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The effect of point defects and nanoparticles on thermal conductivity of magnesium silicide

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ABSTRACT

We compute thermal conductivity (κ) of magnesium silicide (Mg_2Si) with point defects and nanoparticles through molecular dynamics simulation. To describe an alloy with complex defect structures, the extended modified embedded atom method is utilized in this simulation study. The calculated phonon dispersion and κ of pristine Mg_2Si are in close agreement with first-principles calculations and experimental results. We compared the effect of intrinsic point defects and nanoparticles on heat transfer in Mg_2Si at the same stoichiometry. We find that point defects could be more effective than nanoparticles to reduce κ. The geometric size effect is also investigated for Mg and Si nanoparticles. Smaller Mg nanoparticles can significantly reduce κ. However, Si nanoparticles demonstrate little size effect on κ. Our simulation results show that phonon transport in Mg_2Si has more contribution from strain scattering than mass defect scattering. These findings can provide guidance for experiments to more effectively engineer bulk Mg_2Si with nanostructured defects for thermoelectric applications.

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1. Introduction

Thermoelectric devices can be widely used to produce electrical energy from abundant heat sources such as industrial waste heat, nuclear reactor, geothermal and solar energy [1,2]. In many industrial processes, the major energy source is from carbon-based fossil fuel, and over 50% of the consumed energy is released to the environment as waste heat. Therefore, waste heat recovery based on thermoelectric technology can not only reduce carbon dioxide emission, but also improve energy efficiency for a wide spectrum of industries. For heat recovery applications in the medium temperature range (500–900 K), magnesium silicide (Mg_2Si) is an intrinsic n-type semiconductor with cubic anti-fluorite structure, which has shown comparable energy conversion efficiency to other good thermoelectric materials such as PbTe, $CoSb_3$, and SiGe [2]. Considering other attractive properties of Mg_2Si such as high natural abundance, non-toxic and low weight density, it is considered a promising medium temperature thermoelectric material to harvest automobile waste heat energy.

Over recent years, Mg_2Si has been widely investigated both experimentally and theoretically in order to further enhance its thermoelectric figure of merit, which is a dimensionless quantity defined as $ZT = \sigma S^2 T/\kappa$ (σ: electrical conductivity, S: Seebeck coefficient, T: absolute temperature, κ: thermal conductivity). A widely adopted method to enhance the ZT of Mg_2Si is done through impurity doping with various elements, such as Ag for p-type Mg_2Si (ZT = 0.11 at 873 K) and Bi for n-type Mg_2Si (ZT = 0.77 at 862 K) [3]. In this doping method, the power factor, σS^2, can be increased at least by a factor of 2, while κ often remains the same or decreases slightly [4]. Compared with κ of other good thermoelectric materials (<1 W/m K), κ of Mg_2Si doped with Ag is still quite large (>5 W/m K). As phonons are known as the major heat carrier in Mg_2Si [4], it is therefore crucial to further reduce κ without degrading σS^2. In spite of the efforts to extensively study dopants both experimentally [3,5] and theoretically [6–8], doping alone seems to be far from sufficient to develop Mg_2Si with ZT larger than 1. As mentioned in the literature, ZT in the range of 1.5–2.0 is ideal for automobile waste heat recovery [9]. In order to achieve this goal, nanostructured engineering methods, which have been successful with other bulk thermoelectric materials, should be applied to Mg_2Si.

One potentially promising method to reduce κ in bulk materials is to introduce extensive defects, such as grain boundaries. It has been shown that ZT can be effectively increased by controlling the grain size in BiSbTe bulk alloys [10]. In the case of Mg_2Si, a recent theoretical paper suggests that ZT of Mg_2Si cannot be increased by controlling the grain size [11], while another

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modeling study suggests ZT can be increased [12]. Because different theoretical assumptions may lead to opposite conclusions, this methodology needs experimental validation. Another promising method is to introduce nanoparticles in the host matrix to reduce κ [13]. Recently, Si has been embedded in bulk Mg_2Si [14,15]. These results show that Mg_2Si embedded with Si nanoparticles can reduce κ by 25% [14]. In practice, Si nanoparticles are not always chemically inert in Mg_2Si. At higher temperatures, the nanoparticles may partially dissolve into the matrix to create more intrinsic point defects, which can also scatter phonons. Therefore, it is not appropriate to give full credit to Si nanoparticles in Mg_2Si since point defects may also play a critical role in decreasing κ.

In this paper, we use molecular dynamics simulations to study the effect of point defects and nanoparticles on κ for Mg_2Si. Based on the modified embedded atom method [16], we have developed a Mg–Si alloy potential to perform heat transfer simulations. The calculated κ (15 W/m K) for pristine Mg_2Si is close to the first-principles calculations and experimental results (11 W/m K) [17,18]. At the same stoichiometry, the simulation results show that intrinsic point defects are more effective than nanoparticles to reduce κ. In addition, we find that κ is very sensitive to certain types of point defects and nanoparticles in Mg_2Si. Strain effects due to various chemical bonds can account for the different phonon scattering behaviors. Our simulation results can provide guidance for experiments to develop thermoelectric properties of bulk Mg_2Si with higher efficiency.

