An Empirical Refractive Index Model of $A^{I}B^{III}C_2^{VI}$ & $A^{II}B^{IV}C_2^{V}$ Type Ternary Chalcopyrite Semiconductors

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***Abstract*- In this paper a simple empirical relation has been proposed to estimate the refractive-index of I-III-VI2 and II-IV-V2 type chalcopyrite semi-conductors. This relation is based on the principal quantum number of atoms of compounds and the electro-negativities of the constituent atoms. The computed values of refractive-index from the present relation are found to be in good agreement with the known values.**

Index Terms- Refractive-index, Principal quantum number, Electronegativity.

I. INTRODUCTION

Ternary chalcopyrite with the general formula $A^{I}B^{III}C_2^{VI}$ & $A^{II}B^{IV}C_2^{V}$ are of considerable interest because of their potential optoelectronic applications as solar converters, non-linear optical (NLO) devices, light emitting diodes (LED) and detectors. Their mixed crystals are being used for fabrication of detectors, lasers and integrated optic devices such as switches, modulators, filters etc[1-5].

Moss et al. and several other researchers have developed various theories and calculated refractive-index of semiconductor compounds. In practice these theories require elaborate computation and have been developed only for the limited semi-conductors. Therefore, I thought it would be of interest to give an alternative explanation for the refractive-index of semi-conductors. In the proposed relation only two parameters - electro negativity and principal quantum number of valence electrons in atom forming the compounds are required as input to calculate refractive-index of ternary chalcopyrite compounds and the methods turns out to be widely applicable. The results obtained from the present calculation are found in good agreement with the previously calculated results.

II. THEORY

Refractive-index is one of the physico-mechanical properties which not only characteristics the state of the material under but also gives information on some deeper specific features of the materials such as the character of the chemical bonding. Many theoretical approaches have been reported to determine the refractive-index of solids.

Lorentz in 1950 proposed the relation for refractive index of semi-conductors as,

$$n = \sqrt{\varepsilon}$$

where ε is di-electric constant.

In 1950 Moss[6] predicted the first ever relation between the refractive index and energy gap of ternary chalcopyrite crystals. The relation is as,

$$n^4 E_g = 95\ e^V \quad \text{.....(1)}$$

where n and Eg are refractive index and energy gap respectively.

In 1992 Reddy et al. proposed the relation between refractive index(n) and energy gap(Eg) for ternary chalcopyrite crystals as,

$$E_g e^n = 36.6\ e^V \quad \text{... (2)}$$

The model of Herve and vandemme[7] given as:

$$n^2 = 1 + \left(\frac{A}{E_g + B}\right)^2 \quad (3)$$

where A is the hydrogen ionization energy equal to 13.6eV and B =3.4eV is a constant to be the difference between UV resonance energy and band gap energy and Eg is energy gap.

The model of Reddy *et al*[8]. given as:

$$n^2 = \left(\frac{12.417}{E_g - 0.365}\right) \quad \text{... (4)}$$

Equation (4) is the modified form of the original Moss equation.

The model of Ravindra *et al*[9]. given as:

$$n = 4.084 + \beta E_g \quad \text{.. (5)}$$

where $\beta = -0.62\ eV^{-1}$.

The model of Anani *et al*[01]. given as:

$$n^4 = 1 + \frac{A}{{E_g}^2} \quad \text{.....(6)}$$

where A = 40.8 $A = 40.8e^V$.

The model of Kumar and Singh[11] given as:

$$n = KE_g{}^{c} \quad .(7)$$

where K = 3.3668 and C = −0.32234 are the constants. They used simulation software and simulated experimental values of energy gap and refractive index and obtained the relation between n and Eg.

The model of Ahmad and Haq[12] given as:

$$n = (\frac{44}{E_g})^{1/3} \quad (8)$$

where n is the refractive index and Eg is the energy gap.

Tripathy[13] fitted an exponential empirical formula to the experimental values of refractive index and energy gap of some elemental and binary semiconductor over a wide range of energy gap ranging from low value of Eg= 0.1eV to a reasonably high value Eg = 8.5 eV.

The proposed relationship for those data is:

$$n = n_0 + n_1 e^{(\frac{-E_g}{\mu})} \ldots(9)$$

The parameters of the above relation for the best fit are found to be n_0 = 1.65752 ± 0.14605, n_1 = 3.78368 ± 0.21302, and μ = 1.85447 ± 0.25777eV. However, in order to provide the formula to a better shape, equation (9) can be rewritten as:

$$n = n0\ [1 + \alpha e^{-\beta Eg}\ ] \quad (10)$$

The new parameters α, β and n_0 appearing in the above equation are adjusted so as to get good agreement with the experimental values of elemental and binary semiconductors over a wide range of energy gap. The parameters of the modified relation are n_0 = 1.73, α = 1.9017 and $\beta = 0.539(eV)^{-1}$.

