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STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF DEFECT CHALCOPYRITE CDGA2S4 AND HGGA2S4 COMPOUNDS BY FIRST PRINCIPLES

[1]NORHASLINDA OSMAN, [2*]MOHAMAD ALAM SAEED

[1]Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310, UTM Johor Bahru, Johor Darul Ta'azim, Malaysia

[1] miszlinda174@yahoo.com, [2*] saeed@utm.my

*Corresponding author

Abstract. The physical properties of defect chalcopyrite compounds are discussed here. Initial study are carried out under the framework of density functional theory by keeping in view the device manufacturing characteristics relating to structure, energy band configuration and bonding nature of the selected $PbGa_2S_4$ and $HgGa_2S_4$ defect chalcopyrite compounds. The computational work are executed using highly accurate full potential linearized-augmented plane wave + local orbital approach through the latest edition of Wien2k software. In a next step, the electronic properties of $PbGa_2S_4$ and $HgGa_2S_4$ defect chalcopyrite compounds are investigated. Precise band gap are calculated by employing GGA and LDA techniques. This work provided a comprehensive theoretical study of the physical properties with special emphasis on structural and electronic properties of defect chalcopyrite compounds.

Keywords DFT; $PbGa_2S_4$; $HgGa_2S_4$; Wien2K

1.0 INTRODUCTION

Ternary compounds semiconductors have fascinated significantly due to their very inimitable physical properties and applications [1]. Properties of the ternary semiconductors belonging to the family $A^{II}B_2^{III}X_4^{VI}$ of (A^{II}= Pb, Hg; B^{III}= Ga; and X^{IV}= S) are under extensive studied due to their use in optoelectronic and nonlinear device applications. The formula belongs to defect chalcopyrite (DC)

family. $PbGa_2S_4$ (Lead thiogallate) and $HgGa_2S_4$ (Mercury thiogallate) semiconductors have been found to crystallize in the defect-chalcopyrite tetragonal structure and belong to space group *[I-4]*. For device applications it is vital to know the optoelectronic properties of a material [3]; this give motivation to study the structural and electronic properties of $PbGa_2S_4$ and $HgGa_2S_4$. Detailed computational or theoretically study of structural and electronic properties are very vital.

In the structure of $PbGa_2S_4$ and $HgGa_2S_4$, which belongs to defect chalcopyrite (DC) family, gallium atoms occupy the positions of two different types. The gallium atoms of the first type (Ga^1) occupy the half of gallium positions of the compound $AgGaS_2$ (Figure 1), whereas the second type of gallium atoms (Ga^2) are placed in half of the silver positions $AgGaS_2$ leaving the other part of gallium positions in $AgGaS_2$ empty. The second half of the silver positions $AgGaS_2$ are occupied by lead/mercury. As a result, the number of neighboring atoms in the first atomic shell of the atom sulfur is equal to three (Figure 1) in this structure.

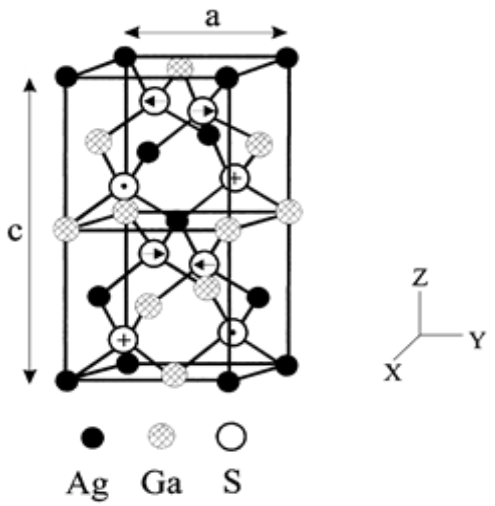

Figure 1. Crystal structure of $AgGaS_2$. The coordinate atom in the left lower corner are: (ua, a/4, c/8) [4]

The study of $A^{II}B_2^{III}X_4^{VI}$ type defect chalcopyrite compounds by first principles is an effort to contribute precise findings in structural and electronic

properties to existing research on this interesting family of compounds. Highly accurate all electron FP-LAPW+lo method under DFT are certainly contribute in removing discrepancies associated with these materials. Precise band gap are presented by employing GGA and LDA techniques. The project's goal are provided accurate structural and electronic for these materials which are helpful in establishing new devices.

