Theoretical investigation of structural properties of ternary alloy CuBr\textsubscript{x}I\textsubscript{1-x} through first principle method

Samandeep Singh Walia\textsuperscript{1}, Gopal Rizal\textsuperscript{2}, Neha Munjal\textsuperscript{*1} Agnibha Das Majumdar\textsuperscript{1}, Uma Kamboj\textsuperscript{1}

\textsuperscript{1}Lovely Professional University, Department of Physics, School of Chemical Engineering and Physical Sciences, Phagwara, Punjab, PIN-144411
\textsuperscript{2}Royal University of Bhutan, Bhutan
\textsuperscript{*}Corresponding Author: neha.18869@lpu.co.in

Abstract. In this research work, the structural parameters of industrially technologically important CuBr\textsubscript{x}I\textsubscript{1-x} ternary alloy compound has been systematically accomplished through computational approach within the DFT parameters. For the compound CuBr\textsubscript{x}I\textsubscript{1-x}, the concentration of dopant has been taken in the range of 0 to 1. CRYSTAL code is the computational software has been used to scrutinize the consequence of dopant on structural parameters. A cutback has been witnessed in the lattice constant with the enlargement in cluster concentration of I into CuBr while the bulk modulus kept on increasing. The results obtained are in good coordination with the previous work done.

1. Introduction

The halides of copper are suitable as they have optical behaviour which is non-linear. There has been a recent advancement in their ability to produce micro crystals and they even are good photosensitive material as well as have maddened semiconductor properties. Copper halides have good miscibility due to the tight binding. The copper halides under conventional behaviour crystallize in the space group F43m under the zinc-blende (B3) structure [1]. An adjacent structural behaviour of the I-VII semiconductor alloys reveals the formation of a proper solid solution for these alloys. Under the implementation of pressure there is a change from tetrahedral to octahedral because of the enhancement of the anion-cation pairs due to which there is a remodelling to the rock salt (B1) structure from the original zinc blende (B3) structure.

The uniqueness that copper halides possess is the presence of hybridized p-d bonding. It has also been remarked through the experimental studies that there is a presence of a lower symmetric intermediate structure in the pressure region of \textasciitilde 10 Gpa. Their degree of ionic band strength reaches to a scale of 0.7 as per of the Phillips scale of iconicity. The other industrial aspects of CuBr are that it is greatly used in the preparation of the organic compounds due to its diamagnetic behaviour whereas CuI is widely used as a reagent due to its ability to form crystals. Presently DFT is being widely used for investigating the several properties of technology important compounds [2-22].

