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2005 J. Phys.: Condens. Matter 17 7319

(http://iopscience.iop.org/0953-8984/17/46/015)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **17** (2005) 7319–7326 doi:10.1088/0953-8984/17/46/015

Enhanced thermoelectric properties of PbTe alloyed with Sb_2Te_3

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Received 24 August 2005, in final form 23 September 2005
Published 1 November 2005
Online at stacks.iop.org/JPhysCM/17/7319

Abstract

We report the enhanced thermoelectric properties of PbTe alloyed with antimony telluride (Sb_2Te_3). The resistivities and absolute values of the Seebeck coefficient for PbTe alloyed with Sb_2Te_3 increase while the thermal conductivities decrease with rising temperature. A maximum figure of merit, ZT, of 1.17 has been achieved for PbTe alloyed with 0.8 mol% Sb_2Te_3 at 560 K. This value is about 30% higher than the ones reported previously for bulk PbTe. The enhanced thermoelectric properties may be due to the low thermal conductivities which are induced by alloying with Sb_2Te_3 and much smaller than that reported for bulk PbTe.

1. Introduction

Solid-state thermoelectric 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 a cold side to a hot side without any moving parts or bulk fluids. Lead telluride (PbTe) is one of the best thermoelectric materials used for thermoelectric generators for temperature ranging between 400 and 800 K [1]. Although the efficiency of thermoelectric generators is rather low, typically ∼5%, the other advantages, such as compactness, being silent, reliability, long life, and long period of operation without attention, lead to a wide range of applications. For example, PbTe has been recently focused on as a constituent material for power supply units using the exhausted heat of gas combustion in incinerators and other industrial furnaces [2].

Good thermoelectric materials must have large Seebeck coefficients, high electrical conductivities, and low thermal conductivities to retain the heat at the junction and to reduce

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the heat transfer losses. These requirements are summarized in what is called the figure of merit Z: $Z = \sigma S^2/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity [1]. The total thermal conductivity κ depends on two parameters, one from the carriers κ_e, and the other one from the lattice thermal vibrations (phonons), κ_{ph}, (i.e. $\kappa = \kappa_e + \kappa_{ph}$, where κ_e is proportional to the carrier concentration) [3].

In general, iodine and PbI_2 are the ordinary dopants for n-type PbTe used to optimize the carrier concentration. But the lattice thermal conductivities of PbTe with these dopants are too high to restrain application (to date, the figure of merit, ZT, has only been ∼0.9 at 650 K) [3]. And thus there are many methods used to reduce the lattice thermal conductivity of PbTe, such as the hot pressing and spark plasma sintering (SPS) techniques [4]. The lattice thermal conductivity of PbTe samples prepared by hot pressing is about 2 W $K^{-1}m^{-1}$ which is much higher than the ideal value of 1 W $K^{-1}m^{-1}$ for good thermoelectric materials proposed by Mahan [5]. Although there are many successful examples of reducing the thermal conductivity in $Pb_{1-x}Sn_xTe$, a product of PbTe alloyed with SnTe, and $(Bi_{1-x}Sb_x)_2Te_3$ solutions [5], only few experimental data exist for the PbTe–SbTe system. On the other hand, since PbTe is similar to BiTe and there are many reports on BiTe–SbTe, one could expect PbTe–SbTe also to be a good thermoelectric material.

In this work, the temperature-dependent thermoelectric properties of PbTe alloyed with Sb_2Te_3 have been studied. The result indicates that the PbTe samples alloyed with Sb_2Te_3 exhibit low thermal conductivity which results in enhanced thermoelectric performance.

2. Experimental details

The compounds PbTe and Sb_2Te_3, made using the elements 6N (99.9999% purity) lead, tellurium, and antimony as sources, were synthesized in evacuated quartz tubes at their respective melting points for 1 h in a stirring furnace. After that, they were mixed in 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; this was followed by cooling with the rate of 98 K h^{-1}. The collected ingots were cut and their surfaces polished before the measurement of thermoelectric properties.

