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Synthesis and Characterization of $AgPb_{18}SbTe_{20}$ doped with PbI_2

S. Yoneda, Y. Hikage, Y. Ohno, Y. Isoda*, Y. Imai* and Y. Shinohara*
Department of Electronics and Informatics Frontiers, Kanagawa University
Rokkakubashi 3-27-1, Kanagawa-ku, Yokohama, Kanagawa 221-8686
Fax: 81-45-491-7915, e-mail: yoneds01@kanagawa-u.ac.jp
* Eco-material Research Center, National Institute for Material Science
Sengen 1-2-1, Tsukuba, Ibaraki 305-0047
Fax: 81-298-59-2601

We attempted to synthesize solidified $AgPb_{18}SbTe_{20}$ doped with PbI_2, which is an *n*-type dopant for PbTe, and evaluated its electrical and thermal conduction properties in order to investigate the possibility of improving its performance. Large amounts of dispersed and interconnected precipitates with a size of approximately 100 μm were observed, and small cobweb-like precipitates were observed in these precipitates. The consistency of Ag, Sb, Te, and I in these areas was found to be higher than that in other areas. It is suggested that the precipitates are $AgSbTe_2$. The consistency of Ag in the small cobweb-like precipitates was found to be higher than that in other areas. It was evident that the carrier density at room temperature was approximately three times higher than that of undoped $AgPb_{18}SbTe_{20}$. It was found that the figure-of-merit at room temperature was 2.4 times higher than that of undoped $AgPb_{18}SbTe_{20}$. The temperature dependence of 1/(resistivity ρ × thermal conductivity κ), which is a factor of the performance of thermoelectric materials, was evaluated. It was found that $1/(\rho\kappa)$ is larger than that of undoped $AgPb_{18}SbTe_{20}$ at temperatures below 170°C. It was suggested that doping of PbI_2 contributed to the improved thermoelectric performance.

Key words: $Ag_{18}PbSbTe_{20}$, PbI_2, carrier density, thermoelectric improvement

1. INTRODUCTION

High efficiency thermoelectric generating system requires superior generating technique and high efficiency thermoelectric generating module. It is necessary to develop a high performance thermoelectric material in order to obtain a highly efficient thermoelectric generating module.

$AgPb_{18}SbTe_{20}$ has attracted worldwide attention as thermoelectric materials with a high figure-of-merit Z or dimensionless figure-of-merit ZT in the mid-temperature range of 400–800 K [1]. We fabricated $AgPb_{18}SbTe_{20}$ and evaluated its electrical and thermal properties in order to investigate possibility of its reproducible performance [2]. The value of ZT at room temperature was found to be 0.07; approximately one order smaller than that reported by Kuei et al [1]. It is suggested that the primary reason for this reduction is its significantly low carrier density. This indicates that its carrier density is smaller than that of a typical thermoelectric material.

In this study, we tried to fabricate $AgPb_{18}SbTe_{20}$ doped with PbI_2, which is an *n*-type dopant for PbTe, and evaluated its electrical and thermal conduction properties in order to investigate any possible improvement in performance.

2. EXPERIMENTAL PROCEDURE

Pb, Te (6N), Ag, Sb (5N), and PbI_2 (5N) in a composition of $AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2 were weighed and encapsulated in a quartz tube with a conical head in a vacuum of 1×10^{-3} Pa. The contents of the tube were then melted and stirred horizontally in a rocking furnace at 1273 K for 1 h [3]. Subsequently, the tube was vertically cooled down to 1173 K at a growth rate of 150 K/h under a temperature gradient of 1 K/mm and a rocking cycle of 0.3 Hz. The rocking was stopped when the lower portion of the top part of the tube cooled down to 1173 K.

The structure of the obtained boule was observed using an OM (BX51M, Olympus Corporation), and its composition was analyzed by EPMA (JXA-8500F, JEOL). The resistivity ρ and Hall coefficient R_H were measured by the dc method at a high speed and resolution in order to prevent errors arising due to the Peltier effect [4]. R_H was measured in a 0.35 T magnetic field. The thermoelectric power α was measured using a cryostat in a vacuum of 1×10^{-4} Pa. The measurement of κ was carried out by the laser flash method.

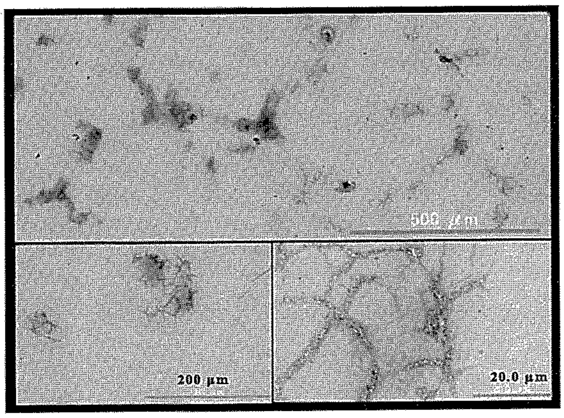

Fig. 1 $AgPb_{18}SbTe_{20}$+ 1.0mass%PbI_2 observed by OM.

