Correlation between Average Inter-Atomic Distance and the Thermal Properties of $A^{I}B^{III}C_2^{VI}$ Chalcopyrite Crystal Structured Solids

Deepak Sharma[1,*], P. K. Sharma[2] and Arti Maheshwari[3]
[1,2] Department of Applied Sciences (Physics), IIMT College of Engineering, Greater Noida, 201306
[3] Department of Chemistry, IET, Mangalayatan University, Beswan, Aligarh, India, 202001
*deepak.shrm1@gmail.com

A striking inter-relation has been evolved for heats of formation determination of ternary chalcopyrite of the type $A^{I}B^{III}C_2^{VI}$. The proposed relation is derived in terms of average inter-atomic distance and melting temperature. A discussion has also been presented among the heats of formation, average inter-atomic distance and melting temperature of these compounds.

Keywords: **C**halcopyrite, Average inter-atomic distance, Melting temperature and Heats of formation.

1. INTRODUCTION

The ternary chalcopyrite compounds form a large number of semiconducting materials with diverse electrical, structural, mechanical, thermal and optical properties. The compounds of the type $A^{I}B^{III}C_2^{VI}$ have attracted considerable attention because of their interesting semiconducting, electrical, structural, mechanical and optical properties. In the recent past $A^{I}B^{III}C_2^{VI}$ group of ternary chalcopyrite semiconductors have become more popular because of their potential applications in the field of light emitting diodes, photovoltaic detectors, solar cells and non-linear optics. The ternary compounds are direct gap semiconductors with tetragonal chalcopyrite crystal structure. Structurally these compounds are derived from that of binary sphalerite structure (III-V and II-VI) with a slight distortion. It is very difficult to prepare high quality crystals of these semiconductors as compared to binary (II-VI and III-V) semiconductors. Thus it is necessary to study the thermodynamical properties of these semiconductors such as heats of formation, melting points etc. [1-14]. The heats of formation play an important role in chemical bonding and crystal physics. Numerous experimental and theoretical works have been done to determine this quantity in case of binary semiconductors [15-19]. Later on, attempts have been made to extend the spectroscopic model of Phillips and Van Vechten [16] of binary semiconductors to the ternary $A^{I}B^{III}C_2^{VI}$ semiconductors. V. Kumar [9,18,] have developed various models based on plasma oscillations theory of solids to explain the thermal expansion coefficient, bond length, inter-atomic force constant of binary and ternary semiconductors. The Plasmon energy is related to effective number of valence electrons in a semiconductor. Bond length is also related to the number of valence electrons. This shows a correlation between bond length and plasmon energy. Phillips and Van Vechten

[16] have shown that heats of formation of binary compounds are also correlated to the bond length. Therefore it has been thought of interest to develope a simple model for the calculation of heats of formation of $A^{I}B^{III}C_2^{VI}$ ternary chalcopyrites.

In the present paper, we have evolved an empirical approach for heats of formation determination of these compounds based on average bong length and melting temperature. The evaluated values of heats of formation are in better agreement with experimental and data as compared to earlier workers so far.

2. THEORY, RESULTS AND DISCUSSION

The heats of formation of a binary tetrahedral compound is given by the relation [16]

$$\Delta H_f(xy) = \Delta H_0 \left(\frac{dGe}{dxy}\right)^S D(xy) fixy \tag{1}$$

Where d_{Ge} and d_{xy} are bond lengths of germanium and the binary compound xy, respectively. $f_i(xy)$ is the bond ionicity [17], and the factor D(xy) is given by the relation [17, 19]

$$D(xy) = 1 - b\left[\frac{E_2(xy)}{E(xy)}\right]^2$$

$$= 1 - b\left[\frac{2E_2(XY)}{E_0(xy)+E_1(xy)}\right]^2 \tag{2}$$

Where $E_0(xy)$ is the lowest direct energy gap, $E_1(xy)$ and $E_2(xy)$ are higher critical energies of the compound (xy), $\bar{E}(xy)$ is the average of $E_0(xy)$, $E_1(xy)$ and $E_2(xy)$ can be either taken from the experimental reflectivity data or calculated theoretical using equations given by Van Vechten [17] and Neumann [19]. The values of scaling factor ΔH_0 and the exponent S in equation 1 have been found by Phillips and Van Vechten [16] for two different sets of ΔH_0 and S.

