Preparation of rare-earth element doped Mg_2Si by FAPAS*

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Abstract: Rare-earth elements (Re) Sc and Y doped Mg_2Si thermoelectric materials were made via a field-activated and pressure-assisted synthesis (FAPAS) method at 1023–1073 K, 50 MPa for 15 min. The samples created using this method have uniform and compact structures. The average grain size was about 1.5–2 μm, the micro-content of Re did not change the matrix morphology. The sample with 2500 ppm Sc obtained the best Seebeck coefficient absolute value, about 1.93 times of that belonging to non-doped Mg_2Si at about 408 K. The electric conductivity of the sample doped with 2000 ppm Y becomes 1.69 times of that of pure Mg_2Si at 468 K, while the former had a better comprehensive electrical performance. Their thermal conductivity was reduced to 70% and 84% of that of non-doped Mg_2Si. Thus, the figure of merit and ZT of these two samples were enhanced visibly, which were 3.3 and 2.4 times of the non-doped samples at 408 K and 468 K, respectively. The maximal ZT belonging to samples doped with 2500 ppm Sc went up to 0.42 at about 498 K, higher than 0.40 of sample doped with 2000 ppm Y at 528 K and 0.25 of non-doped Mg_2Si at 678 K, and the samples doped with Sc seemed to get the best thermoelectric performances at lower temperature.

Key words: Mg_2Si; rare-earth element; thermoelectric material; FAPAS
DOI: 10.1088/1674-4926/33/11/113004 **EEACC:** 2520

1. Introduction

Thermoelectric materials, as kinds of functional material which can convert heat to electricity directly or reversely, are of interest for applications as cooling devices and power generators. Magnesium silicide (Mg_2Si), having a face-centered cubic CaF_2 type of structure, has been identified as a promising advanced n-type thermoelectric material in the temperature range of 500–800 K[1]. Compared with other materials with a figure of merit, ZT > 1, Mg_2Si possesses many outstanding advantages, including the abundance of its constituent elements in nature, the non-toxicity of its processing by-products, and its environmentally benign impact[2]. However, the thermal conductivity of Mg_2Si-based alloys is relatively high for thermoelectric applications, about 6–8 W/(m·K)[3]. Conventionally, heavy doping and solid solutions are regarded as common methods to improve the thermoelectric properties of Mg_2Si, such as the doping of Sb, Te, Bi to Mg_2Si, Mg–Si–Sn and Mg–Si–Ge systems[2,4–10]. Efforts aimed at improving the thermoelectric properties of certain materials have recently focused on the addition of rare earth elements (Re)[11–16]. This has been attributed to the role of the complex electronic shell and sharp energy level splitting[17,18]. Because of their electronegative similarity to and same crystal structure as magnesium, Sc and Y were investigated as dopants for Mg_2Si.

Field-activated and pressure-assisted synthesis (FAPAS) has been successfully applied in the preparation of thermoelectric materials in our previous studies[19–21]. In the case of Mg_2Si, the FAPAS process contributes in two ways: (a) shortens the time of the solid-state reaction process between Mg and Si; and (b) depresses the temperature of the solid-state reaction, thus suppressing the volatilization of Mg[22,23].

2. Experiment

The raw materials were powders of Mg (99.95%, 80–120 mesh), Si (99.95%, 200 mesh) and Re (Sc and Y: 99.99%, 200 mesh). All powders were obtained from the Johnson Matthey Co. Sc and Y were doped to Mg_2Si at different levels, and the compositions and signs are listed in Table 1.

Mixtures of elemental powders corresponding to the chemical constitution of Re-doped Mg_2Si were co-milled at 230 r/min in a planetary mill (Fritsch, Model G5, Germany) for 5 h. Milling resulted in grain size refinement and the creation of three-dimensional multi-interfaces between the magnesium, silicon, and Re particles. The size of the milled powders was below 0.1 μm, as evaluated by Williamson–Hall analysis. In all cases, 5 wt% excess Mg was added to compensate for loss during the sintering process.

The milled powders were cold-compacted into cylindrical blocks in a graphite die, 20 mm in diameter and 2 mm in thickness, and the relative density is in the range of 70%–75%. These samples were then placed in the FAPAS apparatus (Fig. 1) and sintered in the temperature range of 1023–1073 K and under a uniaxial pressure of 50 MPa for 15 min. Then power was turned off and the samples were allowed to cool down to room temperature using recycled water.

