Possibility of improvement of thermoelectric properties of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ by the Functionally Graded Material

傾斜機能構造化による $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ の熱電特性向上の可能性

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Homogeneous $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ crystals with $x = 0.10, 0.15, 0.25, 0.50$ were successfully grown by a new method in that the furnace was being rocked during cooling down under a unidirectional temperature gradient as well as melting. Thermoelectric properties at room temperature were examined as a function of x . They were analyzed on the basis of the Kane model. It was found that reduced the Fermi energy and the effective mass were proportional to x up to 0.25. Temperature dependence of the thermal conductivity was calculated from the measured value of thermal conductivity at room temperature, approximating that the lattice thermal conductivity is proportional to T^{-1} . Temperature dependence of the figure-of-merit was estimated from the calculated value of thermal conductivity and the measured ones of resistivity and thermoelectric power. From these results, the optimum combination of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ crystals for power generation were determined for the temperature range from 300 to 800K. The combination was $x = 0.15, 0.25$ and 0.50 forming 3-step FGM. The maximum energy conversion efficiency was 27 % larger than that of the homogeneous $\text{Pb}_{0.50}\text{Sn}_{0.50}\text{Te}$. It was also confirmed that sufficient FGM effects on power generation can be realized even by 2-step FGM.

Keywords: p -type PbSnTe , thermoelectric property, melt-grown, Kane model, FGM

I. INTRODUCTION

Figure-of-merit Z of thermoelectric materials has the maximum value Z_{max} at a certain temperature T_{opt} , while it shows rather smaller values than Z_{max} at the other temperatures. If Z can be kept high in a wider temperature range and the average in the operating temperature range Z_{av} can be increased, the energy conversion efficiency η

will be effectively improved.¹ Functionally Graded Material (FGM) with the optimum carrier concentration distribution along the temperature gradient is expected as a practical way to widen the high Z_{av} temperature range.¹

$\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ and TAGS (Te-Ag-Ge-Sb) solid solutions are known as the typical p -type thermoelectric materials in the temperature

range from 400 to 900 K.² $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ is particularly thermally stable, i.e., it has no transformation, while GeTe and AgSbTe_2 composing TAGS are suffered from transformations at 700 K,³ and at 418 and 633 K,⁴ respectively. $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ is convenient for FGM because the carrier concentration can be controlled only by changing the ratio of PbTe to SnTe . It is also expected that the formation of PbTe-SnTe solid solution will reduce the lattice thermal conductivity in the same way as Si-Ge and GaAs-InAs .^{5,6}

Although several methods have been applied to grow $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ crystals, large crystals with a high-quality and a homogeneous composition have not been realized because of segregation. An attempt has been made to grow a crystal with a homogeneous composition in a cosmic zero-gravity state. The high-quality spherical crystals obtained,⁷ however, was too small to evaluate their thermoelectric properties.

In 1964, a $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ crystal was grown by the Bridgman-Stockbarger method, and its thermoelectric properties were examined by Machonis and Cadoff.⁸ It was revealed that the temperature distribution in the melt was distorted by thermal convection under the earth gravity.⁹ It is also pointed out that their experiments were made for polycrystalline materials and without sufficient control of the stoichiometry.¹⁰ In order to design the FGM structure of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$, it is necessary to grow homogeneous crystals with an accurately controlled composition and without segregation, and to examine their thermoelectric properties in detail.

In the present study, homogeneous $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ crystals with $x = 0.10, 0.15, 0.25$ and 0.50 were grown by a new method in which the furnace was being rocked during cooling down under a unidirectional temperature gradient as well as melting. Thermoelectric properties were examined as a function of x . They were analyzed on the basis of the Kane model and the optimum combination of crystals for the FGM structure was determined for the temperature range from 300 to 800 K.

II. EXPERIMENTAL PROCEDURE

A. Preparation of samples

$\text{Pb}(6\text{N})$, $\text{Te}(6\text{N})$ and $\text{Sn}(5\text{N})$ were weighed out at the stoichiometric ratios for the mother materials of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$, that is, PbTe and SnTe . They were encapsulated into quartz tubes in a vacuum of 1×10^{-3} Pa. The contents of the quartz capsules were melted and stirred sufficiently in the rocking furnace at 1273 K for PbTe and 1163 K for SnTe during 1 h (Fig. 1(a)) and cooled down with keeping a unidirectional temperature gradient.

