Thermoelectric Properties of the Thallium-Tellurium Binary Compounds

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We are paying attention to extremely low thermal conductivity (\(\kappa\)) materials which have a potential to be next generation thermoelectric materials. Most of the extremely low \(\kappa\) materials that have been reported so far are ternary thallium tellurides such as Ag-Tl-Te ternary system. However, as for Tl-Te binary compounds, \(\text{Tl}_2\text{Te}_3\), \(\text{Tl}_5\text{Te}_9\), \(\text{TlTe}\), and \(\text{Tl}_2\text{Te}_3\) were prepared and their thermoelectric properties were investigated. The \(\kappa\) of \(\text{TlTe}\) was relatively high (approximately 4 \(\text{Wm}^{-1}\text{K}^{-1}\) at 300 K), while those of \(\text{Tl}_2\text{Te}\) and \(\text{Tl}_5\text{Te}_3\) were extremely low (\(<0.5\ \text{Wm}^{-1}\text{K}^{-1}\) at 300 K). These compounds indicated relatively high thermoelectric figure of merit \(ZT\), e.g., \(\text{Tl}_2\text{Te}\) showed the highest value of 0.2 at 586 K.


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1. Introduction

Thermoelectric materials are capable of converting waste heat to usable electricity. The effectiveness of a material for thermoelectric applications is determined by the dimensionless figure of merit, \(ZT = S^2T/\rho\kappa\), where \(S\) is the Seebeck coefficient, \(\rho\) is the electrical resistivity, \(\kappa\) is the thermal conductivity, and \(T\) is the absolute temperature. \(^1\) \(\kappa\) value of the materials used in current devices is approximately 1. In recent years, several classes of bulk materials with high \(\kappa\) have been discovered, including filled skutterudites, \(^2\) zinc antimonide, \(^3\) CsBi\(_4\)Te\(_6\), \(^4\) Ag\(_{1-x}\)Pb\(_x\)SnTe\(_2\), \(^5\) and Tl-doped PbTe. \(^6\)

Against this background, we are paying attention to extremely low \(\kappa\) materials as next generation thermoelectric materials. Here, the extremely low \(\kappa\) means below 0.5 \(\text{Wm}^{-1}\text{K}^{-1}\), which is about one-third or one-fourth of those of typical thermoelectric materials such as Bi\(_2\)Te\(_3\) and PbTe. Most of the extremely low \(\kappa\) materials that have been reported so far are thallium tellurides, e.g., Ag\(_{1-x}\)Tl\(_x\)Te\(_5\) (\(\kappa = 0.22 \text{Wm}^{-1}\text{K}^{-1}\)) \(^7\) and \(\text{Tl}\text{SnTe}_3\) (\(\kappa = -0.5 \text{Wm}^{-1}\text{K}^{-1}\)). \(^8\) Therefore, \(\text{Tl}\) would play some roles in appearing the extremely low \(\kappa\).

In our previous study, \(^9\) TlMTe\(_2\) (\(M = \text{Ga}, \text{In}, \) or \(\text{Tl}\)) were prepared and characterized, in order to discuss the role of \(\text{Tl}\) in the extremely low \(\kappa\) materials, because Ga, In, and Tl are the related elements in the Periodic Table. The correlations among the \(\kappa\) values of TlGaTe\(_2\), TlInTe\(_2\), and TlTlTe\(_2\) (TlTe) were studied. We predicted that TlTe exhibits the lowest \(\kappa\), but the \(\kappa\) of TlTe was unexpectedly high (\(\sim 4 \text{Wm}^{-1}\text{K}^{-1}\)), while those of TlGaTe\(_2\) and TlInTe\(_2\) were extremely low (\(<0.5 \text{Wm}^{-1}\text{K}^{-1}\)). TlTe is well known as a mixed valence compound containing monovalent and trivalent \(\text{Tl}\), i.e., \((\text{Tl}^{1+}) (\text{Tl}^{3+})(\text{Te}^{2-})_2\) \(^10\) while TlGaTe\(_2\) and TlInTe\(_2\) include only monovalent \(\text{Tl}\), i.e., \((\text{Tl}^{1+})(\text{Ga}^{3+})(\text{Te}^{2-})_2\) and \((\text{Tl}^{1+})(\text{In}^{3+})(\text{Te}^{2-})_2\). Therefore, we consider that there are some relations between the unexpectedly high \(\kappa\) of TlTe and the valence state of \(\text{Tl}\).

