Systematic Study of Optoelectronic and Thermoelectric Properties of New Halide Double Perovskites Cs2TlBiX6 (X=Cl, Br and I) for Energy Harvesting Applications

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Research Article

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Abstract

In this study we preferred to substitute hybrid halide perovskites ($\text{CH}_3\text{NH}_3\text{PbI}_3$) by using First principles calculations based on WEIN2K. To achieve renewable energy applications, the expansively investigate structured, optoelectronic, elastic, and thermoelectric characteristics of $\text{Cs}_2\text{TlBiX}_6$ ($\text{X}=\text{Cl}, \text{Br}, \text{and I}$) double perovskite. The elastic properties in these investigations display ductile behavior. Direct band gaps (2.29 eV, 2.26 eV, and 1.63 eV) exhibited by $\text{Cs}_2\text{TlBiX}_6$ ($\text{X}=\text{Cl}, \text{Br}, \text{and I}$) respectively. We have examined dielectric constants, refractive index, absorption coefficient, optical conductivity in optical properties. All compounds have high UV absorption coefficients, indicating that they are suitable for solar cells and other optical devices. In the temperature range of 200-800K, the thermoelectric and thermodynamic properties were calculated.

1. Introduction

Due to substitutional variability double perovskites latterly have greatly grown in the halide perovskites group of materials. The improved flexibility provided a new family of materials showing surprising optoelectronic characteristics. Double perovskite exhibits band structures with altered range of properties appear due to substitutions by distinct atomic site showing different type of band-gaps depending on substitutions causes large sometimes small, direct and also indirect band-gaps [1–10]. Solar cells produced by organ lead halide perovskites have perceived rapid progress that established to be one of the ultimate and capable for photovoltaic technologies, because of their solution-processability, low-cost and high efficiencies in the recent times [11–14]. But perovskite solar cells establish a different evolving technology that has the prospective to dominate due to low cost or concur with silicon solar technology [15]. New scheme of recollecting the promising optoelectronic properties of perovskites is the preparation of halide double perovskite ($\text{A}_2\text{BIIIIIX}_6$), represented as elpasolite, As BI is monovalent & BIII is trivalent cations to substitute Pb$^{2+}$. The encouraging element for BIII is B$^{+3}$ and Sb$^{3+}$ whereas In$^+$, Tl$^+$, Na$^+$, Ag$^+$, Au$^+$ and Cu$^+$ are ideal elements to substitute with BI [16, 17]. The absorption of light in the visible range done proficiently in lead halides and also retain an extensive diffusion length [18]. During radiative recombination [19] recyclable photons are emitted.

The $\text{Cs}_2\text{AgBiBr}_6$ photovoltaic thin film recognized the PCE is 2.5%, have an open-circuit voltage beyond IV [20] which have fast UV photodetectors that originated due to $\text{Cs}_2\text{AgInCl}_6$ single crystals [21] with small detection limit. Furthermore x-ray detectors are established [22] by $\text{Cs}_2\text{AgBiBr}_6$ single crystal. The Bi and Ag effectively substituted by Pb and achieved double perovskite lead-free halides [23–25]. With no phase transition of $\text{Cs}_2\text{BiAgBr}_6$ is stable at 703K and lead-free halides such as $\text{Cs}_2\text{BiAgBr}_6$ is inappropriate for photovoltaic implementation due to indirect bandgap [23]. In order to overcome this challenge, band structure engineering may be used. This may result in an indirect to direct bandgap transition. $\text{Cs}_2\text{InAgCl}_6$ is a lead-free halide double perovskite, according to Volonakis et al. This ground-breaking indium-based double perovskite has a highly adjustable direct bandgap in the visible range.[8]. $\text{Cs}_2\text{AgInCl}_6$ when performed experimentally it displays white pattern having 3.3ev band gap and emission energy is just 2 eV[26].
H slaventy [5] concluded that Cs₂AgI₃IIICl₆ and Cs₂AgI₃IIIIBr₆ shows 1ev direct band gap lesser in comparison with the analogous perovskites, and also predicts that Cs₂AgI₃IIIIBr₆ has the band gap of 0.95 eV. Both Cs₂AgI₃IIICl₆ and Cs₂AgI₃IIIIBr₆ show that bromides and chlorides do not restrict large band gaps.

