EVALUATING STRUCTURAL, OPTICAL & ELECTRICAL CHARACTERIZATION OF ZINC CHALCOGENIDES – FP – LAPW+ lo METHOD

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Abstract: To evaluate the structural, optical & electrical properties of the zinc chalcogenides (ZnO, ZnS, ZnSe & ZnTe), the Full Potential Linearized – Augumented Plane Wave plus Local Orbits (FP – LAPW+lo) method. For the purpose of exchange-correlation energy (E_{xc}) determination in Kohn–Sham calculation, the standard local density approximation (LDA) formalism has been utilized. Murnaghan's equation of state (EOS) has been used for volume optimization by minimizing the total energy with respect to the unit cell volume. With the result of electronic density of states (DOS), the structural, optical and electrical properties of Zinc chalcogenides have been calculated. The second derivative of energy, as a function of lattice strain has been successfully used to estimate the elastic constants of these binary compounds. The results are in good agreement with other theoretical calculations as well as available experimental data.

Keywords: Semiconductors, Chalcogenides, Density Functional Theory, FP-LAPW+lo, Electric properties,.

1. INTRODUCTION

The World of Physics pays much attention to investigate and understand the properties of solids. Because of the high difficulties in experimental work, high cost of chemicals, results accuracy and time consumption researchers are now choosing the theoretical methods. Density Functional Theory (DFT) [1] gives the exact solution to calculate the ground-state properties of all kind of materials. This theory helps to investigate and study the physical properties like electrical, elastic, mechanical, optical, magnetic, thermal and structural of materials. Modern high configuration computer helps researchers to evaluate the physical properties by using this theory.

It is very important to study the band gap and Density of States (DoS) in semiconducting materials. Because of the modern devices and applications are completely based on the band gap and optical absorption. The band structure of ZnX binary compounds have been calculated by using Full Potential Linearized Augmented Plane Wave method Plus local orbits (FP-LAPW+lo) within the Generalized Gradient Approximation (GGA). Many researchers studied the optical parameters of Zinc chalcogenides ZnX (X= S, Se, and Te) belong to II-VI semiconductors [2-8]. There are several methods and theoretical reports available to calculate the band structure and optical properties but some controversies are at there. But the FP-LAPW+lo gives the closer values with the experimental data.

The variation in energy gap is completely based on the method to calculate the band structure. Some theoretical reports are in good agreement with the measured one. They were calculated based on Local Density Approximation (LDA). But we have used FP-LAPW+lo to calculate the band structure. Our values are in good agreement with the earlier reports.

The aim our work is to evaluate the structural, electronic, optical and thermal properties of ZnX binary compounds. FP-LAPW+lo is the method used to investigate the properties and the values are compared with the experimental and other theoretical works for these compounds.

The rest of the paper is organized as follows. After a brief introduction in section 1, the calculation methodology is introduced and the computational details are given in section 2. In section 3, the results of structural, optical, electric and thermal properties of ZnX binary compounds are presented and discussed. In this section we also compared our results with the already available experimental data and as well as theoretical calculations. Finally, the summary of the our main results and concluding remarks is given in section 4.

2. COMPUTATIONAL METHOD

The calculations of the structural, optical, electric and thermal properties are calculated in the frame work of Density Funtional Theory (DFT) [1]. To calculate these properties, we employed the full potential linearized augmented plane wave plus local orbitals (FP-LAPW + lo) as implemented in the Wien2k code [9-10]. We have used the generalized gradient approximation (GGA) as parameterized by Perdew, Burke and Ernzerhof (PBE) to explain the exchange and correlation effects [11]. ZnX compounds crystallize in the zinc-blende structure with space group F-43 m. The Zn atom is set at (0, 0, 0) whereas the X atom is set at (0.25, 0.25, 0.25). We have employed Murnaghan's equation of state [12] for the optimization of the total energy with respect to the unit cell volume.

