

## Mechanical and electronic properties of ZnS under pressure

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Received 01.06.2008; published in revised form 01.11.2008

### Properties

#### ABSTRACT

**Purpose:** The wide-gap semiconductor materials are very important for application in the fields of optical device technology. ZnS is wide-gap semiconductor that is attractive material due to the polymorphic structural transformation and it is suitable semiconductor for applications in infrared optics, ultraviolet laser devices, electronic image display, high-density optical memory, solar cell etc. The goal is to evaluate mechanical and electrical properties of ZnS under pressure.

**Design/methodology/approach:** We report ab-initio calculations of lattice constants, bulk modulus and elastic constants of the B1 (rocksalt), B3 (zincblende) and B4 (wurtzite) structures of ZnS. Ab-initio calculations are based on the density functional theory (DFT) within generalized gradient approximation (GGA) for the exchange-correlation potential.

**Findings:** Phase transition pressures from B4 phase to B3 phase, from B3 phase to B1 phase and from B4 phase to B1 are predicted from intersection of the enthalpy-pressure data for the three phases. These results are consistent with the experimental and other theoretical calculations. Mechanical properties of ZnS under high pressure are also calculated. It is seen that the mechanical properties of ZnS under high pressure are quite different from those ambient condition. The band structure, density of states (DOS) and energy gaps are also given for B3 structure of ZnS.

**Research limitations/implications:** The results are compared with the previous theoretical and experimental data.

**Originality/value:** Evaluation of mechanic and electronic properties of ZnS under pressure.

**Keywords:** Semiconductor; Ab initio calculations; Phase transitions; Elastic and electronic properties

### 1. Introduction

Semiconductor materials are very important because of enormous technological interest. ZnS has gained increasing in the wide band gap semiconductor for applications in optoelectronic devices [1]. Elastic properties of solid are important due to fundamental solid-state phenomena such as equation of state, phonon spectra and atomic potentials. Elastic stiffness coefficients

are essential for many applications related to mechanical properties of a solid such as internal strain, thermoelastic stress and load deflection.

Measure of the deformations is depending on elastic stiffness coefficients that is a very important characterization of the crystals under varying pressure [2, 3]. Moreover, The elastic constants of the materials at high pressures are essential in order to predict and understand material response, strength, mechanical

stability and phase transitions. However, only, a few studies have conducted on the mechanical properties of ZnS at elevated pressures, as well as pressure dependence of its elastic constants, so far. The accurate measurement of these quantities is a difficult task due to difficult experimental conditions at high pressure. With the advances in ab initio methods, it is possible to compute a systematic study of the elastic properties as well as electronic and optical properties of materials at elevated pressure conditions.

ZnS crystallizes in the cubic zincblende (B3) and wurtzite (B4) structures at ambient pressure. There is a phase transition from B4 structure to B3 structure and from B3 structure to B1 (rocksalt) structure when the pressure is applied. In the present study, structural properties of ZnS for three phases: B4, B3 and B1 and electronic properties of ZnS for B3 phase are investigated under hydrostatic pressure by using first-principle calculations based on density functional theory (DFT) within generalized gradient approximation (GGA).

The rest of the paper is organized as follows. After a brief introduction in Section 1, the method of calculation is introduced and the computational details are given in Section 2. The simulation results for structural, mechanical properties, transition pressures as well as electronic properties in three structures being considered in this work are presented and discussed in Section 3. We also compare our results with available experimental data and as well as theoretical calculations in Section 3. Finally, the summary of our main results and conclusion is given in Section 4.

## 2. Computational method

The ab-initio method used in this study by means of the Vienna ab-initio simulation package (VASP) [4, 5] and the implemented projector augmented wave pseudo potential formalism (PAW) [6, 7] employing the GGA within DFT [8]. Reduction of the size of the basis set for transition metals and first row elements is a considerable with this method. Because of the PAW potentials larger problems than usual can be treated by VASP. A cut off 350 eV is chosen, which ensures to convergence with respect to basis set for B4, B3 and B1 structures of ZnS. The Monkhorst-pack meshes used for the B3 and B1 structures of ZnS are  $12 \times 12 \times 12$ , whereas for the B4 structure of ZnS they are  $12 \times 12 \times 8$ . Thus these meshes ensure a convergence of total energy to less than  $10^{-5}$  eV/atom. In the structure of B1 for ZnS, the Zn and S atoms are at the positions: (0,0,0) and (1/2,1/2,1/2). For B3 structure of ZnS, the Zn and S atom positions are (0,0,0) and (1/4,1/4,1/4). For B4 structure of ZnS, there are four atoms per hexagonal unit cell where the positions of the atoms Zn and S are (0,0,0), (1/3,2/3,1/2) and (0,0,u), (1/3,2/3,u+1/2), respectively, where u is the dimensionless internal parameter that represents the distance between the Zn plane and its nearest neighbour S plane. Birch-Murnaghan equation of states (EOS) was used to fit total energy as a function of primitive unit cell volume for ZnS. The phase behaviour, structural parameters, bulk modulus, its pressure derivative and the equilibrium lattice parameters have been obtained by fitting Birch-Murnaghan EOS [9].

