

Optical Properties of CuAlX_4 (X: Cl, Br): A First Principles Study

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Declaration

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A handwritten signature in blue ink, appearing to read "Saty", with a horizontal line drawn underneath it.

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Approval Sheet

This thesis entitled "Optical Properties of CuAlX_4 (X: Cl, Br): A First Principles Study" by SATYANDER SINGH is approved for the degree of Master of Physics from IIT Hyderabad.



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Abstract

We report the electronic structure and optical properties of Copper based halides within the frame work of Density Functional Theory (DFT). The optimized parameters are in good agreement with experimental values. These systems are found to be semiconductor. It is evident from the band structure plots. The calculated optical properties reveal that the investigated systems would have future applications which can be explored.

Contents

Declaration.....	(ii)
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Approval sheet.....	(iii)
Acknowledgements.....	(iv)
Abstract.....	(v)
1 Introduction.....	1
2 Theoretical Background.....	2
2.1 Approximation to solve Many-Body problem.....	3
2.1.1 Born-Oppenheimer Approximation.....	3
2.1.2 The Hartree Approximation.....	3
2.1.3 The Hartree-Fock Approximation.....	4
2.2 Density Functional Theory.....	4
2.2.1 Kohn-Sham method.....	5
2.2.2 Local Density Approximation.....	6
2.2.3 Generalized Gradient Approximation.....	6
3 Results and discussion.....	7
3.1 Structural and Electronic properties.....	7
3.2 Optical Properties.....	9
4 Conclusion.....	11
5 References.....	12

Chapter 1

Introduction

Scintillators exhibit fast scintillation [1] via various mechanisms which include core-valence (CV) transition, inter-configuration transitions, exciton luminescence [2, 3, 4, 5, 6]. Core valence luminescence may be observed due to radiative transition between valence band to core valence band, and this transition is mainly observed in Ba, Cs, Rb-based fluorides, chlorides and bromides [7]. Apart from fast decay time, these core-valence luminescence materials exhibit high thermal stability, and relatively high light yield [8]. Inter-configuration transition can occur in the case of activator compounds with allowed transition between states of 5d-4f particularly in rare earth ions Ce^{3+} , Pr^{3+} and Nd^{3+} [9]. Exciton luminescence is observed in pure compounds also, particularly self-trapped luminescence. This transition is mainly observed in alkali earth fluorides with high light output. Among them, cross luminescence is one of the important criteria for fast scintillation [10]. The compounds which exhibit cross luminescence or core valence luminescence (CVL) are very interesting because of their fast decay and high thermal stability. The radiative transition of electrons from valence band to core valence band will lead to cross luminescence (also called Auger free luminescence) [11, 12, 13, 14, 15, 16, 17, 18]. The general requirement for CVL is that energy difference between top of the valence band and top of core valence band (E_{VC}) should be less than the band gap (E_g) of the compound. The compounds which exhibit CV luminescence are called L -type because of $E_g > E_{VC}$. In the case of compounds like SrI_2 and CaF_2 , the transition is observed from conduction band to valence band and is called Auger luminescence [19]. These are called A -type compounds where $E_g < E_{VC}$, whereas in CsI , it is observed that, $E_g > E_{VC} - \Delta E_v$, it is called AL -type and they exhibit fast scintillation.

Copper based compounds are well-known for catalysis applications due to their ability to readily bind small molecules such as olefins, aromatics and carbonyls [20, 21, 22, 23, 24, 25, 26]. A family of materials based on the structural relationship between $ZnCl_2$ and SiO_2 [27] called as halozeotypes are developed. Synthesis utilizing the Cu (I) and Al (III) tetrahedral cations yield a family of materials of general formula $Cu_mAl_mCl_{4m}$, which are structural analogs of aluminophosphates [28]. These framework materials are constructed from Lewis acidic and redox active building blocks which are known to be reactive toward small molecules and the polymerization of olefins and aromatics. The condensed nature of this framework provides a sufficiently ridged lattice that, in the absence of guest molecules, the isolated Cu (I) centers exhibit brilliant photoluminescence under UV and X-ray excitation. A diverse range of materials in which copper (I) serves as the luminescent activator exhibit emissions across the visible spectrum. When doped into silicate glasses³ or zinc chalcogenide phosphors a blue to green luminescence is observed, whereas a red to orange emission is observed for $Cu_4I_4L_4$ clusters (L=alkylamine) [29]. Similarly, models used to describe Cu(I) luminescence vary widely. Mechanisms including metal-centered $d^{10} \rightarrow d^0$'s absorption, halide to metal charge transfer (XMCT), and the presence of extrinsic or cluster defects, are most relevant to understanding of the luminescence of $CuAlCl_4$.

