Chalcogenide Letters Vol. 7, No. 4, April 2010, p. 263 - 268

THEORETICAL INVESTIGATIONS ON II-VI BINARY SEMICONDUCTORS

RITA JOHN*, D. HANNAH CATHERINE[a], S. PUSHPALATHA
Department of Theoretical Physics, University of Madras, Guindy Campus, Chennai, Tamilnadu, India
[a]*P.G. Department of Physics, Women’s Christian College, Chennail, Tamil Nadu, India*

IIB-VIB chalcogenides are promising semi conducting materials with desirable properties to be used for photonic applications. The theoretical investigation on AB (A= Zn, Cd; B= S, Se, Te) compounds using Tight Binding Linear Muffin Tin Orbital (TBLMTO) method at ambient and high pressures is presented. The structural, physical and mechanical properties are studied and compared with experimental values. The stiffness parameters such as the bulk modulus, melting temperature, and micro hardness are correlated with cell volume.

(Received March 31, 2010; accepted April 15, 2010)

Keywords: II-VI binary semiconductors, Band structure, Bulk modulus, Cell volume

1. Introduction

With the rapid development of advanced technologies in all areas, today much attention is presently paid to binary semi-conductors AB (A= Zn, Cd; B= S, Se, Te) and their alloys because of their applicability to design heterostructures which look promising for optoelectronic applications [1]. Due to their vast technological potential, the electronic and structural properties of these compounds are currently moving into focus of interest [2]. Application of these binary semi-conductors in optical devices has reached a high experimental level of investigation [3]. Experimental findings as well as numerous possibilities for industrial applications initiated a number of theoretical studies of structural and electronic properties of these Zn and Cd chalcogenides semiconductors.

The Tight Binding method has gained certain popularity both because of its realistic description of structural and dielectric properties in terms of chemical bonds and its simplicity, to handle very large systems. So an attempt has been made to study the band structure of binary AB (A= Zn, Cd; B= S, Se Te) chalcogenides using semi-relativistic Tight Binding Muffin –Tin Orbital method within local density approximation with von Barth Hedin exchange correlation scheme [4].

---

*Corresponding author: john_abraham@sify.com

2. Band structure at ambient pressure

The electronic band structure calculations are performed for ZnX (X=S, Se, Te) and CdX (X=S, Se, Te) chalcogenide semiconductors in various competing structures such as zinc blende , wurtzite and Rock salt to determine the equilibrium structure at ambient pressure as possibilities of all these structures are already reported [5]. The present studies support the formation of these compounds in wurtzite structure. This is in agreement with the report of H. Karzel et al who has reported that at ambient pressure most of the chalcogenides crystallizes in either hexagonal wurtzite or cubic zinc blende structure or both [6]. Stanley W.W Liu et al have reported that CdS occurs naturally in hexagonal wurtzite structure [7]. There are number of papers which supports the work where it reports the formation of the compounds (ZnS, CdS, or CdSe) in hexagonal wurtzite structure or cubic zinc blende structure. At high temperature the hexagonal wurtzite structure is reported to be the equilibrium phase of ZnS [8].

Through energy minimization procedure equilibrium lattice parameters has been determined. The self-consistency in Eigen values were achieved and equilibrium cellvolume and lattice parameters were determined by calculating the total energies .by varying V/Vo =1 as shown in Fig.1

