Materials Research Express

PAPER

Toward controlled thermoelectric properties of Pb and Sb co-doped nanostructured Thallium Telluride for energy applications

Waqas Muhammad Khan, Altaf Ur Rahman, Muhammad Tufail, Muhammad Ibrar, Wiqar Hussain Shah, Waqar Adil Syed and Banat Gul

1 Department of Physics, International Islamic University, Islamabad 44000, Pakistan
2 Department of Physics, Riphah Institute of Computing & Applied Sciences, Riphah International University, 13 km Raiwind Rd, Chamru Pur Lahore, Pakistan
3 Department of Physics, Islamia College Peshawar, Khyber Pakhtunkhwa, Peshawar 25120, Pakistan
4 Military College of Engineering, National University of Science and Technology (NUST), Islamabad, Pakistan
* Authors to whom any correspondence should be addressed.

E-mail: altaf.urrahman@riphah.edu.pk and wiqar.hussain@iiu.edu.pk

Keywords: quaternary compound, electronic properties, thermoelectric properties, DFT, GGA

Abstract

Here, the structure-dependent electronic, thermal, and transport properties of nanostructured thallium telluride (Tl8Pb1−xSbxTe6) through controlled variation in Pb and Sb (x = 1.96, 1.97, 1.98, 1.99) concentrations have been investigated. In the temperature and concentration-dependent electrical conductivity measurements, the highest electrical conductivity 131.96 $\times 10^3 \, \Omega^{-1} \, m^{-1}$ at 300 K was measured for x = 1.99 and the maximum observed Seebeck value for the optimized Tl8Pb1.96Sb0.04Te6 nanoparticles was 110.7 $\mu$V/K at 550 K. Such an increased value of the Seebeck coefficient led to the achievement of a significantly improved high-power factor, which was found to be increasing with temperature and decreasing with the increase of Pb concentration. The density functional theory calculations performed for Pb and Sb co-doped Tl5Te3 resulted in the enhanced $\sigma$ and S with a significant reduction in electronic thermal conductivity ($\kappa_e$) and is found consistent with experimentally measured $\kappa_e$. The highest ZT = 0.35 and 0.18 were recorded experimentally and theoretically for Pb and Sb co-doped in Tl5Te3 nanoparticles.

1. Introduction

The current global energy deficit and the environmental challenges ahead is an alarming situation for upcoming generations. The rise in the average temperature of Earth and worldwide pollution has produced far-reaching implications and damage to the ozone. The extraordinary demand and production and conversion of energy for domestic and industrial usage motivate rigorous investigation in the energy sector to explore numerous resources employing a different kind of nanoscale materials and technologies [1]. Also, considerable efforts have been devoted to achieving a possible control over the energy crisis and global warming through the minimization of energy losses in various industrial sectors. In the 21st century, the energy crisis and unrelated waste energy management are two key problems [2]. Various sources of energy are wind, solar, tidal, biofuel, geothermal and nuclear energy. Heat energy is utilized in human actions and industry procedures; at that instant wasted thermal energy has vanished without used energy change [3].

Historically, more than a century ago, the first-ever thermoelectric effect was discovered by Thomas Johanne Seebeck [4, 5] and Jean Charles Athanase Peltier [6, 7]. This effect is based on the principle of the production of electrical energy using a temperature gradient. Notable performance has been reported for Bi2Te3 for being an efficient thermoelectric (TE) material. It is worth mentioning here that for thermoelectric application a high temperature thermodynamically stable materials are desirable [3, 8]. Therefore, thermal stability and good thermoelectric properties make such materials prognosticating for next-generation technologies utilizing waste heat and to convert it into useful electrical energy [9]. On average, industrial processes effectively consume and utilize only about 40% of the total energy and the balance is rejected in the form of waste heat. It is possible to...
capture a fraction of this waste heat by using thermoelectric power conversion (thermoelectric generators) and convert it into useful electric power [10, 11]. The interaction of the chalcogenides in the Tl$_3$X-Bi$_2$X$_3$ (X: S, Se, Te) systems lead to the formation of ternary chemical compounds with different formal compositions. These systems characteristically consist of a quasi-binary character and contain nanoparticles of the Tl$_9$BiX$_6$ and TlBiX$_2$ type [12–14]. The fundamental attraction between the group III and VI such as Tl and Te system creates a specific interest to investigate the thermoelectric properties [15–21]. Substantial efforts have been devoted to manufacturing a new class of thermoelectric materials, in particular, thallium chalcogenides [22, 23]. Therefore, several thalliums containing chalcogenide ternary single crystals among which Tl–Sn–S [24–26], Tl–Sn–Se [27, 28], and Tl–Sn–Te [29, 30] have been investigated.

The thermoelectric properties of cobalt-based metallic anti-perovskite have been investigated by Lin et al [31]. Among all the anti-perovskite families of materials, the highest Seebeck coefficient for the SnCoCo$_3$ of about 50μV/K was reported above room temperature. In the context of thermoelectric properties, the group of Tl$_9$Te$_6$ related nanoparticle has been the subject of numerous earlier investigations, i.e., Latypov and Pradel et al showed that these nanoparticles have poor thermoelectric properties [32, 33]. For example, for Tl$_3$Te$_5$, Latypov et al measured Seebeck coefficient (S) up to 80μV/K and resistivity (ρ) up to 2 × 10$^{-3}$ Ωcm. In contrast, for Tl$_9$BiTe$_6$, Pradel et al measured the Seebeck coefficient of 62 μV/K and $\rho = 1.5 \times 10^{-3}$ Ωcm. The calculated total thermal conductivity $\kappa = 0.7$ W/Km, which shows poor thermoelectric performance at room temperature with a figure of merit $ZT = 0.1$ [33]. It has already been demonstrated for the ternary alloys related to Tl$_3$Te$_5$-group, among these alloys Tl$_9$BiTe$_6$ has the best thermoelectric performance to exhibit. Therefore, it should be considered as a benchmark thermoelectric material for the new thermoelectric devices related to Tl$_3$Te$_5$-group nanoparticles. Compared to the above-mentioned investigations, significant improvements have been made in lattice thermal conductivity ($\kappa = 0.6W/K.m$) and $ZT = 0.4$ by Sb and Bi co-doping in Tl$_3$Te$_5$ nanostructure [34]. As the Tl$_3$Te$_5$ system is a poor thermoelectric material, however, certain modifications through doping have demonstrated to have promising thermoelectric properties, i.e., Tl$_9$BiTe$_6$ has the maximum $ZT$ to date in the temperature range of 300–500K [34]. These measurements make the Tl$_3$Te$_5$ crystal structure exciting for further investigations.

