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On The p-d Hybridization of Some I-III-VI₂ Mixed Chalcopyrites



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Abstract

p-d hybridization resulting from the mixing of the noble metal d-levels with p-levels of other atoms of some mixed ternary I-III-VI₂ chalcopyrites (both amalgamated and persistence type) have been evaluated for the first time using the model of Yooder and Woolley and modifying accordingly for the mixed crystals. In this connection, we have evaluated important characteristic parameters like interaction matrix (M), the fractional d-character and band gap anomaly (ΔE_g) of these compounds. The agreement of these results when compared with those obtained through correlation is encouraging.

Keywords: Band gap anomaly .

Introduction

The ternary chalcopyrite semiconductors belonging to both II-IV-V₂ and I-III-VI₂ have shown considerable technological promise for a wide variety of technological applications, ^{1, 2, 3, 4, 5, 6} nonlinear optical devices i.e. up conversion, down conversion and optical parametric oscillation producing tunable laser radiation, solar energy conversion, optical detectors and as polycrystalline thin films. Because of the similarities of the structure of III-V and II-VI compounds who are binary analogue of II-IV-V₂ and I-III-VI₂ having the same number of bonding electrons, it is quite natural to assume that their bond structures to be related ^{7, 8}. For improving a device-use potential, further advancement are needed on growth methods controlling a degree of perfection, defects, doping and also characterization methods of those compounds.

Objective of the study

Mixed crystals give new possibilities for material engineering as their basic important parameters like lattice constant, band gap energy and valence band can be controlled independently. Although a good number of studies have been carried out on the crystal growth, band structure, dielectric, electrical, thermal dependence, pressure dependence and related parameters but sufficient interpretation of the measured data with the theory are not yet available. In this connection we have studied in detail about some mixed chalcopyrite of the types Cu/AgX_xX'_{1-x}Y₂, Cu/AgX(Y_xY'_{1-x})₂ and Cu_xAg_{1-x}XY₂ (X/X' = Al, Ga, In and Y/Y' = S, Se, Te) and evaluated percentage hybridization and interaction strength of the valence bands between the anion p-level and noble metal d-levels.

Review of Literature

The mixed chalcopyrites compounds are getting considerable interest for potential applications in optoelectronics and photovoltaic solar cells. ^{9,10,11,12,13} Even recently chalcopyrite nano crystals are growing as promising materials for optoelectronic device applications. ^{14,15} The advent of modern crystal growth techniques like Vapour Phase Epitaxy (VPE), Liquid Phase Epitaxy (LPE), Chemical vapour deposition (CVD), Metalloorganic Chemical Vapour Deposition (MOCVD) and highly sophisticated technique like Molecular Beam Epitaxy (MBE) gave further impetus to the study and application of mixed crystals ^{16,17,18,19} as these compounds offer new possibilities for material engineering through the independent control of important design parameters like lowest band gap energy, lattice constant, valence band offset, dielectric constant and birefringence.

The ternary chalcopyrite semiconductors crystallize in the space group $\bar{1}42d$ with eight atoms per unit cell which is a ternary analogue of the diamond structure and is a superlattice zinc blende T_d^2 . In this tetrahedrally coordinated structure like ABY₂, each anion is coordinated by two A and two B cations whereas each cation is tetrahedrally coordinated to four

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anions. Further in case of chalcopyrites, the alternate disposition of two group II atoms and two group IV atoms in case of II-IV-V₂ and two group I atoms and two group III atoms in case of I-III-VI₂ results in a unit cell twice as large as in the c-direction as that corresponding to zinc-blend and results in three characteristic properties of these chalcopyrites namely (i) doubling of the unit cell along the z-axis $c < 2a$, (ii) tetragonal distortion $(2 - c/a)$ and (iii) the displacement of the anion from the sphalerite-like position. Again the departure from the cubic symmetry introduces crystal field interaction and further splitting results from the spin orbit interaction. Studies revealed that the structure of the uppermost valence bands in a II-IV-V₂ chalcopyrite is simply related to the energy bands of its III-V binary analogue while the same is not true for I-III-VI₂ compounds where it is found^{1, 20} that the uppermost valence band is influenced by the proximity of the noble metal d-level resulting in hybridization of the anion p-levels and noble metal d-levels, thus causing the reduction of lowest energy band gap and spin orbit splitting, temperature and pressure dependence of band gap⁷. Again the study of the effect of the d-electrons in the chemical bond²¹ in understanding the complex relationship between crystallographic structure, composition and physicochemical properties of mixed crystals will be very useful.

