Effect of Tellurium Doping on the Thermoelectric Properties of ZnSb

Takashi Ueda*, Chinatsu Okamura*, Yasutoshi Noda and Kazuhiro Hasezaki

Department of Materials Science, Shimane University, 1060 Nishikawatsu-cho, Matsue 690-8504, Japan

N-type tellurium doped ZnSb was prepared by direct melting at 923 K after which it was quenched in water within an evacuated quartz ampoule. All the ingots were heat treated at 723 K for 100 h. The resultant samples were characterized by X-ray diffraction (XRD), differential thermal analysis (DTA) and by measurement of their Seebeck and Hall coefficients. XRD and DTA indicated that the solubility limit of tellurium in ZnSb was less than 3 atomic%. The samples with 0, 1 and 3 atomic% tellurium were *p*-type while those with 1.90 and 2.06 atomic% tellurium were *n*-type. These results indicated that *n*-type ZnSb samples can be obtained by the proper doping of tellurium. Excess doping with tellurium resulted in precipitation of the ZnTe phase and a change in conduction from *n*- to *p*-type. The maximum power factor for the 2.06 atomic% tellurium doped *n*-type sample was found to be 0.84×10^{-3} W m^{-1} K^{-2} at 573 K. [doi:10.2320/matertrans.M2009201]

1. Introduction

ZnSb is one of the most promising thermoelectric materials. It has been reported to show a high figure of merit in an intermediate temperature range (450–700 K).[1] It is relatively low-cost and can be a potential substitute for high performance lead tellurides that contain toxic lead. M. Telkes investigated *p*-type ZnSb for possible use in the production of solar thermoelectric generators.[2,3] The ZnSb phase shows a peritectic reaction at 819 K[4] indicating that prolonged heating is necessary to obtain single phase ZnSb. The preparation of single phase ZnSb has been difficult according to available literature.[5,6]

Furthermore, a thermoelectric module can generally be constructed using a unicouple of *p*- and *n*-type semiconductors. After research[7,8] into impurity doping in *n*-type ZnSb, the *n*-type single phase of ZnSb was obtained by doping with tellurium in 1971.[9] However, the amount of doping was not clarified.

In this study, *n*-type ZnSb samples were preliminary tried to be prepare by doping tellurium. Samples were prepared by quenching and followed by heat treatment after direct melting. The amount of doping was changed from 0 to 3 at%. It was found that tellurium resulted in a change of ZnSb conduction type from *p* to *n*.

2. Experimental Procedures

Undoped and Te-doped single phase samples of ZnSb were synthesized by the direct melting of constituent elements and were quenched in water. The purity of zinc, antimony and tellurium elements was 5 N. The amount of Te used was in the range of 0(undoped) to 3(doped) at%. The raw materials were weighed to be of nominal composition and melted at 973 K for 3 h in an evacuated quartz ampoule. After quenching in water, the ingot was heat treated in the ampoule at 723 K for 100 h. The resultant materials were investigated by differential thermal analysis (DTA) and X-ray diffraction (XRD) using CuKα radiation in the range of 2θ from 20 to 50 degrees. DTA measurements were made by heating in

alumina containers at up to 873 K at a rate of 20 K/min in nitrogen gas flow.

The Seebeck coefficient α was estimated from the linear relationship between thermoelectromotive force (E) and the temperature difference (ΔT) at up to 3 K under vacuum in the temperature range of 300–600 K by $\alpha = E/\Delta T$.

The Hall coefficient R_H and the electric conductivity σ were measured by the van der Pauw method under vacuum with a direct current of 5 mA and a magnetic field of 0.5 T in the temperature range of 300–600 K. The carrier concentration n was determined using the equation $n = 1/eR_H$, where e is electric charge. Thermoelectric performance was evaluated by estimating the power factor $\alpha^2\sigma$.

3. Results and Discussion

3.1 Dependency on the amount of tellurium

Figures 1-(1) and 1-(2) show XRD patterns for the ZnSb samples that were doped with (a) 0, (b) 1, (c) 1.9, (d) 2.06 and (e) 3 at% Te. In 1-(1) 2θ was from 20 to 50 degrees and for 1-(2) 2θ was from 38 to 41 degrees. Most diffraction peaks in Fig. 1(a)–(e) were identified as those from the ZnSb phase, while the peak at 40 degrees, shown in Fig. 1(e), was identified as that from the ZnTe phase. Figure 1(e) indicates that the sample doped with 3 at% Te consists of two phases, ZnSb and ZnTe. Excess tellurium doping in ZnSb is expected to precipitate ZnTe. Figures 1(d) and (e) indicate that the solubility limit of the tellurium in ZnSb was less than 3 at%.