The structure of a- $CuAlCl_4$, in which $CuCl_{4/2}$ tetrahedral units reside in ordered lattice sites that are isolated by corner-sharing to $AlCl_4$ tetrahedral, make this system particularly well

suitable for investigation of the luminescence of the Cu (I) center [30, 31]. Furthermore, the ability to form a complete chloride/bromide solid solution, α -CuAlCl_{4-x}Br_x, provides a measure for the role of the halide ligands in the photoluminescence mechanism [32]. A lot of research has been done on materials based on Boron family and halides in the area of optical applications. The present study on compounds CuAlX₄ are in line with former studies. The present thesis is arranged as follows, second chapter deals with the methodology, third chapter discusses the results part and followed by conclusion.

Chapter 2

Theoretical Background

The branch of physics which deals with the study of solids is the Condensed Matter Physics. It is concerned with the properties of solids. All the properties of the solids can be obtained by solving the Schrodinger wave equation. The complete information about the state of a system is contained in the wave function Ψ . In order to understand the physical properties of a system, the time independent Schrodinger wave equation needs to be solved which is given by:

$$\hat{H}\Psi_i(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) = E_i\Psi_i(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) \quad (2.1)$$

For a one electron system, the solution to this equation is straightforward. But for a system having more than one electron the complexity involved in the solution is more. The electron-electron interaction term makes the solution difficult because of the inherent wave nature in electrons.

The time independent Schrodinger wave equation for a system consisting of M nuclei and N electrons written in atomic units is given by:

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^N \frac{1}{m_i} \nabla_i^2 - \frac{1}{2}\sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (2.2)$$

The Hamiltonian of the system consists of five terms. The first terms represent the kinetic energy of the electrons. The second term represents the kinetic energy of the nucleus. The attractive electrostatic electron-nucleus interaction is represented by the third term. The fourth term and fifth term respectively represent the repulsive interactions between electron-electron and nucleus-nucleus interactions.

The analytical solution to this many body Schrodinger equation is a complex task. Numerical methods should be used for the solution. Many approximations must also be used to solve this equation. Density functional theory (DFT) is developed for getting an

approximating solution to this Schrodinger equation. DFT implemented through various software such as VASP, WIEN2k, CASTEP etc. is very efficient in getting the ground state properties of solids.

2.1 Approximation Methods used in Solution

2.1.1 Born-Oppenheimer Approximation

The nuclei are more massive than electron. Therefore, it can be naively approximated that the nuclei are almost at rest and the electrons are in a potential which is produced by the electrostatic field of nuclei. The basic assumption behind this approximation is that the motion of electrons and nuclei can be made independent. With this assumption, the Hamiltonian is reduced to three terms.

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^N \frac{1}{m_i} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} = \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee} \quad (2.3)$$

The Schrodinger wave equation will be solved with this electronic wave function alone. The nucleus-nucleus interaction energy will be a fixed value. This energy will be added to the electronic energy to obtain the total energy of the system.

$$\hat{H}_{elec} \Psi_{elec} = E_{elec} \Psi_{elec} \quad (2.4)$$

$$E_{tot} = E_{elec} + E_{nuc} \quad \text{where, } E_{nuc} = \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (2.5)$$

Even though the complexity of the equation has reduced, still more approximations are needed to solve the many body problem. Several approximation methods were proposed before the advent of DFT. They will be discussed in the next section.

2.1.2 The Hartree approximation

In this method, the electron is considered to be distinguishable and independent. The total Hamiltonian is written as the product of single particle equation which is given by:

$$\Psi(\vec{r}_i) = C_N \prod_i^n \Phi_i(\vec{r}_i) \quad (2.6)$$

Each electron moves independently and it feels an average electrostatic field created by all other electrons. In fact, electron motion will be correlated. Also, electron is a fermionic particle. These facts are not taken care in this approximation i.e., the exchange and correlation effects are not taken care in this method.

2.1.3 Hartree-Fock Method

The fermionic nature of electron is taken care in this method. The wave function is expressed in this method as Slater determinant and then solved using variational principle to get the ground state energy. Each electron is considered to move in an average field created by all the other electrons. This is known as mean field approximation. As in the Hartree method, here also the wave function is expressed as the product of single particle orbitals. The single particle orbital is consisting of position vector and spin vector. The antisymmetric nature of the wave function is implemented through Slater determinant. The wave function can be represented as:

$$\Psi^D(\vec{r}) = \frac{1}{\sqrt{N!}} \begin{bmatrix} x_1(\vec{r}_1) & \cdots & x_n(\vec{r}_1) \\ \vdots & \ddots & \vdots \\ x_1(\vec{r}_n) & \cdots & x_n(\vec{r}_n) \end{bmatrix} \quad (2.7)$$

If two rows in this determinant is same, which means two electrons having same spin are positioned in the same location. This is not possible according to Pauli's exclusion principle. Since by the property of determinant, if two rows are same, then the determinant will evaluate to zero which implies that the Slater determinant is the manifestation of Pauli's exclusion principle. Also, if two rows are interchanged, the sign of the determinant will be negated which manifest that the Slater determinant takes care of the exchange interaction also.

