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The Miscibility Of $\text{ZnS}_x\text{Se}_{1-x}$ Using A Three-Body Potential



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ABSTRACT

Molecular dynamics simulation is being widely applied in condensed matter physics, rather monte carlo simulation, whenever the dynamic properties are of much interest. Particularity of equilibrium and non-equilibrium phenomena, transport phenomena, diffusivity, specific heat and phase transitions etc. Therefore, we have used this method, in order to obtain more informations about the structural, elastic and thermodynamic properties of $\text{ZnS}_{0.25}\text{Se}_{0.75}$, $\text{ZnS}_{0.5}\text{Se}_{0.5}$ and $\text{ZnS}_{0.75}\text{Se}_{0.25}$. We have also predicted the disorder effect (bowing parameter). © 2007 Trade Science Inc.

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INTRODUCTION

$\text{ZnS}_x\text{Se}_{1-x}$ is an interesting compound semi conductor for optoelectronic applications^[1-3]. The ternary compound has many advantages over binary compounds because the lattice constant, band gap and optical properties can be varied by changing the concentration^[4].

The mixed crystals were prepared and analysed as a complete solid solution and a core-shell type of crystal by the X-ray diffraction method. X-ray diffraction patterns of these alloy systems indicated a cubic zinc-blende structure and showed that the lattice parameter changed linearly with alloy concentration without changes in the crystal structure^[5].

To the best of our knowledge, molecular dynamics calculations of the elastic and especially the thermodynamic properties have not yet been studied.

In this paper, we present the results of molecular dynamics simulation of $\text{ZnS}_x\text{Se}_{1-x}$ for $x=0.25$, $x=0.5$ and $x=0.75$. Based on the Tersoff potential, molecular dynamics simulations are investigated in order to study the miscibility of $\text{ZnS}_x\text{Se}_{1-x}$ and to calculate the structural properties of $\text{ZnS}_{0.25}\text{Se}_{0.75}$, $\text{ZnS}_{0.5}\text{Se}_{0.5}$ and $\text{ZnS}_{0.75}\text{Se}_{0.25}$ which are compared with experimental results^[6]. Various elastic and thermodynamic properties are also predicted, such as C_{11} , C_{12} , thermal expansion coefficient, heat capacity, Debye temperature and melting temperature.

The rest of the paper is organised as follows: in

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section 2, we give a brief description of the model used, and calculation method. Then, the results of our calculation are presented and discussed in Section 3. Finally, a conclusion is given in section 4.

METHODS

A molecular dynamics (MD) calculation is a dynamic study of a many-body system in which the equations of motion are solved explicitly. In the MD calculation one solves the equations motion numerically and from the phase space trajectories one can follow the motions of the atoms in an isolated system (constant N , V and E) or (N , V and T).

The potentials of interactions of the atoms, and hence the force, are necessary input parameters; This trajectory contains all of the microscopic information relevant to the system.

We present an atomistic simulation based on a three-body potential, and we mainly use the Tersoff model to calculate dynamic quantities and, to predict the different thermodynamical properties.

The Tersoff potential

Among the many empirical model potentials that have been developed for tetrahedral semiconductors, that of Tersoff has been the most successful in that it reproduces many of the elemental semiconductors properties particularly for silicon^[7], and carbon^[8].

Another form is developed for multicomponent systems^[9] to treat mixtures of these elements.

This potential developed by Tersoff, are based on the concept of bond order. The strength of a bond between two atoms is not constant, but depends on the local environment^[9].

