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ARTICLE

Thermoelectric Performance of Sb-doped $Mg_{2-x}Zn_xSi$ ($0 \le x \le 0.1$) Solid Solutions

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Abstract: $Mg_{2-x}Zn_xSi_{0.99}Sb_{0.01}$ ($0 \le x \le 0.1$) solid solutions were prepared by a B_2O_3 flux method combined with a spark plasma sintering (SPS) technique. The electrical conductivity, Seebeck coefficient and thermal conductivity were measured as a function of temperature from 300 K to 780 K. It is found that the lattice thermal conductivity reduces with Zn content increasing; however, the electrical conductivity first decreases and then increases. The underlying mechanism was discussed. Results show that among the samples, the maximum PF (power factor) of 1.76 $mW \cdot m^{-1} \cdot K^{-2}$ at x=0.075 is obtained at 780 K, about 18% higher than that of $Mg_2Si_{0.99}Sb_{0.01}$. The lowest lattice thermal conductivity of 2.86 $W \cdot m^{-1} \cdot K^{-1}$ is obtained at 770 K for the x=0.1 sample. As a result, a maximum dimensionless figure of merit of 0.37 is obtained for $Mg_{1.9}Zn_{0.1}Si_{0.99}Sb_{0.01}$ at 780 K.

Key words: magnesium silicides; thermoelectric property; thermoelectric materials; isoelectronic substitution

More and more attention are paid to thermoelectric (TE) materials due to their potential applications in converting heat into electricity. The conversion efficiency depends greatly on the dimensionless TE figure of merit $ZT = \alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity consisting of lattice (κ_L) and electronic (κ_e) components, and T is the temperature. On the other hand, the TE performance can be characterized by the factor β value, $\beta=(T/300)(m^*/m_e)^{3/2}\mu/\kappa_L$, where m^* is the carrier effective mass, and μ is the mobility in $cm^2 \cdot V \cdot s^{-1}$, because the figure of merit ZT is generally proportional to the factor β value in some materials [1]. The magnesium silicides have a larger β value of 14, compared to other traditional TE silicides such as SiGe (1.2~2.6) and β-$FeSi_2$ (0.05~0.8) [1]. Liu *et al*. found the low deformation potential and alloy scattering potential in the Mg_2Si based TE material[2]. The Mg_2Si is expected to have higher ZT values [3]. On the other hand, the Mg_2Si based compounds are cost-effective and eco-friendly candidates for future large-scale commercial application in mid-temperature thermoelectric power generation [4,5], especially in the energy harvesting from the automobile waste heat, which makes it superior to the traditional TE telluride materials.

To reduce the lattice thermal conductivity of Mg_2Si, isoelectric substitution between elements is an effective way. For instance [5], the element Sn is generally used to substitute for Si, which enhances the alloy scattering of phonons[6-10]. Zhang et al [5] studied the effect of Ca isoelectric substitution for Mg on the TE performance of Mg_2Si, and found that the alloying of Ca increased the electrical conductivity and decreased the Seebeck coefficient of Mg_2Si. While the effect of Zn substitution at the Mg site on the TE performance of Mg_2Si is unknown. In the present paper, we prepared Sb-doped $Mg_{2-x}Zn_xSi$ ($0 \le x \le 0.1$) and systematically studied the effect of Zn substitution on the Seebeck coefficient, electrical conductivity and lattice thermal conductivity.

1 Experiment

$Mg_{2-x}Zn_xSi_{0.99}Sb_{0.01}$ ($0 \le x \le 0.1$) solid solutions were synthesized by a B_2O_3 flux method [11]. Stoichiometric amounts of elemental Si (99.9%), Sb (99.5%), Zn (99.99%) and 5.0 mol% excess Mg (99.8%) powders were weighed, homogeneously mixed in an agate mortar, and then

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transferred into an alumina crucible. After the starting materials were covered by B_2O_3 powder and compacted, the crucible was placed into a chamber furnace, heated at 973 K for 10 h and finally cooled down to room temperature. After the alumina crucible was smashed, the B_2O_3 flux and the obtained product were easily separated from each other. The alloy ingots were ground and spark plasma sintered under a pressure of 80 MPa at 1073 K for 15 min.

The phase was identified by X-ray diffraction on a XRD-98 diffractometre using Cu Kα radiation. The thermal conductivity was calculated using $\kappa = D\rho C_p$, where ρ is the sample density estimated by an ordinary dimensional and weight measurement procedure. The thermal diffusivity D and specific heat C_p were measured by a laser flash method on a TC-1200RH apparatus with an inaccuracy of 7% and 5%, respectively. The electrical conductivity and Seebeck coefficient from 300~780 K were measured on a commercial Linseis LSR-3 system using a DC four-probe method and differential voltage/temperature technique, respectively. The errors in the measurement of electrical properties were evaluated to be within 8%. The Hall coefficient, R_H, was measured at 300 K on a Quantum Design PPMS-9T using a four-probe configuration, with the magnetic field sweeping between ± 6.0 T. The carrier concentration was calculated using the relation $n=(1/eR_H)$.

