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Structural phase transition and optoelectronic properties of ZnS under pressure

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ZnS is a wide band gap semiconductor and widely applied in semiconductor industry. In the present study, first principle calculations are performed to obtain the phase transition pressure and optoelectronic response of ZnS under pressure. Calculated transition pressure is in good agreement with the recent experimental results. ZnS has a direct bandgap in zincblende phase and indirect in rocksalt phase. In both phases the chemical bonding is covalent. Optical properties like dielectric function and frequency dependent reflectivity under pressure are calculated and compared with the previous results.

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1. Introduction

Wide band gap semiconductor materials are very important because of their enormous technological interests. Among the wide band gap semiconductors family, Zinc chalcogenides (ZnS, ZnSe, ZnTe) possesses zincblende (B3) and wurtzite crystal structures at ambient conditions. Special attentions have been given to these materials for their use as a blue lasing material, in fabrication of modulated hetrostructures and in optical waveguides [1]. These materials undergo phase transformations under the effect of pressure.

ZnS is a prototype IIB-IVA wide band gap semiconductor. Naturally as a mineral, it crystallizes in the cubic form called zincblende (ZB) structure also known as sphalerite (B3). This wide band gap semiconductor has recently attracted a lot of interest due to polymorphic structural transformations and the blue wavelength regime. The structural phase transition from its natural ZB phase to rock salt (RS) phase has captivated a great deal of interest for materials scientists. This phase transition can be tempted by the application of pressure [2-7].

From the extrapolation of the Bridgman data [2], the pressure induced phase transition of ZnS from ZB to RS was first reported at 24.5 GPa and then at 18.5 GPa based on the shock wave data of Rice *et al.* [3]. Piermarini and Block [4] used the ruby fluorescence line-shift based on the Decker equation of state for ZnS, they measured that the phase transition pressure of ZnS was 15 GPa. Zhou *et al.* [5] used the X-ray diffraction data and determined the transition pressure equal to 15 GPa. The phase transition pressure of ZnS nanocrystalline from B4 to B3 to B1 structure were found by Pan *et al.* [6] to be 11.5 GPa and 16 GPa respectively using the energy dispersive X-ray diffraction technique. Very recently Jun *et al.* [7] performed in situ high pressure x-ray absorption fine structure measurements on the Zn K-edge in zincblende ZnS up to 31.7 GPa at the room temperature and observed a phase transition from zincblende $F\text{-}43m$ to rocksalt $Fm.3m$ at 16.9 GPa.

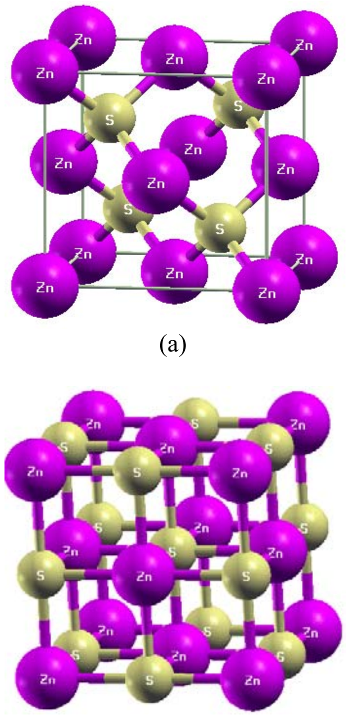
Theoretically, some works have been performed to account the pressure induced phase transition in ZnS from ZB to RS structure. The transformation of ZnS from ZB to RS structure investigated by Jaffe *et al.* [8] using the first principle Hatree-Fock linear combination of atomic-Orbitals (LCAO). The authors sketched the common tangent to the energy-volume curves and predicted that phase transition pressure was 16.1 GPa. Gangadharan *et al.* [9] calculated the structural phase transition pressure to be 15.5 GPa, using the tight binding Muffin-Tin-Orbital (TB-LMTO) method. First principle pseudopotential approach and local density approximation with non-linear core correction methods were used by Nazzal and Qteish [10] and they calculated transition pressure equal to 14.7 GPa. Transition pressure of 14.5 GPa was reported by Miano and Lambrecht [11] using the Troullier-Martins pseudopotential and plane wave basis method. The aim of present study is to report a detailed study of phase transition and opto-electronic properties of ZnS under pressure and to provide theoretical basis to the latest experimental studies on this important compound.

