Theoretical Prediction and Thermal Transport Properties of Novel Monolayer TlPt$_2$Se$_3$

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The theoretical prediction, electronic properties, and thermal transport properties of novel monolayer TlPt$_2$Se$_3$ are investigated using the first-principles calculations and semi-classical Boltzmann transport theory. The calculated phonon band structure and exfoliation energy confirm that monolayer TlPt$_2$Se$_3$ is a stable material and can be exfoliated from its bulk counterpart. The exfoliation energy of the monolayer turns out to be 37 meV Å$^{-2}$, comparable with the exfoliation energy of monolayer PdSe$_2$. The HSE06 indirect bandgap of monolayer (bulk) TlPt$_2$Se$_3$ amounts to 1.18 eV (0.63 eV). The relaxation time is calculated considering three types of scattering mechanisms. The monolayer outperforms the bulk counterpart in the Seebeck coefficient and power factor for both $p$-type and $n$-type dopings. Monolayer TlPt$_2$Se$_3$ shows a high $p$-type Seebeck coefficient of 211 µV K$^{-1}$ compared to the $n$-type Seebeck coefficient of 103 µV K$^{-1}$ at maximum considered temperature (600 K) and a carrier concentration ($10^{20}$ cm$^{-3}$). The calculated lattice thermal conductivity of monolayer TlPt$_2$Se$_3$ is 1.92 W m$^{-1}$ K$^{-1}$ at 600 K which is lower than the monolayer PtSe$_2$ and MoSe$_2$. The $p$-type figure of merit of 0.64 (at 600 K) affirms that the monolayer TlPt$_2$Se$_3$ is an excellent thermoelectric material.

1. Introduction

Thermoelectric materials are efficient candidates for renewable energy resources because they convert the waste heat into electricity and help to reduce the carbon footprint. The dimensionless figure of merit ($ZT = S^2\sigma T/\kappa$) defines thermoelectric efficiency of a material, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, and $\kappa$ is total (electronic and lattice) thermal conductivity. The interdependence of $S$, $\sigma$, and $\kappa$ act as hindrances in obtaining a high $ZT$. 2D materials belong to an exciting class of materials with properties different from their bulk counterpart. Bi$_2$Te$_3$[11], SnSe$_2$[12] PtSe$_2$[13] materials show low lattice thermal conductivity ($\kappa_l$) because of strong in-plane and weak out-of-plane bonding, bonding heterogeneity, and lattice anharmonicity,[4] which result in colossal thermoelectric efficiency of these materials. The electronic and thermoelectric properties of 2D material can be further tuned using band modification,[5] multifunctional alloying,[6] and intercalation.[7]

In addition, 2D ternary semiconductors have attracted much attention in last few years because of having various degrees of freedom that can alter the electronic and thermoelectric properties through stoichiometric variations.[8–9]

Pt-based alkali metal chalcogenides are superior thermoelectric materials because of low $\kappa_l$ and high figure of merit.[10,11] Thallium-based materials show excellent thermal transport properties due to stereoeactive lone pair, contributing to diverse structures,[12,13] and low thermal conductivity due to the high scattering of charge carriers, which is primarily absent in alkali metals. Thallium chalcogenides such as TlAgTe,[14] TlInTe,[15] TlO[16] show excellent thermoelectric performance with low $\kappa_l$ because $\kappa_l$ decreases as heavy atomic mass and suppressed sound velocity. TlPt$_2$Se$_3$ is synthesized experimentally in the late 20th century via a melting reaction of thallium carbonate with Pt and Se powders at temperature range from 400 to 950 °C,[15] and crystallizes in a stacked atomic arrangement similar to Pt-based alkali metal chalcogenides. The thermoelectric properties of thallium platinum chalcogenides have not been conducted so far. Therefore, the electronic structure, stability, and thermal transport properties of bulk and monolayer TlPt$_2$Se$_3$ have been demonstrated using the density functional theory and semi-classical Boltzmann transport theory to fill the gap in the literature. The monolayer TlPt$_2$Se$_3$ shows a higher $p$-type power factor of 3.9 W m$^{-1}$ K$^{-2}$ (4.3 W m$^{-1}$ K$^{-2}$) which contributes to a $ZT$ of 0.62 (0.64) at 300 K (600 K).

