Thermal Conductivity of the Ternary Compounds: AgMTe_2 and AgM_5Te_8 ($M = \text{Ga}$ or In)

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We synthesized AgGaTe_2 , AgGa_5Te_8 , AgInTe_2 , and AgIn_5Te_8 by solid-state reactions of Ag_2Te , Ga_2Te_3 or In_2Te_3 , and Te , and prepared their high-density polycrystalline pellets. The thermal conductivity κ was evaluated by the laser flash method from room temperature to around 870 K. These compounds exhibited low κ , e.g. the room temperature values were 1.94, 0.54, 2.05, and 1.08 $\text{W m}^{-1} \text{K}^{-1}$ for AgGaTe_2 , AgGa_5Te_8 , AgInTe_2 , and AgIn_5Te_8 , respectively. We discussed the magnitude relations of κ from the viewpoints of the crystal structure and the Debye temperature. [doi:10.2320/matertrans.E-M2009810]

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1. Introduction

Solid-state cooling and power generation using thermoelectric effects have potential applications in waste-heat recovery, air conditioning, and refrigeration. The effectiveness of a material for thermoelectric applications is determined by the materials' dimensionless figure of merit, defined as $ZT = (S^2\sigma)T/\kappa$,^{1,2)} where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. Therefore, in order to obtain high performance thermoelectric materials, the large S and the high σ as well as the low κ are required. $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ alloys are known as the best bulk thermoelectric material with high ZT values of near 1 at room temperature.^{1,2)} In recent years, a vigorous research effort has been underway to find bulk materials with higher ZT values, including filled skutterudites,³⁾ zinc antimonides,⁴⁾ CsBi_4Te_6 ,⁵⁾ $\text{AgPb}_m\text{SbTe}_{2+m}$,⁶⁾ and Tl -doped PbTe .⁷⁾

Recently, our group has focused attention on thallium tellurides as advanced thermoelectric materials with extremely low κ ($< 0.5 \text{ W m}^{-1} \text{K}^{-1}$). Because of the extremely low κ , several thallium tellurides exhibit high thermoelectric performance comparable to those of state-of-the-art materials. In particular, among the bulk polycrystalline materials, Ag_9TlTe_5 has been found to exhibit the best, i.e., $ZT = 1.23$ at approximately 700 K.⁸⁾ However, thallium compounds are unsuitable for practical application, because they are toxic. Therefore, we have to find alternative low κ thermoelectric materials that contain no thallium.

In the present paper, we investigated the κ of Ag-Ga-Te and Ag-In-Te ternary compounds, because Ga , In , and Tl are related elements in the Periodic Table. In addition, it has been reported that some of these ternary compounds exhibit complex crystal structure,^{9–11)} which would lead to low κ . We prepared polycrystalline pellets of AgGaTe_2 , AgGa_5Te_8 , AgInTe_2 , and AgIn_5Te_8 and investigated the magnitude relations of κ .

2. Experiment

For polycrystalline samples synthesis, the appropriate amounts of starting materials were sealed in silica tubes, melted at 1273 K for 24 h, and annealed at 873 K for 1 week. The starting materials were chunks of Ag_2Te , Ga_2Te_3 or In_2Te_3 , and Te . The obtained ingots were crushed into fine powders, followed by hot pressing slightly below their melting temperatures in an Ar flow atmosphere. Column-shaped (10 mm in diameter and 15 mm in height) and disc-shaped (10 mm in diameter 1 mm in thickness) pellets were prepared. The density of the pellets was calculated based on the measured weight and dimensions.

To examine the sample purity and determine the lattice parameter, the X-ray diffraction (XRD) data were collected using a diffractometer on RINT2000 (Rigaku) with $\text{Cu K}\alpha$ radiation in air at room temperature. The sample microstructure was observed by the scanning electron microscopy (SEM). The chemical composition of the experimental samples was determined using energy-dispersive X-ray (EDX) analysis in vacuum at room temperature.

Thermal conductivity was calculated from thermal diffusivity (α), heat capacity (C_p), and density (d), using the following standard equation:

$$\kappa = \alpha C_p d. \quad (1)$$

Thermal diffusivity was measured by the laser flash technique using the commercially available apparatus TC-7000 (ULVAC) in vacuum from room temperature to 870 K.

