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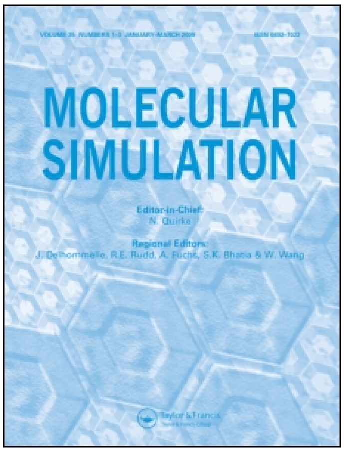

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Thermal expansion of ZnSe by molecular dynamics simulation

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Thermal expansion of bulk ZnSe crystal, grown by physical vapour transport technique, is experimentally measured for various temperatures and molecular dynamics simulation using a three body Tersoff potential is also developed for the same. The resulting expansivity compares well with our experimental results and other reported values.

Keywords: Thermal expansion; Molecular dynamics simulation; PVT; ZnSe

PACS: 65.40De; 61.43Bn; 78.30-j; 61.72Vv

1. Introduction

The recent developments on the fabrication of the II–VI blue light emitting diodes or blue laser diodes demand high quality ZnSe single crystal. Therefore a variety of methods are reported in the literature for the growth of defects free ZnSe bulk crystals without much defects. It is known that the molecular symmetry of ZnSe when doped with phosphorous behave in an unusual way, going from T_d to C_{3v} compared to other II–VI systems [1]. This change in molecular symmetry is now attributed to Jahn Teller (JT) distortion [2] which is negligible in other II–VI systems to alter the symmetry from T_d to C_{3v}. Similarly, the thermal properties of ZnSe particularly an anharmonicity parameter, thermal expansion is extensively studied for these crystals experimentally and the percentage of deviations among them demand theoretical investigations. To our knowledge, theoretical investigations particularly by simulation techniques are not reported in the literature. Readymade softwares are available for simulation but here a new model and the codes are developed to workout the thermal expansion, as this particular system is a peculiar one.

Good quality single crystals of ZnSe are grown here by physical vapour transport technique for this study and the thermal expansion of this crystal is measured by optical method. Theoretical investigation is done by simulation rather than the conventional lattice dynamics.

2. Experiment

Physical vapour transport technique is used to grow the ZnSe crystals. Good single bulk crystals are obtained in cm size with high purity. Though the size of the single crystal grown by this technique is small compared to those obtained from melt method, it shows relatively high crystallinity. The basic XRD and Raman characterizations are carried out on this to verify the crystallinity [3]. Wafers are then sliced from the grown samples in less than 1 mm thick and polished with 10% of bromine in ethyl alcohol for about 2 min. The crystals are cleaved along the (110) faces and they are used in the experiment for the measurement of thermal expansion co-efficient by Fizeau's method [4] from ambient to 400°C. The temperature is maintained at an accuracy of 1°C. The measured thermal expansion of ZnSe is given in figure 4 for various temperatures.

As mentioned, simulation will give more insight and so simulation is carried out for thermal expansion. No readymade softwares are used and we have developed our own model and code to workout the simulation. This will be very useful, as thermal expansion of nano ZnSe is intended for the future.

3. Molecular dynamics simulation (MDS)

MDS is being widely applied in condensed matter physics, rather than Monte Carlo simulation (MCS), as most of the

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time, only the dynamic properties in a physical system are of much interest. Particularly in the study of equilibrium and non-equilibrium phenomena, this method is used for both static and dynamic properties whereas MCS can be applied only to the static physical quantities. Here the exact trajectory of an atom is obtained by solving the equation of motion of atoms. The starting point is the selection of a suitable potential of interaction for the simulation and Tersoff's potential [5] is considered for this as it was found to be successful for III–V systems [6] and it is effective in the case of covalent type crystals. Since Tersoff potential is a three body potential, this is more reliable than other potentials for covalent bonded systems. Microcanonical ensembles are assumed for the convenience of computation. Using initial positions of the atoms in ZnSe, the cohesive energy at 0 K is computed using Tersoff potential employing the equilibrium lattice constant at 0 K. This is explained in detail here. The cohesive energy of the system according to Tersoff potential is defined as

$$U(r,\theta) = f_c(r)[a_{ij} f_{\mathrm{R}}(r) + b_{ij} f_{\mathrm{A}}(r)]$$
$$f_{\mathrm{R}} = A\exp(-\lambda_1 r) \quad \text{and} \quad f_{\mathrm{A}} = -B\exp(-\lambda_2 r)$$

where, f_{R} and f_{A} are the repulsive and attractive potential functions λ_1 and λ_2 are the parameters of attractive and the repulsive potential function, a_{ij} and b_{ij} are the weight factors for the repulsive and attractive parts (table 1).