The $A^{I}B^{III}C_2^{VI}$ semiconductors are the ternary analogs of the II-VI semiconductors and also exhibit tetrahedral coordination. Therefore, it is quite reasonable to suppose that equation (1) can be used to describe the heats of formation of ABC_2 type semiconductors too. Taking this into consideration that the real ABC_2 semiconductors consist of two AB1/2-C units, the heats of formation can be written as [20].

$$\Delta H_f(ABC_2) = 2\Delta H_0 \left(\frac{dGe}{d}\right)^S D(ABC_2) f_i(ABC_2) \tag{3}$$

Where ΔH_0 = -304 KJ/mol and S = 3.575 have the same values as in the case of binary semiconductors, d_{Ge}=2.45A, d=(d_{AC} + d_{BC})/2 is the average bond length of ABC_2 compound and $f_i(ABC2)$ = ($f_i(AC)$ + $f_i(BC)$/2 is the average bond iconicity and $D(ABC_2)$ is again defined by equation 2 but here the energies E_0, E_1 and E_2 are the characteristics of ABC_2 compounds itself. Since all the $A^{I}B^{III}C_2^{VI}$ compounds are direct gap semiconductors the energies E_0, E_1 and E_2 can be taken from experimental data for the fund mental energy

gap in these energy materials.

V. Kumar *et. al.* [9] have given the following equation for heats of formation of ternary semiconductors.

$$\Delta H_0 (ABC_2) = 0.8710 (\hbar\omega_p)^{2.3833} D(ABC_2) f_i(ABC_2) \quad (4)$$

Where $\hbar\omega_p = (\hbar\omega_{p\,(AC)} + \hbar\omega_{p\,(BC)})/2$ is the average Plasmon energy of the A-C and B-C bonds in ABC_2 semiconductors. For the ABC_2 compounds $\hbar\omega_p$ can be written as [21].

$$\hbar\omega_p = 28.8\sqrt{\frac{2\sigma}{W}} \quad (ev) \quad (5)$$

Where Z is the effective number of valence electrons taking part in plasma oscillations, σ is the specific gravity and W is the molecular weight.

V. Kumar *et. al.* [18] have also given the relation between average bond length and Plasmon energy of ternary compounds,

$$d = 15.30 (\hbar\omega_p)^{-2/3} \quad (d \text{ in } A^0 \text{ and } \hbar\omega_p \text{ in ev}) \quad (6)$$

V. Kumar *et. al.* [9] have given the simple empirical relation to calculate the heats of formation values of ternary chalcopyrite semiconductors.

$$-\Delta H_f = A(\hbar\omega_p)^B \quad (7)$$

Where A and B are the constants. The values of A and B are 0.3170 and 2.5310 respectively for $A^{I}B^{III}C_2^{VI}$ semiconductors.

In the above theories, we noted that the authors have used a number of parameters and constants in their relations. We have studied the above relations proposed by these authors and come to the conclusion that the number of constants used by them can reduced to one only. Hence following relation based on the best fit data has been proposed to calculate the heats of formation values for $A^{I}B^{III}C_2^{VI}$ groups of semiconductors.

$$-\Delta H_f = T_m d^{-1.55} \quad (8)$$

The proposed empirical relation (8) has been applied to evaluate heats of formation values for $A^{I}B^{III}C_2^{VI}$ groups of semiconductors. The values so obtained are presented in the following table 1 and compared with the experimental and theoretical data reported so far. We note that the values of heats of formation for these compounds evaluated by proposed simple relation are in close agreement with the experimental data as compared to the values reported by previous workers so far.

