ELSEVIER

International Journal of Minerals, Metallurgy and Materials
Volume 16, Number 5, October 2009, Page 564

Materials

Thermoelectric properties of quaternary $Mg_2Sn_{0.4}Si_{0.6-x}Ge_x$ alloys

Hao Yin, Xin-Bing Zhao, Qian Zhang, and Tie-Jun Zhu

State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China
(Received 2008-10-08)

Abstract: Quaternary alloys $Mg_2Sn_{0.4}Si_{0.6-x}Ge_x$ (x=0, 0.02, 0.05, 0.08 0.1, and 0.2) were prepared using induction melting followed by hot-pressing. Relative densities of the sintered samples were over 97% of the theoretical values. Multiple phases were detected in the samples. It was found that the Seebeck coefficient was sensitive to the content of Mg_2Ge and a maximum value of about 350 $\mu V \cdot K^{-1}$ was obtained. The introduction of Ge increases the electrical conductivity and the thermal conductivity simultaneously. The mechanism of this phenomenon was discussed. A maximum dimensionless figure of merit, ZT, of about 0.28 was obtained for $Mg_2Sn_{0.4}Si_{0.55}Ge_{0.05}$ at 550 K.

Key words: thermoelectric materials; hot-pressing; thermal conductivity; induction melting; quaternary alloys

[*This work was financially supported by the National Natural Science Foundation of China (No.50522203, 50731006) and the National Basic Research Program of China (No.2007CB607502)*.]

1. Introduction

Both energy shortage and environmental burden compel us to seek for all kinds of new resources. New power generators are all characterized by clean, green, or renewable. Among these, thermoelectric (TE) power generators, which can directly convert heat into electricity, are gaining more and more focuses recently because of their unique advantages such as no moving parts, no noise, less maintenance, and long life [1-4]. Dimensionless figure of merit $ZT=\alpha^2\sigma T/\kappa$ of TE materials is usually used to evaluate the efficiency of a TE device, where α is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity, and T the Kelvin temperature. $\alpha^2\sigma$ is also defined as the power factor to determine the electrical property of TE materials. The constituent elements of Mg_2-IV (IV is Si, Sn, or Ge) compound, as a kind of TE materials, are environmental friendly and cheap. Thus, Mg_2Si, Mg_2Sn, and Mg_2Ge are expected to be promising TE materials for power generation in the middle temperature range (400-800 K) [5-9]. In this paper, quaternary alloys $Mg_2Sn_{0.4}Si_{0.6-x}Ge_x$ were prepared by induction melting and hot-pressing to increase electrical conductivity and optimize the semiconductor properties, which has not been reported before.

2. Experimental

The starting materials of Mg_2Si, Mg_2Sn, and Mg_2Ge were prepared by induction melting of constituent elements of granular Mg (99.9% in purity), Si (99.9999%), Sn (99.9%), and Ge (99.999%). The ingots gained were ground into powder (under 40×10^{-6} m in diameter). The powders were mixed to the designed compositions of $Mg_2Sn_{0.4}Si_{0.6-x}Ge_x$, ($x$=0, 0.02, 0.05, 0.08, 0.1, 0.2), and hot-pressed under a pressure of 80 MPa at 973 K for 2 h in vacuum. The disks obtained were 12.6 mm in diameter with a thickness of about 2 mm. Relative densities of the compacts measured by the Archimedes method were about 97% of the theoretical values. X-ray powder diffraction (XRD) was conducted on a RigakuD/MAX-2550PC diffractometer using Cu K_α radiation (λ=1.5406×10^{-10} m). The samples of necessary size for electrical and thermal measurements were cut from the disks. The Seebeck coefficient α and electrical conductivity σ were measured from room temperature to 723 K using a four-probe method. The temperature difference between both ends of the sample for measuring the Seebeck coefficient was about 5 K. Electrical conductivity was calculated from the sample dimensions and the

Corresponding author: Xin-bing Zhao, **E-mail:** zhaoxb@zju.edu.cn
Also available online at www.sciencedirect.com

average resistance measured with the forward and reversed currents [10]. The thermal diffusivity D and the specific heat capacity C_p of the samples were measured by a laser flash apparatus (Netzsch LFA 457) and a thermal analyzer (Netzsch DSC 404), respectively. The thermal conductivity was then calculated from the relationship $\kappa=\rho DC_p$, where ρ is the density of the material.

