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Thermoelectric performance of $Mg_{2-x}Ca_xSi$ compounds

Q. Zhang, X.B. Zhao *, H. Yin, T.J. Zhu

State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China

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Abstract

Thermoelectric materials $Mg_{2-x}Ca_xSi$ ($x = 0$, 0.01, 0.03, 0.05, 0.07, 0.1) compounds have been prepared by vacuum melting followed by hot-pressing. Effects of the substitution of Ca for Mg on phase structures and the thermoelectric properties of the hot-pressed compounds were investigated. It was found that the alloying of Ca in Mg_2Si based compounds increases the electrical conductivity and decreases the Seebeck coefficient of the compounds, due to the electronegativity difference between Ca and Mg. The dimensionless figures of merit of Mg_2Si and $Mg_{1.99}Ca_{0.01}Si$ reach, respectively, 0.41 and 0.34 at 660 K.

Keywords: Thermoelectric materials; Intermetallics; Thermoelectrics

1. Introduction

Thermoelectric materials have received renewed interests due to their potential applications in power generation and solid state cooling with the merits of compactness, static operation, long life and environmental compatibility [1–3]. The quality of a thermoelectric material is evaluated by a dimensionless figure of merit $ZT = \alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity and T the temperature in Kelvin. The electrical property is represented by the power factor $\alpha^2\sigma$, which is generally optimized by doping. The total thermal conductivity κ contains both lattice and electronic contributions κ_{ph} and κ_e, respectively, which must be minimized to maximize ZT.

Continuous work has been done on Mg_2Si based compounds for application in moderate temperature power generation [4–15], since polycrystalline Mg_2Si was first synthesized [16]. Based on the classical thermoelectric theory, the factor $m^{*3/2}\mu/\kappa_{ph}$ can be viewed as the criterion for thermoelectric material filter, where m^* is the density of states effective mass and μ the carrier mobility. The factor is 14 for magnesium silicides, compared to 0.8 for iron silicides, 2.6 for silicon germanium alloys and 1.4 for manganese silicides [17], indicating that Mg_2Si based compounds are promising for thermoelectric applications. Recently Zaitsev et al. [4] reported that the ZT value has reached 1.1 for Sb doped $Mg_2Si_{0.4}Sn_{0.6}$.

Ternary Mg_2B^{IV} (B^{IV} = Si, Ge, Sn) solid solutions are generally applied to decrease the phonon thermal conductivity by the enhanced point defect scattering, because the thermal conductivity of pure binary compounds is too high to result in a good thermoelectric performance [4,11]. However, reports on the solid solutions with elemental substitution at Mg sites are absent. Mg_2Si is a cubic semiconductor crystallizing in the antifluorite structure (space group $Fm3m$), while all the other existing $A_2^{II}Si$ (A^{II} = Ca, Sr, Ba) alloys stabilize in orthorhombic structures (space group $Pnma$) [18]. This reduces the solid solubility of element A^{II} in Mg_2Si. In this paper, $Mg_{2-x}Ca_xSi$ ($x = 0$, 0.01, 0.03, 0.05, 0.07, 0.1) compounds were prepared by melting and hot-pressing. The effects of the content of calcium on the thermoelectric properties were investigated.

2. Experimental methods

$Mg_{2-x}Ca_xSi$ ($x = 0$, 0.01, 0.03, 0.05, 0.07, 0.1) compounds were prepared by directly melting elemental Mg (99.9%), Si (99.999%), and Ca (98%) granules in a medium-frequency induction furnace under argon atmosphere. The ingots were ground, sieved with a 38.5 μm sieve and hot-pressed at 850 °C for 40 min under a pressure of 80 MPa. The densities of the samples were measured by Archimedes method. The crystal structures were characterized by X-ray diffraction (XRD) using a Rigaku D/MAX-2550PC diffractometer with Cu Kα radiation (λ = 1.5406 Å). The electrical conductivity and the Seebeck coefficient were simultaneously measured using a computer-assisted device. The electrical conductivity was calculated from the sample dimensions and the average resis-

* Corresponding author. Tel.: +86 571 87951451; fax: +86 571 87951451.
E-mail address: zhaoxb@zju.edu.cn (X.B. Zhao).