Few comparable calculations using hybrid functionals for inorganic Cs₂TlBiX₆ (X = Cl, Br) were reported by Savory et al. The perovskites TlBi band gaps show very little variation in the A cation for these double perovskites, according to relative calculations (CH₃NH₃) Band gap for Cs₂TlBiBr₆ is 0.71 eV when compared to 0.72 eV for Rb₂TlBiBr₆ when CH₃NH₃ is substituted for Cs. Earlier computed data convinced us to explore Tl-Bi based double perovskites for further characteristics. The structural, elastic, optoelectronic, and thermoelectric properties scrutinized by applying DFT computations via wien2K including Boltztrap code in these material compounds. The calculated results display promising light harvesting features in perovskite solar cell and energy harvesting devices which offer platform for both theoretical and experimental scientists.

2. Computational Methods

Compound exploration in this study discussed the structural, optical, electronic, mechanical, and transport properties of compounds by WEIN2K in DFT simulation carried out by (FP-LAPW+lo) (PBE-GGA) approximation by applying mBJ on cubic Cs₂TlBiX₆ (X=Cl,Br,I) with Fm-3m space group that are optimized for precise lattice constants. Lattice constant and bulk moduli were calculated using Murnaghan's equation of state. The exact ground-state properties determined by using PBE-GGA approximations, however electronic properties (Electronic Band gap) are underrated. In order to exaggerate the electronic band gap, Backe and Johnson resolve the exchange potential that further modified by Trans and Blaha (TB-mBJ) has been merged. The electronic states enhanced by using TB-mBJ by averaging the lattice constant of PBE and GGA approximations. The mBJ potential [27] along with PBE-GGA was carried to run a self-consistent field [28] in order to attain precise band gap depiction. In order to resolve the issue of exchange potential below mention is used The Becke-Roussel potential (BR) in the above equation described by self-consistent charge, electrons density and kinetic energy are represented by , and respectively. The relation for the charge convergence factor is as under

\[
c = \left( \alpha + \beta \frac{1}{V_{\text{cell}}} \int d^3 r \frac{\nabla \rho(r)}{\rho(r)} \right)^{1/2}
\]

In Wein2K are fixed constant factors. In simulation the input parameters (lmax=10, Gmax=14 and R_{MT} x K_{max}=8) are unified. In the convergence 10x10x10 k-mesh has been preferred [29]. Boltzmann transport theory has been employed to determine the thermoelectric and thermodynamic possessions by using the BoltzTrap Code [30]. In BoltzTraP code, relaxation time (τ), k-point (N) and group velocity \( u_\beta (i, k) \) are executed.
3. Results and discussions

3.1. Mechanical Properties

Cs$_2$TlBiX$_6$ (X = Cl, Br and I) double perovskites crystallizes having cubic phase showing Fm-3m (225) space group are measured to grab authentic lattice constant $a_0$ (Å) of optimized structures. Murnaghan's equation of states have been used to plot between energy and volume. Both bulk modulus and lattice constant calculated are inversely associated with one and other are presented in Table 1. Figure 1 shows atomics positions of Cs that occupies the body central position (0.5,0.5,0.5) and X$_6$ forms the corner linked octahedra. The optimized assemblies of Cs$_2$TlBiX$_6$ (X = Cl, Br and I) are found using total energy released versus different unit cell volumes (see Fig. 2).

\[
\sigma_{\alpha\beta}(e) = \frac{1}{N} \sum_{i,k} \sigma_{\alpha\beta}(i,k) \frac{\delta(e - \varepsilon_{i,k})}{\delta(e)}
\]

\[
\sigma_{\alpha\beta}(i,k) = e^2 \tau_{i,k} \nu_{\alpha}(i,k) \nu_{\beta}(i,k)
\]

