Available online at www.sciencedirect.com

SCIENCE DIRECT®

Solid State Communications 138 (2006) 580–584

solid state communications

www.elsevier.com/locate/ssc

Electrical transport and high thermoelectric properties of PbTe doped with Bi_2Te_3 prepared by HPHT

Taichao Su, Pinwen Zhu [a,b], Hongan Ma [a], Guozhong Ren [c], Lixue Chen [a],
Weili Guo [a], Yoshio Iami [b], Xiaopeng Jia [a,d,*]

[a] *National Laboratory of Superhard Materials, Jinlin University, 10 Qianwei Road Qianjin Street, Changchun 130012, Jilin, China*
[b] *Eco-material Research Center, National Institute for Materials Science, Tsukuba 305-0047, Japan*
[c] *Changchun institute of Optics Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China*
[d] *Henan University of Technology, Jiaozuo 454000, China*

Received 18 August 2005; received in revised form 13 March 2006; accepted 18 April 2006 by T.T.M. Palstra

Available online 8 May 2006

Abstract

In this paper, n-type lead telluride (PbTe) compounds doped with Bi_2Te_3 have been successfully prepared by high pressure and high temperature (HPHT) technique. The composition-dependent thermoelectric properties of PbTe doped with Bi_2Te_3 have been studied at room temperature. The figure-of-merit, *Z*, for PbTe is very sentivite to the dopants, which could be improved largely although the doped content of Bi_2Te_3 is very small (<0.08 mol%). In addition, the maximum value reaches to $9.3\times10^{-4}\ K^{-1}$, which is about 20% higher than that of PbTe alloyed with Bi_2Te_3 sintered at ambient pressure ($7.6\times10^{-4}\ K^{-1}$) and several times higher than that of small grain size PbTe containing other dopants. The improved thermoelectric performance in this study may be due to the effect of high pressure and the low lattice thermal conductivity resulting from Bi_2Te_3 as source of dopants.

© 2006 Elsevier Ltd. All rights reserved.

PACS: 81.05; 85.80

Keywords: A. Lead telluride; A. Bismuth telluride; D. Thermal conductivity; D. Thermoelectric properties

1. Introduction

Thermoelectric materials can be used to make refrigerators or power generators [1,2]. These solid state devices have no moving parts and are extremely reliable. Effectiveness of a material for thermoelectric applications is determined by the dimensionless figure-of-merit *ZT*, where *T* is the absolute temperature and $Z=(S^2\sigma)/\kappa$ (*S* is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity). These parameters are determined by the details of the electronic structure (band gap, band shape, and band degeneracy near the Fermi level) and scattering of charge carriers (electrons or holes) and thus they are not independently controllable parameters [3]. The total thermal conductivity k has two contributions, one from the electrical carriers k_e, and the other from the thermal lattice vibrations (phonon) $k_{lattice}$. A good thermoelectric material must have both a large power factor ($P=S^2\sigma$) and a low thermal conductivity.

PbTe is well known as a thermoelectric material, which is generally used for thermoelectric power generation in the medium temperature range between 400 and 800 K [4]. The performance of PbTe with different carrier concentration, however, is not high enough in this temperature range. In order to enhance the thermoelectric properties of PbTe, many methods have been used including hot-pressing and fine grain size with heavy doping [5–7]. Furthermore, several dopants have been used to optimize the carrier concentration of PbTe with the purpose of improving thermoelectric performance.

Comparing to other preparation methods for thermoelectric materials, the method of high pressure and high temperature (HPHT) has many advantages, such as restraining the disorder, phase separation and other complicating factors during the preparation for materials [8]. In our previous result, the room temperature thermoelectric properties of non-doped PbTe samples, which exhibit the same characteristics as the heavily

---

* Corresponding author. Address: National Laboratory of Superhard Materials, Jinlin University, 10 Qianwei Road Qianjin Street, Changchun 130012, Jilin, China. Tel./fax: +86 431 5168858.
E-mail address: jiaxp@jlu.edu.cn (X. Jia).

