

Ag$_9$TlTe$_5$ and AgTlTe: High ZT Materials With Extremely Low Thermal Conductivity

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Abstract

We have studied the thermoelectric properties Ag$_9$TlTe$_5$ and AgTlTe. The thallium compounds have extremely low thermal conductivities around 0.25 W m$^{-1}$K$^{-1}$ from room temperature to about 700 K. The thallium compounds indicate very high ZT values; especially the highest ZT value of Ag$_9$TlTe$_5$ is 1.23 obtained at 700 K. Ag$_9$TlTe$_5$ is a unique material combining extremely low thermal conductivity and relatively low electrical resistivity.

Introduction

Thallium compounds have attracted attention as new thermoelectric materials because they have very low thermal conductivities. For instance, the thermoelectric properties of some thallium compounds, such as Tl$_2$SnTe$_5$, Tl$_9$BiTe$_6$, and thallium-filled skutterudites (Tl$_{0.22}$Co$_4$Sb$_{12}$) have been reported. The maximum ZT values of these thallium compounds are ZT = 0.6 at 300 K for Tl$_2$SnTe$_5$, [1] ZT = 1.2 at around 500 K for Tl$_9$BiTe$_6$, [2] and ZT = 0.8 at 800 K for Tl$_{0.22}$Co$_4$Sb$_{12}$. [3]

On the other hand, some groups have reported the phase equilibria for the Tl$_2$Te-Ag$_2$Te pseudo-binary system. [4-6] A comparison of the data reported in the literature confirms that the Tl$_2$Te-Ag$_2$Te pseudo-binary system contains four ternary compounds: Ag$_3$TlTe$_2$, AgTlTe, Ag$_8$Tl$_2$Te$_5$, and Ag$_9$TlTe$_5$. In our previous study, we measured the thermal conductivity of polycrystalline AgTlTe and confirmed the extremely low values. [7] In this paper, we report on the thermoelectric properties of AgTlTe and Ag$_9$TlTe$_5$, which we selected for study as novel thermoelectric materials. Especially, Ag$_9$TlTe$_5$ seems to have a thermoelectric figure of merit comparable to those of state-of-the-art materials.

Experimental

For polycrystalline sample synthesis, the appropriate amounts of starting materials were sealed in silica tubes, melted at 1173 K, and annealed at 673 K for a few days. The starting materials were Ag$_2$Te and Tl$_2$Te (supplied by Furuuchi Chemical Co. Ltd.). The obtained samples were crushed and pressed into pellets, followed by sintering slightly below their melting temperatures. This preparation method is simple and easy enough that any scientist in the field of solid-state physics or chemistry could prepare the compounds. A photograph of a polycrystalline sample of Ag$_9$TlTe$_5$, together with a 100-yen coin, is shown in Fig. 1.

The polycrystalline samples were taken from the sintered specimens for the measurements of their physical properties. The density of the samples was calculated from the measured weight and dimension. The crystal structure was investigated by the powder X-ray diffraction method at room temperature using Cu Kα radiation. The chemical composition of the samples was determined by the EDX analysis. The melting temperature of the samples was determined by the TG-DTA measurement.

The electrical resistivity ($\rho$) and Seebeck coefficient (S) were measured using a standard four-probe method with a temperature gradient of about 5 K in a helium atmosphere. The thermal conductivity ($\kappa$) was evaluated from the thermal diffusivity, heat capacity, and sample density. The thermal diffusivity was measured using a laser flash method in vacuum. The heat capacity data were obtained from the database.

Figure 1: A photograph of a polycrystalline sample of Ag$_9$TlTe$_5$, together with a 100-yen coin.