2. Computational Details

The calculations are performed using the projector augmented wave method as employed in the Vienna ab initio Simulation Package.[16] The exchange-correlation potential is treated with the Perdew–Burke–Ernzerhof functional of the generalized
gradient approximation scheme. The electronic wave functions are expanded using a plane wave cutoff energy of 400 eV (500 eV) for monolayer (bulk) by considering the valence shell of Tl (6s², 6p³), Pt (5p⁶, 5d⁹, 6s¹), and Se (4s², 4p⁴). The dispersion-corrected density functional theory (DFT-D3) method[17] is employed to treat the van der Waals interactions with a vacuum of 18 Å along a perpendicular direction is used to avoid the artifacts of periodic boundary conditions. The self-consistent calculations are carried out employing the tetrahedron method[18] sampled on 5×5×1 (3×3×3) k-mesh for monolayer (bulk). The exfoliation energy of the monolayer is calculated according to the Ref[19] and using the relation \( E_{\text{ex}} = (E_{\text{mono}} - E_{\text{bulk}})/A \), where \( E_{\text{mono}} \) and \( E_{\text{bulk}} \) are the energy of monolayer and bulk and \( A \) in-plane area. The spin orbit coupling (SOC) is engaged in calculating the electronic properties. The Fermi surface of the conduction band minimum (CBM) and valence band minima (VBM) is calculated using Wannier90.[20]

The phonon band structure of monolayer (bulk) is calculated using 3×3×1 (3×3×3) supercell as implemented in the PHONOPY package.[21] The Boltzmann transport equations are solved using ab-initio scattering and transport (AMSET)[22] and ShengBTE[23] packages. A k-mesh of 41×41×15 (45×45×47) is used to calculate the thermoelectric coefficients of monolayer (bulk). The reliable relaxation time value is obtained considering the acoustic deformation potential scattering, piezoelectric scattering, and ionized impurity scattering. The phonon scattering rate and group phonon velocity are calculated by taking second-order harmonic force constants as input by including the nonanalytical correction in the dynamical matrix. The third-order anharmonic interatomic force constants in real space are calculated using the finite displacement method.[24] The atoms are displaced up to the fourth nearest neighbor (convergence value greater than 0.56 nm) to reduce the interaction between the atoms at the center and the boundary. The converged values of \( k_i \) are calculated using a dense q-grid of 30×30×1 (16×16×16) for monolayer (bulk). The phonon scattering cross-section and phonon group velocity are calculated using the Boltzmann transport equation from third-order force constants and polarization vectors.

### 3. Results and Discussion

Bulk TlPt₂Se₃ crystallizes in the trigonal crystal structure[15] and consists of 12 (2 Tl, 4 Pt, and 6 Se) atoms, as shown in Figure 1. The optimized lattice constants of TlPt₂Se₃ are listed in Table 1. The interatomic distance between Tl and Pt atoms is 3.03 Å, more significant than the covalent radius (2.84 Å) of Tl (1.48 Å) and Pt (1.36 Å), which confirms an ionic bond between them in the plane. The calculated exfoliation energy of the monolayer TlPt₂Se₃ is 37 meV Å⁻¹,[15] comparable with the exfoliation energy (34 meV Å⁻¹) of the monolayer PdSe₂.[25]

The calculated HSE06 (SOC and w/o SOC) band structure of bulk (Figure 2) shows a nearly direct bandgap at the M point. In contrast, an indirect bandgap along \( M \) and \( K \) points for the monolayer because the CBM shift from \( M \) to \( K \) when the dimensionality reduces. The HSE06 calculations with SOC (without SOC) result in a bandgap of 1.96 eV (2.01 eV) and 1.08 eV (1.21 eV) for monolayer and bulk, respectively. The VBM of monolayer are less dispersive than the CBM and result in a high effective mass for holes and thereby a low electrical conductivity, as depicted in Figure 5. The higher Seebeck coefficient of the monolayer than bulk at a given temperature and carrier concentration is due to its larger bandgap. The total and projected density of states (see Figure 3) shows no substantial change in bulk and monolayer.

![Figure 1](image1.png)

**Figure 1.** a) Side and b) top views of bulk TlPt₂Se₃ (Tl: black, Pt: green, and Se: red). A monolayer is represented in a square bracket.

![Figure 2](image2.png)

**Figure 2.** Calculated HSE06 band structure of a,c) bulk and b,d) monolayer TlPt₂Se₃ a,b) without SOC and c,d) with SOC. Red dashed lines represent the VBM.

| TlPt₂Se₃ | Lattice constants [Å] | Bandgap [eV] |
|----------|----------------------|--------------|
|          |                      | PBE | HSE06 |
|          |                      | SOC | W/o SOC | SOC | W/o SOC |
| Bulk     | \( a = 7.55 \) (7.40)[15] | 0.63 | 0.71 | 1.08 | 1.21 |
|          | \( c = 6.09 \) (5.70)[15] |     |     |     |     |
| Monolayer| \( a = 7.50 \) | 1.18 | 1.31 | 1.96 | 2.01 |

Table 1. Calculated lattice constants \((a, c)\) and bandgap with and without \((w/o)\) SOC using the PBE and HSE06 functionals. Experimental lattice constants given in parenthesis.
Figure 3. Calculated projected density of states (DOS) of a) bulk and b) monolayer TlPt$_2$Se$_3$ with HSE06 and SOC.

