [m_0]$ | $m_h^* [m_0]$ |
|----------------|-----------|---------------|---------------|
| Bi$_2$S$_3$    | G-Z       | 2.099         | 3.850         |
|                | G-X       | 1.607         | 4.530         |
| Bi$_2$S$_{2.75}$Se$_{0.25}$ | G-Z     | 0.489         | 1.301         |
|                | G-X       | 1.187         | 2.110         |

![Fig. 6](image-url) Calculated real and imaginary parts of the dielectric function of Bi$_2$S$_3$ (a) and Bi$_2$S$_{2.75}$Se$_{0.25}$ with PBE and PBE + SOC method
addition of the Se element and in the presence of the (SOC) giving rise to a high dielectric constant. To study the stability of the excitons, we calculate the exciton binding energy which can be calculated using the Bohr model (Bushick et al. 2019),

$$E_b = \frac{13.6 \text{ eV} \cdot \mu^*}{\varepsilon_\infty(0)^2}$$  \hspace{1cm} (1)

where $\mu^*$ is the reduced mass given by: $\mu^* = \frac{m_e^* m_h^*}{(m_e^* + m_h^*)}$ and $\varepsilon_\infty(0)$ is the static dielectric constant computed without (SOC) and listed in Table 4. To evaluate $\mu^*$, we considered the directionally averaged value for $m_e^*$ and $m_h^*$ given from the Table 3. Our calculated binding energy $E_b$ for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ are 74.16 meV and 29.10 meV respectively. The calculated values of $E_b$ are of the same order as those of type II–VI compounds (Strzalkowski et al. 2013). The obtained results for $E_b$ indicate that the incorporation of selenium (Se) atoms in the bismithinite Bi$_2$S$_3$ decreases the exciton binding energy which induces a
reduction in recombination, thus improving the efficiency of the extraction of the charge carriers.

It can be seen from Fig. 6a, b, that \( \varepsilon_1(\omega) \) decrease to values below zero indicating that the reflection is maximum in the energy range about (3–7) eV and the materials exhibit...
metallic behavior in this area. The absorptive part $\varepsilon_2(\omega)$ calculated with and without (SOC) for $(E||z)$ is illustrated in Fig. 6a, b for both compounds. $\varepsilon_2(\omega)$ spectra represent a pronounced peak located at 3.233 eV and 3.102 eV for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ respectively, before the inclusion of the (SOC). With the inclusion of the (SOC), these high intensity peak of $\varepsilon_2$ show a red shift. A second peak, who is weaker than the first one, appears at 8.861 eV and 8.512 eV before and after inclusion of the (SOC) for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ respectively. Thus, these differences in the results of the dielectric constants confirm the crucial role of SOC effects in the optical properties of undoped and doped Bi$_2$S$_3$. Our calculated maximum value of $\varepsilon_2$ for $(E||z)$ for Bi$_2$S$_3$ is in accordance with maximum peak values given theoretically by Sharma et al. (2012). It is known that $\varepsilon_2(\omega)$ is directly related to the optical electron transition. From PDOS displayed in Figs. 4 and 5 and for both compounds, the transition between the occupied states Bi 6s to unoccupied states S 3p is at the origin of the appearance of the main peaks, while the second peaks originates from transition occurring between Bi 6s and S 3p electrons. For Bi$_2$S$_{2.75}$Se$_{0.25}$ there is another transition between Se 3p and Bi 6p states participating in the appearance of the main peak in $\varepsilon_2(\omega)$.

