



“BAND STRUCTURE CALCULATIONS ON NOBLE METAL
HALIDES, AND THEIR DERIVATIVES”

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

By

SAHAB UDDIN MAZUMDER

Ph.D. REGN NO.: Ph.D./PHY/00225

DEPARTMENT OF PHYSICS, SCHOOL OF SCIENCES

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Prof. Y. Sundarayya

Submitted

In partial fulfillment of the requirements of the Degree of Doctor of
Philosophy in Physics of Nagaland University



नागालैण्ड विश्वविद्यालय

NAGALAND UNIVERSITY

(संसद द्वारा पारित अधिनियम 1989, क्रमांक 35 के अंतर्गत स्थापित केंद्रीय विश्वविद्यालय)
(A Central University established by an Act of Parliament No.35 of 1989)

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CERTIFICATE

This is to certify that Mr. **Sahab Uddin Mazumder** Registered as a Research Scholar for Ph.D. (Science) degree in Physics in Nagaland University and has been working under my guidance and supervision. His thesis entitled “**BAND STRUCTURE CALCULATIONS ON NOBLE METAL HALIDES AND THEIR DERIVATIVES**” is being forwarded for submission for the Ph.D. (Science) Degree of this University. It is certified that he has fulfilled all the requirements according to the rules of this University regarding investigation embodied in his thesis and the work described in this thesis is original and has not been submitted for any other degree or diploma in this or any other University.

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Supervisor



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DECLARATION

I, Mr. **Sahab Uddin Mazumder**, bearing Registration No. **PhD/PHY/00225** with effect from 23/08/2018, hereby declare that the contents of the thesis entitled “**BAND STRUCTURE CALCULATIONS ON NOBLE METAL HALIDES AND THEIR DERIVATIVES**” hereby declare that the subject matter of this Thesis is the record of work done by me, that the contents of this Thesis did not form basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/Institute. This is being submitted to the Nagaland University for the degree of Doctor of Philosophy in the department of physics.

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Preface

In this thesis work, the full-potential linearized augmented plane wave (FP-LAPW) approach based on density functional theory (DFT) is applied to calculate the structural, electronic and optical properties of binary compounds and their ternary alloys with metal elements (Cu/Ag) substituted in MX (M = Ag, Cu and X = Br, I) type semiconductor alloys system i.e., $Ag_{1-x}Cu_xI$, and $Ag_{1-x}Cu_xBr$ at various substitution concentrations $x = 0.00, 0.03125, 0.0625, 0.09375, 0.125, 0.15625, 0.1875, 0.25, 0.5, 0.75$, and 1.00 . We have employed Generalized Gradient Approximation (GGA) as exchange-correlation potentials for calculation of structural properties for all the compounds under consideration. In addition, we have used Tran-Blaha modified Becke Johnson (TB-mBJ) scheme mainly to calculate exchange-correlation potentials for the calculation of electronic and optical properties, which provide almost accurate energy band gaps as well as their band dispersions near to experimental calculations compared to other theoretical values. Furthermore, the hybrid functional HSE06 scheme has been used for some specific doping concentrations ($x = 0.00, 0.25, 0.5, 0.75$ and 1.00) for electronic and optical properties of $Ag_{1-x}Cu_xI$ and $Ag_{1-x}Cu_xBr$.

For the study of structural properties of the designed materials, we calculated the equilibrium lattice parameters (a) and bulk modulus (B) of each of the designed compounds. In the calculations of electronic properties, we have studied separately the band structure profile of each compound and finally calculated the energy band gap of the materials. We have also calculated the density of states of the compounds to explore the atomic and orbital origin of electronic states, presents in the band structures which provide both partial and total contribution of various electronic states of each

atom. In the optical properties, we have observed the frequency responses of different optical parameters e.g. real and imaginary dielectric function, optical conductivity, absorption coefficient, refractive index, reflectivity, extinction co-efficient and energy loss function of each specimen upon incident electromagnetic radiation. The findings in pre-Ph.D. research work in my selected topic have finally presented in my Ph.D. thesis subjected to seven chapters as follows;

Chapter 1 provides the general introduction, historical background and foundation of solid state ionics, structural properties of AgX and CuX (X= Cl, Br, I), impact of substitution on metals, various types of superionic materials, a brief survey of literature related to my research work, where we mention the various types of superionic materials, aim and object of the present research work.

Chapter 2 provides a brief study on the theory of electronic structure (atoms/molecules), basic quantum mechanics with some approximation methods including a short discussion on density functional theory (DFT). We have also mentioned various types of exchange and correlation potentials such as LDA, GGA, TB-mBJ and HSE06 schemes and different types of plane wave approximation methods, such as APW, LAPW and FP-LAPW methods. The mathematical formulations used in the present computations with various properties are also discussed. We have used WIEN2k code, implemented on the basis of DFT, based on FP-LAPW method to carry out all the computations.

Chapter 3 provides electronic structure calculations on copper substituted silver iodide through modified Becke-Johnson exchange potential. This chapter focuses on the substitution of silver (Ag) with copper (Cu) for various compositions in a $2 \times 2 \times 2$ supercell of $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.03125, 0.0625, 0.125, 0.15625, 0.1875$), ($x = 0.00, 0.25, 0.5, 0.75$ and 1.00 in a unit cell), where we have calculated various

structural parameters, electronic structure, density of states (DOS) and optical properties of the aforementioned compounds.

Chapter 4 provides electronic structure calculations on copper substituted silver iodide using hybrid functional, HSE06 approach. This chapter focuses on the substitution of silver (Ag) with copper (Cu) for various compositions in a unit cell of $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.00, 0.25, 0.5, 0.75$ and 1.00), where we have investigated various structural parameters, electronic structure, density of states (DOS) and optical properties of the aforementioned compounds.

Chapter 5 contains first principles electronic structure calculations on copper substituted silver bromide through modified Becke-Johnson exchange potential. This chapter focuses on the substitution of silver (Ag) with copper (Cu) for various compositions in a $2 \times 2 \times 2$ supercell of $\gamma - Ag_{1-x}Cu_xBr$ ($x = 0.03125, 0.0625, 0.125, 0.15625, 0.1875$), ($x = 0.00, 0.25, 0.5, 0.75$ and 1.00 in a unit cell), where we have calculated the structural parameters, electronic structure, density of states (DOS) and optical properties of the aforementioned compounds.

Chapter 6 provides first principle calculations of structural, electronic and optical properties of copper substituted silver bromide using HSE06 hybrid functional approach. This chapter focuses on the substitution of silver (Ag) with copper (Cu) for various compositions in a unit cell of $\gamma - Ag_{1-x}Cu_xBr$ ($x = 0.00, 0.25, 0.5, 0.75$ and 1.00), where we have investigated the structural parameters, electronic structure, density of states (DOS) and optical properties of the aforementioned compounds.

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Abbreviations

RS-Rock-salt

ZB-Zinc-blende

WZ-Wurtzite

BZ-Brillouin Zone

DFT-Density Functional Theory

LDA- Local Density Approximation

PBE- Perdew-Burke-Ernzerhof

GGA- Generalized Gradient Approximation

TB-mBJ- Tran Blaha modified Becke-Johnson

HSE06- Heyd-Scuseria-Ernzerhof 2006

APW- Augmented Plane Wave

LAPW- Linearized Augmented Plane Wave

FP-LAPW- Full Potential - Linearized Augmented Plane Wave

lo - Local orbital

DOS- Density of States

LMTO- Linear Muffin-Tin Orbitals

HOMO- Highest Occupied Molecular Orbital

LUMO- Lowest Unoccupied Molecular Orbital

TB- Tight Binding

GPa- Giga Pascal

K- Kelvin

Mpa- Mega Pascal

GW- Green's function and screened Coulomb interaction

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CHAPTER 1

Introduction

1.1 A brief review on theoretical material science

In recent decades, theoretical condensed matter physics and theoretical materials science have become increasingly popular areas of science. Due to the developments of algorithms and computer technology, it is now possible to work with systems that contain few tens of atoms in a single unit cell. Thus, these techniques can now be directly applied to a variety of real-world material challenges. Scientific and technological advances depend largely on the development of novel materials and growing understanding of their physical and chemical properties [1]. Simulations can demonstrate important information about the characteristics of matter when employed appropriately. The characteristics of compounds significantly differ from those of their individual constituents. For instance, the mechanical strength and corrosion resistance of a compound can be significantly higher than those of its individual components. Similar to this, semiconductor have different energy gaps than their component parts [2]. For this reason, the materials are employed more often than pure materials. However, the characteristics of a compounds do not progress linearly with those of its constituent elements. Hence, it is challenging to forecast the properties of compounds from the individual characteristics of its constituent parts. Therefore, either theoretical or experimental methods are used to determine the properties of compounds. From scientific point of view, the study of semiconductors is interesting because it opens up new possible applications. A technique that used the total electron density as the basic variable. This idea is the basis of density functional theory (DFT) [3]. A wave function of N electrons has $3N$ spatial variables and is extremely complex to calculate. However, the basic idea of DFT is to replace the complicated many-electron system with the electron density function, which has only three variables. This alternative theoretical technique is capable of identifying energies that are very close to the exact energy. The energy of many electron systems can only be viewed based on the electron density.

1.2 Historical background: Foundations of solid state ionics

In the early 19th century, nothing was known about the structural arrangement of crystals and the idea of disorder. In the beginning of 20th century, the reality of atoms and ions was still refuted by renowned scientists Ernst Mach and Wilhelm Ostwald. The movement of mobile ions in both liquid and solid electrolytes was discovered by Michael Faraday, which was most commendable. He set the groundwork for solid-state ionics and electrochemistry. Alessandro Volta created an electric pile in 1800 using a series of successive plates made of zinc, silver, and linen soaked in salt solution [4]. Using this pile, Anthony Carlisle and William Nicholson, two English scientists, electrolyzed water to produce hydrogen and oxygen.

A few years later, Humphry Davy isolated the elements potassium and sodium through electrolysis using a voltaic pile. Faraday introduced the terminology ion, cation, anion, electrode, anode, cathode, electrolyte, and electrolysis to describe the electric current-based solutions [5]. Indeed, he was the first to recognize that the movement of ions carried charge across an electrolyte and to notice that ions could exchange charges by electrode during electrolysis. Faraday made the quantitative discoveries, referred to as Faraday's laws of electrolysis. The development of solid electrolytes rather than liquid electrolytes was made by Michael Faraday. He stated that ions could move in both liquid and solid electrolytes in the early 1830s. This was the starting of electrochemistry and solid-state ionics. The first electrochemical battery, made by Alessandro Volta around 1800, used a liquid solution [6]. However, he was unaware that ions are needed for the process to work. According to Faraday, the movement of ions is related to the flow of electricity in a medium. He also found that ions can trade charges with an electrode while electrolysis changes them into elements.

In 1834, Faraday studied silver sulphide and lead fluoride, observing that their conductivity was enhanced by heat [5]. When a fragment of the substance was fused and subsequently cooled, being inserted into a voltaic battery interrupted the current. Upon heating, it gained conductive properties prior to becoming clearly red hot in daylight, even its sparks remain solid. In 1976, Michael O'Keeffe noted that this seems to be an initial measurement of the evolution of conducting materials, referred to as solid electrolytes [7]. Today, we differentiate within substances exhibiting mixed ionic/electronic conduction (MIEC), such as Ag_2S and PbF_2 . Lead fluoride (PbF_2)

demonstrates solid electrolytes in which a highly conductive state occurs throughout temperature exceeding 100 K. This transition is referred to as the Faraday transition. Solid-state ionics is the study of ionic electronic materials and ionic conductors, also known as solid electrolytes. Inorganic crystalline and polycrystalline solids, ceramics, glasses, polymers, and composites are some of the elements which come into this category. It is possible for solid-state ionic devices, like solid oxide fuel cells, to be more reliable and last longer than similar devices with fluid electrolytes, especially in extreme conditions. Michael Faraday worked on solid electrolytes Ag_2S and PbF_2 that was the first step of solid-state ionics [8].

1.3 Early development of solid state ionics

During 19th century, three significant developments in Michael Faraday's work were evaluated within the broad category of mobile charge carriers. First two are to deal with charge carrier, and the third one extends the idea of conductivity. Hermann von Helmholtz in 1881, refined the idea of electron by inferring Faraday's law of electrolysis that electricity was most likely granular [9]. The ionic transport numbers were originally measured and subsequently reported by Johann Wilhelm Hittorf [10]. In the 900s, Carl Tubandt also calculated transport number in solid electrolytes [11]. In 1861, James Clerk Maxwell adopted Faraday's field theory that when the specimen is subjected to electric field, it gets changed periodically. The conductivity spectra of solid electrolytes may now be studied over a period of several decades, offering important insights on the dynamics of the mobile ions.

1.4 An approach to structural analysis

The atoms and ions in a solid contribute to the potential for translational transport in a material, which is unfeasible in a precisely structured crystal. The ionic mobility and transport depend on imperfection geometry for the concern material. The glassy structure reveals the presence of empty spaces that mobile ions might use for hopping motion. If the substance is a high-temperature phase of AgI or Ag_2S , the entire Ag sublattice is practically in a molten state, rendering it ionically conductive. Typically, the material in challenging exhibits a rather regular crystal structure characterized by many deficiencies, predominantly point defects, that facilitate the movement of mobile ions [12]. A notable historical journey of advancement, initiated by Michael Faraday's

contributions, eventually results in the Nobel Prize in Physics awarded to Max von Laue in 1914, subsequently giving rise to essential of structural development used. Since crystals were typically categorized based on their external appearance in the 19th century, Miller indices and Bravais lattices were introduced in the year 1839 and 1845, respectively. Yet, the precisely periodic arrangement of atoms and ions in crystals remained unexplained experimentally. Wilhelm Conrad Rontgen's discovery of X-ray radiation in 1895 (for which he was awarded the 1901 Nobel Prize in Physics) was a crucial component of structural analysis. According to Max von Laue's theory (in 1912), X-rays could be electromagnetic waves, as defined by Maxwell, but they would have a shorter wavelength than visible light. Just as visible light that it diffracted by a broader grating, X-rays are also diffracted by the atoms in a crystal if they have the right wavelength.

1.5 Disorder in solids

In a solid electrolyte, ionic transport requires disorder in the materials. But it is more difficult than simple structural analysis to determine the degree of disorder that exists in a specific crystal at a given temperature. Structural developments based on X-ray (or neutron) diffraction data are crucial for identifying disordered structures and predicting the occurrence of mobile ions moving within the crystal. Few examples in PbF_2 , in which order-disorder transition with the maximum heat capacity causes the conductivity of fluoride ions as the temperature rises. Ionic conductivities of solid electrolytes have been known to rise with temperature since Faraday's time. This variation may indicate an ongoing increase in the level of disorder. These factors lead to the conclusion that disorder needs to be observed as a temperature-dependent thermodynamic equilibrium feature [12]. As temperature rises, the number of potential ion configurations might increase as well, reflecting a higher degree of disorder in the crystal lattice. Higher temperatures in thermal equilibrium result in higher ionic conductivities because they cause more disorder. Lead fluoride exhibits a progressive increase in disorder and conductivity, while silver iodide exhibits a first-order phase transition [13].

1.6 The findings and intriguing aspects of alpha silver iodide (α – AgI)

The α -AgI (high-temperature phase), is commonly regarded as solid electrolyte. In 1914, Carl Tubandt and E. Lorenz found the unexpected features of α -AgI while measuring the electrical conductivities of silver halides viz. AgCl, AgBr, and AgI [13]. Tubandt's notations, denoted by α , β , and γ for various phases in the sequence of stability with decreasing temperature. Unlike AgCl and AgBr, AgI exhibits a strongly conducting solid phase, called α -phase, which remains stable between 147°C and 555°C. When AgI changes from β to α -phase, its conductivity increases by three orders of magnitude. Comparable to the best-conducting liquid electrolytes, α -AgI has high electrical conductivity and a relatively minimal temperature dependence. The study of solid electrolyte, a novel family of optimal ion conductors, initiated with the discovery of α -AgI. In addition to the high-temperature phase of Ag_2S , Ag_2Se , Ag_2Te , Carl Tubandt and his colleagues recognized the phases as α -AgI, α -CuI, α -CuBr, and β -CuBr. According to the inter-diffusion experiments and transport number measurements, the ionic charge was migrated by the cations within the conducting phases of AgX and CuX (X= Cl, Br, I) [14]. However, the silver chalcogenide was discovered to be a combination of ionic-electronic conductors [15]. The calculation of the conductivity of Ag_2S was made by Michael Faraday. Since Tubandt's times, the Ag^+ ions in α -AgI have been considered to exhibit liquid-like mobility within the crystal structure generated by the anions. In 1934 and 1936, Strock (Germany) performed the initial analysis of AgI compound [16]. He proposed three distinct types of partially occupied sites, resulting in a total of $6 + 12 + 24 = 42$ positions for the two silver ions within the bcc cell. This concept fails to depict the fluid nature of the arrangement and movement.

In 1977, American scientists Cava, Reidinger, and Wuensch performed neutron-diffraction experiment on a single crystal to construct a map indicating the probable locations of Ag^+ ions in α -AgI. Thus, it can be inferred that the periodic potential barriers created by the anions for the diffusion of cations are approximately equivalent to the thermal energy. In this decade, quasielastic scattering experiments on poly- and single-crystalline α -AgI were carried out at the Institute Laue-Langevin in Grenoble, France, to obtain information regarding the local dynamics of mobile Ag^+ ions. The calculated spectra were accurately represented by a model, obtained the actual Ag^+

motion as a rapid diffusive motion within a cage of approximately 1 Å radius and random hopping through tetrahedral positions. The Hall-effect data obtained from α -AgI were accurately accounted for determining the mobility of silver ions, under the assumption that all ions were mobile within α -AgI. The conductivity of α -AgI exhibited frequency independency up to 40 GHz or more [17]. This indicates that the silver ions exhibit such rapid movement that any recollection of individual trajectories is obliterated after a duration equivalent to the inverse of $2\pi \times 40$ GHz.

1.7 Basic concept of point defects in ionic crystals

Theoretical work on point-defect thermodynamics was done by Walter Schottky and Carl Wagner; Yakov Frenkel and Carl Wagner both contributed to the idea of point defects around 1930. This clarifies the transfer of ions in a crystals, glasses, electrolytes, and nanocomposites. Research in solid state ionics in the late 20th and early 21st centuries centered on developing and studying new solid electrolytes for use in sensors, fuel cells, and solid-state battery systems. Although Takehiko Takahashi first used the term "solid state ionics" in 1967, it wasn't until the 1980s, when a scientific journal of the same name began publishing articles, that it really took off. The inaugural global gathering on this subject took place in 1972 in Belgrate, Italy, and was titled "Fast Ion Transport in Solids, Solid State Batteries and Devices."

Tubandt and Lorenz observed a solid-like condition when studying in other phases of silver halide, as opposed to the disordered and liquid-like mobility of silver ions in α -AgI. The ionic conductivity in these circumstances were non-zero but significantly lower than in α -AgI. Tubandt and colleagues demonstrated that all the phases, the conductivity was transported mostly by silver ions, but the anions remain largely stationary [11, 14]. Schottky and Wagner predicted four extreme scenarios of disorder in a balanced binary crystal composed of types A and B. Type 1: the Frenkel disorder, in which only a few of cations, A^+ are present in extra spaces whereas the regular cation layer contains the same number of vacant spaces. Type 2: includes interstitial anions, B^- and anion vacancies, also known as anti-Frenkel defects. Type 3: has no vacancies but same numbers of interstitial cations and anions. Type 4: crystals have no interstitial ions, yet there are same numbers of anion and cation vacancies. Schottky discovered that close-packed alkali halide show Schottky disorder [12].

1.8 AgI-type solid electrolytes and ionic conductivities

In 1834, Faraday made a significant discovery regarding ionic conductivity in the heated solid electrolytes known as silver sulfide (Ag_2S) and lead fluoride (PbF_2). In PbF_2 , the conductivity exhibits an increase with increasing temperature, yet this phenomenon occurs over a range of approximately $100^\circ C$ [5]. In 1891, Johann Wilhelm Hittorf presented the results on the ion transport numbers in electrochemical cells and established for solid electrolytes in the early 20th century [18]. Among the various solid electrolytes reported during 19th and 20th centuries, α -AgI, the high-temperature crystalline type silver iodide is considered as the most important [11]. Tubandt and Lorenz identified similar behaviour in several materials, including α -CuI, α -CuBr, β -CuBr, and high-temperature phases of Ag_2S , Ag_2Se , Ag_2Te [14]. They associated the conductivity with cations in silver and cuprous halides, as well as ions and electrons in silver chalcogenides. The strongly ion-conducting phases have similar features as several AgI-type other solid electrolytes. Researchers discovered that electron transport number in strongly conducting AgX and CuX are much smaller than one. All silver ion conductors have minimal transport numbers in their solid electrolytes. We made them from AgI through partially substituting different sorts of ions either silver or iodide ions, or both. This procedure resulted in the synthesis of novel compounds, some of them had very higher ionic conductivities at room temperature or below.

1.9 An emerging framework of materials science

The disorder represents a fundamental aspect of solid-state ionics. An evolving framework within materials science presents perfectly ordered crystals at the initial level. At this level, the ions are unable to exit their chosen sites. The appearance of site disorder and point defects represents a significant advancement toward level two, the ionic transport is facilitated by point defects. Nowadays, materials science and engineering predominantly based on the principles associated with level two. Significant alterations are observed when converting to disordered structural materials. In this stage, the ionic transport cannot be characterized by the movement of defects within a static energy framework. This concept is relevant to various materials, such as disordered ionic crystals, nanosized systems, ion-conducting glasses, and polymer

electrolytes. The report articulates a historical advancement that results in the emergence of novel categories of increasingly sophisticated ion-conducting materials. Each new level presented distinct scientific challenges related to the study of structural dynamics. Simultaneously, each newly generated materials presented the prospects for device applications. The improvement of ionic materials is now recognized for enhancing the importance of solid-state ionics in both academic and public domains. The identification of disordered fast-ion conductors, specifically rubidium silver iodide ($RbAg_4I_5$) and sodium-beta-alumina ($Na - \beta - \text{Alumina}$) marked significant milestones in the domain of solid state ionics [19, 20]. The start-up of $RbAg_4I_5$ has generated intriguing possibilities for compact batteries capable of operating at room temperature for applications such as satellites and cardiac pacemakers. Furthermore, $Na - \beta - \text{Alumina}$, developed by Yao and Kummer, has been recognized as solid sodium-ion conductor used in batteries for automotive propulsion [21]. Other structural disorder has been appeared in solids with the consequences of thermodynamic defects and the dynamics of mobile ions, emerged in 1980s with ramifications for defects and the behaviour of mobile ions and electrons [22].

In the early 1970s, remarkable advancements have been correlated by worldwide gatherings and discussions. This included "Solid Electrolytes," "Superionic Conductors," and "Fast Ion Transport in Solids." Over the years and decades, appropriate materials and methods for energy storage, sensing and other applications have become more evident. The current focus on fuel cells and batteries for future revolves within crystalline lithium-ion, oxide-ion, and proton conductors working as electrolytes, in addition to ion-conducting glasses and thin-film polymers [23].

1.9.1 Ion-conducting glasses

The investigation of ionic conductors in which point defects generates excess ions to establish the specific mechanism of conduction was based upon its ionic structure. Glassy and polymeric electrolytes developed in the late 1970's, introducing novel ionic conduction mechanisms. Mobile ions were dynamically decoupled, resulting in a relatively wide variety of conducting glasses [24]. By doping a glass with specific ions or employing a glass mixture, the conductivity could be improved. Ionic conductivity was first demonstrated in 1880's when German scientists discovered that a properly

calibrated thermometer constructed of Thuringian glass would display -0.5°C rather than 0°C when submerged in ice soon after being submerged in hot water. Empirical formulations of several universal laws for ionic glasses have been extended to other ionic conductors, including the frequency dependence of electrical conductivity. This behaviour indicates activated hopping conduction between adjacent sites [5]. Some of the positive aspects of ion-conducting glasses are the lack of grain boundaries, high workability, adjustable composition, and physical isotropy. Because of this, ion-conducting glasses were identified with several potential applications in electrochemistry. Conversely, electrolytic structures and dynamics appeared highly complicated due to the absence of long-range order. In 1834, Emil Warburg established the first evidence of ionic conductivity in glasses when he confirmed Faraday's law for sodium transport number, found to be one, through a glass membrane sandwiched between two amalgams. There are theoretical and practical reasons to devote close attention to unipolar conductivity of glasses. Practically speaking, the unit transport number of glassy materials has a direct correlation with the stability of glasses for use in devices (such as Li-ion-conducting glasses in lithium batteries). During 1970 and 1980's, the revolutionary developments of fast ion conductors, particularly RbAg_4I_5 and β -Alumina, sparked a significant interest in the existence of glassy alternatives [25].

1.9.2 Polymer electrolytes

In 1975, Peter V. Wright, a polymer chemist, synthesized the first polymer electrolyte comprising sodium and potassium salts within a polyethylene oxide (PEO) [26]. Subsequently, a different category of polymer electrolytes, known as polyelectrolytes, was introduced, in which ions pass through an electrically charged polymer matrix instead of a neutral one. Polymer electrolytes exhibited lower conductivities compared to glasses. However, they were more cost-effective, significantly more flexible, commonly manufactured and shaped into diverse forms. Ionic glasses usually work below their glass transition temperatures, whereas polymer conductors are typically heated above these temperatures. As a result, the decay of both electric field and mechanical deformation occurs on a comparable time scale in polymers, but this is not the case in glasses [27]. From 1983 to 2001, it was speculated that the amorphous

fraction contributes to ionic conductivity, suggesting that nearly complete structural disorder is crucial for rapid ionic transport in polymers [24]. Glassy electrolytes are successfully substituted by ion-conducting polymers. This represents a wide category of materials that exhibit greater complexity than glassy systems based on their structural characteristics and ion dynamics. The exciting prospect of ion-conducting polymers for various applications in solid-state devices greatly accelerated their development in the mid-1970's [28]. The polymer exhibits mechanical softness and flexibility, ensuring optimal interfacial contact that experience significant volume changes during charging and discharging cycles. The conductive properties of glasses, ionic liquids, and polymer electrolytes exhibit unexpected first-universality characteristics.

1.9.3 Nanoionics and Nanostructures

During 1970 and 1980's, it became evident that nanosized systems could influence ionic conductivity, thereby establishing a new domain of study known as nanoionics. In 1973, it was discovered that the ionic conductivity of lithium iodide (LiI) crystals could be enhanced by a factor of 50 through the addition of a fine powder of insulating material, specifically alumina [29]. The incorporation of insulating nanoparticles enhanced the conductivity of ionic polymers [30]. The unexpected results can be attributed to charge separation at the matrix of nanoparticle interface, which created additional conductive channels within the matrix. Comparable charge separation phenomena were noted at grain boundaries in crystalline ionic conductors [5]. Surfaces and interfaces are crucial for producing ionic (and electronic) conductivity effects that are surprisingly strong in nanoscale systems like nanocomposites and thin films [22, 31]. Polymer electrolytes were doped heterogeneously with nanosized materials (SiO₂) [32]. Mobile silver vacancies are produced in front of silver ions by the adsorption of silver ions by the grain boundaries in AgCl. In nanocrystalline materials, interfacial effects can be predominant. An illustrative example, CeO_2 , has been investigated and doped with Al_2O_3 . Coarse-grained materials possess a high density of oxygen vacancies, accompanied by a few numbers of electrons, and demonstrate oxygen conduction properties. Furthermore, the material turns into an electronic conductor when it is manufactured in nanocrystalline form.

1.10 Achievements in solid state devices and informative materials

To describe the new science of solid electrolytes, Takehiko Takahashi proposed the concept of “Solid State Ionics” in 1960 [33]. Terminology like “solid electrolytes” and “Fast Ion Transport in Solids” become more prevalent in worldwide common usage. The symposium on “Fast Ion Transport in Solids, Solid State Batteries, and Devices” was organized by the NATO Advanced Study Institute [34]. The β -alumina had only been discovered a few years before the Belgirate meeting, and the majority of the solid electrolytes implemented based on AgI and doped ZrO_2 .

After the discoveries of β -alumina and $RbAg_4I_5$ in 1970s, high expectations about novel battery systems in the applied field of solid-state ionics continuously provided to a more practical perspective. Solid electrolytes have been effectively utilized in cardiac pacemaker batteries and automobile exhaust sensors. Both devices are now utilized globally, thereby attracting international attention in the applied solid state ionics. In 1970, Owens (USA) investigations on cells and batteries using fast silver ion conductor ($RbAg_4I_5$) demonstrated by the configuration $Ag|RbAg_4I_5|RbI_3, C$ [35]. The cells demonstrated functionality at high and low current densities across a broad temperature range. In comparison to $RbAg_4I_5$, lithium iodide (LiI) exhibits low ionic conductivity, approximately at room temperature. In 1972, the inaugural cardiac pacemaker powered by a $Li|LiI|I_2$ battery was implanted in a person in Ferrara, Italy. The pure LiI was then substituted with LiI incorporating scattered Al_2O_3 particles as a secondary phase, leading to significantly improved ionic conductivities.

1.10.1 Sensors, smart windows and supercapacitors

In 1980, M. Kleitz and his team, presented a cell capable of working as a gas sensor for oxygen when chlorine is absent, and for chlorine in presence of oxygen [36]. In this instance, the reference electrode was composed of a layer of AgCl deposited on silver, with the electrolyte being a composite chloride-ion conductor. A slightly greater temperature was needed for the oxygen measurement, but 150°C was sufficient for the chlorine measurement. A distinct oxygen sensor was introduced in France, capable of operating at temperature 150°C [37]. The potentiometric cell designed for the assessment of CO₂ levels in the atmosphere was conceived by Holzinger, Fleig, Maier, and Sitte during mid-1990's [38]. This exceptional sensor provided prolonged stability

and fast response times, while being capable of sustaining ambient temperatures ranging from 350°C to 700°C without the need for sealed electrodes.

Smart windows have been implemented in various regions of the world, mostly to minimize the requirement for air conditioning through effective light management. A novel family of electrochemical energy storage devices, electric double-layer capacitors, often known as supercapacitors, rely significantly on large-surface area, nanostructured electrodes. The fundamental principle of supercapacitors involves the creation of Helmholtz-type or Gouy–Chapman-type double layers by employing ultra-thin, nanostructured electrode materials. Supercapacitors have the ability to quickly supply larger amounts of energy. Supercapacitors, when utilized alongside batteries or cells, are capable of providing a significant amount of short-term power to electric vehicles [39]. The developments of supercapacitors have indispensable global collaboration over the past twenty years, involving researchers and business leaders from multiple nations.

1.10.2 Mixed conduction and new materials

Solid materials have been classified according to their electrical conductivities. The materials are generally classified as, ionic (alkali and silver halides), electronic (metals and semiconductors), or mixed (silver sulphide). All ionic solids clearly demonstrate the ionic-electronic conducting behaviours. The significance of mixed conduction in electrodes, sensors and electrochromic devices, has received substantial attention. The identification of novel materials that enable mixed conduction and the enhancement of their properties required significant effort [40].

During 1990's, extensive research was performed on transport mechanisms in mixed ionic and electronic conductors by the research teams led by Schmalzried and Janek in Germany. This study evaluated the interactions between ionic and electronic flows, as well as the external factors such as temperature gradients. Novel materials can be classified into several criteria, based on their conductivities, historical origins, and potential applications. Carl Tubandt, Walther Nernst, and Michael Faraday were among the pioneers who developed many crystalline materials that are pertinent to solid-state ionics. This includes fluoride-ion-conducting compounds (PbF_2), oxygen-ion-conducting materials, doped ZrO_2 , and solid electrolytes (AgI-type). The category

of rapid ion conductors including disordered sublattices is not confined to AgI-type electrolytes and β -alumina, have been broadened by the identification of other electrolytes. This encompasses the NASICON organic compounds and the pyrochlores. NASICON, an acronym for sodium superionic conductor was initially synthesized by Goodenough et al. [41]. NASICON is a three-dimensional sodium ion conductor, which is beneficial when contrasted with β -alumina. In contrast, the material can be employed as a thin-film material and in sodium-selective electrodes [42, 43]. The aforementioned materials have been introduced as members of the category of historical origins. Among others, a diverse array of oxygen-ion, proton, and lithium-ion conductors are being developed for potential applications.

1.10.3 Battery innovation beyond lithium-ion

We use rechargeable (secondary) batteries in our daily lives, which run at room temperature. The introduction of the lithium-ion battery, characterized by its durability, lightweight design, and reusability, has significantly transformed portable electronic devices, including mobile phones and laptop computers. In electric and hybrid electric vehicles, more powerful versions are now substituting the batteries of the prior generation, predominantly nickel metal-hydride. In a broader sense, secondary battery systems are required for environmental preservation. Energy conversion, storage, and provisions must occur in a sustainable manner. This is the intended purpose of batteries. The global success of the lithium-ion battery can be attributed primarily to use lithium ions (Li^+) as the mobile charge carriers. The alternative includes the utilization of both negative and positive intercalation electrodes. The term ‘intercalation’ (also known as ‘electro-insertion’) denotes a host (guest) solid state redox reaction [44]. This reaction involves the coupling of electrochemical charge transfer with the insertion of mobile ions from the electrolyte into the solid host structure, serving as a mixed electronic and ionic conductor. The ‘rocking chair’ or lithium-ion was first proposed in 1980’s by Lizzari, Scrosati and Armand [34, 45]. The development of the graphite-liquid electrolyte LiCoO_2 battery in Japan was notably initiated, leading to its successful commercialization by SONY in 1991. During charging, Li^+ ions are removed from their LiCoO_2 host, move across the electrolyte, and subsequently intercalate within the layers of anodic graphite. Upon

discharge, the process is reversed. Since, the introduction of the first-generation lithium-ion cell, major developments have been occurred regarding its three primary components; the electrolyte, negative and positive electrode. Scrosati's group in Rome produced a large number of amorphous polymers which conduct Li^+ ions [46]. The crystalline fast Li^+ ion conductor $\text{Li}_7\text{La}_3\text{ZrO}_{12}$ is an example of a non-polymer. The primary features of a lithium-ion battery exist in its safety and durability.

Yttria-stabilized zirconia serves as a solid electrolyte in automotive oxygen sensors, producing a voltage that correlates with the ratio of oxygen to exhaust gas, thereby providing electronic feedback to the fuel injector [47]. These sensors are commonly found in multiple metallurgical and glass-making properties. In the 1980s and 1990s, similar solid silver halide electrolyte-based CO_2 , chlorine, and other gas sensors were proposed [48]. A Li-based solid electrolyte has been employed since the middle of the 1980s to separate the ion-storing film (usually LiCoO_2) and electrochromic film (usually WO_3) in a smart window whose transparency is controlled by an external voltage [49]. Solid-state ionic conductors play a crucial role in lithium-ion batteries, proton exchange membrane fuel cells (PEMFCs), supercapacitors, a new category of electrochemical energy storage devices, and solid oxide fuel cells, which generate electricity through the oxidation of a fuel. Nafion, a versatile fluoropolymer-copolymer identified in the late 1960's, serves a significant role as a polymer electrolyte in PEMFCs [48].

1.11 Structural properties of AgX and CuX ($\text{X}=\text{Cl}, \text{Br}, \text{I}$)

Noble metal halides, MX (where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$ and $\text{M} = \text{Ag or Cu}$), received a lot of interest because of their electronic and optical properties. These are compound of technological importance in photochemistry, electrochemistry, and photography. Metal halides are good candidates for photochemistry because their electrons will absorb light energy and move from the valence band to the conduction band. Additionally, these materials show increased cationic conductivity and super-ionic properties [50, 51]. Metal halides have a fascinating phase diagram that includes crystalline forms of α , β , and γ . The intermediate form, known as the β -phase, has a hexagonal wurtzite structure, while the γ -phase crystallizes in the cubic zincblende configuration at normal temperature and the α -MI creates a stable cubic structure at

higher temperatures. AgCl and AgBr, on the other hand, crystallize in the form of rock salt in ambient conditions [52]. Silver halides have an indirect bandgap feature, while copper halides are categorized as direct bandgap semiconductors. The wide-band gap p-type conductivity of III-V and II-VI materials is marked by notable iconicity and crystallographic changes (α , β , and γ -phases). AgX and CuX (where X = Cl, Br, I) are important compounds for the study of light emitters, transparent conductors, and photocatalysis because of their remarkable features in optoelectronics [53, 54]. The bonding in noble metal halides results from the efficient hybridization of 3d/4d electrons in silver or copper with the p electrons of halogens. The valence band of these compounds derives from the filled d^{10} orbital of the metal and the s^2p^6 configuration of the halogen. Silver halides possess unique electronic structures due to significant hybridization between cation 4d levels and anion p levels [55]. Pressure markedly affects the characteristics of these materials by modifying the structural geometry. AgCl and AgBr undergo a phase transition from the rock salt structure to the CsCl structure at pressures of 8.7 GPa and 8.3 GPa, respectively, while AgI transitions at 9-10 GPa [56, 52]. Silver iodide (AgI) is a metal halide that has been extensively investigated, and α -AgI in particular exhibits superionic behaviour. Above 420 K, α -AgI crystallizes in a stable cubic lattice, with Ag ions distributed randomly across multiple crystallographic positions. At the ambient temperature and pressure, silver iodide (AgI) crystallizes in to β -phase and γ -phase forms. In contrast, the γ -phase crystallizes in a cubic zincblende structure, while the β -phase is distinguished by a hexagonal wurtzite structure. The semiconductor γ -AgI is an n-type semiconductor that remains stable at ambient temperature and pressure, as well as at temperatures of up to 413 K and 588 MPa [57]. These materials are utilized in optoelectronic devices due to their wide band gap range. Copper iodide, CuI, demonstrates isostructural characteristics that are comparable to those of AgI. Copper iodide functions as an electronic and ionic conductor at ambient temperature through electron-hole conduction. The α -CuI exhibits stability at temperatures above 713 K, while the γ -CuI experiences crystallization at temperatures below 663 K. The β -phase exists within the temperature range from 663 to 713 K [58]. γ -CuI, identified as a p-type semiconductor, exhibits extraordinary performance in the realms of solar cells and thermoelectric devices. The efficiency of electronic transport in γ -AgI is enhanced by the mobility of

cationic defects (Ag^+ interstitials), which are generated in larger quantities within the temperature range of 250 - 420K. In contrast, $\gamma\text{-CuI}$ functions as a p-type semiconductor, with its conduction attributed to the existence of Cu^+ Frenkel defects [59]. The study of cation-anion chemical substitution in $\gamma\text{-AgI}$ superionic conductors elucidates the fundamental characteristics of the phase transformation, thereby improving ion transport and mobility within the crystalline framework. A series of experiments have been undertaken to rigorously explore carrier dynamics and recombination behaviours, aiming to improve the efficiency of optoelectronic photovoltaic devices [60 -63].

1.12 Impact of substitution on metal halides

The substitution of Cu atom on AgX ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) compound will relocate the atomic position and remodel the crystal structure of the material. Based on the substitution concentration of Cu atom, the phase structure of the compound changes as rocksalt, wurtzite and zincblende structure. The ionic conductivity of silver halides increases by substitution of copper (Cu^+ ions carrier). It helps to stabilize the superionic phase at low temperature, leading to a higher conductive material. The increased ionic conductivity makes the material ready to use in solid-state batteries and other gas sensing applications. The Cu^+ ions act as charge carriers thereby enhancing the motion of Ag^+ ion within the crystal lattice. Addition of Cu atom in AgX can affect the electronic and optical properties of the material. Hence, the material has possibility of mixed ionic-electronic conduction. The band gap of a material is more important for designing efficient optoelectronic materials. The band gap determines how a material interact with incident light photon of specific energy. The optoelectronic devices such as solar cell, photodetectors rely more on precise band gap for optimal performance.

1.13 Superionic materials

The study of superionic solids becomes a new frontier in materials research and technology. High mobility ions commonly observed are Li^+ , Na^+ , K^+ , Ag^+ , Cu^+ , F^- , and O^{2-} . Solids with high ionic conductivity are referred to as "superionic solids" or "solid electrolytes". The phenomena of migration of ions in solids is a fascinating and challenging in condensed matter science. In the ideal crystal chronology, the superionic state is the ultimate phase [64, 65]. There are three major categories of

materials that show superionic conductivity near room temperature: (a) The AgX family (AgI, AgBr, CuBr, and CuI), (b) Composites of MX– Al_2O_3 (where MX represents AgI, AgCl, LiI, etc.), and (c) Glasses in the AgI – Ag_2O – MO system. The AgI compound displays polymorphism and possesses Frenkel defects, namely Ag^+ vacancies and Ag^+ interstitials, which interact significantly. The conductivity of ionic/superionic conductor exhibits exponential growth with temperature, while the conductivity of metallic conductors reduces with increase in temperature. AgI is an example where both criteria are inherently satisfied. AgI possesses either a stable hexagonal structure or a metastable zincblende structure. The two types of ions, immobile (I^-) and mobile (Ag^+), are regarded as the primitive ions. In the ground state, at low temperatures ($T < 147^\circ C$), the Ag^+ ion is located at the A-site (A-sublattice) and the I^- ion in the C-site (C-sublattice). There is a third sublattice, denoted as B, which is unoccupied in its lowest energy state. At high temperatures, a portion of the flexible Ag^+ ions can undergo excitation into the B-sublattice. These are coupled with the ions of the A sublattice and constitute clusters [66 - 68]. With the heating of AgI, the localized alterations take place in the bonding between Ag and I, which significantly contribute to the phase transition to the superionic state [69]. The localized variations in the bonding provide a strong force field that induces the migration of ions. When the bond variations reach a critical point, the Ag^+ sublattice collapses, causing the transition to the superionic state. In the case of composites, the conductivity of a conventional ionic conductor, MX (AgCl or LiI), is enhanced by combining it with an insulator (Al_2O_3). The superionic conductor is regarded as a lattice-fluid system in which the anionic lattice is suspended in the cation liquid. The movement of mobile ions is better explored within the framework of a hopping model. Superionic glasses are systems in which the presence of short- to intermediate-range structural order generates advantageous potentials for ionic charges (Ag^+ in AgI – Ag_2O – B_2O_3 glass) to undergo rapid hopping motion [70 - 72].

1.14 Classification of superionic solids

Based on crystallographic analysis, a pristine crystal of an ionic substance would exhibit insulating properties [73]. Defects or disorder are most essential for maintaining significant ionic transport. Consequently, all the ions have the ability to

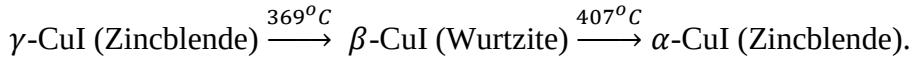
"hop" or "move spontaneously from one location to another. Ionic solids can be classified into three categories based on "free-ion like theory"[74] of superionic solids: Type I: Ionic solids are characterized by a low defect concentration, and Type II: These materials consist of a significant number of imperfections that have merged together to form a cohesive substructure or "extended defects" of sub-microscopic size. Type III: Solids of the "point defects type," transport occurs via Frenkel or Schottky defect pairs that are formed by thermal processes.

1.14.1 Silver ion (Ag^+) conductors

The first demonstrated silver ion conductor in the literature is most likely silver sulphide (Ag_2S) discovered by Faraday in 1833 [75]. The current endeavour to comprehend and explore new silver ion conductors may be the measurement of conductivity in silver halides by Tubandt and Lorenz [76]. The phase with the highest conductivity is referred to as α - AgI (cubic), while the phase with the lowest conductivity is β - AgI (wurtzite). AgI is the primary basis for most silver ion conductors. These conductive phases have been achieved by substitution to a certain extent of (i) various cations for Ag , (ii) various anions for I , or (iii) both cations and anions. Bradley and Greene (1966 – 1967), Owens and Argue independently produced the first and most well-known room temperature silver ion conductors by cation substitution and solid solution $\text{MI} + 4\text{AgI}$ ($\text{M} = \text{K}, \text{Rb}$) [77]. The RbAgI system in the $(\text{MI} + x\text{AgI})$ system is the most excellent among the recently discovered materials, while anion doped materials also show great potential.

1.14.2 Copper ion (Cu^+) conductors

Although the copper ion has a smaller size and coordination number to the Ag ion, the quantity of copper ion conductors is a bit lower. Currently, there is no effective room temperature inorganic copper ion conductor with the exception of partly copper substituted RbAgI . Other inorganic copper ion conductors such as α - CuI and γ - CuI are effective electrolytes only at higher temperatures, making them promising copper ion conductors. Among the copper ion conductors, CuI provides the most exemplary case for exploring the correlation between conductivity and defect structure. CuI undergo phase transition by following the steps:



The conductivity increases on both $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions. The energy needed for the migration of a copper ion in the proton phase (via a Frenkel mechanism) is observed to be quite low, which can be attributed to the random arrangement of the cations [78].

1.15 Literature on noble metal halides

The current status of technological and industrial progress is significantly influenced by the level of development in materials including several domains such as polymers, composite materials, and semiconductors. The specific usage of semiconductors in some areas such as electronics and solar energy has generated significant attention. These materials are crucial in these cutting-edge technologies and appear to be of utmost significance for the industries of the current century. Semiconductor physics is a highly sophisticated and flexible field within solid state physics. The reason for the specific fascination with this material, stems from its highly intriguing electronic properties. Semiconductor material serve as a fundamental aspect of modern electronics. These specific characteristics are used to construct the fundamental unit of electronic logic, the transistor, as well as to manufacture a wide range of devices, including light-emitting diodes and heat sensors. Semiconductors are materials that are of significance in the field of nonlinear optics and for investigating the phenomenon of quantum confinement of excitons [79, 80].

G. S. Nunes et al. [81] used a pseudopotential plane-wave approach to study the metal halides AgCl, AgBr, and AgI using LDA model. They found that the energy of the silver 4d-states is excessively high after comparing the computed density of states with experimental data. M. Boukhtouta et al. [51] investigate the phase stability and electronic properties of AgBr, AgCl, and AgI using FP-LAPW approach within DFT. They employed the WC-GGA potential and adopted the mBJ approximation for band structure calculations. Their findings indicate that AgCl exhibits maximum stability in the NaCl structure, while AgBr and AgI demonstrate optimal stability in the zinc blende structure under ambient pressure. The band gap of these compounds in stable phases, revealing that the mBJ method yields a close correlation with experimental results. C Nirmala Louis et al. [82] investigated the band structure, metallization

process, structural phase transitions, and superconducting transitions of AgCl and AgBr under pressure using the TB-LMTO method. Both AgCl and AgBr are classified as indirect wide bandgap semiconductors. Their results using the FPLAPW method, employing both the LDA and GGA, reveals that band structure of AgBr closely resembles that of AgCl, as the energy levels of the Br 4s electrons are roughly comparable to those of the Cl 3s electrons. They observed that the $X-np$ levels ($X = \text{Cl, Br}; n = 3, 4$) are positioned above the $\text{Ag}+4d$ levels. F. Bassani et al. [83] conducts a theoretical analysis of the electronic characteristics of AgCl and AgBr. The valence bands of AgCl were estimated employing the tight-binding approach, using a screened free-electron exchange potential. The covalent nature of the silver halides was demonstrated through significant p-d mixing at various positions in the Brillouin zone. B. Amrani et al. [84] used the FP-LAPW method to investigate how pressure influences the electronic, and optical properties of CuCl, CuBr, and CuI. Their findings indicated that the zinc blend structure is the most stable for CuCl, CuBr, and CuI at ambient pressure. Weiwei Gao and colleagues [85] conduct a comprehensive analysis of the quasi-particle band structures of the transition metal halides CuCl, CuBr, AgCl, and AgBr. They found that performing GW calculations on cuprous halides can be significantly more complex in extreme circumstances. The LDA+U method offers an improved basis for G_0W_0 calculations. They indicated that, for a converged system, the $G_0W_0/\text{LDA}+U$ method is capable of reproducing the experimental minimum band gaps for these compounds with an accuracy of 0.1 eV. The GW method is employed to explore the quasiparticle band structures of copper and silver halides, highlighting the challenges involved in GW calculations for systems with localized d states. Ali Zaoui and Fouad El Haj Hassan [86] investigated the electronic structure of semiconductor materials containing d electrons on copper halides, using the FP-LAPW method under the GGA potential. Their research demonstrated the effectiveness of the FP-LAPW method when applied to semiconductors with valence electrons. B. Amrani et al. [87] used the FP-LAPW approach to analysed the electronic properties of $\text{Cu}_x\text{Ag}_{1-x}\text{I}$ ternary alloys. They employed both GGA96 and EVGGA as exchange-correlation energies for total energy and potential. They observed that the structural parameters and band gap vary non-linearly with alloy composition x , with the exception of the lattice parameter, which follows Vegard's law. H. Rekab-Djabri et al.

[88] use the FP-LMTO method with LDA potential to investigate the structural, electrical, elastic, and optical aspects of novel $AgBr_{1-x}I_x$ ternary alloys in rock-salt and zinc-blende structures. $AgBr_{1-x}I_x$ alloys in the B3 structure have a direct band gap for all concentrations x , which can be used for long wavelength optoelectronic applications, while the B1 structure has an indirect band gap. Mohan L Verma et al. [89] explore how defects influence the structural, electronic, and optical characteristics of the $Ag_{8-x}Cu_xI_8$ (where $0 \leq x \leq 8$) solid solution by substituting Ag atoms with Cu in AgI, using an ab-initio norm-conserving pseudopotentials. They observed that for $x = 0$ and 1, the solid solution functioning as a conducting system Ag^+ ions, transitions to mixed conduction at $x = 2$, and then exhibits a rise in Cu^+ ion conduction with increasing x . They suggested that the low energy required for defect formation contributes to the rapid ion conductivity of AgI. The energy gap in zb-AgI is measured at 1.46 eV, which progressively decreases as Ag is replaced by Cu atoms. Xianli Liu et al. [90] investigated the series of single β -phase nano $Ag_{1-x}Cu_xI$ ($x = 0.0 - 0.5$) solid solution, manufactured using a wet chemical chelation procedure. The $Ag_{1-x}Cu_xI$ powders were analyzed using XRD and TEM. The crystalline size and lattice parameter of the $Ag_{1-x}Cu_xI$ powders diminish as the quantity of CuI substitution increases. The copper within the lattice of $Ag_{1-x}Cu_xI$ can effectively inhibit the crystalline growth of $Ag_{1-x}Cu_xI$ powders. D. Bharathi Mohan and C.S. Sunandana [62] investigated nanoscale crystallites of Ag-rich $Ag_{12x}Cu_xI$ solid solutions synthesized by attrition through a soft mechanochemical reaction involving Ag, Cu, and I, with sizes ranging from 46 to 13 nm. The lattice parameter of the crystal decreases linearly from 649 to 604 pm as Cu concentration increases in the AgI–CuI system, confirming Vegard’s law. Differential scanning calorimetry reveals systematic alterations in the phase transition temperature with Cu substitution. M. Z. Iqbal [91] have analysed the composite solid electrolytes of AgCuI, generated by the direct mixing method. In his study, the phase structure, and surface morphology of the composites were elucidated using XRD, Far-IR spectroscopy, and SEM. The crystal lattices of pure AgI and CuI are analogous and constitute a full solid solution. The mixed system has been thoroughly investigated experimentally, showing that $Ag_{1-x}Cu_xI$ ($0.0 < x < 0.5$) experiences a phase transition between 430 K and 660 K, transforming into the predominant α form of the crystal structure. Wei et al. [92]

constructed a "direct contact" method to build single-cluster connections of AgCu clusters using three halide anchors. AgCu bimetallic clusters were developed and synthesized with halogens to enhance structural stability. They studied the single-cluster conductance, arranged in decreasing order of conductance: $\text{AgCuCl} < \text{AgCuBr} < \text{AgCuI}$. The connection strength ascended in the sequence $\text{Cl} < \text{Br} < \text{I}$. A theoretical calculation using the tight-binding method confirmed that the conductances of clusters diminished in the order of $\text{AgCuCl} < \text{AgCuBr} < \text{AgCuI}$ when the electrodes were affixed with halides. S. Matsunaga [93] computed the electronic properties of superionic $\text{Ag}_x\text{Cu}_{1-x}\text{Br}$ ($x = 0.5$) alloy in contrast to solid CuBr in zinc blende structure. In this alloy, the occupation probability of the Cu ion has been explored in relation to the charge transfer between ions. The hybridized Cu 3d, Ag 4d, and Br 4p density of states were identified. B. Amrania et al. [94] conducted first-principles calculations to explore the structural, electronic, and thermodynamic properties of rock-salt $\text{AgCl}_x\text{Br}_{1-x}$ alloys using the FP-LAPW method. They studied the effect of Cl composition on lattice constants, bulk modulus, band gap, and effective mass. Bin Cai et al. [95] have synthesized novel ternary alloys of $\text{AgCl}_x\text{Br}_{1-x}$ NCs using a controlled method for crystal growth. The crystalline alloys have a rock-salt structure and feature a uniform cubic shape. Theoretical investigations indicated that the halogen ratio significantly influences the conduction band structures and has a considerable impact on photocatalytic performance. The highest efficiency is attributed to the optimal conduction band levels, which balanced the effects of band gap and electronic interaction. F. EL Haj Hassan and A. Zaoui [96] assessed the electronic structure and the effects of disorder in copper halides $\text{CuCl}_x\text{Br}_{1-x}$, $\text{CuCl}_x\text{I}_{1-x}$ and $\text{CuBr}_x\text{I}_{1-x}$ alloys using the FP-LAPW method. The alloy was arranged in a cubic supercell composed of eight atoms, specifically designed to reflect the pair correlation functions characteristic of a random (disordered) alloy. Ji-Hyun Cha and Duk-Young Jung [97] created transparent AgI-CuI heterojunctions to achieve diode functionality through the iodization of metal layers on conducting oxide substrates. At ambient temperature, films of Ag and Cu underwent transformation into the β -phase of AgI and the γ -phase of CuI, respectively. The AgI and CuI films demonstrated n-type and p-type semiconductor characteristics, respectively, both featuring wide band gaps. The metal ion exchange occurring between the two layers allows the AgI-CuI

heterojunction to exhibit pn-diode characteristics. Their results gave the way for new electronic applications involving AgI materials. Mohammed Ameri et al. [98] have theoretically computed the thermodynamic and electronic properties of $CuCl_{1-x}I_x$. The presence of the direct band gap was identified. S. Touam et al. [99] investigated the ternary alloy $CuBr_xI_{1-x}$ using the FP-LAPW technique. They adapted both the Becke-Johnson and Engel-Vosko methods for band structure calculations. They demonstrated that both binary compounds had a zinc blende (B3) structure, which crystallizes into a two-atom unit cell. A. V. Kosobutsky et al. [100] investigated the fundamental characteristics of $CuCl_{1-x}Br_x$ using LDA and meta-GGA. They demonstrated that in both binary compounds, the valence band was delineated within the range of 2 to 10 eV. The bottom band for both binary compounds CuBr and CuCl is attributed to the 3s state of Cl and the 4s state of Br, while the contribution from Cu arises from the d orbitals in the development of both the lower and upper bands. S. S. Walia and colleague's [101] have presented the research work on $CuBr_xI_{1-x}$ by using CRYSTAL [102] software based on HYBRID2LYP within the framework of DFT. The structural properties of $CuBr_xI_{1-x}$ ($x = 0 - 1$) have been studied in a rock salt configuration by applying the LCAO within the context of DFT. Simulations [14] and computing resources have allowed us to explore structural, electrical, and dynamic properties of materials. This allows us to understand the atomic-level materials behaviour in a better way. The discovery of novel materials and processing techniques is critical for technological advancement in various areas of physics. Based on computational methods, the calculation of solids provides understanding of the physical systems when the mathematical problem cannot be solved analytically. In recent years, there have been multiple approaches to compute the electronic structure, particularly ab initio methods, which have become an essential tool in computation of the structural, electronic and optical properties. The FP-LAPW is among these Ab-initio techniques with a better precision.

1.16 Aim and Scope of the Thesis

We have chosen to focus our computational investigations on binary metal halides (AgCl, AgBr and AgI) and their derivatives, which are formed when noble metal atoms such as copper (Cu) and silver (Ag) are substituted into the corresponding supercells

of these binary compounds. The optimized structure of AgI and AgBr compound substituted with the selected Cu concentrations are mentioned as,

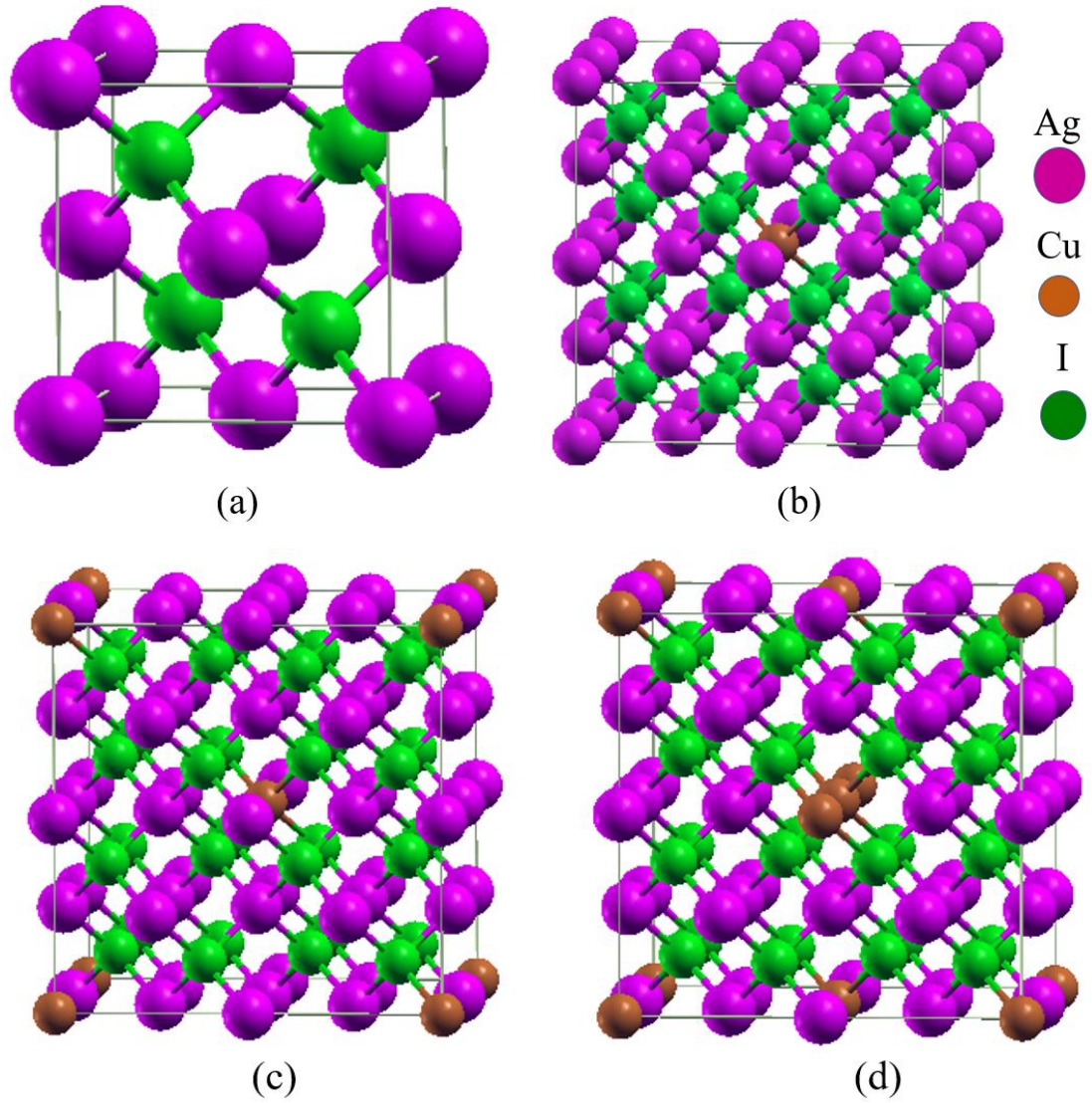


Figure 1.1(a-d): Optimized structure of (a) γ -AgI (unit cell), and $2 \times 2 \times 2$ supercell of γ -Ag_{1-x}Cu_xI for (b) $x = 0.03125$, (c) $x = 0.0625$, (d) $x = 0.125$

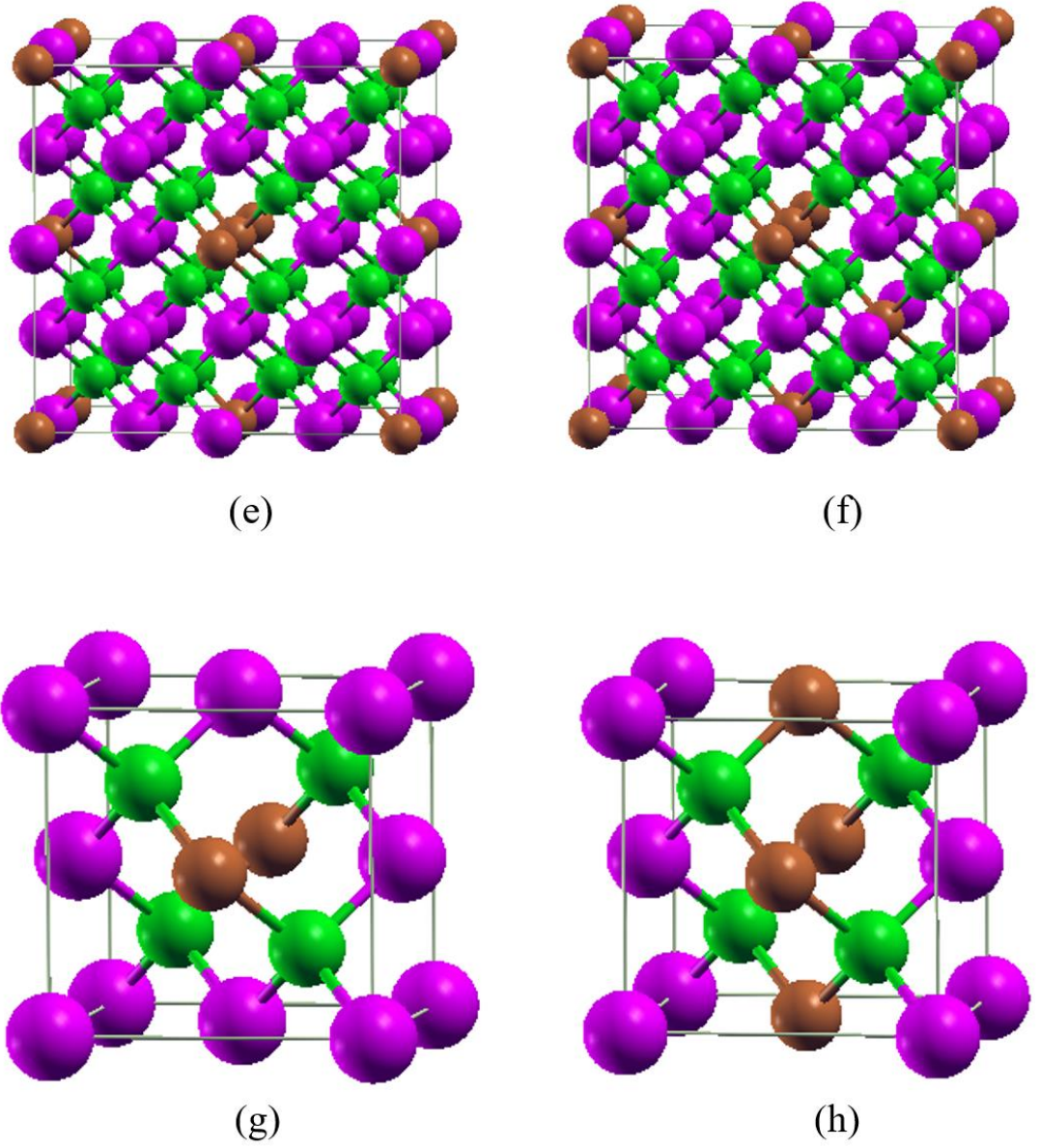


Figure 1.1 (e-h): Optimized $2 \times 2 \times 2$ supercell of $\gamma - Ag_{1-x}Cu_xI$ for (e) $x = 0.15625$, (f) $x = 0.1875$, and unit cell for (g) $x = 0.25$, and (h) $x = 0.5$

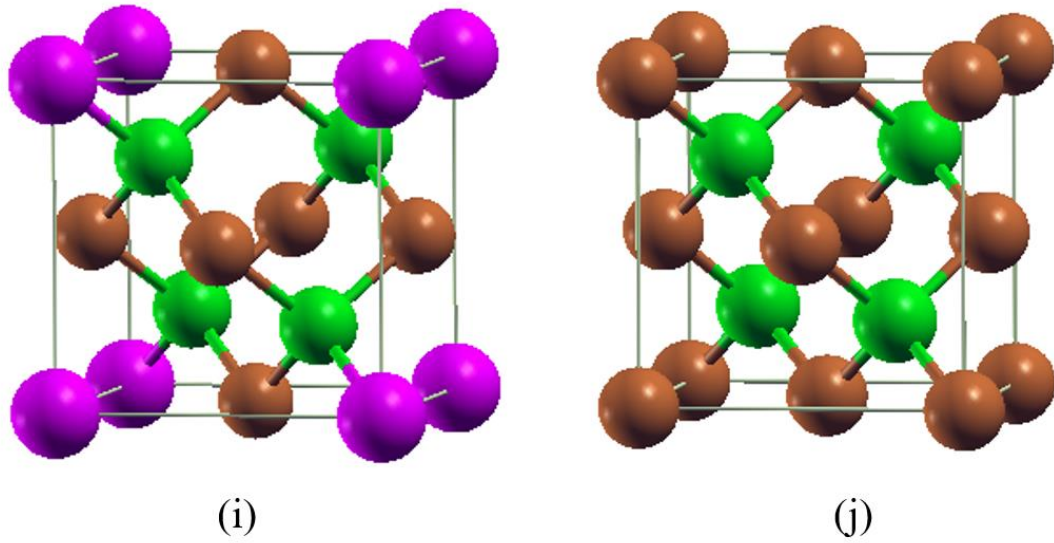


Figure 1.1(i-j): Optimized crystal structure (unit cell) of $\gamma - Ag_{1-x}Cu_xI$ for (i) $x = 0.75$, and (j) $x = 1.00$ (CuI)

In $\gamma - AgI$, the position of Ag and I atoms are at Ag(0.00, 0.00, 0.00); Ag(0.50, 0.50, 0.00); Ag(0.50, 0.00, 0.50); Ag(0.00, 0.50, 0.50), and I(0.25, 0.25, 0.25); I(0.75, 0.75, 0.25); I(0.75, 0.25, 0.75); I(0.25, 0.75, 0.75). For $x = 0.03125$, we have substituted Cu by Ag at (0.50, 0.50, 0.50) in $2 \times 2 \times 2$ supercell of $\gamma - AgI$. For $x = 0.0625$, the position of Cu at (0, 0, 0) and (0.50, 0.50, 0.50). For $x = 0.125$, the position of Cu at (0, 0, 0), (0.50, 0.50, 0.50), (0.00, 0.50, 0.50), and (0.50, 0.00, 0.50). For $x = 0.15625$, the position of Cu at (0, 0, 0), (0.50, 0.50, 0.50), (0.00, 0.50, 0.50), (0.50, 0.00, 0.50), and (0.50, 0.50, 0.00). For $x = 0.1875$, the position of Cu at (0, 0, 0), (0.50, 0.50, 0.50), (0.00, 0.50, 0.50), (0.50, 0.00, 0.50), (0.50, 0.50, 0.00), and (0.25, 0.25, 0.50). For $x = 0.25$, the position of Cu at (0.0, 0.50, 0.50) in unit cell of $\gamma - AgI$. For $x = 0.5$, the position of Cu at (0.0, 0.50, 0.50) and (0.50, 0.00, 0.50) in unit cell. For $x = 0.75$, the position of Cu at (0.0, 0.50, 0.50), (0.50, 0.00, 0.50), and (0.50, 0.50, 0.00) in unit cell. The atomic positions of Cu and I in CuI are Cu(0.00, 0.00, 0.00); Cu(0.50, 0.50, 0.00); Cu(0.50, 0.00, 0.50); Cu(0.00, 0.50, 0.50), and I(0.25, 0.25, 0.25); I(0.75, 0.75, 0.25); I(0.75, 0.25, 0.75); I(0.25, 0.75, 0.75).