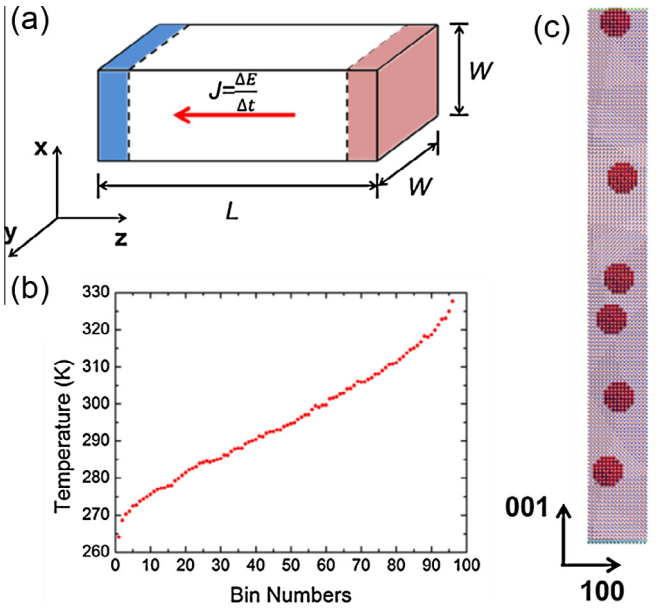

Fig. 1. (a) A diagram to illustrate the thermal conductivity calculation using the non-equilibrium MD simulation method. For bulk material modeling, periodic boundary conditions are applied in *x* and *y* directions. (b) Temperature as a function of bin numbers for Mg_2Si at room temperature. Along the *z*-axis, the bulk sample is uniformly divided into 100 bins. (c) A bulk sample to illustrate nanoparticles (~1 nm in diameter) embedded in Mg_2Si crystal.

2. Theoretical methods

To compute κ for Mg_2Si, we use the non-equilibrium molecular dynamics method implemented in the LAMMPS code [19]. As shown in the diagram in Fig. 1(a), a constant heat flow $J = \Delta E/\Delta t$ across the area $A = W^2$ is established by exchanging kinetic energy (ΔE) between the coldest blue[1] region (left end) and the hottest red region (right end) in each simulation time step (Δt = 0.2 fs). In the simulation, the system is fully relaxed at 300 K by isothermal–isobaric (NPT) ensemble, and afterward microcanonical (NVE) ensemble is used to calculate κ. As the system reached steady state in the NVE ensemble (~10 ns), the temperature profile is linear in the middle region as shown in Fig. 1(b), and a statistical average temperature gradient (∇T) is used to compute κ using Fourier's law expressed as $\kappa = J/A\nabla T$ [20]. In Fig. 1(c), the nanoparticles embedded in the matrix are plotted in red.

In this simulation study, the Mg–Si alloy potential is developed based on the modified embedded atom method (MEAM). According to previous discussion, the nature of bonding in Mg_2Si is mostly covalent and ionicity is only 8% [8]. Therefore, it is valid to study thermal properties of Mg_2Si based on a neutral charge model. The MEAM Mg–Si potential is optimized using density functional theory (DFT) calculations. We use the Vienna ab initio simulation package (VASP) to compute bulk properties of the Mg–Si alloy with local-density approximation for the exchange–correlation potential, and the pseudopotential is described by the projector-augmented-wave method [21]. For bulk elastic properties, we find that the MEAM potential is in good agreement with DFT calculations. However, it is far from accurate in predicting the energy of a bulk Mg–Si alloy with complex defect structures. Although numerical optimization may enhance the prediction of MEAM for defect structures, it is often accomplished by sacrificing accuracy of other bulk properties. To address this problem, Extended MEAM is developed to model the alloy with complex chemical bonds. An implementation of Extended MEAM in LAMMPS and the potential parameters are given in the Supporting information. A later publication will explain more details about Extended MEAM.

[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

3. Results and discussions

The atomic structure of Mg_2Si is shown in Fig. 2(a). We have considered six intrinsic point defects in this simulation study. These intrinsic defects are Mg vacancy (V^{Mg}), Si vacancy (V^{Si}), Mg and Si interstitials on 4*b* sites (I^{Mg}, I^{Si}), Si on Mg Anti-site (Si^{Mg}), and Mg on Si Anti-site (Mg^{Si}). According to a recent first-principles study, the most stable point defects are V^{Mg} for Si-rich conditions, and I^{Mg} for Mg-rich or stoichiometric conditions [8]. Depending on the material synthesis conditions, other intrinsic point defects may also exist in Mg_2Si. In comparison with DFT calculation results, Extended MEAM potential can accurately predict both bulk properties and intrinsic defect formation energies as shown in Table 1. Along the high symmetry *k*-points of the Brillouin zone shown in Fig. 1(b), we also calculated the phonon dispersion of Mg_2Si with DFT and Extended MEAM. The small differences of long-wavelength acoustic phonons shown in Fig. 1(c) suggest that Extended MEAM can provide an accurate prediction for the group velocity of acoustic phonons.

According to kinetic theory, κ for bulk material is given by $\kappa = \frac{1}{3}\int CV\Lambda df$, where *C* is the phonon heat capacity, *V* is the phonon group velocity, and Λ is the phonon mean free path. The mean free path Λ can be expressed as,

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_I} + \frac{1}{\Lambda_D} + \frac{1}{\Lambda_L}$$

Here, Λ_I, Λ_D, and Λ_L refer to the mean free paths due to intrinsic phonon scattering, defect scattering, and boundary scattering, respectively. All of these phonon scattering mechanisms are combined to obtain an overall phonon mean free path, Λ, through

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