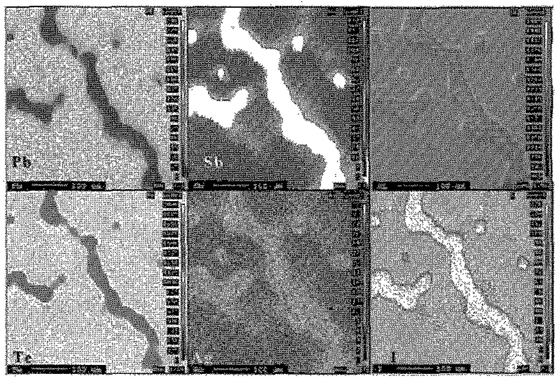

Fig. 2 Pb, Ag, Sb, Te, and I images obtained by EPMA.

3. RESULTS AND DISCUSSION

The obtained PbI_2-doped $AgPb_{18}SbTe_{20}$ was polished to a mirror finish and its surface was etched. The surface tissue observed by an OM is shown in Fig. 1. Large amounts of dispersed and interconnected precipitates with a size of approximately 100 μm were observed. These precipitates were analyzed by EPMA and the corresponding images are shown in Fig. 2. While a higher consistency is observed in the white area, that in blue area is lower. The consistency of Ag, Sb, Te, and I in these areas was found to be higher than that in the other areas. It is suggested that these precipitates are $AgSbTe_2$. Additionally, small cobweb-like precipitates were observed in these precipitates under high-power field. The consistency of Ag in these areas was found to be higher than that in the other areas.

Furthermore, it was expected that the *n*-type dopant PbI_2 for the PbTe was melted into PbTe matrix. Contrary to our expectation, I was detected in the precipitates ($AgSbTe_2$ phase). However, it was confirmed that PbI_2 acted as an *n*-type dopant because the carrier density n_H was approximately three times higher than that of undoped $AgPb_{18}SbTe_{20}$, as shown in Table 1. Moreover, the resistivity ρ was reduced to approximately one-fifth of that of undoped $AgPb_{18}SbTe_{20}$ due to the increasing n_H and this demonstrated the possibility of an improvement in the electrical conduction performance.

Table 2 lists the thermoelectric properties of $AgPb_{18}SbTe_{20}$ and $AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2. The thermoelectric power α decreased with increasing n_H with the doping of PbI_2. It was suggested that κ increased due to the increase in the carrier thermal conductivity κ_{car}. The figure-of-merit *Z* and the dimensionless figure-of-merit *ZT* were 2.4 times higher than that of undoped $AgPb_{18}SbTe_{20}$. The doping of PbI_2 was shown to contribute to the improved thermoelectric performance at room temperature.

Table 1 Electrical properties of $AgPb_{18}SbTe_{20}$ and $AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2.

Sample	ρ (Ωm)	R_H (m³/C)	n_H (1/m³)	μ_H (m²/Vs)
$AgPb_{18}SbTe_{20}$	2.72×10^{-4}	6.5×10^{-6}	9.6×10^{23}	0.024
$AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2	5.49×10^{-5}	2.1×10^{-6}	2.9×10^{24}	0.039

Table 2 Thermoelectric properties of $AgPb_{18}SbTe_{20}$ and $AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2.

Sample	ρ (Ωm)	α (μV/K)	κ (W/(mK))	*Z* (1/K)	*ZT*
$AgPb_{18}SbTe_{20}$	2.72×10^{-4}	–273.0	0.84	3.3×10^{-4}	0.10
$AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2	5.49×10^{-5}	–232.6	1.24	7.9×10^{-4}	0.24

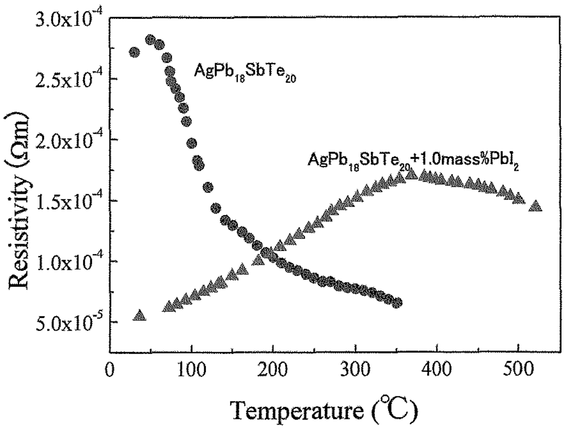

Fig. 3 Temperature dependence of ρ of $AgPb_{18}SbTe_{20}$ and $AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2.

