Thermoelectric Properties of La-Doped BaSi₂

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The authors tried to enhance the thermoelectric figure of merit of BaSi₂ by doping La. Polycrystalline samples of La-doped BaSi₂: Ba_{1-x}La_xSi₂ ($0 \leq x \leq 0.08$) were prepared and characterized. The effect of La-doping was investigated by measuring the thermoelectric properties above room temperature to 973 K. La could dissolve in BaSi₂ up to around $x = 0.03$, while LaSi₂ appeared as the second phase in the higher x range. Both the electrical resistivity and thermal conductivity of the La-doped samples were lower than those of the non-doped BaSi₂. Ba_{1-x}La_xSi₂ ($x = 0.02$) indicated the largest power factor and dimensionless figure of merit (ZT). The ZT value was 0.07 at 970 K, which was approximately 7 times larger than that of non-doped BaSi₂. [doi:10.2320/matertrans.E-MRA2008818]

(Received November 14, 2007; Accepted June 3, 2008; Published July 16, 2008)

Keywords: BaSi₂, thermoelectrics, thermal conductivity, electrical resistivity, Seebeck coefficient

1. Introduction

The technology of energy conversions from waste heat into electrical energy is very important to develop alternative energy technologies in the reduction of our dependence on fossil fuels.¹⁾ A significant reduction in energy consumption through the recovery of waste heat could be achieved by efficient materials for thermoelectric power generation.²⁾ The effectiveness of a material for thermoelectric applications is determined by the dimensionless figure of merit, $ZT = (S^2\sigma)T/\kappa$, where S is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity, and T the absolute temperature.³⁾ The electrical properties are determined by the power factor, defined as $S^2\sigma$ or S^2/ρ , where ρ is the electrical resistivity. The ZT value of the materials used in current devices is approximately 1.

Semiconductor metal silicides, which are composed of less toxic and naturally abundant elements, have attracted attention as candidates of environmentally friendly thermoelectric materials. For example, the thermoelectric properties of FeSi₂ and Mg₂Si have been widely studied, and an excellent ZT value (≈ 1.1) was achieved in the n -type Mg₂(Si,Sn) system.⁴⁾

Recently, BaSi₂ has been studied as a potential candidate for thin-film solar cell material,⁵⁾ because it has a large absorption coefficient and a suitable band gap energy (1.13 eV).⁶⁾ At atmospheric pressure and room temperature, BaSi₂ crystallizes with the orthorhombic BaSi₂-type structure (space group: Pnma).⁷⁾ In our previous study,⁸⁾ it revealed that BaSi₂ indicates quite low thermal conductivity, which is comparable to or less than those of typical thermoelectric materials such as Bi₂Te₃. However, it also revealed that the electrical resistivity of BaSi₂ is quite high, which would be due to its low carrier concentration. Consequently, the dimensionless figure of merit (ZT) of BaSi₂ is not so high: 0.01 at 954 K. At around room temperature, the carrier concentration and the mobility of thin film BaSi₂ were reported to be approximately $5 \times 10^{21} \text{ m}^{-3}$ and $800 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.⁵⁾ Since the optimized carrier concentrations for typical thermoelectric materials are around 10^{25} – 10^{26} m^{-3} , it should be required to tune the carrier concentration through appropriate doping for improvement of the thermoelectric properties of BaSi₂.

In the present study, we tried to improve the thermoelectric properties of BaSi₂ by La-doping. According to the periodic table, La substitution for Ba requires electron doping, leading to increasing of the carrier concentration of n -type BaSi₂. We investigated the effect of La-doping on the thermoelectric properties of BaSi₂ by measuring the ρ , S , and κ of Ba_{1-x}La_xSi₂ ($0 \leq x \leq 0.08$) above room temperature to 973 K.

2. Experiment

Polycrystalline samples of La-doped BaSi₂, i.e., Ba_{1-x}La_xSi₂ ($x = 0, 0.02, 0.04, 0.08$), were prepared by spark plasma sintering (SPS). BaSi₂ (>99%, lumps), LaSi (>99.9%, powder), and Si (>99%, powder) were used as starting materials. The starting materials were put in carbon crucibles and applied an induction heating at 1473 K under a helium flow atmosphere. The obtained ingots were crushed to fine powders through a sieve with the opening of 45 μm , followed by SPS. The SPS condition for the non-doped sample was 1123 K for 2 hours under the pressure of 100 MPa. We tried to prepare the bulk samples of La-doped BaSi₂ under the same SPS condition as that of non-doped BaSi₂. However, we could not obtain high-density fine samples due to the production of micro-crack in the samples. Therefore, we optimized the SPS condition for the La-doped BaSi₂, and we obtained fine samples under the condition of 1123 K for 1 hour under the pressure of 50 MPa and consecutively for 1 hour under the pressure of 10 MPa. The SPS for both non-doped and La-doped BaSi₂ were performed under an argon flow atmosphere.

