Original Article

Electronic and optical properties of Tl₄GeX₃ (X = S, Se and Te) compounds for optoelectronics applications: insights from DFT-computations

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Abstract

In this work, first-principles computational study on the structural, electronic and optical properties of Tl₄GeS₃, Tl₄GeSe₃ and Tl₄GeTe₃ ternary compounds are presented. The computations are performed with pseudopotential plane wave method based on density functional theory with the generalized gradient approximation of Perdew–Burke and Enzerhof (PBE-GGA). The calculated structural, electronic and optical parameters are consistent with the available experimental results. The computed electronic band structures confirm the semiconducting nature for these compounds with direct band gaps of 0.17 eV, 0.085 eV and 0.015 eV for Tl₄GeS₃, Tl₄GeSe₃ and Tl₄GeTe₃, respectively. Furthermore, the electron charge density distribution indicated that the nature of bonds between Ge and S/Se/Te are covalent, whereas Ge and S/Se/Te anions formed ionic bonds. The optical parameters revealed that Tl₄GeS₃, Tl₄GeSe₃ and Tl₄GeTe₃ are highly dielectric materials and has the potential to be beneficial in the optoelectronic device applications.

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1. Introduction

The rapid advancement of novel technologies open up new avenues to search for advanced functional-materials (FM). The desirable chemical and physical properties of such materials rely on the chemical composition depending on the crystal structure and atomic positions. The tuning of structural parameters can bring out huge modification in the electronic structure. In recent studies the attempts are made to develop potential semiconductor materials from single and poly-crystal to meet the specific requirements for technological applications. The prime purpose of this paper is to model and investigate the structural, electrical, and optical properties of three narrow band gap Tl$_4$GeX$_3$ (X=S, Se and Te) semiconductors by using the quantum mechanical first principles calculations [1–7].

Such investigations can help in analyzing the experimental data and as well as design a series of novel materials that may paved a path for the production of new optoelectronic devices [8–10]. The interesting features that can be seen in halides and chalcogenides compounds have a great impact, including little anisotropy, non-linear optical properties and piezoelectric properties [11,12]. The fluorooxoborates materials such as Li$_8$B$_3$O$_9$F, Li$_2$B$_3$O$_9$F$_2$ and Li$_2$B$_3$O$_7$F$_3$ are investigated with the help of first-principles methods study for their nonlinear optical performance and structural features. The nonlinear optical materials played a very important role in solid state laser. A tunable, compact and deep-ultraviolet (wavelength less than 200 nm) laser source could be utilized in large scale in advanced photonic technology [13,14].

The complex-chalcogenides having general formula TlTlB$_{IV}$C$_{VI}$, where B is Sn, Ge having d-block element, are of great interest due to their capacity to solve numerous technological issues. Due to the exceptional chemical and physical properties, these compounds are suitable for use as advanced light-emitting diodes (LED), infrared optoelectronics and photo-detectors working in far and mean spectral infrared regions (SIR) and photo-voltaic systems [15–18]. Tl$_4$X$_3$ (X = Pb, Sn and B = S, Se and Te) (having space group P4/nnc) are ternary semiconductors-chalcogenides with unique properties of excellent thermo-electric features distinguished by low-phonon thermal conductivity [19–24]. The specific importance for the generation of remarkable optical feature is due to the presence of thallium cations, which give attraction to anion co-ordination in a way that ensures the co-existence of covalence and ionic bonds [25–30].

The phase relation in Tl$_4$SeSnS was studied [31,32]. The polymorphic transformation (PT) of Tl$_4$SnS$_3$ compounds is seen at 600 K [33]. The Tl$_4$SnS$_3$ have monoclinic symmetry, \( a = 13.78 \text{ Å}, b = 7.732 \text{ Å}, c = 7.266 \text{ Å} \), (space group 2/c and \( \beta = 105.3^\circ \)) [34]. SnTe-Tl$_2$Te and intermediate phase of Tl$_4$SnTe$_3$ have been synthesized and melts at 817 K [35]. An infinite solid solution is made of tetragonal phase between Tl$_2$Te and Tl$_4$SnTe$_3$ (concentration range 60–100 mole% of Tl$_2$Se) [36–42].