DTA curves for the ZnSb samples are summarized in Fig. 2, where (a) 0, (b) 1, (c) 1.90, (d) 2.06 and (e) 3 at% Te was used for doping. For all samples, the large endothermic peak at 823 K corresponds to the melting point of ZnSb. Another small endothermic peak at 780 K corresponds to the eutectoid reaction between ZnSb and Sb.[4] The peak that was measured for the 3 at% Te doped sample was larger than that of the other samples.

3.2 Thermoelectric properties of undoped and tellurium doped ZnSb

Figure 3 shows plots of the Seebeck coefficient α against the amount x of Te and this was measured at room temperature. The 0, 1 and 3 at% Te doped samples exhibit
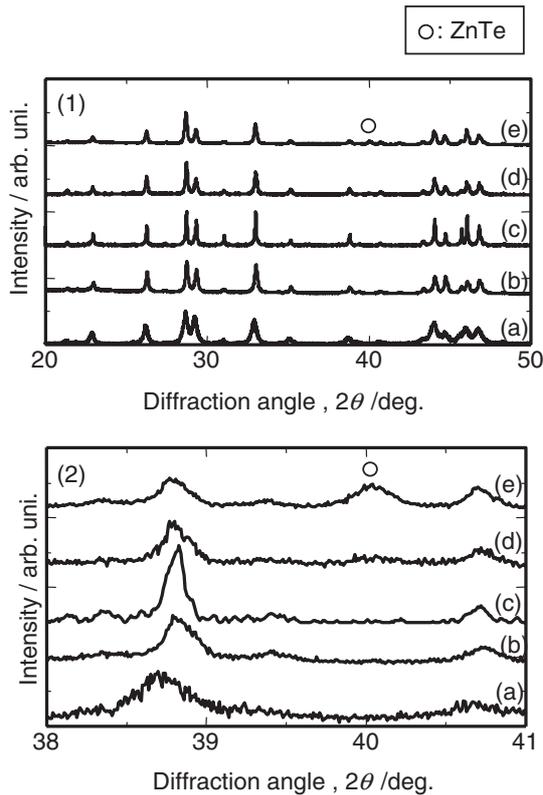
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*Graduate Student, Shimane University

Fig. 1 XRD patterns of the ZnSb samples doped with (a) 0, (b) 1, (c) 1.9, (d) 2.06 and (e) 3 at% Te and (1) 2θ was from 20 to 50 degrees, (2) 2θ was from 38 to 41 degrees.
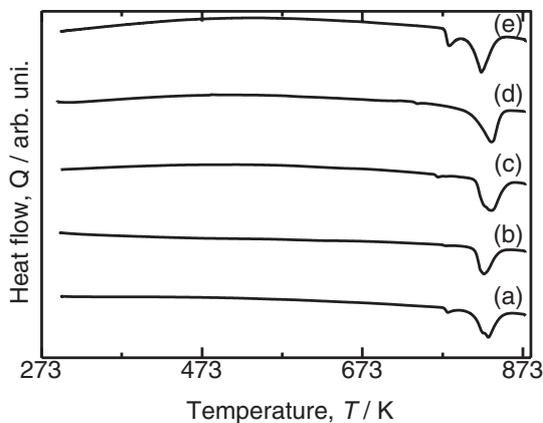

Fig. 2 DTA curves for the ZnSb samples doped with (a) 0, (b) 1, (c) 1.9, (d) 2.06 and (e) 3 at% Te.
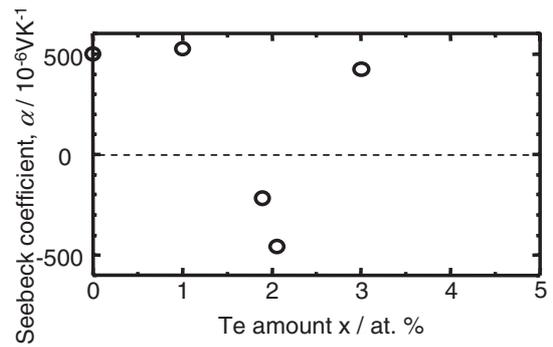