2. Computational details

Present calculations are performed using the full potential linearized augmented plane wave plus local orbitals (FP-LAPW+lo) method [12] based on density functional theory (DFT) as implemented in wien2K package [13], for the volume optimization in the computational investigation of the ground state properties of the material. The exchange-correlation effects are included by generalized gradient schemes of Wu-Cohen (WC) [14], Perdew-Burke-Ernzerh (PBE) [15] and PBEsol [16]. Further modified Becke-Johnson (mBJ) exchange potential is applied to overcome the bandgap underestimation of generalized grad; ient approximations (GGA) [17]. R_{MT}*Kmax (where R_{MT} is the minimum muffin-tin radii and Kmax gives the magnitude of largest K vector in the plane wave basis) is set to 7, Gmax (The potential and the charge density Fourier expansion parameter) is taken to be 12, *lmax* (The valence wave functions inside the atomic muffin-tin-spheres expansion parameter) is 10 and 47 K-points (in the irreducible wedge of the first Brillouin zone (IBZ) has been chosen to obtain self consistent calculations. The self-consistency is achieved up to 0.0001 Ry.

3. Results and discussion

Crystal structure of ZnS in ZB (a) and RS (b) phases are shown in Fig. 1. In the unit cell Zn atom is situated at the (0,0,0) site in both phase, while S Volume atom situated at (0.25,0.25,0.25) site in ZB and (0.5,0.5,0.5) in RS phase. Optimization technique is applied to obtain different structural parameters of ZnS. In the volume optimization process unit cell volume is varied and corresponding variation in the total unit cell energy is calculated. The unit cell volume versus energy data is fitted by the second order Murnaghan's equation of state [18]. The minimum energy is the ground state of the compound. At the ground state, equilibrium lattice constant $a_o\,(A^o)$, bulk moduli B_o (GPa) and its pressure derivative $B_o^{/}$ are calculated and presented in Table 1 along with the available experimental and theoretical data. The analysis of our calculated results reveals good agreement with experimental data. The evaluation of the pressure induced structural phase transition of ZnS from B3 to B1 phase can be observed from the condition of equal enthalpies, where at a certain pressure enthalpy ($H = U + PV$) of the two phases are equal. Using different GGA- schemes, enthalpy of ZnS is calculated in B3 and B1 phases as a function of pressure and is depicted in Fig. 2. Enthalpy difference (ΔH) of B3 and B2 phases is also plotted as a function of pressure and shown in Fig. 3. As thermodynamic requirement, phase transition occurs at certain pressure, where the enthalpies of the two phases become equal i.e. ΔH=0. Enthalpy difference (ΔH) plot as a function of pressure shows that the structural phase transition from B3 to B1 phase in ZnS occurs at 16.05 GPa by Wu-Kohn-GGA, 15.86 GPa by PBE-GGA and 17.82 GPa by PBE-sol-GGA. These results along with the existing experimental and theoretical data are also given in Table 1. Our predicted phase transition pressure is in good agreement with the recent experimental observation [7].



(a)

(b)

Fig. 1: Zinc blende (a) and rock salt (b) crystal structure of ZnS.

Table 1. The calculated equilibrium lattice parameters of ZnS in B3 and B1 phase and under pressure phase transition B3-B1 values along with available experimental and theoretical results.

	This work			Other calculations	Experimental
	Wu- Kohn	PBE	PBE-sol		
ZB structure					
a_o(A^o)	5.39	5.36	5.44	5.58^{a}, 5.409^{c}	5.410^{d}
B_o (GPa)	92.93	83.59	81.30	75.9^{a}, 80.97^{b}, 83.2^{c}	76.9^{d}
$B_o^{/}$	5.72	5.24	9.10	4.7^{a}, 4.43^{c}	4.9^{d}
RS structure					
a_o(A^o)	5.04	5.01	5.11	5.21^{a}, 5.086^{b}, 5.02^{c}	5.21^{e}, 5.13^{f}
B_o (GPa)	100.62	99.48	87.53	83.1^{a}, 95.89^{b}, 104.4^{c}	47.5^{e}, 85.0^{f}
$B_o^{/}$	4.32	4.73	4.3	10.0^{a}, 4.29^{c}	4^{d}
$P_{ZB\rightarrow RS}$ (GPa)	16.05	15.86	17.82	16.1^{a}, 15.5^{b}, 14.7^{c}	14.7–18.1^{c}, 15.0^{g}, 16.0^{h}

^{a}Ref. [9], ^{b}Ref. [10], ^{c}Ref. [11], ^{d}Ref. [19], ^{e}Ref. [20], ^{f}Ref.[12], ^{g}Ref. [6], ^{t}Ref. [7].

