ECHAHID HAMMA LAKHDAR UNIVERSITY - EL-OUED
Under the Supervision of the DGRSDT and in collaboration with the CRTI
International Pluridisciplinary PhD Meeting (IPPM'20)
23-26, 2020 1st Edition, February
Theme: Modern Technology and Fineness Life

4 to 5 pages

Low temperature study of the structural, electronic and thermoelectric behaviors of PbS lead chalcogenide

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Abstract

This paper aims to investigate the structural, electronic and thermoelectric properties of lead sulfide using the first principles calculations. The exchange-correlation potential is treated by two approximations, the local density approximation (LDA) and the generalized gradient approximation (GGA) to calculate the structural and electronic properties. The thermoelectric properties of PbS sample are well predicted by the exchange-correlation potential GGA. The calculated band structure, the density of states (DOS) and electron density shows that lead sulfide is a semiconductor with gap energy of 0.082 and 0.47eV. Finally, temperature dependent thermoelectric properties like electrical and thermal conductivity, Seebeck coefficient and power factor were calculated in detail by employing the Boltzmann transport theory under the BoltzTraP code. The PbS compound has a large power factor at high temperature with a positive Seebeck coefficient which indicates that lead sulfide is p-type semiconductor, and major carrier is predominated by holes. Therefore, it reveals that PbS can be used as promising materials for high potential thermoelectric.

Keywords: Lead chalcogenide, DFT, electronic properties, thermoelectric properties.

1. Introduction

PbS is a promising semiconductor material for various technological applications, it is used successfully in infrared detectors and light emitting devices. They are also used as infrared lasers in optical fibers and as thermoelectric materials in solar panels [1.2], quantum containment devices evolved with PbS, which allows the operation of devices in a technologically important optical range [3], also it presents various interesting properties such as large dielectric constant, a low energy gap [4.5]. Furthermore, to date a large variety of Ag2S nanostructures are synthesized [41.42,46,47,48,49], due to their potential applications in nanocrystals [43], photovoltaic absorber material [44, 45], ...
Earlier theoretical studies of the electronic structure of these material were made by many groups, using a semi-empirical tight-binding (TB) method [6], augmented plane waves (APW) [16], the Green function method [7], orthogonalized plane waves [8], and the emperical-pseudopotentiel method [9,10]. Some volume properties [14], and optical constants [11] were calculated using the Mixed k.p-(APW) and linear combination of atomic orbitals [13] methods. The optical spectra of lead salt have already been calculated using the empirical pseudo-potential method [12]. Ab-initio calculations were also conducted on these materials using the linearized muffin- tin Orbital (LMTO) [15] and the Linearized Augmented Plane Wave (FP-LAPW) methods [17-18]. this theoretical calculations identified a direct band gap at the L point of the Brillouin zone for PbS lead chalchogenide. At ambient temperature and pressure, these compound crystallize in the NaCl structure.
The FP-LAPW method in the framework of the theory of density functional theory (DFT) [25,26] is performed to investigate the structural, electronic and thermoelectric properties of PbS compound.We firstly computed the ground state properties of lead sulfide sample, such as lattice constant and bulk modulus. Then, we calculated the electronic structure including band structure and density of states. Finally, we studied the temperature dependent thermoelectric properties of PbS compound .

2. Computational methods

The structural, electronic and thermoelectric properties of cubic PbS are performed by using a Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method within the framework of density functional theory (DFT) [25,26] implemented in WIEN2K code [19]. The exchange-correlation potential for structural and electronic properties is calculated by the local density approximation (LDA) based on the method established by Perdew and Wang [20] and the generalized gradient approximation (GGA) based on the Perdew et al. [21] method. The optical and thermoelectric properties are computed using the GGA exchange potential.
The wave functions, charge density and potential inside the muffin-tin (MT) spheres are expanded with an angular momentum l_{max}=10. In the interstitial regions, the wave functions are expanded in plane wave with a cut-off of $R_{MT}K_{max}$=9, where R_{MT} is the smallest muffin-tin radius and K_{max} is the largest k vector in the plane wave's expansion. The Pb ($5d^{10}6p^2$), S ($3s^2\,3p^4$), states are treated as valence electrons. The muffin-tin radius for Pb and S are taken as

2.50, 2.39 a.u. The irreducible Brillouin-zone integration is performed using a Monkorst-Pack mesh [23] of *47* special *k*-points (grid of 10 10 10) alloys. Both of plane wave cut-off and the number of *k*-points were chosen in order to ensure total energy convergence. In the current research, we have taken the structure of the PbS in NaCl type (space group Fm-3m, number 225). Primarily, we have calculated the equilibrium lattice constant (a_0), the equilibrium volume (V_0), the bulk modulus (B_0) at zero pressure. These parameters are computed by fitting the total energy versus volume to the Murnaghan's equation of state [22]. Then, the electronic band structure, at the equilibrium lattice constant for studied material is calculated along the high-symmetry directions in the face centered cubic-Brillouin Zone (fcc-BZ) and the total and partial density of states is graphed. Furthermore, We evaluated the thermoelectric properties by means of the semiclassical Boltzmann theory within the constant scattering time approximation (CSTA), as employed in the BoltzTraP code [54].

