The First Principle study of Ground State Properties of Chalcopyrites of the type CuXTe2(where X= Al, Ga, In) using DFT

Nakul Chhetri[1], Purna Chandra Barman[2]
[1,2]Department of Physics, Raiganj University, Uttar Dinajpur, India
Corresponding Author Email: nakulgorkha@gmail.com

Abstract— In pursuit of greener sources of energy, we have probed the ground state properties of the ternary chalcopyrites of the type CuXTe2(where X= Al, Ga, In) using DFT. We have used the Wien2k code in our studies to realise the FP-LAPW (full-potential linearized augmented plane wave method) method within DFT. Our study found them to be direct band gap compounds. We calculated various physical parameters like structural parameters, electrical properties like DOS, band gap, optical properties like absorption, reflectivity,refractive index, etc. and calculated values matched to a great extent with the experimental values. They are found to be the potential candidates to be used as photo voltaic materials because of their suitable optical properties.

Keywords: Chalcopyrites, DFT, FP-LAPW, Wien2k, Structural, Electronic, Optical properties.

I. INTRODUCTION

In realm of present world, the energy crisis has been very much evident. Coupled with rising environmental concerns, the transition from the traditional sources of energy to green energies is need of the hour. In this context chalcopyrites seems to cater this need. The ternary chalcopyrites of the type CuXTe2(where X= Al, Ga, In) are groups of non magnetic semiconductors belonging to space group 122, I-42d. They are structural analogues of ZnS. And they are widely studied materials owing to various diverse structural, electrical and optical properties[1,2,3]. They therefore serve as suitable materials for use as photovoltaic optical detectors, solar cells, and light emitting diodes [4,5,6].

We found the works from various workers regarding chalcopyrites under our studies. In this regard Jaffe and Zunger have carried out the studies of the chemical trends in the band structures, electronic charge densities, density of states and chemical bonding of six Cu-based ternary chalcopyrite semiconductors using the potential-variation mixed-basis (PVMB) approach[7]. Hasan and Reshak studied CuInX 2 (X = S, Se, Te) using FPLAPW as emboided in Wien2k code[8]. They also studied the optical properties like birefringence, llinear optical respone, nonli-linear optical response , etc. From their studies they found that the birefringence of CuInSe to be negative. They also calculated $\varepsilon_2(\omega)$ and found a considerable anisotropy between $\varepsilon_2^{\perp}(\omega)$ and $\varepsilon_2^{II}(\omega)$.Yadav[9] using the concept of plasma oscillations theory of solids has investigated the electronic properties such as homopolar gap (Eh), heteropolar or ionic gap (Ec), average energy gap (Eg), bond ionicity (fi) and electronic susceptibility (χe) for the chemical bonds (A-C and B-C) in complex structured AIBIIICVI2 ternary chalcopyrite crystals. Their studies showed that the homopolar gap, heteropolar gap, and averageenergy gap of these bonds were directly related to the plasmon energy and bond ionicity and electronic susceptibility is inversely related to it. Bouguetaia et al [10] using full potential linear muffin-tinorbital (FP-LMTO) method as employed in the lmtart code to study the structural and elastic properties of Cu(In,Ga)Se 2 using the FP-LMTO method within the LDA approximation in their chalcopyrite (BCT) and rocksalt phase. In addition they also studied the elastic property of the both phases.

II. STRUCTURE AND M ETHOD USED

CuXSe2 are the structural analogues of ZnS and they belong to tetragonal space group 122, I-42d. Each unit cell have within them four formula units. The central atom Te in this structure is linked to four cations at the four corners of regular tetrahedron bonded by sp3 bonds. Owing to different cations at different corners, the bond lengths cannot be expected to be same. Owing to this we observed that the tetrahedron is distorted with deviation of c/a ratio from ideal value of 2.0.

The present paper is being studied using Density Functional Theory. We have employed FPLAPW[23] method implemented in Wien2K code[11]to solve the Kohn–Sham equations which ultimately yields electron density. The exchange correlation potential used here are includes GGA[24] and mBJ[25]. In this method the unit cell volume is divided into the non-overlapping Muffin-Tin spheres surrounding every atom and the remaining interstitial region[21]. Out of their electronic configuration, the valence shell orbitals are chosen to be Cu (3p 6 ,4s 2 , 3d 9), Al (3s 2 , 3p 1), Ga (3d 10 , 4s 2 , 4p 1), In (4d 10 , 5s 2 , 5p 1), and Te (3d 10 , 4s 2 , 4p 4) respectively. For each element, the muffin tin radius have fixed at 2.14 for Cu, 2.19 for Ga, 2.33 for In and 2.13 in a.u. units for Se respectively so that muffin radius does not coalsce each other. For a plane wave expansion, the product of $K_{max} \times R_{max} = 7$ and $l_{max} = 10$ are kept constant throughout the calculations.The corresponding Wyckoff positions in unit cell of crystals are Cu(0,0,0), Ga(0,0,0.5) and Te(0.235,0.25,0.125) respectively. The volume optimisation was done in the first step from experimentally available values of lattice parameters a and c using k=7000 for better results. We have allowed iterations upto 40 times to achieve better self consistency. The convergence criteria for stable system was

considered to have achieved when energy converegence criteria of 10^{-4} Ry and charge convergence criteria of 0.0001 was fulfilled. Now using theoritical values for lattice parameters we have formed the system and studied DOS, PDOS, bandstructure, and optical properties.