The mother materials were weighed out at the composition ratios of $x = 0.10, 0.15, 0.25$ and 0.50 . They were doubly encapsulated into quartz tubes in a vacuum of 1×10^{-3} Pa. The contents of

FIG. 1. The rocking furnace used for melting and crystal growth. (a) For melting, the furnace was being rocked at a rocking cycle of 0.2 Hz and a tilting angle of 30° . (b) For growing crystal, the furnace was being rocked at 0.2 Hz and 30° under a unidirectional temperature gradient in the vertical direction. (c) The temperature gradient during cooling was 0.5 K/mm, and the sweep rate was 15 K/h.

the capsules were melted and stirred sufficiently in the rocking furnace at 1273 K for 1 h and subsequently cooled down at a sweep rate of 15 K/h and a rocking cycle of 0.2 Hz. The temperature gradient given to the capsules was 0.5 K/mm. (Fig. 1(b), (c))

B. Evaluation of thermoelectric properties

Resistivity ρ and Hall coefficient R_H were measured by the DC method with a high speed and a high resolution in order to prevent the error caused by the Peltier effect.¹¹ Temperature dependence of ρ was measured in an Ar atmosphere in the temperature range from 300 to 800 K, with confirming reproducibility of measured values at heating up and cooling down. Thermoelectric power α was determined from the slope of the thermoelectromotive force E_0 vs. the temperature difference ΔT curve, which was obtained by changing the hot side temperature from 300 to 800 K, with the constant cold side temperature of 300 K. Thermal conductivity κ was measured by the static comparative method using transparent quartz as the standard in a vacuum of less than 1×10^{-4} Pa at room temperature. κ is expressed by

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

where κ_{car} and κ_{ph} are the carrier and the phonon contributions, respectively. κ_{car} is given by

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

where T and L are the absolute temperature and the Lorentz number, respectively. L is $2.45 \times 10^{-8} \text{ V}^2/\text{K}^2$, which is valid for the perfectly degenerate case¹². Introducing the approximation $\kappa_{\text{ph}} \propto T^1$, the temperature dependence of κ was extrapolated from the value

TABLE 1. Measured values at room temperature: resistivity ρ , Hall carrier concentration n_H estimated from R_H , thermoelectric power α , Hall mobility μ_H and thermal conductivity κ .

Composition	ρ (Ωm)	n ($1/\text{m}^3$)	α ($\mu\text{V/K}$)	μ_H (m^2/Vs)	κ ($\text{W}/(\text{Km})$)
$x = 0$ (PbTe)	4.67×10^{-5}	1.4×10^{24}	+281.9	0.096	2.1(0)
$x = 0.10$	2.13×10^{-5}	5.6×10^{24}	+146.2	0.052	1.7(4)
$x = 0.15$	1.35×10^{-5}	9.9×10^{24}	+105.4	0.047	1.7(0)
$x = 0.25$	7.54×10^{-6}	1.7×10^{25}	+58.0	0.049	1.7(9)
$x = 0.50$	4.02×10^{-6}	3.7×10^{25}	+13.8	0.042	2.8(0)

at room temperature.² Figure-of-merit $Z = \alpha^2/(\rho\kappa)$ in the temperature range from 300 to 800 K was estimated from the extrapolated κ , and the measured ρ and α .

III. RESULTS AND DISCUSSION

A. Homogeneity of crystals and thermoelectric properties at room temperature

The obtained ingot included a parallel portion without cracks or voids of 12 mm in diam. and 80 mm in length. Only the NaCl-type of sharp X-ray diffraction profile was observed for all the samples. Table I shows the observed values of ρ , α and κ , the Hall carrier concentration n_H estimated from R_H , and Hall mobility μ_H at room temperature. x dependence of ρ and μ_H , and n_H and α are shown in Figs. 2 and 3, respectively. μ_H decreased rapidly with increasing x up to 0.10, while above $x = 0.10$ it decreased gradually with increasing x . μ_H showed the minimum at $x = 0.50$, which suggested that carrier scattering was increased by the crystal lattice distortion caused by Sn substituted for Pb. It is also suggested that the mobility is decreased by substitution of Sn for Pb. ρ decreased with increasing x in the same way as μ_H did. The variation rate of ρ , however, was remarkably different from that of μ_H . n_H increased linearly with increasing x as

shown in Fig. 3, which caused the difference between the variation rates of ρ and μ_H . According to the band structure of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ reported by Harman,¹⁰ the valence band L_6^+ approaches and contact to the conduction band L_6^- with increasing x . After contacting, the positions of L_6^- and L_6^+ are reversed. Two-valence-band model consisting of a non-parabolic valence band and a parabolic valence band is usually applied to the valence bands of PbTe.¹³ In $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$, however, dominant are the non-parabolic valence band and a conduction band because the non-parabolic valence band approaches to the conduction band with increasing x . Non-parabolic single band model was consequently applied to this system, and calculation was carried out by using the calculational procedure of the Fermi-Dirac integral proposed by Ohsugi et al.¹⁴

First, the reduced Fermi energy η (the dimensionless Fermi energy: $\eta = E_F/k_B T$, where E_F is the Fermi energy, k_B the Boltzman constant and T the absolute temperature) was estimated from the experimental α at room temperature by assuming acoustic phonon scattering. η was measured from the top of valence band. In the Kane model,¹⁵ α is expressed by the following equation.