The dependences of the electrical resistivity and the 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 [6]. The sample size for these measurements is 1 mm × 2 mm × 10 mm. The carrier concentration was calculated from the Hall coefficient, assuming a single-carrier model with a Hall scattering factor of unity. The thermal conductivity was measured using disc-shaped samples by the laser flash method with a thermal constant analyser (Shinku-riko TC-7000). The ingots were cut with a sample size of 4 mm × 4 mm × 15 mm and their surfaces polished for measuring the temperature dependence of the Seebeck coefficient, which was determined form the slope of the voltage differences plotted against the temperature gradient (∼5 K) between two points on the samples. The details of the set-up for the measurement are described in detail in elsewhere [6]. The error in the thermoelectric property measurements including those of the Seebeck coefficient, the thermal diffusivity, the Hall coefficient, and the electrical resistivity do not exceed 3%.

3. Results and discussion

In this work, the amounts of Sb_2Te_3 are 0.55, 0.80, 0.93, and 1.02 mol% corresponding to the samples numbered from 1 to 4 in the figures, respectively. The resulting XRD patterns

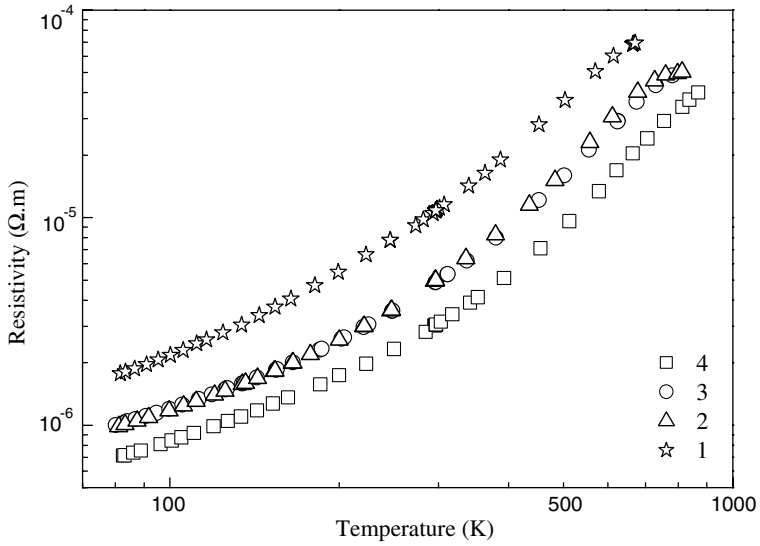

Figure 1. Temperature dependences of the electrical resistivities for PbTe. The carrier concentrations n_e are 1.19×10^{24}, 1.03×10^{25}, 1.16×10^{25}, and 2.15×10^{25} m^{-3} corresponding to the samples numbered from 1 to 4 respectively.

for PbTe alloyed with Sb_2Te_3 were previously described in [7]. The XRD results confirm that all the $(PbTe)_{100-x}(Sb_2Te_3)_x$ samples with $0.3 \leqslant x \leqslant 1.05$ are NaCl structured and the diffraction peaks corresponding to the ternary compounds of $PbSb_xTe_y$ and Sb_2Te_3 are not found. These results indicate that all the samples studied here are single-phase PbTe, and Sb_2Te_3 is the dopant. This result is also consistent with our previous results on PbTe alloyed with $(BiSb)_2Te_3$. The solubility limit for single-phase PbTe-based solid solutions is roughly determined as ~1 mol% in the $(PbTe)_{100-x}(Bi_2Te_3–Sb_2Te_3)_x$ system [8]. On the basis of the results for the temperature-dependent Hall mobility which are shown in our previous work [7], Sb_2Te_3 has the same characteristic as PbTe, and the carrier scattering mechanism for PbTe alloyed with Sb_2Te_3 gradually changes from an ionized impurity scattering to an interaction between an acoustic and an optical phonon scattering as the temperature increases.