Thus the equilibrium structural parameters have been calculated. The calculations were done with RMTkmax = 7, to achieve energy eigen value convergence. RMT is the smallest radius of the muffin-tin (MT) spheres and kmax is the maximum value of the wave vector. The respective values of muffin-tin radii (RMT) for Zn, S, Se and Te were taken to be 2.1, 2.0, 2.2 and 2.5 a.u. (atomic units) for all the calculations. The wave function has been expanded inside the atomic spheres with the maximum value of the angular momentum

lmax as 10. The irreducible Brillouin zone (BZ) of the zinc-blende structure has been decomposed into a matrix of $10\times10\times10$ Monkhorst–Pack k-points [13]. The iteration procedure is continued with total energy and charge convergence to 0.0001Ry and 0.001e, respectively

3. RESULTS & DISCUSSIONS
3.1. Structural and elastic properties

With the Murnaghan's equation of state [12], the variation of the total energy versus unit cell volume yields to the equilibrium lattice parameter (a_0), bulk modulus B_0, and the pressure derivative of the bulk modulus B_0'. The values of $a0$, B_0 and B_0' for the ZB structure of the binary ZnX at zero pressure are presented in Table 1. For ZnS, ZnSe and ZnTe, the energy minima take place for $a0 = 5.371$, 5.632 and 6.198 Å, which agree well with the experimental values of 5.412, 5.667 and 6.103 Å, respectively with the maximal error of 1.53% with respect to experimental values. It is obvious that well defined structural properties are helpful for further study of electronic and optical properties. The elastic constants of ZnX compounds with cubic structure have been determined using the method developed by Charpin incorporated in WIEN2k code [14]. By applying appropriate lattice distortions in a cubic lattice, three independent elastic constants C_{11}, C_{12}, and C_{44} are determined. The following three equations are considered for the calculation of the elastic constants.

$$B_0 = (C_{11}+2C_{12})/3 \tag{1}$$
$$\Delta E_{rhomb} = ((C_{11}+2 C_{12}+4C_{44})V_0\delta^2)/6 \tag{2}$$
$$\Delta E_{tetra} = 6(C_{11}- C_{12})V_0\delta^2) \tag{3}$$

The first equation contains relation between the elastic constants (C_{11} and C_{12}) and the bulk modulus $B0$, obtained from Murnaghan's equation. Second equation is related to the variation of strain energy (ΔE_{rhomb}) versus volume-conserving rhombohedral strain (δ). Third equation is related to the variation of strain energy (ΔE_{tetra}) versus volume conserving tetragonal strain (δ). The calculated elastic constants for the zinc-blende ZnX are displayed in Table 2 with experimental result [15]. Calculated values are in a good agreement with available experimental data. The elastic constants decrease in magnitude with increase in lattice dimension from S to Te, due to cohesive energy decreases with the nearest-neighbour distance [16]. The mechanical stability in a cubic crystal requires the elastic constants satisfying the conditions as, $C_{11} - C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$, $C_{12} < B_0 < C_{11}$. The elastic constants in Table 2 obey these conditions. Calculated values of three elastic constants namely C_{11}, C_{12} and C_{44}, are used to determine Bulk modulus, B_0, Young's modulus, Y , Isotropic shear modulus, G and Poisson ratio, ζ based on the following explicit expressions [17-18],

$$G = (G_V + G_R)/2 \tag{4}$$

Here, G_V is Voigt's shear modulus and G_R is Reuss's shear modulus for cubic crystals, expressed as:

$$G_V = ((C_{11}-C_{12}+3C_{44}))/5 \tag{5}$$

$$G_R = (5C_{44} (C_{11}- C_{12}))/(4C_{44} +3(C_{11}- C_{12}) \tag{6}$$

The expressions for the Young's modulus and Poisson's ratio are given by

$$Y = 9GB/(G+3B) \tag{7}$$
$$\sigma = (3B-2G)/(6B+2G) \tag{8}$$

Table 3 displays the calculated values of elastic modulus. The bulk modulus B_0 represents the resistance to fracture while the shear modulus G represents the resistance to plastic deformation. Ductility of the material can be characterised by B_0/G ratio [19]. The B_0/G ratio for all ZnX are greater than 1.75 (see Table 3) which reveals that the compounds are ductile in nature. The highest value of B_0/G ratio is 2.19 for ZnTe representing it most ductile among all the ZnX compounds. There is a correlation between the binding properties and ductility [20]. The bond character of cubic compounds is expressed in terms of their Cauchy pressure (C_{12}–C_{44}). With increase in positive Cauchy pressure, compound is likely to form metallic bond. Accordingly, the ductile nature of all ZnX compounds can be correlated to their positive Cauchy pressure having the metallic character in their bonds. As depicted in Table 3, the ZnTe has a highest positive Cauchy pressure resulting strong metallic bonding (ductility) in it as compared to other compounds. The calculated value of Young's modulus (Y) is shown in Table 3. It provides the degree of stiffness of the solid, i.e., the stiffer material has the larger value of Y and such materials have covalent bonds. Table 3 shows that the highest value of Y occurs for ZnS demonstrating to be more covalent in nature as compare to other ZnX compounds. Value of Poisson's ratio (ζ), as a measure of compressibility for ZnX compounds are between 0.29 and 0.30 which predict that all the compounds are compressible. Also the Poisson's ratios having values between 0.25 and 0.5 represent central force solids. In our case, the Poisson's ratios are around 0.3, which reveals that the interatomic forces in the ZnX compounds are central forces.

Table 1: Calculated lattice constant (in A˚), bulk modulus B_0 (in GPa), pressure derivative B_0' for ZnX compounds compared to experimental works.

	a_0	B_0	B_0'
ZnS Present Expt.	5.371 5.412	90.12 75	4.32 4.00
ZnSe Present Expt.	5.632 5.667	72.42 69.3	4.76
ZnTe Present Expt.	6.198 6.103	60.39 50.9	4.71 5.04

Table-2: Calculated values of elastic constants (C_{ij} in GPa) at equilibrium for ZnX compound.

	C_{11}	C_{12}	C_{44}
ZnS Present Expt.	111 104	71 65	69 46.2
ZnSe Present Expt.	91 85.9	63 50.6	59 40.6

ZnTe			
Present	79	48	41
Expt.	71.7	40.7	31.2

Table – 3: Calculated values of elastic modulus (in GPa)

	G (GPa)	B0/G	C12-C44 (GPa)	Y (GPa)	σ
ZnS	41.88662	2.15152	1.88	108.8	0.299
ZnSe	33.41409	2.16735	3.93	86.88	0.3
ZnTe	27.48057	2.19755	7.57	71.58	0.302

3.2. Electronic properties

The electronic band structure of Zn chalcogenides has been calculated. The calculated band structure for ZnX at equilibrium is shown in figure 1(a-c). The calculated band structure is in good agreement with other theoretical results [21-23]. The zero of the energy scale is set at the top of the valence band (VB). The energy band structures are calculated along the directions containing high symmetry points of the first Brillouin zone, namely W→ L→ ᴦ→X→ W→K. Each member of ZnX demonstrates the existence of the valence band maximum and conduction band minimum at the same symmetry point. This confirms the direct energy gap between the top of the valence band and the bottom of conduction band at ☐ point. With the increase of the lattice parameters starting from the sulphide to the telluride, the X atom p bands shift up in energy as a common feature of II–VI compounds [24]. The calculated band gap is underestimated in comparison with experimental results, because of the simple form of GGA which cannot account the quasiparticle self-energy [25].

