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Effect of Bi doping on the thermoelectric properties of Zn_4Sb_3

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ABSTRACT

Polycrystalline samples of β-Zn_4Sb_3 doped with bismuth have been fabricated through vacuum melting followed by hot-pressing method. The thermoelectric properties of Bi-doped compounds $Zn_4Sb_{3-x}Bi_x$ ($x = 0, 0.02, 0.04, 0.06$) were investigated in the temperature range of 323–673 K. All the specimens exhibited the behavior of p-type conduction. The thermoelectric figure of merit (ZT) was increased with the increase of Bi content. The maximum ZT value of 1.09 was obtained at 673 K for $x = 0.06$ as compared to the ZT of 0.8 in the undoped Zn_4Sb_3.

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1. Introduction

Thermoelectric materials have been continuously investigated due to their ability to convert waste heat into useable electricity or act as solid-state Peltier coolers [1–4]. Zn_4Sb_3-based compounds have attracted a lot of attention recently in thermoelectric applications [5–8], since they have uniquely low thermal conductivity and exceptional thermoelectric properties in the intermediate temperature range (473–673 K). Although Zn_4Sb_3 is now known to exist in at least four crystalline phases, only the β phase exhibits high performing thermoelectric properties [9,10]. Thermoelectric performance is usually evaluated by using the dimensionless figure of merit (ZT) defined as $ZT = \alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the absolute temperature. The ZT of Zn_4Sb_3 reaches a maximum value of 1.3 [5,11], and this suggests potential commercial applications since the compound is made of relatively cheap and nontoxic elements.

The Zn_4Sb_3-based materials synthesized have severe problems with thermal degradation. Zn_4Sb_3 partly decomposed to ZnSb, Zn/ZnO, and elemental Sb when held at temperature higher than 523 K [12,13]. Many efforts have been made to improve the thermoelectric properties of Zn_4Sb_3, such as investigations of fabrication [14,15], improvements to the preparation method [11,16] and doping of foreign elements. Doping of β-Zn_4Sb_3 has been suggested as a possible approach to improve the stability and optimize the thermoelectric properties by reducing thermal conductivity and changing the carrier concentration. In recent years, doping of Cd, Hg, Mg, In, Cu, Se and Ag in Zn_4Sb_3 has been reported [17–23]. These studies showed that when doped Zn_4Sb_3 with Cd, In or Mg, the thermoelectric performance was not improved obviously. In contrast, the thermoelectric properties of Zn_4Sb_3 were improved substantially after proper doping of Hg, Cu, Se and Ag. For Ag doped compounds $(Zn_{1-x}Ag_x)_4Sb_3$, the lightly doped compound $(Zn_{0.995}Ag_{0.005})_4Sb_3$ exhibited the best thermoelectric performance, whose ZT (at 300 K) was about 1.3 times larger than that of the undoped β-Zn_4Sb_3 [23]. In our previous study, we have reported the thermoelectric properties for doped compounds $Zn_4Sb_{3-x}Te_x$ ($x = 0$–0.08), and found the ZT was increased with the increasing Te content [24].

In the present study, a series of bismuth doped $Zn_4Sb_{3-x}Bi_x$ ($x = 0, 0.02, 0.04, 0.06$) compounds were fabricated. The substitution on Sb site was effective to modulate the power factor and it was expected to reduce thermal conductivity. The effect of isoelectronic Bi substitution at Sb site on the thermoelectric properties has been investigated in the temperature range from 323 to 673 K.

2. Experimental procedures

Bismuth doped compounds $Zn_4Sb_{3-x}Bi_x$ ($x = 0, 0.02, 0.04, 0.06$) were prepared from elements of zinc (powder, 99.999%), antimony (powder, 99.999%) and bismuth (powder, 99.999%) in stoichiometric proportions with the addition of 1.0 at% excess Zn. Slight excess of Zn was taken to compensate the Zn loss at high temperatures processing. The mixtures of constituent elements were sealed into quartz tubes under vacuum (10^{-3} Pa). The quartz tubes were heated in a furnace and held at 1023 K for 5 h, then cooled down to room temperature spontaneously. The resulting ingots were ground in an agate mortar and X-ray diffraction was used to check the phase purity. The powders were then hot pressed (200 MPa, 673 K, 90 min) in a cylindrical stainless steel die in vacuum to form bulk samples. The samples with the size of 2.5 mm × 2.5 mm × 9 mm were cut from the compacts

