



Predicting thermoelectric performance of eco-friendly intermetallic compound p-type CaMgSi from first-principles investigation



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ABSTRACT

In this paper, we report the thermoelectric performance of nontoxic compound CaMgSi using first-principles method combined with Boltzmann transport theory. Our calculation demonstrates that only when using the more accurate HSE06 functional can we correctly reproduce the semiconducting nature of this compound. The result from HSE06 functional shows that CaMgSi compound is a semiconductor with narrow direct band gap of 0.29eV and such narrow band gap may enhance the thermoelectric performance. The calculated thermoelectric transport parameters of p-type CaMgSi, such as Seebeck coefficient, electrical conductivity and lattice thermal conductivity, were described carefully in a wide range of temperature. In addition, the possible techniques to improve ZT value were discussed. The results reveal the thermoelectric performance of CaMgSi exhibits strong temperature dependence and a maximum ZT value of 1.76 can be achieved at 800 K by tuning the carrier concentration, which suggests its appealing thermoelectric application.

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1. Introduction

It is urgent to search for sustainable and clean energy to solve the global energy crisis and environmental pollution. The thermoelectric device can simply and directly convert waste thermal energy into useful electrical power without any mechanical action. For the thermoelectric (TE) material is the most important part of the thermoelectric device, great attentions have been paid to it world widely. The conversion efficiency between thermal and electrical energy is a key parameter for application of TE materials. High conversion efficiency requires TE material has good thermoelectric performance. The thermoelectric performance of TE material is represented by dimensionless figure of merit (ZT) as: $ZT = S^2\sigma T/\kappa$, which is mainly determined by electrical conductivity (σ), Seebeck coefficient (S), absolute temperature (T) and thermal conductivity (κ). The thermal conductivity is consisting of the contributions from electron and phonon two parts ($\kappa = \kappa_e + \kappa_l$). The low efficiency of conversion (ZT value) limits the commercialization of TE material. The TE materials about $ZT \sim 1$ have an opportunity to

be used in commercialized application. Traditional alloy tellurides, such as Be_2Te_3 , Sb_2Te_3 and PbTe [1–3], show large ZT values not only for both n-type but also for p-type TE materials at middle temperatures (ranging from 500 to 800 K). However, these alloys are not widely used in practice due to the toxicity or/and scarce of their constituting elements. Environmental friendly, cheap and earth-abundant TE materials such as oxide-based [4–8] and silicide-based [9,10] materials have sustained attraction for prospective application in thermoelectric technology with reasonable ZT values.

Mg_2Si -based compounds have recently attracted interests due to their remarkable thermoelectric performance by doping for practical applications at middle temperature [11,12]. Benefiting from their inexpensiveness, low density and nontoxic feature, there are many efforts to enhance their thermoelectric performance via different technologies such as dimensional reduction [13], strain [14,15] and doping [16]. Owing to the intrinsic n-type of Mg_2Si , most Mg_2Si -based materials are n-type materials. It's worth noting that the ZT value of p-type Mg_2Si -based materials is roughly a lower order of magnitude than that of n-type Mg_2Si -based materials [17,18]. The n-type materials need to be combined with other p-type materials to achieve thermoelectric devices. The poor match of thermomechanical properties between the n- and p-type materials

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lead to instability of such thermoelectric devices. For the requirement of both n- and p-type Mg₂Si-based materials thermoelectric devices, developing new p-type Mg₂Si-based materials with high thermoelectric performance is strongly desired. Recently, Miyazaki et al. [19] synthesized polycrystalline bulk CaMgSi intermetallic compound and revealed which has p-type conductivity with outstanding thermoelectric performance. However, up to now, the transport properties of intermetallic compound CaMgSi have not been done by first principles. Motivated by the above, we performed the electronic structure, lattice dynamical and transport properties of CaMgSi from first principles calculations in order to better understand the thermoelectric transport properties of CaMgSi and to provide valuable data for further experimental and theoretical research.

2. Computational approach

The structural optimization and electronic properties were performed by using density-functional theory (DFT), which is implemented in the Vienna Ab-initio Simulation Package (VASP) code [20,21]. The structural optimization was performed using generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) functional form and projector augmented wave (PAW) method [22]. The Heyd-Scuseria-Ernzerhof (HSE06) [23] hybrid functional based on DFT was employed to accurately predict the electronic structure. $3 \times 5 \times 3$ k-mesh with Monkhorst-Pack approach was used in the first Brillouin zone (BZ) for the geometry optimization, electronic structure and phonon calculations. The energy convergence threshold was set as 10^{-5} eV. The kinetic energy cut-off value for the wave function expansion in reciprocal space was chosen to be 450 eV.

