Thermoelectric Properties of Thallium Compounds with Extremely Low Thermal Conductivity

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Polycrystalline samples of thallium compounds, Tl_9BiTe_6 , TlBiTe_2 , TlSbTe_2 , and AgTlTe were prepared and the thermoelectric properties such as the electrical resistivity, Seebeck coefficient, and thermal conductivity were measured. The Seebeck coefficients of Tl_9BiTe_6 , TlSbTe_2 , and AgTlTe are positive, while that of TlBiTe_2 is negative. The thermal conductivities of these thallium compounds are very low compared with state-of-the-art thermoelectric materials. Especially, AgTlTe indicates extremely low value, $0.25 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature. The dimensionless figure of merit ZT of thallium compounds are relatively high due to their very low thermal conductivities. The maximum value of ZT is obtained for TlSbTe_2 as 0.87 at 715 K.

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1. Introduction

The effectiveness of a material for thermoelectric applications is determined by the dimensionless figure of merit ZT ,¹⁾ where T is the absolute temperature and $Z = (S^2\sigma)/\kappa$ (S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity). The power factor ($S^2\sigma$) can be optimized as a function of the carrier concentration; therefore, the thermal conductivity must be reduced to obtain maximum ZT . The ZT value of the materials used in the current devices is about 1.

Thallium compounds have been a focus of attention as new thermoelectric materials because they have very low thermal conductivities. For example, the thermoelectric properties of some thallium compounds, such as Tl_2SnTe_5 , Tl_9BiTe_6 , and thallium filled skutterudites ($\text{Tl}_{0.22}\text{Co}_4\text{Sb}_{12}$) have been reported. The maximum ZT values of these thallium compounds are $ZT = 0.6$ at 300 K for Tl_2SnTe_5 ,²⁾ $ZT = 1.2$ at around 500 K for Tl_9BiTe_6 ,³⁾ and $ZT = 0.8$ at 800 K for $\text{Tl}_{0.22}\text{Co}_4\text{Sb}_{12}$.⁴⁾ However, thallium and its compounds are toxic. Thallium may cause cancer. Therefore, they should be handled carefully.

In our previous study, we prepared polycrystalline samples of Tl_9BiTe_6 ,⁵⁾ TlBiTe_2 ,⁶⁾ and TlSbTe_2 ,⁷⁾ and measured the thermoelectric properties such as the electrical resistivity, Seebeck coefficient, and thermal conductivity. In the present study, we prepared polycrystalline samples of AgTlTe and measured the thermoelectric properties. We also studied the heat conduction mechanism of AgTlTe from the Wiedemann–Franz–Lorenz relation and simplest estimation of the minimum lattice thermal conductivity.

2. Experimental

The polycrystalline-sintered samples of Tl_9BiTe_6 , TlBiTe_2 , TlSbTe_2 , and AgTlTe were prepared by solid-state reactions. The preparation methods for polycrystalline-sintered samples of Tl_9BiTe_6 , TlBiTe_2 , and TlSbTe_2 have been reported elsewhere.^{5–7)} The polycrystalline-sintered sample of AgTlTe was prepared from appropriate amounts of Ag_2Te and Tl_2Te . The mixed substances were melted in

sealed quartz ampoules at 923 K for 5 h. And then, the intermediates were crushed and pressed into pellets followed by sintering in sealed quartz ampoules at 623 K for 10 h.

The density of samples was calculated from measured weight and dimension. The crystal structure was analyzed by applying a powder X-ray diffraction method at room temperature using $\text{Cu-K}\alpha$ radiation. The chemical composition was determined by EDX analysis.

In the temperature range between room temperature and about 600 K, the electrical resistivity and Seebeck coefficient were measured simultaneously using an ULVAC ZEM-1 apparatus in helium atmosphere. The Seebeck coefficient was measured in a temperature gradient of about 5 K. The thermal diffusivity was measured by applying a laser flash method from room temperature to about 850 K in vacuum (10^{-4} Pa) using ULVAC TC-7000 apparatus. The thermal diffusivity at a temperature obtained during the heating process was checked with that during the cooling cycle. The thermal conductivity was calculated from the thermal diffusivity α , heat capacity C_p , and density ρ , using the standard expression: $\kappa = \alpha C_p \rho$. The heat capacity of TlBiTe_2 was measured using the triple cell DSC.⁸⁾ The heat capacities of Tl_9BiTe_6 , TlSbTe_2 , and AgTlTe were estimated from those of Tl_2Te , Bi_2Te_3 , Sb_2Te_3 , and Ag_2Te by the Neumann-Kopp law using literature data.^{9,10)} The measured heat capacity of TlBiTe_2 agrees with the estimated data obtained from those of Tl_2Te and Bi_2Te_3 . It is considered that the estimated heat capacities of Tl_9BiTe_6 , TlSbTe_2 , and AgTlTe are almost identical with the measured data.

