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STRUCTURAL OPTIMIZATION, ELECTRONIC BAND STRUCTURE, MECHANICAL AND THERMODYNAMICS PROPERTIES OF LEAD SULPHIDE (PbS)

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Abstract

We calculated the structural, electronic, mechanical and thermal properties of Lead Sulphide (PbS) semiconducting using Quantum ESPRESSO, an open source first principles code based on density-functional theory, plane waves, and pseudopotentials. Structural parameter results (equilibrium lattice parameters, bulk modulus and its derivative pressure) have been reported. The underestimated band gap is obtained along with higher state density and energy bands around the fermi level. Elastic properties of the rock-salt structure of PbS, such as $C_{11}, C_{12}, and\ C_{44}$, shear modulus (G), Young's modulus (E), and Poisson's ratio (σ) were investigated. The thermodynamic parameters are also present. The results are in good agreement with the available experimental and other theoretical results.

1.0 Introduction

Computational materials science is an emerging field of physics of condensed matter. The methods have now entered the research level. Without the experimental data details, the physical properties of a material can be calculated [1].Material science has gained significant interest as it fills the gap between bulk and atoms or molecules, thus enhancing our understanding of the fundamental properties that provide new physical effects [2].

It is reasonable that there is no question that, beyond anything ever thought, semiconductors have changed the world. People probably just had to communicate and process data[3]. In 1874, IV-VI semiconductors were started to be utilized in solid state electronic devices after Ferdinand Braun's report on electrical rectification by PbS [4]. The IV-VI semiconductors consist of binary compounds PbS, PbSe, and PbTe (lead chalcogenide) which have been extensively studied by experiments over the past several decades due to their potential applications as thermoelectric energy converters and electronic devices[5].

At normal temperature and pressure, the rock-salt structure of Lead Sulphide (PbS) is a narrow gap semi-conducting compound of IV-VI. Its band gap is direct and equal to 0.45 eV at room temperature exhibiting outstanding optical and electrical transport properties [6]. PbS is a thermoelectric material with a wide range of heating and cooling applications and power generation applications with many attractive features such as low noise and vibration, no harmful emissions and high reliability. [7].

2.0 Methodology

Due to no restrictions in these techniques, computer techniques have many advantages in material science. It is easy to model all types of materials using computational methods. This work is done by using the computational suite Quantum ESPRESSO (QE) with the first principle pseudopotential Density Functional Theory approach. Quantum ESPRESSO is an interactive suite of open-source computer codes for material quantity simulation using state-of - the-art electronic structure techniques based on density-functional theory, density-functional perturbation theory and multi-body disturbance theory within the pseudopotential and projection-augmented-wave approaches of the plane wave. DFT is typically used to analyze materials ' electronic and mechanical properties, as well as to predict the chemical, optical and magnetic properties of materials such as metals, semi-metals, semiconductors and insulators.The density-functional perturbation theory (DFPT) used in the QE kit is to measure energy derivatives at any arbitrary wavelength, provide dispersions of phonons, interactions between electron-phonons and phonons-phonon, and static response functions. [8].

3.0 Results and Discussion

3.1 Structural Properties

A self-consistent field calculation (scf) was performed to evaluate basic parameters such as kinetic energy cut-off for the base of the plane wave and k-points grid by independently measuring the convergence of total energy with these parameters and calculating the lattice parameter by minimizing energy. The lattice parameter was varied with 0.1 Bohr atomic unit increment (0.052917 Å).

The calculated structural properties of the studied material are lattice constant a (Å), Bulk modulus B (GPa), pressure

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derivative of the bulk modulus B'$_0$, and unit cell energy E_0 as shown in Table 1.The Birch-Murnaghan's [9] equation of state is used to minimize the total energy with respect to unit cell volume which is given as

$$E(V) = E_o + \frac{9V_oB_o}{16}\left\{\left[\left(\frac{V_o}{V}\right)^{\frac{2}{3}} - 1\right]^3 B'_o + \left[\left(\frac{V_o}{V}\right)^{\frac{2}{3}} - 1\right]^2 \left[6 - 4\left(\frac{V_o}{V}\right)^{\frac{2}{3}}\right]\right\} \quad (1)$$

Here, $E(V)$ represents the ground state energy with the cell volume V, V_0 is the reference volume, B_0 is the bulk modulus and B_0' is its pressure derivative at$P = 0$.

