Grain Size Effect on Thermoelectric Properties of PbTe Prepared by Spark Plasma Sintering

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Sintered PbTe materials with average grain sizes of 28–309 \( \mu \)m were prepared by the spark plasma sintering technique. The apparent densities of the sintered PbTe were 8.17–8.23 Mg/m\(^3\), which were higher than 99% of the theoretical ones. Thermoelectric properties of the sintered materials and those of the as-grown boule by Bridgman method were measured in the temperature range from 77 to 550 K. Resistivity, \( \rho \) of the sintered materials increased with decreasing grain size. Temperature dependence of \( \rho \) of the sintered PbTe was remarkably different from that of the as-grown boule below 250 K because of potential barriers at grain boundaries. Hall coefficient, \( R_h \) of the sintered materials at room temperature increased from \( 1.4 \times 10^{-6} \) to \( 3.4 \times 10^{-6} \) m\(^2\)/C, as the average grain size increased from 28 to 309 \( \mu \)m, which suggested that oxidation in the crystal grains was caused in the sintering process. Temperature dependence of the thermoelectric power, \( \alpha \) of the sintered PbTe below 250 K reflected the effect of carrier scattering at grain boundaries. Lattice thermal conductivity of the sintered PbTe decreased with decreasing grain size below 250 K, while it was independent of the grain size above that temperature. Above 250 K, thermoelectric properties of the sintered PbTe, except those in the 28 \( \mu \)m grain case, were consistent with those of the as-grown boule. The values of \( \alpha \) and \( R_h \) at 295 K were calculated by using a two-valence-band model involving a non-parabolic and a parabolic valence band. The calculation results were in good agreement with the experimental data.

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1. Introduction

Sintered material with fine grains is expected to be a thermoelectric material with a high figure-of-merit Z.\(^1\) Lattice thermal conductivity \( \kappa_{ph} \) of sintered material is usually smaller than that of solidified material because of the grain boundary effect and the long wave-length phonon scattering at grain boundaries. Sintered Bi–Te and Si–Ge have already been used for thermoelectric material.\(^1\)

In 1969, Parrot first proposed such a model\(^2\) for Si–Ge alloys, as phonon scattering at grain boundaries effectively reduces \( \kappa_{ph} \). In 1985, Bandari and Rowe applied the Parrott’s model to the \( \kappa_{ph} \) of PbTe. Considering non-parabolicity of the energy bands, \( \kappa \) was calculated on the basis of the acoustic and polar optical phonon scattering. As a result, they reported that \( \kappa \) of sintered PbTe, with a crystal grain size of 1 \( \mu \)m, doped with an optimum amount of dopant is 5% smaller than that of single crystal.\(^3\) Their results suggest that fining the grains reduces \( \kappa \) of PbTe, which is effective in improving the thermoelectric properties.

The objective of this study is to examine the effect of the spark plasma sintering (SPS) on the thermoelectric properties of PbTe. PbTe is known as the typical n-type thermoelectric material in the moderate temperature range, and it has been used below 950 K.\(^4\) It is known that the resistivity \( \rho \) for solidified and SPS n-type PbTe doped with PbI\(_2\) decreases by heating up to 700 K,\(^5–7\) while the \( \rho \) of solidified non-doped p-type PbTe increases up to that temperature.\(^5\) In this experiment, the grain size effect was consequently studied below room temperature in order to prevent the heating effect.