From the temperature dependence of the electrical resistivity of PbTe alloyed with Sb_2Te_3 over a wide temperature range from 80 to 800 K (shown in figure 1), the resistivity increases smoothly with rising temperature, which is consistent with the case for a typical degenerate semiconductor. Furthermore, the resistivities decrease with increase of the carrier concentration. This result indicates that the dopants Sb_2Te_3 have the same characteristic as other dopants for PbTe. Furthermore, the intrinsic temperature for PbTe alloyed with Sb_2Te_3 increases with increase of the carrier concentration. This result indicates that the optimum temperature corresponding to the thermoelectric properties of the sample with high carrier concentration should be raised. This is confirmed by the result shown in figure 4.

The Seebeck coefficients for PbTe alloyed with Sb_2Te_3 as a function of temperature are shown in figure 2. It can be seen that all the values of the Seebeck coefficient are negative, which indicates an n-type semiconductor, and the absolute values rise steadily in nearly a straight line with increase of the temperature. Furthermore, the absolute values of the Seebeck coefficient decrease with increase of the carrier concentration. These results are consistent with those for PbTe alloyed with other dopants, such as PbI_2 [1]. Although the Seebeck coefficient

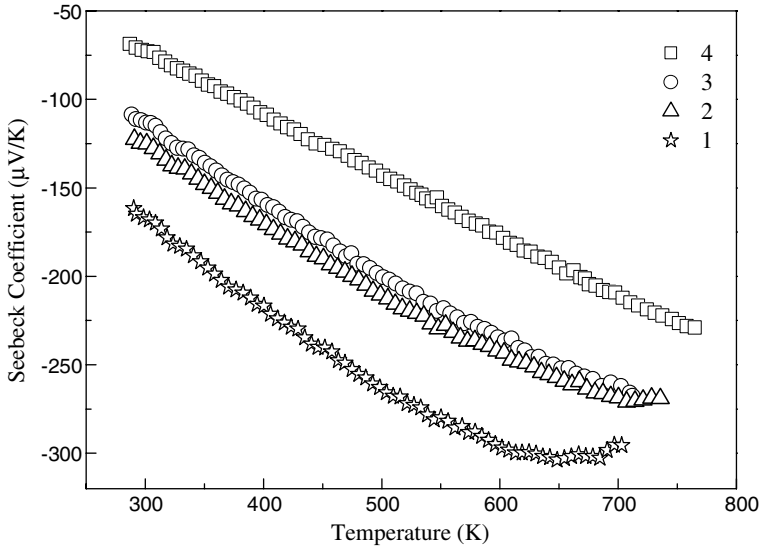

Figure 2. Seebeck coefficient as a function of temperature for PbTe.

at room temperature for PbTe alloyed with 0.8 mol% Sb_2Te_3, ∼124 μV K^{-1}, is near to that for $AgPb_{18}SbTe_{20}$, which is the best thermoelectric material for the temperature range 600–900 K [9], the increase in the Seebeck coefficient with rising temperature is smaller than that for $AgPb_{18}SbTe_{20}$. The Seebeck coefficients for $AgPb_{18}SbTe_{20}$ are −135 and −335 μV K^{-1} corresponding to room temperature and 700 K, respectively. However, the Seebeck coefficient for PbTe alloyed with 0.8 mol% Sb_2Te_3 is only −270 μV K^{-1} at 700 K.

