Carrier Concentration Dependence of Thermal Conductivity of Iodine-Doped n-Type PbTe

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Thermal conductivity ($\kappa$) of iodine doped n-type PbTe with carrier concentration ($n$) in the range of $1.5 \times 10^{24}$ to $3.4 \times 10^{25}$ m$^{-3}$ was measured by using a laser flash method in the temperature range from 300 to 600 K. The scattering factor ($r$) was estimated from the temperature dependence of Hall mobility. The $r$ values below 300 K changed from -0.43 to 0.39 with increasing electron concentration ($n$), while they were almost constant at -0.64 above 300 K. These results indicate that the scattering mechanism gradually changed from an ionized impurity scattering to the interaction between optical and acoustical phonon as the temperature ($T$) increased and $n$ decreased. The $\kappa$ values for all the samples showed the $T^{-1}$ dependence, the slope of which increased with increasing electron concentration in the measured temperature range. The lattice ($\kappa_{\text{lattice}}$) and carrier ($\kappa_{\text{carrier}}$) components of thermal conductivity were estimated using the observed $\kappa$ and $\sigma$ values on the basis of Fermi integration. The $\kappa_{\text{carrier}}$ and $\kappa_{\text{lattice}}$ values showed temperature dependence similar to that of the total $\kappa$ value in the temperature range from 300 to 600 K. This fact suggests that the $\kappa_{\text{lattice}}$ with electron concentration in the range of $1.5 \times 10^{24}$ to $3.4 \times 10^{25}$ m$^{-3}$ is dominated by the Umklapp process in the measured temperature range.

(Received February 17, 2000; Accepted August 16, 2000)

\textbf{Keywords:} lead telluride, scattering mechanism, thermoelectric material, thermal conductivity, Fermi integral, lattice thermal conductivity

1. Introduction

Lead telluride (PbTe) is one of the best materials used in construction of thermolectric (TE) generators operating at intermediate temperatures (450–800 K).\textsuperscript{1} Recently, an attention has been given to PbTe\textsuperscript{2–9} as a constituent material for power supply units using the exhausted heat of gas combustion in incinerators and other industrial furnaces.

The thermoelectric figure of merit ($Z$) of TE materials is expressed using the following equation:\textsuperscript{5}

$$Z = \alpha^2 \sigma / \kappa,$$

where $\alpha$, $\sigma$ and $\kappa$ are the Seebeck coefficient, electrical conductivity and thermal conductivity, respectively. The larger the $Z$ value is, the higher the thermoelectric efficiency of generators is. In order to improve $Z$, the decrease of $\kappa$ and increase of $\sigma$ are indispensable. Since an increase of $\sigma$ generally involves an increase of $\kappa$, it is necessary to experimentally clarify the relationship between these two parameters. The $\kappa$ value is given by the sum of a lattice ($\kappa_{\text{lattice}}$) and carrier ($\kappa_{\text{carrier}}$) components as follows:\textsuperscript{6,7}

$$\kappa = \kappa_{\text{lattice}} + \kappa_{\text{carrier}}$$

Some measurements and analyses of $\kappa$ have been performed for n-type PbTe; Devyatikova \textit{et al.} reported that $\kappa_{\text{lattice}}$ decreases with increasing carrier concentration ($n$) in the region of $n > 5 \times 10^{25}$ m$^{-3}$\textsuperscript{8,9}. Smirnov \textit{et al.} estimated the temperature dependence of thermal resistivity ($W_{\text{lattice}} = 1/\kappa_{\text{lattice}}$) in the temperature range from 100 to 450 K, which was proportional to the temperature below 300 K for $n = 10^{20}$ m$^{-3}$\textsuperscript{10}. Recently, several studies on sintered PbTe materials\textsuperscript{11–13} have indicated that the $\kappa_{\text{lattice}}$ values are modified by the grain boundaries. For the thermoelectric application, the thermal and electrical transportation properties of PbTe single crystals must be clarified in the intermediate temperature range (450 ~ 800 K).

The present study was undertaken to investigate the carrier concentration dependence of thermal conductivity for iodine-doped n-type PbTe single crystals and to clarify the relationship among $\kappa_{\text{lattice}}$, $\kappa_{\text{carrier}}$ and carrier concentration in the temperature range of 300 to 600 K.