2. Experiment

Pb and Te with a purity of 99.9999% were individually weighed out in the atomic ratio of 1 : 1. They were loaded into an evacuated quartz tube of 10 mm in diameter and 120 mm in length. The tube was flushed several times with Ar and sealed off under a pressure of about \( 1 \times 10^{-4} \) Pa. Crystal growth was carried out by the Bridgman technique under the following conditions: the maximum temperature of 1223 K, the temperature gradient of 1.2 K/mm, and the growth rate of 4 mm/h. The conduction type of the grown boule was uniformly p-type. The boule was used for the starting material of sintered PbTe. The starting material was ground into fine powders with mean particle sizes of 6, 39, 180 and 380 \( \mu \)m. The sintered materials were prepared by the SPS\(^9\) at temperatures ranging 732–803 K for durations of 6–9 min in an atmosphere of \( 4.5 \times 10^{10} \) Pa (1 atm) Ar + 5% H\(_2\). The size of the sintered materials was 15 mm in diameter and 6 mm in thickness. The apparent densities were 8.17–8.23 Mg/m\(^3\) (8.17–8.23 g/cm\(^3\)), which were higher than 99% of the theoretical one. All the sintered materials were p-type semiconductors. Some samples were cut out of the sintered
materials for optical-microscopic observation. They were polished and photographed. The average grain size of each sample was determined as follows: A number of random lines were drawn on the obtained photo. The number of intersections at which each line crosses the grain boundaries was counted up. The cord lengths were measured and multiplied by 1.5 to determine \( D \).\(^9\)

Samples with a size of \( 1 \times 2 \times 7 \) mm\(^3\) were cut out of the sintered materials and the boule. \( \rho \) and \( R_H \) were measured in a temperature range from 77 to 350 K by the high speed DC method\(^9\) in order to prevent errors caused by the Peltier effect. \( R_H \) was measured in a magnetic field of 0.5 T. Carrier concentration \( n_H \) and Hall mobility \( \mu_H \) were expressed by \( n_H = 1/(eR_H) \) and \( \mu_H = R_H/\rho \), where \( e \) is the elementary charge. Thermoelectric power \( \alpha \) and thermal conductivity \( \kappa \) were measured at temperatures ranging from 77 to 350 K with a cryostat\(^9\) in a vacuum of \( 1 \times 10^{-4} \) Pa. \( \alpha \) was determined from the slope of the thermoemotive force \( E_0 \) vs. the temperature difference \( AT \) curve. \( \kappa \) was measured by the static comparative method using a transparent quartz as the standard specimen.

3. Results and Discussion

3.1 Sintered material

Figure 1 shows the microstructure of the sintered PbTe with the starting particle sizes of 6 (a), 39 (b), 180 (c) and 380 \( \mu \)m (d). Black and white points are pores in these pictures. For the sintered PbTe with a starting particle size of 6 \( \mu \)m, \( D \) was equal to 28 \( \mu \)m. The shape of the grains was similar to a polygon. The pores were very small and present near the grain boundaries. In the case with a starting particle size of 39 \( \mu \)m, \( D \) equalled 92 \( \mu \)m. A few grains shaped a rectangle, while the most grains shaped a polygon. Small pores were present near grain boundaries and large pores were present inside the grains. In the case of a starting particle size of 180 \( \mu \)m, \( D \) equalled 174 \( \mu \)m. Many grains shaped a polygon, and there were pores near the grain boundaries. In the case of a starting particle size of 380 \( \mu \)m, \( D \) equalled 309 \( \mu \)m. The grains shaped a polygon. A few pores were observed, and they were present near the grain boundaries. In the case of \( D = 28 \) and 92 \( \mu \)m, the grains were effectively grown in the sintering process. In the case of \( D = 174 \) and 309 \( \mu \)m, \( D \) roughly remained equal to the starting particle size, which confirmed that no grain growth occurred in the sintering process. The solidified PbTe was a polycrystal consisting of some large grains, and its properties were compared with those of the sintered materials. The shape of grains was similar to a polygon, and their average size was 3 mm, which was larger than the distance between probes (1.2 mm) used for electric resistivity measurement.

Fig. 1 Microstructures of sintered PbTe: (a), (b), (c) and (d) correspond to the average grain sizes of 28, 92, 174 and 309 \( \mu \)m.
3.2 Conduction parameters

Figure 2 shows the temperature dependences of the resistivity \( \rho \) of the solidified and the sintered PbTe shown in Fig. 1. \( \rho \) increased with decreasing \( D \). Above \( 10^3 / T = 4 \text{ K}^{-1} \) (below \( T = 250 \text{ K} \)), \( \rho \) of the solidified PbTe decreased with decreasing \( D \), while that of the sintered PbTe increased with decreasing \( D \). The temperature dependence of \( \rho \) of the sintered PbTe was remarkably different from that of the solidified PbTe.

