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Opto-Electronic Properties of Ternary Chalcopyrite $A^{I}B^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^{V}$ Semiconductors

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Abstract. An investigation has been carried out for various crystal parameters like homopolar gap (E_h), heteropolar gap (E_c), average gap (E_g) and refractive index (n). These estimated values are used to calculate the ionicity of ternary chalcopyrite semiconductors. Based on the complex crystal chemical bond theory, the Moss formula which is for one type of bond only has been extended to calculate the refractive index (n). The estimated refractive index is used to evaluate the ionicity of ternary chalcopyrite semiconductors. The results have been compared with the literature ones. The calculated values are in fair agreement with previous reported values.

Keywords: refractive index, energy gap, ionicity, ternary chalcopyrite semiconductors

Introduction

The ternary chalcopyrite semiconductors have obtained considerable importance because of their potential applications in the areas of light emitting diodes, nonlinear optics, photovoltaic devices and solar cells. The solid solutions of these semiconductors have been used in electro-optic devices. Their mixed crystals are being used for fabrication of detectors, lasers and integrated optic devices such as switches, modulators, filters. These chalcopyrites have many other practical applications in the field of fibre optics, sensors and communication devices. The properties of these compounds have not been fully investigated inspite of their significant importance. Considerable attention has been given due to their importance for the development and fabrication of various technological devices. Structurally these compounds are derived from binary sphalerite structure with slight distortion. These compounds exhibit a high nonlinear susceptibility and birefringence which leads to efficient second harmonic generator and phase matching. The opto-electronic properties are the fundamental properties of the material. The chalcopyrite crystal structure is noncentrosymmetric and these compounds possess the essential properties of nonzero nonlinear optical tensor which can be quite large. Some chalcopyrite semiconductors, such as $AgGaS_2$, $AgGaSe_2$, etc., have become useful in nonlinear optical device applications with strong commercial possibilities. The evaluation of refractive indices of semiconductors is of considerable importance for potential application in integrated optical devices, whereas the refractive index of materials is the key parameter for designing various devices. Among the various parameters controlling the refractive index, energy band gap may be the most important one. Thus, it is of great interest to develop a correlation between refractive index and energy gap in solid materials. In recent years, various experimental and theoretical works have been done to generalize the trends in the ionicity (f_i) and refractive index (n) of ternary chalcopyrite structures $A^{I}B^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^{V}$ (Gorai and Mahata, 2010; Kumar *et al*., 1994; Neumann, 1987, 1985). The empirical relations between different parameters of the crystal, such as unit cell volume, energy gap, ionicity and plasma energy have been given by different researchers. Some of the chalcopyrites having other practical applications in the field of these compounds, are still being extensively investigated. The crystal ionicity is one of the key parameters of semiconducting materials in discussing problems in the field of elastic constants, cohesive energy, heat of formation, bulk modulus and crystal structure. Singh and Gupta (1986); Levine (1973); Phillips and Van Vechten (1969) and Penn (1962) developed various theories and calculated crystal ionicity in the case of simple compounds. Phillips and Van Vechten (1969) had calculated the homopolar and heteropolar gaps considering the effect of 'd' core electrons. Singh and Gupta (1986) had introduced the justification of Levine's theory. It is clear from the Levine's modifications as well as Phillips and

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Van Vechten theory that the value of homopolar energy gaps (E_h) depends upon the nearest-neighbour distance, while heteropolar energy gaps (E_c) is function of nearest-neighbour distance and valence number of electrons taking part in bond formation. Kumar and Shrivastava (1987) had calculated the homopolar and heteropolar energy gaps in terms of plasmon energy because plasmon energy depends directly on the effective number of valence electrons in a compound. Various experimental studies (Kumar *et al*., 2009; Verma and Bharadwaj, 2006; Meng *et al*., 1998; Moss, 1985) have been done for the determination of the ionicity of some ternary chalcopyrite semiconductors. However, there are big differences among experimental values and calculated ones. Neuman (1985) had developed some empirical relations between ionicity, bulk modulus, microhardness and surface energy. Estimation of ionicity through some semi-empirical models is of interest because of the continuity of the theory developed for the semiconductors. In this paper, Phillips and Van Vechten (PVV) theory (1969) has been applied to investigate homopolar gap (E_h), heteropolar gap (E_c), and average gap (E_g) and hence ionicity can be calculated. Moss (1985) formula is extended to calculate the refractive index (n). The estimated refractive index is then used to evaluate the ionicity of ternary chalcopyrite semiconductors.