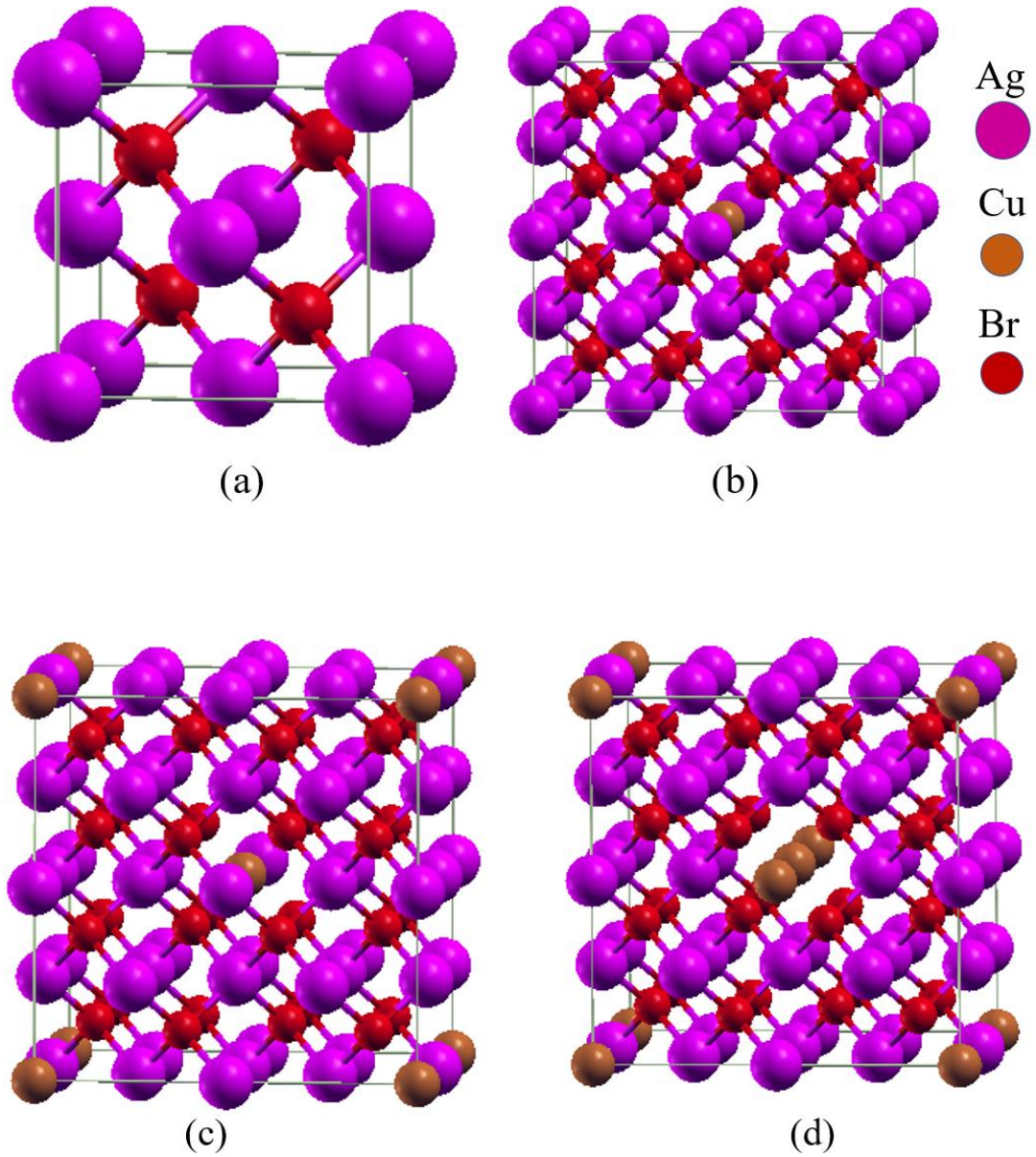


Figure 1.2(a-d): Optimized crystal structure of (a) γ -AgBr (unit cell) and $2 \times 2 \times 2$ supercell of γ -Ag_{1-x}Cu_xBr for (b) $x = 0.03125$ (c) $x = 0.0625$, (d) $x = 0.09375$

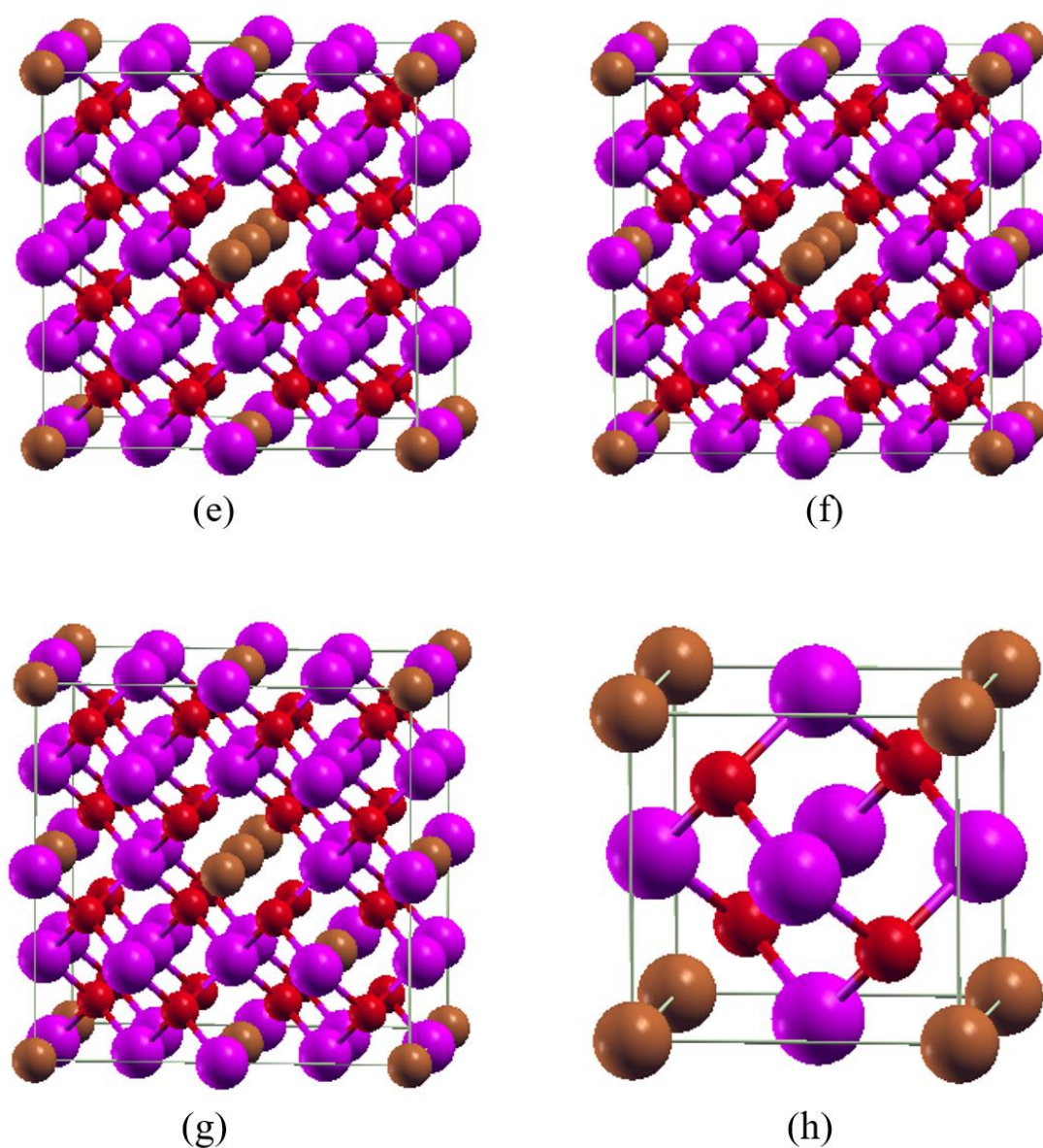


Figure 1.2(e-h): Optimized crystal structure of $2 \times 2 \times 2$ supercell of γ – $\text{Ag}_{1-x}\text{Cu}_x\text{Br}$ for (e) $x = 0.125$, (f) $x = 0.15625$, (g) $x = 0.1875$, and (h) $x = 0.25$ (unit cell).

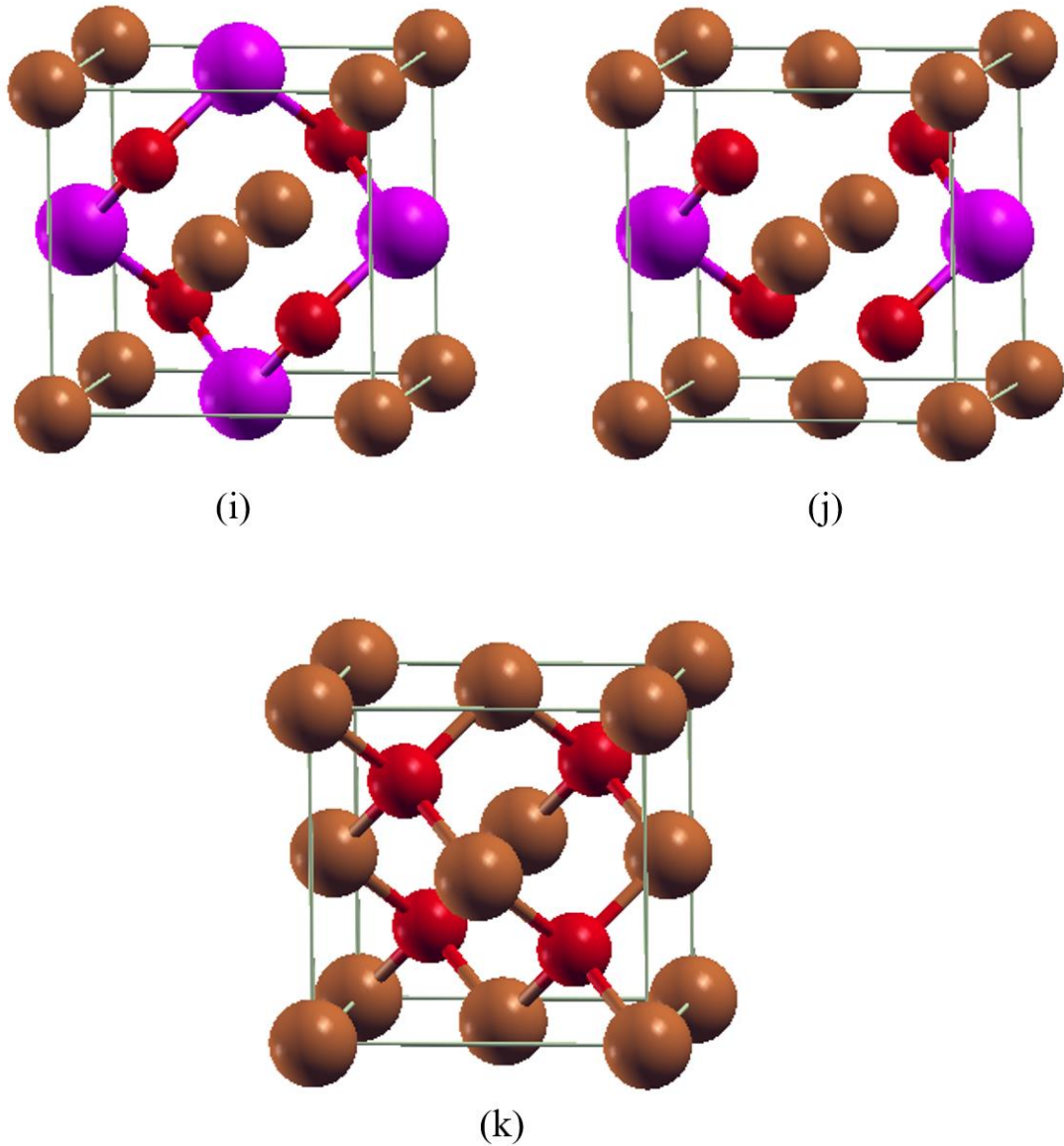


Figure 1.2(i-k): Optimized crystal structure (unit cell) of $\gamma - Ag_{1-x}Cu_xBr$ for (i) $x = 0.5$, (j) $x = 0.75$, and (k) $x = 1.00$ (CuBr)

In $\gamma - AgBr$, the position of Ag and Br atoms are at Ag(0.00, 0.00, 0.00); Ag(0.50, 0.50, 0.00); Ag(0.50, 0.00, 0.50); Ag(0.00, 0.50, 0.50), and I(0.25, 0.25, 0.25); Br(0.75, 0.75, 0.25); Br(0.75, 0.25, 0.75); Br(0.25, 0.75, 0.75). For $x = 0.03125$, we have substituted Cu by Ag at (0.50, 0.50, 0.50) in $2 \times 2 \times 2$ supercell of $\gamma - AgBr$. For $x = 0.0625$, the position of Cu at (0, 0, 0) and (0.50, 0.50, 0.50). For $x = 0.09375$, the position of Cu at (0, 0, 0) and (0.50, 0.50, 0.50), and (0.00, 0.50, 0.50). For $x =$

0.125, the position of Cu at (0, 0, 0), (0.50, 0.50, 0.50), (0.00, 0.50, 0.50), and (0.50, 0.00, 0.50). For $x = 0.15625$, the position of Cu at (0, 0, 0), (0.50, 0.50, 0.50), (0.00, 0.50, 0.50), (0.50, 0.00, 0.50), and (0.50, 0.50, 0.00). For $x = 0.1875$, the position of Cu at (0, 0, 0), (0.50, 0.50, 0.50), (0.00, 0.50, 0.50), (0.50, 0.00, 0.50), (0.50, 0.50, 0.00), and (0.25, 0.25, 0.50). For $x = 0.25$, the position of Cu at (0.0, 0.50, 0.50) in unit cell of $\gamma - AgBr$. For $x = 0.5$, the position of Cu at (0.0, 0.50, 0.50) and (0.50, 0.00, 0.50) in unit cell. For $x = 0.75$, the position of Cu at (0.0, 0.50, 0.50), (0.50, 0.00, 0.50), and (0.50, 0.50, 0.00) in unit cell. In $\gamma - CuBr$, the position of Cu and Br atoms are at Cu(0.00, 0.00, 0.00); Cu(0.50, 0.50, 0.00); Cu(0.50, 0.00, 0.50); Cu(0.00, 0.50, 0.50), and Br(0.25, 0.25, 0.25); Br(0.75, 0.75, 0.25); Br(0.75, 0.25, 0.75); Br(0.25, 0.75, 0.75).

Using the state-of-the-art code WIEN2K and the DFT-based FP-LAPW approach, the structural, electrical and optical properties of these binary compounds and their derivatives of type $\gamma - Ag_{1-x}Cu_xI$ are calculated at specific dopant concentrations (x). To investigate their structural properties, the generalized gradient approximation (GGA) approach was considered. Unlike other schemes, we calculated the electronic and optical properties of the $A_xB_{1-x}C$ using the Tran-Blaha modified Becke-Johnson (TB-mBJ) semi local exchange-correlation potential scheme and HSE06 hybrid functional approach for some specific compounds, to achieve near-precise band dispersions, maximum energy band gaps and precise electronic properties. The main objectives of this study are to investigate the following properties of the above bulk configurations using DFT-based computational calculations.

1.16.1 Structural properties

Under structural properties, the following parameters are calculated; (a) Lattice parameters (a), and bulk modulus (B) of each of the configurations. (b) Linear and nonlinear concentration dependence in ' a ' and ' B '.

1.16.2 Electronic properties

During study of electronic properties of each configuration, we calculate the following parameters

- (i) Band structure of the binary compounds and their derivatives, and hence band gap.
- (ii) Density of State (DOS) for the exploration of atomic and orbital origin of electronic states in the band structures of aforesaid compounds.

1.16.3 Optical Properties

The frequency response of various optical parameters, such as, dielectric function $\varepsilon(\omega)$, refractive index $n(\omega)$, extinction coefficient $k(\omega)$, reflectivity $R(\omega)$, optical conductivity $\sigma(\omega)$, absorption coefficient $\alpha(\omega)$, and energy loss function $L(\omega)$ as function of incident photon energy are computed. The static properties as well as critical points in the respective optical parameters are also computed from these spectra.

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CHAPTER 2

Methodology

2.1 Electronic structure theory of atoms and molecules

The free electron theory is used to describe the properties of metals and it fails to explain the properties of semiconductor and insulators. The material properties are able explained by one-dimensional Kronig-Penny model, which shows that electron in a periodic potential has energy bands with a forbidden energy gap between them. Since solid are three-dimensional entity, cannot be able to explain their physical behaviour by this model. Erwin Schrödinger in 1926 proposed his famous equation which consisting of a remarkable description of many electron system. The Schrödinger equation is now able to calculate the physical properties of a solid with interacting electrons and ions. Through the formulation of accurate Hamiltonian of the system of particles and the subsequent solution of the relevant quantum mechanical Schrödinger's equations of motion, the properties of stationary state of the molecular systems can be determined. Many quantum mechanical terms, including the kinetic energy of each nucleus and electron as well as potential energies arising from the interactions between nuclei, electrons, are contained in the Hamiltonian. Furthermore, the Hamiltonian of a system contains additional terms deriving from other relativistic phenomena in addition to the spin-orbit interaction. Therefore, using of Hamiltonian for solving the Schrödinger's equation of motion is a difficult task. The scenario becomes simpler when we consider the Born-Oppenheimer approximation. Approximate results are possible to obtained when the electronic correlations are properly incorporated into the calculations. In order to solve the non-relativistic Schrödinger equation and determine the electronic structure of quantum mechanical many particle systems as precisely as feasible, approximation techniques have been developed over time to deal with the inter-electronic repulsion term.

2.1.1 The Schrodinger's equation

A quantum mechanical wave function $\psi(r, t)$, which is a function of space and time is describes the state of an N-electron system, and can be expressed as

$$\psi = \psi(r_1, r_2 \dots \dots \dots r_N, t) \quad 2.1$$

The probability density of the wave function can be written as

$$P = |\psi_i(r_i, t)|^2 \quad 2.2$$

The many particle wave function satisfies the time-dependent Schrodinger's equation

$$i \hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \quad 2.3$$

Where $\hat{H}$ is the Hamiltonian operator. If $\hat{H}$ does not contain time explicitly, the time independent and time dependent part of the wave function can be separated for stationary state

$$\psi(r_1, r_2 \dots \dots \dots r_N, t) = \psi_E(r_1, r_2 \dots \dots \dots r_N) e^{-iEt/\hbar} \quad 2.4$$

The stationary wave function ψ_E satisfies the time-independent Schrodinger equation

$$\hat{H} \psi_E = E \psi_E \quad 2.5$$

Here, $\hat{H}$ is not an explicit function of time. There are 3N coordinates in the wave function for N electron system [2]. If we consider the spin coordinates, the total number of co-ordinate become 4N. The spin is considered to be, $S = \pm 1/2$

2.1.2 Hamiltonian for a many-electron system

The time independent Hamiltonian for N-electron system under coulomb interaction between the electrons and nucleus in absence of any external field, spin-orbit, and other relativistic interactions can be expressed as

$$\hat{H} = \frac{\hbar^2}{2} \sum_A \frac{1}{M_A} \nabla_A^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_e^2 + \sum_A \sum_{B>A} \frac{Z_A Z_B e^2}{r_{AB}} - \sum_A \sum_i \frac{Z_A e^2}{r_{iA}} + \sum_j \sum_{i>j} \frac{e^2}{r_{ij}} \quad 2.6$$

Where, A and B represents nuclei and i and j denotes electrons [1]. The first and second terms represents the kinetic energy of the electrons and nuclei respectively. The third term represents the potential energy for nuclear repulsion and r_{AB} is the distance between the nuclei A and B with atomic numbers Z_A and Z_B . The fourth term is the attractive potential energy between electron and the nuclei and $r_{i\alpha}$ is the distance between electron i and nucleus A . The last term is the repulsive potential energy between the electrons and r_{ij} is the distance between electrons i and j . Restricting $B > A$ and $i > j$ to avoid the counting of the self-interaction term in the Hamiltonian.

2.1.3 Born-Oppenheimer Approximation

Born and Oppenheimer in 1927 developed an approximation that nuclei are heavy (slow) and electrons are light (fast). Therefore, mass of nuclei is greater than mass of electron. So, decouple the dynamics of nuclei and electronic part of many body Hamiltonian. In this approximation, the kinetic energy of the nuclei in the Hamiltonian can be assumed to be zero and the potential energy term can be regarded as a constant. Considering that the nuclei are slow and electrons are fast, move at a greater speed than the nuclei. Thus, removing the nuclear kinetic-energy term from equation (6) and assuming that nuclei are stationary [2]. The N-electron Hamiltonian reduces to

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_e^2 + \sum_A \sum_{B>A} \frac{Z_A Z_B e^2}{r_{AB}} - \sum_A \sum_i \frac{Z_A e^2}{r_{Ai}} + \sum_j \sum_{i>j} \frac{e^2}{r_{ij}} \quad 2.7$$

2.1.4 Slater determinant (Anti-symmetrization)

This method is proposed by J. C. Slater [3], to calculate the wave function of a multi-Fermion system, that provides anti-symmetry criteria and thus the Pauli principle in a quantum mechanical system. Since the symmetrization of the quantum mechanical wave function modifies its sign a two-electron interaction, we may express the anti-symmetrization. We may represent the symmetric and anti-symmetric wave functions for a system of non-interacting identical particles [4-5]

$$\psi_s(r_1, r_2 \dots \dots \dots r_N) = \frac{1}{\sqrt{N!}} \sum_P \hat{P} \psi_1(r_1) \psi_2(r_2) \dots \dots \dots \psi_N(r_N) \quad 2.8$$

$$\psi_a(r_1, r_2 \dots \dots r_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \psi_1(r_1) \psi_2(r_2) \dots \dots \psi_N(r_N) \quad 2.9$$

where, P and $\hat{P}$ denotes the parity and its operator respectively.

$$\psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1) & \psi_1(r_2) & \dots & \dots & \dots & \psi_1(r_N) \\ \psi_2(r_1) & \psi_2(r_2) & \dots & \dots & \dots & \psi_2(r_N) \\ \dots & \dots & & & & \dots \\ \dots & \dots & & & & \dots \\ \dots & \dots & & & & \dots \\ \psi_N(r_1) & \psi_N(r_2) & \dots & \dots & \dots & \psi_N(r_N) \end{vmatrix} \quad 2.10$$

2.1.5 Solution of Schrodinger's equation

Schrodinger's equation for a many-electron system cannot be separated due to the inter-electronic repulsion factors, e^2/r_{ij} . Thus, approximation techniques are required in the situations having physical or chemical interest. Different approximation techniques have been designed for handling many-electron system in quantum mechanics.

2.1.6 Methods for solving many-electron system

Various approximation techniques in quantum chemistry and molecular quantum mechanics are mainly classified into three approaches:

(i) Pre Hartree-Fock approaches

(a) Variational method

This method was proposed to solve the time-independent Schrödinger equation for a stationary state of a system that has a time-independent Hamiltonian ($\hat{H}$) with an energy eigenvalue of E_0 . The expected value of the trial energy for the approximated wave function (ψ) is greater or equal to the ground state energy for a normalized, well-behaved function of the coordinates. The quantum-mechanical relation can be expressed as

$$\langle E_{trial} \rangle = \int \psi^* \hat{H} \psi d\tau \geq E_0 \quad 2.11$$

Here, ψ is normalized.

If the function ψ is not normalized, the variation formula can be written as

$$\langle E_{trial} \rangle = \int \frac{\psi^* \hat{H} \psi d\tau}{\psi^* \psi d\tau} \geq E_0 \quad 2.12$$

This expression allowing for calculating the ground state energy in the bound state of the system. This is useful only in the ground state, but not too for excited states [6].

(b) Thomas-Fermi Model

This model was developed by L. Thomas and E. Fermi [7-8] based on semi-classical considerations for the many-electron system. The N electron system is regarded as a ground state Fermi electron gas, by a central potential $V(r)$ that disappears at infinity. For a large number of electrons, the potential $V(r)$, and electron density $\rho(r)$ can be determined through Thomas-Fermi method.

(c) Hartree self-consistent field (SCF) method

This method is one of the simplest ab-initio methods. It provides a mean field approximation to the electron-electron interaction. Considering that electrons move independently in an average field created by all other electrons. D. R. Hartree in 1928 suggested that the wave function of n-electron atom can be expressed as the product of n-one-electron wave function. The wave function of an N-electron system can be expressed as a product of one-electron wave function [9].

$$\psi^0 = \psi_1(r_1, \theta_1, \psi_1) \psi_2(r_2, \theta_2, \psi_2) \dots \dots \dots \psi_N(r_N, \theta_N, \psi_N) \quad 2.13$$

The general form of one electron (H-like) system is

$$\psi_i(r_i, \theta_i, \psi_i) = R_{nl}(r) Y_l^m(\theta, \varphi) \quad 2.14$$

By determining $\psi_1, \psi_2, \dots \dots \dots \psi_N$, which minimizes the integral (2.11). Here, the wave function expressed as the product of spin orbitals with the Pauli Exclusion Principle, which gives the ground state configuration.

(ii) The Hartree-Fock SCF model

The Hartree-Fock Self-Consistent Field (SCF) method is a fundamental approach used to approximate the electronic structure of atoms and molecules. Although the spin and the Pauli exclusion principle have been considered in the Hartree wave functions, the actual wave function should be anti-symmetric including the spin. Hence, instead of spatial orbitals, an anti-symmetric linear combination of products of spin orbitals was considered by Slater and V. A. Fock in 1930. The SCF calculations with these considerations are known as the Hartree-Fock approximation [9]. The antisymmetric criteria for many-electron wave function is satisfied when the product of one-electron functions is expressed in the form of a Slater determinant.

(iii) Beyond Hartree-Fock Models (electron correlation)

In the Hartree-Fock approximation, all electrons undergo the same effective mean field, but there is no explicit correlation between them. It gives precise information in the ground state, but unable to give reliable results in the excited states. Furthermore, the electron correlation between electrons with opposite spins cannot be included in the wave function expressed in the single determinant with this approximation. The correlation energy is the difference between exact non-relativistic energy and Hartree-Fock energy.

$$E_{correlation} = E_{exact} - E_{HF} \quad 2.15$$

Molecular quantum mechanics includes the electron correlation using the post Hartree-Fock technique. Some popular and highly accurate post-Hartree-Fock techniques are:

(a) Configuration Interaction (CI) method

This method is used to solve the non-relativistic Schrödinger equations for a many-electron system following the Born–Oppenheimer approximation. This method is applicable to a comparatively small systems due to the large hardware requirements

[10]. A proper incorporation of electron correlation in the system, the CI approach treated as singles, doubles, and higher order excitations from lower filled orbitals to higher unoccupied orbital.

(b) Coupled-Cluster (CC) method

High level methods like CCSD(T) (Coupled Cluster Singles, Doubles, and Triples) are more accurate but computationally expensive, while DFT is computationally less accurate but computationally efficient. The Moller-Plesset perturbation theory (MPPT) is one of the post-Hartree-Fock ab-initio methods used in computational chemistry. It is an improved version over the Hartree-Fock method, since it applies electron correlation effects [11].

(c) Density functional theory (DFT)

Density functional theory (DFT) is a computational method in quantum chemistry and physics, which provides an efficient framework to describe the electronic structure of atoms, molecules and other alloys. Through the modelling of electronic behaviour of atoms, molecules and solids, DFT is regarded as an important tool for physics, chemistry and material research. DFT optimizes the complicated many body problems by considering electron density as a key variable instead of wave functions as the conventional wave function. This enables DFT to define systems comprising many particles with accurately and efficiently. The fundamentals of the DFT was developed in 1964–1965 by P. Hohenberg, W. Kohn, and L. J. Sham [12-13]. Walter Kohn led the invention of DFT and received the Noble prize in 1998 for his revolutionary contributions in the field of chemistry. His findings modified the methodologies to resolve the Schrodinger equation for many electron systems. Currently, DFT provides an acceptable balance between computing efficiency and accuracy, resulting it for appropriate for complex simulations in both academic and industrial environments. It is more essential for exploring various properties such as chemical reactivity, molecular dynamics and other structural, electronic and optical properties of materials, promoting a new understanding of the underlying essence of matter.

2.2 Density functional approach

The ground state electronic structure of many-body systems can be studied by density functional theory (DFT). Using electron density $\rho(r)$, one can ascertain the properties of a many-electron system. The wave function $\psi(r)$ for a single electron moving in a potential $v(r)$ is obtained using the time-independent Schrodinger's equation in a non-relativistic method as

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v(r) \right] \psi(r) = E\psi(r) \quad 2.16$$

For, many electron systems, Schrodinger's equation can be written as

$$\left[\sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla^2 + v(r_i) \right) + \sum_{i<j} U(r_i, r_j) \right] \psi(r_1, r_2, \dots, r_N) = E\psi(r_1, r_2, \dots, r_N) \quad 2.17$$

Where, N denotes the number of electrons and $U(r_i, r_j)$ denotes the electron-electron interaction.

Kinetic energy operator of the system can be written as

$$\hat{T} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 \quad 2.18$$

Also, the potential energy operator for coulomb interaction

$$\hat{U} = \sum_{i<j} U(r_i, r_j) = \sum_{i<j} \frac{q^2}{|r_i - r_j|} \quad 2.19$$

And

$$\hat{V} = \sum_i v(r_i) = \sum_i \frac{Q_q}{|r_i - R|} \quad 2.20$$

Here, Q is the nuclear charge and R is the position.

For a molecule,

$$\hat{V} = \sum_i v(r_i) = \sum_{ik} \frac{Q_{qk}}{|r_i - R_k|} \quad 2.21$$

The Schrodinger's equation may be represented as sequence

$$v(r) \xRightarrow{SE} \psi(r_1, r_2, \dots, r_N) \xRightarrow{\langle \psi | \dots | \psi \rangle} \text{Observables} \quad 2.22$$

We have specified the system by choosing its accurate potential term $v(r)$ put into the Schrodinger's equation and solve the equation for the wave function ψ to determine observables by taking the expectation values of operator with the same wave function.

The particle density can be obtained as

$$n(r) = N \int d^3r_1 \int d^3r_2 \int d^3r_3 \dots \int d^3r_N \psi^*(r_1, r_2, \dots, r_N) \psi(r_1, r_2, \dots, r_N) \quad 2.23$$

For N electron systems, the electron density $n(r)$ is a function of three coordinates. Thus, the density functional can be represented in sequence as

$$n(r) \Rightarrow \psi(r_1, r_2, \dots, r_N) \Rightarrow v(r) \Rightarrow \text{Observables} \quad 2.24$$

Knowing the values of $\rho(r)$ gives the knowledge of wave functions and potential and finally all other observables.

2.2.1 Hohenberg and Kohn theorem

First theorem: The ground state electron density $n(r)$ of a system that determines the external potential $V_{ext}(r)$ (within a trivial additive constant). Thus, we can say that the external potential $V_{ext}(r)$ can be calculated by the electron density $n(r)$ and for a given density, there will be a single external potential.

Second theorem: The density that minimizes the variational energy, is the true ground state density for the external potential $V_{ext}(r)$. In other words, it determines the ground state energy if and only if the input density is the true ground state density.

2.2.2 Kohn-Sham equation

DFT has reduced the task of dealing with many-electron system to a relatively easy to solve a set of one particle equation. The total energy of an interacting system is

$$E[n] = T[n] + E_{ee}[n] + E_{ext}[n] \quad 2.25$$

For a system of non-interacting electron density $n(r)$, having the same energy functional $E[n]$, and rearranging the terms, we can write it as

$$E[n] = T_S[n] + E_{Hartree}[n] + E_{ext}[n] + \{T[n] - T_S[n] + E_{ee}[n] - E_{Hartree}[n]\} \quad 2.26$$

Where, $T_S[n]$ is the non-interacting kinetic energy corresponding to density ρ . The kinetic energy functional $T[n]$ has been replaced by the non-interacting kinetic energy $T_S[n]$ term. The $E_{Hartree}[n]$ term is the Hartree energy which is the classical coulomb interaction as a functional of the density $n(r)$. The first three terms in the above expression are treated exactly.

Writing

$$T[n] - T_S[n] = E_c[n] \quad 2.27$$

$$E_{ee}[n] - E_{Hartree}[n] = E_x[n] \quad 2.28$$

Rewrite the above equation as

$$E[n] - T_S[n] + E_{ee}[n] - E_{Hartree}[n] = E_c[n] + E_x[n] = E_{xc}[n] \quad 2.29$$

This is called exchange-correlation energy. This part of energy is important in DFT.

The kinetic energy functional of the non-interacting electron system, $T_S[n]$ can be expressed as

$$T_S[n] = -\frac{1}{2} \langle \psi_S[n] | \nabla^2 | \psi_S[n] \rangle \quad 2.30$$

Here, ψ_S is the Slater determinant of orbital ϕ_i obtained from a single particle. The ground state electron density is given by

$$n(r) = \sum_i |\phi_i(r)|^2 \quad 2.31$$

Thus,

$$E[n] = -\frac{1}{2} \sum_i \langle \phi_i[n] | \nabla^2 | \phi_i[n] \rangle + \frac{1}{2} \iint \frac{n(r)n(r')}{|r-r'|} dr dr' + \int V_{ext} n(r) + E_{xc}[n(r)] \quad 2.32$$

After minimizing the energy with respect to orbitals and using the normalization condition $\int \phi_k(r)^* \phi_k(r) dr = 1$, we have

$$\left[-\frac{1}{2} \nabla^2 + \int \frac{n(r')}{|r-r'|} dr' + V_{ext}(r) + V_{xc}(r) \right] \phi_k = \varepsilon_k \phi_k \quad 2.33$$

This equation is known as the Kohn-Sham equation, and is the DFT counterpart of Schrodinger's equation. The function ϕ_k represents the Kohn-Sham orbital and ε_k served as a Lagrange undetermined multiplier, called Kohn-Sham orbital energies. The term V_{ext} and V_{xc} are called external potential and exchange correlation potential respectively [12].

The total energy can be written as

$$E[n] = \sum_{k=1}^N \varepsilon_k - \frac{1}{2} \iint \frac{n(r)n(r')}{|r-r'|} dr dr' - \int V_{ext} n(r) dr + E_{xc}[n(r)] \quad 2.34$$

In our density functional calculations, first we start with an initial density $n(r)$ and solve the Kohn-Sham equation self consistently to obtain a set of Kohn-Sham orbital. And then calculate the ground state energy as a functional of the ground state density.

2.3 Exchange correlation functional

The exchange correlation expression is obtained as the functional derivative of exchange correlation energy as

$$V_{xc} = \frac{\delta E_{xc}[n]}{\delta n(r)} \quad 2.35$$

The exchange correlation energy is separated into exchange and correlation part. Therefore,

$$E_{xc}[n] = E_x[n] + E_c[n] \quad 2.36$$

And the corresponding potentials are represented as

$$V_x = \frac{\delta E_x[n]}{\delta n(r)} \quad \text{and} \quad V_c = \frac{\delta E_c[n]}{\delta n(r)} \quad 2.37$$

For density functional calculations, it is necessary to use appropriate exchange and correlation energy functional. Various exchange correlation potentials are:

2.3.1 Local Density Approximation (LDA)

All exchange-correlation functions are based on the Local Density Approximation (LDA), often referred to as the local functional and first presented by Kohn and Sham in 1965. In LDA, the exchange correlation energy is supposed to give rise to an exchange correlation potential that is dependent on the density value in r rather than its gradient.

$$E_{xc}^{LDA}[n(r)] = \int n(r) \varepsilon_{xc}[n(r)] dr \quad 2.38$$

Where, ε_{xc} is the exchange-correlation energy density of the uniform electron gas of density $n(r)$ [14]. It is exact for a homogenous electron gas. So, it behaves well for systems whose electron density does not vary too rapidly. The LDA functional calculate the ground state properties of systems and predicting less accurately the energy band gap of semiconducting materials.

2.3.2 Generalized Gradient Approximation (GGA)

Apart from the LDA, many non-local approximations are also used. Some materials have a noticeable density gradient. For a strongly correlated systems such as d electrons (transition elements) and f electrons (lanthanides and actinides), the LDA is not appropriate, since it is predicted that the electron density will vary with the spatial co-ordinates. The GGA [14-15] method was established by J. P. Perdew, K. Burke, and M. Ernzerhof in 1996. They suggested that the electron density vary with spatial co-ordinates and the exchange correlation energy would be described as the gradient of electron density. The exchange correlation energy expressed as

$$E_{xc}^{GGA}[n(r)] = \int n(r) \varepsilon_{xc}[n(r), \nabla n(r)] dr \quad 2.39$$

Generally, GGA performs better than LDA by considering bond length, binding energy, lattice constants, and other related properties. The band gap of the semiconductors for transport properties was not provided by LDA and GGA method. GGA has an advantage over LDA [14], it enhances the ground state properties of light molecules, atoms, and clusters.

2.3.3 Tran Blaha modified Becke Johnson (TB-mBJ) exchange correlation potential

The underestimation in the energy band gap calculation within the LDA and GGA is overcome by modified Becke Johnson (mBJ) exchange potential [16-17], which competes in accuracy with the more expensive hybrid and GW approaches. In 2009, Tran and Blah presented the modified version of Becke Johnson potential by introducing a parameter ‘c’ in the original Becke-Johnson exchange potential, which accounts the orbital dependent correction in Hamiltonian. It has a screening term and semi-local approximation to an atomic exchange potential. The modified Becke Johnson potential,

$$V_{X,\sigma}^{mBJ}(r) = cV_{X,\sigma}^{BR} + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{6}} \sqrt{\frac{t_{\sigma}(r)}{n_{\sigma}(r)}} \quad 2.40$$

$$\text{where, } n_{\sigma} = \sum_{i=1}^{N_{\sigma}} |\psi_{i,\sigma}|^2 \text{ is the electron density, and}$$

$$t_{\sigma} = \frac{1}{2} \sum_{i=1}^{N_{\sigma}} \nabla \psi_{i,\sigma}^* \nabla \psi_{i,\sigma}$$

represents the kinetic energy density.

And,

$$V_{X,\sigma}^{BR}(r) = -\frac{1}{b_{\sigma}(r)} \left[1 - e^{-X_{\sigma}(r)} - \frac{1}{2} X_{\sigma}(r) e^{-X_{\sigma}(r)} \right]$$

is called the Becke-Roussel (BR) exchange potential [27]. The quantity,

$$\sqrt{\frac{t_{\sigma}(r)}{n_{\sigma}(r)}} \text{ is the screening term, and } c = \alpha + \beta \left[\frac{1}{v_{cell}} \int_{cell} \frac{|\nabla n(r')|}{n(r')} d^3 r' \right]$$

For any value of c , the exchange potential is calculated for constant electron density. Here, v_{cell} is the cell volume. The constants $\alpha = -0.012$ and $\beta = 1.023 \text{ (bohr)}^{1/2}$ are the two free parameters.

It is possible to apply this semi-local exchange potential to a large system efficiently.

2.3.4 Hybrid functional (HSE06)

In the twenty-first century, hybrid functional, the fourth step on Jacob's ladder became extensively employed in the calculations of solids. Currently the most prevalent is HSE06, a screened version of the other well-known PBE0 and YS-PBE0 functional equivalent to $\alpha = 0.25$. The Hartree-Fock (HF) expression and a semi-local (SL) functional are combined linearly to yield the exchange energy in a (screened) hybrid functional.

$$E_{XC}^{hybrid} = E_{XC}^{SL} + \alpha_X (E_X^{(scr)HF} - E_X^{(scr)SL}) \quad 2.41$$

Where,

$$E_X^{(scr)HF} = -\frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \delta_{\sigma_i \sigma_j} \iint \psi_i^*(r) \psi_j(r) \times v(|r - r'|) \psi_j^*(r') \psi_i(r') d^3 r d^3 r' \quad 2.42$$

Here, v is either the bare Coulomb potential $v = 1/|r - r'|$ for unscreened hybrid potential or a potential that is screened at short or long range for screened hybrid potentials. For solids, it is computationally advantageous to use a potential that is at short range, for instance, the Yukawa potential $v = e^{-\lambda|r-r'|}/|r - r'|$ or $v = \text{erfc}(\mu|r - r'|)/|r - r'|$, where ‘erfc’ is the complementary error function.

The hybrid functionals are particularly notable for qualities derived from the energy band gap, for which they greatly fare better than the normal GGA functional, even if they are employed for the total energy such as geometry optimization and cohesive

energy. The approach of Massidda et al., which is based on the pseudo-charge method for computing the Coulomb potential, is followed in the implementation of the screened and unscreened hybrid functionals. The Yukawa potential is employed by the screened hybrid functional. If the screening value $\lambda=3/2(\mu)$ is chosen correctly, the band gap results from the PBE-based hybrid functional, YS-PBE0 are almost gives the same results as from HSE06, which uses the screened potential. This calculation takes 10–1000 times longer than semi-local methods [17-19] as it uses a double integral and sums over HF-exchange.

2.4 Computational Methodology

The electronic structure of solids can be calculated by using some basic methods. Generally, the core electrons of a material are inactive to the contribution of any physical properties. The methods that used divides the whole electronic population into core electrons and valance electrons regions. The performance of the potential in these regions is more important. We briefly discussed various related methodologies, which are implemented in the present thesis work.

2.4.1 Augmented Plane Wave (APW) Method

DFT developed the framework of highly sophisticated augmented plane wave (APW) method, made feasible to DFT-based calculations. The APW method is a simple method to describe the LAPW and FP-LAPW approaches for electronic structure calculations using Kohn-Sham (KS) equation developed by Slater in 1937. The crystal structure in the APW methodology divide into core (atomic region) and interstitial regions. The core region is called as Muffin-Tin sphere. The corresponding potential for these regions is represented as

$$V(r) = V(r) \quad \text{inside core region} \quad 2.43(a)$$

$$= 0 \quad \text{in interstitial region} \quad 2.43(b)$$

However, the basis of these two regions are also different. According to APW approach [20, 12], the potential and wave function near the nucleus are virtually spherical. The radial solution of Schrodinger's equation is applied inside non-overlapping atomic spheres, while plane waves are applied in the interstitial region.

The wave functions vary rapidly in the atomic region, while it is varying slowly in the interstitial region. This can be expressed as

$$\varphi(r) = \begin{cases} \sum_{lm} A_{lm} u_l(r) Y_{lm}(r) & r \in MT \\ \frac{1}{\sqrt{V}} \sum_G C_G e^{[i(K+G).r]} & r \in I \end{cases} \quad \begin{matrix} 2.44(a) \\ 2.44(b) \end{matrix}$$

Where, G is the reciprocal lattice vector and C_G represents the variational coefficient. This is applicable only for pseudo-potentials. And φ is the wave function, V denotes the volume of the cell and u_l is the solution of radial Schrodinger equation.

The wave functions of the atomic sphere and the interstitial regions are combined to determine the coefficients A_{lm} . The Kohn-Sham electronic wave function would be on the basis of APW as

$$\psi_k(r) = \sum_G C_G^k e^{[i(K+G).r]} \quad 2.45$$

APW is the most effective approach for obtaining valance states within the real potential. Since, an unknown energy term present in the radial wave function, the APW method is quite slow. Improved versions of APW need to be developed to overcome these difficulties in the challenging solid-state systems.

2.4.2 Linearized Augmented Plane Wave (LAPW) Method

In the LAPW [21] approach, the valence electrons are well described by plane waves. These two basis sets are integrated through LAPW approach by inserting a muffin-tin (MT) sphere on each atom. Interstitial region occupies the remaining space within the cell. Inside the muffin-tin spheres, the linear combination of radial function times the spherical harmonics $Y_{lm}(\hat{r})$ can be expressed as

$$\varphi_{K_n}(r) = \begin{cases} \sum_{lm} [A_{lm,K_n} u_l(r, E_l) + B_{lm,K_n} \dot{u}_l(r, E_l)] Y_{lm}(\hat{r}) & r \in MT \\ \frac{1}{\sqrt{V}} \sum_G C_G e^{[i(K+G).r]} & r \in I \end{cases} \quad \begin{matrix} 2.46(a) \\ 2.46(b) \end{matrix}$$

Where, $u_l(r, E_l)$ denotes the solution of radial part of Schrodinger equation of energy E_l , and $\dot{u}_l(r, E_l)$ is the energy derivative of the spherical potential. The linear

combination of these two functions represents the linearization of the radial function. The coefficients $A_{lm.K_n}$ and $B_{lm.K_n}$ determined based on the basis function in the interstitial region. The accuracy of the LAPW method will be augmented by incorporating energy and its derivative in contrast to the APW approach [22].

2.4.3 The Full Potential Linearized Augmented Plane Wave (FP-LAPW) method

The potential in the FP-LAPW approach is described by the muffin-tin (MT) model. It is most commonly employed in electronic band structure and solid includes quantum mechanical models. In this case, the electrons are separated into core and valance electrons. The wave function, charge density, and potential inside the muffin-tin spheres are represented as the product of the radial solution of the single-particle Schrodinger equation with fixed energy (V_{lm}) and the spherical harmonics (Y_{lm}).

$$V(r) = \sum_{l,m} V_{lm}(r) Y_{lm}(r) \quad 2.47$$

On the other hand, the wave function in the interstitial region of the crystal is expanded in the plane wave basis as

$$V(r) = \sum_k V_k e^{i\vec{k} \cdot \vec{r}} \quad 2.48$$

Where, $\vec{k}$ represents the wave vector inside the first Brillouin zone and V_k is the scalar amplitude of the plane wave at fixed $\vec{k}$.

In the FP-LAPW approach [3], smallest muffin-tin radius(R_{MT}) should be chosen carefully to ensure non-overlapping atomic spheres to ensure energy convergence. The various parameters used during DFT calculation based on FP-LAPW method are mentioned as: l_{max} , K_{max} , the product $R_{MT} \cdot K_{max}$ and G_{max} . All these parameters have greater impact during a computational calculation. The value of the parameters should be chosen carefully to ensure the appropriate calculations. Where l_{max} = maximum value of angular momentum for the wave function expansion inside the atomic spheres, K_{max} = Magnitude of the largest k-vector in the plane wave expansion, $R_{MT} \cdot K_{max}$ = Cut-off value of the wave function in the interstitial region

and G_{max} = Fourier expansion parameter of the potential and charge density. The cut-off value and the number of k-points are adjusted to ensure convergence. Until the convergence of total energy, the self-consistent field (SCF) calculations are performed regularly.

2.4.4 Augmented plane Wave (APW) + Local orbital (lo) method

An additional technique for improving the solutions is to incorporate local orbitals (lo) into the linearization of the APW approach. The representation of the basis set used in the APW+lo method as:

$$\varphi_{lm}(r) = \begin{cases} \sum_{lm} [A_{lm,K_n} u_l(r, E_l) + B_{lm,K_n} \dot{u}_l(r, E_l)] Y_{lm}(\hat{r}) & r \in MT \\ 0 & r \in I \end{cases} \quad \begin{matrix} 2.49(a) \\ 2.49(b) \end{matrix}$$

This approach is comparable to the LAPW method in the realm of accuracy, and has the advantage of choosing a smaller basis set than the APW method. The normalization technique is applied to find the coefficients in the aforementioned relation, which implies that the local orbital is zero at the muffin-tin boundary [21-22].

2.5 Computational DFT code based on FP-LAPW method (WIEN2k)

The WIEN2k package is a computer software based on Fortran90 program for quantum mechanical calculations of materials. It initially developed by P. Blaha, K. H. Schwarz, and other colleagues at Institute of Materials Chemistry, Vienna University of Technology. The WIEN code was made available to the public in 1990. Later on, WIEN93, WIEN97 and WIEN2k were developed [19]. The full potential (linearized) augmented plane-wave and local orbitals (FP-(L)APW+lo) basis set is mainly used to solve the Kohn-Sham equations of density functional theory. This package can be used to study mainly, the structural and electronic properties of crystalline solids, including band structure, DOS, charge density, Fermi surface, magnetism (ferromagnetic, antiferromagnetic, and non-magnetic configurations), and many exchange-correlation potentials (e.g., LDA, GGA, TB-mBJ). The package is interlinked via c-shell scripts and a web-based graphical user interface, named as w2web. Figure 2.1 given in the user guide [19] illustrates the program flow of WIEN2k using a flowchart. Over the past two decades, more than 2,500 groups globally working

with the updated code, WIEN2K. This code incorporates multiple intriguing features. The graphic code "XCrySDen" is often used by WIEN2K code users when performing various calculations and visualizing structures [23].

2.5.1 Program flow of WIEN2K code

Initialization

The input process starting with a regular structure file created by WIEN2k code, which contains information about the atomic structure such as, lattice parameters, atomic positions, space group and muffin-tin radii. The programs mentioned below are run during initialization:

(a) NN (nearest neighbor distances)

The nearest neighbor distances of every atom are calculated by the NN program using these structure files, and it also verifies non-overlapping requirements of atomic spheres.

(b) SGROP

The GROUP program uses the created structure files to generate the space group and all point groups of non-equivalent atomic sites. It can also shift the origin, make a new structure file, and reduce unit cells based on the input data.

(c) SYMMETRY

With the help of information of the structure file, the atomic position and lattice type, it can either build space-group symmetry operations or compare ones that have already been created.

(c) LSTART (atomic LSDA program)

This code uses relativistic atomic local spin density approximation (LSDA) to generate atomic densities, which are then used as a starting density for a SCF calculation. It produces atomic potentials and optional atomic valance densities.

(d) KGEN (generates k mesh)

The KGEN uses the given point on the grid to generate the k-mesh within the irreducible wedge of the Brillouin zone (IBZ). The main purpose of convergence tests is to choose a properly large mesh of integration points.

(e) DSTART (superposition of atomic densities)

The DSTART create an initial charge density by the superposition of atomic densities.

2.5.2 Programs for running SCF cycle

(a). LAPW0 (generates potential)

This program calculates the total potential V_{tot} by combining Coulomb potential V_c and the exchange correlation potential V_{xc} , taking electron density as an input parameter.

(b) LAPW1 (generates eigenvalues and eigenvectors)

It determines the diagonalized eigenvalues and eigenvectors and sets up the overlap matrix and Hamiltonian.

(c) LAPW2 (generates valence charge density expansions)

For each occupied state and corresponding k-vector, LAPW2 calculates the Fermi-energy and the expansions of the electronic charge densities. The integration procedure is then used to obtain the relevant partial charges inside the atomic spheres.

(d) LCORE (generates core states)

It generates core eigenvalues, along with the core contribution to atomic forces and the corresponding core densities.

(e) MIXER (adding and mixing of charge densities)

The sum of the electron densities in the core, semi-core, and valance states is what gives the total density in MIXER. The SCF cycle is controlled by combining the input and output densities to create a new density that will be used in the next iteration.

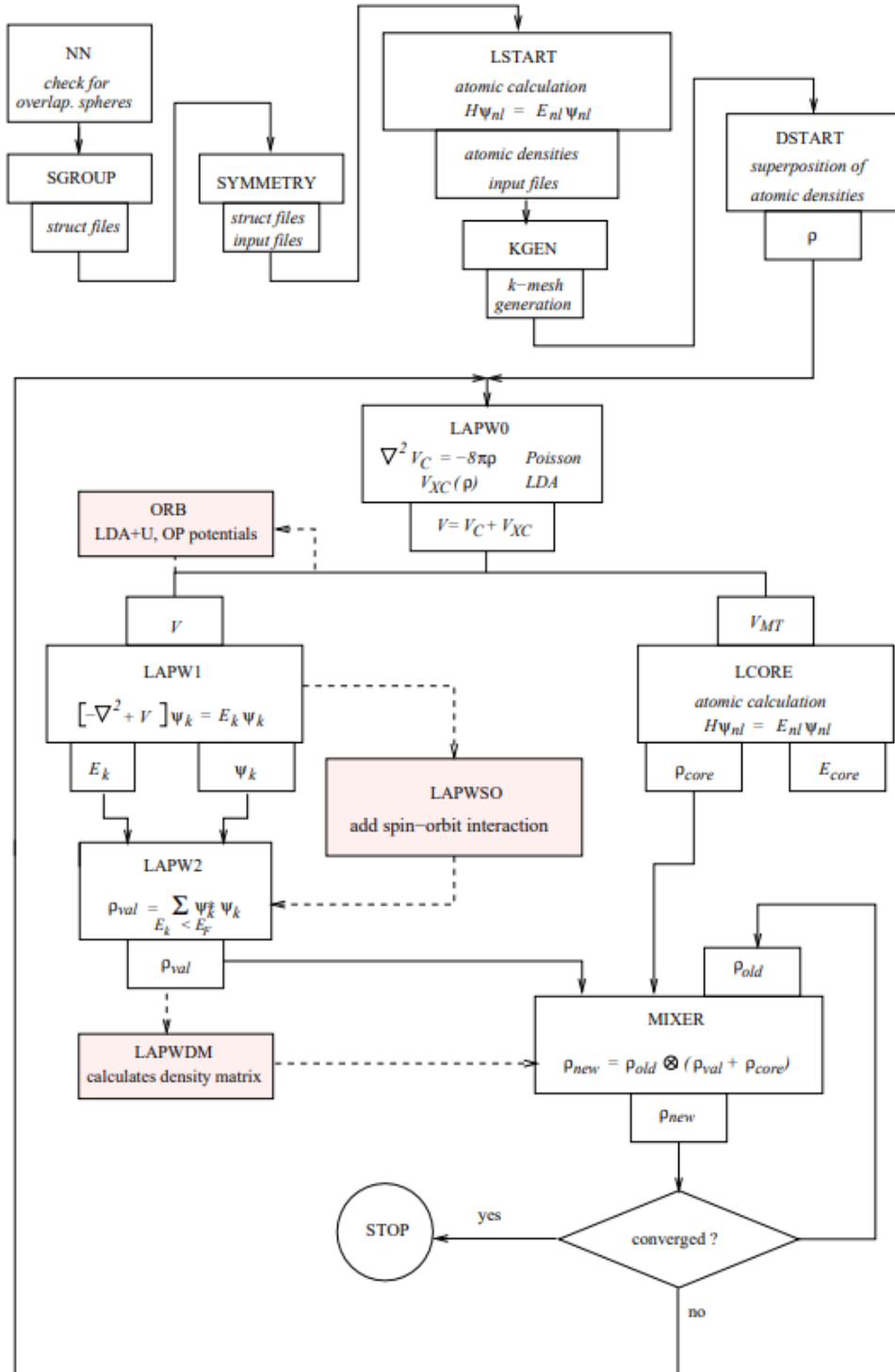


Figure 2.1: Flow chart of WIEN2k program. Source: WIEN2k user guide [19]

2.6 Calculation of various properties of solids

2.6.1 Structural properties

After getting total energy of the crystal volumes around the equilibrium cell volume (V_0), one may fit the data to Birch-Murnaghan's equation of state to find the ground state structural parameters of the compound [24]. The third order Birch-Murnaghan equation of state published in 1947 by Francis Birch, is given by

$$P(V) = \frac{3B_0}{2} \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\} \quad 2.50$$

The energy, $E(V)$ is found by integration of pressure as

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{2/3} \right] \right\} \quad 2.51$$

Where (B_0) the bulk modulus at zero pressure is, (E_0) is the energy of the unit cell at equilibrium, (V_0) is the equilibrium cell volume, and B' is the first order pressure derivative of bulk modulus.

2.6.2 Supercell scheme

This scheme is used to construct supercells from a regular WIEN2k structure file. A large number of electrons present in the surface and interface of system. The current wave function is extremely challenging to calculate such a number of electrons. According to Bloch's Theorem, a large system can be divided into number of small unit cells, which can then be replaced by a finite cell combined in three dimensions. Bloch's Theorem for a periodic function can be represented as.

$$\psi(r) = e^{ik \cdot r} u(r) \quad 2.52$$

$$u(r) = u(r + l) \quad 2.53$$

Where, $\psi(r)$ is Bloch wave, $u(r)$ defines the periodic function, l is the length of the unit cell and k represents the momentum vector within the first Brillouin zone of a reciprocal lattice. The Fourier series expansion in the periodic function $u(r)$ is

$$u(r) = \sum_G C_{i,G} e^{iG \cdot r} \quad 2.54$$

Where, G denotes the reciprocal lattice vector. The extended form of periodic function $u(r)$ can be used to represent the electronic wave functions, expressed as

$$u(r) = \sum_G C_{i,k+G} e^{i(k+G) \cdot r} \quad 2.55$$

This expression is used throughout the calculation to visualize the electronic band structure of compound. In the present thesis, all the calculations are carried out using the $2 \times 2 \times 2$ supercell of 64- atom in a face centered cubic cell. Figure 2.2 shows the supercell of AgI compound.