The completely ab-initio lattice thermal conductivity (k_l) was obtained from a set of interatomic force constants (IFCs) based on Boltzmann transport equation (BTE) as implemented in ShengBTE package [24]. The IFCs includes harmonic (second order) and anharmonic (third-order) IFCs. The harmonic IFCs were investigated using the Phonopy code [25] in the form of supercell approach with finite displacement (0.01 Å). A $3 \times 5 \times 3$ supercell with 540 atoms was considered. All harmonic IFCs were computed from 12 displacement patterns in the approach. In order to obtain the anharmonic IFCs, 272 independent atomic displacement structures ($3 \times 5 \times 3$ supercell) and $3 \times 5 \times 3$ k-mesh in Monkhorst-Pack approach were applied. We included the interatomic interactions up to the third nearest neighbor. Both harmonic and anharmonic IFCs were calculated using VASP code within GGA-PBE functional. Based on the harmonic and anharmonic IFCs, the BTE was iteratively solved by employing ShengBTE code. A $7 \times 11 \times 7$ q-point mesh (270 inequivalent q points) and Gaussian smearing parameter with 1.0 were adopted to guarantee the converged value of k_l . The contribution from natural isotopic scattering was considered as well.

The thermoelectric transport properties of CaMgSi were calculated from semi-classical BTE in the form of constant relaxation time approximation (RTA) and rigid band model, as combined in BoltzTraP code [26]. Under the approximation, the electrical conductivity and Seebeck coefficient tensors as function of temperature T and chemical potential μ can be calculated from the following equations:

$$\sigma_{ij}(T, \mu) = \frac{1}{\Omega} \int g_{ij}(\epsilon) \left[-\frac{\partial f_{\mu}(T, \epsilon)}{\partial \epsilon} \right] d\epsilon \quad (1)$$

$$(\sigma S)_{ij}(T, \mu) = \frac{1}{eT\Omega} \int g_{ij}(\epsilon) \left[-\frac{\partial f_{\mu}(T, \epsilon)}{\partial \epsilon} \right] (\epsilon - \mu) d\epsilon \quad (2)$$

here e , Ω and ϵ represent the electron charge, reciprocal space volume, and band energy, respectively. $\frac{\partial f_{\mu}}{\partial \epsilon}$ is the differential of Fermi function. $g_{ij}(\epsilon)$ denotes transport distribution function, shown as

$$g_{ij}(\epsilon) = \frac{e^2}{N} \sum_{n, \vec{k}} \tau_{n, \vec{k}} v_i(n, \vec{k}) v_j(n, \vec{k}) \frac{\delta(\epsilon - \epsilon_{n, \vec{k}})}{d\epsilon} \quad (3)$$

where N is the k-points number in the entire BZ. $\epsilon_{n, \vec{k}}$ is the energy for n-th band at wave vector \vec{k} , $v_i(n, \vec{k})$ is the corresponding velocity as defined as $v_i(n, \vec{k}) = (1/\hbar) \partial \epsilon_{n, \vec{k}} / \partial k_i$. The relaxation time is treated as independence with n and \vec{k} , namely as a constant ($\tau_{n, \vec{k}} = \tau$). The thermoelectric transport parameters were calculated based on the eigenvalues from HSE06 functional. To accurately predict the thermoelectric properties, much denser k-mesh ($7 \times 11 \times 7$) was used for the integrations in 1st BZ.

In present work, the relaxation time (τ) was considered as a function of temperature (T) using deformation potential theory [27,28]. The τ along arbitrary β direction for 3D material is defined as

$$\tau_{\beta} = \frac{2\sqrt{2}\pi C_{\beta} \hbar^4}{3(k_{\beta} T m_{dos}^*)^{3/2} E_{1\beta}^2} \quad (4)$$

where C_{β} is named as elastic constant along β direction and defined as $C_{\beta} = \frac{1}{V_0} \frac{\partial^2 (E_i - E_0)}{\partial (\Delta l/l_0)^2} |_{l=l_0}$, which is determined by fitting the total energy with strain $\Delta l/l_0$ along the same direction to parabola equation. $E_{1\beta}$ is deformation potential (DP) constant along β direction determined by linear fitting the energy shift of valence band maximum with respect to strain $\Delta l/l_0$. m_{dos}^* is called DOS effective mass and calculated as $m_{dos}^* = \sqrt[3]{m_a^* m_b^* m_c^*}$, here m_a^* is the effective mass along a (wave vector along Γ -X) direction, which was calculated by using: $\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2}$, here E is energy eigenvalue of valence band maximum; \hbar and k are the reduced Plank constant and wave vector, respectively. m_b^* , m_c^* has the corresponding representation as m_a^* .

3. Results and discussion

The CaMgSi has orthorhombic crystal structure with space group Pnma (no.62) as shown in Fig. 1. There are four formula units in each unit cell, in which Ca atoms locating on one of the 4c sites are completely substituted by Mg and other 4c sites are occupied by Ca atoms.

The relaxed lattice parameters and internal parameters by using PBE functional for CaMgSi are given in Table 1; the previous experimental data are also listed.

The calculated lattice constants and internal parameters (x, y, z) of the Ca, Mg and Si are in agreement with experimental reports. Employing the optimized structure, the electronic structures were calculated by using PBE and HSE06 functionals, respectively. Fig. 2 plots the band structures using PBE and HSE06 functionals along high-symmetry k-points in 1st BZ. The high-symmetry k-points paths were chosen as Z(0,0,1/2) - Γ (0,0,0) -X(1/2,0,0) -U(1/2,0,1/2)

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