Calculation of thermophysical properties of magnesium antimonide (α-Mg$_3$Sb$_2$)

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Abstract: Magnesium antimonide (α-Mg$_3$Sb$_2$) is investigated by molecular dynamics simulation to find thermophysical properties. Lattice parameters and heat capacities are calculated from room temperature to the melting point. Nearest neighbor distances of ions are measured from the radial distribution function and compared with experimental values. Bulk properties like elastic constants and bulk and shear moduli are found and tabulated with first-principle and experimental data.

Key words: Magnesium antimonide, Mg$_3$Sb$_2$, lattice parameter, heat capacity, bulk properties

1. Introduction

Magnesium antimonide (Mg$_3$Sb$_2$) is an important material for industry, like the other magnesium alloys. The main reason to use this material, especially for the automobile industry, is its low density compared with the other aluminum alloys [1,2]. Mg$_3$Sb$_2$ was investigated for its thermoelectric properties and was also analyzed for semiconductor properties [3,4]. Studies on the material are performed to find physical properties such as the Seebeck constant, electrical resistivity, and thermal conductivity [5].

Imai and Watanabe [6] published the electronic structure of Mg$_3$Sb$_2$ by using first-principle calculations. Similar methods were utilized to find lattice constants, formation enthalpy, and elastic properties by various groups [7,8]. To our knowledge, there is no classical molecular dynamics simulation investigation in the literature to find the physical properties of Mg$_3$Sb$_2$ by using semiempirical potential.

In this work, classical potential parameters are developed for Buckingham potential. Physical properties of α-Mg$_3$Sb$_2$ are calculated from room temperature up to the melting point with the new potential. In this temperature range, thermal properties like lattice constants and heat capacities are measured and the phase transition temperature from the solid to liquid state is calculated and compared with experimental data. A radial distribution function is obtained at room temperature and nearest neighbor distances are verified by considering the data in the literature. Static properties like bulk properties and elastic constants are calculated and compared with both first-principle and experimental data.

2. Methodology

2.1. Interatomic potential

Buckingham-type interatomic potential is used in the molecular dynamics simulation to obtain physical properties of magnesium antimonide (α-Mg$_3$Sb$_2$). First of all, potential parameters are parameterized and given in

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Table 1. There are some ways to obtain these data; for example, here they are determined by fitting observables, like empirical and first-principle data [9]. The following equation is used for this purpose.

$$F = \sum_{i=1}^{N_{obs}} w_i \left(f_i^{obs} - f_i^{calc} \right)^2 \tag{1}$$

Eq. (1) gives an idea about the quality of the parameters. f_i^{obs} is fitted results, while f_i^{calc} is calculated results. N_{obs} is the number of observables and w is the weight factor.

Table 1. Buckingham-type interaction potential parameters.

		A (eV)	ρ (A)	C (eV A^6)	Z
Sb	Sb	0.0	1.0	201.5396	−2.04
Sb	Mg	1113.544811	0.38333	0.0	0.0
Mg	Mg	0.0	1.0	0.0	1.36

Buckingham interaction potential parameters are tabulated in Table 1 by employing Eq. (1) with first-principle and experimental data of Mg_3Sb_2. The equation of interaction potential is as follows.

$$\varphi = \frac{Z_i Z_j e^2}{r_{ij}} + A \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6} \tag{2}$$

Here, Z_i and Z_j are effective charges, r_{ij} is the distance between ions, and A governs the repulsive and C governs the attraction strength. The first term is the coulombic interaction between ions, the second term is the repulsive parameter, and the third term is the attractive dipole-dipole term. Cut-off distances for the short-range potentials are 20 Å.

2.2. Molecular dynamics simulation

$\alpha-Mg_3Sb_2$ has an anti-La_2O_3 type of structure with space group $P\bar{3}m1$. Experimental lattice constants are a = 4.568 Å and c = 7.229 Å. Density of the molecule is 4.02 g/cm^3 [10]. The supercell of the molecular dynamics simulation is constructed with $8 \times 8 \times 8$ (1024 Sb^{-3}, 1536 Mg^{+2}) unit cells. The Moldy program [11] is used as a classical molecular dynamics program and outputs are examined with its utilities. Total simulation time is 100 ps, where the first 30 ps is for the equilibration process for the initial unstable system. Later on, for 70 ps, physical properties are calculated because in this part it is assumed that the system remains in equilibrium. In order to verify the calculations of the physical properties and control the stability of the potential parameters, molecular dynamics simulation time is increased to 500 ps and physical properties are recalculated by averaging over 470 ps.

