Microstructures and Thermoelectric Properties of Melt-Spun Zn_xSb_3 Ribbons

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Melt-spun Zn_xSb_3 ribbons were fabricated with weight compositions of $x = 3.6, 3.9$, and 4.2 through a single-wheel process and were annealed for 2 h at 673 K. The microstructures of the ribbons were investigated using transmission electron microscopy, together with energy dispersive X-ray analysis. The main structure consisted of $\beta\text{-Zn}_4\text{Sb}_3$ phase, which mainly coexisted with ZnSb phase for $x < 4$ and with Zn phase for $x > 4$. The analyzed composition of the $\beta\text{-Zn}_4\text{Sb}_3$ phase deviated from the stoichiometric composition of 4:3 for all the ribbons. Nanosized voids and zinc inclusions were randomly distributed throughout the $\beta\text{-Zn}_4\text{Sb}_3$ phase. The thermoelectric characteristics of the ribbons were revealed by measuring the Seebeck coefficient, electrical conductivity, power factor, dimensionless figure of merit, and thermal conductivity. The power factor and dimensionless figure of merit increase with increasing x and temperature because either the electrical conductivity or the Seebeck coefficient increases.

Introduction

$\beta\text{-Zn}_4\text{Sb}_3$ -structured Zinc antimonide is promising thermoelectric materials for generating power by directly converting heat into electricity. The conversion efficiency is characterized by the dimensionless figure of merit defined as $ZT = \alpha^2 \sigma T / \kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, T

is temperature, and κ is the thermal conductivity. The preparation process and structure of zinc antimonide have attracted considerable attention since a high ZT was reported for hot-pressed β - Zn_4Sb_3 samples.¹⁻⁸

The structure of a single crystal of β - Zn_4Sb_3 was analyzed, and the β - Zn_4Sb_3 unit cell composed of $\text{Zn}_{36-n+i}\text{Sb}_{30}$ was found to consist of $36-n$ zinc atoms at zinc sites, n zinc vacancies, 30 antimony atoms at antimony sites, and i interstitial zinc atoms.^{9,10} The interstitial zinc atoms are supposed to act as glass-like contributors to reduce the thermal conductivity and increase the ZT of the crystal.

Transmission electron microscopy (TEM) observations have revealed that the β - Zn_4Sb_3 phase in hot-pressed samples of $\text{Zn}_{3.9}\text{Sb}_3$ and $\text{Zn}_{3.99}\text{Sb}_3$ contains randomly distributed voids, while that in a hot-pressed sample of $\text{Zn}_{3.9}\text{Sb}_3$ contains nanosized zinc inclusions.¹¹ The zinc inclusions are expected to effectively scatter phonons, thus contributing to phonon glass behavior, which results in exceptionally low thermal conductivity for increasing ZT .¹¹⁻¹³

The aim of the present paper is to investigate the structures and thermoelectric properties of isothermally annealed Zn_xSb_3 ribbons fabricated with various weight compositions through single-wheel melt-spinning.

Experimental Procedures

High-frequency induction melting was used to prepare Zn_xSb_3 alloy ingots with weight compositions of $x = 3.6, 3.9$, and 4.2 by melting together 99.99 % pure zinc and antimony particles. Ribbons of the alloys were obtained by melt spinning the ingots with a copper wheel. The alloy melt was spouted onto the wheel under 0.12 MPa of Ar gas in a chamber filled with 0.08 MPa of Ar gas. The wheel velocity was 0.6 m s^{-1} . The wheel diameter and width were 200 and 30 mm, respectively. The melt-spinning temperature was 1100 K. The thickness and width of the ribbons were 400 μm and 1.8 mm, respectively. The ribbons were

then isothermally annealed for 2 h at 673 K in quartz tubes filled with Ar gas at 0.18 MPa pressure and were quenched in water at 273 K.

The microstructures of the ribbons were observed using TEM with a JEOL JEM-2010 microscope equipped with an Oxford LINK ISIS energy dispersive X-ray (EDX) spectroscopy system at the Joint Research Center, Nagasaki University. A 15-nm diameter electron beam was used for EDX analysis.

The Seebeck coefficient (α) was measured by heating one end of a ribbon and cooling the other end. The electrical conductivity (σ) was measured using the four-terminal method, and the Harman method¹⁴ was used to measure the dimensionless figure of merit (ZT) in the range 293–473 K under a 10^{-3} Pa vacuum. In the Harman method,¹⁴ ZT was estimated at a ribbon length of zero after measuring ZT as a function of ribbon length in order to eliminate the effect of the heat radiating from the ribbons. The total uncertainty in the ZT measurement was estimated $\pm 10\%$. The power factor (P) and the thermal conductivity (κ) were estimated using $\alpha^2 \sigma$ and PT/ZT , respectively. κ was separated to the contributions of carrier and phonon using Wiedemann–Franz law. $(\pi^2/3)(k/e)^2 = 2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ was used for Lorenz number.

