Enhanced of thermoelectric properties and effects of Sb doping on the electrical properties of Tl\textsubscript{10-x}Sb\textsubscript{x}Te\textsubscript{6} nano-particles

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\textbf{ABSTRACT}

We have prepared the thallium antimony telluride with different doping concentration of Sb, Tl\textsubscript{10-x}Sb\textsubscript{x}Te\textsubscript{6} (x = 1, 1.25, 1.50, 1.75, 2) using solid state reaction techniques. Furthermore, Nano-particles were prepared from the ingot of the respective compound by ball milling techniques. X-rays diffraction analysis confirmed the phase purity of the compound, as no extra peaks were observed. The miller indices and lattice constant has been determined from the XRD data. Energy dispersive x-rays spectroscopy result confirmed the stoichiometric elemental composition of Tl\textsubscript{10-x}Sb\textsubscript{x}Te\textsubscript{6} compound. With increasing antimony (Sb) content the Seebeck coefficient (S) was increased, due to the affected electron hole ratio in the system. The contrary behavior of Seebeck co-efficient and electrical conductivity give rise to enhancement in power factor. Our study allows envisaging the application of Tl\textsubscript{10-x}Sb\textsubscript{x}Te\textsubscript{6} as one of the suitable materials for thermoelectric generator.

\textbf{1. INTRODUCTION}

Achieving large thermoelectric efficient system using a low-cost material, with an appreciable degree of compatibility with the modern technology is need of the time. Keeping in view the progressively of depletion of fossil fuel sources, alternate energy sources, particularly with thermoelectric materials, become increasingly important. These materials are capable of converting thermal energy from a temperature gradient into electrical energy (Seebeck effect) or convert electrical energy into a temperature gradient. (Peltier effect) The Seebeck effect has gained significant interests for application in automotive industry, where the energy from the waste heat could be converted to electrical energy.

The performance of a material for thermoelectric applications is determined by the dimensionless figure of merit ZT \cite{1}, where T is the absolute temperature and $Z = (S^2\sigma)/k$ where \((S)\) is the Seebeck coefficient, \(\sigma\) the electrical conductivity, and \(k\) the thermal conductivity.

The first two quantities need to be as big as possible, while the last one need to be small and should be able to maintain the temperature difference between the hot and cold side. The problem is that all three quantities are inter-related, and cannot be optimized independently. Desirable thermoelectric materials must have large Seebeck coefficient, high electrical conductivity, and low thermal conductivity to preserve the heat at the junction and reduce the heat transport losses.

Thallium telluride’s or thallium Antimonides consist of large group of compounds with complex crystal structures, i.e Tl\textsubscript{3}Sn\textsubscript{2}Te\textsubscript{5} \cite{2}, Ag\textsubscript{2}Te\textsubscript{5} \cite{3}, Tl\textsubscript{2}Te\textsubscript{6} \cite{4, 5}, and Tl\textsubscript{3}Sb\textsubscript{2}Te\textsubscript{5}. More specifically, some ternary groups of Tl\textsubscript{2}Te\textsubscript{5} are more useful such as Tl\textsubscript{2}Bi\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{6} \cite{6, 7}, Tl\textsubscript{3}(Sn/Pb)\textsubscript{2}Te\textsubscript{6} \cite{8, 9} and Tl\textsubscript{4}(Sn/Pb)\textsubscript{3}Te\textsubscript{6} \cite{10, 11} exhibit good thermoelectric properties. In the present study, we have studied Thallium Antimony Telluride, Tl\textsubscript{10-x}Sb\textsubscript{x}Te\textsubscript{6}, based nano materials with similar behavior as of Tl\textsubscript{2}Zr\textsubscript{2}Te\textsubscript{5} \cite{12}, Tl\textsubscript{2}Zr\textsubscript{3}Te\textsubscript{6} \cite{13} and good thermoelectric properties like Tl\textsubscript{3}Sn\textsubscript{2}Te\textsubscript{5} and Tl\textsubscript{3}Bi\textsubscript{2}Te\textsubscript{6} systems. The same phenomenon group I4/mcm and also in iso-structure to Tl\textsubscript{2}Te\textsubscript{5} = Tl\textsubscript{10}Te\textsubscript{6} with different ratio of Tl and Sb elements \cite{14}. The power factor for Tl\textsubscript{10-x}Sb\textsubscript{x}Te\textsubscript{6} nano materials is obtained in the range of 4.4-8.9 $\mu$Wcm\textsuperscript{-1}K\textsuperscript{-2} which is in good agreement with Tl\textsubscript{3}Pb\textsubscript{2}Te\textsubscript{6} - Tl\textsubscript{3}Pb\textsubscript{3}Te\textsubscript{6} i.e. 5.2 - 6.2 $\mu$Wcm\textsuperscript{-1}K\textsuperscript{-2} at 685 K \cite{9, 15}.