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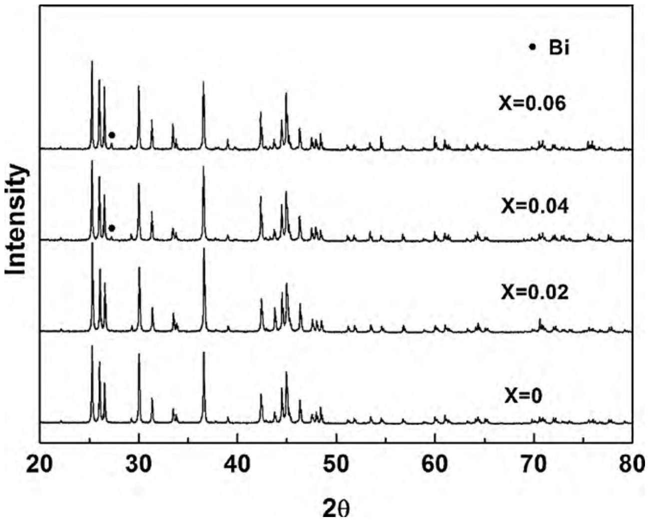

Fig. 1. XRD patterns of $Zn_4Sb_{3-x}Bi_x$ (x = 0, 0.02, 0.04, 0.06) prepared by vacuum melting.

to measure the electrical conductivity and Seebeck coefficient, while the samples with the size of Ø10 mm × 2.5 mm were cut for the measurement of thermal diffusivity.

The power XRD patterns were obtained on a Bruker D8 Advance diffractometer using Cu Kα radiation. Measurements of electrical resistivity and Seebeck coefficient were made with ULVAC ZEM-3 apparatus in the temperature range of 323–673 K under a helium atmosphere (about 0.04 MPa). The thermal conductivity was calculated from thermal diffusivity (λ), heat capacity (C_p) and density (ρ), by $\kappa = \lambda C_p \rho$. The thermal diffusivity (λ) was measured by LFA 427 laser flash apparatus. The heat capacity was measured by a differential scanning calorimeter (Shimadzu DSC-50) under an Ar flow. The bulk density (ρ) of the hot-pressed samples was measured by Archimedes method. The total uncertainty of *ZT* value measured using the equipment in our laboratory was estimated to be ±12%.

3. Results and discussion

The XRD patterns of the $Zn_4Sb_{3-x}Bi_x$ compounds (x = 0, 0.02, 0.04, 0.06) are shown in Fig. 1. It can be seen that the XRD spectrum of the samples with x = 0 and 0.02 is single-phase β-Zn_4Sb_3, while the diffraction peak of Bi appears in XRD spectrum with x = 0.04 and 0.06, indicating that Bi is no longer fully substituted at Sb site. The actual chemical compositions of the samples with x = 0 and 0.06 were determined by electron-probe microanalysis (EPMA) and are listed in Table 1. The Hall coefficients for samples $Zn_4Sb_{3-x}Bi_x$ (x = 0 and 0.06) were measured using an apparatus (PPMS) at room temperature, and then the carrier concentrations were calculated. In undoped sample the carrier concentration is 5.77×10^{20} cm^{-3}, while 9.60×10^{19} cm^{-3} in doped sample $Zn_4Sb_{2.94}Bi_{0.06}$ (Table 1).

The temperature dependence of Seebeck coefficient (α) is shown in Fig. 2, the positive values indicate that all the samples are p-type conduction. The α value of $Zn_4Sb_{2.98}Bi_{0.02}$ is very close to that of the undoped one in the whole temperature range, while for the $Zn_4Sb_{3-x}Bi_x$ (x = 0.04, 0.06) compounds, the α values are larger than that of the undoped one in the temperature range of 323–500 K. The Seebeck coefficient maximum is shifted to lower temperature with increase in Bi content. It is speculated that the main reason for the higher Seebeck coefficient is due to their lower carrier density.

Table 1
The actual basic chemical compositions and carrier concentrations (cm^{-3}) of the $Zn_4Sb_{3-x}Bi_x$ (x = 0 and 0.06).

Samples	Compositions (at.%)		Carrier concentrations (cm^{-3}) at room temperature
	Zn	Sb	
x = 0	57.29	42.71	5.77×10^{20}
x = 0.06	57.52	42.48	9.60×10^{19}

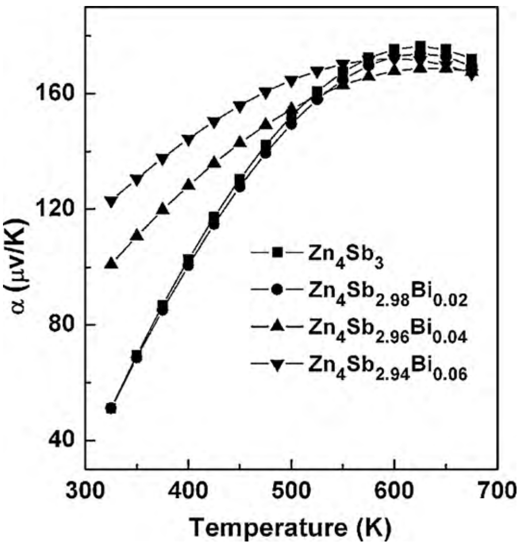

Fig. 2. Temperature dependence of Seebeck coefficient for the hot-pressed samples.

