Heavy thallium based fluoroperovskite TlAF₃ (A = Ge, Sn and Pb) compounds: a computational investigation

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Abstract
The use of heavy elements to build a stable system increases the effective atomic number, making it useful in a variety of applications such as radiation detection and shielding. This study reports the density functional theory (DFT) based investigations on new Thallium based heavy fluoroperovskites TlAF₃ (A = Ge, Sn and Pb). These compounds have a cubic perovskite structure with optimal lattice constants ranging from 4.49 to 4.85 Å. Electronic behaviors of the compounds is found to be insulating with the maximum band gap of up to 1.90 eV, having indirect band nature. In all investigated compounds, the fluorine atom provides a significant number of electronic states to the valence and conduction bands. The optical activity is evaluated by determining the refractive index, extinction coefficient, optical conductivity, reflectivity, and absorption coefficients up to photon energies of 20 eV. The properties of present compounds are being reported for the first time.

Keywords Thallium-based heavy fluoroperovskites · Electronic behavior · Optical properties · Elastic properties

1 Introduction

Perovskites are the class of materials having a simple structure of the form ABX₃, where A and B are alkali metals and alkaline earth metals, respectively, and X might be oxygen or a member of the halogen family. These compounds have potential applications owing to their diverse properties (Chen et al. 2020; Bouich et al. 2021a, b; Chang et al. 2020; Mohseni et al. 2021). Fluoroperovskites are a kind of perovskite in which element X is substituted with the element Fluorine. Growing interest is being witnessed in the investigation of Fluoroperovskites due to their properties such as ferroelectricity (Garcia-Castro et al.
2014), as lens (Nishimatsu et al. 2002), phosphors (Zheng et al. 2007), dosimeters (Daniel et al. 2014), etc.

Density Functional Theory (DFT) can be employed to screen and design future materials. It can also serve to get an insight into the physical properties of interest. Fluoroperovskite systems composed of various elements are being actively investigated using DFT.

A comprehensive study was reported by Körbel et al. (2016) on the search of thermodynamically stable cubic perovskites through high-throughput density functional theory calculations. In this study, the prediction of new stable perovskite systems opened up the way for a detailed investigation of physical properties. The versatile bandgap of perovskites ranging from semiconductors to insulators and the presence of a variety of elements in stable structures makes them worthwhile to investigate for various applications. We reported the study on Thallium-based fluoroperovskites TlXF3 (X = Ca, Cd, Hg and Mg) (Khan et al. 2019) and predicted their use as scintillation material due to high effective atomic number and bandgap in the insulating region. In another study, the InAF3 (A = Ca, Cd and Hg) system (Khan et al. 2021) was investigated by replacing Thallium with Indium, making materials more environment friendly owing to less toxicity of Indium.

The presence of heavy elements in a compound increases the effective atomic number \(Z_{\text{eff}}\). The large value of \(Z_{\text{eff}}\) of a material makes it attractive for numerous applications such as radiation detection and radiation shielding. In general, the detector material must have a high effective atomic number \(Z_{\text{eff}}\) for X-ray and gamma-ray spectroscopy. The large \(Z_{\text{eff}}\), in particular, has strong photoelectric conversion efficiency for X-rays and gamma-rays. The probability of photoelectric absorption is proportional to \(\rho Z_{\text{eff}}^{3-4}\), where \(\rho\) is the density of the detecting medium (Fujimoto et al. 2018). Incorporation of heavy elements in compounds like Bi₄Ge₃O₁₂ (Weber and Monchamp 1973), (Lu, Gd)₃(Ga, Al)₅O₁₂ (Kamada et al. 2011), Tl₂LiGdCl₆ (Kim et al. 2015), and PbWO₄ (Kobayashi et al. 1996) makes materials promising for scintillation applications. Despite intensive research on fluoroperovskite systems, to the best of our knowledge, no research has been done on a heavy element combination with Thallium in fluoroperovskite system TlAF3 (A = Ge, Sn, and Pb) before. Therefore, we found it valuable to choose this system for exploring the structural and optoelectronic properties using DFT with the WIEN2k package and predicting properties for future experiments. Our investigations on TlAF3 (A = Ge, Sn, and Pb) compounds are being performed and communicated for the first time in the literature.

