Composition-Dependent Thermoelectric Properties of PbTe Doped with Sb$_2$Te$_3$

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Although there are many reports on PbTe–SnTe and Bi$_2$Te$_3$–Sb$_2$Te$_3$ systems with improved thermoelectric performance due to reduced lattice thermal conductivity, only few experimental data exist on PbTe–Sb$_2$Te$_3$ system. In this report, the composition-dependent thermoelectric properties of PbTe doped with Sb$_2$Te$_3$ have been studied at room-temperature. It is worth noting that the lattice thermal conductivity is only about 1 W/K m as the contents of Sb$_2$Te$_3$ is larger than 0.8 mol%. In addition, the figure of merit shows a maximum value of 1.03 × 10$^{-3}$ K$^{-1}$ with the content of Sb$_2$Te$_3$ at 0.8 mol% which is the highest value obtained in doped bulk PbTe samples and is several times higher than that of PbTe containing other dopants with small grain sizes. This confirms that Sb$_2$Te$_3$ is one of the best dopants for PbTe to enhance its thermoelectric performance.

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1. Introduction

Solid-state thermoelectric (TE) devices are generally made from heavily doped semiconductors and can be used both as generators that directly convert heat to electricity from a heat source and refrigeration devices that use electricity to pump heat from cold side to hot side without any moving parts or bulk fluids. Lead telluride (PbTe) is one of the best TE materials used for TE generator in a temperature ranging between 400 and 800 K.\textsuperscript{1} Recently, PbTe has been focused as a constituent material for power supply units using the exhausted heat of gas combustion in incinerators and other industrial furnace.\textsuperscript{2} However, the performance of PbTe with different carrier concentration is not high enough in this temperature range.\textsuperscript{3}

The performance of a TE material is usually expressed by the figure-of-merit Z represented by $Z = \sigma S^2/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity and $\kappa$ is the thermal conductivity.\textsuperscript{3} It is evident that the high performance of TE materials can be obtained by maximizing the Seebeck coefficient and electrical conductivity, while simultaneously minimizing the thermal conductivity. The total thermal conductivity $\kappa$ depends on two parameters, one from the carriers, $\kappa_c$, and the other one from the lattice thermal vibrations (phonon). (i.e. $\kappa_p h = \kappa_c + \kappa_{ph}$, where $\kappa_c$ is proportional to the carrier concentration.) In order to reduce the thermal conductivity, the parameter of lattice thermal vibrations can be reduced by the grain boundaries scattering phonon. A broad research has been under way to reduce the lattice thermal conductivity in the heavily doped PbTe samples with small grain size, such as those made by spark plasma sintering (SPS) or hot pressing technique\textsuperscript{4-6} which can also form a preferred orientation for improved TE properties.

Moreover, these undoped PbTe samples exhibit the same characteristics as the heavily doped PbTe samples.\textsuperscript{5} In this result, the high TE performance of PbTe, which is induced by the electronic topological transition (ETT) under high pressure,\textsuperscript{6,8} have been successfully obtained at room-temperature by HPHT. Besides the pressure-tuning, the ETT could be also induced by alloying.\textsuperscript{9} In general, the internal stress achieved by alloying in samples has the same characteristics as a compressive stress achieved by physical pressing. This internal stress occurs due to lattice distortion which is resulted from the occupation of impurity-atom at the crystal lattice. In other words, the high performance of PbTe samples prepared by HPHT may be achieved by alloying of suitable dopants. This is in agreement with the proposal for good TE materials reported by DiSalvo\textsuperscript{3} and Mahan.\textsuperscript{10} Although there are many successful examples of improved TE performance in Pb$_{1-x}$Sn$_x$Te, a product of PbTe alloyed with SnTe,\textsuperscript{10} only few experimental data exist on PbTe–Sb$_2$Te$_3$ system. On the other hand, since PbTe is similar to BiTe and there are many reports on BiTe–Sb$_2$Te$_3$, one could expect that PbTe–Sb$_2$Te$_3$ would also be a good TE material. Compared to the Pb$_{1-x}$Sn$_x$Te and (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ solutions, the solubility of Sb$_2$Te$_3$ in PbTe is only less than 5 mole% according to the phase diagram of PbTe–Sb$_2$Te$_3$.\textsuperscript{11} This is confirmed by our previous result.\textsuperscript{12}

In this work, the room-temperature TE properties of PbTe–Sb$_2$Te$_3$ have been studied. Our results show that the TE performance of PbTe can be greatly improved with Sb$_2$Te$_3$ as a dopant.

