

HPHT synthesis and electrical properties of $\text{AgSbTe}_2\text{--Ag}_2\text{Te}$ thermoelectric alloys

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Abstract

In this letter, p-type pseudo-binary $\text{AgSbTe}_2\text{--Ag}_2\text{Te}$ thermoelectric alloys with the composition of $(\text{AgSbTe}_2)_{1-x}(\text{Ag}_2\text{Te})_x$ ($x=0\text{--}0.2$) were prepared by high pressure and high temperature (HPHT) method. The samples are near single phase AgSbTe_2 with a small quantity of impurities including Sb_2Te_3 and Ag_2Te . The electrical properties including the Seebeck coefficient and the electrical resistivity depending on synthetic pressure and the Ag_2Te content x were studied at room temperature. The measurement results show that the Seebeck coefficient and the electrical resistivity for $(\text{AgSbTe}_2)_{1-x}(\text{Ag}_2\text{Te})_x$ decrease with an increase of the synthetic pressure and x which indicate that high pressure combining alloying with Ag_2Te could modulate the electrical properties of Ag–Sb–Te system effectively.

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1. Introduction

Thermoelectric materials are a class of functional materials which 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 [1,2]. These thermoelectric devices have many advantages such as small sizes, low costs, light weight, no moving parts and extremely reliable [3]. Effectiveness of a material for thermoelectric applications is determined by the dimensionless figure of merit ZT [3], 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). The electrical properties are determined by the power factor, which defined as $S^2\sigma$ or S^2/ρ which could be optimized as a function of the carrier concentration. To be a good thermoelectric material, it is necessary to have both large power factor and low thermal conductivity.

Ternary materials AgSbTe_2 is a high performance p-type thermoelectric material ($ZT=1.4$) with low thermal conductivity ($\kappa_p\sim 0.6\text{ WK}^{-1}\text{ m}^{-1}$) [4]. And it is one of the most important composition of the well known p-type thermoelectric material TAGS (GeTe alloy with AgSbTe_2) which was deemed to be the best thermoelectric material for a time [5]. Recently Hsu reported the highest effective bulk thermoelectric material $\text{AgPb}_m\text{SbTe}_{m+2}$ [6] which could be regarded as AgSbTe_2 alloy with PbTe. Over past years AgSbTe_2 were studied using many methods [7–10] such as Bridgman method and pulse sintering. But it is difficult to control the doping with these methods. And the AgSbTe_2 sample has a large electrical resistivity which impacts its thermoelectric properties.

Compared with 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 [11]. In our previous works, PbTe and its doped alloy have been prepared by HPHT [12,13]. These results show that the non-doped PbTe samples prepared by

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HPHT have the same high thermoelectric performance as that of the heavily doped PbTe samples prepared at normal pressure, and the thermoelectric performance of doped PbTe samples prepared by HPHT are improved further.

Although GeTe, PbTe and SnTe have been used to alloy with AgSbTe₂ [5,6,14] and exciting *ZT* values have been obtained [5,6]. However, little is known of the properties of AgSbTe₂–Ag₂Te alloys. In this work, the advantages of high pressure technique were used to prepare AgSbTe₂–Ag₂Te alloys and the enhanced electrical transport properties were expected. The effects of synthetic pressure and Ag₂Te content *x* on the room temperature electrical properties of the alloys were studied.

2. Experimental

The AgSbTe₂–Ag₂Te samples were prepared with the elements of 99.999% tellurium, antimony and 99.8% silver as sources which were weighed according to the stoichiometry of (AgSbTe₂)_{1–x}(Ag₂Te)_x (*x*=0, 0.05, 0.1, 0.2). After being uniformly mixed in an agate mortar, the mixtures were shaped by press. The pole shaped samples were assembled for HPHT synthesis. The (AgSbTe₂)_{1–x}(Ag₂Te)_x samples were synthesized using a cubic anvil high pressure apparatus with a sample chamber of 23 mm on an edge. The samples were heated to 973 K for 20 min, followed by cooling with the rate of 50 K/s before pressure release. The synthetic pressures were set from 2 to 4.5 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 Chromel–Alumel thermocouples.

