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Phase diagram and thermoelectric properties of $Ag_{3-x}Sb_{1+x}Te_4$ system

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In order to obtain better thermoelectric performance in the composition domain should be stabilized, the phase diagram of the $Ag_{3-x}Sb_{1+x}Te_4$ system by varying the Ag:Sb ratio. The phase diagram is investigated using the differential thermal analysis and the powder X-ray diffraction techniques. The Seebeck coefficient and the electrical resistivity of the grown bulk crystals of the system are also measured. The phase diagram of the $Ag_{3-x}Sb_{1+x}Te_4$ system indicates that a mixed phase of $AgSbTe_2$ and Ag_2Te, which is expected to show higher thermoelectric performance, exists in a wide temperature range between 600 and 830 K at a composition of $Ag_{2.2}Sb_{1.8}Te_4$. The maximum of Seebeck coefficient for $AgSbTe_2$ ($x = 1$) is 0.73 mV/K at about 680 K. The thermoelectric performance is lowered by the compositional deviation from Ag:Sb:Te = 1:1:2. © *2004 Kluwer Academic Publishers*

1. Introduction

Among many materials used in the thermoelectric conversion devices, those belonging to the Ag-Sb-Te_2 system are known to have superior thermoelectric performance around 650–700 K [1, 2]. However, those materials have inevitably complicated domains with different compositions in the growth process [2–4], so that the crystallographic and thermoelectric study using good bulk crystals could not be fully carried out.

In this study, in order to obtain better thermoelectric performance in the composition domain should be stabilized, the phase diagram of the $Ag_{3-x}Sb_{1+x}Te_4$ system by varying the Ag:Sb ratio has been investigated using the differential thermal analysis (DTA) and the powder X-ray diffraction (XRD) techniques. Furthermore, we have grown the bulk crystals of the system and measured the Seebeck coefficient and the electrical resistivity, which are one of the important parameters of the thermoelectric performance.

2. Experimental procedure

DTA curves were observed using an apparatus similar to that reported in a previous paper [5]. Ag, Sb and Te (4–6N purity) elements were weighed to about 0.7 g in total for the composition of $Ag_{3-x}Sb_{1+x}Te_4$ ($x = 0$ to 2). The mixture was sealed in a quartz ampoule under vacuum of $\sim 10^{-4}$ Torr, and synthesized by heating up to about 1100 K. The heating or cooling rate for the DTA measurement was held at a constant value of 2 K/min. The difference in temperature between a sample and a reference material is directly measured by a thermocouple (CA). DTA signals were corrected as the systematic error of the observed temperature was confirmed to be within 2 K at the most. The phase transition points were determined from extrapolated onsets of DTA peaks in the cooling process.

The bulk crystals were grown using the horizontal Bridgman method. The starting materials weighed to 3–5 g in total were sealed in a quartz tube having dimensions of 8 mm × 80 mm under vacuum of $\sim 10^{-6}$ Torr. The quartz tube was first heated to about 973 K for 12 h and held at this temperature for 12 h. Then, the whole zone was cooled electrically at a speed of 5 K/h, keeping the temperature gradient of about 10 K/cm.

The phases of the products synthesized after the DTA measurement and the melt growth were identified by powder XRD measurements using the Cu-Kα radiation of wave length (1.5405 Å) at room temperature. The reference materials of Ag_2Te, Ag_5Te_3, Sb_2Te_3, Ag_3Sb, and SbTe were naturally prepared during the DTA measurements and used for the comparison of XRD patterns. Furthermore, the diffraction patterns were also compared with the JCPDS files [6]. The atomic compositions were determined by an electron probe microanalyzer (EPMA).

The Seebeck coefficients α were determined from the following equation, $\alpha = V_s/\triangle T$, where V_s is the thermoelectric power and $\triangle T$ is the temperature difference in both ends of the sample. The Seebeck coefficients were corrected by the value obtained without the sample in the measurement system. The electrical resistivities, Hall coefficients and mobilities were measured at room temperature by the van der Pauw method using HL5500PC (Nippon Bio-Rad Laboratories).