It is instructive to search for materials of similar nature that can be applied in optoelectronic applications. In this work, the structural, electronic and optical properties of Tl$_4$GeS$_3$, Tl$_4$GeSe$_3$, and Tl$_4$GeTe$_3$ chalcogenides are investigated using the density functional theory. The next section presents the computational methods that are used in the present study.

2. Computational method

The generalized-gradient approximation of Perdew–Burke and Enzerhof (GGA-PBE) is used for all the calculations presented herein. The exchange-correlation function (ECF) through DFT is used in CASTEP method (material studio package) [43,44]. The cut-off energy of the plane wave is fixed at 330 eV. In all processes, the ultra-soft pseudo-potentials are used. The parameters of energy convergence are fixed as the maximum force accuracy is 0.02 eV/Å, the maximum stress component is 0.03 GPa, the total energy accuracy is \( 6 \times 10^{-5} \) eV/atom and the maximum atomic displacement is \( 5 \times 10^{-4} \) Å. The k points of the Brillouin zone are chosen as \( 5 \times 5 \times 3 \) for Tl$_4$GeS$_3$, Tl$_4$GeSe$_3$, and Tl$_4$GeTe$_3$. For fast calculations, the primitive cells are chosen. The electronic configurations are 5d$^2$6s$^2$6p$^1$ for Tl, 4s$^2$4p$^2$ for Ge, 3s$^2$3p$^4$ for S, 4s$^2$4p$^4$ for Se, and 5s$^2$5p$^4$ for Te, respectively.

3. Results and discussions

3.1. Structural properties

Tl$_4$GeS$_3$, Tl$_4$GeSe$_3$, and Tl$_4$GeTe$_3$ compounds are body-centered tetragonal with space group 4/mmm. The crystal unit cell structures of all three compounds are presented in Fig. 1. The Brich–Murnaghan equation of state was used to investigate the ground state structural parameters of chalcogenides compounds under study. Our optimized ground states structural parameters are listed in Table 1. The lattice parameters for Tl$_4$GeS$_3$, Tl$_4$GeSe$_3$, and Tl$_4$GeTe$_3$ are \( a = 8.303 \text{ Å} \), and \( b = 12.96 \text{ Å} \) for Tl$_4$GeS$_3$, \( a = 8.836 \text{ Å} \) and \( b = 12.57 \text{ Å} \) for Tl$_4$GeSe$_3$, \( a = 8.863 \text{ Å} \) and \( b = 12.96 \text{ Å} \) respectively, while other calculated values are \( a = 8.314 \text{ Å} \) where \( b = 12.647 \text{ Å} \), while Tl$_4$GeTe$_3$ are \( a = 8.819 \text{ Å} \), \( b = 64 \text{ Å} \), respectively. The previously
obtained results and our calculated results showed a closed agreement.

3.2. Electronic properties

To understand the nature of materials, the band gap is very important for electromagnetic, optical, and other physical properties. The structural properties of the three compounds are optimized by the procedure mentioned above. The electronic and optical properties are calculated by using GGA-PBE approximation. The Tl4GeS3, Tl4GeSe3, and Tl4GeTe3 ternary compounds show their narrow band gaps. Their direct band energies are 0.170 eV, 0.085 eV and 0.015 eV, respectively, as shown in Table 1. The optimized band structures are shown in Fig. 2(a–c). The conduction band minimum (CBM) and the valence band maximum (VBM) are symmetric and are shown at the vicinity of X and Γ symmetry points for Tl4GeX3 (X = S, Se and Te) compounds in the first Brillouin zone as presented in Fig. 2(a–c). As no experimental work has been done on our compounds yet, we will compare the results to similar compounds of the same group like Tl4SnX3 (X = S, Te); their indirect band gaps are 0.708 eV and 0.027 eV [34]. Our results are closely matched with these compounds. The good point is that the band gaps obtained here are narrow direct band gaps, so the device that will be manufactured from it will be operated by the very low cost of energy. It can be seen from Table 2 that the value of band gaps becomes smaller and smaller and the valence band and the conduction band comes closer and closer to the Fermi level as we doped S, Se, and Te in Tl4GeX3, i.e. for Tl4GeS3 it is 0.170 eV, for Tl4GeSe3 it is 0.085 eV and for Tl4GeTe3 it is 0.015 eV. This is because the conductivity of the elements is enhancing as we go down in groups of periodic table so tellurium has more electrons than selenium and selenium has more electrons than sulfur available for conduction as shown in Fig. 2(d). From all the above discussion, it can be

