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Research note

A study of energy gap, refractive index and electronic polarizability of ternary chalcopyrite semiconductors

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Abstract

A simple relation between the optical electronegativity, energy gap, refractive index and electronic polarizability is given for ternary chalcopyrite semiconductors. Energy gap has been evaluated from the optical electronegativity whereas refractive index and electronic polarizability values have been evaluated from the energy gap by proposing a linear relation between them. The calculated values are in fair agreement with the experimental values and earlier researchers. This work highlights the significance of interrelation between these parameters.

Keywords: semiconductors, electronegativity, energy gap, refractive index and electronic polarizability.

1. Introduction

The correlation between refractive index and energy gap of material is of high interest because such studies lead to manifold application. The refractive index and energy gap of semiconductors represent two fundamental physical aspects that characterize their optical and electronic properties. The applications of semiconductors as electronic, optical and optoelectronic devices are very much determined by the nature and magnitude of these elementary material properties. These properties also aid in the performance assessment of band gap engineered structures for continuous and optimal absorption of broad band spectral sources.

In addition, photonic crystals, wave guides, solar cells and detectors require a pre-knowledge of refractive index and energy gap. Application of specific coating technologies [1] include antirefraction coatings and optical filters [2, 3]. The energy gap determines the threshold for absorption of photons in semiconductors. The refractive index in semiconductors is a measure of its transparency to incident spectral radiation. A correlation between these two fundamental properties has a significant bearing on the band structure of semiconductors. The ternary chalcopyrite semiconductors have obtained considerable importance because of their potential application in area of light emitting diodes, non-linear optics, photovoltaic devices and solar cells. The solid solutions of these semiconductors have been used in electro-optic devices [4 - 6]. Their mixed crystals are being used for the fabrication of detectors, lasers, and integrated optic devices such as switches, modulators, filters, etc. These chalcopyrites have many other practical applications in the field of fiber optics, sensors and communication devices. However, in spite of their significant importance some of the physical properties of these compounds have not been fully investigated. Various attempts have been made to correlate the energy gap of chalcopyrite compounds with many other physical parameters [7-12]. The ternary chalcopyrites have recently received considerable attention due to their importance for the development and fabrication of various technological devices. Structurally these compounds are derived from the binary sphalerite structure with slight distortion. These compounds exhibit a high non-linear susceptibility and birefringence which leads to efficient second harmonic generation and phase matching [13, 14]. The opto-electronic properties are the fundamental properties of the material. Chemla [15] and Kumar *et al*. [16 -18] have extended the calculation of electronic polarizabilities for chalcopyrite semiconductors using plasma frequency formalism. The polarizability has also been calculated using Clausius-Mossotti relations. Electronic polarizability of different crystals has been calculated by several authors [19 - 22] using the dielectric theory of Phillips [23 - 27] and Van Vechten [28, 29] and bond charge model of Levine. Large deviation has been observed between the

experimental and estimated values of energy gap, refractive index and electronic polarizability of these compounds. Moreover, all these models utilize many other parameters and involve a complicated theory. The optical electronegativity is a very useful parameter in understanding the nature of chemical bonding and several important physical parameters can be predicted. It has been suggested that a simple model based on the concept of optical electronegativity and some other parameters should be good enough to study the main properties of ionic crystals and semiconductors with use of only few numerical constants. In the present study a simple model has been developed calculating the energy gap, refractive index and electronic polarizability of ternary chalcopyrite semiconductors. The model is based on the fact that there is a strong correlation between the optical electronegativity, energy gap, refractive index and electronic polarizability.

