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AN EMPIRICAL MICRO-HARDNESS MODEL OF $A^{I}B^{III}C_2^{VI}$ & $A^{II}B^{IV}C_2^{V}$ TYPE TERNARY CHALCOPYRITE SEMICONDUTORS.

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ABSTARCT

In this paper a simple empirical relation has been proposed to estimate the Micro-hardness of I-III-VI_2 and II-IV-V_2 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 Micro-hardness from the present relation are found to be in good agreement with the known values.

Index Terms- Micro-hardness, Principal quantum number, Electronegativity.

I. INTRODUCTION-

Ternary chalcopynites 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]. In spite of their potential applications, elastic properties of I-III-VI_2 and II-IV-V_2semi-conductors are still not sufficiently studied. The elastic properties such as micro hardness, bulk modulus etc. of these semi-conductors have been studied experimentally and theoretically.

Samanta et al.and several otherresearchers have developed various theories and calculated micro-hardness 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 micro-hardness 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 micro-hardness 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

The ground state properties such as micro-hardness, bulk modulus etc. are much important physical quantities responsible for mechanical strength of the bonds in ternary chalcopyrite semi-conductors. Micro-hardness of a crystal is its capacity to resist indentation. Hardness is generally related to the elastic and plastic deformation characteristics of the solid materials. A strictly scientific definition of micro-hardness has not yet been given. The reason for this is that micro-hardness depends on many factors. Due to this reason a wide number of different methods of micro-hardness measurement have been developed. Micro-hardness 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 micro-hardness of solids.

According to Samanta et al.[6]microhardness(H) I-III-VI_2 and II-IV-V_2 type semiconductors may be expressed as-

$$H = H_B\left(\frac{B}{B-V}\right)\left(\frac{1}{P}\right)^{1/2}\left(\frac{1}{d^2}\right)\left(\frac{e_a e_b}{e^2}\right)\left(1-\frac{f_i}{F_i}\right)\left(\frac{T_m}{T}\right) \quad . \qquad \text{.....(1)}$$

where H_B is a numerical constant with the unit of 10^{-14}kg. B is the limiting number of band states per metal atom of interacting set of atoms, V is the number of valance electrons per atom contributing to binding, P is the mean periodicity of atom, d is the effective nearest neighbour distance; $e_a$and e_b are valence numbers of anion and cation, e is the valence of pure covalent crystals, f_i is the mean value of iconicity of A-C and B-C bonds in ternary chalcopyrites and F_i is the critical iconicity.

Gorai et al[7] proposed the following relation for microhardness,

$$H = C(\hbar w_p) - D. \qquad \text{.....(2)}$$

where C and D are constants. The values of C and D are 20.333 and 130.86 for $A^IB^{III}C_2{}^{VI}$&271.64 and 3560.6 for $A^{II}B^{IV}C_2{}^{V}$ type semiconductors.

Kumar et al.[8] have proposed the following equation for the calculation of micro-hardness of $A^{II}B^{VI}$& $A^{III}B^{V}$tetrahedral semiconductors-

$$H = K_1(\hbar w_p) - K_2 \qquad \text{.....(3)}$$

where K_1 and K_2 constants. The numerical values of these constants for $A^{II}B^{VI}$semiconductors are 0.42 and 4.97 & for $A^{III}B^{V}$ semiconductors are 2.19 and 26.82 respectively.

Reddy et al. [9]proposed the following relation,

$$H(GPa) = K_1 e^{k_2 n} - K_3 \qquad \text{.....(4)}$$

where K_1,K_2 and K_3 are constants.

I have studied all the above relations proposed by different researchers for the estimation of micro-hardness of ternary chalcopyrite structure solids and motivated to explore a new alternative empirical relation to estimate the micro-hardness 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 micro-hardness of ternary chalcopyrite structure solids which is based on only Microsoft-excel software and scientific computation.

The above-studied relations reveal that micro-hardness of any material depends on the volume of its constituent atoms, bond length, charge density, Plasmon energy, the lattice constant 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 micro-hardness 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, thelarger will be the principal quantum number. This would show larger electronic polarizability and hence higher micro-hardness. Therefore, electronegativity and principal quantum number, both are assumed to be correlated with the nature of chemical bonding and predicting elastic property like micro-hardness of ternary chalcopyrite structure solids.