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In the present study, \(\text{Tl}_2\text{Te}\), \(\text{Tl}_5\text{Te}_3\), TlTe, and \(\text{Tl}_2\text{Te}_3\) were prepared and characterized in order to make a discussion on the role of the valence state of \(\text{Tl}\) in the Tl-Te binary system. In \(\text{Tl}_2\text{Te}\) and \(\text{Tl}_5\text{Te}_3\), \(\text{Tl}\) would take only monovalent or trivalent, i.e., \((\text{Tl}^{1+})(\text{Te}^{2-})\) and \((\text{Tl}^{3+})(\text{Te}^{2-})_3\), whereas in \(\text{Tl}_3\text{Te}_3\) and TlTe, \(\text{Tl}\) would take mixed valence states, i.e., \((\text{Tl}^{1+})(\text{Tl}^{3+})(\text{Te}^{2-})_3\) and \((\text{Tl}^{1+})(\text{Tl}^{3+})(\text{Te}^{2-})_2\).

2. Experimental Details

\(\text{Tl}_3\text{Te}_3\), TlTe, and \(\text{Tl}_2\text{Te}_3\) were prepared from appropriate amounts of \(\text{Tl}_2\text{Te}\) and Te ingots. \(\text{Tl}_2\text{Te}\) and Te were supplied from the Furuuchi Chemical Co. Ltd. The starting materials were melted in sealed silica tubes at 1273 K for 3 h and annealed at slightly below the melting temperatures for 2 weeks. The obtained intermediate ingots were crushed to fine powders, then hot-pressed at appropriate temperatures for 2 h in an Ar-flow atmosphere. Column-shaped (7 mm in diameter and 14 mm in height) and disc-shaped (10 mm in diameter and 1.7 mm in thickness) pellets were prepared for thermoelectric characterization. The density of the pellets was calculated based on the measured weight and dimensions.

The obtained samples were characterized with a powder x-ray diffraction (XRD) method using Cu \(K\alpha\) radiation at room temperature. Electrical resistivity (\(\rho\)) and Seebeck coefficient (\(S\)) were measured by using a commercially available apparatus (ULVAC, ZEM-1) in a He atmosphere. Thermal conductivity (\(\kappa\)) was evaluated from thermal diffusivity (\(\alpha\)), heat capacity (\(C_p\)), and sample density (\(d\)) based on the relationship \(\kappa = \alpha C_p d^2\). Thermal diffusivity was measured by the laser flash technique in a vacuum using a commercially available apparatus (ULVAC TC-7000). The thermoelectric properties were measured from room temperature to 420~590 K.

3. Results and Discussion

The powder XRD patterns of the polycrystalline \(\text{Tl}_2\text{Te}\), \(\text{Tl}_3\text{Te}_3\), TlTe, and \(\text{Tl}_2\text{Te}_3\) are shown in Fig. 1, together with the peak positions calculated from the reported crystal
The XRD patterns of Tl$_2$Te, TlTe, and Tl$_2$Te$_3$ are well consistent with the literature data, so it can be said that the pure compounds with no impurities could be obtained. As for Tl$_5$Te$_3$, since its structure has not been identified, the XRD pattern of our sample was compared with that of similar compound: Tl$_3$Te$_3$. The XRD pattern of Tl$_2$Te seems to be consistent with that of Tl$_3$Te$_3$.

Assuming that the structure of Tl$_2$Te is identical with Tl$_3$Te$_3$, the tetragonal lattice parameters were calculated to be $a = 0.8931$ nm and $c = 1.2609$ nm. For the possible composition, we considered a case that vacancies occupy only the tellurium site, i.e. Tl$_2$Te [= Tl$_3$(Te$_2$)$_3$V$_{A_{0.5}}$], where VA means vacancy, and the theoretical density was calculated to be 8.86 g cm$^{-3}$. The sample’s bulk density was 8.76 g cm$^{-3}$, corresponding to approximately 99% of the theoretical density. Therefore, the composition considered here would be suitable. Anyway, we are now carrying out the Rietveld refinement. The correct structure will be reported in near future. The lattice parameters of all compounds calculated from the XRD patterns are summarized in Table 1. The theoretical x-ray densities of the compounds were determined and compared to the sample’s bulk densities. The density values are summarized in Table 1. Note that since the hot-press pressure for the disc-shaped pellets was slightly lower than that for the column-shaped pellets, the disc-shaped pellets indicated slightly low density compared to the column-shaped pellets.