The temperature dependence of electrical conductivity (σ) is shown in Fig. 3. The electrical conductivity decreases with increasing temperature, reaches its minimum value and then smoothly increases. The electrical conductivity of compound $Zn_4Sb_{2.98}Bi_{0.02}$ is close to that of the undoped β-Zn_4Sb_3, which is in consistent with that of the Seebeck coefficient. Based on the unchanged electrical conductivity and Seebeck coefficient between x = 0 and x = 0.02 samples in the entire temperature range, we can effectively assume that Bi-substitution does not change the band structure much. For the samples with x = 0.04, 0.06, the values of σ are lower than that of the undoped one in the temperature range of 323–500 K. This is presumably due to the decreased carrier concentration in the doped samples. From σ and α experimental data, the thermoelectric power factor ($\alpha^2\sigma$) is calculated and an improvement on PF is obtained. Take the data at 325 K for example, power factors are 2.6×10^{-4}, 2.9×10^{-4}, 6.0×10^{-4} and 6.6×10^{-4} W/m K^2 for x = 0, 0.02, 0.04, 0.06, respectively.

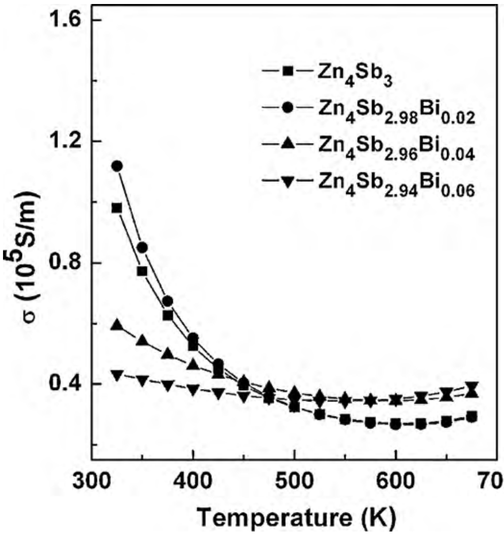

Fig. 3. Temperature dependence of electrical conductivity for the hot-pressed samples.

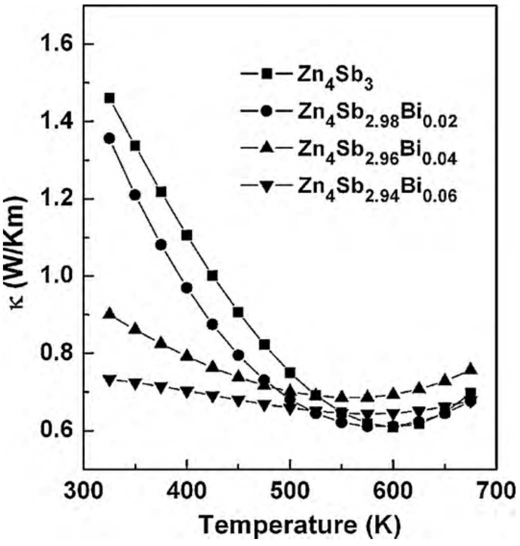

Fig. 4. Temperature dependence of thermal conductivity for the hot-pressed samples.

The temperature dependence of thermal conductivity (κ) is shown in Fig. 4. The thermal conductivity of the Bi-doped samples decreases with increasing Bi content in the temperature range of 323–500 K. The thermal conductivity has carrier (κ_e) and lattice (κ_L) components, $\kappa = \kappa_e + \kappa_L$. According to the Wiedemann–Franz law: $\kappa_e = L\sigma T$, the electronic thermal conductivity (κ_e) can be calculated, where L is the Lorenz number. A value for the Lorenz number of $1.5 \times 10^{-8}\ \mathrm{V^2\,K^{-2}}$ [25] has been used to estimate the electronic contribution to the thermal conductivity. With Bi doping, the electronic contribution to the thermal conductivity is decreased due to the decrease of electrical conductivity. The lattice thermal conductivity ($\kappa - \kappa_e$) for $Zn_4Sb_{3-x}Bi_x$ ($x = 0, 0.02, 0.04, 0.06$) is obtained by subtracting the carrier component (κ_e) from the total thermal conductivity (κ). As shown in Fig. 5, the lattice thermal conductivity decreases with increasing Bi content because of the enhancement of phonons scattering. Isoelectronic substitution introduces mass fluctuation scattering and strain field fluctuation scattering for phonons due to the mass and size differences between alloying atoms and host atoms [26,27]. For the Bi-substituted compounds $Zn_4Sb_{3-x}Bi_x$($x = 0.04, 0.06$), which consist of β-Zn_4Sb_3 as the main phase and Bi as secondary phase, possible mechanisms to explain the reduction of lattice thermal conductivity include grain boundary scattering, mass-difference scattering, point defect scattering and scattering on dislocations besides the intrinsic phonon scattering.