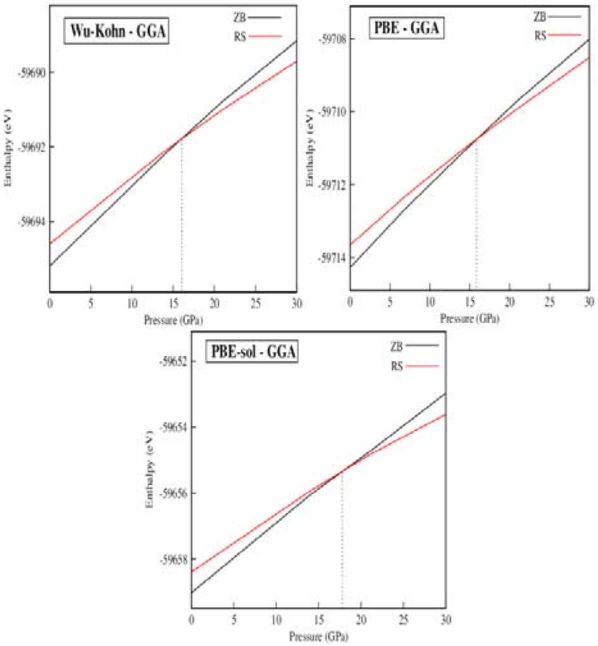


Fig. 2: Enthalpy versus pressure plot of ZnS in B3 and B1 phases.

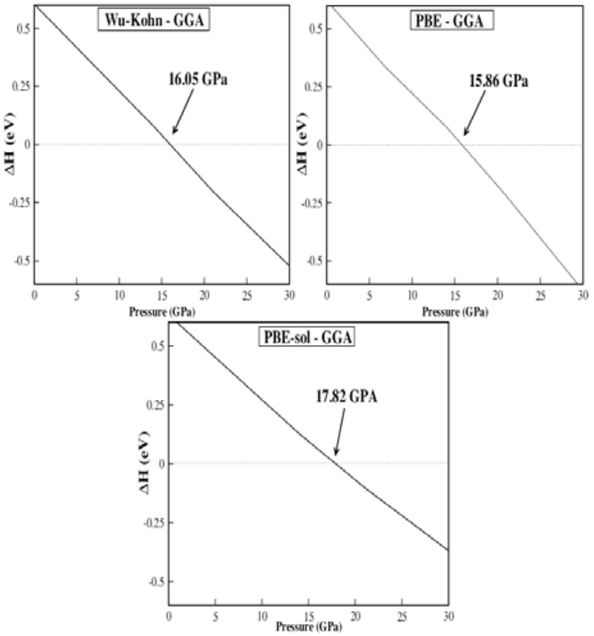


Fig. 3: Plot of enthalpy difference (ΔH) of B3 and B1phases versus pressure for ZnS.

Electronic properties of the compound are described in terms of its band gap and density of states (DOS). The band structure at zero and higher pressures are calculated and shown in Fig. 4 for ZB and RS. Zero pressure band gap of ZnS in ZB-phase is direct at Γ- symmetry point of Brillouin zone with value of 3.86 eV. The bandgap increased with the increase in pressure and at 15 GPa it is 4.2 eV for ZB. In RS-phase band gap is indirect and has value of 1.18 eV at 18 GPa, where valence band maximum (VBM) occurs at L-point and conduction band minimum (CBM) situated at X symmetry point of Brillouin zone. With the increase of pressure above 18 GPa the indirect bandgap decreases and at 30 GPa it is 0.98 eV. Hence ZnS in ZB-structure is a wide band gap semiconductor while zero pressure band gap is in close agreement to the experimental results in Refs. [19, 21] and is improved over the previous theoretical values [22-23].

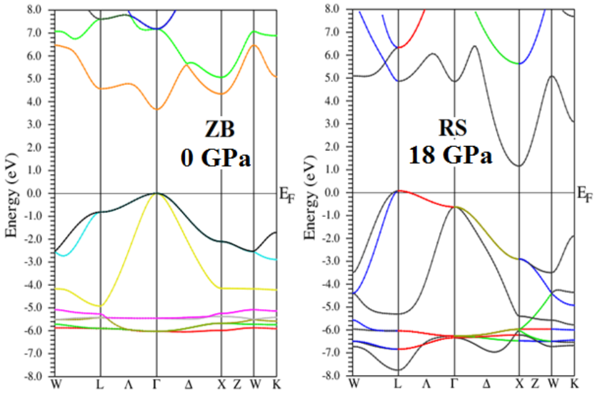


Fig. 4: Band structure for ZnS in ZB-phase (0 GPa) and in RS-phase (18 GPa)

