Improved Thermoelectric Properties in Structure Controlled Ag-Sb-Te System

Seiji Yoneda* Member
Yoshihiro Ohno* Member
Eiji Ohta** Non-member
Nobuhiro Yuhashi*** Non-member
Ichiro Shiota**** Non-member
Yoshikazu Shinohara***** Non-member
Hiromasa T. Kaibe****** Non-member
Isao J. Ohsugi******* Non-member
Isao A. Nishida******* Member

The p-type Ag0.208Sb0.275Te0.517 boule was unidirectionally grown using a Bridgman furnace and, it was subsequently cooled rapidly by an Ar flush to form a high temperature phase AgSbTe2, which could be desirable for power generation. Though the boule looked a homogeneous Widmannstätten structure of the AgSbTe2 phase, XRD patterns revealed that some precipitates of Ag2Te and Sb2Te3 were contained in the boule and increased in volume in the growth direction. The relationship between the transformation and the thermoelectric properties was investigated. Figure-of-merit Z of the p-type Ag0.208Sb0.275Te0.517 boule has been evaluated in the temperature range from 300 to 700 K. The maximum figure-of-merit Zmax was different in the portions of the boule. The value of 2.0×10^-3 /K was for the former half portion of the boule at 620 K and that of 1.7×10^-3 /K was for the latter half portion at 585 K. The Ag0.208Sb0.275Te0.517 boule with less precipitates showed a higher Z at higher temperatures. Possibility of improving thermoelectric properties in Ag-Sb-Te system was pointed out.

Keywords: AgSbTe2, figure-of-merit, Ag2Te, Sb2Te3, Widmannstätten structure, XRD

1. Introduction

The p-type Pb1-xSnxTe solid solution and n-type PbTe doped with PbI2 have been well known as leg materials applied to thermoelectric generating devices in the middle temperature range(1)(2). Figure-of-merit Z of Pb1-xSnxTe solid solution is, however, considerably smaller than that of the n-type PbTe(3), and energy conversion efficiency of the devices still remains low. Though Rosi et al(4). reported that the AgSbTe2 compound was promising as p-type thermoelectric material in the middle temperature range(400-750 K), it has not been practically utilized because of its thermal unstability. According to the phase diagram of Ag1Te-Sb2Te3 (Fig. 1(5)), the AgSbTe2 compound has transformations at 418 and 633 K; α-Ag2Te + Sb2Te3 ↔ α’-Ag2Te + Sb2Te3 at 418 K and α’-Ag2Te + Sb2Te3 ↔ α’-Ag2Te + AgSbTe2 at 633 K. A high temperature single phase of AgSbTe2 has been prepared at a composition of Ag0.208Sb0.275Te0.517, as shown in Fig. 1, and it has been reported that the 2AgSbTe2 → α’-Ag2Te + Sb2Te3 transformation that relations with the temperature dependence of the effective maximum power Pmax have been reported(6)(7). It is, however, still unknon how temperature dependences of the thermoelectric properties (electrical resistivity ρ, Seebeck coefficient α and thermal conductivity κ) and Z is affected by the 2AgSbTe2 → α’-Ag2Te + Sb2Te3 transformation.
We prepared a high temperature single phase of AgSbTe$_2$ at a composition of Ag$_{0.208}$Sb$_{0.275}$Te$_{0.517}$ and investigated the effect of the 2AgSbTe$_2 \rightarrow \alpha'$-Ag$_2$Te + Sb$_2$Te$_3$ decomposition on temperature dependences of the properties and Z.

In this article, the possibility of improving power generating performance in the Ag-Sb-Te system is described.

2. Experimental Procedure

2.1 Preparation of Ag$_{0.208}$Sb$_{0.275}$Te$_{0.517}$ Ag (5N), Sb (5N) and Te (6N) were weighed at a composition of Ag$_{0.208}$Sb$_{0.275}$Te$_{0.517}$, which is shown by the broken line in Fig.1. They were encapsulated into a quartz tube with a conical head in a vacuum of $1 \times 10^{-5}$ Pa. The contents in the tube were melted in a Bridgeman furnace at 873 K for 24 hours, and then a boule was unidirectionally grown at the growth rate of $4.6 \times 10^{-2}$ K/s under the temperature gradient of 3.5 K/mm. When the lower top part of the tube was cooled down to 633 K, the furnace was turned off and cold Ar gas was flushed along the growth direction from the lower top part to the upper part, in order to cool the boule rapidly. The obtained boule was 12 mm in diameter and 90 mm in length.