$$\begin{aligned}
a_{ij} &= (1 + \alpha^n \eta_{ij}^n)^{(-1/2n)} \\
\eta_{ij} &= \sum f_c(r_{ik}) \exp\left[\lambda_3^3 (r_{ij} - r_{ik})^3\right] \\
b_{ij} &= \left(1 + \beta^n \varsigma_{ij}^n\right)^{(-1/2n)} \\
\varsigma_{ij} &= \sum f_c(r_{ik}) g(\theta_{ijk}) \exp\left[\lambda_3^3 (r_{ij} - r_{ik})^3\right] \\
g(\theta) &= 1 + \frac{c^2}{d^2} - \frac{c^2}{[d^2 + (h - \cos\theta)^2]}.
\end{aligned}$$

α, β, λ_3, c, n and h are the Tersoff potential parameters (table 1). These parameters are estimated for this system ZnSe at room temperature, by using the Vegard's Law [7]. For example, these 13 parameters are available in literature for CuCl and CuBr [8] and many other systems. Such zinc blende systems with the parameters are taken to calculate the parameters for ZnSe using Vegards law and least square technique for refinement. The bond length and mass of the constituent atoms are considered for Vegards law. Then the parameters are fitted to the Tersoff potential and the cohesive energy of the system is calculated. By least squares technique, the parameters are adjusted to give the experimental value of the cohesive energy of ZnSe within 0.1%. This refined set of parameters are then used for simulation.

Table 1. Tersoff potential parameters.

A	2548.76 eV
B	225 eV
λ_1	2.822 (Å)$^{-1}$
λ_2	1.7192(Å)$^{-1}$
n	6.3309
h	-0.5196
β	0.3579
c	1.2289
d	0.7921
R	3.5035 (Å)
D	0.1 (Å)

4. Simulation

Simulation cell of size $4 \times 4 \times 4$ is considered here. Since ZnSe possesses Zn blende structure in which the basis has two atoms Zn and Se, 256 atoms are considered in this cell. This is because, there are two interpenetrating fcc cells and in each cell the basis is two atoms. The positions of these atoms are first fixed following the basis of an fcc lattice and boundary conditions. Then the equations of motion of the atoms in this cell are constructed. The initial velocity is fixed from the temperature as $1/2\, mv^2 = kT$ for microcanonical ensemble. From this the displacement of any atom at any instant can be found out. The displacement and velocity of each of these atoms at an interval of Δt are worked out using verlet algorithm [9] where Δt is of femto seconds. For example, the displacement at any instant $r(t + \Delta t)$ is found from $r(t)$, the displacement at previous instant. They are found from the following basic equations obtained from third order Taylor expansion for the position and velocity.
i.e.

$$\begin{aligned} r(t+\Delta t) = r(t) + V(t)\Delta t + 1/2a(t)\Delta t^2 \\ + (1/6)b(t)\Delta t^3 + O(\Delta t)^4 \end{aligned} \tag{1}$$

$$\begin{aligned} r(t-\Delta t) = r(t) - V(t)\Delta t + 1/2a(t)\Delta t^2 \\ - (1/6)b(t)\Delta t^3 + O(\Delta t)^4 \end{aligned} \tag{2}$$

Adding equations (1) and (2),

$$r(t+\Delta t) = 2r(t) + a(t)\Delta t^2 + O(\Delta t)^4 \tag{3}$$

Similarly for velocity, subtracting equation (2) from equation (1), we have

$$V(t) = [r(t+\Delta t) - r(t-\Delta t)]/2\Delta t \tag{4}$$

and $V(t + \Delta t)$ is also found from the equation (4) for various trials. Similarly, the pressure of a classical N-body system is measured from the virial equation. For pairwise additive interactions, it can be written as

$$P = \rho k_{\mathrm{B}} T + 1/\mathrm{d}V \left\langle \sum_{i<j} f(r_{ij}) r_{ij} \right\rangle \tag{5}$$

where d is the dimensionality of the system (here it is $d = 3$) and $f(r_{ij})$ is the force between particles i and j at a distance r_{ij}, ρ is the number density for NVT ensembles.The instantaneous force of interaction $f(r_{ij})$ is obtained from V_{ij} in equation (4).

