Composition-dependent transport properties of $Ag_{1-x}Pb_{18}SbTe_{20}$ prepared by high pressure

Taichao Su [a,*], Hongyu Zhu [b], Hongtao Li [c], Xiaolei Li [a], Shangsheng Li [a], Le Deng [d], Shizao Zheng [d], Hongan Ma [d], Xiaopeng Jia [a,d]

[a] Institute of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China
[b] Institute of Physics and Chemistry, Henan Polytechnic University, Jiaozuo 454000, China
[c] Shanghai Entry-Exit Inspection & Quarantine Bureau, Shanghai 200135, China
[d] National Lab of Superhard Materials, Jinlin University, Changchun 130012, China

ARTICLE INFO

ABSTRACT

Non-stoichiometric $Ag_{1-x}Pb_{18}SbTe_{20}$ ($x = 0, 0.2, 0.5, 0.7, 0.85$) thermoelectric materials were prepared by high pressure method. The composition-dependent transport properties were studied at room temperature. The measurement results show that the carrier concentration and hall mobility of $AgPb_{18}SbTe_{20}$ could be tuned effectively by adjusting the content of Ag. The Seebeck coefficient and resistivity decrease with an increase of x. The maximum power factor of 2.3×10^{-3} W m^{-1} K^{-2} is obtained at $x = 0.7$, which is about 76% higher than that of the sample with stoichiometric composition.

1. Introduction

Extensive interest is currently focused on the search for efficient thermoelectric (TE) materials for solid-state cooling and power generation application based on thermoelectric effects [1–5]. The efficiency of a TE material is usually characterized by the figure of merit ZT, defined as $ZT = T\sigma S^2/\kappa$, where T is the absolute temperature, σ is the electrical conductivity, S is the Seebeck coefficient, and κ is the thermal conductivity. The electrical properties are determined by the power factor, defined as $S^2\sigma$ or S^2/ρ, where ρ is the electrical resistivity. The increase of ZT for TE materials mainly focuses on two ways. One is to maximize the power factor of TE materials without drastically increasing the thermal conductivity, which could be optimized by tuning the carrier concentration. The other way is to minimize the thermal conductivity while retaining large power factor.

In 2004, Hus et al. reported that the quaternary thermoelectric material $Ag_{1-x}Pb_{18}SbTe_{20}$ could achieve an extraordinary high ZT values ($\sim$2.2 at 800 K) [1]. Electron microscopy observations demonstrated that the high figure of merit was originated from nanocrystals of AgSb-rich phase embedded in a PbTe-rich matrix [1]. After that, many other pursuers were inspired by the progress and they started to study the $AgPb_{18}SbTe_{20}$ system by many meth-

ods [6–13]. Although the thermal conductivities of the samples obtained by other pursuers are close to or lower than that of the result reported by Hus, the carrier concentrations of $AgPb_{18}SbTe_{20}$ sample are too low, which results in a high resistivity and a low power factor [8–11]. Recently, Li and his coworkers studied $Ag_{0.8}Pb_{18+x}SbTe_{20}$ system by mechanical alloying (MA) and spark plasma sintering (SPS). They found that large power factor $(1.8–2.0 \times 10^{-3}$ W m^{-1} K$^{-2})$ and high figure of merit (1.2–1.5) could only be obtained when the composition was rich in Pb [12,13].

High pressure method is an effective method to decrease the resistivity and enhance power factor for telluride such as PbTe and Bi_2Te_3 [14]. In our previous study, thermoelectric materials with the composition of $Ag_{0.8}Pb_{18}SbTe_{20}$ were prepared by high pressure method [15]. The results showed that high pressure could reduce the resistivity for $Ag_{0.8}Pb_{18}SbTe_{20}$ effectively and a large power factor of 15.4μW cm^{-1} K^{-2} was obtained at the synthetic pressure of 4.0 GPa.

In order to optimize its carrier concentration further, non-stoichiometric $Ag_{1-x}Pb_{18}SbTe_{20}$ was synthesized by high pressure method (4.0 GPa). The composition dependent transport properties were investigated at room temperature.

2. Experimental

The $Ag_{1-x}Pb_{18}SbTe_{20}$ samples were prepared with tellurium (99.999% in-purity), plumbum (99.9%), antimony (99.999%) and silver (99.9%) powders as sources, which were weighed according to the stoichiometric ratio. After being uniformly mixed in an agate mortar, the mixtures were pressed into a disk with diameter of 10 mm and

* Corresponding author. Tel.: +86 391 3987482.
E-mail addresses: taichao80@hotmail.com, stc@hpu.edu.cn (T. Su).