2. Experimental

Single crystals of iodine doped PbTe were prepared by the Bridgman method. PbI$_2$ was used as the source material of iodine. The constituent elements of Pb and Te (nominal purity, 99.9999%) in the stoichiometric composition (Pb/Te = 1) with PbI$_2$ were vacuum-sealed in a quartz ampoule. The ampoule was 10 mm in diameter and 120 mm in length, and the bottom end had the shape of a columnar cone. The amount of doping ($M$) was controlled by weighing PbI$_2$ in the region of 0.15 to 0.40 at%. Crystal growth was performed in a vertical electric furnace, and the growth conditions were as follows: a maximum temperature of 1223 K, a temperature gradient of about 1200 K/m at the melting point and a growth rate of 4 mm/h.

The Hall coefficient ($R_H$) and electrical conductivity ($\sigma$) were measured by van der Pauw configuration\textsuperscript{14} using Pt-wire electrodes in the temperature range from 300 to 700 K. The measurement of $R_H$ was performed with a magnetic field of 0.4 T and with a current of 10 mA. Thin specimens were cut from the ingots independently of the crystal di-
rection, because the crystal structure of PbTe is free from anisotropy. The carrier concentration \( n \) was estimated by using the equation \( n = 1/eR_H \) \( (e: \) electronic charge), assuming carrier concentration in the region of exhaustion range \( (n\text{-type}) \). Hall mobility \( \mu_H \) was obtained by using the equation \( \mu_H = |R_H|/\sigma \).

Thermal conductivity was measured using disk-shaped samples (10 mm in diameter and 1 mm in thickness) by a laser flash method using a thermal constant analyzer (Shinku-rikok TC-7000) in the temperature range from 300 to 600 K. The source of the energy pulse was a ruby laser with a wavelength of 694.3 nm and an output of more than 6 J/pulse. The measurements were made during heating at a rate of 4 K/min(\( \pm 6.7 \times 10^{-2} \text{ K/s} \)) at a vacuum. For the measurement of heat capacity, glassy carbon was attached to the front surface of the specimen. The thermal conductivity was analyzed in terms of \( \kappa_{\text{lat}} \) and \( \kappa_{\text{car}} \) on the basis of Fermi integration.

3. Results and Discussion

3.1 Scattering mechanism of carrier

Table 1 lists the thermoelectric properties for iodine-doped n-type PbTe at 300 K. The \( n \) values for all samples were almost independent of temperature in the measured temperature range, and increased with increasing the amount of dopant. Figure 1 shows the temperature dependence of \( \sigma \) in terms of carrier concentration. The \( \sigma \) value decreased with increasing \( n \) and decreased with increasing temperature, which indicates that the samples are typical degenerated semiconductors.

The relationship between \( \mu_H \) and \( T \) depends on the carrier scattering mechanism and is generally given by using the scattering factor \( (r) \) as follows,

\[
\mu_H \propto T^{-3/2+r},
\]

where \( r = 0.0, -1.0 \) and 3.0 stand for the scattering by the acoustical phonon, the interaction between acoustical and optical phonon, and ionized impurity scattering, respectively. Matthiessen’s rule\(^{17,18} \) expresses that real mobility is dominant by the smallest mobility component among the existing scattering mechanisms at each temperature.

Figure 2 shows the temperature \( (T) \) dependence of \( \mu_H \) for various electron concentrations. A straight line is drawn for the relationship of \( \mu_H \propto T^{-2.5} \). The \( r \) values were estimated from the slope of the \( \mu_H-T \) curve. The \( r \) values below 300 K changed from \(-0.43 \) to 0.39 with increasing electron concentration. Above 300 K, the \( r \) values for all the samples were equal to \(-0.64 \). These results indicated that the carrier scattering mechanism gradually changed from an ionized impurity scattering to the interaction between an acoustical and an optical phonon scattering as the temperature increased and the electron concentration decreased.