Due to lack of sufficient information about I-III-VI₂ compounds on the p-d hybridization study, it is quite natural and attractive to study in detail the effects of the same on mixed versions of these compounds for explaining the characteristic properties of the compounds. The contribution of d-electrons on the various optoelectronic and band structure parameters including the temperature and pressure dependence of the band gap is the most interesting aspect which draw special attention for studying not only the parent crystals but also their mixed versions^{17,18,19, 22} showing their importance for non-linear and technological devices including solar cells. For I-III-VI₂ chalcopyrites with Cu as group I transition metal ion it has the ground state electronic configuration [Ar]3d¹⁰4s¹ while with Ag is [Kr]4d¹⁰5s¹ and it is the electronic configuration that allows the d-electrons to participate in chemical bonding of the crystal. For I-III-VI₂ compound the uppermost valence band are derived from the combination of p-levels of the anion and the noble metal d-levels whereas the conduction band from the s-states of the cations. In the tetrahedral field, the five fold degenerate d-levels splits into three fold degenerate Γ_{15} and two fold degenerate Γ_{12} levels and these undergo further splitting due to the spin-orbit interaction which is

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responsible for the split of p-like Γ_{15} valence band state^{1,24}. The p-d hybridization results from the strong interaction of p-like and d-like states as the d-level Γ_{15} has the same symmetry as p-level Γ_{15} and is responsible for the reduction in the lowest energy band gap of (Cu,Ag)-III-VI₂ chalcopyrites because of the interaction raising the top of the valence band. The same effect is small in II-VI and III-V compounds where the cation d-orbitals (Zn, Cd, Ga, In) are considerably deeper than the anion p-orbitals but is more significant in Cu based chalcopyrites than the corresponding Ag one. It is further to be noted that I-III-VI₂ chalcopyrites have a direct band gap with the minimum at the Γ point where as for some II-IV-V₂ compounds the band varies from direct to pseudodirect or indirect.

Concept and Hypothesis

Amongst the various approaches^{23,24,25} taking into account the effect of p-d hybridization for studying the electronic structure of the valence band at the Brillouin zone center of I-III-VI₂ chalcopyrites, the approach of Yooder and Woolley has been able to explain some useful parameters like the energy separation E between p-like and d-like Γ_{15} levels, the interaction matrix element M between these levels and also the reduction ΔE_g in the energy band gap compared with the value of the corresponding binary analogue normally called band gap anomaly. In this light, we have made a detailed study for the first time about some I-III-VI₂ mixed chalcopyrites for evaluating the useful parameters like the interaction matrix element M , fractional d-character in the valence band, and related parameters M/E and $\Delta E_g/E$ following the approach of Yooder and Woolley²³ and modifying accordingly for the mixed crystals and these results have been compared with the results obtained by correlation method.

Research design/Methodology

Because of hybridization²⁶ of anion p-levels and noble metal d-levels in I-III-VI₂ chalcopyrites, the electronic structure of the uppermost valence band of these compounds at the center of Brillouin zone is very interesting²². Due to p-d hybridization interaction the level of same symmetry will mix and repel each other, hence the d-level $\Gamma_{15}(d)$ having the same symmetry as p-level $\Gamma_{15}(p)$ in these type of compounds will interact with each other. Following reference [23] the strength of the interaction matrix, fractional d-character of valence band, M/E and $\Delta E_g/E$ of some mixed crystals $Cu/AgX_xX'_{1-x}Y_2$, $Cu/AgX(Y_xY'_{1-x})_2$ and $Cu_xAg_{1-x}XY_2$ ($X/X' = Al, Ga, In$ and $Y/Y' = S, Se, Te$) with variation of both cationic and anionic concentration, ie. for both amalgamated and persistence type of compounds.