3. Results and discussion

3.1. Phase diagram

Typical DTA curves of the $Ag_{3-x}Sb_{1+x}Te_4$ system ($x = 0$ to 2) are shown in Fig. 1. Typical powder XRD

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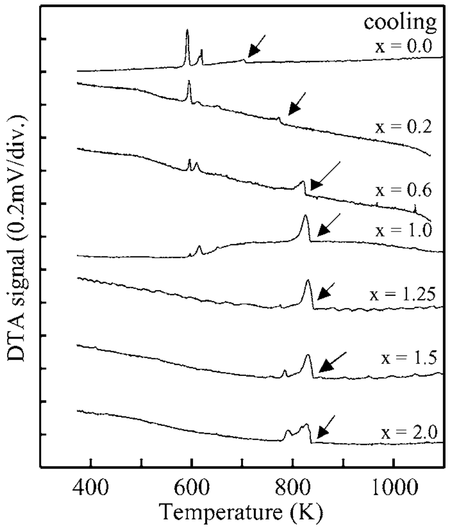

Figure 1 DTA curves of the $Ag_{3-x}Sb_{1+x}Te_4$ ($x = 0$ to 2) system. (arrow: melting point).

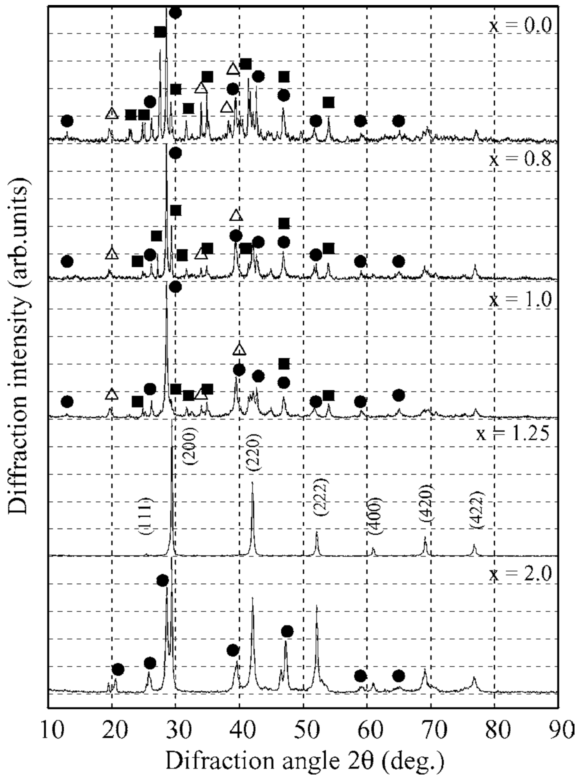

Figure 2 XRD patterns of the $Ag_{3-x}Sb_{1+x}Te_4$ ($x = 0$ to 2) system after DTA measurements. Each spectrum is normalized to the most intense line of the respective samples. (Miller indices: $(Ag,Sb)Te_2$, ■: $Ag_{2-x}Te$, △: Ag_3Sb, and ●: Sb_2Te_{3-x}).

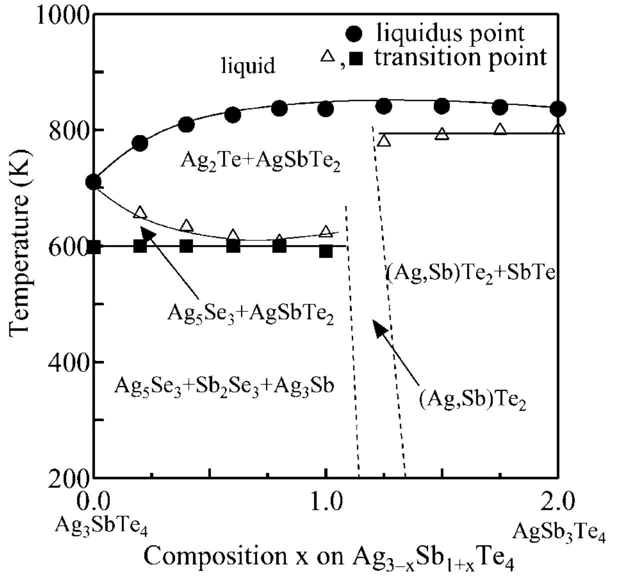

Figure 3 Phase diagram of the $Ag_{3-x}Sb_{1+x}Te_4$ ($x = 0$ to 2) system.