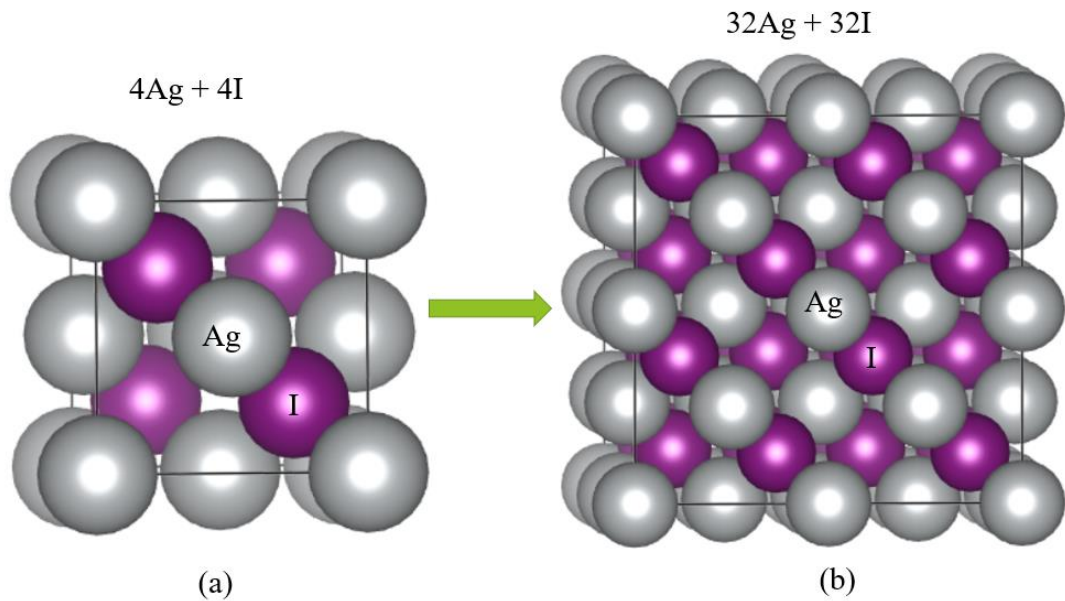


Figure 2.2: (a) $1 \times 1 \times 1$ unit cell, (b) $2 \times 2 \times 2$ supercell of fcc γ – AgI

2.6.3 Optical parameters

The way a material responds to the energy of an incident photon at different frequencies is demonstrated by its optical characteristics. Electronic characteristics, particularly band gap, have a significant impact on the optical properties of the

material. Any frequency-dependent complex dielectric function, $\varepsilon(\omega)$, is used to study its optical properties of material. The complex dielectric function expressed as

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad 2.56$$

The $\varepsilon(\omega)$ is strongly dependent on its electronic properties and its imaginary part $\varepsilon_2(\omega)$ is calculated by the relation,

$$\varepsilon_2(\omega) = \frac{8\pi^2 e^2}{\omega^2 m^2} \sum_n \sum_{n'} \int_{BZ} |P_{nn'}^v(k)|^2 f_{kn}(1 - f_{kn'}) \delta(E_n^k - E_{n'}^k - \hbar\omega) \frac{d^3k}{(2\pi)^3} \quad 2.57$$

The e and m are charge and mass of the electron respectively. The f_{kn} is the Fermi-Dirac distribution function, $P_{nn'}^v(k)$ term defines the projection of the momentum dipole-matrix element between the initial and final states along the direction of v of the electric field and $E_n^k(k)$ is the one-electron energy.

The real part $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$ of dielectric function $\varepsilon(\omega)$ are related by the Kramer's-Kronig transformation [25] are expressed as

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad 2.58$$

$$\varepsilon_2(\omega) = -\frac{2}{\pi} P \int_0^\infty \frac{\varepsilon_1(\omega')}{\omega'^2 - \omega^2} d\omega' \quad 2.59$$

The real part of dielectric function $\varepsilon_1(\omega)$ at zero frequency of the incident photon is called static dielectric constant $\varepsilon_1(0)$ and its energy band gap (E_g) is described by the Penn model [26], according to the relation, based on $\varepsilon_1(0)$ and band gap (E_g) can be written as

$$\varepsilon_1(0) \approx 1 + \left(\frac{\hbar\omega_P}{E_g} \right)^2 \quad 2.60$$

It implies that smaller band gap (E_g) semiconductors exhibits larger static dielectric constant $\varepsilon_1(0)$ and vice-versa.

The frequency dependent refractive index $n(\omega)$ of any material can be calculated from the values of $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ using the relation

$$n(\omega) = \left[\frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}}{2} + \frac{\varepsilon_1(\omega)}{2} \right]^{1/2} \quad 2.61$$

The value of $n(\omega)$ at zero frequency, $n(0)$ of the incident photon is known as static refractive index $n(0)$ and can be calculated by the formula

$$n(0) = \sqrt{\varepsilon_1(0)} \quad 2.62$$

The band gap (E_g) dependence of the $n(0)$ expressed with the Penn model as

$$n(0) \approx \sqrt{1 + \left(\frac{\hbar\omega_p}{E_g} \right)^2} \quad 2.63$$

It implies that smaller band gap (E_g) semiconductors exhibits larger static refractive index $n(0)$ and vice-versa.

The extinction coefficient $k(\omega)$ of any material is associated to its frequency dependent refractive index $n(\omega)$ by the Kramer's-Kronig transformation [27] as

$$n(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{k(\omega')}{\omega' - \omega} d\omega' \quad 2.64$$

$$\text{and } k(\omega) = -\frac{2}{\pi} P \int_0^{\infty} \frac{n(\omega') - 1}{\omega' - \omega} d\omega' \quad 2.65$$

The value of $k(\omega)$ of a material can be calculated from the value of $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ using the relation

$$k(\omega) = \left[\frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}}{2} - \frac{\varepsilon_1(\omega)}{2} \right]^{1/2} \quad 2.66$$

The expression for reflectivity $R(\omega)$ of a material can be calculated using the relation,

$$R(\omega) = \left| \frac{1 - \sqrt{\varepsilon}}{1 + \sqrt{\varepsilon}} = \frac{(1 - n)^2 + k^2}{(1 + n)^2 + k^2} \right| \quad 2.67$$

Where, n and k are the frequency dependent refractive index and extinction coefficient respectively. They are also related to the $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ of complex dielectric function by the relations [28-29]

$$\varepsilon_1(\omega) = n^2 - k^2 \quad 2.68$$

$$\varepsilon_2(\omega) = 2nk \quad 2.69$$

Static reflectivity $R(0)$, also known as zero frequency reflectivity, is defined as the value of $R(\omega)$ at zero frequency of the incoming energy of photon. Therefore, the static reflectivity $R(0)$ at zero frequency of the incident photon may be computed as

$$R(0) = \left[\frac{1 - n(0)}{1 + n(0)} \right]^2 \quad 2.70$$

The band gap (E_g) dependence of $R(0)$ can be also be expressed by

$$R(0) = \left[\frac{1 - \sqrt{\varepsilon_1(0)}}{1 + \sqrt{\varepsilon_1(0)}} \right]^2 \quad 2.71$$

Thus, we can say that smaller band gap (E_g) semiconductor material exhibits larger static reflectivity $R(0)$ and vice-versa.

The optical conductivity [30] $\sigma(\omega)$ has been calculated from the imaginary part $\varepsilon_2(\omega)$ of the complex dielectric function using the expression as

$$\sigma(\omega) = \frac{\omega}{4\pi} \varepsilon_2(\omega) \quad 2.72$$

The optical absorption coefficient $\alpha(\omega)$ and the energy loss function $L(\omega)$ of any material can be derived from its real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of dielectric function [31] by the expression

$$\alpha(\omega) = \sqrt{2\omega} \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2} \quad 2.73$$

$$L(\omega) = -Im\left(\frac{1}{\varepsilon}\right) = \left(\frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}\right) \quad 2.74$$

The relation between extinction coefficients $k(\omega)$ and optical absorption coefficient $\alpha(\omega)$ [31] of any material can be expressed by the relation

$$k(\omega) = \frac{c}{2\omega} \alpha(\omega) \quad 2.75$$

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CHAPTER 3

Electronic structure calculations of $\gamma - Ag_{1-x}Cu_xI$ ($x = 0 - 1$) using TB-mBJ method

3.1 Introduction

Silver iodide (AgI) is a metal halide has been thoroughly studied, with α -AgI exhibiting a superionic behaviour. α - AgI crystallizes into a stable cubic structure above 420 K, in which the Ag ions are arbitrarily distributed among numerous crystallographic sites. Silver AgI crystallizes into the β -phase and γ -phase at ambient temperature and pressure. The β -phase is a member of the hexagonal wurtzite structure, while the γ -phase crystallizes in the cubic zincblende structure. γ -AgI is an n-type semiconductor, demonstrated to be stable at temperatures up to 413 K and 588 Mpa [1, 2]. They are employed in optoelectronic devices as a result of their extensive band gap range. Copper iodide (CuI) is found in a variety of crystalline forms that are isostructural AgI. Copper iodide is an ionic and electronic conductor at ambient temperature, utilizing the electron-hole conduction process. The γ -CuI crystallizes below 663 K, whereas the α -CuI is stable above 713 K. The β -phase is present within the temperature range of 663–713 K [3]. γ -CuI, as a p-type semiconductor, demonstrates excellent performance in both solar cells and thermoelectric devices. The electrical transport in γ -AgI is facilitated by the movement of cationic defects (Ag⁺ interstitials), which are generated more extensively between 250 - 420K. Conversely, γ -CuI functions as a p-type semiconductor, with the conduction attributed to the presence of Cu⁺ Frenkel defects. The electronic properties of AgI have been studied using the tight binding method and the pseudopotential method [4 - 7]. The analysis of the broad band gap of AgI has demonstrated the reliability of calculations based on density functional theory (DFT) [8, 9].

The transport and mobility of ions in the crystal structure are facilitated by the inherent complexities of phase transformation, which are revealed through the study of cation-anion chemical substitution on γ -AgI superionic conductor. Many experimental studies have done to enhance the efficiency of optoelectronic photovoltaic devices by facilitating a critical understanding of carrier dynamics and recombination behaviours.

In $Ag_{1-x}Cu_xI$ films, the recombination of photo-generated carriers and electron transfer is reduced as the Cu content increases [10]. $Ag_{1-x}Cu_xI$ thin films exhibit a substantial change in the geometry of the structure, energy gap, and photoluminescence character for semiconductor behaviour on the Ag (Cu) content [11]. As the composition of Cu increases, the conductivity of mixed Ag-Cu-I compounds diminishes, and the coefficient of thermal expansion reaches zero [12]. The $\gamma - Ag_{1-x}Cu_xI$ system undergoes a structural and phase transition with respect to concentration x , as demonstrated by ionic transport and DC conductivity measurements [13, 14]. $Ag_{1-x}Cu_xI$ alloys exhibit a decrease in ionic conductivity as the Cu content increases [15, 16]. By adjusting the elemental concentrations of Ag (Cu) in silver (copper) iodide based on structural and electronic properties of the Ag-Cu-I system, it is feasible to develop a semiconductor with precise electronic, optical, and chemical characteristics, as Ag and Cu are members of the same metal class. Additionally, the band structure calculation of the combined Ag-Cu-I halide system enables us to concentrate primarily on the formation of phase structure and superionic behaviour [17 - 19]. The electronic properties of $Ag_{1-x}Cu_xI$ is significant due to the unique characteristic of the band structure, which is reflected by the distant valence band from the centre of the Brillouin zone to its maximum extent [20]. This motivates the current investigation, which aims to investigate the impact of copper (Cu) concentration on a $2 \times 2 \times 2$ supercell composed of the ternary $Ag_{1-x}Cu_xI$ compound. Moreover, it is crucial to investigate various structural and electronic properties, including the energy gap (E_g), bulk modulus (B), and lattice parameter (a), of the supercell structure by using the full potential linearized augmented plane wave (FP-LAPW) approach using the TB-mBJ exchange correlation potential.

3.2 Computational method

The valence electronic configuration for Ag: $[Kr] 4d^{10}5s^1$, for Cu: $[Ar] 3d^{10}4s^1$, and for I: $[Kr] 4d^{10} 5s^2 5p^5$ are taken. The assumed Muffin-Tin radii (R_{MT}) values are 2.5 for Ag, Cu and 2.4 for I atom. A k - mesh of $5 \times 5 \times 5$ has been used for all the calculations performed for the present manuscript. The Plane wave energy cut-off, K_{max} has been set at $K_{max} = 7.0/R_{MT}$, where R_{MT} is the smallest muffin-tin radius. In addition, the plane wave cut-off value set at $G_{max} = 12.0 \text{ (a.u.)}^{-1}$ and $l_{max} = 10.0$ in our

computations. For structural properties, we used the generalized gradient approximation (GGA) as exchange-correlation functional. For the calculation of electronic and optical properties, we adopted Tran-Blaha modified Becke-Johnson (TB-mBJ) exchange-correlation functional scheme [21 - 25]. In the FP-LAPW scheme, the wave function, potential and charge density were expanded by the spherical harmonic functions within the non-overlapping spheres surrounded the muffin-tin spheres and by plane wave basis set in the interstitial region. Self-consistent calculations with a convergence of total energy with a stable configuration are performed such that the total energy is within 0.00001 Ry.

3.3 Results and discussion

3.3.1 Structural properties

The original starting binary compound is $\gamma - AgI$ and has been modelled in its zincblende structure (γ -phase, space group $F\bar{4}3m$) with experimental lattice constants [26, 27]. Before performing our computational electronic structural calculations on the copper substituted γ -AgI, we design the supercell of $Ag_{1-x}Cu_xI$ compounds have been prepared for $0.00 < x < 1.00$, by replacing the suitable number of Ag atoms with Cu atoms in $2 \times 2 \times 2$ supercell of the $\gamma - AgI$. By computing total energy as a function of volume around the optimal cell volume V_0 of the binary AgI and CuI structures and their ternary $Ag_{1-x}Cu_xI$ compounds we obtained the optimized structures.

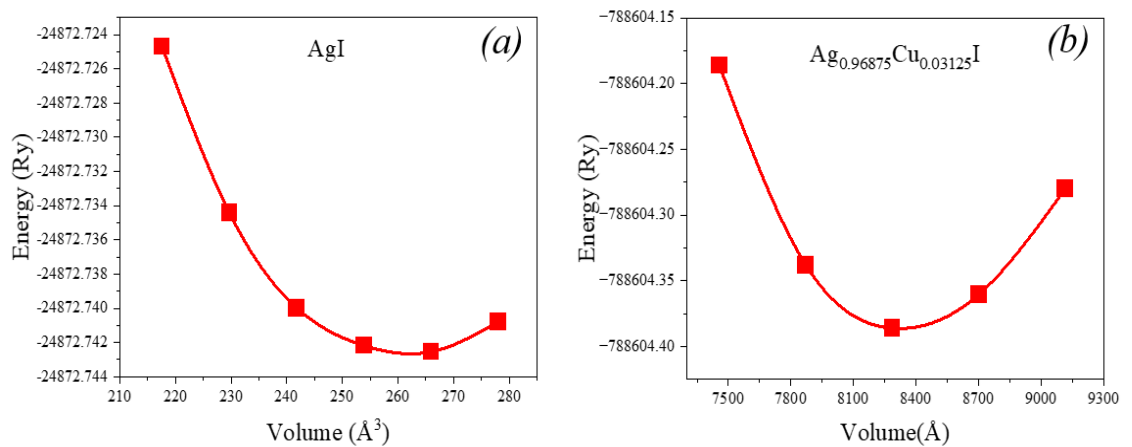


Figure 3.1(a-b): Birch Murnaghan equation of state plots for γ -Ag_{1-x}Cu_xI for (a) $x = 0.00$, and (b) $x = 0.03125$

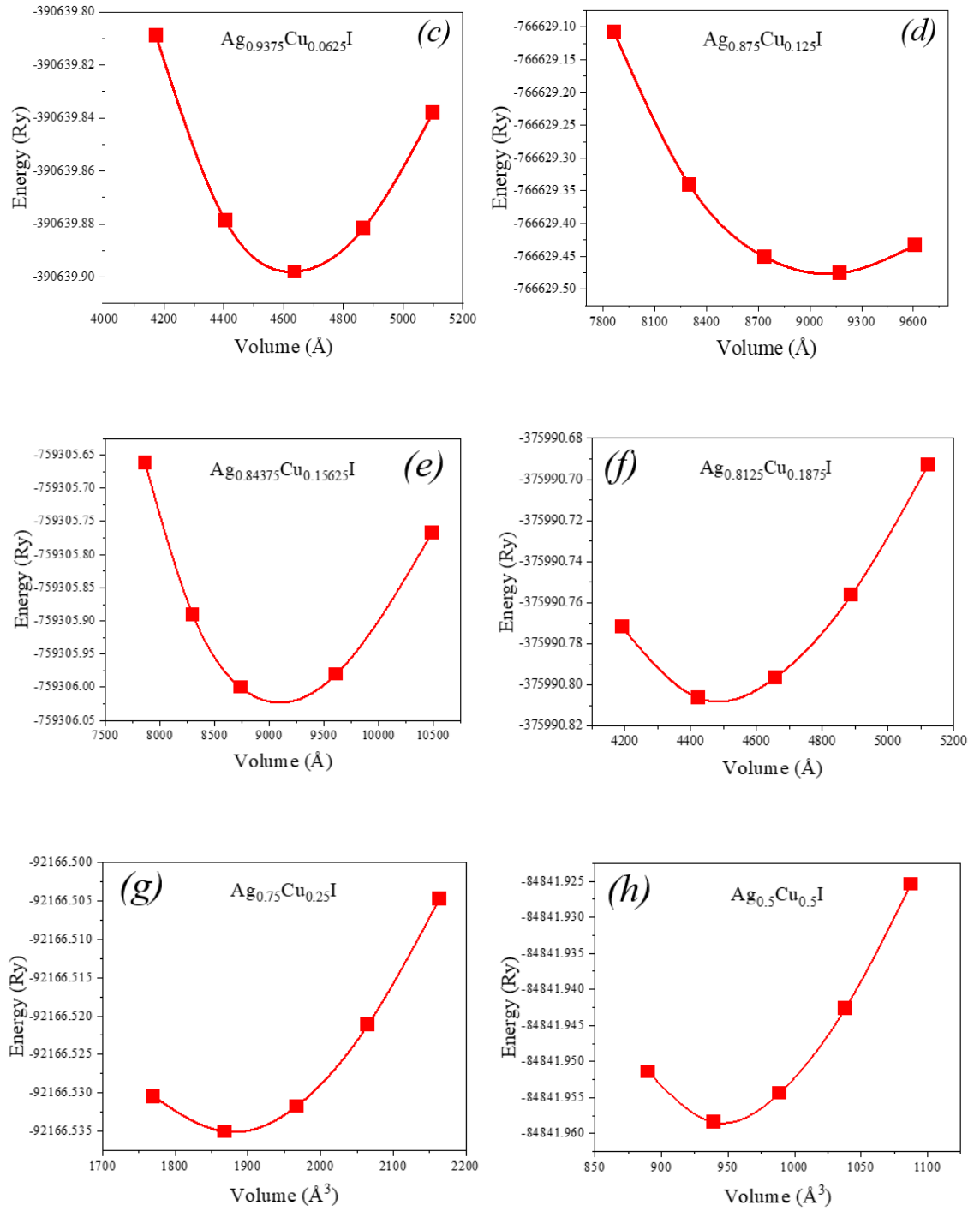


Figure 3.1(c-h): Birch Murnaghan equation of state plots for $\gamma - Ag_{1-x}Cu_xI$ for (c) $x = 0.0625$, (d) $x = 0.125$, (e) $x = 0.15625$, (f) $x = 0.1875$, (g) $x = 0.25$, and (h) $x = 0.5$

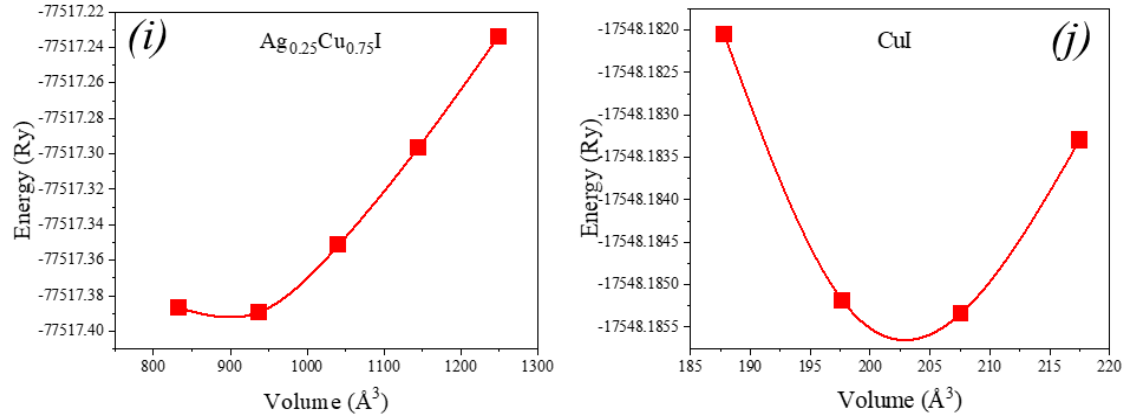


Figure 3.1(i-j): Birch Murnaghan equation of state plots for $\gamma - Ag_{1-x}Cu_xI$ for (i) $x = 0.75$ and (j) $x = 1.00$

To determine the optimal lattice parameter (a) and bulk modulus (B) based on ground state properties, the calculated total energies of the structures were fitted to the theoretical Birch Murnaghan's equation of state to get the optimum lattice parameter for each compound $\gamma - Ag_{1-x}Cu_xI$ [28]. Figure 3.1 shows the fits of the Birch Murnaghan's equation of state for various concentrations ($x = 0.00 - 1.00$) in $\gamma - Ag_{1-x}Cu_xI$. The optimized values of lattice parameter and bulk modulus obtained for binary $\gamma - AgI$ and $\gamma - CuI$ agrees with the earlier reports, demonstrating the validity of the present DFT-based calculation and are given in Table 3.1. The obtained lattice constants of $\gamma - AgI$ and $\gamma - CuI$ are 6.63 and 6.10 $\text{\AA}$ respectively. A continuous decrease of lattice parameter with increase in Cu composition has been observed in $Ag_{1-x}Cu_xI$.

Table 3.1: Calculated lattice parameter a and bulk modulus B compared to experimental and theoretical works of AgI, CuI and $Ag_{1-x}Cu_xI$ compounds

x	Lattice constant a (Å)			Bulk modulus B (GPa)		
	Our work	Expt.	Theoretical	Our work	Expt.	Theoretical
0	6.63	6.49[11]	6.650[16]	26.981	24[28]	26.667[16]
0.03125	6.62	-	-	27.057	-	-
0.0625	6.61	-	-	27.260	-	-
0.125	6.58	-	-	28.113	-	-
0.15625	6.57	-	-	28.337	-	-
0.1875	6.54	-	-	28.922	-	-
0.25	6.52	-	6.516[16]	29.828	-	27.405[16]
0.5	6.41	-	6.396[16]	31.759	-	30.104[16]
0.75	6.28	-	6.256[16]	35.230	-	37.765[16]
1	6.10	6.05[11]	6.098[16]	40.442	36.6[29]	38.872[16]

The number in the square brackets denotes the reference number.

This is due to the decrease of the ionic radii of Ag and Cu respectively given by respectively 1.29 and 0.91 Å. Further the bulk modulus of AgI is found to be lower than that of CuI, which agrees with the inverse dependence of bulk modulus on the lattice parameter.

3.3.2 Electronic Structure

For the purpose of fabricating efficient semiconductor devices, the knowledge of band structure and band gap of the materials are very important. In this study, the band structures of $Ag_{1-x}Cu_xI$ in their γ -phase have calculated by considering TB-mBJ parameterization schemes. Figure 3.2 shows the obtained band structures of $Ag_{1-x}Cu_xI$ for various elemental concentrations ($x = 0.00 - 1.00$). From band structure of AgI and CuI, it is clear that a Γ -centered direct band gap (Γ - Γ) in the IBZ. Also, the same band structure (Γ - Γ) of $Ag_{1-x}Cu_xI$ compounds have been observed.

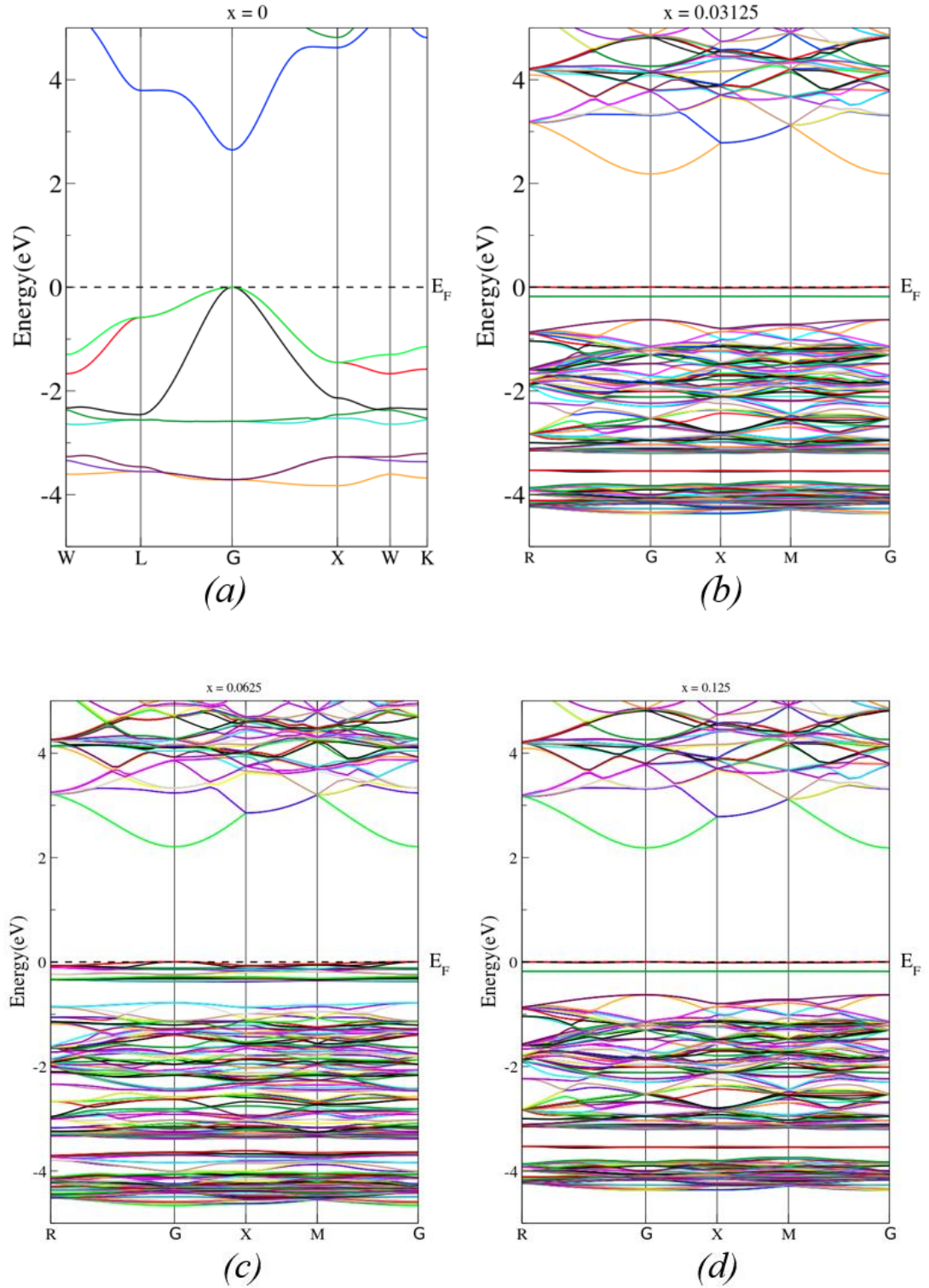


Figure 3.2(a-d): Band structure of $\gamma - Ag_{1-x}Cu_xI$ for (a) $x = 0.00$, (b) $x = 0.03125$, (c) $x = 0.0625$, and (d) $x = 0.125$

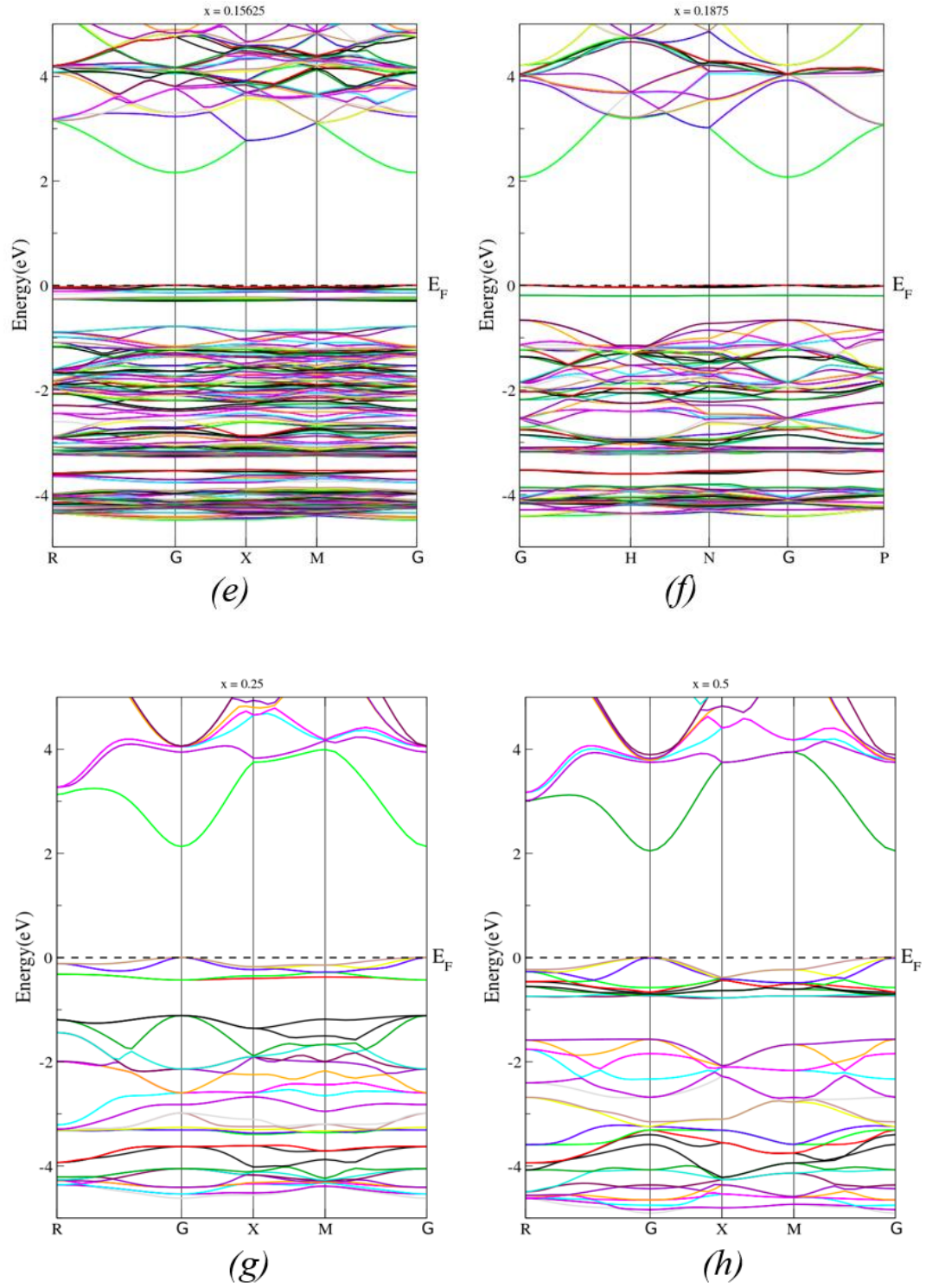


Figure 3.2(e-h): Band structure of $\gamma - Ag_{1-x}Cu_xI$ for (e) $x = 0.15625$, (f) $x = 0.1875$, (g) $x = 0.25$ (h) $x = 0.5$

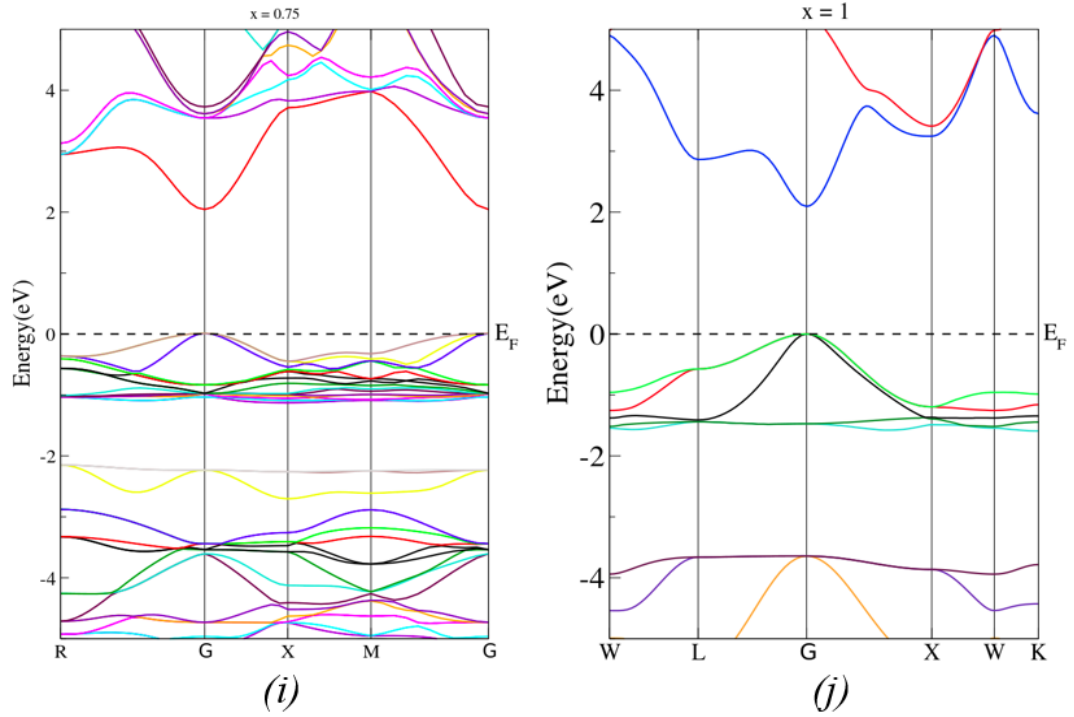


Figure 3.2(i-j): Band structure of $\gamma - Ag_{1-x}Cu_xI$ for (i) $x = 0.75$ and (j) $x = 1.00$

Using TB-mBJ method, we obtained the band gap of 2.645 eV and 2.094 eV for AgI and CuI respectively, predicting a class of semiconducting materials. The observations from calculated AgI and CuI compounds agree with others experimental and theoretical data. The band structure for $Ag_{1-x}Cu_xI$ compounds are obtained by gradual substitution of Ag by Cu atom(s) in the $2 \times 2 \times 2$ supercell of AgI exhibit direct band gap energies. Table 3.2 shows the obtained bandgap values of $Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$), the maximum of valence band and the minimum of conduction band are located at high symmetry Γ -point and thus resulting a direct band gap of both the compounds in zincblende structure, as shown in Figure 3.2. This shows no electronic states cross the Fermi level. The electronic states are moved away from the Fermi level. Figure 3.3 shows the variation of lattice constant, Bulk modulus, and the Bandgap of $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$). The nonlinear variation of band gap with Cu concentrations x for $Ag_{1-x}Cu_xI$ systems with TB-mBJ exchange correlation potential scheme, as depicted in Figure 3.3(c). the obtained values of bandgap for $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$) using TB-mBJ exchange correlation potential are given in Table 3.2 and agrees with earlier theoretical and experimental reports. The

computational calculation is not accurately measuring the exchange correlation energy due to insufficient flexibility of quasiparticle self-energy. In generally, it is mentioned that the experimental values were well mentioned. A small difference in experimental and computational values is that we were not considered the contribution of lattice vibrations at room temperature and considered the crystal is at 0 K temperatures. It is mentioned that some limitations in the density functional calculation in its validity [29].

Table 3.2: Direct band gap energy of $Ag_{1-x}Cu_xI$ alloys with different Cu contents using TB-mBJ scheme.

x	$E_g(eV)$		
	Present work	Experiment	Other calculation
0	2.645	2.78[11]	1.340[16]
0.03125	2.397	-	-
0.0625	2.297	-	-
0.125	2.266	-	-
0.15625	2.244	-	-
0.1875	2.188	-	-
0.25	2.190	-	1.106[31], 1.68286[16]
0.50	2.166	-	0.993[31], 1.59617[16]
0.75	2.148	-	0.962[31], 1.61436[16]
1	2.094	2.95[32]	1.068[14], 1.12[1]

The number in the square brackets denotes the reference number.

Therefore, the calculated values are not fully comparable with the experimental data. There is a small underestimation of our calculated band gap values are probably due to the exclusion of spin-orbit coupling effects in our present calculations.

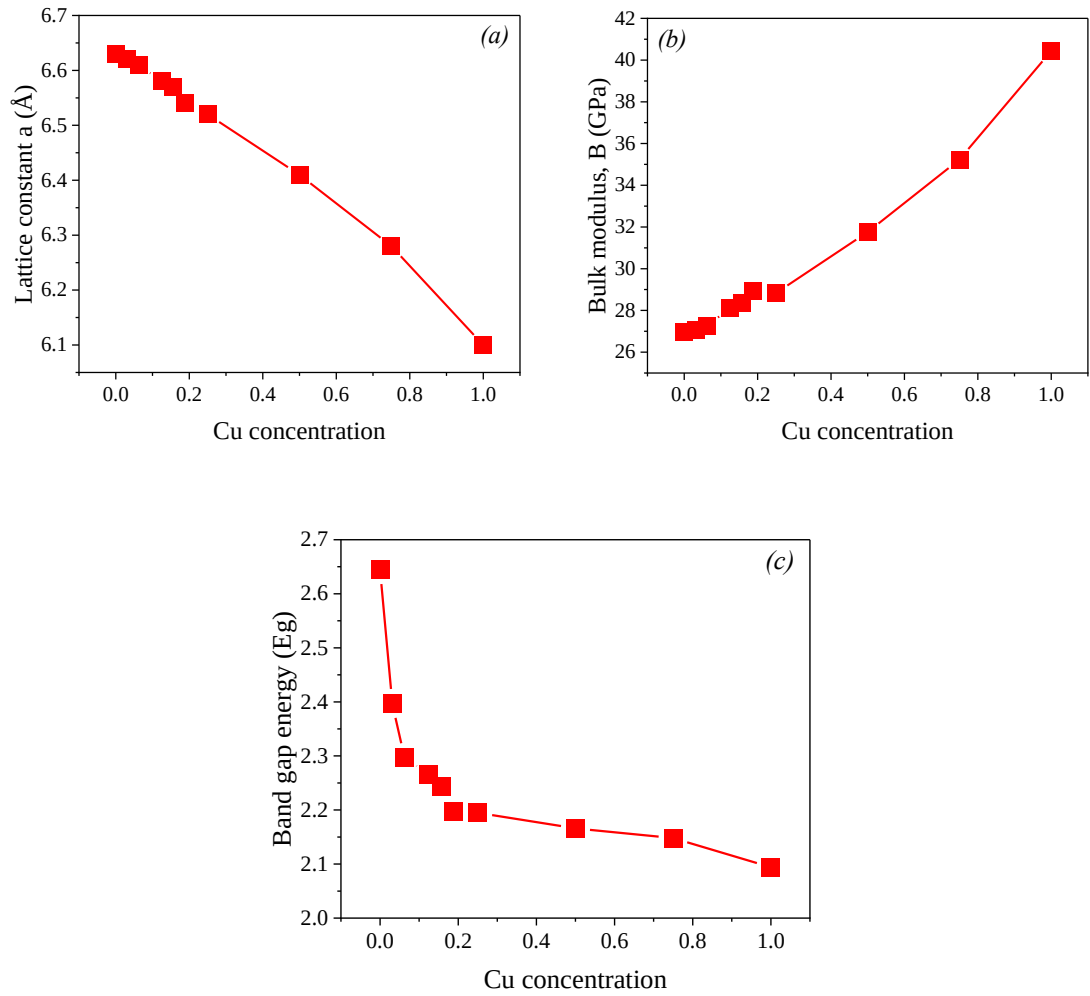


Figure 3.3(a – c): Variation of lattice constant (a), Bulk modulus (B), and the Bandgap (E_g) of $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$).

3.3.3 Density of state

The density of states (DOS) of a compound provides the information about the atomic origin of different electronic states present in band structure. We have displayed the TB-mBJ induced DOS for AgI, CuI and $Ag_{1-x}Cu_xI$ for $x = 0.00 - 1.00$ in Figure 3.4(a, b, c) – 3.13(a, b, c). The density of states (DOS) projected between -4.2 eV to 6.8 eV for AgI and -5.5 eV to 6.5 eV for CuI, the Fermi level has been taken as a source of energy. It is observed that, the first valence region is located from -3.8795 eV to -3.1720 eV for AgI and from -5.4432 eV to -3.5932 eV for CuI. This region is composed between p states of I and d states of Ag/Cu. This is mainly due to the hybridization between I ‘p’ states and the Ag/Cu ‘d’ state. The second valence band is

located between -2.7094 eV to 0.0117 eV for AgI and -1.6336 eV to -0.0281 eV for CuI. This range is predominantly from 'd' states of Ag/Cu and a small amount of I 'p' states. The last region 2.6563 eV to 6.8 eV for AgI and 2.0659 eV to 6.5 eV for CuI is a conduction band dominated mainly by p-I states and d-Ag/Cu states peaks that has a small altitude. However, there is a significant difference in band gap between undoped and Cu doped AgI. The conduction band minimum and the valance band maximum are at the high symmetry Γ -pointcalculated with TB-mBJ scheme.

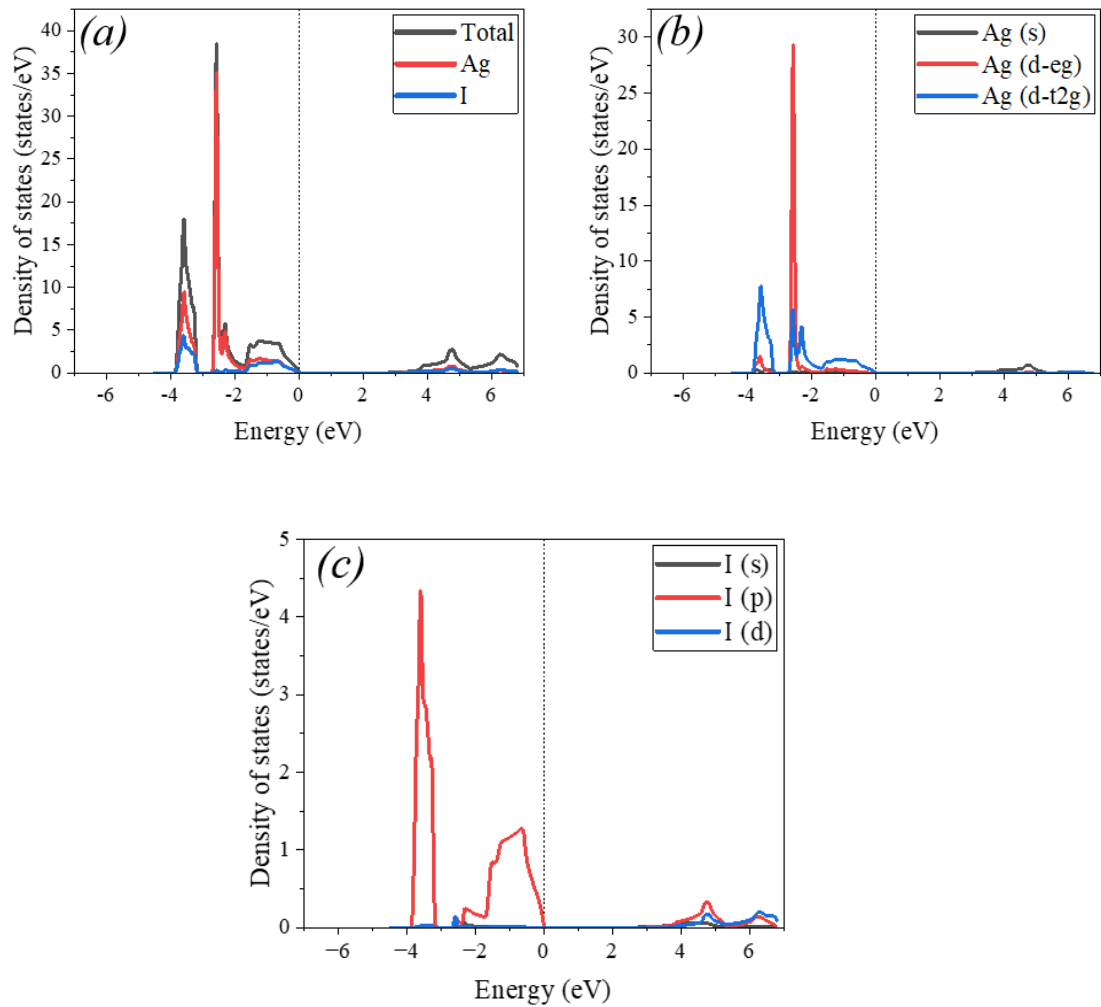


Figure 3.4: (a) Density of states of γ -AgI-total, Ag-total and I-total, (b) Partial density of states of Ag (s, d-eg and d-t2g), and (c) Partial density of states of I (s, p and d) in γ -AgI obtained using TB-mBJ functional.

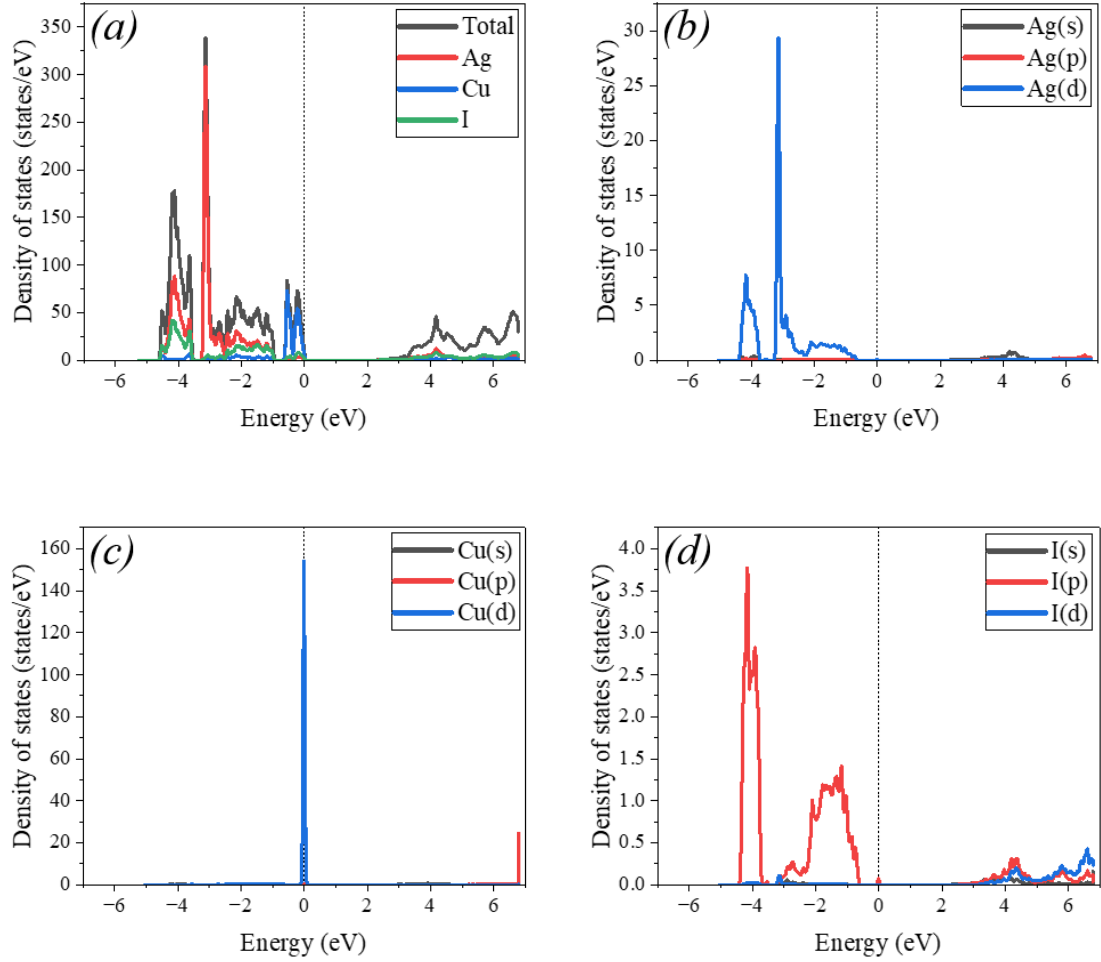


Figure 3.5: (a) Density of states of $\gamma - Ag_{0.96875}Cu_{0.03125}I$ -total, Ag-total, Cu-total and I-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of I (s, p and d) in $\gamma - Ag_{0.96875}Cu_{0.03125}I$ obtained using TB-mBJ functional.

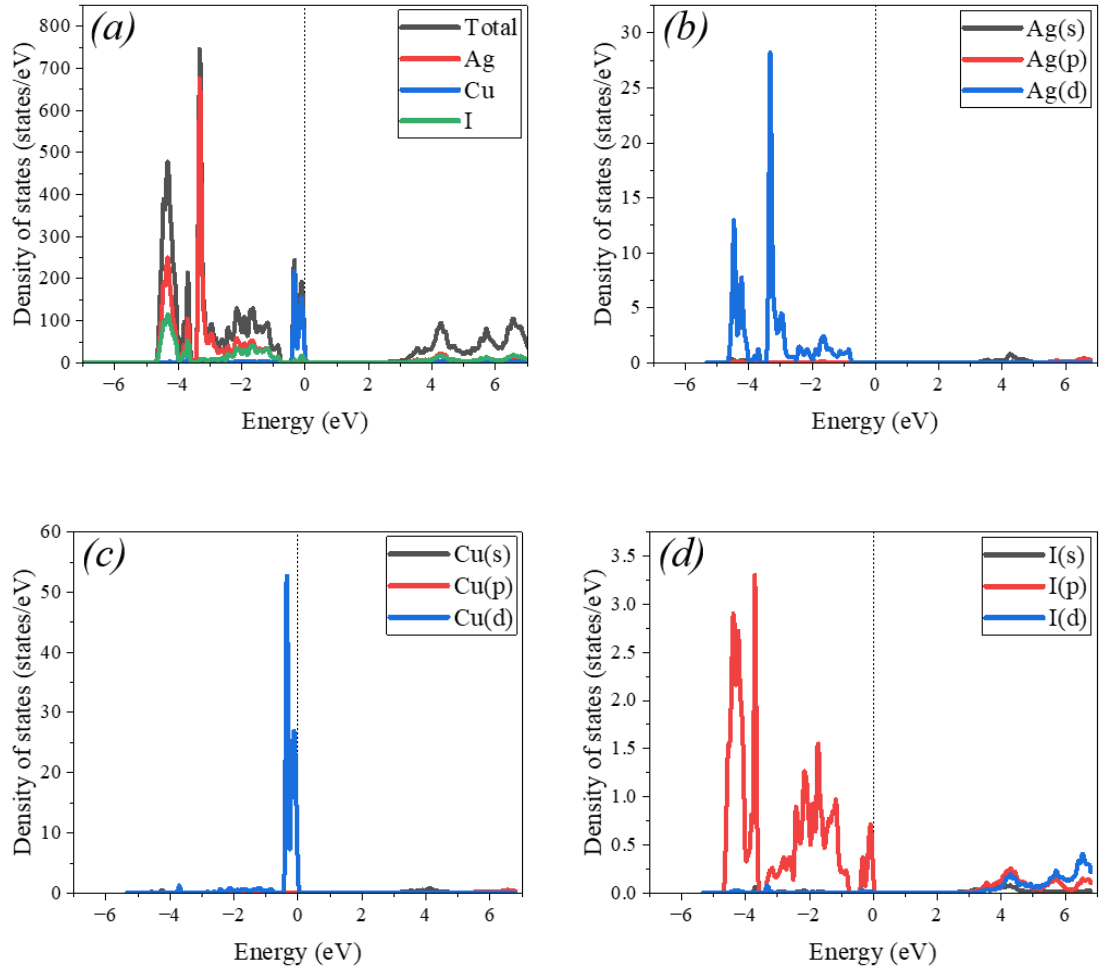


Figure 3.6: (a) Density of states of γ - $Ag_{0.9375}Cu_{0.0625}I$ -total, Ag-total, Cu-total and I-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of I (s, p and d) in γ - $Ag_{0.9375}Cu_{0.0625}I$ obtained using TB-mBJ functional.

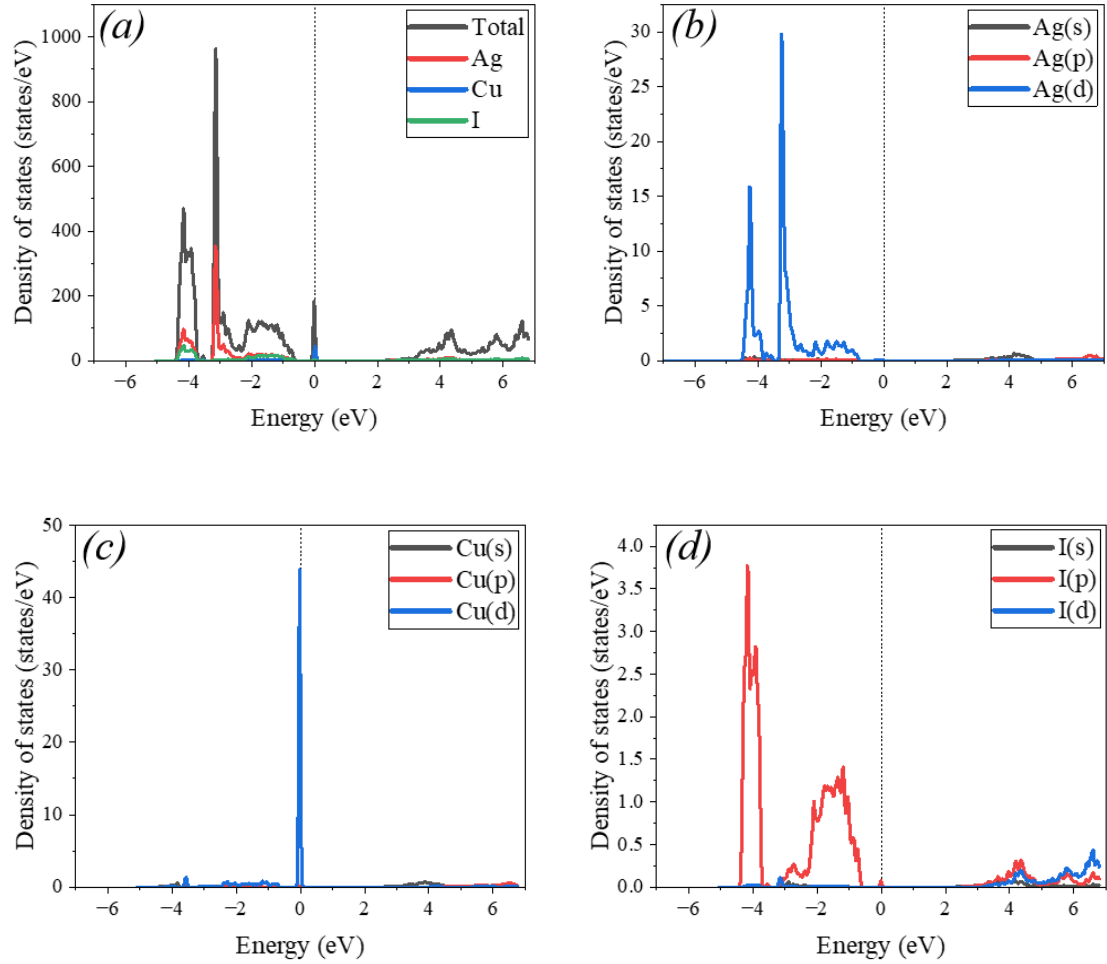


Figure 3.7: (a) Density of states of $\gamma - Ag_{0.875}Cu_{0.125}I$ -total, Ag-total, Cu-total and I-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of I (s, p and d) in $\gamma - Ag_{0.875}Cu_{0.125}I$ obtained using TB-mBJ functional.

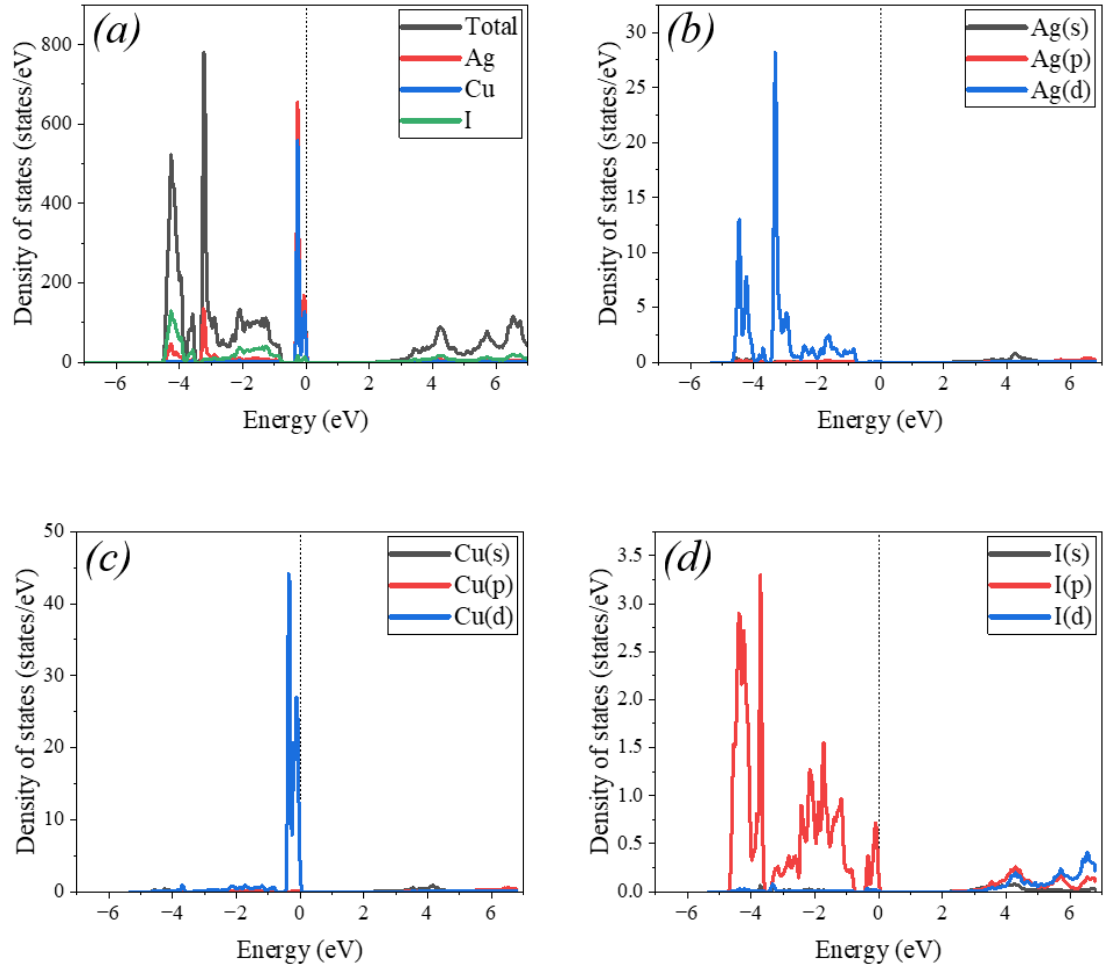


Figure 3.8: (a) Density of states of $\gamma - Ag_{0.84375}Cu_{0.15625}I$ -total, Ag-total, Cu-total and I-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of I (s, p and d) in $\gamma - Ag_{0.84375}Cu_{0.15625}I$ obtained using TB-mBJ functional.

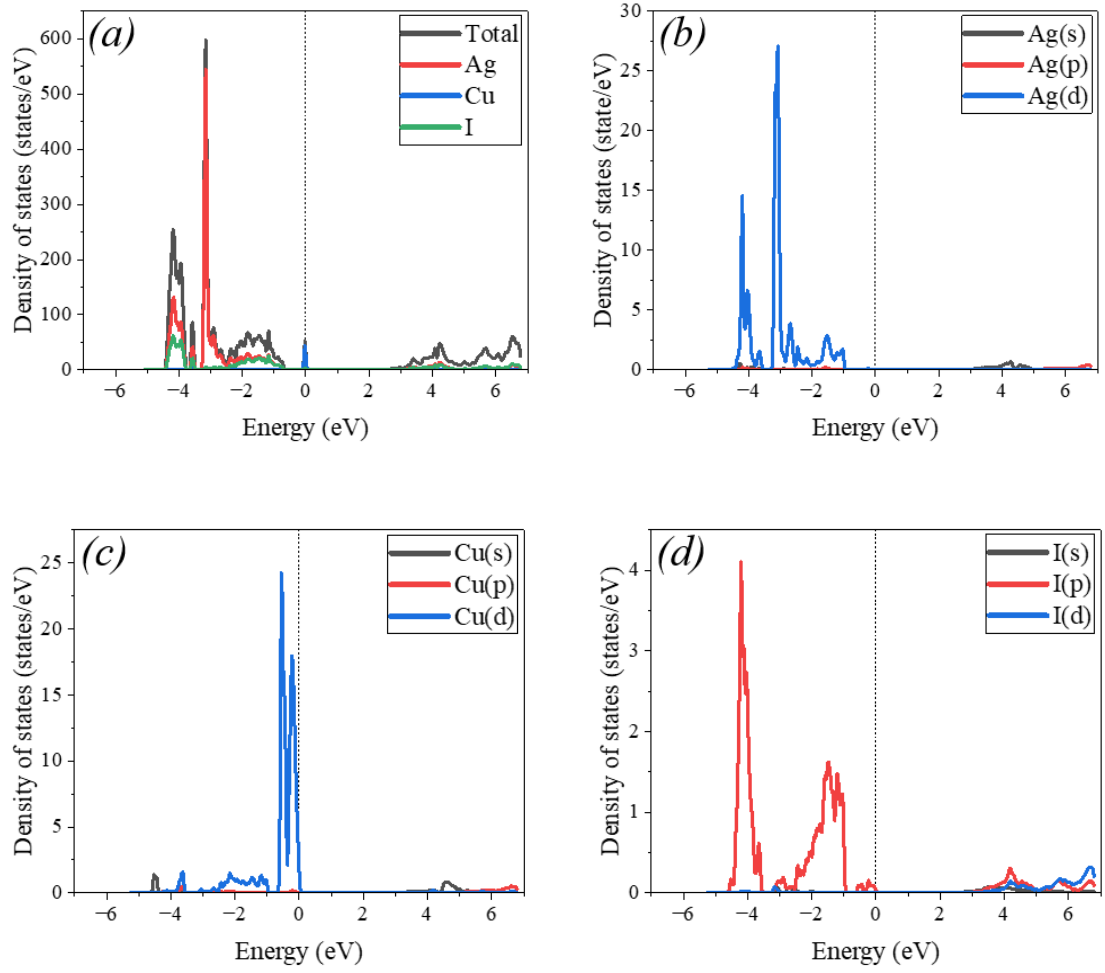


Figure 3.9: (a) Density of states of $\gamma - Ag_{0.8125}Cu_{0.1875}I$ -total, Ag-total, Cu-total and I-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of I (s, p and d) in $\gamma - Ag_{0.8125}Cu_{0.1875}I$ obtained using TB-mBJ functional.