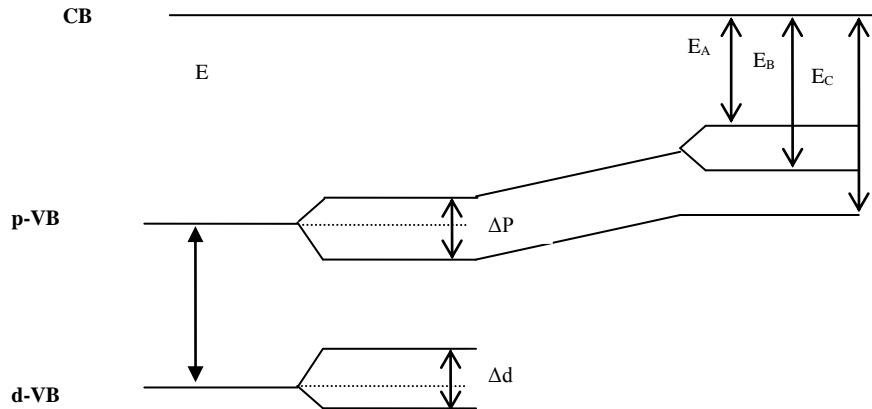


Fig 1: Diagram of Energy Levels

As stated earlier that the valence band splits (fig 1) into three doubly degenerate levels which are given by following reference [23]

$$E_0 = \lambda_0 + \gamma_0 \frac{\delta_p}{3} + (1 - \gamma_0) \frac{\delta_d}{3} \dots\dots\dots(1)$$

$$E_{1,2} = \frac{1}{2} \left[\lambda_1 + \lambda_2 - \gamma_1 \frac{\delta_p}{3} - (1 - \gamma_1) \frac{\delta_d}{3} \right]$$

$$\pm \frac{1}{2} \left[\left\{ \lambda_1 - \lambda_2 - \gamma_1 \frac{\delta_p}{3} - (1 - \gamma_1) \frac{\delta_d}{3} \right\}^2 + \frac{8}{9} \left\{ (\gamma_1 \gamma_2)^{\frac{1}{2}} \delta_p + (1 - \gamma_1)^{\frac{1}{2}} (1 - \gamma_2)^{\frac{1}{2}} \delta_d \right\}^2 \right]^{\frac{1}{2}} \dots\dots(2)$$

And the band gap anomaly $\Delta E_g = E_1 - \Delta P/3 \dots\dots\dots (3)$

Where ΔP is the spin-orbit splitting of p-level and δ_p and δ_d are the crystal field splitting parameters of the p-level and d-level respectively.

$$\text{Now, } E_1 + E_0 + E_2 = -\frac{3}{2} E + \left[\left(\frac{\Delta p}{3} + E + \frac{|\Delta d|}{3} \right)^2 + 4M^2 \right]^{\frac{1}{2}} + \frac{1}{2} \left[\left(-\frac{2}{3} \Delta p + E - \frac{2}{3} |\Delta d| \right)^2 + 4M^2 \right]^{\frac{1}{2}} \dots\dots\dots(4)$$

The values of E_0 , E_1 and E_2 can be obtained using the following relations

$$\left. \begin{aligned} E_1 &= E_g(B.E) - E_A + \frac{\Delta p}{3} \\ E_0 &= E_g(B.E) - E_B + \frac{\Delta p}{3} \\ E_2 &= E_g(B.E) - E_C + \frac{\Delta p}{3} \end{aligned} \right\} \dots\dots\dots(5)$$

And E_A , E_B , E_C for the mixed crystals have been obtained using the relation

$$E(A_x B_{1-x}) = x E(A) + (1-x) E(B) \dots\dots\dots(6)$$

δ_p and δ_d are given by $\delta_p = -1.2(2 - c/a)$ and $\delta_d = -6.45(2 - c/a)$ [16]