Since the three-resistance electrical circuit model\(^{11} \) was known to analyze the temperature dependence of electrical conductivity \( \sigma (=1/\rho) \) of the sintered PbTe doped with Na, it was applied to the temperature dependence of \( \rho \) measured in this experiment.

The same circuit was assumed for the solidified and sintered materials as shown in Fig. 2. The resistances \( R_1 \) and \( R_2 \) correspond to the crystal grains and barriers, respectively, while \( R_3 \) is the resistance in the channels.\(^{11} \) According to this model, the total resistance \( R \) of the whole sample is given by

\[
\frac{1}{R} = \frac{1}{R_1 + R_2} + \frac{1}{R_3}
\]  

(1)

For \( R_1 \) and \( R_3 \), we assume the power laws \( R_1^{-1} \) and \( R_3^{-1} \sim T^{-m} \), where \( m \) is a constant. The temperature dependence of \( R_2 \) is given by the Petritz formula:\(^{12} \) \( R_2^{-1} \sim T^{-1/2} \exp\left(-\frac{\beta}{k_B T}\right) \), where \( \beta \) is the height of the potential barrier. Defining the sample conductivity as \( \sigma = I/(RA) \) (\( I \): sample length, \( A \): cross section), we obtain

\[
\sigma = \left[ a \left( \frac{T}{K} \right)^{-m} \right]^{-1}
+ \left[ b \left( \frac{T}{K} \right)^{-1/2} \exp\left( -\frac{\beta}{k_B T} \right) \right]^{-1} + c \left( \frac{T}{K} \right)^{-m},
\]  

(2)

where \( a, b \) and \( c \) are constant parameters. The values decided in this study are shown in Table 1. In the temperature range from 77 to 350 K, the calculated values are in good agreement with the experimental data. \( \beta \) of the solidified and the whole sintered PbTe were \( 1.6 \times 10^{-21} \text{ J (0.01 eV)} \) and \( 1.3 \times 10^{-20} \text{ J (0.08 eV)} \), respectively. It was found that \( \beta \) of the sintered PbTe was 8 times as large as that of the solidified one. It was also suggested that the band was bent at grain boundaries because of the defects caused by ionized impurities. It was suggested that the difference in temperature dependences of \( \rho \) between the solidified and the sintered materials was caused by energy barrier increase. It was found that the effect mentioned above was dominant above \( 10^3 / T = 4 \text{ K}^{-1} \) (below \( T = 250 \text{ K} \)).

![Fig. 2 Temperature dependence of the resistivities of the as-grown boule and the sintered sample: (a), (b), (c) and (d) correspond to the average grain sizes of 28, 92, 174 and 309 \( \mu \text{m} \).](image)

**Fig. 2** Temperature dependence of the resistivities of the as-grown boule and the sintered sample: (a), (b), (c) and (d) correspond to the average grain sizes of 28, 92, 174 and 309 \( \mu \text{m} \).  

![Fig. 3 Temperature dependence of the Hall mobilities of the as-grown boule and the sintered PbTe sample: (a), (b), (c) and (d) correspond to the average grain sizes of 28, 92, 174 and 309 \( \mu \text{m} \).](image)

**Fig. 3** Temperature dependence of the Hall mobilities of the as-grown boule and the sintered PbTe sample: (a), (b), (c) and (d) correspond to the average grain sizes of 28, 92, 174 and 309 \( \mu \text{m} \).

Figure 3 shows the temperature dependences of \( \mu_H \) of the solidified and the sintered materials. The temperature dependence of \( \mu_H \) of the sintered PbTe disagreed thoroughly with that of the solidified one in the temperature range from 77 to 250 K. It was suggested that scattering mechanisms were dif-

