SNRU JST

Sakon Nakhon Rajabhat University
Journal of Science and Technology

Journal home page: snrujst.snru.ac.th

Thermal properties of GeTe simulated by molecular dynamics

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Received: 24 June 2015; **Revised:** 1 September 2015; **Accepted:** 15 October 2015; **Available online:** 15 December 2015

Paper selected from Sakon Nakhon Rajabhat University - International Conference 2015 (SNRU-IC 2015)

Abstract

The thermal properties of GeTe were simulated by molecular dynamics (MD) method in temperature range 300 K – 700 K and the pressure range 1 MPa – 1.5 GPa. The cluster atomic based on rocksalt structure used Ge 256 atoms and Te 256 atoms in dimension 4×4×4 unit cells. The interatomic interaction used the Morse-type potential functions and the Busing-Ida type potential. Then the potential parameters were determined by fitting calculated lattice constant to agree with the literature at room temperature. The compressibility and linear thermal expansion coefficient were analyzed and contribution to analysis heat capacity. The thermal conductivity was analyzed by the heat flux autocorrelation function. It was found that, the heat capacity of GeTe was increased with increasing temperature agree with the Dulong-Petit law about 97.92 J K^{-1} mol^{-1} at 300 K. The thermal conductivity was decreased with increasing the temperature about 1.97 W m^{-1} K^{-1} to 1.09 W m^{-1} K^{-1} at 300 – 700 K.

Keywords: Molecular dynamics, GeTe, Thermal conductivity, Heat capacity, Lattice parameter

1. Introduction

Thermoelectric (TE) materials can direct conversion of thermal to electrical energy. This conversion has been receiving much attention for their potential applications in solid state cooling and power generation. The quality of thermoelectric materials is related to a dimensionless figure of merit; $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the thermal conductivity [1]. Germanium Telluride (GeTe) is known as appropriate candidate TE materials for the applications in the medium temperature range from 325 K to 750 K [2]. In addition, its TE properties are a few report. Hence,

we focus on TE properties of GeTe with composed of thermal and electrical properties. Moreover, the thermal and electrical properties can study by simulate method for guild line to choose materials before experiment. Recently, we successfully simulated metal substitute on $CaMnO_3$ study of TE properties by molecular dynamics (MD) and molecular orbital (MO) method as well as choose good the case in simulate result to experiment [3]. In this work, we interested simulate lattice parameters, compressibility, thermal expansion coefficient, heat capacity, and thermal conductivity of GeTe by MD method.

2. Materials and Methods

Computational details

The MD simulations of thermal properties for GeTe are employed 512 atoms (256 anions and 256 cations) on MXDORTO program. The parameters of GeTe simulation is determined by trial and error numbers of $Ge^{1.2+}$ and $Te^{1.2-}$ fit with lattice parameter experiment literature. The cluster unit cell was initially arranged 4×4×4 in the rock salt structure. We used a molecular dynamics program based on MXDORTO [4]. A run time of 100,000 steps for total energy and 100,000 steps for heat flux energy was used. The quantum effect is based on the system. The lattice was containing a fixed number of atoms. The temperature was calculated ranging from 300 K to 700 K and pressure control range at 0.001, 0.7501, 1.5001 GPa. The calculation was controlled at both constant pressure and volume equilibrium. The pressure and temperature of the system were controlled independently, through a combination of the Anderson method [5] and Nose method [6]. We employed the semi-empirical, two-body, the potential parameter use the Morse type [7] adding Busing-Ida [8] function contribute to thermodynamics equilibrium and ignored phase transition.

$$U_{ij}\left(r_{ij}\right)=\frac{z_i z_j e^2}{r_{ij}}+f_0\left(b_i+b_j\right)\exp\left(\frac{a_i+a_j-r_{ij}}{b_i+b_j}\right)-\frac{c_i c_j}{r_{ij}^6}$$
$$+D_{ij}\left\{\exp\left[2\beta_{ij}\left(r_{ij}-r_{ij}^*\right)\right]-2\exp\left[-\beta_{ij}\left(r_{ij}-r_{ij}^*\right)\right]\right\} \quad (1)$$

Where f_0 = 4.186, z_i and z_j are the effective partial electronic charges on the i^{-th} and j^{-th} ions, r_{ij} is the interatomic distance, r_{ij}^* is the bond length of the cation-anion pair in vacuum, and a, b and c are the characteristic parameters depending on the ion species. In this potential function, D_{ij} and β_{ij} describe the depth and shape of this potential, respectively.