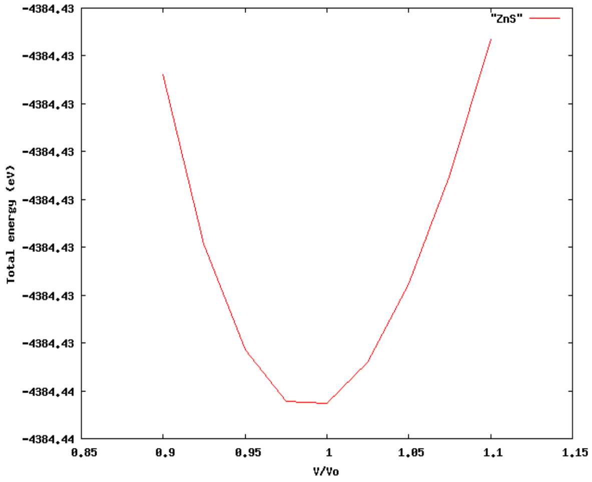

Fig.1 Energy m inimisation curve of Zns at V/Vo =1

Direct band gap is observed for all the compounds. The theoretical energy gaps obtained are underestimated due to the local density formulation of exchange and correlation. From Fig.2 the band structure for all compounds have same generic nature, where the topology of the bands is basically the same. The flat bands occurring in the valence band region -5eV to -10eV is due to the contribution of cationic ‘d’ bands. A group of six mostly anion derived s-p valence band is also observed. The first two conduction are strongly dominated by cationic ‘s’ state. In all chosen Cd compounds the cation ‘d’ bands are clearly separated in energy from the other group of valence bands, this is different from the chosen Zn compounds where the 3d bands lie very close to the upper valence bands. In Cd compounds the ‘d’ orbital shows effects of the interaction with both the anion ‘s’ and ‘p’orbital [9].Moreover upper valence band width for all Cd compounds are less compared with the Zn compounds.

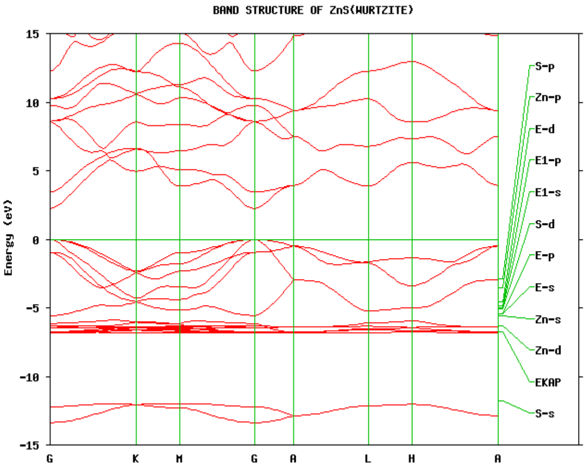

Fig.2 Band structure of ZnS at V/Vo=1

All the six compounds AB (A= Zn, Cd; B= S, Se, Te) have direct band gap occurring along the gamma point G. Among all, ZnS is found have wide band gap and while CdSe seem to have least. The band structure obtained is in similar nature reported by Peter Schroer et al [10]. The band gaps obtained in wurtzite structure for all these have greater value compared to in zinc blende structure which is in agreement with the reported value by Su-Huai Wei and S.B. Zhang [5]. Our calculation yield a width of 7eV for the upper valence band which is 2.5eV higher in energy compared to the experimental values which was reported[10]. The valence band maximum of wurtzite CdX (X=S, Se, Te) is higher than that of valence band maximum of zinc blende CdX. This leads to carrier localization in a mixed zinc blende/wurtzite system and can affect significantly device transport properties [11].

3. Density of states

The DOS obtained for all the compounds in wurtzite structure confirms the existence of band gap for the same. The cation d states which forms the flat bands in the band structure are responsible for the high peaks around -6eV for Zn compounds as shown in Fig.3

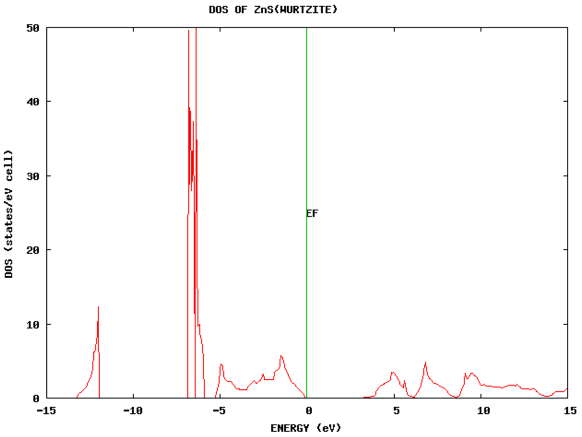

Fig.3 DOS of ZnS at V/Vo=1.