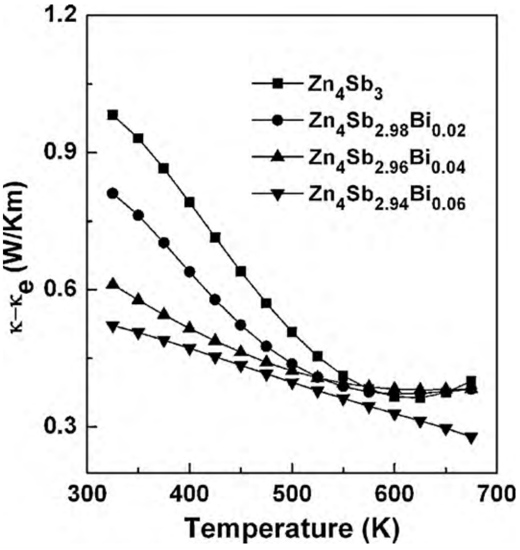

Fig. 5. Temperature dependence of lattice thermal conductivity ($\kappa - \kappa_e$) for the hot-pressed samples.

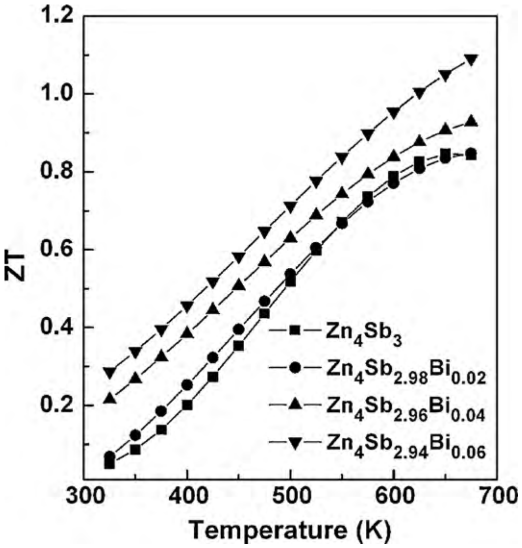

Fig. 6. Temperature dependence of ZT values for the hot-pressed samples.

Based on the date of α, σ and κ achieved above, the thermoelectric figure of merit ZT for all the studied samples can be calculated according to the formula: $ZT = \alpha^2\sigma T/\kappa$. The temperature dependence of dimensionless figure of merit (ZT) is shown in Fig. 6. Although the electrical conductivity of $Zn_4Sb_{3-x}Bi_x$ ($x = 0.04, 0.06$) is smaller than that of the undoped β-Zn_4Sb_3, the ZT values are increased with increasing Bi content. This is due to the improvement of thermoelectric power factor and the decrease of thermal conductivity. The ZT of $Zn_4Sb_{2.94}Bi_{0.06}$ reaches a maximum value of 1.09 at 673 K, which is 0.29 higher than that of the undoped Zn_4Sb_3 at the same conditions.

4. Conclusions

In this study, $Zn_4Sb_{3-x}Bi_x$ with $x = 0, 0.02, 0.04, 0.06$ are synthesized through vacuum melting method followed by hot-pressing method. For the compounds $Zn_4Sb_{3-x}Bi_x$ with $x = 0.04, 0.06$, a second phase of Bi is observed. The carrier concentration of β-Zn_4Sb_3 is decreased by Bi doping. Both the electrical conductivity and thermal conductivity of the doped β-Zn_4Sb_3 are found to reduce. The Seebeck coefficient of the Bi-doped samples is larger than that of the undoped β-Zn_4Sb_3. The ZT values are increased with increasing Bi content and the maximum ZT of 1.09 is obtained for the sample $Zn_4Sb_{2.94}Bi_{0.06}$ at 673 K, which shows that isoelectronic substitution of Bi for Sb is an effective way to reduce the lattice thermal conductivity and optimize the thermoelectric properties.

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