The lattice parameters of the mixed crystals have been evaluated using Vegard's law. The value of spin-orbit splitting Δp is given by

$$\Delta p = G_p \left(\frac{1}{16} \Delta p_I + \frac{3}{16} \Delta p_{III} + \frac{12}{16} \Delta p_{VI} \right) \dots\dots\dots(7)$$

Where G_p takes a value 29/20 for chalcopyrite structure. For Δd (spin-orbit splitting of d-level) only the effect of Cu and Ag d-electrons are effective and Δd is given by $\Delta d = G_d \Delta d_I \dots\dots\dots(8)$

where G_d is also 29/20. The interaction matrix element M has been evaluated using equation (4) while the percentage hybridization of the mixed crystals following the method²³ and modifying accordingly for mixed crystal as well as using linear hybridization model. Also the values of interaction parameter and

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fractional d-character have been evaluated using the correlation of fractional d-character with M, E and ΔE_g .

Findings

Our study about the different parameters of mixed chalcopyrite compounds results in finding a correlation between the parameters M/E and $\Delta E_g/E$. This has been shown in figure 2. The values of M for the mixed crystals have been evaluated using this correlation and compared with results obtained by equation (4) and this has been shown in table 1 and the agreement is encouraging. Analysis of the results shows that the value of interaction parameter M changes more sharply with the change of anion concentration for the compounds containing Ag atoms than those containing Cu. It is also seen that the percentage hybridization also have correlation with M/E and $\Delta E_g/E$. Figure 3 and figure 4 show the correlation of fractional d-character with M/E and $\Delta E_g/E$. Further it is to be noted that though M/E and $\Delta E_g/E$ are dimensionless parameters, they are the characteristics of the structure thus showing their importance in studying the p-d hybridization in the mixed crystals. We have presented here the values of percentage hybridization of the mixed crystals for different compositions from the study of the correlation of percentage hybridization with $\Delta E_g/E$ and M/E and compared the results with those obtained by

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Yooder and Woolley model and the linear hybridization model²³. And these have been shown in table 2. It is interesting to observe that the results obtained from different methods agree well. From our study, it is obvious that the variation of the d-contribution is more prominent for change in Gr.I element (Cu, Ag) concentration than the change in Gr.III or Gr.VI element concentrations which is obvious due to the fact that both Cu and Ag are noble metal. It is also observed that fractional d-character (percentage variation) changes more sharply with the concentration of Gr.VI element for compounds containing Ag atoms than those containing Cu atoms which can be explained considering the fact that for a given change in percentage hybridization, the variation is more prominent in compounds containing Ag compared to Cu one with the same change as the fractional d-character is more in Cu compounds (30-40%) than Ag compounds (10-20%). Further the effect of d-electron on the isotropy point [$n_o(\lambda) = n_e(\lambda)$] of $AgGa(S_xSe_{1-x})_2$ ²⁷ is attractive as the isotropy point changes with the change in anion composition and the change of isotropy point is very useful in connection with the development of device structure with nano layers and to construct narrow band tunable optical filter (MBTOF) in the region 497nm to 804nm which is important, being in the visible region. Further study on this aspect is in progress.