Table 1: Heat of formation ($-\Delta H_f$) of $A^{I}B^{III}C_2^{VI}$ semiconductors.

Compound	d(A^0) [22]	Tm	ΔH_f This work	ΔH_f [9]	ΔH_f [9]	ΔH_f [19]	$\Delta H_{f\ expt.}$ [19](KJ/mol)
$CuAlS_2$	2.29	1570	434.7	443.4	427.9	463.8	-
$CuAlSe_2$	2.40	1336	343.9	357.3	345.9	389.9	-
$CuAlTe_2$	2.58	1163	267.7	287.8	268.5	285.4	-
$CuGaS_2$	2.30	1515	416.6	410.5	418.6	420.4	-
$CuGaSe_2$	2.42	1343	341.3	331.5	349.3	329.5	317
$CuGaTe_2$	2.60	1145	260.4	258.1	266.2	260.8	168
$CuInS_2$	2.40	1363	350.8	319.1	360.5	327.7	-
$CuInSe_2$	2.51	1259	302.4	262.9	305.0	263.5	267
$CuInTe_2$	2.68	1043	228.5	220.9	237.1	228.5	107
$AgAlS_2$	2.42	1420	360.9	388.5	365.6	417.9	-
$AgAlSe_2$	2.53	1223	290.1	334.7	308.6	361.3	-
$AgAlTe_2$	2.69	1002	216.2	308.6	275.7	279.9	-
$AgGaS_2$	2.44	1313	329.5	386.5	359.4	394.8	-
$AgGaSe_2$	2.54	1123	264.8	293.3	288.4	318.2	446
$AgGaTe_2$	2.69	993	214.2	244.9	235.7	252.7	140
$AgInS_2$	2.49	1145	278.4	307.4	311.2	330.6	-
$AgInSe_2$	2.60	1053	239.5	250.5	262.9	268.0	242
$AgInTe_2$	2.77	953	196.5	211.1	210.8	217.9	123

3. CONCLUSION

From the above discussions and results obtained by using the proposed approach, it is quite obvious that the heats of formation reflecting thermodynamical property, can be expressed in terms of average bond length and melting temperature of these materials, which is definitely a surprising phenomenon and need further investigations of the reason. The values of heats of formation evaluated in this work hardly deviates 0 % to 10% from previous theoretical data. The values evaluated show a systematic trend and are consistent with the available data reported so far, which proves the validity of the approach.

REFERENCES

[1] J.E. Jaffe and A. Zunger; "Theory of the band-gap anomaly in ABC_2 chalcopyrite semiconductors", Phys. Rev. B, Vol. 29(4), pp. 1882-1906, 1984.

[2] J.L. Shay, and J.H. Wernick; "Ternary Chalcopyrite Semi-conductors: Growth, Electronic Properties and Applications", Pergamon Press, Oxford, pp. 11, 12 and 73, 1975.

[3] M.I. Alonso, K. Wakita, J. Pascual, and N. Yamamoto; "Optical functions and electronic structure of $CuInSe_2$, $CuGaSe_2$, $CuInS_2$, and $CuGaS_2$", Phys. Rev. B, Vol. 63, 2001. DOI:http://dx.doi.org/10.1103/PhysRevB.63.075203

[4] Xiaoshu Jiang and W.R.L. Lambrecht; "Electronic band structure of ordered vacancy defect chalcopyrite compounds with formula $II-III_2-VI_4$", Phys. Rev. B, Vol. 69, 2004. DOI:http://dx.doi.org/10.1103/PhysRevB.69.035201

[5] R. Marquez and C. Rincon; "On the Dielectric Constants of $A^{I}B^{III}C_2^{VI}$ Chalcopyrite Semiconductor Compounds", Phys. stat. sol. (b), Vol. 191(1), pp. 115-119, 1995.

[6] D.S. Chemla, P.J. Kupecek, D.S. Robertson and R.C. Smith; "Silver thiogallate, a new material with potential for Infrared devices", Opt. Commun., Vol. 3(1), pp. 29-31, 1971.