3.2 Analysis of thermal conductivity

The heat capacity (\( C_p \)) measured for all the samples was almost equal to \( 1.52 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1} \) (=50.90 J mol\(^{-1} \text{ K}^{-1} \)) at 300 K, which was close to the literature data.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Amount of iodine ((\text{M/1%}))</th>
<th>Carrier concentration ((\text{s/m}^{-3}))</th>
<th>Electrical conductivity ((\sigma/\Omega^{-1} \text{ m}^{-1}))</th>
<th>Hall mobility ((\mu_H/\text{m}^2 \text{ V}^{-1} \text{ s}^{-1}))</th>
<th>Seebeck coefficient ((\alpha/\text{V K}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.30</td>
<td>1.50 \times 10^{24}</td>
<td>1.51 \times 10^4</td>
<td>6.30 \times 10^{-2}</td>
<td>-3.20 \times 10^{-4}</td>
</tr>
<tr>
<td>2</td>
<td>0.40</td>
<td>3.32 \times 10^{24}</td>
<td>4.73 \times 10^4</td>
<td>8.92 \times 10^{-2}</td>
<td>-2.40 \times 10^{-4}</td>
</tr>
<tr>
<td>3</td>
<td>0.60</td>
<td>7.98 \times 10^{24}</td>
<td>1.42 \times 10^5</td>
<td>1.12 \times 10^{-1}</td>
<td>-1.51 \times 10^{-4}</td>
</tr>
<tr>
<td>4</td>
<td>0.80</td>
<td>2.15 \times 10^{25}</td>
<td>3.16 \times 10^5</td>
<td>9.20 \times 10^{-2}</td>
<td>-7.40 \times 10^{-5}</td>
</tr>
</tbody>
</table>
(51.95 J mol$^{-1}$ K$^{-1}$ at 350 K)\textsuperscript{20} Figure 3 shows the temperature dependence of $C_p$ of n-type PbTe. The error of $C_p$ at 300 K was less than 2% under three measurements, and the rise of $C_p$ was about 1.08 times from 300 to 700 K. The density ($\rho$) was $8.14 \times 10^3$ kg m$^{-3}$, which corresponded to the literature data.\textsuperscript{20} Thermal conductivity ($\kappa$) was calculated from the measured thermal diffusivity ($\lambda$) and heat capacity\textsuperscript{20} using eq. (4).

$$\kappa = \lambda \rho C_p.$$ \hfill (4)

Figure 4 shows the temperature dependence of $\kappa$ of n-type PbTe samples with various electron concentrations. The error of $\lambda$ was about 1% under three measurements. The $\kappa$ values increased with increasing electron concentration, and were almost proportional to $T^{-1}$. The slope of $\kappa$-T$^{-1}$ plot increased with increasing electron concentration.

$\kappa_{\text{carrier}}$ is expressed by the Wiedemann-Franz law,\textsuperscript{6,7} so that

$$\kappa_{\text{carrier}} = L \sigma T,$$ \hfill (5)

where $L$ is the Lorenz number. $L$ is given by the following equation on the basis of one-electron approximation:

$$L = \left[ \frac{(r+3)F_{r+2}(\xi)}{(r+1)F_r(\xi)} - \left\{ \frac{(r+2)F_{r+2}(\xi)}{(r+1)F_r(\xi)} \right\} \right] \left( \frac{k_B}{e} \right)^2.$$ \hfill (6)

$\xi$ is the reduced Fermi energy ($=\xi/k_B T$, $\xi$: Fermi energy, $k_B$: Boltzmann’s constant), and $F_r(\xi)$ is the Fermi integral defined by\textsuperscript{20}

$$F_r(\xi) = \int_0^\infty \frac{x^r \exp(-x \xi)}{1 + \exp(-x)} dx.$$ \hfill (7)

The Seebeck coefficient ($\alpha$) is expressed as a function of $\xi$ as follows:

$$\alpha = \pm \left( \frac{k_B}{e} \right) \left\{ \frac{(r+2)F_{r+1}(\xi)}{(r+1)F_r(\xi)} - \xi \right\}$$ \hfill (8)

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

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Relationship between temperature and heat capacity for iodine-doped n-type PbTe.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Relationship between temperature and thermal conductivity for iodine-doped n-type PbTe.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{Relationship between temperature and Lorenz number for iodine-doped n-type PbTe.}
\end{figure}

$\xi$ was calculated using the observed $\alpha$ and $r$ values on the basis of eq. (8), where the $r$ values were acquired by differentiating the $\mu$-$T$ curves at each temperature in Fig. 2. Then, $L$ was calculated using eq. (6).

Figure 5 shows the temperature dependence of the calculated $L$ values. Here, the $L_0$ value in Fig. 5 is the Lorenz number of metals ($L = \pi^2/3(k_B/e)^2 = 2.45 \times 10^{-8}$ V$^2$K$^{-2}$). The $L$ values monotonously decreased with increasing temperature and decreased with decreasing carrier concentration, then converged on a constant value ($L_1 = (k_B/e)^2 = 0.745 \times 10^{-8}$ V$^2$K$^{-2}$), which might be attributable to the behavior of the reduced Fermi level in eq. (6). These results indicated that the degeneracy degree decreased with increasing temperature and decreasing carrier concentration because a decrease of reduced Fermi energy means that Fermi energy
leaves the conduction band. In the nondegenerate state, \( L \) is given by\(^{240}\)