Theory. The refractive index is one of the fundamental properties of a material because it is closely related to the electronic polarizability of ions and the local field inside the material. The evaluation of refractive indices of semiconductors is of considerable importance for applications in integrated optic devices, where refractive index of a material is a key parameter for device design (Levin, 1973). The energy gap determines the threshold for absorption of photons in semiconductors. The refractive index in semiconductor is a measure of its transparency to incident spectral radiation. A correlation between these two fundamental properties has significant bearing on the band structure of semiconductors. Moss (1950) proposed a relation between these two properties using the general theory of photoconductivity which was based on photo effect studies. According to this theory, the absorption of an optical quantum will raise an electron in alkali halides to an excited state rather than freeing it from the centre. Thermal energy then moves this electron to the conduction band from the lattice. Such a photo effect takes place in imperfection at certain lattice point and thus the electron behaves similar to an electron in an isolated atom with a dielectric constant of the bulk material. As a result of this effective dielectric constant (ε_{eff}), the energy levels of the electron are scaled down by a factor of $1/\varepsilon^2_{eff}$ approximately corresponds to the square of the refractive index (n). This factor thus, should be proportional to the energy required to raise an electron in the lattice to an excited state. This minimum energy determines the threshold wave length (λ_e), which then varies as the fourth power of the refractive index. Experimental data on different photoconductive compounds show that values of n^4/λ_e were close to 77 throughout a range of refractive indices. The similarities in the quotient show that the photoelectrons stem from the same type of lattice imperfections. Thus the Moss relation was formulated as:

$$\frac{n^4}{\lambda_e} = 77/\mu m \qquad (1)$$

where:

n is the refractive index and λ_e is the wavelength corresponding to the absorption edge. In terms of energy gap, this is:

$$n^4 E_g = 95eV \qquad (2)$$

According to this relation the refractive index can be determined with a known energy gap (E_g). Some empirical models were established that can predict refractive index of compounds from selected atomic properties of their constituent elements. The correlation between band gap and refractive index has been enlightened by Moss (1985) in various binary systems. Moss proposed a general relationship based on the concept that in a dielectric energy levels are scaled by a factor (ε_∞). Various theories have been given to modify the Moss relation and here the empirical relation has been extended in the following form:

$$E_g n^4 = 115eV \qquad (3)$$

The dielectric theory of solids proposed by Phillips and Van Vechten (1969) and the bond charge model developed by Levine (1973) shows us that chemical bonding behaviour and related bond parameters of a crystal are the important indices that allow us to properly express complicated interaction among all the constituent atoms or ions in a real crystal. The chemical bond is thus one of the effective starting points in understanding the complex relationship between composition,

crystallographic structure and chemical and physical properties of solids. The Phillips and Van Vechten theory can successfully deal with multibond crystals. The chemical bond method regards a complex crystal as the combination of all constituent chemical bonds. That means that a multibond crystal can be theoretically decomposed into a complete set of single bonds describing all constituent atoms or ions in their detailed chemical bonding structures. The semiconductors of I-III-VI_2 family are isoelectronic with the zinc blende II-VI compound semiconductors. Both zinc blende and chalcopyrite crystallographic structures are sketched in Fig. 1 for comparison.