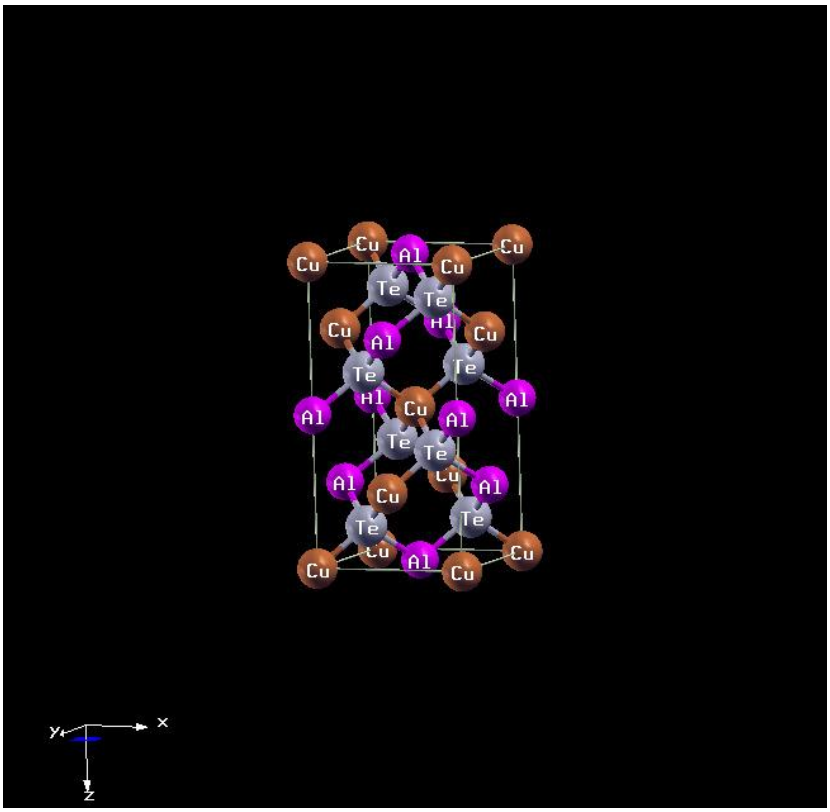


Fig.1: Structure of $CuAlTe_2$

III. RESULTS AND DISCUSSION

III.I. STRUCTURAL PROPERTIES

To start with we performed Volume optimisation by plotting energy against volume using the experimentally obtained lattice constant as given in the table1. The curve is obtained by fitting the calculated values of energies to the Murnaghan equation of state.

The configuration with the minimum energy is the ground state of the system and the corresponding volume was used for determination of theoretical lattice constant and bulk modulus of the compounds. From table 1 it is clear that the calculated lattice parameters matched well with the experimental values and previous results using different theoritical techniques. We can therefore conclude that they are in qualitative agreement with the previous results. The optimized lattice parameters thus obtained were used to calculate the electronic properties, band structures and optical properties the results of which are given in the next sections.

TABLE I. showing the experimental lattice parameters and theoritical lattice parameters of previous works and the present work.

Compound	Exp	Previous works	Present work
a(A°) CuAlTe2	5.976[15]	6.020[12],	6.05[g]

	c(A°)	11.8[15]	11.91[12]	11.95[g]
CuGaTe2	a(A°)	6.013[15]	6.02[13]	6.147[g]
	c(A°)	11.93[15]	11.94[13]	12.037[g]
CuInTe2	a(A°)	6.179[15]	6.179[14]	6.00[g]
	c(A°)	12.36[15]	12.36[14]	12.02[g]

Ref [12,13,14,15] Present calculation using GGA[g]

III.II. DENSITY OF STATES

The density of states represents the occupation of the various states against energy. It means the number of electron states that can be occupied per unit volume per unit energy. DOS influences overall various properties like specific heat and paramagnetic susceptibility, along with aspects of electron transport, etc. The density of states curves also help us to understand the hybridisation of various states of the constituent atoms. The states are plotted against Y axis and energy is plotted against X axis. Furthermore, we have divided energy axis into core energy, valence energy and conduction energy region. The dotted line represents fermi level(E_F) to separate valence band from the conduction band. In our studies we have found that the core region is dominated by s states of Al and p states of Te. In valence band region, we have seen hybridisation between p states of Te and d states of Cu. Beyond E_f , there is no contribution of any states of the constituents atoms.

We found out that these are direct band gap semi conductors. DOS helps us find the energy difference various energy bands. As such DOS can be used to calculate the band gap too. Under different exchange correaltion potential they have shown different gap. Using GGA as exchange correaltion potential , band gap of CuAlTe2 was found out to be 1.5 ev. Using mBJ as xchange correaltion potential , band gap of CuAlTe2 came out to be 2 ev.

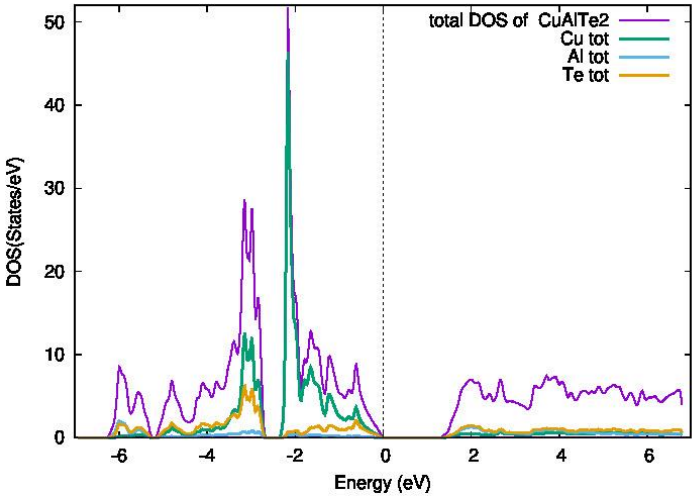


Fig.2(a)