2. Theory

The refractive index is one of fundamental properties of a material because it is closely related to the electronic polarizabilty 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 the material is the key parameter for device design. Based on the concept of dielectric susceptibility, it is possible to relate the dielectric constant of material to the polarizability of atoms or molecules comprising it [30]. Accordingly, The Clausius –Mossotti relation may be written as:

$$\frac{\varepsilon-1}{\varepsilon+2}=\frac{4\pi}{3}\sum N_j a_j \quad , \tag{1}$$

where $\varepsilon, N_j, \alpha_j$ are dielectric constant, number of atoms per unit volume and dielectric polarizability respectively. Lorentz- Lorentz in 1880 describes dielectric constant (ε) and refractive index (n) at optical frequency with the following relation:

$$\sqrt{\varepsilon}=n \ , \tag{2}$$

Moss [31] in 1950 made a proposal on the very general round that all energy levels are in a solid, scaled by factor, $1/\varepsilon_{\text{opt}}^2$ where $\varepsilon_{\text{opt}}=n^2$ the optical dielectric constant. Moss [31] succeeded in systematizing the extensive experimental data on the well-known materials and proposed the following relation:

$$\frac{n^4}{\lambda_g}=77\,\mu\text{m}^{-1}, \tag{3}$$

(n) is the highest frequency refractive index and λ_g is the wave length.

For a class of semiconductors and others, Moss [31] has proposed a relation, which reads as follows:

$$n^4 E_g = 173\,\text{eV}, \tag{4}$$

In 1992, a relation similar to the Moss relation was proposed by Reddy and Anjaneyulu [32]. According to their formula, the relation is:

$$E_g e^n = 36.6, \tag{5}$$

Based on the oscillatory theory, Herve and Vandamme [33] have proposed the following relation, assuming the UV- resonance energy has a constant difference with the energy based gap:

$$n=\sqrt{1+\left(\frac{A}{E_g+B}\right)^2}\ , \tag{6}$$

where $A=13.6\,\text{eV}$ and $B=3.4\,\text{eV}$ are constants.

Duffy [34, 35] has proposed the empirical relation:

$$\Delta x = 0.268 E_g\ , \tag{7}$$

where E_g is the energy gap and Δx is the optical electronegativity.

Using equations (6) and (7), Reddy *et al*. [36] have recently proposed the following relation between (n) and Δx:

$$n=\sqrt{1+\left[\frac{A}{3.72\Delta x+B}\right]^2}\ , \tag{8}$$

where *A* and *B* are constants.

Based on the above correlation the concept of optical electronegativity and its use in estimating, many physico-chemical parameters and the following expression have been obtained between optical electronegativity (Δx) and energy gap (E_g) for ternary chalcopyrite semiconductors:

$$E_g = A\Delta x^B\ , \tag{9}$$

where *A*=3.5 and *B*=0.8 are numerical constants.

Accordingly, the following may be suggested for refractive index (*n*).

$$n=\left[\frac{44}{E_g}\right]^{\frac{1}{3}}, \tag{10}$$

According to the classical theory of dielectric constant, electric polarizibility for a material can be calculated with the help of Lorentz- Lorentz relation:

$$a = 0.395\times10^{24}\times\left[\frac{n^2-1}{n^2+1}\right]\times\frac{M}{d}\,\text{cm}^3\ , \tag{11}$$

where *M* and *d* are molecular weight and density of compounds respectively. Estimated refractive index values from equation (10) are employed in equation (11) and electronic polarizabity values are estimated. It is interesting to investigate the relationship between energy gap (E_g) and electronic polarizability (a). For this purpose, a systematic relationship between these two has been presented. It reads as follows:

$$a = 0.395\times10^{-24}\times[1-0.242(E_g-0.4)^{\frac{1}{2}}]\times\frac{M}{d}\,\text{cm}^3\ , \tag{12}$$

where E_g, *M* and *d* are energy gap (eV), molecular weight (*g*/mol) and density (g/cm^3) of the substances,

Table 1. The calculated values of energy gap and refractive index for ternary chalcopyrite semiconductors.