Fig. 1. XRD patterns of $Ag_{1-x}Pb_{18}SbTe_{20}$ prepared by high pressure.

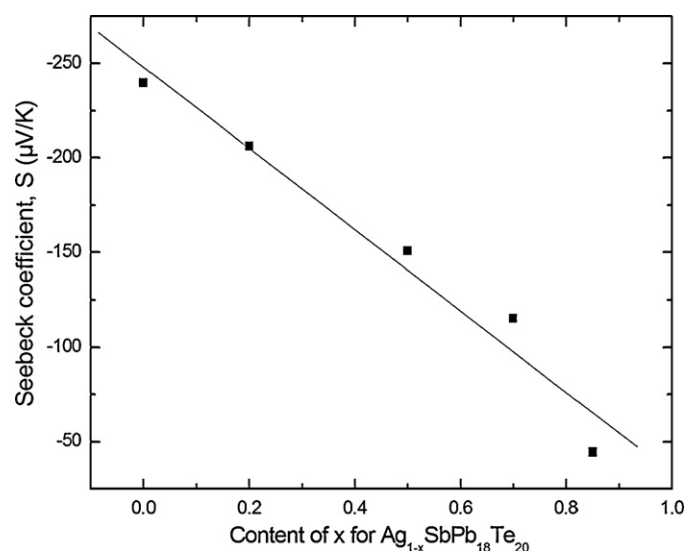**Fig. 2.** Relationship between Seebeck coefficient and x for $Ag_{1-x}Pb_{18}SbTe_{20}$ measured at room temperature, linear line is added for pictorial rendition.
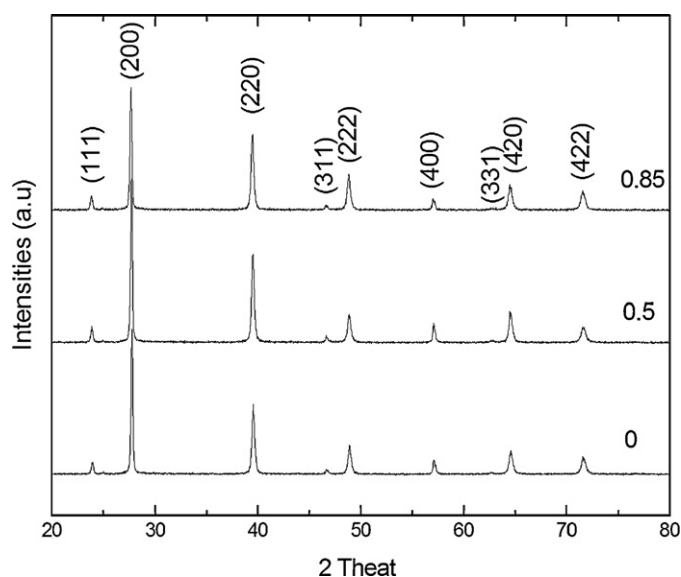
height of 4 mm. The pole shaped samples were assembled for HPHT synthesis. The $Ag_{1-x}Pb_{18}SbTe_{20}$ compounds were prepared in a cubic anvil high pressure apparatus (SPD 6 × 1200) with a sample chamber of 23 mm on an edge at 1200 K and 4.0 GPa. The temperature and pressure were kept for 20 min. After that, the electrical power for heating was cut off and the pressure was released. 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 thermocouples.

The collected samples were cut and polished on the surface for thermoelectric measurements which were carried out at room temperature ($\sim$305 K). The density was measured by the Archimedes method. X-ray diffraction (XRD) measurements with Cu-K$_\alpha$ radiation were performed on an X-ray diffractometer (D/MAX-RA). The electrical conductivity was measured by typical DC four-probe configuration. The Seebeck coefficient S was determined from thermoelectromotive force E_0 given by the temperature difference within 3–5 K between the two ends of the sample with a home-made instrument. The electromotive force was monitored by computer using the VI-Logger program provided by NI-company. Hall coefficient was measured to estimate carrier concentration and Hall mobility using the Van der Pauw method. The equipment was Lakeshore's 7707 Hall measurement system.