Figure 4. Calculated Fermi surface of a,b) bulk and c,d) monolayer TlPt$_2$Se$_3$.

In the case of monolayer TlPt$_2$Se$_3$, the VBM shows a predominant occupation of Pt-d orbitals followed by Se-p and Tl-p orbitals, and the CBM show a dominance of Se-p orbitals followed by Pt-p orbitals. The Fermi surface of CBM and the VBM of TlPt$_2$Se$_3$, shown in Figure 4, show no electron/hole packets localized at the $\Gamma$ point. The less dispersion of VBM in monolayer exhibit large hole packets contribute to a high effective mass. Similarly, high dispersion in the CBM leads to narrow tube-like electron packets, significantly reducing the electrical conductivity due to the low effective mass of electrons.

The phonon band structure (as shown in Figure 5) ensures dynamical stability and contains 36 phonon dispersion relations. The first three branches constitute the acoustic phonons which are the prime factor of thermal conduction. A few low-frequency optical branches also contribute to $\kappa_l$, evident from its low group velocities plotted in Figure 7. The lowest out-of-plane acoustic phonons branch shows a quadratic dispersion at the $\Gamma$ point, whereas the second and third acoustic branches show a linear dispersion. The low $\kappa_l$ of the monolayer is because of the mixing of the acoustic and optical phonons. The phonon density of states of TlPt$_2$Se$_3$ shows that the vibration of Pt and Se atoms is dominant in acoustic phonons and contributes to the $\kappa_l$. It implies that the thermal transport mechanism is dominated by the heat exchange of acoustic phonon in the Pt-Se bonds because Tl atoms govern the high-frequency optical modes.

The $k$-dependent quasi-particle energies, scattering rates, and thermolectric coefficients are calculated using the AMSET code.[22] The calculated Seebeck coefficient, electrical conductivity, thermal conductivity, and power factor function of $p$- and $n$-type concentrations are given in Figure 6. The $n$-type electrical conductivity is larger than the $p$-type due to the low effective mass at the CBM. The large bandgap of monolayer shows that the $n$-type electrical conductivity decreases and approaches to 3.46x10$^3$ $\Omega$ m$^{-1}$ (3.39x10$^5$ $\Omega$ m$^{-1}$) at 300 K (600 K). Several carriers diminish in monolayer and result in a low conductivity of the monolayer.

The $p$-type Seebeck coefficient of the monolayer is more significant than the $n$-type, attributed to the low carrier concentration. The Seebeck coefficient of bulk TlPt$_2$Se$_3$ at a temperature 300 K (600 K) and a carrier concentration of 7x10$^{20}$ cm$^{-3}$ is 31 $\mu$V K$^{-1}$ (87 $\mu$V K$^{-1}$). In the case of the monolayer, the Seebeck coefficient at 600 K is 211 $\mu$V K$^{-1}$ for $p$-type doping, which is 23% greater than for $n$-type doping (171 $\mu$V K$^{-1}$). A potential thermoelectric material has a Seebeck coefficient value greater than or equal to 200 $\mu$V K$^{-1}$.[26] With the increased value of electrical and thermal conductivities, $n$-type doping shows an enhanced value of power factor in the bulk. On the contrary, the monolayer shows
Figure 6. Calculated transport coefficients of a) bulk and b) monolayer TlPt₂Se₃ for p-type and n-type dopings.

The highest power factor with p-type doping due to a high Seebeck coefficient. At the highest p-type doping, the power factor of monolayer is 4.30×10⁻³ W m⁻¹ K⁻² (3.90×10⁻³ W m⁻¹ K⁻²) at 300 K (600 K). The n-type doping at 600 K gives a power factor of 3.60×10⁻³ W m⁻¹ K⁻¹.