Because of the crucial role of bond order and its dependence upon local geometry, it seems attractive to include an environment-dependent bond order explicitly into the potential in the following way. The interatomic potential is taken to have the form^[9]:

$$E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij} \quad (1)$$

$$V_{ij} = f_C(r_{ij}) [a_{ij} f_R(r_{ij}) + b_{ij} f_A(r_{ij})]$$

Here E is the total energy of the system, which

is decomposed for convenience into a site energy E_i and a bond energy V_{ij} . The indices i and j run over the atoms of the system, and r_{ij} is the distance from atom i to atom j .

$$f_R(r_{ij}) = A_{ij} \exp(-\lambda_{ij} r_{ij}) \quad (2)$$

$$f_A(r_{ij}) = -B_{ij} \exp(-\mu_{ij} r_{ij})$$

$$f_C(r_{ij}) = \begin{cases} \frac{1}{2} - \frac{1}{2} \sin \left[\frac{\pi}{2} \frac{(r_{ij} - R_{ij})}{D_{ij}} \right] & R_{ij} - D_{ij} < r_{ij} < R_{ij} + D_{ij} \\ 0 & \text{otherwise} \end{cases} \quad (3)$$

The function f_R represents a repulsive pair potential and f_A represents an attractive pair potential associated with bonding.

f_C is a smooth cutoff function, to limit the range of the potential, since for many applications short-ranged functions permit a tremendous reduction in computational effort.

$$b_{ij} = \chi_{ij} (1 + \beta_{ij}^n \zeta_{ij}^{n_i})^{-\frac{1}{2n_i}} \quad (4)$$

$$\zeta_{ij} = \sum_{k (\neq ikj)} f_C(r_{ik}) g(\theta_{ijk}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3] \quad (5)$$

$$g(\theta_{ijk}) = 1 + \frac{c_i^2}{d_i^2} - \frac{c_i^2}{d_i^2 + (h_i - \cos \theta_{ijk})^2} \quad (6)$$

where b_{ij} is the many-body order parameter describing how the bond-formation energy is affected by local atomic arrangement due to the presence of other neighbouring atoms

The k atoms is many-body function of the positions of atoms i , j and k

where ζ_{ij} is called the effective coordination number and $g(\theta_{ijk})$ is a function of the angle between r_{ij} and r_{ik} that has been fitted to stabilize the tetrahedral structure.

$$a_{ij} = (1 + \alpha^n \eta_{ij}^n)^{-\frac{1}{2n_i}} \quad (7)$$

$$\eta_{ij} = \sum_{k (\neq i,j)} f_C(r_{ik}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3] \quad (8)$$

$$\lambda_{ij} = \frac{(\lambda_i + \lambda_j)}{2} \quad (9)$$

$$\mu_{ij} = \frac{(\mu_i + \mu_j)}{2} \quad (10)$$

$$A_{ij} = (A_i A_j)^{\frac{1}{2}} \quad (11)$$

$$B_{ij} = (B_i B_j)^{\frac{1}{2}} \quad (12)$$

We note that λ_3 and α are set equal to zero^[10], and χ is a parameter which strengthens or weakens the heteropolar bonds, relative to the value obtained by simple interpolation.

Tersoff parameters for ZnSe and ZnS were recently proposed^[11]. From these values and using the above equations (1)–(12), we have calculated the potential parameters (A, B, λ , μ , n, β , h, c, d) for $\text{ZnS}_{0.5}\text{Se}_{0.5}$.

On the basis of the transferability of the tersoff potential^[12,13], all the parameters for $\text{ZnS}_{0.25}\text{Se}_{0.75}$, and $\text{ZnS}_{0.75}\text{Se}_{0.25}$ have been kept constant except the cut-off R and χ , which are adjusted of each structure. All parameters are listed in TABLE 1.

MOLECULAR DYNAMICS SIMULATION

Molecular dynamics a computer simulation technique where the time evolution of a set of interacting atoms is followed by integrating their equations of motion.

In molecular dynamics we follow the laws of classical mechanics, and most notably Newton's law: $F_i = m_i a_i$ for each atom i in a system constituted by N atoms.

