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An improved interatomic potential function for thermoelectric Mg_2Si: A combination study of ab-initio and molecular dynamics method

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ABSTRACT

The appropriate interatomic potential function is of vital importance for the prediction of a material's various properties in theoretical modeling and simulations such as molecular dynamics. Here we develop an improved interatomic potential for use in thermoelectric (TE) Mg_2Si, which is fit to density functional theory and is further verified by the molecular dynamics simulation. We find that this interatomic potential can well predict the structural, elastic, and thermodynamics properties of Mg_2Si such as elastic constants, thermal expansion, heat capacity, and thermal conductivity, while these predicted results show good agreement with the experimental reports. This work is beneficial for the development of powerful theoretical modeling and simulations to accurately predict various properties of Mg_2Si, which can be also applied in other TE or non-TE energy materials.

1. Introduction

Solid-state thermoelectric (TE) technology, which can directly achieve the conversion of thermal energy into electrical energy with high reliability and environmental friendliness, has great application prospects and economic benefits in the fields of refrigeration, power generation, infrared detection, and waste heat recovery [1,2]. The efficiency of TE materials is characterized by the dimensionless figure of merit $zT = \alpha^2 T/\rho\kappa$, where α is the Seebeck coefficient, ρ is the electric resistivity, T is the absolute temperature, and κ is the total thermal conductivity which includes both electric and lattice contributions κ_e and κ_l. A good thermoelectric material requires the perfective combination of the high Seebeck coefficient, decreased electrical resistivity and low thermal conductivity.

Mg_2Si as well as its related compounds have been recognized as the potential high-performance TE material at the intermediate conversion temperature range of 500–850 K [3,4]. In addition to their high thermoelectric performance, their abundant raw materials, low cost, nontoxicity, lightweight (density: 1.99 g/cm^3), elevated compression strength (1640 MPa) and Yong's modulus (120 GPa) make them even more attractive in the commercial applications [5–7]. In recent years, significant experimental characterization efforts [8–12] and theoretical treatments [13–26] have been made on Mg_2Si. Liu et al. [27] reported that the zT value had reached 1.3 for Sb doped $Mg_2Si_{0.3}Sn_{0.7}$ by experimental study. Theoretical treatment, which is mainly adopted by using first principles calculation, was focused on the study of electronic structure [13–15], lattice dynamics [16,17], lattice stability [15,18,19], thermoelectric [20–22]and elastic properties [13–15,23–26] of Mg_2Si and Mg_2X (X = Si,Ge, Sn and Pb) based alloys.

Nowadays, large-scale molecular dynamics (MD) simulations, which is a popular alternative to the experiment, has been also regarded as a well-established and useful tool in material research to evaluate many properties [28–30]. Especially, the MD can provide the fruitful insights into the dynamics of atomic level phenomena that cannot be observed directly from the experiment. However, there are few theoretical investigations on elastic and thermodynamic properties of Mg_2Si by molecular dynamics (MD) method. The difficulty has been due to the establishment of appropriate interatomic potentials. In MD simulation, suitable interatomic potentials are essential for predictions of the elastic and thermodynamic properties of Mg_2Si. Nevertheless, no suitable potential function has been reported so far, which limit the development of theoretical modeling and simulations in the Mg_2Si TE semiconductor.

In this work, we develop multi-body interatomic potentials including bond and angle interactions for Mg_2Si by the first principles calculation. By analyzing the structural stability, the detailed atomic interaction forms including bond and angle items are constructed, respectively. In order to determine the values of parameters in the potential function, the related ground-state equations are established.

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Based on the cohesive energy and elastic properties from first principles calculation and experiments, the potential parameters are determined through the least-square fitting method. Then, the MD simulation is performed to validate the interatomic potentials by calculating the radial distribution function (RDF), structural and elastic properties of Mg_2Si. Finally, the several important thermodynamic properties, including linear thermal expansion coefficient, specific heat capacity and lattice thermal conductivity are also predicted by MD simulation. The potential using in this paper is not complicated in the form. However, this improved Morse potential model has been successfully developed by our group to figure out the atomic interactions and to predict thermodynamic properties in $CoSb_3$ and Zn_4Sb_3 thermoelectric materials, respectively [31,32]. Especially, this potential model can be used to accurately describe the thermodynamic properties under various point defects [33–36] and large structural deformations [37,38]. We believe this improved potential function is not only suitable for a perfect system, but also for a more complicated system such as the one with structural point defect or large structural deformation. Here, using this improved Morse potential model, we probed the atomic interactions in Mg_2Si system and developed the molecular dynamics method for investigation of the structural and thermodynamic properties. These predicted results show good agreement with the experimental reports. Our developed force field method for Mg_2Si is a valuable tool for predicting material properties, which is beneficial for the development of powerful theoretical modeling and simulations to accurately predict various properties of Mg_2Si.