3. Results and discussion

XRD patterns of $Mg_2Sn_{0.4}Si_{0.6-x}Ge_x$, ($x$ =0, 0.02, 0.05, 0.08, 0.1, 0.2) are shown in Fig. 1. All the peaks of the samples can be indexed to Mg_2Si, Mg_2Sn, and Mg_2Ge based solid solution phases with the face-centered cubic structure and the space group of $Fm3m$, indicating that the samples are composed of multiple phases. Furthermore, as Ge increases, the peaks indexed to the same diffraction crystal plane move closer, which means that Ge improves the solid solubility between both Si- and Sn-rich phases. This might be because Ge, whose atom radius (1.22×10^{-10} m) is between Si (1.11×10^{-10} m) and Sn (1.41×10^{-10} m), decreases the lattice size difference between Mg_2Si and Mg_2Sn phases [11].

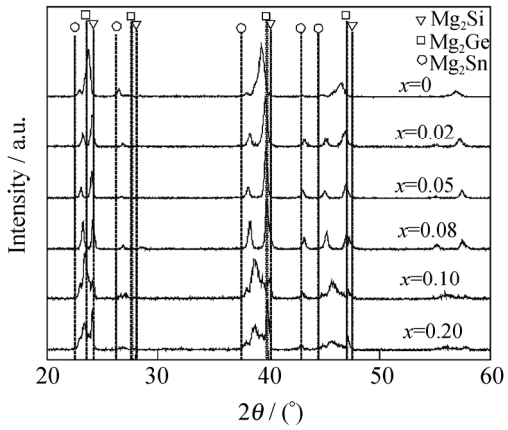

Fig. 1. XRD patterns of $Mg_2Sn_{0.4}Si_{0.6-x}Ge_x$.

Absolute values of the Seebeck coefficient of all the samples are displayed in Fig. 2, plotted as a function of the measuring temperatures. The samples with $x\leq0.08$ are n-type while $Mg_2Sn_{0.4}Si_{0.4}Ge_{0.2}$ and $Mg_2Sn_{0.4}Si_{0.5}Ge_{0.1}$ show p-type characters. This phenomenon might be caused by the conductivity of Mg_2Ge, which is p-type, different from the n-type conduction of Mg_2Si and Mg_2Sn. The maximum value of p-type samples is about 325 $\mu V\cdot K^{-1}$ at 400 K for $Mg_2Sn_{0.4}Si_{0.4}Ge_{0.2}$. The Seebeck coefficient of n-type compacts shows similar trends with the temperature and intensity dependence on composition. All the measured Seebeck coefficients ascend with temperature, reach peak values at about 550 K and go down at higher temperatures because of an increasing number of thermally excited minority carriers. A maximum value of $|\alpha|$=350 $\mu V\cdot K^{-1}$ was obtained in $Mg_2Sn_{0.4}Si_{0.6}$ (x=0).

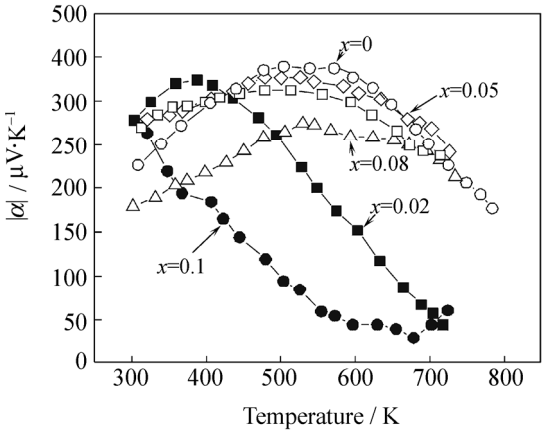

Fig. 2. Temperature dependence of $|\alpha|$ for $Mg_2Sn_{0.4}Si_{0.6-x}Ge_x$ (α of the samples with x=0, 0.02, 0.05, and 0.08 are negative).

