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Thermoelectric Properties of the Thallium-Tellurium Binary Compounds

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We are paying attention to extremely low thermal conductivity (κ) materials which have a potential to be next generation thermoelectric materials. Most of the extremely low κ materials that have been reported so far are ternary thallium tellurides such as Ag-Tl-Te ternary system. However, as for Tl-Te binary system, the thermoelectric properties have been scarcely reported. In the present study, the Tl-Te binary compounds, Tl_2Te, Tl_5Te_3, TlTe, and Tl_2Te_3, were prepared and their thermoelectric properties were investigated. The κ of TlTe was relatively high (approximately 4 $Wm^{-1}K^{-1}$ at 300 K), while those of Tl_2Te and Tl_2Te_3 were extremely low ($\sim$0.5 $Wm^{-1}K^{-1}$ at 300 K). These compounds indicated relatively high thermoelectric figure of merit *ZT*, e.g., Tl_2Te 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, ρ is the electrical resistivity, κ is the thermal conductivity, and T is the absolute temperature.[1] *ZT* value of the materials used in current devices is approximately 1. In recent years, several classes of bulk materials with high *ZT* have been discovered, including filled skutterudites,[2] zinc antimonide,[3] $CsBi_4Te_6$,[4] $AgPb_mSbTe_{2+m}$,[5] and Tl-doped PbTe.[6]

Against this background, we are paying attention to extremely low κ materials as next generation thermoelectric materials. Here, the extremely low κ means below 0.5 $Wm^{-1}K^{-1}$, which is about one-third or one-forth of those of typical thermoelectric materials such as Bi_2Te_3 and PbTe. Most of the extremely low κ materials that have been reported so far are thallium tellurides, e.g. Ag_9TlTe_5 (κ = 0.22 $Wm^{-1}K^{-1}$)[7] and Tl_4SnTe_3 ($\kappa = \sim$0.5 $Wm^{-1}K^{-1}$).[8] Therefore, Tl would play some roles in appearing the extremely low κ.

In our previous study,[9] $TlMTe_2$ (M = Ga, In, or Tl) were prepared and characterized, in order to discuss the role of Tl in the extremely low κ materials, because Ga, In, and Tl are the related elements in the Periodic Table. The correlations among the κ values of $TlGaTe_2$, $TlInTe_2$, and $TlTlTe_2$ (TlTe) were studied. We predicted that TlTe exhibits the lowest κ, but the κ of TlTe was unexpectedly high ($\sim$4 $Wm^{-1}K^{-1}$), while those of $TlGaTe_2$ and $TlInTe_2$ were extremely low ($\sim$0.5 $Wm^{-1}K^{-1}$). TlTe is well known as a mixed valence compound containing monovalent and trivalent Tl, i.e. $(Tl^{1+})(Tl^{3+})(Te^{2-})_2$,[10] while $TlGaTe_2$ and $TlInTe_2$ include only monovalent Tl, i.e. $(Tl^{1+})(Ga^{3+})(Te^{2-})_2$ and $(Tl^{1+})(In^{3+})(Te^{2-})_2$. Therefore, we consider that there are some relations between the unexpectedly high κ of TlTe and the valence state of Tl.

In the present study, Tl_2Te, Tl_5Te_3, TlTe, and Tl_2Te_3 were prepared and characterized in order to make a discussion on the role of the valence state of Tl in the Tl-Te binary system. In Tl_2Te and Tl_2Te_3, Tl would take only monovalent or trivalent, i.e. $(Tl^{1+})_2(Te^{2-})$ and $(Tl^{3+})_2(Te^{2-})_3$, whereas in Tl_5Te_3 and TlTe, Tl would take mixed valence states, i.e. $(Tl^{1+})_9(Tl^{3+})(Te^{2-})_6$ and $(Tl^{1+})(Tl^{3+})(Te^{2-})_2$.

2. Experimental Details

Tl_5Te_3, TlTe, and Tl_2Te_3 were prepared from appropriate amounts of Tl_2Te and Te ingots. Tl_2Te 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 (ρ) and Seebeck coefficient (S) were measured by using a commercially available apparatus (ULVAC, ZEM-1) in a He atmosphere. Thermal conductivity (κ) was evaluated from thermal diffusivity (α), heat capacity (C_p), and sample density (d) based on the relationship $\kappa = \alpha C_p d$. 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$\sim$590 K.

