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Thermoelectric Properties and Electronic Structure of Mg_2Si System

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The Mg_2Si sample with high thermoelectric ability was prepared recently by the solid-state reaction and the spark plasma sintering method. In the present work, its thermal conductivity κ was measured as a function of temperature and the largest figure of merit ZT was obtained to be 0.23 at 773K. The important thermoelectric property, i.e. Seebeck coefficient is analysed by the use of the theoretical electric structure calculation: the electronic structure of Mg_2Si is calculated by means of full-potential linearlized augmented plane wave (FLAPW) method with the generalized gradient approximation (GGA) and then the result is used to calculate thermoelectric property. The band structure of Mg_2Si shows an indirect type semiconductor with band gap 0.20 eV. It has been shown that the experimental Seebeck coefficient was reproduced theoretically by choosing a band gap and an electronic concentration as adjustable parameters.

Key words: Mg_2Si, thermoelectric material, FLAPW

1. INTRODUCTION

The thermoelectric conversion system is the power generation technology by the Seebeck effect where temperature difference between the high-temperature part and the low-temperature part generates an electricity. Since this technology does not have a mechanical drive part and can carry out the direct conversion of the heat to the electric energy, the small lightweight power generation system can be constituted. The thermoelectric conversion was used for the power generation system for satellites, where available space is very much restricted.

In future the thermoelectric technology should be used much more widely. For example, for the environmental view of point, thermoelectric conversion system is suitable to recover the engine waste heat in moving objects, such as a car and a vessel, and the waste heat in the incineration system and in the industrial furnace [1]. However, for the wider utilization, various problems such as the improvement in the system efficiency and in the thermoelectric characteristic of materials, and also the establishment of the mass-production technology of thermoelectric device remain.

The indicator for the efficiency of the thermoelectric conversion is given by the figure of merit ZT, where Z is given by

$$Z=P/\kappa.$$

Here power factor P is given by $P= S^2\sigma$, S is the Seebeck coefficient, σ is the conductivity and κ is the thermal conductivity. The value of ZT=1.0 is a measure for the practical use. Compared with a typical thermoelectric material Bi-Te, metal silicides thermoelectric materials such as Fe-Si, Cr-Si, Mn-Si, Mg-Si and so on are better in environmental points of view and also in low cost, and are attracting much attention [2-4].

In the Mg_2Si system there are few study in the undoped sample Mg_2Si [2-4]. Most study have been devoted to Mg_2Si doped with Al, Ag, In, etc. and its alloys such as $Mg_2Si_XGe_{1-X}$ and Mg_2Si- $MgSn_2$ in order to obtain the better thermoelectric properties [8-11]. The better understanding of the undoped Mg_2Si with higher thermoelectric ability may yield the good starting point for the further improvement.

Thus, in the present work, we pay attention to the undoped Mg_2Si thermoelectric material, whose crystal structure is shown in Fig.1. The β phase (fluorite Mg_2Si) in Fig.1 is the terminal equilibrium structure of the precipitation sequence. It has a fcc primitive unit cell and belongs to the space group Fm-3m (225). Recently for undoped Mg_2Si sample the solid-state reaction and the spark plasma sintering method have been used successfully to obtain the sample with high thermoelectric characteristic in our group [4]. However, the theoretical examination of thermoelectric properties in the Mg_2Si system has not been carried out although electronic structure was recently calculated by some methods [5-7]. Then, the purpose of the present work is to perform further experimental study and the first theoretical examination of thermoelectric properties in undoped Mg_2Si.