Keep in view the importance and potential usefulness, we studied the Pb and Sb doping and co-doping in the Tl$_9$Te$_6$ crystal structure. This manuscript is concerned with the study of structural, electronic, and thermoelectric properties of substitution-ally doped Tl$_3$Te$_5$ using experimental measurements and density functional theory (DFT) calculations. More specifically, this work was aiming at (i) tuning the electronic and thermoelectric properties of Tl$_9$Te$_6$ by Pb and Sb doping and co-doping (ii) to determine whether the power factor (PF) of the Tl$_3$Te$_5$ can be raised above the standard value at room temperature through doping.

## 2. Experimental

### 2.1. Synthesis

The quaternary nanoparticles of thallium telluride (Tl$_9$Pb$_x$Sb$_{2-x}$Te$_6$) with different dopant concentrations of Pb and Sb ($x = 1.96, 1.97, 1.98, 1.99$) were synthesized using the co-precipitation method. Elements as the starting materials Tl$^{+}$, Pb$^{2+}$, Sb$^{3+}$ and Te$^{2-}$ of high purity 99.99% with different concentrations of Pb and Sb have been used for direct synthesis of the stoichiometric amount taken during the reaction. The obtained nanoparticles were annealed at 400 °C for 6 hours followed by grinding into fine powder comprising of the ensembles of the quaternary nanoparticles. For thermoelectric measurements, the quaternary nanoparticles were shaped into rectangular pallets with approximate dimensions of 5 mm × 1 mm × 1 mm.

### 2.2. X-ray diffraction analysis

X-ray diffraction experiments were performed using the intel X-Ray Diffractometer with the Cu $K\alpha$ radiation with $\lambda = 0.154$ nm at the room temperature. The phase confirmation and structural analysis of the nanostructured Tl$_9$Pb$_x$Sb$_{2-x}$Te$_6$ having different Pb and Sb concentrations were performed using x-ray diffraction (see figure 1).

The crystallite size and detailed information about the miller indices and lattice parameters were extracted. The indexed (hkl) values of the identified crystal planes corresponding to the peaks in the x-ray diffraction patterns are; (121), (220), (213), (130), and (024) as shown in figure 1. The crystallite size of Tl$_9$Pb$_x$Sb$_{2-x}$Te$_6$ nanoparticle has been calculated using Debye Scherer’s formula provided below,

$$D = k\lambda / \beta \cos \theta_b$$

In the above equation ‘D’ is the crystallite size and ‘$k$’ is constant having a value as ‘0.91’, $\lambda$ determines the wavelength, and ‘$\theta_b$’ shows an angle. The average crystallite size of the nanoparticle is about 63.50 nm (see table 1).
The concentration ratio of $\text{Tl}_8\text{Pb}_x\text{Sb}_{2-x}\text{Te}_6$ nanoparticles is given as $x = 1.96, 1.97, 1.98$ & 1.99 and $y = 0.04, 0.03, 0.02$, & 0.01. The observed 2θ positions of the various peaks in the x-ray diffraction patterns exactly matched with the JCPD #01-84-2449 (Joint Committee on Powder Diffraction Standards) cards and which confirmed the presence of a single-crystalline tetragonal structure. The preferred orientation is usually determined from the characteristic peak of the XRD which in our case is $(213)$ and $(130)$. The relative intensity of these peaks increases by increasing Sb concentration. This confirmation also supports the purity of the formation of nanostructured material which has been validated by the elemental peak obtained in a typical EDX spectrum provided in figure 2.

### Table 1. The crystallite size (D), the lattice parameters determined by XRD, and calculated by DFT using GGA (generalized gradient approximation) are given in the table.

| Sample   | D (nm) | Experiment $a = b, c$ (Å) | DFT $a = b, c$ (Å) |
|----------|--------|---------------------------|--------------------|
| $\text{Tl}_5\text{Te}_3$ | 63.02 | 8.89, 13.05 | 9.09, 13.08 |
| $\text{Tl}_8\text{Pb}_{1.96}\text{Sb}_{0.04}\text{Te}_6$ | 63.02 | 8.89, 13.05 | — |
| $\text{Tl}_8\text{Pb}_{1.97}\text{Sb}_{0.03}\text{Te}_6$ | 63.64 | 8.84, 12.96 | — |
| $\text{Tl}_8\text{Pb}_{1.98}\text{Sb}_{0.02}\text{Te}_6$ | 63.65 | 8.90, 12.99 | — |
| $\text{Tl}_8\text{Pb}_{1.99}\text{Sb}_{0.01}\text{Te}_6$ | 63.70 | 8.85, 13.07 | — |

The concentration ratio of $\text{Tl}_8\text{Pb}_x\text{Sb}_{2-x}\text{Te}_6$ nanoparticles is given as $x = 1.96, 1.97, 1.98$ & 1.99 and $y = 0.04, 0.03, 0.02$, & 0.01. The observed 2θ positions of the various peaks in the x-ray diffraction patterns exactly matched with the JCPD #01-84-2449 (Joint Committee on Powder Diffraction Standards) cards and which confirmed the presence of a single-crystalline tetragonal structure. The preferred orientation is usually determined from the characteristic peak of the XRD which in our case is $(213)$ and $(130)$. The relative intensity of these peaks increases by increasing Sb concentration. This confirmation also supports the purity of the formation of nanostructured material which has been validated by the elemental peak obtained in a typical EDX spectrum provided in figure 2.