The calculated $\kappa_l$ of TlPt₂Se₃ is shown in Figure 7. The solid line and star represent the inverse relation of $\kappa_l$ with temperature, valid for anharmonic phonon–phonon interaction. The $\kappa_l$ decreases with increasing temperature due to the increased phonon collisions. The $\kappa_l$ of bulk at 300 K (600 K) is 4.37 W m⁻¹ K⁻¹ (2.22 W m⁻¹ K⁻¹) which further decreases to 3.8 W m⁻¹ K⁻¹ (1.92 W m⁻¹ K⁻¹) in the case of monolayer TlPt₂Se₃. The $\kappa_l$ of TlPt₂Se₃ is lower than that of the transition metal dichalcogenides PtSe₂ (18.07 W m⁻¹ K⁻¹) and MoSe₂ (17.6 W m⁻¹ K⁻¹) suggests its potential as an excellent thermoelectric material. Since bipolar effect constrains the thermoelectric effect of Bi₂Te₃ at a higher temperature, monolayer TlPt₂Se₃ can be a better alternative.

The cumulative lattice thermal conductivity ($\kappa_{cl}$) at 300 K (Figure 7) as a function of mean free path is calculated to understand the effect of boundary scattering. The $\kappa_{cl}$ of bulk increases with mean free path up to 1524 nm along in-plane direction and become constant after it, while the $\kappa_{cl}$ of monolayer TlPt₂Se₃ starts with a flat raise and then secure the plateau at 2744 nm. The phonon mean free path decreases with decreasing the dimensionality and results in a low $\kappa_l$ without affecting the electronic counterpart.

Figure 7 shows the scattering rate of acoustic and optical phonon modes along with the phonon group velocities. The peak value of the scattering rate of acoustic phonons for monolayer (bulk) is 0.6 ps⁻¹ (0.19 ps⁻¹), consistent with the lower $\kappa_l$ of the monolayer. The acoustic branches are soft with a maximum velocity of 2.8 km s⁻¹ (3 km s⁻¹) for monolayer (bulk). The $ZT$ of bulk and monolayer (Figure 8) increases with temperature, consistent with the increasing trend of power factor. For n-type doping, the highest $ZT$ of 0.12 (0.02) is obtained at 600 K (300 K) for bulk, whereas it increases to 0.19 (0.09) for monolayer. As the p-type doping increases, the $ZT$ also increases, as expected from the trend shown in the Seebeck coefficient. At higher considered p-type doping of 7×10²⁰ cm⁻³, $ZT$ achieved the peak value of 0.62 (0.64) at 300 K (600 K). Thus, it can be concluded that the monolayer TlPt₂Se₃ shows high thermoelectric importance at both room temperature and above, which can be further enhanced by p-type doping.
4. Conclusion

The electronic and thermal transport properties of TlPt$_2$Se$_3$ have been demonstrated using the first-principles density functional theory and semi-classical Boltzmann transport theory. The AMSET code is used for realistic calculations of thermoelectric performance. The bandgap improves on decreasing the dimensionality and reaches a value as high as 2.01 eV (66% greater than that of bulk). The projected density of states shows that the Pt-$d$ orbitals dominate the CBM. The power factor of the monolayer TlPt$_2$Se$_3$ reaches the highest value of 4.33 W m$^{-1}$ K$^{-2}$ at 300 K and 1.92 W m$^{-1}$ K$^{-1}$ at 600 K of the monolayer is lower than that of PtSe$_2$ (18.07 W m$^{-1}$ K$^{-1}$) and MoSe$_2$ (17.6 W m$^{-1}$ K$^{-1}$) monolayers. The $\kappa_l$ of monolayer TlPt$_2$Se$_3$ starts with a flat raise and then secures the plateau at 2744 nm. The high phonon scattering rate and low group velocity of acoustic phonons and low-frequency optical phonon account for the low $\kappa_l$ of the monolayer. At 600 K, $ZT$ values of 0.64 for $n$-type ($p$-type doping at the 600 K and carrier concentration of 7$	imes$10$^{19}$ cm$^{-3}$). The electronic and thermal transport properties of TlPt$_2$Se$_3$ start with a flat raise and then secure the plateau at 2744 nm. The high phonon scattering rate and low group velocity of acoustic phonons and low-frequency optical phonon account for the low $\kappa_l$ of the monolayer. At 600 K, $ZT$ values of 0.64 for $n$-type doping proposes monolayer TlPt$_2$Se$_3$, an excellent thermoelectric material.

Acknowledgements

The authors acknowledge the financial support from the Abu Dhabi Department of Education and Knowledge (ADEK) under the grant AARE19-126 and the contribution of Khalifa University’s high-performance computing and research computing facilities to the results of this research.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords

first-principles calculations, phonon transport, thermal conductivity

Received: February 1, 2022
Published online: February 23, 2022

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