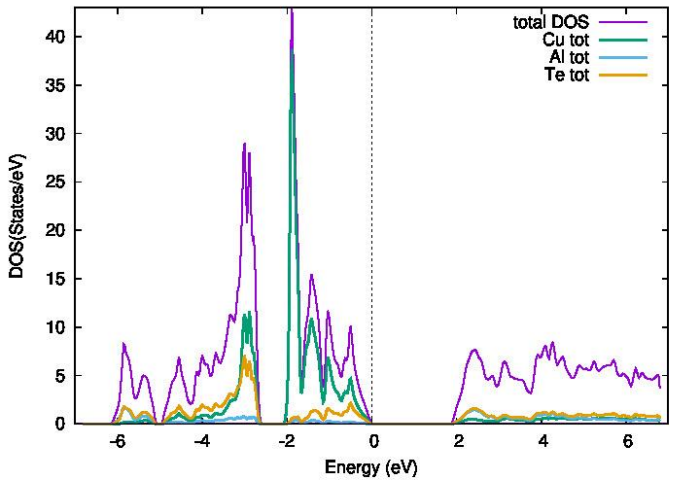


Fig.2(b)

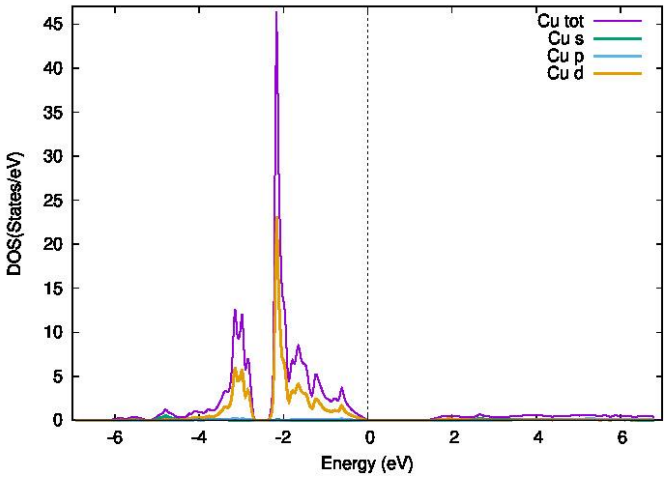


Fig.2(c)

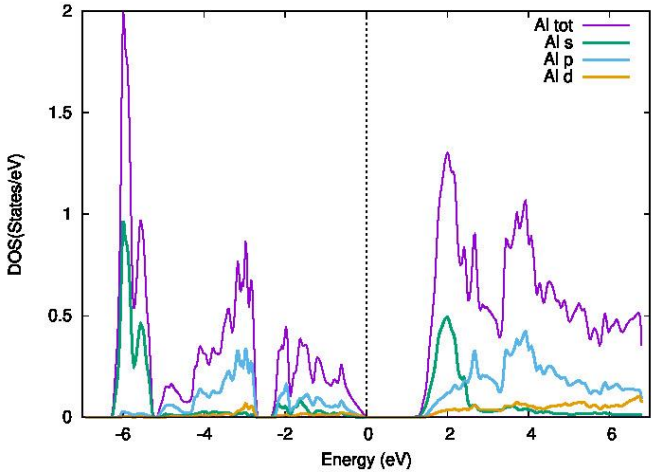


Fig.2(d)

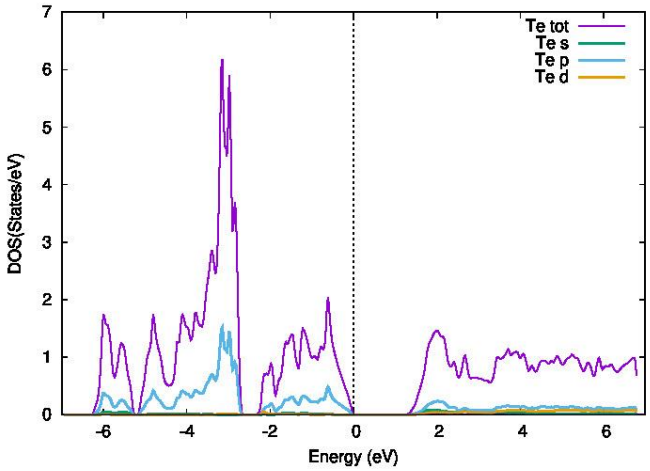
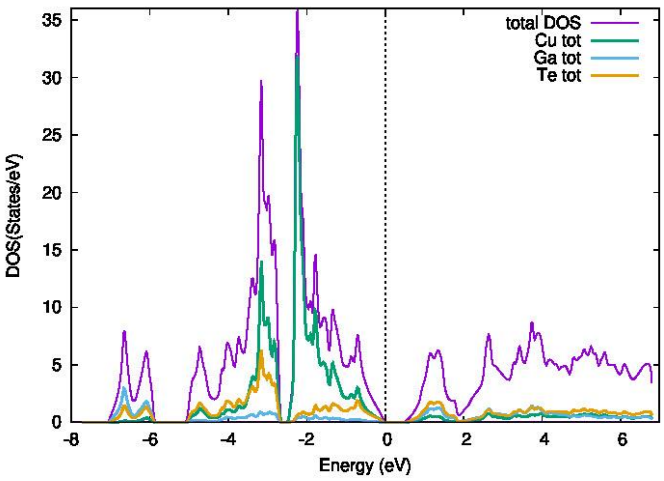