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**Table 1 – The lattice parameters of Tl4GeS3, Tl4GeSe3, and Tl4GeTe3 compounds.**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Present work</th>
<th>Other works [45–47]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl4GeS3</td>
<td>a = 8.303 Å, c = 12.96 Å, V = 879.292 Å³</td>
<td>a = 8.314 Å, c = 12.647 Å, V = 874.195 Å³</td>
</tr>
<tr>
<td>Tl4GeSe3</td>
<td>a = 8.836 Å, c = 12.57 Å, V = 875.1129 Å³</td>
<td>a = 8.819 Å, c = 12.64 Å, V = 872.301 Å³</td>
</tr>
<tr>
<td>Tl4GeTe3</td>
<td>a = 8.863 Å, c = 12.965 Å, V = 1014.443 Å³</td>
<td>a = 8.822 Å, c = 13.03 Å, V = 1012.083 Å³</td>
</tr>
</tbody>
</table>

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**Table 2 – The band values of Tl4GeS3, Tl4GeSe3, and Tl4GeTe3.**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Our proposed (GGA)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl4GeS3</td>
<td>0.17 eV</td>
<td>0.103 eV [45]</td>
</tr>
<tr>
<td>Tl4GeSe3</td>
<td>0.085 eV</td>
<td></td>
</tr>
<tr>
<td>Tl4GeTe3</td>
<td>0.015 eV</td>
<td>0.027 eV [45]</td>
</tr>
</tbody>
</table>

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![Fig. 2](image-url)  
**Fig. 2** – (a) The band gap of Tl4GeS3; (b) the band gap of Tl4GeSe3; (c) the band gap of Tl4GeTe3; (d) the band gap versus composition of Tl4GeX3 (X = S, Se, Te).
figured out that our calculations have good agreement with the other calculations, so our methodology is reasonable.

The electronic density of states (DOS) investigation is really important for the analysis of physical features of Tl₄GX₃ (X = S, Se, Te) semiconductors. To figure out the detail bonding nature of Tl₄GeS₃, Tl₄GeSe₃ and Tl₄GeTe₃ ternary compounds, we have calculated the partial and total densities states (PDOS and TDOS) as shown in Fig. 2(a–c). For Tl₄GeS₃, as in Fig. 3(a), the valance band is originated dominantly from the Tl-5d, Ge-4p, and S-3p bonding orbitals. However, Tl-5d, Ge-4s, Ge-4p states contribute more than the S-3p states. The atomic orbitals Ge-4p, Tl-6p and S-3p constituted the conduction

Fig. 3 – (a) Total and partial densities of states of Tl₄GeS₃, (b) Total and partial densities of states of Tl₄GeSe₃. (c) Total and partial densities of states of Tl₄GeTe₃.
band. Moreover, the lower part of the conduction band is formed by Tl-6p and S-3p and the upper part is formed by the Ge-4p states. The compound TlGeS$_3$ has a narrow energy gap which is 0.17 eV due to the involvement of 5d orbitals of Tl and 4p orbitals Ge during the band formation. In the case of Tl$_2$GeSe$_3$ in Fig. 3(b), the valence band is formed by Tl-5d, Se-4sp Ge-4s, and Ge-4p bonding orbitals but the Se-4sp and Tl-4d give large contribution compared to Ge-4s and Ge-4p. In the conduction band, the Ge-4p, Se-4p and Tl-6p states are contributing. Here we see that the main contributions are due to Ge-4p and the minor contributions are due to Tl-6p and Se-4p orbitals. The small band gap energy of 0.085 eV is due to the inclusion 5d orbital of Tl and 4p orbitals of Ge and Se during band construction.

In the case of the Tl$_4$GeTe$_3$ compound, as presented in Fig. 3(c), the valence band is formed by Te-5p, Tl-5d, and Ge-4s bonding orbitals. The conduction band is comprised of Ge-4p, Tl-6p, and Te-5p. We can see that the large part is given by Ge-4p states and a small part is given by Te-5p state. The energy gap of Tl$_4$GeTe$_3$ is very small (0.015 eV) due to the 5p and 5d bonding orbital contributions of Te and Tl atoms in bond formation.