Table 1
Elastic modules and anisotropy values

<table>
<thead>
<tr>
<th></th>
<th>Young's modulus</th>
<th>Shear modulus</th>
<th>Poisson ratio</th>
</tr>
</thead>
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<tr>
<td></td>
<td>$E_{\text{min}}$</td>
<td>$E_{\text{max}}$</td>
<td>Anisotropy</td>
</tr>
<tr>
<td>Cs$_2$TlBiCl$_6$</td>
<td>4.85</td>
<td>21.97</td>
<td>4.53</td>
</tr>
<tr>
<td>Cs$_2$TlBiBr$_6$</td>
<td>4.876</td>
<td>27.52</td>
<td>5.6</td>
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<td>Cs$_2$TlBiI$_6$</td>
<td>4.87</td>
<td>27.52</td>
<td>5.645</td>
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Table 2
The calculated lattice constant $a_0$ (Å), Band gap $E_g$ (eV), Static dielectric constant $\varepsilon_1$ (0), Static refractive index $n(0)$, Elastic constants ($C_{11}$, $C_{12}$, $C_{44}$), Bulk modulus $B$ (GPa), Pugh's ratio $B/G$, Poisson ratio ($\nu$), Anisotropy (A), and Debye temperature ($\theta$) of Cs$_2$TlBiX$_6$ (X = Cl, Br and I) in the cubic phase.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Cs$_2$TlBiBr$_6$</th>
<th>Others</th>
<th>Cs$_2$TlBiCl$_6$</th>
<th>others</th>
<th>Cs$_2$TlBiI$_6$</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ (Å)</td>
<td>12.606</td>
<td>11.80 a</td>
<td>12.605</td>
<td>11.31 b</td>
<td>12.607</td>
<td>12.8 c</td>
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<tr>
<td>$E_g$ (eV)</td>
<td>2.24</td>
<td>0.71 d</td>
<td>2.9</td>
<td>1.28 e</td>
<td>1.63</td>
<td>1.37 f</td>
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<tr>
<td>$\varepsilon_1$ (0)</td>
<td>3.3</td>
<td>2.6</td>
<td>4.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n(0)$</td>
<td>1.85</td>
<td>1.63</td>
<td>2.1</td>
<td>2.33 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>28.6</td>
<td>23.6</td>
<td>28.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>4.2</td>
<td>4.8</td>
<td>4.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E$</td>
<td>9.9</td>
<td>9.7</td>
<td>9.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>10.6</td>
<td>10.7</td>
<td>10.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$G$</td>
<td>3.7</td>
<td>3.6</td>
<td>3.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B/G$</td>
<td>2.86</td>
<td>2.97</td>
<td>2.86</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$\nu$</td>
<td>0.35</td>
<td>0.33</td>
<td>0.34</td>
<td></td>
<td></td>
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<tr>
<td>$A$</td>
<td>0.14</td>
<td>0.18</td>
<td>0.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\theta$</td>
<td>91.9</td>
<td>90.7</td>
<td>91.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{a,b}$ Ref [44], $^c$ Ref [45] and $^{d,e}$ Ref [46]

Table 3
Cs$_2$TlBiX$_6$ (X = Cl, Br and I) thermoelectric coefficients at room temperature above Fermi level.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma/\tau$</th>
<th>$\kappa/\tau$</th>
<th>Seebeck coefficient (V/K)</th>
<th>PF</th>
<th>ZT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Ωms)$^{-1}$</td>
<td>(W/mKs)</td>
<td></td>
<td>(W/mK²s)</td>
<td></td>
</tr>
<tr>
<td>Cs$_2$TlBiCl$_6$</td>
<td>$3\times10^{17}$</td>
<td>$7.4\times10^{12}$</td>
<td>$2.3\times10^{-4}$</td>
<td>$7\times10^{10}$</td>
<td>0.752</td>
</tr>
<tr>
<td>Cs$_2$TlBiBr$_6$</td>
<td>$2.3\times10^{17}$</td>
<td>$5.1\times10^{12}$</td>
<td>$2.4\times10^{-4}$</td>
<td>$6\times10^{10}$</td>
<td>0.751</td>
</tr>
<tr>
<td>Cs$_2$TlBiI$_6$</td>
<td>$1.7\times10^{17}$</td>
<td>$4.4\times10^{12}$</td>
<td>$2.6\times10^{-4}$</td>
<td>$5.7\times10^{10}$</td>
<td>0.746</td>
</tr>
</tbody>
</table>
Understanding elastic constants demonstrates how a material behaves under stress, which is necessary to verify the mechanical stability of the crystal structure [31]. The mechanical stability and cubic symmetry properties can be explained by just three independent elastic constants (C₁₁, C₁₂, and C₄₄). Mechanical stability is confirmed by the Born stability criterion conditions \( C_{11} - C_{12} > 0, C_{44} > 0, C_{11} + 2 C_{12} > 0 \) and \( C_{12} < B₀ < C_{11} \) [32, 33]. In order to show mechanical behavior, the Bulk modulus (B) is calculated using the formula \( B = (C_{11} + 2 C_{12})/3 \). This mechanical behavior demonstrates that Rb₂SnI₆ is less valuable than Cs₂SnI₆ and is consistent with the Bulk modulus obtained through optimization. The Pugh ratio \( B/G > 1.75 \) and the Poisson limiting value \( (> 0.26) \) distinguish between ductile and brittle materials, respectively [34]. Materials that have values above critical are ductile; otherwise, they are brittle. Table 1 shows the ductile nature of our studied material. The anisotropy factor \( A = 2 C_{44}/ \) is a significant parameter that defines the directional properties of the materials being studied \( (C_{11} - C_{12}) \). For materials that are isotropic, its value is 1, while those that are anisotropic show anisotropy at a smaller value or greater than unity, as shown in Table 1. Elastic moduli can be used for calculating Debye temperature to enlighten \( C_v \) [35, 36] by the expression