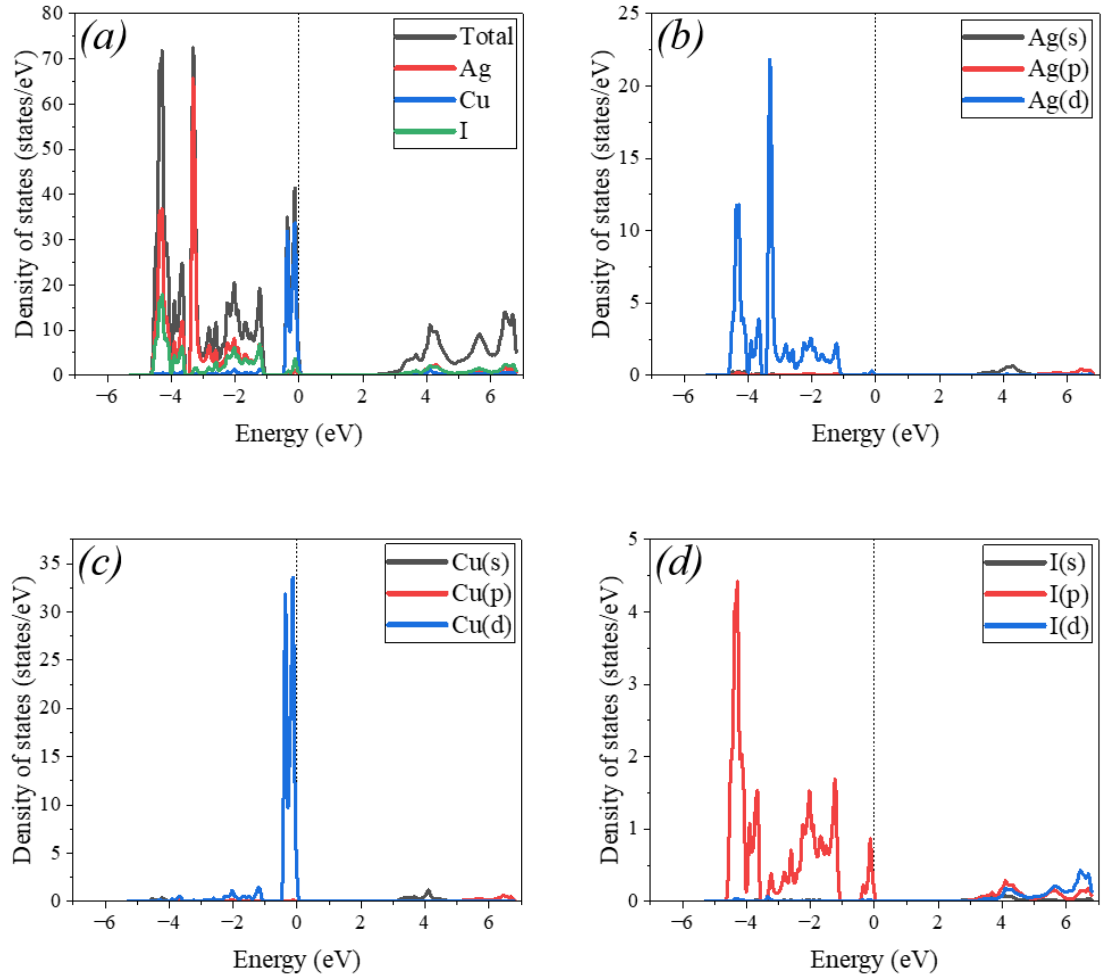


Figure 3.10: (a) Density of states of $\gamma - Ag_{0.75}Cu_{0.25}I$ -total, Ag-total, Cu-total and I-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of I (s, p and d) in $\gamma - Ag_{0.75}Cu_{0.25}I$ obtained using TB-mBJ functional.

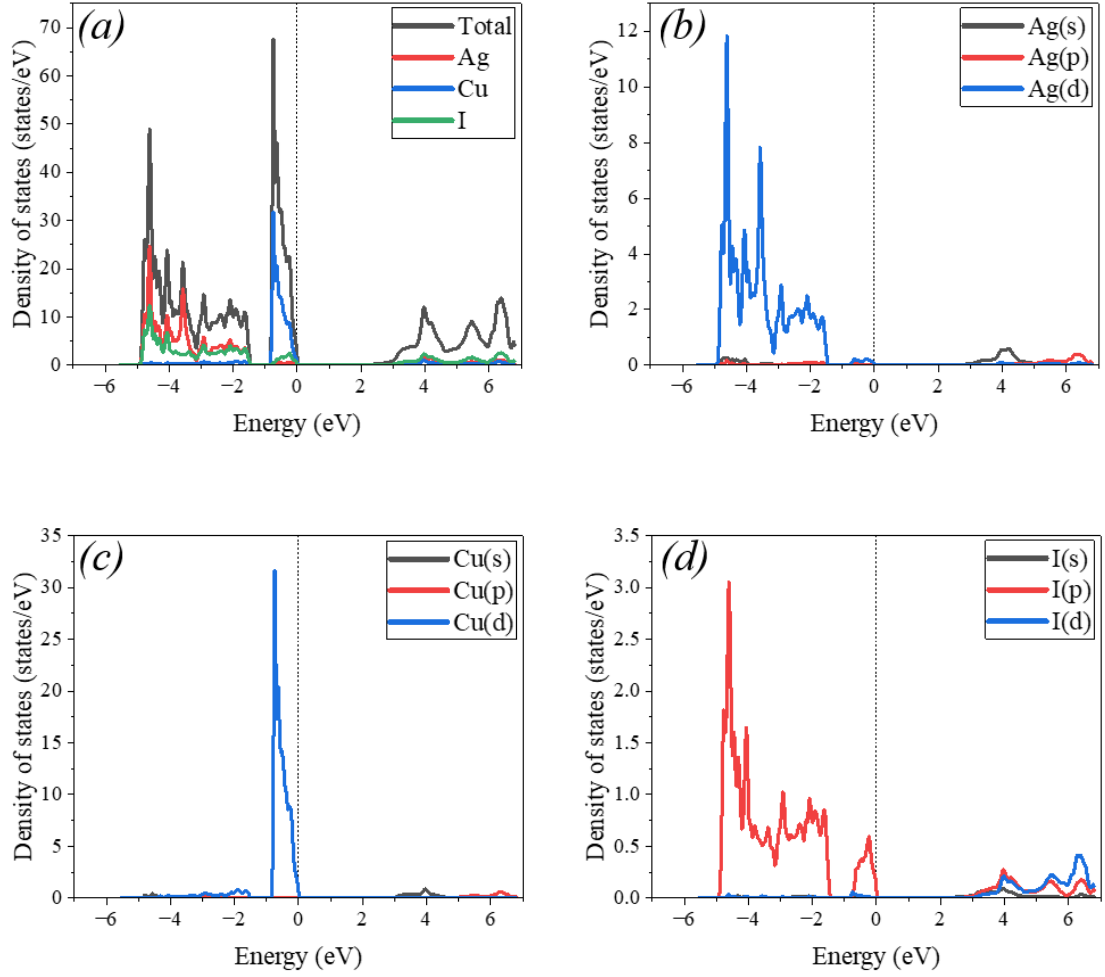


Figure 3.11: (a) Density of states of $\gamma - Ag_{0.5}Cu_{0.5}I$ -total, Ag-total, Cu-total and I-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of I (s, p and d) in $\gamma - Ag_{0.5}Cu_{0.5}I$ obtained using TB-mBJ functional.

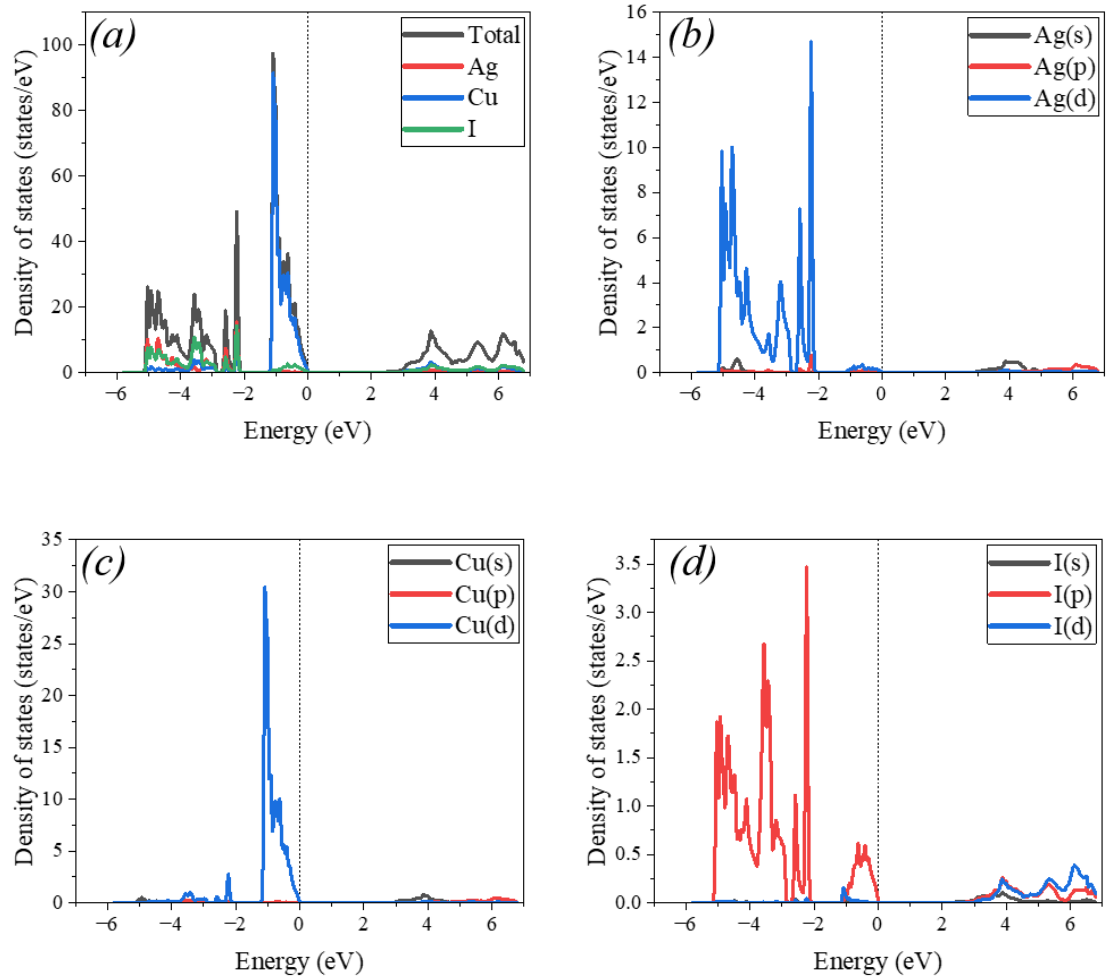


Figure 3.12: (a) Density of states of $\gamma - Ag_{0.25}Cu_{0.75}I$ -total, Ag-total, Cu-total and I-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of I (s, p and d) in $\gamma - Ag_{0.25}Cu_{0.75}I$ obtained using TB-mBJ functional.

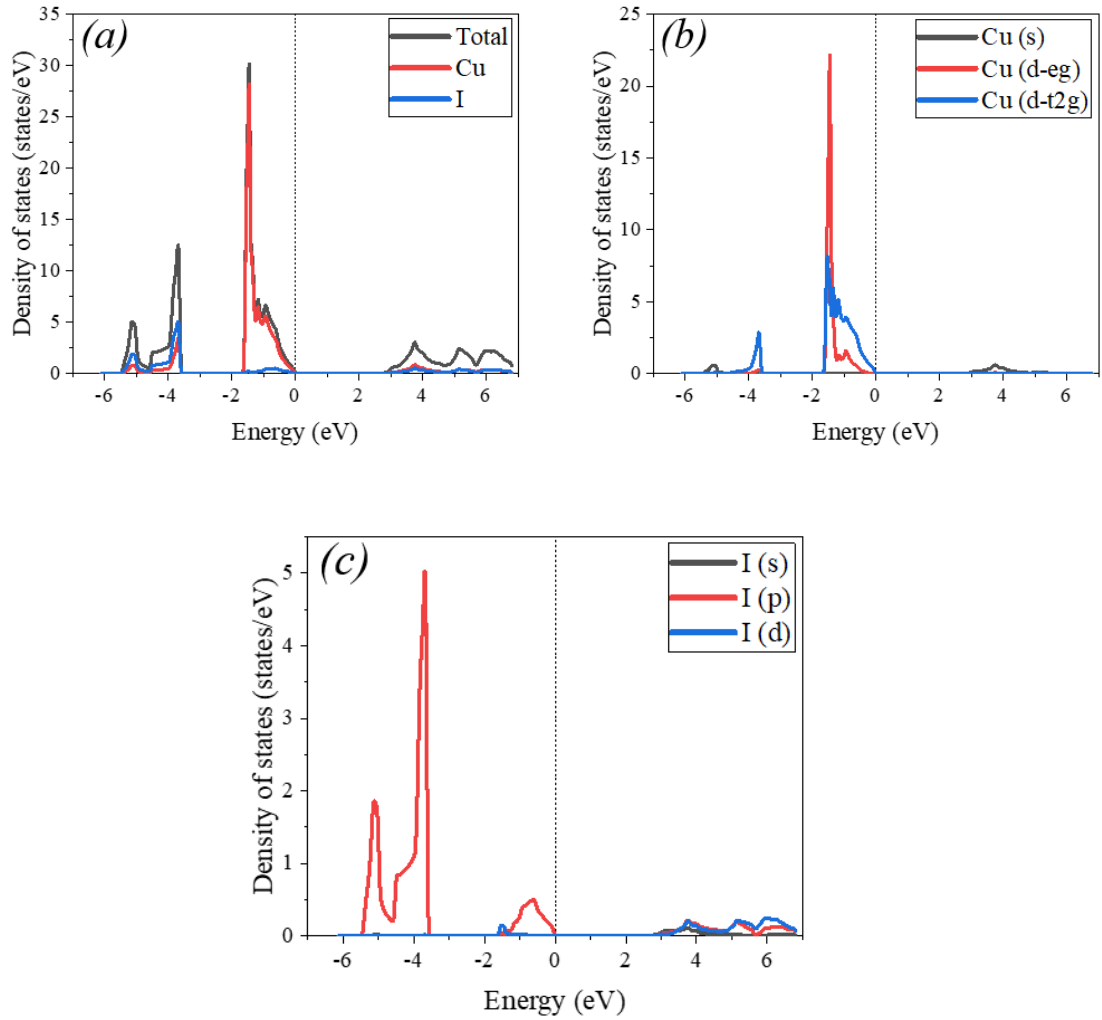


Figure 3.13: (a) Density of states of γ -CuI-total, Cu-total and I-total, (b) Partial density of states of Cu (s, d-eg and d-t2g), and (c) Partial density of states of I (s, p and d) in γ -CuI obtained using TB-mBJ potential.

We have seen that the decrease in percentage of substitution of Cu increases the significant difference in energy between conduction band valence band, for which we get the band gap energy values equal to 2.397 eV, 2.297 eV, 2.266 eV, 2.244 eV, 2.189 eV, 2.195 eV, 2.166 eV, 2.148 eV, for their respective atomic percentage, $0.00 < x < 1.00$. Based on DOS calculation, it is seen that substitution of Ag by Cu atom in the AgI zincblende structure not drastically change the behaviour of the doping material,

the density of states still symmetric, the hybridization between d states of Ag/Cu and p states of I. The pattern of the DOS for the $\gamma - Ag_{1-x}Cu_xI$ nearly matches with the earlier report [30]. The gradual replacement of Ag atom by Cu atom in $Ag_{1-x}Cu_xI$ alloy does not affect the total DOS of alloys. For Cu-Ag-I ternary alloys, the lattice parameters are in between Ag and Cu. The lattice parameters gradually decrease on increasing the Cu concentration. It is observed that the d- bands of Cu-Ag-I systems are enlarged in comparison to the pure Ag and Cu atom. The expansion of d- bands of the alloys is slightly increasing with the Cu/Ag atomic concentrations. Further, it is noticed that the hybridization of d- states with the s and p- states increases near Fermi level upon increasing Cu compositions. This suggests the d-sp band transition rates become greater. Also, the position of sp-hybridized band varies with the Cu concentration near Fermi level. From the inter-intra band concept, the d-sp inter band and sp intra band transitions, the above results indicating that the mismatching Ag atom with Cu atom in Ag-Cu-I system may be significantly change the distribution of energy of the system. To analyse the behaviour of the band structures of Cu-Ag-I alloys, we further calculate the total partial density of states (TDOS) of Ag, Cu and Cu-Ag-I alloys. In addition, we have calculated the PDOS of Cu and Ag of Cu-Ag-I compounds. It is seen that the width of d-band is gradually increasing with Cu composition. However, the limiting values for lower and upper d-band edges are lies between Ag and Cu atoms respectively. Detailed study of DOS for d-orbital of Cu and Ag content in Cu-Ag-I alloys shows the d-band extension arising due to the strong d-d hybridization of Cu and Ag atom. The width of d-orbital of Ag and Cu increases with Cu concentration. The changes in electronic structure of Cu-Ag-I alloy are because of the reduced volume of Cu-Ag-I alloys with varying atomic concentration. As we know the atomic radius of Ag atom is greater than that of Cu atom, therefore replacing Ag atoms with Cu atoms results the decrease in volume of the Cu-Ag-I alloys. Band structure can be conceptually explained by density of states (DOS). We have calculated both total density of states (TDS) and partial density of states (PDOS) of ternary alloy systems AgCuI. It has been noticed from the TDOS that the valence band (VB) of ternary alloys are shifted towards the Fermi level with changing of cation from doping concentration $0.00 < x < 1.00$ of Ag-Cu-I system, this is due to the contribution of 4d states of Ag and 3d states of Cu cation. The computational work has

done for composition effect of Cu on structural and electronic properties using full potential linear muffin-tin orbital (FP-LMTO) [31].

3.3.4 Optical properties

The optical properties of solids are due to the incoming light which causes a response from electron systems to a time dependent electromagnetic perturbation. The method used for calculation of optical properties is related to joint density of states modified with proper dipole matrix elements [32, 33]. In the present study, the optical properties of $Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$) compounds have been calculated as a frequency response of various optical parameters. Figure 3.14(a – b) shows the (a) real part of dielectric constant $\epsilon_1(\omega)$ and (b) imaginary part of dielectric constant $\epsilon_2(\omega)$ for $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$). The obtained values of real part of the complex dielectric function with energy in eV, as shown in Figure 14(a). It is observed that the dielectric constant exhibits a multi-peak pattern for each of the compounds, and attains a negative value. The zero-frequency limit $\epsilon_1(0)$ of the real part of dielectric constant, called static dielectric constant. The $\epsilon_1(0)$ values of all the compounds are listed in table 3.3. From the table 3, it is noticed that the $\epsilon_1(0)$ values increases with the increase in doing concentration x and nature of variation is in reverse nature of variation of band gap with concentration x .

The decrease in real dielectric constant towards negative values indicates its reflectiveness of the materials that demonstrate a metallic behaviour. Hence, the material can be used as either a radiation protection in the energy window, or a radiation detector. The static dielectric constant of $\gamma - Ag_{1-x}Cu_xI$ at zero temperature and pressure are found to be 3.5829, 3.7077, 3.7995, 3.8072, 3.9502, 3.9089, 3.9147, 4.1420, 4.2025, 4.3944 and 4.7533 corresponding to Cu concentration $x = 0.00, 0.03125, 0.0625, 0.125, 0.15625, 0.1875, 0.25, 0.5, 0.75$ and 1.00 respectively. It is noticed that the static dielectric constants are located between 3.5829 and 4.7533 i.e., maximum, and minimum at higher and lower Cu concentrations

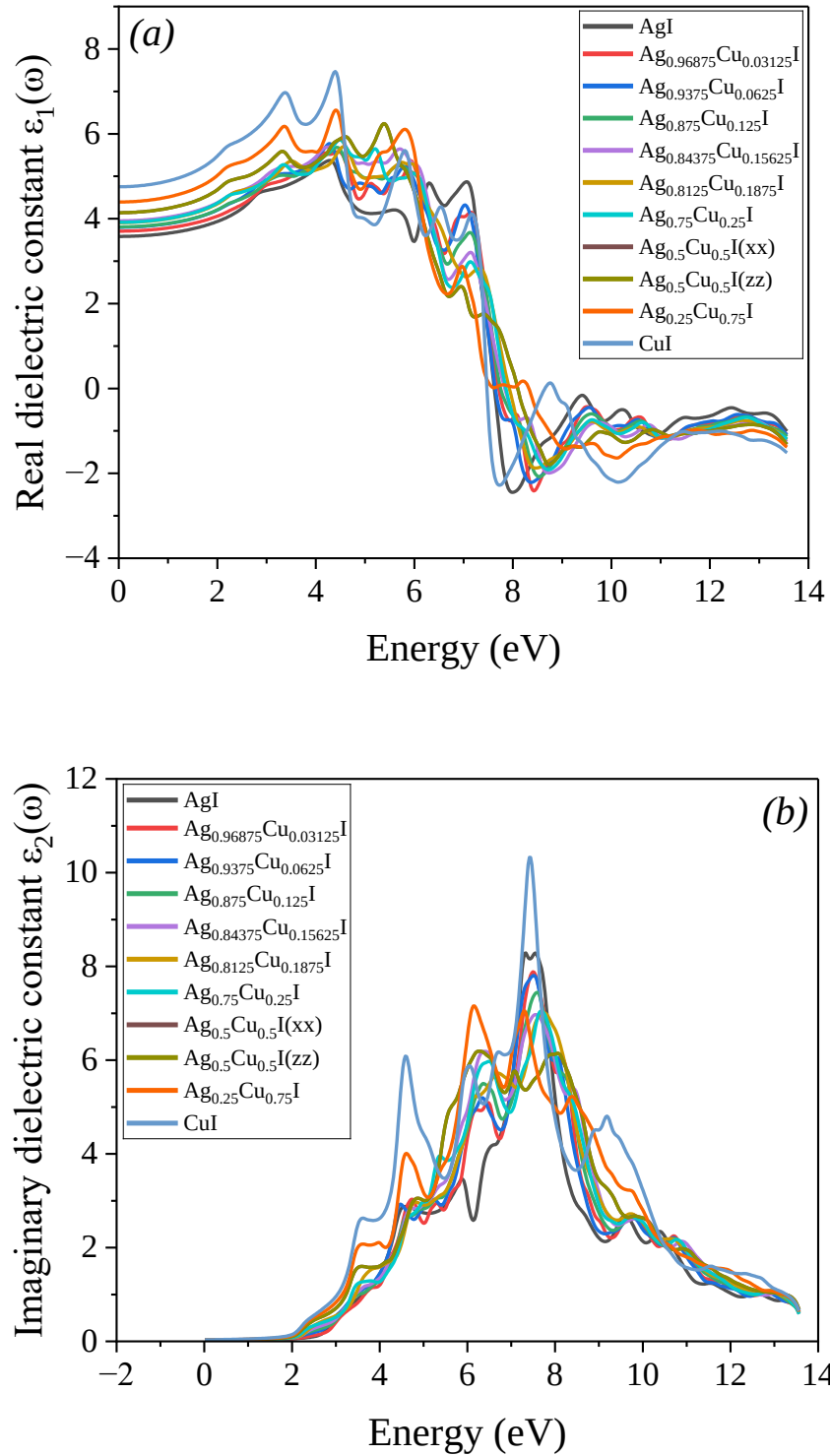


Figure 3.14(a - b): Variation of (a) Real part and (b) Imaginary part of dielectric constant of $\gamma - Ag_{1-x}Cu_xI$

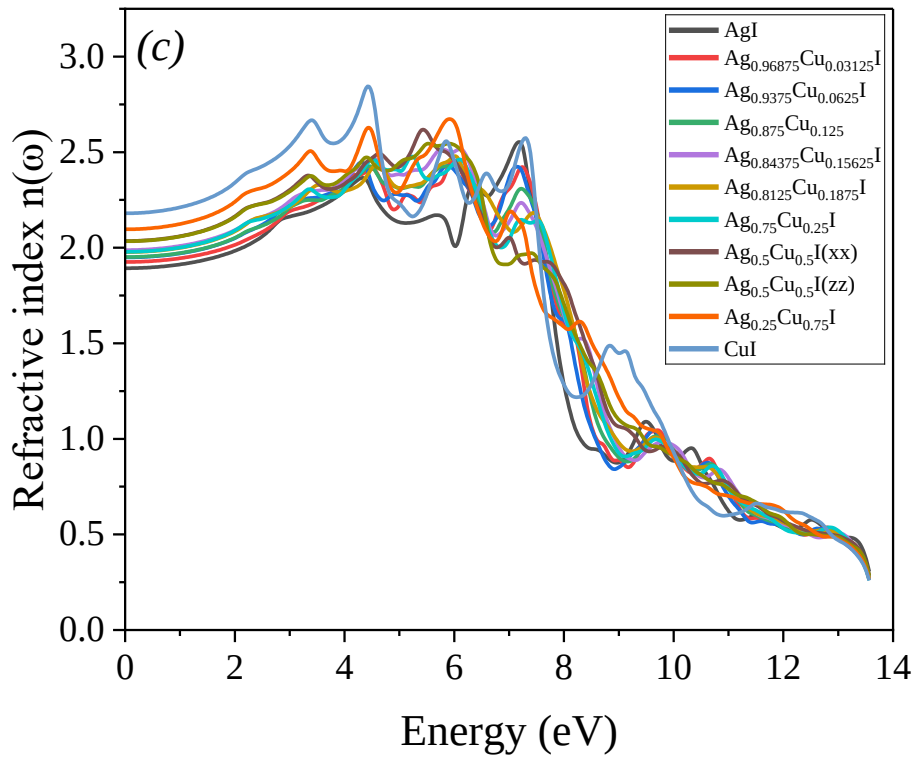
Table 3.3: Zero-frequency limits in the real dielectric constant $\varepsilon_1(\omega)$, refractive index $n(\omega)$, and reflectivity $R(\omega)$ spectra and threshold values (critical points) in the imaginary dielectric constant $\varepsilon_2(\omega)$, extinction coefficient $k(\omega)$, absorption coefficient $\alpha(\omega)$, and optical conductivity $\sigma(\omega)$ spectra in $\gamma - Ag_{1-x}Cu_xI$ alloys with different Cu contents using TB-mBJ scheme.

Compound	Zero-frequency limits			Threshold values (eV)			
	$\varepsilon_1(0)$	$n(0)$	$R(0)$	$\varepsilon_2(\omega)$	$\kappa(\omega)$	$\alpha(\omega)$	$\sigma(\omega)$
<i>AgI</i>	3.582	1.892	0.095	2.653	2.653	2.898	2.843
<i>Ag_{0.96875}Cu_{0.03125}I</i>	3.707	1.925	0.100	2.353	2.408	2.707	2.843
<i>Ag_{0.9375}Cu_{0.0625}I</i>	3.799	1.949	0.103	2.277	2.272	2.680	2.789
<i>Ag_{0.875}Cu_{0.125}I</i>	3.807	1.951	0.103	2.253	2.247	2.625	2.816
<i>Ag_{0.84375}Cu_{0.15625}I</i>	3.950	1.987	0.109	2.222	2.232	2.435	2.680
<i>Ag_{0.8125}Cu_{0.1875}I</i>	3.908	1.977	0.107	2.163	2.217	2.435	2.544
<i>Ag_{0.75}Cu_{0.25}I</i>	3.914	1.978	0.107	2.160	2.190	2.356	2.544
<i>Ag_{0.5}Cu_{0.5}I(xx)</i>	3.142	2.035	0.116	2.108	2.136	2.326	2.353
<i>Ag_{0.5}Cu_{0.5}I(zz)</i>	3.202	2.033	0.116	2.105	2.135	2.222	2.353
<i>Ag_{0.25}Cu_{0.75}I</i>	4.394	2.096	0.125	2.104	2.054	2.272	2.326
<i>CuI</i>	4.753	2.180	0.137	2.050	2.027	2.244	2.272

Figure 3.14(b) illustrates the variation of imaginary component of dielectric functions with energy. The threshold energy values are listed in table 3.3, which correspond to various Cu concentrations. It is observed that the $\varepsilon_2(\omega)$ value increases with the increase in doping concentration x , and the nature of variation is corresponding to the variation of band gap with concentration x . It is seen that soon after the threshold energy, the imaginary dielectric function rises with an increase in energy, reaching peaks that correspond to their respective energy values. The highest peaks of $\gamma - Ag_{1-x}Cu_xI$ occur at 7.8611, 7.8030, 7.4428, 7.0477, 7.0476, 6.9665, 6.0929, and 7.0512, corresponding to the energy values 7.4695, 7.4969, 7.5783, 7.6872, 7.6871, 7.0512, corresponding to the energy values 7.4695, 7.4969, 7.5783, 7.6872, 7.6871,

7.5783, 7.8504, and 7.3062, respectively. The peaks in all the curves of $\varepsilon_2(\omega)$ are due to the transitions from the valance band to the conduction band.

The variation of refractive index with energy is shown in Figure 3.14(c). Similar to the behaviour of dielectric constant, exhibits a multi-peak pattern for each of the compounds, and attains a negative value at the higher values of energy. This shows that the material loses its transparency in higher energies. Therefore, these compounds cannot be used as a transparent material in higher values of energies. The decreasing value of refractive index less than one signifies that the speed of light in vacuum is less than its phase velocity in that medium. The value of refractive index at zero-frequency limit of incident photon is known as static refractive index $n(0)$. All calculated $n(0)$ values are listed in table 3.3.



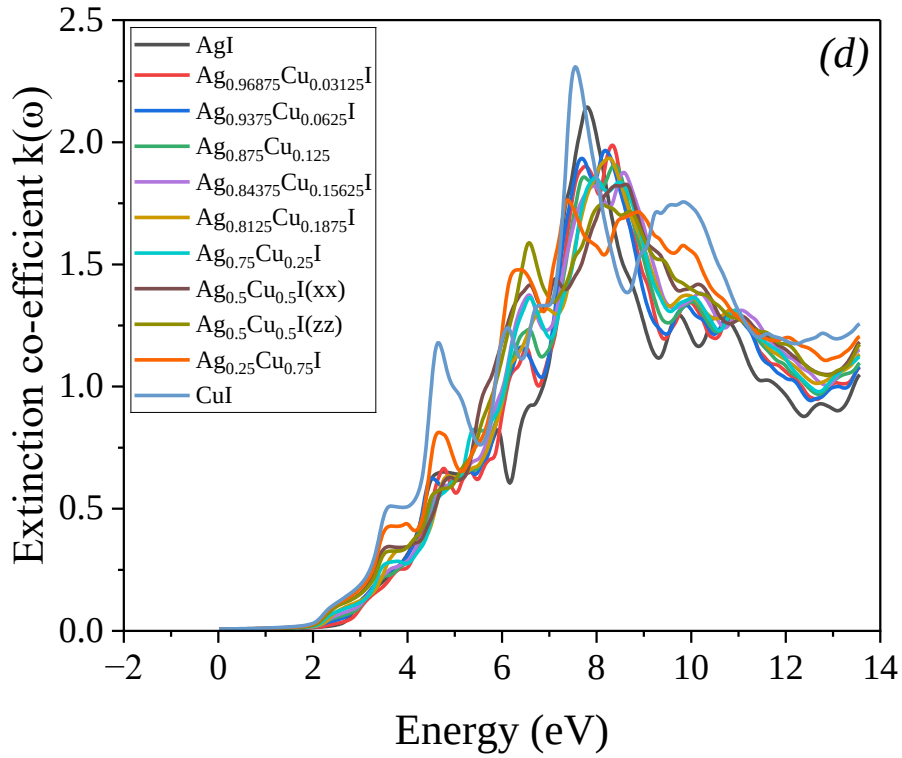


Figure 3.14(c – d): Variation of (c) Refractive index and (d) Extinction coefficient of $\gamma - Ag_{1-x}Cu_xI$

The absorption of incident light is directly corresponding to the extinction coefficient of a material. Figure 3.14(d) illustrates the variations in extinction coefficients as they relate to energy. This measures the extent to which a material is capable of absorbing a particular wavelength of incoming light. The pattern of the extinction coefficient indicates that increased concentrations of Cu in $\gamma - Ag_{1-x}Cu_xI$ correspond to an expanded level of light absorption. The absorption coefficient $\alpha(\omega)$ is a measure of the degree to which an optical material absorbs light. It is related to the proportion of power absorbed for each unit length of a medium.

Figure 3.14(e) presents the changes of the absorption coefficient of $\gamma - Ag_{1-x}Cu_xI$ as a function of energy (eV) for $x = 0.00 - 1.00$. At low Cu concentrations, the compound exhibits high absorptive power. Photons energies higher than the threshold energy will be absorbed by the compounds. Due to their lower absorption coefficient, compounds behave like transparent materials below the threshold energy. In this

region, higher transmission is indicated by a lower absorption coefficient. As a result, the compounds can be used in a variety of optical devices within this range.

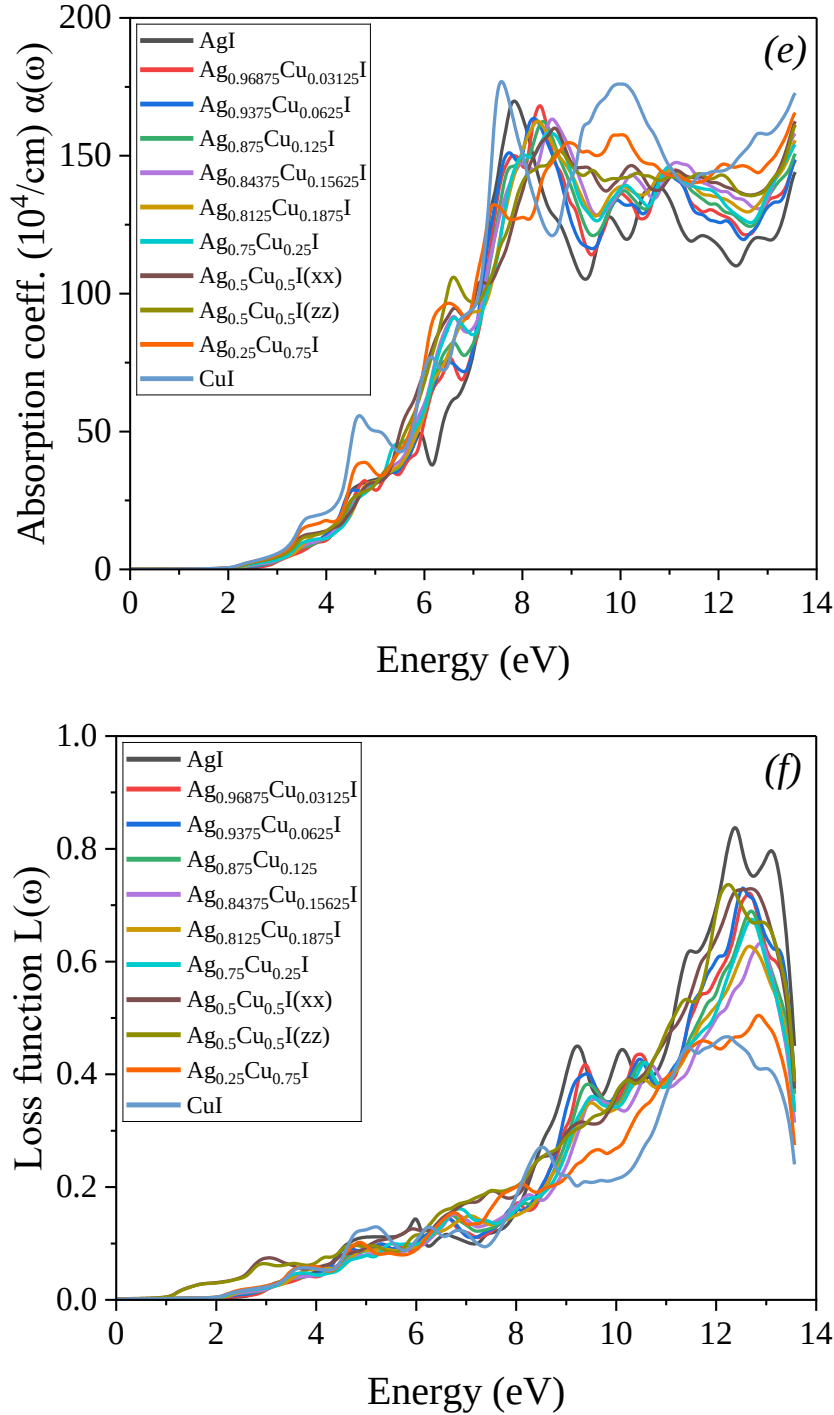
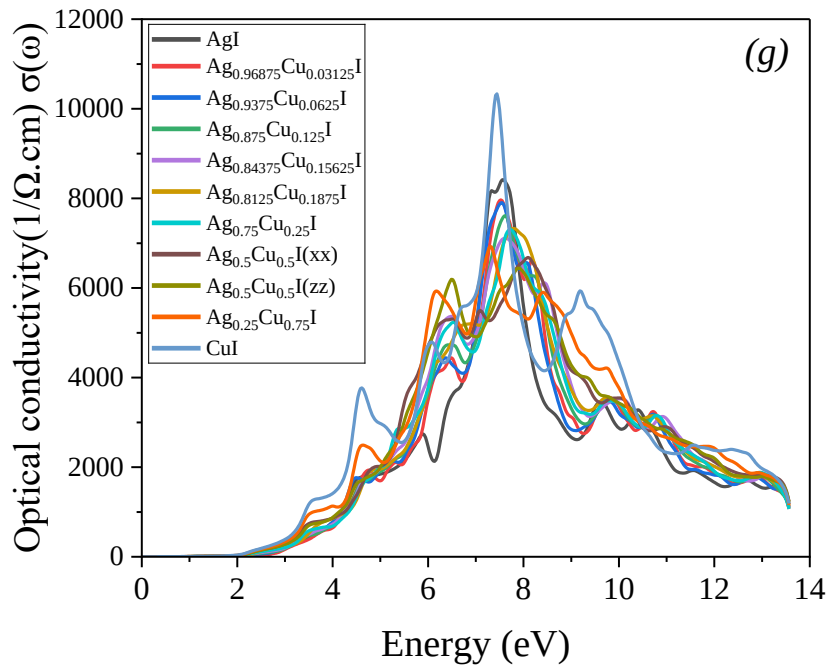


Figure 3.14(e – f): Variation of (a) Absorption coefficient $\alpha(\omega)$ and (b) Loss function $L(\omega)$ of $\gamma - Ag_{1-x}Cu_xI$.

Figure 3.14(f) shows the energy loss function changes as a function of energy. Below the threshold energy, the plot mainly retains flat. The low-frequency electronic interband transition is indicated as a gap on the energy axis. The largest peaks for concentration of Cu are located at energies 12.612 eV, 12.600 eV, 12.664 eV, 12.911 eV, and 12.666 eV. A standard coupling with plasma resonance is shown by the prominent peaks in the energy loss function; the corresponding frequency is known as the plasma frequency. The material behaves as a solid at frequencies below this threshold value and as a dielectric at frequencies beyond it.

The optical conductivity $\sigma(\omega)$ of γ - $Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$) varies with photon energy is shown in Figure 3.14(g). When incident energy reaches a threshold value, conductivity starts to react to the electric field. It is observed that the critical points in optical conductivity go towards lower energy levels as the concentration of Cu increases.



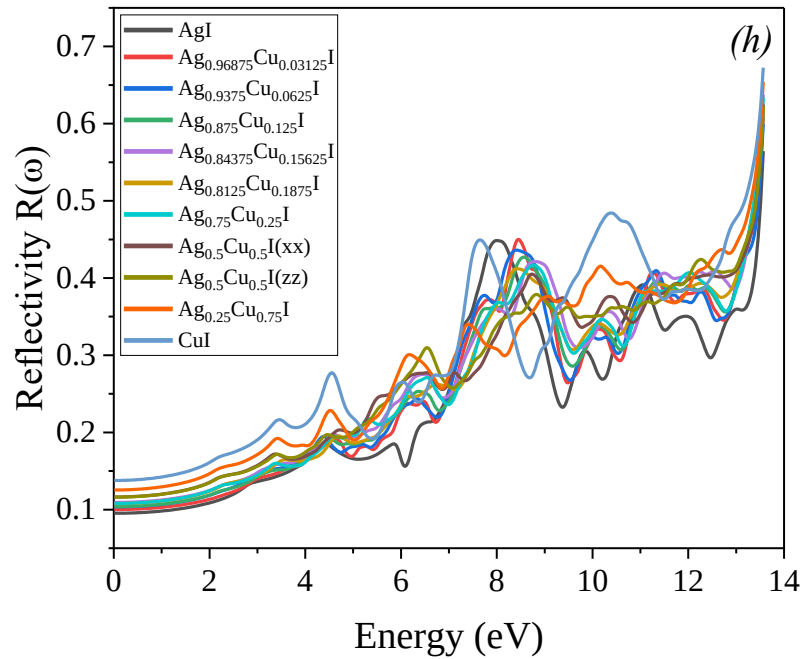


Figure 3.14(g – h): Variation of (a) Optical conductivity $\sigma(\omega)$, and (b) Reflectivity $\sigma(\omega)$ of $\gamma - Ag_{1-x}Cu_xI$

Reflectivity $R(\omega)$ is defined as the energy ratio of incident to reflected photons or the ratio of incident power to reflected power on the surface of a material. Transmission (T) is defined as the transmitted power divided by the incident power. If a material does not scatter or absorb light, then $T + R = 1$. Using reflectivity, specifically the reflection coefficient, one can study how light is reflected at the surface of a crystalline solid. In connection with their structural properties, the materials' reflectivity spectra can be employed to comprehend the scattering length density (SLD) of different layers [34]. The relationship between reflectivity and the energy of $\gamma - Ag_{1-x}Cu_xI$ is seen in Figure 3.14(h). The reflectivity of these materials attains its peak within the energy range of 8 eV to 9.5 eV, depending upon the selected Cu concentrations used. The engagement of light with the generated electrons within the material explained the peaks observed at different energy levels. A reduction in the reflection coefficient is observed within the energy range of 8.85 to 9.56 eV. Table 3.3 shows the values of $R(0)$, at the zero-frequency limit of normal incidence reflectivity $R(\omega)$. An electron

undergoing an interband transition experiences a finite loss of energy, which may explain the observed discrepancy in peak values. This scenario pertains to the annihilation of an individual electron within the material, results energy loss spectrum.

3.4 Conclusions

In summary, the first principle computational calculations based on FP-LAPW method were able to study the electronic structural calculations of $Ag_{1-x}Cu_xI$ compounds using TB-mBJ exchange correlation potential. We presented the concentration dependent various structural and electronic parameters such as lattice parameter, bulk modulus, and band gap energy. We have found these parameters vary with Cu concentration. A direct band gap has been observed from the calculated band structure and density of states (DOS). Optical properties calculation shows the Cu doped AgI behaves as a radiation detector. The materials lose the transparency in the higher energies and becomes transparent at low energy. Low energy cubic γ - $Ag_{1-x}Cu_xI$ compounds are suitable for making various optical instruments. The absorption spectra of $Ag_{1-x}Cu_xI$ compounds have higher ability to absorb in compare to pure AgI.

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CHAPTER 4

Electronic structure calculations of $\gamma - Ag_{1-x}Cu_xI$ ($x = 0 - 1$) using HSE06 method

4.1 Introduction

Silver and cuprous halides (AgX and CuX , $X = Cl, Br, I$) had a practical interest for their electronic properties. Silver halides were treated as the first photographic materials have been used as a light conversion material owing to their exceptional performance in photosensitivity and photovoltaic cell. Due to their large excitation energy, the materials are used in optoelectronic devices [1-10]. The achievements in semiconductors have broadly used for various light emitting devices such as solar cells and other display panels [11]. AgI has n-type electrical conductivity and found to be promising material used in photo catalysts due to the favorable band gap (2.8 eV) and strong oxidizing capacity. CuI with an excellent p-type material used in photovoltaic and photodiode [12-16]. These materials are wide band gap semiconductor and have a tetrahedral orientation executed by eight atoms per basis. CuI exhibits an acceptable lattice mismatch with AgI , allowing for the combination of CuI and AgI to make a solid solution [17]. The phase diagrams of metal halides, which exist in α , β , and γ -phase, change with various temperature ranges, are usually complex in nature. Furthermore, the stable γ phase of AgI and CuI , form a crystalline material of $Cu_xAg_{1-x}I$ type with a controlled energy band gap by changing the concentrations of Ag/Cu [18,19]. Among all these metal halides, silver iodide (AgI) is one of the most common superionic material. Above 420 K, the α -phase of AgI crystallizes into its stable cubic form, the γ - AgI has been found to be stable at 413K and 587Mpa [20-22]. Silver iodide (AgI) and copper iodide (CuI) are structurally identical and can exist in different crystalline forms. At normal temperature, CuI exhibits electron-hole conduction as an ionic-electronic conductor. Above 713 K, the α -phase of CuI remains stable, but below 663 K, the γ - CuI crystallizes [23]. Ag^+ interstitials (cationic defects) produced between 250 and 420 K, generally migrate and

mediate the electrical transport in γ -AgI. Conversely, in γ -CuI, conduction process is primarily driven by the Cu^+ (Frenkel defects). There is a significant hybridization that exists between the p-electrons in halogens and the 3d/4d electrons in Ag/Cu is the cause of orbital bonding within these metal halides. The d^{10} orbital of the metal and the s^2p^6 configuration of the halogen are essentially give rise to the valance band origin of metal halides [24 - 27]. The ion mobility in crystals is better understood by calculating the intrinsic behavior of structural transformation in cation-anion chemical substitutions on the γ -AgI ionic conductor. Research has shown that as Cu concentration rises, the conductivity of Ag-Cu-I alloy considerably decreases [15]. As the concentratiосn of Cu increases, the ionic conductivity of the γ - $Ag_{1-x}Cu_xI$ alloy decreases due to a structural and phase change, as demonstrated by the ionic transport [28 - 30]. Amrani et al. [16] recently demonstrated the electronic structure properties of $Ag_{1-x}Cu_xI$ compound. Goldmann deduced the electronic structure of $Ag_{1-x}Cu_xI$ alloys by analyzing the X-ray spectra of CuI and AgI systems [31].

Now-a-days, the first principle electronic structure modeling is performed systematically to predict the various properties of solids. Among various techniques, the density functional theory (DFT) within local density approximation (LDA) and generalized gradient approximation (GGA) have been considered most widely due to its accuracy and efficiency. However, the presence of self-interaction in LDA and GGA, the band gap of these material is expected to be underestimated i.e., inflated metallic states that affect the accuracy of LDA and GGA based DFT calculations. Earlier theoretical calculations on AgX and CuX confirmed that the band gaps are typically smaller in comparison to experimentally calculated values [10]. To overcome the partly remediate when using the most popular extensively used hybrid functional, HSE06 [15, 16] where the exchange energy is expressed as a combination of semi-local(SL) functionals and the Hartree-Fock (HF) exact exchange. Since both Ag and Cu are members of the same metal group, adjusting the Ag/Cu elemental composition on AgI/CuI, therefore, various electronic structure properties of Ag-Cu-I combination makes it simple to construct a semiconductor with controllable electrical and optical features. Furthermore,

concentrating on the creation of phase structure and the superionic character is made possible by the calculations of electronic properties on a coupled Ag-Cu-I material [32]. It is essential to investigate the various electronic aspects of Ag-Cu-I for its distinct band structure, that broadens the center of BZ to the extremum. This encourages us to look into the effects of copper on γ -Ag_{1-x}Cu_xI ternary alloy systems with a $1 \times 1 \times 1$ supercell structure.

4.2 Computational method

In the present calculation, we use density functional calculation, based on the FP-LAPW scheme, performed using the WIEN2K code [33 - 36], to determine the structural parameters, electronic and optical properties on $\gamma - Ag_{1-x}Cu_xI$ compound for specific Cu concentrations ($x = 0.00 - 1.00$). We employed GGA as an exchange-correlation potential for estimating various structural parameters. We have used the screened hybrid functional, which is widely used in the computational calculations for solids. The potential parameters were calculated by Heyd-Scuseria-Ernzerhof screened hybrid functional (HSE06) scheme [33, 10] to achieve the utmost reliable band gap with accurate band-dispersions, compared to other schemes like LDA and GGA [37, 38]. For all the calculations in the present work, we used a k-point mesh of $10 \times 10 \times 10$. During the calculations, the electronic configuration of Ag: [Kr] $4d^{10}5s^1$, Cu: [Ar] $3d^{10}4s^1$ and I: [Kr] $4d^{10}5s^25p^5$ is considered. Within FP-LAPW scheme, the spherical harmonics inside the non-overlapping spheres along with the plane wave, augmented the wave function, potential, and charge density. The predicted muffin-tin radii (R_{MT}) for the Ag/Cu and I atoms are 2.5 and 2.48, respectively. Where, R_{MT} defines the measurement of the minimal muffin-tin radius. The cut-off energy (K_{max}) of plane wave was determined at $K_{max} \cdot R_{MT} = 7.0$. Furthermore, the cut-off value of the plane wave has been set at $l_{max} = 10.0$, and $G_{max} = 12.0$ (a.u) in the present calculations. We used a computational approach in our computations in which we obtained the corresponding equivalent configurations for every substitution of Ag with Cu atom. Self-consistent computations are performed on a stable structure with a convergence of total energy, ensuring that the system is within 0.00001 Ry. Through self-consistent calculation, a stable $1 \times 1 \times 1$

supercell of $\gamma - Ag_{1-x}Cu_xI$ that is equivalent to a lowest level of total energy has been chosen for the electronic structure calculation.

4.3 Results and Discussion

4.3.1 Structural properties

In the present study, we have chosen a stable cubic structure of $\gamma - AgI$ as an initial starting material, and has been modelled by using its experimental lattice parameters in its zincblende structure (γ -phase, space group $F\bar{4}3m$) [28]. In this regard, we designed the $\gamma - Ag_{1-x}Cu_xI$ type supercell and prepared it for $x = 0, 0.25, 0.5$ and 0.75 by substituting the appropriate amount of Ag by Cu atoms in the $1 \times 1 \times 1$ supercell of $\gamma - AgI$ before conducting computational calculations. In the crystal structure of $\gamma - AgI$, the Ag and I atoms are arranged at $(0,0,0)$ and $(1/4, 1/4, 1/4)$ respectively. We calculated the optimized crystal structures with the lowest energy by measuring the total energy as a function of cell volume close to the most optimal unit cell volume V_0 for AgI, CuI, and $\gamma - Ag_{1-x}Cu_xI$ compounds.

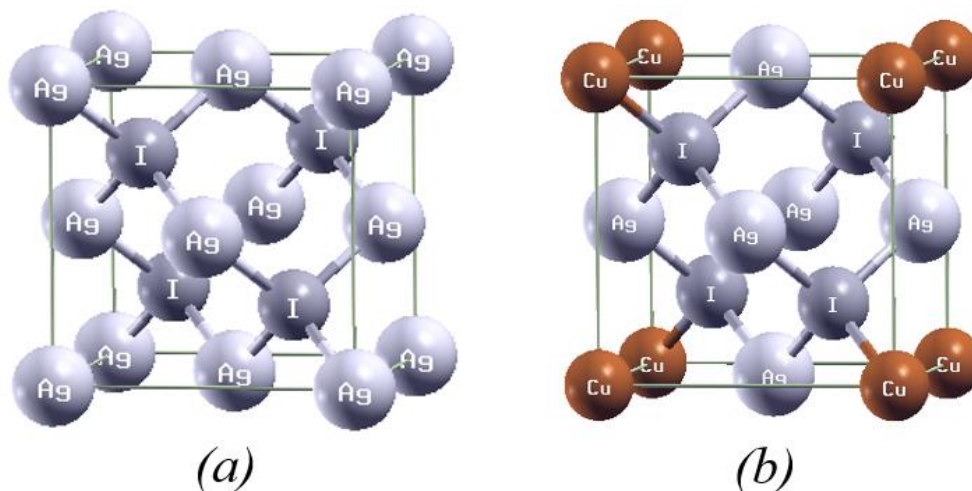


Figure 4.1(a-b): Optimized crystal structure of $\gamma - Ag_{1-x}Cu_xI$ for (a) $x = 0$, and (b) $x = 0.25$

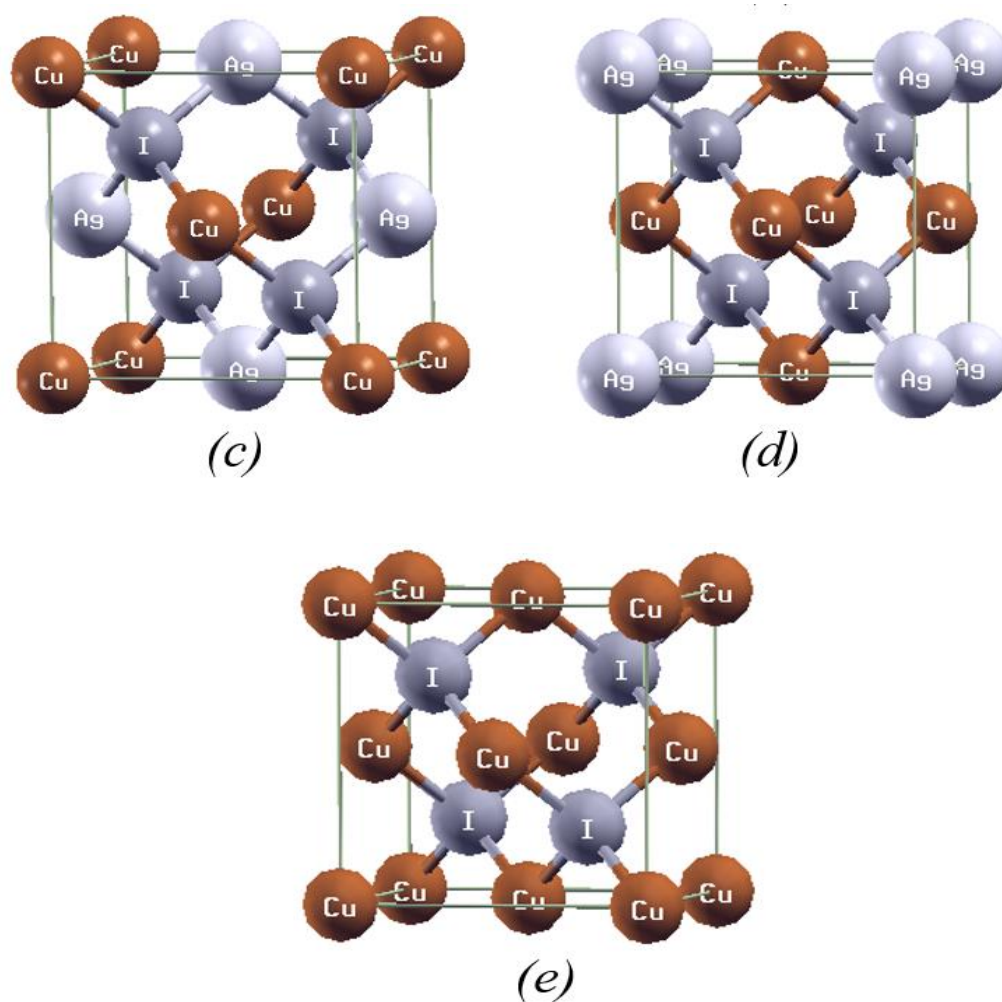


Figure 4.1(c-e): Optimized crystal structure of $\gamma - Ag_{1-x}Cu_xI$ for (c) $x = 0.5$, (d) $x = 0.75$, and (e) $x = 1$

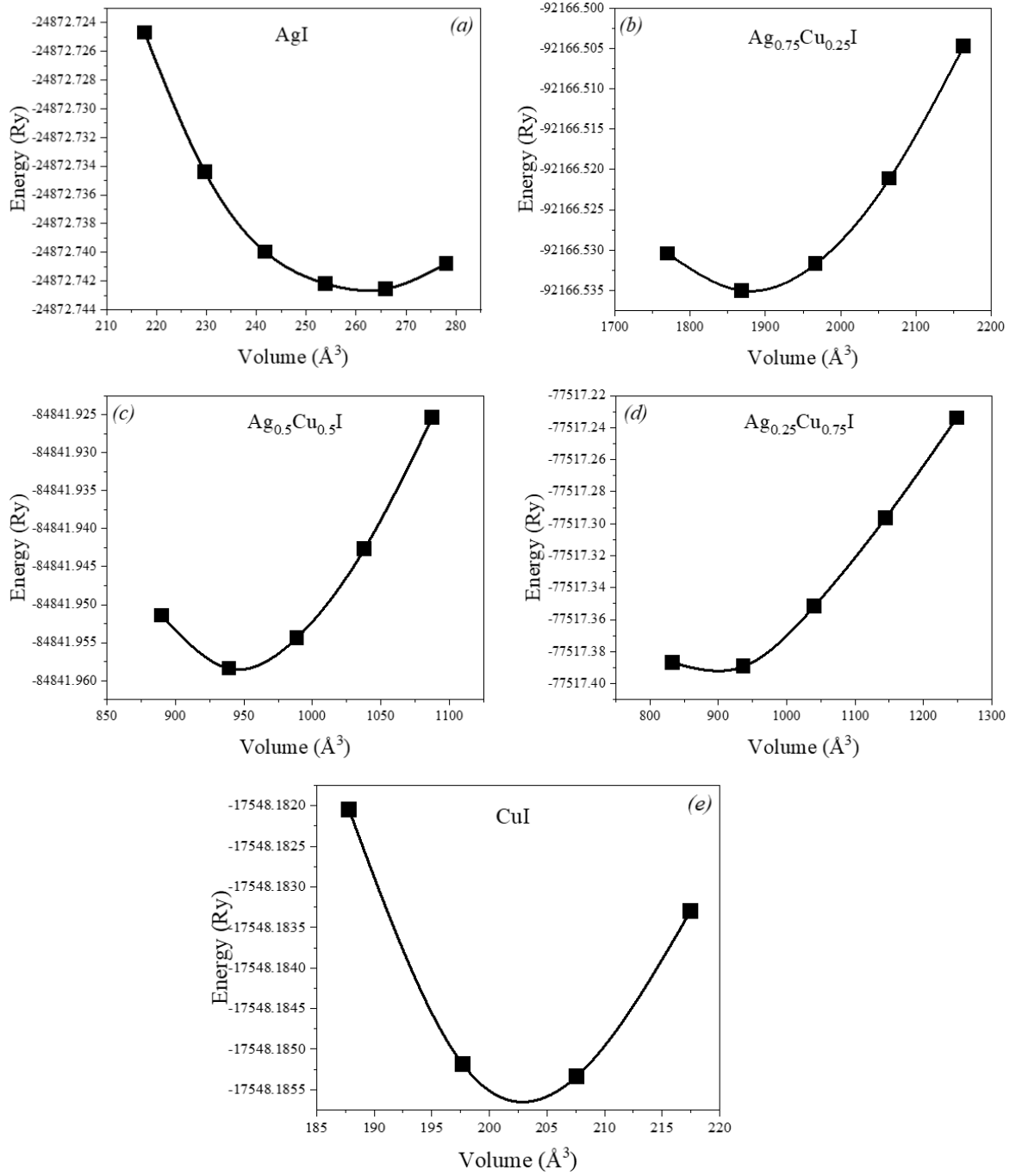


Figure 4.2: Birch Murnaghan equation of state plots for $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{I}$ for (a) $x = 0.00$, (b) $x = 0.25$, (c) $x = 0.5$, (d) $x = 0.75$ and (e) $x = 1.00$

The optimized crystal structures as shown in Figure 4.1. For each of the compounds $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{I}$ ($0.00 < x < 1.00$), the obtained total energy of the crystal structures is fitted to Birch-Murnaghan's equation [33] to get the optimal lattice constant (a) and bulk modulus (B) generated by ground state properties. Figure 4.2 displays the plot of total energy with cell volume of $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{I}$ for $x = 0.00, 0.25, 0.5, 0.75$, and 1.00 . The crystal structures were kept within the computational ability by the substitution of various concentrations.

Table 4.1: Calculated lattice parameter a and bulk modulus B compared to experimental and theoretical works on $\text{Ag}_{1-x}\text{Cu}_x\text{I}$ ($x = 0, 0.25, 0.5, 0.75$ and 1) compound.

x	Lattice constant a (Å)			Bulk modulus B (GPa)		
	Our work	Expt.	Theoretical	Our work	Expt.	Theoretical
0	6.63	6.49[16]	6.65[17]	26.98	24[42]	26.66[17]
0.25	6.52	---	6.52[17]	29.82	---	27.41[17]
0.5	6.41	---	6.39[17]	31.75	---	30.11[17]
0.75	6.28	---	6.26[17]	35.23	---	37.77[17]
1	6.10	6.05[16]	6.09[17]	40.44	36.6[44]	38.87[17]

The number in the square brackets means the reference number.

The integration across the Brillouin zone was done by using 3000 k-points throughout the structural minimization as well as in self-consistent field calculations in all the cases. Table 4.1 shows the optimized lattice parameter (a) and bulk modulus (B) for $\gamma\text{-AgI}$, $\gamma\text{-CuI}$ and $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{I}$ ($x = 0.25, 0.5$ and 0.75) compounds that agree with previous studies, proving the accuracy of our present DFT-based computation. The lattice parameters for $\gamma\text{-AgI}$ and $\gamma\text{-CuI}$ were found to be 6.63 and 6.10 Å, respectively. In $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{I}$, an increasing concentration of Cu substitution has been found to bring about in a continuous decreasing of the lattice parameter. This is consistent with the ionic radii of Cu and Ag decreasing by 0.91 and 1.29 Å, respectively. Furthermore, it is found that

AgI has a smaller value of bulk modulus than CuI, which is predicted by the inverse relationship bulk modulus with the lattice parameter.

4.3.2 Electronic Structure

The understanding of band structure of a material is crucial for developing various semiconductor devices. In this investigation, the band structures of $\text{Ag}_{1-x}\text{Cu}_x\text{I}$ in γ -phase were computed using HSE06 hybrid functional as exchange-correlation potential. Figure 4.3(a-e) displays the calculated band structures of $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{I}$ with their specific Cu contents ($x = 0.00 - 1.00$). From band structure of $\gamma - \text{AgI}$ and $\gamma - \text{CuI}$, it is observed that a Γ -centered direct band gap is observed within the IBZ. Also, the same electronic band structure (Γ - Γ) of $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{I}$ compounds have been observed.