Curves of electrical conductivity against temperature are plotted in Fig. 3(a). With the increase in Ge content, the electrical conductivities increase, reaching the maximum in sample x=0.05. All the electrical conductivities measured go up at lower temperatures, which are induced by increasing the carrier numbers. A mild platform can be observed which might be caused by the decrease of carrier mobility, and then a remarkable increase follows over 650 K which is believed to be affected by intrinsic excitations. Samples with x=0.02, 0.05, 0.08 show higher values in the whole temperature range. The band gaps, E_g, are 0.77, 0.74, and 0.35 eV for Mg_2Si, Mg_2Ge, and Mg_2Sn, respectively [11]. E_g might decrease after adding Mg_2Ge, which makes it easier for electrons to jump from the valence band to conduction band. Thus, the electrical conductivity might increase. Fig. 3(b) is the relationship of $\ln\sigma$ and $1000/T$. The calculated E_g values for all the samples with Ge are shown in Table 1 [12].

The temperature dependence of thermal conductivity κ of all the samples is shown in Fig. 4(a). κ consists of electronic contribution κ_{el} and lattice contribution κ_{ph}. According to the Wiedemann-Franz rule, $\kappa_{el}=L_0\sigma T$, where L_0 is the Lorenz number 2.45×10^{-8} $V^{-2}\cdot K^2$ for heavily doped semiconductors [13-14]. All the electronic thermal conductivities calculated in these samples are far smaller than total κ. That is to say, lattice thermal conductivity plays predominant role in total κ [15]. In the ternary system Mg-Si-Sn, the difference in volume of atoms between Si and Sn strengthens the phonons scattering of crystal defects which dramatically reduce the thermal conductivity compared with Mg_2Si. However, in the quaternary system, Ge, whose atom volume is in the middle of Si and Sn, abates this effect. The upward trends that all

the samples show with the increase of x could support the conclusion. When the temperature exceeds 650 K, intrinsic excitations increase the κ values. The lowest thermal conductivity is obtained from $Mg_2Sn_{0.4}Si_{0.6}$, which is about 1.65 $W \cdot m^{-1} \cdot K^{-1}$. The ratios of σ/κ are also calculated and presented in Fig. 4(b), from which we can see that the ratios of the samples with $0<x<0.2$ are higher than that of $Mg_2Sn_{0.4}Si_{0.6}$ (x=0). This indicates that the solubility of Ge is an effective way to increase the thermoelectric properties.

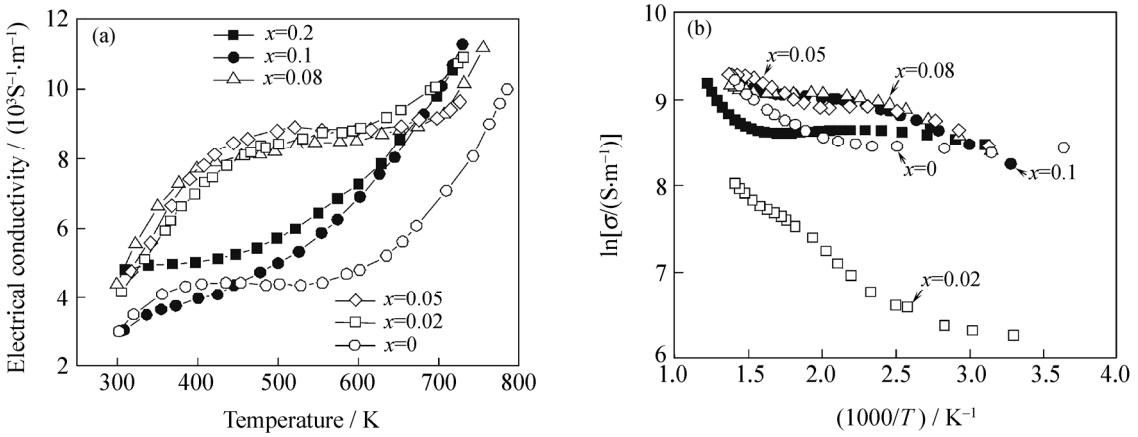

Fig. 3. Temperature dependence of electrical conductivity for $Mg_2Sn_{0.4}Si_{0.6-x}Ge_x$ (a) and the relationship between $\ln\sigma$ and $1000/T$ (b).