Phase and microstructure were characterized by using

Table 1. Compositions and signs of Re-doped Mg_2Si.

Content of Re	Sc (ppm)		Y (ppm)	
	1000	2500	1000	2000
Sign	A-1	A-2	B-1	B-2

* Project supported by the National Natural Science Foundation of China (Nos. 50671070, 50975190) and the SXSCC (No. 200826).
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Received 14 March 2012, revised manuscript received 8 July 2012

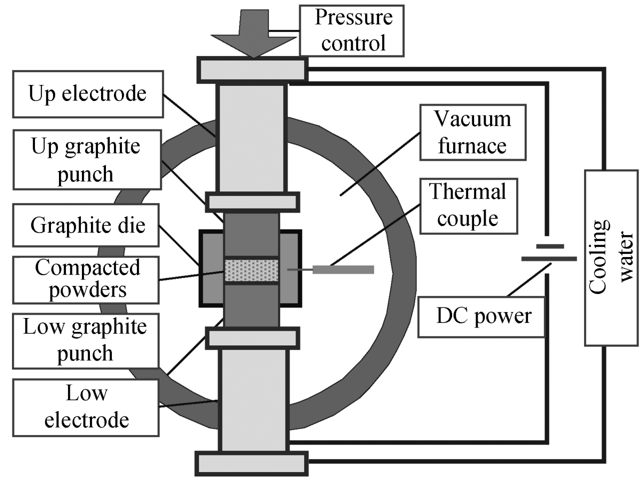

Fig. 1. Schematic diagram of the FAPAS apparatus.

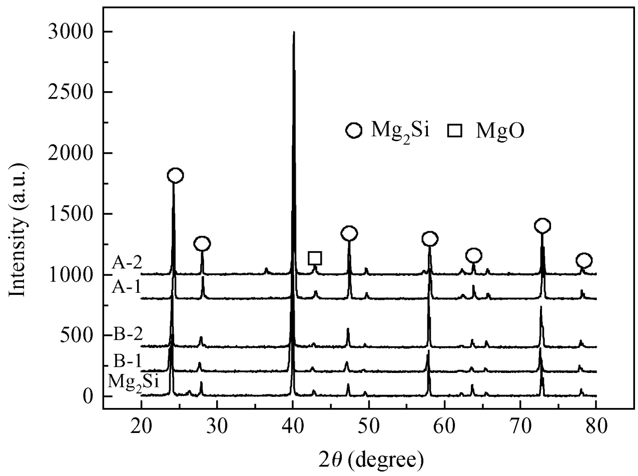

Fig. 2. XRD patterns of sintered samples.