Hartree-Fock method employs solving the Schrodinger wave equation by considering wave function in the form of Slater determinant. Since in this model also, the electrons are considered to be independent, the correlation effect is not considered in this model. This is the major drawback of this model.

2.2 Density Functional Theory

The density functional theory evolved as a technique to solve the many body Schrodinger equations. The idea behind DFT is that the wave function can be replaced by density. The electrons are moving in an electrostatic potential of the nucleus. The electrons can't be localized due to Heisenberg uncertainty principle. The exact position of an electron can't be located. The probability of an electron at a particular location can only be specified. The corresponding probability is given by the square of the wave function. The electrons are moving in a potential which is generated by the electron as well as all the other electrons. In DFT studies, the quantity of interest is the electron density rather than wave function. Here Energy is expressed as a function of density which itself is a function of position. Since energy is a function of a function, the theory is called as the density functional theory. The idea that density can be used instead of wave function was first put by Thomas and

Fermi through their statistical model of homogeneous electron gas and then Hohenberg and Kohn were the one who verified it through their theorems.

The advantage of this method over other conventional method to solve the many body problem is that it is computationally efficient. The electron wave function is a function of $3N$ variables where N is the number of electrons in the system. But irrespective of the number of electrons, the electron density is a function of only three variables x , y and z .

$$\rho(r) = N \int d^3r_2 d^3 \dots d^3r_N \Psi(r_1, r_2 \dots r_N) \Psi^*(r_1, r_2 \dots r_N) \quad (2.8)$$

There are two important theorems in DFT which was formulated by Hohenberg and Kohn. The first theorem states that there is a one to one correspondence between external potential and the electron density. The external potential is nothing but the attractive electrostatic interaction between nucleus and electron. Since every atom has different number of electrons, external potential will be different for different atoms and so there will be a unique density associated with that potential. The second theorem states that the density which minimize the total energy is the exact ground state energy of the system. The two theorems together state that the knowledge of density of a system can predict the ground state energy of the system.

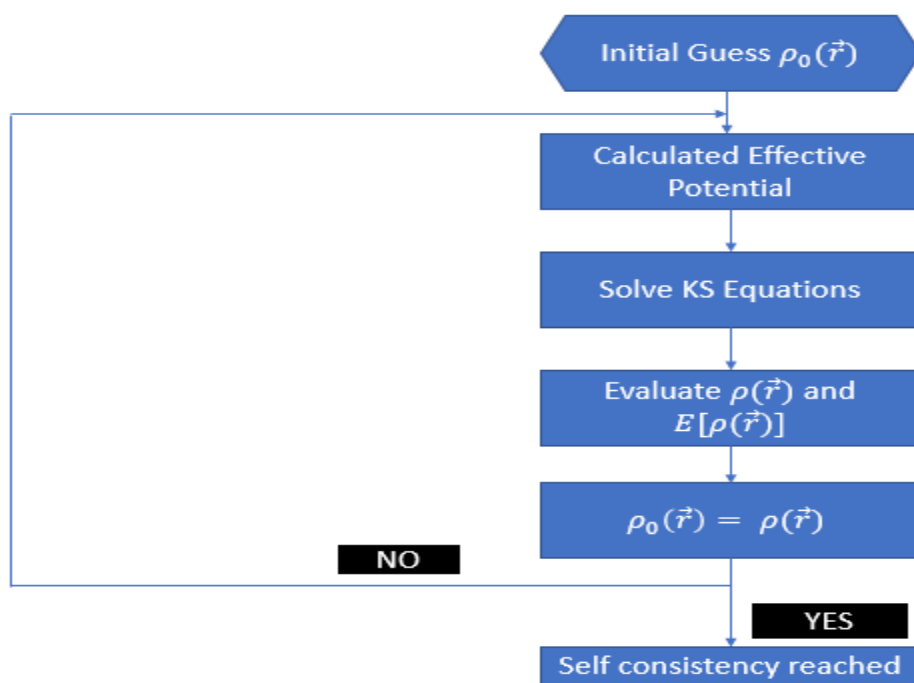
2.2.1 Kohn-Sham Method

Density functional theory has set up its functionality by Kohn Sham method. The theorems put forward by Hohenberg and Kohn has been practically implemented through Kohn-Sham method. Here the original system which is consisting of interacting electrons is mimic through non interacting system of electrons. This non-interacting system will have exactly the same density as that of the non-interacting system of electrons. As the solution stems on just one unknown quantity electron density rather than a large number of unknown wavefunctions, the method is computationally cheaper. The total energy of this system is given by the equation:

$$E = T_o[\rho] + \int V_{ext} \rho(\vec{r}) d\vec{r} + \frac{1}{2} \int \frac{\rho(\vec{r}) \rho(\vec{r}') d\vec{r} d\vec{r}'}{|\vec{r} - \vec{r}'|} + E_{xc}[\rho] \quad (2.9)$$

The first term corresponds to the kinetic energy of the non-interacting electrons, the second term is the external potential which is same as the Hartree potential, the third term corresponds to the Coulomb interaction between the electrons and the forth term is the exchange correlation energy which consist of two energies exchange energy and correlation energy. The above energy functional corresponds to the energy as a function of density for each of the single particle wave equation. The first three terms of this equation can be calculated exactly. The important part of this equation is the exchange correlation energy which takes care of the interaction energy between electrons which was

left out as the system is assumed to be made up of non-interacting electrons. The exchange energy is same as calculated in the Hartree-Fock method and the correlation energy is the difference between the exact energy of the system and the exchange energy. The exchange energy deals with interaction of electrons having opposite spin and correlation energy the interaction energy between electrons of the same spin. As in the mean field approximation, the electrons are not in an average field, the spatial position of each electron relative to the other electron must be properly considered for obtaining the true ground state energy of the system. The Kohn Sham method of solving for the ground state property has been shown in the flowchart below.



Each of the system has a unique external potential which basically makes DFT as an ab initio method in which the atomic number is the only input which is given for calculation. The initial guess of the electron density is obtained by superposing the atomic densities of neutral atoms placed at their proper position. With this charge density the effective potential will be calculated. The obtained effective potential will be used in the Kohn Sham equation and the new charge density will be calculated. If this new charge density is equal to the initial guessed charge density, then this is the true charge density of the system otherwise the iteration will be continued until the required convergence meets. The true

ground state energy can be calculated with this charge density. This is the method of solution implemented in DFT.

The interaction between electrons is not known accurately and therefore the true functional form of the exchange correlation potential cannot be explicitly understood. The exchange correlation functional should be chosen effectively for the efficient account of this interaction between the electrons. Several approximation methods are there which calculates this interaction like Local Density Approximation (LDA), Generalized Gradient Approximation (GGA) etc. Each of these approximation works well according to the system we have chosen.

2.2.2 Local Density Approximation (LDA)

In the LDA treatment the system of electron actually being an inhomogeneous system is considered to be a homogeneous system like electron gas. Since the system of homogeneous electron gas has solution, similar method can be adopted here also. The exchange correlation energy is written as

$$E_{XC}^{LDA}[\rho] = \int \rho(\vec{r}) \epsilon_{XC}[\rho(\vec{r})] d\vec{r} \quad (2.10)$$

Here $\epsilon_{xc}[\rho(\vec{r})]$ is the exchange-correlation energy per particle of a uniform electron gas of density (\vec{r}). Since the system of uniform gas can be solved with conventional methods such as Monte Carlo approach, LDA employs this approach for obtaining exchange correlation energy.

The exchange correlation energy is split into exchange and correlation energy.

$$\epsilon_{XC}[\rho(\vec{r})] = \epsilon_X[\rho(\vec{r})] + \epsilon_C[\rho(\vec{r})] \quad (2.11)$$

The LDA is more suitable for homogeneous systems. It has several disadvantages as well. It does not predict the properties of strongly correlated systems. The band gap prediction with this method is not fairly accurate. It does not give accurate results for systems with Vander Waals attraction.

2.2.3 Generalized Gradient Approximation (GGA)

The main problem with the Local density approximation is that it considers the system as homogeneous in spite of the fact that the real systems are not homogeneous. There will be a finite variation in the density. This needs to be considered. GGA method considers this

finite variation in electron density. The exchange correlation energy in this method is given by:

$$E_{xc}^{GGA}[\rho] = \int \varepsilon_{xc}^{GGA}[\rho(\vec{r}), \nabla\rho(\vec{r})]dr \quad (2.12)$$

GGA method gives fairly better results compared to LDA in terms of ground state energy calculation, prediction of band gaps etc.