By ab initio or first principles means an approach of doing calculations which rely on the well established and fundamental laws of science and does not involve any special models, suppositions or fitting techniques. In physics, such calculations of electronic structure which do not incorporate fitting models to experimental results and which make use of Schrodinger equation as a starting point along with a group of estimations may be called as ab intio or first principle calculations [5].

There are two possible ways by which materials can be analyzed. One way is to characterize the material experimentally for the description of its properties. Though in some cases, it is almost impossible to furnish experiments with required conditions for synthesis or characterization. Atomic scale calculations are difficult to handle even by modern experimental techniques. The other option is to solve many body problems by solving complex quantum mechanical equations, but this also takes a large time [5]. Recently computational approaches have gained enormous attention because of their ability to solve many body problems in less time with the advancement in computer processing technology [1]. Now simulation and modeling of materials is possible in ideal conditions which were impossible to achieve before. Computational approaches are a cheaper way of discovering new possibilities for preparing and understanding materials for device manufacturing. The valuable properties which are difficult to explore through experimentation are now can be revealed through simulation techniques.

In this calculation, within the framework of density functional theory (DFT), we used the Wien2k package which is based on the full potential linearized-augmented plan waves plus local orbital's (FP-LAPW+lo) method. Lattice parameters, bulk modulus, pressure derivative, band gap for both compounds in zinc-blend (ZB) structure, using experimental lattice parameters,

with different exchange-correlation approximation are reported in this paper. To calculate the ground state properties, the local density approximation (LDA) and generalize gradient approximation (GGA) shows good result but underestimate the band gaps energy values. This work leads to more systematic understanding of the structural and electronic properties of these group defect chalcopyrite.

2.0 PROBLEM STATEMENT

Research shows that, PbGa2S4 and HgGa2S4 have been studied almost few years ago and the main emphasis was generally on their structural and electronic properties [1,2]. The structural properties and the electronic properties using LDA and GGA are proposed, which offered a better results for our calculations. Moreover, these results help in analysis and proper comparison with existing literature. Therefore, structural and electronic properties are expected to significantly improve.

The properties and underlying physics of certain materials are very important for the development of new devices as well as operating characteristics of such devices. To comprehend the physical properties of such compounds a lot of research has been carried out but there are yet many characteristics needs clarity, like electronic band gap disagreement among different studies. This motivate us to perform more advance calculations using the all electron full-potential linearized augmented plane wave plus local orbital method (FP-LAPW+lo) which has confirmed to be one of the most accurate method for the calculation of the electronic structure of solids within DFT with different kind of exchange correlation. Therefore, an inclusive theoretical analysis of structural and electronic properties along with experimental results is therefore essential.

3.0 SIMULATIONS & RESULTS

Our calculations are carried out within the framework of DFT using the highly accurate all-electron full potential linear augmented plane wave plus local orbitals method as employed in WIEN2k code [5]. In this method Kohnan-Sham wave functions, charge density and potential are expanded in the different sets of basis functions. For the wave functions, inside the MT spheres of radius (RMT) around each atom, a linear combination of the atomic wave functions times the spherical harmonic expansion is used and in the interstitial region a plane wave expansion is used. The charge density and potential are expanded into lattice harmonics inside MT spheres and as a Fourier series in the remaining space.

The dependency of the total energy on the number of k-points in the irreducible wedge of Brillouin zone optimized with the size of k-mesh is set to 10x10x10 k-points. Self-consistency is considered to be reached when total energy difference between successive iterations is less than 10^{-5} Ry. For the unit cell parameters of the tetragonal lattice, first we need to optimize the total energy for various ratios c/a keeping unit cell volume constant. Once the c/a ratio is fixed, we optimized the total energy for various unit cell volumes. The obtained set of unit cell volume and total energy was used to make a fit to the Murnaghan equation of state to determine the equilibrium unit cell volume V_0, the optimized lattice constants 'a', the bulk modulus B_0 and the pressure derivative of the bulk modulus B_0'. The Murnaghan equation of state (1944) is written as

$$E(V) = E_{0+} \frac{B_0 V}{B_0'} \left[\frac{(\frac{V_0}{V})^{B_0'}}{B_0'} + 1 \right] - \frac{V_0 B_0}{B_0' - 1}$$