2 Results and Discussion

The XRD patterns are shown in Fig.1a. The most peaks of the samples can be indexed to the face-centered cubic structure with the space group of Fm3m according to JCPDS 35-0773, in addition to the weak peak at ~43° which corresponds to MgO (JCPDS 45-0946) and identified SiO_2 (JCPDS 46-1045) at $x \geq 0.075$. This indicates the formation of the Sb-doped $Mg_{2-x}Zn_xSi$ solid solution. The lattice constants of $Mg_{2-x}Zn_xSi_{0.99}Sb_{0.01}(0 \leq x \leq 0.1)$ samples, which are estimated from the XRD data in Fig.1a and plotted in Fig.1b, remain almost unchanged ~0.6356 nm with increasing of the Zn content, because the ionic radius of Zn is very close to that of Mg.

The temperature dependences of electrical conductivity are shown in Fig.2a. The fitted room temperature (RT) electrical conductivity of $Mg_2Si_{0.99}Sb_{0.01}$ is about 6.8×10^4 $S\cdot m^{-1}$, in agreement with that (~6.0×10^4 $S\cdot m^{-1}$) reported by Nolas[12]. With increasing of the Zn content, the electrical conductivity at RT decreases to ~3.6×10^4 $S\cdot m^{-1}$ until at x=0.025 and then increases to ~9.3×10^4 $S\cdot m^{-1}$ at x=0.1. The carrier concentration is 5.8×10^{19}, 4.7×10^{19}, 7.7×10^{19} and 1.0×10^{20} cm^{-3} for the x=0, 0.025, 0.075, 0.1 samples respectively, consistent with the change in the electrical conductivity. For the x=0.075 and x=0.1 samples, the increase in n may be due to the extra generation of the electrons in Mg_2Si caused by the enhancement of the point defect concentration (i.e. Mg interstitial and Si vacancy),

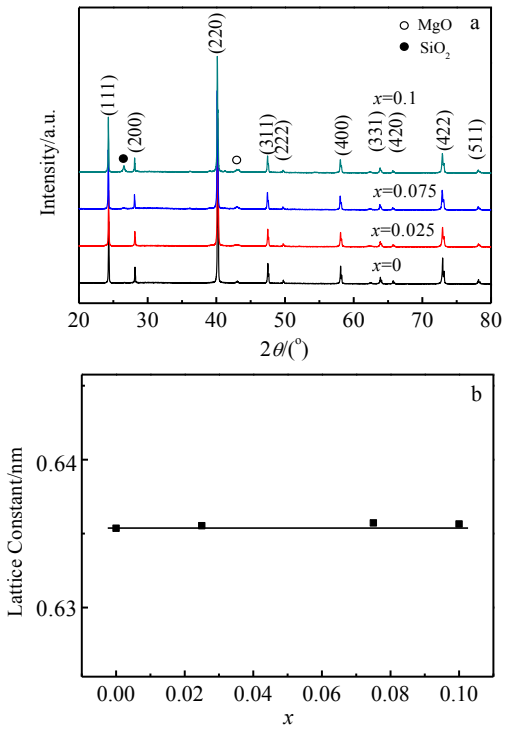

Fig.1 XRD patterns (a) and lattice constants (b) of the $Mg_{2-x}Zn_x$-$Si_{0.99}Sb_{0.01}(0 \leq x \leq 0.1)$ samples

according to Kato [13], because the formed impurity phase SiO_2 directly results in the deficiency of Si in the major Zn-substituted $Mg_2Si_{0.99}Sb_{0.01}$ phase.

The temperature dependences of Seebeck coefficient are shown in Fig.2b. All the Seebeck coefficients are negative in the temperature range studied for all the samples, indicative of n-type conduction. The Seebeck coefficients of all the samples increase with increasing of temperature. Because Seebeck coefficient is inversely proportional to the reduced Fermi energy $\alpha \propto (r + 3/2)/\eta_F$, where r is the scattering factor, η_F the reduced Fermi level, the increase of the Seebeck coefficient with the increase of temperature is due to the decrease of reduced Fermi level with increasing temperature. The Zn-substituted samples have lower Seebeck coefficients than the parent compound. The positive effect of enhancement in the electrical conductivity exceeds the negative effect of decrease in Seebeck coefficient and leads to the improvement of the PF for x= 0.075, 0.1 compared with x=0 (see Fig.2c). The maximum PF of 1.76 $mW\cdot m^{-1}\cdot K^{-2}$ at x=0.075 is obtained at 780 K, about 18% higher than that of $Mg_2Si_{0.99}Sb_{0.01}$.

The thermal conductivity as a function of temperature for all the samples is shown in Fig.3a. The RT thermal conductivity of the parent compound is 6.3 $W\cdot m^{-1}\cdot K^{-1}$, larger than that (4.5 $W\cdot m^{-1}\cdot K^{-1}$) reported by Zhang [5]. The lattice thermal conductivity, κ_L, values are estimated by subtracting the carrier thermal conductivity, κ_e, from