### 2.3. Morphological and elemental analysis of $\text{Tl}_{10-x-y}\text{Pb}_x\text{Sb}_y\text{Te}_6$

Scanning electron microscopy (SEM) for imaging and the Energy-dispersive x-ray spectroscopy (EDX) have been employed to study the morphology and elemental composition of the nanostructured $\text{Tl}_8\text{Sb}_1\text{Te}_6$. By the concentration of Pb doped with $\text{Tl}_8\text{Pb}_x\text{Sb}_{2-x}\text{Te}_6$ nanoparticles which cause the production of grains in the miner region and provided the path for the large scattering of electrons. The increase in Pb concentrations, grains enhances the electron scattering, causes an increase in thermopower [35]. The $\text{Tl}_8\text{Pb}_x\text{Sb}_{2-x}\text{Te}_6$ nanoparticles are shown in the image at a scale of 100 nm.

EDX was used for the qualitative and quantitative analysis of the composition. The EDX of $\text{Tl}_8\text{Pb}_{1.97}\text{Sb}_{0.03}\text{Te}_6$ nanoparticle is shown in figure 2. In this method, the elements present in the material are identified such as Pb, Sb, Te, TI (wt.% 14.38, 0.13, 27.78, 57.69), respectively, this percentage tells about the amount of each element present in the system. While At% as Pb (14.51%), Sb (0.12%), Te (27.22%), TI (58.13%). It shows that there is no extra peak observed in the chemical composition. The highest peak of the thallium (TI) shows a high concentration than others.
2.4. Seebeck coefficient measurements

The first-ever thermoelectric effect based on the principle of generating electrical energy using a temperature gradient $\Delta T$ was discovered by Thomas Johann Seebeck [5], and Jean Charles Athanase Peltier [6, 7]. The temperature dependence Seebeck coefficients of the rectangular-shaped pallets with approximate dimensions of 5mm $\times$ 1 mm $\times$ 1 mm were measured using the experimental setup as shown in figure 3(a). Two types of thermoelectric materials have been used for the probing tips: material denoted as labeled A is an alloy of nickel and chromium having a positive Seebeck coefficient 28.1 $\mu$V/K [36], material denoted as labeled B is an alloy of nickel, manganese, aluminum and silicon having a negative Seebeck coefficient $-12.9 \mu$V/K [36]. Both materials are commonly used to make K-type thermocouples and have been considered as reference materials. The voltage difference appears due to different types of materials labeled as A and B are heated. The emf (electromotive force) generated depends on the temperature difference between the two junctions. The temperature was controlled by a K2000 digital controller. The Seebeck coefficient is defined as

$$ S = \frac{\Delta V}{\Delta T} \quad \text{and} \quad S = \frac{V_{\text{cold}} - V_{\text{hot}}}{T_{\text{cold}} - T_{\text{hot}}} $$

The conducting wire A in a circuit connected with the voltmeter using wire B from both tips of the voltmeter. Both the ends of wire A are held at two different temperatures $T_1$ and $T_2$. The voltage $V$ is measured by varying $T_1$ or $T_2$. If $T_1 > T_2$ electrons flow towards $T_1$ leaving $T_2$ more positive and results as a positive value of the Seebeck coefficient.
2.5. Four-point probe electrical resistivity method

To measure the electrical resistivity of all six samples of Tl$_{8.33}$Sb$_{1.67}$, Pb$_{0.6}$Te$_{0.4}$, where (x = 1.29, 1.31, 1.33, 1.35, 1.36 and 1.38), a four-probe method was used as shown in figures 3(b)–(c). Where I denotes electrical current crosses the material in alternating direction. The voltage $V$ is measured across the horizontal probe for the measurement of electrical resistivity. Keeps the continuous flow of current through the area of the pellet. The potential difference is calculated between the terminal and across the physical length from which the resistance of the material is measured. The four-probe resistivity method was employed for electrical conductivity measurements of the sample pallets by passing a current through two outer probes and measuring the voltage through the inner probes allows such measurements [37]. The electrical conductivity is calculated by applying the following equations

\[ R = \frac{V}{I}, \quad \text{and} \quad \sigma = \frac{L}{RA}. \]

3. Theoretical framework

The electronic and thermoelectric properties of pure and doped bulk Tl$_5$Te$_3$ crystal structure (denoted as Tl$_{10-x}$Pb$_x$Sb$_y$Te$_6$; x = [0:2] and y = [0:2]) were investigated using the DFT calculations [38] with Plane-Wave (PW) basis is implemented in Quantum Espresso (QE) code [39]. We employed the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) [40, 41] for the electronic exchange-correlation energy functional. A. Dal Corso ultra-soft pseudopotential within the PBE form was employed [42], in which only the outermost electrons were taken into consideration. We have used the following pseudopotentials: Tl.pbe-dn-rrkjus psl.1.0.0.UPF, Te.pbe-n-rrkjus psl.1.0.0.UPF, Pb.pbe-dn-rrkjus psl.1.0.0.UPF, and Sb.pbe-n-rrkjus psl.1.0.0.UPF, for Tl-, Te-, Pb- and Sb-atom respectively. These pseudopotentials are freely available on the web page: http://www.quantum-espresso.org/pseudopotentials. The wave function in the electronic calculation was expanded in a PW-basis set with kinetic energy and charge-density cut-offs of 70 Ry and 300 Ry, with $1 \times 10^{-7}$ eV electronic convergence criteria, respectively. The irreducible Brillouin-zone (BZ) is sampled with a Monckhorst-Pack $k$-point grid [43] of 16 $\times$ 16 $\times$ 16 for geometry optimization and $30 \times 30 \times 30$ are used for the electronic structures of both pure Tl$_5$Te$_3$ and doped Tl$_5$Te$_3$ crystal structures. The structural relaxation and optimization of forces on ions are converged to less than 0.002 eV/Å. The transport properties of pure and doped Tl$_5$Te$_3$ structures were studied using the BolzTrap code developed by D. J. Singh’s group [44] based on Boltzmann transport theory. The corresponding dispersion relations $E(n, k)$ in terms of wave vector ($k$) and band ($n$) were obtained from the electronic band structures calculations using the above-mentioned QE code. To find the temperature-dependent transport coefficient, i.e., electronic conductivity $\sigma_{\alpha\beta}(T, \mu)$, the Seebeck coefficient, and electronic thermal conductivity $\kappa_{\alpha\beta}^{\text{el}}(T)$, the Boltzmann transport equations are solved and expressed by the following equations,

