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Molecular Dynamics Simulation of Thermal Conductivity and Vibrational Density of States of Cadmium Telluride

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Abstracts: This study aims to calculate the thermal conductivity and vibrational density of states of CdTe using MD simulation. The lengths of CdTe varied from 10 nm, 20 nm, 30 nm, 40 nm, and 50 nm, with fixed width and height of 10 nm at room temperature (300 K). The results show the decrease of thermal conductivity as a function of length due to phonon-phonon interaction. The width varied from 10 nm, 20 nm, 30 nm, 40 nm, and 50 nm at room temperature (300 K) with a fixed length and height of 10 nm. Similarly, the height varied from 10 nm, 20 nm, 30 nm, 40 nm, and 50 nm with fixed length and width at room temperature (300 K). It was found that the phonon spread less in the boundaries of the mean free path which follows the creation processes resulting to the decrease of thermal conductivity. The temperatures varied from 50 K, 75 K, 100 K, 300 K, 500 K, 700 K, 900 K, 1,000 K, and 1,365 K with fixed dimensions of 50 nm in length, 50 nm in width, and 50 nm in height. As observed, the thermal conductivity decreases with a further increase in temperature. There were four major peaks found in the vibrational density of states of cadmium telluride: ~1.3 THz and ~3.5 THz which corresponds to transverse and longitudinal acoustic modes, ~4.5 THz and ~5 THz which corresponds to transverse and longitudinal optical modes.

Keywords: LAMMPS, thermal conductivity, vibrational density, molecular dynamics, acoustic modes, optical modes, cadmium telluride.

1. INTRODUCTION

Electronic gadgets have large dimensions that usually have disadvantages; less efficient, non-portable, and high electric consumption. The nanocomponents of the latest generation especially in electronic devices are approaching atomic dimensions. An important part of the development of many nano-devices is the thermal design of a material [1].

A semiconductor is a material that has an electrical conductivity between a conductor and an insulator [2]. Several compounds of semiconductors, which are composed of binary materials were also studied, and buckled structures were also observed in its 2D structure.

A new promising material for semiconductors is the three-dimensional cadmium telluride because of its peculiar properties. Cadmium Telluride (CdTe) belongs to the group II-VI. The interest in the different properties of CdTe is considerable, due to its practical importance in technological applications such as solar energy conversion and electro-optic modulators [3]. In this study, the thermal conductivity of cadmium telluride with the structure propagating along x, y, and z axes is simulated using molecular dynamics simulation. To determine the effect of thermal conductivities of cadmium telluride, the length, width, height, and temperature are varied. The study also investigated the vibrational properties of cadmium telluride. The study of structure, thermal conductivity, and vibrational density of states of cadmium telluride will be significant in its applications in electronics.

2. THEORETICAL FRAMEWORK

2.1. Thermal Conductivity

Thermal conductivity k of a material is the property of a material to conduct heat that is transferred from high to low-temperature regions. Thermal conductivity can also be stated from the kinetic transport theory by the heat carrier’s heat capacity, velocity, and mean free path [4].

$$k = \frac{1}{3} C_v v_g l$$

where $\boldsymbol{C_v}$, is the heat carriers' specific heat per unit volume, $\boldsymbol{v_g}$ is the group velocity, and $\boldsymbol{l}$ are the mean free path of heat carriers. The main carriers of heat are the phonons defined as quantized lattice vibrations.

2.2. Cadmium Telluride

Cadmium Telluride (CdTe), II and VI compounds, could have the structure of cubic zinc-blend (Figure 1).