For ternary chalcopyrite of I-III-VI_2 and II-IV-V_2 types, graphs has been plotted between micro-hardness (H) 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.

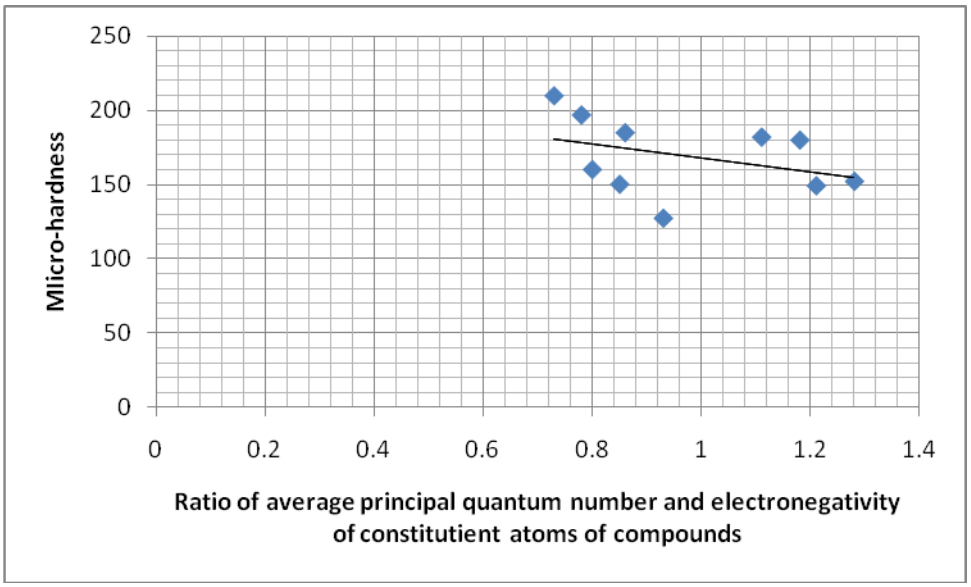

Fig.1: Plot of Micro-hardness Vs Ratio of average principal quantum number and Electronegativity of constituent atoms of compounds for II-III-VI_2 .

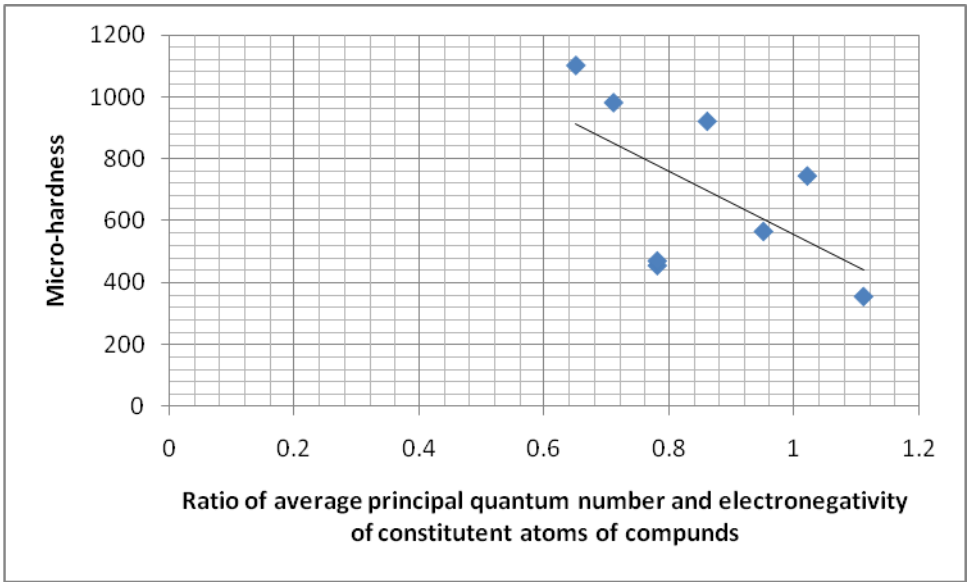

Fig.2: Plot of Micro-hardness Vs Ratio of average principal quantum number and Electronegativity of constituent atoms of compounds for II-IV-V_2.

