Preparation and thermoelectric properties of K-doped p-type lead telluride

K添加p型PbTeの作製と熱電特性

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(Received 8, November 1996 Accepted 17, February 1997)

Single crystals of K-doped p-type PbTe were prepared by Bridgman method. The carrier concentration and Hall mobility were measured from 77 to 300K. The hole concentration was successfully controlled in the range from 8.0×10^{24} to $4.0 \times 10^{25} \text{ m}^{-3}$ with 1000 to 20000 molppm K at 300 K. By calculating κ_{el} on the basis of Fermi integration, κ_{ph} was estimated to be $2.15 \text{ Wm}^{-1}\text{K}^{-1}$.

By using the observed thermoelectric power and electrical conductivity value and the calculated κ value, figure-of-merits Z of PbTe at 300K were $8.0 \times 10^{-4} \text{ K}^{-1}$ for p-type at a hole concentration of $1.0 \times 10^{25} \text{ m}^{-3}$ (2000 molppm K). The μ_{H} monotonously decreased with an increase of carrier concentration. Z remains low due to the low values of μ_{H} and $\mu_{\text{H}}/\kappa_{\text{ph}}$.

Keywords: Lead telluride, p-type dopant, scattering mechanism, thermoelectricity, figure-of-merit, Fermi integral

1. INTRODUCTION

Lead telluride is among the best material used in construction of thermoelectric generators working at intermediate temperature (450-840 K). The PbTe generators were developed as the special application in space exploration in 1960s, and now constitute the power supply unit using heat of gas combustion.

The figure of merit Z of PbTe reaches its maximum Z_{opt} at a certain optimum temperature T_{opt} and rapidly decreases on deviation from T_{opt} .¹⁻³ The T_{opt} value of

n-type PbTe is known to shift from low to high temperature with an increase of electron concentration.

Recently, an attempt to attain high conversion efficiency of PbTe thermoelectric material is based on the preparation of functionally graded material (FGM) carrier concentration. The carrier concentration has been controlled by doping iodine for n-type⁴ and Ag or Na for p-type,^{5,6} although the thermoelectric properties have not fully been clarified.

The study for the homogeneous materials is indispensable to preparation and evaluation of the carrier concentration FGM of PbTe.

As a series of the study on PbTe, the purpose of the present study was to investigate the thermoelectric properties for K-doped p-type PbTe single crystals. The thermoelectric properties were analyzed on the basis of Fermi integration assuming the single valence band as the 0th approximation.

II. EXPERIMENTAL

The single crystals of PbTe were prepared by Bridgman method after direct melting of constituent elements of Pb and Te (nominal purity, 99.9999%). The weighed amount of the elements in stoichiometric composition (Pb/Te=1) was vacuum sealed in a quartz ampule with metallic K as the p-type dopant. The ampule was 10 mm in dia. and 120 mm in length, and the bottom end was shaped in a circular cone. The control of the doping amount was made by weighing K in the region of 1000 to 24000 molppm. The crystal growth was performed in the vertical electric furnace, where the maximum temperature was 1223 K, and the temperature gradient was about 1200 K/m at melting point. The growth rate was 4 mm/h.

The Hall coefficient R_H and electrical conductivity σ were measured by van der Pauw configuration using the Pt-wire electrodes. The carrier concentration $|N_A - N_D|$ and Hall mobility μ_H were calculated using the equation $|N_A - N_D| = 1/eR_H$ (e : electric charge) and $\mu_H = R_H \sigma$, respectively. The thermoelectric power α at 300 K was estimated from the linear relationship between thermoelectromotive force EMF and temperature difference within 5K.

The valence band of PbTe is rather complexed, for which single and two band models were proposed.^{7,8} The analysis of the thermoelectric properties was performed on the basis of Fermi integration by assuming a dominant single band for heavily doped PbTe as the 0th approximation. In the present study, we performed the analysis of thermoelectric properties of K-doped p-type PbTe by calculating Fermi-Dirac integration.

FIG.1. Plots of carrier concentration versus amount of dopant in K-doped p-type PbTe.