Fig.2(e)

Fig. 2(a)-Total DOS of CuAlTe2 using GGA; Fig. 2(b)-Total DOS of CuAlTe2 using mBJ: Fig.2(c-e)-Partial DOS :

On analysing the DOS and PDOS of CuGaTe2, curves were found to be similar in nature. The core region showed the hybridisation of s states of Ga and p states of Te. The valence band region showed the domination of Cu d states. The conduction band however had very little to negligible contribution from all states of the constituent elements. This compound too was found out to be direct band gap compound. Under GGA approximation, the band gap was obtained to be 0.7ev wheras using mBJ as exchanage correlation potential, the value turned out to be 1.15 ev.



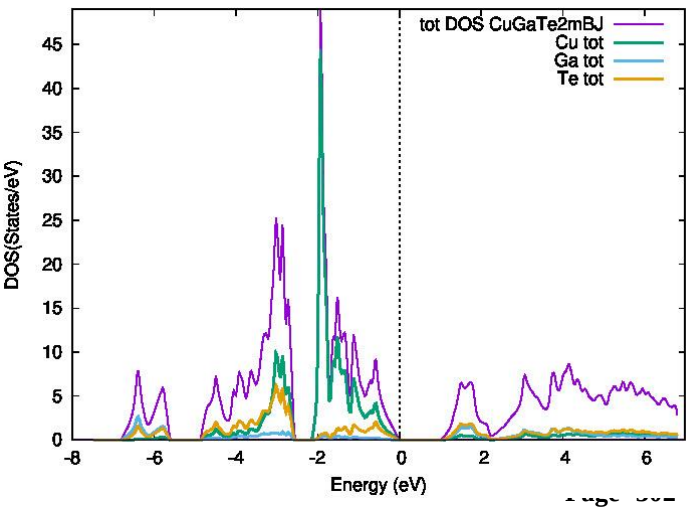


Fig.3(a)

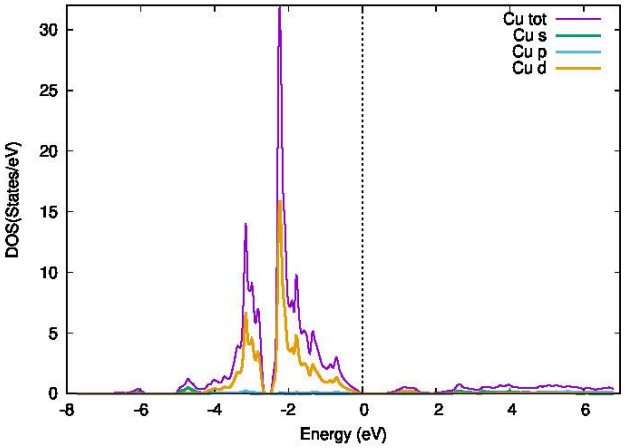


Fig.3(b)

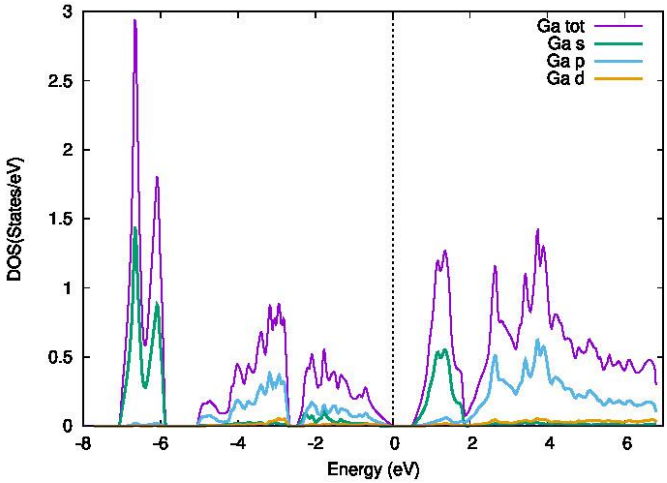


Fig.3(c)

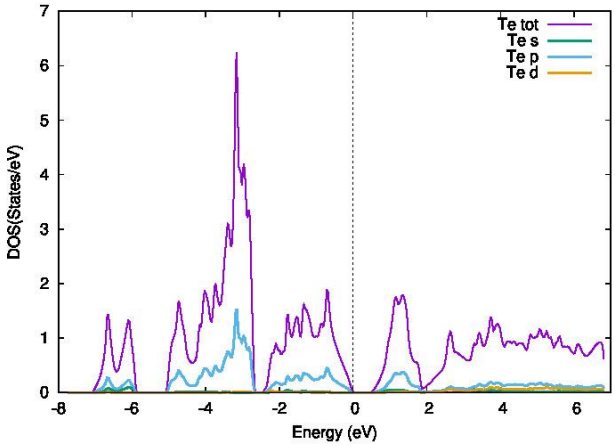
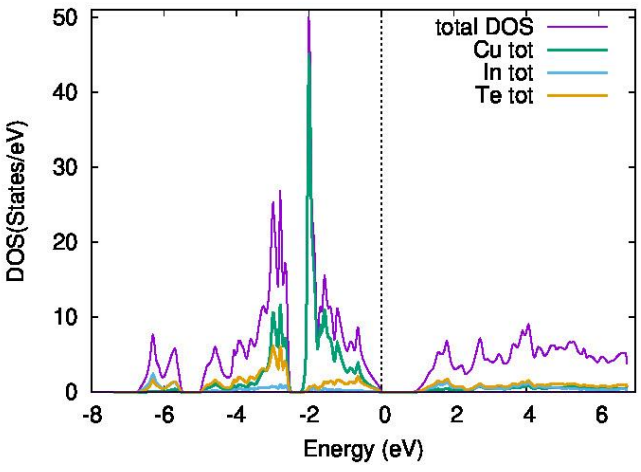