The collected samples were cut and polished on the surface for thermoelectric measurements which were carried out at room temperature. X-ray diffraction (XRD) measurements with Cu-K_α radiation were performed on an X-ray diffractometer (D/MAX-RA). The electrical resistivity was measured by typical DC four-probe configuration. The Seebeck coefficient

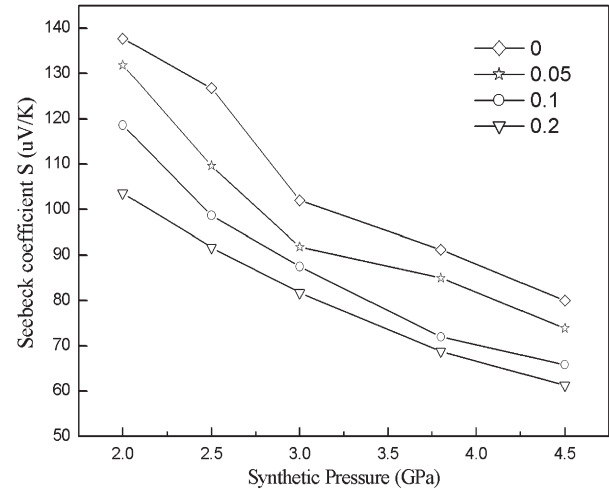


Fig. 2. Relationship between Seebeck coefficient and synthetic pressure for AgSbTe₂ measured at room temperature.

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 is monitored by computer using the VI-Logger program provided by NI-company.

3. Results and discussions

Fig. 1 shows the diffraction patterns for the samples of (AgSbTe₂)_{1–x}(Ag₂Te)_x prepared under 2.0 GPa. The XRD patterns of (AgSbTe₂)_{1–x}(Ag₂Te)_x prepared under different synthetic pressures are nearly same. All the samples are near single phase except a small quantity of Sb₂Te₃ and Ag₂Te impurities.

Especially the sample of AgSbTe₂ (*x*=0) is near single phase except the slight remnant of Sb₂Te₃ which is much purer than that of the same composition synthesized at normal pressure reported by H. Matsushita [8]. These results indicate that high pressure is helpful to restrain the phase disorder which supports the results reported by J.V. Badding [11]. As seen from Fig. 1, a secondary phase Ag₂Te was found in the XRD patterns except the main phase AgSbTe₂ when the content

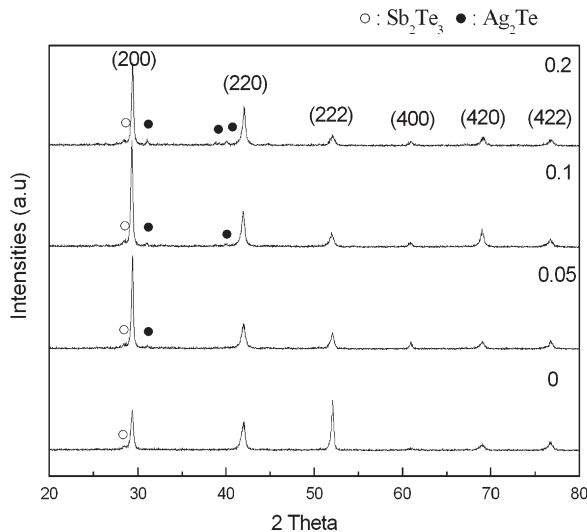


Fig. 1. XRD patterns of (AgSbTe₂)_{1–x}(Ag₂Te)_x prepared by HPHT.

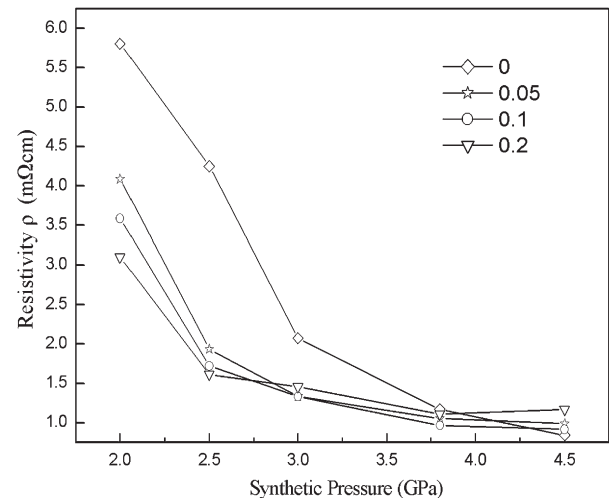


Fig. 3. Electrical resistivity of (AgSbTe₂)_{1–x}(Ag₂Te)_x as a function of synthetic pressure measured at room temperature.