3. Results and Discussion

The powder XRD patterns of the polycrystalline Tl_2Te, Tl_5Te_3, TlTe, and Tl_2Te_3 are shown in Fig. 1, together with the peak positions calculated from the reported crystal

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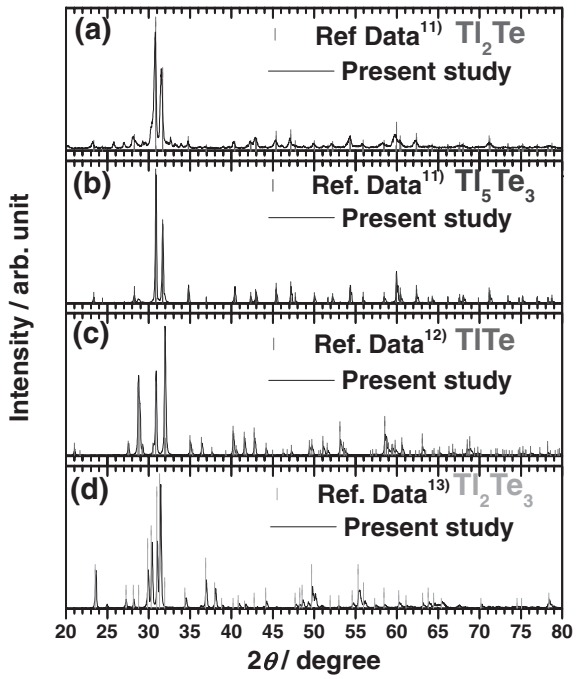

Fig. 1 Powder XRD patterns of the samples. (a) Tl_2Te, (b) Tl_5Te_3, (c) TlTe, and (d) Tl_2Te_3.

structures.[11–13] The XRD patterns of Tl_5Te_3, TlTe, and Tl_2Te_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_2Te, since its structure has not been identified, the XRD pattern of our sample was compared with that of similar compound: Tl_5Te_3. The XRD pattern of Tl_2Te seems to be consistent with that of Tl_5Te_3.

Assuming that the structure of Tl_2Te is identical with Tl_5Te_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_2Te [$= Tl_5(Te_{2.5}VA_{0.5})$, where VA means vacancy], and the theoretical density was calculated to be 8.86 gcm^{-3}. The sample's bulk density was 8.76 gcm^{-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_2Te, Tl_5Te_3, TlTe, and Tl_2Te_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_2Te_3 exhibited the largest S and ρ with negative temperature dependences. On the other hand, Tl_5Te_3 and TlTe showed typical metallic characteristics, i.e. low ρ with small S and they showed tendencies to increase with increasing

Table 1 Crystallographic data, sample bulk density, and Debye temperature of Tl_2Te, Tl_5Te_3, TlTe, and Tl_2Te_3.

		Tl_2Te	Tl_5Te_3	TlTe	Tl_2Te_3
Crystal system		Tetragonal			Monoclinic
Space group		I4/mcm			Cc
Number of atoms /unit cell		30	32	32	20
Lattice parameters at room temperature	a (nm)	0.8931	0.8929	1.2915	1.7413
	b (nm)	—	—	—	0.6564
	c (nm)	1.2609	1.2607	0.6179	0.7919
	β (degree)	—	—	—	133.16
Column-shaped (7 mm × 14 mm)	(gcm^{-3})	8.67	9.20	8.41	6.59
	(%T.D.)	98	99	99	83
Disc-shaped (10 mm × 1.7 mm)	(gcm^{-3})	8.76	8.98	8.20	6.43
	(%T.D.)	99	97	96	81
Debye Temperature	(K)	107	124	110	108