Furthermore, to know about the bonding character clearly, the 2D charge density distribution of Tl$_3$GeS$_3$, Tl$_4$GeSe$_3$, Tl$_4$GeTe$_3$ compounds have been calculated and plotted in Fig. 4. It is revealed from the charge density calculations that these materials have similar bond characteristics. One can observe from charge distribution maps that there are covalent chemical bonds between Ge and S/Se/Te anions and there are ionic bonds between Tl and S/Se/Te. Obviously, these compounds consist of a mixture of covalent and ionic characters. The various charge densities of space hybridizations are due to the geometrical structure of the compounds under consideration. The space hybridization degree is a good technique for the mobility charge detection mainly made by p S/Se/Te holes in the valence band and s, d cationic electron in conduction band near the Fermi level.

### 3.3 Optical properties

A comprehensive understanding of the basic optical characteristics, i.e., photonics, and optoelectronics of a compound is of great interest. We should mention in this section that the studied compounds have tetragonal structure, hence we need to calculate two non-zero independent components of the dielectric tensors, namely, $\varepsilon_{xx}$ = $\varepsilon_{yy}$, and $\varepsilon_{zz}$ to completely characterize their linear optical properties. These components, i.e., $\varepsilon_{xx}$ and $\varepsilon_{zz}$, correspond to incident radiations with electric field vector $\vec{E}$ polarized parallel to x- and z-axes ([100] and [001] directions), respectively. We find that the calculated components $\varepsilon_{xx}(\omega)$ and $\varepsilon_{zz}(\omega)$ spectra of each studied compound overlap perfectly. This indicates that the optical properties of the title compounds are perfectly isotropic, i.e., they are independent of the crystallographic direction. The frequency-dependent dielectric function (DF) $\varepsilon(\omega)$ = $\varepsilon_1(\omega)$ + i$\varepsilon_2(\omega)$ is used to figure out the optical properties of Tl$_3$GeS$_3$, Tl$_4$GeSe$_3$, and Tl$_4$GeTe$_3$ ternary compounds. The $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the two parts of the dielectric function (DF). Where $\varepsilon_1(\omega)$ is the real part of DF and $\varepsilon_2(\omega)$ is the imaginary part of DF. The imaginary part can be derived from the momentum matrix elements (MME) of filled and unfilled bonding orbitals by applying the following equation:

$$\varepsilon_2(\omega) = \frac{2\omega^2}{\Omega c^2} \sum k, u, v \mid \psi_k^u \mid^2 \mid \psi_k^v \mid^2 \delta(E_k^u - E_k^v - \omega)$$

where $u$ represents the incident electric field polarization, $\omega$ is the frequency of light, $e$ defines the electron charge, $\mid \psi_k^u \mid$ and $\mid \psi_k^v \mid$ denotes the conduction and valance band wave functions at a particular $k$, respectively.

Reflectivity is an optical parameter that characterizes the optical response of the surface of the material. From Fig. 5(a), it is seen that the reflectivity spectra of Tl$_4$GeX$_3$ (X = S, Se and Te) compounds show similar characteristics. The reflectivity of Tl$_4$GeS$_3$ gets to a maximum value of 4.1. On the other hand, the reflectivity of Tl$_4$GeSe$_3$ begins at 4.6, goes up and gets to a max-

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**Fig. 4** - The charge densities of states for Tl$_4$GeS$_3$ (a), Tl$_4$GeSe$_3$ (b) and Tl$_4$GeTe$_3$ (c).
maximum value of \(\sim 4.8\) in the energy range from 0 to 15 eV. For the Tl\(_4\)GeTe\(_3\) compound, the reflectivity starts at 5.3 and get to the highest value of 5.8. It can be noted that all three compounds have similar same spectra and show good characteristics of coating materials. Next, the absorption parameter that shows the depth light of specific photon (energy) or wavelength which can go into the material before being fully absorbed. Fig. 5(b) shows the absorption-spectra of Tl\(_4\)GeS\(_3\), Tl\(_4\)GeSe\(_3\), and Tl\(_4\)GeTe\(_3\) compounds showing that these compounds have semiconducting nature. The absorption spectra of these compounds grow sharply close to 5.8 eV. On the other hand, for polarization direction [100], the maximum peaks have an appearance at 6.3 eV, after this it undergoes drastic decrement at about 13.6 eV. The real parts of refractive-indices of Tl\(_4\)GeX\(_3\) (X=S, Se and Te) compounds are depicted in Fig. 5(c). The refractive indices of the compounds under investigation are about 3.6, 4.2 and 4.8 respectively. These materials are, therefore, suitable for applications where large refractive indices are prerequisites. It can be noted from the refractive indices spectra that they are high in infrared (IR) region, then slowly decrease in the visible and then in the ultraviolet (UV) regions. The results also illustrate that the refractive indices have an inverse relation with the band gaps of the compounds under consideration. It can be observed that the refractive indices are increasing as the bang gap decreasing. From this observation, it can be claimed that our calculations, methodology, and results are reasonable.

