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Elastic constants and thermodynamic properties of $Mg_2Si_xSn_{1-x}$ from first-principles calculations*

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This paper stuides the elastic constants and some thermodynamic properties of $Mg_2Si_xSn_{1-x}$ ($x = 0$, 0.25, 0.5, 0.75, 1) compounds by first-principles total energy calculations using the pseudo-potential plane-waves approach based on density functional theory, within the generalized gradient approximation for the exchange and correlation potential. The elastic constants of $Mg_2Si_xSn_{1-x}$ were calculated. It shows that, at 273 K, the elastic constants of Mg_2Si and Mg_2Sn are well consistent with previous experimental data. The isotropy decreases with increasing Sn content. The dependences of the elastic constants, the bulk modulus, the shear modulus and the Debye temperatures of Mg_2Si and $Mg_2Si_{0.5}Sn_{0.5}$ on pressure were discussed. Through the quasi-harmonic Debye model, in which phononic effects were considered, the specific heat capacities of $Mg_2Si_xSn_{1-x}$ at constant volume and constant pressure were calculated. The calculated specific heat capacities are well consistent with the previous experimental data.

Keywords: first-principles, $Mg_2Si_xSn_{1-x}$, elastic constants, heat capacity
PACC: 7115M, 8160C, 6220D, 6540E

1. Introduction

There has been increasing attention paid to semiconducting magnesium based materials which are composed of non- or less toxic and naturally abundant elements in the earth's crust for applications to photoelectronic and thermoelectric devices. In recent years a number of works on synthesis methods of magnesium based materials have been carried out.[1,2] In 2006, Song *et al*[3] studied the thermoelectric properties of $Mg_2Si_xSn_{1-x}$ synthesized by bulk mechanical alloying. It indicated that thermoelectric materials of $Mg_2Si_xSn_{1-x}$ have better comprehensive properties than Mg_2Si. However, there are many difficulties because of large difference in melting temperature among elemental constituents, various contaminations in material processing and so on.[4,5] So in recent years a number of works based on first principles calculations about magnesium based materials have been carried out in order to know more properties of them. In 2001, Araud and Alouani[6] calculated the elastic properties of Mg_2Si and Mg_2Ge using the all-electron GW approximation. In 2007, Tani and Kido[7] calculated the lattice dynamics of Mg_2Si and Mg_2Ge using first-principles. However, there is a group of ternary compounds that has been studied very little theoretically. To our knowledge, no detailed first-principles elastic constants and thermodynamic properties such as specific heat capacity and Debye temperature on the pressure have been reported on ternary $Mg_2Si_xSn_{1-x}$ thermoelectric materials.

In this paper, we present first-principles calculations of elastic constants and some thermodynamic properties of ternary Mg-based thermoelectric materials. The elastic constants and specific heat capacities C_v of $Mg_2Si_xSn_{1-x}$ and the Debye temperatures θ_D of Mg_2Si and $Mg_2Si_{0.5}Sn_{0.5}$ are calculated and discussed. They are compared with previous experimental data.

2. The calculation model and method

The semiconducting compounds Mg_2Si and Mg_2Sn have an anti-CaF_2 type structure (space group $Fm3m$ No.255). According to Vegard's law,[8] the lattice constants of $Mg_2Si_xSn_{1-x}$ ($x = 0$, 0.25, 0.5, 0.75,

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1) are given as

$$a(x) = 6.35(1-x) + 6.76x. \quad (1)$$

The lattice constants of Mg_2Si and Mg_2Sn are 0.635 nm and 0.676 nm. The calculated lattice constants are listed in Table 1. The present results are close to the experimental data.[1] The Sn replaces some Si atoms and is solutionized in the intermediate compound Mg_2Si to form $Mg_2Si_xSn_{1-x}$, which has the same crystal structure as Mg_2Si. The crystal structure of $Mg_2Si_{0.5}Sn_{0.5}$ is shown in Fig.1.