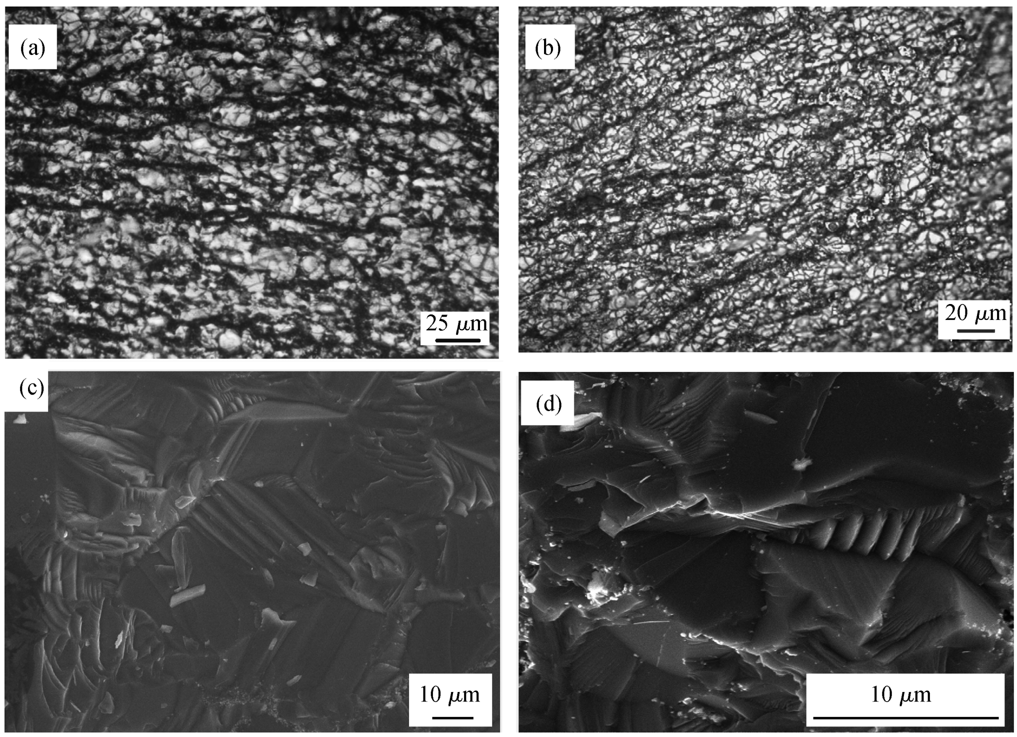

Fig. 3. Microstructure of Mg_2Si and B-2. (a, b) OM structure. (c, d) SEM structure.

a X-ray diffractometer (XRD, Model D5000, Siements AG, Karlsruhe), a scanning electron microscope (SEM, Philips FEIXL30-SFEG) and an optical microscope (OM, Olympus-GX71). The Seebeck coefficient and the electrical conductivity were simultaneously determined by using a Seebeck coefficient/electric resistance measuring system (ZEM-1, ULVAC Inc., Japan). A temperature difference of about 2–5 K between the cool and hot ends of the sample was used for the electromotive force (V) measurement, Seebeck coefficient ($\alpha = V/\Delta T$) can be obtained. The thermal conductivity (κ) was calculated from $\kappa = \alpha D C_{\rm p}$, where a is the thermal diffusivity measured with a laser flash apparatus (Netsch, LFA457), D is the sample density measured by a gravimetric method, and $C_{\rm p}$ is the specific heat capacity measured on a thermal analyzer (Netsch, DSC404).

3. Results and discussion

3.1. Phases and microstructures

Figure 2 depicts the XRD patterns of sintered Sc and Y doped Mg_2Si samples by the PAPAS process. There are mainly Mg_2Si peaks, showing that the formation of Mg_2Si took place during the sintering process. As Mg, Y, and Sc have the same hexagonal crystal structure, Y and Sc are inclined to replace Mg in the CaF_2 type structure, the micro-content of earth elements did not change the crystal structure. The relative density of the sintered samples is in the range of 95%–97% by using the Archimedes method at room temperature.

The fracture microstructures of Mg_2Si and B-2 measured by using an OM and an SEM are shown in Fig. 3. The samples

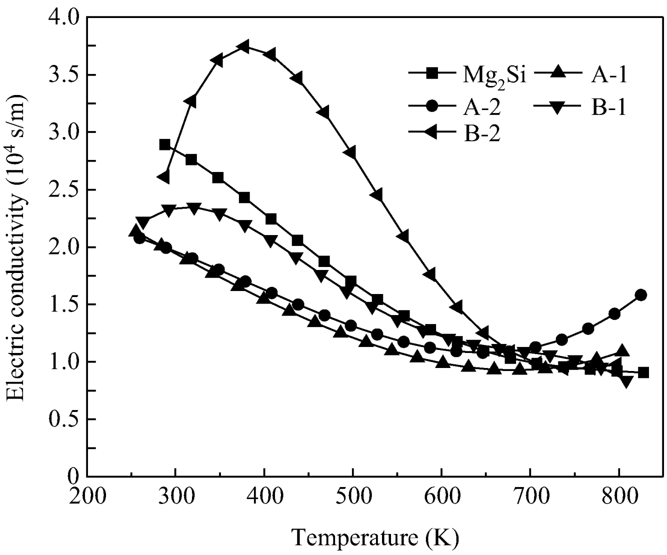

Fig. 4. The electric conductivity of Re-doped Mg_2Si.

