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Thermoelectric properties of Zn–Sb alloys doped with In

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ABSTRACT

Several samples of Zn–Sb alloys were prepared by doping with different amount of In (0, 5, 10 and 15 at%) using cold-pressing and sintering techniques. The X-ray powder diffraction patterns reveal that In-doped samples are complex phase mixture, which consist of β-Zn_4Sb_3 as the main phase and ZnSb, InSb and In as secondary phases. The thermoelectric properties for these alloys were studied by means of thermal and carrier transport measurement in the temperature range between 40 and 700 K. For all studied samples, the Seebeck coefficients were found to be positive in whole the temperature range under investigation. It suggests that the hole-type carriers dominate the thermoelectric transport. Temperature dependence of electric resistivity, Seebeck coefficient and thermal conductivity for these alloys were analyzed. From the experimental analysis, the indium doping in Zn–Sb alloys leads to an increase in Seebeck coefficient and electric resistivity and leads to a decrease in thermal conductivity of β-Zn_4Sb_3-based materials. The dimensionless figure of merit, ZT for these alloys were evaluated and discussed. It was found that the sample with 10 at% indium doping exhibits a larger figure of merit in the 40–700 K temperature range.

1. Introduction

Zn_4Sb_3 and $(Zn_{1-x}Cd_x)_4Sb_3$ alloys were proposed as a high performance p-type thermoelectric materials [1,2]. p-Type β-Zn_4Sb_3-based materials have the highest thermoelectric figures of merit ZT of about 1.3 at a temperature of 673 K. $(Zn_{0.8}Cd_{0.2})_4Sb_3$ exhibits a ZT value of 1.4 at 520 K and it is the best result in the medium temperature [1,2]. The figure of mrerit ZT is defined as $ZT = \alpha^2 T/\rho\kappa$, where ρ is the electrical resistivity, α is the Seebeck coefficient, κ is the thermal conductivity and T is the temperature in Kelvin. The power factor is also defined as α^2/ρ.

For Zn_4Sb_3, three phases are known: α-, β-, γ-Zn_4Sb_3 which are stable below 263 K, between 263 and 765 K, and above 765 K, respectively. According to the phase diagram ZnSb [3], β-Zn_4Sb_3 phase is produced through peritectical reactions and the phase transformation occurs upon cooling at 765 K, hence it is difficult to obtain crack-free alloy by melting growth. Other difficulties are compositional changes during high-temperature synthesis and poor tendency to form a compound since Zn_4Sb_3 decomposes into ZnSb and Zn at high temperature due to the relative poor stability [1,4,5]. Most of studies have been focused on the β-Zn_4Sb_3 phase to optimize its thermoelectric properties above room temperature. It was also reported that the power factor of the α-Zn_4Sb_3 phase is twice as large as that of β-Zn_4Sb_3 phase and could be a good candidate for thermoelectric material for cryogenic use [6]. Although there is no doubt that the highest thermoelectric figure of merit is obtained with melt-grown alloys, there are considerable practical advantages in the use of powder-metallurgy process. Such a process lends itself much more economically to large-scale automated production and can be less wasteful of materials, particularly if the elements are pressed as individual dice.

Indium is a typical metal with low melting point and good electrical conductivity but low Seebeck coefficient. Metal doping in Zn–Sb alloys may alters the Zn/Sb ratio of the bulk material and provide additional scattering mechanism. This doping changes the electronic structure of the material and offers opportunities for optimizing its thermoelectric performance. In order to investigate the effect of In doping on the thermoelectric properties, several samples of Zn–Sb alloys were prepared by doping with different amount of In (0, 5, 10 and 15 at%) using cold-pressing and sintering techniques. The crystal structure and crystalline quality were investigated by X-ray diffraction as well as electron-probe microanalysis (EPMA). The thermoelectric behaviors for the as-prepared samples were studied by means of thermal and carrier transport measurements. Temperature dependences of resistivity, Seebeck coefficient, and thermal conductivity for these In-doped Zn–Sb alloys were analyzed. The dimensionless figure of merit, ZT for these alloys were evaluated and discussed.

