A study on thermochemical properties of ZnS Nanomaterial:A computational Approach

T.Mathavan[1*], Anitta Varghese[1], G.Vanitha Kumari[2], M.A Jothirajan[2], A.Milton Franklin Beniel[1], Demeter Tzeli[3], S.Umapathy[4]
[1] Department of Physics, N.M.S.S.Vellaichamy Nadar College, Nagamalai, Madurai-625019, Tamilnadu, India
[2] Department of Physics, Arul Anandar College, Karumathur, Madurai-625514, Tamilnadu, India
[3] Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens 116 35, Greece
[4] School of Physics, Madurai Kamaraj University, Madurai-625021, Tamilnadu, India
[*] Email: tjmathavan@yahoo.co.in

Abstract— We report the electronic and thermochemical properties of semiconductor ZnS at various temperature and pressure using density functional theory(DFT), in conjunction with the 6-311+G(d) basis sets. ZnS subjected to electronic calculations in order to calculets its bond length, Mulliken atomic charges, HOMO-LUMO energy, vibrational spectral analysis of FT-IR and Raman. Thermochemical parameters such as thermal energy, thermal correction to enthalpy (ΔH) and thermal correction to Gibbs free energy (ΔG), constant volume molar heat capacity(C_v) and entropy(S) were calculated and their results were analysed and interpreted. The results obtained with DFT method give new insight of the ZnS semiconductor material. It was found that for higher temperature the stability of the species high whereas for higher pressure the stability was found to be reducing.

Index Terms— Zinc Sulfide, density functional theory(DFT), HOMO-LUMO, FT-IR, Raman, thermal correction to enthalpy(ΔH), thermal correction to Gibbs free energy(ΔG), constant volume molar heat capacity(C_v) and entropy(S).

1 INTRODUCTION

ZINC Sulfide is an inorganic component with the chemical formula of ZnS. In the series of II-VI compounds, the zinc sulfide which posses wide band gap 3.65eV have drawn get attention for their application in the fabrication of optoelectronic devices such as blue, or UV light emitting diodes, emissive flat screens, and laser diode [1-5].. ZnS is an important semiconductor compound of the group with a wide band gap at room temperature and relatively large exciton binding energy approximately 40meV and has been exensively investigated. Several ZnS nanostructures including nano wires, nano belts, nanoribbon, and nanocables have been successfully synthesized using a variety of methods such as thermal evaporation, etc. [6-10]. ZnS nanowires have attracted much research attention because they promise to open huge potential applications for optoelectronics and interdisciplinary utilities such as nano LED, nano FET and laser that can operate at still lacking. In the present study, the structure, the thermal and the electronic properties of ZnS have been investigated at various temperatures and pressures. All calculations are done by using B3LYP/6-311G(d) basis set level.

2 Computational Procedure

The geometryical structure is fully optimized using the hybrid gradient-corrected functional (B3YLP) within density functional theory frame in the Gaussian-09 code. The optimization are done by using B3LYP/6-311+G(d) [9] basis set level and the job unit time is 16 seconds. Bond length, Mulliken atomic charge, dipole moment, IR spectrum, thermal correction to Gibbs free energy, thermal correction to enthalpy, thermal correction to energy, entropy, constant volume molar heat capacity have been determined and analysed via B3LYP/6-311G(d) method [11-12]. The theoretical thermodynamic quantities are derived from the enthalpy and entropy values. It has been shown that the B3LYP calculation of the entropy for a series of diatomic and polyatomic molecules is in excellent agreement with available experimental values [13]. All computational works have been carried out with the Gaussian09 package [14].

3 Results and Discussion

3.1 Stability of structure

The optimized molecular structure of ZnS is shown in Fig. 1. The global minimum energy obtained by the DFT structure is -2177.4683 Hatrees.

Fig: 1 Optimized structure of ZnS

The optimized bond length of the ZnS molecule is 2.174 Å with respect to the electronic energy or the electronic energy corrected for the zero point energy. The optimized bond lengths with respect to electronic +thermal free enthalpies and electronic +thermal free energies for different temperatures are shown in Table 1. We observe that the geometry optimization with respect to the electronic +thermal free energies leads to enlogated bond comparing to the length obtained via the geometry optiomization with respect to the electronic +thermal free enthalpies. While, the optimized bond length with respect to electronic +thermal free enthalpies remains

almost the same as the temperature is increased, the optimized value with respect the electronic +thermal free energies is increased, as it is expected.

The large dipole moment is observed of 7.25 Debye and a positive charge of Zn of 0.75 e^- is calculated[15].

TABLE 1

Bond length in Åof the ZnS for various temperature at the B3LYP/6-311+G(d) level of theory.