2 Computational details

The thallium-based fluoroperovskite compounds TlAF3 (A = Ge, Sn and Pb) crystallize in the cubic perovskite-type crystal structure having space group Pm3m (# 221). The Tl and A atoms are positioned at (0,0,0) and (1/2,1/2,1/2), respectively, while F atoms are placed at (0,1/2,1/2), (1/2,0,1/2) and (1/2,1/2,0) sites of the Wyckoff coordinates as shown in Fig. 1.

In this work, we used the WIEN2k code (Blaha et al. 2020) to implement the full-potential linearized augmented plane wave technique (FP-LAPW) (Singh 2006). Coulomb interactions are taken into account, and calculations are performed using the generalized gradient approximation (GGA + U) with an extra Hubbard-U component to compensate for on-site Coulomb interactions. (GGA + U) (Perdew et al. 1996). We did GGA + U calculations by considering Hubbard correction U = 5 eV, for both Tl and X (X: Ge, Pb, Sn) atoms and found that Hubbard correction slightly increase
the electronic bandgap bandgap. Both Tl and X atoms are heavy elements containing d-orbital electrons due to which we used GGA + U method. Quite standard approaches are applied and in particular to go beyond PBE-GGA to obtain a reasonable band-gap which is the main property of interest for optoelectronic applications. It is well known that PBE underestimates the band-gap and therefore more sophisticated approach is used for evaluating this property.

First of all, we optimized lattice parameters for the present series of compounds. Optimization plots of all compounds are shown in Fig. 2. Ground state lattice parameters are found to be 4.49, 4.70, and 4.85 Å by fitting the curves using Burch Murnaghan’s equation of state (Murnaghan 1944). The valence-core energy difference is considered to be −6 Ry. Inside the muffin tin-spheres, spherical harmonic functions are employed with a cut-off of l-max = 10. The total k-Points are chosen to be 1500 and the Fourier expanded charge density was truncated at Gmax = 12 a.u.−1 for self-consistent calculations. Moreover, the RMT (denotes the minimum radius of the muffin-tin sphere) values for Tl is 2.5 a.u. for all compounds. In TlGeF3, 2.15 and 2.11 a.u. are chosen for Ge, F, respectively, while in TlPbF3, 2.11 a.u. is chosen for both Pb and F. In TlSnF3, the value chosen for both Sn and F atoms was 2.12 a.u.

To check the crystal structure stability, we calculated the formation energy, which can be defined as

$$E_f = E_{tot}[TlXF_3] - E_{tot}[Tl] - E_{tot}[Ge] - 3E_{tot}[F]$$

where $E_{tot}[TlXF_3]$ is the total electronic energy of TlXF3 (X: Ge, Sn, Pb), and $E_{tot}[Tl]$ (X) is the chemical potential energy per Tl(X) atom in its natural state. The chemical potential for the F atom is calculated from the molecular phase’s total energy, which contains two F atoms. The calculated formation energies are −3.45 eV, −2.30 eV and −1.92 eV for TlGeF3, TlSnF3 and TlPbF3 compounds, respectively. The negative formation energy indicates the thermodynamic stability of these compounds. The negative $E_f$ values indicate the exothermic system, which means without any difficulty they can be experimentally realized.
3 Results and discussion

3.1 Elastic properties

In this section, we present our calculation results on the elastic behavior of the studied compound. Elastic properties can be deduced from elastic constants. The behavior of the crystal to external forces is determined by these constants. Information regarding the stability and stiffness of materials is found from the elastic constants. There are a total of 21 elastic constants, but three of them, \( C_{11}, C_{12}, \) and \( C_{44} \), are relevant for a cubic system. The elastic constants \( C_{ij} \) from first-principles calculations for present compounds are listed in Table 1. The criteria for mechanical stability are described below which put limitations on elastic constants (Grimvall 1999)

\[
C_{11} > 0; \quad C_{44} > 0; \quad (C_{11} - C_{12}) > 0; \\
(C_{11} + 2C_{12}) > 0; \quad C_{12} < B < C_{11}.
\]