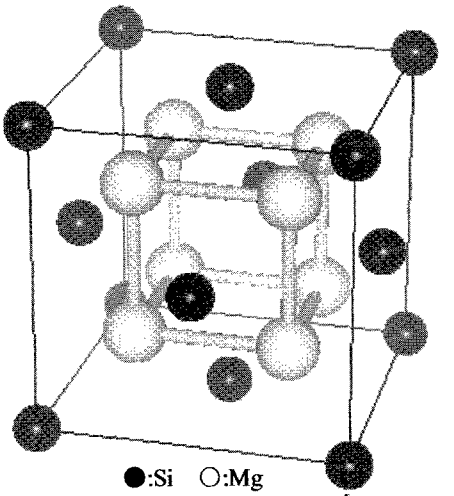

Fig.1 Crystal structure for Mg_2Si

2. EXPERIMENT

Recently we have synthesized the undoped Mg_2Si thermoelectric sample. The solid-state reaction and the spark plasma sintering method were used in order to examine the effects of sample density to the thermoelectric properties. By sintering the powder with the smaller size in higher temperature, high density samples were obtained. The high density sample yields good thermoelectric property [4]. With the increase in density, Seebeck coefficient doesn't change much, but the electrical conductivity and then the power factor increase. The obtained power factor is comparable to the previous best results recently obtained by Komatu group [3]. Our best result of the Seebeck coefficient, electrical conductivity and the power factor for the samples with the highest density are summarized in Fig.2-4 together with the recent results by Komatu group. In the present work we extended our work: the laser flash method is used to measure the thermal conductivity from the room temperature to a higher temperature of 850 K for the undoped Mg_2Si, whose data exist little. Then we can

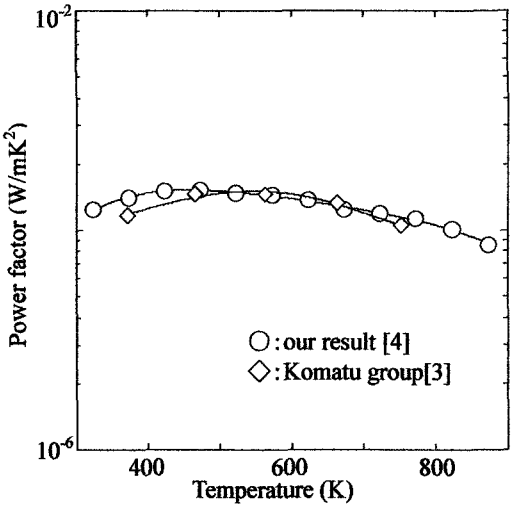

Fig.4 The temperature dependence of the power factor.

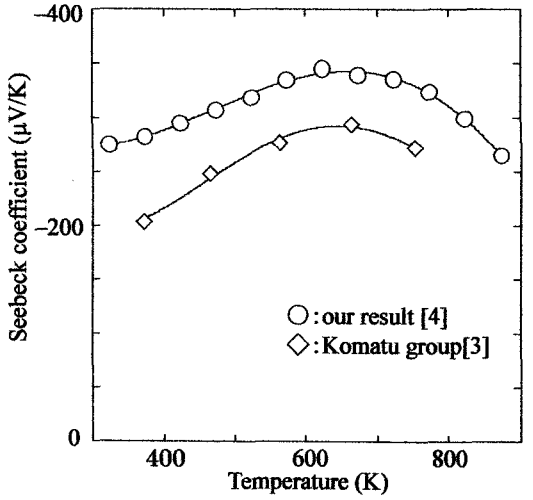

Fig.2 The temperature dependence of the Seebeck coefficient.

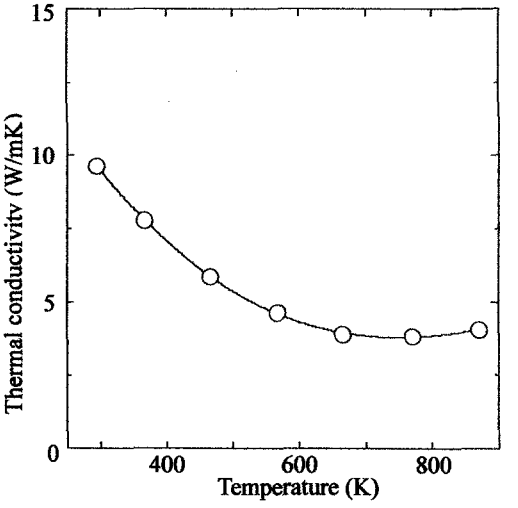

Fig.5 The temperature dependence of thermal conductivity.