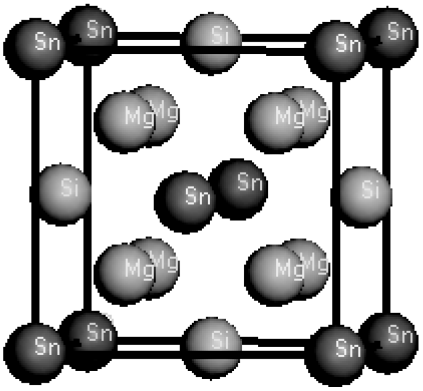


Fig.1. Crystal structure of $Mg_2Si_{0.5}Sn_{0.5}$.

Table 1. Lattice constants of $Mg_2Si_xSn_{1-x}$ in comparison with previous experimental data.

x	0	0.25	0.5	0.75	1
present work a/nm	0.635	0.645	0.656	0.666	0.676
x	0	0.2	0.6	0.8	1
experiment a/nm [1]	0.6353	0.6426	0.6586	0.66683	6.765

The first-principles calculations are performed by employing a pseudo-potential plane-waves (PP-PW) approach based on density functional theory (DFT) and implemented in the most recent version of CASTEP (Cambridge Serial Total Energy Package) code.[9] The exchange–correlation potential is treated within the generalized gradient approximation (GGA).[10] In order to reduce the number of plane waves required, chemically inactive core electrons are effectively replaced with ultra-soft pseudo-potentials. Two parameters that affect the accuracy of calculations are the kinetic energy cutoff which determines the number of plane waves in the expansion and the number of special k-points used for the Brillouin zone (BZ) integration. The valence electronic wave function in a plane-wave basis is set up to an energy cutoff of 330eV (ultra-fine) and self-consistent calculation (SCF) tolerance of 10^{-6} eV/atom (fine). In the total-energy calculations, integrations over the BZ are performed by using a $4 \times 4 \times 4$ Monkhorst–Pack set,[11] which gives 20 symmetrized k points in the irreducible BZ.

3. Results and discussion

The elastic properties define the properties of a material that undergoes stress, deforms and then recovers and returns to its original shape after the stress ceases. Elastic properties of solids are closely related to many fundamental solid-state properties, such as equations of state (EOS), specific heat thermal expansion, Debye temperature melting point and many others. From the elastic constants, one can obtain valuable information about the anisotropic character of the bonding, the structural stability and mechanical stability.

It is well established that first-principles studies based on DFT can be used to obtain reliable elastic properties.[12,13] Several methods are available for computation of stiffness coefficients, but currently the finite strain method seems to be most commonly used and this one is used in the present work. In this approach, the ground state structure is strained according to symmetry-dependent strain patterns with varying amplitudes and a subsequent computation of the stress tensor after a reoptimization of the internal structure parameters. The elastic stiffness coefficients are then the proportionality coefficients relating the applied strain to the computed stress, $\sigma_i = C_{ij}\varepsilon_{ij}$.[14] A cubic crystal has only three different symmetry elements (C_{11}, C_{12} and C_{44}), each of which represents three equal elastic constants ($C_{11} = C_{22} = C_{33}$; $C_{12} = C_{23} = C_{31}$; $C_{44} = C_{55} = C_{66}$). A single strain with non-zero first and fourth components can give stresses relating to all three of these coefficients, yielding a very efficient method for obtaining elastic constants for the cubic system.

From the results of the elastic stiffness (C_{ij}), bulk modulus (B), Young's modulus (E), shear modulus (G) and Poisson's ratio (ν) were determined by using the Voigt–Reuss–Hill averaging scheme.[15–17] According to the Voigt approximation, the Voigt's shear modulus ($G_{\rm V}$) in the cubic system is given by

$$G_{\rm V} = \frac{C_{11} - C_{12} + 3C_{44}}{5}. \quad (2)$$

According to the Reuss approximation, however,

the Reuss's shear modulus (G_R) is given by

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})}. \quad (3)$$

The bulk modulus B is the same in both the Voigt and Reuss averages in the cubic system and it is given by

$$B = \frac{C_{11} + 2C_{12}}{3}. \quad (4)$$

Hill has proved that the Voigt and Reuss equations represent upper and lower limits of the polycrystalline constants and the arithmetic mean value of the Voigt and Reuss moduli, $G = (G_V + G_R)/2$ is taken for an estimation of the elastic modulus.