The initial configuration is heated from 300 K up to 2000 K for every interval of 50 K. The Parrinello–Rahman constant pressure method [12] and Nosé–Hoover thermostat method [13, 14] are chosen for the NPT ensemble. This constant pressure ensemble method constrains the supercell from uniform expansion or contraction.

3. Results and discussion
3.1. Bulk properties

Calculations of bulk properties are performed with the GULP program [9], such as bulk and shear moduli. They are calculated by the Birch–Murnaghan equation and given in Table 2. Elastic constants C11, C12, C13, C33,

and C44 are calculated by:

$$C_{ij} = \frac{1}{V} \left(\frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j} \right), \tag{3}$$

which gives information about the crystal. Constants are calculated by second derivatives of the energy to the strain. Here ε is the strain and U is the energy. As the strain is increased, elastic constants contain information about the hardness of the material. These properties are compared with first-principle results in Table 2.

Table 2. Lattice constants and bulk properties of α-Mg_3Sb_2.

	Exp. [10]	First-principle [7]	Present work
Lattice constant a (Å)	4.568	4.5062	4.617 (MD)
C (Å)	7.229	7.1582	7.306 (MD)
Bulk modulus (GPa)		48.8	42.95
Shear modulus (GPa)		22.6	17.11
C11 (GPa)		87.5	71.42
C33 (GPa)		91.9	38.16
C12 (GPa)		43.6	48.95
C13 (GPa)		21.7	26.93
C44 (GPa)		17.8	24.14

Moreover, lattice constants are compared with both experimental and first-principle results. The program searches the minimum energy structure and calculates the values a = 4.597 Å and c = 7.096 Å. Lattice constants a and c from the molecular dynamics simulation at 300 K are given in Table 2.

3.2. Radial distribution function

The radial distribution function displays information of the crystal structure and the ionic positions. Nearest neighbor distance data may also be obtained from Figure 1.
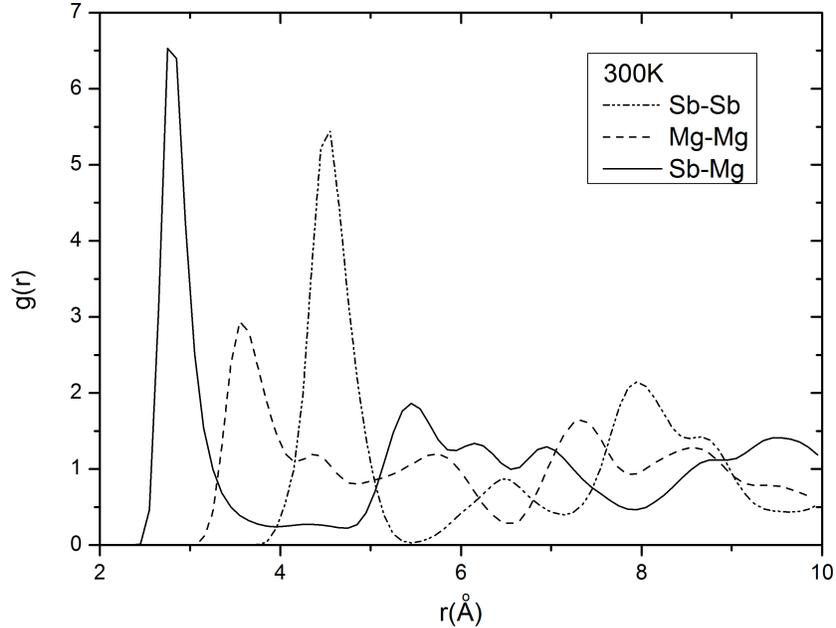

Figure 1. Radial distribution function of α-Mg_3Sb_2.