Chapter 3

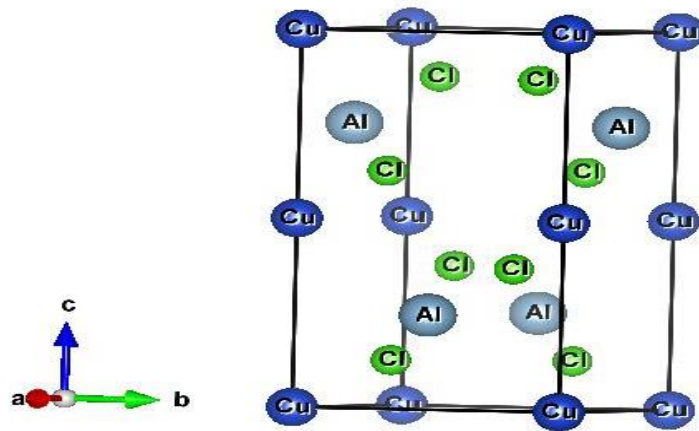
Results and Discussion

Structural and Electronic Properties

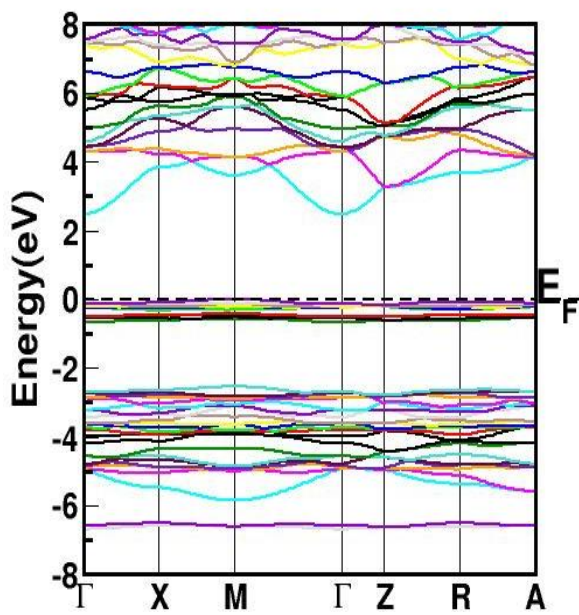
The investigated compounds CuAlX_4 (X: Cl, Br) crystallize in tetragonal structure with space group $P\bar{4}2c$ (112). The crystal structure is shown in Fig. 1(a). We have optimized the lattice parameters of the investigated compounds by using experimental parameters as inputs, and given in Table 1. For both the compounds, our optimized parameters are in good agreement with the experimental values. The band structure of the investigated compounds is shown in Fig. 1(b, d). These compounds found to be a wide band gap semiconductor with band gap around 2.4 eV. The band gap nature is found to be indirect for both the compounds. The bands are more dispersive in conduction band compared to valence band. From the band structure it is evident that, the difference between valence band and next deeper core valence band is lesser than band gap, and this might provide scintillating properties. Further we have analyzed the total and partial density of states of both the investigated compounds and presented in Fig. 1(c, e). Cu and halides (Cl, Br) states are contributing more to total density of states in valence band near Fermi level and deeper core valence band both. Halides (Cl, Br) are contributing most in conduction band. We can see that p – orbital of Cu and (Cl, Br) atoms are contributing most near Fermi level as well as deeper core valence band. Next, we have checked effects of spin orbit coupling on the electronic properties, but we could not find any change.

Table1: The optimized parameter along with experimental values.

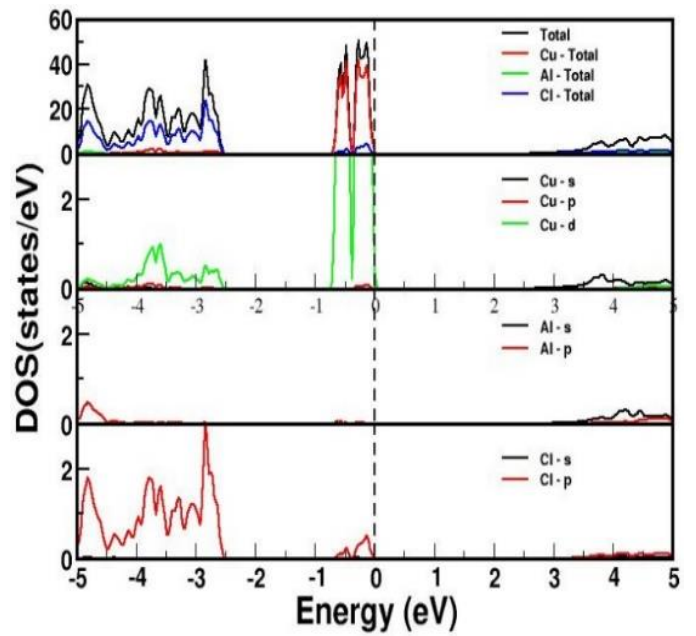
Compound	Experiment (Å)			Optimized parameter (Å)		
	a	b	c	a	b	c
CuAlCl_4	5.55	5.55	10.084	5.64	5.64	9.98
CuAlBr_4	5.72	5.72	10.59	5.72	5.72	10.59