The atomic forces are derived from the potential

TABLE 1 : The adjusted tersoff parameters for $\text{ZnS}_x\text{Se}_{1-x}$ ($x=0.25, 0.5, 0.75$)

	$\text{ZnS}_{0.25}\text{Se}_{0.75}$	$\text{ZnS}_{0.5}\text{Se}_{0.5}$	$\text{ZnS}_{0.75}\text{Se}_{0.25}$
A(eV)	2756.03	2756.03	2756.03
B(eV)	210.0	210.0	210.0
$\lambda(\text{A}^\circ^{-1})$	3.0599	3.0599	3.0599
$\mu(\text{A}^\circ^{-1})$	1.7322	1.7322	1.7322
β	1.1000×10^{-6}	1.1000×10^{-6}	1.1000×10^{-6}
n	0.78734	0.78734	0.78734
c	100390.0	100390.0	100390.0
d	16.217	16.217	16.217
h	-0.59825	-0.59825	-0.59825
R(A°)	3.00725	3.00725	3.00725
D(A°)	0.15	0.15	0.15
χ	0.9747	0.9854	0.9975

energy function $F_i = -\partial U / \partial r_i$, which is, in general, a complicated function of the positions of all of the atoms in the system.

Starting from an initial configuration of the N-particle system and a specified potential energy function, the equation of motion are numerically integrated to provide the atomic trajectories $r_i(t) = \{r_i(t_0 + \Delta t)\}$ at any given time by moving each particle forward in time by discrete steps (Δt).

The basic steps in an MD simulation can be summarized as:

- 1) Specify the initial simulation model, e.g. the number of particles, the potential energy function, the initial system configuration, boundary conditions and the system state (desired pressure, temperature and volume).
- 2) Initialize the system by assigning each atom an initial kinetic energy, generally assigned from a Boltzmann distribution for the specified temperature.
- 3) Calculate the forces on each atom and integrate the equations of motion to determine each atoms acceleration, velocity and change in position.
- 4) Repeat step 3 until the desired time has elapsed.

Using Molecular dynamic calculations, the interactions are described for different concentrations by the the Tersoff potential. In our simulation, we assume that the system is treated as two components (ZnS and ZnSe).

Indeed, ZnS and ZnSe are considered as an equivalent one-component system.

Initially, ZnS and ZnSe are always located at the nodes of a zinc blende structure with interaction via the tersoff potential.

The integral energy of the system is a sum of interactions between pairs of ZnS-ZnS, ZnSe-ZnSe, ZnS-ZnSe.

In order to obtain more information about the structural, elastic and thermodynamic properties of $\text{ZnS}_x\text{Se}_{1-x}$ we run molecular dynamics simulation using the tersoff potential with 216 molecules. This simulation is carried out within the canonical NVT-ensemble where the control is investigated using Andersen's method^[14].

The MD cell is formed in a cube of side L with $3 \times 3 \times 3$ FCC unit cells, where 216 molecules with

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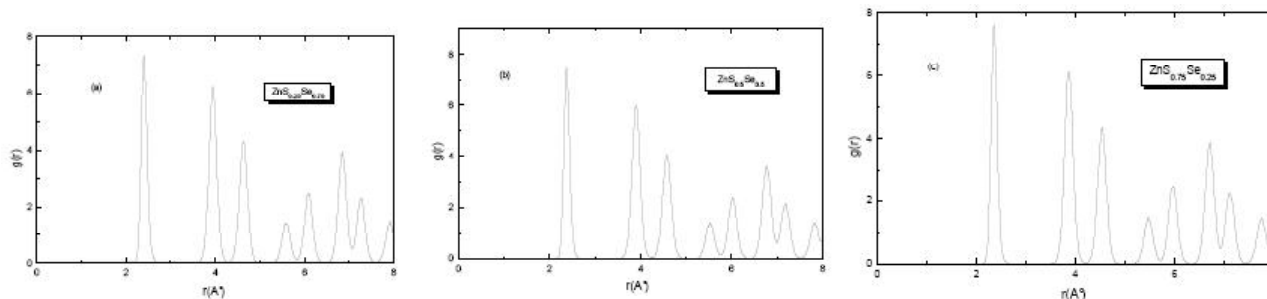


Figure 1 : The pair distribution function of: (a) $ZnS_{0.25}Se_{0.75}$; (b) $ZnS_{0.5}Se_{0.5}$; (c) $ZnS_{0.75}Se_{0.25}$