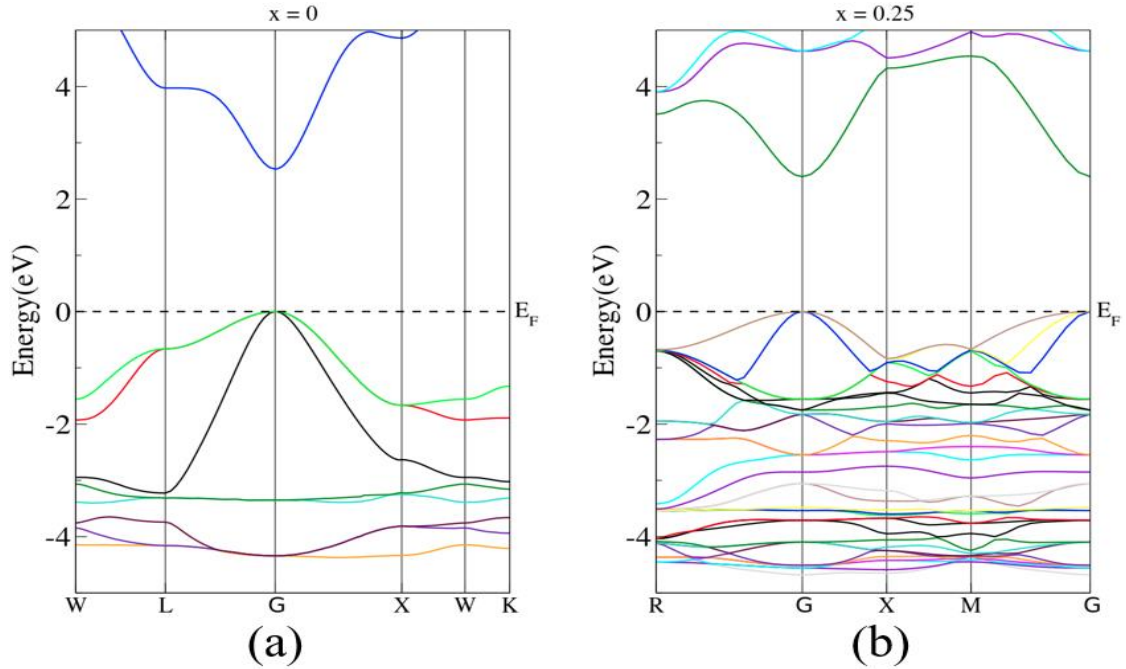


Figure 4.3(a-b): Band structure of $\gamma\text{-Ag}_{1-x}\text{Cu}_x\text{I}$ for (a) $x = 0$, and (b) $x = 0.25$, obtained using HSE06 hybrid functional.

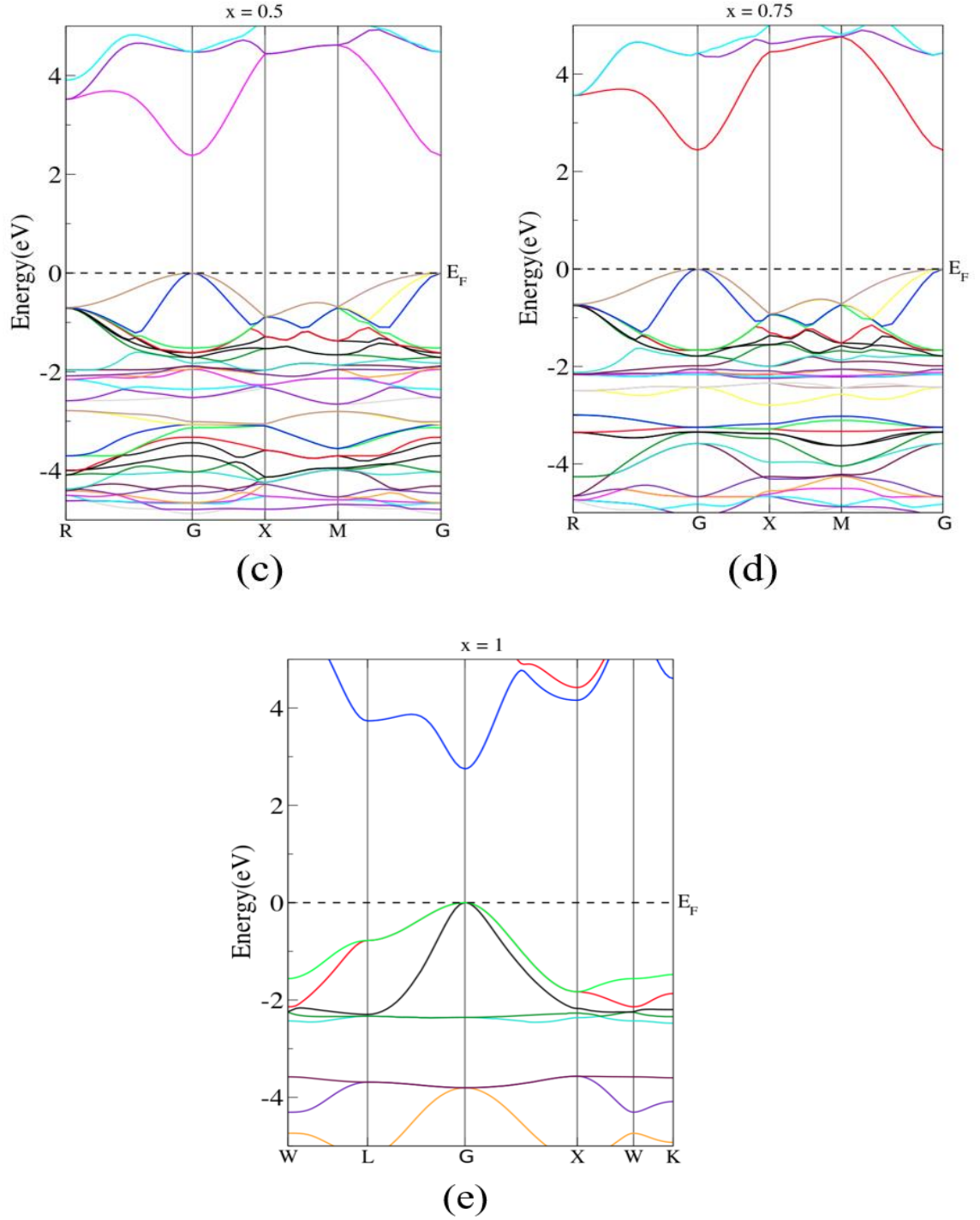


Figure 4.3(c-e): Band structure of $\gamma - Ag_{1-x}Cu_xI$ for (c) $x = 0.5$, (d) $x = 0.75$, and (e) $x = 1$ obtained using HSE06 hybrid functional.

The obtained band gap corresponding to AgI and CuI are observed to be 2.525 and 2.750 eV, respectively, with the HSE06 hybrid functional, indicating that the compounds are belong to semiconducting material. Other experimental and theoretical findings are consistent with the computed AgI and CuI compounds. By gradually substituting of Ag with one or more Cu atoms in the 1 x 1 x 1 supercell of AgI, the band structure for $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$) compounds shows direct band gap energies. The obtained energy gap values in $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$) are displayed in Table 4.2. The valance and conduction band are pointed with their respective maximum and minimum position close to high symmetry Γ -point, generates a direct band gap for both compounds within zincblende structure, as displays in the Figure 4.3. This does not demonstrate that any electronic states beyond fermi level. The electronic states are displaced from the fermi level. Figure 4.4 illustrates the variations of lattice parameter, bulk modulus, and the band gap energies with Cu composition in $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$). Figure 4.4(c) shows a non-linear variation associated with fundamental energy gap with various Cu concentrations x for $\gamma - Ag_{1-x}Cu_xI$ systems using the HSE06 hybrid functional scheme.

Table 4.2: Direct band gap energy of $\gamma - Ag_{1-x}Cu_xI$ alloys with different Cu concentrations using HSE06 potential.

Concentration	E_g (eV)		
x	Our work	Experiment	Other calculation
0	2.525	2.78[16]	1.340[17]
0.25	2.370	-	1.106[44], 1.682[17]
0.5	2.379	-	0.993[44], 1.596[17]
0.75	2.440	-	0.962[44], 1.614[17]
1	2.750	2.95[43]	1.068[17], 1.12[10]

The number in the square brackets means the reference number.

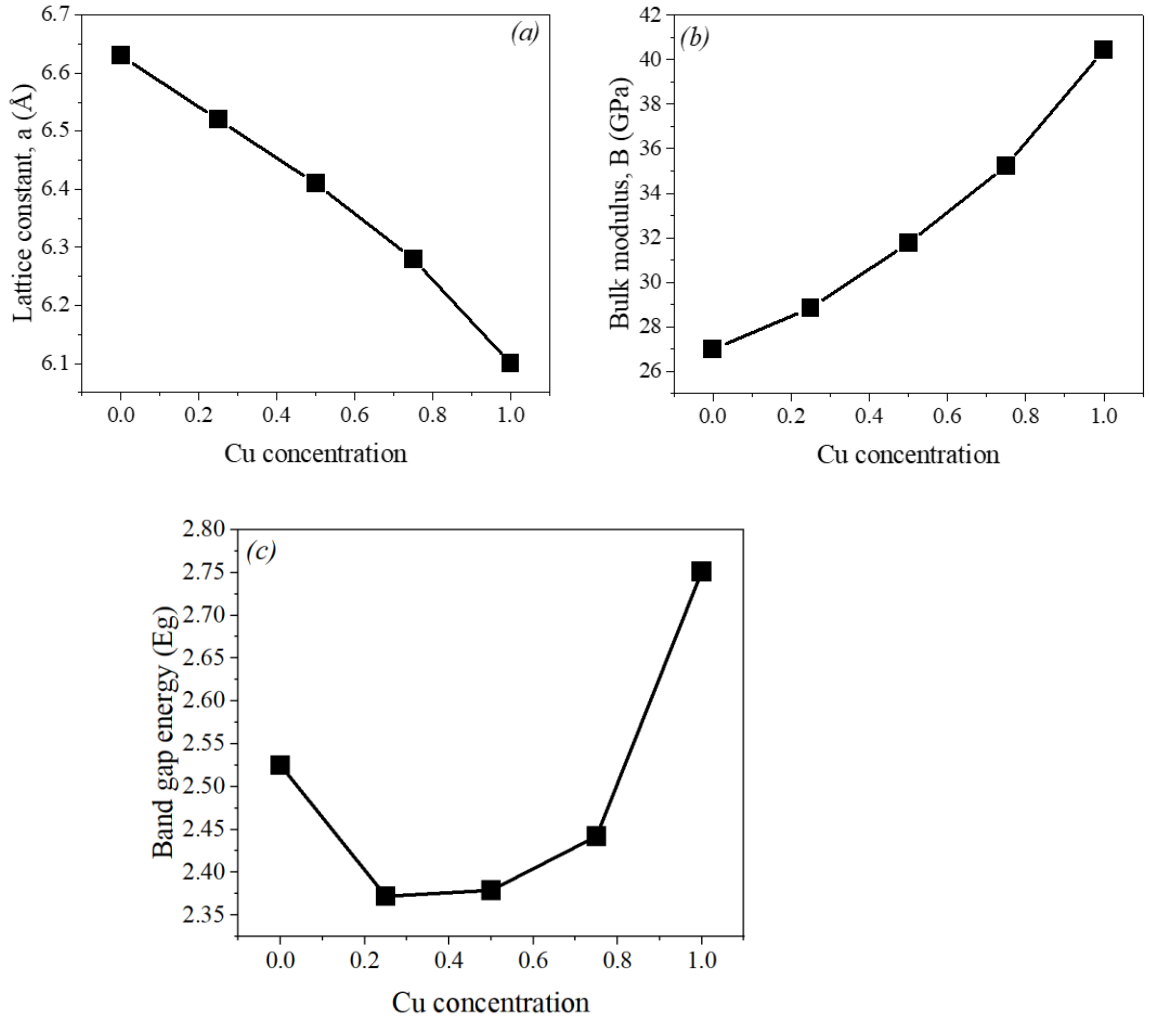


Figure 4.4: Variation of (a) lattice constant, (b) Bulk modulus, and (c) Band gap with Cu concentration in $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.00, 0.25, 0.5, 0.75$ and 1.00).

The band gap values calculated using the HSE06 hybrid functional for $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$) are shown in Table 4.2, are consistent with previous theoretical and experimental studies. The exchange correlation energy is being measured incorrectly by the computational calculation due to the rigidity of the quasi-particle self-energy. In general, there was clear and concise manifestation of the experimentally calculated values. A small difference in between experimental and computational predictions can be attributed to our assumption that the crystal was at 0 K temperatures and our inability

to account for the contribution of lattice vibrations at ambient temperature. There are limitations to the validity of the density functional calculation [39]. This results in a little difference between the calculated and experimental values. Our current calculations do not consider spin-orbit coupling effects into account, which is probably explains our calculated band gap are a little underestimated.

4.3.3 Density of states

The density of states (DOS), which defines the electronic states at particular energies that can be occupied, helps in the investigation and understanding of the nature of chemical bonds in a material. The density of states (DOS) of a material gives insights into the atomic origins of various electronic states observed within the band structure. We have displayed the HSE06 hybrid functional induced DOS for $\gamma - Ag_{1-x}Cu_xI$ for $x = 0, 0.25, 0.5, 0.75$ and 1 in Figure 4.5 - 4.9. The DOS projected between -4.8224 to 6.7968 eV in AgI compound, and -6.2941 to 6.7946 eV in CuI compound. The fermi level is considered as base of energy source. It has been noted that the starting valence region extends from -4.1693 to -3.3529 eV for AgI, while for CuI, it extends from -5.6409 to -3.5184 eV. This part consists of p states of halide (I) and d states of metal (Ag/Cu). This primarily results from the hybridization between I -p states and Ag/Cu - d states. The second region is situated within the energy range of -2.9992 to -0.0604 eV in AgI, and -1.9401 to -0.0625 eV for CuI. This is mainly composed of 'd' states of Ag/Cu along with a minor contribution from I 'p' states. The final region covers from 2.5243 to 6.8 eV in AgI and from 2.6855 to 6.7946 eV in CuI, characterized by conduction band primarily formed via I-p states and Ag/Cu-d states, exhibiting a minimal peak height. Although, a clear difference exists in band gap when comparing undoped AgI with Cu doped AgI. We have seen that the decrease in percentage of Cu substitution, decreases the intriguing discrepancy in the energy involving conduction band and valence band, for which we get the band gap energy values equal to 2.5242, 2.370, 2.379, 2.440, and 2.750 eV respectively for their specific atomic percentage, $x = 0, 0.25, 0.5, 0.75$, and 1. It has been noticed that, the first valence region in the substituted system is lies between -4.5754 eV to -0.9291 eV for γ -Ag_{0.75}Cu_{0.25}I, from -4.9282 eV to -1.2547 eV for γ -

$Ag_{0.5}Cu_{0.5}I$, and from -5.2244 eV to -2.0135 eV for $\gamma - Ag_{0.25}Cu_{0.75}I$. The entire regions are formed by the hybridization across the I-p states and Ag/Cu-d states.

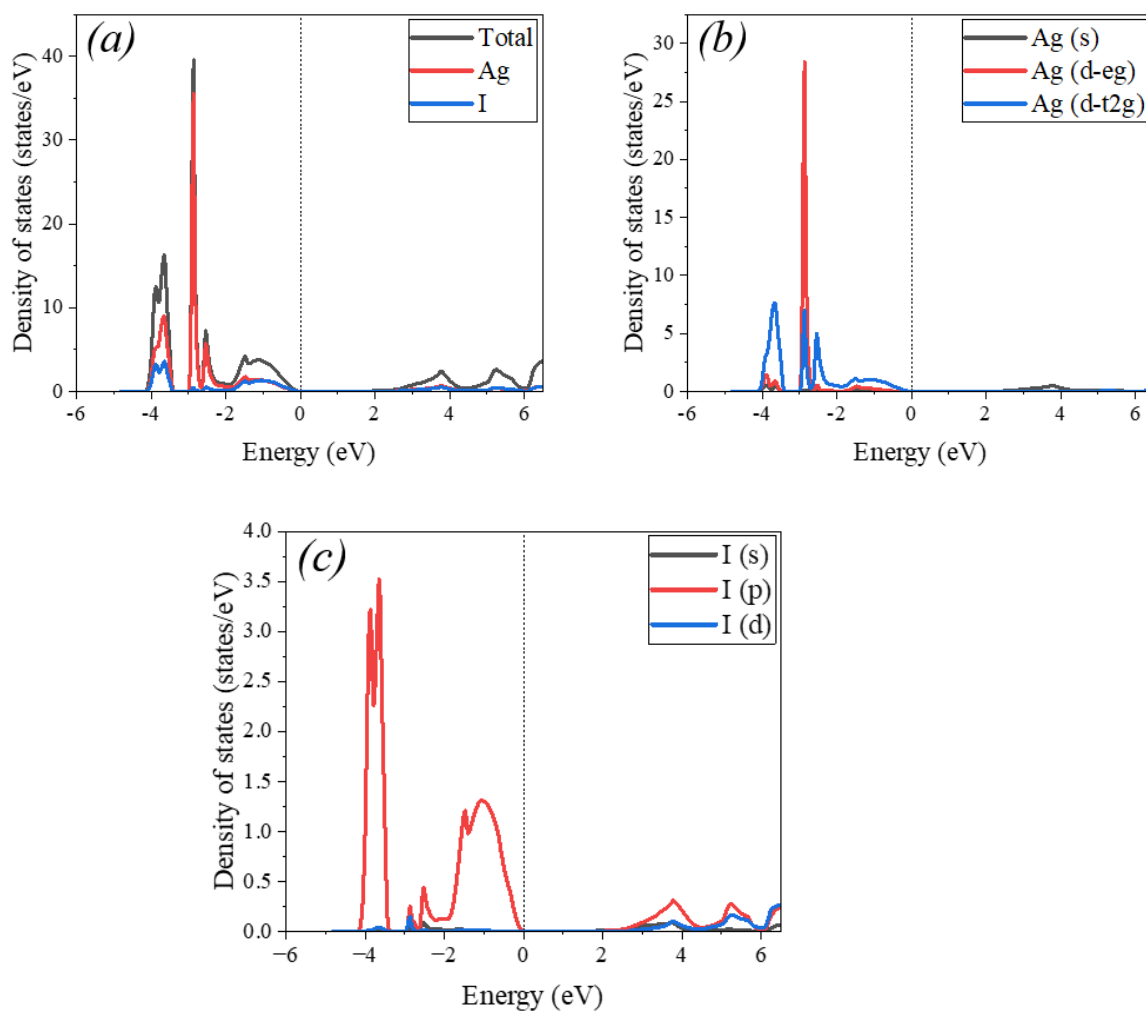


Figure 4.5: (a) Density of states of AgI-total, Ag-total and I-total, (b) Partial density of states Ag (p, d-eg and d-t2g), and (c) Partial density of states of I (s, p and d) in $\gamma - AgI$ obtained using HSE06 functional.

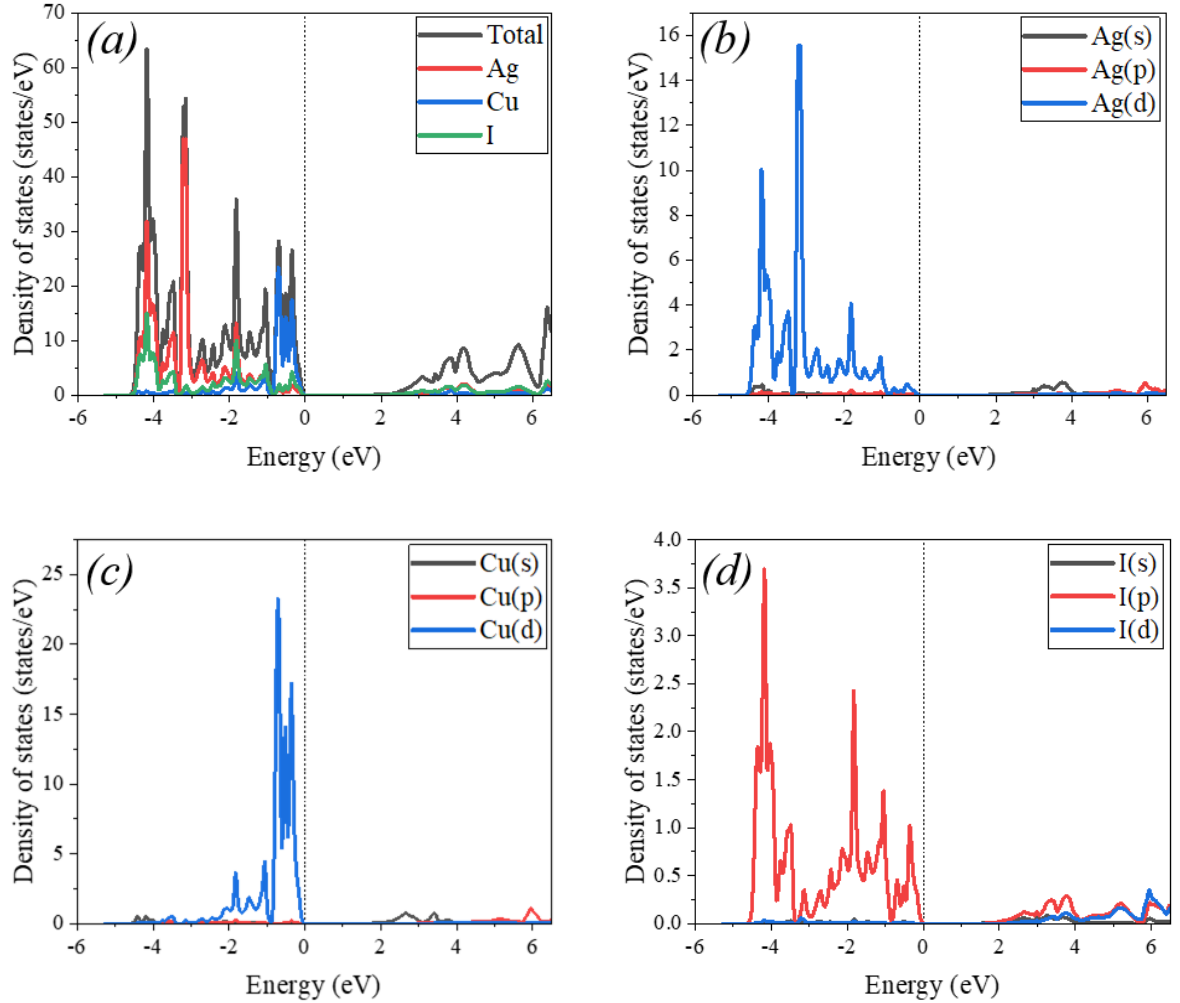


Figure 4.6: (a) Density of states of $\gamma - Ag_{0.75}Cu_{0.25}I$ -total, Ag-total, Cu-total and I-total, (b) Partial density of states of Ag(s, p and d), (c) Partial density of states of Cu(s, p and d), and (d) Partial density of states of I(s, p and d) in $\gamma - Ag_{0.75}Cu_{0.25}I$ obtained using HSE06 functional.

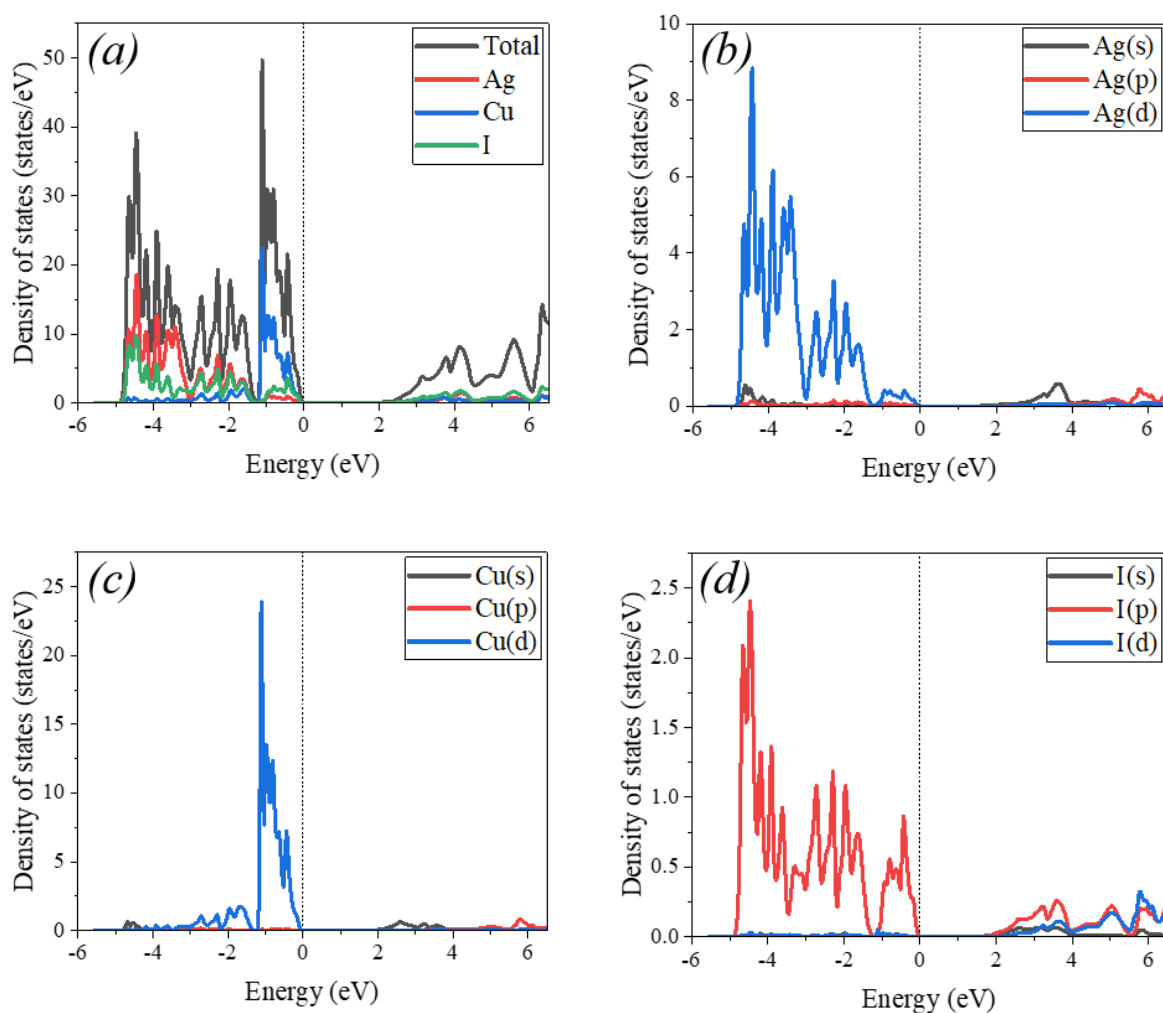


Figure 4.7: (a) Density of states of $\gamma - Ag_{0.5}Cu_{0.5}I$ -total, Ag-total, Cu-total and I-total, (b) Partial density of states of Ag(s, p and d), (c) Partial density of states of Cu(s, p and d), and (d) Partial density of states of I(s, p and d) in $\gamma - Ag_{0.5}Cu_{0.5}I$ obtained using HSE06 functional.

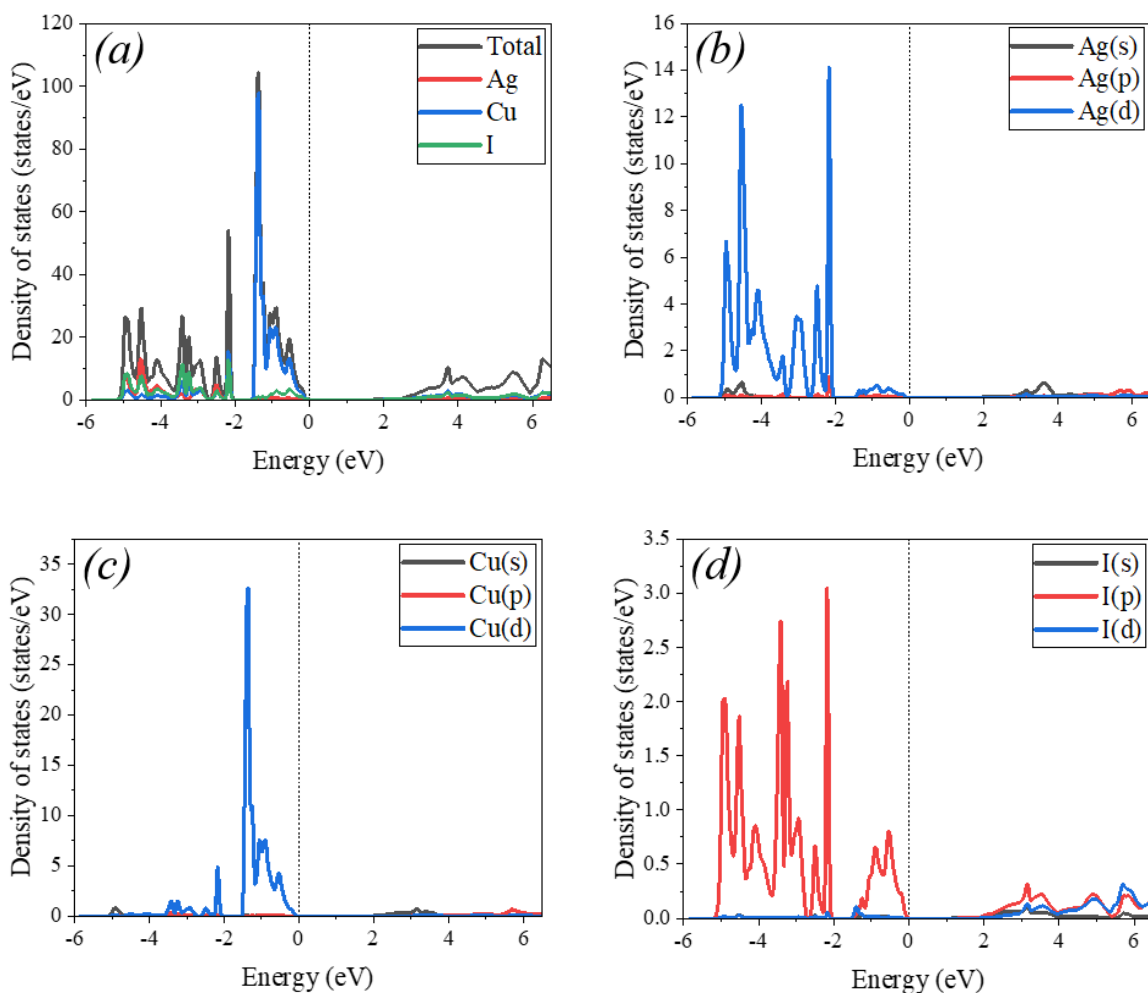


Figure 4.8: (a) Density of states of $\gamma - Ag_{0.25}Cu_{0.75}I$ -total, Ag-total, Cu-total and I-total, (b) Partial density of states of Ag(s, p and d), (c) Partial density of states of Cu(s, p and d), and (d) Partial density of states of I(s, p and d) in $\gamma - Ag_{0.25}Cu_{0.75}I$ obtained using HSE06 functional.

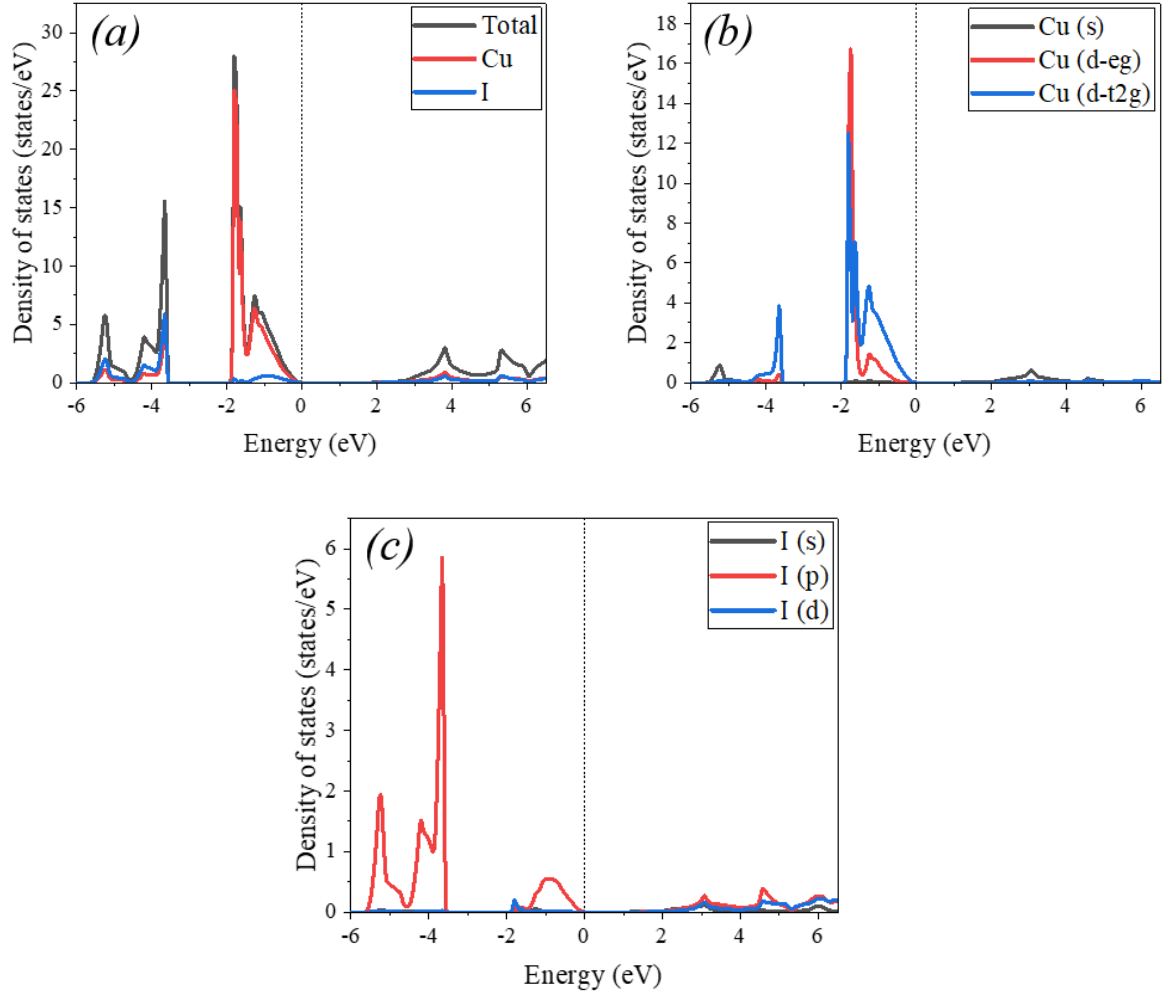


Figure 4.9: (a) Density of states of CuI-total, Cu-total and I-total, (b) Partial density of states Cu (p, d-eg and d-t2g), and (c) Partial density of states of I (s, p and d) in γ -CuI obtained using HSE06 functional.

The second region of valence bands are lying between -0.9290 to -0.0311 eV, -1.2547 to -0.0846 eV, and -1.578 to -0.0815 eV, for $\gamma - Ag_{1-x}Cu_xI$ with Cu content $x = 0.25, 0.5$ and 0.75 respectively. These ranges are mostly from the Ag/Cu-d and a less contribution of I-‘p’ states. In the last region, it is ranges from 2.3459 to 6.7968 eV,

2.2950 to 6.7968 eV, 2.3590 to 6.7968 eV for Cu composition $x = 0.25, 0.5$ and 0.75 respectively in $\gamma - Ag_{1-x}Cu_xI$. This conduction band region is occurred due to p-I states and d-Ag/Cu states with a small peak height. The DOS calculation shows that the substitution of Cu atom by Ag atom in AgI, the zincblende structure of the compound does not significantly alter the characteristics of the doped material; rather, the hybridization of the I-p states and d-Ag/Cu d states remains symmetrical. The DOS pattern for the $\gamma - Ag_{1-x}Cu_xI$ is almost identical. The total DOS of alloys is unaffected by the gradual substitution of Cu atoms for Ag atoms in $\gamma - Ag_{1-x}Cu_xI$ alloy. The lattice parameters of $\gamma - Ag_{1-x}Cu_xI$ ternary alloys lie between Ag and Cu. The lattice parameters exhibit a continuous reduction as the concentration of Cu increases. The d-bands $\gamma - Ag_{1-x}Cu_xI$ alloys are observed to be slightly enlarged when compared to undoped AgI and CuI compounds. The d-band expansion in the alloys exhibits a small increase in correlation with the concentrations of Cu/Ag atoms. Furthermore, as Cu concentration increases, the hybridizing d-states with s and p-states increases close to fermi level. This implies that the rate of transition associated with d-sp band will be higher. Additionally, the hybridized 's' and 'p' band location changes when the Cu concentration gets closer to the fermi level. Based on the idea of inter-intra band, the aforementioned results suggest that the mismatching between Ag and Cu atoms in the combined $Ag_{1-x}Cu_xI$ alloys could alter the energy distribution of the system. Moreover, the hybridized states get closer to the fermi level as the percentage of Cu concentration is more. Additionally, as the concentration of Cu approaches the maximum extent, the position of the hybridization bands 's' and 'p' shifts. The results indicated above imply that the mismatch within Cu and Ag atoms in the combination of Ag-Cu-I alloys change their energy distribution on the basis of the concept of inter-intra band and band transition. We also, compute the TDOS associated with Ag, Cu, and $Ag_{1-x}Cu_xI$ system in order to investigate the characteristics of the band structure of these compounds along with PDOS of Cu and Ag in $Ag_{1-x}Cu_xI$ compounds. It is observed that when Cu concentration increases, width of d-band decreases. But the values of higher and lower d-band limits are located within the atoms itself (Ag and Cu). A comprehensive analysis

of DOS in the d-orbital of Cu/Ag concentration in $Ag_{1-x}Cu_xI$ alloys reveals that the significant d-d hybridization in Ag and Cu atoms is the origin of the d-band extension. With the increase in Cu concentration, width of the d-orbitals in Ag and Cu decreases as well. The increased volume of $Ag_{1-x}Cu_xI$ alloys with different atomic concentrations is a result of altering of band structure of $Ag_{1-x}Cu_xI$ alloy. The decrease of volume in $Ag_{1-x}Cu_xI$, when Ag atoms are substituted with Cu atoms because, Ag atoms have a larger atomic radius than Cu atoms. DOS provides the conceptual explanation of the band structure. For the $Ag_{1-x}Cu_xI$ ternary alloy systems, we have computed both PDOS and TDOS. The TDOS calculation shows that the total contribution of 4d-orbital in Ag, and 3d-orbital in Cu cation causes the valence band (VB) of alloys to shift towards the fermi level when the cation of the combined $Ag_{1-x}Cu_xI$ system is changed the dopant percentage from 0 to 1. The impact of Cu composition on electronic properties have been analyzed through FP-LMTO calculation [40].

4.3.4 Optical properties

The optical properties of a material result from the interaction of incident photon with electron, leading to a time-dependent response to electromagnetic perturbations. The response of a material to electromagnetic radiation, commonly known as light, when it impinges on its surface, or its interaction with such radiation, defines its optical behavior. Variations in physical, chemical, and mechanical attributes among different materials give rise to distinct optical properties. Comprehensive understanding of optical properties holds great significance in both industrial and scientific realms. In applications such as selecting materials for non-contact temperature measurement devices, heat transfer techniques, and laser technology, thorough perspective of materials, the study of optical properties is important for optimal performance. The method employed for calculating optical properties is connected with the joint density of states that has been altered by appropriate dipole matrix elements [41].

Table 4.3: Calculated values of zero-frequency limits in $\epsilon_1(0)$, $n(0)$ and $R(0)$ spectra and threshold values in $\epsilon_2(\omega)$, $k(\omega)$, $\alpha(\omega)$ and $\sigma(\omega)$ spectra using HSE06 hybrid functional.

Compound	Zero-frequency limits			Threshold values (eV)			
	$\epsilon_1(0)$	$n(0)$	$R(0)$	$\epsilon_2(\omega)$	$k(\omega)$	$\alpha(\omega)$	$\sigma(\omega)$
<i>AgI</i>	5.157	2.271	0.151	1.129	1.238	1.483	1.456
<i>Ag_{0.75}Cu_{0.25}I</i>	5.244	2.290	0.154	1.129	1.156	1.564	1.564
<i>Ag_{0.5}Cu_{0.5}I(xx)</i>	5.712	2.389	0.168	0.993	0.993	1.265	1.238
<i>Ag_{0.5}Cu_{0.5}I(zz)</i>	5.691	2.386	0.168	0.966	0.966	1.211	1.156
<i>Ag_{0.25}Cu_{0.75}I</i>	6.011	2.452	0.178	0.993	0.993	1.238	1.183
<i>CuI</i>	6.671	2.583	0.195	1.184	1.183	1.510	1.455

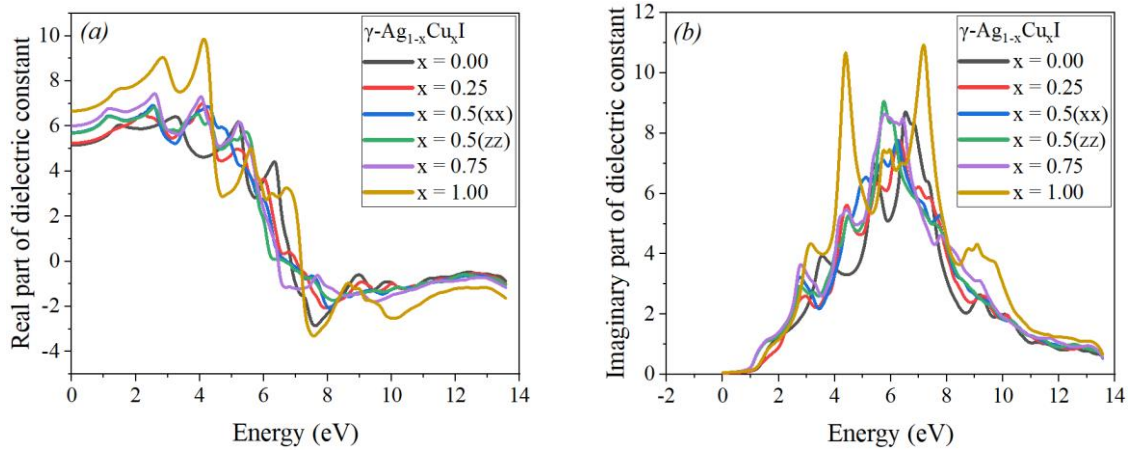


Figure 4.10(a – b): Variation of (a) Real part of dielectric constants, and (b) Imaginary part of dielectric constant of $\gamma - Ag_{1-x}Cu_xI$

The optical characteristics of $Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$) compounds have been analysed in the present research in the sense of frequency response for multiple optical parameters. The calculated real component of dielectric function with incident photon

energy expressed in eV is displays in Figure 4.10(a). From the figure, it is found that the dielectric function reaches a negative value and reflects a multiple peak of every compound. The decreasing value of the real dielectric function approaching negative values signifies the reflectiveness of the material, exhibiting metallic behaviour. Therefore, the material may be utilized behind the energy window as radiation shielding or as a radiation sensing device. At zero-frequency limit, the values of the dielectric constants are called the static dielectric constant. The calculated values of static dielectric constants in $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$) are listed in the Table 4.3. It is found that the static value increasing with increase in Cu concentration. It is noticed that the static dielectric constants with higher and lower Cu concentrations fluctuate between 5.1574 and 6.6706, respectively.

Figure 4.10(b) illustrates the variation of imaginary component of dielectric functions with energy. The zero-frequency limits in energy values are called threshold values, the threshold energy values corresponding to Cu concentrations of 0.00, 0.25, 0.5, 0.75, and 1.00 are listed in Table 4.3. Moreover, the imaginary dielectric function increases with energy following the threshold energy, attaining peaks that comply with their corresponding energy values. The peak values of $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$) are 8.4611, 8.391, 8.472, 9.234 and 10.476, corresponding to energy values of 7.4969, 7.5783, 7.6872, 7.6871, 7.8504, respectively.

The impact of refractive index with incident photon energy is depicts in Figure 4.10(c). Refractive index shows many peaks for every compound and turns negative at higher energy levels. The refractive index $n(\omega)$ at zero-frequency of incoming photon energy is called static refractive index $n(0)$. The static refractive index is listed in the Table 4.3. This demonstrates that with higher energy, the material becomes less transparent. As a result, these materials may not be employed as a transparent material. The velocity of light in vacuum is lower to its phase velocity inside a medium, when the refractive index reduces to the below one.

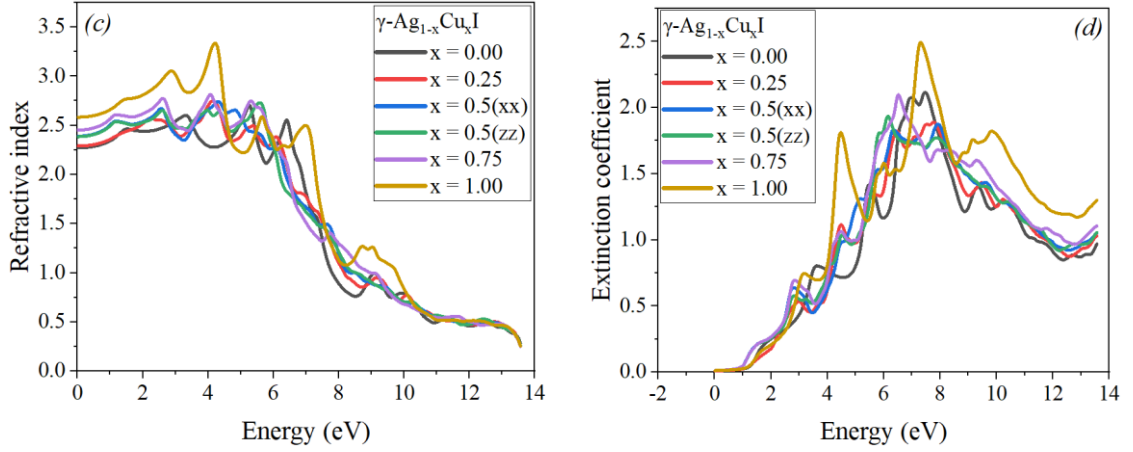


Figure 4.10(c – d): Variation of (a) Refractive index, and (b) Extinction coefficient of $\gamma - Ag_{1-x}Cu_xI$

The absorption of incident photon occurs in direct correlation with the extinction coefficient of a material. Variations in extinction coefficients with energy are depicted in figure 4.10(d). The oscillating nature of the curves in extinction coefficient is a consequence of the interface effect in a material. It quantifies the degree to which a substance can absorb a specific wavelength of incident light. The extinction coefficient pattern suggests that higher concentrations of Cu in $\gamma - Ag_{1-x}Cu_xI$ manifest a greater degree of light absorption. The critical values of extinction coefficient are displays in the Table 4.3.

Figure 4.10(e) demonstrates the variation in optical conductivity of $\gamma - Ag_{1-x}Cu_xI$ ($x = 0.00 - 1.00$) with energy. Optical conductivity defines the property of a material which gives the relationship between the material and magnitude of the electric field. Conductivity begins to respond to the electric field when incident energy reaches a critical point. The critical values are mentioned in Table 4.3. It is noted that an increase in Cu concentration results in a shift of the critical points in optical conductivity towards lower energy levels.

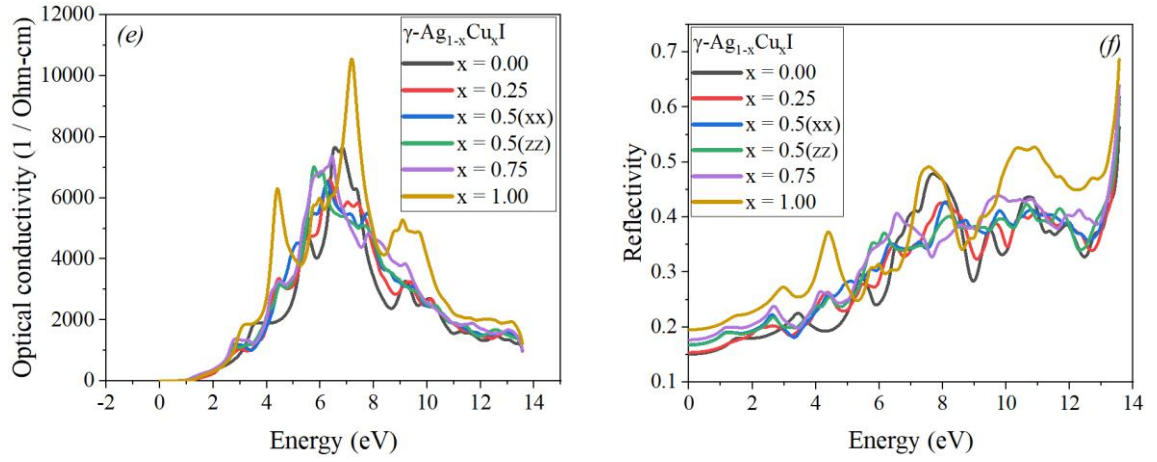


Figure 4.10(e – f): Variation of (a) Optical conductivity, and (b) Reflectivity of $\gamma - Ag_{1-x}Cu_xI$

Reflectivity describes the energy ratio of incident to reflected photons on the surface of a material. The reflection of light at the surface of a crystalline solid is studied using reflectivity, particularly the reflection coefficient. The reflectivity spectra of the materials can be used to understand the scattering length density (SLD) of various layers in relation to their structural characteristics [38]. Figure 4.10(f) depicts the correlation between reflectivity and the energy of $\gamma - Ag_{1-x}Cu_x$ ($x = 0.00 - 1.00$). The values of reflectivity at zero-frequency limit are listed in the Table 4.3. As illustrated in Figure 4.10(f), the reflectivity of these materials reaches its maximum energy limits of 8 eV to 9.5 eV when the specified Cu concentrations are used. The interaction of light with generated electrons in the substance is responsible for the peaks at various energy values. There is a decrease in the reflection coefficient between 8.85 and 9.56 eV. A finite quantity of energy is lost by the incident electron during an interband transition, which could account for the difference in peak values. This scenario involves the extinction of a single electron within the material, which leads to the energy loss spectrum.

The absorption coefficient quantifies the extent of light absorption by an optical material. Figure 4.10(g) illustrates the variation of the absorption coefficient of $\gamma -$

$Ag_{1-x}Cu_xI$ with energy (eV) for $0.00 < x < 1.00$. The critical values of absorption coefficient of all the compounds are listed in the Table 4.3. High absorptive power is exhibited by the compound when the Cu concentration is low. The compounds will absorb photons with energies exceeding the threshold energy. Below the threshold energy, compounds behave like transparent materials due to their reduced absorption coefficient. A lower absorption coefficient indicates greater transmission within this range. Consequently, within this range, the compounds may be utilized in various optical instruments.

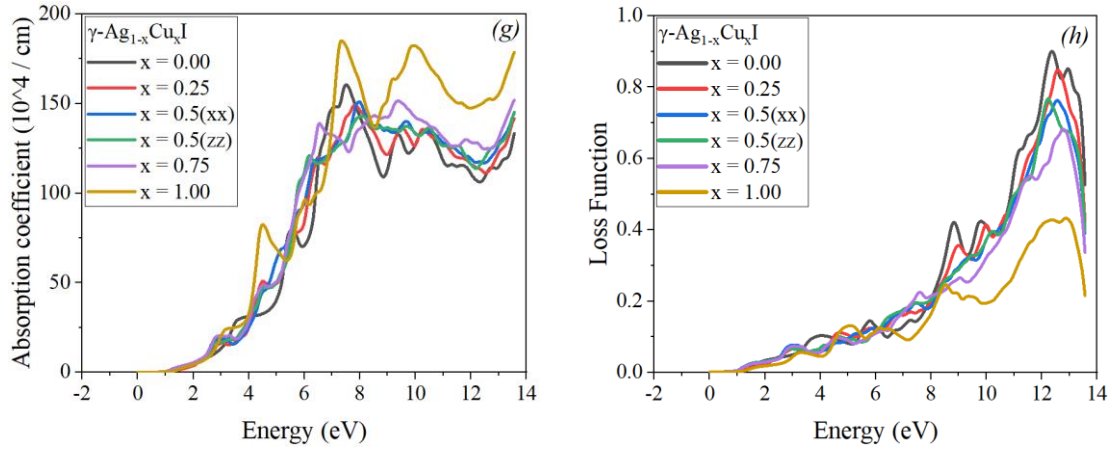


Figure 4.10(g – h): Variation of (a) Absorption coefficient, and (b) Energy loss function of $\gamma - Ag_{1-x}Cu_xI$

Figure 4.10(h) illustrates the energy loss function of material with photon energy. The plot remains primarily flat below the threshold energy. A gap exists on the energy axis, indicating the electronic interband transition at low frequency. The highest peaks for each Cu concentrations are found at energies 12.612, 12.600, 12.664, 12.911, and 12.666 eV, with corresponding loss of energies 0.731, 0.730, 0.689, 0.629, and 0.627 respectively. $\gamma - Ag_{1-x}Cu_xI$ exhibits the highest and lowest peak at $x = 0.00$ (AgI) and 1.00 (CuI). The notable peaks in the energy loss function indicates a standard coupling

with plasma resonance, with the associated frequency referred to as the plasma frequency. At frequencies above this threshold value, the material exhibits dielectric properties, while at frequencies below, it behaves as a solid.

4.4 Conclusions

As a summary, the electronic structural calculation of $\gamma - Ag_{1-x}Cu_xI$ compounds employing the HSE06 hybrid functional have been performed the computational calculations using the FP-LAPW approach. The parameters such as lattice constant, bulk modulus, and the band gap were introduced as concentration dependent structural and electronic parameters. Our findings indicate that these parameters vary with the concentration of Cu. The band structure along with the density of states (DOS) both are demonstrate a direct band gap. The optical properties are calculated to demonstrate that Cu doped AgI operates as a radiation sensor material. Higher energies cause the materials to become opaque, whereas lower energies enable them to become transparent. The low-energy cubic $\gamma - Ag_{1-x}Cu_xI$ compounds can be used to make a wide variety of optical devices. The absorption spectra of $\gamma - Ag_{1-x}Cu_xI$ combinations are more absorbent than those of pure AgI.

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CHAPTER 5

Electronic structure calculations of $\gamma - Ag_{1-x}Cu_xBr(x = 0 - 1)$ using TB-mBJ method

5.1 Introduction

AgX and CuX, where X = Cl, Br, and I, are semiconductors with diverse applications in photography and other electrolytic materials. The materials are important because of their significant p-d hybridization. In these materials, electrons are promoted by a light-capturing mechanism from valance to the conduction band [1-5]. The significance of these compounds lies in their superionicity and higher Ag⁺ conductivity levels. Their ionic characteristics differ from others because of the d-electrons present in the Ag⁺ ion. With increasing pressure, these materials modified their structural parameters without making any changes to the atomic arrangement of the fundamental unit [6]. The modelling of the electronic structure of silver halides is crucial for exploring the diverse physical and chemical properties. Significant hybridization occurs due to the presence of 4d-levels of Ag⁺ in the valence band and p-levels of Br⁻. Scop [7] theoretically computed the electronic structure of silver halides (AgCl, AgBr) using the APW approach. A self-consistent band structure calculation for AgF, AgCl, and AgBr showed the changes in band structure with atomic size of halogen [8]. In addition, the CuX (X = Cl, Br) in the zinc blende structure at ambient conditions have been thoroughly analysed to know about the behaviour of tetrahedral compounds [9-11]. The significance of group IB-VIIA materials is increasing due to their prospective applications in micro-crystals fabricated from these compounds. It offers a short-range wavelength application for its strong binding energy (about 108 MeV) in solar cells. Copper bromide is an inorganic, non-toxic chemical that is common in the Earth's crust. It demonstrates above 80% transparency in the visible spectrum. It exhibits significant absorption in the UV region of the electromagnetic spectrum [12-13]. The Ag/Cu atoms create tetrahedrally coordinated metal halide compounds with a diamond-like structure. The metal transfers its loosely bound electrons to the electronegative halogens, forming a metal halide

complex [14-15]. Cuprous and silver halides are ionic conductors, are of research interest for understanding the fundamental concepts of semiconductor physics for practical applications [16]. The superionic conductors exhibit ionic conductivity, used in solid-state batteries, optical instruments, and fuel cells. CuBr, CuI, and AgI are the examples of superionic metal halides, while AgCl and AgBr do not show this behaviour until the melting point. A simulation (MD) study has been carried out to investigate the structural properties of $Ag_xCu_{1-x}Br$ ($x < 0.5$). The concentration dependence investigation reveals the allocation of Cu and Ag ions around the tetrahedral and octahedral sites in the superionic phases, which facilitates an integral distribution of Ag ions [17-18]. The Cu^+ and Ag^+ cations form a band around the octahedral sites in the $Ag_{1-x}Cu_xBr$ compound [19]. Typical ionic crystals are alkali halides characterized by low ionic conductivity ($10^{-2} \text{ Ohm.cm}^{-1}$). The ionic conductivity of these materials originates from the intrinsic vacancies within the superionic phase. The higher intrinsic ionic conductivity originates from a cationic Frenkel defect in these crystals. Tubandt and Lorentz [20] investigated the electronic characteristics of silver halides that AgI exhibits ionic conductivity comparable to that of liquid electrolytes. Furthermore, the conductivity of AgI in the alpha phase goes beyond that of AgCl and AgBr, and it remains stable at temperatures 150 to 440 °C [21]. The unique characteristics of ionic mobility in the solid electrolytes α -AgI and β -CuBr have been investigated. In β -CuBr, the cations exhibit structural order, unlike in AgBr silver salt. Even so, approximately 10 mole percent of CuBr contributes to the conductivity of a mixed crystal [22-23]. Researchers have investigated and elucidated the structural variations among each phase of the AgBr-CuBr system. Slykhouse and Drickamer [24] have been proposed an experimental work on AgCl and AgBr, focusing on the crystallographic phase transformation from rocksalt (RS) to the CsCl structure at pressures of 8.7GPa and 8.3GPa for AgCl and AgBr respectively [25-26]. The review on AgCl and AgBr, performed both theoretically and empirically using the FP-LAPW technique, gave an analytical comparison of their impact of hydrostatic pressure on optoelectronic properties [27]. The computational analyses of CuCl and CuBr using the FP-LAPW method shows the structural transformations within zincblende structure, which

transforms to the rocksalt structure at approximately 10 GPa pressure [28,29,10]. Bouhafs and colleagues have investigated the band structures of the $\gamma - Cu_xCl_{1-x}Br$, $CuCl_{1-x}I_x$, and $CuBr_{1-x}I_x$ alloys with FP-LAPW method [30-31] and observed the disorder effect of on copper halide alloys. M. Ameri et al. [32] have investigated the ionic transport of $Ag_{1-x}Cu_xI$ using full potential linear muffin-tin orbitals (FP-LMTO). They noted that electronic conductivity of the material varies with copper concentration. The electronic and optical properties, which are important in solids for various aspects, have not been calculated either theoretically or experimentally for $\gamma - Ag_{1-x}Cu_xBr$ in the zincblende structure. The main objective of this study is to present fundamental aspects of $\gamma - Ag_{1-x}Cu_xBr$ employing first principle calculations. The main focus on this calculation is based on electronic structure, density of states (DOS), and optical properties with a minimal discussion of structural properties of the designed compounds.

5.2 Computational method

The electronic configuration of Ag, Cu and Br atom are Ag: $[Kr]4d^{10}5s^1$, Cu: $[Ar]3d^{10}4s^1$ and Br: $[Ar]3d^{10}4s^24p^5$. For the structural minimization, we use GGA as exchange correlation functional for obtaining optimized parameters. For calculating the electronic and optical properties, we use modified Becke-Johnson (TB-mBJ) correlation functional proposed by Tran and Blaha in addition to GGA approach [33-35]. The FP-LAPW method relies on muffin-tin model in the crystal potential. The value of muffin-tin radii (R_{MT}) is calculated at 2.5, 2.5, and 2.48 a.u. in Ag, Cu, and Br respectively. The energy which defines the core and valance state separation is set at -6.0 Ry. The cut-off energy, K_{max} of the plane wave is measured at $R_{MT} \times K_{max} = 7$, which defines the size of the matrix. Where, R_{MT} represents the smallest radius in the muffin tin sphere, and K_{max} limits the largest k vector on expansion of plane wave. The input parameter is set at $l_{max}=10$, which defines the maximum angular momentum in the expansion of wave function within atomic sphere and $G_{max} = 12 \text{ (a.u.)}^{-1}$, defines the Fourier expansion of charge density and potential. These parameters providing an accurate functioning and maintenance in computational time. In the present study, all calculations are carried out

on a $2 \times 2 \times 2$ supercell of γ -AgBr and γ -CuBr, which consists of 32 positions of cation (Ag^+/Cu^+ ions) and 32 for anions (Br^- ions). We implemented a computational approach in our investigation such that for every substitution of Ag with Cu in AgI (or Cu with Ag in CuBr), we accomplished a corresponding identical configuration. We execute self-consistent calculations on all these configurations to ensure total energy of the configuration within 0.00001 Ry. of a stable state. The stable configuration of $\gamma - Ag_{1-x}Cu_xBr$ corresponding to a minimal energy obtained from self-consistent calculations has been chosen for electronic structure calculation.

5.3 Results and discussions

5.3.1 Structural properties

The pure AgBr compound is considered as a starting material and is modelled in its zincblende phase (space group #216, $F\bar{4}3m$) with its experimental lattice parameter [36-39]. Before conducting computational calculations, we have modelled a $2 \times 2 \times 2$ supercell structure of the original AgBr crystal to enable appropriate substitutions. The cubic AgBr has lattice constant 6.63 Å, with Ag and Br atoms situated at (0, 0, 0) and (1/4, 1/4, 1/4) respectively. The supercells of the compound have been constructed for the doping compositions $x = 0.00, 0.03125, 0.0625, 0.09375, 0.125, 0.15625, 0.1875, 0.25, 0.5, 0.75$, and 1 by substituting Ag atoms with Cu atoms in $Ag_{1-x}Cu_xBr$. For $x = 0.03125, 0.09375, 0.125, 0.15625, 0.25$, and 0.75 , each calculated crystal structure corresponds to a 64-atom cubic lattice (space group #215, $P\bar{4}3m$). And, for $x = 0.0625$ and 0.1875 , we obtain a cubic lattice (space group #217, $I\bar{4}3m$), except for $x = 0.5$ (space group #111, $P\bar{4}2m$), and $x = 0.875$ (space group #216, $F\bar{4}3m$). The structural parameters of AgBr, CuBr, and their ternary alloys in the cubic structure is first obtained by using the FP-LAPW method.