(a)



(b)



(c)

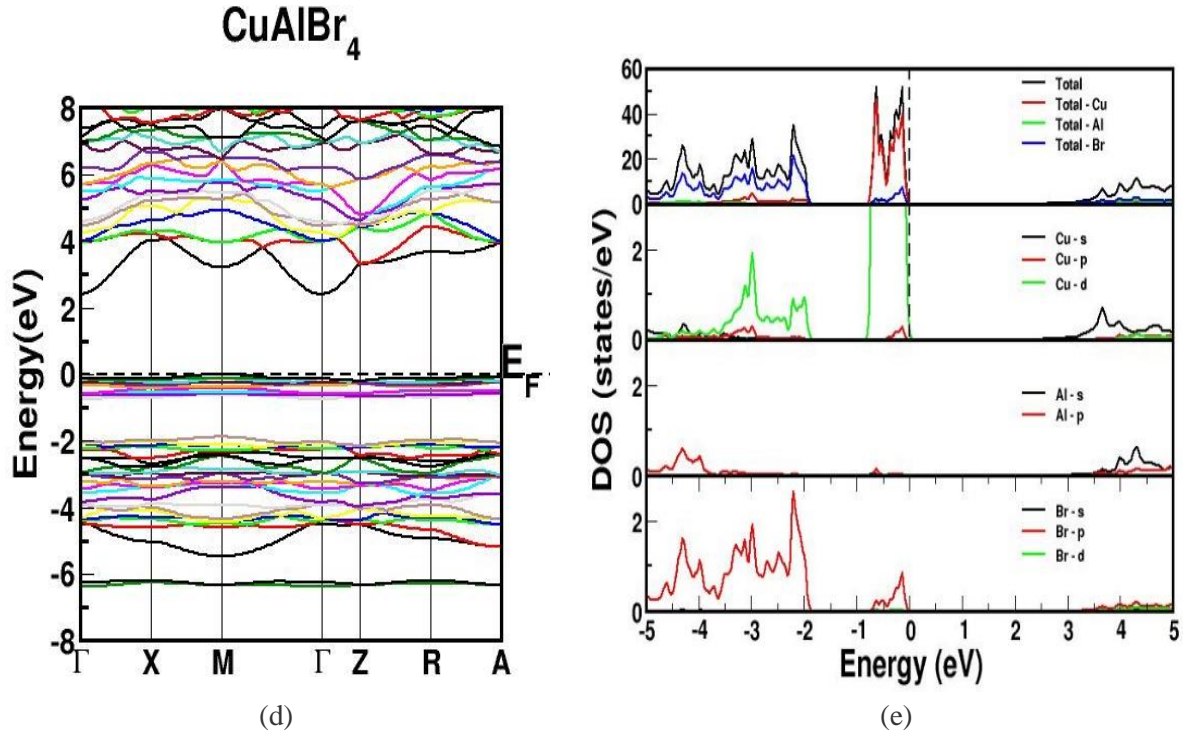
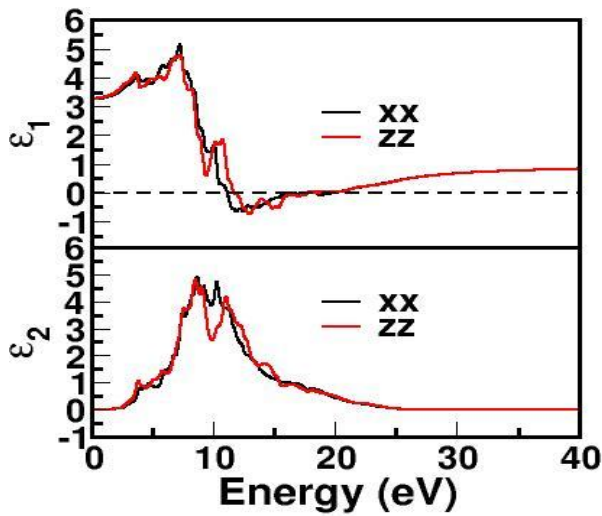