## 3. Results and discussions

### 3.1. Structural and elastic properties

Total energy versus volume data for the B4, B3 and B1 structures of ZnS is shown in Fig. 1. As shown in the Fig. 1, B4 structure is more stable than the other structures. That is, the energy state of B4 structure is the lowest ones among the other structures showing here. In this case it is most stable structure although a small energy difference can be shown between the B4 and B3 structures.

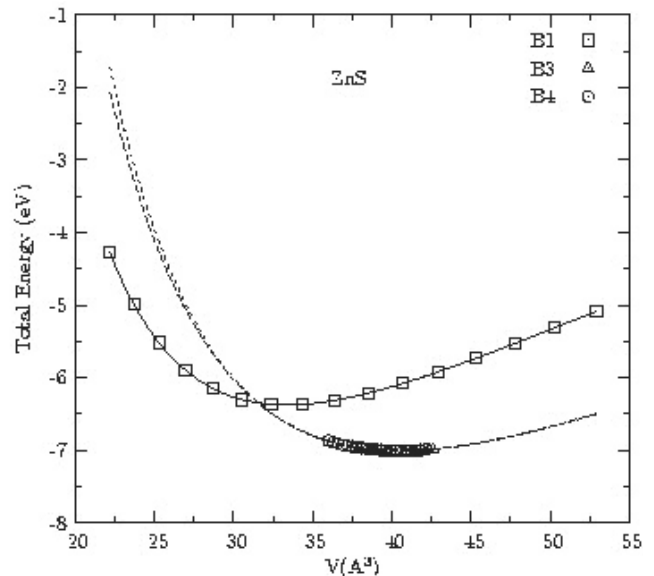


Fig. 1. Total energy as function of primitive unit cell volume for ZnS in the phases of B1, B3 and B4

In order to obtain the equilibrium structural parameters the curves of Fig.1 have been fitted to Murnaghan's EOS. These results are listed in Table 1 and our results for B4, B3 and B1 structures are in good agreement with the other theoretical calculations and experimental values [2, 10, 11, 12, 13]. We have presented the transition pressure from B4 to B1 for the ZnS. It is found that transition pressure of B4→B1 is found as 14.84 GPa from the slope of the common tangent of both enthalpy-pressure (H-P) curves as seen in Fig. 2a. It is estimated that the pressure for transition from B3 to B1 structures is 18.50 GPa from the slope of the common tangent of both H-P curves as done in Fig. 2b.

The enthalpies of both B4 and B1 structures are the same for transition pressure from the usual condition of equal enthalpies. Also B3 and B1 structures are the same at the enthalpies  $H=E+PV$ . The mechanical stability conditions in the cubic structures can be expressed in terms of elastic constants as:  $c_{11}-c_{12}>0$ ,  $c_{44}>0$ ,  $c_{11}+2c_{12}>0$ . We also present lattice parameter, elastic constants, and bulk modulus of ZnS in the B1 and B3 structures at various pressures in the Table 2.

Table 1.