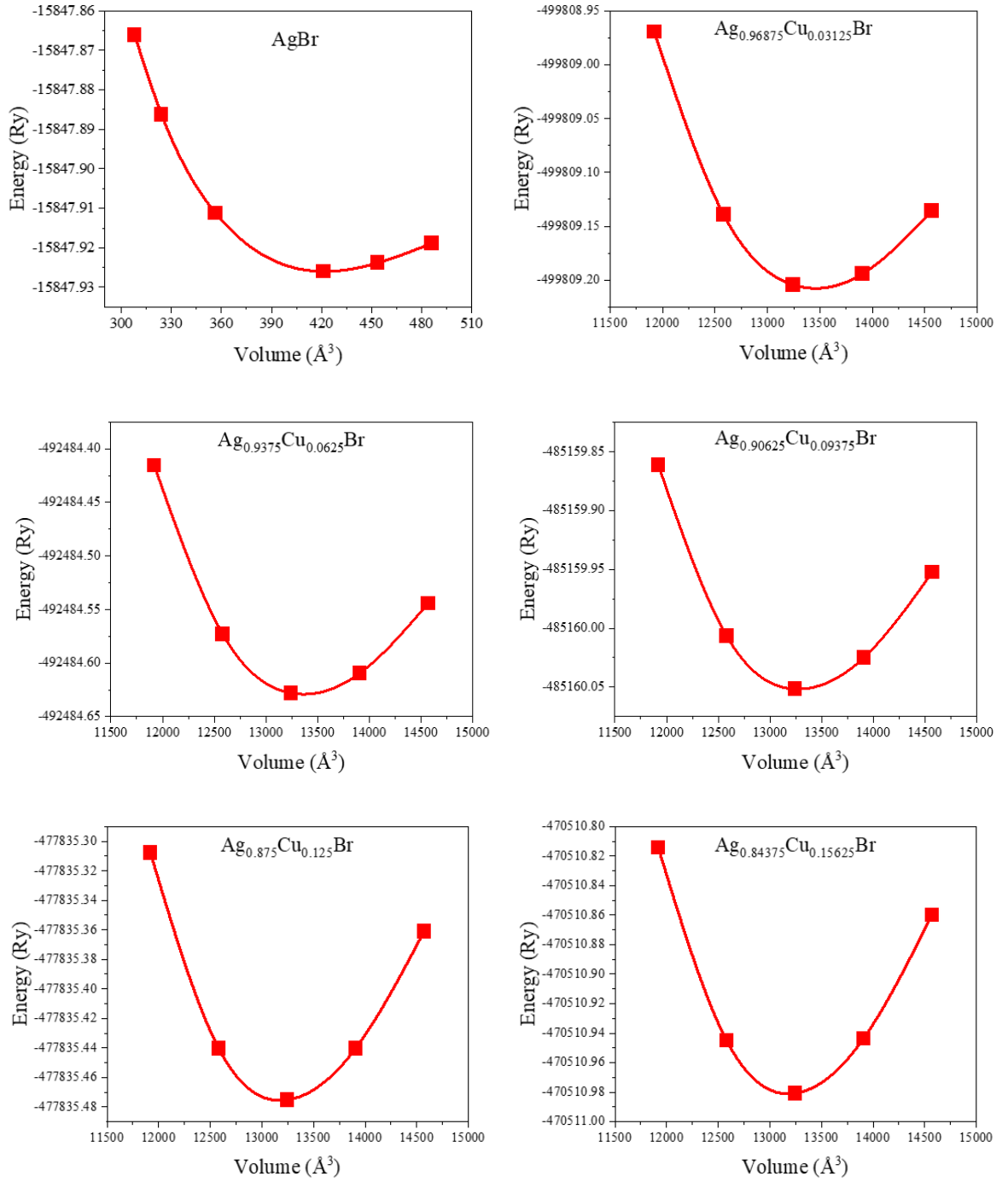


Figure 5.1: Birch Murnaghan equation of state plots for $\gamma - Ag_{1-x}Cu_xBr$ for $x = 0.00 - 0.15625$.

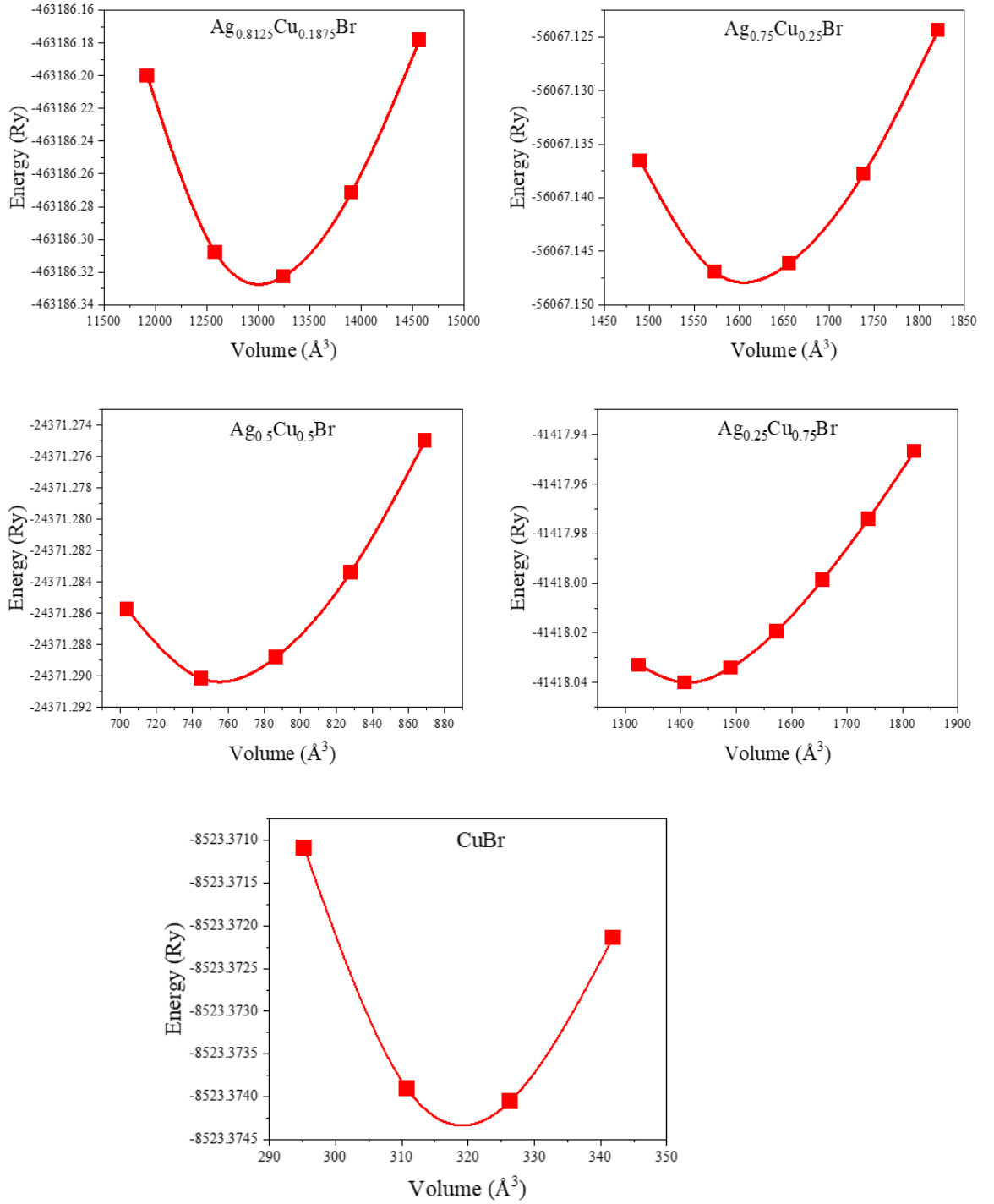


Figure 5.1: Birch Murnaghan equation of state plots for $\gamma - Ag_{1-x}Cu_xBr$ for $x = 0.1875 - 1.00$

In order to determine the equilibrium parameters, all atoms are required to reconfigured within the structure by applying the appropriate forces. A total of 64 atoms, 32 cations and 32 anions present in the crystal structure. We determine the structural minimization for each of these created structures by considering the total energy of the crystal structure as a function of cell volume for AgBr, CuBr and $Ag_{1-x}Cu_xBr$ alloys. **Figure 5.1** shows the fit of Birch Murnaghan equation of $\gamma - Ag_{1-x}Cu_xBr$ ($x = 0.00 - 1.00$). The ground state properties of these compounds were calculated by fitting the computed total energy to the Birch-Murnaghan's equation [40-41].

Table 5.1: Calculated lattice parameter a and bulk modulus B compared to experimental and theoretical works of $\gamma - AgBr$, $\gamma - CuBr$ and $\gamma - Cu_xAg_{1-x}Br$ compounds.

x	Lattice constant a (Å)			Bulk modulus B (GPa)		
	Our work	Expt.	Theoretical	Our work	Expt.	Theoretical
0	6.31	-	6.33[37]	28.025	-	37.910[6]
0.03125	6.29	-	-	28.817	-	-
0.0625	6.28	-	-	29.375	-	-
0.09375	6.26	-	-	29.930	-	-
0.125	6.25	-	-	30.467	-	-
0.15625	6.25	-	-	31.153	-	-
0.1875	6.23	-	-	31.584	-	-
0.25	6.19	-	-	32.630	-	-
0.5	6.12	-	-	34.178	-	-
0.75	5.93	-	-	38.756	-	-
1	5.74	5.677[36]	-	44.771	-	-

The number in the square brackets represents the reference number.

The calculated values of the lattice parameters vary slightly, which is compatible with the computational technique and their general behaviours. It is observed that the predicted lattice parameters of AgBr are larger than those of CuBr. As both these compounds include the same anion atom, the results are easily explained using the atomic radius of the Ag and Cu atoms. Ag and Cu have atomic radii of 1.60Å and 1.35Å, respectively, hence the lattice parameter decreases as the size of the cation atom decreases. In addition, AgBr has a lower bulk modulus (B) than CuBr. The relationship between lattice parameters and bulk modulus follows an inverse sequence to the optimal volume of the cell, i.e., the calculated values of bulk modulus (B) increase as the lattice constants (a) decrease from AgBr to CuBr, implying that the compressibility of AgBr to CuBr decreases. In the analysis of ternary compounds, it is assumed that the atoms occupy their respective lattice sites within the lattice structure. The lattice parameters exhibit a linear change in response to the doping of Cu concentration on AgBr, in accordance with theoretical Vegard's law [42]. The calculated optimized lattice parameters and bulk modulus with doping concentration x are presented in the **Table 5.1**. The calculated values of optimized lattice parameters for the ternary $Ag_{1-x}Cu_xBr$ alloy demonstrate a clear correlation with Vegard's law [42]. As the doping concentration x (Cu) increases, the lattice constants of ternary alloys $Ag_{1-x}Cu_xBr$ decrease, attributed mainly for smaller atomic size of Cu in comparison to Ag atom. The calculated values are closely matched with those obtained with FP-LAPW approach [21] on a unit cell calculation.

5.3.2 Electronic structure

To fabricate efficient semiconductor devices, it is essential to understand the band structure of a compound and its energy band gap. To achieve this, we evaluate the electronic band structure of $\gamma - Ag_{1-x}Cu_xBr$ by incorporating the exchange and correlation potentials, GGA and TB-mBJ parameterization approach. The energy band structures of $\gamma - Ag_{1-x}Cu_xBr$ for Cu concentrations $x = 0.00 - 1.00$ are displayed in **Figure 5.2** and **Figure 5.3**. A direct energy gap (Γ - Γ) at the irreducible Brillouin zone (IBZ) has been noticed from the predicted band structures of $\gamma -$

$Ag_{1-x}Cu_xBr$ compounds. Using the GGA approach, we found that the energy band gap for AgBr and CuBr is 1.094 eV and 0.413 eV, respectively. The difference in energy values at the Γ -points in the first BZ is significantly smaller than the experimentally calculated values. The band structures of $Ag_{1-x}Cu_xBr$ compounds, which identically show a direct energy band gap, are produced by gradually substituting one or more Cu atoms for Ag in the $2 \times 2 \times 2$ supercell of AgBr.

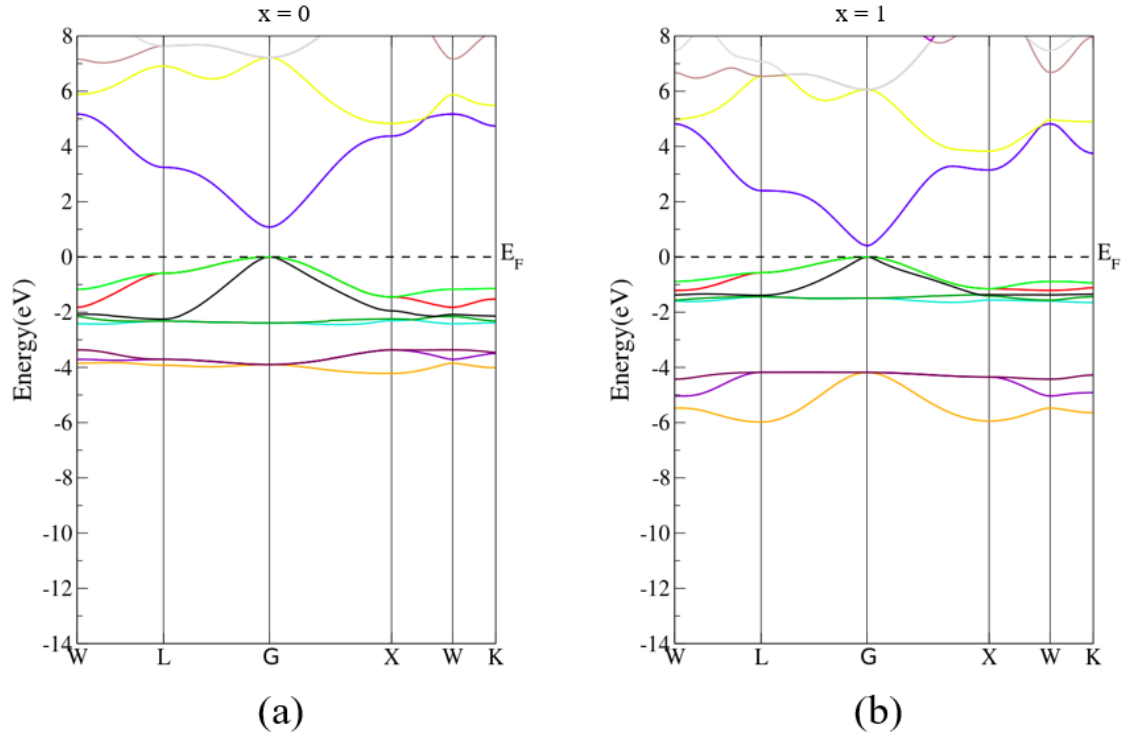
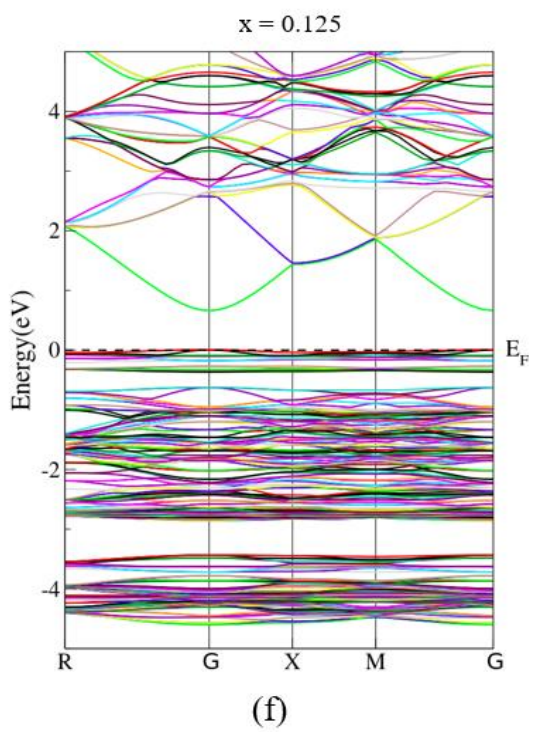
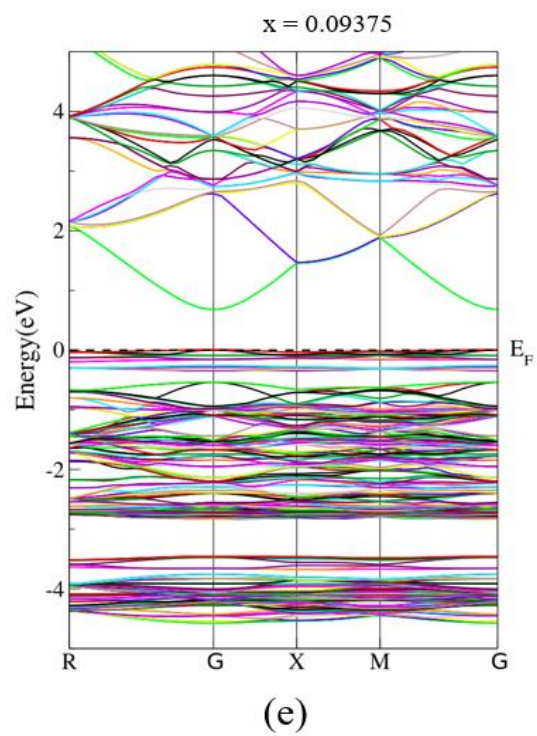
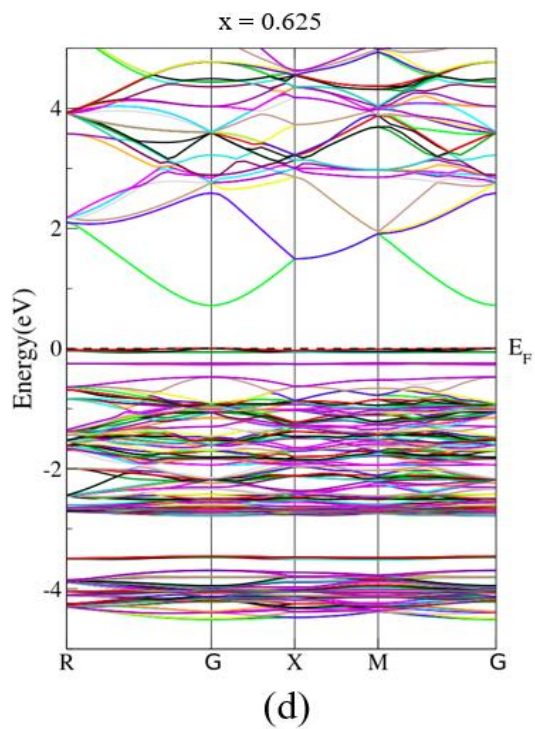
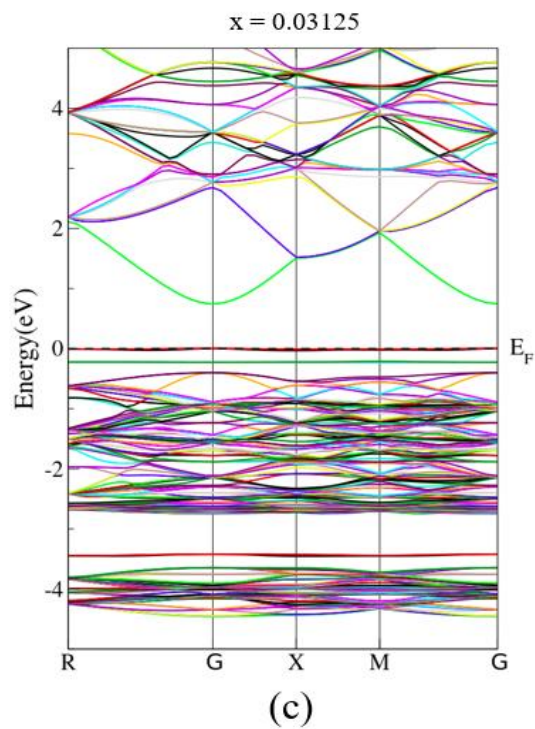
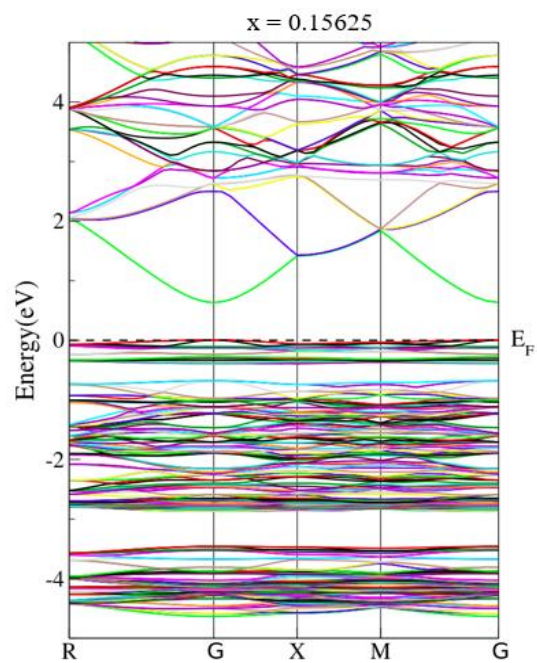
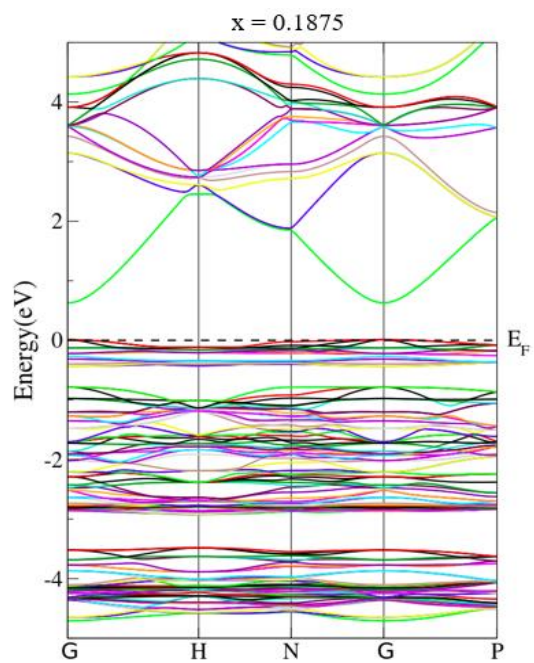


Figure 5.2(a-b): Band structure of (a) γ -AgBr, and (b) γ -CuBr obtained using GGA potential.

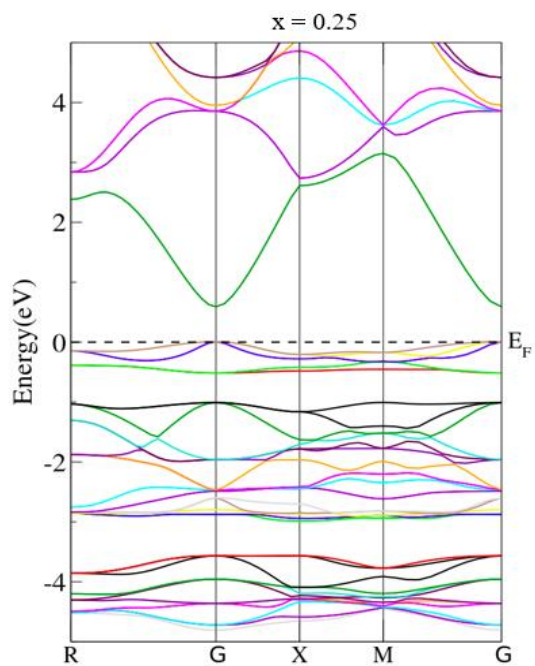




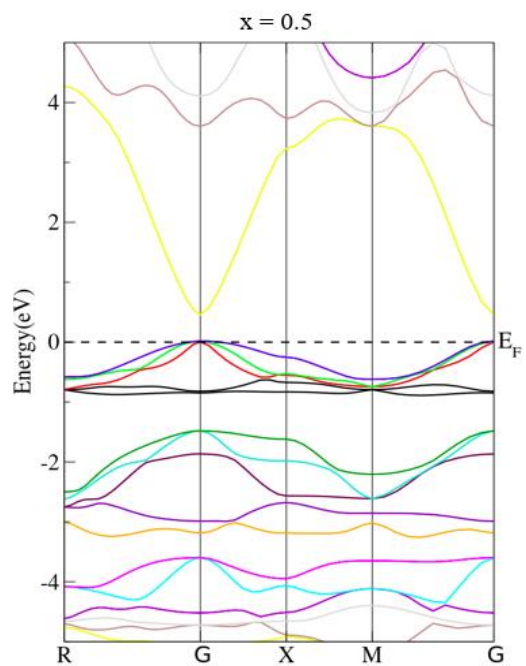
(g)



(h)



(i)



(j)

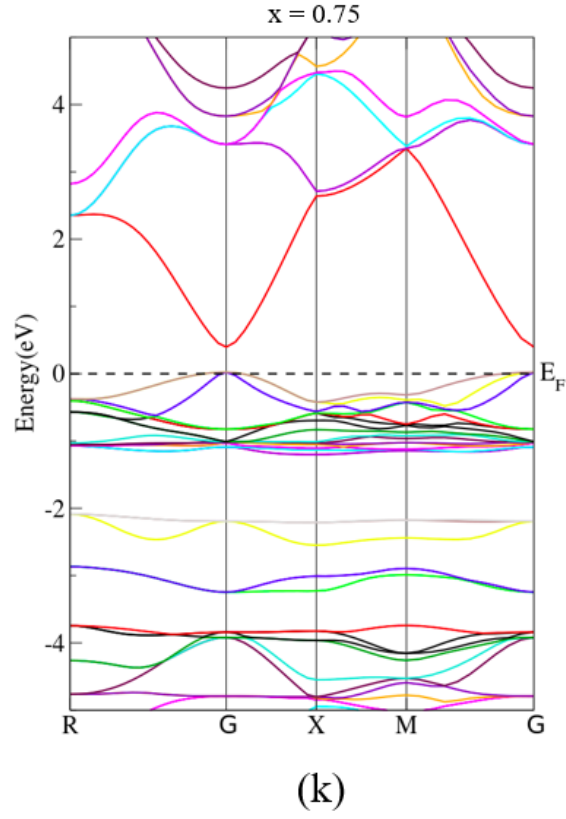


Figure 5.2(c-k): Band structure of $\gamma - Ag_{1-x}Cu_xBr$ for (c) $x = 0.03125$, (d) $x = 0.0625$, (e) $x = 0.09375$, (f) $x = 0.125$, (g) $x = 0.15625$, (h) $x = 0.1875$, (i) $x = 0.25$, (j) $x = 0.5$, and (k) $x = 0.75$ obtained using GGA potential.

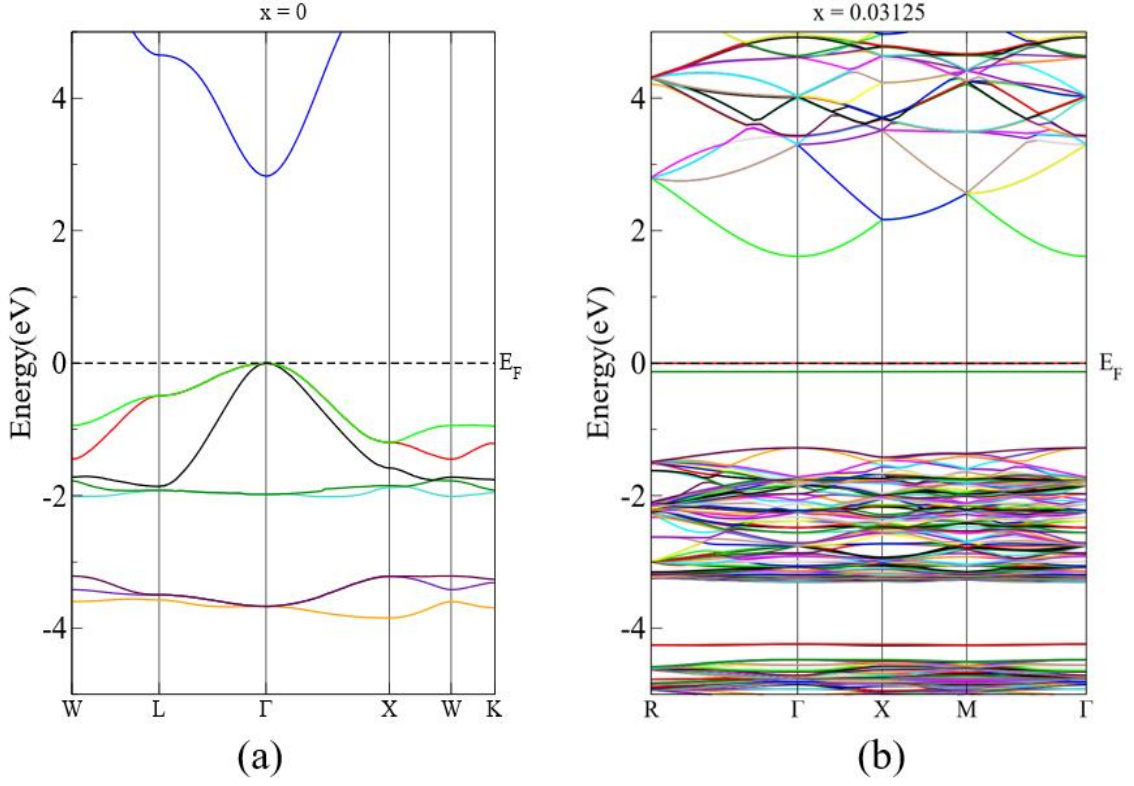


Figure 5.3(a-b): Band structure of $\gamma - Ag_{1-x}Cu_xBr$ for (a) $x = 0.00$, (b) $x = 0.03125$, obtained using TB-mBJ functional.

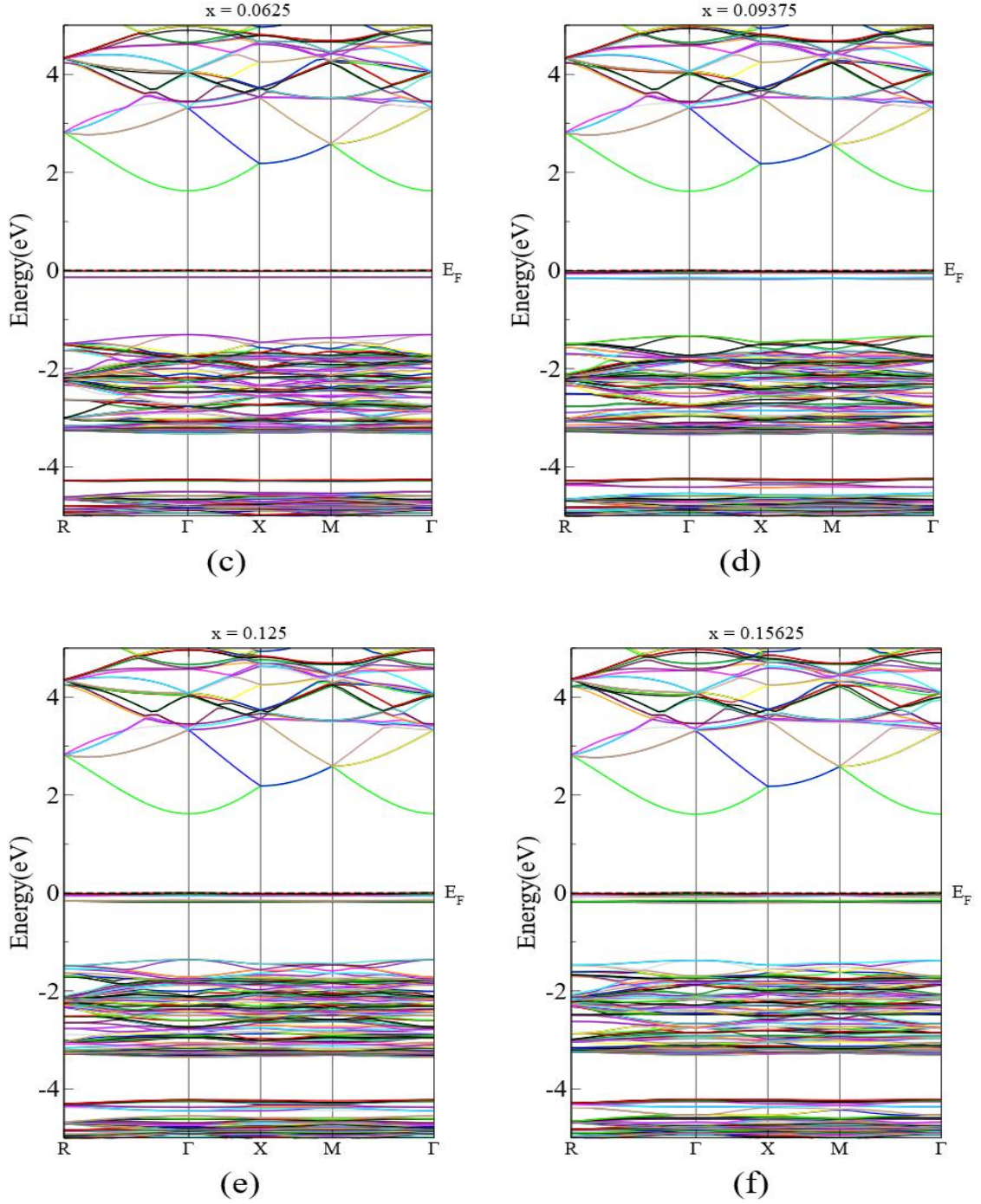


Figure 5.3(c-f): Band structure of $\gamma - Ag_{1-x}Cu_xBr$ for (c) $x = 0.0625$, (d) $x = 0.09375$, (e) $x = 0.125$, (f) $x = 0.15625$, obtained using TB-mBJ functional.

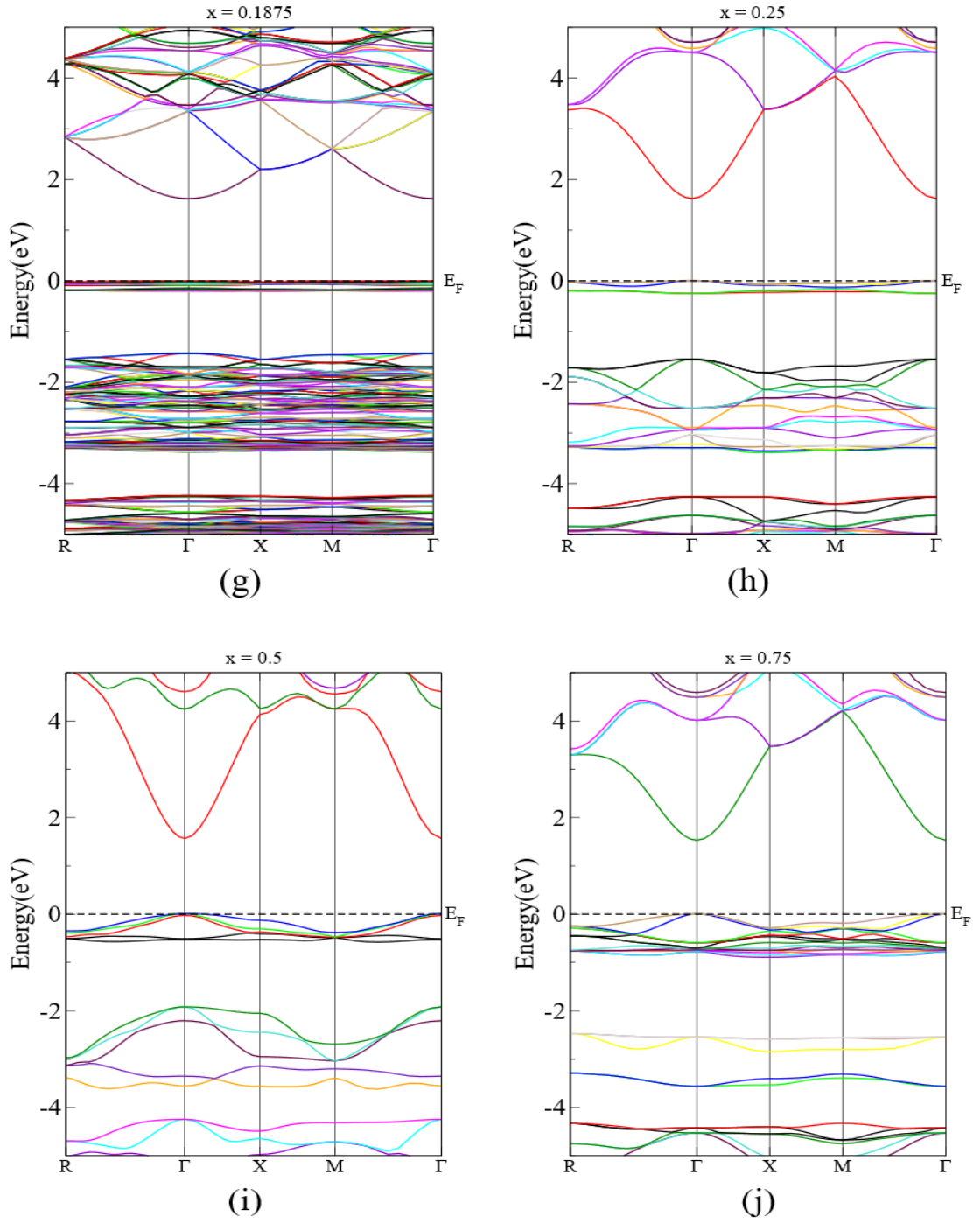


Figure 5.3(g-j): Band structure of $\gamma - Ag_{1-x}Cu_xBr$ for (g) $x = 0.1875$, (h) $x = 0.25$, (i) $x = 0.5$, and (j) $x = 0.75$, obtained using TB-mBJ functional.

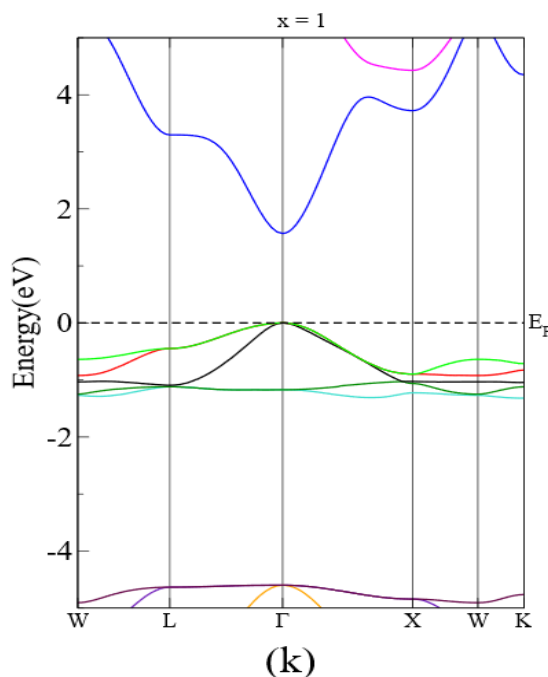


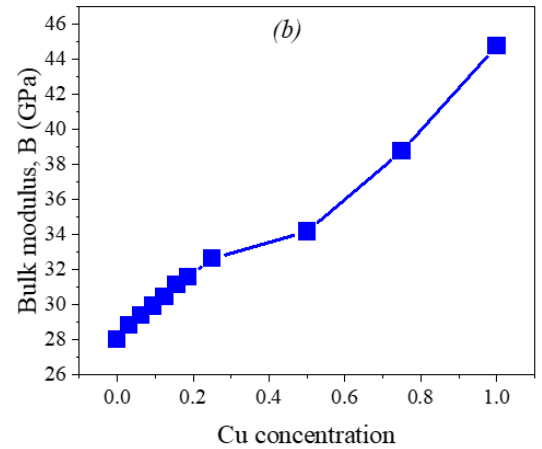
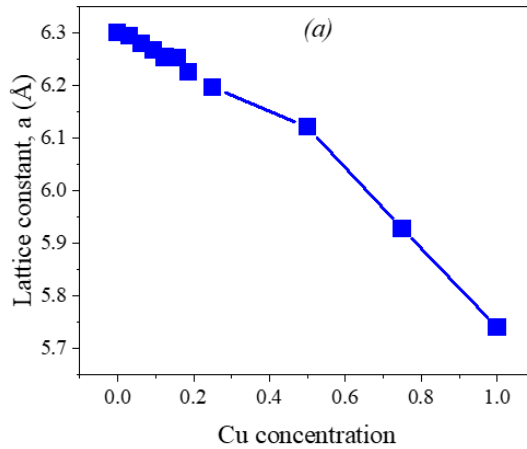
Figure 5.3(k): Band structure of $\gamma - Ag_{1-x}Cu_xBr$ for (k) $x = 1.00$ obtained using TB-mBJ functional.

To achieve improved results for energy gap, we employ the TB-mBJ potential developed by Tran and Blaha. The calculated band gap values of $Ag_{1-x}Cu_xBr$ compounds are mentioned in the **Table 5.2**. The calculated energy gap for AgBr and CuBr are estimated to be 2.823 eV and 1.569 eV, while using TB-mBJ method. The band gap values are matching closely with previously reported values [21]. In this scheme, the valance and conduction bands are separated from one another which lead to a direct band gap at high symmetry Γ - point. The improved estimation of band gap provided the enhanced potential of d-states with TB-mBJ potential. A minimal variation in energy band gap values may arise from inconsistencies in the muffin-tin radii at outer orbital, leading to an underestimating of bandwidth due to electronic dispersion [31].

Table 5.2: Direct band gap energy of $\gamma - AgBr$, $\gamma - CuBr$ and $\gamma - Cu_xAg_{1-x}Br$ alloys with various Cu concentration.

	$E_g(eV)$			
x	Our work		Experiment	Other calculations
	GGA	TB-mBJ		
0	1.094	2.823	2.713[38]	2.886[6], 2.40[16]
0.03125	0.870	1.747	-	-
0.0625	0.840	1.718	-	-
0.09375	0.812	1.701	-	-
0.125	0.792	1.699	-	-
0.15625	0.768	1.695	-	-
0.1875	0.760	1.690	-	-
0.25	0.730	1.701	-	-
0.50	0.725	1.705	-	-
0.75	0.714	1.627	-	-
1	0.413	1.569	3.07[39]	0.44, 1.32[16]

The number in the square brackets represents the reference number.



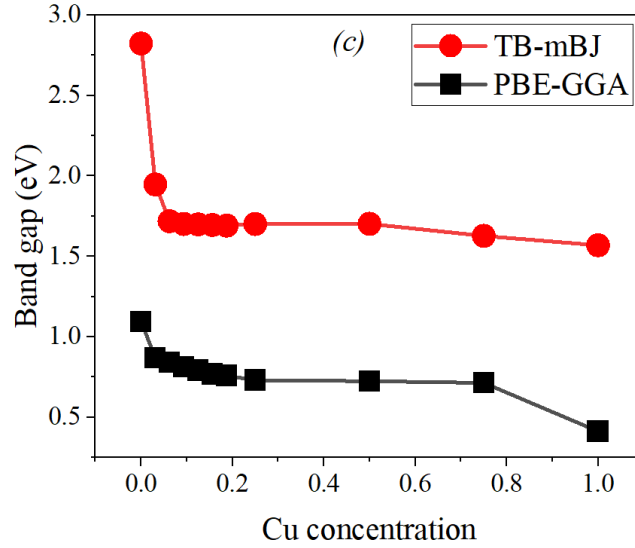


Figure 5.4: Variation of (a) lattice constant, (b) Bulk modulus, and (c) Band gap with Cu concentration in $\gamma - Ag_{1-x}Cu_xBr$ ($x = 0.00 - 1.00$)

The lower band gap results are due to the confined adaptability of the correlation energy functional in GGA framework. The estimated band structure profile of $\gamma - Ag_{1-x}Cu_xBr$ using GGA and mBJ schemes are comparable with the exception of higher band gap values in TB-mBJ exchange correlation potential. The computed energy gaps derived from the TB-mBJ methodology shows a correlation with the experimentally calculated values. A slight decrease in energy gap arises on CuBr due to its poor convergence of the computational analysis while using GGA with TB-mBJ potential which results from the irrelevant expansion of correlation energy. The primary cause for the inadequate representation of electronic structure of CuBr is the difficulties in defining the localized electronic states in the correlation functional. The electronic dispersion bandwidth may be underestimated as a result of improper muffin-tin radii (R_{MT}) for outer orbital, which would explain the differences between experimental and computational measurements. The band structure indicates that the electronic states are displaced from one another and

no electronic states touches the fermi level. **Figure 5.4** illustrates the changes in the lattice parameter (a), bulk modulus (B), and energy gap of $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{Br}$. The data indicates a nonlinear relationship between the band gap and Cu composition (x) in $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{Br}$ compounds, as illustrated in **Figure 5.4(c)**. The computed energy band gap of $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{Br}$ applying both GGA and TB-mBJ correlation potentials have presented in the **Table 5.2**, demonstrating a consistency with previous experimental and theoretical work. The limited flexibility of quasiparticle self-energy resulting an inaccurate estimation of correlation energy in a computational calculation. The observed discrepancy between computational and experimental results is predicted, as the contribution of lattice vibration at absolute zero temperature in the crystal is minimal [42]. The current estimated energy band gap values appear to be slightly underestimated, with the absence of spin-orbit coupling effect.

5.3.3 Density of states

The details regarding the origin of atoms for many electronic states that are exists in the electronic structure can be obtained through the idea of DOS of a material [14-15]. The calculated atom orbital-projected DOS using TB-mBJ method in $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{Br}$ (x = 0.00 – 1.00) is shown in **Figure 5.5 – 5.15**. Based on the TB-mBJ calculation, the DOS projected between -4.588 to 6.786 eV in AgBr, and -6.870 to 6.789 eV in case of CuBr, with fermi level considered as the measuring energy source. It has been noticed that, the starting valence region is embedded from -3.962 to 3.254 eV in AgBr, and -6.244 to -4.530 eV in CuBr. The region is generated mainly with the presence of p states of Br and d states of Ag/Cu. The second region is lies within -2.220 to 0.037 eV in AgBr and -1.319 to 0.068 in CuBr. This region is mainly due to Ag/Cu-d with a little contribution of Br-p states. In the last conduction band region, the DOS lies between 3.167 to 6.323 eV for AgBr, and 1.946 to 6.463 eV in CuBr with a minor peak height, arising specifically due to the contribution of Br-p states with the Ag/Cu-d states. However, the band gap in pure AgBr and Cu-doped AgBr is very different, computed with the GGA and TB-mBJ schemes at the Γ -point only. The observed reduction in the doping

concentration of Cu correlates with a notable change in the band gap between conduction and valence band.

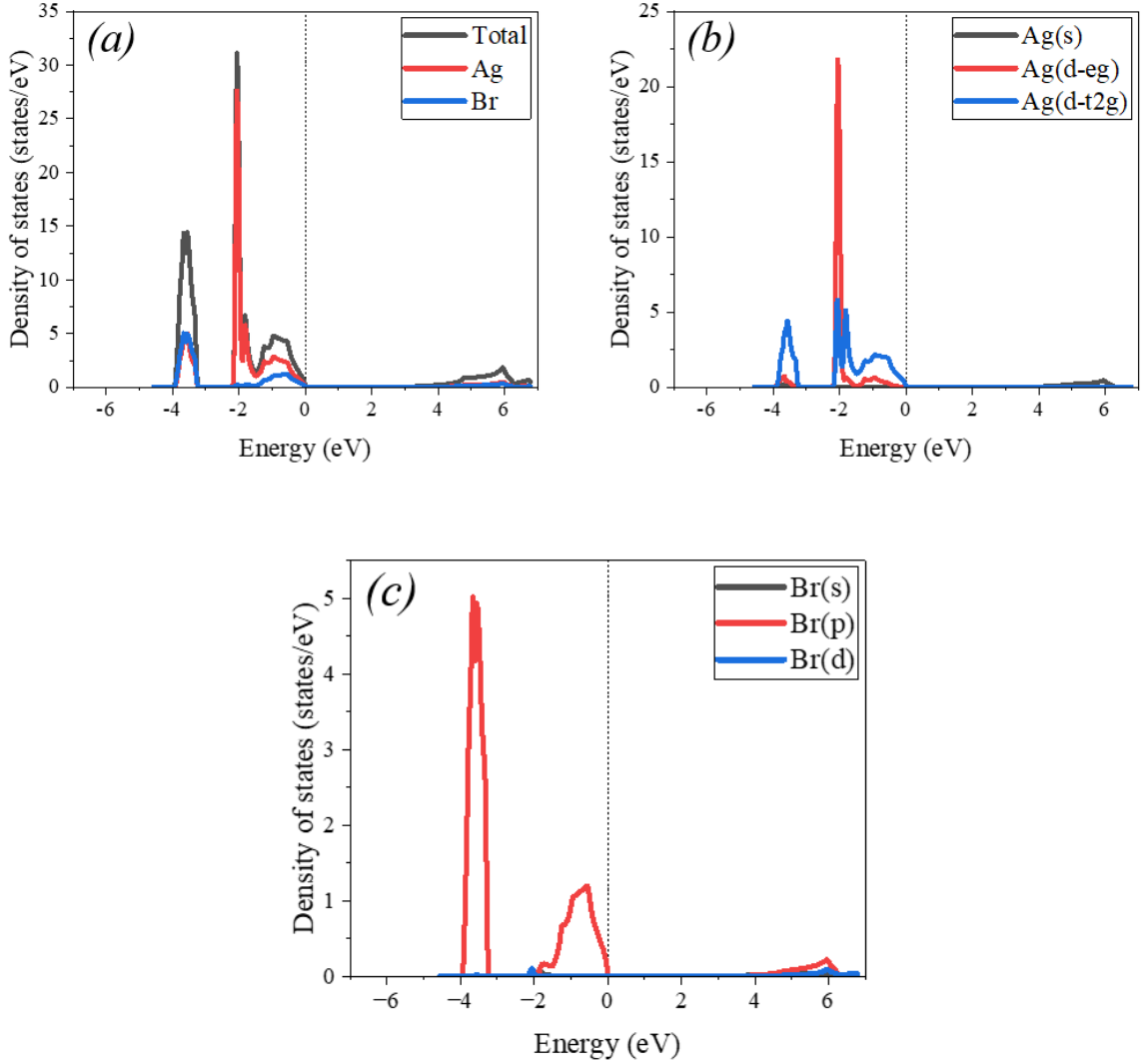


Figure 5.5: (a) Density of states of AgBr-total, Ag-total and Br-total, (b) Partial density of states Ag (p, d-eg and d-t2g), and (c) Partial density of states of Br (s, p and d) in γ -AgBr obtained using TB-mBJ functional.

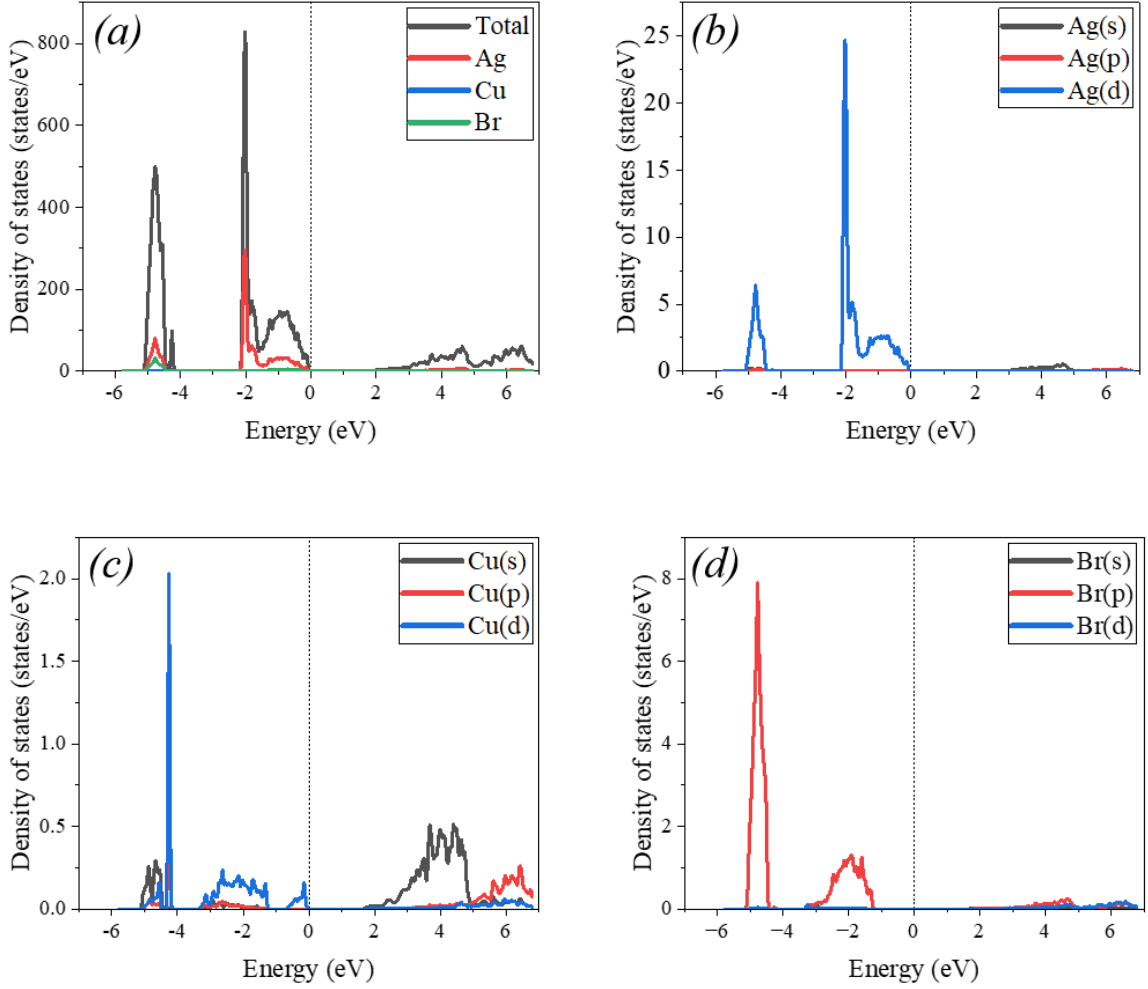


Figure 5.6: (a) Density of states of $\gamma - Ag_{0.96875}Cu_{0.03125}Br$ -total, Ag-total, Cu-total and Br-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of Br (s, p and d) in $\gamma - Ag_{0.96875}Cu_{0.03125}Br$ obtained using TB-mBJ functional.

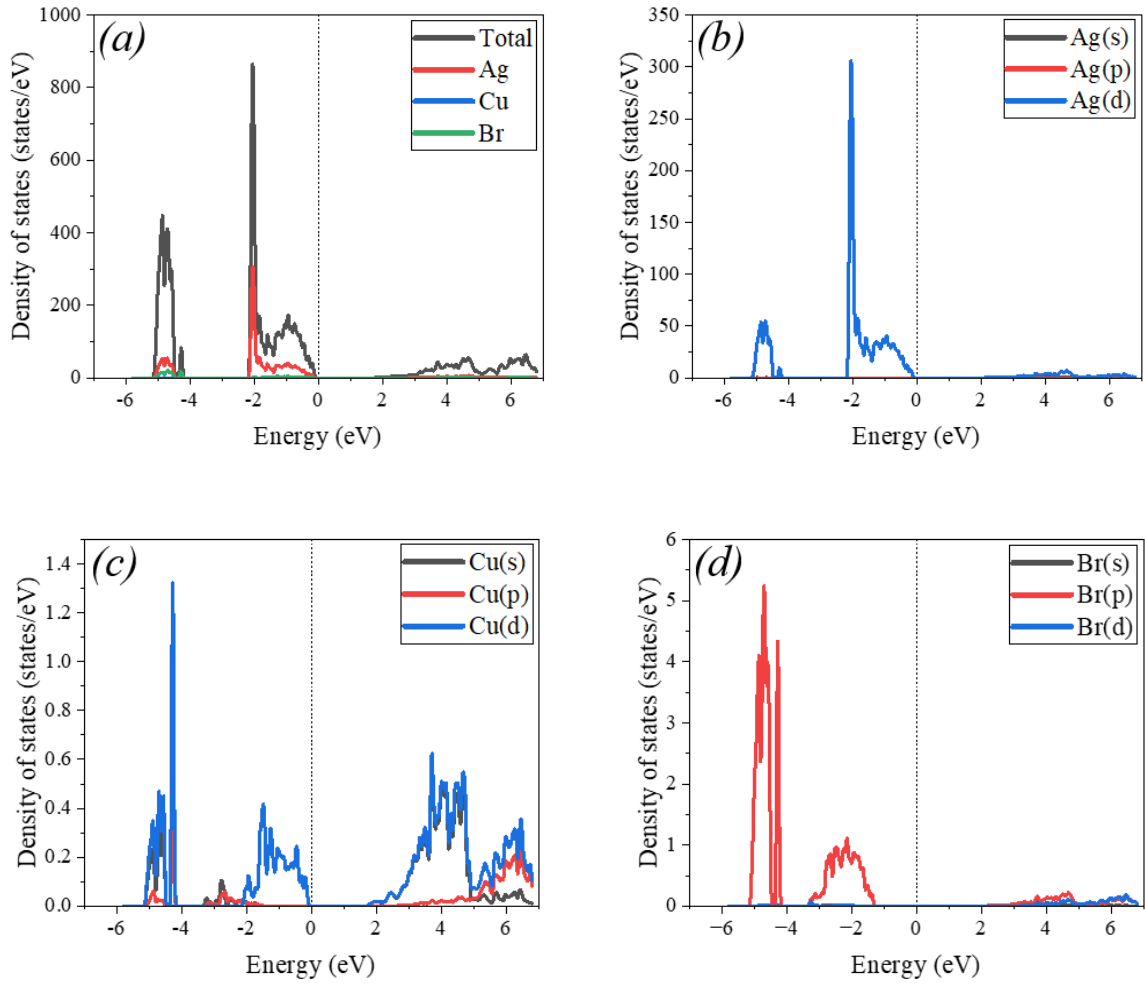


Figure 5.7: (a) Density of states of $\gamma - Ag_{0.9375}Cu_{0.0625}Br$ -total, Ag-total, Cu-total and Br-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of Br (s, p and d) in $\gamma - Ag_{0.9375}Cu_{0.0625}Br$ obtained using TB-mBJ functional.

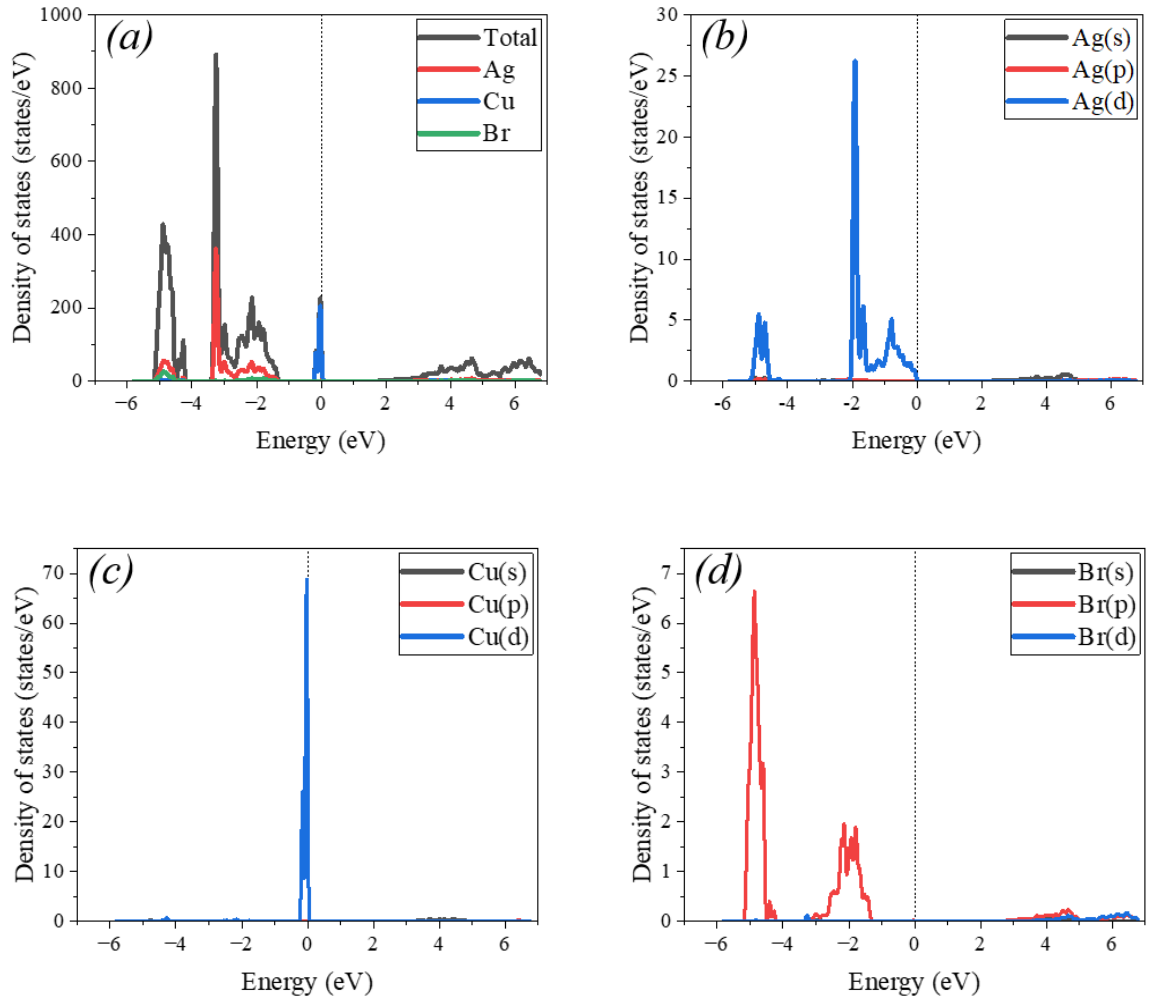


Figure 5.8: (a) Density of states of $\gamma - Ag_{0.90625}Cu_{0.09375}Br$ -total, Ag-total, Cu-total and Br-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of Br (s, p and d) in $\gamma - Ag_{0.90625}Cu_{0.09375}Br$ obtained using TB-mBJ functional.

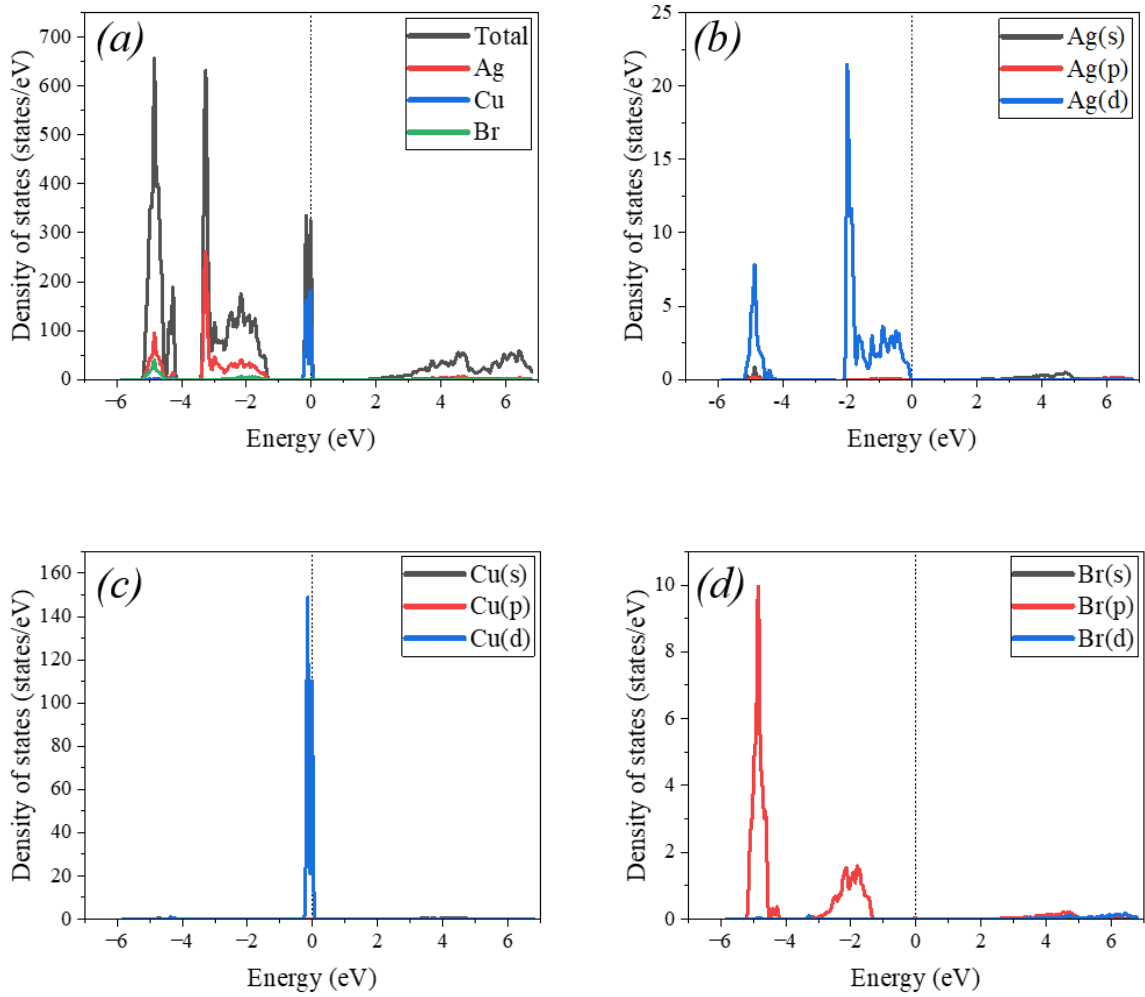


Figure 5.9: (a) Density of states of $\gamma - Ag_{0.875}Cu_{0.125}Br$ -total, Ag-total, Cu-total and Br-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of Br (s, p and d) in $\gamma - Ag_{0.875}Cu_{0.125}Br$ obtained using TB-mBJ functional.