The anionic ‘s’ state which forms the lowest lying conduction band at about -12eV in band structure is also responsible for the occurrence of peak around -12eV from Fig.3. But the peaks seem to be higher in the case of Cd compounds to Zn compounds. Stoffel [9] attributed the occurrence of three peaks in the photoemission spectrum of the 4d bands of CdS to the influence of s-p and p-d interactions. The peaks obtained from DOS diagram seem to be highest for Telluride compounds compared to Sulphide and Selenide compounds but width of the peaks seem to be the least for telluride compounds.

4. Band structure at high pressure

The band structure calculations are performed for all compounds in the compressed volume range from 0.9Vo to 0.2Vo. The calculations are performed carefully to ensure the accuracy of metallization volumes. Under pressure the direct band gap changes to indirect and the metallization occurs indirectly between the point G and K. For CdS and CdSe compounds the 'd' bands are deeper in the valence bands hence they show higher metallic nature due to the reduced interaction of 'd' bands with upper valence band Fig.[4].

Table 1. Lattice Parameter (a), Energy Gap (Eg), Cell Volume (V_o), Bulk modulus(B_o).

Compound	**Lattice parameter a (Å)**		**Energy Gap (eV)**		**Cell volume Vo($Å^3$)**	**Bulk modulus B_o(GPa)**
	Theoretical	**Experim**	**Theoretical**	**Experim**		
ZnS	a=3.7656;c=6.1563, [1] a=3.71;c=6.06, [2] a=3.83;c=6.28[3]	a=3.82;c=6.26[4]	2.25[1]	3.68[3]	226.68	77.1
ZnSe	a=3.9690;c=6.4846, [1]		1.32[1]	2.70[3]	265.40	62.4
ZnTe	a=4.2651;c=6.9815, [1]		1.038[1]		329.96	51.0
CdS	a=4.1740; c=6.8173, [1] a=4.1009; c=6.6866, [2] a=4.03; c=6.54, [3]	a=4.136;c=6.71[4]	1033[1]	2.485[3]	308.58	62.0
CdSe	a=4.2642;c=6.9743, [1] a=4.2717;c=6.9786, [2] a=4.21;c=6.86, [3]	a=4.300;c=7.01[4]	0.55[1]	1.751[3]	329.48	53.0
CdTe	a=5.5496;c=7.4389, [1] a=4.5499;c=7.4512, [2]		0.614[1]	0.80[3]	400.04	42.4

[1] Present (TBLMTO); [2] Ref. 10; [3] Ref.12; [4] Ref.5

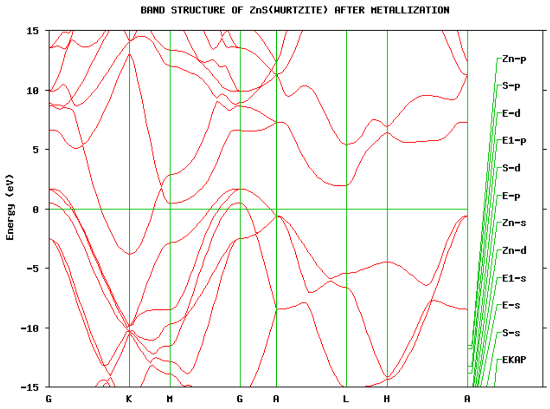

Fig.4 Band structure of ZnS after metallization.

5. Cell volume and stiff parameters

Bulk modulus (Bo) is the hardness parameter which has been linked with the structural parameter such has cell volume[13]. As the microhardness (H) and melting point (Θm) also reflect the stiffness of the solid an attempt is made to correlate these parameters Bo, H, Θm with Vo. We observe a linear trend between each of these parameter with Vo. From Fig.5 the hardness parameter (bulk modulus) show a systematic reduction with the increase in cell volume. Similar nature is observed for other parameters with cell volume.