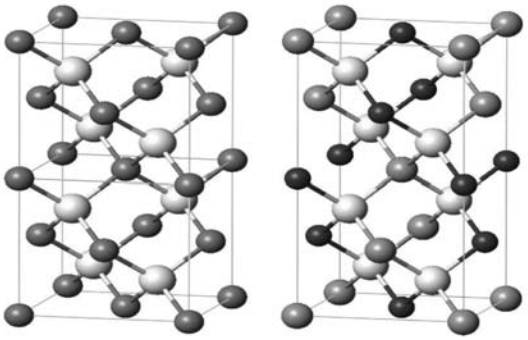

Fig. 1. Zinc blende (left) and chalcopyrite (right) crystallographic structures. **Left:** two unit cells of the zinc blende lattice (dark grey, group II ion; light grey, group II ion). **Right:** one unit cell of chalcopyrite lattice (black, group I ion; dark grey, group III ion; light grey, group VI ion).

From the crystallographic view point, the tetragonal unit cell of chalcopyrite can be regarded as a concatenation of two cubic unit cells of the zinc blende structure stacked on top of each other along the c-axis. The group II ions of the zinc blende structure are alternately replaced by group I transition metal ions and group III ions. Furthermore, the structure suffers a tetragonal distortion, the unit cell is slightly strained in the c-axis direction. According to the following equation the chalcopyrite structure can be decomposed into two sorts of bonds:

$$\text{I-III-VI}_2 = \text{I-VI+III-VI} \tag{4}$$

The macroscopic properties of I-III-VI_2 compounds can be referred to the macroscopic contribution from these two basic structure units I-VI and III-VI connected in an infinite network. For crystals, due to their periodicity, this infinite network can be reduced to a finite network consisting of only a single formula unit; the graph of this network for I-III-VI_2 type compounds is shown in Fig. 2. From this description the formal number of valence electrons can be derived to be used in further calculations of each of the ions. While the number of valence electrons for the group III and group VI ions can be treated as fixed, for the value of a substantial portion of the d electrons of the transitions metal must be formally included into the number of valence electrons. The amount depends on the specific compound. How to treat this d electron problem is one of the key points and one of the most interesting aspects of the current calculations, same is the situation for II-IV-V_2 semiconductors.

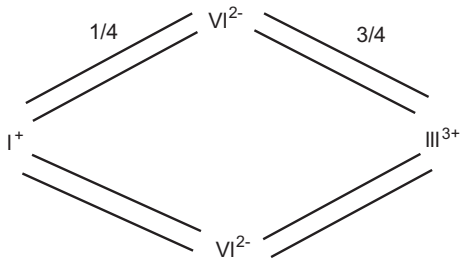

Fig. 2. Bond gap of I-III-VI_2 type ternary semiconductors. Valence of atoms and theoretical bonds are shown.

The average energy gap (E_g) can be decomposed into a heteropolar (E_c) and a homopolar part (E_h). The heteropolar part of (E_c) is related to the ionic bonding and represents the dielectrically screened potential difference between the fields produced by the ion cores of the atoms participating in given bond at bond centre. According to modified Phillips and Van Vechten (PVV) theory, E_h, E_c and E_g are given by the following relations:

$$E_g^2(AC) = E_h^2(AC) + E_c^2(AC) \tag{5}$$

where:

$$E_h(AC) = ar^{-2.5}(AC) \tag{6}$$

and

$$E_c(AC) = be^2\left(\frac{Z_A}{r_A} + \frac{Z_c}{r_c}\right) \exp\left[-K_s \frac{r_A + r_c}{2}\right)] \tag{7}$$

where, *a* and *b* are constants, r(AC) is the interatomic distance between A and C atoms, Z_A, Z_c and r_A, r_c are the valence numbers of electrons, covalent radii of A and C atoms, respectively, and K_s is the Thomas-Fermi screening parameter. The screening factor, as well as the bond length, is related to the effective number of free electrons in valence band. The ionic charge also depends directly on the effective number of free electrons in the valence band. Thus, there must be some correlation between the physical process, which involves the ionic contribution (E_c) to the average energy gap (E_g) and the product to ionic charge of a compound. Several researchers present clear picture on the ionicity and the covalency. The ionic picture involved the electron energy transfer from one atom to another giving rise to the closed-shell ions which interact mainly by Coulomb force and short-range repulsion, while the covalent picture involves sharing of electrons between the atoms instead of charge transfer. In order to determine the crystal ionicity, the first major approach was given by Pauling (1960) based on thermo-chemical effect. Penn (1962) had proposed a theory based on the one-electron model. According to the Penn (1962) model, the Penn gap (E_p) or average energy gaps (E_p) can be evaluated as:

$$E_p = \hbar\omega_p \Big/ \sqrt{\varepsilon_\infty - 1} \quad (8)$$

where, ε_∞ is the dielectric constant and $\hbar\omega_p$ is the valence electron Plasmon energy. Using above relations, we can calculate the Phillips and Van Vechten (1969) and Tubbs (1970) ionicity.