The main objective of this work is to optimize the temperature dependence of the thermoelectric properties of Sn doped Tellurium Telluride Tl\textsubscript{10-x}Sb\textsubscript{x}Te\textsubscript{6} over a wide temperature range and evaluates their potential for thermoelectric power generator. The purposes and importance of this study is to see the effects of charge carrier’s concentrations on the Seebeck co-efficient, electrical conductivity and, power factor different dopants on thallium telluride nano-system. In order to develop high-performance nano-thermoelectric materials, we have investigated thallium nano-particles as these types of nano-materials have extremely low thermal conductivity as well as moderate electrical performance \cite{16}.

We have studied the effect of induction/reduction of the charge carriers on thermal and transport characteristics using different dopants content. The charge carrier’s concentration affects the ratio of electron-hole concentration which in turns increases the electron scattering in the chalcogenide system consequently affecting the electrical conductivity and thermopower. We have investigated the properties of Tl\textsubscript{10-x}Sb\textsubscript{x}Te\textsubscript{6} compound due to their low thermal and high electrical conductivity and potential for their use as high performance nano-thermoelectric materials.
2. EXPERIMENTAL SECTION

Tl$_{10-x}$Sb$_x$Te$_6$ compound (where $x$=1, 1.25, 1.50, 1.75, 2) has been prepared by solid state reaction method from the Sb doped element with different concentration of respective elements (Tl granules, 99.4%; Sb powder, 99.5% and Te broken ingots, >99.9%). Different Samples with different masses were measured between 60 mg and 120 mg. Tl$_{10-x}$Sb$_x$Te$_6$ system was prepared by heating different elements of Tl, Sb and Te in their stoichiometric molar ratio and kept in a silica tube (approx. $10^{-2}$mbar) stored in an argon-filled glove box to prevent it from the reaction of other environmental elements. The silica tubes were coated under H$_2$O$_2$ flame. All samples were gradually heated in a furnace with appropriate temperature. The profile for these compound is (12 h-650 K-24 h-650 K 60 h- 650 K and cooled down to 550 K within 100 h). If the reaction mixture were inhomogeneous after heating, the material was again placed in a silica tube in the argon filled glove box and kept in heat furnace for one week. Keeping the process continues till desired homogeneous compound were obtained. The prepared ingot was then put in the Ball milling machine to produce nanoparticles of different sizes as mentioned latter.

3. RESULT AND DISCUSSION

Figure 1 shows the powder XRD spectrum of the thallium antimony telluride’s compounds, Tl$_{10-x}$Sb$_x$Te$_6$ with varying doping concentration ($x$ = 1, 1.25, 1.50, 1.75, 2). In the XRD patterns, the strongest intensity of the (213) diffraction peak around 31.80$^\circ$ indicates a preferred oriented tetragonal phase with polycrystalline structure for all the doping concentrations in the host matrix. The peaks associated to the (130), (121), (220), (024), (006), (240), (413), (044) and (136) crystallographic planes were also observed. The XRD result implies that a single pure phase of Tl$_{10-x}$Sb$_x$Te$_6$ is obtained in the present study. Further, the particle size of the prepared samples was estimated using Debye-Scherrer formula, ($D = \frac{0.9\lambda}{Bcos\theta}$) [21]. The crystallite size value of the prepared samples is in the range (21-25 nm) indicating that Sb incorporations in TlSbTe$_6$ do not affect significantly its crystallite size. The XRD data are summarized in table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size, (nm)</th>
<th>Lattice constant, a, b, c (Å)</th>
<th>Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl)$<em>{9}$Sb$</em>{1}$Te$_{6}$</td>
<td>25.247</td>
<td>a = b = 8.8930</td>
<td>1004.51</td>
</tr>
<tr>
<td>Tl)$<em>{8.75}$Sb$</em>{1.25}$Te$_{6}$</td>
<td>21.795</td>
<td>c = 13.0050</td>
<td>1023.95</td>
</tr>
<tr>
<td>Tl)$<em>{8.5}$Sb$</em>{1.5}$Te$_{6}$</td>
<td>21.170</td>
<td>a = b = 8.8250</td>
<td>1013.45</td>
</tr>
<tr>
<td>Tl)$<em>{8.25}$Sb$</em>{1.75}$Te$_{6}$</td>
<td>21.118</td>
<td>c = 13.0000</td>
<td>1009.09</td>
</tr>
<tr>
<td>Tl)$<em>{8}$Sb$</em>{2}$Te$_{6}$</td>
<td>21.455</td>
<td>a = b = 8.8484</td>
<td>1022.72</td>
</tr>
</tbody>
</table>