0038-1098/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2006.04.018

doped PbTe samples, prepared by high pressure and high temperature (HPHT) have been largely improved. In this result, the high performance of PbTe, which is induced by the electronic topological transition (ETT) under high pressure [10], has been successfully quenched at room temperature by HPHT. Besides the pressure-tuning, the ETT could be also induced by the alloying. Up to date, there have no reports on Bi_2Te_3 as the sources of dopants of PbTe prepared under HPHT. We report that high performance in $(PbTe)_{100-x}(Bi_2Te_3–Sb_2Te_3)_x$ samples, prepared at ambient pressure, with NaCl structure at $x \geq 1$ is obtained [11]. This result confirms that the heavy atom is effective to improve the thermoelectric performance for PbTe. In order to further improve the properties of PbTe, the advantages of high-pressure technique and Bi_2Te_3 as source of dopants have been used. Our results show that the thermoelectric performance of PbTe has been greatly improved with Bi_2Te_3 as the sources of dopants.

2. Experimental

2.1. Sample preparation

The PbTe samples doped with Bi_2Te_3 were prepared with the elements of 6 N lead, tellurium, and bismuth as sources, which were weighed according to the respective stoichiometry. After being uniformly mixed in an agate mortar under argon protection, the mixtures were shaped by press. The pole shaped samples were assembled to high-pressure and high-temperature synthesis. The $(PbTe)_{100-x}(Bi_2Te_3)_x$ compounds were prepared in a cubic anvil high-pressure apparatus with a sample chamber of 18 mm on an edge under high temperature around 1200 K and high pressure 3 GPa. The pressure was estimated by the oil press load, which was calibrated by the pressure induced phase transitions of bismuth, thallium, and barium metals. The temperature was estimated by the relationship of input heater power and temperature, which was measured by the platinum–rhodium thermocouple.

2.2. Physical measurements

The collected samples were cut and polished on the surface for thermoelectric measurements, which were carried out at room temperature. X-ray powder diffraction (XRD) measurements with Cu K_α radiation were performed on an X-ray diffractometer (JDX-3500). The electrical resistivity and Hall coefficient were obtained using the five-probe method with a constant magnetic field in the range ±5 T and the electrical current ±10 mA [12]. The carrier concentration was calculated from the Hall coefficient, assuming a single carrier model as a Hall scattering factor of unity. The voltage sensing electrodes and current electrodes were 50 μm-diameter platinum wires, which were mounted at the ends of the samples. 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 using a standard transparent quartz (SiO_2, 1.37 W/Km) with the same size as the standard sample [12]. The Seebeck coefficient S was determined from thermoelectromotive force E_0 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 does not exceed 5% at room temperature.

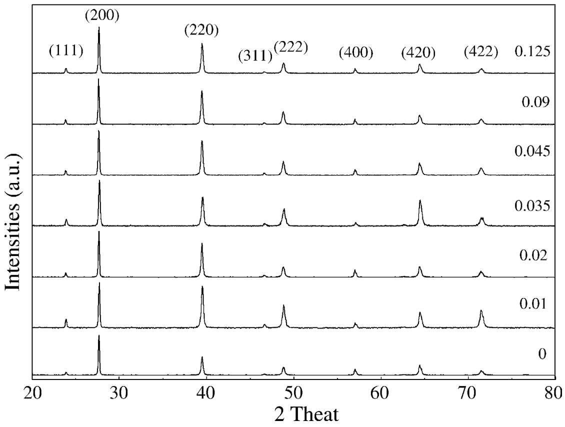

Fig. 1. XRD patterns of PbTe doped with Bi_2Te_3 prepared at HPHT.