$$f_i = \frac{E_c^2(AC)}{E_g^2(AC)} \quad (9)$$

and

$$f_i = \frac{E_p}{\hbar\omega_p} \quad (10)$$

Resuls and Discussion

The value of homopolar gap (E_h), heteropolar gap (E_c), average gap E_g, Penn gap (E_p) and refractive index (n) are listed in the Table 1-2. The crystal ionicity evaluated from equations (6) and (7) are listed in the Table 2 and compared with the values reported by Reddy *et al*. (1999). These values are in fair agreement with literature ones. Plasmon energy, dielectric constants and Penn gap E_p are also listed in Table 2. It is obvious that the values evaluated by equations (2) and (5) are in close agreement for ternary chalcopyrite semiconductors. The calculated values of refractive index (n) from equation (1) are listed in Table 1 and compared with values reported by Reddy *et al*. (1999). There is an agreement between calculated and reported one. The ionic charges of these materials are the key informations in understanding the optical and electric properties of these compounds. The ionic gap (E_c) and average energy gap (E_g) of these materials is inversely related to the interatomic distance. The product of ionic charges and refractive index of these materials is directly related to interatomic distance and the product of ionic charges.

Table 1. Calculated values of refractive index (n) compared with literature ones

Compounds	Energy gap (E_g) (Gupta and Ravindra, 1980)	Refractive index (n)	
		Present study (Eq. 3)	Experimental (Reddy *et al*., 1999)
$A^IB^{II}C_2^{VI}$			
$CuAlS_2$	9.50	2.40	2.40
$CuAlSe_2$	2.70	2.55	2.60
$CuAlTe_3$	0.90	2.36	3.30
$CuGaS_2$	2.40	2.63	2.67
$CuGaSe_2$	1.70	2.86	2.80
$CuGaTe_2$	1.00	3.27	3.30
$CuInS_2$	1.50	2.95	2.60
$CuInSe_2$	0.96	3.30	2.90
$CuInTe_2$	0.95	3.32	3.40
$AgAlS_2$	3.46	2.35	-
$AgAlSe_2$	2.90	2.50	2.34
$AgAlTe_2$	2.6	2.68	2.53
$AgGaS_2$	2.70	2.55	2.40
$AgGaSe_2$	1.80	2.82	2.80
$AgGaTe_2$	1.10	2.20	3.30
$AgInS_2$	2.00	2.75	2.50
$AgInSe_2$	2.16	2.70	3.36
$AgInTe_2$	0.93	3.33	2.40
$A^{II}B^{IV}C_2^V$			
$ZnSiP_2$	2.10	2.72	3.10
$ZnGeP_2$	1.99	2.76	3.10
$ZnSnP_2$	1.62	2.90	3.10
$ZnSiAs_2$	1.70	2.87	3.30
$ZnGeAs_2$	0.85	3.41	3.90
$ZnSnAs_2$	0.65	3.64	3.10
$CdSiP_2$	2.20	2.70	3.10
$CdGeP_2$	1.72	2.86	3.50
$CdSnP_2$	1.17	3.14	3.50
$CdSiAs_2$	1.55	2.93	3.40
$CdGeAs_2$	0.68	3.60	3.60
$CdSnAs_2$	0.61	3.70	3.70