EDX analysis whose carried out quantitative percentage to get of the elements present in the samples. For Tl$_{10-x}$Sb$_x$Te$_6$ sample highly rich in thallium has (69.9 % Tl, 25.8 % Te, and 4.2 % Sb). In Figure 2, the spectra show the Tl:Te ratio and the Sb concentration appear in the compound.

The electrical conductivity $\sigma$, for Tl$_{10-x}$Sb$_x$Te$_6$ samples (where $1 \leq x \leq 2$) in the temperature range 300 K and 550 K is shown in Figure 3. Electrical conductivity decreases gradually with increasing temperature, shows similar trend to Tl$_6$BiTe$_6$ system. This behavior of our Sb doped is true in case of intrinsic semiconductors with $x=1$ as well as for doped semiconductors with $x$ up to 2.00, like the compounds Tl$_{10-x}$Sn$_x$Te$_6$ and Tl$_{10-x}$Bi$_x$Te$_6$ [6, 8]. The decreasing behavior of electrical conductivity with temperature indicates the p-type conductivity.

Tl$_8$Sb$_2$Te$_6$ has the highest electrical conductivity of 698.7 $\Omega$ cm$^{-1}$ at 300 K, which decreases gradually with increasing temperature, i.e. 664 $\Omega$ cm$^{-1}$ 550 K (figure 3). The electrical conductivity for Tl$_{10-x}$Sb$_x$Te$_6$ also decreases with increase in concentration of $x$. As an example in varying concentration of...
x from 1 to 2, the electrical conductivity, decreased from 698.7 $\Omega \cdot \text{cm}^{-1}$ to 658.6 $\Omega \cdot \text{cm}^{-1}$ at 300 K. Similarly at 550 K, it decreased from 664 $\Omega \cdot \text{cm}^{-1}$ at $x = 1$ to 617.4 $\Omega \cdot \text{cm}^{-1}$ at $x = 2$.

Figure 3. Image of energy dispersive X-ray spectroscopy

Table 3. The electrical conductivity at 300 and 550 K for all samples (1.0 ≤ $x$ ≤ 2.0)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrical conductivity (Ω·cm$^{-1}$) at 300 K</th>
<th>Electrical conductivity (Ω·cm$^{-1}$) at 550 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Tl}_9\text{Sb}_1\text{Te}_6$</td>
<td>699</td>
<td>663</td>
</tr>
<tr>
<td>$\text{Tl}<em>{8.75}\text{Sb}</em>{1.25}\text{Te}_6$</td>
<td>694</td>
<td>659</td>
</tr>
<tr>
<td>$\text{Tl}<em>{8.50}\text{Sb}</em>{1.50}\text{Te}_6$</td>
<td>680</td>
<td>656</td>
</tr>
<tr>
<td>$\text{Tl}<em>{8.25}\text{Sb}</em>{1.75}\text{Te}_6$</td>
<td>674</td>
<td>642</td>
</tr>
<tr>
<td>$\text{Tl}_8\text{Sb}_2\text{Te}_6$</td>
<td>657</td>
<td>617</td>
</tr>
</tbody>
</table>

Seebeck coefficient (S) measured for $\text{Tl}_{10-x}\text{Sb}_x\text{Te}_6$ systems with different concentration of Sb ($x = 1, 1.25, 1.50, 1.75, 2$) is shown in figure 4. All samples show an increasing trend of Seebeck coefficient with increasing temperature for example, for sample $\text{Tl}_8\text{Sb}_2\text{Te}_6$ Seebeck coefficient is increased from 78.66 $\mu \text{VK}^{-1}$ at 300 K to 125 $\mu \text{VK}^{-1}$ at 550 K. In the same way for $\text{Tl}_8\text{Sb}_2\text{Te}_6$ compound the Seebeck coefficient increased from 45 $\mu \text{VK}^{-1}$ at 300 K to 75 $\mu \text{VK}^{-1}$ at 550 K.