FIG. 2. x dependence of resistivity and Hall mobility of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ at room temperature.

FIG. 3. x dependence of thermoelectric power and Hall carrier density of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ at room temperature.

FIG. 4. x dependence of effective mass and reduced Fermi energy of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ at room temperature.

$$\alpha = \frac{k_B}{e} \left\{ \frac{2F_1(\eta) + 3\alpha^* k_B T F_2(\eta)}{F_0(\eta) + 2\alpha^* k_B T F_1(\eta)} - \eta \right\} \quad (3)$$

Here, k_B is the Boltzman constant, e the change of carriers, T the absolute temperature and α^* the parameter defined by $\alpha^* = 1/E_G^*$, where E_G^* is the effective energy gap representing the degree of non-parabolicity. The E_G^* value by Dixon and Bis¹⁶ was used in this work. The function $F_r(\eta)$ is the Fermi-Dirac integral defined by

$$F_r(\eta) = \int_0^\infty \frac{\varepsilon^r}{\exp(\varepsilon - \eta) + 1} d\varepsilon \quad (4)$$

where r is the scattering parameter.

Next, m^* was derived from η and the experimental n_H by using the following equation of the carrier density p in a non-parabolic band.

$$p = 2 \left(\frac{2\pi m^* k_B T}{h^2} \right)^{\frac{3}{2}} \left\{ F_{\frac{1}{2}}(\eta) + \frac{15}{4} \alpha^* k_B T F_{\frac{3}{2}}(\eta) \right\} \quad (5)$$

Table II shows the experimental values of n_H and α , the calculated values of η and m^* , and the E_G^* value by Dixon and Bis.¹⁶ x dependences of η and m^* are shown in Fig. 4. η increased linearly with increasing x up to 0.25, while it showed an exceptionally large

FIG. 5. x dependence of thermal conductivity of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ at room temperature.

value at $x = 0.50$. m^*/m_0 (m_0 is the rest mass of free electron) decreased linearly with increasing x up to 0.25, while it showed an exceptionally small value approximately equal to zero at $x = 0.50$. The estimated value of m^* at $x = 0.50$ is remarkably smaller than that of SnTe, namely $0.066m_0$.¹⁷ These facts suggest that the band model assumed in this work is not applicable to the case of $x = 0.50$, in which strong interactions might occurs between the conduction band and the valence band.

Figure 5 shows x dependence of κ , κ_{ph} and κ_{car} at room temperature. κ decreased with increasing x in the range of $x \leq 0.20$, while in the range of $x > 0.20$ it increased. κ was 15% smaller than that of PbTe in the range of $x \leq 0.20$. The primary cause of κ reduction is the decrease in κ_{ph} as shown in Fig. 5. It is suggested that lattice distortion was caused by substitution of Sn for Pb to increase the scattering of phonons with a wave length roughly equal to the lattice distortion. It is also found in Fig. 5 that the decrease in κ_{ph} caused by Sn substitution was saturated around $x = 0.50$. It is concluded from the above discussions that solid solutions with a homogeneous composition were successfully prepared by our new method in that the furnace is rocked during melting and cooling down with keeping the unidirectional temperature gradient.

TABLE 2. Experimental values of Hall carrier concentration n_H and thermoelectric power α , calculated values of effective mass m^* and reduced Fermi energy η , and energy gap parameter E_G^* estimated by Dixon and Bis.

Composition	n_H (m^{-3})	α ($\mu\text{V K}^{-1}$)	m^*	η	E_G^* (eV)
$x = 0$ (PbTe)	1.4×10^{24}	+281.9	0.257	-0.95089	0.30
$x = 0.10$	5.6×10^{24}	+146.2	0.178	1.47636	0.27
$x = 0.15$	9.9×10^{24}	+105.4	0.147	2.91007	0.24
$x = 0.25$	1.7×10^{25}	+58.0	0.070	7.04769	0.19
$x = 0.50$	3.7×10^{25}	+13.8	0.005	39.6977	0.07

FIG. 6. Temperature dependence of resistivity of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$.

B. Temperature dependence of thermoelectric properties in the temperature range of 300–800 K

Temperature dependence of ρ of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ in the temperature range from 300 to 800 K is shown in Fig. 6. ρ in the range $x > 0.10$ decreased with increasing amount of SnTe in the whole temperature range because the carrier degeneracy of SnTe is higher than that of PbTe. Temperature dependence of ρ in all the samples at high temperatures showed the effect of intrinsic conduction. The temperature at which conduction enters the intrinsic region increased with increasing x . Temperature dependence of α in the temperature range from 300 to 800 K is shown in Fig. 7. α at room temperature decreases with increasing x . The temperature at which α reaches the maximum, α_{max} , increased with increasing x . The variation in α below α_{max} decreased with increasing x . The Fermi en-

FIG. 7. Temperature dependence of thermoelectric power of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$.

