Ag_9TlTe_5 and AgTlTe: High ZT Materials With Extremely Low Thermal Conductivity

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Abstract

We have studied the thermoelectric properties Ag_9TlTe_5 and AgTlTe. The thallium compounds have extremely low thermal conductivities around 0.25 $Wm^{-1}K^{-1}$ from room temperature to about 700 K. The thallium compounds indicate very high ZT values; especially the highest ZT value of Ag_9TlTe_5 is 1.23 obtained at 700 K. Ag_9TlTe_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_2SnTe_5, Tl_9BiTe_6, and thallium-filled skutterudites ($Tl_{0.22}Co_4Sb_{12}$) have been reported. The maximum ZT values of these thallium compounds are ZT = 0.6 at 300 K for Tl_2SnTe_5, [1] ZT = 1.2 at around 500 K for Tl_9BiTe_6, [2] and ZT = 0.8 at 800 K for $Tl_{0.22}Co_4Sb_{12}$. [3]

On the other hand, some groups have reported the phase equilibria for the Tl_2Te-Ag_2Te pseudo-binary system. [4-6] A comparison of the data reported in the literature confirms that the Tl_2Te-Ag_2Te pseudo-binary system contains four ternary compounds: Ag_3TlTe_2, AgTlTe, $Ag_8Tl_2Te_5$, and Ag_9TlTe_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_9TlTe_5, which we selected for study as novel thermoelectric materials. Especially, Ag_9TlTe_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_2Te and Tl_2Te (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_9TlTe_5 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 (ρ) 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 (κ) 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.

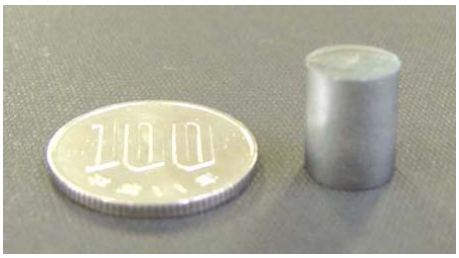

Figure 1: A photograph of a polycrystalline sample of Ag_9TlTe_5, together with a 100-yen coin.

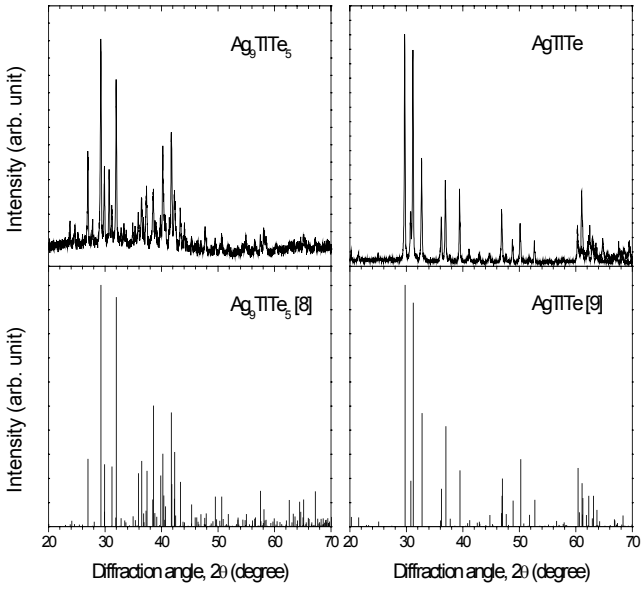

Figure 2: X-ray diffraction patterns of Ag_9TlTe_5 and AgTlTe, together with the literature data. [8,9]

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 Ag_9TlTe_5 and AgTlTe are shown in Fig. 2. Ag_9TlTe_5 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 Ag_9TlTe_5 are a= 1.1431 nm and c= 4.1945 nm. The unit cell contains 12 molecules. Ag_9TlTe_5 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 Ag_9TlTe_5 and AgTlTe are shown in Fig. 3.