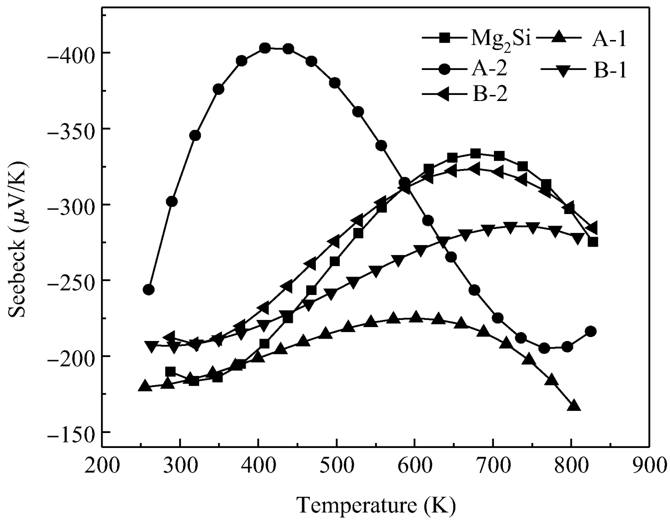

Fig. 5. Seebeck coefficient of Re-doped Mg_2Si.

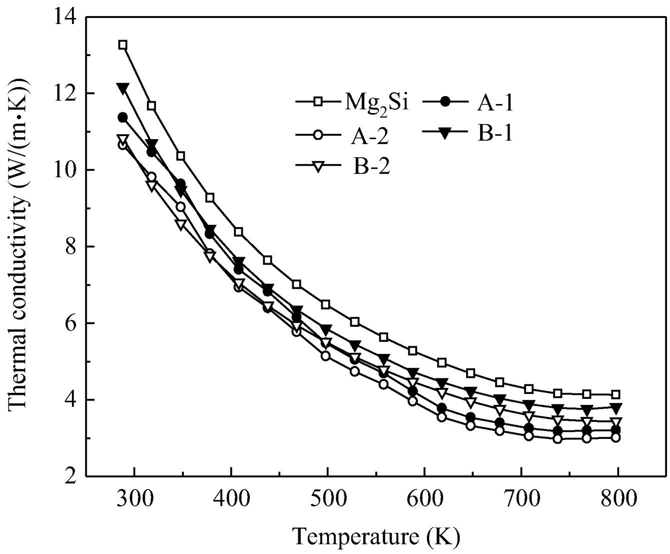

Fig. 6. The thermal conductivity of Re-doped Mg_2Si.

prepared by this method have uniform and relatively fine-grain size microstructures. The average grain size was about 1.5–2 μm, and both of the samples consist of small parallel and thin slices, which can enhance lattice scattering to reduce thermal conductivity and ensure good thermoelectric performance.

3.2. Thermoelectric properties of Re-Mg_2Si samples

3.2.1. Electrical properties

The temperature dependence of the conductivity (σ) of Re-doped Mg_2Si is delineated in Fig. 4. The electric conductivity of Sc doped samples had a similar trend to Mg_2Si. While the electric conductivity of the sample doped with Y revealed a distinct characteristic, taking B-2 as an example, its electric conductivity increased from 2.61×10^4 to 3.74×10^4 S/m in the range of 288 to 378 K, which can be attributed to an increase in carrier concentration due to the introduction of Y, then it decreased to 0.98×10^4 S/m with increasing temperature to 700 K, the decrease in σ is believed to be the consequence of a decreasing mobility with increasing temperature[24]. With a further increase in temperature, the electric conductivity of all samples trended to slightly increase, which contributed to the intrinsic conduction of Mg_2Si with a band gap of 0.77 eV[25]. The adsorption to outer-shell electron of Sc is stronger than that of Y, so the effect on σ in most temperature was smaller than Y.

The temperature dependences of the Seebeck coefficient (α) of Re doped Mg_2Si are shown in Fig. 5. The signs of the Seebeck coefficients are negative, confirming that n-type conduction is dominant in these materials[26]. The Seebeck coefficient of the samples had a similar relationship with temperature. It first increased with temperature to a maximum absolute value, which can be attributed to the increase of effective carrier quality[27]. Then the Seebeck coefficient decreased with a further increase in temperature, because the increasing of the carrier concentration plays a main role[27]. It was indicated that sample A-2 got the best Seebeck coefficient at lower temperature and had been enhanced obviously, about 1.93 times of that belonging to non-doped Mg_2Si at about 408 K. It was also inferred that the Seebeck coefficient can be enhanced to some degree when the doping ratio is increased, resulting from the rising of the diffusion barrier by doping.