\[
L = (r + 2) \left( \frac{k_B}{e} \right)^2
\]

and depends only on the scattering parameter. In the higher temperature range, it is known that the scattering parameter of PbTe approaches \( r = -1.0 \) (the interaction between acoustical and optical phonon scattering).\(^{172}\) When \( r = -1.0 \), \( L \) becomes the value of \( \left( \frac{k_B}{e} \right)^2 = 0.745 \times 10^{-8} \) \( \text{V}^2 \text{K}^{-2} \). The result that \( L \) converged on a constant means that the state changed from a degenerate one to a nondegenerate one. The \( L \) values were smaller than those of Smirnov’s data, where all \( r \) values were assumed to be temperature-independent (\( r = 0 \)).

After \( \kappa_{\text{carrier}} \) was obtained by using observed \( \sigma \) (in Fig. 1) and calculated \( L \) in eq. (5), the \( \kappa_{\text{lattice}} \) values were estimated by using observed \( \kappa \) values.

Figure 6 shows the temperature dependence of the \( \kappa_{\text{carrier}} \) with various electron concentrations. \( \kappa_{\text{carrier}} \) was found to be inversely proportional to the temperature. The \( \kappa_{\text{carrier}} \) value was sensitive to electron concentration and too small to influence the total \( \kappa \) value when \( n \) was below \( 10^{24} \) m\(^{-3} \). However, \( \kappa_{\text{carrier}} \) rapidly increased with electron concentration and the \( \kappa_{\text{carrier}} \) was sufficiently large to influence the \( \kappa \) value when \( n \) was larger than \( 3 \times 10^{24} \) m\(^{-3} \).

Figure 7 shows the temperature dependence of thermal resistivity (\( W_{\text{lattice}} = 1/\kappa_{\text{lattice}} \)) with the literature data\(^{10}\) for various electron concentrations. The values reported in the literature rapidly increased with increasing temperature above 300 K. On the contrary, all \( W_{\text{lattice}} \) values obtained in this study were proportional to temperature indicating that the behavior of thermal resistivity obeys the Umklapp processes\(^{25}\) in the measured temperature range. The values reported by Smirnov et al. exceeded those in the present study above 300 K, perhaps due to the large \( L \) values obtained by assuming that the \( r \) values were constant.\(^{10}\) Devyatova et al. also reported \( W_{\text{lattice}} \) values for p-type PbTe with hole concentrations of \( 10^{23} \) and \( 10^{25} \) m\(^{-3} \). Devyatova’s data, which deviated from the linear \( W_{\text{lattice}} \propto T \) relationship above 300 K,\(^{26}\) was in the direction opposite that of Smirnov’s data; this can be attributed to the bipolar diffusion of electrons and holes in the intrinsic region. This fact suggests that the \( \kappa_{\text{lattice}} \) with carrier concentration in the range of \( 1.5 \times 10^{24} \) to \( 3.4 \times 10^{25} \) m\(^{-3} \) is limited by the Umklapp processes in the measured temperature range because the carrier was in the exhaustion region.

4. Summary

Iodine-doped n-type PbTe single crystals were prepared by the Bridgman method and the influence of carrier concentration on the thermal conductivity was investigated.

(1) The scattering factor (\( r \)) was estimated from the result of temperature dependence of Hall mobility. The \( r \) value below 300 K changed from -0.43 to 0.39 with increasing electron concentration. Above 300 K, \( r \) values for all samples were almost equal to -0.64. These results indicated that the carrier scattering mechanism changed from ionized impurity scattering to the interaction between acoustical and optical phonon scattering as the temperature increased and the electron concentration decreased.

(2) The \( \kappa \) values for all samples were inversely temperature-dependent and monotonously increased with increasing electron concentration. The \( \kappa_{\text{lattice}} \) and \( \kappa_{\text{carrier}} \) values were estimated from the observed \( \kappa \) values. The \( \kappa_{\text{lattice}} \) behavior obeyed the Umklapp processes in the measured temperature region and electron concentration region.

Acknowledgment

We thank Prof. T. Goto of IMR, Tohoku University for discussing the results in this work.

This work was partly supported by the Research Fellowship of the Japan Society for the Promotion of Science for Young Scientist (JSPS Research Fellow) (No. 6231) and the Grant-in-Aid for Scientific Research on Priority Areas (No. 08243102) from the Ministry of Education, Science, Sports and Culture.
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