The lattice constant,  $a$  (Å), bulk modulus,  $B_0$  (GPa), and its pressure derivatives,  $B_0'$ , internal parameter,  $u$ , axial ratio,  $c/a$ , elastic constants,  $c_{11}$ ,  $c_{33}$ ,  $c_{44}$ ,  $c_{66}$ ,  $c_{12}$ ,  $c_{13}$ , together with the transition pressures  $P_T$  (GPa)

B4 Structure	This work	Other theoretical calculations	Experiments
$a$	3.852	3.840 <sup>k</sup> , 3.777 <sup>l</sup> , 3.982 <sup>m</sup>	3.811 <sup>n</sup> , 3.823 <sup>o</sup>
$c$	6.313	6.267 <sup>k</sup> , 6.188 <sup>l</sup> , 6.500 <sup>m</sup>	6.234 <sup>n</sup> , 6.261 <sup>o</sup>
$c/a$	1.639	1.632 <sup>k</sup> , 1.638 <sup>l</sup>	1.636 <sup>n</sup> , 1.638 <sup>o</sup>
$u$	0.375	0.375 <sup>k</sup> , 0.375 <sup>l</sup> , 0.377 <sup>m</sup>	0.375 <sup>n</sup>
$B_0$	68.519	68.96 <sup>k</sup>	75.8 <sup>k</sup>
$B_0'$	4.135	4.39 <sup>k</sup>	4.41 <sup>k</sup>
$c_{11}$	115.611	118 <sup>m</sup>	122 <sup>n</sup> , 124.2 <sup>p</sup>
$c_{33}$	132.522	135 <sup>m</sup>	138 <sup>n</sup> , 140.0 <sup>p</sup>
$c_{44}$	27.783	31 <sup>m</sup>	29 <sup>n</sup> , 28.6 <sup>p</sup>
$c_{66}$	30.997		32.0 <sup>p</sup>
$c_{12}$	48.971	52 <sup>m</sup>	60.1 <sup>p</sup>
$c_{13}$	37.101	39 <sup>m</sup>	45.5 <sup>p</sup>
$P_T$ (from B4 to B1)	14.844	17.20 <sup>k</sup>	14.1-14.6 <sup>f</sup> , 16 <sup>k</sup>
$P_T$ (from B4 to B3)	8.75		
B3 Structure			
$a$	5.449 <sup>a</sup>	5.404 <sup>b</sup> , 5.58 <sup>c</sup> , 5.40 <sup>d</sup>	5.410 <sup>h</sup>
$B_0$	69.806 <sup>a</sup>	71.22 <sup>b</sup> , 75.9 <sup>c</sup> , 80.97 <sup>d</sup>	76.9 <sup>h</sup>
$B_0'$	4.413 <sup>a</sup>	4.705 <sup>b</sup> , 4.7 <sup>c</sup> , 4.43 <sup>e</sup>	4.9 <sup>h</sup>
$c_{11}$	96.283 <sup>a</sup>	99.6 <sup>b</sup> , 123.7 <sup>f</sup> , 104.0 <sup>g</sup>	104.0 <sup>i</sup>
$c_{12}$	55.555 <sup>a</sup>	57.0 <sup>b</sup> , 62.1 <sup>f</sup> , 53.55 <sup>g</sup>	65.0 <sup>i</sup>
$c_{44}$	62.497 <sup>a</sup>	50.5 <sup>b</sup> , 59.7 <sup>f</sup> , 50.72 <sup>g</sup>	46.2 <sup>i</sup>
$P_T$	18.50 <sup>a</sup>	17.5 <sup>b</sup> , 16.1 <sup>c</sup> , 15.5 <sup>d</sup>	18.1 <sup>e</sup>
B1 Structure			
$A$	5.107 <sup>a</sup>	5.07 <sup>b</sup> , 5.21 <sup>c</sup> , 5.086 <sup>d</sup>	5.06 <sup>j</sup> , 5.21-5.13 <sup>j</sup>
$B_0$	85.107 <sup>a</sup>	89.54 <sup>b</sup> , 83.1 <sup>c</sup> , 95.89 <sup>d</sup>	103.6 <sup>j</sup> , 47.5-85.0 <sup>j</sup>
$B_0'$	4.510 <sup>a</sup>	4.58 <sup>b</sup> , 10.0 <sup>c</sup> , 4.29 <sup>e</sup>	4.0 <sup>j</sup>
$c_{11}$	133.075 <sup>a</sup>	136.1 <sup>b</sup>	
$c_{12}$	61.124 <sup>a</sup>	65.0 <sup>b</sup>	
$c_{44}$	47.10 <sup>a</sup>	54.1 <sup>b</sup>	

<sup>a</sup>From Ref. [13], <sup>b</sup>From Ref. [2], <sup>c</sup>From Ref. [15], <sup>d</sup>From Ref. [16], <sup>e</sup>From Ref. [17], <sup>f</sup>From Ref. [18], <sup>g</sup>From Ref. [19], <sup>h</sup>From Ref. [20], <sup>i</sup>From Ref. [21], <sup>j</sup>From Ref. [14], <sup>k</sup>From Ref. [10], <sup>l</sup>From Ref. [23], <sup>m</sup>From Ref. [12], <sup>n</sup>From Ref. [24], <sup>o</sup>From Ref. [25], <sup>p</sup>From Ref. [26], <sup>r</sup>From Ref. [11].