And the bulk modulus B_0 corresponding to the equilibrium unit cell volume V_0 is given by the relation:

$$B_0 = V_0 \frac{d^2 E(V)}{dV^2}$$

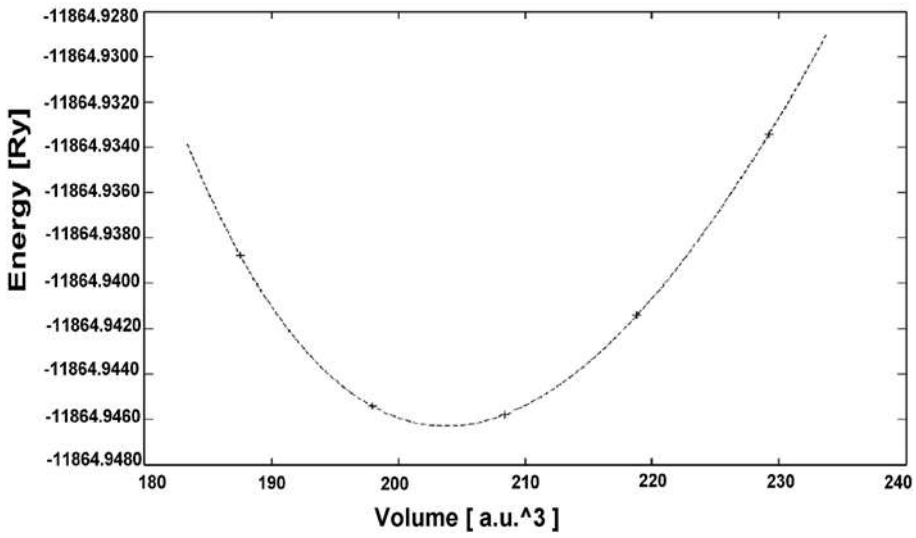

Figure 2. The total energy vs. Primitive cell volume for ZB- $HgGa_2S_4$ within LDA

3.1 Structural properties

In order to study the structural properties of $PbGa_2S_4$ and $HgGa_2S_4$, LDA and GGA has been used. The equilibrium lattice constant, bulk modulus and it's pressure derivative in this section are calculated by using fitting the Murnaghan equation of state as shown in Figure 2. The obtained values are listed in Table 1, with the experimental results and other computations. From Table 1, it may be observed that our results with LDA/GGA are closed to the experiment and in agreement with previous theoretical calculation. However, it appears that the lattice constants (compared with the experiment) are slightly underestimated within LDA, and overestimated within GGA. All results agree with the experimental numbers within 1-2%.

Bulk modulus which determines the hardness of crystals (large compressibility corresponds to a high crystal hardness) was calculated for both compounds (Table 1). Our computed values show that the LDA slightly overestimates whereas GGA underestimates as compared to the experimental results. The calculated pressure derivatives of bulk modulus are also presented in Table 1.

Table 1. The lattice parameters of $PbGa_2S_4$ and $HgGa_2S_4$ taken from Reference

Compounds	Method	a (Å)	V (a.u.)3	B (GPa)	B_0
$PbGa_2S_4$					
Our work	FP-LAW-GGA	5.56	121.23	111	4.56
	FP-LAW-LDA	5.279	118.56	110	4.53
Experiment		5.545[1]	-	102[1]	-
$HgGa_2S_4$					
Our work	FP-LAW-GGA	5.507	155.12	156	4.52
	FP-LAW-LDA	5.230	149.54	149	4.28
Experiment	-	5.435[2]	-	148[2]	–

3.2 Electronic properties

The electronic band structure plays a vital role in determination the electronic properties of materials. Figure 3 and 4, shows the calculated band structures of $PbGa_2S_4$ and $HgGa_2S_4$ by using LDA and GGA methods along high symmetry direction in the first Brillion zone, respectively. It is obvious that the LDA and GGA gap values are samaller than the experimental values.