The absorption coefficient $\alpha(\omega)$ spectra for $(E||z)$ calculated with and without (SOC) for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ are given by Fig. 7. As can be seen from the $\alpha(\omega)$ spectra, the threshold of absorption is around 1.391 eV and 1.305 eV for undoped and doped Bi$_2$S$_3$ respectively. This shows that there was a shift towards low energies on the absorption edge with the incorporation of the Se atoms. This confirms the experimental results carried out on Bi$_2$S$_{3-x}$Se$_x$ (Chen et al. 2019). With the addition of (SOC), the threshold of absorption decrease and take the values of 1.192 eV and 1.010 eV for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ respectively. The calculated energies of the threshold of absorption are close to the energy band gaps of Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ evaluated with and without the addition of (SOC) (see Table 2). In the energy range up to 3 eV, the absorption is maximum for Bi$_2$S$_{2.75}$Se$_{0.25}$ has a value of 94.79310$^4$ cm$^{-1}$, while at the same energy the undoped bismuthinite presents an absorption of the order of 90.22810$^4$ cm$^{-1}$ in agreement with the experimental values (104–10510$^4$ cm$^{-1}$) (Rahman et al. 2016). This clearly shows that Bi$_2$S$_3$ becomes more absorbent in the visible range by doping it with selenium. For higher energy extending up to 3 eV, Bi$_2$S$_3$ crystal has a higher absorption than that of Bi$_2$S$_{2.75}$Se$_{0.25}$. The calculated high absorption coefficient of the ternary Bi$_2$S$_{2.75}$Se$_{0.25}$ shows that this material is very promising in photovoltaic applications. The optical conductivity $\sigma(\omega)$ describes the electron conduction produced by an incident photon crossing a material. The optical conductivity spectra for $(E||z)$ calculated with and without addition of the (SOC) for both compounds are presented in Fig. 8. The optical conductivity presents a sharp peak in the visible range for both compounds Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$. The maximum value of the optical conductivity decreases in the case of the calculation with (SOC) effect. $L(\omega)$ is the electron energy loss function describing the energy loss of a fast electron crossing a medium. The energy loss (Eloss) spectra for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ calculated with and without (SOC) for $(E||z)$ are given by Fig. 9. $L(\omega)$ present a prominent peak called the plasma resonance (Ouerghui et al. 2021a) located around 7.231 eV and 7.138 eV for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ materials, respectively. The corresponding plasma frequencies are 10.98010$^{15}$ Hz and 10.83910$^{15}$ Hz. The calculated value of the plasma excitations for Bi$_2$S$_3$ is in accordance with theoretical results (Sharma et al. 2012) and experimental measurements (Nascimento et al. 1999).

The refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$ for $(E||z)$ are plotted in the Fig. 10. It can be seen that $n(\omega)$ curves present an important value in low energy region.
and remarkable reduction in high energy region. To analyze the refractive index at lower optical frequencies one can use the Wemple—DiDomenico (WDD) single-oscillator model (Ouerghui et al. 2021b) which is the most applied concept for the chalcogenide semiconductors. The (WDD) model is given by the following expression:

\[
(n^2 - 1)^{-1} = \frac{E_0}{E_d} - \frac{1}{E_0 E_d} (h\nu)^2
\]

(2)

here, \(E_0\) and \(E_d\) are the dispersion energy parameters, \(h\) is Planck’s constant and \(h\nu\) is the photon energy.

The dispersion energy \(E_d\) corresponds to the dispersion of the electronic dielectric function related to the interband transition force, while \(E_0\) is the single oscillator energy connected with the optical energy gap called WDD band gap (Ouerghui et al. 2021b). The dispersion parameters for Bi\(_2\)S\(_3\) and Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\) were estimated by fitting the plot \((n^2 - 1)^{-1}\) versus \((h\nu)^2\) in low energy region as shown in Fig. 11. Our calculated values of \(E_d\) and \(E_0\) for Bi\(_2\)S\(_3\) and Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\) calculated with and without (SOC) are listed in Table 4. From Table 4, the dispersion energy \(E_d\) decreased while passing from Bi\(_2\)S\(_3\) and Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\) after and before the inclusion of (SOC). This is essential due to the addition of the Se atoms in Bi\(_2\)S\(_3\) lattice which induced a weak force of the interband transitions. Similarly, the oscillatory energy \(E_0\) decreases for Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\) due to the decrease in the energy band gap. Based on the (WDD) model, we can calculate the static refractive index \(n(0)\) from equation: \(n(0) = \sqrt{1 + \left(\frac{E_0}{E_d}\right)}\). The static refractive indexes \(n(0)\) for Bi\(_2\)S\(_3\) and Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\) calculated with and without (SOC) are given in Table 4. Another important parameter given by the WDD model is the oscillator strength given by: \(F = \frac{E_0}{E_d}\). The calculated values of \(F\) for Bi\(_2\)S\(_3\) and Bi\(_2\)S\(_{2.75}\)Se\(_{0.25}\) are reported in Table 4.

### 3.3.2 Non-linear optical parameters

The optical non-linearity of materials is directly related to the control of the light in optical switching devices. In the present work, the nonlinear optical properties (NLO) were studied from the calculation of the 3rd order nonlinear optical susceptibility \(\chi^{(3)}\) and the

![Fig. 11 (n^2 - 1)^{-1} versus (h\nu)^2](image-url)
non-linear refractive index $n_2$ for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ within the Miller’s rule and the static refractive index $n(0)$ (Ouerghui et al. 2021b). It is known that the non-linearity occurs when the electromagnetic field becomes high enough. $\chi^{(3)}$ can be evaluated by the following expression:

$$\chi^{(3)} = \frac{A}{(4\pi)^4} \left( \frac{E_d}{E_0} \right)^4$$ (3)

where $A$ is a constant independent of the frequency and equal to $1.710^{-10}$ esu (Ouerghui et al. 2021b), $E_d$ and $E_0$ are the dispersion parameters given by the (WDD) single-oscillator model. The non-linear refractive index $n_2$ is related to $\chi^{(3)}$ and the static refractive index $n_0$ which given by:

$$n_2 = \frac{12\pi \chi^{(3)}}{n(0)}$$ (4)

The calculated values of $\chi^{(3)}$ and $n_2$ for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ are summarized in Table 5.