\[
\sigma_{\alpha\beta}(\varepsilon) = \frac{1}{N} \sum_{\mathbf{k}} \frac{\delta(\varepsilon - \varepsilon_{\mathbf{k}})}{\partial \varepsilon}
\]

\[
\sigma_{\alpha\beta}(T, \mu) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\varepsilon) \left[ \frac{-\partial f_{\mathbf{k}}(T, \varepsilon, \mu)}{\partial \varepsilon} \right] \partial \varepsilon
\]

\[
S_{\alpha\beta}(T, \mu) = \frac{1}{e T \Omega \sigma_{\alpha\beta}(T, \mu)} \int \sigma_{\alpha\beta}(\varepsilon - \mu) \left[ \frac{\partial f_{\mathbf{k}}(T, \varepsilon, \mu)}{\partial \varepsilon} \right] \partial \varepsilon
\]

\[
\kappa_{\alpha\beta}^{\text{el}}(T, \mu) = \frac{1}{e^2 T \Omega \sigma_{\alpha\beta}(T, \mu)} \int \sigma_{\alpha\beta}(\varepsilon - \mu)^2 \left[ \frac{-\partial f_{\mathbf{k}}(T, \varepsilon, \mu)}{\partial \varepsilon} \right] \partial \varepsilon
\]

Where $\alpha$ and $\beta$ are the tensor indices, $\varepsilon$ is the electronic charge, $\Omega$ is the unit cell volume, $f_{\mathbf{k}}(T, \varepsilon, \mu)$ is the Fermi distribution function with $\mu$ denoting the Fermi level energy, and $\sigma_{\alpha\beta}(\varepsilon)$ is the conductivity tensor [45]. The transport properties for electrons in Tl$_5$Te$_3$ and Tl$_{10-x}$Pb$_x$Sb$_y$Te$_6$ structures were investigated using a rigid band and constant relaxation time approximations applied to semiclassical Boltzmann transport theory. In addition, the Seebeck coefficient ($S$), electrical conductivity $\sigma_{\alpha\beta}$ power factor $PF (\sigma^2 S)$, and electronic part of thermal conductivity denoted by $\kappa_{\alpha\beta}$ were investigated in this work. The dimensionless figure of merit $ZT = \frac{\sigma^2 T}{\kappa_{\text{lat}}} T$ was evaluated by taking the lattice thermal conductivity ($\kappa_{\text{lat}}$) as a parameter and its values were set to $\kappa_{\text{lat}} = 0.7$ W/Km for pure Tl$_5$Te$_3$, Pb or Sb-doped Tl$_5$Te$_3$, and $\kappa_{\text{lat}} = 0.4$ W/Km for Pb and Sb co-doped Tl$_5$Te$_3$ nanoparticles [34]. The relaxation time $\tau$ was determined by comparing the experimental and theoretical electrical conductivity values at different temperatures. The calculated values $\tau = 2.9 \times 10^{-15}$ s, $2.24 \times 10^{-15}$ s and $1.96 \times 10^{-16}$ s at 300K, 400 K, and 500 K respectively are in the same order as that of the measured value of SrTiO3 is $7.2 \times 10^{-15}$ s [45]. Therefore, the average of these calculated values was used in the following results.
4. Results and discussion

4.1. Crystal structure

Before considering the substitutional doping in the Tl5Te3 crystal structure, we have first presented the structural properties of Tl5Te3 in figures 4(a)–(c) and table 1. A primitive unit cell is shown in the figures 4(a)–(b) containing 20 Tl- and 12 Te-atoms on four different crystallographic positions termed as Tl-1, Tl-2, Te-1, and Te-2, respectively. Among the four possible positions two of the crystallographic positions are occupied by Tl atoms (Wyckoff position 4c and 16d) and the two are occupied by Te atoms with Wyckoff position 4a and 8h. The equilibrium crystal structure of Tl5Te3 has a tetragonal crystal structure like a Br3Cr3 type crystal structure having space group I4/mcm [46]. Figure 4(c) shows the PBE-GGA optimized volume 1080.9 Å³ for the Tl5Te3 crystal structure.

The table 1 shows that the calculated optimized lattice parameters, a = 9.09 Å and c = 13.08 Å (bond length bTl–Te = 2.44 Å) is larger than the experimentally measured lattice parameters, a = 8.92 Å and c = 12.62 Å (bond length bTl–Te = 2.51 Å) [47]. This is likely due to the reason that GGA overestimates the optimized volume or lattice parameters [48]. However, these results are found consistent with previously reported work on Tl5Te3 [32–34, 39]. Once, the optimum crystal structure is achieved, the electronic and thermoelectric properties of the Tl5Te3 via substitutional doping and co-doping by introducing Pb and Sb atoms at Tl-sites were studied.

4.2. Electronic properties

To understand the electronic structure of Tl5Te3 at optimized lattice parameters, the electronic band structure, and the total density of state (TDOs) along with the partial density of states (PDOS) are calculated as shown in the figures 5A(a)–(d). Figure 5A(a) shows that Tl5Te3 is non-magnetic and metallic behavior which is consistent with the previous theoretical and experimental results [39, 47]. Figure 5(a) black line shows the TDOs, which further confirmed the conducting and non-magnetic behavior of the Tl5Te3 crystal structure.

