Determination of Debye Temperature and Debye-Waller Factor of $A^{i}B^{iii}C_2^{vi}$ & $A^{ii}B^{iv}C_2^{v}$ Type Chalcopyrite Semi-Conductors

Ajay Kumar Sharma
Assistant Professor, B.C.College, Asansol, Research Scholar, JRU, Ranchi

***Abstract*- For more than 30 years, chalcopyrite semi-conductors with the forms AIBIIIC2VI & AIIBIVC2V have attracted much attention due to their potential applications in non-linear optical devices, detectors, solar cells etc. Numerous researchers have proposed a numbers of models to study the mechanical, electronic, chemical and optical properties of these types of solids. In the present work a simple empirical model has been proposed to estimate the Debye temperature (ΘD) of ternary chalcopyrite structure solids of AIBIIIC2VI & AIIBIVC2V type from the electro-negativities of the constituent atoms and the principal quantum number of atoms of the compounds. The empirical relation is based on the chemical bond theory. The Debye-Waller factors for the ternary chalcopyrite semi-conductors are determined from the calculated values of Debye Temperature.**

Index Terms- Debye temperature, Ternary Chalcopyrite, Debye-Waller Factor, Electronegativity, principal quantum number

I. INTRODUCTION

Chalcopyrite compounds can be classified in two broad categories. The group of compounds under first category is called ternary chalcogenides and are represented by AIBIIIC2VI where A=Cu, Ag; B=Al, Ga, In , Tl and C= S, Se, Te. These groups of compounds are isoelectronic with the zinc blende AII-BVI compound semiconductors. Second group of compounds are named as ternary pnictide's and are represented by AIIBIVC2V where A=Zn,Cd; B= Si, Ge, Sn, and C= P, As , Sn. This group of compounds are iso-electronic with the AIII-BV compound semiconductors. Chalcopyrite semiconductors have potential applications in the fields of light emitting diodes, photo-voltaic devices, solar cells and non-linear optics. The solid solutions of these semi-conductors have been used for fabrication of detectors, lasers and integrated optic devices such as switches, modulators, and filters etc1-29. In spite of their numerous applications, their many fundamental properties are less investigated- among them, the lattice vibrational properties are one.

The Debye temperature (ΘD) of material is a suitable thermodynamic quantity to describe several phenomena of solid-state physics which are associated with lattice vibrations. It is naturally depends on several other quantities, such as the pressure, elastic constants, and other thermal quantities, such as specific heat and lattice thermal conductivity. The development of new optoelectronic materials depends mostly on the materials engineering at a practical level, and also on a good understanding of the properties of materials. Knowledge of different thermodynamic properties such as Debye temperature helps engineers in the improvement of the manufacturing of the semiconductor devices. And due to technological importance of AIBIIIC2VI & AIIBIVC2V semiconductors, several experimental and theoretical works on their electronic, optical, mechanical and thermal properties were published. The present work aims to establish simple empirical expression for Debye temperature of the ternary chalcopyrite compounds. 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 Debye temperature of ternary chalcopyrite compounds and the method turns out to be widely applicable. The results obtained from the present calculation are found in good agreement with the previously calculated results. The Debye-Waller factors are determined with the help of calculated values of

Debye temperature and mean square displacements of the ternary chalcopyrite solids.

2. THEORY

In Debye theory, the Debye temperature is the temperature of a crystal's highest normal mode of vibration i.e. the highest temperature that can be achieved due to a single normal vibration. The Debye Temperature is given by Debye as,

$$\theta_D = \frac{h\vartheta_m}{k} \quad \text{.....(1)}$$

where h is Planck's constant, k is Boltzmann constant and υ_m is the Debye frequency.

Kumar et al[30]. proposed a relation for Debye temperature of ternary chalcopyrite crystals as,

$$\theta_D = K_1 \left[(M)^{-\frac{1}{2}} (V)^{\frac{1}{6}} \left(\hbar\omega_p\right)^{1.1666}\right] - \text{.....(2)}$$

where K_1 and K_2 are two empirical parameters, slightly depend on the nature group of material, M is the mean atomic weight, $(\hbar\omega_p)$ is Plasmon energy, and V is the mean atomic volume.

Sheba et.al[31]. proposed a relation for Debye temperature of ternary chalcopyrite semiconductors based on interionic separation and reduced mass. The relation is as follow,

$$\theta_D = \frac{h}{2\pi k_B}\sqrt{\frac{A}{\mu}} \quad \text{...} \quad (3)$$

where $A=3r_0K$, h= Planck's constant, k_B=Boltzmann constant, μ=reduced mass, r_0=inter-ionic separation distance and K= Bulk modulus.