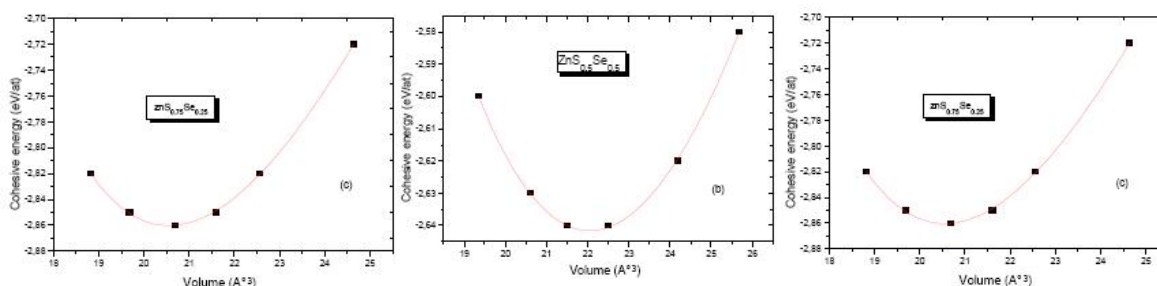


Figure 2 : The cohesive energy of the system as a function of volume for: (a) $ZnS_{0.25}Se_{0.75}$; (b) $ZnS_{0.5}Se_{0.5}$; (c) $ZnS_{0.75}Se_{0.25}$

108 ZnSe and 108 ZnS (molecules) are included. The periodic boundary conditions are applied.

The molecular dynamics routine is based on a fifth-order gear-predictor-corrector algorithm of the Newtonian equations of motion using a neighbor list technique with a time step $h=5.02$ fs. After 100 ps, different properties are computed along the trajectory of the system in phase space.

RESULTS AND DISCUSSION

We display, in figure 1 the pair distribution function $g(r)$ for $ZnS_{0.25}Se_{0.75}$, $ZnS_{0.5}Se_{0.5}$ and $ZnS_{0.75}Se_{0.25}$ alloy.

The results for the fourth peaks listed in TABLE 2 are in good agreement with the values in Ref^[19]. Thus, we confirm the stability of the structure during the simulation.

In order to calculate the structural and elastic properties of ZnS_xSe_{1-x} , we plot in figure 2 the variation of the cohesive energy with the volume for $ZnS_{0.25}Se_{0.75}$, $ZnS_{0.5}Se_{0.5}$ and $ZnS_{0.75}Se_{0.25}$ in the zincblende structure. The curves are fitted to the Murnaghan equation of state^[16] from which the equilibrium cohesive energy, the lattice parameter,

the bulk modulus, and its derivative are obtained.

From the results listed in TABLE 3, we notice the agreement of the lattice parameter with experiments^[6], the accuracy is between 0.1 and 0.8%.

Our results of the bulk modulus are in good agreement with other calculations based on the Cohen's relation^[17]:

$$B = 17.61d^{3.5} \quad (13)$$

where d is the nearest-neighbor distance in \AA , and B is the bulk modulus given in Mbar. Using this equation, we found good values of the bulk modulus for $ZnS_{0.25}Se_{0.75}$ (0.78 Mbar), $ZnS_{0.5}Se_{0.5}$ (0.82 Mbar),

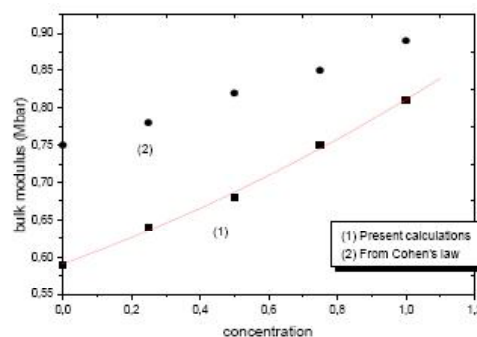


Figure 3 : The bulk modulus versus concentration of ZnS_xSe_{1-x} . Squares correspond to our results circles correspond to calculations from Cohen's relation