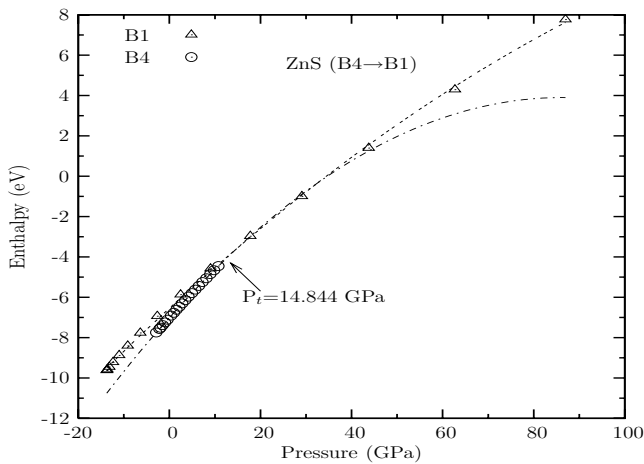


Fig. 2a. Enthalpy as function of pressure for the B4 and B1 phases of ZnS

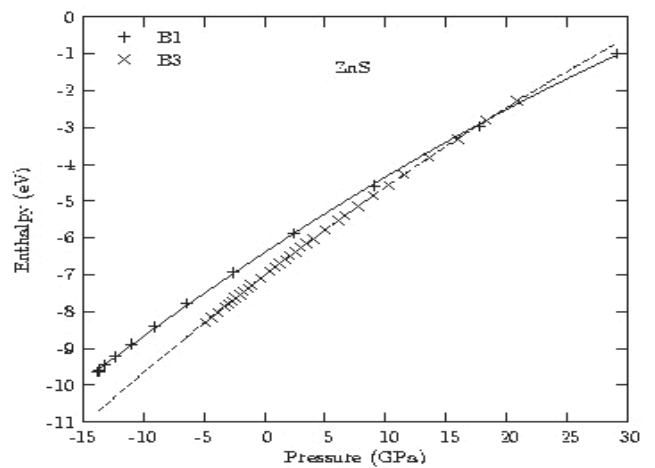


Fig. 2b. Enthalpy as function of pressure for the B3 and B1 phases of ZnS

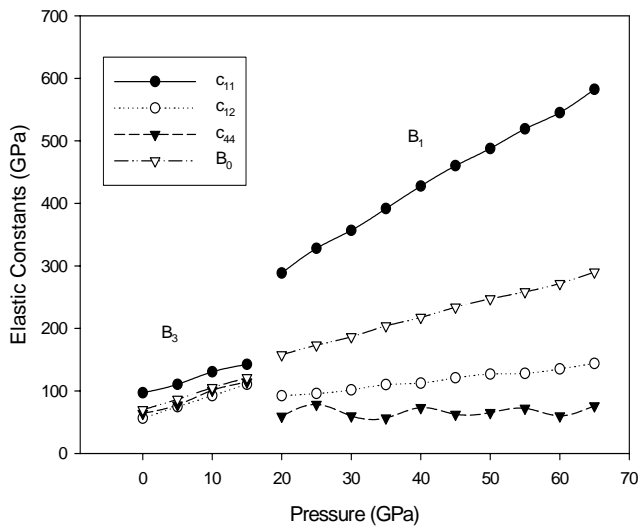


Fig. 3. Pressure dependence of the elastic constants  $c_{ij}$  and the bulk modulus  $B$  of ZnS

The variations of the elastic stiffness coefficients and the bulk modulus  $B$  as a function of pressure for the both B3 and B1

Table 2.