In order to discuss the magnitude relations of κ , we evaluated the Debye temperature (θ_D) of AgGaTe_2 , AgGa_5Te_8 , AgInTe_2 , and AgIn_5Te_8 . The longitudinal (V_L) and shear sound velocities (V_S) were measured through an ultrasonic pulse-echo method at room temperature in air. The experimental samples were bonded to a 5-MHz longitudinal or shear sound wave echogenic transducer. From the measured sound velocities, the θ_D was calculated based on the following equation:

Fig. 1 Powder XRD patterns of the Ag-(Ga or In)-Te ternary compounds, together with the peak positions calculated from the crystal structures reported in Refs. 9), 10), and 11).

Table 1 Room temperature values of the crystallographic data and the thermophysical properties for AgGaTe₂, AgGa₅Te₈, AgInTe₂, and AgIn₅Te₈. δ^3 , M , N , θ_D , κ is the average volume occupied by an atom in the crystal, the average atomic mass of the crystal, the number of atoms per unit cell, the Debye temperature, and the thermal conductivity at room temperature, respectively.

Compounds	AgGaTe ₂	AgGa ₅ Te ₈	AgInTe ₂	AgIn ₅ Te ₈
Crystal structure	Tetragonal	Orthorhombic	Tetragonal	Tetragonal
Lattice parameter (nm) []:Reference	a	0.6324 [0.6300] ^{[11)}	0.6022 [0.6000] ^{[11)}	0.6419 [0.6406] ^{[9)}
	b	1.2113 [1.2020] ^{[11)}	0.6204 [0.6199] ^{[10)}	—
	c	1.2001 [1.1940] ^{[11)}	1.2630 [1.2560] ^{[9)}	1.2423 [1.2425] ^{[10)}
Sample density (g/cm ³)	5.99	5.08	5.96	5.61
Relative density (% T.D.)	99	92	98	95
δ (nm)	0.3107	0.3173	0.3192	0.3245
M (amu)	108.20	105.52	119.47	121.63
N	16	56	16	14
θ_D (K)	206	127	202	164
κ (Wm ⁻¹ K ⁻¹)	1.94	0.54	2.05	1.08

$$\theta_D = \left(\frac{h}{k_B} \right) \left[\frac{9N}{4\pi V_C (V_L^{-3} + 2V_S^{-3})} \right]^{1/3}, \quad (2)$$

where h is Planck's constant, k_B is the Boltzmann constant, N is the number of atoms per unit cell, and V_C is the unit cell volume.

3. Results and Discussion

The powder XRD patterns of our polycrystalline samples agreed well with the patterns reported in Refs. 9), 10), and 11), as shown in Fig. 1. The lattice parameters and densities of our samples are summarized in Table 1. In this table, the

literature data of the lattice parameters are also shown for comparison. The lattice parameters of our samples were consistent with the literature values. From the SEM/EDX analysis, we confirmed that the chemical compositions did not deviate a lot from the stoichiometric one. Relatively high-density pellets were obtained in the present study. The bulk densities of the pellets were 99, 92, 98, and 95% of the theoretical density for AgGaTe₂, AgGa₅Te₈, AgInTe₂, and AgIn₅Te₈, respectively.

The θ_D values determined in the present study as well as the N values are summarized in Table 1. It was confirmed that these compounds indicated very low θ_D , which would be attributable to the weak interatomic bonding. On the other

Fig. 2 Temperature dependences of the thermal conductivities κ of AgGaTe₂, AgGa₅Te₈, AgInTe₂, and AgIn₅Te₈. Inset: Temperature dependences of the thermal resistivity $1/\kappa$.

hand, the N values are relatively large, indicating the complex crystal structures. Especially, the N value of AgGa₅Te₈ is 56. From the viewpoint of the low θ_D and the large N , these compounds would exhibit low κ .

