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HEAT OF FORMATION OF I-III-VI2 AND II-IV-V2 TYPE TERNARY CHALCOPYRITES ON THE BASIS OF OPTICAL ELECTRONEGATIVITY

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Abstract

In this paper an empirical formula for the calculation of heat of formation of I-III-VI2 and II-IV-V2 type of ternary chalcopyrites has been proposed. The empirical relation is based on the optical electronegativity of the ternary chalcopyrites. Values of heat of formation calculated using the empirical formula show fairly good agreement with the experimental values and the values reported by earlier researchers.

Keywords: ***Ternary Chalcopyrites, Heat of formation, Optical electronegativity***

1. INTRODUCTION

I-II-VI2 and II-IV-V2 types of ternary chalcopyrites have attracted considerable attention in last few years because of their potential applications in the field of electronics, medical sciences, non-linear optics and communication [1-5]. Various researchers have derived different theoretical models for the calculation of Bulk modulus [6-18], Lattice energy [19], Microhardness [20-39], refractive index [40-41], ionicity [42], Debye temperature [43] and other mechanical, optical and electronic properties but very few researchers have been done on their thermodynamic properties such as melting point, heat of formation etc. The heat of formation plays an important role in explaining the nature of bonding and crystalline structure of materials. It is the amount of heat absorbed or evolved when one mole of a compound is formed from its constituent elements, each substance being in its normal physical state. Optical electronegativity is one of the important parameter of ternary chalcopyrites and helps in explaining the chemical bonding and various factors of a material. Duff [44] defined the optical electronegativity as,

$$\Delta x^* = x^*_{anion} - x^*_{cation} \quad \text{.....(i)}$$

where x^*_{anion} is the optical electronegativity of anion and x^*_{cation} is the optical electronegativity of cation. In this, I have tried to co-relate heat of formation with optical electronegativity.

2. THEORY

Numerous theoretical and experimental works has been done to calculate the heat of formation binary and ternary chalcopyrite semiconductors [45-47]. Phillips and Van Vechten [48] were the first who have determined the heat of formation for I-III-VI_2 type chalcopyrites. Newman [49] has also calculated the values of heat of formation of I-III-VI_2 type chalcopyrites. V. Kumar and B.S.R. Sastry [50] has proposed the relations for heat of formation as

$$\Delta H_f(ABC_2) = 0.8710\ (\hbar\omega_P)^{2.3833} D(ABC_2) f_i(ABC_2) \quad \text{.....(ii)}$$

where f_i is bond ionicity and D(ABC_2) is a constant.

$$-\Delta H_f = A\ (\hbar\omega_P)^B \quad \text{.....(iii)}$$

where A=0.3170, B=2.5310 for I-III-VI_2 and A=11.4136, B=1.1624 for II-IV-V_2 type chalcopyrites.

Optical electronegativity of ternary chalcopyrites depends on Plasmon energy. Again, heat of formation also depends on Plasmon energy [50]. So, there must be some relation

between heat of formation and optical electronegativity. I used this concept to propose my empirical relation.

To derive the relation I have plotted the variation (Fig. 1 and 2) of experimental values of optical electronegativity with heat of formation using the best fit data method.

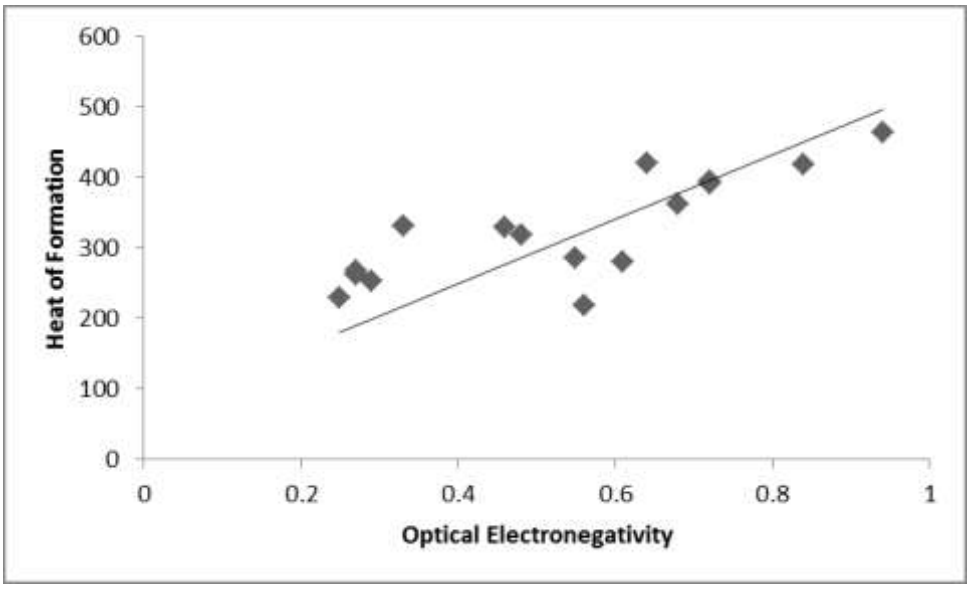

Fig 1 Variation of Heat of formation with Optical electronegativity of I-III-VI_2