Figure 4. Electrical conductivity of $\text{Tl}_{10-x}\text{Sb}_x\text{Te}_6$ with $x$ varying between 1 and 2

The Seebeck Coefficient significantly increased upon Sb doping. At 300 K, it is enhanced from 44.1 $\mu \text{VK}^{-1}$ at $x = 1$ to 78.6 $\mu \text{VK}^{-1}$ at $x = 2$. Similarly, increasing Sb composition from 1 to 2, S increased from 78.66 $\mu \text{VK}^{-1}$ 125 $\mu \text{VK}^{-1}$ at 550 K.

We have observed that the Seebeck coefficient linearly increases with temperature for all the composition studied here. P-type deficiency is frequently observed in heavy metal, telluride’s, as found in $\text{Tl}_{10-x}\text{Ln}_x\text{Te}_6$ series and $\text{Tl}_8\text{Bi}_2\text{Te}_6$, causing a high number of charge carriers ($> 10^{19}$ cm$^{-3}$) [7], $\text{Tl}_{10-x}\text{Ln}_x\text{Te}_6$ series ($\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Gd, Tb}$) having almost similar trend of Seebeck coefficient of $\text{Tl}_{10-x}\text{Sb}_x\text{Te}_6$ [7]. Increasing of Seebeck coefficient with temperature by the creation of a small energy band gap can be easily excited from the valance band to conduction band [16].

The temperature dependencies with variation of dopant, can be attributed to the relationship between Seebeck coefficient, temperature and charge carrier concentration according to the following formula [21],

$$S = T \frac{8\pi^2 k^2 m^*}{3eh^2} \left( \frac{\pi}{3n} \right)^{2/3}$$

(1)

Here, $k_B$ is the Boltzmann constant, $e$ is electronic charge, $h$ is Planck constant, $m^*$ is effective mass, and $n$ is charge carrier concentration in system.

The above equation shows that $S$ would depend on which dominated parameter in a particular situation and in specific system. Compounds with $x \geq 1$ is supposed to be p-type semiconductor as $\text{Tl}_8\text{Sb}_2\text{Te}_6$ is formally an intrinsic semiconductor as observed from the experimental positive value of $S$.

As electrical conductivity, increases carriers concentration which is as per equation $\sigma = n e \mu$, where $\mu$ and $e$ = charge of carriers respectively, as mentioned above, $S$ has $n^{-2/3}$ dependence, $S$ and $\sigma$ are related inversely through $n$. The experimental results endorse that increased $x$ causes $\sigma$ decreases for a given Sb due to decrease in $n$ (see Figure 3).

Furthermore, as $T$ increases, $\sigma$ to decreases, because $\mu = \frac{T}{m^* \tau}$ where $\tau$ is the relaxation time, inversely related to temperature.

Table 4. Temperature dependence of the Seebeck coefficient of $\text{Tl}_{10-x}\text{Sb}_x\text{Te}_6$ samples at 300 and 550 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>Seebeck coefficient($\mu \text{VK}^{-1}$) at 300 K</th>
<th>Seebeck coefficient($\mu \text{VK}^{-1}$) at 550 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Tl}_8\text{Sb}_2\text{Te}_6$</td>
<td>46.76</td>
<td>82</td>
</tr>
<tr>
<td>$\text{Tl}<em>{8.33}\text{Sb}</em>{1.66}\text{Te}_6$</td>
<td>50.47</td>
<td>82.96</td>
</tr>
<tr>
<td>$\text{Tl}<em>{8.50}\text{Sb}</em>{1.50}\text{Te}_6$</td>
<td>58.75</td>
<td>84.5</td>
</tr>
<tr>
<td>$\text{Tl}<em>{8.75}\text{Sb}</em>{1.25}\text{Te}_6$</td>
<td>60.78</td>
<td>96.59</td>
</tr>
<tr>
<td>$\text{Tl}_9\text{Sb}_1\text{Te}_6$</td>
<td>80.95</td>
<td>126.93</td>
</tr>
</tbody>
</table>

A significant non-linearity electrical and thermal behavior is observed from 300-550 K, signifying the decomposition of semiconducting network into non-metallic clusters which are supported by a study of the transport and thermal characteristics. This investigation further testifies that the semi-conducting states are suppressed with the doping of Sb, obviously a clear evidence of increase of Seebeck co-efficient.