The structure of the obtained boule was observed by OM(optical microscope), and the phases were analyzed by XRD(X-ray diffraction).

2.2 Evaluation of the Thermoelectric Properties $\rho$ and Hall coefficient $R_H$ were measured by the dc method with high speed and high resolution to prevent errors by Peltier effect.$^{(8)}$ Temperature dependence of $\rho$ was measured in an Ar atmosphere in the temperature range from 300 to 720 K. $\alpha$ at room temperature and $\kappa$ below 350 K were measured with a cryostat$^{(9)}$ in a vacuum of $1 \times 10^{-2}$ Pa. The measurement of $\kappa$ was carried out by the static comparative method using a transparent quartz as the standard specimen. $\alpha$ was obtained from a slope of the thermoelectromotive force $E_0$ - temperature difference AT curve using a Seebeck coefficient / electric resistance measuring system in the temperature range from 300 to 720 K. $\kappa$ was measured by the laser-flash instrument in the temperature range from 300 to 720 K. Figure-of-merit $Z = \alpha^2/(\rho \kappa)$ in the temperature range from 300 to 720 K was estimated from the measured $\rho$, $\alpha$, and $\kappa$.

3. Results and Discussions

3.1 Evaluation of Ag$_{0.208}$Sb$_{0.275}$Te$_{0.517}$ Boule and Thermoelectric Properties at Room Temperature

Figure 2 shows the morphology in the cross section normal to the growth direction. A homogeneous Widmannstätten structure was observed in the early-grown part I, and the middle part II and late-grown part III showed the same morphology.

Powder diffraction patterns obtained by XRD are shown in Fig. 1. It was concluded that every part of I, II and III consists of Ag$_2$Te, Sb$_2$Te$_3$, AgSbTe$_2$. The early-grown part I was nearly a phase of AgSbTe$_2$, while the late-grown part contained larger amounts of Ag$_2$Te and Sb$_2$Te$_3$. Like this difference in the phase is caused by the difference in the cooling rate, though the morphology looks the same by OM. The cooling rate is determined to be higher in the order of I, II and III.

Thermoelectric properties of the former half (A) between I and II, and the latter half (B) between II and III were evaluated at room temperature. The results are listed in Table 1. The $\rho$ of (B) is approximately one order smaller than that of (A), while the apparent Hall concentration, $n_H$ of (B) is approximately one order larger than that of (A). This is caused by the decomposition of 2AgSbTe$_2 \rightarrow$ Ag$_2$Te + Sb$_2$Te$_3$, which is deduced from the phase diagram and the results of the XRD experiment. The $\alpha$ of (B) was one half times of that of (A), and the $\kappa$ was 0.7 and 1.0 W/(Km) for (A) and (B). Lattice thermal conductivity $\kappa_{ph}$ calculated from the Wiedemann-Franz law was 0.6 W/(Km) for both (A) and (B), which is smaller than the value for the sintered Bi$_2$Te$_3$ (1.1

<table>
<thead>
<tr>
<th>Part</th>
<th>$\rho$ [10$^\Omega$m]</th>
<th>$n_H$ [10$^{16}$/m$^3$]</th>
<th>$\mu_H$ [10$^3$ m$^2$/Vs]</th>
<th>$\kappa_{ph}$ [10$^2$ W/(Km)]</th>
<th>$\alpha$ [10$^2$ /K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>16.2</td>
<td>2.62</td>
<td>1.47</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>(B)</td>
<td>2.19</td>
<td>23.8</td>
<td>1.20</td>
<td>123</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Part</th>
<th>$\kappa$ [W/(Km)]</th>
<th>$\kappa_{ph}$ [W/(Km)]</th>
<th>$\alpha^2/\rho$ [10$^5$ W/(Km)$^2$]</th>
<th>$Z$ [10$^{-7}$/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>0.7</td>
<td>0.6</td>
<td>4.50</td>
<td>0.65</td>
</tr>
<tr>
<td>(B)</td>
<td>1.0</td>
<td>0.6</td>
<td>6.91</td>
<td>0.71</td>
</tr>
</tbody>
</table>
decrease with decreasing temperature. However, $\kappa_{\text{ph}}$ and $\kappa_{\text{carrier}}$ below 350K. Generally, the phonon mean free path increases with decreasing temperature because phonon collisions decrease with decreasing temperature. However, $\kappa_{\text{ph}}$ did not depend on the temperature. The phonon scattering must occur in the shorter range than the mean free path, for example at structure or grain boundaries. We consider that the Widmanstätten structure contributes to decreasing $\kappa_{\text{ph}}$ in AgSbTe$_2$. [It is noted that decreasing $\kappa_{\text{ph}}$ by phonon scattering at structure boundaries occurs for such as sintered Bi$_2$Te$_3$ with a fine crystal grain size.]