2. Construction of interatomic potentials

2.1. Crystal structure

Mg_2Si is a cubic TE semiconductor crystallizing in the antifluorite structure with one molecular unit per primitive cell and four formulas per fcc conventional cell [23]. The structure symmetry of Mg_2Si is O_h^3 with the space group of $Fm\bar{3}m$. The silicon atom locates at the 4*a* (0 0 0) Wyckoff site and Magnesium atom locates at the 8*c* (0.75 0.25 0.25) Wyckoff site, respectively [14]. The crystal structure of Mg_2Si is shown in Fig. 1. The axis angle is 90°, 90°, 90° and the experimental lattice constants $a = 6.338$ Å [39].

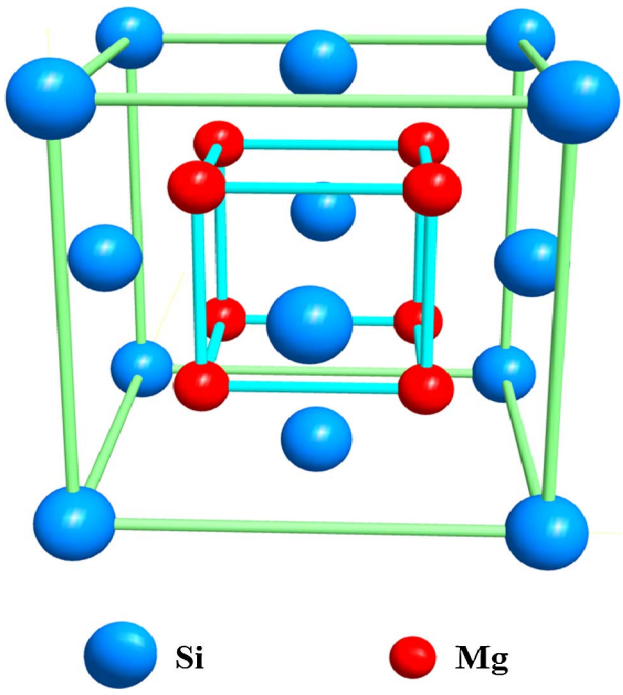

Fig. 1. Crystal structure of the Mg_2Si semiconductor.

2.2. Function form for interatomic potentials

The adopted interatomic potentials comprise of bond and angle atomic interaction functions. The long range electrostatic interaction was not considered in our MD simulation, because this interatomic potential function focuses on studying the structural and thermodynamic properties of Mg_2Si, rather than the electric properties. The total interatomic potential energy (φ) is given by

$$\varphi = \varphi_{Bond} + \varphi_{Angle} \tag{1}$$

where φ_{Bond} and φ_{Angle} are interatomic potentials which represent the bond and angle interaction respectively. The bond interaction, a central-force bond between two atoms, is described by Morse function, revealing the bond-bending and bond-stretching characteristics [40,41]. It can be defined as

$$\varphi_{Bond} = \sum_{i<j} B_{ij}, B_{ij} = D(e^{-2\alpha(r_{ij}-r_0)} - 2e^{-\alpha(r_{ij}-r_0)}) \tag{2}$$

where B_{ij} is the bond interaction potential energy function between atoms i and j, and r_{ij} is the distance between atoms i and j. r_0, α and D represent the equilibrium bond distance, stiffness parameter, and depth of the potential well, respectively.

The angle interaction is described by the bond-angle function which is the angle bending deviation from an ideal geometry [42]. It is defined as

$$\varphi_{Angle} = \sum_{j} A_{ijk}, A_{ijk} = \frac{1}{2}K(\cos\theta_{ijk} - \cos\theta_0)^2 \tag{3}$$

where A_{ijk} is the angle interaction potential energy function between atoms i, j and k, force constant (K) is the parameter to be determined, θ_{ijk} is the angle with a center atom j, and θ_0 is the equilibrium value of the angle.

2.3. Determination of parameters of the interatomic potentials

For bond interaction potential energy function, three kinds of bond interaction are constructed. They are Mg-Mg, Mg-Si, and Si-Si interactions, respectively. For each bond interaction, there are three parameters to be determined. Thus, there are nine parameters to be solved in the bond interaction potential energy function.

For the angle interaction potential energy function, there are two kinds of angle interactions are considered. One is the angle form by two Mg atoms and one Si atom (Mg-Si-Mg angle interaction), the other is the angle form by two Si atoms and one Mg atom (Si-Mg-Si angle interaction). There are two parameters to be determined for the angle interatomic potential, since θ_0 can be obtained from the equilibrium atomic coordinates.

The equilibrium bond distances and angles are listed in Table 1. Totally, there are eleven parameters to be determined for the interatomic potentials. These parameters would be determined according to the ground-state equations as discussed below.

When a unit cell reaches the equilibrium state, the internal stress is

Table 1
Equilibrium bond distances and angles for Mg_2Si.

Bond interactions	Equilibrium bond distances
Mg-Mg	3.1814 Å
Mg-Si	2.7552 Å
Si-Si	4.4992 Å
Angle Interactions	Equilibrium angles
Mg-Si-Mg	70.529°or 109.471°
Si-Mg-Si	109.527°