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Thermoelectric Performance of Quaternary Mg$_2$Si$_{0.27}$Ge$_{0.05}$-Sn$_{0.65}$Sb$_{0.03}$ Solid Solutions

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Abstract: Single–phased Mg$_{2(1+x)}$Si$_{0.27}$Ge$_{0.05}$Sn$_{0.65}$Sb$_{0.03}$ (x=0.05, 0.08) quaternary solid solutions were prepared by B$_2$O$_3$ flux method followed by spark plasma sintering (SPS). The electrical conductivity, Seebeck coefficient and thermal conductivity were measured from 300 to 800 K. The results show that the electrical conductivity increases while the Seebeck coefficient decreases with temperature rising for these samples. The lattice thermal conductivities of all the samples are higher than the calculated value using the Abeles model. A maximum ZT of 1.0 at 800 K is obtained in the sample with x=0.08.

Key words: magnesium silicides; thermoelectric properties; thermoelectric materials; quaternary solid solution

Driven by energy shortage and climate change, more and more attention are being paid on thermoelectric (TE) devices that are all solid-state assembly, quiet, and maintenance-free and can directly convert heat into electricity from different sources such as solar heat, geothermal heat, and the exhaust of automobiles. The conversion efficiency is decided by the dimensionless figure of merit, ZT, of the materials of which the device is made. $ZT = \alpha^2 \sigma T/\kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the temperature in Kelvin.

ZT is proportional to the factor $\beta = (m^*/m_0)^{3/2}\mu/\kappa_L$, where m^* is the carrier effective mass, μ is the mobility in cm$^2\cdot$V$^{-1}\cdot$s^{-1}, and κ_L is the lattice thermal conductivity in mW$\cdot$cm$^{-1}\cdot$K^{-1} [1]. The β value of Mg$_2$X (X=Si, Ge, Sn) compounds is 3.7~14 which is larger than that of other traditional TE silicides such as SiGe (1.2~2.6) and β-FeSi$_2$ (0.05~0.8). Therefore, the Mg$_2$X based TE material is expected to have higher ZT values[2]. In addition, Mg$_2$X based TE materials are cost-effective and eco-friendly candidates for future large-scale commercial application in mid-temperature thermoelectric power generation, especially in the energy harvesting from the automobile waste heat. These advantages make it superior to the traditional TE telluride materials.

To date, the investigation on Mg$_2$X based TE material focuses on Mg$_2$(Si,Sn) ternary solid solutions[3]. For example, the effect of antimony and bismuth doping, magnesium excess and conduction band convergence on the TE properties of the Mg$_2$(Si,Sn) ternary solid solutions are studied in Ref. [4-6]. However, the investigation on Mg$_2$(Si,Ge,Sn) quaternary solid solutions is rather limited. In this research, we prepared quaternary Mg$_{2(1+x)}$Si$_{0.27}$Ge$_{0.05}$Sn$_{0.65}$Sb$_{0.03}$ (x=0.05,0.08) solid solutions and studied their TE properties.

1 Experiment

Mg$_{2(1+x)}$Si$_{0.27}$Ge$_{0.05}$Sn$_{0.65}$Sb$_{0.03}$ (x=0.05, 0.08) solid solutions were synthesized by a B$_2$O$_3$ flux method[7]. Stoichiometric amounts of elemental Si (99.9%), Sn (99.9%), Ge (99.999%) and Mg (99.8%) powder were weighed, homogeneously mixed in an agate mortar in a glove box, and then transferred into an alumina crucible. After the starting materials were covered by B$_2$O$_3$ powders 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$_2$O$_3$ flux and the obtained product were easily separated from each other. The alloy ingots were ground in the glove box and sintered by the spark plasma

sintering (SPS) method under a pressure of 50 MPa at 978~ 993 K for 10 min.

