Improvement of Thermoelectric Properties by Dispersing Ag$_2$Te Grains in AgBiTe$_2$ Matrix: Composition Effects in (AgBiTe$_2$)$_{1-x}$(Ag$_2$Te)$_x$

Tsutomu SAKAKIBARA,*** Yasuo TAKIGAWA,***
Akhiro KAMEYAMA**** and Kou KUROSAWA****

*Second Development Department, Aisin Seiki Co., Ltd., 2-1, Asahi-machi Kariya-shi Aichi 448-8650
**Department of Materials Science and Engineering, University of Miyazaki, 1-1, Gakuenkibana-dai Nishi, Miyazaki-shi 889-2192
***Department of Electronic Engineering, Osaka Electro-Communication University, 18-8, Hatsu-machi, Neyagawa-shi, Osaka 572-8530
****Department of Electrical and Electronic Engineering, University of Miyazaki, 1-1, Gakuenkibana-dai Nishi, Miyazaki-shi 889-2192

AgBiTe$_2$マトリックスにAg$_2$Te粒子を分散させることによる熱電特性の向上: (AgBiTe$_2$)$_{1-x}$(Ag$_2$Te)$_x$の複合化効果

Key-words: Ag$_2$Te, AgBiTe$_2$, Composite, Thermoelectric, Figure-of-merit

1. Introduction

Based on the theoretical law that thermoelectric figure-of-merit $Z \propto m^{3/2} \mu/\kappa_g$ ($m^*$: effective mass; $\mu$: mobility; $\kappa_g$: lattice thermal conductivity), $Z$ values have been enhanced by enhancing short wavelength phonon scattering in solid solutions of high-performance thermoelectric materials such as the reference. There are only a few elements which become solid solutions with Bi$_2$Te$_3$ and remain the crystal structure unchanged, and therefore the figure of merit has not been enhanced by introducing foreign elements into Bi$_2$Te$_3$ any more. Our idea is that lattice thermal conductivity would be decreased by enhancing phonon scattering at boundaries, if an appropriate size of grains is dispersed in a thermoelectric material matrix. The phonons must be scattered efficiently, if the dispersed grains have the same order of dimensions as the mean free path of long wavelength phonons. Sawade et al. has reported$^6$ that RuSi$_3$ prepared by an arc-melt method shows the figure of merit twice as large as single phase Ru$_2$Si$_3$. This is because a small amount of RuSi grains dispersed in the Ru$_2$Si$_3$ matrix enhanced the electrical conductivity. In other words, the figure of merit must be effectively enhanced in composites in which not only thermal conductivity but also electrical conductivity is much improved. There are only a few works after us$^7$ for detailed studies about the relations between thermoelectric properties in composite materials, although here are a lot of studies about thermal conductivity.$^8-10$ electrical conductivity$^{11-13}$ or power factor$^{14,15}$ for composite materials. Our final target is to get a guideline for enhancement of thermoelectric figure of merit by dispersing grains in a matrix of thermoelectric material.

We have carried out the experimental studies about the thermoelectric properties of such a composites that Ag$_2$Te grains are dispersed in an AgBiTe$_2$ matrix in a system of (AgBiTe$_2$)$_{1-x}$(Ag$_2$Te)$_x$ with 0$\leq$x$\leq$1.$^7$ In this paper, we present experimental results about textures and thermoelectric properties of (AgBiTe$_2$)$_{1-x}$(Ag$_2$Te)$_x$ composites prepared by cooling from liquid phase of (AgBiTe$_2$)$_{1-x}$(Ag$_2$Te)$_x$.

2. Experiments

An appropriate ratio of high-purity Ag (above 99.99% purity) grains and Bi (99.999%) and Te (99.999%) lumps was introduced in a silica glass tube. After being evacuated to 10$^{-3}$ Pa and then sealed off, the tube was placed in a vertical furnace in which the upper end was kept at 1273 K and the lower end at 1373 K. The raw materials circulated to be mixed well in the tube by convection when they were kept for 100 h at 1373 K which is much higher than the melting points 1323 K for Ag$_2$Te and 828 K for AgBiTe$_2$. The liquid phases were cooled down to 923 K at a rate of 1.0 K/min and then kept for 5 h at 923 K for precipitation of Ag$_2$Te grains. At this stage, a solid phase of Ag$_2$Te dispersed in a liquid phase of AgBiTe$_2$. It was dropped into water and finally quenched at room temperature.