The thermal conductivity (κ) is calculated from the thermal diffusivity (λ) data, which are measured in this study, and the heat capacity (C_p) data, which are from the literature [10], using the formula $\kappa = \lambda\rho C_p$ [11], where ρ is the density. The measurement accuracy for the heat capacity is 3–5% and the heat capacity at 350 K is 51.95 J mol^{-1} K^{-1} [10]. This value has been confirmed by Orihashi for PbTe doped with PbI_2 [12]. Figure 3(a) shows the temperature-dependent thermal conductivity of PbTe alloyed with different Sb_2Te_3 contents. It can be seen that the thermal conductivities decrease with increase of the temperature. When the amount of Sb_2Te_3 is lower than 0.8 mol%, the thermal conductivities are near to that of undoped PbTe and comparable to that of $AgPb_{18}SbTe_{20}$ [9]. Although the values of the thermal conductivity for PbTe alloyed with Sb_2Te_3 increase with the carrier concentration, the values of the thermal conductivities obtained in this study are much smaller than those for alloying with other dopants with the same carrier concentration. For example, the value of κ for PbTe alloyed with 1.02 mol% Sb_2Te_3 (carrier concentration: 1.03×10^{25} m^{-3}) is 1.25 W K^{-1} m^{-1} at 500 K. Bhandari reported that the thermal conductivity of PbTe alloyed with PbI_2 (carrier concentration: 1×10^{25} m^{-3}) is higher: 1.9 W K^{-1} m^{-1} at 500 K [13]. The low thermal conductivity of PbTe alloyed with Sb_2Te_3 may be expected for the generally good thermoelectric properties.

The figures of merit, Z and ZT, are calculated using experimental S and ρ data and using κ data measured from 300 to 700 K. The temperature dependences of Z and ZT are shown in figures 4(a) and (b) respectively. The values of Z exhibit strong temperature dependence and the temperature corresponding to the maximum Z shifts upward with carrier concentration increase, which is consistent with the findings for other dopants used for PbTe. Compared to

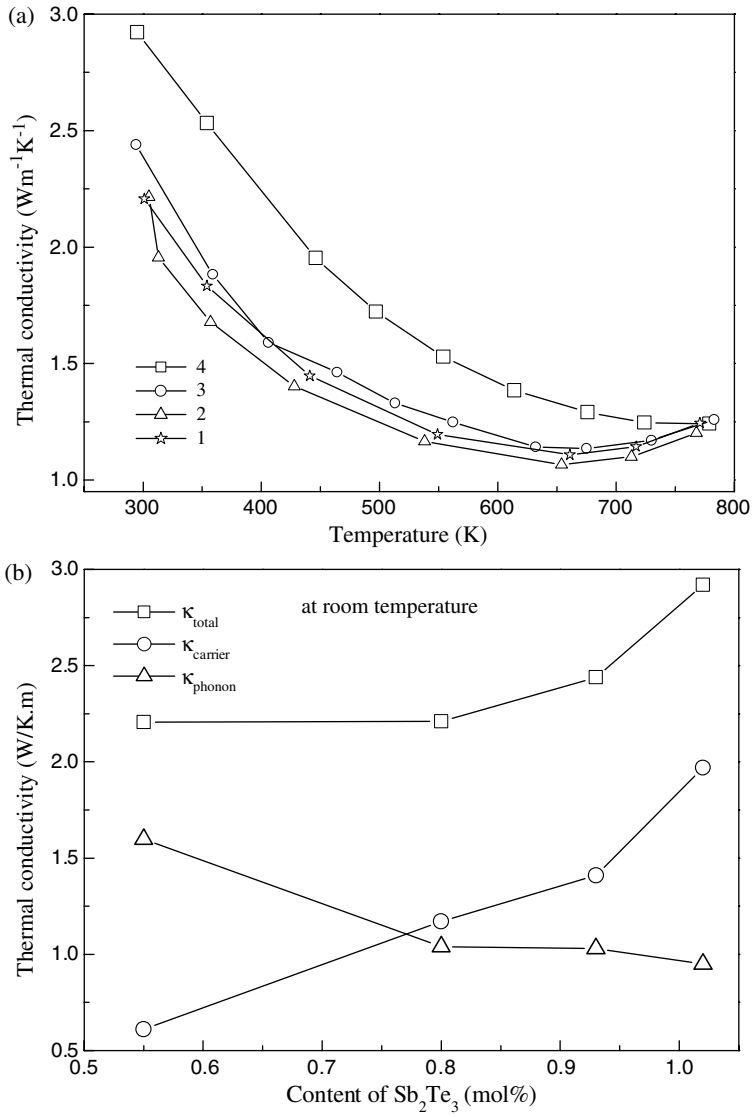

Figure 3. (a) Variation of thermal conductivities of PbTe with temperature; (b) carrier and phonon parts of the thermal conductivity at room temperature.