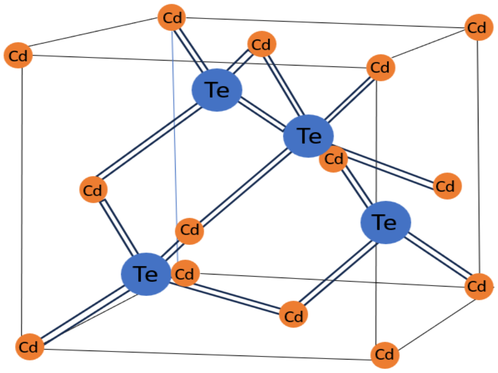

Figure 1. Zincblende crystal structure (sphalerite)

Zinc blende is named after its archetype and is closely related with diamond which consists of two interpenetrating lattices. The structure described the face centered cubic (fcc), cadmium and tellurium offset from each other by one quarter of a unit cell body diagonal.

2.3. Molecular Dynamics Simulation

Molecular dynamics is one of the methods to simulate atoms and molecules on an atomic scale. Solving problems in classical, molecular dynamics is essential in the context of the study of matter at the atomic scale. There are lots of techniques used in computer simulation. Molecular dynamics (MD) and Monte Carlo (MC) are the two main families of simulation technique. For this study it only focuses on the MD simulation.

Tersoff Potential is based on the bond-order concept. The form of the energy E, between two neighboring atoms $\boldsymbol{i}$**,** and $\boldsymbol{j}$ is taken to be [5]:

$$E = \sum_{i} E\, i = \frac{1}{2} \sum_{i \neq j} Vij$$

with

$$V_{ij} = f_c\left(r_{ij}\right) \left[\, a_{ij}\, f_r\left(r_{ij}\right) + b_{ij}\, f_a\left(r_{ij}\right) \right]$$

where V_{ij} is a pair potential function, $f_c\left(r_{ij}\right)$ is a smooth cutoff function to limit the range of the potential in which it ensures only nearest neighbor interaction. The function $f_r\left(r_{ij}\right)$ is the repulsive pair potential and the function $f_a\left(r_{ij}\right)$ is the attractive pair potential. For b_{ij} the bond order parameter describing many interactions which makes the potentials a three-body potential that depends on the positions of all neighboring atoms (Figure 2).

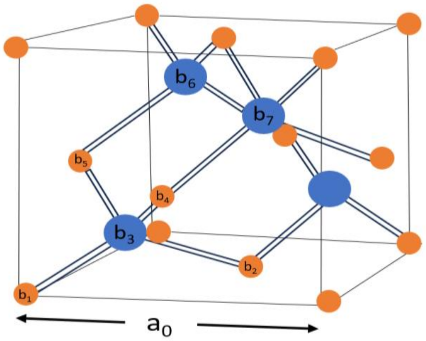

Figure 2. A unit cell of zincblende crystal structure with lattice constant a_0, and the position of atoms (b_1, b_2, b_3, b_4, b_5, b_6, b_7).

2.4. LAMMPS

Large – scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is a classical molecular dynamics simulation code that models an ensemble of particles in a liquid, solid, or gaseous state. It can model atomic, polymeric, biological, metallic, granular, and coarse-grained systems using a variety of force fields and boundary conditions designed to run efficiently on parallel computers.

2.5. Vibrational Density of States

Vibrational density of states (VDOS) is the measure of phonon distribution in a material. It is the number of phonon modes per unit frequency per unit space volume.

Moreover, the vibrational density of states is strongly influenced by the thermal properties like heat capacity and thermal conductivity as well as many other material properties. It is important to calculate the VDOS in order to calculate the frequencies of individual vibrational modes with specific range of diameters using MD simulation. For the calculations of vibrational properties, the simulations were relied on the velocity-autocorrelation function.

3. METHODOLOGY

3.1. Obtaining the Crystal Structure of CdTe

The simulation starts in creating the structure of the materials through code::blocks software with C++ language program considering the four conditions for this study: (a) first, the width and height of cadmium-telluride (CdTe) are held fixed varying its length by 10 nm to 50 nm at standard room temperature (300 K); (b) second, length and height were held fixed varying its width by 10 nm to 50 nm at standard room temperature (300 K); (c) third, length and width are held fixed varying its height by 10 nm to 50 nm at standard room temperature (300 K); (d) fourth, dimensions of CdTe are held fixed by 10 nm x 10 nm x10 nm varying its temperature by 50 K, 75 K, 100 K, 300 K, 500 K, 700 K, 900 K, 1000 K and 1365 K.