The thermophysical properties composed of the compressibility β, the linear thermal expansion coefficient α_{lin}, the heat capacity at constant volume C_v, the heat capacity of lattice dilational term C_d, the heat capacity at constant pressure C_P and the thermal conductivity κ. The β is evaluated by:

$$\beta=\frac{3}{a\left(P_0\right)}\left(\frac{\partial a\left(P\right)}{\partial P}\right)_T \quad (2)$$

where $a\left(P\right)$ is the lattice parameter at pressure $P\left(Pa\right)$ and P_0 is atmospheric pressure. The α_{lin} is evaluated by:

$$\alpha_{lin} = \frac{1}{a(T_0)}\left(\frac{a(T)-a(T_0)}{T-T_0}\right)_P \tag{3}$$

where $a(T)$ is the lattice parameter at $T(K)$ and T_0 is room temperature. The C_V, C_d and C_P are evaluated by:

$$C_d = \frac{(3\alpha_{lin})^2 V_m(T)}{\beta} T \tag{4}$$

$$C_V = \left(\frac{\partial E(T)}{\partial T}\right)_V \tag{5}$$

$$C_P = C_V + C_d \tag{6}$$

where $E(T)$ is the internal energy at $T(K)$ and V is the molar volume. The κ was calculated by the Green–Kubo relation [8]:

$$\begin{aligned}\kappa &= \frac{V}{3k_B T^2}\int_0^\infty \langle S(t)S(0)\rangle dt \\ &= \frac{1}{3}C_V \upsilon_T l\end{aligned} \tag{7}$$

where k_B is the Boltzmann constant, T is the absolute temperature and $S(t)$ is the heat flux autocorrelation function (ACF). The heat flux $S(t)$ is described as:

$$S(t) = \frac{1}{V}\left[\sum_j E_j v_j + \frac{1}{2}\sum_j \sum_{i\neq j} r_{ij}\left(f_{ij} v_j\right)\right] \tag{8}$$

The instantaneous excess energy of atom j is E_j, described as:

$$E_j = \left\{\frac{1}{2}m_i v_j^2 + \frac{1}{2}\sum_{i\neq j} U_{ij}\left(r_{ij}\right)\right\} - E_{av} \tag{9}$$

where m_j and v_j are the mass and velocity of atom j, r_{ij} and f_{ij} are the interatomic distance and force between atom i and j, U_{ij} is the potential between atom i and j, and E_{av} is the average energy of the system.

The values of the interatomic potential parameters used in the present are summarized in Table 1.

Table 1 Values of the interatomic potential function parameters for GeTe

Ions	Atoms	*Z*	*a*	*b*	*c*
Ge	256	+2	1.723	0.16	0
Te	256	-2	2.015	0.16	20
Pair Ge–Te		D_{ij}	β_{ij}	r_{ij}^*	
		12.232	1.872	3.0530	

3. Results and discussion

Fig. 1 shows that the lattice constant with values 5.9874±0.0008 Å at 300 K was obtained by MD calculation which good agreement with experimental of Kabalkina *et al.* [10]. To examine the expansion of crystal structure of GeTe we was calculated by vary temperature as increase 50 K at temperature range 300 –700 K. It was found that, the structure was expanded due to the lattice constant increased with increasing temperature. Consequently, the lattice constant has increase value error too and it shown metal behavior.

Fig. 2 to evaluate contraction of crystal structure the lattice constant was carried out by MD calculation as vary pressure range 1 MPa – 1.5 GPa. We found that, the crystal structure was decreased with increasing temperature which indicates with pressure affect to behavior of crystal.

Fig. 3 the lattice constant varies at temperature and pressure contribute to evaluate the compressibility and linear thermal expansion coefficient as following by equation (3) - (4). It was found that, the compressibility was tend constant about 9.5 MPa^{-1} at 300 – 700 K and the linear thermal expansion coefficient has value 6.2 μK^{-1} at 300 K increase to 7.5 μK^{-1} at 700 K. Hence, the GeTe has been good resistivity because of the compressibility tend constant and low or not good expansion due to its have small expansion coefficient.

Fig. 4 the heat capacity viz., constant pressure term (C_p), constant value term (C_V) and lattice dilation term (C_d) was calculate by MD method combination compressibility and linear thermal expansion coefficient. We found that, lattice dilation term is a small value because the lattice small vibration. Then the constant pressure term can evaluate with sum of constant value term and lattice dilation term is calls that total heat capacity. The last result, the total heat capacity was contributed to evaluate thermal conductivity which MD calculation was carry lattice thermal conductivity, as following by equation (7).