Compounds	Optical electronegativity	Energy gap E_g(eV)		Refractive index (n)	
	(Δx)	eq. (9)	ref. [37-39]	eq. (10)	refs. [8,11,31]
$CuAlS_2$	0.938	3.32	3.50	2.41	2.40
$CuAlSe_2$	0.723	2.70	2.67	2.59	2.60
$CuAlTe_2$	0.552	2.17	2.06	2.78	3.30
$CuGaS_2$	0.643	2.45	2.43	2.67	2.67
$CuGaSe_2$	0.455	1.86	1.68	2.93	2.80
$CuGaTe_2$	0 268	1.22	1.23	3.37	3.30
$CuInS_2$	0.403	1.69	1.53	3.02	2.60
$CuInSe_2$	0.279	1.26	1.04	3.34	2.90
$CuInTe_2$	0.254	1.16	0.95	3.43	3.40
$AgAlSe_2$	0.683	2.58	2.55	2.63	2.47
$AgAlTe_2$	0.608	2.35	2.27	2.71	2.54
$AgGaS_2$	0.723	2.70	2.60	2.59	2.40
$AgGaSe_2$	0.482	1.95	1.83	2.86	2.80
$AgGaTe_2$	0.294	1.31	1.20	3.29	3.30
$AgInS_2$	0.534	2.11	1.80	2.81	2.50
$AgInSe_2$	0.332	1.45	1.24	3.18	3.32
$AgInTe_2$	0.268	1.22	1.00	3.37	3.40
$ZnSiP_2$	0.562	2.20	2.96	2.77	3.40
$ZnGeP_2$	0.533	2.11	2.34	2.81	3.10
$ZnSnP_2$	0.444	1.82	1.66	2.95	2.90
$ZnSiAs_2$	0.456	1.86	2.12	2.93	2.90
$ZnGeAs_2$	0.308	1.36	1.15	3.25	3.10
$ZnSnAs_2$	0.269	1.22	0.73	3.37	_
$CdSiP_2$	0.656	2.49	2.45	2.66	3.10
$CdGeP_2$	0.461	1.73	1.72	3.00	3.30
$CdSnP_2$	0.313	1.38	1.17	3.24	3.10
$CdSiAs_2$	0.415	1.73	1.55	3.00	3.50
$CdGeAs_2$	0.164	0.82	0.57	3.85	3.40
$CdSnAs_2$	0.069	0.41	0.26	4.85	3.70

respectively. The estimated energy gap (E_g) values from equation (9) are substituted in equation (12) and electronic polarizability values are estimated.

3. Result and discussion

The accuracy of the estimated physical parameters energy gap, refractive index and electronic polarizability mainly depends on the reliability and precision of the electronegativity difference (input data).The proposed relationships between optical electronegativity, energy gap, refractive index and electronic polarizability give an access to study the nature of chemical bonding using the electronegativity concept. It can be observed from the tables that as the electronegativity difference for the groups of semiconductors with common cation decreases with the energy gap, refractive index and electronic polarizability increases. The ionic character can be understood from the proposed relations. Electronegativity difference of the atoms forming a compound and band gap is interrelated. Compounds with the ionic bonding have the largest band gaps and covalent bond have the smallest ones. Electronegativity describes the pre-disposition of an atom to absorb electrons, its units are the square root of bond strength. Thus an atom with higher electronegativity will be more reactive chemically than one with lower electronegativity. When the electronegativities of atoms engaged in covalent bonding are similar, this factor has little influence on bonding. However, when the electronegativity difference of the two species is equal or

Table 2. The calculated values of electronic polarizability of ternary chalcopyrite semiconductors.