Lattice constant  $a$  (Å), elastic constants  $c_{11}$ ,  $c_{12}$  and  $c_{44}$  (GPa), bulk modulus  $B$  (GPa) calculated at elevated pressures (GPa)

B3 Structure					
P	a	$c_{11}$	$c_{12}$	$c_{44}$	B
0	5.449	97.2	56.4	64.2	70.0
5	5.337	110.6	74.8	77.6	86.7
10	5.246	130.7	92.6	101.1	105.3
15	5.170	142.6	110.7	114.3	121.3
20	5.104	155.9	129.0	121.3	138.0
B1 Structure					
0	5.107	133.1	61.1	47.1	85.1
5	5.018	172.2	71.3	44.6	104.9
10	4.948	214.6	77.8	57.9	123.4
15	4.888	255.8	81.5	65.2	139.6
20	4.837	288.5	92.4	59.6	157.8
25	4.792	328.1	95.9	78.5	173.3
30	4.752	356.8	101.6	60.0	186.6
35	4.715	391.7	110.2	56.8	204.0
40	4.682	427.6	112.6	73.4	217.6
45	4.651	460.2	121.0	62.6	234.0
50	4.623	487.7	126.9	65.3	247.2
55	4.597	519.1	128.2	72.3	258.5
60	4.572	545.0	135.2	59.9	271.8
65	4.549	582.3	144.0	76.1	290.1

phases of ZnS are shown in Fig. 3. The elastic stiffness coefficients and bulk modulus increase as the pressure is applied to material for the structures of B1 and B3 except for  $c_{44}$  of the B1. As shown in the Fig. 3. There is a linear dependence between the elastic constants and pressure except for  $c_{44}$  of the B1.

### 3.2. Electronic properties

The structure of B3 phase of ZnS is optimized at the pressure of 0 GPa. Fig. 4 shows the calculated band structure at equilibrium volume for B3 phase of ZnS. In all cases, the maximum valance band and minimum conduction band occur at the  $\Gamma$  point. Thus, the energy gap is difference between the top of the valance band and the bottom of conduction band at  $\Gamma$  point. Imai et al. [27] calculated the band gap value as 2.2 eV by using CASTEP code. Laihia et al. [28], using x-ray diffraction data, reported it as 2.0 eV. We have also found that the band gap is 2.016 eV at  $\Gamma$  point. It is seen that our result of band gap for B3 structure shows errors of 0.8%, 9.9% when it is compared to the experimental and theoretical results, respectively.

Fig. 5 shows the total DOS and Zn, 4s, 4p, 3d and S 4s, 3p partial DOS of ZnS in B3 structure.

The overall band profiles are in fairly good agreement with previous theoretical and experimental results [26, 27].

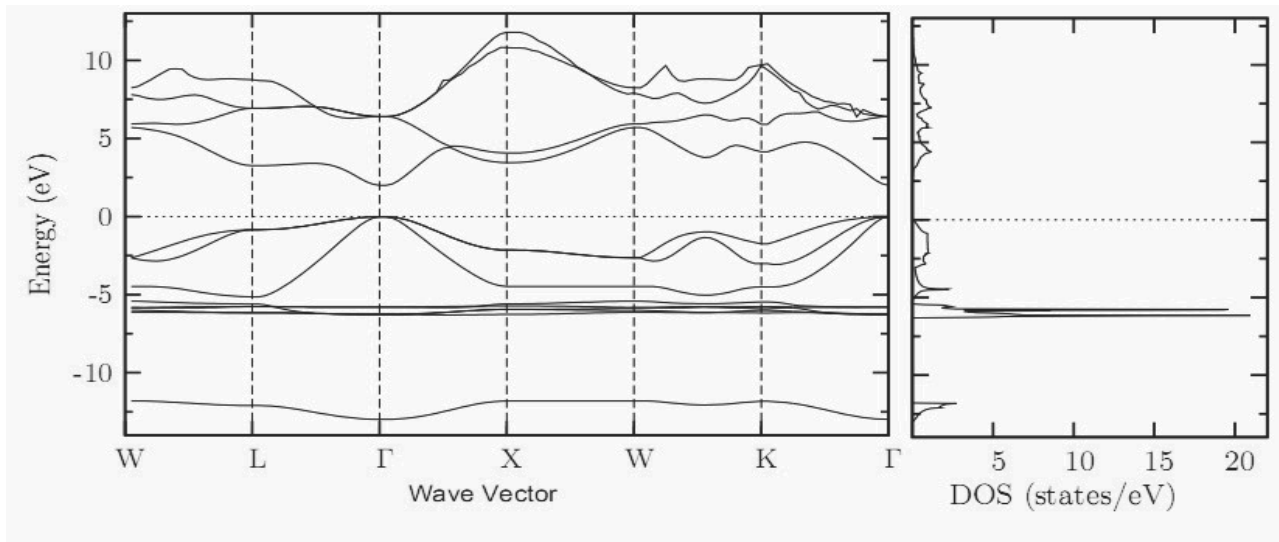


Fig. 4. Left panel is related to the band structures and right one is the total densities of states of ZnS in B3 structure