Results and Discussions

Figure 1 shows a TEM image of a $\text{Zn}_{3.6}\text{Sb}_3$ ribbon. The structure consisted of the Zn_4Sb_3 and ZnSb phases, as previously reported based on X-ray diffraction data.¹⁵ The abundance ratio of the Zn_4Sb_3 and ZnSb phases is considered to be 0.6:0.4 according to the lever rule. The compositions analyzed using EDX were $\text{Zn}_{3.45 \pm 0.10}\text{Sb}_3$ for the Zn_4Sb_3 phase and $\text{Zn}_{0.86 \pm 0.01}\text{Sb}$ for the ZnSb phase, where a 15-nm-diameter electron beam was used for the analysis. From the analyzed compositions of the ribbon, the ratio of zinc inclusions in the Zn_4Sb_3 phase was estimated as $(4 - 3.45)/4 = 0.14$.

Figure 2 shows a TEM image of a $\text{Zn}_{3.6}\text{Sb}_3$ ribbon containing Zn_4Sb_3 phase diffraction spots. The white and black spots correspond to 10–20-nm diameter voids and zinc inclusions, respectively, as previously reported.¹¹⁻¹³

Figure 3 shows a TEM image of the Zn_4Sb_3 phase in a $\text{Zn}_{4.2}\text{Sb}_3$ ribbon. A zinc phase was also observed in other fields, and the abundance ratio of the Zn_4Sb_3 and Zn phases is considered to be 0.95:0.05 according to the lever rule.¹⁵ The analyzed composition of the Zn_4Sb_3 phase was $\text{Zn}_{3.39\pm0.05}\text{Sb}_3$. The white and black spots, which correspond to voids and zinc inclusions were more frequently observed in the $\text{Zn}_{4.2}\text{Sb}_3$ ribbon than in the $\text{Zn}_{3.6}\text{Sb}_3$ one. Analysis of the white spots revealed that they were composed of more than 80 at% Zn, although the Zn_4Sb_3 phase was included in addition to the white spots in the electron-irradiated area. The white spot was hexagonal when the image was observed along the [001] direction in the Zn_4Sb_3 phase, as shown in Fig. 4.

Figure 5 shows the numbers of zinc vacancies (n), interstitial zinc atoms (i), and zinc atoms ($z = 36 - n + i$) in a unit cell of the Zn_4Sb_3 phase composed of $\text{Zn}_z\text{Sb}_{30}$, which were calculated as a function of absolute temperature under the equilibrium state. They were calculated from the minimum free energy:

$$F = E - TS, \quad (1)$$

where E is energy and is given by

$$E = nU_1 + iU_2, \quad (2)$$

where U_1 and U_2 are the energies of formation of a zinc vacancy and an interstitial zinc atom, respectively. The latter term comes from the configuration entropy (S) of zinc atoms and vacancies at zinc and interstitial sites, respectively. The entropy (S) is given by

$$S = -k\{(36 - n)\ln(36 - n) + n\ln n\} + 3kT\{(36 - j)\ln(36 - j) + j\ln j\}, \quad (3)$$

where three kinds of interstitial sites were considered to be equivalent for the sake of simplicity, and $i = 3j$.

$U_1 = 659\text{kJ}$ and $U_2 = 855\text{kJ}$ were estimated using the reported values of $n = 3.6$ and $i = 5.9$,^{9,10} where the temperature was assumed to be 350 K. n , i , and z in the figure all decrease with decreasing temperature, while i decreases more than n . If Kröger-Vink notation is used, the process may be explained by the following reactions when the temperature decreases:

although there is no information about charged values. Interstitial zinc atoms precipitate as zinc inclusions through reaction (4), and i decreases. The zinc atoms in the zinc inclusions diffuse and occupy zinc vacancies, and the places where there had been zinc inclusions became voids through reaction (5). As a result, n decreases and voids appear. If interstitial zinc atoms are near zinc vacancies, the interstitial zinc atoms may directly occupy the zinc vacancies through reaction (6), and i and n decrease.

When the temperature increases, the process may be explained by the following reactions:

Zinc atoms in the Zn_4Sb_3 phase precipitate as zinc inclusions, which produce zinc vacancies through reaction (7), and n increases. The zinc atoms in the zinc inclusions diffuse and enter interstitial sites, and the places where there had been zinc inclusions become voids through reaction (8). As a result, i increases. If zinc atoms in the Zn_4Sb_3 phase can enter nearby interstitial sites, the zinc atoms may directly occupy the interstitial sites through reaction (9), and i and n increase. Consequently, zinc inclusions and voids were

produced in the Zn_4Sb_3 phase, as observed in the TEM image shown in Fig. 4, because the ribbons were prepared by cooling and heating.