In each case, the equilibration is monitored, i.e. when 30,000 trials are effected to simulate the velocity

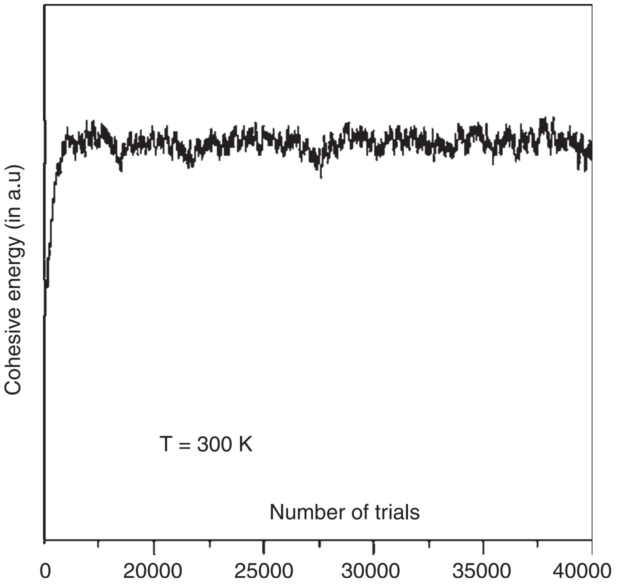

Figure 1. Typical equilibration pattern.

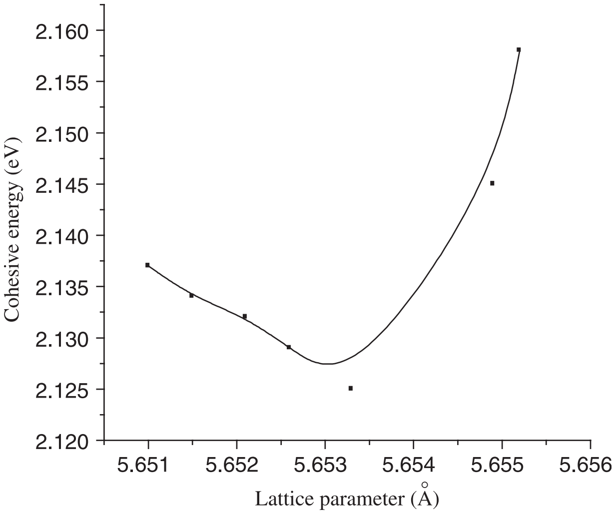

Figure 2. Lattice parameter with cohesive energy at 350 K.

Table 2. Thermal expansion co-efficient of ZnSe.

Sl No.	*Method*	*α (10^{-6})/°C*
1	Fizeau (present expt)	(8.9 ± 0.5)
2	Simulation by MDS	7.5
3	Others [8]	7.6

correlation function, after how many trials one has to take measurements should be decided. Here the equilibration is reached only after 15,000 trials, i.e. the energy reaches a constant value only after 15,000 trials. Therefore, 15,001th trial will be taken as the first trial and suitably the averaging is done. Once the equilibration is reached, then the cohesive energy is worked out by executing the program (already written and verified) for various values of lattice constant around a_o at various temperatures from 300 to 425 K. The pressure given in equation (5) is also monitored at each temperature and no appreciable variation is found. This is essential here as thermal expansion is intended (volume expansion) in this work where the pressure should be maintained constant. A sample output for equilibration is given in figure 1. Here a_o is the lattice constant at room temperature. To start with, for room temperature, the cohesive energy is known and so the simulation program was validated.

This cohesive energy reaches its minimum value for a particular lattice constant when the system is in equilibrium. A graph is drawn connecting this energy and lattice constant for each temperature and the particular lattice constant is found from this graph as shown in figure 2 as an example. This is repeated for various temperatures and in each case, the minimum energy is seen and the lattice constant is found out. Now the co-efficient of thermal expansion is found out from

$$\alpha = 1/a_o(\Delta a/\Delta T) \tag{6}$$

where 'a_o' is the lattice constant at room temperature and Δa is the change in lattice constant when the temperature is changed by ΔT. Each run of this simulation program took about 4 h in P IV, 2.4 GHz PC with 30,000 time steps. The simulation results are given in table 2.