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The density of states (DOS) for ZnS is shown in figure 2(a-c). It is similar to that of ZnSe and ZnTe. The first structure in the total DOS is small and centered at around -12.29 eV, -12.37 eV and -11.18 eV for ZnS, ZnSe and ZnTe respectively. This structure arises from the chalcogen s states and it corresponds to the lowest lying band with the dispersion in the region around the ᴦ point in the Brillouin zone. The next structure appears at -6.20 eV, -6.56 eV and -7.09 eV for ZnS, ZnSe and ZnTe, respectively. It is an attribute of Zn d states with some p states of the chalcogen atoms and occupies largest number of states with flat bands clustered between -5.6 eV and -6.5 eV (for ZnS).
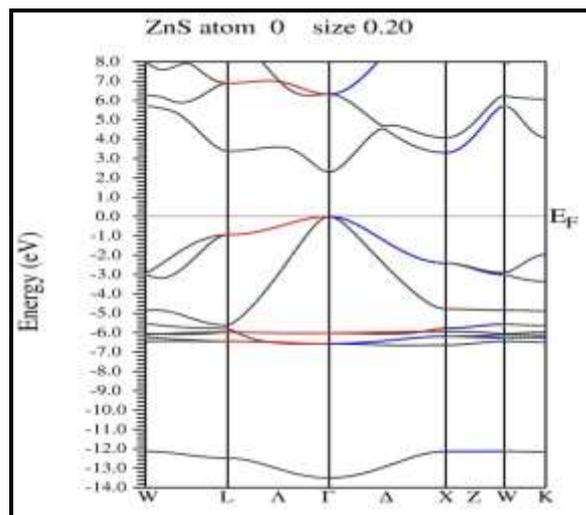
Figure 1a. Shows the Band Structure of ZnS
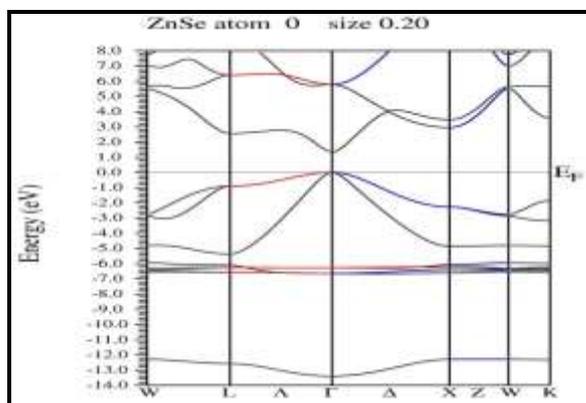
Figure 1b. Shows the Band Structure of ZnSe
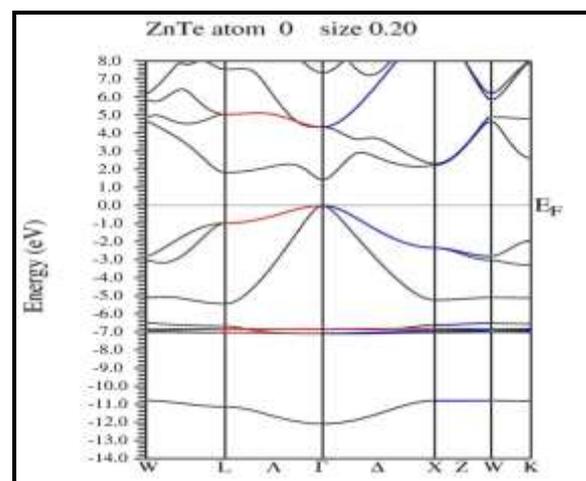
Figure 1c. Shows the Band Structure of ZnTe
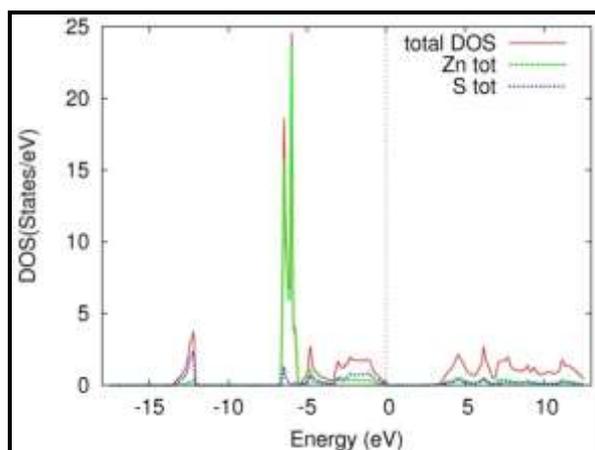
Figure 2a. Shows the Density of States of ZnS
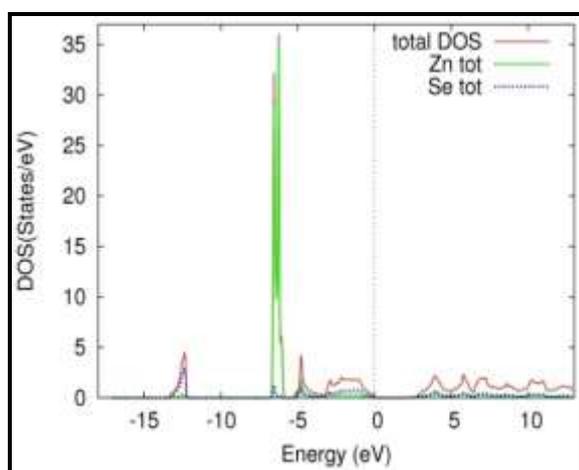
Figure 2b. Shows the Density of States of ZnSe
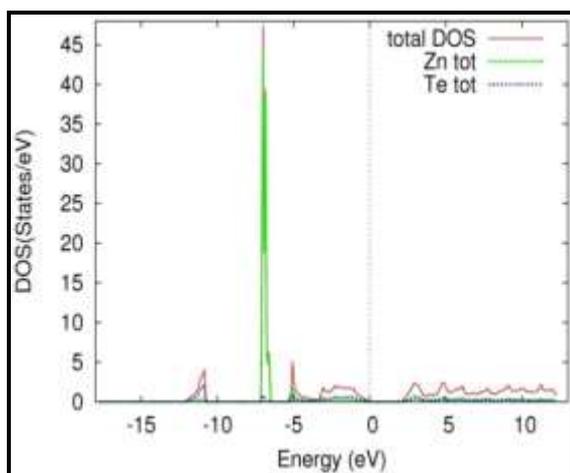
Figure 2c. Shows the Density of States of ZnTe

