Study of structural, electronic and optical properties of the chalcopyrite $AgGaSe_2$

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Abstract-Ternary compounds with structures of the family of chalcogenide chalcopyrite I-III-VI2 (I = Ag, III = Ga, VI = S, Se) form an extensive semiconductor materials group with diverse optical and electrical properties. Ternary alloys with this composition are well known for their potential applications in the industry of electronic devices and photovoltaics. From a structural point of view, they crystallize with a tetragonal symmetry in the space group I42d (No. 122). The objective of the present work is to predict the structural properties, such as lattice parameter, bulk modulus as well as its derivative compound AgGaSe2 and their mechanical and electronical properties such as band structure and optical properties using the first principle methods (FP-LMTO).

1. Structural properties:

The fundamental state properties of our material were obtained by the use of a mathematical calculation based on the FP-LMTO method, by a GGA treatment of the exchange energy and correlation. The commonly used procedure to determine the structural properties in the vicinity of equilibrium consists in evaluating the total system energy for different values of c/a at constant volume (see Figure 1). Finally we calculated the total system energy for various values of network parameter for a constant c/a (see Figure 2). The obtained results are then adjusted to the Murnaghan state equation [1].

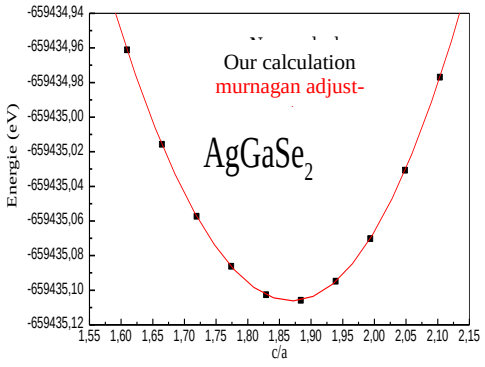

Figure (1): variation of the total energy as a function of c/a of the $AgGaSe_2$ compound with the FP-LMTO-GGA approximation.

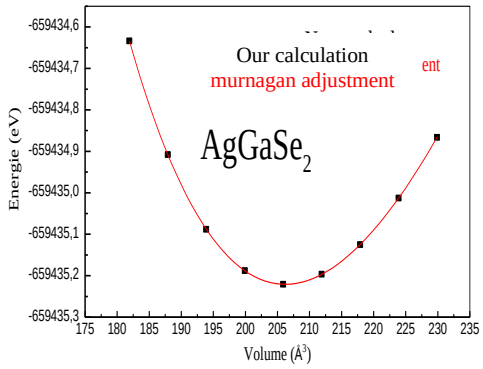

Figure (2): variation of the total energy based on the volume of the $AgGaSe_2$ compound with the FP-LMTO-GGA approximation.

Table (1): Setting parameters a (Å), c (Å), c/a, u (Å) stiffness modulus B0 (GPa), its derivative B' chalcopyrite $AgGaSe_2$, compared with experimental, theoretical and other work values.

com-pound	method	a(Å)	c(Å)	c/a	u(Å)	B(GPa)	B'(GPa)
Ag-$GaSe_2$	Our GGA calcula-tions	6.0473	11.2771	1.8648	0.27788		
	other calculations[a]	6.0579	11.2943	1.8644	0.2788	53.07	4.0076
	theory[c]	6.0629	11.2284	1.852	0.2794	50.7	5.02
	Experience[b]	5.985	10.904	1.822	0.272	63.8	4.00

Ref[a] [2] ,Ref[b] [3], Ref[c][4].

2-Elastic properties:

The mechanical stability of crystals has been the subject of extensive theoretical studies. The systematic study of the stability of the network was made by Born and Huang who formulated the criterion of stability. This criterion is expressed in terms of the elastic constants Cij which in the case of our material, is given by:

$\mathbf{C_{11}, C_{33}, C_{44}, C_{66} > 0, (C_{11}+C_{12})C_{33}>2C_{13}^2}$, $\mathbf{C_{11}> |C_{12}|}$, $\mathbf{C_{66} > 0}$, $\mathbf{C_{44} > 0}$

It is clear from the above expressions that the condition on the criteria for this chalcopyrite mechanical structure stabilitiy is satisfied for all three materials.