3. Results and Discussion

The calculated total energy of PbS, (NaCl) phase compound using LDA and GGA approximation is fitted with the Murnaghan equation of states to obtain structural parameters which are reported in Table 1, and compared The lattice parameters for PbS are found to be **5.8537** and **6.0144** (Å) for LDA and GGA respectively. A sub-estimation of mesh parameters by the LDA approximation in relation to the experimental values is in the order of **1.37%** and an overestimation of the latter by the GGA is in the order of **1.33%**.
Our calculated structural parameter for both material are in good agreement with other theoretical results [27, 33,34]. Bulk modulus is overestimated by the two approximations LDA and GGA. This over-estimation in relation to the experiment is in the order of **0.14%**, **24.1%**, for the LDA and the GGA respectively. So our result obtained by the GGA approximation is in very good agreement with previous theoretical studies and Experiment results.

Table 1. Structural parameters and bulk modulus of PbS compound

Lattice constant (Å)				
Exp	Theoretical		Present	
	LDA	GGA	LDA	GGA
5.929 [a] 5.936 [b,c] 5.940 [d]	5.860 [a] 5.906 [e] 5.854 [f]	6.012 [a] 6.012 [e]	5.8537	6.0144
Bulk modulus (GPa)				
Exp	Theoretical		Present	
	LDA	GGA	LDA	GGA
52.9 [a]	64.8 [a] 66.3 [e] 67.3 [f]	53.3 [a] 53.2 [f]	65.65	53.04

[a] Ref.[27] , [b] Ref.[28], [c] Ref.[29], [d] Ref.[30], [e] Ref.[31], [f] Ref.[32].

3.1. Electronic properties

The PbS compound is a semiconductor with low energy gap, the bond between Pb and S is considered to be predominantly ionic [28]. The electronic band structures for PbS along the high symmetry directions in the Brillouin Zone (BZ) are obtained by using their equilibrium lattice parameters in the NaCl structure. The band structures for PbS are shown in Figure 1.
It is clearly seen that PbS has a direct band gap with a value of 0.082, 0.474 eV at L point for LDA and GGA approaches, respectively . Our results are compared with experimental and theoretical data available in table 2. It should be noted that our results obtained by LDA and GGA disagree with those of the experience.
The value of the gap is underestimated by the LDA and overestimated by the GGA, the value of the experimental gap is very low compared with that determined by the ab-initio methods. Generally speaking, these controversial values can be explained by the low energy gap value of this lead chalcogenide. Moreover, the difference between our calculated of energy gaps values, and those calculated in the other works using the same method, is due to the fact that they introduced the interaction spin orbit in their calculations, which resulted in a shift of the Conduction band.
To better understand the band structure, it is interesting to determine the spectra of the total and partial state densities in order to analyze and know the type of hybridization and the states responsible for the liaison. The density of states (DOS) of PbS was calculated by the GGA approximation. The projected total and partial DOS calculated are illustrated in Figure.2.
The deepest part of the valence band in the PbS compound is located in the range of energies (-13.23 →-11.75 eV), this region is essentially formed of the s states of the Chalcogen atom (S) as shown in the partial density curve Figure 2, this peak corresponds to the lowest valence band shown on the band structure curve (Figure. 1), and its width comes from the area surrounding the Γ point in the Brillouin area, where dispersion is quite appreciable. The structure centered at 8

eV below the Fermi level is predominated by the s states of lead, with a slight contribution of the s states of the chalcogen atom. For conduction strips that are located above the Fermi level, the dominant component is the p state of lead. Our analyses of the density of states are perfectly consistent with those of a. Delin et al. [11] and M. Lach-hab et al. [27].