Figure 2: X-ray diffraction patterns of Ag$_9$TlTe$_5$ and AgTlTe, together with the literature data. [8,9]
Results and discussion

The X-ray diffraction pattern of our polycrystalline sample agrees well with the powder pattern calculated from the reported crystal structure. The X-ray diffraction patterns of Ag₉TlTe₅ and AgTlTe are shown in Fig. 2. Ag₉TlTe₅ exhibits a hexagonal crystal system with the space group R-3c. On the other hand, AgTlTe exhibits an orthorhombic crystal system with the space group Pnma. The hexagonal lattice parameters of Ag₉TlTe₅ are a= 1.1431 nm and c= 4.1945 nm. The unit cell contains 12 molecules. Ag₉TlTe₅ has a large crystal cell with a complex structure. The orthorhombic lattice parameters of AgTlTe are a= 0.8800 nm, b= 0.4880 nm, and c= 0.7770 nm. The unit cell contains 4 molecules. The lattice parameters of the compounds are almost the same as those reported in the literature. [8,9] The chemical compositions determined by the EDX analysis do not deviate from the stoichiometric compositions. The structures of Ag₉TlTe₅ and AgTlTe are shown in Fig. 3.

Figure 3: The structure of (a) Ag₉TlTe₅ and (b) AgTlTe. The green, yellow, and blue balls represent tellurium, silver, and thallium, respectively. In Ag₉TlTe₅, silver atoms occupy randomly 70 % of the sites.

The electrical properties of Ag₉TlTe₅ and AgTlTe are shown in Fig. 4. The electrical resistivities (ρ) of Ag₉TlTe₅ and AgTlTe decrease with temperature across the whole temperature range, indicating semiconducting characteristics. The values of the Seebeck coefficient (S) of Ag₉TlTe₅ and AgTlTe are positive, indicating that the majority of the charge carriers are holes. The Seebeck coefficient decreases with temperature, for Ag₉TlTe₅ it reaches a minimum at around 650 K, and for AgTlTe it reaches a minimum at around 550 K. Both the electrical resistivity and Seebeck coefficient of AgTlTe are higher than those of Ag₉TlTe₅, which is because that the carrier concentration of AgTlTe is lower than that of Ag₉TlTe₅.

The electrical resistivity value of Ag₉TlTe₅ at 700 K is 2.63x10⁻⁴ Ωm, which is higher by about an order of magnitude or more than those of state-of-the-art thermoelectric materials. This high electrical resistivity indicates a contribution from both the low carrier concentration and polycrystalline sample’s microstructure such as cracking and/or grain boundary resistance. The Seebeck coefficient value of Ag₉TlTe₅ at 700 K is 319 µVK⁻¹. A maximum power factor (S²/ρ) of 3.87x10⁻⁴ Wm⁻¹K⁻² was calculated at 700 K. The power factor of Ag₉TlTe₅ is higher than that of AgTlTe in the whole temperature range.

The values of the power factor of Ag₉TlTe₅ are lower than those of state-of-the-art thermoelectric materials. Although its electrical performance is not very high, Ag₉TlTe₅ exhibits a very high value of the dimensionless figure of merit because of its extremely low thermal conductivity.

The thermal conductivities κ of Ag₉TlTe₅ and AgTlTe are shown in Fig. 5, together with the data for other substances. [7,10] The thermal conductivity (κ) was evaluated using the following standard equation:

\[ \kappa = \alpha \cdot \frac{C_p \cdot d}{\rho} \]

where \( \alpha \) is the thermal diffusivity, \( C_p \) is the heat capacity, and \( d \) is the sample density. Apparently the thermal conductivities of Ag₉TlTe₅ and AgTlTe are extremely low. The values at room temperature are 0.23 and 0.25 Wm⁻¹K⁻¹ for Ag₉TlTe₅.
and AgTlTe, respectively. These values are about one-fifth the value for pure Bi$_2$Te$_3$. The temperature dependence of thermal conductivity is rather flat, indicating that the thermal conductivity approaches a glass-like limit. At room temperature, the electronic contributions to thermal conductivities that can be estimated from the Wiedemann Franz Lorenz relation are very small estimated to be less than about several percent of the total thermal conductivity. 

