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Thermoelectric Properties of Solidified PbTe Doped with $AgSbTe_2$

S. Yoneda, Y. Ohno, Y. Isoda*, Y. Imai* and Y. Shinohara*
Department of Electrical, Electronics and Information, 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

Solidified PbTe doped with $AgSbTe_2$ was grown in a rocking furnace. The solidified $Pb_{18}AgSbTe_{20}$ ingot thus obtained was cut along the growth direction, and the cross section was observed using an optical microscope. It was confirmed that participates, which had a size of approximately 100 μm, were dispersed. By EPMA analysis, it was determined that the mother phase was PbTe and the other phases consisted of Ag, Sb and Te atoms. The diffraction pattern of a single phase of PbTe was obtained by XRD. The figure-of-merit the dimensionless figure-of-merit at room temperature was found to be 2.2×10^{-4} K^{-1} and 0.07, respectively.
Key words: thermoelectric property, figure-of-merit, dimensionless figure-of-merit, $Pb_{18}AgSbTe_{20}$

1. INTRODUCTION

Thermoelectric generation has received considerable attention because it efficiently utilizes energy and reduces the emission of CO_2 by recycling unused thermal energy and/or exhaust heat energy. On a relevant note, the national research project with regard to the development of a high efficiency thermoelectric generating system is progressing.

High efficiency thermoelectric generating systems are required in superior generating technique and high efficiency thermoelectric generating modules. For obtaining these modules, the development of high performance thermoelectric material is required.

TAGS (Tellurium-Antimony-Germanium-Silver), Zn_4Sb_3, and $AgSbTe_2$ have been reported in several articles as thermoelectric materials with high figure-of-merit Z or dimensionless figure-of-merit ZT in the middle temperature ranges 400-800 K; their reproducible performance has also been confirmed. However, these materials are p-type conductive. Thus, it is considered that high performance n-type thermoelectric materials are required.

In 2004, the ZT of n-type $Pb_{18}AgSbTe_{20}$ was reported to be 2.2. [1] This material has great potential as a high performance n-type thermoelectric material. Therefore, some research institutes are currently conducting research on this material. However, the reproducibility of its performance has not been confirmed thus far.

In this study, we attempted to synthesize $Pb_{18}AgSbTe_{20}$ and evaluated its electrical and thermal properties in order to investigate the possibility of the reproducibility of its performance.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of $Pb_{18}AgSbTe_{20}$

Pb (6N), Ag (5N), Sb (5N) and Te (6N) were weighed at a composition of $Pb_{18}AgSbTe_{20}$ and encapsulated in a quartz tube with a conical head in a vacuum of 1×10^{-3} Pa. The contents of the tube were melted and stirred horizontally in a rocking furnace[2] at 1273 K for 1 h, and 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 by an OM (optical microscope), the phases were analyzed by XRD (X-ray diffraction, RINT-RAPID Rigaku) and the composition was analyzed by EPMA (electron probe microanalysis, JXA-8500F, JEOL).

2.2 Evaluation of the thermoelectric properties

The resistivity ρ and Hall coefficient R_H were measured by the dc method at a high speed and high resolution to prevent errors due to the Peltier effect.[3] R_H was measured in a magnetic field of 0.35 T. The Hall carrier density n_H and Hall mobility μ_H were expressed as $n_H = 1/(eR_H)$ and $\mu_H = R_H/\rho$, respectively, where e denotes the elementary charge. The thermoelectric power α and thermal conductivity κ were measured

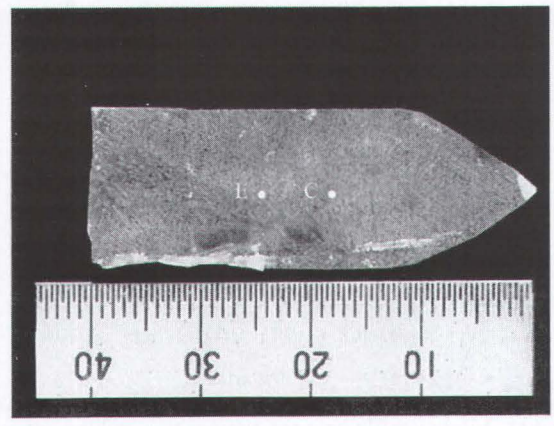

Fig. 1 $Pb_{18}AgSbTe_{20}$ boule.