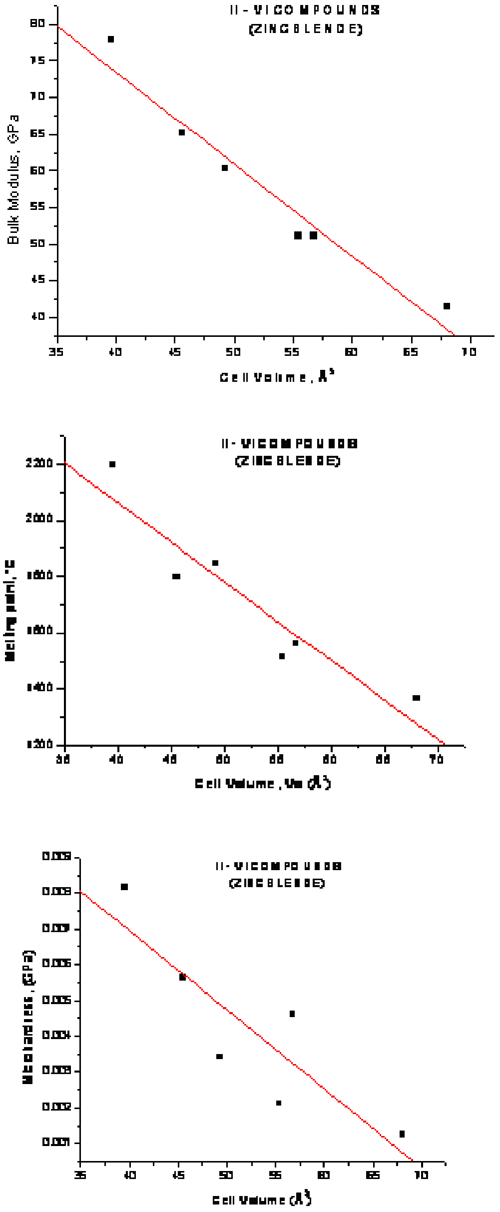

Fig. 5. Cell volume versus stiffness parameters (Vo versus Bo , H, Θm)

6. Conclusions

Band structure calcuation for six binary AB (A= Zn, Cd; B= S, Se, Te) semiconductors are reported. The present TB-LMTO calculations show their formation in wurtzite structure at ambient pressure. Their direct band gap values are compared. They undergo metallisation on pressure with band closure between G and K. The cell volume of these compounds are correlated with some stiffness parameters, and linear trend is observed for all the compounds.

References

[1] M. J. McMahon, R. J. Nelmes, N. G. Wright nad D. R. Allan, Phys. Rev. B **48**, 16246 (1993).
[2] Chin – Yu Yeh, Su – Huai Wei, and Alex Zunger, Phys. Rev. B **50,** 2715 (1994).
[3] R. J. Nelmes, M. J. Mc Mahon, N. G. Wright, D. R. Allan, Phys. Rev. B **51,** 15723 (1995).
[4] O.K. Anderson and O.Jepsen Phys.Rev. Lett **53,** 2571 (1984),
[5] Su Huai Wei, S.B. Zhang Phys. Rev. B.**62** (2004)
[6] H. Karzel, W. Potzel, M. Kofferlein, W. Schiessl, M. Steiner, U. Hiller, G. M. Kalvius, Phys. Rev. B **53**, 11425 (1996).
[7] V Stanely W. W. Liu and Sohrab Rabii, Phys. Rev. B **13**, 1675 (1976).
[8] G. E. Engel and R. J. Needs, Phys. Rev. B **41**, 7876 (1990).
[9] A. San – Miguel, A. Polian, M. Gautheir, and J. P. Itie, Phys. Rev. B **48**, 8683 (1993).
[10] Peter Schroer, Peter Kruger, and Johannes Pollmann, Phys. Rev. B **47**, 6971 (1993).
[11] Fuyuki Shimojo, Sanjay Kodiyalam, Ingvar Ebbsjo, Rajv K. Kalia Aiichiro Nakaho and Priya Vashista, Phys. Rev. B **70**, 184111 (2004).
[12] Dirk Voger, Peter Kruger and Johannes Pollman Phys. Rev. B.**48,** 6971 (1993).
[13] Rita John, Journal of Computational Physics **44**, 2008.