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Polycrystalline Mg_2Si thin films: A theoretical investigation of their electronic transport properties

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ABSTRACT

The electronic structures and thermoelectric properties of a polycrystalline Mg_2Si thin film have been investigated by first-principle density-functional theory (DFT) and Boltzmann transport theory calculations within the constant-relaxation time approximation. The polycrystalline thin film has been simulated by assembling three types of slabs each having the orientation (001), (110) or (111) with a thickness of about 18 Å. The effect of applying the relaxation procedure to the thin film induces disorder in the structure that has been ascertained by calculating radial distribution functions. For the calculations of the thermoelectric properties, the energy gap has been fixed at the experimental value of 0.74 eV. The thermoelectric properties, namely the Seebeck coefficient, the electrical conductivity and the power factor, have been determined at three temperatures of 350 K, 600 K and 900 K with respect to both the energy levels and the *p*-type and *n*-type doping levels. The best Seebeck coefficient is obtained at 350 K: the S_{yy} component of the tensor amounts to about $\pm 1000\ \mu V\ K^{-1}$, depending on the type of charge carriers. However, the electrical conductivity is much too small which results in low values of the figure of merit ZT. Structure–property relationship correlations based on directional radial distribution functions allow us to tentatively draw some explanations regarding the anisotropy of the electrical conductivity. Finally, the low ZT values obtained for the polycrystalline Mg_2Si thin film are paralleled with those recently reported in the literature for bulk chalcogenide glasses.

1. Introduction

Among the thermoelectric materials, the Mg_2X (X=Si, Ge, Sn) alloys have been identified as promising advanced ones for use in the temperature range from 500 K to 800 K [1,2]. By contrast with PbTe and $CoSb_3$, which are thermoelectric materials operating in the same conversion temperature range as Mg_2X alloys, the latter ones are environmentally friendly, bearing nontoxic and Earth crust abundant chemical elements [3].

The efficiency of thermoelectric materials can be characterized by the figure of merit $ZT = TS^2\sigma/\kappa$, a dimensionless quantity in which S is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity, and T the temperature. This expression, identified by Ioffe in the late 1950s [4], shows that a good thermoelectric material should have a high S and σ values, and a low κ value in the temperature range of interest. High performance thermoelectric materials are usually regarded as having ZT equal to or greater than unity.

The thermoelectric efficiency can be improved by means of nanoscale engineering techniques. The use of thermoelectric thin films should be an attractive route for at least two reasons. Firstly, the 3D to 2D-dimension lowering of materials leads to the quantum confinement of electrons and discretization of the quantum states that in turn increases the Seebeck coefficient. Secondly, by decreasing the grain size, and as a consequence by increasing the number of interfaces, the thermal conductivity in thin films should be lower than that in bulk materials due to more phonon scattering. In addition, the ongoing miniaturization of electronic components implies that thermoelectric generators must be reduced in size so as to reach higher power density [5]. Thin films permit this miniaturized technology.

Although an abundant literature exists on the fabrication of Mg_2Si thin films [6–14], their thermoelectric properties have not been experimentally investigated. Only a few theoretical studies have been reported on the calculations of Mg_2Si thin films, either dealing with the structural and electronic characteristics [15], or the thermoelectric properties of the films [16]. Whereas experimentally grown thin films are always polycrystalline with preferential orientations (001, 110 and 111), the theoretical studies deal only with monocrystalline thin films. In the present work, our objective is to calculate thermoelectric properties of polycrystalline thin films by means of first-principle

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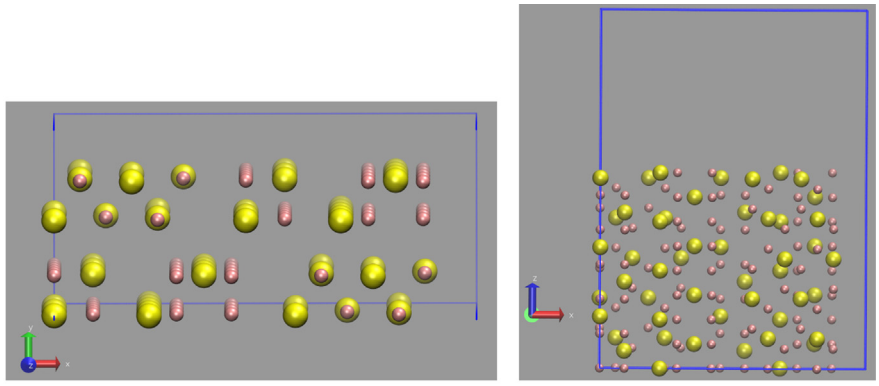
density-functional theory (DFT) and Boltzmann transport theory approaches. The studied polycrystalline Mg_2Si thin film is build from three monocrystalline films each having a different orientation, namely, (001), (110) or (111).