patterns of the samples after DTA measurements are shown in Fig. 2, where each spectrum is normalized to the most intense line of the respective samples. The $AgSbTe_2$ single phase at higher temperature has the cubic structure [6]. The diffraction lines are shown as the Miller indices (*hkl*) at $x = 1.25$, which can be analogical structure for ordering Ag-Sb from the $AgSbTe_2$ phase, i.e., Sb-rich (Ag, Sb)Te_2 solid solution. The solid solution substituted Sb in Ag site was also expected from the results using the Rietved Method [7]. The diffraction lines from the $Ag_{2-x}Te$, Ag_3Sb and Sb_2Te_3 phases were found in the composition ranging from $x = 0$ to 1, and their melting points decreased to about 700 K with an increase of Ag concentration. The samples of Ag-rich compositions have the transition points, which are due to the decomposition of $AgSbTe_2$ and the phase transition of $Ag_{2-x}Te$, respectively, because two DTA peaks at about 600 K were observed in this concentration range. On the other hands, the diffraction lines form $(Ag,Sb)Te_2$ and Sb_2Te_{3-x} phases were found at the Sb-rich compositions ($x > 1.25$). Their melting points decreased a little with an increase of Sb concentration. The DTA peak observed at about 800 K may be due to the phase transition of Sb-Te system, since the SbTe sample has both the melting and transition points.

The phase diagram constructed from the results of DTA and XRD measurements is shown in Fig. 3. Here, the samples of respective compositions prepared by quenching method from respective temperatures were also obtained, and their phases at higher temperatures were identified using the powder XRD technique. In the case of the Ag-rich compositions, the $Ag_2Te + AgSbTe_2$ phase exists at the high temperature, and the $Ag_5Te_3 + AgSbTe_2$ phase exists at the middle temperature. These phases were obtained from the investigations of the quenched samples. The phase diagram indicates that a mixed phase of $AgSbTe_2$ and Ag_2Te, which is expected to show higher thermoelectric performance, exists in a wide temperature range between 600 and 830 K at the composition of $Ag_{2.2}Sb_{1.8}Te_4$ ($x = 0.8$). The $Ag_5Te_3 + Sb_2Te_3 + Ag_3Sb$ phase exists at the low temperature. In the case of the Sb-rich compositions, the $(Ag,Sb)Te_2 + SbTe$ phase exists. In addition, the phase transition of SbTe is also observed and the detail of this transition is not found at this stage. The single phase of $AgSbTe_2$ do not exit at the composition of Ag:Sb:Te = 1:1:2, but the phase of $(Ag,Sb)Te_2$ solid solution in the region of slightly Sb-rich composition.

3.2. Thermoelectric properties

Fig. 4 shows the temperature dependence of Seebeck coefficients of the $Ag_{3-x}Sb_{1+x}Te_4$ system. The

TABLE I Conduction type, electrical resistivities, Hall concentrations and mobilities of the $Ag_{3-x}Sb_{1+x}Te_4$ system at room temperature

Composition x	Conduction type	Electrical resistivity (ohm-cm)	Hall concentration (cm^{-3})	Hall mobility (cm^2/Vs)
0.4	p	3.5×10^{-3}	5×10^{19}	30
0.6	p	3.5×10^{-3}	2×10^{19}	80
0.8	p	6.3×10^{-3}	1×10^{19}	70
1.0	p	1.8×10^{-2}	8×10^{18}	40
1.25	p	2.7×10^{-2}	7×10^{18}	30
1.5	p	8.7×10^{-3}	5×10^{19}	15