<table>
<thead>
<tr>
<th>Sample</th>
<th>( a/\Omega^{-1}\text{m}^{-1} )</th>
<th>( b/\Omega^{-1}\text{m}^{-1} )</th>
<th>( c/\Omega^{-1}\text{m}^{-1} )</th>
<th>( \beta/\beta )</th>
<th>( m )</th>
<th>( K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>( 1.11 \times 10^9 )</td>
<td>( 2.90 \times 10^7 )</td>
<td>( 6 \times 10^7 )</td>
<td>( 1.3 \times 10^{-20} )</td>
<td>1.9</td>
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</tr>
<tr>
<td>(b)</td>
<td>( 1.80 \times 10^9 )</td>
<td>( 1.51 \times 10^8 )</td>
<td>( 4 \times 10^8 )</td>
<td>( 1.3 \times 10^{-20} )</td>
<td>1.9</td>
<td>1</td>
</tr>
<tr>
<td>(c)</td>
<td>( 1.92 \times 10^9 )</td>
<td>( 2.45 \times 10^8 )</td>
<td>( 5 \times 10^8 )</td>
<td>( 1.3 \times 10^{-20} )</td>
<td>1.9</td>
<td>1</td>
</tr>
<tr>
<td>(d)</td>
<td>( 2.02 \times 10^9 )</td>
<td>( 7.14 \times 10^8 )</td>
<td>( 7 \times 10^8 )</td>
<td>( 1.3 \times 10^{-20} )</td>
<td>1.9</td>
<td>1</td>
</tr>
<tr>
<td>asg*</td>
<td>( 2.90 \times 10^9 )</td>
<td>( 3.85 \times 10^8 )</td>
<td>( 1 \times 10^{10} )</td>
<td>( 1.6 \times 10^{-71} )</td>
<td>1.9</td>
<td>1</td>
</tr>
</tbody>
</table>

\*asg: as-grown boule
ferten between the solidified and the sintered materials; i.e., in the sintered PbTe carriers were scattered by the energy barrier at grain boundaries also. The boundary scattering mechanism should depend on the formation conditions of the grain boundaries. $\mu_H$ of the sintered PbTe approached that of the solidified one with increasing $D$'s above 200 K. This is due to the decrease of the carrier mean-free-path with increasing temperature and to decrease of the scattering probability at grain boundaries with increasing $D$'s. Above 250 K, $\mu_H$ was proportional to $T^{-2.5}$. In common semiconductors, $\mu_H$ is proportional to $T^{-1.5}$ when the acoustic phonon scattering is dominant. However, PbTe is a narrow band-gap degenerate semiconductor with an energy gap of $5.0 \times 10^{-20}$ J (0.31 eV) and a relative dielectric constant of 400, which suggests strong temperature dependences.

Table 2 shows the experimental and calculated thermoelectric power $\alpha$ and Hall coefficient $R_H$, and the estimated parameters of solidified and sintered PbTe at 295 K. The Harris' model consisting of a non-parabolic valence band $v_b_1$ and a parabolic valence band $v_b_2$ was applied to this system, and calculation was carried out by using the calculation procedure of the Fermi-Dirac integral proposed by Ohzugi et al. $\alpha$ and $R_H$ are expressed as

$$\alpha = \frac{\alpha_1 \sigma_1 + \alpha_2 \sigma_2}{\sigma_1 + \sigma_2}$$

$$R_H = \frac{R_{H1} \sigma_1^2 + R_{H2} \sigma_2^2}{(\sigma_1 + \sigma_2)^2}$$

where $\sigma_0^*$ is the effective mass of carriers, $p_i$ the carrier density, $\eta_i$ the reduced Fermi energy, $\sigma_i$ the electrical conductivity. The suffix $i = 1$ and 2 denote the contribution from the valence band $v_b_1$ and $v_b_2$. The Kane model was applied to $v_b_1$, and the above parameters were calculated by the following equations:

$$\alpha_1 = p_1 \epsilon \mu_1$$

$$\alpha_2 = p_2 \epsilon \mu_2$$

$$\sigma_1 = \frac{k_B}{e} \left( \frac{2 F_1(\eta_1) + 3 \alpha^* k_B T F_2(\eta_1)}{F_0(\eta_1) + 2 \alpha^* k_B T F_1(\eta_1)} - \eta_1 \right)$$

$$\sigma_2 = \frac{k_B}{e} \left( \frac{2 F_1(\eta_2)}{F_0(\eta_2)} - \eta_2 \right)$$