The Young's modulus (E) and Poisson's ratio (ν) can be calculated using the Hill's shear modulus (G) and bulk modulus (B), and they are given by

$$E = \frac{9GB}{3B + G}, \quad (5)$$

$$\nu = \frac{3B - 2G}{2(3B + G)}. \quad (6)$$

Table 2 shows the calculated elastic constants of $Mg_2Si_xSn_{1-x}$. It shows that the calculated elastic constants of Mg_2Si and Mg_2Si are in good agreement with the experimental data.[18,19] These results indicate that the method used in our case is reasonable. To the best of our knowledge, no experimental data have been reported so far for the elastic constants of $Mg_2Si_xSn_{1-x}$ in the $0 < x < 1$ composition range. From Table 2, it is noted that C_{11}, C_{12} and the bulk modulus decrease with increasing Sn content, while for C_{44} there is no obvious change.

Table 2. The calculated elastic properties of $Mg_2Si_xSn_{1-x}$ and the experimental data of Mg_2Si.

properties	Mg_2Si		$Mg_2Si_{0.75}Sn_{0.25}$	$Mg_2Si_{0.5}Sn_{0.5}$	Mg_2Sn	
	calculated	experiment[18]			calculated	experiment[19]
elastic constant C_{11}/GPa	118.82	126	107.76	94.24	81.10	82.4
C_{12}/GPa	22.27	26	22.05	21.63	20.16	20.8
C_{44}/GPa	44.96	48.5	40.92	38.43	34.85	36.6
$S = (C_{11} - C_{12})/(2C_{44})$	1.07		1.05	0.95	0.87	
bulk modulus B/GPa	54.45	59	50.60	46.08	43.73	
Young's modulus E/GPa	111.79		100.14	85.05	69.15	
shear modulus G/GPa	46.25		41.68	37.57	31.7	
Poisson ratio ν	0.15		0.17	0.20	0.24	

The isotropy coefficient, $S = (C_{11} - C_{12})/(2C_{44})$, which has the value 1 for an isotropic crystal, is calculated to be 1.07 and 0.87 for Mg_2Si and Mg_2Sn. Mg_2Si is more isotropic than Mg_2Sn and the isotropy of $Mg_2Si_xSn_{1-x}$ decreases with the increasing Sn content.

The key criteria for mechanical stability of a crystal are that the strain energy must be positive, which for a cubic crystal means that the elastic stiffness constants should satisfy the following criteria:

$$C_{11} + 2C_{12} > 0,\ C_{44} > 0,\ \text{and}\ \ C_{11} - C_{12} > 0. \quad (7)$$

Table 2 shows that the elastic stiffness constants of $Mg_2Si_xSn_{1-x}$ satisfy the above conditions, implying that they are mechanically stable.

The calculated ratios of bulk modulus B to shear modulus G are 1.21, 1.24, 1.20, 1.25 for Mg_2Si, $Mg_2Si_{0.75}Sn_{0.25}$, $Mg_2Si_{0.5}Sn_{0.5}$ and Mg_2Sn respectively. Pugh[20] proposed that the ratio of B/G represents a measure for machinable behaviour. A high B/G value is associated with ductibility and the low value indicates brittleness. The critical value which separates ductile and brittle is around 1.75. Based on Pugh's notion,[20] these compounds are brittle, which may have technological applications.

Table 3 presents the pressure dependences of the elastic constants, the bulk modulus B and the shear modulus G of Mg_2Si and $Mg_2Si_{0.5}Sn_{0.5}$ at 273 K. It is found that the constant C_{11} varies largely under the effect of pressure in comparison with the variations in elastic constants C_{12} and C_{44}. The elastic constant C_{11} represents elasticity in length. A lon-

gitudinal strain produces a change in C_{11}. On the other hand, the elastic constants C_{12} and C_{44} relate to the elasticity in shape, which is a shear constant. A transverse strain causes a change in shape without a change in volume. Therefore, C_{12} and C_{44} are less sensitive to pressure in comparison with C_{11}. As pressure increases, C_{11}, C_{12} and B of Mg_2Si, $Mg_2Si_{0.5}Sn_{0.5}$ increase monotonically, while for C_{44} there is no obvious change.

Having calculated the Young's modulus E, bulk modulus B, and shear modulus G, one can calculate the Debye temperature θ_D, which is an important fundamental parameter closely related to many physical properties such as elastic constants, specific heat, and melting temperature.