3. Results and Discussion

The X-ray diffraction pattern of AgTlTe is shown in Fig. 1, together with the pattern calculated from the reported crystal structure.¹¹⁾ The XRD patterns of our AgTlTe well agree with literature data. In case of Tl_9BiTe_6 , TlBiTe_2 , and TlSbTe_2 , it is confirmed that the single phases are obtained in the present study. The lattice parameters of the compounds evaluated from the X-ray diffraction patterns are shown in Table 1. The lattice parameters are almost the same as literature data.¹¹⁾ The chemical compositions determined by

Fig. 1 X-ray diffraction pattern of AgTlTe, together with literature data.¹¹⁾

Fig. 2 Temperature dependence of electrical properties of thallium compounds,^{5–7)} together with literature data:^{1,12)} (a) electrical resistivity, (b) Seebeck coefficient.

Table 1 Sample characteristics and thermoelectric properties of Tl₉BiTe₆, TlBiTe₂, TlSbTe₂, and AgTlTe.

		Tl ₉ BiTe ₆	TlBiTe ₂	TlSbTe ₂	AgTlTe
Crystal system		Tetragonal	Hexagonal	Hexagonal	Orthorhombic
Lattice parameter	<i>a</i> (nm)	0.886	0.451	0.442	0.880
	<i>b</i> (nm)	—	—	—	0.488
	<i>c</i> (nm)	1.305	2.310	2.330	0.777
Sample density	(%T.D.)	98	96	95	90
Maximum power factor	(Wm ⁻¹ K ⁻²)	6.2 × 10 ⁻⁴ (590 K)	3.8 × 10 ⁻⁴ (340 K)	8.9 × 10 ⁻⁴ (570 K)	2.5 × 10 ⁻⁴ (580 K)
Thermal conductivity at room temp.	(Wm ⁻¹ K ⁻¹)	0.39	1.73	1.42	0.25
Maximum ZT	(—)	0.86 (590 K)	0.15 (760 K)	0.87 (715 K)	0.61 (580 K)

the EDX analysis do not deviate from the stoichiometric compositions. The bulk densities of all samples are above 90% of the theoretical densities.

The temperature dependence of electrical resistivities ρ and Seebeck coefficients of thallium compounds^{5–7)} is shown in Fig. 2, together with the data of other substances.^{1,12)} In this figure, TAGS refers to the alloys (GeTe)_{1–x}(AgSbTe₂)_x, which is derived from the names of the major constituents, tellurium, antimony, germanium, and silver. In case of Tl₉BiTe₆, TlBiTe₂, and TlSbTe₂, the electrical resistivities increase with temperature, indicating simple metallic behavior. On the other hand, the electrical resistivity of AgTlTe decreases with temperature, indicating semiconducting be-

havior. The values of electrical resistivities of Tl₉BiTe₆, TlBiTe₂, and TlSbTe₂ are of an order of magnitude of 10⁻⁴ (Ωm), which is slightly higher than those of state-of-the-art thermoelectric materials. The Seebeck coefficients of Tl₉BiTe₆, TlSbTe₂, and AgTlTe are positive in the whole temperature range, showing that the majority of charge carriers are holes. On the other hand, the Seebeck coefficient of TlBiTe₂ is negative. The maximum absolute values of Seebeck coefficients of Tl₉BiTe₆ and TlSbTe₂ are 235 μVK⁻¹ at 588 K and 224 μVK⁻¹ at 666 K, respectively. These values are comparable to those of state-of-the-art thermoelectric materials.

The power factor, which is defined as $S^2\sigma$ or S^2/ρ , was

Fig. 3 Temperature dependence of thermal conductivities of thallium compounds,^{5–7)} together with literature data:^{1,12)} (a) measured thermal conductivity, (b) several contributions to thermal conductivity of AgTlTe.

calculated from the data of electrical resistivity and Seebeck coefficient. It is known that the power factor is required to have an order of magnitude of about 10^{-3} ($\text{Wm}^{-1}\text{K}^{-2}$) for the materials used in current devices. The maximum values of power factors of thallium compounds are summarized in Table 1, which are about one order lower than those of state-of-the-art thermoelectric materials.