All the constants are positive and fulfill the criteria which shows the stability of studied compounds. Many properties of interest can be computed from elastic constants. The following mathematical expressions (Hill 1952) have been used to calculate Bulk Modulus (\( B \)), Young’s modulus (\( E \)), Poisson’s ratio (\( \nu \)), and Pugh’s index ratio (\( B/G \)) and obtained values are listed in Table 1.

Fig. 2 Optimization plots were obtained for TIGeF\(_3\), TISnF\(_3\) and TIPbF\(_3\) by calculating energy corresponding to varying unit-cell volume
The ductility and brittleness nature are studied by using the bulk modulus to shear modulus ratio ($B/G$), Cauchy’s pressure, and Poisson’s ratio ($\nu$). For under-study compounds, according to Pugh’s ratio (Pugh 1954), values of $B/G$ exceed the limit of 1.75 which is considered as its threshold value. Cauchy’s pressure is obtained by calculating the difference of elastic constants $C_{11} - C_{44}$. The positive or negative outcome of this difference indicates whether the compound is brittle or ductile. The positive value indicates ductile nature while the negative value represents brittle nature (Pettifor 1992). For all the present compounds, the obtained difference is positive, leading to ductile nature. While according to the Poisson ratio (Frantsevich and Voronov 1982), calculated values of $\nu$ for all compounds are greater than 0.26, which is another confirmation of ductility. The degree of elastic anisotropy of a crystal can be inferred from the anisotropy factor $A = 2C_{44}/(C_{11} - C_{12})$. If the value of $A$ approaches unity, the crystal reveals an isotropic character. The calculated values of $A$ for all compounds are deviating from 1 as listed in Table 2, so we can conclude that the compounds under consideration in this work are anisotropic mechanically.

| Parameter | TlGeF$_3$ | TlSnF$_3$ | TlPbF$_3$ |
|-----------|-----------|-----------|-----------|
| $a_0$     | 4.49      | 4.70      | 4.85      |
| $C_{11}$  | 163.40    | 442.52    | 274.55    |
| $C_{12}$  | 60.46     | 147.22    | 112.47    |
| $C_{44}$  | 36.03     | 62.96     | 63.53     |
| A         | 0.70      | 0.57      | 0.78      |
| B         | 94.77     | 245.65    | 166.50    |
| G         | 41.57     | 105.67    | 70.03     |
| E         | 108.81    | 277.26    | 184.27    |
| $\nu$     | 0.43      | 0.44      | 0.44      |
| $B/G$     | 2.27      | 2.32      | 2.37      |

$$B = \frac{C_{11} + 2C_{12}}{3}$$  \hspace{1cm} (1)$$E = \frac{9BG}{3B + G}$$  \hspace{1cm} (2)$$\nu = \frac{3B - 2G}{2(2B + G)}$$  \hspace{1cm} (3)$$G = \frac{G_v + G_R}{2}$$  \hspace{1cm} (4)$$G_v = \frac{C_{11} - C_{12} + 3C_{44}}{5}$$  \hspace{1cm} (5)$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})}$$  \hspace{1cm} (6)
3.2 Electronic properties