\[
\theta_D = \frac{\hbar}{k_B} \left[ \frac{3n}{4\pi} \frac{N_A \rho}{M} \right]^{\frac{1}{3}} u_m
\]

where \( N_A \) is Avogadro number, \( \theta_D \) is Debye temperature, \( \rho \) is the material density, \( u_m \) is the average sound velocity, and \( M \) is molar mass. Navier’s equations are used to calculate \( u_m \) are denoted as relation

\[
u_m = \left[ \frac{1}{3} \left( \frac{2}{\nu_l^3} + \frac{1}{\nu_t^3} \right) \right]^{-\frac{1}{3}}
\]

where \( \nu_l \) and \( \nu_t \) is longitudinal and transverse velocity respectively \( \nu_l = \left( \frac{G}{\rho} \right)^{\frac{1}{2}} \) and \( \nu_t = \left( \frac{3B + 4G}{3\rho} \right)^{\frac{1}{2}} \)

### 3.2. Electronic Properties

The fundamental physical belongings of studied compounds evaluated antedated for Band gap as well as for density of states (DOS) in the investigation of the compounds [37, 38]. The computed band structures for Cs₂TlBiX₆ (X = Cl, Br, I) are presented in Fig. 3 (a, b, c) show that in all the three bandgaps, The maximum conduction band (CBM) and minimum valence band (VBM) are situated at \( (\Gamma \) point). Therefore Cs₂TlBiX₆ (X = Cl, Br, I) showing (2.29 eV, 2.26 eV and 1.63 eV) direct band gap at \( \Gamma \) point. It depicts that VB and CB displays dispersibility close to the edges. Usually, the electronic properties largely rely on the atomic orbitals as well as on the occupation of \( B^{1+} \) and \( B^{3+} \) site cations. It has been reported that B site cations essentially maintain the lone pair states for the direct band and for permitted optical alterations. [17, 26]. Due to completely identical occupied s shells for Tl₁⁺ and Bi₃⁺, the computed direct band gaps of Cs₂TlBiX₆ are brought on by Tl and Bi’s 6s lone pair states. Halide atoms’ interactions with lone pairs of electrons result in the distinctive
structural and electronic characteristics of halide perovskites. Since the Bi-s contribution pales in comparison to the role of the Tl-s orbital, the X atoms interact with it symmetrically. Indirect and middle band gaps experienced VBM as a result of the symmetric interaction and orbital matching between Tl and Bi. Total density of states (TDOS) calculations can be used to study the energy band structure, and partial density of states calculations can provide more specific information (PDOS). Due to orbital involvement with the electronic structure in PDOS in Fig. 4, understanding is improved.