Blackmann et.al[32]. establish a relation for Debye temperature of ternary chalcopyrite solids as,

$$\theta_D = \frac{h}{2\pi k_B}\sqrt{\frac{5A}{6\mu}} \quad \text{.....} \quad (4)$$

Reddy et.al[33]. modified the Sheba et.al.'s relation as,

$$\theta_D = \frac{h}{2\pi k_B}\sqrt{\frac{A}{\mu}} + 128.587 \quad \text{.....} \quad (5)$$

for I-III-VI_2 type semiconductors.

$$\theta_D = \frac{h}{2\pi k_B}\sqrt{\frac{A}{\mu}} + 177.299 \quad \text{.....} \quad (6)$$

for II-IV-V_2 type semiconductors.

I have studied all the above relations proposed by earlier researchers for the estimation of Debye temperature of ternary chalcopyrite structure solids and motivated to explore new alternative empirical relation to estimate the Debye temperature of the solids. Most of the above relations require commercial computer code and high-speed computer with more memory for running the program of these relations for finding the result. In this research work, I have presented an alternative method for the estimation of Debye temperature of ternary chalcopyrite structure solids using a scientific calculator and Excel software. This is quite easy and economical for finding the trends in physical and chemical properties in solid state material science research.

For I-III-VI2 and II-IV-V2 type chalcopyrite semi-conductors, graphs (fig.1 and fig.2) has been plotted between Debye temperature and the ratio of average principal quantum number of atoms constituting compounds and electro-negativity of atoms. In this case least square fitting method has been used.

Figure.1: Graph between Debye temperature and ratio of average value of principal quantum number and electronegativity of constituting atoms of compound I-III-VI2.

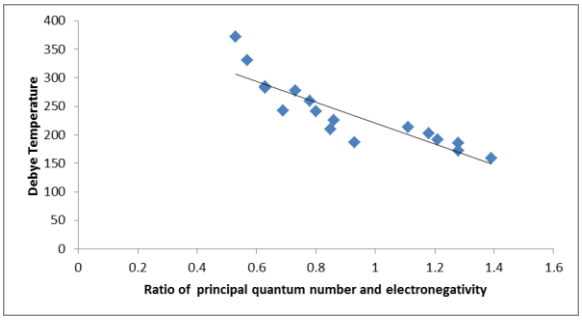
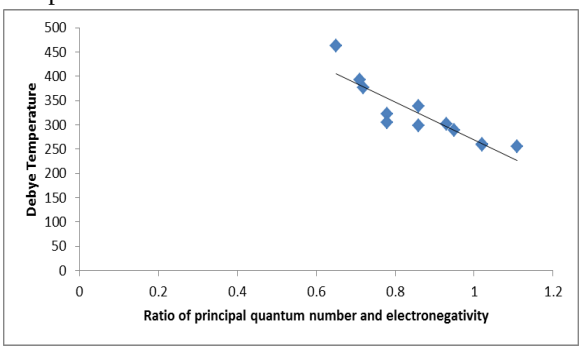


Figure.2: Graph between Debye temperature and ratio of average value of principal quantum number and electronegativity of constituting atoms of compound II-IV-V2.



The graph shows that Debye temperature is linearly related with the ratio of principal quantum number and electro-negativity in both types of ternary chalcopyrites. Thus this variation can be used to derive an empirical relation for the determination of Debye temperature of the compounds. For ternary chalcopyrites structure solids, the Debye temperature 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 Debye temperature of ternary chalcopyrite semi-conductors using the graphs can be expressed as-

$$\theta_D = \propto \left[\frac{\eta_{av}}{(\chi_A\chi_B)^{\frac{1}{4}}\ (\chi_C)^{1/2}}\right] + \beta \quad \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

where $\alpha = -3.996958306958878$ and $\beta = 18.705438804833044$ for I-III-VI_2 type semiconductors and $\alpha = -5.309488297383955$ and $\beta = 20.291371615419713$ for II-IV-V_2 type semi-conductors.

Now Debye-Waller factor at any temperature T is calculated using the relation,

$B_{DWF} = 8\pi^2 < u^2 >$

where $<u^2>$ is the mean square displacement at temperature T. The value of $<u^2>$ is calculated using the relation,

$$< u^2 >= \frac{9h^2T}{4\pi^2 m k_B {\theta_D}^2}$$

3. RESULTS AND DISCUSSION:

The Debye temperature of I-II-VI2 and II-IV-V2 type chalcopyrite structure solids is estimated using Equation(8). In Table-1, the estimated values for I-II-VI2 and in Table-2 estimated values for II-IV-V2 are listed. It is observed that the calculated values are in better agreement with the other reported values.