Compounds	Molecular weight, M(g/mol)	Density, D(g/cm)	Electronic polarizability, $\alpha \times 10^{-24}$ cm^3				
			Present study eq. (12)	Present study eq. (11)	Reddy et al. ref. [11]	Gupta et al. ref. [19]	Kumar et.al. ref. [16]
$CuAlS_2$	154.65	3.47	10.29	10.84	10.84	6.73	6.62
$CuAlSe_2$	248.45	4.70	13.17	13.68	14.48	10.09	9.02
$CuAlTe_2$	345.73	5.50	16.76	17.17	18.31	17.17	7.37
$CuGaS_2$	197.39	4.35	11.67	12.03	12.27	7.25	7.61
$CuGaSe_2$	291.19	5.56	14.57	14.82	15.73	10.91	10.29
$CuGaTe_2$	388.47	5.99	19.89	19.86	20.09	19.20	11.74
$CuInS_2$	242.49	4.75	14.55	14.72	15.50	8.4	10.59
$CuInSe_2$	336.29	5.77	17.75	17.77	18.26	12.47	12.73
$CuInTe_2$	433.57	6.10	17.89	21.95	22.39	20.86	15.29
$AgAlSe_2$	292.77	5.07	14.60	15.13	16.03	11.31	10.42
$AgAlTe_2$	390.05	6.18	16.44	16.92	18.03	19.35	12.06
$AgGaS_2$	241.71	4.72	12.75	13.25	14.14	8.22	8.46
$AgGaSe_2$	335.51	5.84	15.78	16.08	17.06	12.13	11.35
$AgGaTe_2$	432.79	6.05	21.61	21.64	22.05	20.79	13.17
$AgInS_2$	286.87	5.00	15.42	15.79	17.08	9.04	10.91
$AgInSe_2$	380.61	5.18	19.36	19.46	20.28	13.51	14.69
$AgInTe_2$	447.86	6.12	22.44	22.41	22.98	23.23	16.88
$ZnSiP_2$	155.40	3.39	12.18	12.49	12.12	12.45	10.70
$ZnGeP_2$	199.90	4.17	12.88	13.19	13.60	14.24	11.28
$ZnSnP_2$	246.00	3.16	21.78	21.13	23.38	16.36	13.80
$ZnSiAs_2$	242.20	4.70	14.34	14.58	15.93	18.12	12.89
$ZnGeAs_2$	287.80	5.32	16.21	16.26	16.84	20.52	12.62
$ZnSnAs_2$	333.90	5.53	18.51	18.49	19.24	23.84	14.99
$CdSiP_2$	202.43	4.00	12.94	13.38	14.42	14.34	12.29
$CdGeP_2$	246.94	4.48	15.62	15.83	16.51	15.95	12.88
$CdGeAs_2$	334.83	5.60	19.76	19.40	19.21	23.16	12.15
$CdSnAs_2$	380.93	5.72	24.95	23.21	21.71	26.68	17.32

more than about 0.2 units, small amounts of ionic bonding may take place along with the covalent bonding. Larger electronegativity difference involves the higher degree of ionicity in the bonding. It is probable that perfectly pure covalent bonding normally does not exist in compounds because no two atoms have identical electronegativity, small degree of ionicity is present. After careful examination of crystal structure, it is known that the wurzite structure is more favorable for crystals with larger difference of electronegativity between the two kinds of atoms. In other words, the general tendency is such that the wurzite structure has proven that zinc blende structure has a higher degree of ionicity. The nature of bonding is clearly evident from this discussion.

Estimated physical parameters in the present study are in good agreement with the values reported by different investigators. Several other workers have also estimated these parameters with distinct ideas. But all the methods enumerated in the literature involve many experimental parameters. The main advantage of the present model is the simplicity of the formula, which does not require any experimental data except electronegativity difference of the materials. The empirical relationship proposed in the present study will stimulate basic research in describing the physical characterization of compounds. In most of the cases, the values coincide with the others. Hence it is possible to predict the above parameters of the compounds with the knowledge of only one parameter called electronegativity difference.

4. Conclusion

The computed values of energy gap, refractive index

and electronic polarizability on the basis of the above proposed relations for the ternary chalcopyrite semiconductors are presented in tables (1) and (2). The values of energy gap, refractive index and electronic polarizability in the present study are in good agreement with the available experiment data. The minimum average percentage deviation obtained in the present study indicates the improvement over the previous works and also expresses the equivalence between Lorentz-Lorentz approach and optical electronegativity concept. It is pertinent to mention here that the inclusion of optical electronegativity has a direct bearing on the concept of chemical bonding. Highest optical electronegavity for a material indicates its strength of ionicity. Low optical electronegativity represents its covalency. This work highlights the significance of interrelation between energy gap, refractive index and electronic polarizability.