5. Results and discussion

The cohesive energy of the system ZnSe is worked out for various lattice constant by molecular dynamics simulation. Tersoff Potential is assumed for the interaction. The variation of this energy with the lattice constant is shown in figure 2 for a particular temperature. For example, here the lattice constant is varied from 5.651 to 5.659 Å in steps of 0.001 Å. For each of these values, the simulation program was run and the cohesive energy is found. This is 2.1371 eV for $a = 5.651$ Å from the figure 2. As the lattice constant a varies, this energy also

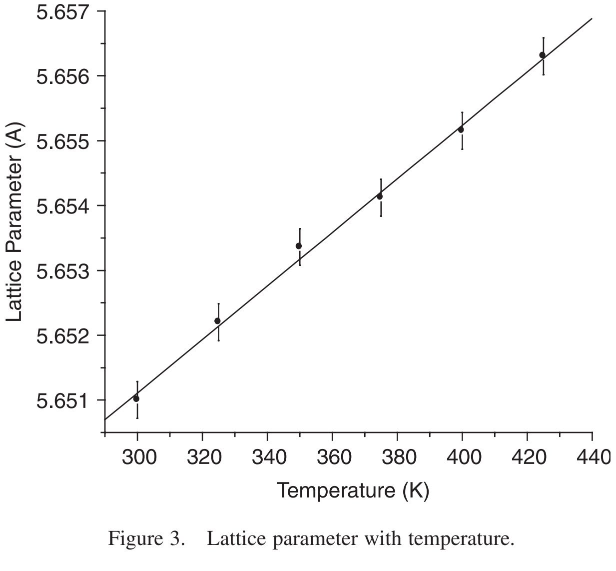

Figure 3. Lattice parameter with temperature.

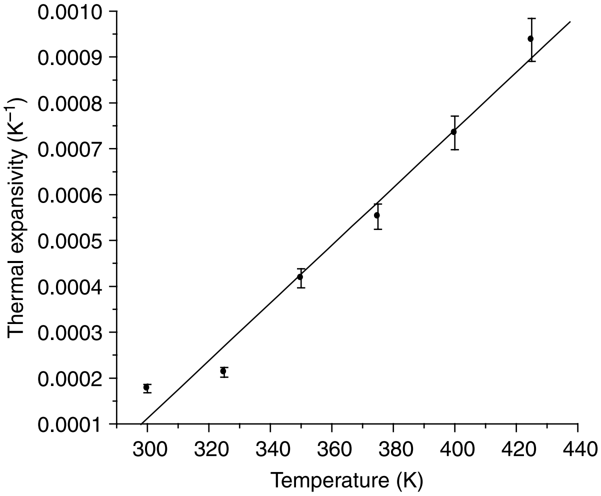

Figure 4. Variation of thermal expansivity with temperature.

varies and reaches a minimum at $a = 5.6534$ Å. This is the state of equilibrium. So for the temperature 350 K, the lattice constant is $a = 5.6534$ Å. The lattice constant at which the cohesive energy is minimum is thus found for all the temperatures. This lattice parameter is found to increase with the temperature and the variation is as shown in figure 3. Similarly the thermal expansion coefficient is calculated from equation (6) and the expansivity is found to increase with the temperature linearly as shown in figure 4. Thermal expansion of ZnSe from simulation is 7.5×10^6/°C which is compared with our experimental results obtained for the as grown ZnSe crystal by Fizeau's method at room temperature and other reported values as in table 2. The statistical errors are also estimated for the simulation result which is about 2% for thermal expansion. There is no other better potential be used than Tersoff, eventhough Buckingham and Born Mayer potentials are tried for II–VI and III–V systems. The values obtained for thermal expansion from simulation agrees well with the literature and the deviation of experimental value from simulation value, reveals that the Fizeau's method needs modification as there is always an isothermal expansion of ZnSe. This way also it differs from other II–VI systems.

Tersoff potential is the most suitable one for covalent crystals like III–V and II–VI systems in the calculation of cohesive energy. Above all, within the limit, it is found out that the lattice parameter varies directly as temperature, atleast upto 400°C, means that the quadratic term in the expansion co-efficient for ZnSe is negligible.

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