Less dispersion of these bands results in sharp peaks. There is a wide spread in DOS in the energy range of -5.6 eV and zero energy for these compounds. The peaks in this energy interval arise from the chalcogen p states partially mixed with Zn s states and they contribute to the upper Valence Band. Above the Fermi level, the feature in the DOS originate mainly from the s and p states of Zn partially mixed with little of chalcogen d states. Band width of valence band as determined from the

width of the peaks in DOS dispersion below Fermi level equal to 13.42 eV, 13.13 eV, 12.17 eV for ZnS, ZnSe and ZnTe, respectively. The results showing valence band width minimum for ZnTe, clearly indicate that the wave function for ZnTe is more localized than that for ZnS. This is in consistence with the fact that when the atomic number of the anion increases, a material becomes non-polar covalent with valence band states being more localized.

3.3. Optical properties

The dielectric function $\varepsilon(\omega)$ can describe the interaction of photons with electrons in the form of linear response of the system to electromagnetic radiation [26]. Dielectric function comprises of the imaginary part $\varepsilon_2(\omega)$ and the real part $\varepsilon_1(\omega)$. They are shown in figures 3 & 4. The absorption of ZnX binary compounds are shown in figure 5. Figures 6 and 7 represents the dielectric loss and the reflectivity of ZnO, ZnS, ZnSe and ZnTe. $L(\omega)$ describes the energy-loss of a fast electron traversing in the material [27]. Its highest peak gives rise to plasma frequency ωP. Generally it happens where $\varepsilon_2(\omega)<1$ and $\varepsilon_1(o)$ turns to the zero value [28]. The main peaks in the energy-loss spectra for different chalcogen atom (S, Se, and Te) are located at 12.78, 12.61 and 12.85 eV, respectively. Moreover, the main peaks of $L(\omega)$ start to decrease while the peaks in reflection spectra $R(\omega)$ start to increase. For example, the abrupt reduction of $L(\omega)$ occurs by 55% where the peak of $R(\omega)$ appears at 13.56eV. The reflectivity $R(\omega)$ of ZnX possesses small value approximately in the photon energy range from 0 to 3.1 eV. It demonstrates the transmitting nature of the material for the photon energy <3.1 eV. It is clear from the reflectivity spectrum that ZnS possesses more transmitting nature than ZnTe in the visible range.