I have studied all the above relations proposed by different researchers for the estimation of refractive-index of ternary chalcopyrite structure solids and motivated to explore a new alternative empirical relation to estimate the refractive-index of the solids. Most of the above relations require highly complex mechanism. In this research work, I have presented an alternative method for the estimation of refractive-index of ternary chalcopyrite structure solids which is based on only Microsoft-excel software and scientific computation.

The above-studied relations reveal that refractive-index of any material depends on the volume of its constituent atoms, micro-hardness and bulk-modulus etc. The volume of the ternary chalcopyrite is related to its specific structure. The structure of ternary chalcopyrite is body center tetragonal (bct). The deformation of the body center tetragonal structure is correlated with three lattice parameter a, c and u. These parameters are optimized through minimization of the total energy and accordingly refractive-index is estimated. The measurement of stiffness of the crystal is related to deformation produced in the crystal. The anisotropic strain of tetragonal structure is reflected by tetragonal deformation (2-c/a).This will also lead to a change in bond length ($R_{AC} \neq R_{BC}$) which reveals anion displacement. This whole scenario will change the bond length and bond strength of the compounds. In order to take all these into account and to define the ground state property of ternary chalcopyrite solids, I have used two parameters, one parameter is the electronegativity value which is the tendency of an atom to attract electrons to itself during the formation of bonds, and another parameter is the principal quantum number. The longer the distance between the valence electrons and nuclei, the larger will be the principal quantum number. This would show larger electronic polarizability and hence higher micro-hardness and bulk modulus and this leads higher refractive-index. Therefore, electronegativity and principal quantum number, both are assumed to be correlated with the nature of chemical bonding and predicting refractive-index of ternary chalcopyrite structure solids.

For ternary chalcopyrite of I-III-VI_2 and II-IV-V_2 types, graphs has been plotted between refractive-index and the ratio of average principal quantum number of atoms constituting compounds and electronegativity of atoms. Fig.1 shows the variation for of I-III-VI_2 and Fig.2 shows the variation for II-IV-V_2. In this case, least square fitting method has been used.

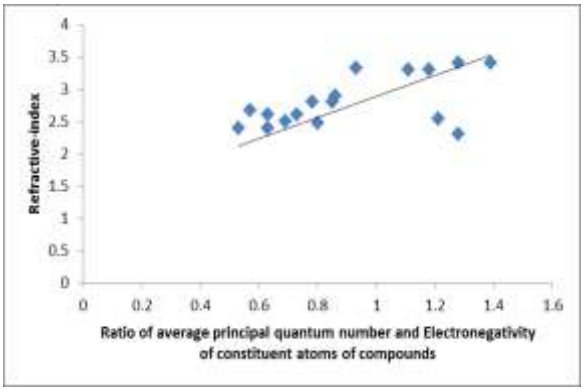

Fig.1: Plot of refractive-index Vs Ratio of average principal quantum number and Electronegativity of constituent atoms of compounds for I-III-VI2 .

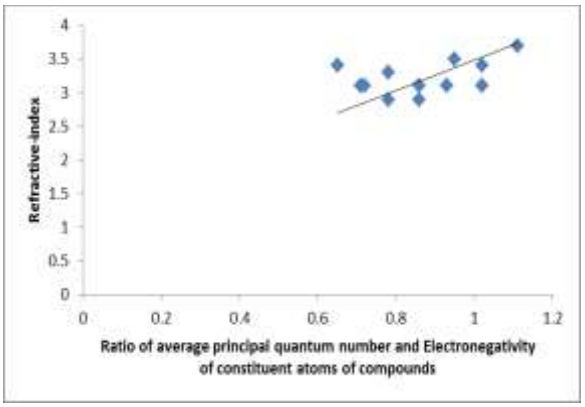

Fig.2: Plot of refractive-index Vs Ratio of average principal quantum number and Electronegativity of constituent atoms of compounds for II-IV-V_2.

From the figures it is found that refractive-index and the ratio of average principal quantum number of atoms constituting compounds and electronegativity of atoms are exponentially related. Therefore the effectiveness of least square fitting is reliable and the normal mathematical expression between refractive-index and the ratio of average principal quantum number of atoms constituting compounds and electronegativity of atoms is given in equation (11).

For ternary chalcopyrite structure solids, the refractive-index is assumed to be co-related to the contribution of three atoms A,B and C_2. Let $\eta_{av} = \frac{(\eta_A+\eta_B+2\eta_C)^{1/4}}{4}$ is the average principal quantum number of the four constituents' atoms in ABC_2.

The refractive-index of ternary chalcopyrite semi-conductors using the graphs can be expressed as-

$$n = \propto \left[\frac{\eta_{av}}{(\chi_A\chi_B)^{\frac{1}{4}}\ (\chi_C)^{1/2}}\right] + \beta \qquad (11)$$

where $\alpha = 1.6378$ and $\beta = 1.25$ for I-III-VI_2 type semiconductors and $\alpha = 2.2336$ and $\beta = 1.25$ for II-IV-V_2 type semi-conductors.