At low temperature the vibrational excitation arises solely from acoustic modes. Hence, at low temperatures the Debye temperature calculated from elastic constants is the same as that determined from specific heat measurements. One of the standard methods to calculate the Debye temperature θ_D is from the data of elastic constants, since θ_D may be estimated from the average sound velocity v_m by[21,22]

$$\theta_D = \frac{\hbar}{k}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{1/3} v_m, \tag{8}$$

where $\hbar$ is Planck constant, κ Boltamann constant, N_A Avogadro number, n number of atoms in the molecule, M the molecular weight and ρ the density. The average wave velocity v_m is approximately calculated from

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_s^3} + \frac{1}{v_p^3}\right)\right]^{-1/3}, \tag{9}$$

where v_s and v_p are the compressional and shear wave velocity, respectively which are obtained from Navier's equations

$$v_s = \sqrt{\frac{G_H}{\rho}}, \tag{10}$$

$$v_p = \sqrt{\frac{\left(B + \frac{4}{3}G\right)}{\rho}}. \tag{11}$$

The Debye temperatures θ_D and the average wave velocities v_m obtained under various pressures are listed in Table 3, respectively. It is noted that as pressure increases up to 100 GPa, the Debye temperature θ_D and bulk modulus B increase monotonically.

It is observed that, at 273 K and zero pressure, our obtained Debye temperature θ_D of Mg_2Si is 359.0 K, which is well consistent with the experimental data (419 K).[23]

Table 3. The lattice constants (Å), elastic constants (GPa), average wave velocity (m/s) and the Debye temperature (K) of Mg_2Si and $Mg_2Si_{0.5}Sn_{0.5}$ at 273 K.

	P	a	C_{11}	C_{12}	C_{44}	B	G	v_m	θ_D
Mg_2Si	0	6.35	118.82	22.27	44.96	54.45	46.25	5316.2	359.0
	10	6.06	173.73	49.41	71.90	90.85	67.83	6457.7	436.1
	30	5.73	249.5	106.16	97.65	153.94	86.27	6865.7	494.7
	50	5.53	314.3	163.75	98.86	213.95	88.64	7485.4	505.5
	100	5.22	470.42	301.03	118.27	357.49	103.46	8125.6	548.7
$Mg_2Si_{0.5}Sn_{0.5}$	0	6.56	94.24	21.63	38.43	46.08	37.57	4695.2	307.4
	10	6.21	139.70	54.02	57.88	83.05	51.32	5526.4	361.9
	30	5.86	210.29	116.78	70.69	147.53	59.90	6027.3	394.7
	50	5.64	268.31	173.31	78.27	205.04	64.06	6264.9	410.2
	100	5.30	431.99	312.92	72.27	356.86	66.9	6447.6	422.2

The results of a linear response calculation of the phonon spectra can be used to compute the specific heat capacity C_v. Within CASTEP, the vibrational contributions to the thermodynamic properties are evaluated to compute C_v at the finite temperature as discussed below. As the phonon dispersion relation is determined, the vibrational density of states $g(w)$ also can be determined. The lattice contribution to the heat capacity, C_v,[24] is

$$C_v(T) = k\int \frac{(\hbar\omega/kT)^2 \exp(\hbar\omega/kT)}{[\exp(\hbar\omega/kT) - 1]^2} g(\omega)\mathrm{d}\omega, \tag{12}$$

where $\hbar$ and k are the Planck constant and the Boltz-

mann constant respectively.

The calculated specific heat capacities of $Mg_2Si_xSn_{1-x}$ are shown in Fig.2. With regard to the calculated data of $Mg_2Si_xSn_{1-x}$, $Mg_2Si_xSn_{1-x}$ compounds show the same changing trend while increasing Sn content. Knowledge of the heat capacity of a substance not only provides essential insight into its vibrational properties but is also mandatory for many applications. Two famous limiting cases are correctly predicted by the standard elastic continuum theory.[25] At high temperature, the constant-volume heat capacity C_v tends to the Petit and Dulong limit.[26]