Fig. 3 Seebeck coefficient α versus the tellurium doped amount x, measured at room temperature.
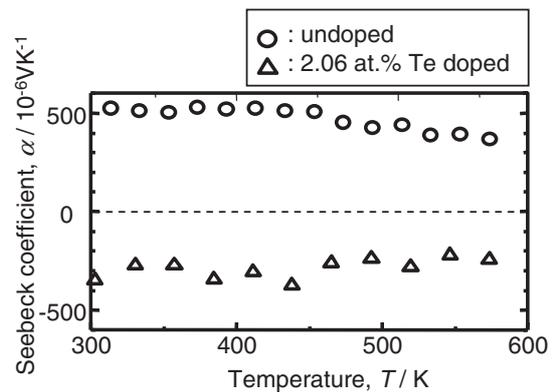

Fig. 4 Seebeck coefficient versus temperature for the undoped p-type and the 2.06 at% Te doped n-type samples.
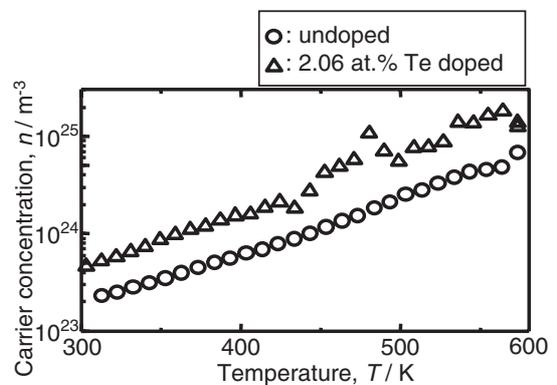

Fig. 5 Carrier concentration versus temperature for the undoped p-type and the 2.06 at% Te doped n-type samples.

p-type character, while the 1.9 and 2.06 at% Te doped samples exhibit n-type character. The 1.9 and 2.06 at% Te doped samples indicate that n-type ZnSb can be obtained if a proper amount of Te is used for doping. Excess Te results in the precipitation of a ZnTe phase from Fig. 1(e). ZnTe has a direct band gap of 2.2–2.3 eV at room temperature and it is usually a p-type semiconductor.[10] Therefore, 3 at% Te doped sample changed in conduction from n- to p-type.

The thermoelectric properties of the n-type sample doped with 2.06 at% Te is shown in Figs. 4–8 and compared with the undoped p-type sample.

Figure 4 shows plots of the Seebeck coefficient α versus temperature for the undoped p-type and the 2.06 at% Te doped n-type samples. It is noteworthy that the Seebeck coefficient of the 2.06 at% Te doped sample was negative in the temperature range from 300 to 600 K.

Figure 5 shows plots of the carrier concentration n versus temperature for the undoped p-type and the 2.06 at% Te doped n-type samples. The carrier concentration increased as the temperature increased. The carrier concentration of the n-type sample was almost equivalent to that of the undoped p-type sample.

The Hall mobility μ_H is shown as a function of temperature in Fig. 6 and its value decreased as the temperature increased. The Hall mobility of the n-type sample was almost equivalent to that of the p-type sample. Figure 7 shows plots
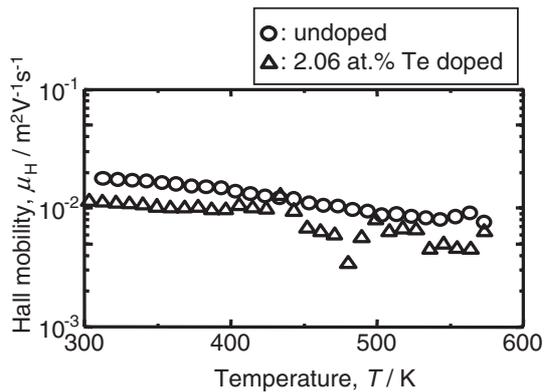
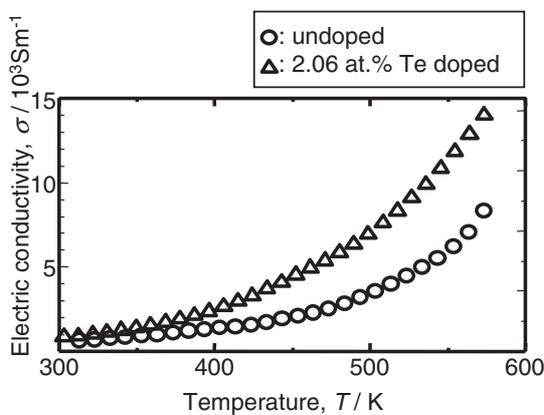Fig. 6 Hall mobility versus temperature for the undoped *p*-type and the 2.06 at% Te doped *n*-type samples.
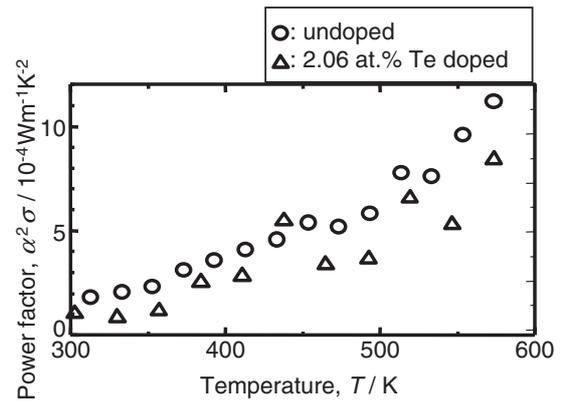