Electronic properties play a key role in deciding the area of utilization of a material. We looked at energy band structure and density of states to learn in detail about electronic characteristics. The investigations are made, like all other properties by employing GGA approximation with additional U-term. For the accurate prediction of electronic bandgap, we did Heyd-Scuseria-Ernzerhof (HSE) calculations (Heyd et al. 2003). For HSE calculations, we used the optimized norm-conserving Vanderbilt pseudopotentials. In HSE calculation the mixing parameters, $\alpha = 0.25$, and screening-parameter $\beta = 0.15$ used for all compounds. For the best comparison we plotted the GGA + U and HSE calculated electronic band structure together as shown in Fig. 3. The GGA + U calculated electronic bandgap are without bracket and HSE calculated are listed with in the bracket in the Table 2. The states are plotted in the first Brillouin zone (BZ) along with the high

| Compounds   | $E_g^{M-M}$ | $E_g^{X-X}$ | $E_g^{\Gamma-\Gamma}$ | $E_g^{R-M}$ | $E_g^{\Gamma-X}$ |
|-------------|-------------|-------------|-----------------------|-------------|------------------|
| TlGeF$_3$   | 2.71 (4.07) | 4.53 (5.85) | 8.74 (10.25)          | 1.59 (2.82) | 3.38 (5.79)      |
| TlSnF$_3$   | 1.83 (2.90) | 3.73 (4.83) | 7.65 (8.38)           | 0.63 (1.69) | 5.90 (6.58)      |
| TlPbF$_3$   | 2.83 (4.07) | 4.04 (5.48) | 7.26 (8.89)           | 1.90 (3.10) | 5.56 (7.17)      |

Table 2 Bandgap values of TlAF$_3$ (A = Ge, Sn and Pb) compounds were obtained through GGA + U. The GGA + U calculated electronic bandgap are without bracket and HSE calculated bandgaps are listed with in the bracket.

Fig. 3 Energy band structure of TlAF$_3$ (A = Ge, Sn and Pb) computed along with high symmetry directions of first Brillouin zone.
symmetry directions in the energy range of $-6 \text{ eV} \text{ to } +6 \text{ eV}$. The horizontal dashed line represents Fermi level, set at zero energy level, and is indicated by a horizontal dashed line. Irreducible BZ’s high symmetry points are denoted with alphabetic letters. The bandgap nature is determined by the location of valence band maxima and conduction band minima. If both lie at the same symmetry point, then the material is known to have a direct band gap, otherwise, the band gap nature is indirect. All the compounds are showing similar profiles. Valence band maxima are located at the R point while conduction band minima lie at the M point for all compounds exhibiting indirect band gap nature. Energy band gap values are found to be 1.59, 0.63, and 1.90, respectively, for TlGeF₃, TlSnF₃, and TlPbF₃ as listed in Table 2. Apart from band splitting, no major difference in the distribution of states is observed.

Atom-specific density of states is evaluated to investigate the contribution coming from individual elements and presented in Fig. 4. In the case of TlGeF₃, shown in part (a), it is clear that in the valence region, maximum states are contributed by the F atom in which among all of its orbitals, p-state has a major share. Whereas the conduction band has mixed contributions from Ge and Tl atoms. The total and partial density of states of TlSnF₃ are shown in Fig. 4b. The valence region is dominated by the states of the F atom, especially the p-state of the F atom. In the conduction band, there is a mixed contribution from the F and Sn and Tl atoms. On the other hand, in the case of TlPbF₃, the valence region is dominated by the p states of F atom while the conduction band is having mixed behavior contributed by the p-states of Pb and Tl atoms as shown in Fig. 4c.

![Fig. 4](image_url) The major contribution of electronic states in valence and conduction band of (a) TlGeF₃, (b) TlSnF₃, and (c) TlPbF₃ in terms of total and partial density of states.
3.3 Optical properties

This subsection reports the detailed investigation of optical properties. We performed calculations using the GGA + U method with varying incident photon energies up to 20 eV and plotted in Fig. 5. Among all the optical properties, dielectric function calculations play an important part, and they may be linked to electronic structure for the necessary explanations. The dielectric function $\varepsilon(\omega)$ is given by the following relation (Ambrosch-Draxl and Sofo 2006)

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

(7)

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ stand for the real and imaginary part of dielectric function, respectively. This complex function computes the linear response of any material to external electric and magnetic fields.