Density of states of ZnS in B3-phase and B1-phase is depicted in Fig. 5. In zero pressure DOS of ZnS in B3 phase, just below the Fermi level (0 eV) S-3p, Zn-3p,3d states form the upper part of the valence band, where leading contribution comes from S-3p state. In the lower part of valence band, again S-3p state dominating with high DOS with reasonable contribution from Zn-4s,3d states. Above the Fermi level, the lower part of the conduction starts at 3.72 eV with the contribution of the mixed s, p and d states of S and Zn ions. DOS for ZnS in RS-structure at 18 GPa reveals that due to structural phase transition, the conduction band squeezing and valence band broadens also another band appears below the valence band. The overall contribution from the various states remains same while the band below the valence band is composed of S-3s state mainly with small contribution from Zn-4s,3d.

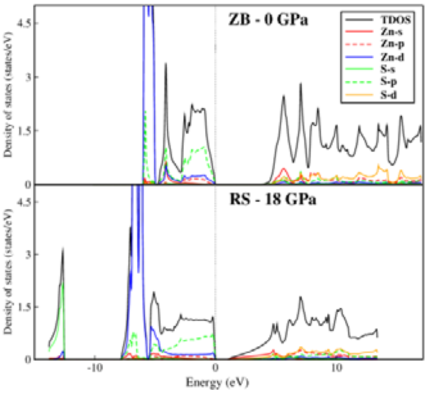


Fig. 5: DOS of ZnS (at 0 GPa) in ZB structure and at 18 GPa in RS structure.

In Fig. 6 the electron charge density in 2-D and 3-D map plotted in (110) plane for ZnS in ZB-structure at zero GPa and RS-structure at 18 GPa. In ZB-phase at zero GPa, strong covalent bonding is seen because of the large sharing of charges among the cation and anion. On structural phase transition from ZB to RS phase, again the strong covalent bonding nature is observed. Electron charge density around cation and anion is again to the same extent as in ZB structure. This strong covalent bonding is because of the pd-hybridization of the states as clear from the DOS in Fig. 5.

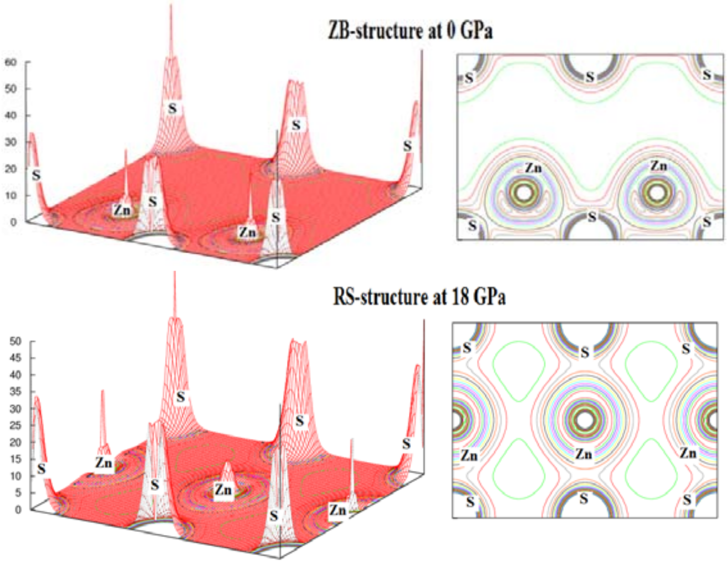


Fig. 6: Electron charge density plot for ZnS in ZB structure at 0 GPa.

Dielectric function can be used to describe completely the optical response of the compound under the applied light power. Dielectric function, $\varepsilon(\omega)$, is a complex quantity with real part, $\varepsilon_1(\omega)$, describe the optical polarizibility and imaginary part, $\varepsilon_2(\omega)$, describe the absorption. The Imaginary part of the dielectric function of ZnS is displayed in Fig. 7(a) at pressure ranging from 0—30 GPa in ZB (0-15 GPa) and RS (18-30 GPa). The analysis of the $\varepsilon_2(\omega)$ plot shows that the first critical point at zero pressure in ZB-structure is at 3.89 eV. This point corresponds to the threshold for the direct optical transition between valence band maximum and conduction band minimum at *Γ*- symmetry point consistent with band structure (shown in Fig. 4). The other small edge at 5.52 eV is due to direct *L-L* optical transition from S-3p and Zn-3d,3p states of the valence band to the unoccupied Zn-4s and S-3p states of the conduction band.