III. RESULTS AND DISCUSSION-

The refractive-index of I-II-VI_2 and II-IV-V_2 type chalcopyrite structure solids is estimated using Equation (11). In Table-1, the estimated values of refractive-index for I-II-VI_2 and in Table-2 the estimated values of refractive-index for II-IV-V_2 are listed along with the results of earlier researchers. It is observed that the calculated values are in better agreement with the experimentally reported values and values estimated by other researchers

Table-1: Refractive-index of I-III-VI_2 type chalcopyrite semiconductors-

Compounds	Calculated from Eq.(11)	Eq.[1]	Eq.[3]	Eq.[7]	Eq.[8]	Eq.[4]	Eq.[6]	n [16-17]
$CuAlS_2$	2.11	2.28	2.21	2.25	2.33	1.99	1.44	2.40
$CuAlSe_2$	2.44	2.44	2.45	2.45	2.55	2.32	1.61	2.60
$CuAlTe_2$	3.06	2.61	2.68	2.67	2.78	2.71	1.81	3.30
$CuGaS_2$	2.18	2.50	2.54	2.53	2.63	2.45	1.68	2.67
$CuGaSe_2$	2.52	2.74	2.86	2.85	2.97	3.07	1.98	2.80
$CuGaTe_2$	3.18	1.06	3.10	3.15	3.30	3.79	2.30	3.30
$CuInS_2$	2.28	2.81	2.93	2.94	3.06	3.27	2.07	2.60
$CuInSe_2$	2.65	3.09	3.22	3.33	3.48	4.29	2.50	2.90
$CuInTe_2$	3.34	3.16	3.28	3.42	3.59	4.61	2.61	3.40
$AgAlS_2$	2.21	-	-	-	-	-	-	-
$AgAlSe_2$	2.56	2.47	2.50	2.49	2.58	2.38	1.64	2.47
$AgAlTe_2$	3.23	2.54	2.60	2.59	2.69	2.55	1.73	2.54
$AgGaS_2$	2.28	2.46	2.48	2.47	2.57	2.36	1.63	2.40
$AgGaSe_2$	2.64	2.68	2.79	2.77	2.89	2.91	1.91	2.80
$AgGaTe_2$	3.34	2.98	3.12	3.18	3.32	3.86	2.33	2.30
$AgInS_2$	2.38	2.70	2.80	2.79	2.90	2.94	1.92	2.50
$AgInSe_2$	2.77	2.96	3.10	3.14	3.29	3.77	2.29	3.32
$AgInTe_2$	3.52	3.12	3.25	3.37	3.53	4.42	2.54	3.40

Table-2: Refractive-index of II-IV-V_2 type chalcopyrite semiconductors

Compounds	Calculated from Eq.(11)	Eq.[1]	Eq.[3]	Eq.[7]	Eq.[8]	Eq.[4]	Eq.[6]	n[16-17]
$ZnSiP_2$	2.70	2.38	2.36	2.37	2.46	2.19	1.54	3.40
$ZnGeP_2$	2.83	2.52	2.57	2.56	2.66	2.51	1.71	3.10
$ZnSnP_2$	2.99	2.75	2.87	2.86	2.98	3.10	1.99	2.90
$ZnSiAs_2$	3.17	2.59	2.66	2.64	2.75	2.66	1.78	2.90
$ZnGeAs_2$	3.32	3.02	3.15	3.22	3.37	3.98	2.38	3.10
$ZnSnAs_2$	3.52	3.38	3.44	3.73	3.92	5.83	2.91	3.10
$CdSiP_2$	2.85	2.50	2.53	2.52	2.62	2.44	1.67	3.10
$CdGeP_2$	2.99	2.73	2.84	2.83	2.95	3.03	1.96	3.30
$CdSnP_2$	3.17	3.00	3.14	3.20	3.35	3.93	2.36	3.10
$CdSiAs_2$	3.37	2.80	2.92	2.92	3.05	3.24	2.06	3.50
$CdGeAs_2$	3.52	3.59	3.57	4.04	4.26	7.78	3.35	3.40
$CdSnAs_2$	3.72	4.37	3.85	5.20	5.53	-	4.96	3.70

It is clear from the tables that II-IV-V2 type ternary chalcopyrite solids show greater refractive-index than I-III-VI2 type chalcopyrite solids.

IV. CONCLUSION

It is clear from the above calculations that refractive-index of ternary chalcopyrite semiconductors depend on principal quantum number and electronegativity of the constituting atoms of the compounds. It is evident from the above relation, that no experimental data is essential for the determination of refractive-index of ternary chalcopyrite compounds. Just by knowing electronegativity and principal quantum number of atoms, one can easily determine the refractive-index of ternary chalcopyrite compounds from the above relation.

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