2. Theoretical procedure

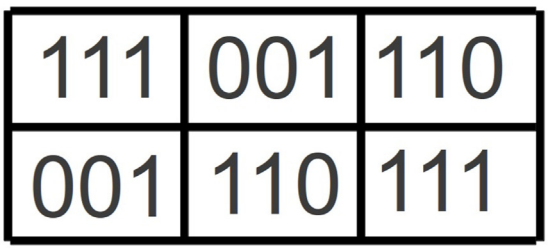
Mg_2Si crystallizes in the antifluorite structure within the space group $Fm\bar{3}m$, with a cell parameter of 6.35 Å. The Si atom occupies the 4*a* (0,0,0) site and the Mg atoms occupy the 8*c* (0.25,0.25,0.25) sites. The $Fm\bar{3}m$ space group fixes the fractional coordinates of all atoms.

The polycrystalline thin film (Fig. 1) has been built by assembling three different types of monocrystalline films together each having a different orientation that can be (001), (110) or (111). Two of each films, hence six films in total, have been used to build the polycrystalline film and arranged together in such a way to avoid that two identical films share the same face, as shown in Fig. 1(iii). The construction of the (001), (110) and (111) slabs has been performed by cleaving the bulk Mg_2Si structure perpendicular to the directions [001], [110] and [111], respectively. The thickness of these three slabs was chosen to be as close as possible to each other while keeping the Mg_2Si stoichiometry. Hence, the thickness was of 18.015 Å for the (110) slab ($Mg_{18}Si_9$), 17.516 Å for the (001) slab ($Mg_{12}Si_6$), and 17.467 Å for the (111) slab ($Mg_{20}Si_{10}$). Since the calculations have been performed by combining two slabs of each orientation, the total number of atoms in the resulting slab is 150 and the size of the simulation box is 24.5 Å × 11.0 Å × 33.0 Å. The slab structure belongs to the orthorhombic crystal system and is depicted in Fig. 1(i) and (ii). In order to avoid that the periodic images of the slab interact with each other, a vacuum above the slab of about 15 Å has been chosen. The size of the vacuum has been determined by the calculation of the potential energy curve (not shown here) with respect to the length of the simulation box perpendicular to the slab surface, which corresponds to the *z*-axis. The procedure to calculate the ideal vacuum size is as follows. We select a large *c* parameter of the simulation box (perpendicular to the slab surface) and we calculate the energy. Then we decrease *c* and recalculate the energy, and so forth until the slab meets its periodic image. We then plot the potential energy curve with respect to *c*. The curve resembles a Lennard–Jones curve with a leveling off of long-range tail. The size of *c* is selected in this long-range tail region of the curve which ensures that the slab is nearly isolated.

The calculations have been performed using the first-principle density-functional theory (DFT) [17,18] as implemented in the Quantum Espresso package [19]. The self-consistent, total energy calculations have been carried out using the plane-wave and ultrasoft pseudopotential approaches [20]. The generalized gradient approximation (GGA) exchange and correlation functionals designed by Perdew, Berke and Ernzerhof (PBE) [21] have been used for treating the exchange-correlation terms. Kutorasinski et al. have recently shown that spin–orbit coupling impacts the valence band structure of the Mg_2X series [22]. The spin–orbit coupling breaks the threefold degeneracy of the topmost valence bands down into twofold and single degenerate bands; for Mg_2Si the energy difference is 36 meV. In addition, the curvature of the bands at the Γ-point is slightly increased. It is then expected that the Seebeck coefficient should be slightly enhanced in *p*-doped bulk Mg_2Si. By contrast, there is no effect on the conduction bands. Since the errors made on the calculation of transport properties as estimated using the Boltzmann theory are much larger than the spin–orbit coupling effects, relativistic effects have not been accounted for explicitly in the present calculations. A cutoff energy of 340 eV has been used throughout this work. The *k*-point



(i) (ii)



(iii)

Fig. 1. Structure of the simulated polycrystalline Mg_2Si thin film before optimization. (i) Polycrystalline thin film structure before optimization. View of the slab surface parallel to the *c*-axis. The blue frame denotes the basis cell of the simulated thin film along the *a* and *b* directions. The location of the constituting monocrystalline films (MCF) can be seen in Fig. 1(iii): the top two atomic layers are, from left to right, the (111), (001) and (110) MCF; the bottom two atomic layers are the (001), (110) and (111) MCF. Pink: Mg atoms; Yellow: Si atoms; (ii) same slab surface though viewed perpendicularly to the *c*-axis. The vacuum is depicted above the polycrystalline thin film; (iii) mode of assemblage of the various monocrystalline thin films to create the polycrystalline thin film. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this paper.)