III. RESULTS AND DISCUSSION

A. CONTROL OF CARRIER CONCENTRATION

Figure 1 shows plots of carrier concentration versus amount M of K.⁹ The dashed line is derived by assuming that the K atom occupies the Pb site and acts a singly ionizable acceptor. In the region of 1000 to 10000 molppm, the carrier concentration monotonously increased with an increase of doping amount, which was lower than that of the calculation. The hole concentration was successfully controlled in the range of 1.0×10^{25} to $2.0 \times 10^{26} \text{ m}^{-3}$ at 77K. The maximum carrier concentration was about $2.0 \times 10^{26} \text{ m}^{-3}$ at 77 K and about $4.0 \times 10^{25} \text{ m}^{-3}$ at 300 K. The difference of carrier concentration between at 77 K and 300 K may be due to the contribution from heavy hole or decrease in mobility at temperature T less than 300 K.⁷ In the region of $M > 10000$ molppm K, carrier concentration decreased with an increase of M . The result suggests that interstitial K or n-type precipitation may have caused carrier concentration or R_H increases because of increasing of heavy hole density.

Figure 2 shows plots of μ_H versus carrier concentration for K-doped PbTe. The μ_H value of all samples monotonously decreased with an increase of carrier concentration at 77 and 300 K.

Figure 3 shows the temperature dependence of μ_H for K-doped PbTe, which indicates that μ_H monotonously decreased with an increase of temperature.

Hall mobility μ_H is expressed in terms of

FIG.2. Plots of Hall mobility versus carrier concentration in K-doped p-type PbTe.

FIG.3. Temperature dependence of Hall mobility in K-doped p-type PbTe (the numbers indicate amount of K in molppm).

temperature T as follows;¹⁰

$$\mu_H \propto T^{-3/2+r}, \quad (1)$$

where r is scattering factor, and $r=0$ and $r=3.0$ for acoustical and ionized impurity scattering, respectively.

As for K-doped PbTe, r was estimated to be changing from -0.17 to 0.95 with increased amount of dopant from 1000 to 25000 molppm. This result suggests that the scattering mechanism of the hole changed from phonon scattering to ionized impurity scattering with an increase of M .

Figure 4 shows plots of σ and α versus carrier concentration. The α at 77 and 300 K value monotonously decreased and the σ value increased

FIG.4. Plots of electrical conductivity versus carrier concentration in K-doped p-type PbTe.

FIG.5. Plots of carrier concentration versus thermal conductivity in K-doped p-type PbTe.

with an increase of carrier concentration.

B. ANALYSIS OF THERMOELECTRIC PROPERTIES

The κ is expressed by the sum of components of phonon κ_{ph} and electron κ_{el} as follows,^{2,11}

$$\kappa = \kappa_{ph} + \kappa_{el}. \quad (2)$$

κ_{el} is expressed by the Wiedemann-Franz law, so that

$$\kappa_{el} = L \sigma T, \quad (3)$$

where Lorentz number, L is given by the following equation;

$$L = (k/e)^2 \left[\frac{(r+3)/(r+1) F_{r+2}(\xi)/F_r(\xi) - \{(r+2)/(r+1) F_{r+1}(\xi)/F_r(\xi)\}^2}{\} \right]. \quad (4)$$

FIG.6. Plots of carrier concentration versus reduced Fermi energy in K-doped p-type PbTe.

Here k is the Boltzman constant. r is the scattering factor which was determined from the temperature dependence of Hall mobility. ξ is the reduced Fermi energy ($= \xi/kT$, ξ :Fermi energy), $F_r(\xi)$ is the Fermi integral defined by¹²

$$F(\xi) = \int_0^\infty x^r / \{\exp(x - \xi) + 1\} dx. \quad (5)$$

ξ is expressed as follows;

$$\alpha = \pm (k/e) \{ (r+2)/(r+1) F_{r+1}(\xi) / F_r(\xi) - \xi \}, \quad (6)$$

where the positive and negative signs stand for the p- and n-type conductions, respectively.

For the undoped p-type PbTe, ξ was calculated using the observed α and r values. Thus, κ_{el} was obtained by using calculated L in eq.(4) and observed σ value, which results in κ_{ph} to be $2.15 \text{ Wm}^{-1}\text{K}^{-1}$ on the basis of literature data of κ value.¹³ Table 1 lists the κ -, ξ -, and L -values for undoped p-type PbTe. The κ_{ph} value was hereafter assumed to be independent of the carrier concentration. Since κ_{el} was calculated using eq.(3), the κ values were estimated using κ_{ph} and κ_{el} as a function of the carrier concentration as shown in Fig. 5. The κ value was found to increased monotonously with an increase of carrier concentration at 77 and 300 K.