$$R_{H1} = \frac{1}{p_1 \epsilon}$$

$$R_{H2} = \frac{1}{p_2 \epsilon}$$

where $\mu_1$ and $\mu_2$ are the mobilities in $v_b_1$ and $v_b_2$, and $\sigma^*$ is defined to be $1/E_C^*$, where $E_C^*$ is the effective energy gap of the non-parabolic band. In this calculation, $E_C^*$ was assumed to be $4.3 \times 10^{-20}$ J (0.27 eV). $\eta_2$ equals $\eta_1 + \Delta E/(k_B T)$, where $\Delta E$ is the energy gap between $v_b_1$ and $v_b_2$. In this calculation, $\Delta E$ was assumed to be $1.3 \times 10^{-20}$ J (0.08 eV). The function $F_i(\eta)$ is well known Fermi-Dirac integral,

$$F_i(\eta) = \int_0^\infty \frac{e^\eta}{\exp(e - \eta) + 1} \, d\epsilon.$$
an $n$-type semiconductor, while PbTe with 5% excess Pb was a $p$-type one. Lawton's experiments on the rectifying properties of these crystals have revealed that an oxide film forms easily on the telluride crystal. It is suggested that oxygen acts as an accepter in PbTe. In the sintering process, the surface area contacting oxygen increases with fining crystal grains. This suggested that oxidation was accelerated with decreasing crystal grain size. Therefore, the $n_H$ increased and $R_H$ decreased with decreasing $D$. $R_H$ of the whole sample increased with increasing temperature. This should be explained by the two-valence-band model\(^\text{(16)}\) rather than the usual single band model. In a low temperature range, $v_b_1$ with a small effective mass is dominant. Around room temperature, $v_b_1$ approaches $v_b_2$ with a large effective mass with increasing temperature. Increase in $R_H$ expressed by the formula (4) as a weighed average of Hall coefficients $R_H$ of $v_b_1$ and $R_H$ of $v_b_2$ is explained on the basis of the hole transit from $v_b_1$ to $v_b_2$.

Figure 5 shows the temperature dependences of $\alpha$ of the solidified and the sintered PbTe. The temperature dependence of $\alpha$ of the solidified PbTe was showed by a straight line in the temperature range from 77 to 350 K. The temperature dependence of $\alpha$ of the sintered PbTe was showed by a straight line above 250 K and by a deflected line below 250 K. Such a dependence tended to increase with decreasing $D$. In Fig. 3, the temperature dependences of $\mu_H$ of the sintered and the solidified PbTe below 250 K were remarkably different from each other. It was suggested that a different scattering mechanism existed in the grain boundaries. The temperature dependence was showed by a deflected line, because $\alpha$ of the sintered PbTe was increased by the change of scattering mechanisms below 250 K.

3.3 Thermal conductivity

Figure 6 shows the temperature dependences of the thermal conductivity $\kappa$ of the solidified and the sintered PbTe. $\kappa$ tended to decrease with decreasing $D$ below 250 K. $\kappa$ is expressed by\(^\text{(1)}\)

$$\kappa = \kappa_{\text{car}} + \kappa_{\text{ph}},$$

where $\kappa_{\text{car}}$ and $\kappa_{\text{ph}}$ are the carrier and the lattice contributions. $\kappa_{\text{car}}$ is estimated by\(^\text{(1)}\)

$$\kappa_{\text{car}} = LT/\rho,$$

where $L$ is the Lorentz number. $\kappa_{\text{ph}}$ was calculated from the observed $\kappa$ using $L = 2.45 \times 10^{-8} \text{Wm}^2/\text{K}^3$ in the perfectly degenerate case.

