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Ab initio study of structural, electronic and optical properties of ternary chalcopyrite semiconductors

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ABSTRACT

In this paper, structural, electrical and optical properties of $AgGaX_2$ (X=S, Se, Te) were studied by using Full Potential Linear Augmented Plane Wave (FP-LAPW) based on density functional theory. Perdew Becke Ernzerhof (GGA-PBE) and Wu Cohen Generalized gradient approximation (GGA-Wc), Engel Voskov Generalized Gradient Approximation (EV) and modified Becke-Johnson exchange potential (MBJ) were used for the exchange correlation potential. GGA-PBE was closed to the other and experimental data for lattice constant, bulk modulus (B) and its first derivative (B'), and MBJ potential was in good agreement with the experiment and other calculations for band gap energy and the optical properties. Band structure, total and partial density of states were plotted to obtain electronic properties and the band gap was direct for all components. By using imaginary and real part of dielectric functions, some optical properties such as reflection coefficient (R), refractive index (n), extinction coefficient (k) were obtained and the role of X atoms (X=S, Se, Te) in optical properties were investigated.

1. Introduction

$A^{I}B^{III}C_2^{VI}$ semiconductor compounds have attracted considerable interest because of their fascinating electronic and optical properties and wide transparency band in visible and infrared regions [1]. $A^{I}B^{III}C_2^{VI}$ semiconductor compounds are good candidates for the formation of p–n hetero-junction with II–VI group semiconductors, because both structures are similar [2]. In this paper $AgGaS_2$, $AgGaSe_2$ and $AgGaTe_2$ compounds were studied. These ternary compounds belong to the tetragonal chalcopyrite structure, which is considered as two zinc-blende super lattice along C-lattice constant. Chalcopyrite ternary compounds are divided into two groups, silver (Ag-III–VI_2) and copper (Cu-III–VI_2) based compounds. For the first group, Ag-based attracts much attention due to their potential usage in non-linear optical and photonic applications. Among the Ag-based, the $AgGaS_2$ and $AgGaSe_2$ were studied extensively due to their direct band gap of about 2.51 eV and 1.82 eV respectively and good transparency in 500–1200 nm wavelength [3–5]. For the second group, Cu-based, following compounds Cu (In, Ga, Se) (CIGS) were studied extensively due to their suitability for the construction of thin film solar cells and high absorption coefficient, suitable optic band gap (1.04 eV) and ease of production [2]. Chalcopyrite compound is used as solar cell, Light Emitted Diode (LED), Non-Liner Optical devices (NLO) and photonic sensors. The chalcopyrite composition with narrow band gap is suitable for infrared detector used in photovoltaic solar cells as thin films [6,7]. Mentioned semiconductors can shift wavelength and can tune over wide spectra range because of their Non-Liner Optical properties (NLO), so they increase laser performance and can be used as mid- and far-IR lasers [7,8]. In previous works with first principle calculations, Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA) were used for exchange-correlation potential and calculate the structural, optical and electronic properties [9]. On the other hand, the Becke–Johnson exchange potential (MBJ) and Engel Voskov Generalized Gradient Approximation prove better performance than LDA and GGA in predicting band gap energy. That is why in the present work the GGA approximation was used to calculate lattice constants and MBJ potential and EV approximation were used to calculate band gap energy and optical properties.

2. Computational details

All calculations were performed employing Density Functional Theory (DFT) [10] as embodied in the Wien2k code [11]. Perdew Becke Ernzerhof (GGA-PBE) [12] and Wu Cohen Generalized gradient approximation (GGA-WC), Engel Voskov Generalized Gradient Approximation (EV) [13], Local Density Approximation (LDA) [14] and modified Becke-Johnson exchange potential (MBJ) [15] were used for exchange-correlation potential. Full relaxation was exerted on all atoms until the total force became smaller than

Abbreviation: EV, Engel Voskov Generalized Gradient Approximation; MBJ, Modified Becke–Johnson exchange potential

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1 mRy/Bohr. The muffin-tin radii for Ag, Ga, S, Se and Te atoms were chosen to be 2.5, 2.36, 2.03, 2.28 and 2.49 a.u. respectively. The expansion of the wave functions and charge densities were cut off by the $R_{MT}K_{MAX}=7$ and $G_{MAX}=12$ parameters. We generated 40 special k-points in the first Brillouin zone (1BZ) corresponding to the shifted Monkhorst–Pack grids of $7\times7\times7$ for all compounds.