3.3. Optical properties

To look into the optical characteristics of double perovskites of various applications, and their performance’s complex dielectric function, extinction coefficient k(ω), absorption coefficient α(ω), refractive index (ω), and reflectivity R(ω) are computed. The dielectric function (ω) commonly designates optical performance of any material and it consists of two parts i.e $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ that refer to spectral reaction of the material when photons incident on it [39]. Dispersion as well as polarization of the electromagnetic radiations are closely associated with the real part $\varepsilon_1(\omega)$ while absorptivity designates only imaginary component of dielectric function $\varepsilon_2(\omega)$. The elements of the Kramers-Kronig relation comprises of both these components that are joined apiece [40]. Kramer-Kronig transformation can be utilized to evaluate the $\varepsilon_1(\omega)$ from $\varepsilon_2(\omega)$ dielectric constant [41] which is presented below

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

$$\varepsilon_2(\omega) = \frac{\varepsilon^2 h \hbar}{\pi m^2 \omega^2} \sum_{v,c} \int_{BZ} |M_{cv}(k)|^2 \delta [\omega_{cv}(k) - \omega] d^3 k$$

The zero-frequency limit, or $\varepsilon_1(0)$, which only represents the electronic component of the dielectric function, plays a significant role in $\varepsilon_1(\omega)$ spectra. Static point for Cs$_2$TlBiX$_6$ (X = Cl, Br and I) are 2.6, 3.3 and 4.7 and the maximum peaks for real dielectric Cs$_2$TlBiX$_6$ (X = Cl, Br and I) are 3.82 eV, 3.09 and 2.34 correspondingly. Imaginary part $\varepsilon_2(\omega)$ of dielectric constant provides information about the absorption of light by any material medium. Cs$_2$TlBiX$_6$ (X = Cl, Br and I) extreme peaks for $\varepsilon_2(\omega)$ at 4.54 eV, 3.78 eV and 2.91 eV as shown in Fig. 5. Kramer-Korong relation and DFT approximation limitations may be to blame for the small band gap difference. Minor variation as shown can rise due to of discrete transitions from VB to CB. Absorption coefficient $\alpha(\omega)$ for all Cs$_2$TlBiX$_6$ (X = Cl, Br and I) are 59.2 cm$^{-1}$, 61.1 cm$^{-1}$ and 116.5 cm$^{-1}$ in UV are shown in Fig. 5(d). Materials light absorption on behalf of changeable density is symbolized by k(ω) is termed as the extinction coefficient. This property of computed compounds for Cs$_2$TlBiX$_6$ (X = Cl, Br and I) with noticeable peak are at (4.5 eV, 3.8 eV and 3.6 eV) in Fig. 5 (d). $\varepsilon_2(\omega)$ and k(ω), are similar peaks to each other.
Whenever a photon interacts with the lattice, it examines that the material bonding and relationship in the phenomenon of Refraction n(ω) [41]. Refraction n(ω) in terms of comparability is larger in Materials that are covalently bonded to ionic bonds for solid exchange in the compounds when shared between electrons and incoming photons decreases its energy. The refraction n(ω), domain of (2–3) in semiconductors [32]. Refraction n(ω) for Cs$_2$TlBiX$_6$ (X = Cl, I and Br) are originating from (1.6, 1.85 and 2.17) and touches the highest peak at (3.9, 3.1 and 2.38 eV) respectively. The results provided by the relationship. n (0)$^2 = \varepsilon_1 (0)$ were supported by static refraction and dielectric constant (0). The results produced by the relation were supported by static refraction and the dielectric constant. For Cs2TlBiX6 (X = Cl, I, and Br), R(0) is (0.057, 0.13 and 0.088). According to Paul Drude’s model [42], all compounds might develop superluminal properties for UV light waves. When interrelated, the group velocity of light in this domain it is less than the speed of light in vacuum. The measured optical parameters declared that the studied double perovskites reveal effective optical responses. Therefore, it is proposed that these materials may be grown experimentally for designing attractive novel optical devices.