3. Results and discussion

X-ray diffraction patterns of PbTe doped with Bi_2Te_3 (from 0 to 0.125 mol%) are shown in Fig. 1. It is confirmed that single phase of PbTe, with NaCl structure and space group $Fm3m$ is obtained in the present study. The diffraction peaks corresponding to the ternary compounds of $PbBi_xTe_y$ were not found. The ternary compounds $PbBi_2Te_4$ can only be formed at $x=50$ under the temperature 850 K according to the phase diagram of PbTe–Bi_2Te_3 [13,14]. Note that, in this study, the mole percents of Bi_2Te_3 are not exceeding 0.13 and the cooling rate is exceeding 200 K/min. Under these conditions, the ternary compounds should not be formed.

Fig. 2 shows the dependence of electrical resistivity for PbTe doped with Bi_2Te_3 on the composition x. It first decreases dramatically for a small Bi_2Te_3 content and then decreases slowly for larger x. Furthermore, an abnormal peak of resistivity emerges corresponding to the sample with 0.02 mol%

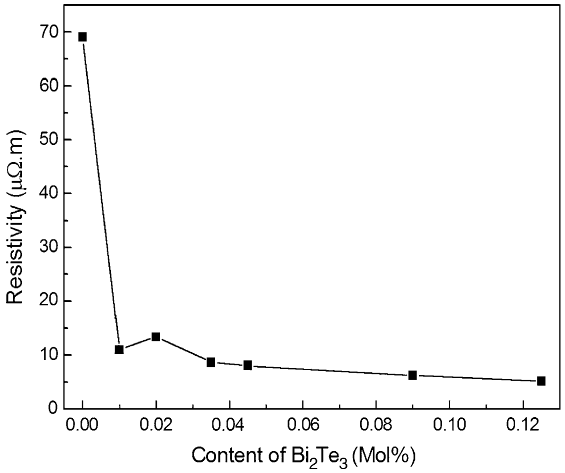

Fig. 2. The relationship between the electrical resistivity and Bi_2Te_3 content for PbTe at room temperature.

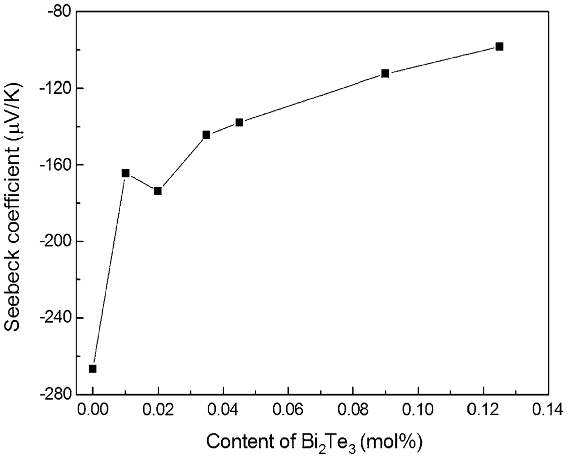

Fig. 3. The Seebeck coefficient for PbTe as a function of Bi_2Te_3 content at room temperature.

Bi_2Te_3 doped. The electrical resistivity of non-doped PbTe is 6.9×10^{-5} Ω m, which is much smaller than that of non-doped samples prepared at ambient pressure and consistent with our previous result [9]. While x is only 0.01 mol%, the electrical resistivity for PbTe is lower than 1.1×10^{-5} Ω m. This result indicates that the electrical resistivity of PbTe prepared by HPHT is more sensitive to the contents of dopants Bi_2Te_3 than that sintered at ambient pressure [15].

The Seebeck coefficient for PbTe as a function of Bi_2Te_3 content is shown in Fig. 3. It can be found that the Seebeck coefficients for all PbTe samples are negative. This result indicates that all the samples prepared by HPHT are n-type semiconductors. The Seebeck coefficient for non-doped PbTe is about −270 μV/K, which is much smaller than that prepared at ambient pressure and comparable with our previous result [9]. The absolute value of Seebeck coefficient for PbTe decreases dramatically when the amount of Bi_2Te_3 is smaller than 0.01 mol% and then slowly when the amount is larger than 0.01 mol% with an increase of Bi_2Te_3. Furthermore, an abnormal peak of Seebeck coefficient emerges corresponding to the sample with 0.02 mol% Bi_2Te_3 doped.