3.2 Temperature Dependence of Thermoelectric Properties in the Temperature Range from 300-720 K

3.2.1 Resistivity Figure 5 shows the temperature dependence of $\rho$ for the former half (A) and the latter half (B) of the Ag$_{0.208}$Sb$_{0.275}$Te$_{0.517}$ boule. The $\rho$ of (A) was larger than that of (B) in the whole temperature range. It was reported that the $\rho$ at room temperature, $\rho_{\text{RT}}$, of single phase Sb$_2$Te$_3$ was $2.0\times10^{-6}$ $\Omega$m.

Thus, the $\rho$ in AgSbTe$_2$ single phase by the transformation of $\alpha'\rightarrow\alpha'$-Ag$_2$Te + Sb$_2$Te$_3$ during the measurement in the temperature range from 418K to 633K. The $\rho$ of (A) was independent of temperature above the transformation temperature of 418 K. This is caused by the transformation of $\alpha\rightarrow\alpha$-Ag$_2$Te. Then, the $\rho$ decreased with increasing temperature. As above mentioned, this is mainly due to the increased $\rho_{\text{RT}}$ caused by the decomposition of 2AgSbTe$_2\rightarrow\alpha'\rightarrow\alpha$-Ag$_2$Te + Sb$_2$Te$_3$ during the measurement in the temperature range from 418K to 633K. The $\rho$ of (A) was almost AgSbTe$_2$ single phase, while that of (B) tended to increase with temperature. It is considered that (B) is increasing the amount of Ag$_2$Te single phase by the transformation of $\alpha'\rightarrow\alpha'$-Ag$_2$Te + Sb$_2$Te$_3$ above 633 K.

3.2.2 Seebeck coefficient Figure 6 shows temperature dependence of the $\alpha$ for the former half (A) and the latter half (B) of the Ag$_{0.208}$Sb$_{0.275}$Te$_{0.517}$ boule. The $\alpha$ of (A) was larger than that of (B) in the whole temperature range. This is caused by larger $n_i$ of (B) than that of (A) due to which is corresponding to the different amount of Ag$_2$Te and Sb$_2$Te$_3$ precipitates between (A) and (B). The $\alpha$ of both (A) and (B) increased at 418 K. This is caused by the transformation of $\alpha\rightarrow\alpha$-Ag$_2$Te + Sb$_2$Te$_3$ makes only a little influence on decreasing the tendency of the $\alpha$ of (A). The transformation of $\alpha'\rightarrow\alpha$-Ag$_2$Te + Sb$_2$Te$_3$ makes only a little influence on $\alpha$ at 633K. On the other hand, the $\alpha$ of (B) increased slightly with temperature up to 600 K and decreased above 600 K. The $\alpha$ of (B) also changes the slope at 633K as well as that of (A). More amounts of Ag$_2$Te and Sb$_2$Te$_3$ precipitates are included in (B) than in (A). Not only the Ag$_2$Te$_2$ phase but also the Ag$_2$Te and Sb$_2$Te$_3$ precipitates contribute to the $\alpha$ of (B). The intrinsic region of Sb$_2$Te$_3$ is at least less than 550K, which indicates Sb$_2$Te$_3$ increases $\alpha$ with temperature up to 550K. It is suggested that the
maximum $\alpha$ of (B) at 600K is a result of the complicated AgSbTe$_2$, Ag$_2$Te and Sb$_2$Te$_3$ phases.