Fig.3(d)

Fig.3(e)

Fig. 3(a)-Total DOS of CuGaTe2 using GGA; Fig. 3(b)-Total DOS of CuGaTe2 using mBJ: Fig.3(c-e)-Partial DOS :

Finally we moved on to study the DOS and PDOS of CuInTe2. The nature of the curves were similar to that of previous two materials. The core region showed the contribution of s states of In and p states of Te . The valence had prominet presence of d states and hence its dominance. The conduction band as in previous materials showed no contributions from constituents atoms. We calculated the band gap to be 1.1eV under GGA whereas the value climbed upto 1.7 eV under mBJ.



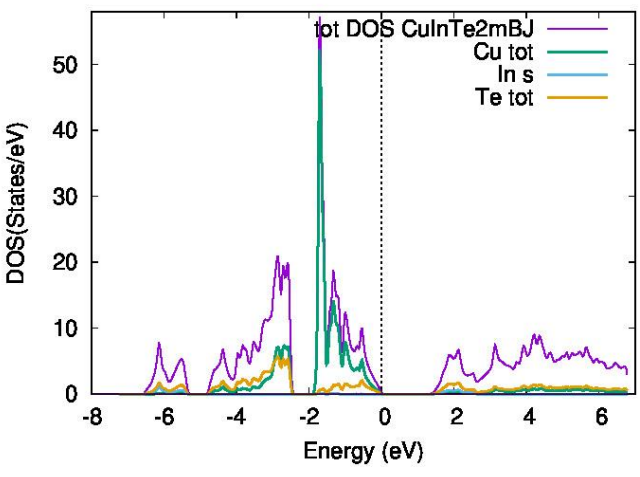


Fig.4(a)

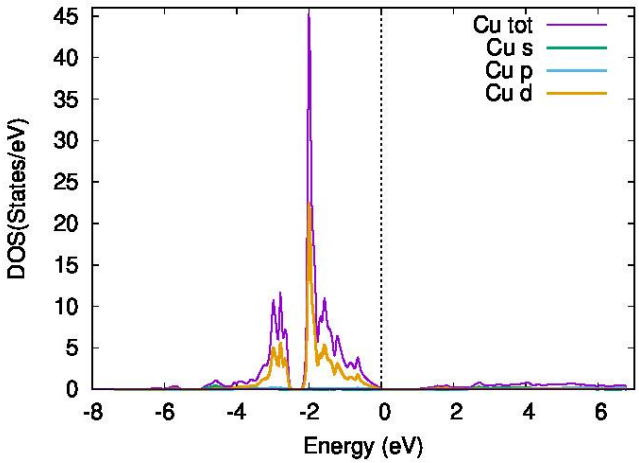


Fig.4(b)

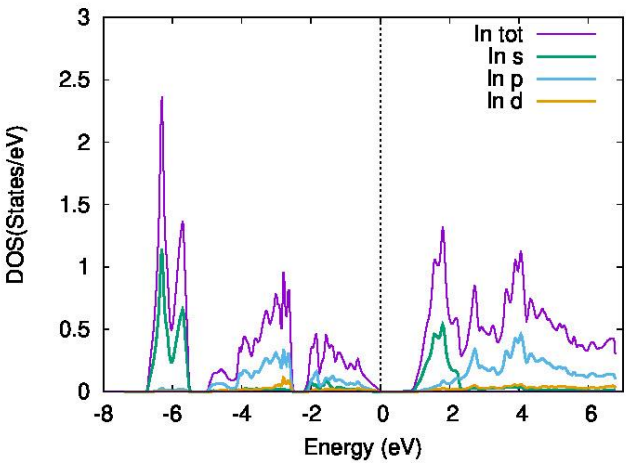


Fig.4(c)

Fig.4(d)

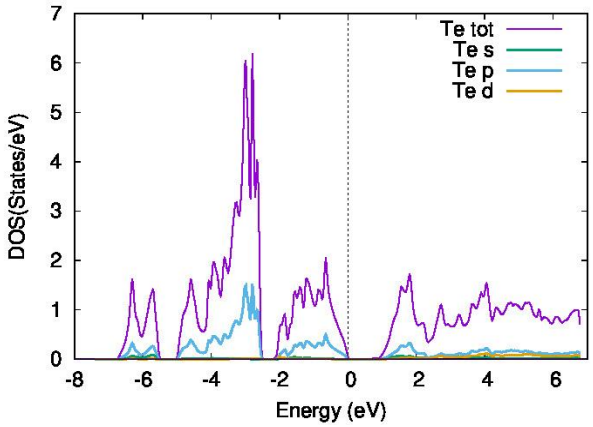


Fig.4(e)

Fig.4(a)-Total DOS of CuInTe2 using GGA; Fig. 4(b)-Total DOS of CuInTe2 using mBJ:

Fig.4(a-e) Partial DOS :

Table II: Bandgap of CuXTe2 compounds.