As seen from Figs. 2 and 3, both the electrical resistivity and the absolute value of Seebeck coefficient decrease with an increase of the content of Bi_2Te_3 except the abnormal doping rate of 0.02 mol%. The factors, which result in the anomaly could be originated from a chemical inhomogeneity. One of the sources of chemical inhomogeneity is the lossing of Bi in PbTe, which may result from clusterization or sticking in the mortar during the mixing process for the Bi_2Te_3 contents are very small in this study. The other source may be contributed to the excess of Bi in the PbTe sample doped with 0.01 mol% Bi_2Te_3. In addition, the inhomogenity in PbTe doped with Bi_2Te_3 is also conformed by XRD patterns shown in Fig. 1. The intensities of some diffraction peaks in PbTe doped with Bi_2Te_3 from 0.01 to 0.035 mol% are different. For example, the intensities of the (111) and (420) for PbTe doped with 0.01 mol% Bi_2Te_3 are higher and the intensity of the (222) for PbTe doped with 0.02 mol% is lower than that of others.

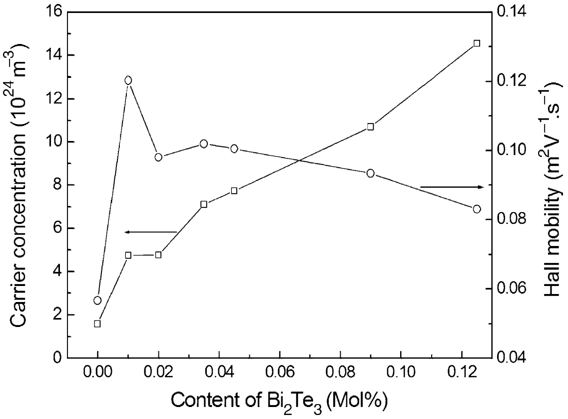

Fig. 4. The dependence of carrier concentration and Hall mobility of PbTe on Bi_2Te_3 content at room temperature.

Hall effect measurements are performed to estimate the concentration and mobility of carriers in the samples. Fig. 4 shows the dependence of Hall mobility and the carrier concentration of PbTe as a function of content of Bi_2Te_3. The Hall mobility increases dramatically first and then decreases slowly with an increase in Bi_2Te_3 content. The maximum value of the Hall mobility, 1202.6 cm^2/s, is obtained in the sample with 0.01 mol% Bi_2Te_3 doped. The value is larger than the best value of 1000 cm^2/s for good thermoelectric materials reported by Mahan [16]. The high value in Hall mobility should result in high thermoelectric performance, which is confirmed by the following result (Fig. 6). The dependence of carrier concentration on Bi_2Te_3 dopants for PbTe is similar to that on other dopants. However, the carrier concentration for PbTe in this study is more sensitive to dopants than that sintered at ambient pressure. The carrier concentration in the PbTe sample alloyed with 0.035 mol% Bi_2Te_3 is 7.1×10^{24} m^{-3}, while that with 0.2 mol% Bi_2Te_3 and Sb_2Te_3 sintered at ambient pressure is only 6.46×10^{24} m^{-3} [11]. These results may be attributed to the pressure effect.

In general, the charge transport properties of narrow gap semiconductors are sensitive to extremely small changes in effective mass, mobility, and concentration of carriers around the Fermi level, which are affected by the changes in the dopants composition. The band gap of PbTe becomes smaller under high pressure. The Bi acts as a donor and the introduction of Bi increases the electron concentration. So, the effect of the pressure and alloying makes the electrical resistivity and Seebeck coefficient decrease. But, the power factor is much more than that of the pure PbTe. In particular, the maximal power factor reach 24.6 $\mu W/cm\,k^2$ in the sample with 0.01 mol% Bi_2Te_3 doped, which is near to the best bulk thermoelectric material ($AgPb_mSbTe_{2+m}$) reported by Hus [17]. Based on these results, high thermoelectric performance are expected if a low thermal conductivity is obtained at the same time in the PbTe samples prepared at HPHT.