Crystal structures were checked by an X-ray powder diffraction method. Textures and Ag$_2$Te grain sizes were examined with an electron probe microanalyzer (EPMA; Shimadzu EPMA-850A). Electrical conductivity, Seebeck coefficients, Hall coefficients and thermal conductivity were measured at room temperature. For electrical conductivity, Hall coefficients and Seebeck coefficients measurements, $2 \times 2 \times 12$ mm$^3$ rods were cut out of the blade. Electrical conductivity was measured with a four-point probe method, and Seebeck coefficients were measured by applying temperature difference of 10 degrees under 10$^{-3}$ Pa. Hall coefficients were measured with a Van der Pauw method by applying 0.73 T magnetic field. Thermal conductivity was measured for 3.5 $\times$ 3.5 $\times$ 4 mm$^3$ samples with a comparison method in vacuum, in which transparent silica glass was
Improvement of Thermoelectric Properties by Dispersing Ag₂Te Grains in AgBiTe₂ Matrix: Composition Effects in (AgBiTe₂)₁₋ₓ(Ag₂Te)ₓ

3. Experimental results

The composites (AgBiTe₂)₁₋ₓ(Ag₂Te)ₓ were prepared with x = 0, 0.25, 0.375, 0.5, 0.75, 0.875 and 1.0. In Fig. 1, are shown the back-scattered electron images taken with an EPMA. The bright parts are identified to be AgBiTe₂ and the dark parts are Ag₂Te according to a quantitative analysis with a ZAF method. It was confirmed that the samples consisted of AgBiTe₂ and Ag₂Te crystals with X-ray diffraction patterns, as an example of the diffraction patterns is reproduced in Fig. 2. The EPMA images show an important fact that Ag₂Te is not soluble in AgBiTe₂ and thus Ag₂Te grains disperse in AgBiTe₂ matrices. The grain sizes vary from 200 μm for the x = 0.75 sample to 1 μm for the x = 0.25 sample. Fine structures are included in some samples, and the textures of precipitated Ag₂Te vary from a dot like shape to a vein like one with increasing x. The textures and sizes may become important for electron and phonon scattering and thus alter the thermal and electrical conductivity.

Figures 3 and 4 show the electrical and thermal conductivity at room temperature of (AgBiTe₂)₁₋ₓ(Ag₂Te)ₓ. The electrical conductivity is the highest (57.1 kS/m) for Ag₂Te and the lowest (11.9 kS/m) for AgBiTe₂, and the intermediate values for the composites. They increase with increasing x, but the x = 0.5 sample shows the highest value of 30 kS/m among the composites. In the case of thermal conductivity, the pure materials show higher values around 1.1 W/m·K than the composites, namely the conductivity is decreased by mixing the two kinds of materials. The lowest value of 0.68 W/m·K is obtained for the x = 0.5 sample.

Hall and Seebeck coefficients measured are plotted in

![Fig. 2. X-ray diffraction patterns of (AgBiTe₂)₁₋ₓ(Ag₂Te)ₓ composites.](image)

![Fig. 1. Back-scattered electron photographs of (AgBiTe₂)₁₋ₓ(Ag₂Te)ₓ composites. The relatively bright parts are AgBiTe₂ and the dark ones are Ag₂Te.](image)
They hardly vary by mixing the two kinds of materials. The lowest value 0.3 cm$^3$/C of Hall coefficient is observed for AgBiTe$_2$. It should be noticed here that the Hall coefficients increase significantly by dispersing Ag$_2$Te in the matrix AgBiTe$_2$. The majority carriers are electrons for all of the pure materials and composites, because the Seebeck coefficients have the minus sign. They show almost the same value as the pure materials.

4. Discussion

The electrical conductivity of the composites are able to be calculated with the equation derived after Maxwell$^{[11]}$ by assuming that the carrier is not scattered at the boundary,

$$\sigma_{\text{mix}} = \sigma_0 + 2\sigma_1 - 2(1 - V_x) (\sigma_1 - \sigma_0) $$

where $\sigma_0$ and $\sigma_1$ mean electrical conductivity of AgBiTe$_2$ and Ag$_2$Te, respectively, $\sigma_{\text{mix}}$ that of the composites, and $V_x$ volume ratio of in the composites. The calculated values are plotted as the dotted line in Fig. 3. The conductivity of the $x = 0.5$ sample is on the line, which implies that the carrier is hardly scattered at the boundary. In the cases of the $x = 0.25, 0.75$ and 0.875 samples, on the other hand, the carrier is significantly scattered at the boundary and thus the conductivity is lower than the line. By comparing the textures, the fine structures in Ag$_2$Te might enhance the carrier scattering, resulting in the degradation of the carrier diffusion.

The carrier concentration $n$ and mobility $\mu$ are estimated from the Hall coefficient $R_H$ and electrical conductivity $\sigma$ by using $n = 1/R_H\mu$ and $\mu = \sigma/en$, which are illustrated in Figs. 7 and 8, respectively. The concentration of AgBiTe$_2$ is $2 \times 10^{25}$ m$^{-3}$ which is one order higher than $2 \times 10^{24}$ m$^{-3}$ of Ag$_2$Te. The composites show the intermediate values between them which are close to that of Ag$_2$Te. On the contrary, the mobility is almost linearly increase with $x$.

With respect to the mobility, the values of the composites are calculated by the following Eq. (2) derived on the analogy of the Maxwell’s equation for the conductivity, Eq. (1).

$$\mu_{\text{mix}} = \frac{\mu_0 + 2\mu_1 - 2(1 - V_x) (\mu_1 - \mu_0)}{\mu_0 + 2\mu_1 + (1 - V_x) (\mu_1 - \mu_0)} \mu_1$$

where $\mu_{\text{mix}}$, $\mu_0$, and $\mu_1$ mean the mobility of the composites,
Improvement of Thermoelectric Properties by Dispersing Ag7Te3 Grains in AgBiTe2 Matrix: Composition Effects in (AgBiTe2)1-(Ag7Te3)x Composites

Fig. 7. Carrier concentration of \((\text{AgBiTe}_2)_{1-x} (\text{Ag}_7\text{Te}_3)_x\) composites calculated from Hall coefficients.