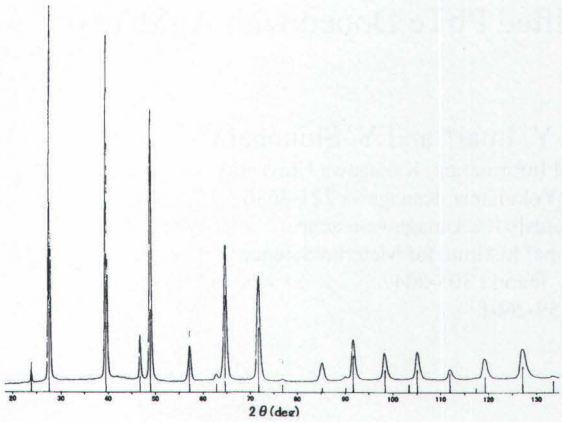

Fig. 2 X-ray diffraction pattern of $Pb_{18}AgSbTe_{20}$ ingot.

with a cryostat in a vacuum of 1×10^{-4} Pa. The measurement of κ was carried out by the static comparative method using transparent quartz as the standard specimen. α was obtained from the slope of a thermoelectromotive force - temperature difference ΔT curve. The figure-of-merit $Z = \alpha^2/(\rho\kappa)$ was estimated from the measured ρ, α and κ.

3. RESULTS AND DISCUSSION

3.1 Evaluation of the obtained boule

A section of the obtained $Pb_{18}AgSbTe_{20}$ boule measuring 15 mm in diameter and 40 mm in length is shown in Fig. 1. Line analysis for growth direction and vertical growth direction was carried out by EPMA. The homogeneous distribution of individual atoms was confirmed. Points C and E shown in Fig. 1 were then analyzed by XRD. As a representative case, the XRD pattern at point C is shown in Fig. 2. All diffraction peaks roughly corresponded to the diffraction peaks of PbTe, and no unidentified diffraction peak was observed. A single phase was confirmed in the boule by XRD analysis. The lattice constant d was derived from each diffraction peak, and was found to be 6.444 Å at point C and 6.441Å at point D. The d values of PbTe and $AgSbTe_2$ in the JCPDS cards are 6.459 and 6.080 Å, respectively. The relationship between the composition ratio of PbTe-$AgSbTe_2$ and d is shown in Fig. 3. d values at points C and D were plotted; these values were

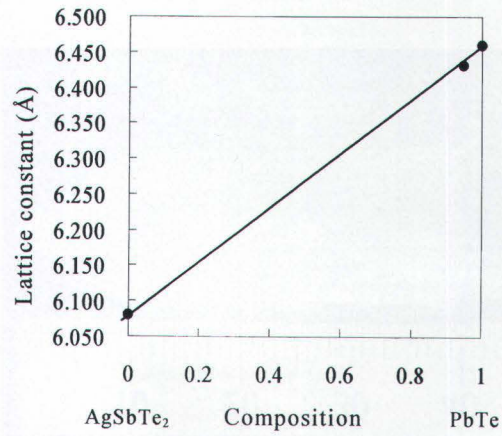

Fig. 3 Relationship between composition and the lattice constant.

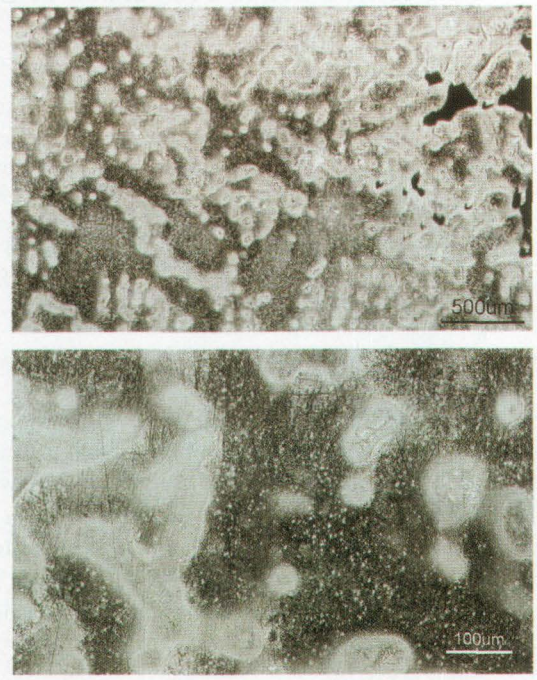

Fig. 4 $Pb_{18}AgSbTe_{20}$ observed by OM.

found to lie on the line drawn from the d value of PbTe to that of $AgSbTe_2$. The d value on the line at the $Pb_{18}AgSbTe_{20}$ composition is 6.439 Å and it corresponds to the experimental values. Thus, the d values were found to follow Vegard's law.

Next, the boule section was polished to a mirror and the surface was etched. The surface tissue observed by an OM is shown in Fig. 4. Large amount of participates with a size of approximately 100 μm, were found to be dispersed. In addition, thickness coats were observed around the participates.