It is well known that thermal conductivity is composed of the electronic thermal conductivity κ_e and the lattice thermal conductivity κ_L. Here, κ_e is expressed by the Wiedemann-Franz law, $\kappa_e = L\sigma T$, where L is the Lorenz number and T is in

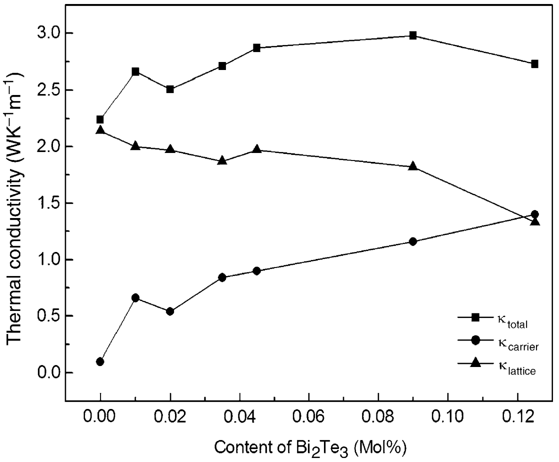

Fig. 5. Variation of thermal conductivity for PbTe as a function of Bi_2Te_3 content at room temperature.

absolute temperature. The value of Lorenz number for PbTe ($L = 2.45\times10^{-8}$ W Ω K^{-2}) [18] is used to estimate κ_e. Fig. 5 shows the thermal conductivity of PbTe doped with Bi_2Te_3 as a function of content of dopants. The total thermal conductivities slightly increase when the Bi_2Te_3 content is lower than 0.09 mol% and then decrease with an increase in Bi_2Te_3 content. The lattice thermal conductivity decreases while the carrier thermal conductivity increases with an increase in Bi_2Te_3 content. Compared to other methods to reduce the thermal conductivity, the total thermal conductivity for PbTe doped with Bi_2Te_3 prepared at HPHT does not obviously increase with an increase of the carrier concentration. This is due to the lattice thermal conductivity decreases with the Bi_2Te_3 content increasing. The decrease of the lattice thermal conductivity with the content of dopants might be attributed to the phonons scattered by the impurity atoms. The impurity atoms and ions provided by Bi_2Te_3 have large atomic number, which might result in the lower lattice thermal conductivity.

Fig. 6 shows the composition dependence of the figure-of-merit, Z, for PbTe doped with Bi_2Te_3 calculated from the measured quantities. It can be seen that the value of Z increases dramatically first and then decreases slowly with an increase of the Bi_2Te_3 content. In particular, the figure-of-merit, Z, for doped PbTe samples is much higher than that non-doped PbTe as the content of Bi_2Te_3 is less than 0.08 mol%. The maximum value reaches to $9.3\times10^{-4}\,K^{-1}$, which is larger than that of fine grains PbTe samples alloyed with PbI_2 (4×10^{-4} and $2.3\times10^{-4}\,K^{-1}$ at the grain size of ~0.5 and 0.7 μm, respectively, [5,6]). Especially, the figure-of-merit obtained in this study is about 20% higher than that of PbTe alloyed with 0.3 mol% Bi_2Te_3 sintered at ambient pressure ($7.6\times10^{-4}\,K^{-1}$) [15]. This result indicates that high-pressure technique is a useful tool to improve the thermoelectric performance. Compared to other dopants at ambient pressure, the large number of Z obtained in this study should be attributed to both ETT induced by pressure effect, which results in the large values of conductivity, Seebeck coefficient and alloying with Bi_2Te_3, which results in the low thermal conductivity.