Using the following relationship, the imaginary component of the dielectric function may be calculated using a solid’s electronic band structure:

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2\omega^2} \sum_{i,j} \int <i|M|j>^2 f_i(1 - f_j) \times \delta(E_{j,k} - E_{i,k} - \omega)d^3k.$$  

(8)

The starting and end states during electronic transition are denoted by $i$ and $j$, respectively, while the dipole matrix is represented by $M$. $E_i$ is the electron energy in the $i^{\text{th}}$ state, while $f_j$ is the Fermi distribution function for that state.

The Kramers–Kroning relation is used to find $\varepsilon_1(\omega)$, which is written as:

*Fig. 5* Optical behavior of TlGeF$_3$, TlSnF$_3$, and TlPbF$_3$ in terms of real and imaginary part of dielectric function, refractive index, reflectivity, optical conductivity and absorption coefficient for the varying photon energies ranging from 0 to 20 eV
\[ \varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'. \] (9)

Here \( P \) stands for the principal part of the integral.

The absorption behavior of a solid, which is directly tied to electronic band structure, is related to the imaginary component of the dielectric function. The electronic transitions between the valence and conduction bands are described by this part. The refractive index, extinction coefficient, absorption coefficient, and reflectivity are all calculated using both real and imaginary components of dielectric function.

In Fig. 5a, h and o the real part of the dielectric function \( \varepsilon_1(\omega) \) is plotted. As indicated in Table 3, the static dielectric constants \( \varepsilon_1(0) \) for TiGeF\(_3\), TiSnF\(_3\), and TiPbF\(_3\) are 4.1, 18.5, and 3.4, respectively. These findings are consistent with the Penn model which states that inverse relationship exists between \( \varepsilon_1(0) \) and \( E_g \) (Penn 1962). As TiSnF\(_3\) has smallest band gap of 0.84 eV and therefore possess largest value of \( \varepsilon_1(0) \) among the present compounds. Figure 5b, i and p illustrates the imaginary part \( \varepsilon_2(\omega) \), which characterizes the absorption behavior of all compounds as a function of photon energy. The absorption edges of a compound correspond to the transition from valence band maxima to conduction band minima and are related to the energy bandgap. For present compounds, these edges emerge from transitions between R to M points. As can see from the band structure plot, TiSnF3 has the narrowest band gap of all the compounds studied, therefore having absorption edge at the lowest photon energy.

Then, in order of increasing band gaps, the edges for TiGeF\(_3\) and TiPbF\(_3\) are identified, in agreement with the band structure plot in Fig. 3. Beyond absorption edges, as more states are available to take part in transitions, there is rapid increase in intensity of absorption curves. TiGeF\(_3\), TiSnF\(_3\), and TiPbF\(_3\) possess major peaks corresponding to photon energy of 7.6 eV, 0.7 eV, and 5.7 eV, respectively.

Refractive index and extinction coefficient have been computed by using the following relations (Dressel and Gruener 2002)

\[ n(\omega) = \left[ \frac{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}{2} + \frac{\varepsilon_1(\omega)}{2} \right]^{1/2}, \] (10)

\[ k(\omega) = \left[ \frac{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}{2} - \frac{\varepsilon_1(\omega)}{2} \right]^{1/2}. \] (11)

| Compound    | \( \varepsilon_1(0) \) | \( n(0) \) | \( R(0) \) | Maximum \( \sigma(\omega) \) [in \( \Omega^{-1} \text{ cm}^{-1} \)] | Maximum \( \alpha(\omega) \) |
|-------------|-----------------|-------------|-----------|-----------------|-----------------|
| TiGeF\(_3\) | 4.1             | 2.0         | 11%       | 5472.7          | 137.5           |
| TiSnF\(_3\) | 18.5            | 4.3         | 40%       | 5649.1          | 155.2           |
| TiPbF\(_3\) | 3.4             | 1.8         | 10%       | 4814.8          | 131.8           |