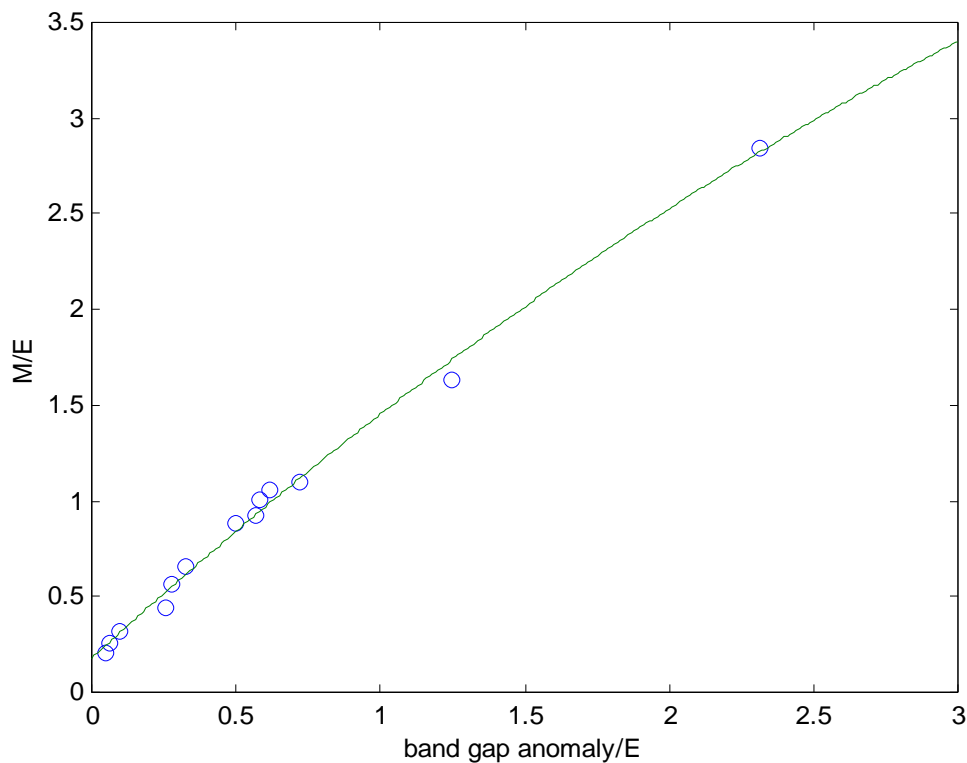


Figure 2: Correlation between band gap anomaly and M/E

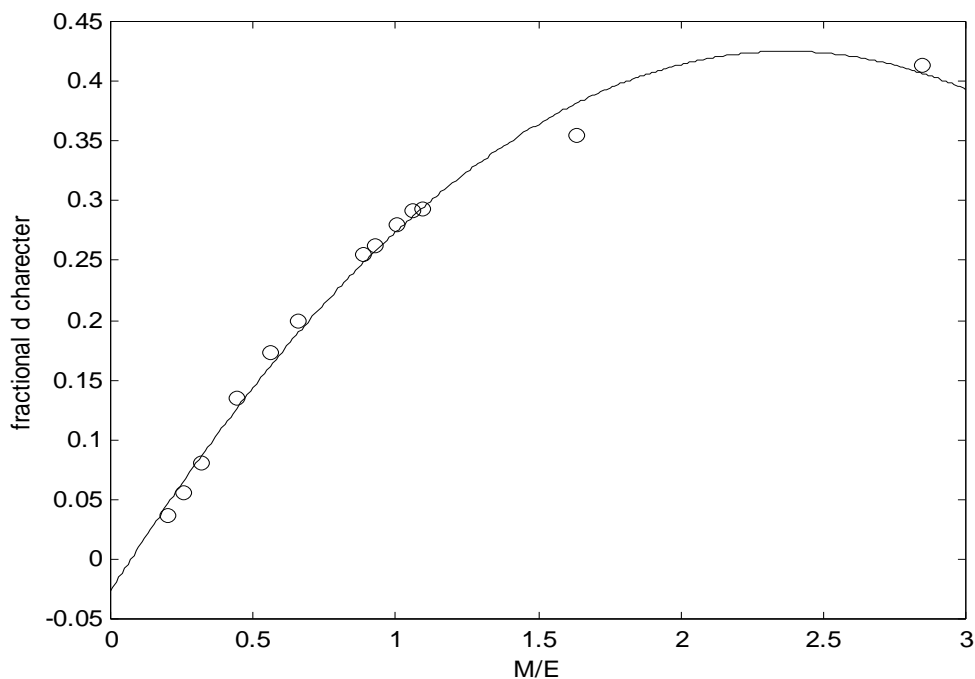


Figure 3: Correlation between fractional d-character and M/E

Values of interaction matrix (M) and $\Delta E_g/E$ of some mixed chalcopyrites

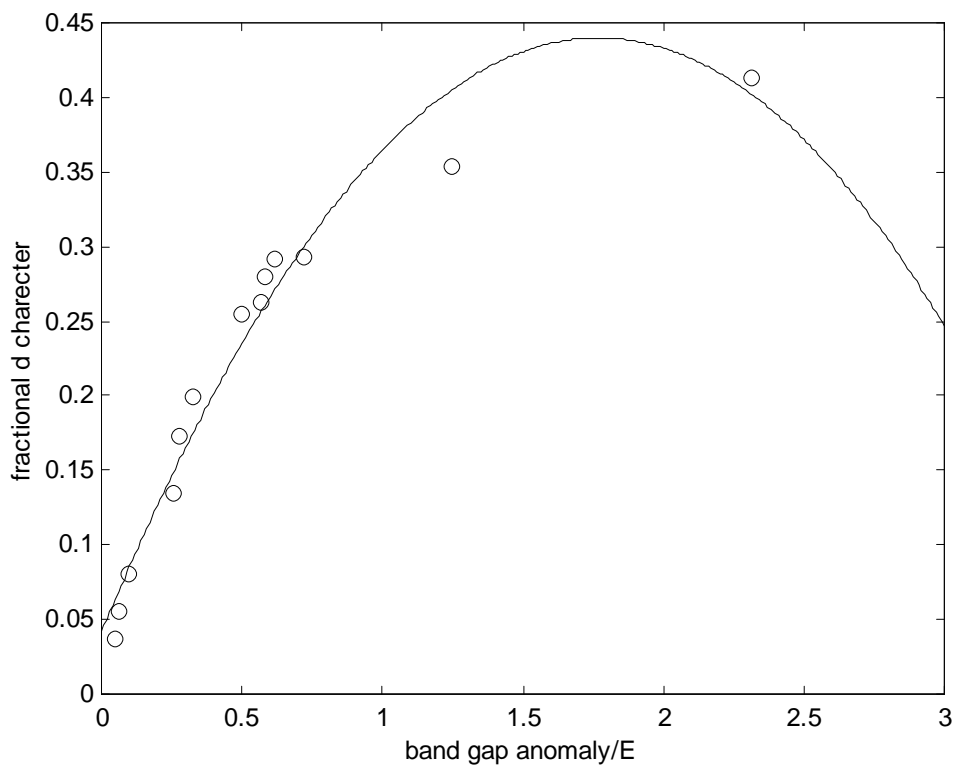


Figure 4: Correlation between fractional d-character and $\Delta E_g/E$

Table 2

| Compounds | Concentration | Values of $\Delta E_g/E$ | Interaction matrix (M) from | |
|--|---------------|--------------------------|-----------------------------|--------------------------------------|
| | | | from eqn.(4) | from correlation with $\Delta E_g/E$ |
| CuAl _x In _{1-x} Se ₂ | x = 0.25 | 0.52 | 2.32 | 2.23 |
| | x = 0.50 | 0.53 | 2.34 | 2.27 |
| | x = 0.75 | 0.55 | 2.34 | 2.33 |
| CuGa _x In _{1-x} Se ₂ | x = 0.25 | 0.44 | 2.25 | 2.11 |
| | x = 0.50 | 0.41 | 2.15 | 2.03 |
| | x = 0.75 | 0.37 | 2.12 | 1.95 |
| CuAl _x In _{1-x} S ₂ | x = 0.25 | 1.35 | 2.44 | 2.51 |
| | x = 0.50 | 0.99 | 2.85 | 2.93 |
| | x = 0.75 | 0.82 | 3.26 | 3.33 |
| CuGa _x In _{1-x} Te ₂ | x = 0.25 | 0.60 | 2.02 | 1.89 |
