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Theoretical study on thermoelectric properties of Mg_2Si and comparison to experiments

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ABSTRACT

Mg_2Si has been regarded as a potential candidate for thermoelectric applications in middle-temperature range (500–900 K). In order to better understand the temperature, doping level and composition dependent thermoelectric properties, we performed simulations that are based on the semi-classical electronic transport theory and the empirical lattice thermal conductivity model. The temperature and doping level dependence of the calculated Seebeck coefficients and electrical conductivity agree qualitatively with the previous experiments. By considering the influence of the chemical composition on the lattice thermal conductivity, we further estimated the thermoelectric figure-of-merit (ZT) for the Sb-doped Mg_2Si samples. The results reproduced the temperature variation trends of the ZT values in the literature. The current work represents an attempt to combine the first-principles tools and the empirical models to evaluate the TE properties of the Mg_2Si materials. It may shed some light on developing Mg_2Si-based thermoelectric devices in the future.

1. Introduction

In recent years, increasing concerns on global warming and depletion of fossil fuels have renewed the interest in academia and industry to develop technologies of converting low grade heat into electricity with thermoelectric (TE) generator. The efficiency of a TE material is characterized by its dimensionless figure-of-merit $ZT = S^2\sigma T/\kappa$, where S, σ, κ and T are Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. To build a thermoelectric generator, the TE properties of the material should be optimized for the temperature at which the device is aimed to operate. In practice, the temperature difference between heat source and sink in many heat-to-electricity applications may reach several hundred degrees. It is impossible to find a homogenous material with maximized TE performance over such a large temperature range. Therefore it has been proposed to fabricate segmented thermoelectric devices (STD) to ensure that the TE efficiency of the individual segment is optimized over a specific narrow temperature range [1].

Mg_2Si has long been regarded as a promising TE material that works between 500 K and 900 K [2–9], a temperature span where many needs for waste heat recovery exist. In addition, magnesium and silicon are non-toxic and earth-abundant elements, which is a competitive advantage of Mg_2Si-based devices. Aiming at practical uses, Sakamoto et al. recently reported Mg_2Si-based segmented devices that were made of Sb-doped segment for high temperature end and Al-doped segment for low temperature end [10]. In such a case, tuning the chemical composition and carrier concentration is crucial to further optimize the performance of individual segment around a certain temperature. It is therefore necessary to have a better understanding on the dependence of the TE properties of Mg_2Si upon doping level, chemical composition and temperature.

In this paper, we intend to combine the first-principles calculations and the empirical models to interpret and predict the TE performance of the doped Mg_2Si samples. We first performed semi-classical transport calculations with the BoltzTraP code [11] to investigate the electronic transport properties of Mg_2Si on the basis of the electronic structures obtained from the first principles calculations. The approach has been used widely to interpret the TE properties of various TE materials [12–17]. In fact, Akasaka et al. have used a similar method to compute the Seebeck coefficients of the Mg_2Si crystals and found a good agreement with their experiments [9]. However, other properties like electrical conductivity and electronic thermal conductivity were not considered in their simulations. In the current study, we explored the temperature and doping-level dependent electronic transport properties of Mg_2Si in a relatively systematic way. The results were compared to the previous experimental data ranging over several decades. The ZT values of Sb-doped Mg_2Si were then estimated by including the composition dependent lattice thermal conductivity.

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2. Theoretical methods

The Mg_2Si crystal belongs to $Fm\bar{3}m$ space group and has a cubic antifluorite structure. In the primitive cell, there are two Mg atoms which are ocated at $\pm\mu$ ($\mu = (\frac{1}{4},\frac{1}{4},\frac{1}{4})a$, *where a is the lattice constant), and one Si atom which occupies a face-centered cubic (fcc) site.*

In the simulations, the experimental lattice constant (a = 6.338 Å) [18] was used for Mg_2Si. The electronic structures were computed within the density functional theory (DFT) framework by using the WIEN2K program [19] which utilizes full potential, linearized augmented plane-wave (FLAPW) and local orbital methods. We used the general gradient approximations (GGA) proposed by Perdew, Burke and Ernzerhof [20] for the exchange–correlation potential. The muffin-tin radii were set to be 2.5 Bohr for Mg and Si. The core bands and the valence bands were separated at −6 Ry. A $R_{MT} \cdot K_{MAX}$ value of 9 and a G_{max} value of 14 were adopted. To calculate the transport properties, we used a mesh of 40,000 k points in the Brillouin zone to compute the electronic bands. The BoltzTraP code was then employed to calculate the thermoelectric properties based on the analytical expressions of the electronic bands. The constant relaxation time approximation and the rigid band approximation were used in the calculations.