The structure of a unit cell is considered in this study. Taking seven positions of atoms (1,2,3,4,5,6,7) in creating the structure (Figure 2) then manually determine the coordinates of every atom type having $\boldsymbol{a_0}$ as the cell parameter of CdTe equivalent to 5.4060 Angstrom. It first generates a loop of seven position of atoms that duplicates through x, then through y and through z. From code::blocks, the coordinates of atoms were then carried out through LAMMPS for the structure optimization for the steady state temperature.

3.2. Molecular Dynamics (MD) Simulation through LAMMPS

This study used MD simulation which is the time evolution for multiple particles in a system and describe the system with the dimensions, length, width and the initial position of the atoms that are needed to be able to recognize. After defining these elements, a potential function was chosen to calculate the total force on every particle and a time step has chosen as well. By using Newton's 2nd law, we calculate the acceleration of each particle from the force acting on it by other atoms in the system. Then the acceleration of each atom is integrated numerically to get new positions and velocities at each time step. This new state results an output wherein the properties of the system: kinetic energy, potential energy, temperature etc. are calculated. To continue with the simulation then these steps are repeated every time step.

3.3. Investigating Thermal Conductivity

The heat flow in the system of particles in equilibrium fluctuates around zero. MD simulation used in this study is based on the Green Kubo method thus, the thermal conductivity equation:

$$k = \frac{V}{3k_\beta T^2}\int < \vec{J}(0)\cdot\vec{J}(t) > dt$$

where k is the thermal conductivity, k_β is the Boltzmann constant, V is the volume of the system, T is the temperature $\vec{J}$ is the heat current: $\vec{J}(0)$ is the heat current at time zero, $\vec{J}(t)$ is the heat current at time t, and the bracket denotes an average over all atoms in the simulation domain. The equation inside the integrand $\langle\vec{J}(0)\cdot\vec{J}(t)\rangle\, dt$ is the heat current auto-correlation function (HCACF).

3.4. Determining the Vibrational Density of States

For the calculations of vibrational properties from the simulations, the velocity-autocorrelation function (VAF) is used. At a chosen origin in time the velocity v_i in three components,

$$v_i = (v_x(t_o), v_y(t_o), v_z(t_0))_i$$

for every atom (*i*) in the system. The first contribution to the VAF, corresponding to time zero (*t=0*) is presented by the following equation:

$$C_{VAF}(t=0) = \frac{1}{N}\sum_{i=1}^{N}(v_i(t=0)\cdot v_i(t=0)).$$

At the next time step in the simulation $(t = t_o + \Delta t)$ the corresponding velocity for each atom is

$$v_i = \; v_x(t_o+\Delta t), v_y(t_o+\Delta t), v_z.$$

Then, we can repeat the procedure at each subsequent time step and so obtain a sequence of points in the VAF, $C_{VAF}(t) = \langle v_i(0)\cdot v_i(t)\rangle$.

All simulations were carried out using Lenovo ideapad 100-15 with Intel Quad Core Pentium N3540 @ 2.42Ghz.

4. RESULTS AND DISCUSSION

4.1. Length dependence of thermal conductivity

Results in Figure 3 show that there is a decrease in the thermal conductivity as length increases. This behavior is probably due to the decrease of the number of phonons resulting from phonon-phonon interaction. Furthermore, the contribution of acoustic phonons (ZA) modes may play an important role of providing a significant source of heat. It is speculated that as the length increases, the phonons become fewer in the boundaries which gives more influence to $\boldsymbol{k}$, resulting to the decrease of thermal conductivity.