Sb-Mg, Mg-Mg, and Sb-Sb nearest neighbor distances are 2.79 Å, 3.57 Å, and 4.53 Å, respectively, at 300 K by molecular dynamics simulation. Experimental values for Sb-Mg are between 2.819 Å and 3.11 Å with an average value of 2.961 Å. Mg-Mg distances are between 3.272 Å and 3.736 Å. The predicted theoretical value of the sum of the metallic radii is 3.15 Å [10]. It has been observed that increasing the total simulation time has almost no effect on the radial distribution function.

3.3. Lattice parameters and heat capacity

Lattice parameters of the supercell are calculated by the molecular dynamics simulation program from 300 K to 2000 K for every interval of 50 K. Lattice parameters (a, c) increase with the temperature and a discontinuity is observed at around 1300–1500 K, which signals the onset of a melting transition, as shown in Figures 2 and 3. The experimental melting temperature of α-Mg_3Sb_2 is about 1518 K [15]. The melting point of crystal is better determined by the energy data of the system as the temperature increases, which will be demonstrated in the following paragraph. Polymorphic transition from the α phase to the β phase is not observed with the present potential parameters. In addition, unusual behavior in the lattice structure occurs between 1800 K and 1900 K, which could be interpreted as the boiling point. The experimental boiling point is 1860 K [15].
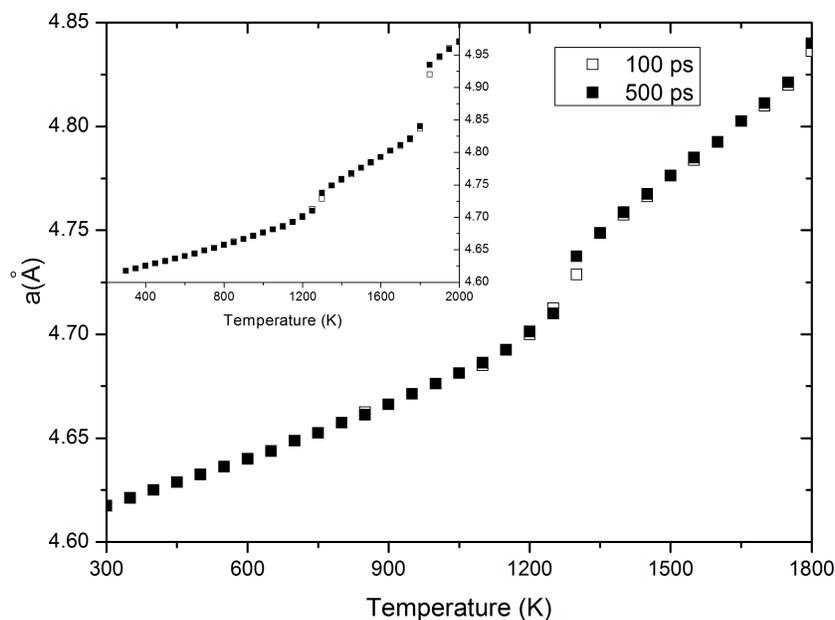

Figure 2. Lattice parameter, a, changing with the temperature.

Constant pressure heat capacity of the magnesium antimonide molecule is given in Figure 4, which is calculated from the first-order derivative of the system total energy.