From the figures it is found that Micro-hardness 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 Micro-hardness and the ratio of

average principal quantum number of atoms constituting compounds and electronegativity of atoms is given in equation(5).

For ternary chalcopyrite structure solids, the Micro-hardness 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 Micro-hardness(H) of ternary chalcopyrite semi-conductors using the graphs can be expressed as-

$$H = \propto \left[\frac{\eta_{av}}{(\chi_A\chi_B)^{\frac{1}{4}}(\chi_C)^{1/2}}\right] + \beta \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

where $\alpha = -47.21$ and $\beta = 215.14$ for I-III-VI_2 type semiconductors and $\alpha = -1183.48$ and $\beta = 1759.22$ for II-IV-V_2 type semi-conductors.

III. RESULTS AND DISCUSSION-

The Micro-hardness of I-II-VI_2 and II-IV-V_2 type chalcopyrite structure solids are estimated using equation(5). In Table-1, the estimated values of micro-hardness for I-II-VI_2 and in Table-2 the estimated values of micro-hardness 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. From the tables it is clear that $CuAlS_2$ has the highest value of micro-hardness in I-III-VI_2 type semiconductors and $ZnSiP_2$ has the highest value of micro-hardness in II-IV-V_2 type semi-conductors.

Table-1 : Micro-hardness (in Kg/mm^2) of I-III-VI_2 type chalcopyrite semiconductors-

Compounds	Calculated from Eq.(5)	Expt.[10]	Reported[7]	Reported[6,11]
$CuAlS_2$	190.11		219.88	216,250
$CuAlSe_2$	180.67	210	191.31	228,226
$CuAlTe_2$	162.73	182	164.57	210,225
$CuGaS_2$	188.22		220.45	245,230
$CuGaSe_2$	178.31	197	192.80	210,197

$CuGaTe_2$	159.42	180	160.00	185,240
$CuInS_2$	185.39		196.96	140,140
$CuInSe_2$	174.53	185	175.96	141,160
$CuInTe_2$	154.70	152	146.97	140,166
$AgAlS_2$	187.28			
$AgAlSe_2$	177.36	160	177.38	135,176
$AgAlTe_2$	158.00	149	163.98	142,167
$AgGaS_2$	185.39		196.46	130,175
$AgGaSe_2$	175.00	150	178.18	124
$AgGaTe_2$	154.70		146.09	142,166
$AgInS_2$	182.56			
$AgInSe_2$	171.23	127	158.53	82,102
$AgInTe_2$	149.51			

Table-2 :Micro-hardness (in Kg/mm^2) of II-IV-V_2 type chalcopyrite semiconductors-

Compounds	Calculated from Eq.(5)	Expt.[10]	Reported[7]	Reported[6,11]
$ZnSiP_2$	989.96	1100	1061.35	1065,900
$ZnGeP_2$	918.95	980	958.94	770,635
$ZnSnP_2$	836.10	455	663.40	500,530
$ZnSiAs_2$	741.42	920	808.72	890,820
$ZnGeAs_2$	658.58	680	694.09	680,630

$ZnSnAs_2$	552.07	744	466.46	445,430
$CdSiP_2$	907.11		838.33	765,730
$CdGeP_2$	836.10	470	654.43	515,470
$CdSnP_2$	741.42			
$CdSiAs_2$	634.91	565	609.07	640,615
$CdGeAs_2$	552.07		486.29	490,470
$CdSnAs_2$	445.55	335	267.35	315,310

It is clear from the tables that II-IV-V_2 type ternary chalcopyrite solids show greater Micro-hardness than I-III-VI_2 type chalcopyrite solids. It is evident from the tables that higher the Bulk-modulus means higher the Micro-hardness.

IV. CONCLUSION-

It is clear from the above calculations that Micro-hardness 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 Micro-hardness of ternary chalcopyrite compounds. Just by knowing electronegativity and principal quantum number of atoms, one can easily determine the Micro-hardness of ternary chalcopyrite compounds from the above relation.

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