### 3.4. Thermoelectric Properties

Since a short time ago, many applications have relied heavily on semiconductors’ thermoelectric properties for the conversion of heat energy to electrical energy. The charge movement transfer of energy is responsible for thermoelectric effect which is used in fabricating heat gradient that generates potential difference. Cs$_2$TlBiX$_6$ (X = Cl, I and Br) calculated for thermoelectric properties displayed in Figure. 6 (a, b), electrical conductivity (σ/τ) and thermal conductivity (κ/τ) versus temperature. Electrical conductivity at ambient condition for Cs$_2$TlBiX$_6$ (X = Cl,Br and I) are (3x10$^{17}$, 2.3x10$^{17}$ and 1.7x10$^{17}$) (Ω.m.s)$^{-1}$ respectively. The electrical conductivity (σ/τ) shows linear increasing trend by increase in temperature is shown in Fig. 6 (a).

Lattice vibration increase due to increase in temperature that is the primary cause of elastic waves for phonons participation, but free carriers are due to electrons contribution. In a crystal lattice thermal conductivity (κ/τ) is owing to electrons and phonons energy that measures the thermal current. The increasing temperature offers energy for carriers to travel to the conduction band for the conduction process. The slope for Cs$_2$TlBiCl$_6$ is higher than other two compounds that is due to the larger energy of electrons. According to the Wiedemann-Fraz law, LT = κ/σ represents the ratio of thermal to electrical conductivity [46]. The thermoelectric materials computations are desirable when is ratio is small. At room temperature the thermal conductivity for Cs$_2$TlBiX$_6$ (X = Cl,Br and I) are (7.4×10$^{12}$, 5.1×10$^{12}$ and 4.4×10$^{12}$). The lower thermal conductivity and higher electrical conductivity usually prefer thermoelectric efficiency.

The term Seebeck coefficient (S), also known as thermopower, is typically used to refer to the ratio of voltage to temperature change [47]. Seebeck coefficient is represented by equation S = ΔV/ΔT. It may be positive or negative according to the nature of the charges (positive charge is for holes and negative is for electrons) [48].

Figure 7(a) displays that Seebeck coefficient decreased by rising temperature. Cs$_2$TlBiI$_6$ is greater than Cs$_2$TlBiCl$_6$ and Cs$_2$TlBiBr$_6$ at room temperature. Seebeck coefficient (S) squared and electrical conductivity (σ/τ) are the components of power factor (PF), which is determined by equation PF = S$^2$σ/τ t. The value of
PF for Cs₂TlBiX₆ (X = Cl, I & Br) are (7x10¹⁰, 5.7x10¹⁰ & 6x10¹⁰) W/mk²s at 800 K are shown Fig. 7(b) that shows linearly growing behavior as rising temperature. The dimensionless figure of merit (ZT) is expressed by equation ZT = S²σ/kT is shown in Fig. 7(c).

The expression for figure of merit displays direct proportional manner for thermal and electrical conductivity with temperature. The supreme rate of ZT for Cs₂TlBiX₆ (X = Cl, Br and I) are (0.752, 0.751 & 0.746) at 800K. The ZT value pattern which for Cs₂TlBiX₆ (X = Cl, Br and I) shows linearly increasing behavior at room temperature but ZT values for all compounds attained room temperature starts decreasing with increase in temperature at 800K. The thermodynamic characteristics by specific heat capacity, susceptibility, hall coefficient, and number electron density are displayed in Fig. 8(a-d) for the temperature range of 200–800 K. In solid the specific heat capacity (Cᵥ) is caused by charge carriers and phonons [48]. Indirect band gap in semiconductors is primarily by the contribution of phonons however direct band gap is caused by very slight contribution of phonons inn case of electrons. BoltzTraP code is deployed for the specific heat capacity owing to the participation of electrons that participation is by BoltzTrap code limitations in this study. It follows Debye law (Cᵥ α T³) which is displayed in Fig. 8 (a) shows increase while increasing temperature.