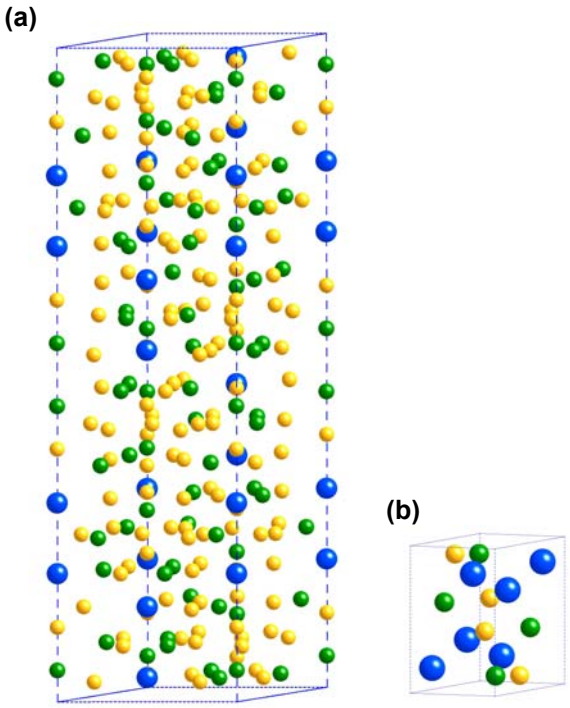

Figure 3: The structure of (a) Ag_9TlTe_5 and (b) AgTlTe. The green, yellow, and blue balls represent tellurium, silver, and thallium, respectively. In Ag_9TlTe_5, silver atoms occupy randomly 70 % of the sites.

The electrical properties of Ag_9TlTe_5 and AgTlTe are shown in Fig. 4. The electrical resistivities (ρ) of Ag_9TlTe_5 and AgTlTe decrease with temperature across the whole temperature range, indicating semiconducting characteristics. The values of the Seebeck coefficient (S) of Ag_9TlTe_5 and AgTlTe are positive, indicating that the majority of the charge carriers are holes. The Seebeck coefficient decreases with temperature, for Ag_9TlTe_5 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 Ag_9TlTe_5, which is because that the carrier concentration of AgTlTe is lower than that of Ag_9TlTe_5.

The electrical resistivity value of Ag_9TlTe_5 at 700 K is 2.63×10^{-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 Ag_9TlTe_5 at 700 K is 319 μVK^{-1}. A maximum power factor (S^2/ρ) of 3.87×10^{-4} $Wm^{-1}K^{-2}$ was calculated at 700 K. The power factor of Ag_9TlTe_5 is higher than that of AgTlTe in the whole temperature range.

The values of the power factor of Ag_9TlTe_5 are lower than those of state-of-the-art thermoelectric materials. Although its electrical performance is not very high, Ag_9TlTe_5 exhibits a very high value of the dimensionless figure of merit because of its extremely low thermal conductivity.

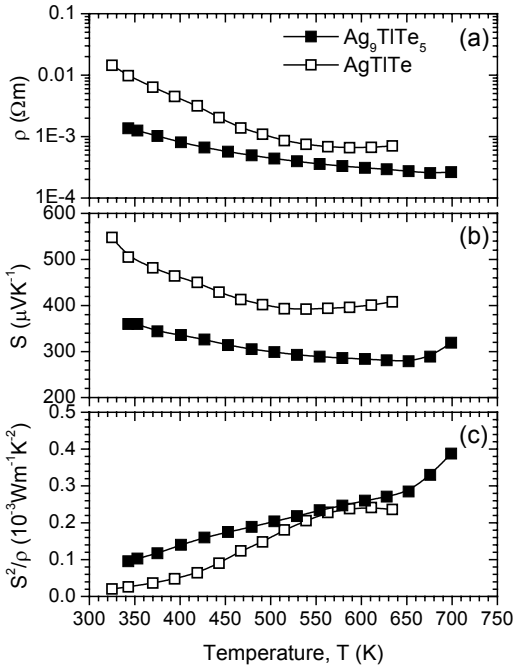

Figure 4: Temperature dependence of the electrical properties of Ag_9TlTe_5 and AgTlTe: (a) electrical resistivity, ρ (b) Seebeck coefficient, S (c) power factor, P that is described as S^2/ρ.