Compound		Exp(eV)	Previous calculation (eV)	Present calculation (eV)
CuAlTe2	Band gap(eV)	2.45[16]	1.61[17]	1.5[g], 2.0[m]
CuGaTe2	Band gap(eV)	1.2[18]	0.57[19]	0.7[g], 1.15[m]

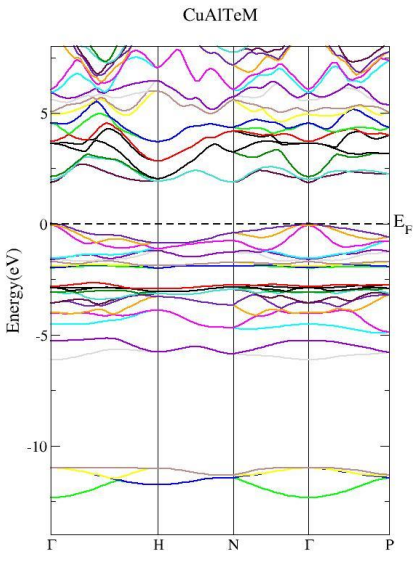
CuInTe2	Band gap(eV)	1.04[20]	0.18[21]	1.1[g] , 1.7[m]

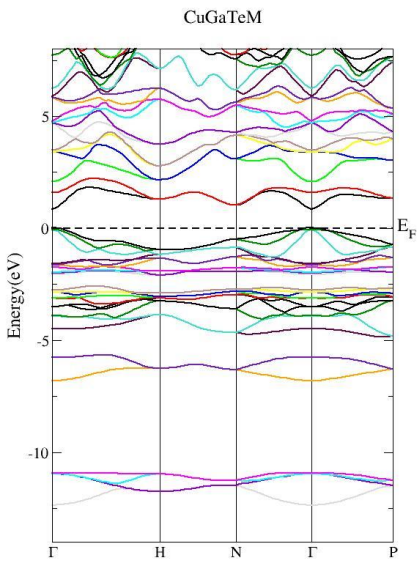
Ref [k,l,p,q,r,s] Present calculation using GGA[g] and mBJ[m]

III.III. BAND STRUCTURE

In addition to DOS, we also studied the bandstructure for CuGaX2 conpunds under GGA and MBJ approximations. Band structure forms one of ways of studying fundamental principle within condensed matter physics and materials science. It represents the organization and dispersion of electronic energy bands within a crystalline solid, delineating permissible energy states for electrons within the material. This band arrangement profoundly influences the electronic, thermal, and mechanical properties of a material, encompassing aspects like electrical conductivity and optical behavior.

In all of these CuXTe2 compounds, the curves showed similar nature. The top of the valence band and bottom of the conduction fell at different points on the Γline. This proved they are direct band gap materials. In our calculation we coalsed the top of the valence band with origin. Measuring the gap between top of valence band and bottom of the conduction band also yields bandgap. The pattern of showed that the band gaps increased when Ga in the middle is replaced by In and Al respectively. The increase in the band gap is due to shifting of valence band towards conduction band and due to interplay of s and p orbitals.





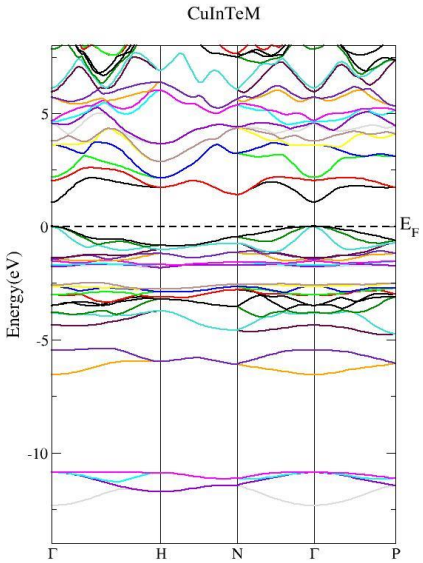


Fig.5(a) Fig.5(b) Fig.5(c)

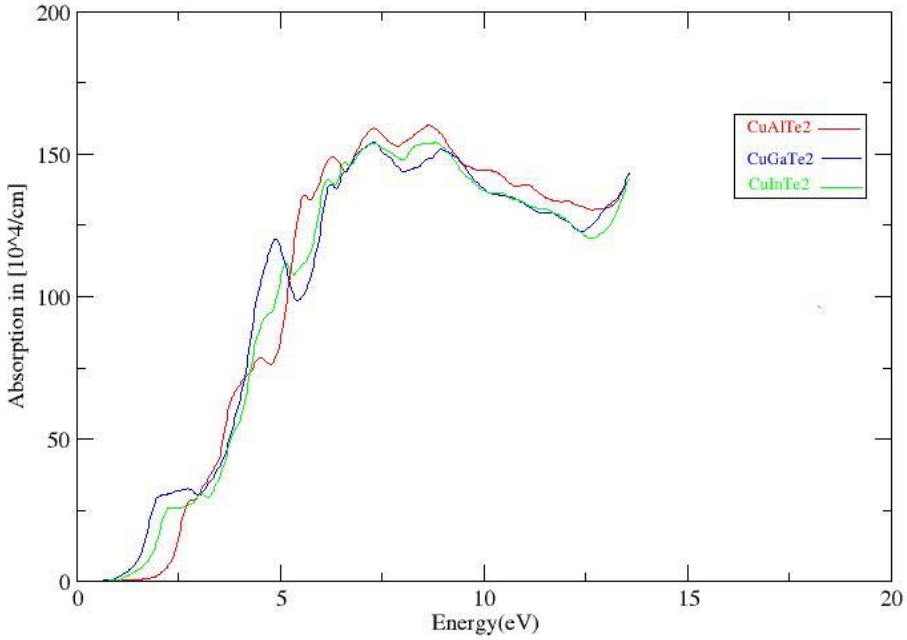
Fig.5(a-c): Bandstructures of CuAlTe2, CuGaTe2 and CuInTe2.