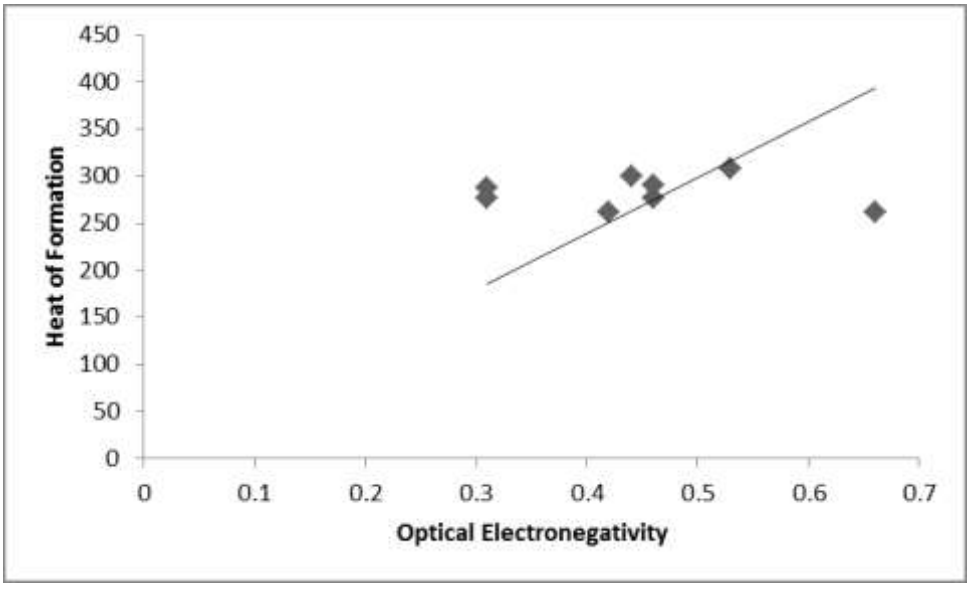

Fig 2 Variation of Heat of formation with Optical electronegativity of II-IV-V

The graphs are linear in nature and R2 values are respectively 0.3394 for I-III-VI2 and -18.73 for II-IV-V2. From the graphs it is clear that heat of formation bears a linear

relation with optical electronegativity in case of both type ternary chalcopyrite groups of compound.

Using the best fit data and linearity, the following relation is proposed by me,

$$\Delta H_f = \alpha \Delta x^* \beta \quad \text{.....(iv)}$$

where α=457.56, β=65.56 for I-III-VI2 and α=595.64, β=0.05 for II-IV-V2 type chalcopyrites.

3. DISCUSSION AND CONCLUSION

The values of heat of formation of I-III-VI2 and II-IV-V2 types chalcopyrites are calculated using equation (iv) and the calculated values are listed in Tables 1 and 2 along with experimental values and values reported by other researchers.

Table-1: Heat of formation (-ΔH_f in kJ/mole) of I-III-VI2 type chalcopyrite semiconductors

Compounds	Calculated from equation (iv) $-\Delta H_f$	Ref.[50] $-\Delta H_f$	Ref. [50]- ΔH_f	Ref.[49] $-\Delta H_f$	Expt.[49] $-\Delta H_f$
$CuAlS_2$	495.66	443.4	427.9	463.8	-
$CuAlSe_2$	395.00	357.3	345.9	389.9	-
$CuAlTe_2$	317.21	287.8	268.5	285.4	-
$CuGaS_2$	358.39	410.5	418.6	420.4	-
$CuGaSe_2$	276.03	331.5	349.3	329.5	317
$CuGaTe_2$	189.10	258.1	266.2	260.8	168
$CuInS_2$	398.66	319.1	360.5	327.7	-
$CuInSe_2$	312.18	262.9	305.0	263.5	267
$CuInTe_2$	179.95	220.9	237.1	228.5	107
$AgAlS_2$	449.91	388.5	365.6	417.9	-
$AgAlSe_2$	376.70	334.7	308.6	361.3	-
$AgAlTe_2$	344.67	308.6	275.7	279.9	-
$AgGaS_2$	395.00	386.5	359.4	394.8	-
$AgGaSe_2$	285.18	293.3	288.4	318.2	446
$AgGaTe_2$	198.25	244.9	235.7	252.7	140
$AgInS_2$	216.55	307.37	311.2	330.6	-
$AgInSe_2$	189.10	250.5	262.9	268.0	242
$AgInTe_2$	321.79	211.1	210.8	217.9	123

Table-2 : Heat of formation of II-IV-V$_2$ ($-\Delta H_f$ *in kJ/mole*) type chalcopyrite semiconductors-

Compounds	Calculated from equation (iv) $-\Delta H_f$	Ref.[49] $-\Delta H_f$	Expt.[49] $-\Delta H_f$
$ZnSiP_2$	315.73	307.8	312
$ZnGeP_2$	262.13	290.4	-
$ZnSnP_2$	274.04	299.8	293
$ZnSiAs_2$	184.69	276.5	289
$ZnGeAs_2$	183.50	277.1	275
$ZnSnAs_2$	393.17	262.0	270
$CdSiP_2$	274.04	287.5	290
$CdGeP_2$	184.69	273.0	-
$CdSnP_2$	250.21	279.4	271
$CdSiAs_2$	-	263.7	266
$CdGeAs_2$	194.82	262.0	252
$CdSnAs_2$	160.27	247.7	247

Fairly good agreement has been obtained between the calculated values and other reported values of heat of formation of both types of ternary chalcopyrites. In some cases deviation is greater, but as optical electronegativity is a fixed quantity so the values may be used for future calculations. On the other hand, the relations proposed by other researchers depend on factors which are variable.

The main advantage of the equation is its simplicity. It does not require any experimental data except the optical electronegativity. Using optical electronegativity other physical parameters relating ternary chalcopyrites can be explained in similar manner.

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