Fig. 8. Mobility of \((\text{AgBiTe}_2)_{1-x} (\text{Ag}_7\text{Te}_3)_x\) composites calculated from Hall coefficients.

Fig. 9. Lattice thermal conductivity of \((\text{AgBiTe}_2)_{1-x} (\text{Ag}_7\text{Te}_3)_x\) composites calculated from thermal conductivity.

AgBiTe2 and Ag7Te3, respectively. They are plotted as the dotted line in Fig. 8. Except for the x=0.5 sample, the mobility decreases by the carrier scattering.

Thermal conductivity usually consists of phonon and carrier parts. The phonon part \(\kappa_{\text{ph}}\) is calculated from the measured thermal conductivity by subtracting the carrier part \(\kappa_{\text{car}}\), which is calculated after Eq. (3)

\[
\kappa_{\text{car}} = \sigma T \left( \gamma + \frac{5}{2} \right) \left( \frac{k_B T}{\epsilon} \right)^2
\]

where \(\sigma\) is electrical conductivity, \(T\) absolute temperature, \(\gamma\) scattering coefficient and \(k_B\) Boltzmann’s constant. \(\gamma\) is assumed to be equal to 1 based on a fact that the mobility of composite follows \(T^{-1/2}\). The lattice thermal conductivity calculated is plotted in Fig. 9. The lattice thermal conductivity is much lowered by adding the Ag7Te3 grains to the AgBiTe2 matrix, which shows the highest value of 0.95 W/m·K. The lattice thermal conductivity is also calculated with same manner as the electrical conductivity after the following Eq. (4) derived after Maxwell.

\[
\kappa_{\text{min}} = \kappa_{\text{ph0}} + 2\kappa_{\text{ph1}} - 2(1 - V_1) (\kappa_{\text{ph0}} - \kappa_{\text{ph1}})
\]

where \(\kappa_{\text{min}}, \kappa_{\text{ph0}}\) and \(\kappa_{\text{ph1}}\) mean lattice thermal conductivity of the composite, AgBiTe2 and Ag7Te3, respectively. Of course, the phonon scattering at the boundary is assumed to be neglected. The thermal conductivity calculated is plotted as the dotted line in Fig. 9. All of the composites show the lower values of the lattice thermal conductivity than that of the pure materials. This is explained by what the phonon is effectively scattered at the boundary. The x=0.5 sample shows the lowest value among the pure materials and composites prepared here, and the degradation reach 30% from that without the scattering. It should be pointed out here that the scattering at the boundary is the most significant for the x=0.5 sample, although the reduction cannot be explained well at this stage.

Thermoelectric figure of merit Z is the most convenient factor to evaluate the performance in the practical viewpoint. The Z values are usually calculated from Seebeck coefficient \(\alpha\), electrical conductivity \(\sigma\) and thermal conductivity \(\kappa\) by using the Eq. (5).

\[
Z = \frac{\alpha \sigma}{\kappa}
\]

where \(\alpha\) is Seebeck coefficient, \(\kappa\) thermal conductivity, and \(\sigma\) electrical conductivity. They are plotted against the composition in Fig. 10. The dotted line is Z values calculated by using pair-type model:

\[
Z_{\text{mix}} = \left\{ \frac{\alpha_0 (1 - V_1) + \alpha_1 V_1}{\left( \frac{\sigma_0}{\sigma_1} \right)^{1/3} (1 - V_1) + \left( \frac{\sigma_1}{\sigma_0} \right)^{1/3} V_1} \right\}
\]

where the subscripts 0 and 1 mean the values of matrix and grain, respectively. If neither carrier nor phonon is scattered at the boundary, the figure of merit of a composite has a value volume-averaged between those of the pure materials. The x=0.5 sample has the figure of merit larger than that of the averaged value without scattering. It should be pointed out that the lattice thermal conductivity is significantly decreased by dispersing the Ag7Te3 grain into the AgBiTe2 matrix.

5. Conclusions
We prepared a series of composite materials with
AgBiTe$_2$ and Ag$_2$Te with the composition of $(\text{AgBiTe}_2)_{1-x}(\text{Ag}_2\text{Te})_x$ ($x=0-1.0$). The Ag$_2$Te grains are dispersed in the AgBiTe$_2$ matrices. The phonon scattering is enhanced at the boundary, resulting in the enhancement of the figure of merit. Such composites may open a way to improve the thermoelectric property.

Fig. 10. Thermoelectric figure-of-merit of $(\text{AgBiTe}_2)_{1-x}(\text{Ag}_2\text{Te})_x$ composites calculated from Seebeck coefficient, electrical conductivity and thermal conductivity.

References