Figure 3 shows the temperature dependence of ρ of $AgPb_{18}SbTe_{20}$ and $AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2. Resistivity ρ of $AgPb_{18}SbTe_{20}$ decreased rapidly up to 125°C and then decreased slowly with increasing temperature. This behavior was similar to that of an impurity semiconductor. On the other hand, ρ of $AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2 increased slowly up to 380°C and then decreased. This behavior was similar to that of a degenerated semiconductor.

Figure 4 shows the temperature dependence of κ of $AgPb_{18}SbTe_{20}$ and $AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2. Thermal conductivity κ of $AgPb_{18}SbTe_{20}$ increased

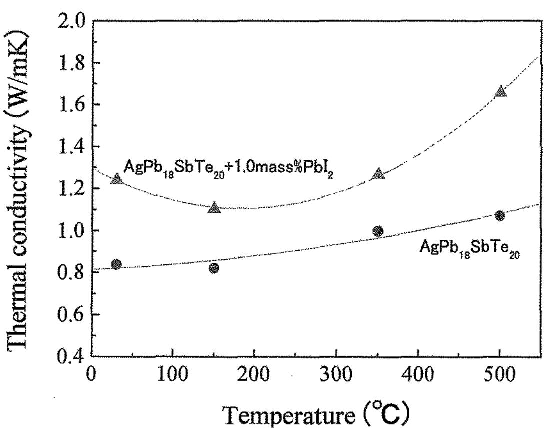

Fig. 4 Temperature dependence of κ of $AgPb_{18}SbTe_{20}$ and $AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2.

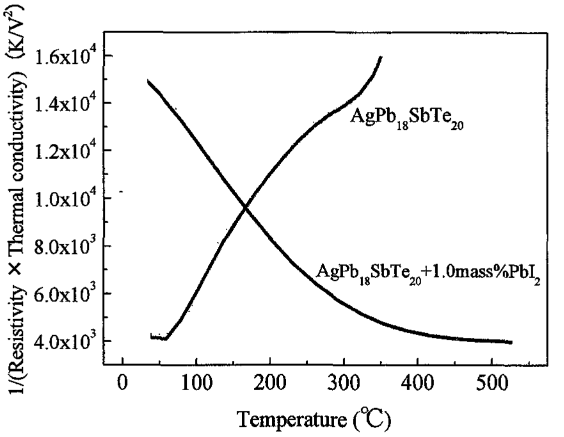

Fig. 5 Temperature dependence of $1/(\rho\kappa)$ of $AgPb_{18}SbTe_{20}$ and $AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2.

linearly with temperature. It is suggested that κ of $AgPb_{18}SbTe_{20}$ was not dependent on ρ because the lattice thermal conductivity κ_{ph} dominates κ [2]. Thermal conductivity κ of $AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2 tended to increased rapidly for temperature above 350°C. This temperature corresponds to that where the tendency in ρ reversed from increasing to decreasing. From these results, it is suggested that the contribution of κ_{car} in κ was increased.

Here, the formula for the performance of thermoelectric materials was expressed as $Z = \alpha^2/\rho\kappa$. Then, the temperature dependence of $1/(\rho\kappa)$, which was the denominator of Z, was estimated and shown in Fig. 5. It was found that $1/(\rho\kappa)$ of $AgPb_{18}SbTe_{20}$ + 1.0mass%PbI_2 is larger than that of undoped $AgPb_{18}SbTe_{20}$ at temperatures below 170°C. Therefore, it was suggested that the doping of PbI_2 contributed to the improved thermoelectric performance.

4. CONCLUSIONS

We attempted to synthesize $AgPb_{18}SbTe_{20}$ doped with PbI_2, which is an *n*-type dopant for PbTe, and evaluated electrical and thermal conduction properties in order to investigate the possibility of improving its performance.

Our conclusions are as follows:

(1) The surface tissue was observed by an OM. Large amounts of dispersed and interconnected precipitates with a size of approximately 100 μm were observed, and small cobweb-like precipitates were observed in these precipitates.

(2) The precipitates were analyzed by EPMA. The consistency of Ag, Sb, Te, and I in these areas was found to be higher than that in other areas. It is suggested that the precipitates are $AgSbTe_2$. The consistency of Ag in the small cobweb-like precipitates was found to be higher than that in other areas.

(3) It was evident that the carrier density at room temperature was approximately three times higher than that of undoped $AgPb_{18}SbTe_{20}$.

(4) It was found that the figure-of-merit at room temperature was 2.4 times higher than that of undoped $AgPb_{18}SbTe_{20}$.

(5) The temperature dependence of $1/(\rho\kappa)$, which is a factor of the performance of thermoelectric materials ($=\alpha^2/\rho\kappa$), was evaluated. It was found that $1/(\rho\kappa)$ is larger than that of undoped $AgPb_{18}SbTe_{20}$ at temperatures below 170°C. It was suggested that doping of PbI_2 contributed to the improved thermoelectric performance above 170°C.

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