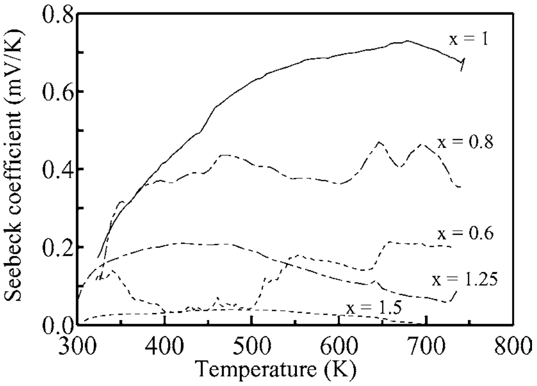

Figure 4 Temperature dependence of Seebeck coefficients of the $Ag_{3-x}Sb_{1+x}Te_4$ system.

coefficient Seebeck of $AgSbTe_2$ ($x = 1$) has a maximum value of 0.73 mV/K at about 680 K and $Ag_{2.2}Sb_{1.8}Te_4$ ($x = 0.8$), where a mixed phase of $AgSbTe_2$ and Ag_2Te with higher thermoelectric performance exists in the wide temperature region, has a value of 0.45 mV/K at about 650 K. Furthermore, the Seebeck coefficient of Ag-rich composition decreases with increasing the Ag concentration. In the case of $Ag_{2.8}Sb_{1.2}Te_4$ ($x = 0.2$) with the Ag-richest composition, the conduction changed from p- to n-type with temperature variation. On the other hand, the Seebeck coefficient of $Ag_{1.75}Sb_{2.25}Te_4$ ($x = 1.25$), which has the $AgSbTe_2$ single phase of the cubic structure, is found to have the maximum value of 0.20 mV/K at about 450 K. The maximum of the Seebeck coefficient of Sb-rich composition decreases drastically with increasing the Sb concentration. According to the result of EPMA, the Te concentration at the surface of the bulk sample lowered after the temperature dependence Seebeck coefficient measurements, but no change of Te concentration of the whole bulk sample was observed. Thus, the crystals of the system are stabile in the air below 750 K.

Table I shows the conduction type, electrical resistivities, Hall concentrations and mobilities of the system at room temperature. All crystals prepared by the horizontal Bridgman method showed p-type conduction. The electrical resistivities are independent of temperature from 300 to 750 K and the changing values are less than an order of magnitude. The electrical resistivity seems to increase as the content of $(Ag,Sb)Te_2$ phase increases. The Hall mobility may depend on an increase of the content of Ag_5Te_3 phase. The power factors considering the electrical resistivities to Seebeck coefficients can be estimated. As these results, the power factor of the samples close to $AgSbTe_2$ ($x = 1$) composition was found to be the largest of all samples prepared in this study.

4. Summary

The phase diagram of the $Ag_{3-x}Sb_{1+x}Te_4$ system by varying the Ag:Sb ratio was constructed using the differential thermal analysis and the powder X-ray diffraction techniques. The phase diagram of the $Ag_{3-x}Sb_{1+x}Te_4$ system indicated that a mixed phase of $AgSbTe_2$ and Ag_2Te, which is expected to show higher thermoelectric performance, exists in a wide temperature range between 600 and 830 K at a composition of $Ag_{2.2}Sb_{1.8}Te_4$ ($x = 0.8$).

The Seebeck coefficient and the electrical resistivity of the bulk crystals of the system grown by the horizontal Bridgman method were measured, and the power factors considering both of those values were also estimated, which is the important parameters for the thermoelectric performance. The Seebeck coefficient of $AgSbTe_2$ ($x = 1$) was found to become maximum (0.73 mV/K) at about 680 K, and the thermoelectric performance is lowered by the compositional deviation from Ag:Sb:Te = 1:1:2.

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