Electrical transport and thermoelectric properties of $AgPb_{10}SbTe_{12}$ prepared by high pressure method

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Abstract. Thermoelectric material, $Ag_{1-x}Pb_mSbTe_{m+2}$ ($x = 0.2, m = 10$), have been successfully prepared by high pressure method. The pressure-dependent electrical transport and thermoelectric properties of $Ag_{0.8}Pb_{10}SbTe_{12}$ were studied at room temperature. Electrical resistivity and Seebeck coefficient decreases with an increase of synthetic pressure. Thermal conductivities are nearly constant when the pressure is lower than 4 GPa. The carrier concentrations of $Ag_{0.8}Pb_{10}SbTe_{12}$ were tuned by more than a factor of 100 through changing of synthetic pressure. These results indicate that high pressure technique provides a viable and controllable way of tuning the electrical transport properties for $AgPb_mSbTe_{m+2}$.

Keywords. Thermoelectric properties; high pressure; $Ag_{0.8}Pb_{10}SbTe_{12}$.

1. Introduction

Thermoelectric devices based on thermoelectric materials could convert heat to electricity or use electricity to pump heat from cold side to hot side (Rowe 1995). They have many advantages, such as lightweight, small, and without any moving parts or bulk fluids (Disalvo 1999). However, the efficiency of thermoelectric device is not high enough to apply widely due to the low efficiency of thermoelectric materials. In recent years there has been a strong impetus to improve the efficiency of thermoelectric materials.

The efficiency of thermoelectric materials is expressed by the figure-of-merit, Z ($Z = S^2/\rho\kappa$), where S is the Seebeck coefficient, ρ the electrical resistivity, and κ the thermal conductivity. The electrical properties are determined by the power factor, S^2/ρ. The total thermal conductivity, κ, has two contributions, one from carrier (κ_e), and the other from lattice vibrations (κ_{ph}). Optimization of the carrier concentration is crucial for better thermoelectric performance because S, ρ and κ are highly dependent on carrier concentration.

PbTe is well known as a thermoelectric material, which is generally used for power generator functions in the intermediate temperature region (400–800 K) (Wood 1988). Over the years PbTe prepared by many methods such as hot-pressing (Kishimoto and Koyanagi 2002) and spark plasma sintering (Martin *et al* 2007) was studied. Furthermore, several dopants have been used to optimize the carrier con-

centration of PbTe with the purpose of improving thermoelectric performance (Kishimoto and Koyanagi 2002; Imai *et al* 2007). In 2004, Hsu *et al* reported that the Ag and Sb co-doped PbTe samples ($Ag_{1-x}Pb_mSbTe_{m+2}$, $m = 10$, 18) had extremely high figure-of-merit (Hsu *et al* 2004). After that, $AgPb_mSbTe_{m+2}$ samples were studied by many researchers using different methods (Kosuga *et al* 2005; Yan *et al* 2007; Zhou *et al* 2007; Dow *et al* 2009). However, the high TE performance reported by Hsu and co-workers is difficult to reproduce. One of the main reasons is that the resistivity is too high due to its low carrier concentration of $AgPb_mSbTe_{m+2}$ samples (Kosuga *et al* 2005; Yan *et al* 2007; Zhou *et al* 2007; Dow *et al* 2009). For example, the highest carrier concentration is just about 5×10^{18} cm^{-1} for the sample reported by Yan *et al* (2007). While an appropriate carrier concentration, above 10^{19} cm^{-3}, is the primary requirement for high ZT (Rowe 1995).

Compared to other preparation methods of thermoelectric materials, high pressure method has many advantages, such as restraining the disorder, phase separation and other complicating factors during the preparation of materials (Badding 1998). In our previous studies, the thermoelectric material, PbTe, with enhanced performance was prepared successfully by high pressure method (Zhu *et al* 2004).