3. Results and discussion

3.1. Electronic structures

The calculated electronic structures of Mg_2Si are plotted along several high symmetry lines in Fig. 1. It confirms that Mg_2Si is an indirect semiconductor with the valence band maximum (VBM) located at the Γ point and the conduction band minimum (CBM) at the X point [21]. The values of the band gaps are summarized in Table 1 along with the previous theoretical and experimental results [2,21–27]. The indirect band gap ($\Gamma_{15V} \rightarrow X_{1C}$) is found to be 0.21 eV in this work, which is significantly smaller than the experimental values but is comparable to other DFT calculations. On the other hand, the calculated direct band gap ($\Gamma_{15V} \rightarrow \Gamma_{1C}$) is 1.91 eV, which is only about 12% smaller than the experimental value. The underestimation of the band gap is a known deficiency of the DFT calculation. The problem can be alleviated by using more elaborate but generally time consuming methods. By employing a GW approximation in conjunction with the all-electron full-potential projector augmented wave method, Arnaud and Alouani obtained the values of the indirect and direct band gaps for Mg_2Si that agreed fairly well with experiments [22].

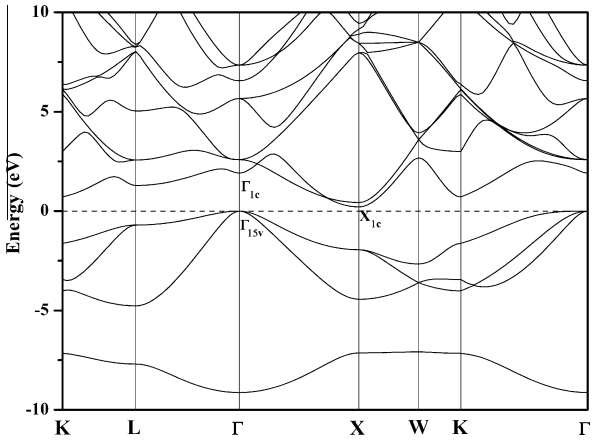

Fig. 1. Calculated electronic band structure of Mg_2Si along several high symmetry lines.

Fig. 2a displays the calculated total electronic density of states (TDOS) and atom projected density of states for Mg_2Si. The basic shape of DOS is consistent with the previous calculations [23,24]. The valence bands near the Fermi level are mainly derived from Si atom, while the conduction bands from Mg atoms. This can be understood by a simplified picture, where Mg is prone to lose electrons and thus provides empty states for electron transport. The plots of orbital resolved density of states are presented in Fig. 2b which indicates that the valence bands near the Fermi level are mainly contributed by Si-p states and a small portion of Mg-p and Mg-d states. The bottom of the conduction bands consists primarily of Mg-s states and Si-d states.

The TE properties are very sensitive to the values of band gap. In the current study, a temperature-dependent band gap, $E_g = E_g^0 - \beta T$, is applied, where E_g^0 represents the value of the indirect band gap at 0 K and β is a positive constant. It is well known that the band gap of a semiconductor shrinks with increasing temperature due to the effects of electron–phonon interaction and thermal expansion [28]. Since it is still challenging to obtain the temperature dependent band gap from the first-principles calculations, the band gap derived from the experiments was often used in the temperature dependent transport studies of TE materials, including Mg_2Si [9] and Bi_2Te_3 [14]. This is equivalent of a rigid shift of all the calculated conduction bands with respect to the VBM. The feasibility of the treatment is supported by the fact that the main features of the conduction bands and valence bands near the band gap can be in general well captured by the DFT calculations.

In this paper, we adopted a value of 0.78 eV for E_g^0 which was derived from electrical conductivity and Hall measurements [26] and was previously used in Akasaka et al.'s calculations [9]. For β, we use a value of 4×10^{-4} eV/K, with which the calculated Seebeck coefficients were found to agree well with the experimental results for the samples with doping levels larger than 9×10^{17}/cm^3 (see below).

3.2. Chemical potential

The transport properties were evaluated based on the rigid-band approximation in which the electronic structure of the material is supposed to remain unchanged in the doped regions. A series of experimental results [2–4,7,9] ranging from the 1950s to the 2000s were compared to the current theoretical predictions. The basic information of those samples is summarized in ascending order of doping concentration in Table 2. It should be noted that only n-type Mg_2Si samples were considered in this work. Though the experimental samples mentioned in Table 2 were prepared by different methods and existed in either single crystal or polycrystalline form, they were differentiated in the electronic transport simulations only through the doping concentrations.

To obtain the TE properties of a material at a certain temperature T, it is essential to know the chemical potential μ at that temperature through the following relation [14]:

$$N_D - N_A = \int_{E_g}^{+\infty} \frac{D(E)dE}{e^{(E-\mu)/k_BT}+1} dE - \int_{-\infty}^{0} \frac{D(E)dE}{e^{(\mu-E)/k_BT}+1}, \quad (1)$$

where N_D and N_A are the concentrations of donors and acceptors, respectively, $D(E)$ represents the electron density of states, k_B is the Boltzmann's constant and E_g is the temperature dependent band gap mentioned above. The experimental residual carrier concentrations of the samples were used for (N_D–N_A) in the calculations. The electron and hole concentrations (denoted by n_e and n_h, respectively) were approximated at the same time as μ was computed by assuming N_D–$N_A \approx n_e$–n_h [14].

Fig. 3a displays the calculated chemical potential at three doping concentrations (4.3×10^{17}/cm^3, 2.2×10^{19}/cm^3 and 1.5×10^{20}/