III.IV. OPTICAL PROPERTIES

We also explored to study the optical properties of CuXTe2 materials. The optical properties of solids provide an important tool for studying energy band structure, as well as impurity levels, excitons, localized defects, lattice vibrations, and certain magnetic excitations[26]. For studying optical properties, the knowledge of frequency-dependent complex dielectric function $\mathscr{E}$. As is known the dielectric function consists of real and imaginary parts, i.e $\mathscr{E} = \varepsilon\mathscr{E}_1 + i\mathscr{E}_2$. We used the following expressions for the calculations of the real and imaginary parts of dielectric function.

Once we have the knownledge of the real and imaginary parts of dielectric function we can calculate the various optical properties like absorption, reflectivity, refractive indices, etc.

III.V. ABSORPTION



"Optical absorption is primary criterion for selection of material for use as phtovoltaic materials. The absorption coefficient is a significant parameter in absorption studies. The **absorption coefficient** gives us indication to measure at how far light can go through material before it gets absorbed."[22] From the absorption spectra it can be seen absorption threshold of CuXTe2 materials. The absorption threshold represents the energy from where absorption take place is actually the energy of the fundamental gap. The threshold of absorption for CuAlTe2, CuGaTe2 and CuInTe2 commences at 1.55 eV, 0.95 eV, and 1.12 eV respectively. From the curves, we saw that the values of absorption keeps on increasing with the increase of energy and have maximum between 7.1 ev and 9.01 eV. The peaks values for CuAlTe2 is maximum followed by CuInTe2 and then CuGaTe2. Given the nature of curve obtained we can safely say that the the CuXSe2 materials serves as good absorption materials when utilised for energy ranges 7.1 ev and 9.01 eV.

Fig. 6: Plot of absorption vs energy

Optical reflectivity: "represents the fraction of the radiant energy that is reflected from the surface. In our analysis we found out the optical different percentage of reflectivity of the CuXTe2 materials at various energies". [22]For CuAlTe2 at 2.5eV, 5.55eV and 10.5eV the reflectivities were 34.5%, 44.56% and 50% respectively. Similarly for CuGaTe2 at the same energy values, the reflectivities were respectively 30.7%, 34.67% and 47.71%. And finally for CuInTe2, the observed values of reflectivities were 29.6%, 37.8% and 48.5% respectively. From our analyses reflectivity is energy dependent parameter. The proportion reflectivity is the highest at around 10eV for all compounds.

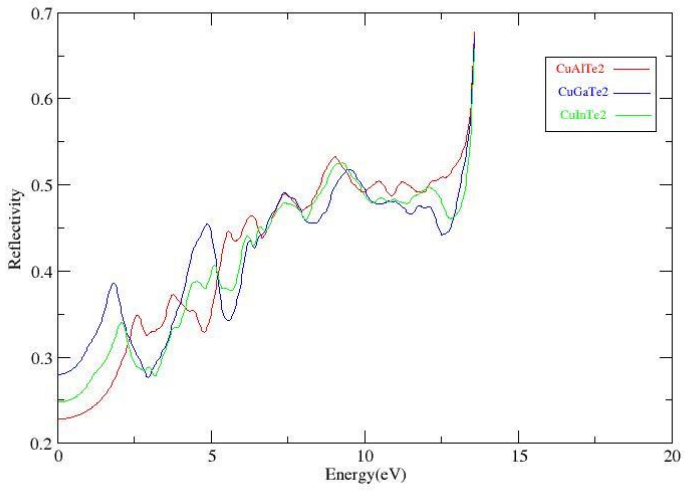


Fig.7: Plot of Reflectivity vs energy

III.VI. REFRACTIVE INDEX

Continuing with our probe, we have also calculated the refractive index which can be calculated from dielectric function. We know at zero frequency or theinfinite wavelength the real part of the dielectric function is equal to the refractive index of the material. The zero frequency refractive indices for CuAlTe2, CuGaTe2 and CuInTe2 was obtained to be 2.82, 3.32 and 2.9 respectively.

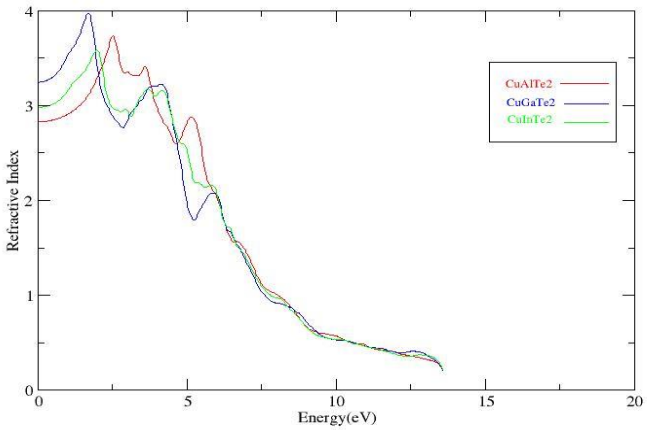


Fig.8 Refractive index vs Energy.