| | x = 0.50 | 0.60 | 2.10 | 1.98 |
| | x = 0.75 | 0.58 | 2.18 | 2.05 |
| CuAl _x Ga _{1-x} S ₂ | x = 0.25 | 0.98 | 2.26 | 2.38 |
| | x = 0.50 | 0.85 | 2.73 | 2.82 |
| | x = 0.75 | 0.77 | 3.19 | 3.28 |
| AgGa _x In _{1-x} Se ₂ | x = 0.25 | 0.08 | 1.95 | 2.20 |
| | x = 0.50 | 0.07 | 1.81 | 2.15 |
| | x = 0.75 | 0.06 | 1.61 | 2.08 |
| CuGa(S _x Se _{1-x}) ₂ | x = 0.25 | 0.43 | 1.98 | 1.91 |
| | x = 0.50 | 0.57 | 1.94 | 1.94 |
| | x = 0.75 | 0.81 | 1.88 | 1.93 |
| CuGa(S _x Te _{1-x}) ₂ | x = 0.25 | 0.67 | 2.16 | 2.08 |
| | x = 0.50 | 0.80 | 2.04 | 2.04 |
| | x = 0.75 | 0.97 | 1.92 | 1.97 |
| CuIn(S _x Se _{1-x}) ₂ | x = 0.25 | 0.65 | 2.25 | 2.18 |
| | x = 0.50 | 0.89 | 2.19 | 2.17 |
| | x = 0.75 | 1.33 | 2.11 | 2.14 |
| AgGa(S _x Se _{1-x}) ₂ | x = 0.25 | 0.06 | 1.75 | 2.05 |
| | x = 0.50 | 0.08 | 1.46 | 1.64 |
| | x = 0.75 | 0.12 | 1.14 | 1.28 |
| AgGa(S _x Te _{1-x}) ₂ | x = 0.25 | 0.07 | 2.77 | 2.88 |
| | x = 0.50 | 0.09 | 2.12 | 2.22 |
| | x = 0.75 | 0.13 | 1.40 | 1.49 |
| Cu _x Ag _{1-x} InS ₂ | x = 0.25 | 0.46 | 1.58 | 1.55 |
| | x = 0.50 | 0.74 | 1.76 | 1.76 |
| | x = 0.75 | 1.25 | 1.89 | 1.94 |