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Table 1
Calculated lattice parameters and relative densities for $Mg_{2-x}Ca_xSi$ compounds

x	0	0.01	0.03	0.05	0.07	0.1
a (Å)	6.349	6.354	6.363	6.367	6.375	6.384
Relative density (%)	98	95	97	92	91	95

tance of the sample measured with the forward and reversed currents, in order to eliminate any induced thermoelectromotive force. For the Seebeck coefficient measurements, a small heater was powered to produce a temperature difference ΔT between two ends of the sample. The thermoelectric voltage ΔV and temperature difference ΔT were measured from $\Delta T \approx 0\,^{\circ}C$ to about 5 °C by an Agilent 34401A multimeter. The Seebeck coefficient was then calculated by the slope of the line of ΔV versus ΔT fitted with about 100 pairs of measured data. The thermal diffusivity a 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 calculated from the relationship $\kappa = \rho a C_p$, where ρ is the density of the material.

3. Results and discussion

The XRD results of $Mg_{2-x}Ca_xSi$ ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.1$) samples are presented in Fig. 1. The major peaks of the binary silicide, Mg_2Si, can be indexed to the face-centered cubic structure with the space group of *Fm3m* according to JCPDS 35-0773. With increasing content of calcium, the fluidity during melting and therefore the homogeneity of the ternary compounds become poorer. We see the increasing amount of the MgO phase with increasing x value in Fig. 1. Because the ionic radius of calcium is larger than that of magnesium, a little left shift indicates the solubility of calcium according to the Bragg equation. The lattice parameters of $Mg_{2-x}Ca_xSi$ samples are estimated from the XRD data in Fig. 1 and summarized in Table 1. The lattice parameter for $x = 0$ is consistent with the previous report [12], and increases with increasing calcium content.

The electrical conductivity σ and Seebeck coefficient α of the $Mg_{2-x}Ca_xSi$ samples are plotted in Fig. 2 versus measuring temperature. The electrical conductivities of all the samples decrease with increasing temperature, showing metal-like conduction.

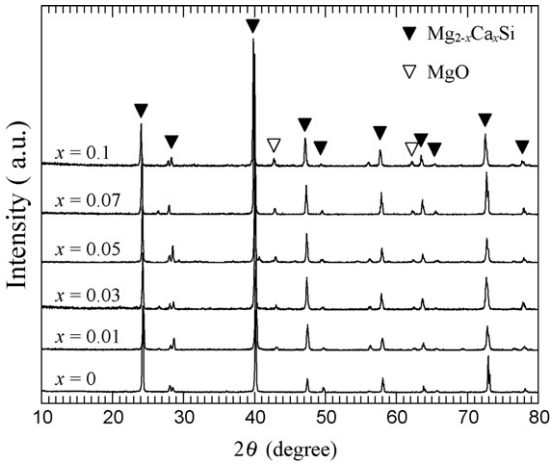

Fig. 1. XRD patterns for $Mg_{2-x}Ca_xSi$ compounds.

This is in accordance with the previous reports that the scattering of the lattice vibration is predominant [9]. The decreasing mobility results in the decreasing electrical conductivity in spite of the increasing carrier concentration with increasing temperature. Correspondingly, all the measured Seebeck coefficients increase with temperature, reach peak values at about 700 K and decrease at higher temperatures because of an increasing number of thermally excited minority carriers. For $x = 0$, a maximum value of $-271\ \mu V\ K^{-1}$ is obtained at about 640 K. All the compounds are n-type conduction with the negative Seebeck coefficients.