Temperature (K)	Bond length[a] (Å)	Bond length[b] (Å)
273	2.1764	2.1828
373	2.1757	2.1854
473	2.1754	2.1883
573	2.1750	2.1911
673	2.1749	2.1939
773	2.1747	2.1973

[a] Geometry optimization with respect to the electronic +thermal free enthalpies

[b] Geometry optimization and electronic +thermal free energies

TABLE 2

The thermal correction to Gibbs free energy, thermal correction to energy, thermal Correction to enthalpy of ZnS at the B3LYP/6-311+G(d) level of theory.

Temperature K	273	373	473	573	673	773
Thermal correction to Gibbs free energy (KJ/Mol) x10^{-2}	-2.3	-2.9	-3.9	-4.9	-5.9	-6.9
Thermal correction to enthalpy (KJ/Mol)	4.5 x10^{-3}	5.5 x10^{-3}	6.9 x10^{-3}	8.3 x10^{-3}	9.7 x10^{-3}	11 x10^{-2}

The thermal correction to Gibbs free energy, thermal correction to enthalpy, thermal correction to energy and the entropy of the ZnS species with respect to temperature are shown in Figs. 2-5.

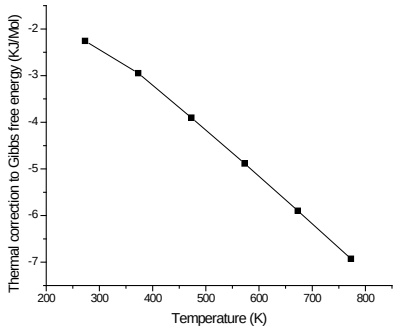

Fig. 2 Thermal correction to Gibbs free energy

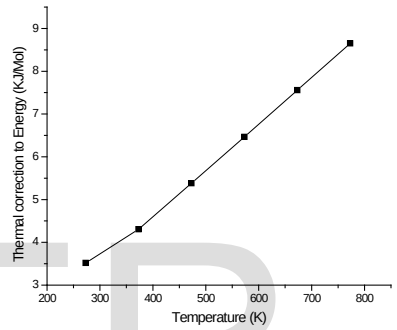

Fig.3 Thermal correction to Energy

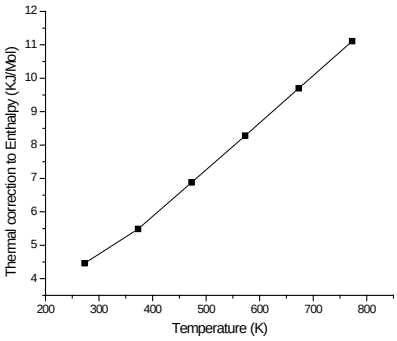

Fig.4 Thermal correction to Enthalpy

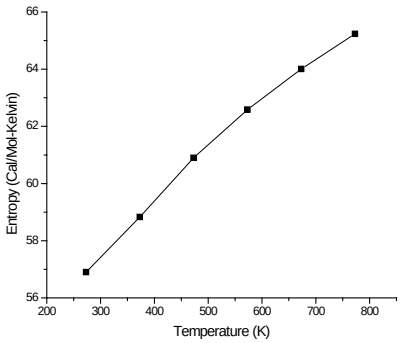

Fig. 5 Thermal correction to Entropy

The Gibbs free energy is found to decrease with increase in temperature, see Fig. 2. The thermal correction to enthalpy is increased positively indicating endothermic reaction, see Fig. 3. The calculated values of the constant value heat capacity and entropy with temperature are reported in Table 3. The entropy of the system varied when increasing temperture. Increasing value of entropy indicates the disorder of the title compound increased[11].

TABLE 3
Variation of constant value heat capacity and entropy with temperature of the ZnS molecule at the B3LYP/6-311+G(d) level of theory.

Temperature K	**273**	**373**	**473**	**573**	**673**	**773**
$C_{v(Cal/Mol-Kelvin)}$	**6.27**	**6.54**	**6.68**	**6.76**	**6.81**	**6.85**
$S_{tot(Cal/Mol-Kelvin)}$	**57**	**59**	**61**	**63**	**64**	**65**

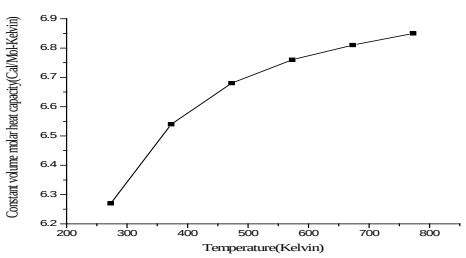

Fig. 6 Thermal correction to Entropy

3.2 Vibrational spectral analysis

The present calculations predict an IR band identified at 349(cm^{-1}) which correspond to the bond stretch. The Raman intensity identified at 16.30(cm^{-1}) and HOMO-LUMO identified at 1.9eV[2,11]. The IR and the Raman spectra are depicted

