AB INITIO CALCULATIONS OF STRUCTURAL AND THERMAL PROPERTIES OF WURTZITE $ZN_{1-X}CD_XO$ ALLOYS WITH DEBYE-GRUNEISEN MODEL

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Abstract. In this paper, structural and thermal properties of Zn1-xCdxO alloys for x=0, 0.125, 0.25, 0.375, 0.5, and 0.625 have been investigated by Ab initio calculations method. Both lattice constants a and c of wurtzite structure follow Vegard's law and are in a good agreement with the experimental data for x=0. The diagrams of specific heat at constant volume versus temperature for different values of x have been plotted and values of specific heat at constant pressure for different concentrations of x at 300K, 600K and 900K have been obtained. The value of specific heat at constant pressure for ZnO has a good consistency with experimental data. Specific heat at constant volume increased by increasing temperature and specific heat at constant pressure decreased by increasing x. The diagrams of Debye temperature versus x at 0K, 300K, 600K and 900K have been plotted, too. These diagrams state that Debye temperature decreases by increasing x or increasing temperature.

Keywords: ab initio calculations, thermal properties, Debye-Gruneisen model, $Zn_{1-x}Cd_xO$ alloy.

1. Introduction

Wurtzite Zn1-xCdxO ternary alloys were investigated because of applications for the light emitting diodes. For this reason, the study of the thermodynamic properties of the $Zn_{1-x}Cd_xO$ ternary alloy is very significant in the point of view of the fabrication of effective LEDs [1].

So far, Wang Zhi et al. [2], have obtained structural and corrected band properties of $Zn_{1-x}Cd_xO$ by first principle study. They found that the band gap decreases by increasing concentration of Cd. Xin Tang et al. [3], have investigated the doping stability and electronic structure of $Zn_{1-x}Cd_xO$. They found that by increasing Cd concentration, formation enthalpy of $Zn_{1-x}Cd_xO$ alloy increases. I.I. Shtepliuk et al. obtained the critical temperature for $Zn_{1-x}Cd_xO$ system about 1140K. Yabin Chen et al. [4], have investigated pressure-induced structural transition of $Zn_{1-x}Cd_xO$ alloys. According to their experiment, at x=0.67 where the alloy is intrinsically stable in the rock-salt phase even at ambient pressure.

Since theoretical works on electronic properties were successful [2, 3], we decided to investigate the structural and thermal properties of $Zn_{1-x}Cd_xO$ for x=0, 0.125, 0.25, 0.375, 0.5, 0.625 by Debye-Gruneisen model that scarcely has been paid attention by researchers.

In this paper, in addition to obtaining the related lattice constants and testing the correction of Vegard's law about them the thermal quantities like, specific heats at constant volume and pressure, Debye temperature at different temperatures and concentration of x have been investigated.

2. Computational Details

The calculations are on the basis of Density Functional Theory (DFT). Ab initio calculations have been done by Quantum Espresso [5] package. The exchange correlation functional GGA(PBE) has been used. In these calculations the cut off energy equals 60 Rydberg and uniformed k-mesh 5*5*5 has been considered. Using third-order Brich-Murnaghun Eos, the fitting of energy versus volume data was done by code Gibbs 2 [6, 7] and the thermal properties also were calculated by this code.

In code Gibbs 2, non-equilibrium Gibbs function is written in the following form:

$$G^*(V;P,T) = E(V) + PV + A_{vib}[\theta_D(V),T], \tag{1}$$

where $E(V)$ is the total energy per unit cell, PV is corresponding hydrostatic pressure conditions, $\theta_D(V)$ is Debye temperature and A_{vib} is vibration term which can be written as:

$$A_{vib} = nk_BT[\frac{9\theta}{8T} + 3\ln(1 - e^{\frac{-\theta}{T}}) - D(\frac{\theta}{T})]. \tag{2}$$

In above relation $D(\frac{\theta}{T})$ is Debye integral. In quasi-harmonic model Debye temperature can be obtained by:

$$\theta_D(V) = \theta_D(V_0)\frac{(B_{Stat}/B_0)^b}{(V/V_0)^a}, \tag{3}$$

where V_0 and B_0 are equilibrium volume and bulk modulus, respectively. The values of parameters a and b are assumed to be -0.5 and 0.5, respectively in the Dugdale-McDonald approximation [7].

By minimizing non-equilibrium Gibbs Free energy proportional to volume, the thermal properties of the system like C_v and C_p can be calculated.