Fig. 5(d) shows the DF that is the basic optical parameter for the description of polarization and absorption feature of materials. It is clear from Fig. 5(d), that the imaginary part of dielectric function is zero near 9.2 eV for Tl\(_4\)GeS\(_3\), 9.8 eV for Tl\(_4\)GeSe\(_3\), and 10.2 eV for Tl\(_4\)GeTe\(_3\). The materials are transparent above this energy. The non-zero portion of the imaginary part indicates that absorption occurs in this range of energy. These calculated results by DFT for the three compounds are aligned with the band structure results, showing that these materials have good absorption quality. Dielectric materials with value of dielectric constant \(k \times 8.854 \, \text{F/cm} > 7\) that of silicon nitride \((k > 7)\) are categorized as high dielectric materials and that materials having \(k\) values less than the dielectric constant of silicon dioxide \((k \sim 3.9)\) are categorized as low dielectric materials. So, by comparing the \(k\) values of the materials under study with the above-mentioned reference values, we found that our materials have \(k\) value more than 7 and could be classified as high dielectric materials and they may have applications in optoelectronics such as memory cell dielectrics, gate dielectrics and passive components [47].

Moreover, the photoconductivity is an optical phenomenon that illustrates that the conductivity of the material goes up due to the absorption of radiation or light energy. Fig. 5(e) shows the photoconductivity of Tl\(_4\)GeS\(_3\), Tl\(_4\)GeSe\(_3\), and Tl\(_4\)GeTe\(_3\) begins at 0.05 eV. These materials are significantly electrically conductive for the incident photon energy.
in the range between 1.3 and 3.8 eV. The conductivity becomes
small in the energy range 12.2–14.3 eV. For energies higher
than 15 eV, there is no photoco nductivity at all. The energy
loss function is presented in Fig. 5(f). This shows the energy
loss of an electron passing through the materials. It can be
seen from the energy loss function that effective plasma fre-
quencies reside within an energy range of 12.5–13.6 eV. Also,
the compounds are transparent when the frequency of the
incident photon energy is larger than the plasma frequency.

4. Conclusions

In this study, we find out the structural, electronic and optical
properties of Tl$_4$GeS$_9$, Tl$_4$GeSe$_3$, and Tl$_4$Te$_3$ com-
ounds by using the GGA-PBE approach. All three compounds are
narrow band gap semiconductors with band gap energies of 0.170 eV
for Tl$_4$GeS$_9$, 0.085 eV for Tl$_4$GeSe$_3$ and 0.015 eV for Tl$_4$Te$_3$.
The calculation of band gaps, densities of states and optical
features of Tl$_4$GeS$_9$, Tl$_4$GeSe$_3$, and Tl$_4$Te$_3$ semiconduc-
tors showed good alliance with each other and other related cal-
culations. The DOS calculations showed that the maximum
contribution near the Fermi level is due to Tl-d, Ge-p, Se-p, and
Te-p bonding orbitals. It can be seen from charge distribution
maps that the compounds under study have covalent bonds be-
tween Ge and S/Se/Te atoms and there are ionic bonds between
Tl and S/Se/Te. One can clearly see a mixture of covalent and ionic
character in these compounds. The optical properties, such as the re-
flexivity, absorption, refractive index, dielectric function, conduc-
tivity and loss function of materials revealed that our materials may have optoelectronic
applications. As it is the first time that we have figured out the
physical features of Tl$_4$GeS$_9$, Tl$_4$GeSe$_3$, and Tl$_4$Te$_3$ com-
ounds, confirmation with experimental results are expected in the future. It is hoped that our findings will open new gate-
ways in this advanced field of research.

Conflicts of interest

The authors declare no conflicts of interest.

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