The phase was checked by X-ray diffraction on a XRD-98 diffractometer operating at 50 kV and 40 mA. Cu Kαradiation (λ=0.154 06 nm) and a scan rate of 4°·min^{-1} were used to record the patterns. The thermal conductivity was calculated using $K=D\rho C_p$, 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. Since the composition of the samples is very close to each other and a small amount of magnesium excess does not affect the C_p markedly. We only measured the C_p for x=0.08 (Fig.1) and used it to calculate K for all the samples. The Seebeck coefficients (α) and electrical conductivities (σ) as a function of temperature were measured using an ULVAC ZEM-3 instrument system in a helium atmosphere between RT and 800 K. A temperature difference of approximately 5 °C was applied between the two terminals of the samples in order to measure the Seebeck coefficient, whereas the electrical conductivity was measured using the four-probe method. The measurement uncertainties were 5% for α and 6% for σ.

2 Results and Discussion

Fig.2 presents the XRD patterns of Mg$_{2(1+x)}$Si$_{0.27}$Ge$_{0.05}$-Sn$_{0.65}$Sb$_{0.03}$ (x=0.05, 0.08) quaternary solid solutions. All diffraction peaks can be indexed to an anti-fluorite-type structure (space group, Fm-3m). No magnesium oxide and other impurities were detected in the diffraction patterns, indicating the effectiveness of the preparation method. All the peaks are located between that of binary Mg$_2$Si (JCPDS #35-0773) and Mg$_2$Sn (JCPDS #07-0274), confirming the formation of the Mg$_2$(Si,Ge,Sn) solid solution.

The temperature dependences of electrical conductivity and Seebeck coefficient of Mg$_{2(1+x)}$Si$_{0.27}$Ge$_{0.05}$Sn$_{0.65}$Sb$_{0.03}$ (x=0.05, 0.08) samples are shown in Fig.3a and 3b, respectively. The electrical conductivity dereases with temperature for all the samples, indicating a metal-like behavior. The RT electrical
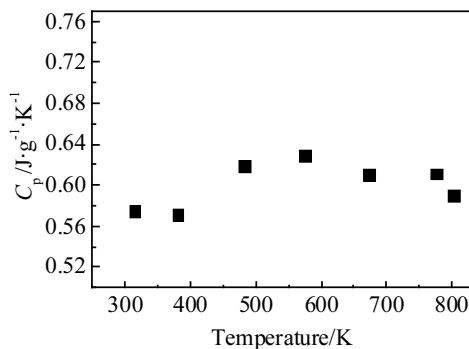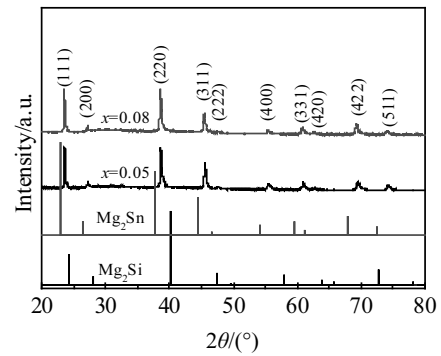

Fig.2 XRD patterns of the Mg$_{2(1+x)}$Si$_{0.27}$Ge$_{0.05}$Sn$_{0.65}$Sb$_{0.03}$ (x=0.05, 0.08) samples

conductivity σ increases markedly from 1.7×10^5 S·m^{-1} for x=0.05 to 2.5×10^5 S·m^{-1} for x=0.08, consistent with that of ternary Mg$_2$Si$_{0.4}$Sn$_{0.6}$ solid solution[5]. This enhancement is due to the interstitial magnesium which donates electrons to the conduction band[5]. The Seebeck coefficients for all the samples are negative in the whole temperature range, indicating n-type conduction behavior. It decreases with increasing Mg excess amount, in junction with the behavior of electrical conductivity. With increasing temperature the Seebeck coefficient of all the samples monotonically increases. This can be explained in the light of the following relation. $\alpha \propto (r+3/2)/\eta_F$, where r is the scattering factor, and η_F is the reduced Fermi level. The increase of the Seebeck coefficient is a result of the decrease of reduced Fermi level with increasing temperature. We calculated the temperature dependences of power factor (PF) for the samples, as shown in Fig.3c. The PF for x=0.08 is higher than that of the x=0.05 mainly due to the enhanced electrical conductivity. A maximum PF of 3.8 W·m^{-1}·K^{-2} is obtained at ~770 K for x=0.08.

