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Research paper

Atomistic study of stability and new phase transitions of zinc selenide using FP-LMTO-PLW method

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Abstract

By full potential linear muffin-tin orbitals (FP-LMTO-PLW) method, we have studied the phase transitions of ZnSe under high pressures. The local density approximation (LDA) was used for the exchange and correlation energy. The most important result is the prediction of the possibility of four phase transitions from the cubic zincblende (ZnS-B3) to the B81 (NiAs) structure at 8.00 GPa, the second from B3 to the B32 (NaTi) and Bh (WC) structures at above 45 GPa for each one of them, and from B3 to B2 (CsCl) phase at around 31GPa. The first one (ZnS–NiAs) occurring at a lower pressure than the well knownZnS to NaCl transition (found here to be 11.5 GPa).

Keywords: *FP-LMTO-PLW; LDA; Properties Structurales; Transition Phases,Znse.*

1. Introduction

The semiconductor II-VI compounds play an important role in developing new technologies due to some of their extreme physical properties [1, 2]. Specifically, zinc selenide semiconducting material has attracted increasing research interest in recent years. The zinc selenide has quite different behaviors in its electronic, elastic and structural properties from the other II–VI compounds.

The zinc selenide (ZnSe) is a very important wide-band-gap semiconductor of II-VI group (also known as dilute magnetic semiconductor group) having many technological applications such as high-density optical memories, transparent conductors, ultrasonic transducers, solar cells etc. due to its direct band gap, low resistivity and photosentivity. The structural, electrical and elastic properties for ZnX (X = S, Se, Te) compounds have been widely investigated by many researchers using experimental measurement and first principal calculation [3-5]. Ahuja and Heda [3] have measured experimental Compton profiles of ZnSe along [100] and [110] directions using our 740GBq 137Cs Compton spectrometer. They have alsocomputed the momentumdensities, energy bands, density of states (DOS) and band gaps using DFT (LDA and GGA) and pseudopotential (PP) approach. The elastic and thermodynamicproperties of ZnSe have investigated by Khatta et al. [4] usingthermo_pw package implemented in Quantum espresso code within the framework of DFT. Authorsused PP methodwithin the LDA for the exchange-correlationpotential. Recently, Structural, thermoelastic, and mechanicalproperties of ZnX (X = O, S and Se) in wurtzite and zinc blende phase have been studied by Valdez et al. [5] using SIESTA code.

The investigation of physical properties of the binary compounds under hydrostatic pressure has been an active topic of researches in condensed matter physics over the previous decades [6–8]. Withthis background, the presentpapergives a detailedstudy on the structural properties and energy band gap of ZnSe and compares theseresultswithothersexperimental and theoriacl data.

2. Methods

The calculations presented in this work were performed using FP-LMTO-PLW method as implemented in the LMTART (Mindlab) code [9] within the framework of density functional theory (DFT) [10], [11]. For the electron-electron interaction, in the total energy calculations, we used the local density approximation (LDA) for exchange correlation potential, as parameterized by Perdew et al. [12]. The crystal potential and the electron charge density within muffin-tin (MT) spheres were expanded using spherical harmonics up to $l_{max} = 6$. Table 1 contains the parameters used in the present calculations; the kinetic energy necessary to ensure the convergence (E_{cutoff}), the number of plane waves (NPLW) used, and the radius of the muffin-tin (RMT) spheres, for each of the eight crystal structure that were studied. The NaCl (B1), CsCl (B2), NaTl (B32) and ZnS (B3) structures have cubic symmetry, where the unit cell volume depends on one parameter only which is the lattice constant a. Other structures, namely wurtzite (B4), NiAs ($B8_1$), and WC (B_h), so the unit cell volume in these structures depends on different lattice constants (z, a, c/a ratio and internal parameter u), all of them should be optimized. The position of zinc (Zn) and selenide (Se) atoms in each of the above structures of ZnSe compound are listed in Table 2.These structures have the following space groups: B1: $Fm\bar{3}m$, B2: $Pm\bar{3}m$, B3: $F\bar{4}3m$, B4: $P6_3mc$, B_h: P6m2, B32:Fd3m, and $B8_1$: $P6_3/mmc$

Table 1: The Plane Wave Number NPLW, Energy Cut-Off (In Ry) and the Muffin-Tin Radius (RMT) (in A.U.) Used in Calculation for Binary Znse

Structure	NPLW	E_{cut}tot(Ry)	RMT(u.a)				K-Point
	ZnSe	ZnSe	Zn		Se		
NaCl(B1)	3942	98.5	2.368		2.566		(24;24;24)
CsCl(B2)	4168	104.14	2.559		2.772		(22;22;22)
ZnS(B3)	5064	100.79	2.207		2.391		(26;26;26)
Wz(B4)	13200	97.17	2.426	2.426	2.628	2.628	(28;28;46)
NiAs($B8_1$)	7786	97.06	2.384	2.384	2.583	2.385	(24;24;40)
NaTl(B32)	5064	117.66	2.128	2.128	2.128	2.128	(26;26;46)
WC (B_h)	2996	80.64	2.783		2.79		(18;18;28)