Table 3 The calculated values of static dielectric constant \( \varepsilon_1(0) \), static refractive index \( n(0) \), static reflectivity \( R(0) \), maximum optical conductivity \( \sigma(\omega) \) [in \( \Omega^{-1} \text{ cm}^{-1} \)] and maximum absorption coefficient for TiGeF\(_3\), TiSnF\(_3\) and TiPbF\(_3\) using GGA + U scheme.
Figure 5c, j and q shows the refractive indices of TlGeF₃, TlSnF₃ and TlPbF₃. The static refractive indices have values of 2.0, 4.3, and 1.8 for TlGeF₃, TlSnF₃, and TlPbF₃, respectively as listed in Table 3. Values of static refractive indices are endorsed by the relation \( \eta(0) = \sqrt{\varepsilon_1(0)} \). The refractive index of TlGeF₃ and TlPbF₃ is almost constant at lower photon energies. This represents optically isotropic behavior at lower energies. On the other hand, refractive index of TlSnF₃ varies, exhibiting its optically anisotropic nature. While for high photon energies, the curve attains a maximum positive value. Beyond that, it displays a declining trend at higher photon energies. Figure 5d, k and r shows the extinction coefficients \( k(\omega) \). TlGeF₃, TlSnF₃, and TlPbF₃ have extinction coefficient maxima of 1.6 at 8.2 eV, 1.9 at 3.3 eV, and 1.5 at 6.9 eV, respectively, corresponding to the zero of \( \varepsilon_1(\omega) \).

The following relation can be used to calculate the Reflectivity of a solid.

\[
R(\omega) = \left| \left( \frac{\varepsilon_1(\omega) + i \varepsilon_2(\omega)}{\varepsilon_1(\omega) + i \varepsilon_2(\omega)} \right)^{1/2} - 1 \right|.
\]  \(12\)

Figure 5e, l and s shows plots demonstrating optical reflectivity. TlGeF₃, TlSnF₃, and TlPbF₃ had zero-frequency reflectivities of 11%, 40%, and 10%, respectively, as indicated in Table 3. For the energy range below the bandgap energy, a solid’s reflectivity is either constant or has a lower value. The energy range in which the absorption capacity of a solid is maximum is the region in which the maximum reflectivity can be noted as shown by plots of \( \varepsilon_2(\omega) \).

The following equations are used to calculate optical conductivity and absorption coefficient.

\[
\sigma(\omega) = \frac{\omega}{4\pi} \varepsilon_2(\omega),
\]  \(13\)

\[
\alpha(\omega) = \sqrt{2\omega} \left[ \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2}.
\]  \(14\)

Figure 5f, m, and t show the optical conductivity of TlAF₃ (A=Ge, Sn, and Pb), whereas figure (g), (n), and (u) show the absorption coefficients for all three compounds.

In all energy ranges, both parameters exhibit similar behavior. TlGeF₃ has a maximum absorption coefficient of 142 at 8.2 eV, 153 at 18.7 eV for TlSnF₃, and 140 at 9.6 eV was observed for TlPbF₃. Above the bandgap energy, all the compounds show considerable absorption.

### 4 Conclusions

We examined the structural, elastic, and electronic characteristics of Thallium-based heavy fluoropervoskites TlAF₃ (A=Ge, Pb, and Sr), as well as their optical response to incoming photons using density functional theory with GGA+U approximation for the first time. The present compounds crystallize in cubic structure having ground state lattice parameters in range (4.49–4.85 Å). The elastic parameters such as elastic constants, bulk modulus, anisotropy factor, Poisson’s ratio, and Pugh’s ratio are predicted. The Cauchy’s pressure and B/G ratio reveal that understudy compounds are ductile. Electronic behavior is evaluated by investigating the band structure and densities of states DOS for all compounds.
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TlGeF₃, TlSnF₃, and TlPbF₃ have band gaps of 1.59, 0.63, and 1.90 eV, respectively. In lower energy range, TlGeF₃ and TlPbF₃ show isotropic behavior while TlSnF₃ is optically anisotropic. As the properties of these compounds are being reported for the first time, they could not be compared with other studies. Owing to cubic nature, structural stability and high effective atomic numbers, these compounds have potential to be used as X-ray and gamma-ray radiation detectors in single crystal form.

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