Fig.4a presents the temperature dependence of thermal conductivity, κ, of the Mg$_{2(1+x)}$Si$_{0.27}$Ge$_{0.05}$Sn$_{0.65}$Sb$_{0.03}$ (x=0.05, 0.08) samples. The thermal conductivity increases with increasing Mg content due to the enhanced electrical conductivity. The lattice thermal conductivity, κ_L, values were estimated by subtracting the carrier thermal conductivity, κ_e, from κ using the Wiedemann–Franz relation, $\kappa_e = L_0\sigma T$, where Lorentz number $L_0 = 2\times10^{-8}$ V^2·K^{-2} is used for estimation. The temperature dependence of the lattice thermal conductivity is plotted in Fig.3b. The room temperature lattice thermal conductivity decreases as Mg excess increases in the range of 2.8 W·m^{-1}·K^{-1} to 2.5 W·m^{-1}·K^{-1}. It was reported that the bismuth interstitial can decrease the lattice thermal conduc-tivity obviously in the Mg$_2$(Si,Sn) ternary solid solution[8]. The decrease of the lattice thermal conductivity may be due to the Mg interstitials. Because the interstitial atoms act as phonon scattering centre and reduce the lattice thermal conductivity. The smallest lattice thermal conductivity of 1.6 W·m^{-1}·K^{-1} is obtained in the sample with x =0.05 at 800 K.

Fig.1 Specific heat capacity of the Mg$_{2.16}$Si$_{0.27}$Ge$_{0.05}$Sn$_{0.65}$Sb$_{0.03}$ sample
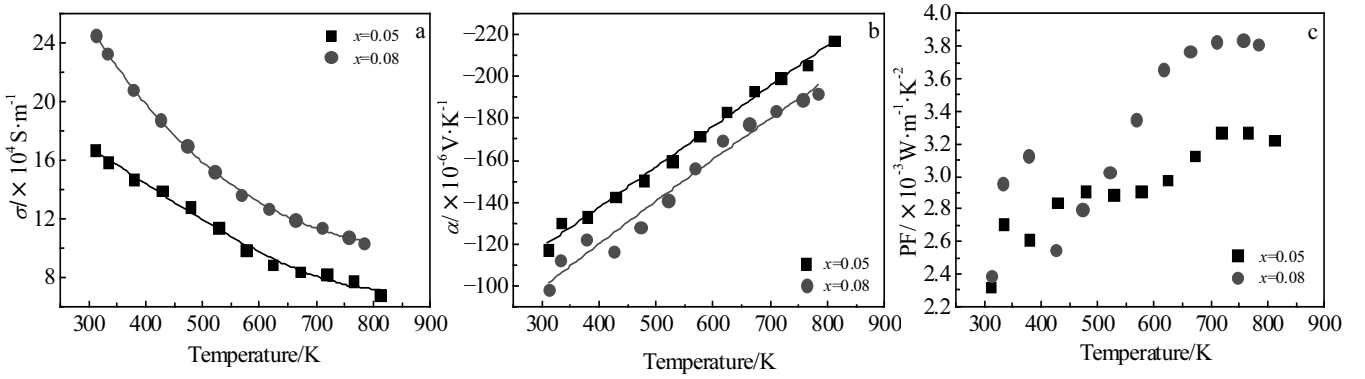
Fig.3   Temperature dependences of electrical conductivity σ (a), Seebeck coefficient α (b), and power factor (PF) (c) for the $Mg_{2(1+x)}Si_{0.27}Ge_{0.05}$-$Sn_{0.65}Sb_{0.03}$ (x=0.05, 0.08) samples
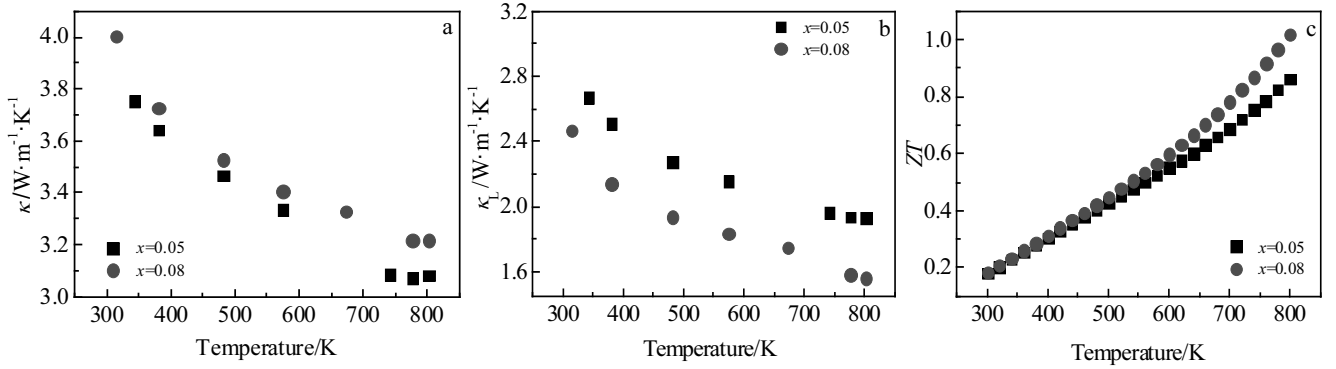