Table (2): The elastic constants Cij (GPa) calculated for $AgGaS_2$.

material	methods	C11	C12	C13	C33	C44	C66
$AgGaSe_2$	our calc	74.556	43.306	36.0905	50.44067	33.8303	32.57028
	Experience[d]	89.8	65.7	45.1	58.0	21.7	13.3
	theory[e]	86.4	55.2	52.9	72.4	20.3	52.9
	theory[f]	74.95	41.03	43.03	59.57	30.10	21.62

Ref[d] [5], Ref[e] [6],Ref[f][7]

3-Electronic properties:

In solid state physics, band theory is a model of energy values that can electrons acquire from within a solid. We calculated the energy bands of chalcopyrite $AgGaSe_2$, using the FP-LMTO method. The material has the following topology.

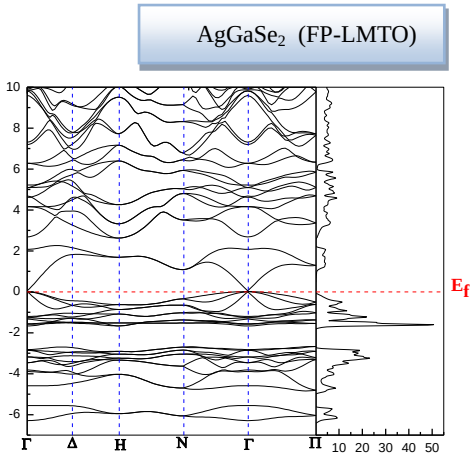

Figure (3): band structure $AgGaS_2$ obtained by FP-LMTO.

For this material the maximum of the valence band and the minimum of the conduction band are at the same level even at high symmetry point Γ, resulting in a direct gap. The experimental values available to us for this material show a significant underestimation of the energy gap. This was predictable since we have been using the GGA [8]. It is well established that GGA underestimate gap energy values due to the fact that they have simple shapes that are not sufficiently flexible to accurately reproduce the energy exchange and correlation.

The energy gap and valence band widths calculated for these compounds are shown in Table 3

Table (3): energy gap $AgGaSe_2$.

	method	Energy gap
$AgGaSe_2$	FP-LMTO	0.04201
	Experience	1.73[g]
Ref[g]	[9]	

4-Optical properties:

Figure (4) shows the real and the imaginary part of the dielectric function at normal pressure for a radiation lower than 20 eV for the AgGaSe2compound. By using the calculated band structures, it would be interesting to identify the inter band transitions that are responsible for the structure of ε2 (ω).

The analysis of the absorption spectrum shows that the energy threshold of the dielectric function is around 0.394 eV for $AgGaSe_2$. This energy value corresponds to the static dielectric stant $\varepsilon_1(0)$, which is given by the lower limit of $\varepsilon_1(\omega)$. It has to be noted that we did not take into account the phonon contribution to the effect of the optical dielectric screen calculated at normal pressure of 9,799 for the $AgGaSe_2$.

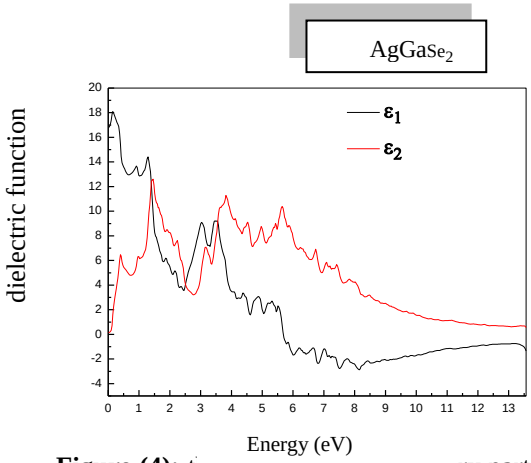

Figure (4): the real part and imaginary part of the dielectric function of $AgGaSe_2$.

Conclusion:

We have set an objective thorough out this work which mainly consist in determining the structural, electronic, mechanical and optical properties of the chalcopyrite $AgGaSe_2$, for this purpose we have used the (FP- LMTO) method.

Our results for the structural properties such as lattice parameters (a0 and c0) and internal parameter (u), modulus and its derivative are in good agreement with the experimental input values. The elastic coefficients predicted by

Table (4): refractive index and static dielectric constants of composite $AgGaSe_2$.

compound	n	Ɛ0
$AgGaSe_2$	3.1304	9.79969

the Mehl models show that our materials are stable in this structure phase. As far as the band structure is concerned we have used the GGA approach.

The latter gives a better topology of the band structure and the values of gap energy we then have optimized the refraction index and dielectric constants.

Values are less than those given by experimental work, which is evident with the use GGA functional. As far as the density state is concerned, we reported contributions of states of each band strips

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