Further investigation of the electronic structure shows a narrow bandgap opening above the Fermi energy, which is consistent with those results calculated by Nordell et al., using the tight-binding method [19]. Surprisingly, Pb substitutional doping in the Tl5Te3 structure (see figures 5B(a)–(d)) at Tl-site ensued the incremental rise in the Fermi level by amount 0.25eV confirmed the concentration-dependent semiconducting nature of Tl5Te3. Such a semiconducting nature was previously predicted for Bi or Sb doped Tl5Te3 crystal structure [49]. Therefore, the tunable semiconducting nature of Tl5Te3 makes it promising to be doped with other heavy elements to exhibit excellent electronic properties for thermoelectric applications [50].

To understand the orbital character the PDOS as shown in the figures 5A(b)–(d), which shows that in pure Tl5Te3 nanoparticle, valence band maximum (VBM) mainly contributed by Tl2 atom s-orbitals and Te1 atom p-orbitals, which partially hybridized with d-orbital of Tl atoms (see figure 5(d)). Moreover, the p-orbitals states of Tl atoms dominate the conduction band minimum (CBM) with partial contribution from p-orbital states of Te atoms, which results in strong hybridization. The detailed calculation of the PDOS of Pb doped at Tl-site in Tl5Te3 crystal structure, as shown in figures 5B(b)–(d), which demonstrates that Pb doping induces impurities states in the conduction band and reduces the repulsion between bonding and anti-bonding states. Consequently, the pseudo-band gap in the conduction band reduces by an amount of 0.12 eV. Therefore, the contribution to CBM is mainly from p-orbital states of the dopant Pb-atoms depicted from the figures 5B(b)–(d). These results were also
confirmed by the TDOS (see figure 6(a)), which demonstrates that the band-gap window in the CBM for Pb-doped is shifted lower as compared to the TDOS of pure Tl₅Te₃ crystal structure.

4.3. Thermoelectric properties

Thermoelectric properties of pure, Pb, or Sb doped and co-doped nanostructured Tl₅Te₃ were analyzed using experimental measurements and DFT calculations. The optimized electrical and thermal properties were achieved through doping and have been an efficient method [49]. The electrical conductivity, the Seebeck coefficient, and the power factor were calculated experimentally for TlₓPb₁₋ₓSb₀.₅Te₆ at concentrations (x = 1.96, 1.97, 1.98, 1.99) in the temperature range of 300K to 550 K are shown in figures 7(a)–(c). We demonstrated that the electrical conductivity gets increased, and the Seebeck coefficient gets decreased, by increasing the Pb concentration, in the temperature range studied here. As a result, the power-factor decreases with an increase of Pb concentration, which reveals that a decrease in the Seebeck coefficient does not compensate by the increase of electrical conductivity in all compositions studied here. The smallest (largest) Seebeck value of 29.72 μVK⁻¹ (78.70 μVK⁻¹) at room temperature (550 K) was found for Tl₁.₉₉Sb₀.₀₁Te₆ nanoparticle. Figure 7(b) shows that the smallest electrical conductivity (602.9 Ω⁻¹m⁻¹) and the highest Seebeck values (110.7 μVK⁻¹) are found for Tl₁.₉₆Sb₀.₀₄Te₆ nanoparticle. For comparison, these values are enhanced from previously calculated results [21].
Figure 7(a) shows electrical conductivity decreases with an increase in the temperature range for all the composition studied here. A sightly flat line was observed to that of Tl₈Pb₁.₉₆Sb₀.₀₄Te₆ nanoparticle. The Pb (Sb) atoms have one (two) more electrons in the valance p states as compared to Tl atom valance p states. The excess of charge carriers electrons due to dopants enhanced the electrical conductivity at a particular temperature.

Figure 7(b) shows the Seebeck coefficient having an increasing or decreasing trend for all the composition due to variation in temperature or concentration. In the chalcogenide system, to enhance the electrical conductivity, Pb and Sb doping concentration play an important role. As we further increase the dopant concentration, the electrical conductivity starts decreasing due to the scattering of electrons with defective states. The enhancement in electrical conductivity and the Seebeck coefficient is required strongly to enhance the power factor (PF = S² × σ) of these nanoparticles. The optimized PF (738.84 μWK⁻²m⁻¹) were calculated for Tl₈Pb₁.₉₆Sb₀.₀₄Te₆ nanoparticle at 550 K. Figure 7(c) shows that by an increase in Pb dopant concentration the ZT gets decreased. Furthermore, ZT gets increased by increasing Sb co-dopant concentration. Here the nanoparticles with changing Sb co-dopant concentrations are given such as Tl₈Pb₁.₉₆Sb₀.₀₄Te₆ compound shows the lowest value of 0.05 at 300 K while it shows the highest value of ZT = 0.35 at 550 K.

The highest (lowest) PF value of 861.39 μWK⁻²m⁻¹ (205.50 μWK⁻²m⁻¹) is observed for Tl₈Pb₁.₉₆Sb₀.₀₄Te₆ nanoparticle at 550 K. In the middle of the last century, A. F. Ioffe’s [51] states that in narrow electronic bandgap semiconductors formed by 5p and 6p electrons high thermoelectric efficiency and a low thermal conductivity κ should be expected. For the reason that their crystal structures consist of heavy elements. Following these predictions, the first thermoelectric material was synthesized from doped Bi (bismuth), Sb (antimony), and Pb (lead) Te (telluride) with the thermoelectric figure of merit of about 0.8 at 300K. Figure 7(e) shows that by an increase in Pb dopant concentration the ZT gets increased. Furthermore, ZT gets increased by increasing Sb co-dopant concentration. Here the nanoparticles with changing Sb co-dopant concentrations are given such as Tl₈Pb₁.₉₆Sb₀.₀₄Te₆ compound shows the lowest value of 0.05 at 300 K while it shows the highest value of ZT = 0.35 at 550 K. Furthermore, to complement these experimental results we study here Pb-doping, Sb-doping, Pb, and Sb co-doping in Tl₁₀−ₓ₋₅PbxSb₅Te₆ using the first-principles calculations.
TDOS shows a sharp peak above the $E_F$ in the conduction bands, and it switches to $n$-type doping in the Tl$_5$Te$_3$ crystal structure. Among all the studied compounds, the pure Tl$_5$Te$_3$ nanoparticle has a larger TDOS at $E_F$, and it goes down with the Pb and Sb doping or co-doping at Tl-site. The decrease in TDOS at $E_F$ offers possible enhancement in the Seebeck coefficient. In reality, the Seebeck coefficient is also jointly related to the TDOS around the Fermi level in valance bands (conduction bands) for $p$-type ($n$-type) doped Tl$_5$Te$_3$ crystal structure.