The temperature dependences of κ are shown in Fig. 2. These compounds exhibited low κ . The room temperature values were 1.94, 0.54, 2.05, and 1.08 Wm⁻¹K⁻¹ for AgGaTe₂, AgGa₅Te₈, AgInTe₂, and AgIn₅Te₈, respectively. The κ of all samples decreased with temperature roughly according to a $1/T$ law, as shown in the inset of Fig. 2. This means that the dominant phonon scattering mechanism in the temperature range investigated here is intrinsic phonon-phonon Umklapp processes.

Under the assumptions that none of optical phonons carry heat and that the T is in a temperature range in which intrinsic phonon scattering is dominant, the general lattice thermal conductivity (κ_{lat}) can be expressed as the following equation proposed by Slack:¹²⁾

$$\kappa_{\text{lat}} \propto \frac{M\delta(\theta_D)^3}{N^{2/3}T}, \quad (3)$$

where M is the average atomic mass of the crystal and δ^3 is the average volume occupied by an atom in the crystal. This equation is applicable to a wide range of crystal structures and compounds.¹³⁾ Here, we calculated M and δ based on the reported crystal structure, as summarized in Table 1. And then, we calculated the parameter $M\delta(\theta_D)^3/N^{2/3}/T$ at 300 K for AgGaTe₂, AgGa₅Te₈, AgInTe₂, and AgIn₅Te₈ to be 1.54, 0.15, 1.65, and 0.99 (10^{-4} umK²), respectively. Figure 3 shows the relationship between the κ_{lat} at room temperature and the parameter $M\delta(\theta_D)^3/N^{2/3}/T$ ($T = 300$ K) for AgGaTe₂, AgGa₅Te₈, AgInTe₂, and AgIn₅Te₈. In the present study, we assumed that measured κ corresponds to κ_{lat} because these four compounds indicated quite low σ values. For example, the room temperature values of the electrical resistivities of AgGaTe₂, AgGa₅Te₈, and AgIn₅Te₈ were reported to be around 2×10^5 , 5×10^6 , and 3×10^5 Ω cm, respectively.^{14,15)} By using these values and the Lorenz number, the electronic contribution to the κ (κ_{el}) at room temperature were calculated to be 3.7×10^{-9} , 1.5×10^{-10} ,

Fig. 3 Relationship between the parameter $M\delta(\theta_D)^3/N^{2/3}/T$ ($T = 300$ K) and κ at room temperature for AgGaTe₂, AgGa₅Te₈, AgInTe₂, and AgIn₅Te₈.

2.4×10^{-9} Wm⁻¹K⁻¹ for AgGaTe₂, AgGa₅Te₈, and AgIn₅Te₈, respectively. Therefore, in the present study, the κ_{el} could be considered to be zero. From Fig. 3, it was confirmed that decreasing the value of the parameter $M\delta(\theta_D)^3/N^{2/3}/T$ ($T = 300$ K) led to decrease in the value of the κ_{lat} at room temperature. Since, generally, θ_D depends mostly on M and δ , while does not depend on N , the present results demonstrate a quantitative statement that low κ_{lat} requires low θ_D and large N . Ag-*M*-Te ($M = \text{Ga or In}$) ternary compounds investigated here were found to meet these requirements.

4. Summary

We prepared high-density polycrystalline pellets of AgGaTe₂, AgGa₅Te₈, AgInTe₂, and AgIn₅Te₈, and the κ was measured from room temperature to 870 K. The magnitude relations of κ of these compounds were explained by the general lattice thermal conductivity theory. AgGa₅Te₈ exhibited the lowest κ around 0.5 Wm⁻¹K⁻¹ at room temperature, due to the combination of the weak interatomic bonding and the complex crystal structure (i.e. low θ_D and large N). The Ag-*M*-Te ($M = \text{Ga or In}$) ternary compounds, especially AgGa₅Te₈, would have a potential to be alternative low κ thermoelectric materials that contain no thallium. Unfortunately, however, the σ values of these compounds are too low to apply them as thermoelectric materials at this moment. Since the κ_{lat} is significantly low, it can be considered that AgGa₅Te₈ could maintain the total κ at sufficiently-low level even if the κ_{el} rises due to increasing the σ by tuning the carrier concentration. Now, we are trying to increase the σ by tuning the carrier concentration. These results will be reported in the near future.

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