Fig. 8 Power factor estimated from the value of the electric conductivity and the Seebeck coefficient for the undoped *p*-type and the 2.06 at% Te doped *n*-type samples.

Fig. 7 Electric conductivity versus temperature for the undoped *p*-type and the 2.06 at% Te doped *n*-type samples.

of the electric conductivity σ versus temperature in the range from 300 to 600 K for the undoped *p*-type and the 2.06 at% Te doped *n*-type samples. The electric conductivity increases as the temperature increases. The temperature dependence of these thermoelectric properties corresponds to those of a semiconductor.

In Fig. 8 the power factor, estimated from the value of the electric conductivity and the Seebeck coefficient are shown in the temperature range from 300 to 600 K for the undoped *p*-type and 2.06 at% Te doped *n*-type samples. Local maxima were found at 573 K for both samples and their values were $1.12 \times 10^{-3} \, \mathrm{W \, m^{-1} K^{-2}}$ for the undoped *p*-type sample and $0.84 \times 10^{-3} \, \mathrm{W \, m^{-1} K^{-2}}$ for the 2.06 at% Te doped *n*-type samples, respectively.

4. Conclusion

For this study, *n*-type ZnSb samples were prepared by doping with tellurium as an impurity element. The results are summarized as follows:

(1) The *n*-type single phase ZnSb sample was successfully prepared by a direct melting method.
(2) X-ray diffraction indicates that the solubility limit of tellurium in ZnSb was less than 3 at%.
(3) The 0, 1 and 3 at% Te doped samples had *p*-type conduction, while the 1.90 and 2.06 at% Te doped samples had *n*-type conduction. Results indicated that a proper amount of tellurium doping resulted in a change of ZnSb into an *n*-type material and that excessive tellurium doping resulted in precipitation of the ZnTe phase and in a change of conduction from *n*-type to *p*-type.
(4) The maximum power factor of the undoped *p*-type and 2.06 at% Te doped *n*-type samples were determined to be $1.12 \times 10^{-3} \, \mathrm{W \, m^{-1} K^{-2}}$ and $0.84 \times 10^{-3} \, \mathrm{W \, m^{-1} K^{-2}}$ at 573 K, respectively.

REFERENCES

1) Y. Suga: *Thermoelectric Semiconductor*, (Maki Syoten, Tokyo, 1966) pp. 314–317.
2) M. Telkes: J. Appl. Phys. **25** (1954) 765–777.
3) M. Telkes: J. Appl. Phys. **18** (1947) 1116–1127.
4) H. W. Mayer, I. Mikhail and K. Schubert: J. Less Common Metals **59** (1978) 43–52.
5) T. Koyanagi, K. Adachi, K. Kishimoto and K. Matsubara: Trans. Inst. Elect. Engnr. Jpn. **116-A** (1996) 258–267.
6) K. Hasezaki, M. Nishimura, M. Umata, H. Tsukuda and M. Araoka: 12th Int. Conf. on Thermoelectrics, (ICT 1993) pp. 307–310.
7) H.-G. Müller und G. Schneider: Z. Naturforsch. **26a** (1971) 1316–1322.
8) G. Schneider: Phys. Status Solidi **33** (1969) K133–K136.
9) A. Abou-Zeid and G. Schneider: Phys. Status Solidi (a) **6** (1971) K101–K103.
10) M. S. Hossain, R. Islam and K. A. Khan: Renewable Energy **33** (2008) 642–647.