$$C_p = \left(\frac{\partial U}{\partial T} \right)_p \tag{4}$$

The room temperature heat capacity value is almost equal to the theoretical Dulong–Petit value. At high temperatures, temporary Frenkel pairs are the reason for a slight increase in the heat capacity. A significant change of heat capacity in Figure 4 indicates the phase transition, which is also observed from the lattice parameter data. This phase transition is the melting of Mg_3Sb_2 that occurs around 1200–1400 K.
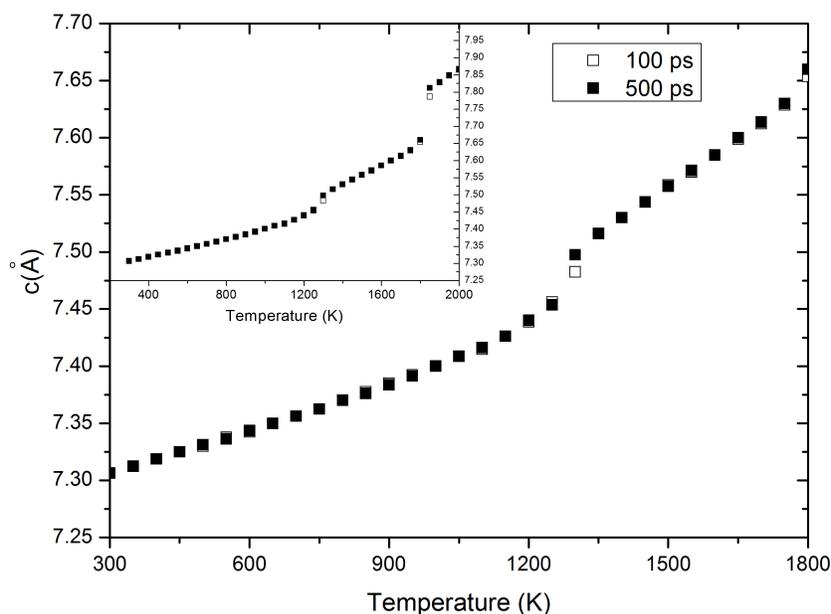
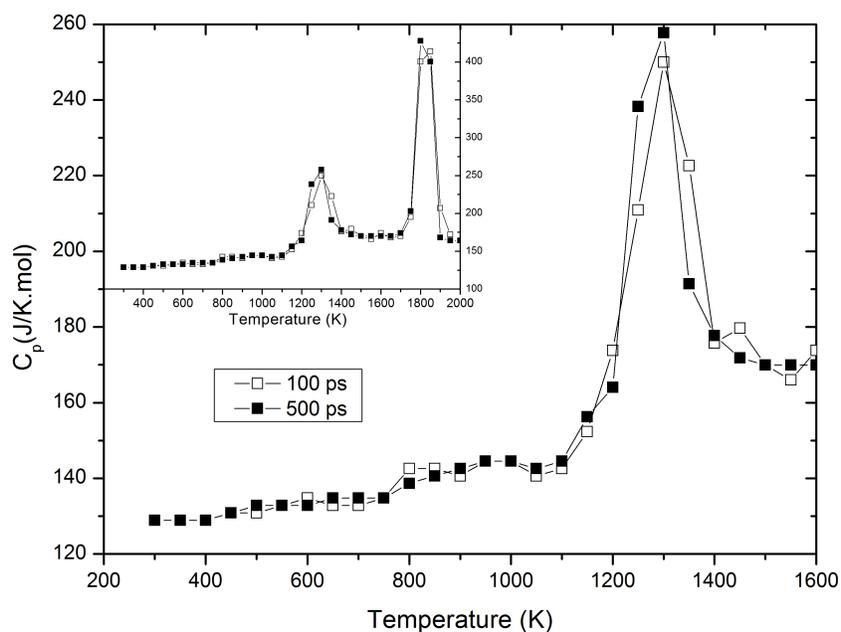**Figure 3.** Lattice parameter, c, changing with the temperature.

Figure 4. Heat capacity changing with temperature.

Again, a prominent change in the curve exists around 1700–2000 K, as seen in the inset of Figure 4. Detailed examination is needed to draw any conclusion from this phenomenon at such high temperatures. It could be a sign of boiling point or an anomaly caused by potential.

In addition to the above discussions, as the total simulation time is increased from 100 ps to 500 ps, physical properties like lattice parameters and heat capacity demonstrate small changes but the general behavior of the curves remains the same.

4. Conclusion

In this study, classical potential parameters of Buckingham type are proposed for magnesium antimonide. Physical properties like lattice constants, bulk modulus, shear modulus, and elastic constants are found and compared with available first-principle and experimental results. The radial distribution function is calculated at room temperature and nearest neighbor distances of Sb-Mg and Mg-Mg are in agreement with experimental results. In addition, molecular dynamics simulations are performed from room temperature up to 2000 K. Lattice parameter and heat capacity are observed as the temperature increases and the melting point of the material is estimated. All the physical properties calculated from molecular dynamics simulation show agreement with the data in the literature.

To our knowledge, no classical interaction potentials have been suggested in the literature for Mg_3Sb_2, and in this work it is shown that this interaction potential could be a good candidate for this material. In addition to this, for future work, molecular dynamics simulation could be performed in more realistic ways with this material, like introducing extended defects, grain boundaries, Schottky-type and Frenkel-type defects, and defect clusters with this potential.

Acknowledgment

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