3. Results and discussion

The XRD patterns of $Ag_{1-x}Pb_{18}SbTe_{20}$ are shown in Fig. 1. The patterns indicate that all samples crystallize in the NaCl-type structure without any noticeable secondary phase. As seen from Table 1, the lattice constant of $Ag_{1-x}Pb_{18}SbTe_{20}$ decreases with an increase of x, which is similar to the result of Kosuga et al. [9]. The densities of the samples prepared by high pressure are all above 98.5% of the theoretical value. The high densities may be helpful to decrease the resistivity of $AgPb_{18}SbTe_{20}$.

The composition-dependence of Seebeck coefficient for $Ag_{1-x}Pb_{18}SbTe_{20}$ samples prepared by high pressure is presented in Fig. 2. The Seebeck coefficients of all the samples are negative, which indicate that the majority of charge carriers are electrons (n-type). The Seebeck coefficient in absolute value for $Ag_{1-x}Pb_{18}SbTe_{20}$ decreases with an increase of x (from 239.8 μV/K to 44.5 μV/K). The composition dependent Seebeck coefficient

is similar to the results of $Ag_{1-x}Pb_{18}SbTe_{20}$ prepared by other methods [9–11].

The electrical resistivity of $Ag_{1-x}Pb_{18}SbTe_{20}$ as a function of x is shown in Fig. 3. Similar to the result of Seebeck coefficient, the electrical resistivity decreases with an increase of x. In particular, the electrical resistivity of $Ag_{1-x}Pb_{18}SbTe_{20}$ prepared by high pressure is much lower than that of the samples prepared by other methods [8–10]. For example, the highest resistivity for the $AgPb_{18}SbTe_{20}$ sample prepared by high pressure is about 4.4×10^{-5} Ωm, which is about two order less in magnitude than that of the sample prepared at normal pressure reported by Yan (2.8×10^{-3} Ωm) [8]. The low resistivity may be helpful to improve its thermoelectric properties, which is confirmed by the following experimental results (see Fig. 5).

There are many factors affecting the variation of electrical resistivity. One of the factors is that the carrier concentration varies with x. Another is the mean free path of carrier which is affected by the impurity atoms scattering. The mean free path of the car-
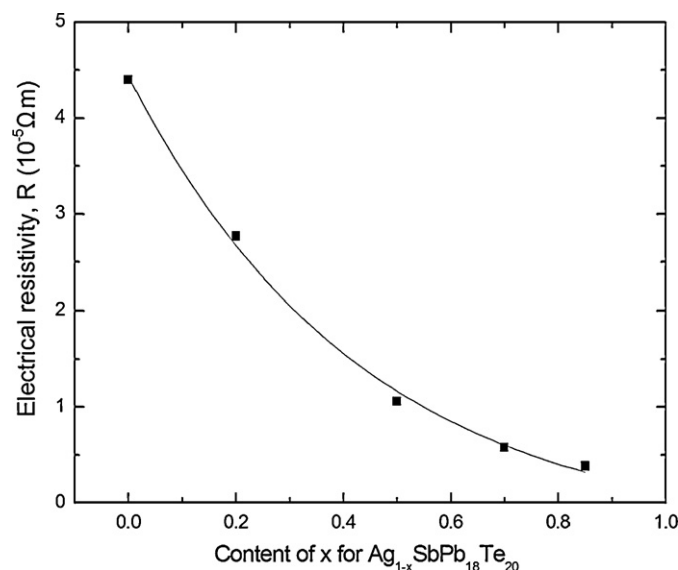
Table 1
Lattice constant and relative density for $Ag_{1-x}Pb_{18}SbTe_{20}$ prepared by high pressure.

X	Lattice constant (nm)	Relative density (%)
0	0.6462(4)	98.6
0.5	0.6461(3)	99.1
0.85	0.6458(7)	98.5