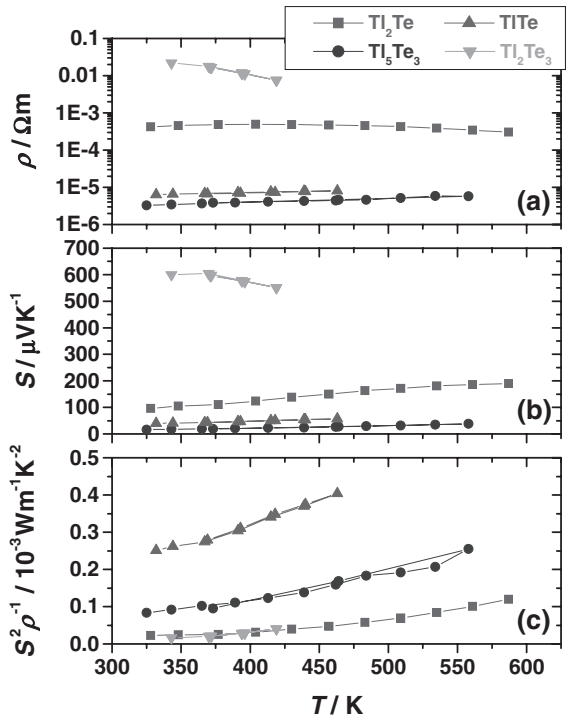

Fig. 2 Temperature dependence of the electrical properties of Tl_2Te, Tl_5Te_3, TlTe, and Tl_2Te_3. (a) electrical resistivity ρ, (b) Seebeck coefficient S, and (c) power factor, $S^2\rho^{-1}$.

temperature. Tl_2Te exhibited the intermediate characteristics; it indicated moderate S values for thermoelectric materials but the ρ values were too high, leading to low power factor. The power factor ($S^2\rho^{-1}$) which determines the electrical performance of thermoelectric materials, increased with increasing temperature for all compounds. The highest values were 0.12×10^{-3} $Wm^{-1}K^{-2}$ at 587 K, 0.26×10^{-3} $Wm^{-1}K^{-2}$ at 558 K, 0.40×10^{-3} $Wm^{-1}K^{-2}$ at 463 K, and 0.04×10^{-3} $Wm^{-1}K^{-2}$ at 419 K for Tl_2Te, Tl_5Te_3, TlTe, and Tl_2Te_3, respectively.

The temperature dependences of κ of Tl_2Te, Tl_5Te_3, TlTe, and Tl_2Te_3 are shown in Fig. 3. The κ of Tl_5Te_3 and TlTe were considerably high (3.5~4.0 $Wm^{-1}K^{-1}$), while those of

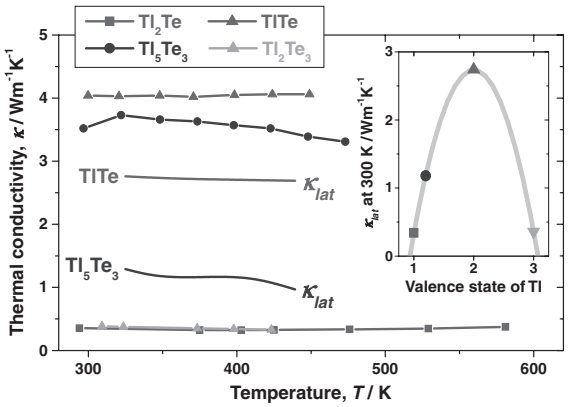

Fig. 3 Temperature dependence of the thermal conductivity κ of Tl_2Te, Tl_5Te_3, TlTe, and Tl_2Te_3. Inset: Relationship between the κ_{lat} at 300 K and the valence state of Tl.

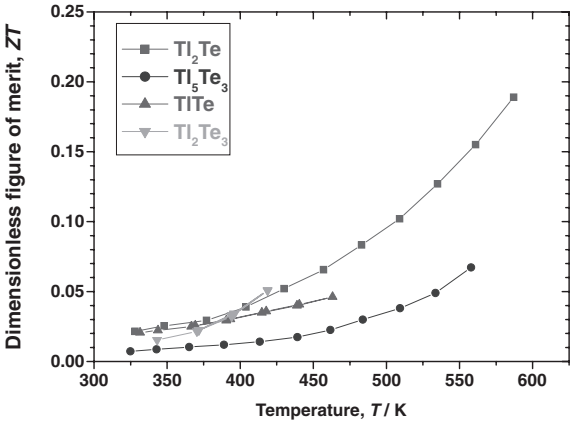

Fig. 4 Temperature dependence of the dimensionless figure of merit ZT of Tl_2Te, Tl_5Te_3, TlTe, and Tl_2Te_3.