Powder x-ray diffraction (XRD) measurements were performed using a diffractometer on RINT2000 (Rigaku Corporation) with Cu $K\alpha$ radiation in air at room temperature. The lattice parameter was calculated from the XRD pattern. The microstructure of the samples was observed by using a scanning electron microscope (SEM). The chemical composition was determined using an energy-dispersive x-ray (EDX) analysis.

The electrical resistivity (ρ) and Seebeck coefficient (S) were measured using a commercially available apparatus: ZEM-1 (ULVAC Co. Ltd.) under a helium atmosphere from 323 K to 973 K, in which ρ was measured by the four-probe

method and S was measured by the steady method. We tried to measure the Hall coefficient by the van der Pauw method. However we could not obtain the data probably due to the lower carrier concentration of the samples than the measurable limits. The thermal conductivity (κ) was evaluated from the thermal diffusivity (α), heat capacity (C_p), and sample density (d) using the standard relationship of $\kappa = \alpha C_p d$. The thermal diffusivity was measured by the laser flash method using a commercially available apparatus: TC-7000 (ULVAC Co. Ltd.) in a vacuum from room temperature to 973 K. The heat capacity was estimated from the model of Dulong-Petit, viz. $C_p \text{ (JK}^{-1} \text{ mol}^{-1}) = 3nR$, where n is the number of atoms per formula unit and R is the gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$).

3. Results and Discussion

The XRD patterns of the La-doped BaSi_2 samples are shown in Fig. 1, together with that of the non-doped BaSi_2 sample. It can be confirmed that the XRD patterns for all samples corresponded to that of orthorhombic BaSi_2 . However, all the samples contained a small amount of impurities such as the cubic phase of BaSi_2 . In addition, some peaks corresponding to the tetragonal LaSi_2 were observed in the samples of $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$ ($x = 0.04$ and 0.08).

The SEM and EDX images of the La-doped BaSi_2 samples are shown in Fig. 2. The EDX mapping images revealed that Ba, Si, and La were homogeneously distributed throughout the sample of $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$ ($x = 0.02$). On the other hand, for the samples of $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$ ($x = 0.04$ and 0.08), La was not homogeneously distributed but precipitated with Si. These results were well consistent with the results of the XRD.

The average chemical compositions, lattice parameters of the BaSi_2 phase, and densities of the samples are summarized in Table 1. Relationships between the lattice parameters and

Fig. 1 Powder XRD patterns of the La-doped BaSi_2 samples, together with that of BaSi_2 .

Fig. 2 SEM and EDX mapping images of the La-doped BaSi_2 samples: $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$ ($x = 0.02, 0.04, \text{ and } 0.08$).

Table 1 Chemical compositions, lattice parameters, and bulk densities of the non-doped and the La-doped BaSi_2 samples.

La content x in $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$		0	0.02	0.04	0.08
Chemical composition determined by the	Ba	30.4	34.6	33.3	32.7
	Si	69.6	64.6	65.4	65.1
EDX analysis (at%)	La	—	0.7	1.3	2.5
Lattice parameter (nm)	a	0.8919	0.8929	0.8928	0.8915
	b	0.6801	0.6731	0.6718	0.6716
	c	1.1578	1.1532	1.1525	1.1519
Sample bulk density $d \text{ (gcm}^{-3}\text{)}$		3.35	3.44	3.24	3.30
Relative density (%T.D.)		91.4	92.8	—	—

the La content x in $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$ are shown in Fig. 3. The chemical composition of the non-doped sample was slightly Si-rich, while those of the La-doped samples were almost stoichiometric. From Fig. 3, it was confirmed that the lattice parameter a was constant regardless of the La content, and the lattice parameters b and c decreased with increasing the La content. In addition, both the lattice parameters b and c become constant above the La content of around $x = 0.03$. From these results, it can be concluded that the solid solubility limit of La for BaSi_2 is around $x = 0.03$ in $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$. The densities of the samples of $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$ ($x = 0$ and 0.02) were 91.4 and 92.8% of the theoretical density (T.D.), respectively.

Temperature dependences of the electrical resistivity (ρ), Seebeck coefficient (S), and power factor (S^2/ρ) of the samples are shown in Figs. 4(a), 4(b), and 4(c), respectively. The electrical properties of BaSi_2 varied dramatically with La-doping. The ρ of all samples decreased with increasing

Fig. 3 Relationships between the lattice parameters a , b , and c and the La content, x in $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$.