2. Experimental

The compounds of PbTe and Sb$_2$Te$_3$ using the elements of 6N (99.9999% in-purity) lead, tellurium and antimony as sources, were synthesized in evacuated quartz tubes at their respective melting points for 1h in a stirring furnace, respectively. After that, they were mixed with the corresponding stoichiometric ratio and then sealed in an evacuated quartz tube. The quartz tubes containing the mixtures were...
then placed in a stirring furnace and melted at 1250 K for 1 h followed by cooling at the rate of 98 K/h. The collected ingots were cut and polished on the surface for the measurement of TE properties.

X-Ray powder diffraction (XRD) measurements with Cu-Kα radiation were performed on an X-ray diffractometer (JDX-3500). The microstructure image of PbTe was obtained on the surface splitted along the growth direction under optical microscope. The electrical resistivity and Hall coefficient were obtained using the five-probe method with a constant magnetic field in the range ± 0.5 T and an electrical current ± 10 mA by a five-probe technique. The carrier concentration was calculated from the Hall coefficient, assuming a single carrier model as a Hall scattering factor of unity. The error in the measurement of the Hall coefficient and electrical resistivity is about 3%. The thermal conductivity was measured by the static comparative method with a sample size 5 × 5 × 5 mm using a standard transparent quartz (SiO₂, 1.37 W/K-m) with the same size as the standard sample. The Seebeck coefficient S was determined from thermoelectromotive force E₀ given by the temperature difference within 2–3 K with the same equipment as thermal conductivity measurement. The error in the Seebeck coefficient and thermal conductivity measurement do not exceed 5% at room temperature.

3. Results and Discussions

The results of X-ray powder diffraction patterns, shown in Fig. 1, confirm that all the (PbTe)₁₀₀₋ₓ(SbₓTe₃)₀ samples with 0.3 ≤ x ≤ 1.05 are NaCl-structure and the diffraction peaks corresponding to the ternary compounds of PbSbₓTe₇ are not found. The ternary compounds PbₓSb₂Te₁₁, PbSb₂Te₄ and PbSb₄Te₇ can only be formed at x ≥ 30 under the temperature 860 K according to the phase diagram of PbTe–Sb₂Te₃. Note that, in this study, the mole percents of Sb₂Te₃ do not exceed 1.5 and the cooling rate is 98 K/h. Under these conditions, the ternary compounds should not be formed. Based on this result, the samples studied here are single phase PbTe while Sb₂Te₃ is the source of dopant for PbTe. The microstructure of PbTe, as shown in Fig. 2, has a grain size much larger than 100 µm, which is consistent with those solidified directly.

Figure 3 shows the dependence of electrical resistivity for (PbTe)₁₀₀₋ₓ(SbₓTe₃)ₓ on the composition x. It can be seen that the electrical resistivity increases with a decrease of x. The electrical resistivity decreases dramatically at x ≤ 0.8 and slightly at x ≥ 0.8 with an increase of x. There are many factors affecting the variation of electrical resistivity. One of the factors is that the carrier concentration varies with Sb₂Te₃ which is shown in Fig. 4. Another is the mean free path of carrier which is affected by the impurity atoms path scattering.

Fig. 1 Powder XRD patterns of (PbTe)₁₀₀₋ₓ(SbₓTe₃)ₓ.

Fig. 2 Microstructure of PbTe.

Fig. 3 Electrical resistivity of (PbTe)₁₀₀₋ₓ(SbₓTe₃)ₓ as a function of x.