In order to study the effect of high-pressure on the thermoelectric materials of $Ag_{1-x}Pb_mSbTe_{m+2}$ system, $Ag_{0.8}Pb_{10}SbTe_{12}$ (with $x = 0.2$ and $m = 10$) was prepared by high pressure method first. Our results show that high pressure is an effective method to synthesize $Ag_{0.8}Pb_{18}SbTe_{20}$, which could modulate its carrier concentration and transport properties effectively.

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2. Experimental

The samples were prepared using 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 of $Ag_{0.8}Pb_{10}SbTe_{12}$. After being uniformly mixed in an agate mortar, the mixtures were pressed into a disk with a diameter of 10 mm and height of 4 mm. The pole shaped samples were assembled for high pressure synthesis. The $Ag_{0.8}Pb_{10}SbTe_{12}$ 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 2~5 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. The density was measured by the Archimedes method. X-ray diffraction (XRD) measurements with Cu-K_{α} radiation were performed on an X-ray diffractometer (D/MAX-RA). The carrier concentration and electrical conductivity were measured by Van der Pauw method. The Seebeck coefficient, S, was determined from thermoelectric motive 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 thermal conductivity, κ, was calculated by using $\kappa = D\rho C_P$, where ρ is the sample density measured by the Archimedes method. The thermal diffusivity, D and specific heat, C_P, were measured on a Netzsch LFA457 laser flash apparatus.

3. Results and discussion

The results of X-ray diffraction patterns of $Ag_{0.8}Pb_{10}SbTe_{12}$ are shown in figure 1. It can be seen that all the samples crystallize in the NaCl-type structure. There are no structural changes for $Ag_{0.8}Pb_{10}SbTe_{12}$ in the range of experimental pressure. These results confirm that single phase $Ag_{0.8}Pb_{10}SbTe_{12}$ compounds with PbTe-based structure have been synthesized by high pressure in a relatively short period of time.

The lattice constant of $Ag_{0.8}Pb_{10}SbTe_{12}$ evaluated from the X-ray diffraction pattern is shown in table 1. The lattice constants are all about 0·645 nm, which indicates that the compositions for the samples prepared at different pressures are similar. The density increases with an increase in synthetic pressure. The high density obtained in this study may be helpful to decrease the resistivity of $Ag_{0.8}Pb_{10}SbTe_{12}$.

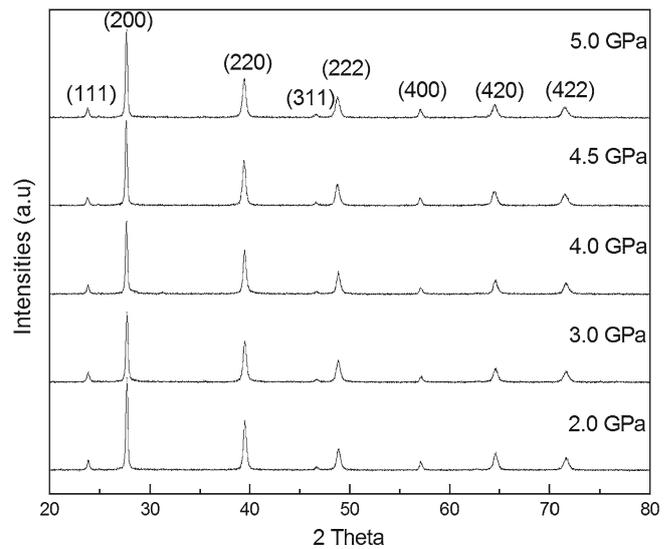Hall effect measurements are performed to estimate the carrier concentrations which are shown in figure 2. The

Figure 1. X-ray diffraction patterns of $Ag_{0.8}Pb_{10}SbTe_{12}$ prepared by high pressure.

Table 1. Lattice constants and densities for $Ag_{0.8}Pb_{10}SbTe_{12}$ prepared by high pressure.

Synthetic pressure (GPa)	Lattice constant (nm)	Density (g/cm^3)
2	0·6454	8·01
3	0·6452	8·12
4	0·6452	8·28
4·5	0·6456	8·33
5	0·6453	8·34

carrier concentration increases from 1.70×10^{18} cm^{-3} to 2.63×10^{20} cm^{-3} with an increase of synthetic pressure. These results indicate that high pressure could modulate the carrier concentration for $Ag_{0.8}Pb_{10}SbTe_{12}$ in a large range.