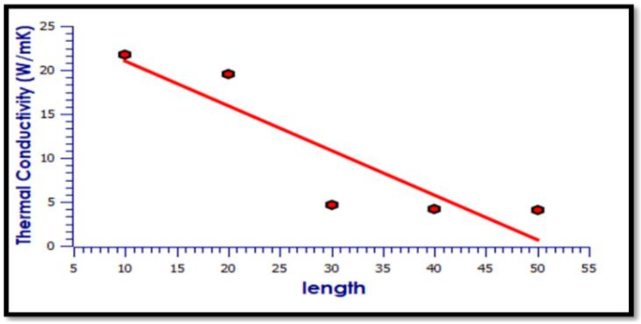

Figure 3. Thermal conductivity of cadmium telluride as a function of length at 300 K at constant width (10 nm) and height (10 nm).

4.2. Width dependence of thermal conductivity

Figure 4 shows the dependence of width of the thermal conductivity on CdTe. The increase in width results to a smaller number of phonons which is probably due to remarkable phonon's Umklapp effect and by the influence of boundary in which phonons are distributed less in the boundaries of the mean free path. So as the width is increased, the number of phonons become less resulting to the decrease of thermal conductivity.

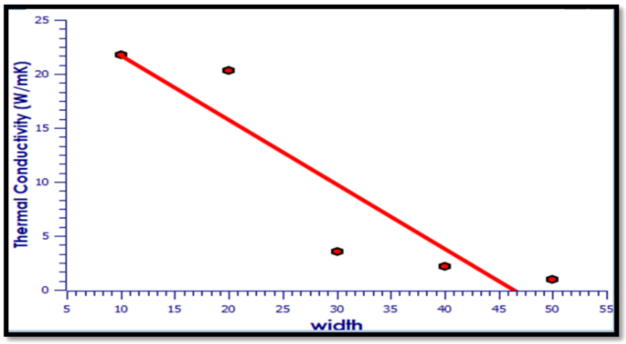

Figure 4. Thermal conductivity of cadmium telluride as a function of width at 300 K at constant length (10 nm) and height (10 nm).

4.3. Height dependence of thermal conductivity

The graph in Figure 5 shows that as the height of CdTe increases, thermal conductivity decreases which is possibly due to the less scattered number of phonons in the boundary of the mean free path [6]. At ~10 nm phonons reached the maximum height which at this point phonons interact more with other phonons then after the interaction, phonons drop continuously which is believed that phonons follow creation processes resulting to the decrease of phonons and thus the thermal conductivity.

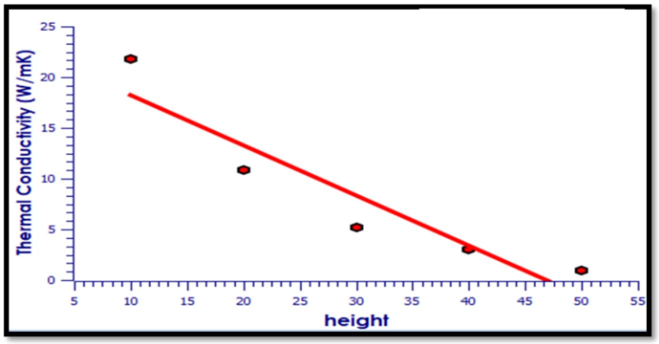

Figure 5. Thermal conductivity of cadmium telluride as a function of height at 300 K at constant length (10 nm) and width (10 nm).

4.4. Temperature dependence of thermal conductivity

Figure 6 shows that the thermal conductivity of cadmium telluride decreases as the temperature is increased. According to the kinetic formula for the thermal conductivity of the specific heat, phonon velocity and phonon mean free path, when T is above the Debye temperature θ_D [2], the specific heat C is constant and is equivalent to $3\mathbf{R}$, where $\mathbf{R}$ is the universal gas constant satisfying the Dulong and Petit Law [6]. It implies that the specific heat capacity is independent of material properties and the thermal conductivity is strongly dependent on the phonon mean free path l which is inversely proportional to temperature T.