**3.2.3 Thermal conductivity** Figure 7 shows the temperature dependence of the $\kappa$ for the former half (A) and the latter half (B) of the Ag$_{0.208}$Sb$_{0.275}$Te$_{0.517}$ boule. The $\kappa$ of both (A) and (B) tends to increase slightly with increasing temperature. The $\kappa$ of (B) was larger than that of (A) in the whole temperature range. The values of $\alpha_{\text{RT}}$ were 0.7 and 1.0 W/(Km), and the $\alpha$ values at 720 K were 1.0 and 1.3 W/(Km), respectively. The increases in $\kappa$ were small, viz., smaller than only 0.3 W/(Km). The Ag$_{0.208}$Sb$_{0.275}$Te$_{0.517}$ boule indicates low temperature dependence of the $\kappa$.

**3.2.4 Figure-of-merit** Figure 8 shows temperature dependence of the figure-of-merit $Z$ calculated from measured $\rho$, $\alpha$ and $\kappa$ for the former half (A) and the latter half (B) of the Ag$_{0.208}$Sb$_{0.275}$Te$_{0.517}$ boule. The temperature at which $Z$ reached $Z_{\text{max}}$ for (A) and (B) are 620 and 585 K, respectively. The $Z_{\text{max}}$ value for (A) was $2.0 \times 10^{-3}$/K, and that for (B) was $1.7 \times 10^{-3}$/K. The $Z$ values of both the parts were higher than 1. It was found that the AgSbTe compounds possessed superior performances as $p$-type thermoelectric material in the middle temperature range. The $Z$ of both (A) and (B) tended to increase with temperature in the temperature range from 418 to 600 K, which was caused by decreases in $\rho$ of (A) and (B) due to increasing decomposition of 2AgSbTe$_2$ $\rightarrow$ $\alpha'$- Ag$_2$Te + Sb$_2$Te$_3$ caused during the measurement. The $Z$ curves of (A) and (B) were crossed around 600 K, and the $Z$ curve of (B) decreased drastically. It is concluded that Ag$_2$Te and Sb$_2$Te$_3$ precipitates are inferior in $Z$ to AgSbTe$_2$ phase above 600 K.

**3.2.5 Possibility of improving thermoelectric properties in Ag-Sb-Te system** From these results, (A) possesses a high power generating performance above 600 K, and (B) possesses a high power generating performance below 600 K. The total power generating performance will be improved by arranging Ag$_2$Te phase for the portion above 600 K and arranging Ag$_{0.208}$Sb$_{0.275}$Te$_{0.517}$ phase for the portion below 600 K. It is concluded that the thermoelectric properties in Ag-Sb-Te system can be improved by controlling the size of Widmannstätten structure, the precipitation ratio of Ag$_2$Te and Sb$_2$Te$_3$, crystallization of Ag$_2$Te, Sb$_2$Te$_3$ and AgSbTe$_2$ and anisotropy of precipitated Sb$_2$Te$_3$.

**4. Conclusion**

A high temperature single phase of AgSbTe$_2$ was prepared at a composition of Ag$_{0.208}$Sb$_{0.275}$Te$_{0.517}$, and the effect of the 2AgSbTe$_2$ $\rightarrow$ $\alpha'$- Ag$_2$Te + Sb$_2$Te$_3$ decomposition on temperature dependences of the thermoelectric properties and $Z$ was investigated. The relationship between the transformation and the thermoelectric properties was clarified and possibility of improving thermoelectric properties in Ag-Sb-Te system was indicated.

(Manuscript received May 19, 2003, revised Oct. 8, 2003)

**References**

7. N. Yuhashi, I. Shiota, I.A. Nishida, Y. Shimohara S. Yoneda, and H.T. Kaibe : "Preparation of Ag$_{0.208}$Sb$_{0.275}$Te$_{0.517}$ and the thermoelectric properties", Proc. 19th Int. Conf. Thermoelectrics, pp.160-163 (2000)
Seiji Yoneda (Member) was born in Fukuoka, Japan, on August 1, 1972. He received his M.E. degree in electrical engineering from Tokyo Metropolitain University in 1997 and his Ph.D. degree in material science from Keio University in 2000, and is presently a research associate at Kanagawa University. He was a visiting researcher at the NRIM in the STA between 1995 and 2000. His research interests are in the areas of thermoelectrics and fuel cell. He is a member of the IEE of Japan, the Japan society of applied physics, the Japan institute of metals, the solid state ionics society of Japan, the thermoelectric conversion research committee of Japan and the society of advanced science.