The major peak arises at 6.63 eV is mainly due to the transition of electrons from Zn-3d and S-3p states of valence band to the unoccupied states in the conduction. Following the major peak a small peak is situated at 8.2 eV due to the direct *K-K* optical transition from the VB maximum to the conduction band minimum. Pressure increase upto 15 GPa in the ZB-structure shifted the fundamental absorption edge including the high peaks towards higher energies. This result is consistent with band structure where band gap increases on application of pressure. The $\varepsilon_2(\omega)$ spectra in RS structure at 18 GPa shows that the fundamental absorption edge occurs at 1.18 eV, while at 30 GPa it shifts towards the lower energy due to decrease in the energy bandgap. The main peak occurs at 5.76 eV is mainly due to the optical transition from Zn-3d and S-3p states of valence band to unoccupied Zn-4s state of the conduction band.

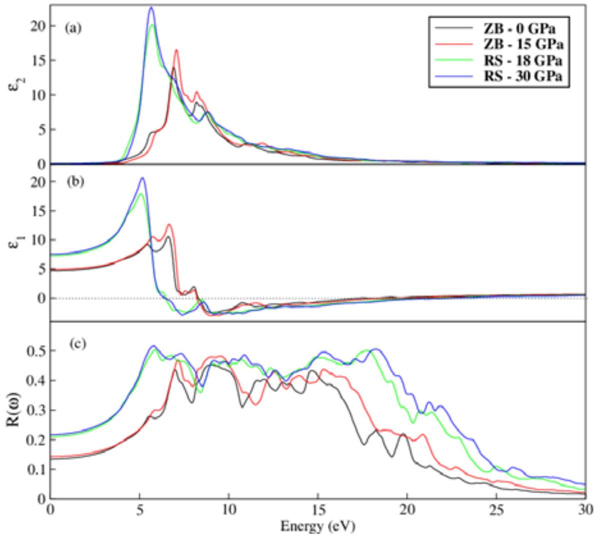


Fig. 7. Imaginary part of dielectric function (a) real part of dielectric function and (b) reflectivity (c) as a function of energy.

The frequency dependant real part of the dielectric function $\varepsilon_1(\omega)$ is displayed in Fig. 7(b). At zero pressure in ZB phase, the static dielectric constant $\varepsilon_1(0)$ is found to be 4.72 which is close to the experimentally found value 5.2 [24] and with improvement over the theoretical calculations 6.18 [25], 5.71 [26] and 5.63 [27]. Its value increases to 7.53 at 30 GPa for RS-structure. In both structures, $\varepsilon_1(\omega)$ increases with the increase in energy and reaches to maximum value and then decreases sharply and eventually goes below zero in various energy intervals as shown in the figure. With the increase in pressure, polarizibility of the compound also increases in both structures.

Reflectivity spectra of ZnS in ZB (0-15 GPa) and RS (18-30 GPa) structures is presented in Fig. 7(c). Static value of reflectivity, R(0), is found to be 3% while increases with the increase in pressure and is 22% at 30 GPa. In ZB structure, high reflecting behavior can be seen from the spectra in the 7-17 eV energy intervals with maximum reflectivity of 45% at zero pressure. With the application of pressure, the high reflection energy range broadened and maximum reflectivity attained up to 52% for RS at 30 GPa. This behavior is in agreement to the spectra of the real part of the complex dielectric function $\varepsilon_1(0)$ where the maximum reflectivity range of the compound under pressure enhances in accordance to the negative value of $\varepsilon_1(\omega)$ [28].

4. Conclusion

In conclusion, first principle calculations have been performed to obtain the phase transition pressure and optoelectronic response of ZnS under pressure by FP-LAPW+lo method. Calculated transition pressures by GGA schemes are in close agreement to the recent experimental results. ZnS has wide direct bandgap in zincblende phase and indirect badgap in rocksalt phase. Also the calculated bandgaps are in better agreement to the experimental results compared to previous calculations. In both phases the chemical bonding is observed to be covalent. Polarizibility and absorption ability of the compound increases with the increase in pressure. ZnS absorbs highly in the ultraviolet (UV) region of the energy spectrum. Reflectivity is noted to be high in UV. These characteristics make the compound attractive for the optoelectronic devices.

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