The participates shown in Fig. 4 were analyzed by EPMA and the corresponding images are shown in Fig. 5. While a higher consistency is observed in the white

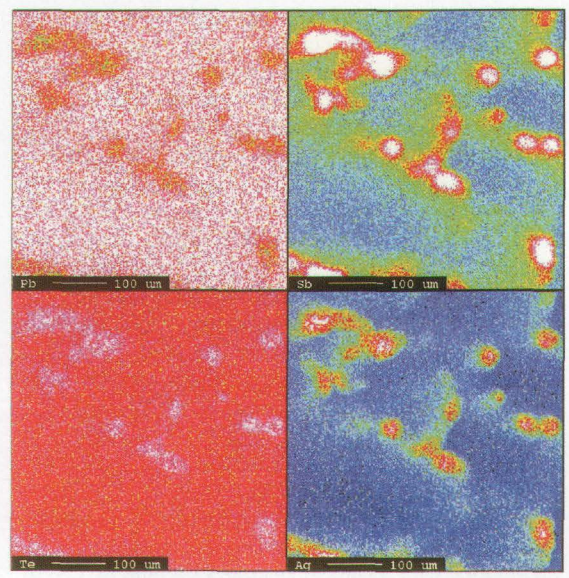

Fig. 5 Pb, Ag, Sb and Te images obtained by EPMA .

Table 1 Resistivity ρ, thermoelectric power α, thermal conductivity κ, figure-of-merit Z and dimensionless figure-of-merit ZT.

ρ (Ωm)	α (μV/K)	κ (W/(mK))	Z (1/K)	ZT
2.72×10^{-4}	-273.0	1.23	2.2×10^{-4}	0.07

area, that in blue area is lower. The consistency of Ag, Sb and Te in the participates was higher in this area than that in the other area. On the basis of XRD experiment results, it is suggested that the precipitates are $AgSbTe_2$.

3.2 Evaluation of the thermoelectric properties

Table 1 lists the resistivity ρ, thermoelectric power α, thermal conductivity κ figure-of-merit Z and dimensionless figure-of-merit ZT. Table 2 lists that the Hall coefficient R_H, Hall carrier density n_H, Hall mobility μ_H, carrier thermal conductivity κ_{car} and lattice thermal conductivity κ_{ph}. Then, κ_{ph} is expressed as

$$\kappa_{ph} = \kappa - \kappa_{car} \quad (1)$$

and κ_{car} is estimated as

$$\kappa_{car} = LT/\rho \quad (2)$$

where T and L denote the absolute temperature and the Lorentz number, respectively, and a value of 2.45×10^{-8} V^2/K^2 was used for L. The value of κ_{car} thus obtained was found to be significantly small. It was also found that κ_{ph} was dominant in κ.

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] Similarly, the value of ρ was approximately two orders larger than the reported value. The value of κ was one-half of the reported value, and κ_{ph} was dominant. The value of α was twice as large as the reported value. The physical factor common to all these electrical and thermal parameters is a carrier density. In general, the optimum carrier density of a thermoelectric material is approximately of the order 10^{25} ($1/m^3$). However, the value of n_H was of the order of 10^{23} ($1/m^3$). It is suggested that main reason for the difference between the values of the specimen in this study and those reported in the article is the significantly small carrier density of the specimen in this study. As mentioned in the above composition analysis, Ag, Sb and Te were observed to be precipitated. Thus, it was supposed that the reduction in carrier density resulted from the micro scale scant dispersion of Ag, Sb and Te. It can be said that there is a possibility of the reproducibility of its performance by controlling the carrier density.

Table 2 Hall coefficient R_H, Hall carrier density n_H, Hall mobility μ_H, carrier thermal conductivity κ_{car} and lattice thermal conductivity κ_{ph}.

R_H (m^3/C)	n_H ($1/m^3$)	μ_H (m^2/Vs)	κ_{cal} (W/(mK))	κ_{ph} (W/(mK))
6.5×10^{-6}	9.6×10^{23}	0.024	0.03	1.20

4. CONCLUSIONS

We attempted to synthesize $Pb_{18}AgSbTe_{20}$ and evaluated its electrical and thermal properties in order to investigate the possibility of the reproducibility of its performance. We arrived at the following conclusions:

(1) All diffraction peaks of solidified $Pb_{18}AgSbTe_{20}$ roughly corresponded to the diffraction peaks of PbTe and no unidentified diffraction peak was observed. A single phase was confirmed in the boule by X-ray diffraction analysis.

(2) Lattice constant d of solidified $Pb_{18}AgSbTe_{20}$ was located on the line drawn from the d value of PbTe to that of $AgSbTe_2$. It was found that the lattice constant followed Vegard's law.

(3) The solidified $Pb_{18}AgSbTe_{20}$ boule section was polished to a mirror. The surface was etched and the surface tissue was observed by an OM. Large amounts of participates with a size of approximately 100 μm were found dispersed.

(4) The participates were analyzed by EPMA. The consistency of Ag, Sb and Te in the participates was found to be higher than that in the other area. On the basis of X-ray diffraction experiment results, it is suggested that the precipitates are $AgSbTe_2$.

(5) The value of dimensionless figure-of-merit ZT at room temperature was found to be 0.07. It is suggested that main reason for the reduction in it is the significantly small carrier density resulted from the micro scale scant dispersion of Ag, Sb and Te.

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