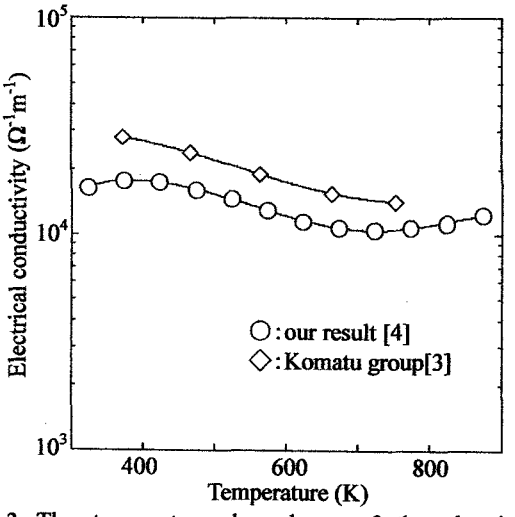

Fig.3 The temperature dependence of the electrical conductivity.

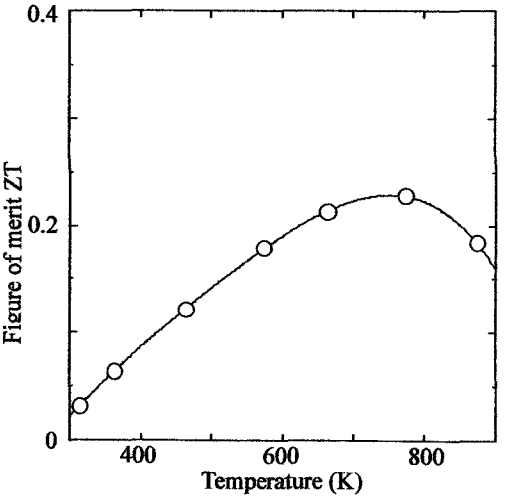

Fig.6 The temperature dependence of figure of merit ZT

obtain the figure of merit ZT which is the indicator of the thermoelectric conversion. The experimental results of κ and ZT are shown in Fig.5 and 6. According to the increase of the temperature, thermal conductivity κ decreases from the value κ = 9.66 W/mK at room temperature to about 4 W/mK around 600 ~ 800 K. As a increase of the temperature, figure of merit ZT increases from ZT = 0.03 at room temperature and reaches the maximum value ZT = 0.23 at 770 K and then start to decrease.

3. ELECTRIC STRUCTURE

In the present work, the full potential linearized augumented plane wave (FLAPW) method with the density functional theory was used to calculate the electronic structure [13]. Kohn-Sham equation was solved self-consistently in the electronic structure calculation. The exchange correlation energy was treated by the Perdew-Burke-Ernzerhof expression [14]. We used the following APW parameters in the calculations: Mg: R_{mt}=2.1 a_B, Si: R_{mt}=2.1 a_B, $R_{mt}K_{max}$=7 and G_{max}=14$R_{mt}^{1/2}$. Here, R_{mt} is the muffin-tin radius. K_{max} is the plane-wave cutoff, and G_{max} is the maximum Fourier component of the electron density. For all the calculations we used the modified tetrahedron method for Brillouin-zone integrations. All the k-point meshes were checked for convergence.

Firstly, the lattice constant of Mg_2Si is calculated theoretically from the minimization of the total energy. In order to calculate the total energy we need to know the electronic structure, which is calculated by the above first principle FLAPW method. The total energy dependence on the lattice parameter is shown in Fig.7

The calculated optimized value 6.36 Å differs by 0.6 % from the experimental value 6.338 Å [14]. The calculated bulk modulus, derived from a second-order Birch fit, was 56 GPa compared to 59 GPa from the experiment [14].