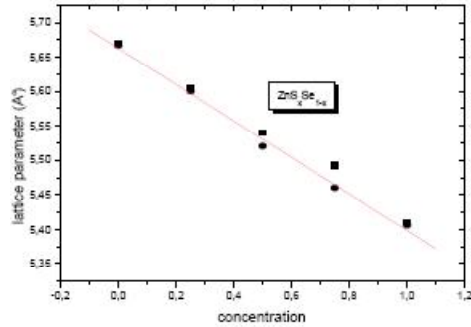


Figure 4: The lattice parameter versus concentration of $\text{ZnS}_x\text{Se}_{1-x}$. The solid line is a prediction of ideal mixing according to Vegard's law. Squares correspond to our simulation

$\text{ZnS}_{0.75}\text{Se}_{0.25}$ (0.85 Mbar) with an accuracy about 17%, 17% and 15% respectively

As we see in Figure 3, the variation of B with concentration is quadratic and is given by the following equation:

$$B(\text{Mbar}) = 0.586 + 0.1474x + 0.068x^2 \quad (14)$$

The quadratic term stands for the bowing parameter. This bowing is known to be an effect caused by disorder. Indeed, the disorder effect contributes in two different ways: the chemical disorder (contribution due to the compositional disorder in the anionic sublattice).

The volume deformation effect (contribution due to the compression and the dilatation of the two binary alloys into the ternary alloy volumes).

According to van Vechten and Bergstresser^[18], the disorder contribution (which is related to the difference of electronegativities of the alloyed atoms) plays a dominant role in determining the bowing parameter.

In $\text{ZnS}_x\text{Se}_{1-x}$, the difference of electronegativities of S and Se atoms is equal to 0.1.

Moreover, our results show that the bowing parameter is equal to 0.068. This value is close to the value found for $\text{CuAg}_x\text{I}_{1-x}$ (0.08)^[19].

In figure 4, we plot the lattice parameter for $\text{ZnS}_x\text{Se}_{1-x}$ solid solution. We notice that for all concentrations ($x=0.25$, $x=0.5$, $x=0.75$), the calculated lattice parameters are in good agreement with experimental results^[6] for which the variation is linear and follow Vegard's law very closely. In conclusion, we can say that there is an ideal mixing between ZnSe and ZnS.

To compute elastic constants, we will follow the treatment established in Ref^[15] which we shall outline here briefly. To compute C_{11} - C_{12} , we use a volume-conserving strain matrix:

$$\begin{pmatrix} (1+\beta)^{\frac{1}{3}} - 1 & 0 & 0 \\ 0 & (1+\beta)^{\frac{1}{3}} - 1 & 0 \\ 0 & 0 & (1+\beta)^{\frac{2}{3}} - 1 \end{pmatrix} \quad (15)$$

which yields an energy change $\Delta E = \beta^2(C_{11} - C_{12})V/3 + O(\beta^3)$ where V is the volume. We compute the total energy at several values of β and drop the terms of order β^3 and higher. Plotting ΔE versus β^2 yields a straight line with slope $= (C_{11} - C_{12})V/3$.

Based on the fact that our results for C_{11} and C_{12} agree well with experimental results for ZnS and ZnSe (see TABLE 3), we have extended our calculations to predict these quantities for $\text{ZnS}_{0.25}\text{Se}_{0.75}$, $\text{ZnS}_{0.5}\text{Se}_{0.5}$ and $\text{ZnS}_{0.75}\text{Se}_{0.25}$.