Fig. 1. (a) Crystal structure, (b) The electronic structure of CuAlCl₄ (c) Total DOS along with partial density of states of CuAlCl₄ (d) The electronic structure of CuAlBr₄ (e) Total DOS along with partial density of states of CuAlBr₄

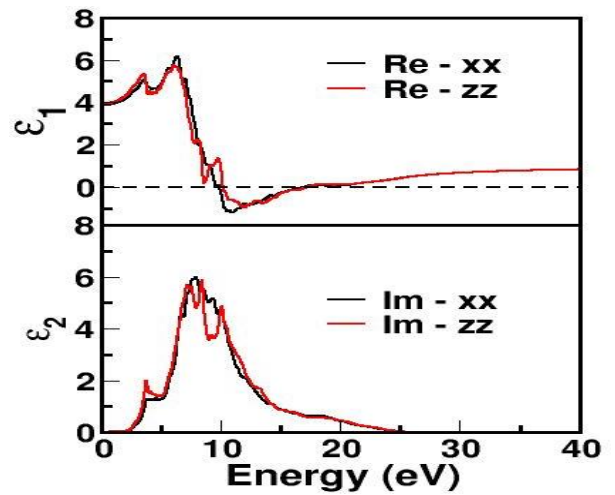
Optical Properties

In this section, we discuss the calculated optical properties of the compounds using GGA functional. Since optical property calculations need a dense mesh of uniformly distributed k-points, we use $44 \times 44 \times 25$ mesh with 3168 k in the Irreducible Brillouin Zone (IBZ) for the investigated compounds. The calculated absorptive part ϵ_2 and the dispersive part ϵ_1 of the complex dielectric function $\epsilon(\omega)$ as a function of the photon energy are shown in Fig. 2 (a, b). Imaginary part of dielectric function illustrates the optical transition mechanism. The real part ϵ_1 of the dielectric function can be derived from the imaginary part using the Kramers - Kronig relations. The knowledge of both the ϵ_1 and ϵ_2 allows the calculation of important optical functions such as refractive index, reflectivity and absorption coefficients. The calculated dielectric functions of both compounds are shown in Fig.2[a, b], which is the sum of all transitions from valence band to conduction band. Imaginary part of dielectric function starts at a particular energy called threshold energy, and threshold energy is 3.5 eV for both compounds. The higher energy spectra are due to transition of electrons from core valence band to conduction band. The peak in the higher energy region of dielectric function indicate the transition of electrons from core valence band to conduction band creating hole in the core valence band which plays a major role

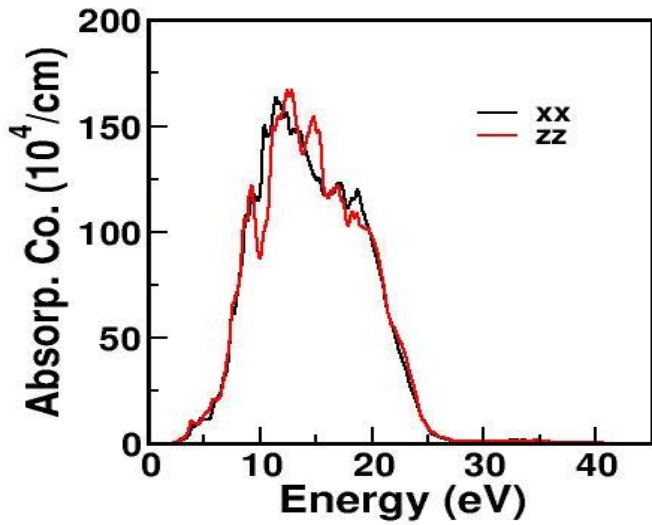
in CVL, and this hole recombine with the electrons in the valence band giving rise to the cross luminescence with fast decay. We have predicted A - type luminescence to occur in compound CuAlCl_4 because of the energy difference between top of the valence band to top of the core valence band is more than the band gap of the compound and the transition from valence band to core valence band is less probable. The peak near band gap in the spectra of imaginary dielectric function indicate the transition of electrons from valence band to conduction band. In case of CuAlBr_4 , the energy difference between top of the valence band to top of core valence band is less than the band gap of compound and the transition of electrons is possible from the valence band to the core valence band which may lead to the fast luminescence. The compound CuAlCl_4 is found as A-type scintillator and the compound CuAlBr_4 is found as L-type scintillator. Next, we have calculated the refractive index along two crystallographic directions and are shown in Fig.2[c, d]. We have found the optically isotropic nature of both compounds in long energy range. The investigated compounds are optically isotropic while these are structurally anisotropic which can be considered as the basic requirement for scintillators. The value of refractive index is around 2 for both the compounds. The absorption coefficient of both compounds as a function of photon energy is calculated and are shown in Fig.2[e, f]. The absorption coefficient reveals the manner in which the compounds absorb the incident radiation. Absorption spectra together with the electronic structure permits a basic understanding of scintillating characteristics of materials. The imaginary part of the dielectric spectra is directly proportional to absorption spectra. In both compounds, below 2.5-3 eV, there is no response from these systems which indicate the optical gap of the compounds being around 2.5 eV. Below this energy range these materials behave like transparent materials. The absorption spectra are observed in the range of 2.5-30 eV i.e., in the ultraviolet region for both compounds. We predict that both compounds studied are good scintillators.