The Seebeck coefficient and electrical resistivity of $Ag_{0.8}Pb_{10}SbTe_{12}$ as a function of synthetic pressure are shown in figure 3. It can be seen that the values of Seebeck coefficient for all $Ag_{0.8}Pb_{10}SbTe_{12}$ samples are negative, which indicate that all the samples prepared by high pressure are *n*-type semiconductors. The Seebeck coefficient in absolute value for $Ag_{0.8}Pb_{10}SbTe_{12}$ decreases with an increase of synthetic pressure from 195·4 μV/K at 2 GPa to 27·3 μV/K at 5 GPa, which is similar to the results of PbTe reported by Zhu (2004). The resistivity of $Ag_{0.8}Pb_{10}SbTe_{12}$ decreases with an increase of pressure except that of the sample prepared at 4 GPa. The lowest resistivity reaches to 3.19×10^{-4} Ω cm for the sample prepared at 5 GPa, which is much lower than that of $AgPb_mSbTe_{m+2}$ samples prepared by other methods (Kosuga *et al* 2005; Yan *et al* 2007; Zhou *et al* 2007; Dow *et al* 2009). The low resistivity may be helpful to improve the thermoelectric performance of $AgPb_mSbTe_{m+2}$ based system sample.

The simultaneous decrease of Seebeck coefficient and electrical resistivity is a common phenomenon in many other thermoelectric materials such as metallic elements, intermetallic compounds and heavily doped semiconductors, reported by other groups (Mahan 1998). Godwal *et al* (1998) attributed the observed anomalies in electric resistivity and Seebeck coefficient under pressure to the electronic topological transition (ETT). It is known that an ETT occurs when a band extremum, which is associated with a Van Hove singularity in the density of states, crosses the Fermi energy, resulting in a change in topology of the Fermi surface and a strong energy dependence of the electronic density of states near the Fermi energy (Chandra Shekar *et al* 2005). An ETT does not induce a structure phase transition. This is consistent with the XRD results obtained in this study.

As mentioned above, the thermal conductivity is composed of the electrical thermal conductivity, κ_e and the
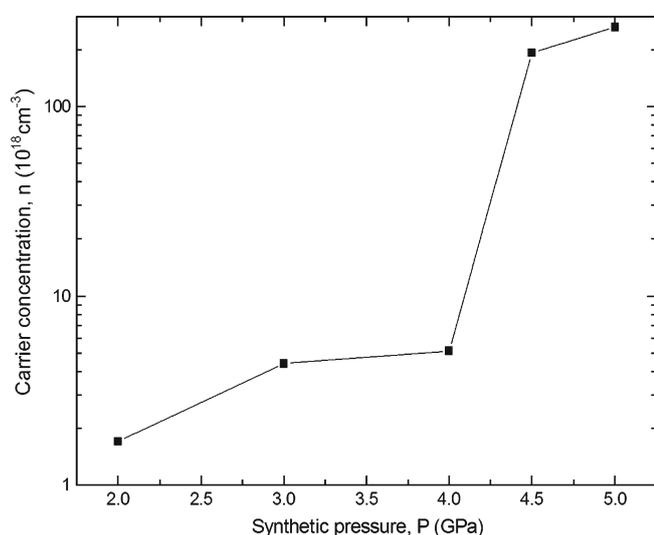