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2. Experimental procedure

The source material for the cold-pressing was prepared by synthesizing $(Zn_4Sb_3)_{1-x}In_x$ with $x = 0$, 0.05, 0.10 and 0.15. Appropriate amount of zinc, antimony and indium with 99.999% purity were put into a carbon-coated ampoule of 1.1 cm i.d., which was then evacuated and sealed under vacuum. The ampoule was slowly heated to the melting point of alloy in a rocking furnace and was held at this temperature for one day. At the end of the process, the ampoule was quenched to room temperature. Resulting ingots were ground in an agate mortar and analyzed by X-ray diffractometry (XRD). The powders were then sieved with mean powder size smaller than 44 μm. Powders were cold pressed at 700 kg/cm^2 to form 15 mm in diameter and 2 mm in thickness compacts and sintering was conducted in argon atmosphere at 300 °C for 24 h.

Electron-probe microanalysis was performed for examining the composition of samples. Electrical resistivity, Seebeck coefficient and thermal conductivity were measured in the temperature range from 40 to 700 K. Thermal conductivity and Seebeck coefficient measurements were performed simultaneously in a closed-cycle helium refrigerator by the heat pulse technique. Samples were cut into a rectangular shape of typical size of 1.5 mm × 1.5 mm × 5.0 mm. Very thin differential thermocouple junctions were fixed at the two ends of the sample using thermal epoxy. To measure the Seebeck electromotive force (emf), thin copper leads were placed on the sample at close vicinity to the thermocouple junctions using silver paste. One end of the sample was mounted on a copper block and a small chip resistor serving as a heater was fixed at the other end of the sample. The temperature difference was controlled to be less than 1 K to minimize the heat loss through radiation, and the sample space is maintained in a good vacuum (10^{-4} Torr) during measurements. All data were recorded at a slow warm-up rate of about 20 K/h. The details of the measurement techniques can be found elsewhere [7,8].

3. Results and discussion

Electron-probe microanalysis studies showed that the compositions are homogeneous to within 2% in each ampoule. The X-ray diffraction patterns of two representative samples, Zn_4Sb_3 and $(Zn_4Sb_3)_{0.9}In_{0.1}$, are shown in Fig. 1. For Zn_4Sb_3 sample, peaks of β-$Zn_4Sb_3$and ZnSb are observed. The growth of ZnSb phase is attributed to the deficiency of Zn, which is commonly observed in high-temperature process of this alloy system as stated above [1,4,5]. For In-containing sample as $(Zn_4Sb_3)_{0.9}In_{0.1}$, additional peaks of In and InSb are observed. The main peaks of β-Zn_4Sb_3 phase do not shift obviously with In-doping and some peaks are broadened due to overlap between closely spaced peaks of β-Zn_4Sb_3, ZnSb and InSb phases as indexed in Fig. 1. It indicate that In does not incorporate into the lattice of β-Zn_4Sb_3. These results also suggest that In-containing samples are complex phase mixture which consist of β-Zn_4Sb_3 as the main phase and InSb, ZnSb and In as secondary phases.

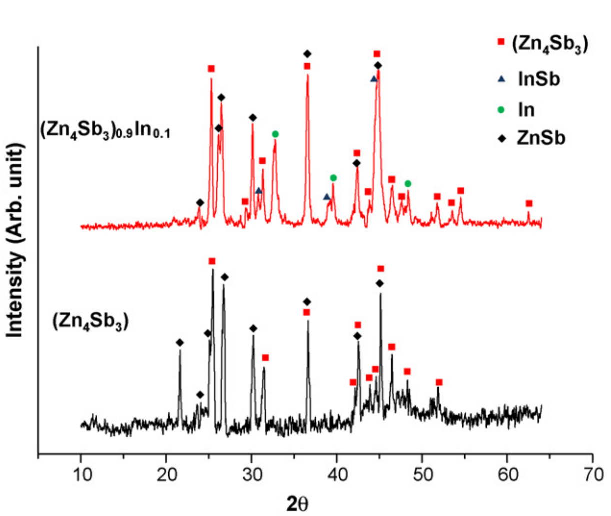

Fig. 1. The X-ray diffraction patterns of two representative samples, Zn_4Sb_3 and $(Zn_4Sb_3)_{0.9}In_{0.1}$.