IV. CONCLUSION

We have carried out the first principles method of calculations of the study of structural, electronic, and optical properties of CuXTe2 compounds. In our study we found out that these comounds showed DOS and bandstructure which is in line with direct band gap semiconductors. This shows that they are direct band gap materials. DOS showed core region being dominated by s states Al, Ga, Te and p states of Te wheras the valence band being dominated by d states of Cu. The conduction band had little to no states which proves that they are semiconductors. The band gap calculation was done using both GGA and mBJ exchange correlation potentials. The values of band gap were closer to experimental values when treated with mBJ exchange correlation potentials. The optical properites like absorption, reflectivity and refraction were studied. The optical paramters like refractive indices too were close to experimental values. The materials also showed good absorption coefficients when analysed between 7.1 ev and 9.01 eV energy range.

REFERENCES

1. E. Parthe, Crystal Chemistry of Tetrahedral Structures, Gordon and Breach, New York, 1964.
2. J.L. Shay, J.H. Wernick, Ternary Chalcopyrite Semiconductors: Growth, Electronic properties and Applications, Pergamon, Oxford, 1974.
3. U. Kaufmann, J. Schneider, in: J. Treusch (Ed.), FestkorperproblemeXIV, Vieweg, Braunschweig, 1974, p. 229.
4. R. W. Birkmire and E. Eser, Annu. Rev. Mater. Sci.27, 625~1997.
5. J.L. Shay, L.M. Schiavone, E. Buehier, J.H. Wernick, J. Appl. Phys. 43 (1972) 2805.

6. S. Wagner, J.L. Shay, B. Tell, H.M. Kasper, Appl. Phys. Lett. 22 (1973) 351

7. Jaffe JE, Zunger A, ' Theory of band gap anamoly in ABC2 chalcopyrite semicondutors, Physical Review B, vol. 29, number 4, 1882-1906.

8. [8] Reshak AH, Auluck S, 'Electronic structure, linear, nonlinear optical susceptibilitiesand birefringence of CuInX 2 (X = S, Se, Te) chalcopyrite-structure compounds' PMC Physics B 2008,1:12.

9. Yadav, D.S, Electronic Properties of Bonds in AIBIIICVI2 Chalcopyrite Semiconductors, Journal of Materials Physics and Chemistry, 2015, Vol. 3, No. 1, 6-10

10. Bouguetaia et al 'Structural Phase Transition Elastic and Electronic Properties of CuXSe2 (X= In, Ga) Chalcopyrite' , Surface Review and Letters, Vol. 19, No. 2 (2012) 1250021.

11. Blaha P, Schwarz K, Madsen GKH, Kvasnicka D, Luitz J: WIEN2k, An augmented plane wave plus local orbitals program for calculating crystal properties Vienna University of Technology, Austria; 2001.

12. Boyd GD, Kasper HM, McFee JH (1971) Linear and nonlinear optical properties of AgGaS 2 , CuGaS 2 , and CuInS 2 , and theory of the wedge technique for the measurement of nonlinear coefficients. IEEE J Quantum Electron 7:563.

13. Gudelli VK, Kanchana V, Vaitheeswaran G, Svane A, Christensen NE (2013) Thermoelectric properties of chalcopyrite type CuGaTe 2 and chalcostibite CuSbS 2 . J Appl Phys 114:223707.

14. Pearson WB (1967) Handbook of lattice spacing and structures of metals and alloys, vol 2. Pergamon Press, Oxford.

15. David R. Lide, CRC Handbook of Chemistry and Physics, 79th Edition, CRC Press, Boca Raton, FL, 1998.

16. B.V. Korzun, A.A. Fadzeyeva, A.V. Mudryi, S. Schorr, Phys. Status Solidi C 3 (8) (2006) 2626–2629.

17. A.H. Reshak, S. Auluck / Solid State Communications 145 (2008) 571–576

18. Plirdpring, K. Kurosaki, A. Kosuga, T. Day, S. Firdosy, V. Ravi, G. J. Snyder, A. Harnwunggmoung, T. Sugahara, Y. Ohishi, H. Muta, and S.Yamanaka, Adv. Mater. 24, 3622–3626 (2012).

19. V.K. Gudelli, V. Kanchana, G. Vaitheeswaran, A. Svane, and N. E. ChristensenThermoelectric properties of chalcopyrite type CuGaTe2 and chalcostibite CuSbS2, Journal of Applied Physics 114, 223707 (2013); doi: 10.1063/1.4842095

20. Kazmerski L L and Juang Y J 1977 Journal of Vacuum Science & Technology 14 769

21. Rashkeev S N, Lambrecht W R L 2001 Phys. Rev. B 63 165212

22. Nakul Chhetri, and Purna Chandra Barman, "The study of Ground State Properties of Chalcopyrites of the type CuXSe2 (where X= Al, Ga, In) using DFT," International Research Journal of Advanced Engineering and Science, Volume 8, Issue 4, pp. 81-88, 2023.

23. Wimmer, E.; Krakauer, H.; Weinert, M.; Freeman, A. J. (15 July 1981). "Full-potential self-consistent linearized-augmented-plane-wave method for calculating the electronic structure of molecules and surfaces: O2 molecule". Physical Review B.

24. Perdew, J. P., Burke, K., and Ernzerhof, M.(1996). Phys. Rev. Lett., 77:3865. 8, 126, 134, 136, 137, 138, 139.

25. Tran, F. and Blaha, P. (2009). Phys. Rev. Lett., 102:226401. 8, 58, 59, 60, 84, 134, 136, 138