The structure of the binary compound PbS is a rock-salt structure which represents a face centered cubic. The structure of PbS is shown in Figure 1. Plots of total energy as a function of volume of PbS is shown in Figure 2.

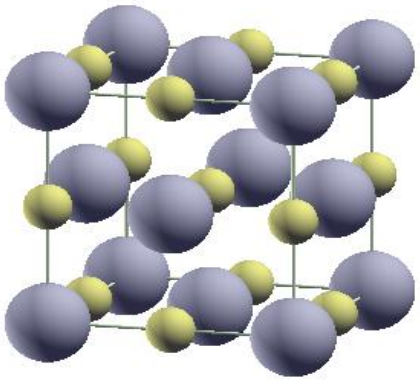

Figure 1: Structure of PbS

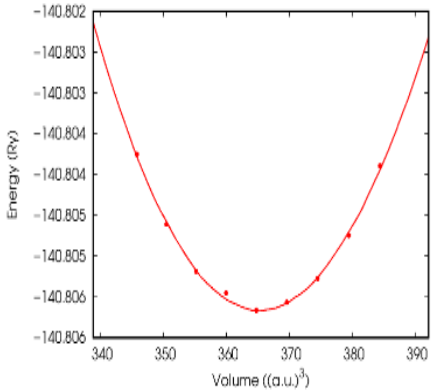

Figure 2: Plot of energy as a function of volume

Table 1: Calculated structural parameters

	a (Å)	B(Gpa)	B_0'	E_0
PbS				
This work	6.002	52.9	4.61	-140.81
Experiment	5.950[a]	52.9[b]	-	-
Others	6.012[c]	52.1[c]	4.10[d]	-

[a]Ref [10]
[b]Ref [11]
[c]Ref [12]
[d]Ref [13]
]

3.2 Electronic Properties

We also study the band structure which gives useful information about the structure of materials.

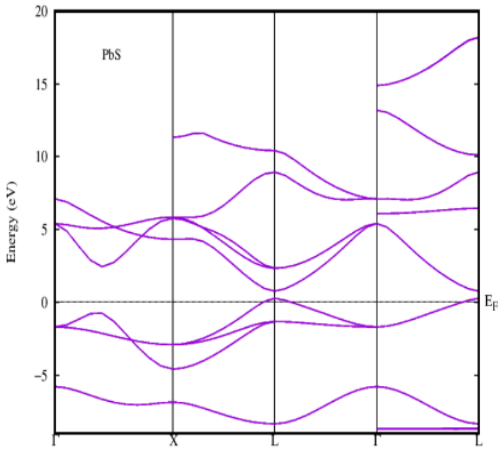

Figure 3: Electronic band structure of PbS. The zero energy is set to be Fermi level.

The band structure of PbS is shown in Figure 3 which is in rock salt phase. From the figure the minimum of conduction band (CB) and maximum of the valence band (VB) are at L-symmetry point having a direct band gap of 0.4924eV.

Table 2: The calculated and experimental energy gaps (in eV) at L-symmetry point for PbS.

	Energy Band gaps (eV)
PbS	
This work	0.49
Experiment	0.42[d]
Others	0.28[c]