Figure 3(a) shows the temperature dependence of thermal conductivities of thallium compounds,^{5–7)} together with the data of other substances.^{1,12)} To be a good thermoelectric material, it is necessary to have a low thermal conductivity. As can be seen in Fig. 3, the thermal conductivities of thallium compounds are very low. The values at room temperature are summarized in Table 1. Especially, the thermal conductivity of AgTlTe is extremely low, and the value at room temperature is $0.25 \text{ Wm}^{-1}\text{K}^{-1}$, which is about 1/4 of those of state-of-the-art thermoelectric materials.

It is well known that the total thermal conductivity κ_{total} of solids can be written as follows:

$$\kappa_{\text{total}} = \kappa_{\text{lat}} + \kappa_{\text{el}} \dots,$$

where κ_{lat} is the lattice contribution and κ_{el} is the electronic contribution. κ_{el} can be calculated using the Wiedemann–Franz–Lorenz relation:

$$\kappa_{\text{el}} = L\sigma T,$$

where L is the Lorenz number, σ is the electrical conductivity, and T is the absolute temperature. κ_{lat} is obtained by

subtracting κ_{el} from κ_{total} . Variations of the κ_{total} , κ_{lat} , and κ_{el} of AgTlTe with temperature are shown in Fig. 3(b). The κ_{el} increases slightly with increasing temperature, but it is very small compared to κ_{total} . Therefore, it can be said that almost all contribution to κ_{total} is κ_{lat} .

The simplest estimation of the minimum lattice thermal conductivity κ_{min} of AgTlTe is obtained by using the following relation:

$$\kappa_{\text{lat.min}} = C_V vl/3,$$

where C_V is the lattice heat capacity, v is the average sound velocity, and l is the mean free path of the heat carrying phonons. The C_V can be evaluated from the Debye temperature as follows:

$$C_V = 3nRD(\theta_D/T),$$

where n is the number of atoms per molecule, R is the gas constant, θ_D is the Debye temperature, and $D(\theta_D/T)$ is the Debye function. The average sound velocity v can be calculated from the longitudinal sound velocity V_L and shear sound velocity V_S as follows:

$$v = (V_L + 2V_S)/3.$$

In the present study, the sound velocities and Debye temperature were evaluated from an ultrasonic pulse-echo method.^{8,13)} Assuming that the mean free path of the heat carrying phonons equals to the cubic root of the lattice volume, the κ_{min} can be estimated to about $0.28 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature as shown in Fig. 3(b). From this figure, it is confirmed that the measured κ_{lat} is almost same as estimated κ_{min} , indicating that the heat carrying phonons are scattered very efficiently in the AgTlTe crystal.

The dimensionless figure of merit ZT of thallium compounds is evaluated by using the data of electrical resistivity, Seebeck coefficient, and thermal conductivity. The temperature dependence of ZT of thallium compounds^{5–7)} is shown in Fig. 4, together with the data of other substances.^{1,12,14)} The ZT of Tl_9BiTe_6 has a peak at around 600 K and reaches a maximum value of 0.86, indicating that Tl_9BiTe_6 can be a good thermoelectric material in a medium temperature

Fig. 4 Temperature dependence of ZT of thallium compounds,^{5–7)} together with literature data.^{1,12,14)}

region. TlSbTe_2 shows the maximum ZT value among the thallium compounds studied in the present study. The ZT of TlSbTe_2 increases linearly with temperature and reaches 0.87 at 715 K. The maximum ZT values of thallium compounds are summarized in Table 1. Based on our findings, the thallium compounds, especially Tl_9BiTe_6 and TlSbTe_2 are promising candidates for p-type thermoelectric materials at medium temperature region from 600 to 700 K.

4. Conclusion

Tl_9BiTe_6 , TlSbTe_2 , and AgTlTe are p-type materials with large Seebeck coefficients and extremely low thermal conductivities, while TlBiTe_2 shows n-type characteristics. The thermal conductivities of thallium compounds are very low; especially AgTlTe indicates extremely low thermal conductivity ($0.25 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature). The dimensionless figures of merit of thallium compounds are relatively high; the maximum ZT values are 0.86 at 590 K for Tl_9BiTe_6 , 0.15 at 760 K for TlBiTe_2 , 0.87 at 715 K for TlSbTe_2 and 0.61 at 580 K for AgTlTe . It is concluded that thallium compounds can be good thermoelectric materials because they have both moderate power factors and very low thermal conductivities.

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