Fig. 4 Dependence of Hall mobility and the carrier concentration for (PbTe)₁₀₀₋ₓ(SbₓTe₃)ₓ on x.
The scattering effect of the heavy impurity atoms should be stronger than that of light impurity atoms and be enhanced with an increase of Sb$_2$Te$_3$ content. The mean free path of the carriers should be reduced by the scattering effect. This is confirmed by the following results of Hall mobility (Fig. 4) which decreases with an increase of $x$ at $x \geq 0.8$. Furthermore, the grain boundary microstructure also has great effect on the electrical resistivity.

Hall Effect measurements are performed to estimate the concentration and Hall mobility of carriers. Figure 4 shows the dependence of Hall mobility and the carrier concentration of (PbTe)$_{(100-x)}$(Sb$_2$Te$_3$), as a function of $x$. The Hall mobility increases first and then decreases with an increase of $x$. All the carriers exhibit high Hall mobility and the maximum value of the Hall mobility is $0.1168 \, \text{m}^2\text{V}^{-1}\text{s}^{-1}$ at $x = 0.8$. This value is larger than the best value of $0.1 \, \text{m}^2\text{V}^{-1}\text{s}^{-1}$ for good TE materials reported by Mahan.$^{10}$ The high Hall mobility should be resulted in high TE performance. This is confirmed by the following results (Fig. 7). Furthermore, the carrier concentration of (PbTe)$_{(100-x)}$(Sb$_2$Te$_3$), increase slowly at $x < 0.93$ and quickly at $x \geq 0.93$ with an increase of Sb$_2$Te$_3$ content. This result is in a good agreement with Rogacheva’s result.$^{11}$ Rogacheva attributed the relationship between carrier concentration and Sb$_2$Te$_3$ to that the Te atoms partially fill the cation vacancies to produce antistructural defects or that some of the Sb atoms show the maximum valency (+5). The donor action of the Sb replacing the Pb is not balanced by the acceptor action of the vacancies formed in the lattice, and the concentration of n-type carriers increases with an increase of Sb$_2$Te$_3$.

The Seebeck coefficients for PbTe as a function of $x$ are shown in Fig. 5. It can be seen that all (PbTe)$_{(100-x)}$(Sb$_2$Te$_3$)$_x$ samples exhibit an n-type behavior. The Seebeck coefficient in the absolute value increases slowly at $0.55 \leq x \leq 0.93$ while dramatically increases at $x \leq 0.55$ with a decrease of $x$. At $x \geq 0.93$, the Seebeck coefficients in the absolute value for (PbTe)$_{(100-x)}$(Sb$_2$Te$_3$)$_x$ decrease considerably with a further increase of $x$. The relationship between the Seebeck coefficients and the compositions of Sb$_2$Te$_3$ obtained in this study is consistent with the result of PbTe prepared at HPHT.$^7$ The more dopants added, the higher internal compressive residual stress is obtained.

As is mentioned above, the thermal conductivity $\kappa$ has two contributions, one from the carrier $\kappa_e$, and the other one from the lattice thermal vibration (phonon) $\kappa_{ph}$. Here $\kappa_e$ is expressed by the Wiedemann-Franz law, $\kappa_e = L \sigma T$, where $L$ is the Lorenz number and $T$ is in absolute temperature scale. The value of Lorenz number for PbTe ($L = 2.45 \times 10^{-8} \, \text{W} \, \text{K}^{-2}$)$^{14}$ is used to estimated $\kappa_e$. Figure 6 shows the thermal conductivity of (PbTe)$_{(100-x)}$(Sb$_2$Te$_3$)$_x$ as a function of $x$. At $x \leq 0.8$, the thermal conductivity, $\kappa$, is kept nearly constant at $2.30 \, \text{W/Km}$, which is consistent with that in literature.$^{15}$ In this case, the total thermal conductivity of (PbTe)$_{(100-x)}$(Sb$_2$Te$_3$)$_x$ is mainly from the contribution of thermal lattice vibrations. At $x \geq 0.8$, the total thermal conductivity rapidly increases with increasing $x$. However, the lattice thermal conductivity decreases at $x \leq 0.8$ and keeps constant, $1 \, \text{W/Km}$, at $x \geq 0.8$ with an increase of $x$. It is worth noting that the value of lattice thermal conductivity, $1 \, \text{W/Km}$, is the ideal value for TE materials as proposed by Mahan.$^{10}$ This value is much lower than that of heavily doped PbTe with small grain size prepared by SPS ($\sim 2.5 \, \text{W/}$
K·m)\(^{10}\) and comparable to our previous result.\(^{12}\) Based on the result of microstructure, the low lattice thermal conductivity should be resulted from the heavy atom as the additive for PbTe. The very small lattice thermal conductivity obtained in this study should be attributed to the phonons scattered by the impurity atoms. This result is consistent with DiSalvo\(^3\) and Mahan.\(^{10}\) Compared to other dopants, the impurity atoms and ions provided by Sb\(_x\)Te\(_{3-x}\) have larger atomic number, which have a more strong scattering effect on the phonons.