[c]**Ref [12]**
[d]**Ref [13]**

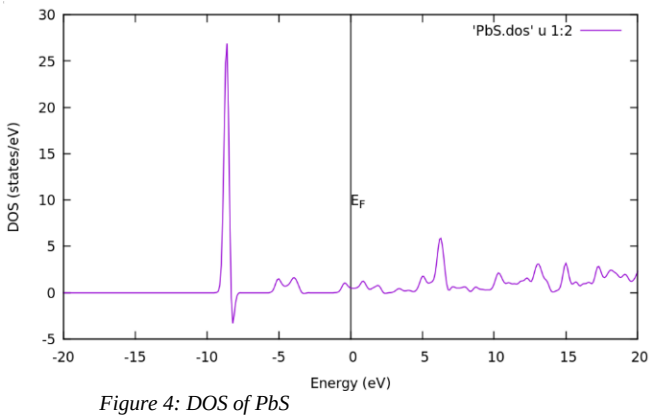

Figure 4: DOS of PbS

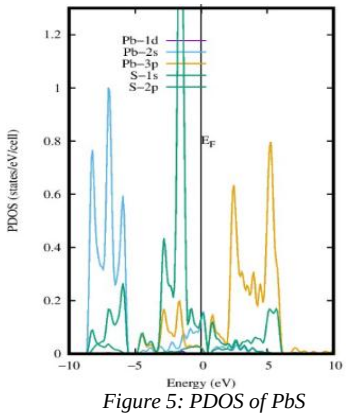

Figure 5: PDOS of PbS

Density of states (DOS) describe the number of states of a system per unit interval of energy which are occupied by the electrons. The study of band structure requires the knowledge of electron density of states. Moreover, the density of states provides numerical information on the states that are available at each energy level. The DOS of PbS is shown in Figure 4. The results of partial densities of states (PDOS) of PbS helps to further elaborate the nature of band gap as shown in Figure 5. The partial density of states gives information about the origin of bands. In Figure 5, left side from zero energy point indicates valance band whereas right side of zero indicates conduction band. The valence band is formed by 2p-orbital of S with slight contribution of 2s-orbital of Pb whereas the conduction band is formed by 3p-orbital of Pb with smaller contribution of 1s-orbital of S.

3.3 Mechanical Properties

The elastic constants of solids provide a relation between the mechanical and dynamic behavior of crystals and provide valuable information about the nature of the forces in solids. [14]. The elastic constants, bulk modulus B, shear modulus G, Young's modulus E, and Poisson ratio *n*, have been calculated. AlAs and PbS have three distinct elastic constants in the cubic structures; C_{11}, C_{12}, and C_{44}[15]. A minimum square fit solves this set of the three linear equations. Using the calculated elastic constants, the code calculates other elastic moduli such as the Reuss-Voigt-Hill bulk, shear, Young modulus, Poisson's ratio.
The calculated values of the bulk modulus from the elastic constants is given by

$$B = \frac{(C_{11}-2C_{12})}{3} \quad (2)$$

Using the data in Table 3, one can show that the traditional mechanical stability conditions on the elastic constants in cubic crystals, i.e.

Table 3: Calculated elastic parameters of PbS. The bulk modulus (B), shear modulus (G), Young's modulus (E) and elastic constant $C_{ij}$are in the unit of GPa.

	Elastic Constant			Independent Elastic constant			Poisson's Ratio (σ)
	B (GPa)	**G (GPa)**	**E (GPa)**	**C_{11} (GPa)**	**C_{12} (GPa)**	**C_{44} (GPa)**	
PbS	52.55	29.10	73.55	124.12	16.76	18.83	0.26359
Experiment	55.7[g]	-	-	135.1[g]	16.9[g]	20.4[g]	-

[g]**Ref [5]**

$C_{11} - C_{12} > 0$,$C_{11} + 2C_{12} > 0$, $C_{11} > 0$, and $C_{44} > 0$are well satisfied for PbS structure. Also the calculated elastic moduli satisfy the cubic stability condition of the material under study i.e. $C_{12} < B < C_{11}$. Poisson's ratio,σ is a measure of the Poisson effect, the phenomenon in which a material tends to expand (compress) in directions perpendicular to the direction of compression (expansion). The defined numerical limits for Poisson's ratio is$-1.0 \leq n \leq 0.5$, for ionic materials a typical value of σ is 0.25. The Poisson's ratio is also a measure of the ductility-brittleness of materials. If $\sigma \leq 0.33$, the material is brittle, otherwise it is ductile. From Table 3, the calculated value of σ lie below the critical value (0.33) which means that PbS is brittle at ambient conditions. To determine the ductile-brittle nature, the empirical formula $\frac{B}{G}$ which 1.75 is

empirically a critical value that separates ductile and brittle response of materials. If $\frac{B}{G}$ <1.75 the material behaves in a brittle manner and if $\frac{B}{G}$ > 1.75 the material behaves in a ductile manner. PbS B to G ratio was calculated to be 1.81 indicating a brittle nature.