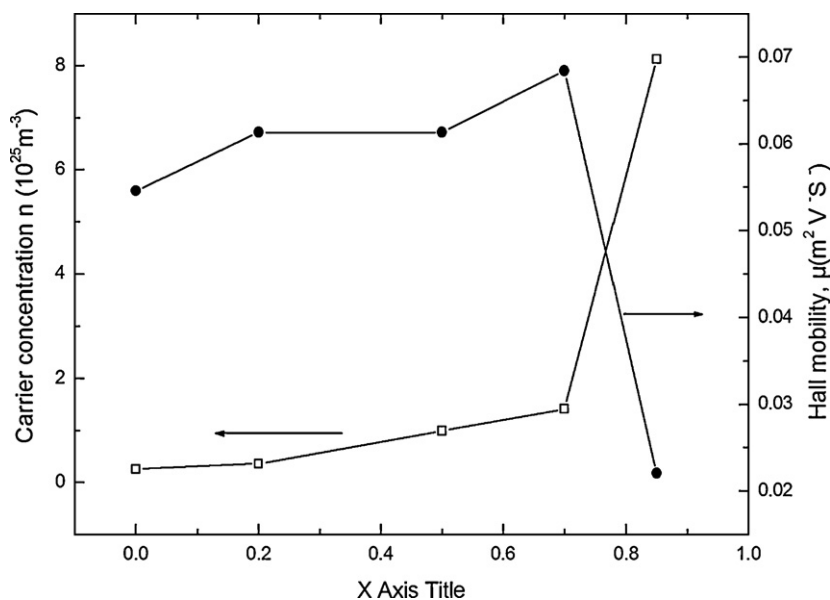**Fig. 3.** Electrical resistivity of $Ag_{1-x}Pb_{18}SbTe_{20}$ as a function of x measured at room temperature.

Fig. 4. Power factor, S^2/ρ, vs x for $Ag_{1-x}Pb_{18}SbTe_{20}$ at room temperature.

riers should be reduced by the scattering effect. As seen from Fig. 4, the carrier concentration of $Ag_{1-x}Pb_{18}SbTe_{20}$ increases with an increase of x. The maximum carrier concentration reaches $8.13 \times 10^{25}\,m^{-3}$, which is much higher than that of the maximum value for $Ag_{1-x}Pb_{18}SbTe_{20}$ sample prepared by melt-quench-SPS ($5 \times 10^{24}\,m^{-3}$) reported by Yan [10]. The $AgPb_{18}SbTe_{20}$ can be seen the PbTe co-doped with Ag and Sb. As well known, the band gap of PbTe becomes smaller under high pressure [16]. So it is reasonable to assume the band gap of $AgPb_{18}SbTe_{20}$ become smaller under high pressure. The high carrier concentration obtained in this study could be attributed to the narrower band gap of $Ag_{1-x}Pb_{18}SbTe_{20}$ under high pressure.

As seen from Fig. 4, the Hall mobility increases first and then decreases with an increase of x. The maximum value reaches $684.22\,cm^2\,V^{-1}\,S^{-1}$ for the $Ag_{0.3}Pb_{18}SbTe_{20}$ sample. The value is about 25% higher than that of the stoichiometric sample, and matches that of the $Ag_{0.8}Pb_{22.5}SbTe_{20}$ sample prepared by MA and

SPS ($558\,cm^2\,V^{-1}\,S^{-1}$) [13]. According to the report of Badding [17], high pressure method has the advantages of restraining the disorder and phase separation for synthesis materials, which was confirmed in the XRD patterns. The sample with pure phase obtained in this study may help to reduce the scatter of carrier, which result in high hall mobility.

The power factor for $Ag_{1-x}Pb_{18}SbTe_{20}$ samples, S^2/ρ calculated in terms of the Seebeck coefficient and electrical resistivity as function of x is shown in Fig. 5. It can be seen that the power factor increases first and then decreases with an increase of x. The optimized composition of $Ag_{1-x}Pb_{18}SbTe_{20}$ prepared by high pressure is different from those obtained prepared with normal pressures reported by others ($x \sim 0.2$) [9–13]. In particular, the maximum value of high pressure synthetic $Ag_{1-x}Pb_{18}SbTe_{20}$ reaches $2.3 \times 10^{-3}\,W\,m^{-1}\,K^{-2}$ at $x = 0.7$. The value is lower than that of the result reported by Hus ($\sim 33.7 \times 10^{-3}\,W\,m^{-1}\,K^{-2}$). However, it is much higher than the results obtained by other pursers [8–11], which can be attributed to the carrier concentration and hall mobility of $Ag_{1-x}Pb_{18}SbTe_{20}$ prepared by high pressure.