PbI_2 as a dopants for PbTe, the highest value of Z, 2.07×10^{-3} K^{-1}, has been achieved in PbTe alloying with Sb_2Te_3. This value is much higher than that ($\sim 1.5 \times 10^{-3}$ K^{-1}) obtained for PbTe alloyed with other dopants [1]. The high value of Z results in $ZT \sim 1.17$ for PbTe alloyed with 0.8 mol% Sb_2Te_3 at 560 K. This value is about 30% higher than the highest value obtained for bulk PbTe alloyed with PbI_2 ($\sim$0.9) [3]. Furthermore, this sample exhibits a wide temperature region (from 470 to 730 K) with $ZT > 1$. As the carrier concentration increases, the temperature corresponding to $ZT > 1$ shifts upward. Although $AgPb_{18}SbTe_{20}$ is the best material, the results obtained in this study are comparable to those for $AgPb_{10}SbTe_{12}$ ($\sim$1 at 700 K) [9]. Furthermore, the result of the wide temperature region with $ZT > 1$ is helpful

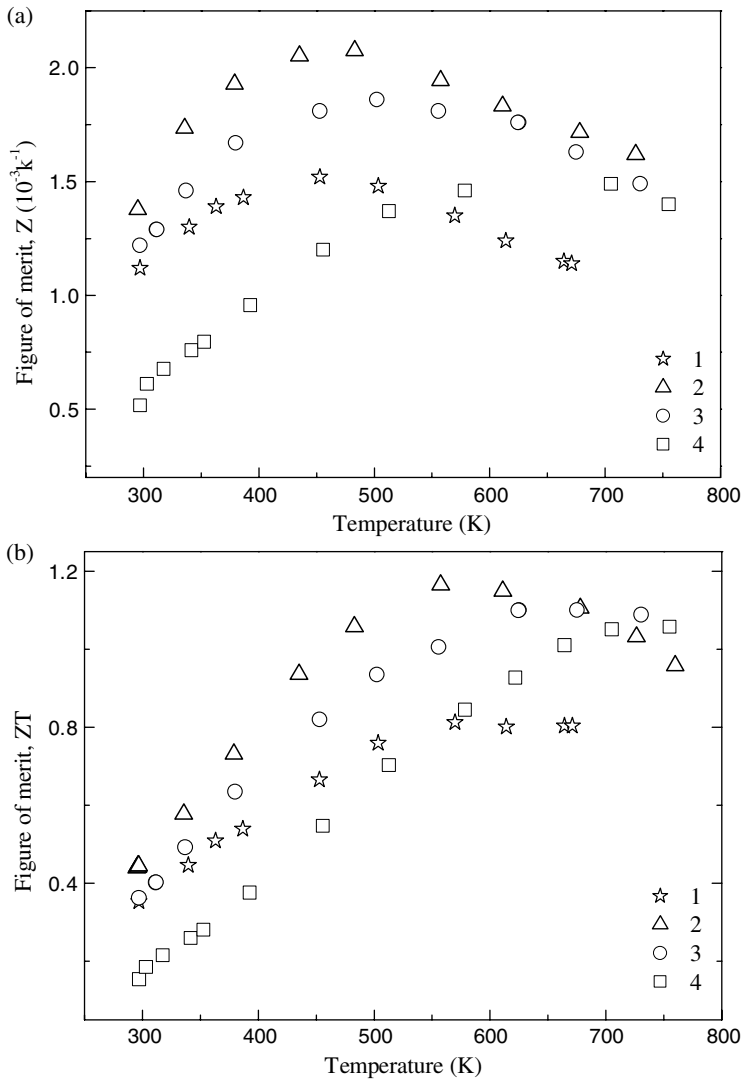

Figure 4. Figure of merit, ZT, versus temperature for PbTe: (a) Z versus T; (b) ZT versus T.

as regards applying PbTe in power supply units using the exhausted heat of gas combustion in incinerators and other industrial furnaces, since most exhausted heat is at about 500 K.