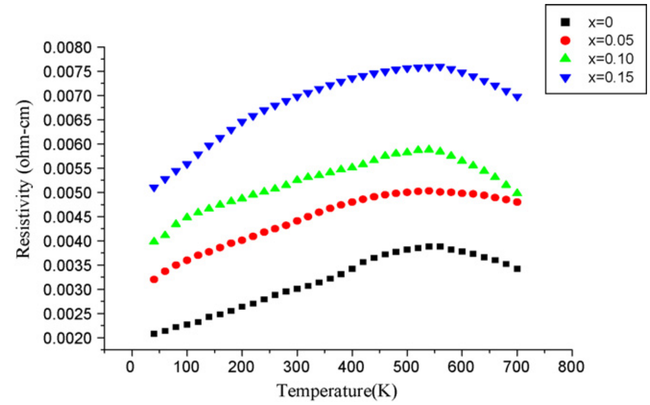

Fig. 2. The temperature-dependent electrical resistivity for all studied samples, $(Zn_4Sb_3)_{1-x}In_x$ with $x = 0$, 0.05, 0.10 and 0.15.

The temperature-dependent electrical resistivity for all studied samples, $(Zn_4Sb_3)_{1-x}In_x$ with $x = 0$, 0.05, 0.10 and 0.15, is shown in Fig. 2. All the samples exhibit semiconducting behavior: resistivity increase with increasing temperature, reach its maximum value and then decrease. The electrical resistivity maximum is shifted to higher temperature with increase in In composition. The electrical resistivity of samples also increase with increase in In composition.

The temperature-dependent Seebeck coefficient for all studied samples, $(Zn_4Sb_3)_{1-x}In_x$ with $x = 0$, 0.05, 0.10 and 0.15, is shown in Fig. 3. The Seebeck coefficients of the investigated alloys were found to be positive in the entire temperature range under investigation, suggesting that the hole-type carriers dominate the thermoelectric transport. The Seebeck coefficients of all the In-containing samples, $(Zn_4Sb_3)_{1-x}In_x$ with $x = 0.05$, 0.10 and 0.15, are larger than that of the sample Zn_4Sb_3 in the entire investigated temperature range as shown in Fig. 3.

The temperature-dependent thermal conductivity for all studied samples, $(Zn_4Sb_3)_{1-x}In_x$ with $x = 0$, 0.05, 0.10 and 0.15, is shown in Fig. 4. The thermal conductivity of all the In-doped samples, $(Zn_4Sb_3)_{1-x}In_x$ with $x = 0.05$, 0.10 and 0.15, are obviously smaller than that of the sample Zn_4Sb_3 in the entire investigated temperature range. It reveals that indium doping in Zn–Sb alloys may provide additional scattering mechanism, leading to reduction of the thermal conductivity of Zn–Sb alloys. In general, the total thermal conductivity consists of two parts and in semiconductors both have to be considered. That is an electronic contribution which increases with increasing temperature and a lattice contribution which decreases with increasing temperature. The thermal con-

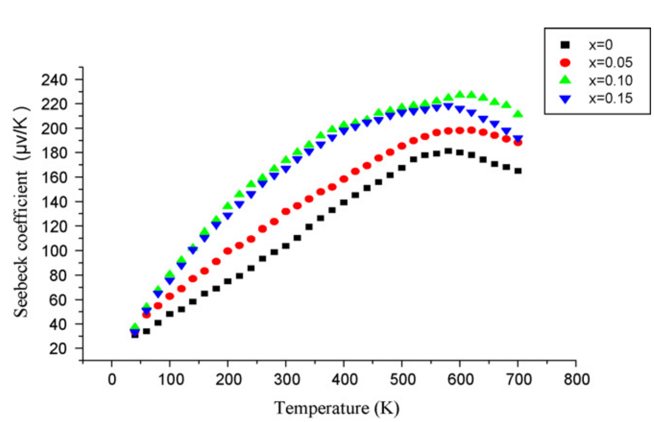

Fig. 3. The temperature-dependent Seebeck coefficient for all studied samples, $(Zn_4Sb_3)_{1-x}In_x$ with $x = 0$, 0.05, 0.10 and 0.15.