The susceptibility of a given material endorses its magnetic behavior. In semiconductors its value is typically 10⁻⁹ [48]. The susceptibility for Cs₂TlBiX₆ (X = Cl, Br and I) at 200K is 1.3 x10⁻¹¹ (m³mol⁻¹), 7.9 x10⁻¹² (m³mol⁻¹) and 5.5 x10⁻¹² (m³mol⁻¹) which increases to (2.7x10⁻¹¹ (m³mol⁻¹), 2.20x10⁻¹¹ (m³mol⁻¹) and 2.02x10⁻¹¹ (m³mol⁻¹) at 800K may cause by the thermal effect on electrons spin movement as shown in Fig. 8 (b). Hall coefficient (Rₜₜ) is applied for the investigation of the free carriers (negative for electrons and positive for holes) are presented in Fig. 8 (c). The (Rₜₜ) values with low temperature is larger than decreases by very slight increasing temperature because carriers turn too conductive at higher temperatures. Analysis suggest that the positive value of Rₜₜ fulfill the electronic and Seebeck coefficient properties exhibiting p-type of examined mixtures. In electron density curve against temperature increases by increasing temperature due to thermal excitations of electrical conductivity displayed in Fig. 8 (d)

4. Conclusions

The elasticity and structural characteristics of halide double perovskites effectively supported the stability for Cs₂TlBiX₆ (X = Cl, Br and I) space group of Fm-3m (225) in cubic phase. Modified Back and Johnson are used to describe the electronic and optical properties, while BoltzTraP code is used to examine the thermoelectric and thermodynamic properties. Electronic band-structure for Cs₂TlBiX₆ (X = Cl, Br and I) shows direct bandgap (2.29, 2.26 & 1.63 eV) respectively at Γ point. Cs₂TlBiI₆ have maximum absorption in comparison to the Cs₂TlBiCl₆ and Cs₂TlBiBr₆ in ultra violet range. The optoelectronic applications of these compounds are very flexible due to smaller reflection and higher absorption in ultra violet range. The thermoelectric properties certify high electrical conductivity and low thermoelectric conductivity ratio. The specific heat capacity and number of electrons density increase by increasing temperature. Thorough investigations of this study affirm the highest absorption in the UV range and large thermal efficiency fabricate them for optoelectronic and energy harvesting applications.
References

36. Feng, J.: Mechanical properties of hybrid organic-inorganic CH3NH3BX3 (B = Sn, Pb; X = Br, I) perovskites for solar cell absorbers. Apl Mater. 2(8), 081801 (2014)


Figures

Figure 1
$\text{Cs}_2\text{TlBiX}_6 (X = \text{Cl, Br, and I})$ structural optimization in electronic form (left side) and polyhedral form (Right side) via VESTA software.

![Optimization curve for total energy versus volume using PBE-GGA](image)

**Figure 2**

$\text{Cs}_2\text{TlBiX}_6 (X = \text{Cl, Br, and I})$ optimization curve for total energy versus volume using PBE-GGA.
Figure 3

Energy band structure and density of state for (a) Cs$_2$TIBiCl$_6$, (b) Cs$_2$TIBiBr$_6$ and (c) Cs$_2$TIBiI$_6$ by TB-mbj Potential.
Figure 4

Partial density of states for Cs$_2$TlBiX$_6$(X= Cl, Br, and I) by TB-mBJ potential.
Figure 5

(a) Real dielectric constant $\varepsilon_1(\omega)$, (b) Imaginary dielectric function $\varepsilon_2(\omega)$, (c) Reflectivity spectra $R(\omega)$, (d) Absorption coefficient $\alpha(\omega)$, (e) Refractive index $n(\omega)$ and (f) Extinction coefficient $k(\omega)$ \(\text{Cs}_2\text{TIBiX}_6\) (X = Cl, Br, and I)
Figure 6

Computation of (a) Electrical conductivity ($\sigma/\tau$) and (b) Thermal conductivity ($\kappa/\tau$) plotted against Temperature $T$ (200-800)K using BoltzTraP code for Cs$_2$TlBiX$_6$ (X = Cl, Br, and I).

Figure 7

Computation of (a) Seebeck coefficient ($S$) (b) Power factor ($\sigma S^2/\tau$) and (c) Figure of merit ($ZT$) plotted against Temperature $T$ (200-800) K using BoltzTraP code for Cs$_2$TlBiX$_6$ (X = Cl, Br, and I).
Figure 8

Computation of (a) specific heat capacity, (b) susceptibility, (c) Hall coefficient and (d) number electron density plotted against Temperature $T$(200-800) K using BoltzTraP code for $\text{Cs}_2 \text{TIBiX}_6$($X$= Cl, Br, and I).