4. Conclusions

Thermoelectric materials $Ag_{1-x}Pb_{18}SbTe_{20}$ were prepared by high pressure method. The transport properties measurements show that the carrier concentrations of $Ag_{1-x}Pb_{18}SbTe_{20}$ were tuned by a factor of more than 10 through adjusting x. The electrical resistivity and Seebeck coefficient decrease with an increase of x. The power factor increases first and then decreases with an increase of x. The maximum value reaches $23 \times 10^{-3}\,W\,m^{-1}\,K^{-2}$ at $x = 0.7$, which is about 76% higher than that of stoichiometric sample. The results indicate that it is an effective method to modulate the transport properties of $AgPb_{18}SbTe_{20}$ by means of high pressure technique combining with adjusting the content of Ag.

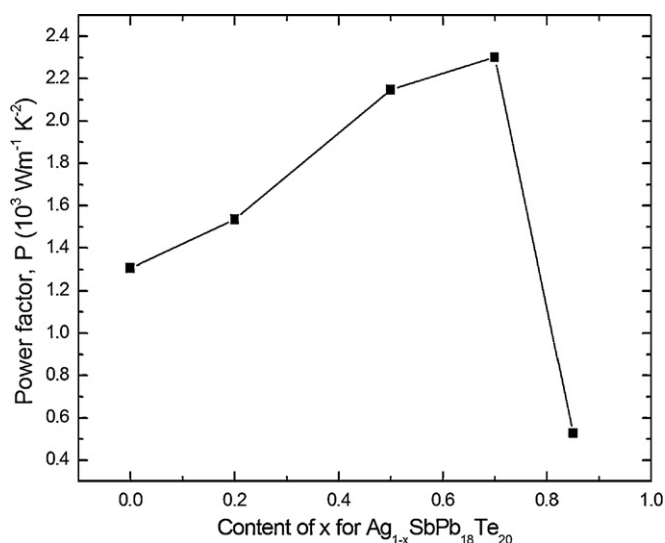**Fig. 5.** The dependence of carrier concentration and Hall mobility of $Ag_{1-x}Pb_{18}SbTe_{20}$ on x at room temperature.

References

[1] K. Hsu, S. Loo, F. Guo, W. Chen, J. Dyck, C. Uher, T. Hogan, E. Polychroniadis, M. Kanatzidis, Science 303 (2004) 818–821.
[2] J. Shen, S. Zhang, S. Yang, Z. Yin, T. Zhu, X. Zhao, J. Alloys Compd. 509 (2011) 161–164.
[3] Y. Lan, A. Minnich, G. Chen, Z. Ren, Adv. Funct. Mater. 19 (2009) 1–20.
[4] L. Zhao, D. Berardan, N. Dragoe, J. Alloys Compd. 508 (2010) 606–609.
[5] J. Wu, J. Yang, H. Zhang, J. Zhang, S. Feng, M. Liu, J. Peng, W. zhu, T. Zou, J. Alloys Compd. 507 (2010) 167–171.
[6] W. Ao, W. Sun, J. Li, F. Liu, Y. Du, J. Alloys Compd. 475 (2009) L22–L24.
[7] J. Androulakis, K. Hsu, R. Pcionek, H. Kong, C. Uher, J. D'Angelo, A. Downey, T. Hogan, M. Kanatzidis, Adv. Mater. 18 (2006) 1170–1173.
[8] F. Yan, T. Zhu, S. Yang, X. Zhao, Phys. Scr. 129 (2007) 116–119.
[9] A. Kosuga, K. Kurosaki, M. Uno, S. Yamanaka, J. Alloys Compd. 386 (2005) 315–318.
[10] Y. Yan, X. Tang, H. Liu, L. Yin, Q. Zhang, Acta Phys. Sin. 56 (2007) 3473–3478.
[11] K. Cai, C. Yan, Z. He, J. Cui, C. Stiewe, E. Müller, H. Li, J. Alloys Compd. 469 (2009) 499–503.
[12] M. Zhou, J. Li, H. Wang, Chin. Sci. Bull. 52 (2007) 990–996.
[13] M. Zhou, J. Li, T. Kita, J. Am. Chem. Soc. 130 (2008) 4527–4532.
[14] S. Ovsyannikov, V. Shchennikov, Chem. Mater. 22 (2010) 635–647.
[15] T. Su, S. Li, H. Ma, X. Li, L. Deng, Y. Yan, W. Guo, X. Jia, J. Alloys Compd. 497 (2010) 432–435.
[16] S.-H. Wei, A. Zunger, Phys. Rev. B 22 (1997) 605–610.
[17] J.V. Badding, Annu. Rev. Mater. Sci. 28 (1998) 631–658.