With increasing calcium content, the electrical conductivity increases up to the maximum value at $x = 0.03$, then decreases. Calcium has a lower ionization energy relative to magnesium. The presence of calcium as the ionized impurities in the samples enhances the scattering of carriers, results in a slower decrease of electrical conductivity with increasing temperatures. However, with higher contents of calcium, the overall electrical conductivities of the samples decrease due to the existence of MgO as shown in Fig. 1. The valence electron number of calcium is equal to that of magnesium, making it neither a donor or an acceptor. However, the lower electronegativity of Ca makes the outer-shell electrons of calcium atoms be more easily lost than those of magnesium. Therefore the alloying of Ca in Mg_2Si based compounds increases the electronic carrier concentration and hence the electrical conductivity, while the Seebeck coefficient is obviously decreased. The total electrical properties weighted by the power factors are calculated. The highest value for pure Mg_2Si is $2.37 \times 10^{-3}\ W\ m^{-1}\ K^{-2}$, which is higher than the results in other works [6,13]. The solubility of calcium degraded the power factors of all the compounds. The negative effect of the decrease in the Seebeck coefficient exceeds the positive effect of the increase in the electrical conductivity.

The thermal conductivities of $Mg_{2-x}Ca_xSi$ samples are presented in Fig. 3(a) plotted against temperature. The κ values of all samples decrease with increasing temperature at 300–600 K. The results in Fig. 3(a) show that the alloying of calcium in Mg_2Si could not reduce the thermal conductivity. There are many effects on the thermal conductivity when calcium is alloyed in Mg_2Si, including the increase of κ due to the electronic contribution and the decrease of κ due to the enhancement of phonon scattering by alloyed calcium atoms and also by the MgO inclusions. In Fig. 3(b), we see that the ratios of electron- to phonon-conduction, σ/κ, of all calcium alloyed ternary silicides are remarkably higher than the pure Mg_2Si. This means that the electronic conduction for the samples containing calcium is more dominative in the total thermal conductivity than that for pure Mg_2Si.

Fig. 4 shows the dimensionless figure of merit of the $Mg_{2-x}Ca_xSi$ samples. The ZT values for all samples increase with increasing temperature, mainly because the α increase with temperature shown in Fig. 2(b) and the σ/κ ratios are nearly independent of temperature as shown in Fig. 3(b). In Fig. 4 we see that the alloying of calcium in Mg_2Si decreases ZT due to the decrease of the Seebeck coefficient. The highest ZT is 0.41 for the pure Mg_2Si and 0.34 for $Mg_{1.99}Ca_{0.01}Si$ at 660 K, respectively. Although the ZT values measured in the present

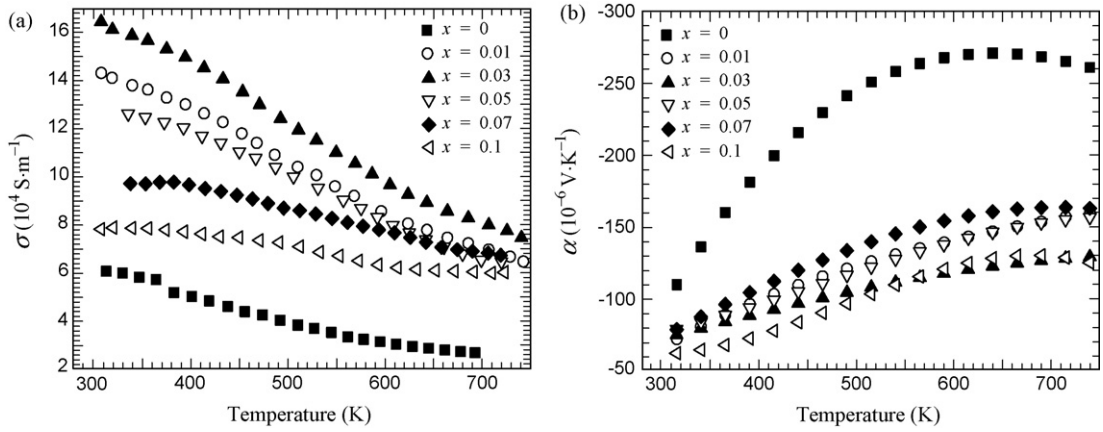

Fig. 2. Temperature dependences of electrical conductivity σ (a) and Seebeck coefficient α (b) for $Mg_{2-x}Ca_xSi$.