**Figure 7.** Experimentally measured (a) electrical conductivity, (b) Seebeck coefficient, (c) total thermal conductivity, (d) PF, and (e) figure of merit for Pb and Sb doped Tl$_5$Te$_3$ nanoparticles at equilibrium lattice constant.
Figure 6 shows the sharp peak in the TDOS near the Fermi energy that occurred in the conduction bands, which results in $n$-type doped Tl$_5$Te$_3$ crystal structures. The Seebeck coefficient and electronic conductivity are closely related to the total density of states near the Fermi energy and provide a necessary test to electronic and thermoelectric properties of the materials.

The thermoelectric properties of Tl$_5$Te$_6$, Tl$_{9.5}$Pb$_{0.5}$Te$_6$, Tl$_{9.5}$Sb$_{0.5}$Te$_6$, Tl$_{9.0}$Pb$_{0.5}$Sb$_{0.5}$Te$_6$, and Tl$_{8.0}$Pb$_{2.0}$Te$_6$ crystal structure were calculated in the temperature range of 0-800 K, as shown in figures 8(a)–(e). The electrical
conductivity and the Seebeck coefficient follow the similar trend for Pb-doping \((x = 0.5, y = 0.0)\), Sb-doping \((x = 0.0, y = 0.5)\) and co-dopants of Pb and Sb at intermediate concentration \((x = 0.5 \text{ and } y = 0.5)\).

Figures 8(a), (c) shows electrical conductivity \((\sigma)\) and electronic thermal conductivity \((\kappa)\) were get significantly smaller with introducing the co-dopants in the Tl\(_3\)Te\(_6\) crystal structure. The \(\sigma\) shows a decreasing trend above 200 K with increasing temperature, while \(\kappa\) shows an increasing trend in the temperature range of 0–800 K. These results show evidence of a metallic character, despite these, the \(\sigma(T)\) of Tl\(_{9.0}\)Pb\(_{0.5}\)Sb\(_{0.5}\)Te\(_6\) compound displayed comparatively flat dependence on temperature. The electrical resistivity calculated for these compounds were in the range of \(1.6 \times 10^{-5} - 0.75 \times 10^{-5} \Omega \times m\), which is comparable to those of state of the art nanoparticles [52].

Figure 8(a) shows, the electrical conductivity \((\sigma)\) first increases with Pb-doping and then start decreasing by a further increase of Pb atoms substitutions or Sb as a co-dopant substitution. The \(\sigma\) follows a similar trend in the whole temperature range. It can be seen in figure 8(a) that the \(\sigma\) of the un-doped Tl\(_3\)Te\(_6\) and doped Tl\(_{3}\)Pb\(_{0.5}\)Te\(_6\) compounds are very high about \(160 \times 10^{-5} \Omega^{-1}m^{-1}\) and \(158 \times 10^{-5} \Omega^{-1}m^{-1}\), respectively at room temperature. The \(\sigma\) gets decreased with an increase of temperature, which is the indication of metallic behavior consistent with the electronic band-structure calculated here. The \(\sigma\) has large values, and the Seebeck has small values in case of an un-doped crystal structure except at the high Pb concentration. As with the increase of the Sb co-dopants concentration, the \(\sigma\) get decreased, and the Seebeck increased consistent with experimental results. The electrical conductivity of the Tl\(_{0.5}\)Sb\(_{0.5}\)Te\(_6\) crystal structure lowered by a small amount and the Seebeck coefficient increased by a larger amount, which results in higher PF in the temperature range of 0–800 K. The variances in electrical conductivity caused by Pb-dopant and Sb-dopant are evident and indicate the strong effect of electron-hole doping in the Tl\(_3\)Te\(_6\) crystal structure. This is consistent with the donor-doped and acceptor-doped SrTiO\(_3\) [53]. In addition to this hole (electron) produced by substitutional dopants would fill the valance band (conduction band), which is confirmed by the positive (negative) sign of the Seebeck coefficient. But in our study, we have presented thermoelectric properties at a fixed chemical potential equal to the Fermi energy, and all dopants behave like a hole-doping in Tl\(_3\)Te\(_6\) crystal structure. Thus, we consider holes are the dominating carriers in all these compounds tested through DFT.

Figure 8(b) shows the Seebeck coefficient which increased with temperature in the entire temperature range except for the pure and heavily Pb-doped Tl\(_3\)Te\(_6\) crystal structure. The Seebeck coefficient in all cases is measured positive, which provides a sensitive test of the electronic structures of the materials in proximity to the Fermi energy. For efficient thermoelectric devices, large values of the Seebeck coefficient are required. Figure 8(b) shows the tuning of the Seebeck coefficient owing to the doping and co-doping of Pb and Sb atoms. The enhanced Seebeck values of \(60 \mu V/K\) were calculated at 800 K for Tl\(_{0.5}\)Sb\(_{0.5}\)Te\(_6\) and Tl\(_{9.0}\)Pb\(_{0.5}\)Sb\(_{0.5}\)Te\(_6\) compounds. Further investigation shows that beyond these concentration values the Seebeck coefficient gets decreased as demonstrated for the Tl\(_{5.0}\)Pb\(_{2.0}\)Te\(_6\) compound. Thus it is evident that we are expecting the good thermoelectric response of Tl\(_3\)Te\(_6\) crystal structure at the intermediate concentration values i.e., Pb and Sb co-doping \((x = 0.5 \text{ and } y = 0.5)\). Interestingly, the theoretically calculated Seebeck values (see figure 8(b)) follow the similar trend of experimentally measured Seebeck values (see figure 7(b)) owing to substitutional doping concentration. The theoretically calculated values differ from the experimentally measured values because these compounds are optimized at their ground states in DFT at 0 K, while experimentally, the ground state is not used to obtain the thermoelectric properties [54]. So besides the advantages of the DFT method, it has limitations [55, 56].