The temperature dependences of the electrical properties of Tl$_2$Te, Tl$_3$Te$_3$, TlTe, and Tl$_2$Te$_3$ are shown in Fig. 2. It is confirmed that the all four compounds show positive values of $S$ indicating that the majority of charge carriers are holes. Tl$_2$Te$_3$ exhibited the largest $S$ and $\rho$ with negative temperature dependences. On the other hand, Tl$_3$Te$_3$ and TlTe showed typical metallic characteristics, i.e. low $\rho$ with small $S$ and they showed tendencies to increase with increasing temperature. Tl$_2$Te exhibited the intermediate characteristics; it indicated moderate $S$ values for thermoelectric materials but the $\rho$ values were too high, leading to low power factor. The power factor ($S^2/\rho^{1/2}$) which determines the electrical performance of thermoelectric materials, increased with increasing temperature for all compounds. The highest values were $0.12 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ at 587 K, $0.26 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ at 558 K, $0.40 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ at 463 K, and $0.04 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ at 419 K for Tl$_2$Te, Tl$_3$Te$_3$, TlTe, and Tl$_2$Te$_3$, respectively.

The temperature dependences of $\kappa$ of Tl$_2$Te, Tl$_3$Te$_3$, TlTe, and Tl$_2$Te$_3$ are shown in Fig. 3. The $\kappa$ of Tl$_3$Te$_3$ and TlTe were considerably high (3.5–4.0 W m$^{-1}$ K$^{-1}$), while those of

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Fig. 1 Powder XRD patterns of the samples. (a) Tl$_2$Te, (b) Tl$_3$Te$_3$, (c) TlTe, and (d) Tl$_2$Te$_3$.

Fig. 2 Temperature dependence of the electrical properties of Tl$_2$Te, Tl$_3$Te$_3$, TlTe, and Tl$_2$Te$_3$. (a) electrical resistivity $\rho$, (b) Seebeck coefficient $S$, and (c) power factor, $S^2/\rho^{1/2}$.

Fig. 3 Temperature dependence of the electrical properties of Tl$_2$Te, Tl$_3$Te$_3$, TlTe, and Tl$_2$Te$_3$.
Tl$_2$Te and Tl$_2$Te$_3$ were extremely low (~0.5 Wm$^{-1}$K$^{-1}$). Since thallium tellurides studied so far indicate very low $\kappa$, it can be said that the $\kappa$ of Tl$_2$Te$_3$ and TITe are exceptionally high. It is well known that the total thermal conductivity ($\kappa_{\text{total}}$) of solids is mainly composed of two components: the lattice term ($\kappa_{\text{lat}}$) and the electronic term ($\kappa_{\text{el}}$). The $\kappa_{\text{el}}$ was roughly estimated based on the Wiedemann-Franz relation using the $\rho$ data and the Lorenz number ($2.45 \times 10^{-8}$ W$^2$K$^{-2}$), and the $\kappa_{\text{lat}}$ was obtained by subtracting the $\kappa_{\text{el}}$ from the $\kappa_{\text{total}}$. At room temperature, the fractions of $\kappa_{\text{el}}$ to $\kappa_{\text{total}}$ were near zero for Tl$_2$Te and Tl$_2$Te$_3$, whereas it reached 65% and 30% for Tl$_5$Te$_3$ and TITe, respectively. In Fig. 3, the $\kappa_{\text{lat}}$ of Tl$_5$Te$_3$ and TITe are also plotted. From this figure, it can be confirmed that the high $\kappa$ of TITe was due to not only its high $\kappa_{\text{el}}$ but also its intrinsically high $\kappa_{\text{lat}}$. However, as for Tl$_5$Te$_3$, the $\kappa_{\text{lat}}$ was not so high to be around 1 Wm$^{-1}$K$^{-1}$, and the high $\kappa$ was mainly attributed to the large electronic contribution.