| Cu _x Ag _{1-x} GaS ₂ | x = 0.25 | 0.43 | 1.07 | 1.16 |
| | x = 0.50 | 0.65 | 1.34 | 1.44 |
| | x = 0.75 | 0.91 | 1.58 | 1.68 |
| Cu _x Ag _{1-x} InSe ₂ | x = 0.25 | 0.14 | 2.18 | 2.02 |
| | x = 0.50 | 0.21 | 2.29 | 2.10 |
| | x = 0.75 | 0.37 | 2.32 | 2.35 |

Table 2

Values of Fractional D-Character of The Mixed Chalcopyrites At Various Concentrations From Different Approaches

| Compounds | Concentration | fractional d-character | | | |
|---|---------------|-----------------------------|--------------------------------|---------------------------|--------------------------------------|
| | | By Yoodee and Woolley model | By linear hybridization method | From correlation with M/E | from correlation with $\Delta E_g/E$ |
| CuAl _x In _{1-x} Se ₂ | x = 0.25 | 0.257 | 0.265 | 0.250 | 0.240 |
| | x = 0.50 | 0.259 | 0.267 | 0.252 | 0.244 |
| | x = 0.75 | 0.259 | 0.266 | 0.252 | 0.250 |
| CuGa _x In _{1-x} Se ₂ | x = 0.25 | 0.239 | 0.245 | 0.229 | 0.215 |
| | x = 0.50 | 0.228 | 0.236 | 0.218 | 0.204 |
| | x = 0.75 | 0.217 | 0.225 | 0.207 | 0.190 |
| CuAl _x In _{1-x} S ₂ | x = 0.25 | 0.348 | 0.361 | 0.398 | 0.410 |