The thermal conductivities κ of Ag_9TlTe_5 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:

$$\kappa = \alpha \cdot C_P \cdot d ,$$

where α is the thermal diffusivity, C_P is the heat capacity, and d is the sample density. Apparently the thermal conductivities of Ag_9TlTe_5 and AgTlTe are extremely low. The values at room temperature are 0.23 and 0.25 $Wm^{-1}K^{-1}$ for Ag_9TlTe_5

and AgTlTe, respectively. These values are about one-fifth the value for pure Bi_2Te_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.

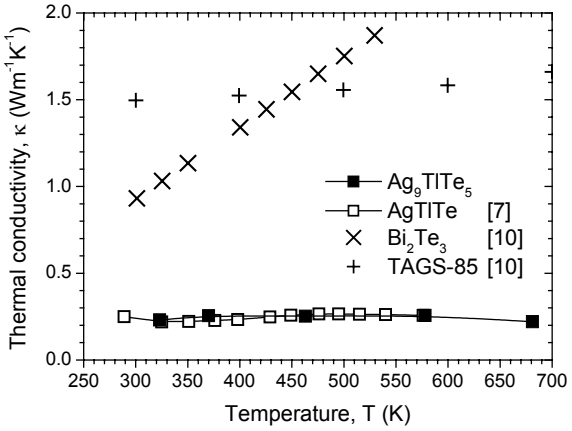

Figure 5: Temperature dependence of the thermal conductivities of Ag_9TlTe_5 and AgTlTe, together with the data of other substances. [7,10]

To examine the extremely low thermal conductivities of Ag_9TlTe_5 and AgTlTe, we performed ultrasonic pulse echo measurement for Ag_9TlTe_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:

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

Young's modulus (E) and the Debye temperature (θ_D) can be calculated from the sound velocity as follows:

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

$$\theta_D = \frac{h}{k_B} \left[\frac{3N}{4\pi V} \right]^{\frac{1}{3}} v_a ,$$

where r is the sample density, h is Plank'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_9TlTe_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_2Te_3 and PbTe are 165 and 160 K, respectively. [10] The low Young's modulus and Debye temperature of Ag_9TlTe_5 are 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_9TlTe_5 as well as AgTlTe fulfill these conditions.

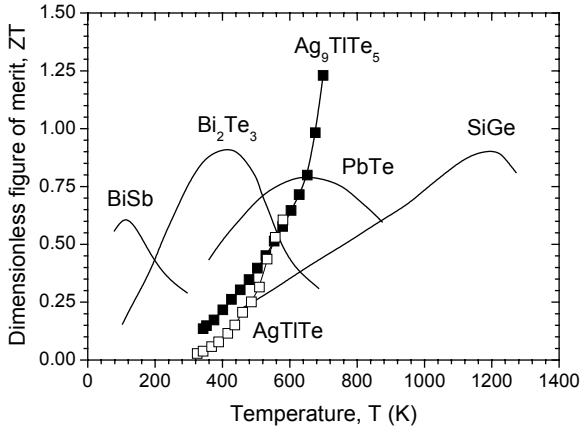

Figure 6: Temperature dependence of dimensionless figure of merit ZT of Ag_9TlTe_5 and AgTlTe, together with the data of other substances. [12]

The dimensionless figure of merit ZT of Ag_9TlTe_5 and AgTlTe is shown in Fig. 6, together with the data for other substances. [12] The figure reveals that Ag_9TlTe_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_9TlTe_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_9TlTe_5 and AgTlTe. Polycrystalline samples were prepared and characterized. Ag_9TlTe_5 and AgTlTe show p-type conduction characteristics and have extremely low thermal conductivities. Ag_9TlTe_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_9TlTe_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_9TlTe_5. This compound combines extremely low thermal conductivity and relatively low electrical resistivity, making it a very interesting high-performance thermoelectric material.

References

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