The band structure and DOS of Mg_2Si are shown in Fig.8. The present calculation yields the band gap 0.23 eV at $\Gamma_{15}^{(V)} \rightarrow X_1^{(C)}$, which is about 30 % of the experimental value 0.66~0.77 eV [15]. The smaller calculated band gap is considered to reflect the well-known smaller band gap in the calculation based on the density function method. This deficiency is known to be recovered in the much elaborate more involved calculation in the GW approximation, which yield the lager band gap. The valence band of Mg_2Si was constituted by the mixed states of s, p orbital of Mg and p orbital of Si. The state near the bottom of the conduction band consists of s and p orbitals of both Mg and Si.

Here we mention the results of the previous calculations [5, 6]. The over all band structure of the present and other calculation agrees well with each other. Band gap is an indirect gap between Γv-Xc by both the pseudopotential method [6] and GW approximation [5] as in the present work. However, only the calculated band gap differ much. The calculation of the usual density function method, i.e., the present LAPW method and the pseudopotential method yield 0.23 eV and 0.28 eV, respectively. The much elaborate calculation in the GW approximation yields the larger band gap value E_g = 0.65 eV, which roughly agrees with the experiment.

4. SEEBECK COEFFICIENT

Here, based on the electronic structure calculation, we now calculate the thermoelectric property, i.e., Seebeck coefficient. Basic expression to calculate the Seebeck

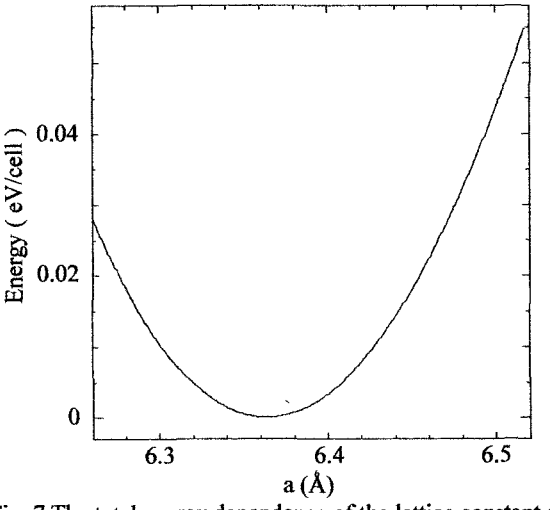

Fig. 7 The total energy dependence of the lattice constant a

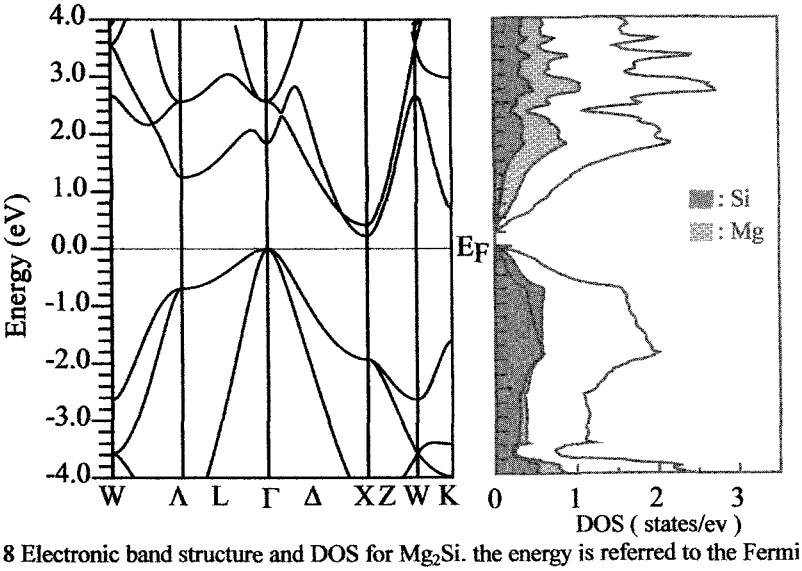

Fig. 8 Electronic band structure and DOS for Mg_2Si. the energy is referred to the Fermi level.