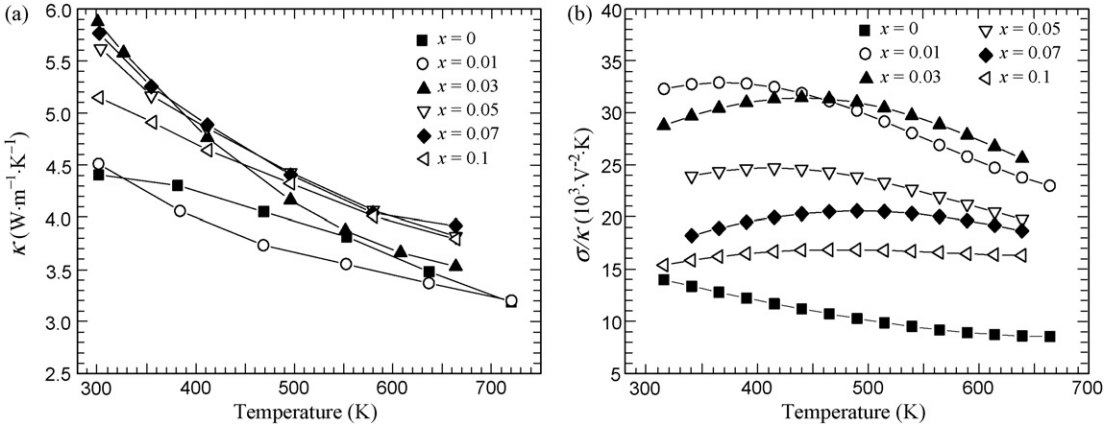

Fig. 3. Temperature dependences of thermal conductivity κ (a) and the electron- to phonon-conduction ratio σ/κ (b) for $Mg_{2-x}Ca_xSi$.

work are a little lower than, but still comparable to, that of the state-of-the-art PbTe based thermoelectric alloys, Mg_2Si based thermoelectric materials are more attractive due to the low cost and non-toxicity. High figures of merit of Mg_2Si based materials would be available above the measuring temperature of the present work according to the tendency in Fig. 4. It should be noted that the present work demonstrates the effectiveness of increasing the electron- to phonon-conduction ratio, σ/κ, by alloying of calcium in Mg_2Si. The improvement of the figure of merit could be expected through the enhancement in the Seebeck coefficients by, for example, nanostructuring the microstructures and optimizing the compositions of the materials.

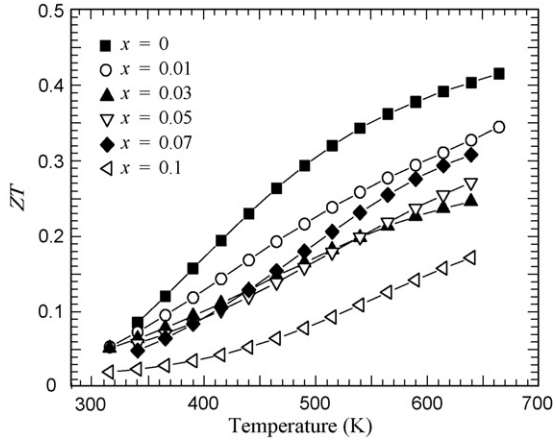

Fig. 4. Temperature dependences of the dimensionless figure of merit, *ZT*, for $Mg_{2-x}Ca_xSi$.

4. Conclusion

Ternary $Mg_{2-x}Ca_xSi$ ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.1$) compounds were prepared by melting followed by hot-pressing. The XRD analysis shows that the lattice parameters of the compounds increase with the increase of x in $Mg_{2-x}Ca_xSi$, indicating the solution of Ca in the Mg_2Si based compounds. The alloying of Ca increases the electronic carrier concentration and hence the electrical conductivity of the Mg_2Si based compounds, due to the lower electronegativity of Ca than Mg. The σ/κ value of $Mg_{1.99}Ca_{0.01}Si$ is about three times higher than pure Mg_2Si. The maximum *ZT* value of 0.34 is obtained at 660 K for $Mg_{1.99}Ca_{0.01}Si$, which is lower than that of the pure Mg_2Si, 0.41, due to the low Seebeck coefficient.

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