Table 2: Location of Zinc (Zn) and Silenide(Se) Atoms for the Seven Structures

	Zn		Se	
	1statom	2ndatom	1statom	2ndatom
NaCl(B1)	0.0 ;0.0 ;0.0		1/2;1/2 ;1/2	
CsCl(B2)	0.0 ;0.0 ;0.0		1/2;1/2 ;1/2	
ZnS(B3)	0.0 ;0.0 ;0.0		1/4;1/4 ;1/4	
Wz(B4)	0.0 ;0.0 ;0.0	1.2 ;-1/2√3 ;1/2	0.0 ;0.0 ;u	1.2 ;-1/2√3 ;(0.5+u)
NiAs($B8_1$)	3/4 ;1/4 ;0.0	1/4;3/4 ;0.0	1/4;1/4 ;0.3	3/4;3/4 ;-0.3
NaTl (B32)	1/8 ; 1/8 ;1/8	-1/8 ; -1/8 ;-1/8	3/8 ; 3/8 ;3/8	-3/8 ; -3/8 ;-3/8
WC (B_h)	0.0 ;0.0 ;0.0		1/2 ;$-12^{-1/2}$;1/2	

3. Results and discussion

3.1. Structural properties

In ab-initio calculations, the equilibrium structural parameters can usually be predicted by calculating either the pressure as a function of unit cell volume P(V), or the energy as a function of the unit cell volume E(V) [6]. In the presentwork, the structural parameters of ZnSesemiconducting compound wereobtainedfrom E(V) (Fig 1), for each of the eight structures consideredhere: NaCl (B1), CsCl (B2), ZnS (B3),Wurtzite (B4), NaTl (B32), and WC (B_h). The equilibrium lattice constant a_0, bulk modulus B_0 and pressure derivative of bulk modulus B_0' have been computed by minimizing the total energy by means of Murnaghan’s equation of state (EOS) [13] (For more details, please see our previous works [6, 8]). Total energy versus volume data for the rocksalt, CsCl, zincblende, wurtzite, NiAs, NiAs, NaTi and WC structures of ZnSe crystal shown in Fig. 1.

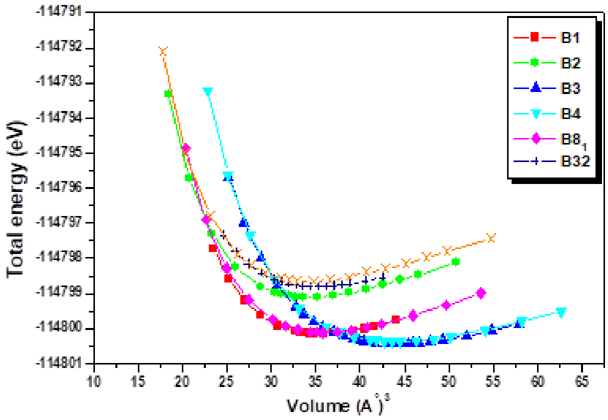

Fig. 1: Total Energy versus Volume for Different Structures of Znse Compound Using LDA.

Energies and volumes are per single ZnSe formula unit. By exploiting the curves of minimization, it follows that ZnS (B3) structure represents the most stable phase at zero pressure; we also show that the WZ(B4) structure is metastable in ZnSe, which is consistent with the results of Saini et al.[13]. It can also be seen that the NaCl phase has a higher total energy than the Wz(B4) phase (by 0.029 eV/2atoms). The total energy difference between the minima of the B3 phase curve and of the Wz(B4) phase curve is very low (-0.005 eV/2atoms). Our results are summarized in Table 3 together with those of other ab-initio calculations and experimental works [13-17].

The data shown in Table 3 for the ZnS (B3) phase indicates that LDA underestimates the lattice parameter by 2.29% compared to experimental value [15]. To the best of our knowledge, there are no data available for structural properties of ZnSe in B1, B2, B4, $B8_1$, B32 and WC phases.