coefficient S is obtained from the linearized Boltzmann equation with the relaxation time approximation and is given by the following equation,

$$S = \frac{e}{3T\sigma_e}\int d\varepsilon\left(-\frac{\partial f(\varepsilon)}{\partial \varepsilon}\right)\rho_e(\varepsilon)v(\varepsilon)^2(\varepsilon-\mu)\tau(\varepsilon).$$

with

$$\sigma_e = \frac{e^2}{3}\int d\varepsilon\left(-\frac{\partial f(\varepsilon)}{\partial \varepsilon}\right)\rho_e(\varepsilon)v(\varepsilon)^2\tau(\varepsilon).$$

Here, the expression involves the integration with respect to the energy ε for the quantities containing the energy differentiation of the Fermi distribution function f (ε), DOS (density of states) ρ_e (ε), the velocity of an electron v (ε), the chemical potential μ, and the relaxation time τ (ε). It is noted that Seebeck coefficient includes the electrical conductivity σ_e in the denominator.

In the present work, the relaxation time τ is assumed to be state (energy) independent constant. Then the relaxation time τ (ε) =τ of a denominator and a numerator is canceled, and thus Seebeck coefficient S depends only on the electronic structure. We also assume there are finite carriers (extra electrons) in the conduction band and both structures of the conduction band and the valence band are not affected by the existence of carrier (extra electrons). The Seebeck coefficient depends strongly on the electron concentration N_e and the band gap E_g. Thus we choose both the electronic concentration N_e and the band gap E_g as adjustable parameters, so that the calculated curve reproduse the experimental result as much as possible. The best fitted results are shown in Fig.9. It is noted that the calculated Seebeck coefficient with the band gap value of about E_g = 0.4 eV yields the good agreement with the experiment. However, the calculated and the experimental band gaps E_g = 0.23 eV and 0.70 eV dose not describe well the experiment by adjusting the electron concentration. At present the reason of the discrepancy for the band gap is not clear.

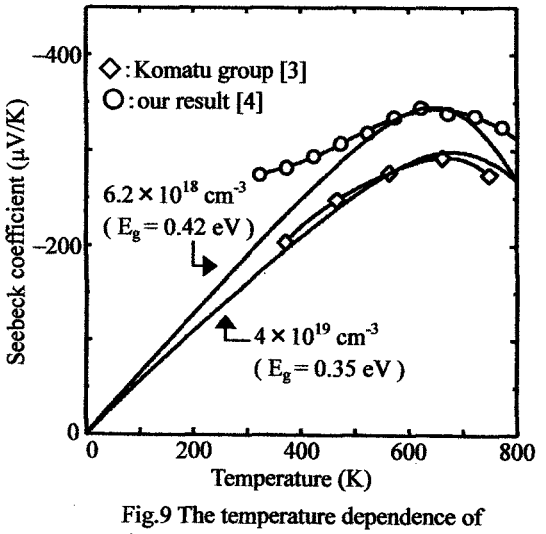

Fig.9 The temperature dependence of the Seebeck coefficient

5. CONCLUSIONS

The undoped sample Mg_2Si with good thermoelectric characteristic was prepared by using the solid-state reaction and the spark plasma sintering process. The measurement of the thermal conductivity has yielded the figure of merit ZT, whose largest value is 0.23 at 773K. This preparation process may be the good starting point to improve the figure of merit ZT by an impurity doping.

The electronic structure of Mg_2Si has been calculated using the first principle calculation. The calculated band structure of Mg_2Si shows an indirect type semiconductor with band gap 0.20 eV. Based on the electronic structure the Seebeck coefficient, one of the basic thermoelectric quantity, has been calculated. It has been found to be possible to reproduce experiment by choosing band gap E_g and electronic concentration N_e as adjustable parameters.

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