Table 2: The energy band gap (E_g) properties of $PbGa_2S_4$ and $HgGa_2S_4$

Compounds	Methods	XC	E_g (eV)	Type of band gap
$PbGa_2S_4$				
	FP-LAPW	GGA	1.767	Direct (Γ-Γ)
		LDA	1.757	Direct (Γ-Γ)
Experiment		-	3.231[1]	Direct (Γ-Γ)
$HgGa_2S_4$				
	FP-LAPW	GGA	0.00	Direct (Γ-Γ)
		LDA	0.00	Direct (Γ-Γ)
Experiment		-	0.700[2]	Direct (Γ-Γ)

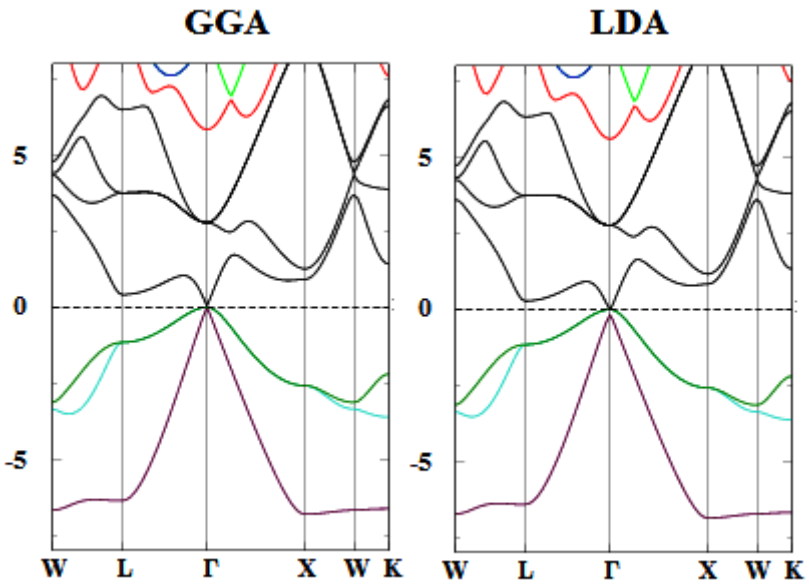

Figure 3. Band structure of $PbGa_2S_4$ calculated by the LDA and GGA

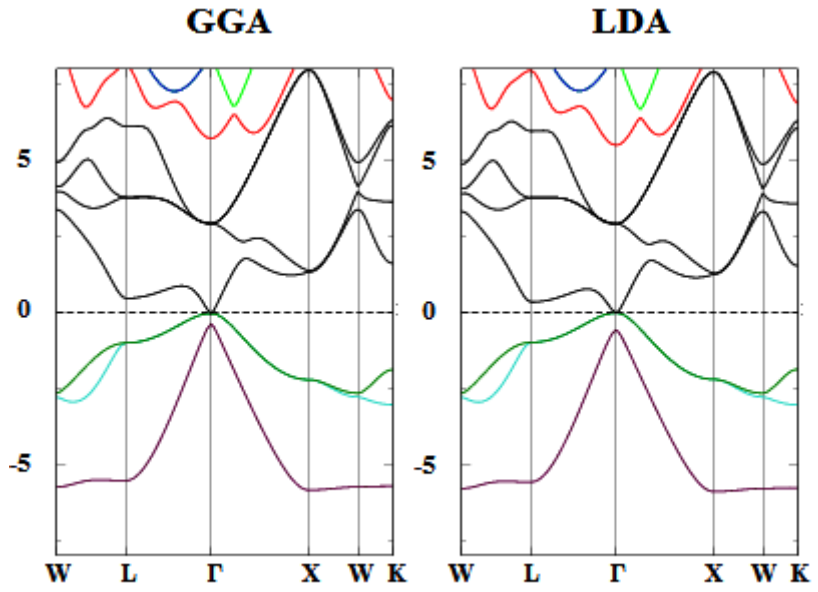

Figure 4. Band structure of $HgGa_2S_4$ calculated by the LDA and GGA

4.0 CONCLUSIONS

The structural and electronic properties of $PbGa_2S_4$ and $HgGa_2S_4$ have been studied by first principles based on DFT within the LDA and GGA methods. The results show that the LDA/GGA yields quite reliable structure properties, but seriously underestimates the band gap values.

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