3.4 Thermodynamic Properties

Thermal parameters; heat capacity at constant volume, sound velocity and Debye temperature have been determined as shown in Table 4. The sound velocity and Debye temperature are two fundamental parameters for evaluating the chemical bonding characteristics and thermal properties of materials. Plot of heat capacity as a function of temperature is given in Figure 6.

Table 4: Thermodynamic Parameters

	Soundvelocity(m/s)	Debye Temperature, θ_D (K)	Heat Capacity C_v (J/N mol)
PbS	**2152.698**	**213.494**	**48.7469**

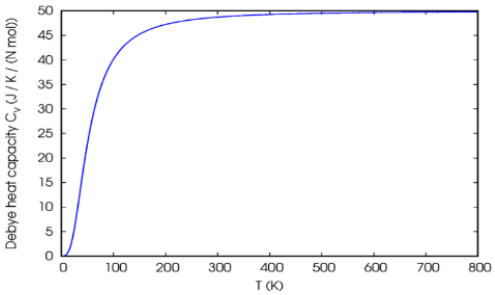

Figure 6: Debye heat capacity C_v*(J/K/ (N mol))* *with temperature variation (K) for PbS.*

4.0 Conclusion

In this present work, we report a systematic study of structural, electronic structures, lattice dynamics, mechanical and thermodynamic properties of PbS. We calculate the structural parameters, electronic band structure along with energy band gap, and partial density of state, elastic moduli. Also, the heat capacity, sound velocity and Debye temperature have been calculated. The obtained results are in god agreement with experiment and other data except for the thermal parameters which was not compared with experiment or other works.

References

[1] Asghar, K.M., Shah, Z.A., Khan,J., Arafat, Y., Hayat, S, *et al*., (2017):Principle Investigation of Structural, Electronics and Chemical Properties of Sn Doped PbX `(X=S, Se, Te). Journal of Theoretical and Computational Science 4:159.

[2] Elfurawi, U., (2012). Optical and electronic properties of PbS colloidal nanocrystals. Ph.D thesis, University of Nottingham.

[3] Lidia, L., and Andrzej, J., (2012). History of Semiconductor, Journal of Telecommunication and Information Technology. 6(11)

[4] Braun, F., (1874). On current Flow through Metallic Sulfides. Annalen der Physik und Chemie 153:556.

[5] Yi, Z., Xuezhi, K., Changfeng, C., Yang, J., and Kent, P., (2009); Thermodynamic properties of PbTe, PbSe and PbS: First-principles study. The American Physical Society.

[6] Qadri, S.B., Singh, A., and Yousuf, M.., (2003). Structural stability of PbS films as a function of temperature. Thin Solid Films 431:506-510.

[7] Venkatasubramamian, E, Siivola, E., Colpius, T., and O'Quinn, B.,(2001). Nature (London). 413:597.

[8] Giannozzi, P., Baroni, S., Bonini, N., Calandra, M.., *et al.,* (2009). QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. Journal of Physics: Condensed Matter 21 395502 19.

[9] Birch, F., (1947). Finite elastic strain of cubic crystals. Physical Review 71:809.

[10] Kumar S, Khan MM, Zulfequar M, Husain M, (2007); Optical, structural and electrical investigation on PbTe1-xSx alloys. J Mater Sci 42:363-367.

[11] Kacimi S, Zaoui A, Abbar B, Bouhafs B, (2008); Ab initio study of cubic PbSxSe1-x alloys. Journal of Alloys and Compounds 462:135-141.

[12] Asghar, K.M., Shah, Z.A., Khan, J., Arafat, Y., Hayat, S, *et al*., (2017);Principle Investigation of Structural, Electronics and Chemical Properties of Sn Doped PbX `(X=S, Se, Te). Journal of Theoretical and Computational Science 4:159.

[13] Bencheriff, Y., Boukra, A., Zaoui, A., and Ferhat, M., (2011); High-pressure phases of lead chalcogenides. Materials Chemistry and Physics 126:707-710.

[14] Afrin, S., Shalauddin, and Hossain, M.K., (2012). First principle study of the structural, electronic, optical and thermodynamic properties of binary compound (AlB_2).

[15] Olademeji, D., Linu, M., Barbara S., Ericmore, J., and Jerzy, S., (2017). First principles study of thermos-mechanical properties of Gallium Phosphide. Int J Metall Met Physics 2017, 2:006.