To what can we attribute the enhanced thermoelectric properties of PbTe alloyed with Sb_2Te_3 systems? As mentioned above, the total thermal conductivity $\kappa = \kappa_{\text{carrier}} + \kappa_{\text{ph}}$. Here κ_{carrier} is expressed by the Wiedemann–Franz law, $\kappa_{\text{carrier}} = L\sigma T$, with L being the Lorenz number and T being the absolute temperature scale. The values of the Lorenz number decrease monotonically with temperature increase and depend on the scattering parameter r [12]. However, there are some arguments as regards the temperature dependence of L. The values of L calculated from the different theories at high temperature are different. At room temperature, the Lorenz number for PbTe, $L = 2.45 \times 10^{-8}$ W Ω K^{-2}, is generally accepted for estimating κ_{carrier} [12]. So we calculate the carrier and phonon parts of the thermal conductivity only at

room temperature to analyse the contribution of the total thermal conductivity. On the basis of the calculated results at room temperature (shown in figure 3(b)), the thermal conductivity arises mainly from the contribution of carriers, and the lattice thermal conductivity stays constant, $\sim$1 W K^{-1} m^{-1}, which is the lowest value for bulk PbTe samples and much smaller than those for doping with other dopants prepared by hot pressing ($\sim$2.0 W K^{-1} m^{-1}) [4], with increase of the carrier concentration. Although materials prepared by hot pressing techniques hold great promise for reducing the lattice thermal conductivity via scattering of phonons at the grain boundaries, theoretical calculations indicated that a reduction of 7% in lattice thermal conductivity κ_L in optimally alloyed PbTe can be obtained with a mean grain size of the order of 0.5 μm [13]. Grain boundary scattering of phonons is more pronounced in alloys where the atoms of the constituents have large differences in atomic mass. Short wavelength phonons are scattered by alloy disorder, while the long wavelength phonons are effectively scattered at the grain boundaries. The differences in atomic mass and ionic radius between Pb and Sb are 85.45 g mol^{-1} and 0.26 Å, respectively [14]. The donor action of the Sb replacing the Pb is not balanced by the acceptor action of the vacancies formed in the lattice, which results in the low lattice thermal conductivity of PbTe alloyed with Sb_2Te_3. This result is in good agreement with Tani on Bi-doped Mg_2Si, for which the lattice thermal conductivity decreases with increase of the content of Bi [15]. Furthermore, Hsu reported that quantum 'nanodots', which were formed by Ag and Sb atoms substituted for Pb in the lattice of PbTe, were present in $Ag_nPb_mSb_nTe_{n+2m}$ members and resulted in substantially lower thermal conductivity [9].

4. Conclusions

In summary, the temperature-dependent thermoelectric properties of PbTe alloyed with Sb_2Te_3 have been studied. The resistivities and the absolute values of the Seebeck coefficients of PbTe alloyed with Sb_2Te_3 increase with rising temperature, as for a typical degenerate semiconductor. The thermal conductivities for all the samples exhibit a linear dependence with the reciprocal temperature and are much lower than those for alloying with other dopants. A lattice thermal conductivity of $\sim$1 W $K^{-1}m^{-1}$ has been achieved for PbTe alloyed with Sb_2Te_3. This value is much lower than those obtained for PbTe alloyed with other dopants with fine grain size. The maximum ZT, of $\sim$1.17, is achieved for PbTe alloyed with 0.8 mol% Sb_2Te_3 at 560 K. This value is about 30% higher than those obtained for bulk PbTe alloyed with other dopants so far. The enhanced thermoelectric properties may be due to the low thermal conductivity induced by alloying with Sb_2Te_3.

Acknowledgments

This work was supported in part by the Japan Society for the Promotion of Science (JSPS) and the National Science Foundation of China under Grant (No 50171030) and National Basic Research Program of China (also called 973) (No 2005CB7224400).

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