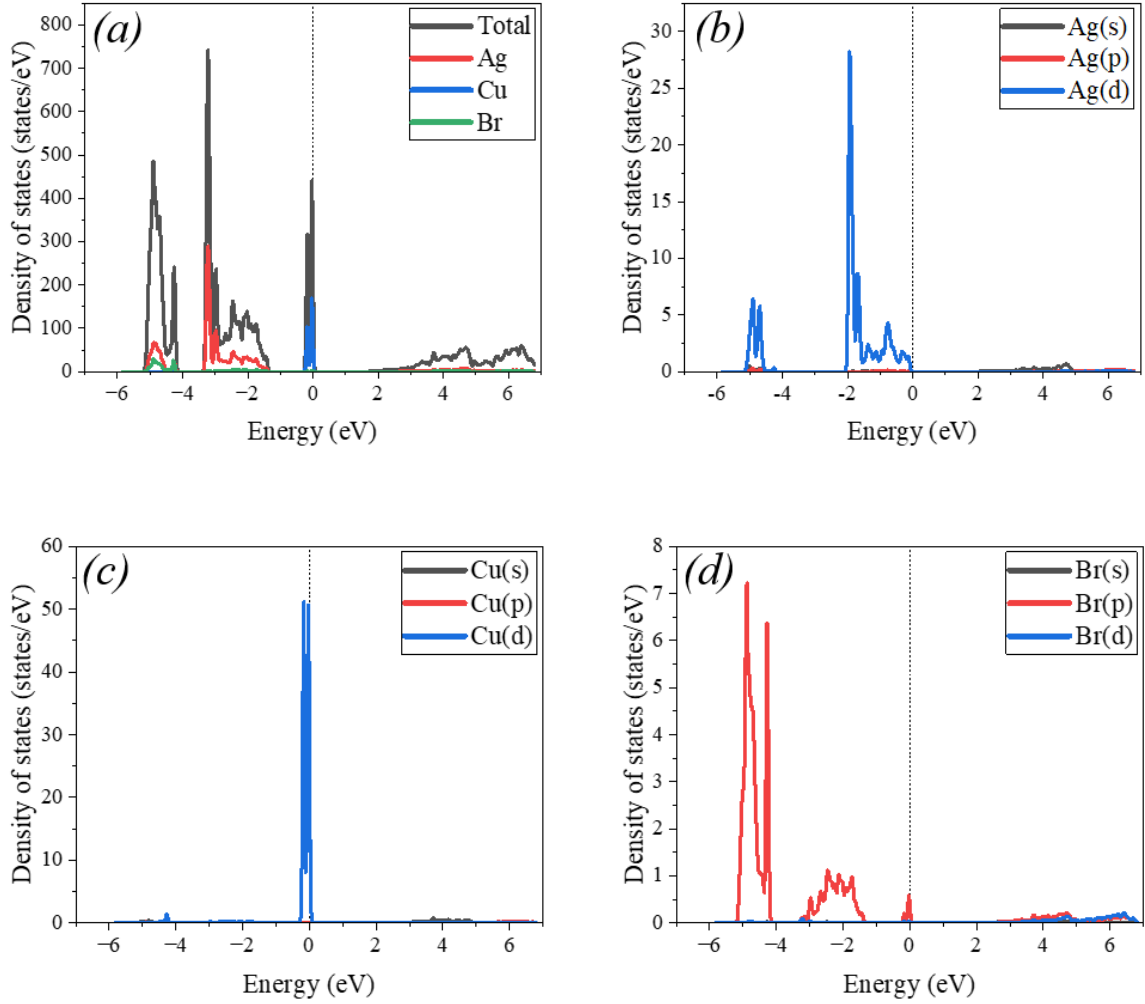


Figure 5.10: (a) Density of states of $\gamma - Ag_{0.84375}Cu_{0.15625}Br$ -total, Ag-total, Cu-total and Br-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of Br (s, p and d) in $\gamma - Ag_{0.84375}Cu_{0.15625}Br$ obtained using TB-mBJ functional.

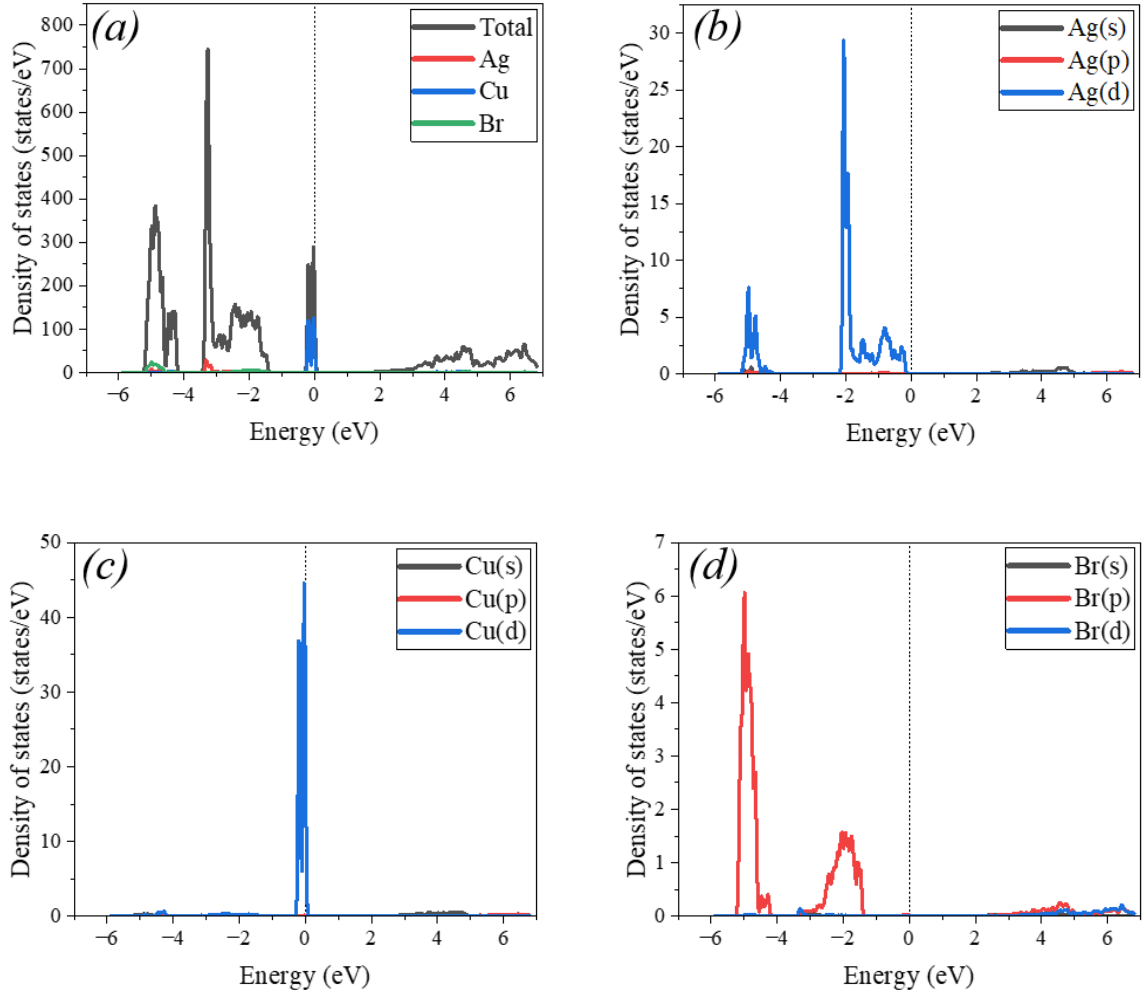


Figure 5.11: (a) Density of states of $\gamma - Ag_{0.8125}Cu_{0.1875}Br$ -total, Ag-total, Cu-total and Br-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of Br (s, p and d) in $\gamma - Ag_{0.8125}Cu_{0.1875}Br$ obtained using TB-mBJ functional.

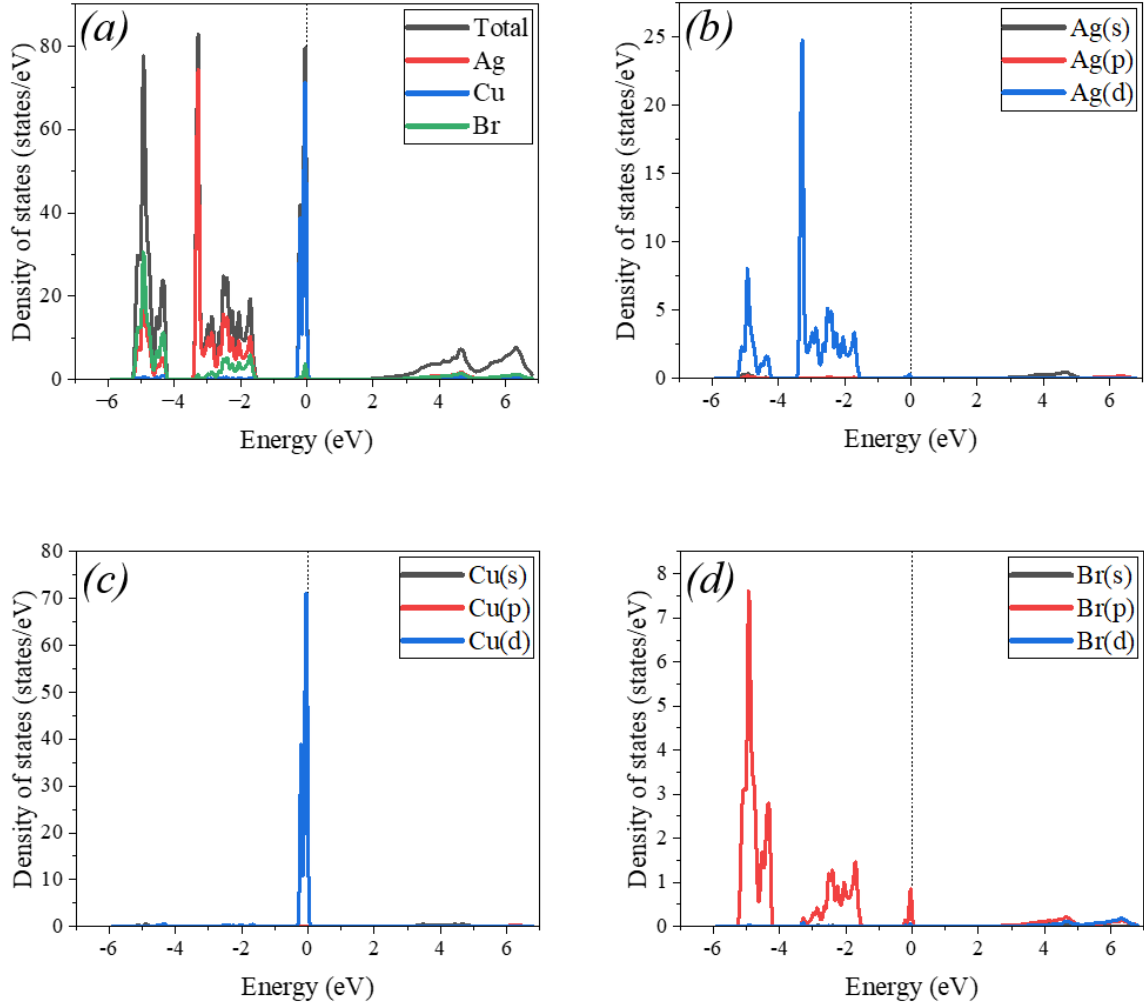


Figure 5.12: (a) Density of states of $\gamma - Ag_{0.75}Cu_{0.25}Br$ -total, Ag-total, Cu-total and Br-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of Br (s, p and d) in $\gamma - Ag_{0.75}Cu_{0.25}Br$ obtained using TB-mBJ functional.

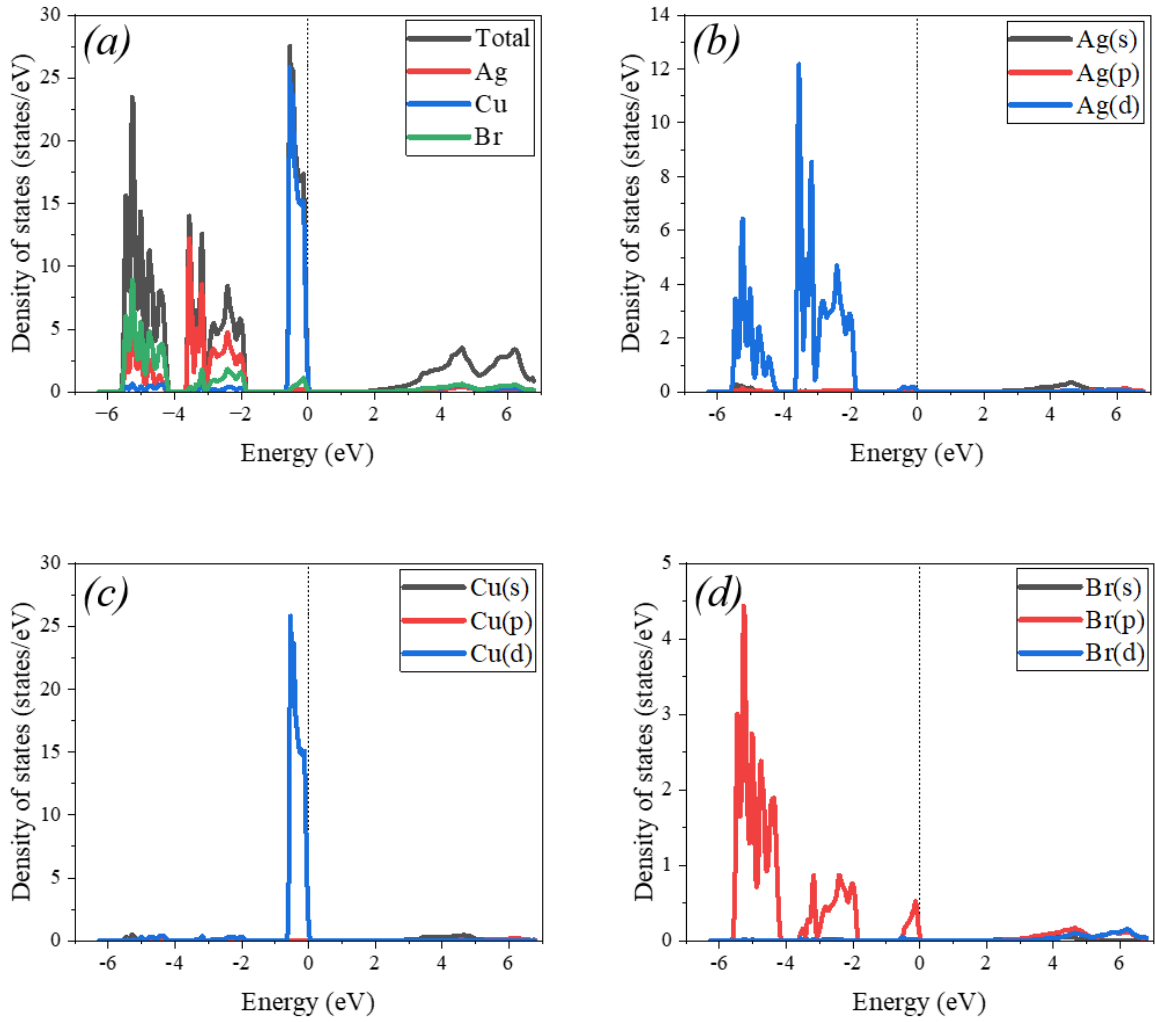


Figure 5.13: (a) Density of states of $\gamma - Ag_{0.5}Cu_{0.5}Br$ -total, Ag-total, Cu-total and Br-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of Br (s, p and d) in $\gamma - Ag_{0.5}Cu_{0.5}Br$ obtained using TB-mBJ functional.

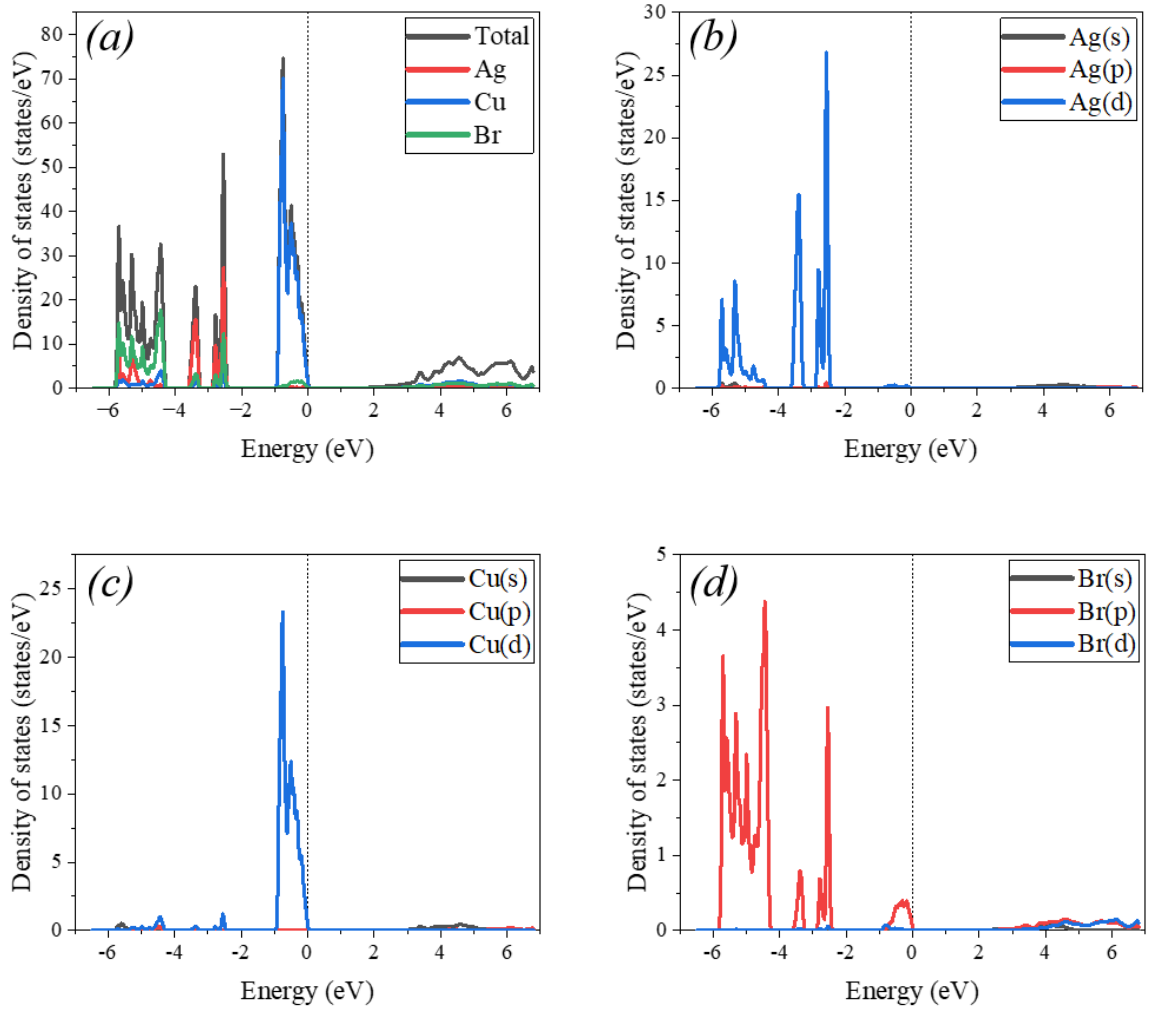


Figure 5.14: (a) Density of states of $\gamma - Ag_{0.25}Cu_{0.75}Br$ -total, Ag-total, Cu-total and Br-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of Br (s, p and d) in $\gamma - Ag_{0.25}Cu_{0.75}Br$ obtained using TB-mBJ functional.

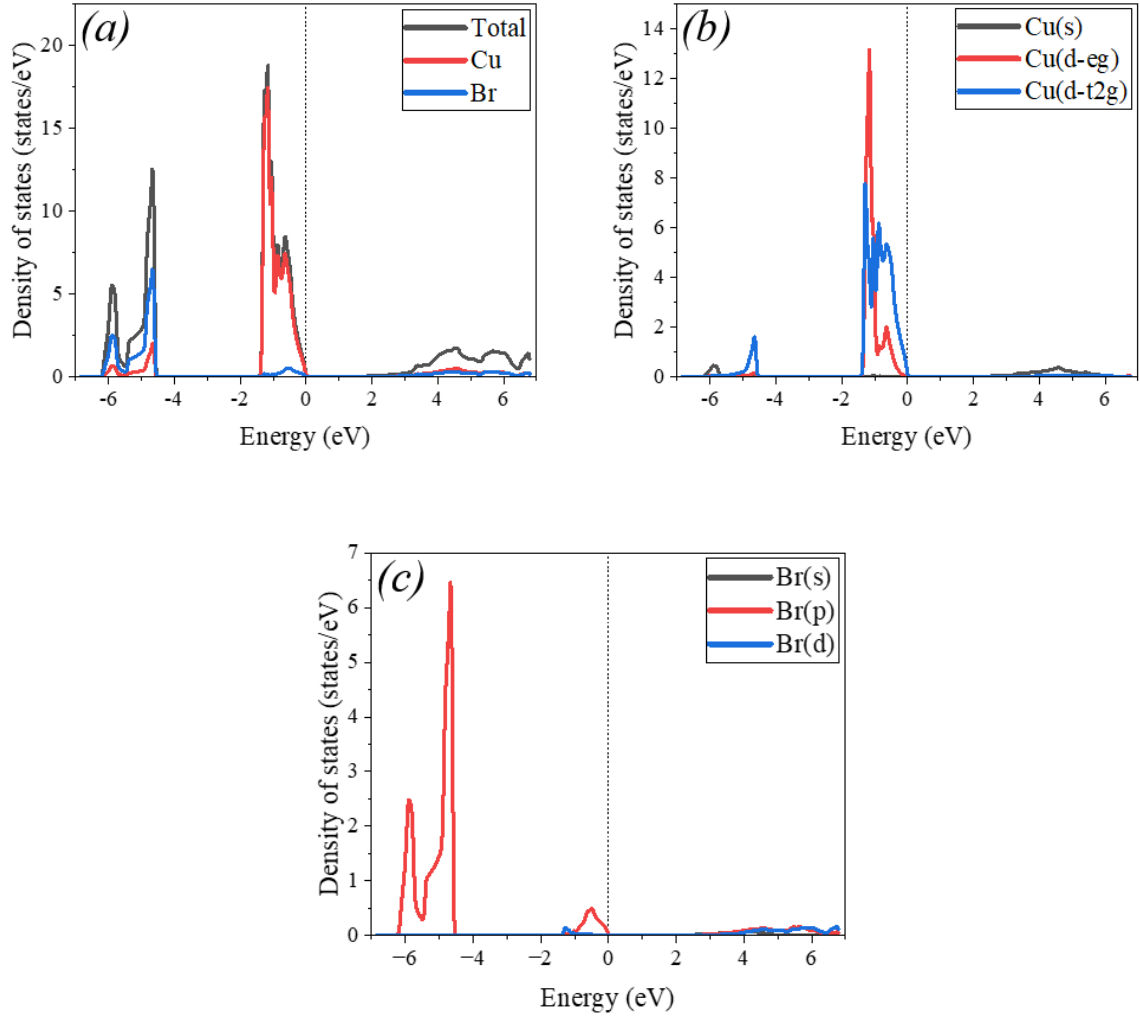


Figure 5.15: (a) Density of states of γ -CuBr-total, Cu-total and Br-total, (b) Partial density of states of Cu (s, d-eg and d-t2g), and (c) Partial density of states of Br (s, p and d) in γ -CuBr obtained using TB-mBJ functional.

Consequently, the band gap values lying between 1.094 eV to 0.413 eV by employing the GGA method. The band gap values ranging from 2.823 eV to 1.569 eV while using the TB-mBJ potential. The doping of Cu atom in AgBr does not significantly affecting the properties of the material. The DOS pattern remains symmetric in the hybridized d-p states of Ag/Cu and Br. It is noted from the DOS, the d-bands in Ag-Cu-Br system show

an expansion when compared to those of Ag and Cu atoms. The extension of d-bands within alloys exhibits an increase in magnitude corresponding to the atomic concentrations in Ag and Cu. The upper edge of d-bands in $\gamma - Ag_{1-x}Cu_xBr$ alloys approaches the Fermi level, embedded at approximately -1.6 eV, just below the Fermi level, which closely resembles that of a pure Cu atom and exceeds that of a pure Ag atom (≈ 1.0 eV). Furthermore, it has been noted that the d-sp hybridized states expands close to Fermi level as the composition of Cu is increased. Consequently, the transition rates of the d-sp band increase. Based on the concept of inter-intra band transition, the aforementioned transitions providing a mismatching behaviour of these atoms which may slightly modify the energy distribution of the alloy systems. To investigate the actual characteristics of electronic structure, we calculate the atom orbital contribution for Ag, Cu, and $Ag_{1-x}Cu_xBr$ system. Some of the changes in DOS have been found in the energy range that occurs between -5.126 and 0.101 eVs. In the energy range close to the Fermi level, the DOS undergoes a slight modification. As the percentage of copper is increased, the size of the d-band is gradually expanding. It is important to note that the restricting value of the lower and higher d-band lines are located within the Cu and Ag atoms, respectively. The broadening of the d-band in Ag-Cu-Br alloys is explained by the hybridization of d-orbital of silver and copper atoms, as demonstrated by a detailed investigation of PDOS for the d-orbital of their respective atoms. As the concentration of copper increases, the height of the d-bands of both silver and copper rises. The decreased structural volume in $Ag_{1-x}Cu_xBr$ alloys is the cause of the changes that occur in the electronic band structures. Because of the higher atomic radius in Ag compared to Cu, substitution of Ag by Cu atoms leads to a reduction in the volume of Ag-Cu-Br alloys. The band structure of a crystal can be conceptually elucidated using TDOS and PDOS. The TDOS indicates that the shifting of valance band towards the Fermi level when the cation concentration varies from 0.00 to 1.00 in the Ag-Cu-Br system.

5.3.4 Optical properties

Optical properties of a material are important since it is employed in a wide variety of optoelectronic devices. The optical properties of a material are caused by the incident light photon, which produces a response of electronic system to a perturbing system. In this aspect, dielectric functions are the fundamental parameter that describe a response of a material. The optical spectra of solids are solely determined by the band transition of atoms. The approach of calculating optical characteristics are mainly based on the joint density of states defined by the dipole matrix [43]. The optical parameters are calculated based on dielectric function of the materials, represented as $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, where $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are real and the imaginary part of dielectric constants [43-45]. We have studied various features on $\gamma - Ag_{1-x}Cu_xBr$ ($x = 0.00 - 1.00$) system in its zincblende phase, such as dielectric function, refractive index, absorption coefficient, optical conductivity, extinction coefficient, and loss function.

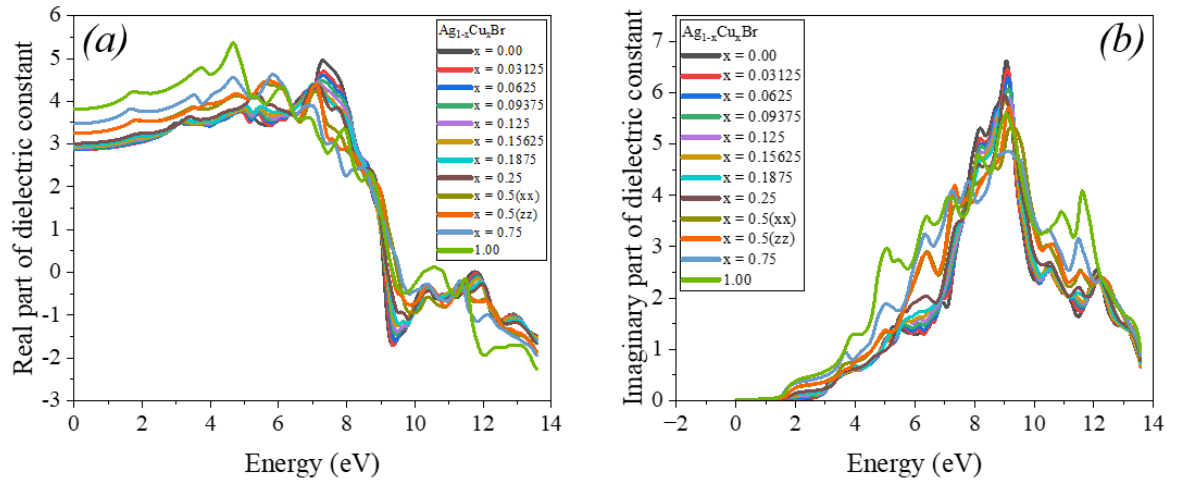


Figure 5.16(a – b): Variation of (a) Real part of dielectric constant, and (b) Imaginary part of dielectric constant for $\gamma - Ag_{1-x}Cu_xBr$ using TB-mBJ functional.

Table 5.3: Calculated values of zero-frequency limits in $\varepsilon_1(0)$, $n(0)$ and $R(0)$ spectra and threshold values in $\varepsilon_2(\omega)$, $k(\omega)$, $\alpha(\omega)$ and $\sigma(\omega)$ spectra in $\gamma - Ag_{1-x}Cu_xBr$ using TB-mBJ functional.

Compound	Zero-frequency limits			Threshold values (eV)			
	$\varepsilon_1(0)$	$n(0)$	$R(0)$	$\varepsilon_2(\omega)$	$k(\omega)$	$\alpha(\omega)$	$\sigma(\omega)$
<i>AgBr</i>	2.888	1.699	0.067	2.816	2.925	2.979	2.925
<i>Ag_{0.96875}Cu_{0.03125}Br</i>	2.869	1.694	0.066	2.843	2.979	3.006	3.006
<i>Ag_{0.9375}Cu_{0.0625}Br</i>	2.880	1.697	0.067	2.789	3.006	3.034	3.006
<i>Ag_{0.90625}Cu_{0.09375}Br</i>	2.902	1.703	0.068	2.517	2.979	3.061	3.006
<i>Ag_{0.875}Cu_{0.125}Br</i>	2.925	1.710	0.069	2.190	2.952	3.088	3.034
<i>Ag_{0.84375}Cu_{0.15625}Br</i>	2.939	1.714	0.069	1.891	2.843	3.115	3.006
<i>Ag_{0.8125}Cu_{0.1875}Br</i>	2.969	1.723	0.071	1.836	2.734	3.142	2.952
<i>Ag_{0.75}Cu_{0.25}Br</i>	3.014	1.736	0.072	1.836	2.108	3.224	2.680
<i>Ag_{0.5}Cu_{0.5}Br(xx)</i>	3.251	1.803	0.082	1.700	1.809	3.224	2.087
<i>Ag_{0.5}Cu_{0.5}Br(zz)</i>	3.253	1.804	0.082	1.727	1.836	3.360	1.972
<i>Ag_{0.25}Cu_{0.75}Br</i>	3.476	1.864	0.091	1.537	1.646	3.333	1.809
<i>CuBr</i>	3.810	1.952	0.104	1.564	1.700	3.278	1.836

The parameters that determine the frequency-dependent dielectric functions mainly consist of electron wave functions and eigenvalues. The real component indicates that the material exhibits dielectric behaviour at $\varepsilon_r(\omega) > 0$ up to a photon energy. However, at $\varepsilon_r(\omega) < 0$, beyond its energy range, it exhibits metallic characteristics. The limiting value of the $\varepsilon_r(\omega)$ provides the static dielectric constant, denoted as $\varepsilon_r(\omega) = 0$. The real part $\varepsilon_1(\omega)$ is associated with the band structure of materials, which reveal the absorptive

capacity. Multiple peaks are observed at the inter-band transitions within materials at different energy ranges. These peaks move towards higher energy regions. The highest peak observed at maximum intensity is approximately 7.0957 eV in the TB-mBJ method. Therefore, the material has the potential to function as a filter in the ultraviolet-visible region for a broad range of energies.

Figure 5.16(a-b) depicts the variation dielectric function of the $\gamma - Ag_{1-x}Cu_xBr$ ($x = 0.00 - 1.00$) with energy in eV. **Figure 5.16(a)** shows the obtained real part of the complex dielectric function $\epsilon_1(\omega)$. The dielectric constant of the materials displays a multiple peak pattern for all compound and reaches its minimum value. The decreasing trend of real dielectric constants towards negative values demonstrates the reflectivity of metallic compounds. The compounds can be served as a radiation detector, and a radiation shield within the energy window. The values of static dielectric constant of $\gamma - Ag_{1-x}Cu_xBr$ are listed in the **Table 5.3**. The higher value of static dielectric constants suggests that the material has high value of refractive index and thus high optical density. Figure 5.16(b) shows how the imaginary part $\epsilon_2(\omega)$ of dielectric function varies with photon energy. The threshold energy values are listed in **Table 5.3** with their corresponding Cu concentration. Furthermore, we have seen that the imaginary dielectric function rises with an increase in energy right after the threshold energy value, reaching peaks that correspond to their respective energy values. The highest peak values of $\gamma - Ag_{1-x}Cu_xBr$ occur at 7.8611, 7.8030, 7.4428, 7.0477, 7.0476, 6.9665, 6.0929, and 7.0512, which correspond to the energy values 7.4695, 7.4969, 7.5783, 7.6872, 7.6871, 7.5783, 7.8504, and 7.3062 eV, respectively.

Figure 5.16(c) displays the variation of refractive index $n(\omega)$ with photon energy. The data reveals a multiple peak, attributed to various interband transitions, analogous to the dielectric character. A minimum value is reached at higher energy levels, suggesting a loss of transparency in the material at the higher energy values. The **Figure 5.16(c)** illustrates that the refractive index of the material increases with an increasing energy of incident photon. After reaching a maximum value of 4.693 eV, the value decreases with an increase in photon energy, attributed to stronger electronic interactions with photons in this region. The value of refractive index $n(\omega)$ at zero-energy is called static

refractive index $n(0)$. The values of $n(0)$ have shown in **Table 5.3**. **Figure 5.16(d)** illustrates the variations of extinction coefficients as a function of energy. The extinction coefficient of a material correlates with the absorption of incident light. It quantifies the extent to which a substance can absorb a particular quantity of incident light at a specific wavelength. The highest peaks are observed at 1.971, 1.972, 1.920, 1.831, 1.911, 1.831, 1.835, and 1.810, with corresponding energy values of 8.180, 8.151, 8.425, 8.646, 8.386, 8.153, 8.617, and 7.410 eV, respectively.

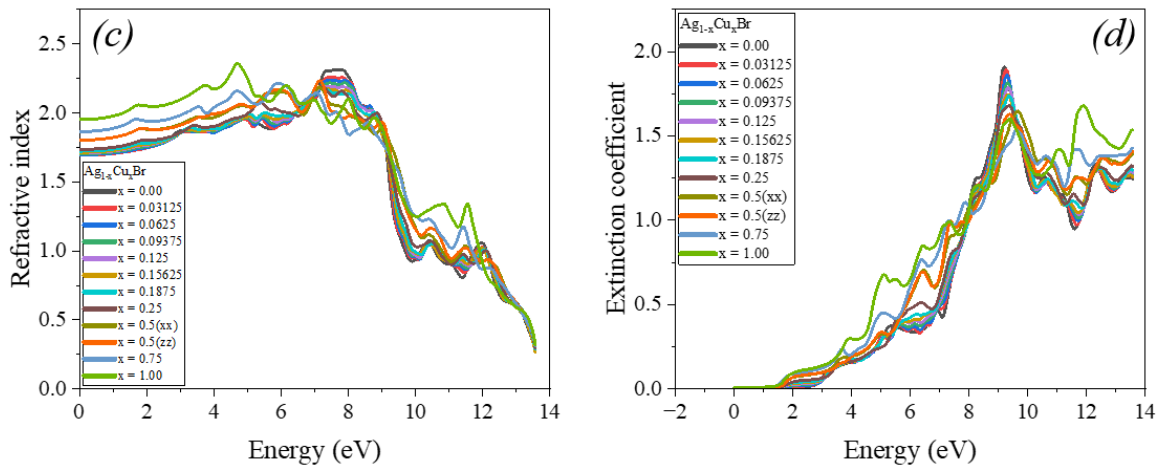


Figure 5.16(c – d): Variation of (c) Refractive index, and (d) Extinction coefficient of $\gamma - Ag_{1-x}Cu_xBr$ using TB-mBJ functional.

The extinction coefficient spectrum indicates that higher concentrations of Cu in $\gamma - Ag_{1-x}Cu_xBr$ exhibit more light absorption compared to lower values.

Figure 5.16(e) illustrates the optical conductivity of $\gamma - Ag_{1-x}Cu_xBr$ varies with photon energy. At the critical point of incident energy, conductivity starts to respond to the electric field. We observe that when Cu concentration increases, the critical points in optical conductivity adapt towards lower energy. The critical values of the extinction coefficient are listed in Table 5.3.

Reflectivity is the measure of the energy ratio between incident and reflected photons on the surface of a material. The reflection of light at the surface of a crystalline solid is analysed through the use of reflectivity. The scattering length density (SLD) of different layers related to their structural properties can be inferred from the reflectivity spectra of the materials [38]. **Figure 5.16(f)** demonstrates that the specific Cu concentrations result highest peaks in the reflectivity of these materials within 8 to 9.5 eV. The peaks at various energy values are caused by the interaction of light with free electrons in the substance. The reflectivity decreases between 8.85 and 9.56 eV. The highest energy peaks are at 0.4500, 0.4361, 0.4265, 0.4209, 0.4118, 0.4168, 0.4040, and 0.4363, corresponding to Cu concentrations of 8.4491, 8.4219, 8.5307, 8.7484, 8.3947, 8.7756, 8.6940, and 12.666 eV, respectively. The difference in peak values may be associated with an interband transition for which the incident electron loses a finite amount of energy. In this scenario, the loss of energy results from the extinction of a single electron within the material. The absorption coefficient describes the amount of light absorbed by an optical material. It is also defined as a percentage of the power absorbed per unit length of a medium. **Figure 5.16(g)** depicts the variation of absorption coefficient of $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{Br}$ with energy (eV). When the Cu content is low, the compound exhibits high absorptive power. This means that the compounds will absorb photons with energies higher than the threshold energy. Because of their lower absorption coefficient, compounds behave like transparent materials below the threshold energy. A lower absorption coefficient value implies the highest transmission within this range. As a result, in this range, the compounds can be employed in a variety of optical instruments.

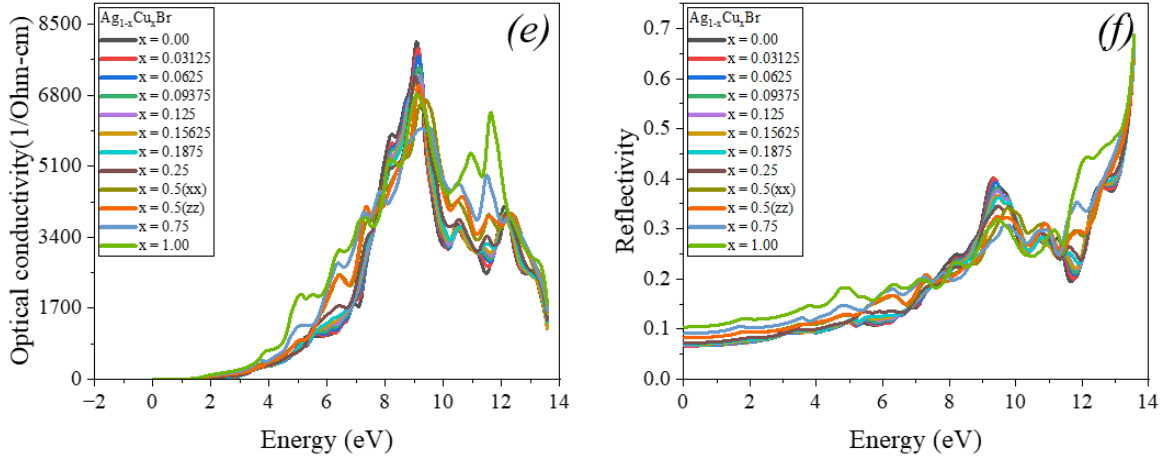


Figure 5.16(e – f): Variation of (e) Optical conductivity, and (f) Reflectivity of $\gamma - Ag_{1-x}Cu_xBr$ using TB-mBJ functional.

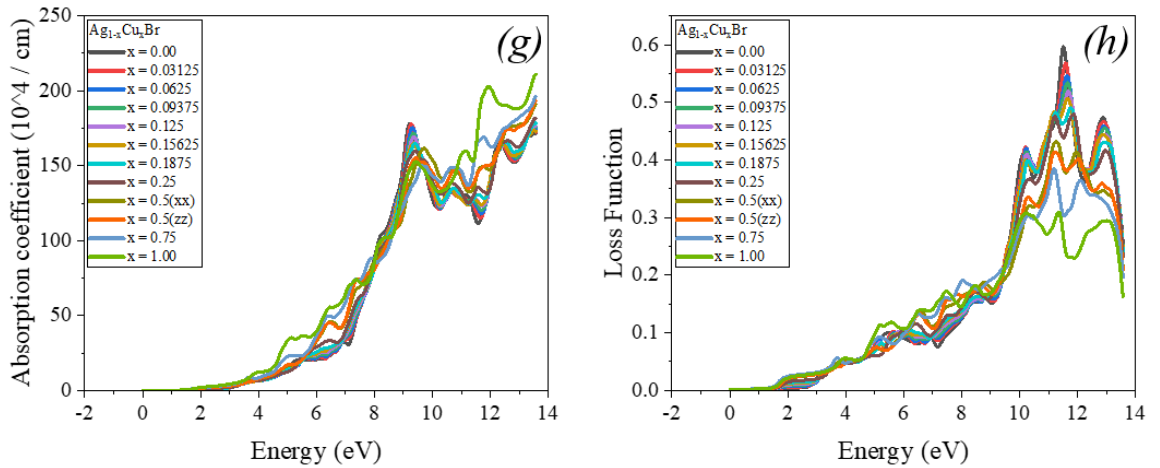


Figure 5.16(g – h): Variation of (g) Absorption coefficient, and (h) Energy loss of $\gamma - Ag_{1-x}Cu_xBr$ using TB-mBJ functional.

Figure 5.16(h) displays the variation of energy loss function with the incident photon energy. Below the threshold energy, the plot is almost entirely flat. As a result, a gap exists on the energy axis, which represents the electronic interband transition at a low

frequency. The greatest peaks for their respective Cu concentrations occur at energies of 12.612, 12.600, 12.664, 12.911, 12.666, 12.694, 12.830, and 12.840 eV, occurring at 0.731, 0.730, 0.689, 0.629, 0.627, 0.674, 0.574, and 0.505, respectively. $\gamma - Ag_{1-x}Cu_xBr$ has the highest peak at $x = 0.03125$ and 0.0625 , and the lowest peak at $x = 0.75$. The energy loss function shows two significant peaks for $\gamma - Ag_{1-x}Cu_xBr$ at $x = 0.03125 - 0.5$ compounds. This significant peak in the energy loss function suggests a typical coupling with plasma resonance. The associated frequency is known as the plasma frequency. Above this frequency, the material behaves like a dielectric, and below it behaves like a solid.

5.4 Conclusions

In conclusion, the first principle calculations using the FP-LAPW approach successfully determined the electronic structure of $\gamma - Ag_{1-x}Cu_xBr$ alloys. We assessed various properties such as lattice parameters, bulk modulus, and band gap, all of which depend exclusively on concentration. We have identified these parameters exhibiting nonlinearity with alloy concentration, with the exception of lattice constant and bulk modulus, which adhere to Vegard's law. A direct energy gap has been shown from the computed band structure and DOS calculation. Substitution of copper typically narrows the band gap of AgBr, with the extent of narrowing depending on the copper concentration. The materials are losing their transparency at higher energy levels, indicating that they become transparent at lower energy levels. The low energy $\gamma - Ag_{1-x}Cu_xBr$ materials are primarily useful for the fabrication of many different optical devices. The absorption spectra of $\gamma - Ag_{1-x}Cu_xBr$ materials demonstrate an extra capacity for light absorption when compared to the pure AgBr compound. The incorporation of copper as a dopant results in an expansion of the absorption spectrum, allowing it to extend into the visible and near-infrared regions. This makes the compounds more suitable for various applications, including photocatalysis and devices that are sensitive to light.

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CHAPTER 6

Electronic structure calculations of $\gamma - Ag_{1-x}Cu_xBr$ using HSE06 method

6.1 Introduction

Silver bromide (AgBr) has stronger ionic conductivity than alkali halides due to the occurrence of cation Frenkel defects (silver ion vacancies and interstitials), which differ from Schottky defects (cation and anion vacancies). Copper halides (CuBr) on the other hand, has vacancies, could be a less expensive alternative to silver ion conductors. [1-2]. Band structure modelling on AgBr is critical for calculating their physical and chemical properties due to the existence of 'd' electrons in Ag^+ , and 'p' electrons in Br^- , which leads to significant hybridization [3-5]. Self-consistent band structure calculations on AgCl and AgBr demonstrate the variations of electronic features with the percentage of atoms in the halogens. Through this process, the forbidden gap between d-p states of metals halides become broadened. The closer the conduction band bottom, the smaller the energy band gap [6-9]. Group IB-VIIA materials are becoming more important due to their potential uses in microcrystals made of this particular compound. Due to the higher binding energy (108 MeV), the materials are characterized by a short-range wavelength that is employed in solar cells. Copper bromide shows the maximum absorption near ultraviolet region of the electromagnetic spectrum [10–11]. The Ag and Cu atoms combine to form diamond-like tetrahedral metal halide structures [12–13]. The study of ionic conductors, including cuprous and silver halides, is of more interest to understand the fundamental concept of semiconductor physics in real world applications [14]. Superionic conductors depict a class of materials defined by their excellent ionic conductivity, are used in various devices such as fuel cells, solid-state batteries, and optical instruments. A simulation study (MD) shows the fundamental features of the superionic phase containing Ag^+ and Cu^+ cations verify the concentration dependency on Ag-Cu-Br system. The structural changes of cations affect the migration of ions in the superionic phase. The Ag^+ and Cu^+ cations created a band surrounding the octahedral

sites inside the system [15-17]. The inherent vacancies in the superionic phase of these materials are the source of ionic conductivity. Silver halides have been studied for their electronic properties, showing ionic conductivity similar to the liquid electrolytes [18]. [19-20]. The study on AgCl and AgBr using the FP-LAPW technique, provided an analytical comparison on optoelectronic properties [21-22]. The calculation of CuCl and CuBr using the FP-LAPW approach reveals the structural change within the zincblende structure, transformed to the rocksalt structure at around 10 GPa pressure [23-24, 8]. Tubandt et al. [25] and coworkers were the first to study that the electrical conductivity of γ -CuBr increases with temperature from 500 to 657 K. M. Ameri et al. [26] studied the ionic transport using full potential linear muffin-tin orbitals (FP-LMTO). However, at higher temperatures, the superionic phase is insufficient to study the electronic and optical properties of Cu-rich AgBr materials. So, to investigate the AgCuBr system in its gamma phase, we do computational calculations on AgBr containing Cu. These properties have not been determined theoretically or empirically within a zincblende phase. The primary goal of this effort is to offer fundamental information on the physical properties through first-principles calculations. This calculation primarily concerns towards band structure, density of states (DOS), and the optical properties.

6.2 Computational method

The electronic configurations of Ag, Cu, and Br atoms are Ag: [Kr]4d¹⁰5s¹, Cu: [Ar]3d¹⁰4s¹ and Br: [Ar]3d¹⁰4s²4p⁵. We used generalized gradient approximation (GGA) as exchange correlation potential for structural minimization and determination of structural parameters within Kohn-Sham equation. To calculate electronic and optical properties, we employed the screened hybrid functional. The parameters were calculated by employing the Heyd-Scuseria-Ernzerhof screened hybrid functional (HSE06) methodology [27, 12] to attain the maximum feasible energy gap with accurate band dispersion as comparison to alternative methods like LDA and GGA [28]. A k-mesh of $10 \times 10 \times 10$ is used for all the calculations. The muffin-tin radii (R_{MT}) for Ag, Cu, and Br is taken to be 2.5, 2.5, and 2.48 a.u., respectively. The separation between the core

and valance states is defined by the cut-off energy, is set at -6.0 Ry. The size of the matrix is defined by cut-off energy of the plane wave, K_{max} , has been measured as $K_{max} = 7/R_{MT}$. The K_{max} restricts the range of biggest k vector through the plane wave expansion, while R_{MT} indicates the minimum muffin tin radius. We also included $G_{max} = 12 (a.u.)^{-1}$ and $l_{max} = 10$ in our present calculation. G_{max} specifies the Fourier expansion of potential and charge density, while l_{max} is the largest angular momentum within atomic sphere. These factors ensured precise operation and maintenance within computational time. All computations are conducted using a $1 \times 1 \times 1$ unit cell of γ -Ag (Cu)Br, which represents 4 atomic locations for each anions and cations (Ag^+/Cu^+ and Br^-). We employed the computational methods of our present calculation to construct a corresponding equivalent configuration for every substitution of Ag with Cu in AgBr. Self-consistent calculations are performed on all comparable configurations to achieve a total energy convergence at 0.00001 Ry, ensuring the stable configuration. The stable configuration of the $1 \times 1 \times 1$ unit cell of $\gamma - Ag_{1-x}Cu_xBr$, corresponding to a minimal energy determined by self-consistent calculations, has chosen for aforementioned properties.

6.3 Results and Discussions

6.3.1 Structural properties

The pure AgBr compound, has been modelled by its experimental lattice parameter in the zincblende structure (γ -phase, space group (#216, $F\bar{4}3m$) [29–30]. To allow for suitable substitutions, we have designed a $1 \times 1 \times 1$ unit cell structure of the AgBr crystal prior to performing our computational calculations. The lattice constant of the cubic AgBr crystal is 6.63 Å, and the positions of the Ag and Br atoms are (0, 0, 0) and (1/4, 1/4, 1/4), respectively. By replacing Ag atoms in $Ag_{1-x}Cu_xBr$ with Cu atoms with doping compositions $x = 0.00, 0.25, 0.5, 0.75$, and 1 for generating the zincblende structure in $Ag_{1-x}Cu_xBr$ alloy. Each calculated crystal structure for the selected substitution concentration results in an 8-atom cubic lattice (space group #215, $P4\bar{3}m$),

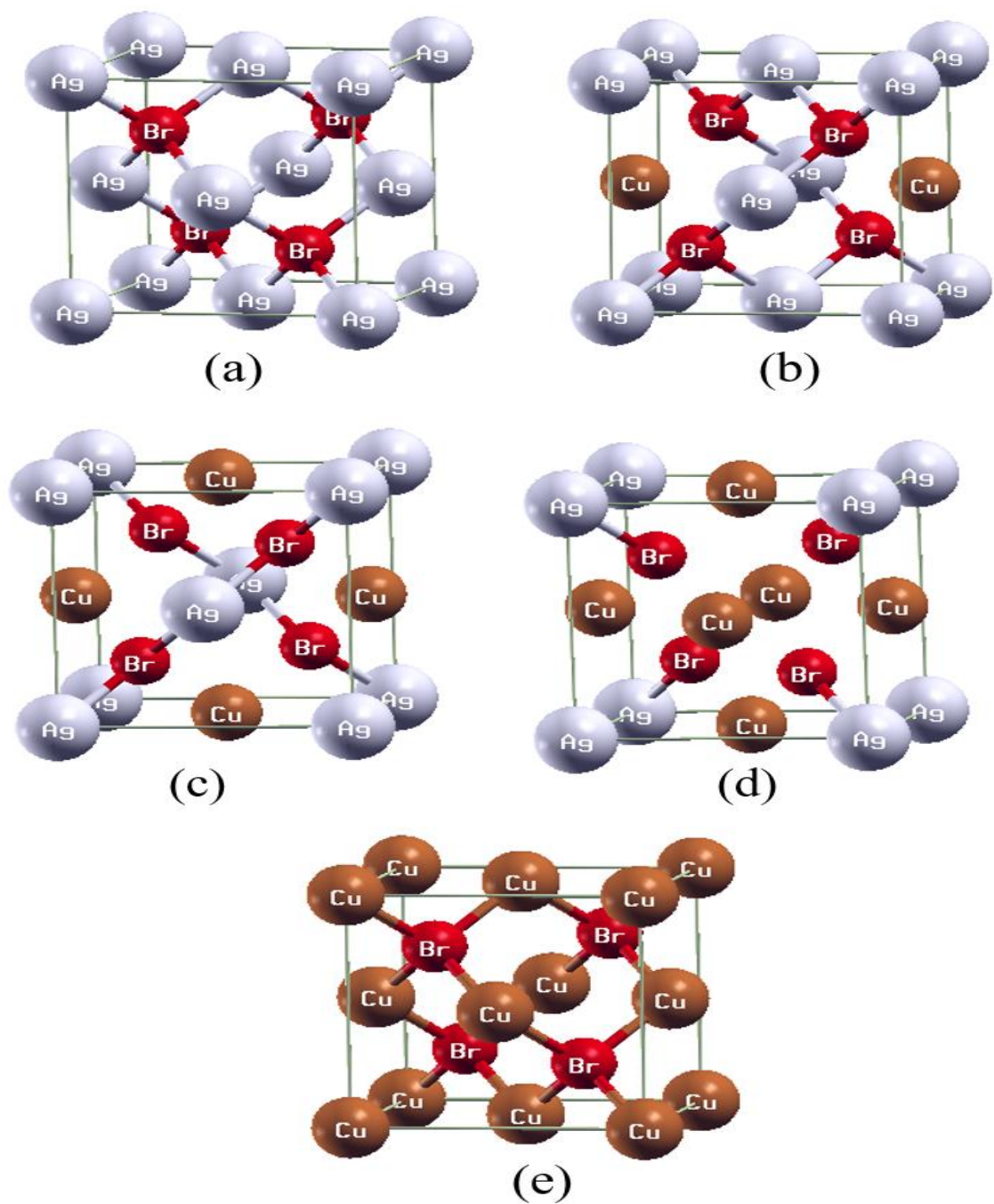


Figure 6.1: Optimized unit cell of $\gamma - Ag_{1-x}Cu_xBr$ for (a) $x = 0.00$, (b) $x = 0.25$, (c) $x = 0.5$, (d) $x = 0.75$ and (e) $x = 1.00$

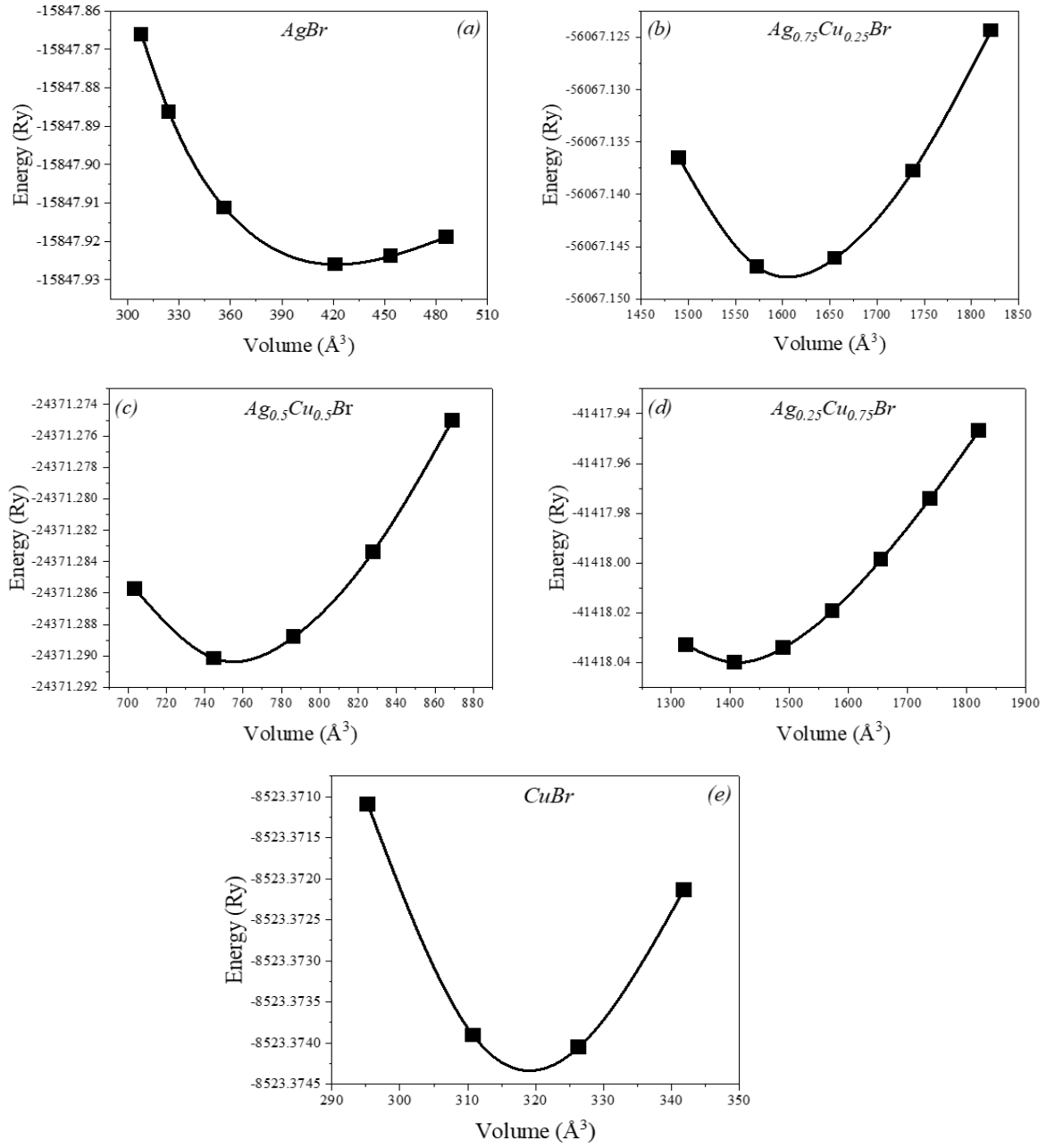


Figure 6.2: Birch Murnaghan equation of state plots for $\gamma - Ag_{1-x}Cu_xBr$ for $x = 0.00 - 1.00$

with the exception of $x = 5$ (space group #111, $P4\bar{2}m$), which produces a different structure. Using FP-LAPW method, we first determined the optimized parameters of AgBr, CuBr, and $Ag_{1-x}Cu_xBr$ alloys. All the atoms are required to rearranged within the crystal structure by applying the necessary forces in order to ascertain the equilibrium parameters of the mentioned compounds. For each newly generated structure, we calculate the structural minimization by considering total energy as a function of optimized cell volume V_0 . The ground state properties were ascertained by fitting the theoretical Birch-Murnaghan's equation of state to the calculated total energy of the crystal structure [31]. Figure 6.2 displays the Birch Murnaghan equation of state plots for $Ag_{1-x}Cu_xBr$ ($x = 0.00 - 1.00$). Table 6.1 displays the computed lattice constants (a) and bulk modulus (B), which includes the results of earlier calculations and experimental data.

Table 6.1: Calculated lattice parameter a and bulk modulus B compared to experimental and theoretical works of $\gamma - Cu_xAg_{1-x}Br$ compounds.

x	Lattice constant a (Å)			Bulk modulus B (GPa)		
	Our work	Expt.	Theoretical	Our work	Expt.	Theoretical
0	6.312	-	6.33[27]	28.026	-	37.91[8]
0.25	6.191	-	-	32.631	-	-
0.5	6.120	-	-	34.179	-	-
0.75	5.934	-	-	38.757	-	-
1	5.741	5.67[29]	-	44.772	-	-

The number in the square brackets denotes the reference number.