2. Literature review

B.Amrani et.al [4] have used the FP-LAPW method to understand the behaviour of copper doped in Cl, Br and I using the GGA approximations. They observed a transition from ZnS to NaCl under high pressure. They calculated the parameters related to the structural aspects for both these phases. They also calculated the constants of elasticity. Further, they studied optical properties like
refractive index and dielectric constants under the photon range of 11 eV. F. Haj Hassan et.al [5] have cast off FLAPW method using the WIEN97 code for the alloys of copper halides and related to this they carried out the structural studies using the VCA approximation and even used this to calculate the band gap and its structure. A. Berghout et.al [6] have studied the optical, structural and thermodynamic properties of cubic crystal semiconductor alloy of Zn$_{1-x}$Be$_x$Se using 8 atoms supercell by the first-principles density functional theory DFT with the local-density approximation LDA. They calculated the bandgap as 1.08 eV and compared it with the experimental data. The bond length results showed a little deviation of about 0.04 Å as calculated by the Vegard’s Law formulae. The Phase diagram as shown by them predicted the miscibility gap having a critical temperature of about 1327.36 K. They concluded that the Zn$_{1-x}$Be$_x$Se alloy is unstable at normal temperatures for a wide range of in-between compositions. Yang Xiao-Cui et.al [7] have worked on the electronic as well as structural stabilities of SrX (X= S, Se, and Te) under high-pressure conditions. The computational method used is the plane wave set in the CASTEP code. They showed that the energy band gap decreases with the increasing pressure due to the reason for the wave function overlapping with shrinking atomic size under high pressure. The transition pressure (dv/V)% from B1 to B2 metallization was similar to the experimental data for SrS as 11.04% while there was a slight difference in the values for SrSe and SrTe due to the absence of the relativistic effects of spin-orbit interactions as the valence band of Se and Te consists of triple degenerate levels and in addition they also concluded that the bandgap is always indirect for B1 structures of all three crystals. M.G Brik [8] has studied the optical and electronic properties of ternary CuXS$_2$(X=Al, Ga, In) compounds using the CASTEP code. The crystal has a space group of 142d and crystallizes into a zinc blende (B3) structure. The experimental band gap of CuAlS$_2$ is about 3.50 eV but the calculated value was about 1.94 eV because of the DFT limitations of not accounting the exchange-correlation potential and he used scissor operator to remove this discrepancy. Further, the dielectric constant was also calculated by considering the matrix elements where the real part was calculated by Kramers-Kronig transform while the imaginary part in CASTEP. The refractive index for the crystals (X= Al, Ga, In) increases with the increasing atomic number as (2.26, 2.46, 2.57) respectively. The main results that were calculated were in good contrast with the experimental data available G. Gokoglu et al [9] have worked on the magnesium chalcogenides, MgTe, MgS, and MgSe using both GGA and LDA approximations and found the structural stability for different phases of the crystals like B1, B2, B3, B8. They observed the structural transition about 1.2GPa pressure as according to LDA both MgS and MgSe were found to have rock salt (B1) while MgTe to have B8 structure whereas the GGA calculations showed that MgTe and MgSe have wurtzite (B4) structure and MgS was the same as that was shown by LDA approximation. Moreover, they also showed that the presence of indirect band in B1 and B8 crystallographic structures with the lowest bandgap for all B1 structures around 0.44 eV while the highest bandgap was observed to be around 2 eV. Whereas the B4 and B3 phases of all had direct bandgap. Y. Saeed et.al [10] have reported the structural, electronic and magnetic properties of Zn$_{1-x}$TM$_x$S where TM= Fe, Co and Ni at x=0.25 through first principle study using the FP-LAPW based on the spin density functional theory. They discussed that the cohesive energy of the doped crystal is more than that of the ZnS crystal. They obtained the results by fitting the calculated energies to the Birch equation of state. Furthermore, Co doping generates only five majority spin states and even this semiconductor alloy is half-metallic for x=0.25. They even showed that these compounds have direct bandgaps at the transition points. They concluded that the TM ions produced the local magnetic moments on the non-magnetic moment sites of Zn and S sites. N.A. Noor et.al [11] retained worked on the structural properties and other atomic parameters of Cd$_x$Zn$_{1-x}$S through the (LDA) as well as generalized gradient approximant (GDA). They showed that the direct bandgap deplete from 2.0 eV to 0.9 eV as x mushroomed from 0 to 1.
and moreover the dielectric response also increases from 6.38 to 6.61. They showed that the thin films of the ternary compounds can be used as solar cells and even in photoconductive devices due to the wide bandgap heterojunction window. They also showed that the individual atoms possesses different orbitals for the determination of electronic patrimony like $s$ and $d$ orbitals of Cd, $d$ orbital of Zn and $p$ orbital of S. A. Schleife et.al [12] have worked on the electronic and optical properties of heterostructure and isostructural alloys using the cluster expansion method. They undergo the theoretical calculations of the bandgap and observed strong non-linear behaviour. They used the Beth-Salpeter equation to calculate the dielectric constants for each of the clusters of alloys. To calculate the density of states they decomposed the alloy into 16 atom cluster. They also found out that when doped with Se, S the crystal has similar band features but the bandgap of Cu$_2$SnS$_3$ has larger bandgap than Cu$_2$SnSe$_3$ since the electronegativity of S is more than that of Se C. Vargas-Hernandez et.al [14] performed the calculations to study the structural, magnetic and electrical behaviour of Zn$_{0.75}$Mn$_{0.25}$O alloy. Their study showed that the alloy has a half-metallic behaviour for the variation in x as 0.25, 0.50, and 0.75 and has a magnetic moment of 5 magneton per atom They also showed that the alloy over the various values of x has large bulk modulus thus providing good rigidity and making it suitable for the devices operating under high temperature and pressure. Q. Mahmood et.al [15] have worked on the ternary alloy Zn$_{1-x}$V$_x$S in the zinc blende (B3) phase and studied the structural, electronic, mechanical and optical properties. The computational method used by them was the Projected Augmented Wave (PAW) method. They also found out that when doped with V atoms, ZnS has almost similar band features but the bandgap of Cu$_2$SnSe$_3$ has larger bandgap than Cu$_2$SnSe$_3$ since the electronegativity of S is more than that of Se. S. Touam et.al [17] have worked on the ternary alloy CuBr$_x$I$_{1-x}$ using the FP-LAPW method. They used modified both Becke-Johnson as well as Engel-Vosko techniques for the calculations of the band structure. They used a different mesh of k points 72 and 32 for binary and ternary compounds respectively. They also showed that both the binary compounds have a zinc blende (B3) structure that crystallizes into a two-atom unit cell. A. V. Kosobutsky et.al [18] have worked on the fundamental properties of CuCl$_{1-x}$Br$_x$ using the LDA as well as meta GGA. They showed that in both the binary compounds the valence band separated in the range of 2 and 10 eV. They also observed that the lower band for both binary compounds CuBr and CuCl is by 3$s$ state of Cl and
4s state of Br whereas the contribution from Cu was from the d orbitals in the formation of the lower and the upper bands.