Table 2. Calculated values of crystal ionicity compared with the literature ones

Compounds	Plasmon energy $\hbar\omega_p$ (Kumar *et al*., 1994)	Dielectric constant $\varepsilon_\infty = n^2$	E_p (eV) Eq. (8)	E_h (eV) Eq. (6)	E_c (eV) Eq. (7)	E_g (eV) Eq. (5)	Ionicity (f_i) Exp. Phillips Eq. (9)	Tubbs Eq. (10)	(Reddy *et al*., 1999)
$A^{I}B^{II}C_2^{VI}$									
$CuAlS_2$	21.70	5.76	9.95	5.08	5.93	7.81	0.58	0.46	0.59
$CuAlSe_2$	20.14	6.50	8.59	4.49	4.97	6.70	0.55	0.43	0.56
$CuAlTe_3$	18.19	11.30	5.67	3.79	3.03	4.85	0.39	0.31	0.16
$CuGaS_2$	20.90	6.92	8.59	5.05	6.03	7.12	0.72	0.41	0.60
$CuGaSe_2$	19.55	8.20	7.29	4.46	3.94	5.95	0.44	0.73	0.56
$CuGaTe_2$	17.95	10.70	5.76	3.70	3.21	4.90	0.43	0.32	0.47
$CuInS_2$	19.34	8.70	6.97	4.52	4.24	6.20	0.47	0.36	0.64
$CuInSe_2$	19.28	10.90	6.13	4.05	3.02	5.05	0.63	0.32	0.61
$CuInTe_2$	17.25	11.02	5.45	3.45	2.92	4.52	0.42	0.32	0.53
$AgAlS_2$	20.13	5.52	9.47	4.46	6.05	7.52	0.65	0.47	-
$AgAlSe_2$	18.80	6.25	8.20	3.98	5.03	6.42	0.61	0.44	0.59
$AgAlTe_2$	17.05	7.18	6.86	3.40	3.67	5.00	0.54	0.40	0.52
$AgGaS_2$	19.90	6.50	8.49	4.37	5.60	7.10	0.62	0.43	0.61
$AgGaSe_2$	18.65	7.95	6.61	3.94	4.60	6.05	0.58	0.35	0.59
$AgGaTe_2$	17.03	10.24	5.60	3.40	3.17	4.65	0.46	0.33	0.51
$AgInS_2$	17.90	7.56	7.48	1.14	4.50	4.10	0.54	0.39	0.61
$AgInSe_2$	19.15	7.30	7.13	3.70	4.53	5.85	0.60	0.40	0.64
$AgInTe_2$	16.30	11.10	5.13	3.16	3.00	4.35	0.48	0.31	0.57
$A^{II}B^{IV}C_2^{V}$									
$ZnSiP_2$	17.46	7.40	6.90	4.96	4.42	6.65	0.44	0.40	0.26
$ZnGeP_2$	17.52	7.62	6.92	4.75	4.03	6.24	0.41	0.40	0.30
$ZnSnP_2$	16.72	8.41	6.14	4.32	3.52	5.57	0.39	0.36	0.32
$ZnSiAs_2$	17.42	8.24	6.47	4.50	3.66	5.80	0.39	0.37	0.18
$ZnGeAs_2$	17.53	11.63	5.38	4.33	1.86	4.72	0.16	0.30	0.22
$ZnSnAs_2$	16.90	12.00	5.12	3.96	2.17	4.52	0.23	0.30	0.33
$CdSiP_2$	16.87	7.30	6.72	4.42	2.44	6.24	0.49	0.40	0.28
$CdGeP_2$	16.93	8.20	6.30	4.30	3.62	5.62	0.41	0.37	0.32
$CdSnP_2$	16.17	9.86	5.43	4.95	3.21	5.09	0.39	0.33	0.44
$CdSiAs_2$	16.90	8.58	6.14	4.06	3.71	5.50	0.45	0.36	0.19
$CdGeAs_2$	17.00	13.00	4.90	3.94	1.89	4.37	0.19	0.29	0.23
$CdSnAs_2$	16.38	30.70	4.60	3.64	1.78	4.05	0.19	0.28	0.36

Conclusion

The values evaluated show a systematic trend and support the validity of the approach. It is also noted that the proposed relations are simpler and widely applicable. It is concluded from the present study that there exists the correlation between energy gap, refractive index and ionicity. This study could act as guide for developing some more general correlations.

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