Table-1: Debye temperature and Debye-Waller factor of I-III-VI2 type chalcopyrite semiconductors-

Compounds	Calculated from Eq.(8)	Debye-Waller factor
$CuAlS_2$	306.66	0.47
$CuAlSe_2$	269.91	0.54
$CuAlTe_2$	200.09	0.66
$CuGaS_2$	299.31	0.47
$CuGaSe_2$	260.73	0.52
$CuGaTe_2$	187.23	0.66
$CuInS_2$	288.29	0.51
$CuInSe_2$	246.03	0.60
$CuInTe_2$	168.86	0.69
$AgAlS_2$	295.63	0.60
$AgAlSe_2$	257.05	0.72
$AgAlTe_2$	181.72	0.72
$AgGaS_2$	288.10	0.54
$AgGaSe_2$	247.68	0.69
$AgGaTe_2$	168.86	0.80
$AgInS_2$	277.26	0.60
$AgInSe_2$	233.17	0.78
$AgInTe_2$	148.65	0.86

Table-2: Debye temperature and Debye-Waller factor of II-IV-V2 type chalcopyrite semiconductors-

Compounds	Calculated from Eq.(8)	Debye-Waller factor
$ZnSiP_2$	405.46	0.52
$ZnGeP_2$	382.14	0.54
$ZnSnP_2$	354.93	0.57
$ZnSiAs_2$	323.84	0.61
$ZnSeAs_2$	296.63	0.65
$ZnSnAs_2$	261.65	0.64
$CdSiP_2$	378.25	0.68
$CdGeP_2$	354.93	0.67
$CdSnP_2$	323.84	0.72
$CdSiAs_2$	288.86	0.69
$CdGeAs_2$	261.65	0.54
$CdSnAs_2$	226.67	0.62

4. CONCLUSION

It is evident from the above relation, that no experimental data is essential for the determination of Debye temperature of ternary chalcopyrite compounds. Just by knowing electronegativity and principal quantum number of atoms, one can easily determine the Debye temperature of ternary chalcopyrite compounds from the above relation.

The Debye-Waller factor of a crystal is helpful in understanding many aspects of the binding in the crystal as well as explaining the phenomena of melting and phase transition. Also it plays an important role in the crystal structure determination by X-ray or neutron diffraction. In the present work, Debye-Waller factor s of the ternary chalcopyrites calculated and they can help to understand the above said phenomena of those materials.

REFERENCES

[1] Shay J L, Wernic J H 1975 Ternary chalcopyrite semiconductors growth, in: Electronic properties and application, pergamon press, Newyork
[2] Kazmerski L L, 1983 NuovoCimento 20 2013
[3] Deab S K and Zunger A, 1987 Ternary Multinary Compounds.Mater.Res.SocConf.Proc.37
[4] Yan C and Xue D 2008 Funct.Mater.Lett.1 37
[5] Zhu Y 2008 Funct.Mater.Lett.1239.

[6] J C Phillips Bonds and Bands in Semiconductors (New York:Academic Press) (1973)
[7] J C Phillips and Van Vechten Phys. Rev. B2 2147 (1970)
[8] J C Phillips and Van Vechten Phys. Rev. 183 709 (1969)
[9] J A VanVechten Phys. Rev. B1 3351 (1970)
[10] J A VanVechten Phys. Rev. 182 891 (1961)
[11] J A VanVechten Phys. Rev. 187 1007 (1969)
[12] B F Levine Phys. Rev. B7 2591 (1973)
[13] J A VanVechten Phys. Rev. 7 2600 (1973)
[14] J A VanVechten J. Chem. Phys. 59 1463 (1973)
[15] J A VanVechten Phys. Rev. Lett. 25 44 (1970)
[16] S Q Wang and H Q Ye J. Phys. Condens. Matter 17 4475 (2005)
[17] N Guezmir, J Querfelli and S Belgacem Mater. Chem. Phys. 96 116 (2006)
[18] G Devi, K K Sarma, P Datta and A K Mahanta Indian J. Phys.86 77 (2012)
[19] N Nimje, S Dubey and S Ghosh Indian J. Phys. 84 1567 (2010)
[20] S P Singh, S K Srivastava and A Bahadur Indian J. Phys. 85 1897 (2011)
[21] S K Gorai and P Mahto Indian J. Phys. 84 587 (2010)
[22] A Garcia and M L Cohen Phys. Rev. B47 4215 (1993)
[23] A S Verma and S R Bhardwaj J.Phys. Condens. Matter 18 8603(2006)
[24] A S Verma and S R Bhardwaj J.Phys. Condens. Matter 19 026213 (2007)
[25] A S Verma and S R Bhardwaj Phys. Stat. Sol(b) 243 4025 (2006)
[26] S Mohanty and S Ravi Indian J. Phys. 84 735 (2010)
[27] M F C Ladd and W H Lee J. Chem. Phys. 60 1954 (1974)
[28] V Kumar J. Phys. Chem. Solid 48 827 (1987)
[29] V Kumar Srivastava J. Phys. C. Solid State Phys. 11 837 (1978)
[30] V Kumar, A K Shrivastava, R Banerji, D Dhirhe, Solid State Communication, 149 (2009),pp.1008-1011
[31] S G S Sheba, K Sadayandi, IJPAP, Vol 7, No.2(2011), pp.139-144.
[32] M Blackmann, Handbuch der Physik VII/I, Springer Verlag, Berlin (1955)(p.325)
[33] R R Reddy, Y N Ahammed, K R Gopal and D V Raghuramm, IJPAP,Vol.37,January 1999,pp.25-28.