From Table 5, the calculated values of the (NLO) parameters $\chi^{(3)}$ and $n_2$ for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ are large and this can be related to the electronic and geometrical structure of these two materials. The obtained value of $\chi^{(3)}$ coefficient of the bulk Bi$_2$S$_3$ is larger than measured experimentally for Bi$_2$S$_3$ nanocrystal: $6.2510^{-11}$ esu (Li et al. 2008). This difference is due in particular to the quantum confinement effect in the nanocrystals. In addition, the results presented in Table 5 show that doping Bi$_2$S$_3$ with Se atoms further expanded the (NLO) coefficients $\chi^{(3)}$ and $n_2$ thus showing the effect of Se doping Bi$_2$S$_3$ in improving the nonlinear optical properties and consequently in the realization of a promising nonlinear optical materials.

### 4 Conclusion

The effect of spin orbit coupling on the electronic and optical properties of Bi$_2$S$_{2.75}$Se$_{0.25}$ are investigated by means of Wien2k code based on the density functional theory. Firstly, the structural properties such as lattice constants, the bulk modulus and its pressure derivative of Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ are calculated within the PBE-GGA scheme. The calculated electronic band structures show that Bi$_2$S$_{2.75}$Se$_{0.25}$ is a direct band gap semiconductor with and without the inclusion of (SOC). The energy band gap reduction with respect to that of undoped Bi$_2$S$_3$ is due to the splitting states near the Fermi level if the (SOC) is taken into account. The carrier effective masses of Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ were calculated along high symmetry directions showing an increase in both the anisotropy and the

| Compound          | Method         | $\chi^{(3)} 10^{-10}$ (esu) | $n_2 10^{-10}$ (esu) |
|-------------------|----------------|-----------------------------|---------------------|
| Bi$_2$S$_3$       | Present (GGA-PBE) | 2.699                       | 4.363               |
|                   | Present (PBE-SOC) | 2.701                       | 4.369               |
| Bi$_2$S$_{2.75}$Se$_{0.25}$ | Present (GGA-PBE) | 6.512                       | 9.493               |
|                   | Present (PBE-SOC) | 4.797                       | 7.493               |

Table 5 Non-linear optical parameters: third-order nonlinear optical susceptibility $\chi^{(3)}$ and nonlinear refractive index $n_2$ for Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ calculated with and without (SOC)
carrier mobility when Se atoms were incorporated. The linear optical properties of Bi$_2$S$_3$ and Se doped Bi$_2$S$_3$ (dielectric function, absorption, optical conductivity and energy loss function) were investigated for polarization parallel to the z axis. All linear optical spectra show a red shift when incorporating Se atoms in Bi$_2$S$_3$ lattice and after inclusion of (SOC). Bi$_2$S$_{2.75}$Se$_{0.25}$ exhibits a high absorption coefficient in the visible region showing its potential use in future for applications in solar cells. The static dielectric constant increase in Bi$_2$S$_{2.75}$Se$_{0.25}$ with (SOC) effect giving rise to a decrease in the exciton binding energy. The oscillator parameters such as the oscillator energy, the dispersion energy and the static refractive index for both Bi$_2$S$_3$ and Bi$_2$S$_{2.75}$Se$_{0.25}$ materials were estimated using the (WDD) single-oscillator model. It was found that the inclusion of Se content in Bi$_2$S$_3$ leads to the increase of the static refractive index but a decrease in the oscillator parameters.

The nonlinear optical properties (NLO) of doped and undoped Bi$_2$S$_3$ were also reported. A large values of (NLO) parameters were obtained for Bi$_2$S$_{2.75}$Se$_{0.25}$ indicating that it can be a useful device for all-optical communication and computer network. We strongly believe that our study on the electronic, linear and nonlinear optical properties of the ternary bismuth sulfide Bi$_2$S$_{2.75}$Se$_{0.25}$ is important for the development of a new high-performance optoelectronic material in the Bi-based compounds.

Authors contribution
HBA Formal analysis, Methodology, Investigation, Writing—original draft, Supervision, Validation, Conceptualization
WO Formal analysis, Validation, Investigation, Conceptualization, Writing—review & editing.

Declarations
Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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