References

1. N M Ravindra, "*NJIT International memorandum, application specific coaling technology*", New Jersey Institute of Technology (2005).
2. F M Tong, M Nuggehalli Ravindra, and W F Kosonocky, *Opt. Eng*. **36** (1997) 549.
3. N M Ravinder, P Ganapathy, and J choi, *Infrared Phys. Tech*. **50** (2007) 21.
4. J L Shay and J H Wernik, "*Electronic properties and applications*", Pergamon press, New York (1975).
5. L L Kazmerski, *Nuova Cimento* **20** (1983) 2013.
6. S K Deab, A Zunger, *Res. Soc. Conf. Proc*. (1987) 37.
7. R R Reddy, Y NazeerAhmad, K Rama Gopal, P Abdul Azeem, T V R Rao, and P Mallikarjuma Reddy, *Opt. Materials* **14** (2000) 355.
8. R R Reddy *et al*., *Opt. Materials* **22** (2003) 7.
9. S K Goria and P Mehta, *Ind. J. Phys*. **84** (2010) 587.
10. V Kumar and J K Singh, *Ind. Pure Appl. Phys*. **48** (2010) 571.
11. R R Reddy *et al*., *J. Alloys Comp*. **473** (2009) 28.
12. A S Verma and S R Bhardwaj, *Phys. Stat. Sol.* **243** (2006) 2858.
13. D S Chemla, P J Kupecek, D S Robertson, and R S Smith, *Opt. Comm*. **3** (1971) 29.
14. N A Goryunova, L B Zlatkin, and E K Ivanov, *J. Phys. Chem. Solids* **31** (1970) 2557.
15. D S Chemla, *Phys. Rev. Lett.* **26** (1971) 827.
16. V Kumar, G M Prasad, and D Chandra, *Ind. J. pure App. phys*. **32** (1994) 272.
17. V Kumar, *J. Phys. Chem. Solids* **48** (1987) 827.
18. V Kumar, G M Prasad, and D Chandra, *J. Phys. Chem. Solids*, **57** (1996) 503.
19. V Gupta and V K Shrivatava, *J. Phys. Chem. Solids*, **42** (1981) 1079.
20. R R Reddy, M Ravi Kumar, and T V R Rao, *Infrared Phys*. **34** (1993) 99.
21. R R Reddy, Y Nazeer Ahmad, K Rama Gopal, and T V R Rao, *Infrared Phys. Tech*. **39** (1998) 55.
22. B P Singh, V S Beghel, and K S Beghel, *Ind. J. Pure Appl. Phys*. **47** (2009) 793.
23. J C Phillips, *Phys. Rev. Lett*. **19** (1967) 415.
24. J C Phillips, *Phys. Rev*. **166** (1968) 832.
25. J C Phillips, *Rev. Mod. Phys.* **42** (1970) 311.
26. J C Phillips, "*Bonds and Bands in semiconductors*", Academic Press, New York (1973).
27. J C Phillips, *Phys. Rev*. **168** (1986) 905.
28. J A Van Vechten, *Phys. Rev.* **182** (1969) 891.
29. J A Van Vechten, *Phys. Rev.* **187** (1969) 1007.
30. J D Jackson, "*Classical electrodynamics*", Wiley Eastern, New Delhi (1998).
31. T S Moss, *Phys. Stat. Sol*. **131** (1985) 415; T S Moss, *Proc. Phys. Soc*. B **63** (1950) 167.
32. R R Reddy, S Anjaneyulu, *Phys. Stat. Sol.* **174** (1992) K91.
33. P Herve and K L Vandamme, *J. Infrared Phys.* **35** (1994) 609.
34. J A Duffy, *J. Phys.*C: *Solid State Phys.* **13** (1980) 2979.
35. R R Longman, "*Bonding energy levels and bonds in organic solids*", England (1990).
36. Reddy, K Rama Gopal, K Narasimhulu, *Opt. Matter* **31** (2008) 209.
37. W A Harrison, "*Electronic structure and properties of solids*", W H Freeman Co., San Fransisco (1980).
38. N V Joshi, "*Photoconductivity*", Merida Veneznela, Marcel Dekker Inc., New York (1990).
39. C M Wolfe, N Holonyak, G E Stillman, "*Physics properties of semiconductors*", Prentice Hall, New Jersey, (1989).