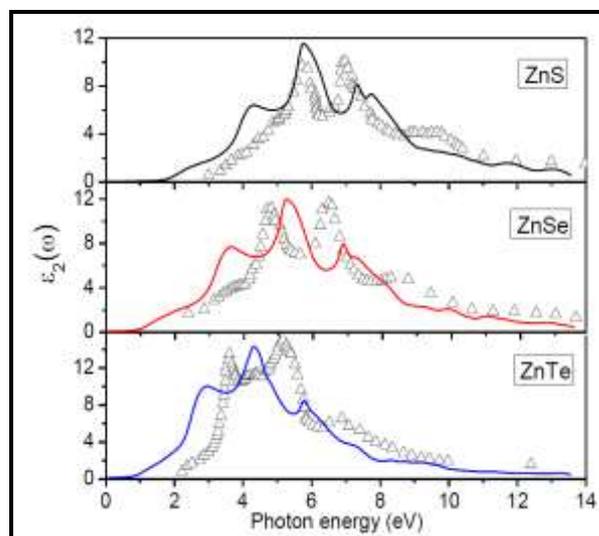
Figure 3. Shows the Imaginary part (ε_2) of ZnX calculated based on DFT
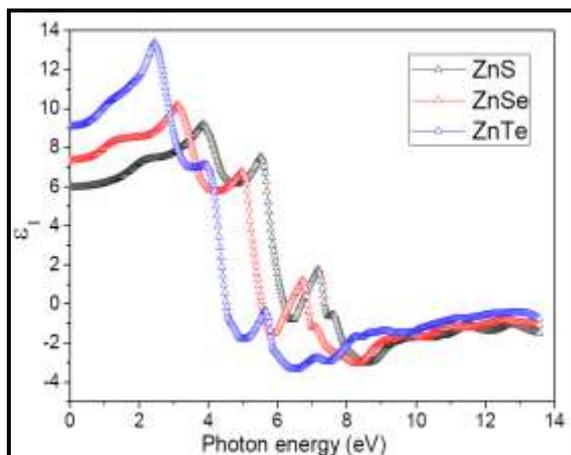
Figure 4. Shows the Imaginary part (ε_1) of ZnX calculated based on ε_2

Figure 5. Shows the Absorption of ZnX
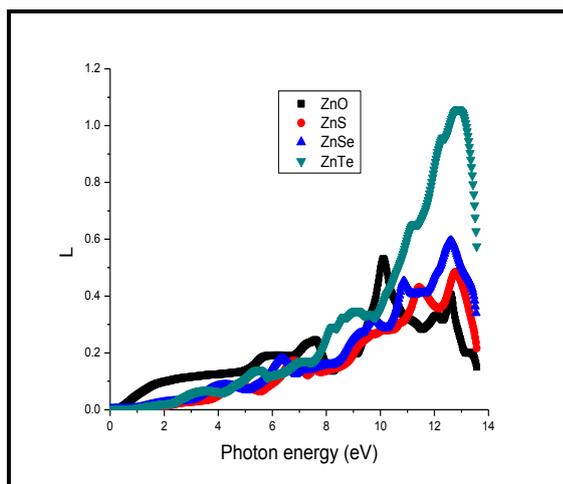
Figure 6. Shows the Dielectric Loss of ZnX

Figure 7. Shows the Reflectivity of ZnX

4. CONCLUSION

This paper reports a systematic study of the structural, electronic, elastic and optical properties of Zn-chalcogenides (ZnTe, ZnSe and ZnTe) have been studied with FP-LAPW + lo method in the framework of density functional theory. The quantities such as elastic constant, band structure, dielectric constants, dielectric loss and refractive index were obtained. The generalized gradient approximation (GGA) was considered for the exchange and correlation effects calculations. The results from FP-LAPW + lo method were found to be in better agreement with the experimental data in comparison to other calculation methods. The elastic constants maintain all conditions to be satisfied for mechanical stability of the compound. The profound ductility in ZnX compound was observed with the increase in chalcogen atomic number. The metallic character in their bonds is well demonstrated from the positive Cauchy pressure (C_{12}–C_{44}) values. The band structure of all Zn-chalcogenides confirms the direct energy gap between the top of the valence band and the bottom of conduction band at ᴦ point. In the linear optical response, the absorption threshold shifts toward lower energy with the increase in chalcogen atomic number. The strong interband transitions between the chalcogen outermost s state and Zn 3d states play the main role in the optical response.

5. REFERENCES

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