3. Results and Discussions

Structural Properties. The diagrams of lattice constants of $Zn_{1-x}Cd_xO$ alloy versus x have been shown in Fig.1.
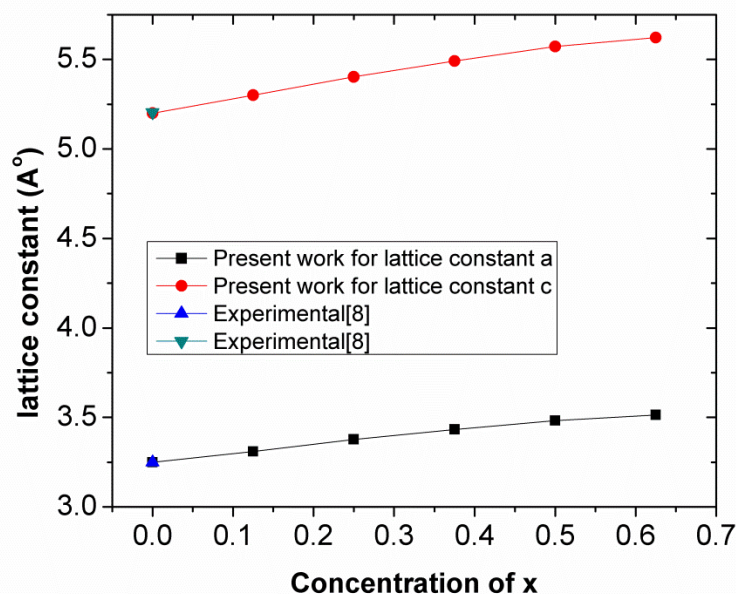
Fig. 1. The diagrams of lattice constants of $Zn_{1-x}Cd_xO$ alloy versus x

It is obvious that the lattice constants increase by increasing concentration of Cd. It is because of weaker bonding of CdO than ZnO due to more ionic bonding of ZnO than CdO caused by higher difference of electronegativity between Zn (1.65) and O (3.44) than Cd (1.69) and O (3.44). Also, more atomic radius of Cadmium and more distance of valence electrons from nucleus of Cd might be the other reasons of weaker bonding of wurtzite ZnO. The experimental results confirm above sentences where binding energy of wurtzite ZnO is 7.52(ev/pair) [9], while, as we know, the highest calculated value of wurtzite CdO binding energy equals 5.97(ev/pair) [9].

Our calculated lattice constants a and c at different concentration of Cd together with experimental and other theoretical values results are listed in Table 1.

Table 1. Calculated lattice constants a and c at different concentration of Cd together with experimental and theoretical results in Angstrom unit

	X=0	X=0.125	X=0.25	X=0.375	X=0.5	X=0.625
Present work	a=3.2496, c=5.1993	a=3.31, c=5.3	a=3.3767, c=5.4027	a=3.4323, c=5.4917	a=3.4831, c=5.5729	a=3.514, c=5.622
Experimental work [8]	a=3.2496, c=5.2042	-	-	-	-	-
Theoretical work [8]	a=3.286, c=5.241	-	-	-	-	-

Lattice constants of $Zn_{1-x}Cd_xO$ alloy follow Vegard's law and experiment confirms this result up to x=0.69[2]. The reasons of following lattice constants from Vegard's law include:

i) The relative atomic sizes of the elements;

ii) The relative volume per valence electron in crystals of the pure elements;

iii) Brillouin-zone effects;

iv) electrochemical differences between the elements [10].

Thermal properties. The diagrams of specific heat at constant volume versus temperature for different values of x for $Zn_{1-x}Cd_xO$ have been plotted in Fig. 2. The diagrams at low temperatures have T^3 behavior and at high temperatures tend to saturation limit.
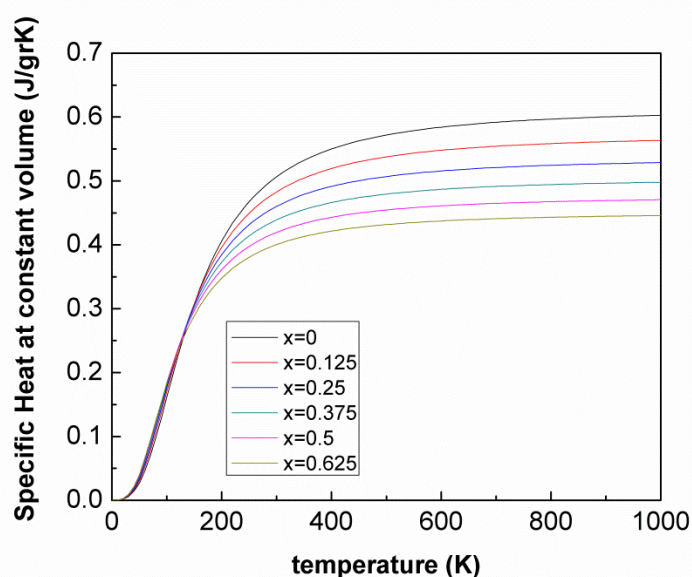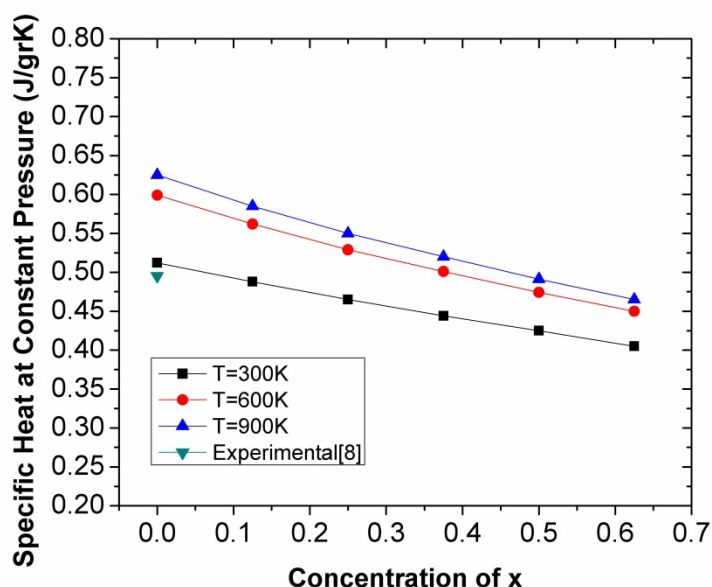