We are interested now in calculating the thermodynamic properties of $\text{ZnS}_x\text{Se}_{1-x}$ for $x = 0.25$,

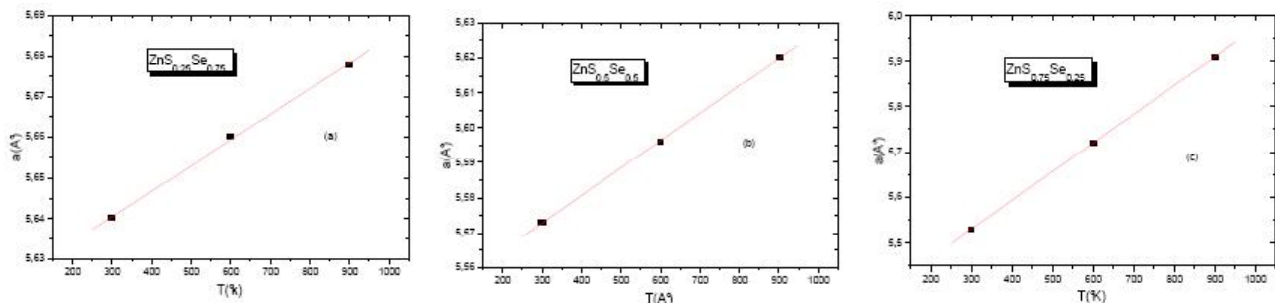


Figure 5: The lattice parameter as a function of temperature for: (a) $\text{ZnS}_{0.25}\text{Se}_{0.75}$ (b) $\text{ZnS}_{0.5}\text{Se}_{0.5}$ (c) $\text{ZnS}_{0.75}\text{Se}_{0.25}$

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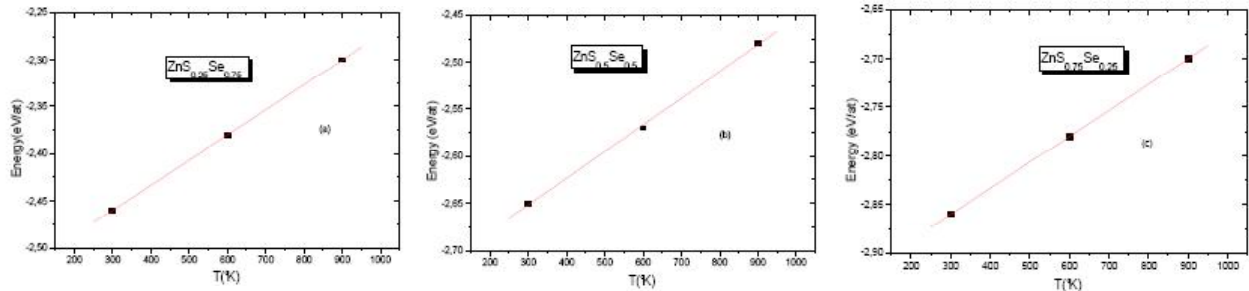


Figure 6 : The total energy as a function of temperature for: (a) $ZnS_{0.25}Se_{0.75}$; (b) $ZnS_{0.5}Se_{0.5}$; (c) $ZnS_{0.75}Se_{0.25}$.

$x=0.5$, and $x=0.75$.

In MD simulation, the linear thermal expansion coefficient α can be computed directly from the definition:

$$\alpha = \left. \frac{1}{a} \frac{\partial a}{\partial T} \right|_P \quad (16)$$

Where a is the lattice parameter. Therefore, we consider the temperature variation of the lattice constant at zero pressure (see figure 5).

A molecular dynamics simulation is performed in an NVT ensemble at each temperature to equilibrate the system and then to determine the corresponding zero pressure lattice constant.

From the slope of the total energy versus temperature curve (see Figure 6), we can estimate the specific heat of the system according to the following equation:

$$C_v = \left. \frac{\partial E}{\partial T} \right|_V \quad (17)$$

TABLE 3. Structural and thermodynamic properties of $ZnS_{0.25}Se_{0.75}$, $ZnS_{0.5}Se_{0.5}$, $ZnS_{0.75}Se_{0.25}$