Figure 7 shows the dependence of the figure-of-merit Z for (PbTe)\(_{100-x}\)(Sb\(_x\)Te\(_3\))\(_x\) samples at room temperature, calculated from the quantities measured, on the composition x. It can be seen that the value of Z increases initially and then decreases with increasing x. In particular, the figure-of-merit at room temperature shows a maximum value of 1.03 \times 10^{-3} K\(^{-1}\). This value is the highest value obtained in doped bulk PbTe samples and is about several times larger than the value of PbTe samples alloyed with PbI\(_2\) with small grain size reported in the literature.\(^{4,5}\) Kishimoto reported that the figure-of-merit, 4 \times 10^{-4} and 2.3 \times 10^{-4} K\(^{-1}\), were obtained in PbTe doped with PbI\(_2\) at the grain size of \(~0.5\) and 0.7 \(\mu\)m, respectively.\(^{4,5}\) The maximum value of Z in (PbTe)\(_{100-x}\)(Sb\(_x\)Te\(_3\))\(_x\) is about 20\% higher than that of (PbTe)\(_{100-x}\)(Bi\(_2\)Te\(_3\)–Sb\(_x\)Te\(_3\))\(_x\) sample\(^{12}\) and about 80\% of that of AgPb\(_{10}\)SbTe\(_{12}\) sample.\(^{15}\) The TE performance of PbTe should be further improved by the suitable dopant according to our previous result.\(^{7}\) This is confirmed by the result that the figure-of-merit, 1.67 \times 10^{-3} K\(^{-1}\), is obtained in the alloy of AgPb\(_{10}\)SbTe\(_{20}\) at room temperature.\(^{15}\) Compared to other dopants such as PbI\(_2\), the large number of Z obtained should be attributed to the large values of Seebeck coefficient and the low lattice thermal conductivity for Sb\(_x\)Te\(_3\) as dopants in PbTe. The high Seebeck coefficient might be due to the ETT resulted from alloying. The low lattice thermal conductivity should be due to the heavy atom as source of dopant which is effective to scatter the phonon. The high value of figure-of-merit for (PbTe)\(_{100-x}\)(Sb\(_x\)Te\(_3\))\(_x\) samples confirms that the dopant Sb\(_x\)Te\(_3\) is one of the best dopants for PbTe to enhance its TE performance.

4. Conclusion

The TE properties dependence on the composition x for (PbTe)\(_{100-x}\)(Sb\(_x\)Te\(_3\))\(_x\) have been studied at room temperature. At x \leq 0.55, the electrical resistivity and the Seebeck coefficient in absolute value increase dramatically with a decrease of x. The thermal conductivity and the Seebeck coefficient increase whereas the electrical resistivity nearly keeps constant with increasing x at x > 0.97. The lattice thermal conductivity, 1 W/K m, is kept at x > 0.8. The figure-of-merit, Z, increases at first to a maximum value of 1.03 \times 10^{-3} K\(^{-1}\) at x = 0.8 and then decreases with an increase of Sb\(_x\)Te\(_3\). This value is the highest value obtained in doped bulk PbTe samples and is several times higher than that of small grain size PbTe containing other dopants. This confirms that the dopant Sb\(_x\)Te\(_3\) is one of the best dopants for PbTe to enhance its TE performance.

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