Figure 7 shows the temperature dependences of $\kappa_{\text{ph}}$ of the solidified and the sintered PbTe. $\kappa_{\text{ph}}$ of all the specimens were proportional to $T^{-1}$ above 200 K. Since the Debye temperature $\theta_D$ of PbTe is 136 K,\(^\text{(20)}\) the condition of $T \gg \theta_D$ is satisfied in the temperature range. $\kappa_{\text{ph}}$ is expressed by\(^\text{(21,22)}\)

$$\kappa_{\text{ph}} = \frac{Cv_l}{3},$$

where $C$ is the phonon specific heat, $v$ the average velocity.
of phonons and \( l \) the mean-free-path of phonons. \( C \) and \( v \) are constant, when the temperature is above \( \theta_D \). \( \kappa_{\text{ph}} \) is proportional to \( l \). The phonon energy in the umklapp process is \( k_B \theta_D / 2 \). Excitation probability of phonons \( P \) caused by this energy is expressed by \( 1 / (\exp(\theta_D/2T) - 1) \), using the Boltzmann factor.\(^{21}\) \( P \) is proportional to the collision frequency \( f \) of phonons. \( l \) is inversely proportional to \( f \), and it is expressed by

\[
 l \propto \exp(\theta_D/2T) - 1
\]

(17)

Exponential function of the formula (17) may be approximated by a linear equation of \( \theta_D/2T \) in the temperature range of \( 2T \ll \theta_D \). Then, \( \kappa_{\text{ph}} \) is proportional to \( T^{-1} \) as described by the following equation:

\[
 \kappa_{\text{ph}} \propto l \propto \exp(\theta_D/2T) - 1 \approx \theta_D/2T \propto T^{-1}
\]

(18)

This fact confirms that the umklapp process is dominant. \( \kappa_{\text{ph}} \) decreased with decreasing \( D \) below 250 K. It suggests the long-wave-length phonon scattering at grain boundaries. \( \kappa_{\text{ph}} \) was independent of \( D \) above 250 K. This result is in good agreement with the calculation by Yoshino.\(^{23,24}\) \( D \) reduction is not expected to improve \( Z \) of PbTe above 250 K. However, \( \rho \) and \( \mu_H \) of the sintered PbTe (excepting the case of the average crystal grain size of 28 \( \mu \)m (a)) were in good agreement with those of the solidified one above 250 K. Therefore, sintered PbTe (above the average crystal grain size of 92 \( \mu \)m) is superior to solidified one because it has sufficient mechanical strength and it may be manufactured into desired shapes.

4. Conclusions

In order to examine the possibility of improvement in the thermoelectric properties of sintered PbTe, the thermoelectric properties were investigated for the sintered PbTe by the spark plasma sintering technique.

(1) \( \rho \) of the sintered PbTe increased with decreasing average grain sizes in the temperature range from 77 to 350 K. The temperature dependence of \( \rho \) of the sintered PbTe is remarkably different from that of the solidified one below 250 K. We applied a simple electrical model consisted of 3 electrical resistances to the temperature dependence of \( \rho \). It was found that the difference of temperature dependence in the \( \rho \) between the solidified PbTe and the sintered PbTe was caused by increasing energy barrier at crystal grain boundaries.

(2) Thermoelectric power and Hall coefficient of the solidified and the sintered PbTe at 295 K were calculated. Effective mass of the non-parabolic band and that of the parabolic band were 0.2\( n_0 \) and 1.0\( m_0 \), except the 28 \( \mu \)m grain case. The calculated values of thermoelectric power and Hall coefficient were in good agreement with the experimental data.

(3) Hole density increased with decreasing average grain size. It was suggested that oxidation was caused in the sintering process at the grain boundaries and/or in the crystal grains.

(4) The temperature dependence of thermoelectric power of the solidified PbTe was showed by a straight line, while that of the sintered PbTe by a deflected line below 250 K. The temperature dependences of \( \mu_H \) of the sintered and the solidified PbTe below 250 K was remarkably different from each other. It was suggested that the different carrier scattering mechanisms existed at the grain boundaries.

(5) The lattice thermal conductivity tended to decrease with decreasing average grain size below 250 K. However, the lattice thermal conductivity was independent of the average grain size above 250 K. Decrease in \( \kappa_{\text{ph}} \) by the phonon scattering at crystal grain boundaries was not effective for improving the thermoelectric properties in PbTe.

Acknowledgments

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REFERENCES

19) W. D. Lawson: J. Appl. Phys. 23 (1952) 495–496.