Table 1. Calculated E_g values of $Mg_2Sn_{0.4}Si_{0.6-x}Ge$

x	0	0.02	0.05	0.08	0.10	0.20
E_g / eV	0.58	0.44	0.35	0.37	0.39	0.62

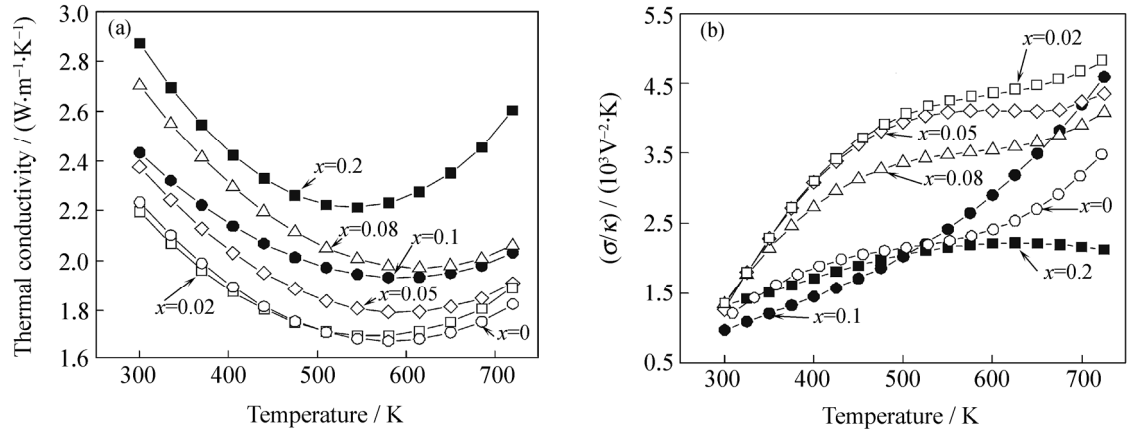

Fig. 4. Temperature dependences of thermal conductivity (a) and σ/κ (b) for $Mg_2Sn_{0.4}Si_{0.6-x}Ge_x$.

Fig. 5 shows the dimensionless figure of merit ZT of all the samples against temperature.

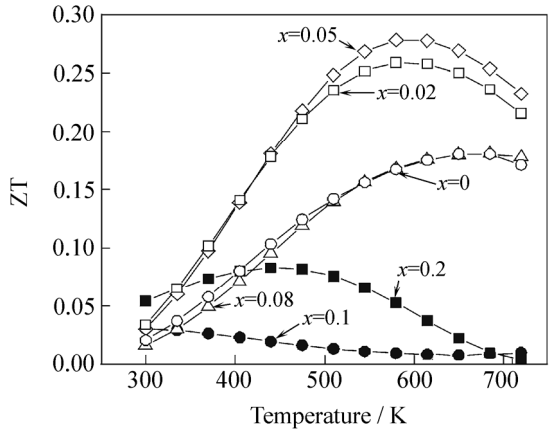

Fig. 5. Temperature dependence of the dimensionless figure of merit ZT for $Mg_2Sn_{0.4}Si_{0.6-x}Ge_x$.

Because of the higher electrical conductivities and lower thermal conductivities of $Mg_2Sn_{0.4}Si_{0.55}Ge_{0.05}$ and $Mg_2Sn_{0.4}$-$Si_{0.58}Ge_{0.02}$, the ZT values of these samples exceed those of other ones. The maximum ZT value of ~0.28 at about 550 K is obtained for $Mg_2Sn_{0.4}Si_{0.55}Ge_{0.05}$.

4. Conclusion

Thermoelectric properties of the quaternary system $Mg_2Sn_{0.4}Si_{0.6-x}Ge_x$ prepared by induction melting followed by hot-pressing were evaluated. XRD patterns revealed that all the compacts contained multiple phases. The maximum Seebeck coefficient and electrical conductivity were measured to be about 325 $\mu V \cdot K^{-1}$ for p-type and -350 $\mu V \cdot K^{-1}$ for n-type and over 11000 $S \cdot m^{-1}$, respectively. σ/κ increases after

adding Ge though a higher lattice thermal conductivity was obtained. The maximum ZT value was about 0.28 for $Mg_2Sn_{0.4}Si_{0.55}Ge_{0.05}$.