| | | | | | |
|--|----------|-------|-------|-------|-------|
| | x = 0.50 | 0.332 | 0.304 | 0.351 | 0.362 |
| | x = 0.75 | 0.310 | 0.303 | 0.318 | 0.320 |
| CuGa _x In _{1-x} Te ₂ | x = 0.25 | 0.289 | 0.303 | 0.284 | 0.267 |
| | x = 0.50 | 0.284 | 0.297 | 0.279 | 0.266 |
| | x = 0.75 | 0.281 | 0.291 | 0.275 | 0.262 |
| CuAl _x Ga _{1-x} S ₂ | x = 0.25 | 0.327 | 0.337 | 0.343 | 0.361 |
| | x = 0.50 | 0.312 | 0.323 | 0.321 | 0.332 |
| | x = 0.75 | 0.300 | 0.308 | 0.304 | 0.313 |
| AgGa _x In _{1-x} Se ₂ | x = 0.25 | 0.103 | 0.108 | 0.054 | 0.077 |
| | x = 0.50 | 0.070 | 0.073 | 0.054 | 0.072 |
| | x = 0.75 | 0.050 | 0.052 | 0.052 | 0.067 |
| CuGa(S _x Se _{1-x}) ₂ | x = 0.25 | 0.230 | 0.235 | 0.220 | 0.211 |
| | x = 0.50 | 0.266 | 0.272 | 0.260 | 0.258 |
| | x = 0.75 | 0.307 | 0.315 | 0.313 | 0.322 |
| CuGa(S _x Te _{1-x}) ₂ | x = 0.25 | 0.295 | 0.309 | 0.293 | 0.286 |
| | x = 0.50 | 0.311 | 0.320 | 0.317 | 0.318 |
| | x = 0.75 | 0.333 | 0.339 | 0.346 | 0.350 |
| CuIn(S _x Se _{1-x}) ₂ | x = 0.25 | 0.289 | 0.290 | 0.288 | 0.282 |
| | x = 0.50 | 0.325 | 0.340 | 0.339 | 0.342 |
| | x = 0.75 | 0.367 | 0.363 | 0.399 | 0.415 |
| AgGa(S _x Se _{1-x}) ₂ | x = 0.25 | 0.044 | 0.046 | 0.054 | 0.069 |
| | x = 0.50 | 0.054 | 0.056 | 0.063 | 0.077 |
| | x = 0.75 | 0.074 | 0.078 | 0.081 | 0.094 |
| AgGa(S _x Te _{1-x}) ₂ | x = 0.25 | 0.059 | 0.061 | 0.069 | 0.073 |
| | x = 0.50 | 0.065 | 0.069 | 0.074 | 0.079 |
| | x = 0.75 | 0.087 | 0.091 | 0.091 | 0.098 |
| Cu _x Ag _{1-x} InS ₂ | x = 0.25 | 0.243 | 0.252 | 0.227 | 0.222 |
| | x = 0.50 | 0.308 | 0.304 | 0.302 | 0.305 |
| | x = 0.75 | 0.359 | 0.383 | 0.388 | 0.405 |
| Cu _x Ag _{1-x} GaS ₂ | x = 0.25 | 0.218 | 0.214 | 0.196 | 0.211 |
| | x = 0.50 | 0.276 | 0.291 | 0.264 | 0.279 |
| | x = 0.75 | 0.322 | 0.333 | 0.326 | 0.346 |
| Cu _x Ag _{1-x} InSe ₂ | x = 0.25 | 0.113 | 0.111 | 0.114 | 0.104 |
| | x = 0.50 | 0.153 | 0.149 | 0.148 | 0.132 |
| | x = 0.75 | 0.199 | 0.201 | 0.189 | 0.189 |

Conclusion

It is obvious that the d-electrons of the Gr.I metal ions play an important role in some important characteristic properties of the chalcopyrites and the fractional d-contribution for these compounds have been investigated from different approaches. The similarity of the results from different approaches is one of the key features of the present work. Following the trends in investigations of the chalcopyrite compounds, the present work on I-III-VI₂ mixed chalcopyrites definitely throws some light in this field for finding out new crystals for device applications in nonlinear optics, optoelectronic as well as solar cells as the design related properties can be adjusted by varying the concentration of the component elements in the crystals which in turn will help the crystal growers for growing the proper crystals because the knowledge about the parameters related to device design affected by p-d hybridization is known beforehand.

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