Fig. 4 Temperature dependences of the electrical resistivity (ρ), Seebeck coefficient (S), and power factor (S^2/ρ) of the non-doped and the La-doped BaSi_2 samples.

temperature, showing semiconductor-like behavior. The ρ also decreased largely at low temperature region by addition of a small amount of La, viz. $x = 0.02$ in $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$, indicating that the electron doping was successfully done

Fig. 5 Temperature dependence of the thermal conductivity (κ) of the non-doped and the La-doped BaSi_2 samples.

in this system. However, the ρ values of the non-homogeneous samples containing LaSi_2 as the second phase, viz. $x = 0.04$ and 0.08 in $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$ were larger than that of the homogeneous sample: $x = 0.02$ in $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$. This result can be attributed to the carrier scattering at interfaces between the matrix and second phases. In addition, the ρ values of the non-homogeneous samples became lower as increasing the La content. This would be due to the very low ρ of tetragonal LaSi_2 as the second phase: $4 \times 10^{-7} \Omega\text{m}$ at 300 K.⁹⁾

The sign of S of all samples was negative, indicating that the majority carriers are electron. The absolute S values decreased with increasing temperature at high temperatures, showing semiconductor-like behavior. The absolute S values of the La-doped samples were lower than that of the non-doped sample at low temperature region, implying that La-doping led to an increase of the carrier concentration. On the other hand, the S values of the La-doped samples were similar over the whole temperature range regardless of the La content. It seems that the effect of the carrier doping rather than that of the precipitation of LaSi_2 is effective for the absolute values of S .

In the temperature range from room temperature to 973 K, La-doping enhanced the power factor of BaSi_2 , as shown in Fig. 4(c). The $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$ ($x = 0.02$) sample exhibited the highest power factor; the maximum value was $44.8 \times 10^{-6} \text{ Wm}^{-1} \text{ K}^{-2}$, obtained at 726 K.

Temperature dependence of the thermal conductivity (κ) of the samples is shown in Fig. 5. In the $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$ system, the electronic contribution to the thermal conductivity (κ_{el}) is quite low compared with the total thermal conductivity, and then almost all of κ is composed of the lattice contribution (κ_{lat}). The measured κ values of the La-doped samples were slightly lower than that of the non-doped sample. In case of $x = 0.02$ in $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$, the lower κ than that of the non-doped sample would be the result of the alloy scattering effect. On the other hand, in cases of $x = 0.04$ and 0.08 in $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$, the phonon scattering at interfaces between the matrix phase (a small amount of La-containing BaSi_2) and the second phase (LaSi_2) likely occurred. In addition, the κ of LaSi_2 was expected to be significantly

Fig. 6 Temperature dependence of the dimensionless figure of merit (ZT) of the non-doped and the La-doped BaSi_2 samples.

higher than that of the matrix phase, because the ρ of LaSi_2 was reported to be $4 \times 10^{-7} \Omega\text{m}$ at 300 K⁹⁾ leading to the κ_{el} to be $18 \text{ W m}^{-1} \text{ K}^{-1}$ according to the Wiedemann-Franz law. This high- κ LaSi_2 existed as the second phase would result in the high κ of the sample for $x = 0.08$ in $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$ compared with that of the sample for $x = 0.04$. Nevertheless, the κ values of all the samples were quite low, which is a great opportunity to enhance the ZT .

The dimensionless figure of merit (ZT) of the samples is shown in Fig. 6 as a function of temperature. The maximum ZT value was 0.07 at 970 K, obtained in the composition of $\text{Ba}_{0.98}\text{La}_{0.02}\text{Si}_2$, which was approximately 7 times higher than that of non-doped BaSi_2 . In the present study, the power factor of BaSi_2 can be improved through the carrier concentration tuning by La-doping while the κ was maintained quite low, leading to enhancement of the ZT of La-doped BaSi_2 .

4. Summary

We investigated the thermoelectric properties of poly-

crystalline samples of La-doped BaSi_2 : $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$ ($x = 0, 0.02, 0.04, 0.08$) prepared by induction heating followed by SPS. La dissolved up to around $x = 0.03$ in $\text{Ba}_{1-x}\text{La}_x\text{Si}_2$, while LaSi_2 appeared as the second phase above this concentration. For the homogeneous sample, the power factor was improved significantly due to decreasing the electrical resistivity by La doping. In addition, the thermal conductivity was maintained quite low. From these results, we were able to realize an enhancement of the thermoelectric figure of merit of BaSi_2 . The 2 at% La-doped BaSi_2 , $\text{Ba}_{0.98}\text{La}_{0.02}\text{Si}_2$, exhibited the highest ZT . The maximum value was 0.07 obtained at 970 K, which was approximately 7 times higher than that of non-doped BaSi_2 .

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 18760667) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. Additional support was kindly provided by Kansai Research Foundation for Technology Promotion, The Kinki District Invention Center, and Foundation for the Promotion of Material Science and Technology of Japan.

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