When the serious phonon scattering is taken into account for κ_{ph} in heavily doped PbTe, κ value at high carrier concentration will not become so large as that in Fig. 5. The ξ value in Fig. 6 monotonously increased from 0 to 7 with an increase of carrier concentration. The result indicates that K-doped p-

FIG.7. Plots of figure of merit versus carrier concentration in K-doped p-type PbTe.

type PbTe is heavily degenerated semiconductor.¹⁰

C. EVALUATION OF THERMOELECTRIC FIGURE OF MERIT

The thermoelectric figure of merit Z was estimated from the observed α and σ values using the equation;

$$Z = \alpha^2 \sigma / \kappa. \quad (7)$$

Figure 7 shows plots of Z value versus carrier concentration. The maximum figure of $Z(300\text{K}) = 7.0 \times 10^{-4} \text{ K}^{-1}$ was obtained at $p = 2.34 \times 10^{24} \text{ m}^{-3}$ (nominal doping concentration; 2000 molppm K)

The effective mass m^* was estimated from the relationship,^{10,14}

$$p = 4\pi (2m_d^* kT)^{3/2} F_{1/2}(\xi) / h^3, \quad (8)$$

where h is Plank constant, and m_d^* is state of effective mass.

m_d^* is given in the following expression in terms of m^* ;¹⁴

$$m_d^* = N^{2/3} (m_{\perp}^{*2} m_{\parallel}^*)^{1/3}, \quad (9)$$

where N is number of equivalent band edge ($N=4$ for PbTe), and the two components of effective mass are the longitudinal $m_{\parallel}^*$ and transverse $m_{\perp}^*$. m^* was calculated using eq.(9) on the hypothesis of $m^* = m_{\perp}^* = m_{\parallel}^*$. Table 2 lists effective mass ratio, m^*/m_0 (m_0 : free electron mass). The m^*/m_0 value for hole is consistent with the literature data.¹⁴

The maximum figure of merit Z_{max} is expressed in terms of the semiconducting parameters;¹⁴

$$Z_{max} \propto N m^{*3/2} \mu T^{3/2} \exp(r+1/2) / \kappa_{ph}. \quad (10)$$

Therefore Z increases with an increase of the m^* and

mobility to thermal conductivity ratio μ/κ_{ph} . Table 2 shows semiconductive properties and maximum figure-of-merit of K-doped PbTe at 300K. The μ_H value was smaller than that of the literature data,¹⁴

and consequently the Z and μ_H/κ_{ph} values were smaller than the literature data.

TABLE 1. Thermal conductivity and calculated values of carrier and lattice thermal conductivities of undoped PbTe at 300K.

κ (W·m ⁻¹ K ⁻¹)	ξ	L (10 ⁻⁸ V ² K ⁻²)	κ_{el} (W·m ⁻¹ K ⁻¹)	κ_{ph} (W·m ⁻¹ K ⁻¹)
2.30	-2.4	0.805	0.15	2.15

κ : literature data¹³. ξ , L and κ_{el} were calculated in the present study using the observed α and r values for an undoped p-type PbTe single crystal.

TABLE 2. Semiconductive properties and maximum figure-of-merit of PbTe at 300K.

Type	Amount of dopant (molppm)	m^*/m_0	μ_H (10 ⁻⁴ m ² V ⁻¹ s ⁻¹)	κ_{el} (W·m ⁻¹ K ⁻¹)	μ_H/κ_{ph} (10 ⁻² mKW ⁻¹ V ⁻¹ s ⁻¹)	Z_{max} (10 ⁻³ K ⁻¹)
p	2400(K)	0.301	310	0.24	1.44	0.70

V. CONCLUSION

- (1)The p-type PbTe single crystals were prepared by Bridgman method. The hole concentration was successfully controlled in the range of 8.0×10^{24} to 4.0×10^{25} m⁻³ with 1000 to 20000 molppm K at 300 K. These data will be important in the further study on preparing the carrier concentration FGM of PbTe.
- (2)By calculating κ_{el} on the basis of Fermi integration, κ_{ph} was estimated to be 2.15 Wm⁻¹K⁻¹. By using the observed α and σ value and the calculated κ value, Z_{max} 's were estimated to be 0.7×10^{-3} K⁻¹ at $p=1.0 \times 10^{25}$ m⁻³. The Z_{max} value was lower than those of the thermoelectric materials in the middle temperature range.
- (3)The μ_H monotonously decreased with an increase of carrier concentration. The low μ_H and μ_H/κ_{ph} values cause the Z value low-lying. The sintered-PbTe might be effective to improve the Z_{max} by decreasing κ_{ph} value.
- (4)The detailed analysis of the thermoelectric properties is rest in the further studies by considering the valence band structure.

ACKNOWLEDGMENTS

The authors wish to thank Dr. I. A. Nishida for permitting us to utilize the computation system.

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