Comprehensive electrical performance can be expressed as $P = \alpha^2\sigma$; by comparing, we knew that sample A-2 got a better electrical property.

3.2.2. Thermal conductivity

The thermal conductivity of samples showed the same trends with temperature in Fig. 6, they decreased monotonously in the measured temperature range, and decreased with more addition of Re due to the lattice distortion. It was revealed the thermal conductivity of A-2 and B-2 reduced to 70% and 84% of that belonged to the undoped Mg_2Si.

3.2.3. Figure of merit

The thermoelectric figure of merits ($\mathrm{ZT} = \alpha^2\sigma/k$) for all samples were calculated. From the thermal and electrical performances, among detected samples, A-2 and B-2 were bound

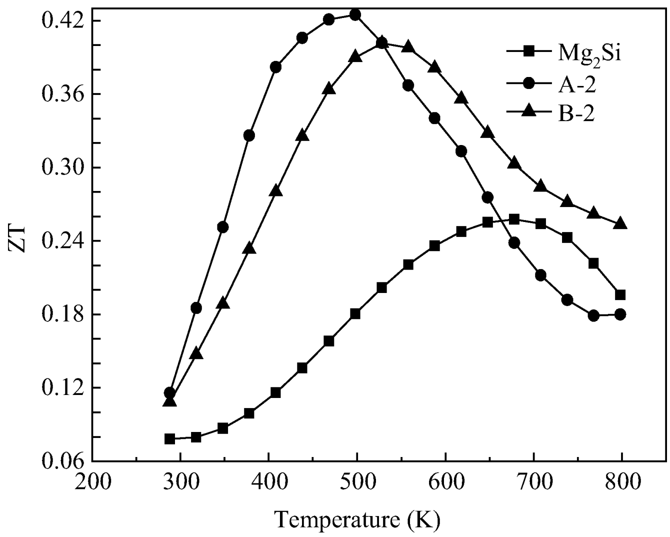

Fig. 7. Figure of merit of Re-doped Mg_2Si.

to have a higher ZT than the non-doped Mg_2Si, as displayed in Fig. 7, which were 3.29 and 2.28 times of the latter at 408 K and 468 K, respectively. The ZT_{max} of A-2 and B-2 were 0.42 at 498 K and 0.40 at 528 K, higher than 0.25 of non-doped Mg_2Si at 678 K. So, it was demonstrated that micro-scale Re Sc and Y could both enhance the thermoelectric properties of Mg_2Si, and Sc seemed to do the best at lower temperature.

4. Conclusion

Re-doped Mg_2Si thermoelectric materials (Sc: 1000, 2500 ppm and Y: 1000, 2000 ppm) were fabricated by FAPAS process, at 1023–1073 K, 50 MPa for 15 min. The XRD pattern of the samples indicated that the reaction of powders had taken place thoroughly. SEM and OM images showed that samples had uniform and relatively fine-grain microstructures; the average grain size was about 1.5–2 μm. The sample with 2500 ppm Sc got the best absolute value of Seebeck coefficient, about 1.93 times of that belonging to non-doped Mg_2Si at about 408 K. The electric conductivity of the sample doped with 2000 ppm Y became 1.69 times of that of pure Mg_2Si at 468 K, while the comprehensive electrical performance of the sample with 2500 ppm Sc was better. The thermo-conductivity of samples doped with Sc and Y reduced apparently compared with that of the pure Mg_2Si, which was only 70% and 84% of that belonged to the latter, proving that the addition of Sc and Y can improve both thermal and electrical properties of Mg_2Si based thermoelectric materials. The ZT of 2500 ppm Sc and 2000 ppm Y doping samples were 3.29 times and 2.28 times of non-doped Mg_2Si at 408 K and 468 K, respectively. The maximum ZT among the obtained samples belonged to the sample with 2500 ppm Sc was 0.42. It seemed that samples doped with Sc had the best thermoelectric performances at lower temperature. In short, it was confirmed Sc and Y were promising dopants in a Mg_2Si system.

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