[7] N.A. Gorynova, L.B. Zlatkin and E.K. Ivanov; "Optical anisotropy of $A_2B_4C_{25}$ crystals", J. Phys. Chem. Solids, Vol. 31, pp. 2557-2561, 1970.

[8] N. Yamamoto, Ph.D. thesis, University of Osaka, Japan, 1976.

[9] V. Kumar and B.S.R. Sastry; "Heat of formation of ternary chalcopyrite semiconductors", J. Phys. Chem. Solids, Vol. 66(1), pp. 99-102, 2005.

[10] A.S. Verma and S.R. Bhardwaj; "Electronic and optical properties of zinc blende and complex crystal structured solids", Phys. Status Solidi (b), Vol. 243(15), pp. 4025-4034, 2006.

[11] A.S. Verma and D. Sharma; "Dielectric constants of $A^{I}B^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^{V}$ chalcopyrite semiconductors", Phys. Scr., Vol. 76(1), pp. 22-24, 2007.

[12] A.S. Verma and S.R. Bhardwaj; "Correlation between ionic charge and ground-state properties in rock-salt and zinc blende structured solids", J. Phys.: Condens. Matter, Vol. 18(37), pp. 8603-86012, 2006.

[13] A.S. Verma and S.R. Bhardwaj; "Correlation between ionic charge and the mechanical properties of complex structured solids", J. Phys.: Condens. Matter, Vol. 19(2), article no. 026213, 2007.

[14] C. Rincon; "Debye Temperature and Melting Point in $A^{I}B^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^{V}$ Chalcopyrite Compounds", Phys. Stat. Sol. (a), Vol. 134(2), pp. 383-389, 1992.

[15] B.F. Levine; "d-Electron Effects on Bond Susceptibilities and Ionicities", Phys. Rev. B, Vol. 7(6), 1973. DOI: 10.1103/PhysRevB.7.2591

[16] J.C. Phillips and J.A. Van Vechten; "Spectroscopic Analysis of Cohesive Energies and Heats of Formation of Tetrahedrally Coordinated Semiconductors", Phys. Rev. B, Vol. 2, 1970. DOI:http://dx.doi.org/10.1103/PhysRevB.2.2147

[17] J.A. Van Vechten; "Quantum Dielectric Theory of Electronegativity in Covalent Systems. I. Electronic Dielectric Constant", Phys. Rev., Vol. 182(3), 1969. DOI:http://dx.doi.org/10.1103/PhysRev.182.891; and "Quantum Dielectric Theory of Electro-negativity in Covalent Systems. II. Ionization Potentials and Inter-band Transition Energies", Phys. Rev., 187(3), 1969. DOI:http://dx.doi.org/10.1103/ PhysRev.187.1007

[18] V. Kumar and B.S.R. Sastry; "Relationship between the thermal expansion coefficient, Plasmon energy, and bond length of ternary chalcopyrite semiconductors", J. Phys. Chem. Solids, Vol. 63(1), pp. 107-112, 2002.

[19] H. Neumann; "Spectroscopic analysis of the heat of formation in $A^{I}B^{III}C_2^{VI}$ compounds", Cryst. Res. Technol., Vol. 18(12), pp. 1567-1574, 1983.

[20] H. Neumann; "About the average bond ionicity in $A^{I}B^{III}C_2^{VI}$ compounds", Cryst. Res. Technol., Vol. 18(11), pp. 1391-1396, 1983.

[21] L. Martin, L.B. Leder and H Mandlouitz; "Advances in Electronic and Electron Physics", Academic press, New York, Vol. 7, pp. 225, 1955.

[22] D. Sharma, G.S. Sharma, A.S. Verma and S.R. Bhardwaj; "Microhardness of Ternary Chalcopyrite Semiconductors", Proceedings National Conference on Advanced condensed matter Physics (ACMP), Thapar Institute of engineering and technology, Patiala, pp. 307-311, 2005.