Fig.4   Temperature dependences of thermal conductivity κ (a), lattice thermal conductivity κ_L (b), and ZT (c) of the $Mg_{2(1+x)}Si_{0.27}Ge_{0.05}Sn_{0.65}Sb_{0.03}$ (x=0.05, 0.08) samples

Abeles[9] has proposed a phenomenological approach to calculate a lattice thermal conductivity of disordered solid solutions at high temperatures. His theory has been based on the model presented by Klemens[10] and Callaway[11]. This model has been successfully used for many semiconductor solid solutions [12]. We used the model to estimate the lattice thermal conductivity of $Mg_2Si_{0.3}Ge_{0.05}Sn_{0.65}$ quaternary solid solution. The lattice thermal conductivity containing the contributions of the normal process, Umklapp process and point defect scattering process can be expressed by [9,13]

$$\frac{\kappa_L}{\kappa_u} = (1 + \frac{5}{9}\lambda)\left[\frac{\arctan y}{y} + \frac{(1 - \arctan y/y)^2}{\left[(1+\lambda)y^4/5\lambda - y^2/3 + 1 - (\arctan y/y)\right]}\right] \quad (1)$$

where

$$y^2 = \frac{\pi^2 \kappa_u \Theta_D \overline{M}}{(1 + 5\lambda/9)\overline{v}^2 \rho h}\left[\frac{1}{\overline{M}^2}\sum_i x_i(M_i - \overline{M})^2 + \frac{\varepsilon}{\delta^2}\sum_i x_i(\delta_i - \delta)^2\right] \quad (2)$$

$$\overline{M} = \sum_i x_i M_i \quad (3)$$

$$\delta = x_i \delta_i \quad (4)$$

κ_u is the theoretical thermal conductivity of the material without any defects, ρ is the density, h is the Planck constant,

and λ is the parameter indicating the contribution of normal processes in thermal conductivity, which is 0.04 for the $Mg_2A_xB_{1-x}$ system[13]. δ_i and δ are a cubic root of average volume per an atom or molecule in the lattice of component and solid solution, respectively. x_i is the concentration of a component. M_i and $\overline{M}$ is atomic (molecular) weight of a component and the alloy, respectively. ε is a fitting parameter[9], which is about 23 for $Mg_2A_xB_{1-x}$ system[13], $\overline{v}$ is the average sound velocity. For a solid solution the following parameters can be determined by linear interpolation [13].