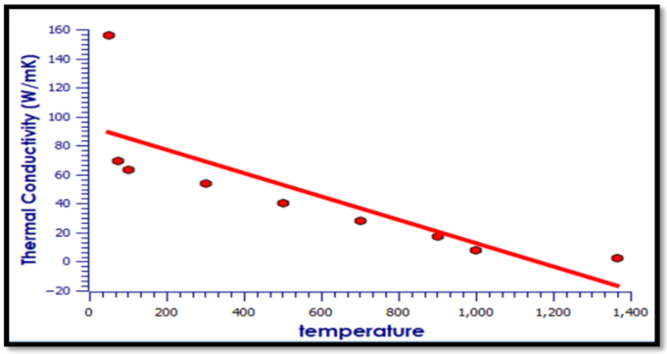

Figure 6. Thermal conductivity of cadmium telluride as a function of temperature at constant dimension 10 nm x 10 nm.

The number of phonons intermingle in the collision due to the dominant role of the Umklapp processes in phonon-phonon interactions over a wide temperature range. As a result, thermal conductivity decreases with the increase of temperature.

4.5. Vibrational Density of States of CdTe

Figure 7 shows the graph of vibrational density of states of CdTe with respect to the frequency. It is observed that there are four major peaks: (i) transverse acoustic (TA) mode at ~1.3 THz, (ii) longitudinal acoustic (LA) mode at ~3.5 THz, (iii) transverse optical (TO) mode at ~4.5 and (iv) longitudinal optical (LO) mode at ~5.0 THz. The first peak contributes the line broadening in which shifted to lower frequencies. The curve in the second peak becomes sharper at low frequency of ZA. Correspondingly the transverse optical (TO) mode was found in the third major peak that phonons correspond with longer mean free paths that phonons propagate longer in distance. The fourth peak longitudinal optical (LO) mode losses its height rapidly, by the fact that in high frequency flank of these modes drops continuously without line broadening.

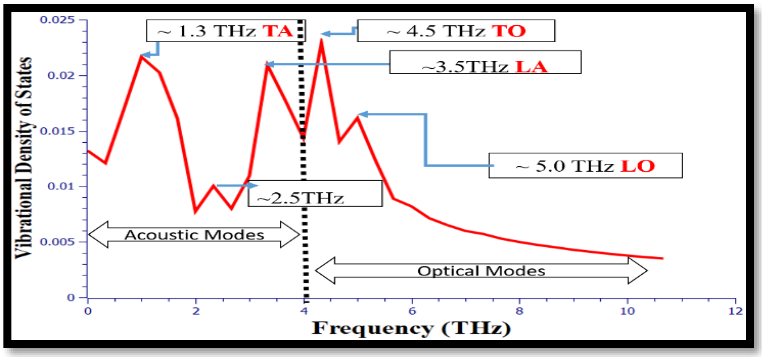

Figure 7. Vibrational density of states of CdTe in various frequencies.

5. CONCLUSION

This study presents a method of calculating the thermal conductivity and vibrational density of states of cadmium telluride. Results showed that the thermal conductivity decreases as the length is varied by 10 nm to 50 nm at room temperature (300 K) due to the smaller number of phonons in the phonon-phonon interaction. The thermal conductivity decreases monotonically as the width increases from 10 nm to 50 nm nm due to smaller number of phonons which resulted from phonon's Umklapp effect in which phonons are distributed less in the boundaries of the mean free path. Moreover, as height is increased, the thermal conductivity decreases which is believed that phonons follow creation processes resulting to the decrease of phonons and thus the thermal conductivity. It is also found that the specific heat capacity is constant and is independent of material properties and the thermal conductivity is strongly dependent on the phonon mean free path and as a result, thermal conductivity decreases with the increase of temperature.

The thermal conductivity is strongly influenced by the vibrational density of states. In the result of VDOS, it is observed that there are four major peaks: (i) transverse acoustic (TA) mode at ~1.3 THz, (ii) longitudinal acoustic (LA) mode at ~3.5 THz, (iii) transverse optical (TO) mode at ~4.5 and (iv) longitudinal optical (LO) mode at ~5.0 THz. First peak is found in the acoustic mode (ZA).

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