In general, $\kappa_{\text{lat}}$ is related with crystal structure and interatomic bonding, that is, complex crystal structure and weak interatomic bonding would lead to low $\kappa_{\text{lat}}$. In the present study, in order to estimate the strength of interatomic bonding, we performed ultrasonic pulse echo measurements on the column-shaped pellets of Tl$_2$Te, Tl$_5$Te$_3$, TITe, and Tl$_2$Te$_3$, and evaluated the Debye temperature ($\theta_D$), because low $\theta_D$ generally means weak interatomic bonding. The $\theta_D$ values are summarized in Table 1. We obtained reasonable results, i.e. the $\theta_D$ values are very low for all compounds. On the other hand, the numbers of atoms per unit cell ($N$) are also summarized in Table 1. Generally, $N$ gives an indication of complexity of the crystal, i.e. the larger $N$ means more complex structure. The $N$ values of Tl$_5$Te$_3$ and TITe are 32, which are larger than those of Tl$_2$Te (30) and Tl$_2$Te$_3$ (20). Therefore, from the viewpoints of both crystal structure and interatomic bonding, Tl$_5$Te$_3$ and TITe should exhibit low $\kappa_{\text{lat}}$. However, we got the opposite results. In addition, the $\kappa_{\text{lat}}$ values at 300 K of the TI-Te binary compounds are plotted as a function of the valence state of TI, as shown in the inset of Fig. 3. It seems that there is a clear relationship between the $\kappa_{\text{lat}}$ and the valence state of TI, i.e. the $\kappa_{\text{lat}}$ described a parabolic curve and exhibited a maximum at Tl$^{2+}$. It can be said that the magnitude relations of $\kappa$ for the TI-Te binary compounds are closely related with the valence state of TI.

![Fig. 3](image1.png)  
**Fig. 3** Temperature dependence of the thermal conductivity $\kappa$ of Tl$_2$Te, Tl$_5$Te$_3$, TITe, and Tl$_2$Te$_3$. Inset: Relationship between the $\kappa_{\text{lat}}$ at 300 K and the valence state of TI. 

Since thallium tellurides studied so far indicate very low $\kappa$, it can be said that the $\kappa$ of Tl$_2$Te$_3$ and TITe are exceptionally high. It is well known that the total thermal conductivity ($\kappa_{\text{total}}$) of solids is mainly composed of two components: the lattice term ($\kappa_{\text{lat}}$) and the electronic term ($\kappa_{\text{el}}$). The $\kappa_{\text{el}}$ was roughly estimated based on the Wiedemann-Franz relation using the $\rho$ data and the Lorenz number ($2.45 \times 10^{-8}$ W$^2$K$^{-2}$), and the $\kappa_{\text{lat}}$ was obtained by subtracting the $\kappa_{\text{el}}$ from the $\kappa_{\text{total}}$. At room temperature, the fractions of $\kappa_{\text{el}}$ to $\kappa_{\text{total}}$ were near zero for Tl$_2$Te and Tl$_2$Te$_3$, whereas it reached 65% and 30% for Tl$_5$Te$_3$ and TITe, respectively. In Fig. 3, the $\kappa_{\text{lat}}$ of Tl$_5$Te$_3$ and TITe are also plotted. From this figure, it can be confirmed that the high $\kappa$ of TITe was due to not only its high $\kappa_{\text{el}}$ but also its intrinsically high $\kappa_{\text{lat}}$. However, as for Tl$_5$Te$_3$, the $\kappa_{\text{lat}}$ was not so high to be around 1 Wm$^{-1}$K$^{-1}$, and the high $\kappa$ was mainly attributed to the large electronic contribution.