Figure 2. Pressure dependence of carrier concentration for Ag₀.₈Pb₁₀SbTe₁₂.
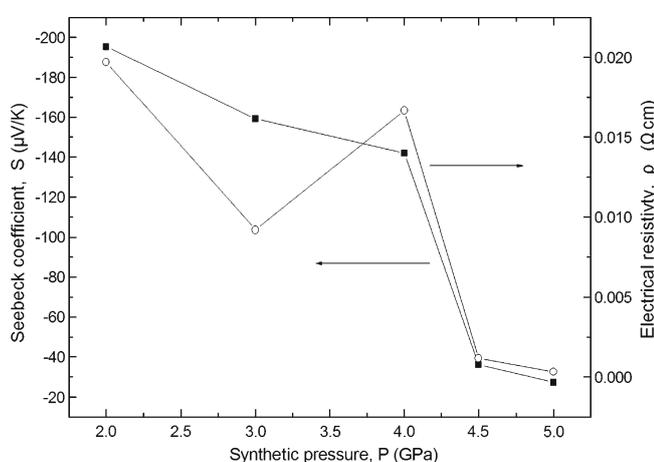
Figure 3. Pressure dependence of Seebeck coefficient and electrical resistivity for Ag₀.₈Pb₁₀SbTe₁₂.

Table 2. Thermal conductivities and figure-of-merit of Ag₀.₈Pb₁₀SbTe₁₂ prepared by high pressure.

Properties	2·0 GPa	3·0 GPa	4·0 GPa	4·5 GPa	5·0 GPa
κ_{total} (W/mk)	1·67	1·74	1·66	2·28	3·94
κ_{ph} (W/mk)	1·63	1·66	1·62	1·65	1·64
$Z(10^{-4}\text{K}^{-1})$	1·16	1·59	0·73	0·49	0·59

phonon thermal conductivity, κ_{ph}. Here, κ_e is expressed by the Wiedemann–Franz law, $\kappa_e = L\sigma T$, where L (2·45 × 10⁻⁸ WΩ/K²) is the Lorenz number. As seen from table 2, the thermal conductivity for Ag₀.₈Pb₁₀SbTe₁₂ is nearly constant with a value of 1·7 W/(mK) when the synthetic pressure is lower than 4 GPa. The thermal conductivity increases sharply to 3·94 W/(mK) for the sample prepared at a pressure of 5 GPa. The high thermal conductivity obtained at high pressure is induced by its high electrical thermal conductivity. The phonon thermal conductivities are constant with a value of 1·6 W/(mK) for all the samples, which is much lower than that of PbTe (2·3 W/(mK)) (Martin *et al* 2007). The low phonon thermal conductivity obtained in these samples may be due to the following factors: (i) the impurity atoms of Ag and Sb with large atomic numbers, which have a strong scattering effect on the phonon and (ii) ETT effect induced by high pressure and alloying effect may soften phonon which also decreases the phonon thermal conductivity (Chandra Shekar *et al* 2005).

The pressure dependence of figure-of-merit, Z, for Ag₀.₈Pb₁₀SbTe₁₂ calculated from the measured quantities is shown in table 2. It can be seen that the value of Z increases first and then decreases with an increase of pressure. The maximum value reaches to 1·59 × 10⁻⁴ K⁻¹ at a pressure of 3 GPa. Although the value is too low compared to that of the state-of-the-art thermoelectric materials (Disalvo 1999), high pressure technique provides a viable and controllable way of tuning the transport properties for AgPb₁₀SbTe₁₂. A better thermoelectric performance of AgPb$_m$SbTe$_{m+2}$ based systems can be expected by further systematic studies such as the high pressure synthesis techniques, composition optimization and alloyed with Se or Sn.

4. Conclusions

N-type thermoelectric material, Ag₀.₈Pb₁₀SbTe₁₂, has been successfully prepared by high pressure method. XRD patterns show that all the samples are single phase with the structure of NaCl. The carrier concentration increases with an increase of synthetic pressure from 1·70 × 10¹⁸ cm⁻³ to 2·63 × 10²⁰ cm⁻³. The electrical resistivity and Seebeck coefficient in absolute value decrease with an increase of synthetic pressure. Thermal conductivities are nearly constant with a value of 1·7 W/(mK) when the pressure is lower than 4 GPa. These results indicate that high pressure technique

is an effective method to tune the carrier concentration and transport properties for $Ag_{0.8}Pb_{10}SbTe_{12}$.

Acknowledgements

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