Table 3: Calculated Structural Parameters (Equilibrium Lattice Constants A_0, and Structural Parameter C/A), Bulk Modulus B_0, the First Pressure Derivatives B_0’ and the Total EnergyE_{min}:^{B}ref-[14]^{C}ref-[13]^{F}ref-[15]^{G}ref-[16]^{H}ref-[17]

Parameters			NaCl(B1)	CsCl(B2)	ZnS(B3)	Wz(B4)	NiAs($B8_1$)	NaTi (B32)	WC (B_h)
a_0 (A°)	This work		5.222	3.257	5.618	3.96	3.716	5.200	5.586
	Otherworks	Theo			5.66^b 5.57^c, 5.54^g				
		Exp			5.75^f				
B_0 (GPa)	This work		87.382	78.85	67.67	65.75	82.96	76.34	72.67
	Otherworks	Theo			64.7^b, 57.30^c, 72.44^g				
		Exp			72.7^f				

B'_0	This work		4.247	3.96	3.881	3.81	4.05	4.288	3.70
	Otherworks	Theo			4.56^c 4.02^g, 4.36^h				
c/a	This work					1.656	1.633		1.630
E_{min}	This work		-8441.18	-8441.1	-8441.209	-8441.204	-8441.1	-8441.08	-8441.07

3.2. Phase transition

The stability of any particular structure corresponds to the lowest Gibbs free energy, which is given by G = E+ PV-TS, where E is the internal energy, S is the vibrational entropy, P is the pressure, and V is the volume [6, 8]. Since our calculations were performed at T = 0 K, the Gibbs free energy G is then equivalent to the enthalpy H = E + PV and the pressure Pt for which Gibbs energies of two phases are equal is defined as the transition between these two phases [6, 8].

In order to show these phase transitions more clearly, we display in Fig.2, the enthalpy differences for B2, B1, B32, B81 and Bh phases as a function of pressure with reference to B3. The obtained results show that ZnSe undergoes five transitions. The first one is the transition from the cubic zincblende (ZnS-B3) structure to the B32 (NaTi) and Bh (WC) structures above 45 GPa for each one of them, and to the B81 and B2 structuresat 8 and 31 GPa, respectively.

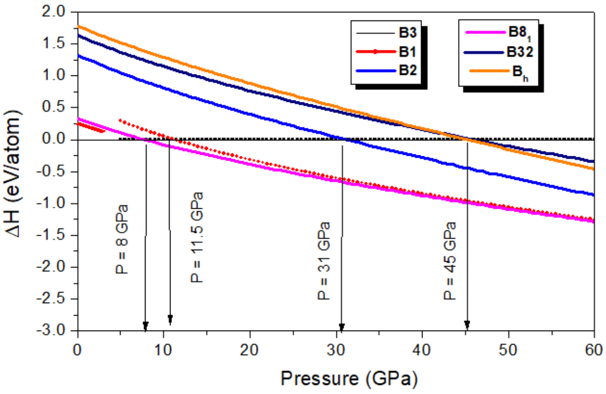

Fig. 2: Variation of the Enthalpy Differences ΔH (Ev/Atom) Versus Pressure (Gpa) For Zns (B3),Nacl (B1), Cscl(B2), Nias(B81), Nati(B32) And WC(Bh) Phases of Znse. The Reference Gibbs free energy in Set for the Zincblende Phase

The calculated values of Pt and the transition volume are listed in Table 4. The latter (B3-B1 pressure transition) was found here to occur at 11.5 GPa, which is consistent with previous theoretical data (10.8 GPa[18], 12.1 GPa [19], 11.8-14.5 GPa [20], 13 GPa [21], and 13.8 GPa [22]). To the best of our knowledge there are no experimental or theoretical results in literature to compare our results for the pressures, which induce phase transitions from B3 to the four (B2, $B8_1$, B32 and B_h) phases.

Table 4: Calculated Values of the Transition Pressure Ptand Transition Volumes forZnSe

Materials	ZnS(B3)→NaCl(B1)	ZnS(B3)→CsCl (B2)	ZnS(B3)→NiAs($B8_1$)	ZnS(B3)→NaTi(B32)	ZnS(B3)→WC(B_h)
Pt(GPa)	11.50	31.00	8.00	45.00	45.00
V_{B3} (Pt) $(A^{\circ})^3$	44.34	44.34	44.34	44.34	44.34
V_{Bx} (Pt) $(A^{\circ})^3$	35.61	34.56	36.30	35.16	35.36
Vr(%)	19.68	22.06	18.13	20.69	20.25

4. Conclusion

In this work, we have studied ZnSe in the rocksalt NaCl(B1), CsCl (B2), zinc-blende (B3), wurtzite (B4), NiAs (B81), NaTi (B32) and WC (B_h), structures by the ab-initio FP-LMTO-PLW method within the local density approximation (LDA). The ground state properties such as the equilibrium lattice parameter and the bulk modulus and its pressure derivative were determined and compared with other available experimental and theoretical data. Our most important result is that concerned with the possibility of phase transition from ZnS to CsCl, NiAs, NaTi and WC at lower pressures (31, 08, 45 and 45 GPa, respectively), than the well knownZnS to NaCl transition (11.50 GPa). The phase transition ZnS–NiAs was found to occur at the lower pressure.

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