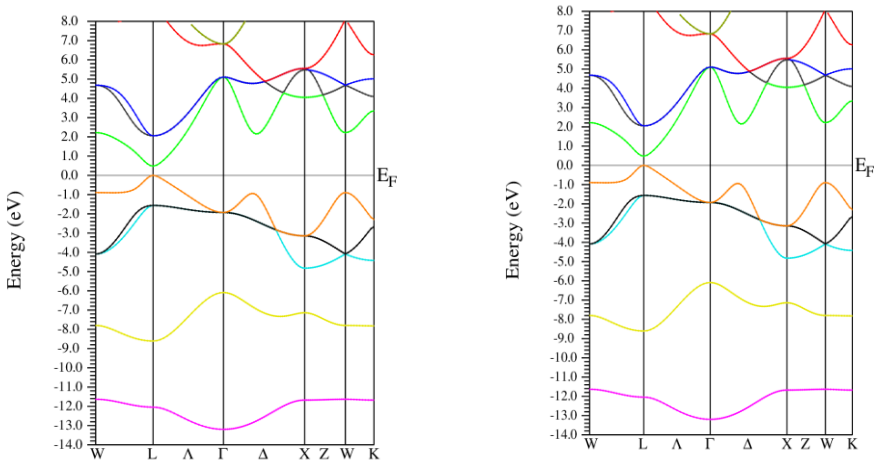

Fig.1. Electronic band structure of PbS compound, (a) LDA and (b) GGA approaches.

Table 2. Energy gap of PbS semiconductor compound

Gap energy $E_{L\to L}$ (ev) of PbS compound					
Exp	Theoretical			Present	
	FP-LAPW		LMTO		
	LDA	GGA	LDA	LDA	GGA
0.286 [j, k] 0.29 [l]	0.26[m] 0.22 [a] 0.29 [n]	0.38 [a] 0.44 [h]	0.069 [d]	0.082	0.47

[a] Ref.[27] , [h] Ref.[17], [j] Ref.[35], [k] Ref.[36], [l] Ref.[37], [m] Ref.[38], [n] Ref.[39].

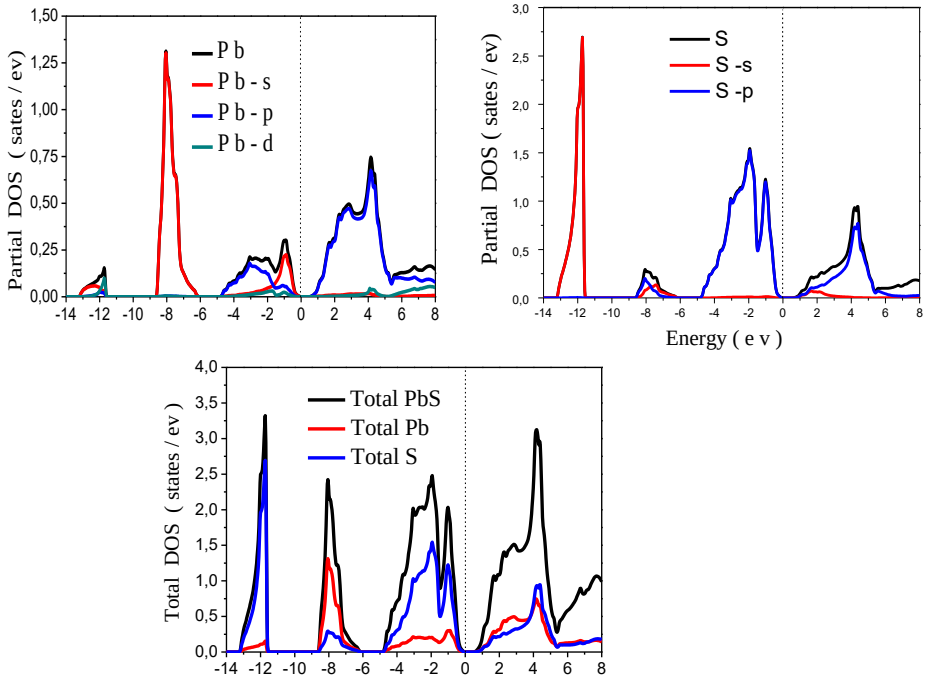

Fig. 2. Calculated total and partial density of states of PbS compound Using the GGA approach.

4. Conclusion

We have studied structural, electronic and thermoelectric properties of PbS using the LDA and GGA approximations within the density functional theory as implemented in the WIEN2k. The structural results for both material is in general agreement with previous studies of PbS sample. Our calculations prove that PbS has a direct gap semiconductor in the direction L→L. The thermolectric study shows that PbS has large Seebeck coefficients and thermoelectric power factor values, with a positive Seebeck coefficient which indicates that lead sulfide is p-type semiconductor .Therefore, it reveals that PbS can be used as promising materials for high potential thermoelectric.

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