Yoshihiro Ohno (Member) was born in Shimane, Japan, on December 30, 1941. He received his M.E. degree from Waseda University in 1967, and is presently a professor at Keio University. He has worked at the ELT. He holds a Ph.D. degree. His research interests are in the areas of fuel cell. He is a member of the IEE of Japan, the energy society of Japan, the ceramic society of Japan and the solid state ionics society of Japan.

Eiji Ohta (Non-member) was born in Hyogo, Japan, on May 3, 1949. He received his M.E. degree and Ph.D. degree from Keio University in 1979, and is presently a professor at Keio University. His research interests are in the areas of fundamental and electronic properties of semiconductor materials. He is a member of the Japan society of applied physics, the physical society of Japan, and the surface science society of Japan.

Nobuhiro Yuhashi (Non-member) was born in Chiba, Japan, on August 13, 1976. He received his M.E. degree in material science from Kogakuin University in 2001 and presently work at Maruyama Mfg Co. He is a member of the Japan institute of metals, the society of rubber industry Japan.

Ichiro Shiota (Non-member) was born in Okayama, Japan, on September 19, 1941. He obtained his M.E. degree in metal physics from Tohoku University in 1968. After finishing his graduate course, he worked for Tohoku University as a research associate and moved to NRIM, STA in 1969. He obtained his Ph.D. degree in material science from Tokyo Institute of Technology in 1980. He moved to Kogakuin University as a professor in 1993. His research interests are in the fields of thermoelectrics and composite materials. He is a member of the Japan society of applied physics, the Japan institute of metals, the Japan Society for composite materials and the thermoelectric conversion research committee of Japan.

Isao A. Nishida (Member) was born in Nagano, Japan, on January 1, 1940. He worked for NRIM, STA since 1960. He obtained his M.E. degree from Kogakuin University in 1966. He was a professor at Tohoku University in 1998 concurrently with NRIM. He is presently a professor of Salesian Polytechnic - Ikuei Kosen. He holds a Ph.D. degree. His research interests are in the areas of thermoelectric materials. He is a member of the IEE of Japan, the physical society of Japan, the Japan institute of metals, Materials Science Society of Japan and the thermoelectric conversion research committee of Japan.

Yoshikazu Shinohara (Non-member) was born in Hyogo, Japan, on July 24, 1960. He received his M.E. degree in material science from Tokyo University in 1986 and his Ph.D. degree in material science from Tokyo University in 1989, and is presently an associate professor at Tohoku University. He was a researcher at the NIMS between 1989 and 2002. His research interests are in the areas of thermoelectrics and ecomaterials. He is a member of the Japan society of applied physics, the Japan institute of metals, the society of polymer science of Japan, the thermoelectric conversion research committee of Japan, the Ecomaterials forum and the functionally graded materials forum.

Hiromasa T. Kaibe (Non-member) was born in Hyogo, Japan, on February, 1962. He obtained Ph.D. degree in instrumentation engineering from Keio University in 1991. After 10 years in Tokyo Metropolitan University as a research associate, he moved to Komatsu Ltd. He is now involved in the research and development for the thermoelectric application as well as the basic activity. From 1987 until 1990 and from 1995 until 1997 he was a visiting researcher of National Research Institute for Metals (NRIM). From 1997 during one year he stayed at German Aerospace Center (Cologne) as a guest scientist. He is a member of the Japan society of applied physics, the Japan institute of metals, and the thermoelectric conversion research committee of Japan and the society of advanced science.

Isao J. Ohugi (Non-member) was born in Ibaraki, Japan, on January 23, 1954. He received his Ph.D. degree in materials science from Keio University in 1996. He is a professor of Salesian Polytechnic - Ikuei Kosen. His research interests are in the areas of thermoelectric materials and degenerate semiconductors. He is a member of the Physical Society of Japan, the Japan Society of Applied Physics, the Japan Institute of Metals, the Society of Materials Science, Japan, the Crystallographic Society of Japan, the Thermoelectric Conversion Research Committee of Japan and the Society of Advanced Science.