Figure 6 shows the Seebeck coefficient, electrical conductivity, and thermal conductivity for each ribbon. The plot of the Seebeck coefficient versus the natural logarithm of the electrical conductivity (i.e., Jonker plot) of the ribbons is also shown. The ribbons were p-type because the Seebeck coefficient was positive for all ribbons. The Seebeck coefficient was almost the same for each ribbon and was independent of the composition parameter x in Zn_xSb_3 because the Seebeck coefficients for the Zn_4Sb_3 and ZnSb phases were almost identical. The electrical conductivity of the ribbons increases with increasing x because the electrical conductivity of the Zn_4Sb_3 phase is higher than that of the ZnSb one. The Seebeck coefficient increases with increasing temperature, while the electrical conductivity decreases with increasing temperature. The linear relation in the Jonker plot depends on x and becomes nonlinear in the high electrical conductivity or high temperature regions. The nonlinear behavior of the Jonker plot suggests that the number of zinc vacancies, interstitial zinc atoms, zinc inclusions, and voids changes with increasing temperature. These results correspond to the increase in n , i , and z at high temperature as calculated in Fig. 5 although the sample don't completely reach to the equilibrium state. The nonlinear behavior of the Jonker plot for large x may be attributed to the precipitate of Zn phase. The thermal conductivity is the same for all the ribbons and is high when the temperature is high. This result also suggests that the number of zinc vacancies, interstitial zinc atoms, zinc inclusions, and voids changes with increasing temperature. The thermal conductivity is mainly due to phonon conduction for all ribbons at all temperatures.

Figure 7 shows the power factor and the dimensionless figure of merit (ZT). The power factor and figure of merit increase with increasing x and temperature. The increase in the power factor and in ZT with increasing x is mainly attributed to the increase in electrical conductivity, and the increase in those values

with increasing temperature is caused by the increase in the Seebeck coefficient .

Conclusions

Melt-spun Zn_xSb_3 ribbons were fabricated with weight compositions of $x = 3.6, 3.9$, and 4.2 through a single-wheel process at a wheel speed of 0.6 m s^{-1} and were annealed for 2 h at 673 K. The microstructures of the ribbons were determined using TEM, together with EDX analysis. The $\beta\text{-Zn}_4\text{Sb}_3$ phase mainly coexisted with the ZnSb phase for $x < 4$ and with the Zn phase for $x > 4$. The analyzed composition of the $\beta\text{-Zn}_4\text{Sb}_3$ phase was Zn_ySb_3 for $y < 3.5$ for all the ribbons because nanosized voids and zinc inclusions precipitated. The voids and zinc inclusions may form through reactions of zinc atoms at zinc sites and zinc vacancies, and between interstitial and zinc atoms during ribbon cooling and heating. The thermoelectric characteristics of the ribbons were revealed by measuring the Seebeck coefficient, electrical conductivity, power factor, dimensionless figure of merit, and thermal conductivity of the ribbons. The power factor and dimensionless figure of merit increase with increasing x because the electrical conductivity increases, while those properties increase with increasing temperature because the Seebeck coefficient increases with increasing temperature. The thermoelectric properties may originate in the complex structure, which contains voids, zinc inclusions, zinc vacancies, interstitial zinc atoms in the $\beta\text{-Zn}_4\text{Sb}_3$ phase, and a coexisting ZnSb or Zn phase.

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Figure Captions

Fig. 1 Bright-field TEM image of ZnSb and Zn₄Sb₃ phases in Zn_{3.6}Sb₃ ribbon. Diffraction pattern for [001] incident direction of ZnSb phase.

Fig. 2 Bright-field TEM image and diffraction pattern for [$\bar{1}$ 11] incident direction of Zn₄Sb₃ phase in Zn_{3.6}Sb₃ ribbon.

Fig. 3 Bright-field TEM image of Zn₄Sb₃ phases in Zn_{4.2}Sb₃ ribbon.

Fig. 4 Bright-field TEM image and diffraction pattern for [$\bar{1}$ 11] incident direction of Zn₄Sb₃ phase in Zn_{4.2}Sb₃ ribbon.

Fig. 5 Numbers of zinc vacancies (n), interstitial zinc atoms (i), and zinc atoms ($z = 36 - n + i$) in unit cell of Zn₄Sb₃ phase composed of Zn_zSb₃₀, calculated as a function of absolute temperature under the equilibrium state.

Fig. 6 Seebeck coefficient, electrical conductivity, and thermal conductivity of Zn_xSb₃ ribbons. Plot of Seebeck coefficient versus natural logarithm of electrical conductivity (i.e., Jonker plot) is also shown.

Fig. 7 Power factor and figure of merit for Zn_xSb₃ ribbons.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7