	ZnSe	$ZnS_{0.25}Se_{0.75}$	$ZnS_{0.5}Se_{0.5}$	$ZnS_{0.75}Se_{0.25}$	ZnS
a (Å)	5.667 ^a	5.6 ^b , 5.605 ^c	5.52 ^b , 5.54 ^c	5.46 ^b , 5.492 ^c	5.406 ^a
B (Mbar)	0.59 ^a , 0.75 ^d	0.64 ^b , 0.78 ^d	0.68 ^b , 0.82 ^d	0.72 ^b , 0.85 ^d	0.816 ^a , 0.89 ^d
B'	5.41 ^a	3.54 ^b	3.11 ^b	3.65 ^b	4.73 ^a
C_{11} (Mbar)	0.72 ^a	0.644 ^b	0.682 ^b	0.753 ^b	0.98 ^a
C_{12} (Mbar)	0.52 ^a	0.638 ^b	0.679 ^b	0.748 ^b	0.73 ^a
θ_D (K)	277 ^b	299 ^b	316 ^b	336 ^b	372 ^b
T_m (K)	978 ^b	933 ^b	956 ^b	998 ^b	1132 ^b
C_v (J/K.mol)	23.54 ^b	25.6 ^b	26.16 ^b	25.53 ^b	24.02 ^b
α ($10^{-5} K^{-1}$)	1.17 ^b	1.12 ^b	1.4 ^b	0.11 ^b	1.22 ^b

^a [11], ^b [DM], ^c [6], ^d [17].

Our calculations can be used to determine an approximate melting. Fine et al^[20] noticed empirically that the melting temperature and elastic constants of cubic materials are related by the approximate expression:

$$T_m = 553K + (591KMbar^{-1})C_{11} \pm 300K \quad (18)$$

Debye temperature is calculated from the bulk modulus using the empirical relation taken from Ref [21].

$$\theta_D = 24.0062 + 0.42939 \times B(\text{kar}) \quad (19)$$

All the predicted thermodynamic properties are listed in TABLE 3.

Based on the fact that the values of θ_D and T_f agree well with experimental calculations for ZnSe and ZnS, we have predicted these quantities for ZnS_xSe_{1-x} at $x=0.25$, $x=0.5$, and $x=0.75$ using Equations (18) and (19).

According to our results, we see that the Debye temperature increases with concentration (x) according to the following equation (see Figure. 7):

$$\theta_D = 277.6 + 70.8x + 24x^2 \quad (20)$$

The specific heat for $ZnS_{0.25}Se_{0.75}$, $ZnS_{0.5}Se_{0.5}$ and $ZnS_{0.75}Se_{0.25}$ alloy is around $24.6 J K^{-1} mol^{-1}$.

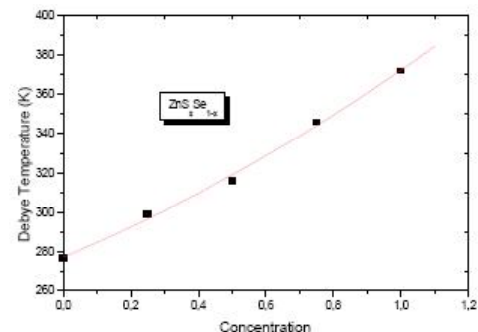


Figure 7 : Debye temperature versus concentration for ZnS_xSe_{1-x}

This constant value corresponds to the classical Dulong-Petit result ($\approx 24 \text{ JK}^{-1}\text{mol}^{-1}$) which is obtained at high temperatures for all solids.

CONCLUSIONS

We have presented the results of simulation calculations based on the well-tested Tersoff potential. We found that the lattice parameter varies linearly with alloy concentration. However, the apparition of a bowing in the variation of the bulk modulus with concentration can be due to the volume deformation effect and to the difference in electronegativity between Se and S. Based on molecular dynamics calculations, we have predicted elastic and thermodynamic properties such C_{11} , C_{12} , heat capacity, melting point, Debye temperature and linear thermal expansion coefficient for $\text{ZnS}_{0.25}\text{Se}_{0.75}$, $\text{ZnS}_{0.5}\text{Se}_{0.5}$ and $\text{ZnS}_{0.75}\text{Se}_{0.25}$.

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