The low Young’s modulus and Debye temperature of Ag$_9$TlTe is attributable to weak interatomic bonding. Recently, Clarke reported materials selection guidelines for low thermal conductivity thermal barrier coatings. According to those guidelines, a material will have a low thermal conductivity at high temperatures if it satisfies four principal conditions: A large molecular weight, a complex crystal structure, non-directional bonding, and a large number of different atoms per molecule. [11] Ag$_9$TlTe fulfills these conditions.

Figure 5: Temperature dependence of the thermal conductivities of Ag$_9$TlTe$_5$ and AgTlTe, together with the data of other substances. [7,10]

To examine the extremely low thermal conductivities of Ag$_9$TlTe$_5$ and AgTlTe, we performed ultrasonic pulse echo measurement for Ag$_9$TlTe$_5$ and studied the lattice properties. The longitudinal ($v_l$) and shear ($v_s$) sound velocities can be evaluated by the ultrasonic pulse echo measurement. The average sound velocity ($v_a$) is given using the following expression:

$$ v_a = \left( \frac{1}{3} \left[ \frac{1}{v_l} + \frac{2}{v_s} \right] \right)^{1/3}. $$

Young’s modulus ($E$) and the Debye temperature ($\theta_D$) can be calculated from the sound velocity as follows:

$$ E = \rho \left( \frac{3v_l^2 - 4v_s^2}{v_l^2 - v_s^2} \right), $$

$$ \theta_D = \frac{h}{k_B} \left[ \frac{3N}{4\pi^3} \right]^{3/2} v_a, $$

where $\rho$ is the sample density, $h$ is Planck’s constant, $k_B$ is the Boltzmann constant, $N$ is the number of atoms in a unit cell, and $V$ is the unit cell volume. We calculated the average sound velocity, Young’s modulus, and Debye temperature of Ag$_9$TlTe$_5$ to be 1203 ms$^{-1}$, 23.4 GPa, and 120 K, respectively. These values are very low compared with those of state-of-the-art thermoelectric materials. For example, the Debye temperatures for Bi$_2$Te$_3$ and PbTe are 165 and 160 K, respectively. [10] The low Young’s modulus and Debye temperature of Ag$_9$TlTe$_5$ are attributable to weak interatomic bonding.

Figure 6: Temperature dependence of dimensionless figure of merit ZT of Ag$_9$TlTe$_5$ and AgTlTe, together with the data of other substances. [12]

The dimensionless figure of merit ZT of Ag$_9$TlTe$_5$ and AgTlTe is shown in Fig. 6, together with the data for other substances. [12] The figure reveals that Ag$_9$TlTe$_5$ has a very high ZT value, comparable to those of state-of-the-art materials. Maximum ZT values are 1.23 at 700 K for Ag$_9$TlTe$_5$ and 0.61 at 600 K for AgTlTe. These high ZT values are attributable to the material’s extremely low thermal conductivities.

Conclusions

We have reported the thermoelectric properties of Ag$_9$TlTe$_5$ and AgTlTe. Polycrystalline samples were prepared and characterized. Ag$_9$TlTe$_5$ and AgTlTe show p-type conduction characteristics and have extremely low thermal conductivities. Ag$_9$TlTe$_5$ shows a relatively high thermoelectric figure of merit, 1.23 at 700 K. In addition, the preparation method is simple and easy. The thermal conductivity values of Ag$_9$TlTe$_5$ and AgTlTe are very low around 0.25 Wm$^{-1}$K$^{-1}$, similar to those of glass. However, glass-like materials usually have high electrical resistivity, which is not desirable for achieving high figures of merit. But this is not the case for Ag$_9$TlTe$_5$. This compound combines extremely low thermal conductivity and relatively low electrical resistivity, making it a very interesting high-performance thermoelectric material.

References