In general, $\kappa_{\text{lat}}$ is related with crystal structure and interatomic bonding, that is, complex crystal structure and weak interatomic bonding would lead to low $\kappa_{\text{lat}}$. In the present study, in order to estimate the strength of interatomic bonding, we performed ultrasonic pulse echo measurements on the column-shaped pellets of Tl$_2$Te, Tl$_5$Te$_3$, TITe, and Tl$_2$Te$_3$, and evaluated the Debye temperature ($\theta_D$), because low $\theta_D$ generally means weak interatomic bonding. The $\theta_D$ values are summarized in Table 1. We obtained reasonable results, i.e. the $\theta_D$ values are very low for all compounds. On the other hand, the numbers of atoms per unit cell ($N$) are also summarized in Table 1. Generally, $N$ gives an indication of complexity of the crystal, i.e. the larger $N$ means more complex structure. The $N$ values of Tl$_5$Te$_3$ and TITe are 32, which are larger than those of Tl$_2$Te (30) and Tl$_2$Te$_3$ (20). Therefore, from the viewpoints of both crystal structure and interatomic bonding, Tl$_5$Te$_3$ and TITe should exhibit low $\kappa_{\text{lat}}$. However, we got the opposite results. In addition, the $\kappa_{\text{lat}}$ values at 300 K of the TI-Te binary compounds are plotted as a function of the valence state of TI, as shown in the inset of Fig. 3. It seems that there is a clear relationship between the $\kappa_{\text{lat}}$ and the valence state of TI, i.e. the $\kappa_{\text{lat}}$ described a parabolic curve and exhibited a maximum at Tl$^{2+}$. It can be said that the magnitude relations of $\kappa$ for the TI-Te binary compounds are closely related with the valence state of TI. The present study implies that the extremely low $\kappa$ observed in many thallium tellurides cannot be explained by only the existence of TI. It was revealed that the valence state of TI should be considered to discuss the magnitude relations of $\kappa$ of the thallium tellurides.

Finally, the temperature dependences of $ZT$ of Tl$_2$Te, Tl$_5$Te$_3$, TITe, and Tl$_2$Te$_3$ are shown in Fig. 4. Tl$_2$Te indicated the highest $ZT$ value of around 0.2 at 586 K. Since the electrical performance of Tl$_2$Te was not superior, this high $ZT$ value was caused by its very low $\kappa$ (~0.5 Wm$^{-1}$K$^{-1}$) comparable to those of several thallium tellurides known as the extremely low $\kappa$ materials. Meanwhile, the $ZT$ values of Tl$_5$Te$_3$, TITe, and Tl$_2$Te$_3$ were quite low compared with that of Tl$_2$Te. Although Tl$_5$Te$_3$ and TITe exhibited high power factor, the $\kappa$ values were also high leading to the low $ZT$.

### 4. Summary

Polycrystalline samples of Tl$_2$Te, Tl$_5$Te$_3$, TITe, and Tl$_2$Te$_3$ were prepared and the thermoelectric properties were studied from room temperature to slightly below the melting temperatures. The electrical performance of these materials was not so good, e.g. the maximum power factor was obtained for TITe to be $0.40 \times 10^{-3}$ Wm$^{-1}$K$^{-2}$ at 463 K. As expected, the $\kappa$ values of Tl$_2$Te and Tl$_2$Te$_3$ were extremely low to be around 0.5 Wm$^{-1}$K$^{-1}$, while those of Tl$_5$Te$_3$ and TITe were unexpectedly high (about 4 Wm$^{-1}$K$^{-1}$). This high $\kappa$ of TITe was caused by not only its large $\kappa_{\text{el}}$ but also its intrinsically high $\kappa_{\text{lat}}$. On the other hand, the $\kappa_{\text{lat}}$ of Tl$_5$Te$_3$ was not so high to be around 1 Wm$^{-1}$K$^{-1}$, and the high $\kappa$ was attributed to the large $\kappa_{\text{el}}$. The magnitude relations of $\kappa_{\text{lat}}$ did not follow a general lattice thermal conductivity theory in which complex crystal structure and weak interatomic bonding lead to low $\kappa_{\text{lat}}$. The present study revealed that the valence state of TI was very important to discuss the magnitude relations of $\kappa_{\text{lat}}$ in the TI-Te binary compounds, that is, the $\kappa_{\text{lat}}$ exhibited a maximum when TI took bivalence. Tl$_2$Te exhibited relatively high $ZT$ to be around 0.2 at 586 K. Now we continue to investigate the relationship between the $\kappa_{\text{lat}}$ and the valence state of TI in various thallium tellurides. These results will be reported in near future.
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REFERENCES