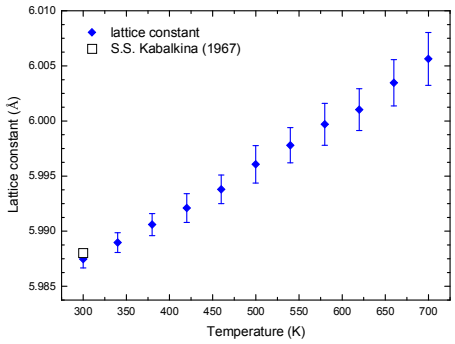

Fig. 1 Lattice constant of GeTe at various Temperature

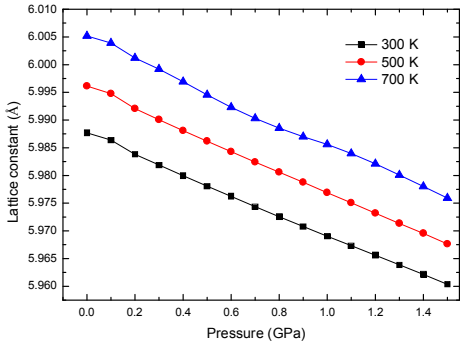

Fig. 2 Lattice constant of GeTe at various pressure

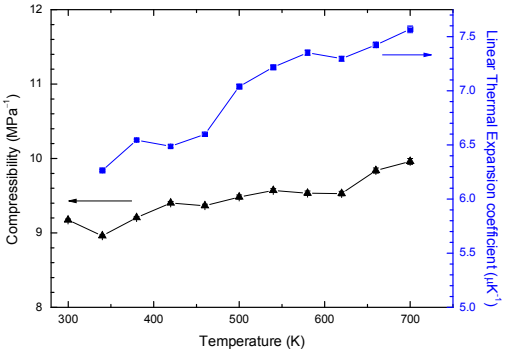

Fig. 3 Calculated of compressibility and linear thermal expansion coefficient for GeTe at various temperature

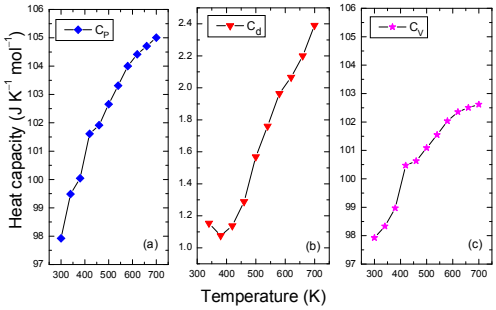

Fig. 4 Calculated of heat capacity for GeTe at various temperature

It was found that, the lattice thermal conductivity is value 3.4 $\mathrm{W\,m^{-1}\,K^{-1}}$ at 300 K not agree with literature because of this result is lattice thermal conductivity term but literature are total thermal conductivity term which can evaluate by $\kappa_{total} = \kappa_{lat} + \kappa_e + \kappa_{other}$ were κ_e is electron thermal conductivity and κ_{other} is other thermal conductivity term.

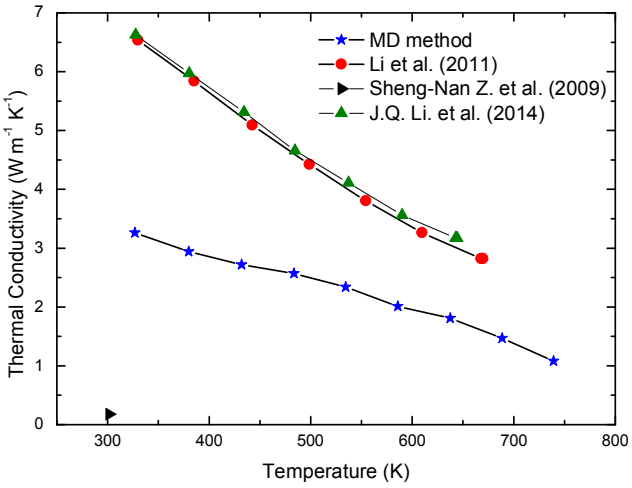

Fig. 5 Thermal conductivity various temperature of GeTe at 300-700 K

Fig. 5 the thermal conductivity has decreased with increasing temperature agree with literture of Li *et al.* [2], S.N. Zhang *et al.* [11] and Li *et al.* [12].

4. Conclusion

The lattice constant, compressibility, linear thermal expansion, heat capacity and thermal conductivity of GeTe have been completely simulated by MD simulation at temperature range from 300 K to 700 K. The thermal expansion coefficient and heat capacity were increased with increasing temperature agree with the Dulong-Petit law. The thermal conductivity was decreased with increasing temperature agree with literature data.

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