In material, heat is conducting through lattice vibrations and electrons. Lattice vibration in the semiconductor is mostly responsible for the conduction of heat, while in metals free electrons are good sources of thermal conductivity. In conductors, the lattice thermal conductivity can be safely neglected because it is smaller than 2\% of the total thermal conductivity. In thermoelectric generators good thermoelectric materials are desirable which have less thermal conductivity, to maintain the temperature gradient across the material (see figure 8(d)). The thermoelectric PF is determined by the interplay of \(S\) and \(\sigma\). The power factor \((PF = \sigma S^2)\), for all compounds at the four doping levels as a function of temperature, were investigated. The temperature dependence of PF is observed, indicating the increase in temperature rises results in the increase of the PF for all the samples under investigation. The efficiency of a TE generator can be measured by its figure of merit (ZT), which will be large for high Seebeck coefficient, high electrical conductivity, and low thermal conductivity. Both figures 7(e) and 8(e) shows the experimental and theoretical dimensionless figure of merit. It is clear from both the figures that the experimental value of \(ZT = 0.35\) and the theoretical value of \(ZT = 0.12\) are the largest, for Pb and Sb co-doped crystal structure among all the studied crystal structures. This result is possible because the co-doped crystal structure has the highest Seebeck coefficient as shown in figure 8(b) consistent with experimental results, i.e., maximally Sb co-dopants concentration corresponds to high ZT value. Although, the ZT values both experimental and theoretically predicted are not over one. Pb and Sb doped or co-doped Tl\(_3\)Te\(_3\) based materials may be a good candidate for thermoelectric applications. There are some conventional ways to enhanced ZT by reducing the thermal conductivity by phonon engineering, such as elemental isotope doping [57], which will introduce large phonon scatterings that result in smaller phonon mean-free paths. Interestingly,
with the inclusion of Sb co-dopants, our experimental and theoretical results show larger ZT than those of other crystal structures. For example, this is consistent with previously reported work for bulk silicon ZT = 0.003, then with phonon engineering nanostructured Si have enhanced ZT two order larger in magnitude [57, 58].

5. Conclusion

The co-precipitation method was successfully employed to synthesized Tl₅PbₓSb₂₋ₓTe₆ quaternary nanoparticles with different concentrations of Pb and Sb dopants (x = 1.96, 1.97, 1.98, 1.99). The thermoelectric properties of nanostructured Thallium Telluride were successfully improved by simply co-doping of Pb and Sb using various concentrations. The XRD revealed the iso-structural phase for the Tl₅Te₃ nanoparticles. The same is also accurately predicted by the DFT calculations. The electrical conductivity measurements provide the confirmatory evidence for the nanostructured Tl₅PbₓSb₂₋ₓTe₆ as a degenerative semiconductor. The positive Seebeck coefficient over a range of temperatures confirmed the leading contribution of holes conduction at the nanoscale. The Seebeck coefficient decreases with increasing Pb contents due to the increase in electron scattering behavior. Nevertheless, the optimization of electrical conductivity and the Seebeck coefficient through controlled doping of Sb concentration lead to the achievement of a significantly improved power factor of 738.85 μWm⁻¹K⁻². The DFT calculations confirmed that the doping and co-doping Pb and Sb concentrations in the Tl₅Te₆ crystal structure caused a dramatic reduction in the electronic thermal conductivity with the dramatic increase in the Seebeck coefficient and electrical conductivity. The experimentally measured ZT = 0.35 and theoretically calculated ZT = 0.18 through Pb or Sb doping and co-doping expand the thermoelectric efficiency of the Tl₅Te₆ nanoparticles. Therefore, owing to the enhanced thermoelectric properties of Tl₅Te₆ nanoparticles demonstrated in a controlled manner has the substantial potential for designing and fabrication of efficient thermoelectric devices to be used for energy harnessing with a new class of nanostructured materials.

Acknowledgments

Density Functional Theory calculations were performed using the Exabyte.io platform [59] a web-based computational ecosystem for the development of new materials and chemicals, employing parts of its infrastructure hosted on the Oracle Cloud Infrastructure [60]. A. U. Rahman acknowledges National Center for Physics (NCP), Islamabad, and Ghulam Ishaq Khan Institute (GIKI), Swabi, for providing a supercomputing facility.

Conflict of interest

We have no conflict of interest for this work to be declared.

ORCID iDs

Altaf Ur Rahman @ https://orcid.org/0000-0001-7772-3272
Waqar Adil Syed @ https://orcid.org/0000-0001-8917-520X
Banat Gul @ https://orcid.org/0000-0003-3223-9596