3. Structural properties

$AgGaX_2$ (X=S, Se, Te) composition has tetragonal chalcopyrite structure, the space group is $I\bar{4}2d$, which is considered as two zinc-blende super lattice along C-lattice constant, both structures are shown in Fig. 1. There are eight atoms in the chalcopyrite structure and the positions are as follows:

A: (0, 0, 0), (0, 1/2, 1/2)

B: (1/2, 1/2, 0), (1/2, 0, 1/2)

C: (u, 1/4, 1/8), (0, 1/2, 1/2), (3/4, u, 7/8), (1/4, u, 7/8)

$$u = 1/2 - (c^2/32a^2 - 1/16) \quad (1)$$

The calculated and experimental data of lattice constants, bulk modulus (B) and its first derivative (B') are given in Table 1 for $AgGaX_2$ (X=S, Se, Te). The results of GGA approximation are in good agreement with the experiment and other calculations. The bond lengths before and after relaxation are given in Table 2 which indicates that Ag–X and Ga–X (X=S, Se, Te) bond length decreases.

4. Electronic properties

The electronic properties of $AgGaX_2$ (X=S, Se, Te) composition were computed by using GGA, LDA, EV approximation and MBJ

Table 1
Lattice constant in angstrom (Å), bulk modulus and its first derivative.

Compound	Exchange	$a=b$	c	B (GPa)	B'
$AgGaS_2$	LDA	5.640	10.734	98.65	9.93
	GGA	5.678	10.587	100.04	4.95
	WC	5.663	10.647	100	5
	Other[a]	5.587	10.401	81.23	4.74
	Other[b]	5.77	10.578	60.8	4.00
	Exp[a]	5.755	10.278	77.6	4.00
$AgGaSe_2$	LDA	5.878	11.313	100.02	5.09
	GGA	5.915	11.172	100.00	5.00
	WC	5.895	11.346	100.00	5.00
	Other[a]	5.838	11.022	64.621	4.70
	Other[b]	6.05	11.210	50.7	5.02
	Exp[a]	5.992	10.886	65	4
$AgGaTe_2$	LDA	6.138	11.669	99.39	1.91
	GGA	6.272	11.925	99.99	5.83
	WC	6.254	12.037	99.99	5.00
	Other[c]	6.288	11.949		
	Exp[d]	6.280	11.940	76.6	

[a] Ref. [17].
[b] Ref. [16].
[c] Ref. [8].
[d] Ref. [18].

Table 2
Bond lengths of $AgGaX_2$ (X=S, Se, Te), before and after relaxation in angstrom (Å).

Type	Before	After
Ag–S	4.690	4.680
Ga–S	4.420	4.416
Ag–Se	4.919	4.855
Ga–Se	4.595	4.977
Ag–Te	5.137	5.136
Ga–Te	4.977	4.976

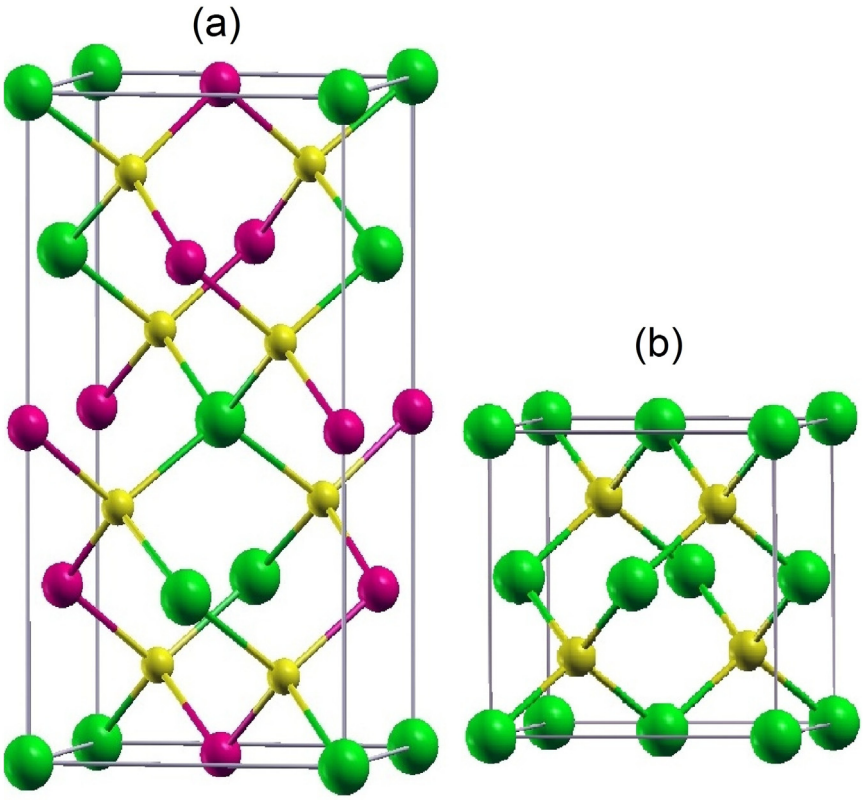

Fig. 1. (a) Chalcopyrite and (b) zincblende structure.