FIG. 8. Temperature dependence of figure-of-merit of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$. The bold line indicates an ideal figure-of-merit curve of 4-step FGM.

ergy E_F was calculated by using the Eq. (3) from the experimental α below α_{max} and α^* at 300 K, assuming that the temperature dependence of α^* is negligible. E_F of all the samples decreased with increasing temperature. The gradients of the E_F -curves decreased with increasing x , which is consistent with those of the α -curves. It is concluded from this fact that the temperature dependence of α is caused by the temperature dependence of E_F .

Temperature dependence of Z calculated from ρ , κ and α is shown in Fig. 8. The temperature at which Z reaches Z_{max} for $x = 0.10, 0.15, 0.25$ and 0.50 are 420, 470, 540 and 660 K, respectively. In the case of $x = 0.25$, the reduction of κ_{ph} is remarkable. In the case of $x = 0.50$, a rather high Z is maintained at high temperatures because of gradual decrease in α . It has been reported that ρ of PbTe is changed by heating up to 700 K.¹⁸ In this study, however, no change of ρ was observed for $x = 0.50$ up to 800 K as shown in Fig. 6. It is consequently concluded that $\text{Pb}_{0.50}\text{Sn}_{0.50}\text{Te}$ prepared in this work is thermally stable up to 800 K.

C. Design of FGM structure for the temperature range 300–800 K

On the basis of the above results, the optimum FGM consisting of segments with different carrier concentrations was estimated for the temperature range from 300 to 800 K. The maximum conversion efficiency η_{max} is given by the following equation:¹²

$$\eta_{\text{max}} = \frac{T_h - T_c}{T_h} \times \frac{M - 1}{M + \left(\frac{T_c}{T_h}\right)} \quad (6)$$

where T_h and T_c are the hot and the cold side temperatures, respectively. M is the factor defined by

TABLE 3. Estimated combination of x , joint temperature, average figure-of-merit Z_{av} and maximum energy conversion efficiency η_{max} calculated for $T_c = 300$ K and $T_h = 800$ K.

Combination	Joint Temp. (K)	Z_{av} (K^{-1})	η_{max} (%)
$x = 0.10, 0.15, 0.25, 0.50$	339, 400, 603	0.978×10^{-3}	9.29
$x = 0.15, 0.25, 0.50$	400, 603	0.975×10^{-3}	9.27
$x = 0.10, 0.25, 0.50$	376, 603	0.974×10^{-3}	9.26
$x = 0.25, 0.50$	603	0.950×10^{-3}	9.09
$x = 0.50$	—	0.720×10^{-3}	7.29

$$M = \sqrt{1 + \frac{1}{2} Z_{av} (T_h + T_c)} \quad (7)$$

and Z_{av} is the average of Z expressed by

$$Z_{av} = \frac{1}{T_h - T_c} \int_{300K}^{800K} Z dT \quad (8)$$

Fixing T_h and T_c , it is necessary to distribute Z to maximize η_{max} for the operating temperature range.¹² For $T_c = 300$ K and $T_h = 800$ K, the estimated combination of x , the joint temperature, Z_{av} and the theoretical η_{max} are shown in Table III. It was found that the largest Z_{av} is realized by the 4-step FGM in which Z_{av} is expressed by

$$Z_{av} = \frac{1}{T_h - T_c} \left[\int_{300K}^{339K} Z_1 dT + \int_{339K}^{400K} Z_2 dT + \int_{400K}^{603K} Z_3 dT + \int_{603K}^{800K} Z_4 dT \right] \quad (9)$$

where Z_1, Z_2, Z_3 and Z_4 correspond to $x = 0.10, 0.15, 0.25$ and 0.50 , respectively. No remarkable difference in η_{max} , however, was found between the 4- and the 3-step cases. The performance of the 3-step FGM will be practically higher than that of the 4-step case because of electrical resistances at joints. In the case of 3-step FGM, the combination maximizing Z_{av} was $x = 0.15, 0.25$ and 0.50 . Z_{av} was estimated at $0.975 \times 10^{-3} / K$. Z_{av} and η_{max} of the 3-step case were 35% and 27% larger than those of homogeneous $Pb_{1-x}Sn_xTe$ with $x = 0.50$, whose maximum efficiency η_{max} is equal to 7.29%. In the case of 2-step FGM, the combination maximizing Z_{av} was $x = 0.25$ and 0.50 , and Z_{av} was estimated at $0.950 \times 10^{-3} / K$. Z_{av} and η_{max} of the 2-step case were 32% and 25% larger than

those of the homogenous material with $x = 0.50$. It is consequently concluded that sufficient FGM effect on power generation can be produced even by the 2-step FGM.

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