Fig. 2. The diagrams of variations of specific heat at constant volume by increasing temperature at different concentration of Cd

The diagrams of specific heat at constant pressure of $Zn_{1-x}Cd_xO$ at 300K, 600K and 900K and different Cd concentrations have been shown in Fig. 3. At low temperatures, the specific heat depends on strength of bonding between atoms and their molecular mass. Because of weaker bonding between cadmium and oxygen in comparison with zinc and oxygen plus heavier molecular mass of cadmium oxide than zinc oxide that decreases the velocity of phonon vibrations, the Specific heat at constant pressure and low temperatures decreases linearly by doping of Cd atoms as it is confirmed with our calculations. At higher temperatures due to ionic nature of these bonding, Coulomb interactions have the most important role in optical modes. Hence, the specific heats of this alloy decrease with increasing Cd concentration because of higher lattice constants, higher difference of electronegativity of ZnO wurtzite than CdO wurtzite and more screening of ionic potential in cadmium.

Fig. 3. The diagrams of variations of specific heat at constant pressure of $Zn_{1-x}Cd_xO$ at 300K, 600K and 900K
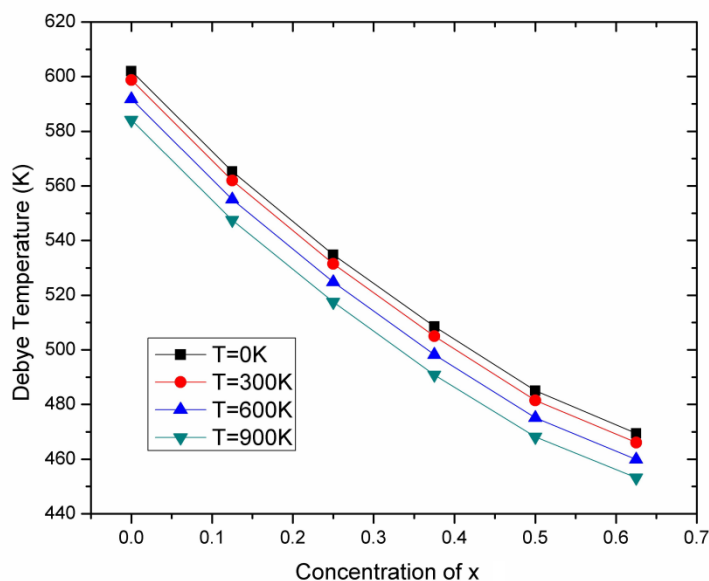
Fig. 4. The diagrams of Debye temperature versus x at 0K, 300K, 600K and 900K

As we know from literatures, Debye temperature is the highest temperature that can be achieved due to a single vibration in alloys and has a direct relation with static bulk modulus. The diagrams of Debye temperature of $Zn_{1-x}Cd_xO$ versus x at different temperatures have been shown in Fig. 4. As it is seen, Debye temperature decreases by increasing the concentration of Cd in $Zn_{1-x}Cd_xO$ so that the difference of this parameter is about 130K when x varies between 0 and 0.67.

4. Conclusion

In this paper, structural and thermal properties of $Zn_{1-x}Cd_xO$ alloy for x=0, 0.125, 0.25, 0.5, 0.625 have been investigated. The values of lattice constants a and c were calculated 3.2496 and 5.1993, respectively, for x=0 which are in good agreement with the experimental and theoretical reports. Also lattice constants for different values of x follow Vegard's law. The diagrams of specific heat at constant volume at low temperatures have T^3 behavior and at high temperatures tend to saturation limit. Specific heat at constant pressure versus x at 300K, 600K and 900K has been plotted. Specific heat at constant pressure decreases linearly by increasing x and specific heats increases by increasing temperature. Debye temperature diagram versus x at different temperature shows to be decreased by increasing x and temperature.

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