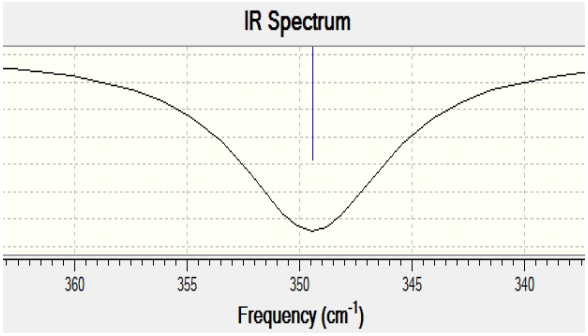

Fig. 7. IR spectrum of optimized structure of ZnS

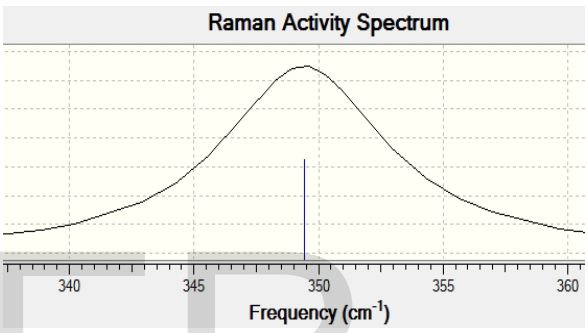

Fig.8. Raman spectrum of optimized structure of ZnS

3.3 Thermal correction to Gibbs free energy (ΔG) and entropy(S) values of ZnS at various pressure

Thermal correction to Gibbs free energy and entropy values of ZnS at various pressures (atm) are listed in Table 4. Thermal correction to Gibbs free energy values for ZnS were plotted against the pressure in Fig. 9 negatively increasing values of Gibbs free energy indicates reducing stability of structure when inceasing the pressure. The entropy values of ZnS were plotted against the pressure in Fig. 10. Entropy values of ZnS decresing the pressure which can be attributed to reducing disorder of chemical compounds[2,14-16].

TABLE 4
Variation of Thermal correction to Gibbs free energy and entropy values of ZnS at various pressures (atm) at the B3LYP/6-311+G(d) level of theory.

Pressure (atm)	ΔG(x10^{-2}) (KJ/Mol)	S (Cal/ Mol-Kelvin)
10	-2.039	52.323
20	-1.974	50.946
30	-1.936	50.140
40	-1.908	49.568
50	-1.887	49.125
60	-1.870	48.762
70	-1.856	48.456
80	-1.843	48.191
90	-1.832	47.957
100	-1.822	47.747

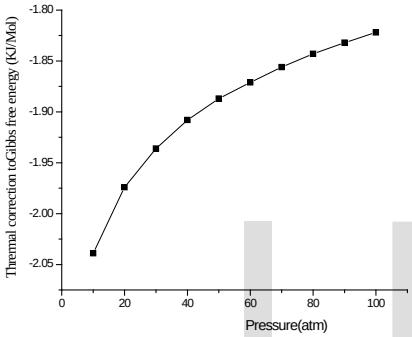

Fig.9. Variation of thermal correction to Gibbs free energy as a function of Pressure

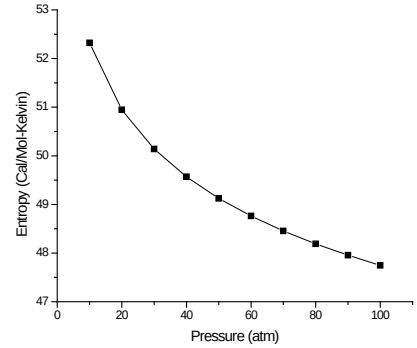

Fig.10. Variation of Entropy as a function of Pressure

4 Conclusion

The ZnS nanomaterial is an excellent semiconductor with a high thermal stability. The thermochemical properties of ZnS were examined theorectically. The optimized geometry parameters were calculated by using B3LYP/6-311+G(d) at Gaussian-09 package. Bond length, Mulliken atomic charge, dipole moment, IR spectrum, thermal correction to Gibbs free energy, thermal correction to enthalpy, thermal correction to energy, entropy, constant volume molar heat capacity have been determined and analysed at B3LYP/6-311+G(d) basis set. Decreasing of Gibbs free energy indicate the ZnS is having the high thermal stability and indicated that the system has a high thermal resistivity. Thermal correction to Gibbs free energy and entropy values were calculated for various pressures.The thermal correction to Gibbs free energy is negatively increases as a function of pressure which indicates the reducing stability of both chemical compounds.

Acknowledgment

One of the author T.Mathavan, thank the managemeasnt and Department of Physics, NMSSVN College to carry out this work.

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