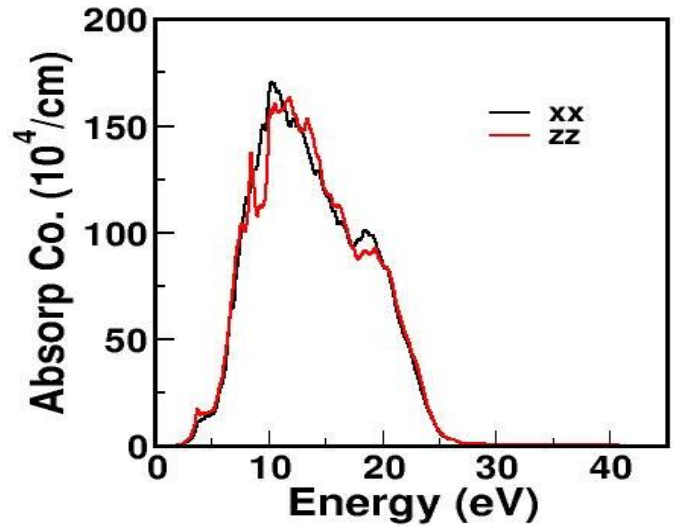
(a)



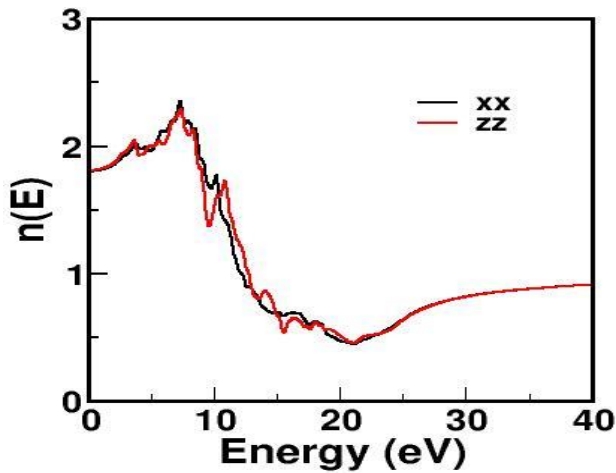
(b)



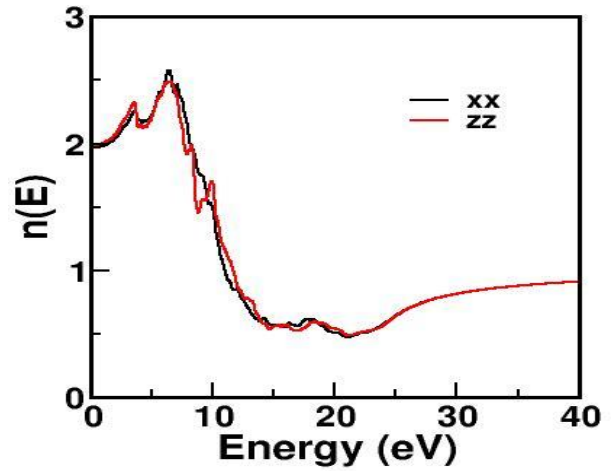
(c)



(d)



(e)



(f)

Fig.2. The optical properties calculated, The dielectric function (a) CuAlCl_4 (b) CuAlBr_4 , The absorption coefficient (c) CuAlCl_4 (d) CuAlBr_4 and Refractive index (e) CuAlCl_4 (f) CuAlBr_4

Chapter 4

Conclusions

We have studied the electronic structure and optical properties of CuAlX_4 (X: Cl, Br) within the frame work of Density Functional Theory using GGA functionals. Both the compounds are found to be indirect band gap semiconductor with band gap value around 2.4 eV. The compound CuAlCl_4 and CuAlBr_4 are reported as A – type and L – type scintillators respectively. Both the compounds are optically isotropic while they are

structurally anisotropic which project these compounds as better candidates for transparent ceramic scintillators.

Chapter 5

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