4. POWER FACTOR

The power factor, characterized by $\alpha^2 \sigma$, shows overall thermal efficiency of thallium antimony telluride. The power factor increases with increasing temperature for all of the samples. The increasing values of power factor for Sb doped thallium telluride system are mainly attributed to increasing Seebeck coefficients. The Sb doped system show a power factor in the range from 1.31 $\mu \text{Wcm}^{-1} \text{K}^{-2}$ to 9.8 $\mu \text{Wcm}^{-1} \text{K}^{-2}$ at 300 K and 550 K respectively. The samples with $x = 1, 1.25$ and 1.50 show slight increase with temperature and aggregate at s
ame point at 4.0 μW·cm⁻¹·K⁻² as shown in Figure 5. All Sb dop
ined samples investigated here shows better performance of p
ower factor as compared to un-doped system. Tl/LnTe₆ series
was reported that the doping of different elements i.e (Ce, Pr)
in ternary group show different values of power factor in the
range of 2.8–4.6 μW·cm⁻¹·K⁻² at 550K [7]. Ternary group (TlₓS
nTe₆) substitute of Sn has reported the value of power factor a
t x = 2.05 are 3.6–4.9 μW·cm⁻¹·K⁻² at 320 K and 685 K respec
tively [18]. Which is quite low value compared to the one repo
rted in the present study, i.e. for TlₓSb₂Te₆ power factor is 8.9
μW·cm⁻¹·K⁻² at 550 K. This is the main goal and achievement
of this research work to enhance the power factor and thermo
electric properties in modified system of Tl₁₀Te₆ system.

![Figure 5. Seebeck coefficient of Tl₁₀-xSbxTe₆ with x varying between 1 and 2](image)

Figure 5. Seebeck coefficient of Tl₁₀-xSbxTe₆ with x varying between 1 and 2

![Figure 6. Power factor of Tl₁₀-xSbxTe₆ with x varying between 1 and 2](image)

Figure 6. Power factor of Tl₁₀-xSbxTe₆ with x varying between 1 and 2

5. CONCLUSION

We conclude that the structural and compositional analyses
of Tl₁₀-xSbxTe₆ shows tetragonal structure with space group
(4/mcm), no impurities or secondary phases were found in th
is system. We have concluded from the electrical and thermo
electric properties that our system shows p-type behavior due
to the Sb doping in binary thallium telluride group as they ha
ve positive Seebeck coefficient in the whole range of tempera
ture. There is substantial increment in the Seebeck coefficient
with respected to temperature as well as Sb doping concentra
tion in Tl₁₀Sb₂Te₆, i.e. at 300 K. We have observed ‘S’ value
s of 78.1 μV·K⁻¹ for TlₓSb₂Te₆ and 126 μV·K⁻¹ at 500 K respec
tively. Similarly the values of S at 300 K for x=1.00 is 47 μV
K⁻¹ and for x=2.00 it increased up to 81μV·K⁻¹. On the other h
and, at higher temperature, Seebeck coefficient at for x=1.00
is 82.0 μV·K⁻¹ and for x=2.00 it increased up to 127 μV·K⁻¹, th
erefore, greater the ‘Sb’ content lower the electrical conductiv
ity and high the Seebeck coefficient. The high Seebeck coeffi
cient in turn gives the enhanced value of power factor. A pro
minent non-linear electrical and thermal behavior is observed
in the temperature range studied here, signifying the decomp
osition of the semiconducting network into non-metallic clus
ters which are supported by a study of the transport and therma
l behavior. This investigation further clarifies that the semi-c
conducting behavior becomes weekend with the addition of Sb,
which is the clear evidence of increase of Seebeck co-efficien
t and suppression of metallic behavior. The results show here
important information about the cluster co-existence, suppres
sion of the metallic state with the addition of Sb. The resistivi
ty changes with Sb concentration but there is no structural ch
anges observed. We conclude that the relative higher values o
f ‘Sb’ based compound made them interesting for further stud
y and practical application, of high efficient thermoelectri
gerators.

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