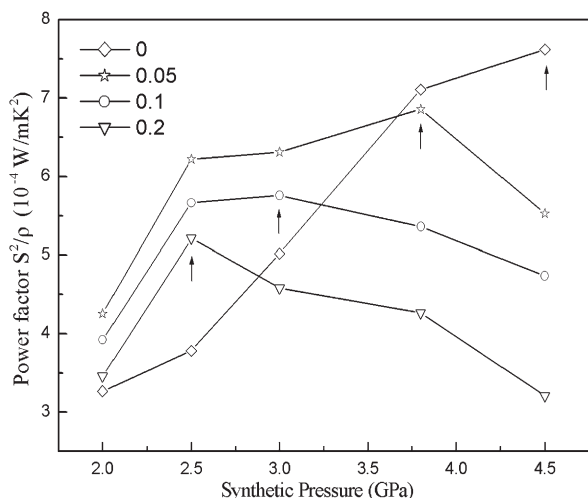


Fig. 4. Power factor, S^2/ρ , VS synthetic pressure for $(\text{AgSbTe}_2)_{1-x}(\text{Ag}_2\text{Te})_x$ at room temperature.

$x \geq 0.05$ and the concentration of Ag_2Te increases with an increase of x . The result indicates that with the increase of the content x , the Ag_2Te was not completely alloyed with AgSbTe_2 , and a little secondary phase Ag_2Te formed.

Fig. 2 shows the Seebeck coefficient for the $(\text{AgSbTe}_2)_{1-x}(\text{Ag}_2\text{Te})_x$ alloys prepared by HPHT. The Seebeck coefficients of all the samples are positive which imply that they are p-type semiconductors. As can be seen from Fig. 2, the high pressure and alloying with Ag_2Te have the same effect on the Seebeck coefficient of AgSbTe_2 which decreases gradually with an increase of the synthetic pressure and the content x .

In general, as the doping level and the carrier concentration of a semiconductor are increased, the electrical conductivity increases but the Seebeck coefficient decreases. According to our early study high pressure has the same effect as doping which can increase the carrier concentration [12]. Moreover, the increase of the carrier concentration reduces the mobility of the carriers, which causes the Seebeck coefficient to decrease with the increase of synthetic pressure and x . These results are in consistent with other experiments [15,16].

The dependence of electrical resistivity for $(\text{AgSbTe}_2)_{1-x}(\text{Ag}_2\text{Te})_x$ alloys on synthetic pressure is shown in Fig. 3. Similar to the result of PbTe we reported early [12], the electrical resistivity for the samples of $(\text{AgSbTe}_2)_{1-x}(\text{Ag}_2\text{Te})_x$ decreases with an increase of synthetic pressure. The highest resistivity of $5.8 \times 10^{-3} \Omega \text{ cm}$ was obtained at the pressure of 2.0 GPa for AgSbTe_2 ($x=0$) which is much lower than that of the sample synthesized at ambient pressure reported by H. Matsushita ($1.8 \times 10^{-2} \Omega \text{ cm}$) [8]. The result indicates that the HPHT technique has conquered the disadvantage of high electrical resistivity for AgSbTe_2 prepared at ambient pressure effectively. In our study, the relative density for $(\text{AgSbTe}_2)_{1-x}(\text{Ag}_2\text{Te})_x$ increases with the increase of synthetic pressure, which may affect the microstructure of the synthetic samples and further result in the decrease of the resistivity. The electrical resistivity for $(\text{AgSbTe}_2)_{1-x}(\text{Ag}_2\text{Te})_x$ at 2 GPa as seen from Fig. 3 decreases with an increase of the Ag_2Te content x , which

should partially be attributed to the form of a little secondary phase Ag_2Te because of its lower electrical resistivity ($9.0 \times 10^{-4} \Omega \text{ cm}$) [17]. As the synthetic pressure increases, the composition dependence of the electrical resistivity becomes weak.

The power factor for $(\text{AgSbTe}_2)_{1-x}(\text{Ag}_2\text{Te})_x$ calculated by the Seebeck coefficient and the electrical resistivity is shown in Fig. 4. From Fig. 4, we can see that the power factor for $(\text{AgSbTe}_2)_{1-x}(\text{Ag}_2\text{Te})_x$ with different x has a maximum at different synthetic pressure, which shifts to the low pressure side with increasing x . These results indicate that high pressure and alloying have the similar effect on improving the thermoelectric property of Ag-Sb-Te system.

4. Conclusion

Near single phase pseudo-binary $\text{AgSbTe}_2\text{-Ag}_2\text{Te}$ thermoelectric alloys were prepared by HPHT method. The electrical transport properties including the electrical resistivity and Seebeck coefficient studied at room temperature indicate that high pressure combined with alloying could modulate the electrical properties of thermoelectric material of Ag-Sb-Te system effectively.

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