References

[1] B.C. Sales, D. Mandrus, and R.K. Williams, Filled skutterudite antimonides: A new class of thermoelectric materials, *Science*, 272(1996), p.1325.

[2] T.C. Harman, P.J. Taylor, M.P. Walsh, and B.E. LaForge, Quantum dot superlattice thermoelectric materials and devices, *Science*, 297(2002), p.2229.

[3] T.M. Tritt, Thermoelectrics run hot and cold, *Science*, 272(1996), p.1276.

[4] X.B. Zhao, X.H. Ji, Y.H. Zhang, T.J. Zhu, J.P. Tu, and X.B. Zhang, Thermoelectric bismuth telluride nanotubes synthesized by hydrothermal method, *Appl. Phys. Lett.*, 86(2005), Art. No.062111.

[5] V.K. Zaitsev, M.I. Fedorov, E.A. Gurieva, I.S. Eremin, P.P. Konstantinov, A. Yu. Samunin, and M.V. Vedemikov, Highly effective $Mg_2Si_{1-x}Sn_x$ thermoelectrics, *Phys. Rev. B*, 74(2006), Art. No.045207.

[6] Q. Zhang, J. He, T.J. Zhu, S.N. Zhang, X.B. Zhao, and T.M. Tritt, High figures of merit and natural nanostructures in $Mg_2Si_{0.4}Sn_{0.6}$ based thermoelectric materials, *Appl. Phys. Lett.*, 93(2008), Art. No.102109.

[7] M. Akasaka, T. Ilda, A. Matsumoto, K. Yamanaka, Y. Takanashi, T. Imai, and N. Hamada, The thermoelectric properties of bulk crystalline n- and p-type Mg_2Si prepared by the vertical Bridgman method, *J. Appl. Phys.*, 104(2008), Art. No. 013703.

[8] G.S. Nolas, D. Wand, and M. Beekman, Transport properties of polycrystalline $Mg_2Si_{1-y}Sb_y$ ($0 \leqslant y < 0.4$), *Phys. Rev. B*, 76(2007), Art. No.235204.

[9] Q. Zhang, H. Yin, X.B. Zhao, J. He, X.H. Ji, T.J. Zhu, and T.M. Tritt, Thermoelectric properties of n-type $Mg_2Si_{0.6-y}Sb_ySn_{0.4}$ compounds, *Phys. Status Solidi A*, 205(2008), No.7, p.1657.

[10] Q. Zhang, J. He, X.B. Zhao, S.N. Zhang, T.J. Zhu, H. Yin, and T.M. Tritt, *In Situ* Synthesis and thermoelectric properties of La-doped Mg_2(Si, Sn) composites, *J. Phys. D*, 41(2008), Art. No.185103.

[11] G.A. Slack and D.M. Rowe, *CRC Handbook of Thermoelectrics*, CRC Press, Boca Raton, 1995.

[12] T. Kajikawa, K. Shida, K. Shiraishi, and T. Ito, Thermoelectric figure of merit of impurity doped and hot-pressed magnesium silicide elements, [in] *Proceedings of the 17th International Conference on Thermoelectrics*, Nagoya, 1998, p.362.

[13] Y. Noda, H. Kon, Y. Furukawa, I.A. Nishida, and K. Masumoto, Temperature dependence of thermoelectric properties of $Mg_2Si_{0.6}Ge_{0.4}$, *Mater. Trans. JIM*, 33(1992), No.9, p.845.

[14] T. Aizawa, R. Song, and A. Yamamoto, Solid-state synthesis of thermoelectric materials in Mg-Si-Ge system, *Mater. Trans.*, 46(2005), No.7, p.1490.

[15] M. Riffel and J. Schilz, Mechanically alloyed $Mg_2Si_{1-x}Sn_x$ solid solutions as thermoelectric materials, [in] *Proceedings of the 17th International Conference on Thermoelectrics*, Pasadena, 1996, p.133.