Tl_2Te and Tl_2Te_3 were extremely low ($\sim 0.5\,Wm^{-1}K^{-1}$). Since thallium tellurides studied so far indicate very low κ, it can be said that the κ of Tl_5Te_3 and TlTe are exceptionally high. It is well known that the total thermal conductivity (κ_{total}) of solids is mainly composed of two components: the lattice term (κ_{lat}) and the electronic term (κ_{el}). The κ_{el} was roughly estimated based on the Wiedemann-Franz relation using the ρ data and the Lorenz number (2.45×10^{-8} $W\Omega K^{-2}$), and the κ_{lat} was obtained by subtracting the κ_{el} from the κ_{total}. At room temperature, the fractions of κ_{el} to κ_{total} were near zero for Tl_2Te and Tl_2Te_3, whereas it reached 65% and 30% for Tl_5Te_3 and TlTe, respectively. In Fig. 3, the κ_{lat} of Tl_5Te_3 and TlTe are also plotted. From this figure, it can be confirmed that the high κ of TlTe was due to not only its high κ_{el} but also its intrinsically high κ_{lat}. However, as for Tl_5Te_3, the κ_{lat} was not so high to be around $1\,Wm^{-1}K^{-1}$, and the high κ was mainly attributed to the large electronic contribution.

In general, κ_{lat} is related with crystal structure and interatomic bonding, that is, complex crystal structure and weak interatomic bonding would lead to low κ_{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_2Te, Tl_5Te_3, TlTe, and Tl_2Te_3, and evaluated the Debye temperature (θ_D), because low θ_D generally means weak interatomic bonding. The θ_D values are summarized in Table 1. We obtained reasonable results, i.e. the θ_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_5Te_3 and TlTe are 32, which are larger than those of Tl_2Te (30) and Tl_2Te_3 (20). Therefore, from the viewpoints of both crystal structure and interatomic bonding, Tl_5Te_3 and TlTe should exhibit low κ_{lat}. However, we got the opposite results. In addition, the κ_{lat} values at 300 K of the Tl-Te binary compounds are plotted as a function of the valence state of Tl, as shown in the inset of Fig. 3. It seems that there is a clear relationship between the κ_{lat} and the valence state of Tl, i.e. the κ_{lat} described a parabolic curve and exhibited a maximum at Tl^{2+}. It can be said that the magnitude relations of κ for the Tl-Te binary compounds are closely related with the valence state of Tl. The present study implies that the extremely low κ observed in many thallium tellurides cannot be explained by only the existence of Tl. It was revealed that the valence state of Tl should be considered to discuss the magnitude relations of κ of the thallium tellurides.

Finally, the temperature dependences of ZT of Tl_2Te, Tl_5Te_3, TlTe, and Tl_2Te_3 are shown in Fig. 4. Tl_2Te indicated the highest ZT value of around 0.2 at 586 K. Since the electrical performance of Tl_2Te was not superior, this high ZT value was caused by its very low κ ($\sim 0.5\,Wm^{-1}K^{-1}$) comparable to those of several thallium tellurides known as the extremely low κ materials. Meanwhile, the ZT values of Tl_5Te_3, TlTe, and Tl_2Te_3 were quite low compared with that of Tl_2Te. Although Tl_5Te_3 and TlTe exhibited high power factor, the κ values were also high leading to the low ZT.

4. Summary

Polycrystalline samples of Tl_2Te, Tl_5Te_3, TlTe, and Tl_2Te_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 TlTe to be $0.40 \times 10^{-3}\,Wm^{-1}K^{-2}$ at 463 K. As expected, the κ values of Tl_2Te and Tl_2Te_3 were extremely low to be around $0.5\,Wm^{-1}K^{-1}$, while those of Tl_5Te_3 and TlTe were unexpectedly high (about $4\,Wm^{-1}K^{-1}$). This high κ of TlTe was caused by not only its large κ_{el} but also its intrinsically high κ_{lat}. On the other hand, the κ_{lat} of Tl_5Te_3 was not so high to be around $1\,Wm^{-1}K^{-1}$, and the high κ was attributed to the large κ_{el}. The magnitude relations of κ_{lat} did not follow a general lattice thermal conductivity theory in which complex crystal structure and weak interatomic bonding lead to low κ_{lat}. The present study revealed that the valence state of Tl was very important to discuss the magnitude relations of κ_{lat} in the Tl-Te binary compounds, that is, the κ_{lat} exhibited a maximum when Tl took bivalence. Tl_2Te exhibited relatively high ZT to be around 0.2 at 586 K. Now we continue to investigate the relationship between the κ_{lat} and the valence state of Tl in various thallium tellurides. These results will be reported in near future.

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