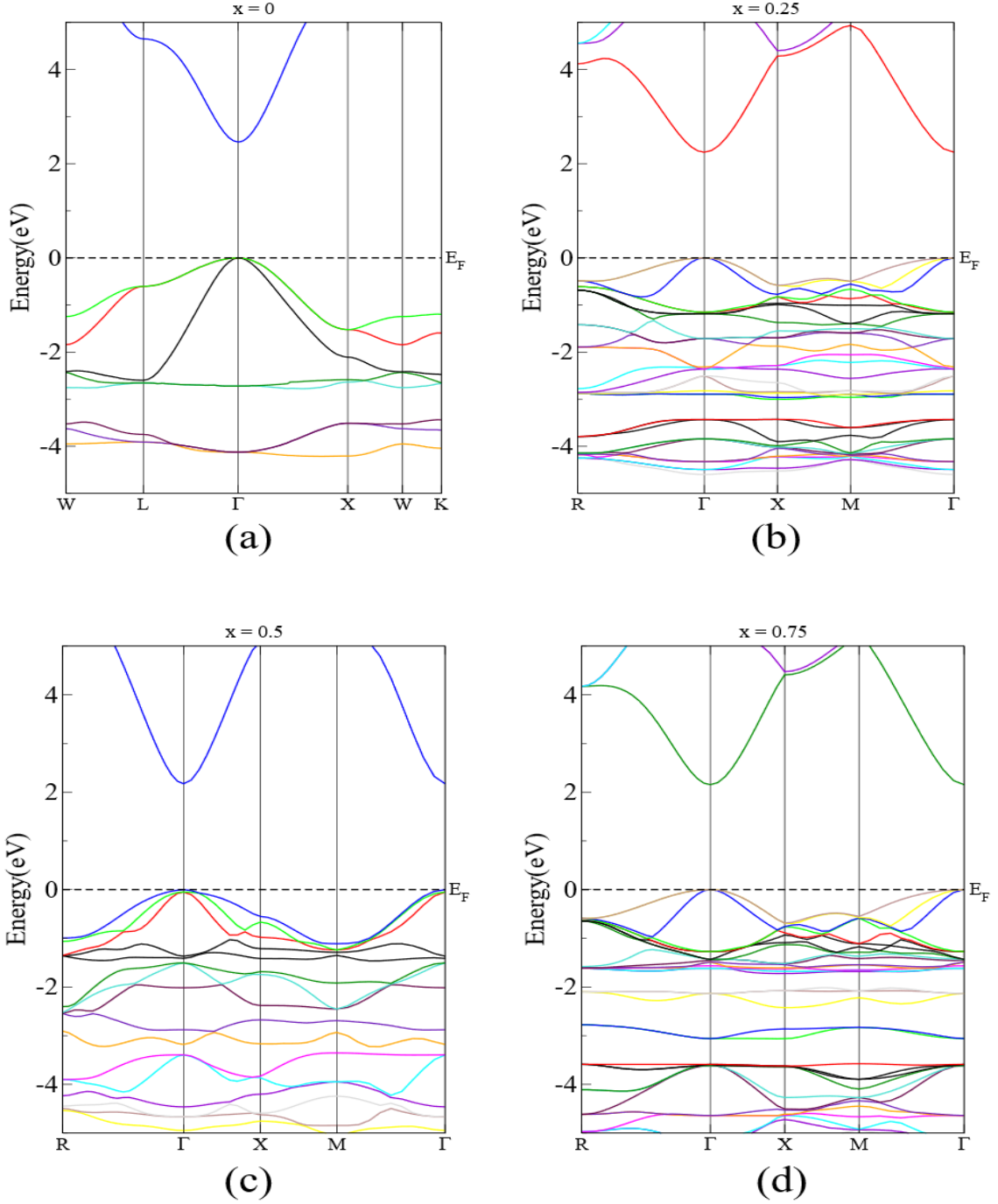
The calculated lattice parameter of AgBr is found to be greater than those of CuBr. Since the identical anion atom is present in both of these compounds, the atomic radius of the Ag and Cu atoms readily explains the results. Due to their respective atomic radii of 1.72Å and 1.57Å, Ag and Cu exhibit a decreasing trend in lattice parameter as the

cation atom size decreases. Furthermore, the bulk modulus (B) of AgBr is lower than that of CuBr. The relationship between lattice parameters and bulk modulus follows an inverse sequence, i.e., the calculated values of the bulk modulus (B) increase as the lattice constants (a) decrease from AgBr to CuBr, implying that the compressibility of AgBr to CuBr decreases. Furthermore, the atoms are expected to occupy their appropriate lattice spaces within the lattice structure while analyzing ternary compounds. The lattice parameters indicate a linear change in response to the doping of Cu concentration on AgBr, in accordance with theoretical Vegard's law [28]. Figure 6.4(a-b) displays the calculated bulk modulus and lattice parameters with substitution concentration $x = 0.00 - 1.00$. In the $Ag_{1-x}Cu_xBr$ compound, the computed values of optimized lattice parameters show a significant relationship with Vegard's law [28]. As the doping concentration x (Cu) increases, the lattice constants of ternary alloys $Ag_{1-x}Cu_xBr$ decrease, attributed mainly to the smaller atomic size of the Cu atom compared to that of the Ag atom. It has been observed that as the concentration of Cu increases, the bulk modulus B increases as well, as shown in Figure 6.4(b). The calculated values are closely comparable with those obtained by FP-LAPW approach [32].

6.3.2 Electronic structure

Understanding of band structure and band gap of any material is crucial in order to achieve efficient semiconductor devices. The energy band structures of $Ag_{1-x}Cu_xBr$ for Cu concentrations $x = 0.00 - 1.00$ are illustrated in Figure 6.2. A direct band gap (Γ - Γ point) has been observed for the predicted band structures of $Ag_{1-x}Cu_xBr$ compounds. The energy band gap for AgBr and CuBr is 2.454 eV and 2.282 eV, respectively, as determined by the HSE06 approach. The energy values at the Γ - Γ points are significantly smaller than the experimentally determined values. The band structures of $Ag_{1-x}Cu_xBr$ compounds, which identically exhibit a direct energy band gap, are obtained by gradually substituting one or more Cu atoms for Ag in the $1 \times 1 \times 1$ unit

cell of AgBr. The band gap values of $Ag_{1-x}Cu_xBr$ compounds are given in the Table 2. The values are in close agreement with those that were previously reported [32].



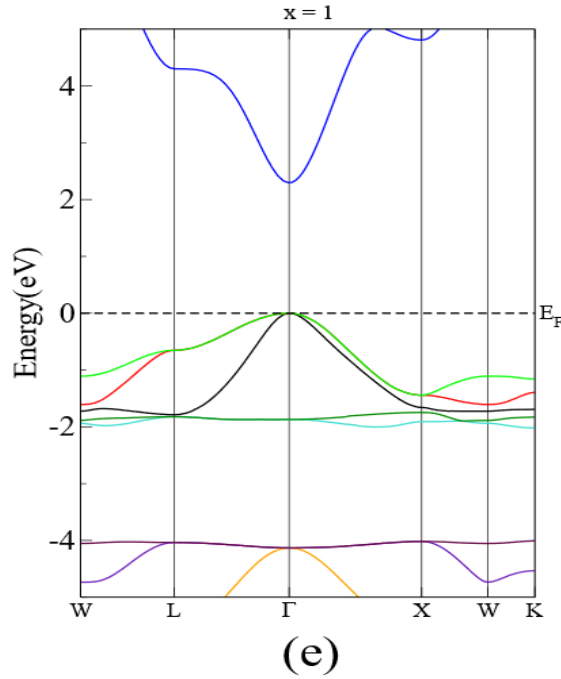


Figure 6.3 Band structure of $\gamma - Ag_{1-x}Cu_xBr$ for (a) $x = 0.00$, (b) $x = 0.25$, (c) $x = 0.5$, (d) $x = 0.75$, and (e) $x = 1.00$ are obtained using HSE06 hybrid functional.

The HSE06 scheme results in the formation of a direct band gap at high symmetry Γ - Γ point as the valance and conduction bands are displaced from one another. This improved measurement of the band gap value was attributed to the enhanced predicting ability of the d-states of the element with HSE06 scheme. The cause of minimal variation arises in the band gap may be the inconsistencies of muffin-tin radii of the outer orbital, which results in an underestimation of bandwidth as a result of electronic dispersion [33].

Table 6.2: Direct band gap energy of $\gamma - Cu_xAg_{1-x}Br$ alloys with various Cu concentration.

Compound	E_g (eV)		
	Our work	Experiment	Other calculation
$AgBr$	2.454	2.78[18]	1.340[19], 3.78[14]
$Ag_{0.75}Cu_{0.25}Br$	2.244	-	
$Ag_{0.5}Cu_{0.5}Br$	2.173	-	
$Ag_{0.25}Cu_{0.75}Br$	2.153	-	
$CuBr$	2.282	2.95[29]	1.068[19], 1.12[12], 2.76[14]

The number in the square brackets means the reference number

The estimated energy gaps generated by the HSE06 methodology are more closely related to the experimental values than those obtained using the GGA method [12]. The underestimation in the band gap value on CuBr is caused by inadequate convergence of the computational analysis, while using the HSE06 hybrid functional scheme, which comes from the unnecessary expansion of the exchange and correlation energy. The main reason for the inadequate representation of the electronic band structure of CuBr is due to the challenges associated with describing the localized electronic states within the correlation functional.

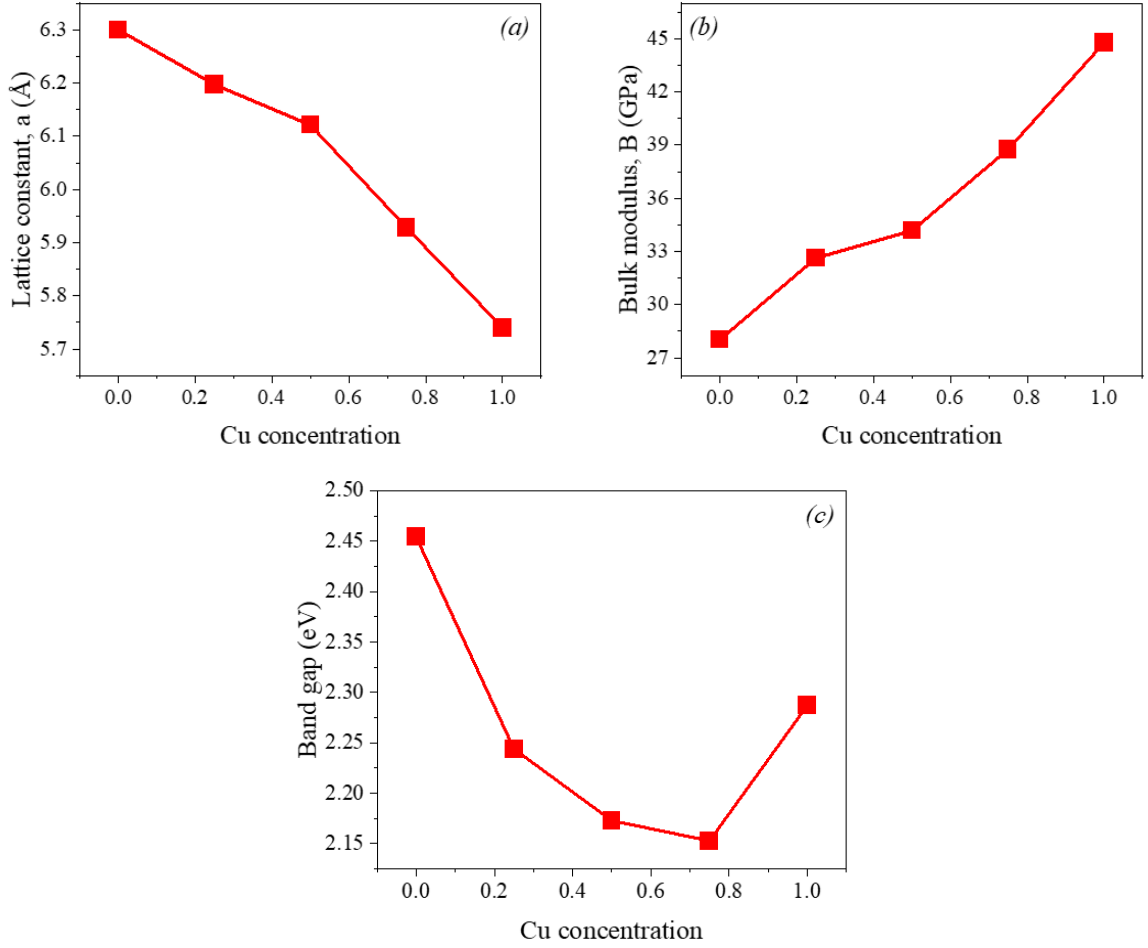


Figure 6.4: Variation of (a) lattice constant, (b) Bulk modulus, and (c) Band gap with Cu concentration in $\gamma - Ag_{1-x}Cu_xBr$ ($x = 0.00 - 1.00$)

The electronic dispersion bandwidth may be marginalized due to inaccurate estimation of muffin-tin radii (R_{MT}) for the outer orbital. The band structure exhibiting a direct band gap material in their zincblende structure is illustrated in Figure 6.3. It is evident from the band structure that the Fermi level is not in contact with any electronic states; rather, the electronic states are widely separated.

Figure 6.4 illustrates the variations in the lattice constant (a), bulk modulus (B), and energy band gap (E_g) of $\gamma - Ag_{1-x}Cu_xBr$ ($x = 0.00 - 1.00$). The data shows a nonlinear relationship between the band gap and Cu composition (x) has shown in figure 4(c). The computed band gap of $\gamma - Ag_{1-x}Cu_xBr$ using HSE06 hybrid functional, consistent with previous experimental and theoretical studies are listed in Table 6.2. The limited flexibility of quasiparticle self-energy causes a slight under estimation of the exchange correlation energy in the computational calculation. [28]. The present energy band gap measurements appear to be slightly underestimated, due to the absence of the spin-orbit coupling effect (SOC).

6.3.3 Density of states

The band structure can be demonstrated through the concept of density of states (DOS) of a material. It defines the number of electronic states per unit energy interval. The atom orbital-projected DOS calculated using a hybrid functional scheme for $\gamma - Ag_{1-x}Cu_xBr$ ($x = 0.00 - 1.00$) is presented in **Figure 6.4 – 6.10**. The HSE06 hybrid functional calculation indicates that the density of states for AgBr ranges from -4.256 to 6.791 eV, while for CuBr, it ranges from -6.754 to 6.796 eV. The Fermi level serves as the reference point for energy measurements. The first valence zone is identified between -4.256 and -3.304 eV for AgBr, and between -6.046 and -4.169 eV for CuBr. This area comprises by the Br-4p and Ag-4d/Cu-3d states. The second valence band ranges from -2.569 to -0.065 eV for AgBr due to highly localized Ag-4d orbital, and from -1.638 to -0.087 eV in CuBr for hybridized Cu-3d orbitals with minor contribution from Br-4p states. In the final region, the DOS ranges from 2.546 to 6.791 eV for AgBr and from 2.089 to 6.796 eV for CuBr, characterized by a conduction band mostly influenced by Br-4p and Cu-4s/Ag-5s states, exhibiting a minor peak height. However,

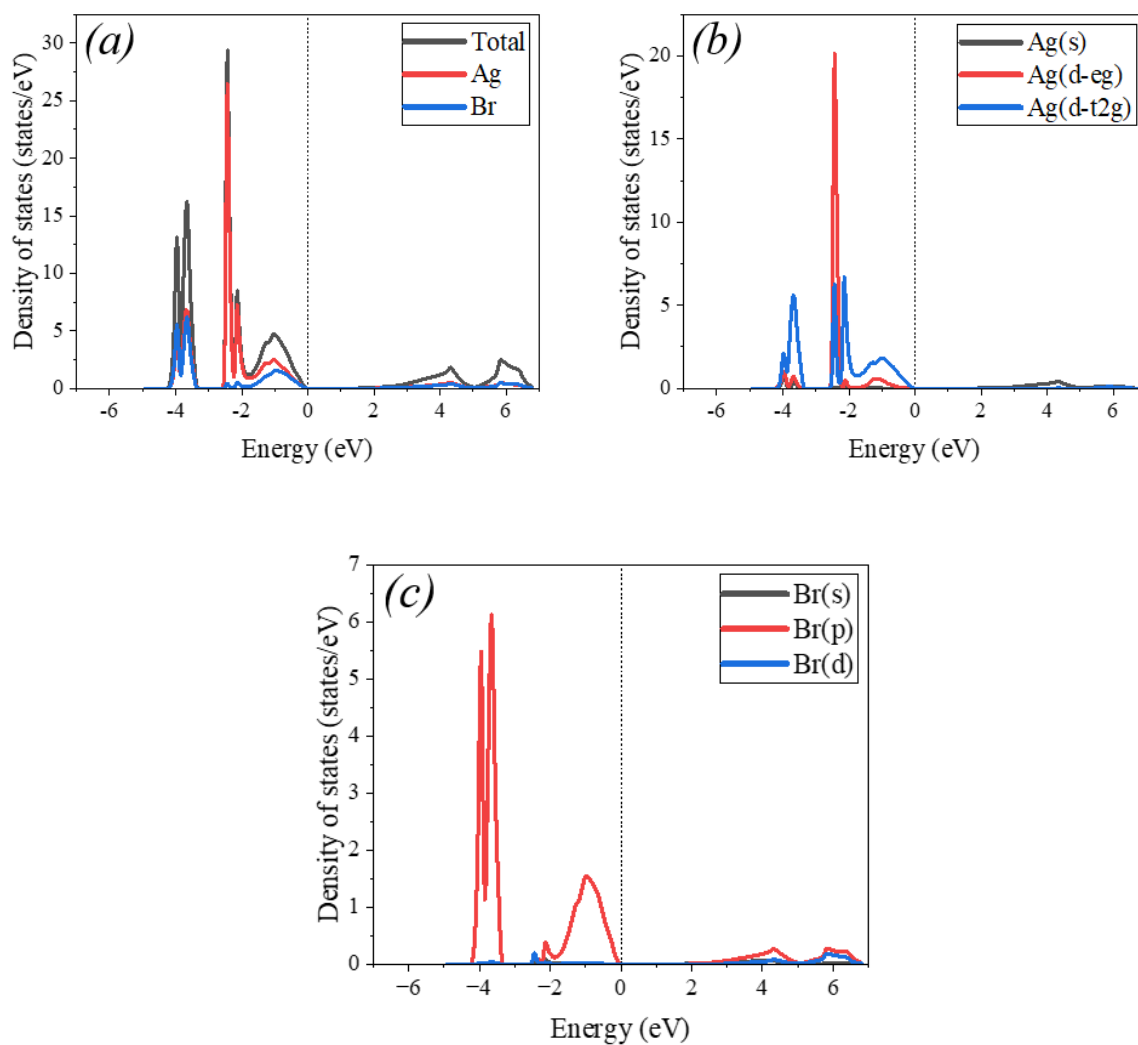


Figure 6.5: (a) Density of states of AgBr-total, Ag-total and Br-total, (b) Partial density of states Ag (p, d-eg and d-t2g), and (c) Partial density of states of Br (s, p and d) in γ -AgBr obtained using HSE06 hybrid functional.

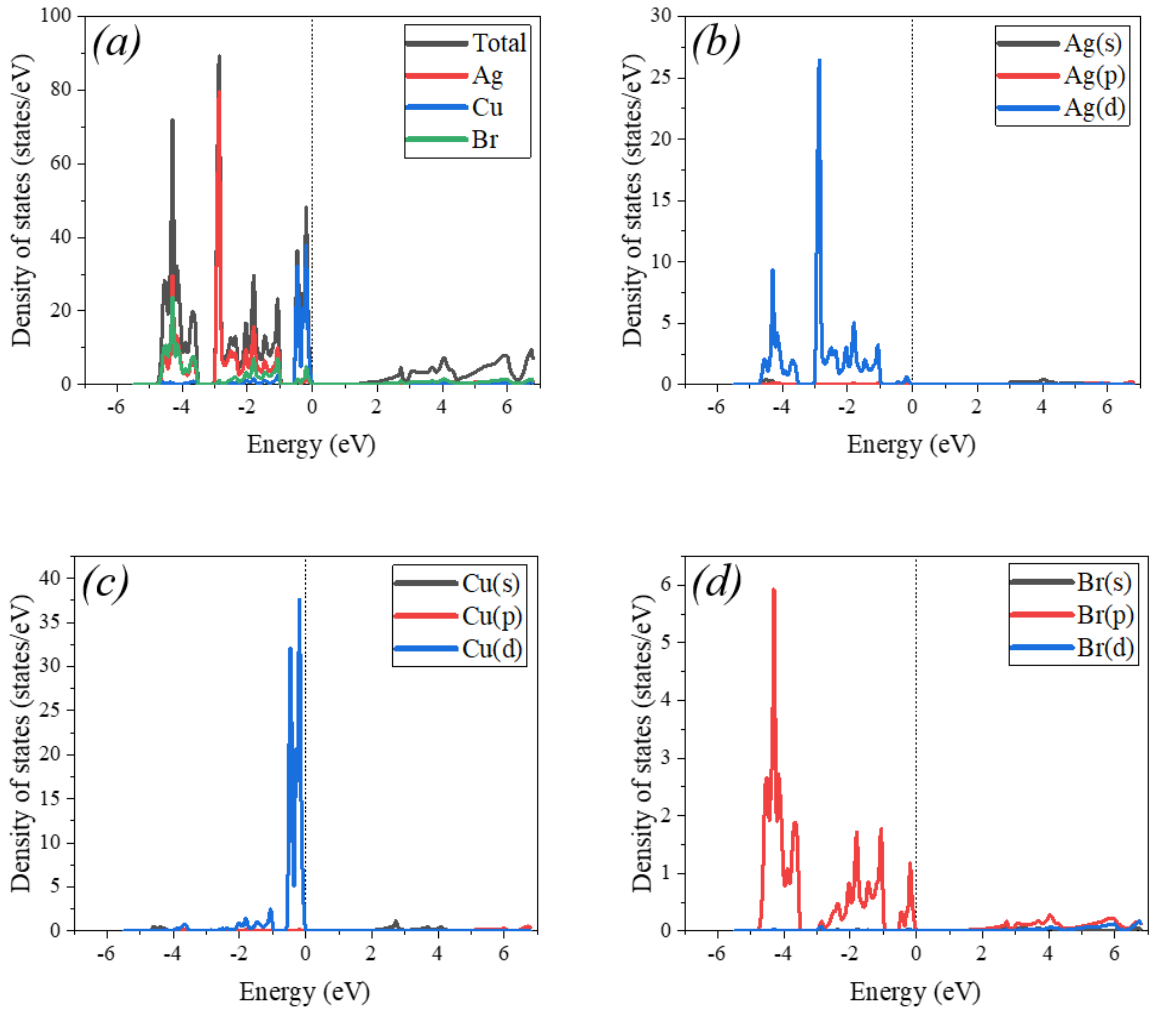


Figure 6.6: (a) Density of states of $\gamma - Ag_{0.75}Cu_{0.25}Br$ -total, Ag-total, Cu-total and Br-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of Br (s, p and d) in $\gamma - Ag_{0.75}Cu_{0.25}Br$ obtained using HSE06 hybrid functional.

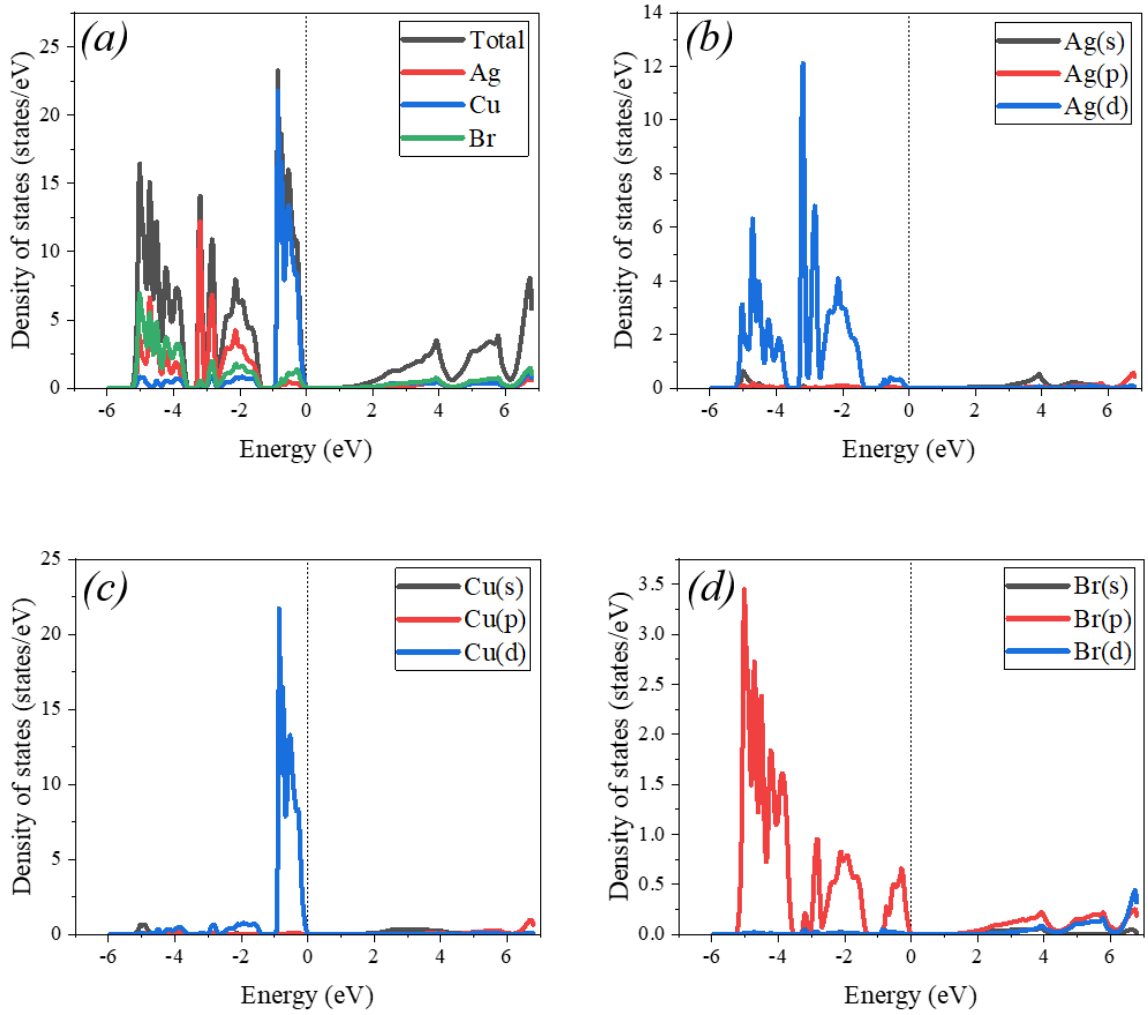


Figure 6.7: (a) Density of states of $\gamma - Ag_{0.5}Cu_{0.5}Br$ -total, Ag-total, Cu-total and Br-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of Br (s, p and d) in $\gamma - Ag_{0.5}Cu_{0.5}Br$ obtained using HSE06 hybrid functional.

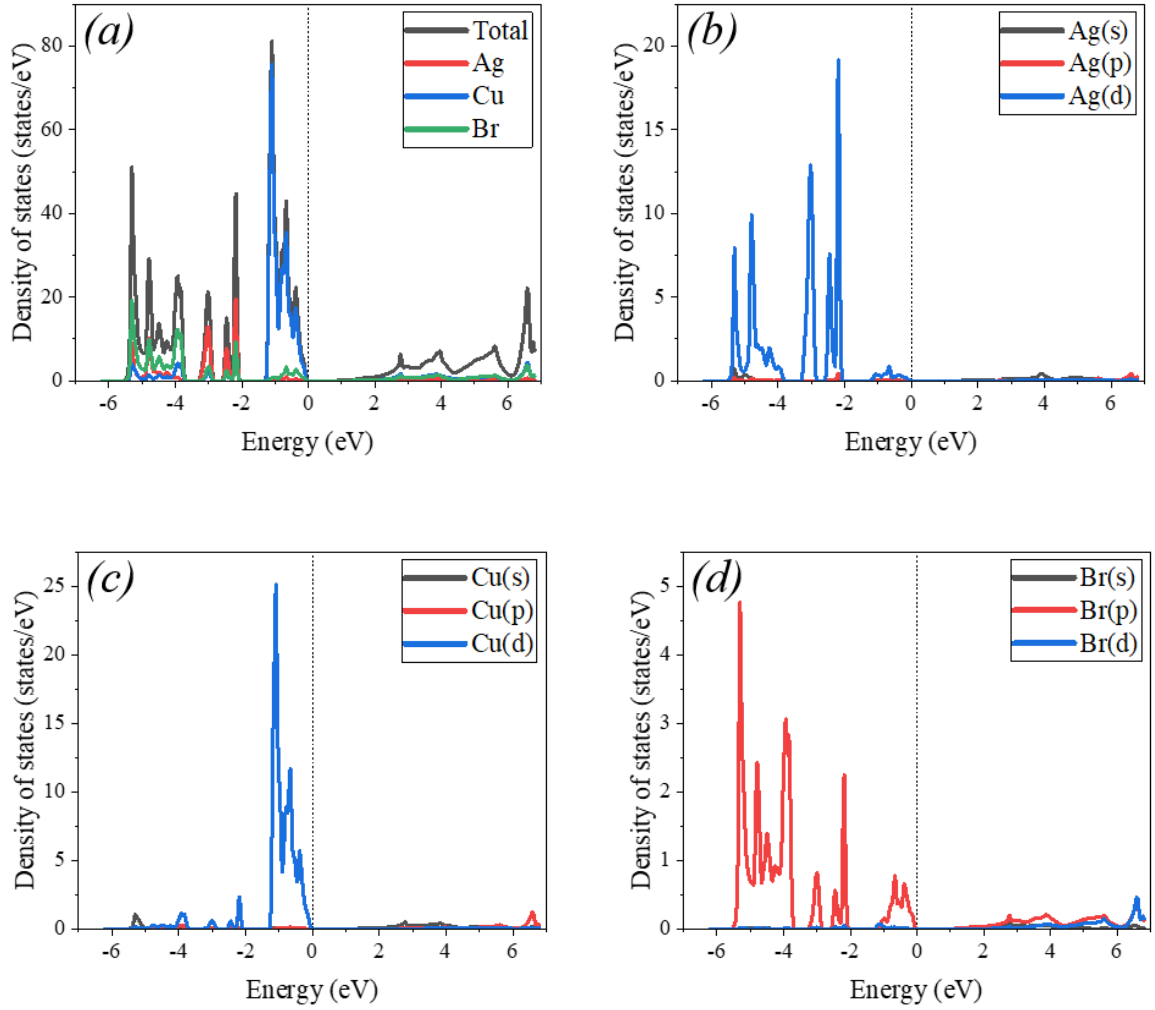


Figure 6.8: (a) Density of states of $\gamma - Ag_{0.25}Cu_{0.75}Br$ -total, Ag-total, Cu-total and Br-total, (b) Partial density of states of Ag (s, p and d), (c) Partial density of states of Cu (s, p and d), and (d) Partial density of states of Br (s, p and d) in $\gamma - Ag_{0.25}Cu_{0.75}Br$ obtained using HSE06 hybrid functional.

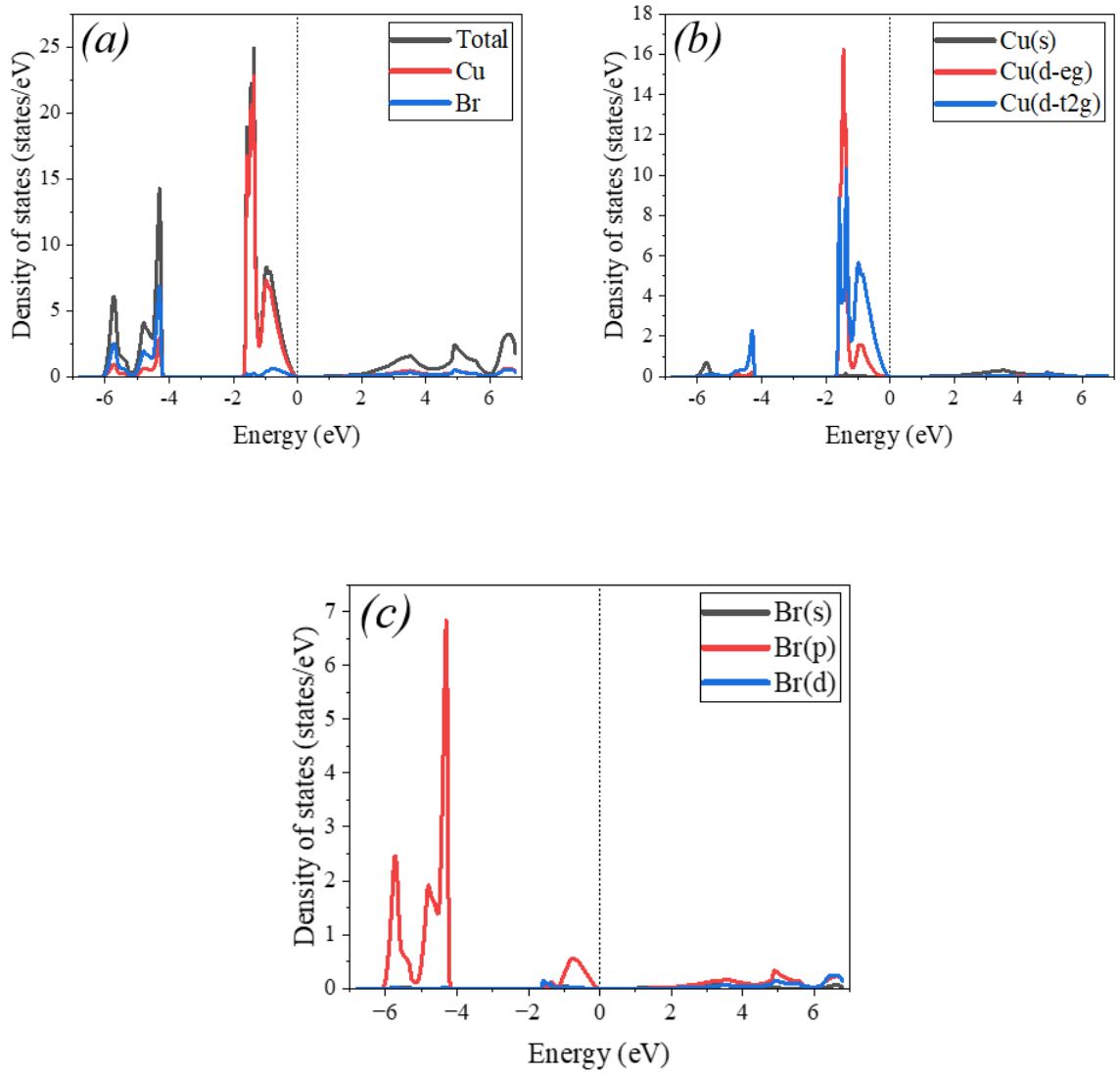


Figure 6.9: (a) Density of states of γ -CuBr-total, Cu-total and Br-total, (b) Partial density of states of Cu (s, d-eg and d-t2g), and (c) Partial density of states of Br (s, p and d) in γ -CuBr obtained using HSE06 hybrid functional.

the band gap of pure AgBr and Cu-doped AgBr differs significantly. The HSE06 techniques are used to calculate the valence and conduction band at its maximum and minimum extent through high symmetry Γ -point. The observed reduction in Cu doping

concentration is associated with a comparable rise in the band gap of the compounds. The band gaps are lies within 2.244 eV to 2.153 eV by using the HSE06 method for the substituted compounds. The doping of Cu atom in AgBr zincblende structure doesn't largely varies the nature of the generated compounds. The DOS exhibits a symmetrical nature, and the d-p hybridization within Ag/Cu and Br closely resembles the observed pattern in the DOS for the $\gamma - Ag_{1-x}Cu_xBr$ alloys, as observed in Ref. [17]. The d-bands of the Ag-Cu-Br combination exhibit an expansion compared to those of Ag/Cu atoms, when increasing the Cu content, as seen from the DOS in $\gamma - Ag_{1-x}Cu_xBr$ alloys. The extension of d-bands within the alloys exhibits an increase in magnitude corresponding to the atomic concentrations (Cu/Ag). The upper edge of d-bands is set at about -1.7 eV, just below the Fermi level, higher than that of Ag atom (≈ 1.0 eV) nearly matches Cu atom. Furthermore, it has been noted that the interaction of d-states with s and p-states increases close to Fermi level as the composition Cu increases. Consequently, the transition rates of the d-sp band increase. The d-sp and s-p band transitions providing mismatching behaviour of Cu and Ag in Ag-Cu-Br compound, may slightly modify its energy distribution. In order to explore the intrinsic characteristics of the electronic structure, we have studied the total partial density of states (TDOS) for each atom along with their combined system. Furthermore, we also presented the orbital contribution (PDOS) of Ag and Cu in Cu-Ag-Br system. Certain modifications in the density of states have been identified within the energy spectrum that extend from -4.828 to 0.151 eV. The density of states experiences a slight change in the energy range near the Fermi level. With an increase in the percentage of copper, there is a gradual expansion of the d-band size. The broadening of d-band in Ag-Cu-Br alloys can be explained through the significant hybridization occurring between d-orbitals of Cu and Ag atoms, as indicated by a comprehensive analysis of the projected density of states for the d-orbitals of these atoms. The electronic band structure of the Ag-Cu-Br system undergo modifications as a result of the reduction in structural volume through atomic composition. The substitution of Ag by Cu atom results in a reduction in volume, as the atomic radius of Ag is greater than that of Cu. By employing the density

of states (DOS), it is possible to conceptualize the electronic structure of a crystal. The TDOS suggests that the valence bands on Ag-Cu-Br alloys shift toward the Fermi level as the cation concentration in the Ag-Cu-Br system varies from 0 to 1.

6.3.4 Optical properties

Optical properties generally defined their interaction with incident light. The study of the optical characteristics of any material is crucial due to their importance in various optoelectronic devices. The phenomenon occurs by means of incoming light photon, which generates a response in the electronic system to a time-dependent perturbing system. In this regard, dielectric functions are a key parameter that characterizes the response of the material. The optical spectra of solids are solely determined by the electronic band transition of an element. In the zincblende phase of $\gamma - Ag_{1-x}Cu_xBr$ ($x = 0.00 - 1.00$) system, we investigated multiple features, characterized by various parameters such as, dielectric function, refractive index, absorption coefficient, optical conductivity, extinction coefficient, reflectivity, and energy loss function. The dipole matrix elements modify the joint density of states, which is the primary basis for the method of calculating the optical properties. The optical properties are obtained from the dielectric function of the materials, and can expressed as $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, where $\varepsilon_1(\omega)$ represents the real part, and $\varepsilon_2(\omega)$ denotes the imaginary part of complex dielectric equation [34-36]. The electron wave functions and eigenvalues are the main parameters that govern the frequency-dependent dielectric functions. Real component of dielectric function signifies a material, which demonstrates dielectric behaviour at $\varepsilon_r(\omega) > 0$, extending up to a specific photon energy. However, at $\varepsilon_r(\omega) < 0$ beyond its energy range, it behaves metallic characteristics. The static dielectric constant, represented as $\varepsilon_r(\omega) = 0$, is obtained from the limiting value (zero energy limit) of the real component of the dielectric constant. At various energy ranges, multiple peaks appear at the inter-band transitions within materials. These peaks shift in the direction of greater energy regions. The highest peak observed at maximum intensity is approximately 7.215 eV. therefore, the material may serve as a filter for a broad

spectrum of energy in the UV-visible spectrum. The variation dielectric function of the $\gamma - Ag_{1-x}Cu_xBr$ ($x = 0.00 - 1.00$) with energy in eV is shown in Figure 6.10(a-b). Calculated real part of complex dielectric function $\epsilon_1(\omega)$ is displayed in Figure 6.10(a). Each compound exhibits a multi-peak pattern, which attains minimum limits. The reflecting ability of metallic compounds is indicated by the real dielectric constants' decreasing tendency towards negative values. The substances can act as a radiation

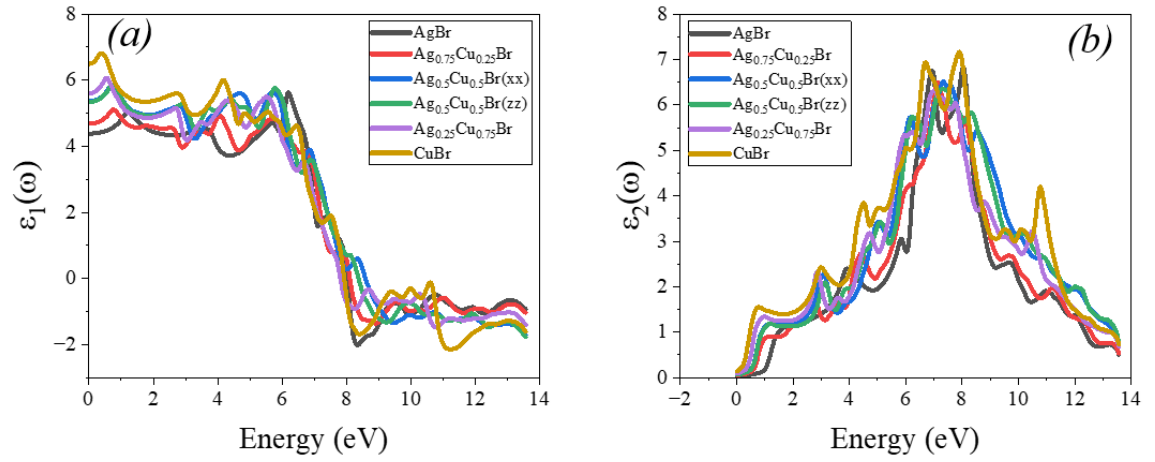


Figure 6.10(a-b): Variation of (a) Real part $\epsilon_1(\omega)$, and (b) Imaginary part $\epsilon_2(\omega)$ of dielectric constant with incident photon energy for $\gamma - Ag_{1-x}Cu_xBr$.

Table 6.3: Calculated values of zero-frequency limits in $\epsilon_1(0)$, $n(0)$ and $R(0)$ spectra and threshold values in $\epsilon_2(\omega)$, $\kappa(\omega)$, $\alpha(\omega)$ and $\sigma(\omega)$ spectra in $\gamma - Ag_{1-x}Cu_xBr$ using HSE06 hybrid functional.

Compound	Zero-frequency limits			Threshold values (eV)			
	$\epsilon_1(0)$	$n(0)$	$R(0)$	$\epsilon_2(\omega)$	$\kappa(\omega)$	$\alpha(\omega)$	$\sigma(\omega)$
<i>AgBr</i>	4.383	2.094	0.125	0.612	0.694	1.292	1.184
<i>Ag_{0.75}Cu_{0.25}Br</i>	4.690	2.166	0.136	0.204	0.367	0.966	0.857
<i>Ag_{0.5}Cu_{0.5}Br(xx)</i>	5.364	2.316	0.158	0.177	0.231	0.911	0.775
<i>Ag_{0.5}Cu_{0.5}Br(zz)</i>	5.345	2.312	0.157	0.259	0.231	0.857	0.775
<i>Ag_{0.25}Cu_{0.75}Br</i>	5.604	2.367	0.165	0.041	0.122	0.803	0.612
<i>CuBr</i>	6.494	2.548	0.191	0.014	0.041	0.666	0.503

barrier and detector inside the energy window. Table 6.3 lists the static dielectric function values for $\gamma - Ag_{1-x}Cu_xBr$ ($x = 0.00 - 1.00$). Using the HSE06 approach, the static dielectric constants are found to range from 4.383 to 6.494, with the highest and lowest values occurring at greater and lower Cu concentrations, respectively. The higher value of static dielectric constants indicates a greater refractive index and, thus, a higher optical density for the material.

Figure 6.10(b) illustrates how the imaginary part of dielectric function $\epsilon_2(\omega)$, changes with energy. The threshold value of the dielectric function with Cu concentration are reported in Table 6.3. With immediately following the threshold value, we observe that the imaginary dielectric function increases as energy increases with immediately following the threshold value, reaching peaks that correspond to their respective energy values. The highest peak values of $\gamma - Ag_{1-x}Cu_xBr$ occur at 6.916, 6.478, 6.427, 6.346, 6.303, and 7.151, which correspond to the energy values 8.013, 7.034, 7.061, 7.333, 6.979, and 7.932 eV, respectively.

Figure 6.10(c) represents the variation of refractive index $n(\omega)$ with incoming photon energy. The data indicates a multiple peak for each compound, which can be attributed

to different interband transitions, similar behaviour observed in the dielectric constant. At the increasing value of energy, a minimum value is attained, indicating that the material loses transparency. The Figure 6.10(c) illustrates that the refractive index increases with an increase in photon energy. Because of the greater electronic interactions with photons in this region, the value drops as photon energy increases after reaching a maximum of 6.132 eV. The value of refractive index $n(\omega)$ at zero-frequency of photon energy is known as static refractive index $n(0)$. The value of the static refractive index is listed in Table 6.3.

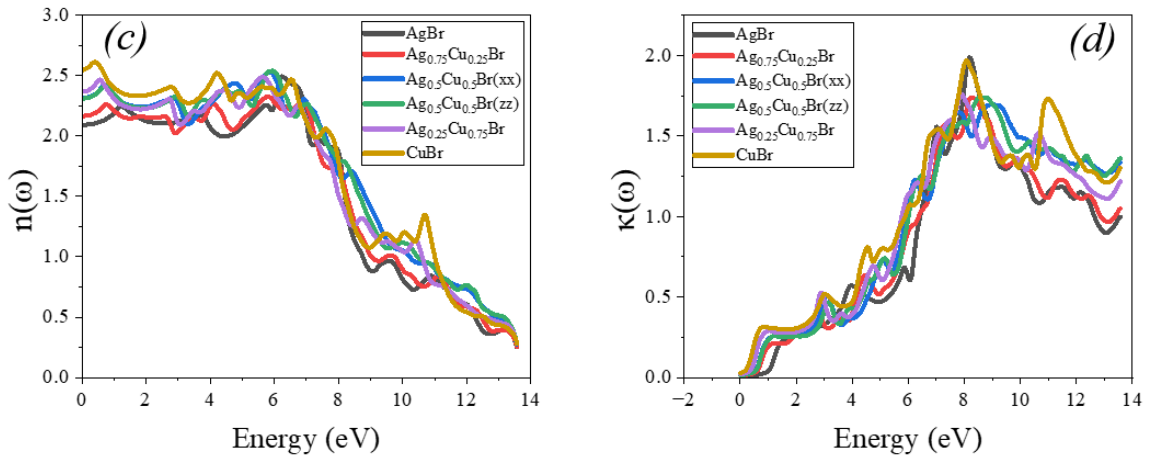


Figure 6.10(c-d): Variation of (c) Refractive index $n(\omega)$, and (d) Extinction coefficient $\kappa(\omega)$ with incident photon energy for $\gamma - Ag_{1-x}Cu_xBr$.

Figure 6.10(d) illustrates the variations of extinction coefficients with the photon energy. The ability of a material to absorb incident light is associated with its extinction coefficient. It calculates how much of a given amount of incident light at a certain wavelength a substance can absorb. The highest peaks are found at 1.987, 1.736, 1.700, 1.751, 1.756, and 1.969 with comparable energy values of 8.177, 8.258, 8.993, 8.557, 7.796, and 8.068 eV respectively. The spectrum of extinction coefficient shows that more light is absorbed by higher Cu concentrations in $\gamma - Ag_{1-x}Cu_xBr$ than by lower concentrations.

Figure 6.10(e) illustrates the optical conductivity of $\gamma - Ag_{1-x}Cu_xBr$ varies with photon energy. Conductivity begins to respond to the electric field when incident energy reaches a crucial threshold. We see that when Cu concentrations rise, the critical points in optical conductivity shift towards lower energy. Table 6.3 presents the critical values for the extinction coefficient.

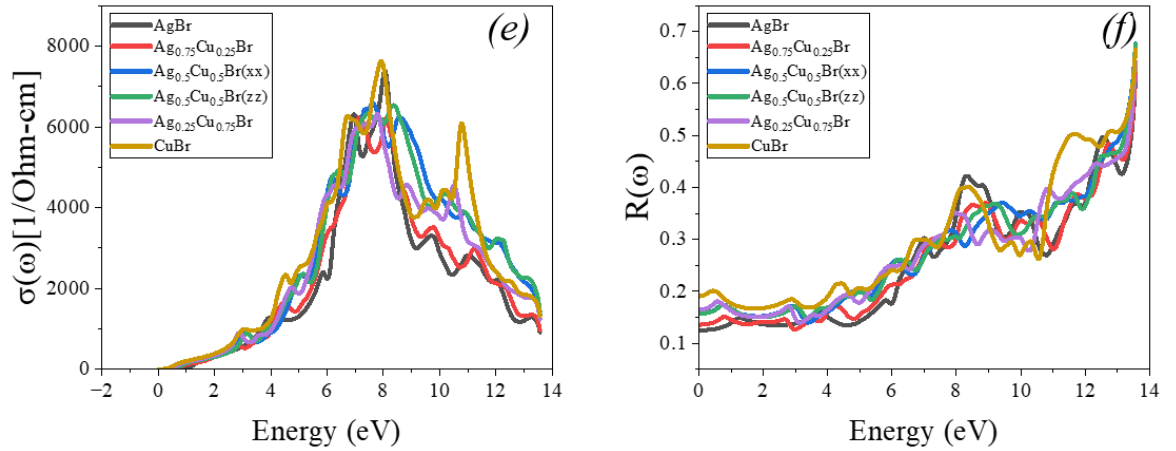


Figure 6.10(e-f): Variation of (e) Optical conductivity $\sigma(\omega)$, and (f) Reflectivity $R(\omega)$ with incident photon energy for $\gamma - Ag_{1-x}Cu_xBr$.

The energy ratio between incident and reflected photons, or the ratio of incident power to reflected power on a material's surface, is known as reflectivity. Reflectivity is used to analyse how light is reflected at a crystalline solid surface. The reflectivity spectra of the materials can be used to estimate the scattering length density (SLD) of various layers in relation to their structural characteristics [29]. Figure 6.10(f) demonstrates that the specific Cu concentrations result in the maximum reflectivity of these materials occurs within the energy of 8.35 eV to 9.05 eV. When light interacts with the substance's unbound electrons, it produces peaks at different energy levels. A decrease in reflectivity occurs between 8.35 and 10.56 eV. A finite amount of energy is lost by the incident electron during an interband transition from valence to conduction band, may be

responsible for of the variation in peak values. The extinction of a single electron within the material in this case produces the energy loss spectrum. The absorption coefficient describes the amount of light absorbed by an optical material. It is also defined as a percentage of the power absorbed per unit length of a medium. Figure 6.10(g) depicts the variation of absorption coefficient of $\gamma - Ag_{1-x}Cu_xBr$ with energy (eV).

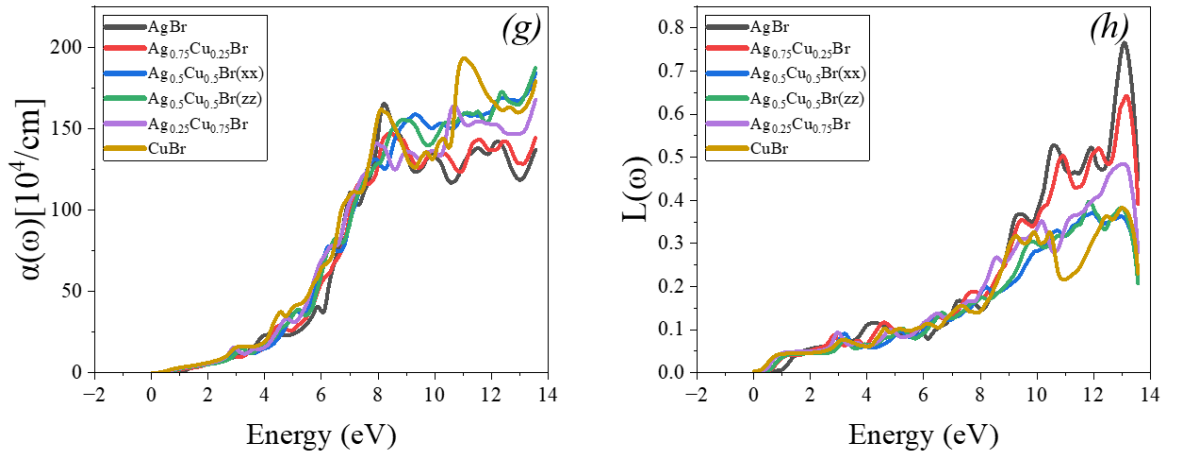


Figure 6.10(g-h): Variation of (g) Absorption coefficient $\alpha(\omega)$, and (h) Energy loss $L(\omega)$ with incident photon energy for $\gamma - Ag_{1-x}Cu_xBr$.

The compound has a strong absorptive power when the Cu concentration is low. This indicates that photons with energies greater than the threshold energy will be absorbed by the atoms. Below the threshold energy, compounds behave like transparent materials due to their reduced absorption coefficient. The highest transmission range is indicated by a lower value of absorption coefficient with this range. This means that the compounds can be used in a wide range of optical devices. The plot is nearly flat below the threshold energy. Consequently, the electronic interband transition at a low frequency is represented by a gap on the energy axis. The highest peaks corresponding to Cu concentrations are found at 0.766, 0.642, 0.371, 0.484, and 0.382 with energies of 13.075, 13.156, 11.877, 11.932, 13.021, and 13.020 eV, respectively. Figure 6.10(h)

shows the energy loss function of $Ag_{1-x}Cu_xBr$. The compounds at $x = 0.00$ and 0.25 , the energy loss function displays two prominent peaks. A typical coupling with plasma resonance is suggested by this noticeable peak in the energy loss function, and the associated frequency is referred to as the plasma frequency [37]. The material exhibits dielectric behaviour above this frequency and solid behaviour below it.

6.4 Conclusions

The FP-LAPW method has been successfully used to calculate the band structure of $\gamma - Ag_{1-x}Cu_xBr$ alloys. A variety of properties, including lattice parameters, bulk modulus, energy gap, and optical properties, which are all concentration dependent. We identified these properties that display nonlinearity with alloy concentration, except lattice constant and bulk modulus, which follow Vegard's law. The calculated band structure and state density (DOS) revealed a direct band gap material. Cu substitution often decreases the band gap of AgBr, the extent of which varies with copper content. The materials lose transparency at higher energy levels, implying that they become transparent at lower energy levels. The low energy $\gamma - Ag_{1-x}Cu_xBr$ materials are essentially employed in the fabrication of optical devices. The absorption plot exhibits a higher capability for light absorption relative to the pure AgBr compound. The use of copper as a dopant leads to an expansion of the absorption spectrum, enabling it to extend into the visible and near-infrared regions. This promotes the compatibility compounds for multiple uses, including photocatalysis and light-sensitive devices.

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CHAPTER 7

Overall conclusions and future scope of work

As a summary, the first principle computational calculations based on FP-LAPW method were able to study the electronic structural calculations of $\gamma - Ag_{1-x}Cu_xX$ ($X = Br$ and I) compounds using TB-mBJ exchange correlation potential and HSE06 hybrid functional scheme.

- We presented the concentration dependent various structural and electronic parameters such as lattice parameter, bulk modulus, and band gap energy. We have found these parameters vary with Cu concentration. A direct band gap has been observed from the calculated band structure and density of states (DOS).
- The direct band gap semiconductor material exhibits significant absorption capabilities, classifying it as an optically active material. A direct bandgap semiconductor is required by a large variety of optoelectronic and semiconductor devices due to its high efficiency and quick responses. As a result, we may increase the efficiency of various devices such as sensors, detectors, and storage by using $\gamma - Ag_{1-x}Cu_xI$, and $\gamma - Ag_{1-x}Cu_xBr$ compounds.
- The variations in the zero frequency limits $\epsilon_1(0)$, $n(0)$, and $R(0)$ with dopant concentration x are inversely related to the variations in the fundamental band gap. The various peaks observed in the $\epsilon_2(\omega)$ curves of each specimen result from electronic transitions occurring between the valence band and the conduction band. The observed transitions result from HOMO-LUMO

electronic transitions occurring from the p-state of halogen in the valence band to the d-state of Ag/Cu in the conduction band for all compounds investigated.

- The designed compounds, characterized by high efficiency and quick responses, may function as valuable materials for optoelectronic, microelectronic, and other solid-state devices that operate within the visible and UV regions of the spectrum.
- Optical properties calculation shows the Cu doped AgI behaves as a radiation detector. The materials lose the transparency in the higher energies and becomes transparent at low energy. The absorption spectra of doped materials exhibit a higher capability for light absorption relative to the pure compound.
- Low energy cubic γ - $\text{Ag}_{1-x}\text{Cu}_x\text{I}$ compounds are suitable for making various optical instruments. The use of copper as a dopant leads to an expansion of the absorption spectrum, enabling it to extend into the visible and near-infrared regions. This promotes the compounds for multiple uses, including photocatalysis and light-sensitive devices.

We are actively involved in the design of materials characterized by a substantial number of atoms per unit cell, aiming to investigate their diverse properties for prospective applications. We are employing the most advanced potentials, such as TB-mBJ and hybrid functional HSE06, which are exceptionally suited for highly accurate calculations, especially in the pursuit of experimental validation. We are involved in the calculations of structural, electronic and optical properties of $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{Cl}$, $\gamma - \text{Ag}_{1-x}\text{Cu}_x\text{F}$. Other related variations of these compounds that we preparing for calculations are $\gamma - \text{AgCu}_x\text{I}_{1-x}$, $\gamma - \text{AgCu}_x\text{Br}_{1-x}$, $\gamma - \text{AgCu}_x\text{Cl}_{1-x}$, $\gamma - \text{AgCu}_x\text{F}_{1-x}$, $\gamma - \text{AgBr}_{1-x}\text{I}_x$, $\gamma - \text{AgCl}_{1-x}\text{I}_x$, $\gamma - \text{AgCl}_{1-x}\text{Br}_x$, $\gamma - \text{AgBr}_{1-x}\text{F}_x$, $\gamma -$

$AgCl_{1-x}F_x$. The other class of compounds such as $\alpha - Ag_{1-x}Cu_xI$, $\alpha - Ag_{1-x}Cu_xBr$, $\alpha - Ag_{1-x}Cu_xCl$, $\alpha - Ag_{1-x}Cu_xF$, $\alpha - AgCu_xI_{1-x}$, $\alpha - AgCu_xBr_{1-x}$, $\alpha - AgCu_xCl_{1-x}$, $\alpha - AgCu_xF_{1-x}$, $\alpha - AgBr_{1-x}I_x$, $\alpha - AgCl_{1-x}I_x$, $\alpha - AgCl_{1-x}Br_x$, $\alpha - AgBr_{1-x}F_x$, $\alpha - AgCl_{1-x}F_x$, $\alpha - AgCu_xBr_{1-x}$, $\alpha - AgCu_xCl_{1-x}$, $\alpha - AgCu_xF_{1-x}$, $\beta - Ag_{1-x}Cu_xI$, $\beta - Ag_{1-x}Cu_xBr$, $\beta - Ag_{1-x}Cu_xCl$, $\beta - Ag_{1-x}Cu_xF$, $\beta - AgCu_xI_{1-x}$, $\beta - AgCu_xBr_{1-x}$, $\beta - AgCu_xCl_{1-x}$, and $\beta - AgCu_xF_{1-x}$ are in line with our calculations. The materials have the ability to generate hybrid ionic-electronic conduction. The growth of especially efficient optoelectronic materials depends on the band gap of a material. It controls the interaction of material with light as well as whether it absorbs, emits, or transmits particles of a certain energy. Optimal performance of optoelectronic devices such as solid-state batteries, gas sensor, electrochemical sensor, fuel cell, solar cells and photodetectors depends on accurate band gaps. Some of the selected compounds other than metal halides like AgO , CuO , Ag_2S , Ag_2Se , and Cu substituted AgO , Ag_2S , Ag_2Se eg. $Ag_{1-x}Cu_xO$, $Ag_{1-x}Cu_xS$, and $Ag_{1-x}Cu_xSe$. We are preparing for calculations of these compounds to study the structural, electronic and optical properties, and thermodynamic properties for various device applications.

Paper published

(i) *"Electronic structure calculations on copper substituted silver iodide through modified Becke-Johnson exchange potential."*

Sahab Uddin Mazumder, C.S. Sunandana, S. Mahapatra, Y. Sundarayya

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Paper to be communicated

(i) Electronic structure calculations on copper substituted silver iodide using Hybrid functional, HSE06 potential. (This work is under review)

(ii) First principle electronic structure calculations on copper substituted silver bromide through Modified Becke-Johnson Potential. (This work is under review)

(iii) Impact of Cu substitution on the structural, electronic and optical properties of AgBr: A first principle study using HSE06 potential. (This work is under review)

(iv) Theoretical investigations on structural, electronic and optical properties of Cu substituted AgCl through Tran-Blaha modified Becke-Johnson exchange potential. (This work is preparing for communication)

(vi) First principle investigation of copper substituted silver chloride using the HSE06 hybrid functional. (This work is preparing for communication)

Conferences and Workshops participated/attended

- (i). International Conference on Contemporary Researches in Engineering, Science, Management & Arts (ICCRESMA 2022) created & powered by Centre for Research and Training (CRT), National Foundation for Entrepreneurship, Development (NFED), Coimbatore, Tamil Nadu, India on 27-29 January 2022.
- (ii). Fourth International Conference on Material Science (ICMS-2024) organized by Department of Physics, Tripura University (A Central University), 31st January-2nd February 2024.
- (iii). International Conference on Chemistry in Multidisciplinary Research (ICCMR-2025) organized by Department of Chemistry, Nagaland University (A Central University), 25th -27th March 2025
- (iv). 30th National Conference on Condensed Matter Physics, Condensed Matter Days-2022 (CMDAYS-2022), 14th -16th December 2022, Organized by the Department of Science and Humanities, National Institute of Technology Nagaland, India.
- (v) Two-day National Level Workshop on the “Fundamental Aspects of Nano Horizon” organized by the Department of Physics, Nagaland University on 6th & 7th March, 2025.

List of webinars participated.

- (i). International Webinar on Nanoscience and Nanomaterials, organized by Department of Physics, Assam University, Silchar, from 16th -17th November, 2020.
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Electronic structure calculations on copper substituted silver iodide through modified Becke-Johnson exchange potential

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ABSTRACT

Silver iodide (AgI) has a rich phase diagram with the γ -AgI being one of the forms. γ -AgI is a *n*-type semiconductor that crystallizes into zinc blende structure and found to be stable at ambient temperature and pressure. The electrical transport in γ -AgI is mediated by the migration of Ag^+ cationic interstitial defects, while the Cu^+ Frenkel defects are responsible for the conduction in γ -CuI, a *p*-type semiconductor. This intrigues to understand the transition of the nature of electrical transport with the replacement of Ag by Cu. In this regard, we report the computational study on the Cu substituted γ -AgI using the density functional theory (DFT) with Tran-Blaha modified Becke-Johnson (TB-mBJ) scheme. The calculations are performed on γ - $\text{Ag}_{1-x}\text{Cu}_x\text{I}$ ($x = 0.00$ – 1.00) supercell through full potential linearized augmented plane wave (FP-LAPW) method. The lattice parameter and bulk modulus are found to vary nearly linear with copper concentration x , whereas band gap values follow a non-linear variation.

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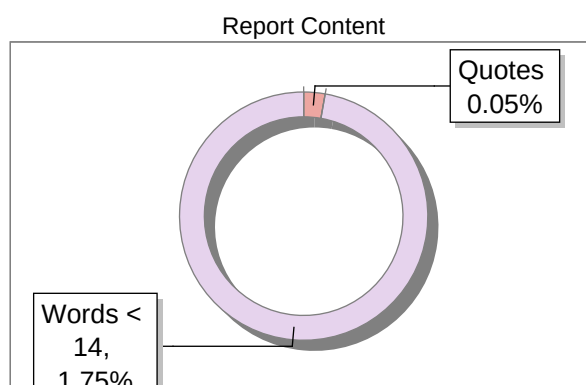
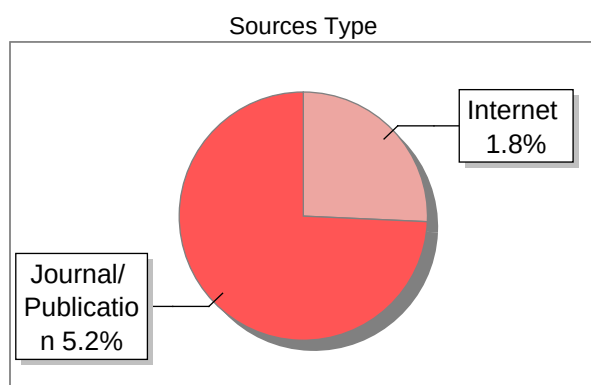
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