References

[1] Minnich A J, Dresselhaus M S, Ren Z F and Chen G 2009 Cambridge: Energy Environ. Sci. 2 466–79
[2] Alama H and Ramakrishnab S 2013 Nano Energy 2 190–212 (https://www.scribd.com/document/43756559/1-s2-0-
S231128512002078-main-pdf)
[3] Polozinea A, Sirotinskayab S and Schaeffera S 2014 Materials Research, Brasil 17 1260
[4] Rahman G and Rahman A U 2017 Physica B 526 122
[5] Seebeck TJ 1822 Magnetic Polarization of Metals and Ores by Temperature Differences 289–346 (https://en.wikipedia.org/wiki/
Thomas_Johann_Seebeck#cite_ref-3)
[6] Pelletier J C A 1834 Annales de Chimie et de Physique (in French) 56 371–86
[7] Thomson W 1851 Proc. of the Royal Society of Edinburgh 3 91–8
[8] Ali A, Rahman A U and Rahman G 2019 Physica B 565 18
[9] Rowe D M (ed) 2006 Thermoelectric, Handbook, Macro to Nano (Boca Raton: CRC Press, Taylor & Francis) (https://doi.org/10.1201/
9781420038903)
[10] Chiang P W and Gluck J V 1967 J. Appl. Phys. 38 4671
[11] Pradel A, Tadencac J C, Brun G and Maurin M 1982 J. Solid State Chem. 45 99
[12] Barchii I E, Lazarev V B, Peresh E Y, Voroshilov Y V and Tkachenko V I 1988 Izv. Akad. Nauk. SSSR, Neorg. Mater. 24 1791
[13] Barchii I E, Lazarev V R, Peregry V Y and Tkachenko V I 1988 Inorg. Mater. (USSR) 24 1526
[14] Jusakah A and Kannewurf A 1968 C. R. J. Appl. Phys. 39 3003
[15] Rahman A U, Ullah H, Verma M and Khan S 2020 J. Magn. Magn. Mater. 515 167212
[16] Cruseau E and Sladaru S 1969 J. Mater. Sci. 4 410
[17] Ikari T and Hashimoto K 1978 Phys. Stat. Sol. 86 239
[18] Jensen J D, Burke J R, Ernst D W and Allgaier RS 1972 Phys. Rev. B 6 319
[19] Nordell K J and Miller J J 1996 J. Alloys Compd. 241 51
[20] Lippens P E and Aldon L 1998 Solid State Commun. 108 913
[21] Kuroptaw B A, Assoud A and Kleinhe H 2011 J. Alloys Compd. 509 6768
[22] Kosuga A, Kurosaki K, Muta H and Yamanaka S 2006 J. Appl. Phys. 99 063705
[23] Ajovan A L, Eholie R, Pi Frieder E and Tournoux M 1983 Rev. Chim. Miner. 20 421
[24] Ibanez A, Jumas J C, Philipott E, Ajavo A L and Eholie R 1986 Rev. Chim. Miner. 23 281
[25] Malakhovskaya-Rosokh T A, Sabov M Y, I E Barchyand and Peregry E Y 2011 Russ. J. Inorg. Chem. 56 118
[26] Houenou P, Eholie R and Fhaut J 1979 C. R. Seances Acad. Sci., Ser. C 283 193
[27] Houenou P and Eholie R 1981 J. Less-Common Met. 81 181
[28] Houenou P, Ajavan A L and Fatsoue A G A 1982 C. R. Seances Acad. Sci., Vie Acad. 295 455
[29] Dichi E, Kra G, Eholie R and Legendre B 1993 J. Alloys Compd. 194 155
[30] Dichi E, Kra G, Eholie R and Legendre B 1993 J. Alloys Compd. 194 7
[31] Lin S, Tong P, Wang B, Lin J, Huang Y and Sun Y 2014 Inorg. Chem. 53 3709
[32] Latypov Z M, Faiudullina N R, Sotov K N and Savelev V P 1988 Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy 24 1920
[33] Pradel A, Tenedac J C, Coquillion D and Brun G 1982 Rev. of Chimie Minerale 19 43
[34] Teubner J 2001 Diploma Thesis Universität Konstanz (https://kops.uni-konstanz.de/bitstream/123456789/8921/jb2001_ Solid_State_and_Cluster.pdf;sequence=1)
[35] Kittel C 1971 Introduction to Solid State Physics Edition: IV (New York: Wiley & Sons Inc.)
[36] Kasap S 1997–2001 Thermoelectric Effects in Metals: Thermocouples (http://courses.nus.edu.sg/course/elengy/cc3406/seebeck%20and%20thermocouple.pdf)
[37] Kurosaki K, Kosuga A, Goto K, Muta H and Yamanaka S 2006 Mater. Trans. 47 1938
[38] Hohenberg P and Kohn W 1964 Phys. Rev. B 136 71
[39] Giannozzi P et al 2009 J. Phys. Condens. Matter 21 395502
[40] Blochl P E 1994 Phys. Rev. B 50 17953
[41] Allen P B, Picket W E and Krakauer H 1988 Phys. Rev. B 37 7482
[42] Corso A D 2014 Comput. Mater. Sci. 95 337
[43] Monakhst H I and Pak J D 1976 Phys. Rev. B 13 5192
[44] Madsen G K H and Singh D J 2006 BoltzTraP Comput. Phys. Commun. 175 67
[45] Sun J and Singh D J 2016 APL Mater. 4 104803
[46] Bhan S and Schubert K 1970 J. Less-Common Met. 20 229
[47] Persson K et al 2013 APL Mater. 1 011002
[48] Rahman A U, Morbec J M, Rahman G and Kratzer P 2018 Phys. Rev. Materials 2 094002
[49] Tao X, Jund P, Viennoms R and Tenedac J C 2011 J. Phys. Chem. A 115 8761
[50] Snyder G J and Toberer E S 2008 Nat. Mater. 7 105
[51] Joffe A F 1957 Semiconductor Thermoelements and Ther-moelectric Cooling (London: Infosearch)
[52] Rose D M (ed) 1995 CRC Handbook of Thermoelectrics (New York: CRC)
[53] Rahman J U, Nam W H, Van Du N, Rahman G, Rahman A U, Ho Shin W, Seo W S, Kim M H and Lee S 2019 J. Eur. Ceram. Soc. 39 358–65
[54] Xu B, Liang J, Li X, Sun J F and Yi L 2011 Eur. Phys. J. B 79 275
[55] Onda G, Reining L and Rubio A 2002 Rev. Mod. Phys. 74 601
[56] Rashkeev S N and Lambrecht W R I 2001 Phys. Rev. B 63 165212
[57] Yang N, Gang E and Li B 2007 Nano. Lett. 8 276
[58] Bux S K et al 2009 Adv. Funct. Mater. 19 2445
[59] https://arxiv.org/abs/1902.10838 (accessed May. 12, 2020)
[60] https://www.oracle.com/cloud/ (accessed May. 12, 2020)