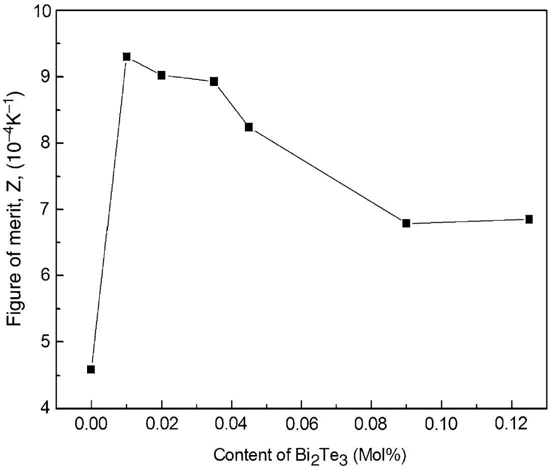

Fig. 6. The figure-of-merit, Z, for PbTe as a function of Bi_2Te_3 content at room temperature.

4. Summary

N-type lead telluride (PbTe) compounds doped with Bi_2Te_3 have been successfully prepared at high pressure and high temperature (HPHT). XRD patterns show that all the samples have the NaCl structure. The electrical resistivity and the absolute value in Seebeck coefficient decrease with an increase of Bi_2Te_3 content. The total thermal conductivities slightly increase when the Bi_2Te_3 content is smaller than 0.09 mol% and then decrease, while the lattice thermal conductivity decreases with an increase of Bi_2Te_3 content. The figure-of-merit, Z, is sentivite to the dopants, which could be enhanced dramatically for PbTe doped with very small content of Bi_2Te_3(0–0.08 mol%) and the maximum value of $9.3\times10^{-4}\,K^{-1}$ is obtained. The value is about 20% higher than that of PbTe alloyed with Bi_2Te_3 sintered at ambient pressure ($7.6\times10^{-4}\,K^{-1}$) and several times higher than that of small grain size PbTe containing other dopants. The improved thermoelectric performance in this study may be due to the effect of high pressure and the low lattice thermal conductivity resulting from Bi_2Te_3 as source of dopants.

References

[1] H.J. Goldsmid, Electronic Refrigeration, Pion, London, 1986. pp. 10.
[2] D.M. Rowe, C.M. Bhandari, Modern Thermoelectrics, Reston Publishing, Reston, VA, 1983. pp. 104.
[3] F.J. Disalvo, Science 285 (1999) 703.
[4] G.L. Bennett, in: D.M. Rowe (Ed.), CRC Handbook of Thermoelectrics, CRC Press, New York, 1995, pp. 515–537.
[5] K. Kishimoto, T. Koyanagi, J. Appl. Phys. 92 (2002) 2544–2549.
[6] K. Kishimoto, K. Yamamoto, T. Koyanagi, Jpn. J. Appl. Phys. 42 (2003) 501–508.
[7] D.M. Rowe, C.M. Bhandari, Appl. Phys. Lett. 47 (1985) 255–257.
[8] J.V. Badding, Annu. Rev. Mater. Sci. 28 (1998) 631–658.
[9] P.W. Zhu, Y. Imai, Y. Isoda, et al., Mater. Trans. 45 (2004) 3102–3105.
[10] B.K. Godwal, A. Jayaraman, S. Meenakashi, et al., Phys. Rev. B 57 (1998) 773.

[11] P.W. Zhu, Y. Imai, Y. Isoda, et al., Mater. Trans. 46 (2005) 761–764.
[12] K. Uemura, I.A. Nishida, Nikkan-Kogyo, Tokyo, (1988) 180–197 (In Japanese).
[13] O.G. Karpinskii, L.E. Shelimova, E.S. Avilov, et al., Inorg. Mater. 38 (2002) 17–24.
[14] H. Liu, L.L.Y. Chang, Am. Mineral. 79 (1994) 1159.
[15] P.W. Zhu, Y. Imai, Y. Isoda, et al., Chin. Phys. Lett. 22 (2005) 2103–2105.
[16] G.D. Mahan, Solid State Phys. 51 (1998) 81–157.
[17] K.F. Hsu, S. Loo, F. Guo, et al., Science 303 (2004) 820.
[18] M. Orihashi, Y. Noda, H.T. Kaibe, I.A. Nishida, Mater. Trans., Jim 39 (1998) 672–678.