$$\kappa_u = x_i \kappa_i \quad (5)$$

$$\Theta_D = x_i \Theta_{Di} \quad (6)$$

$$\overline{v} = x_i v_i \quad (7)$$

The parameters used in the calculation are listed in Table 1. The lattice constant, thermal conductivity of Mg_2X (X=Si, Ge, Sn) in Ref. [14, 15] was used in the calculation.

According to the model, the RT lattice thermal conductivity of $Mg_2Si_{0.3}Ge_{0.05}Sn_{0.65}$ quaternary solid solution is 1.6 $W \cdot m^{-1} \cdot K^{-1}$, which is obviously smaller than the experimental value. This suggests that the Si, Ge and Sn atoms mix inhomogeneously at the atomic scale. Only a part of atomic weight and radius

Table 1   Lattice constant, Debye temperature, longitudinal and transversal sound velocity used in the calculation using Abeles model

Parameters	Mg$_2$Si	Mg$_2$Ge	Mg$_2$Sn
Lattice constant/nm	0.638[13]	0.638[16]	0.676[16]
Debye temperature/K	578[17]	488[18]	339[19]
Longitudinal sound velocity/km·s^{-1}	7.7[17]	6.3[18]	5.0[19]
Transversal sound velocity/km·s^{-1}	4.9[17]	3.8[18]	3.0[19]
Average sound velocity/km·s^{-1}	5.4	4.2	3.3

difference between Si/Ge, Si/Sn and Ge/Sn scatter the phonons, resulting in the higher lattice thermal conductivity in the Mg$_2$Si$_{0.3}$Ge$_{0.05}$Sn$_{0.65}$ quaternary solid solution. These defects and their effect needs further study. With σ, α, and κ known, the temperature dependence of ZT for Mg$_{2(1+x)}$Si$_{0.27}$Ge$_{0.05}$Sn$_{0.65}$Sb$_{0.03}$ (x=0.05, 0.08) was calculated and is presented in Fig3c. Due to the obviously enhanced electrical conductivity, a maximum ZT value of 1.0 is obtained at 800 K for x=0.08.

3   Conclusions

1) The electrical conductivity of Mg$_{2(1+x)}$Si$_{0.27}$Ge$_{0.05}$Sn$_{0.65}$Sb$_{0.03}$ (x=0.05, 0.08) decreases while the Seebeck coefficient increases with temperature.

2) The lattice thermal conductivity of the samples is higher than the calculated value using the Abeles model.

3) Due to high electrical conductivity and moderate Seebeck coefficient, the sample with x=0.08 has the maximum ZT of 1.0 at 760 K.

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四元 Mg$_2$Si$_{0.27}$Ge$_{0.05}$Sn$_{0.65}$Sb$_{0.03}$ 固溶体的热电性能

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摘　要：通过氧化硼助熔剂法和放电等离子烧结技术制备了 Mg$_{2(1+x)}$Si$_{0.27}$Ge$_{0.05}$Sn$_{0.65}$Sb$_{0.03}$ (x=0.05，0.08) 四元固溶体热电材料。在 300~800 K 的温度区间内测试了所有四元固溶体试样的塞贝克系数、电导率和热导率。结果表明随着温度的升高电导率单调降低而塞贝克系数单调升高，所有样品的晶格热导率明显高于通过 Abeles 模型计算所得到的理论值。最高无量纲热电优值 ZT 出现在 x=0.08 样品中，在 800 K 时达到最高值 1.0。

关键词：硅化镁；热电性能；热电材料；四元固溶体

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