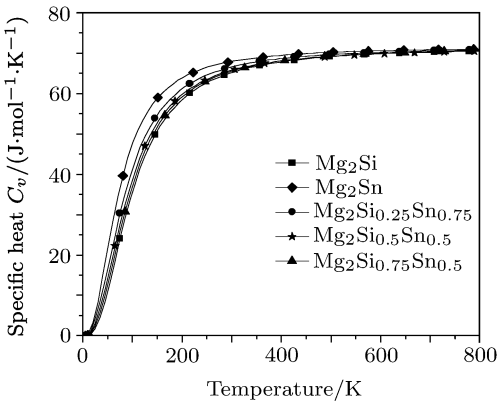


Fig.2. The calculated heat capacity, C_v, of $Mg_2Si_xSn_{1-x}$.

At sufficiently low temperature, C_v is proportional to T^3.[25] At intermediate temperature, however, the temperature dependence of C_v is governed by the details of vibrations of the atoms and for a long time could only be determined from experiments. Figure 2 shows the specific heat capacity C_v, as function of the temperature, respectively. This quantity indicates a sharp increase up to 300 K which is due to the anharmonic approximation of the Debye model used here. However, at higher temperature, the anharmonic effect on C_v is suppressed, and C_v is very close to the Dulong–Pettit limit ($C_v(T)-3R$ for monoatomic solids), which is common to all solids at high temperature.

As it can be seen, the concentration of Sn has little influence on the heat capacity behaviour. The C_v of $Mg_2Si_xSn_{1-x}$ increases at low temperature but tends to be similar at high temperature. This means that C_v is not sensitive to the presence of defects as the temperature increases. Thus, the anti-CaF_2 type structure can be assimilated to a perfect crystal.

The calculated C_v of Mg_2Si and Mg_2Sn (as shown in Fig.3) are compared with the experimental data[23,27] available in the temperature range 0 K to 300 K. The calculated C_v of Mg_2Si and Mg_2Sn are 65 J·mol^{-1}·K^{-1} and 68 J·mol^{-1}·K^{-1}, while the experimental data are 67.9 J·mol^{-1}·K^{-1} and 72.5 J·mol^{-1}·K^{-1} at 300 K, respectively. The errors are 4.5% and 6.6%. From this, we find that there is closer resemblance between the calculated and the experimental C_v. These results indicate that the method used in our case is reasonable.

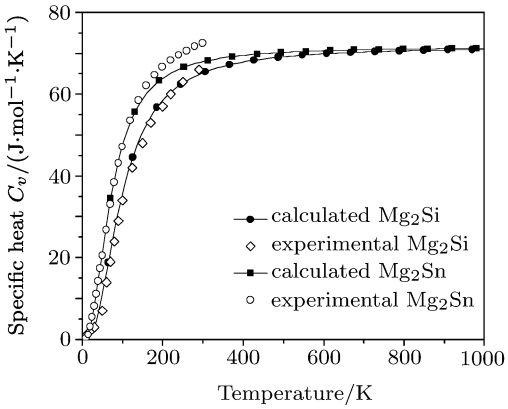


Fig.3. The calculated heat capacity, C_v, of Mg_2Si and Mg_2Sn in comparison with previous experimental data.

4. Conclusions

In this paper, first-principles calculations were used to investigate the elastic constants and thermodynamic properties of $Mg_2Si_xSn_{1-x}$. The results were obtained from the PP-PW method, in the framework of DFT, with the GGA. The main results and conclusions can be summarized as follows:

(1) The elastic constants of $Mg_2Si_xSn_{1-x}$ were calculated at zero pressure. The results are well consistent with the previous experimental data. C_{11}, C_{12} and the bulk modulus increase with increasing Sn content, while for C_{44} there is no obvious change with x. The isotropy of $Mg_2Si_xSn_{1-x}$ decreases with increasing Sn content.

(2) The Debye temperatures θ_D of Mg_2Si and $Mg_2Si_{0.5}Sn_{0.5}$ were calculated from elastic constants, as pressure increased up to 100 GPa. The Debye temperatures increase with the increase of pressure.

(3) The specific heat capacities C_v of $Mg_2Si_xSn_{1-x}$ were calculated. The C_v is not sensitive to the presence of defects as the temperature increases. Thus, the anti-CaF_2 type structure can be assimilated to a perfect crystal.

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