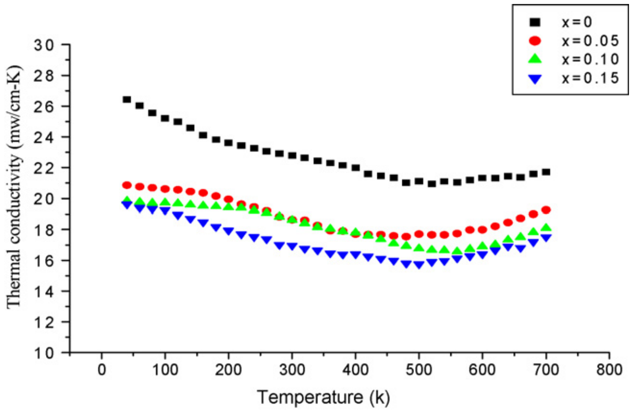

Fig. 4. The temperature-dependent thermal conductivity for all studied samples, $(Zn_4Sb_3)_{1-x}In_x$ with $x = 0$, 0.05, 0.10 and 0.15.

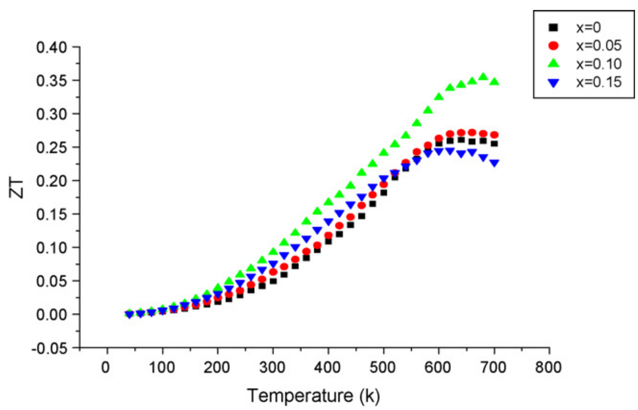

Fig. 5. The dimensionless figure of merit ZT for all studied samples, $(Zn_4Sb_3)_{1-x}In_x$ with $x = 0$, 0.05, 0.10 and 0.15.

ductivity of all the investigated samples, $(Zn_4Sb_3)_{1-x}In_x$ with $x = 0$, 0.05, 0.10 and 0.15, were decrease with increasing temperature in the temperature region below 500 K but increases gradually with increasing temperature in the temperature region above 500 K as shown in Fig. 4. Hence the lattice contribution is the dominant term in the temperature region below 500 K and the electronic contribution is the dominant term in the temperature region above 500 K.

Using the data of electrical resistivity (ρ), Seebeck coefficient (α), and thermal conductivity (κ), the dimensionless figure of merit (i.e. $ZT = \alpha^2 T/\rho\kappa$) for all studied samples, $(Zn_4Sb_3)_{1-x}In_x$ with $x = 0$, 0.05, 0.10 and 0.15, can be evaluated and depicted in Fig. 5. The ZT increases with increasing temperature, reach its maximum value and then decrease. The maximum value of ZT is 0.35 for the sample $(Zn_4Sb_3)_{0.9}In_{0.1}$ at 680 K, which is larger than that of the sample Zn_4Sb_3.

4. Conclusions

Several In-doped samples, $(Zn_4Sb_3)_{1-x}In_x$ with $x = 0$, 0.05, 0.10 and 0.15, were successfully prepared by using cold-pressing and sintering techniques. For Zn_4Sb_3 sample ($x = 0$), phase of β-$Zn_4Sb_3$and ZnSb are observed and for In-doped samples ($x = 0.05$, 0.10 and 0.15), additional phase of In and InSb are observed. It indicate that In-doped samples are complex phase mixture and In does not incorporate into the lattice of β-Zn_4Sb_3. All the samples exhibit semiconducting behavior and the electrical resistivity of samples increase with increase in In composition. The Seebeck coefficients of all the In-doped samples are larger than that of the sample Zn_4Sb_3 and the thermal conductivity of all the In-doped samples are obviously smaller than that of the sample Zn_4Sb_3 in the entire investigated temperature range. It reveals that indium doping in Zn–Sb alloys may provide additional scattering mechanism, leading to reduction of the thermal conductivity of Zn–Sb alloys. The maximum value of ZT is 0.35 for the sample $(Zn_4Sb_3)_{0.9}In_{0.1}$ at 680 K, which is larger than that of the sample Zn_4Sb_3.

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