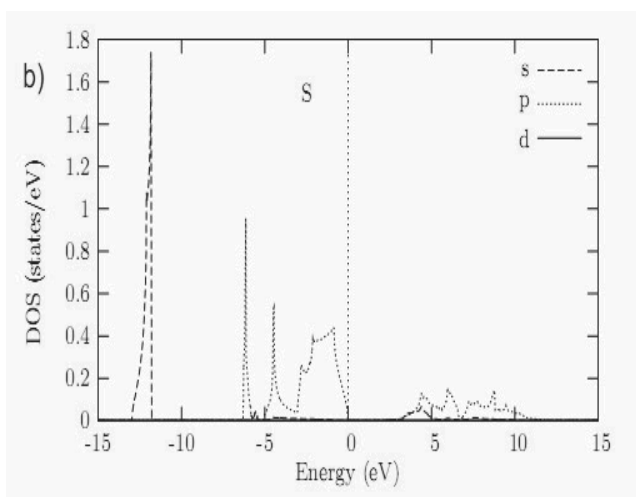
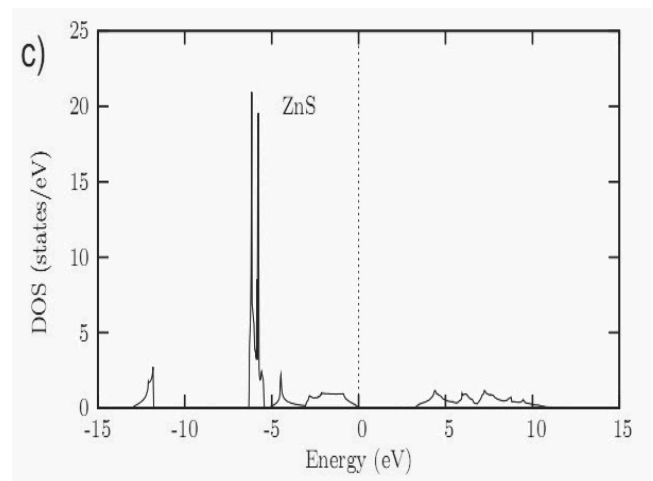
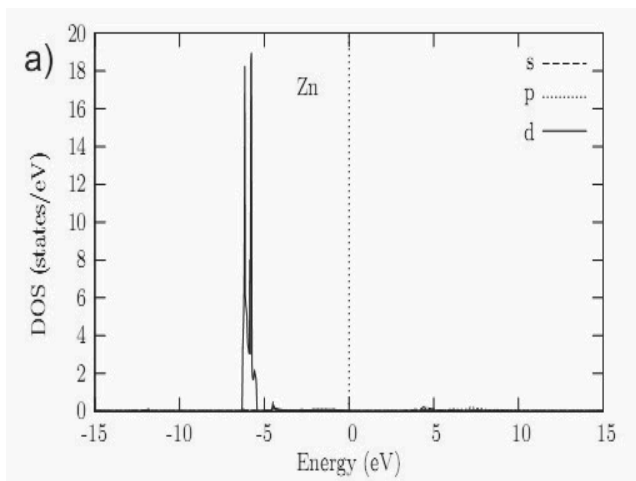


Fig. 5. a. Zn 4s, 4p, 3d partial DOS; b. S 4s, 3p partial DOS; c. total DOS of ZnS in B3 structure

## 4. Conclusions

We have presented an ab-initio study of the mechanic and electronic properties of ZnS using the density functional theory with GGA. It is found that the transition pressures of the B4→B1, B4→B3 and B3→B1 structures are 14.84 GPa, 8.75 GPa and 18.50 GPa, respectively. Our results for the band structure and DOS show that these compounds have similar structures with direct energy band gap. The numerically calculated values showed generally reasonable agreement with the available experimental and other calculations.

## Acknowledgements

Authors would like to thank the following institutions and agencies in carrying out this work. Computations are carried out on TUBITAK-ULAKBIM clusters. Some parts of the calculations are fulfilled by using the opportunity of project in the Department of Physics supported by Pamukkale University (BAP Project No: 2006FEF019).

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