In this present paper, we have worked on the CuBr<sub>x</sub>I<sub>1-x</sub> (for x=0 to 1) with the help of CRYSTAL [19] software within the substructure of DFT as very less work has been through this procedure within this variation

3. Research Methodology

The first principle computational method of DFT of (LCAO) within the framework has been used to analysed the structural parameters of CuBr<sub>x</sub>I<sub>1-x</sub>. For the building of the K-S Hamiltonian, the scheme that has been considered is HYBRID2LYP. The optimization for calculating the structural properties of CuBr<sub>x</sub>I<sub>1-x</sub> (x=0 to 1) was governed through diminishing the total energy in contrast to the volume for each component of each cell. The self-consistency is obtained within the 14 cycles. The k-points are used with adequate tolerance.

4. Result and Discussion

For the determination of overall energies of (B3) structures of CuBr<sub>x</sub>I<sub>1-x</sub> for the variation in x for the range in the volumes (LCAO) has been used. With the help of plots shown below, we have illustrated the fluctuation of volume versus net energy. The energies has been deliberated according to the BM equation of the state which is fitted by the continuous lines in the plots which are summarized below

\[
E(V) = E_0 + \frac{9V_0B_0}{16} \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]^3 B_0' + \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]^2 \left[ 6 - 4 \left( \frac{V_0}{V} \right)^{2/3} \right]
\]

In this equation, E(V) depicts to the energy at the specific volume while E<sub>0</sub> and V<sub>0</sub> specifies the equilibrium energy and the analogous volume, further we have bulk modulus B<sub>0</sub> and also its derivative with respect to pressure B<sub>0</sub>'/ These structural parameters are put forth in Table 1.

The plots depicts the CuBr<sub>x</sub>I<sub>1-x</sub> as an undertaking of x and the variation in the Bulk Modulus and the Lattice Constant is plotted.
Table 1. Previously calculated and the presently calculated lattice parameter (a), bulk modulus ($B_0$) for the alloy CuBr$_x$I$_{1-x}$ (x=0.00, 0.25, 0.50, 0.75 and 1.00)

5. Conclusion
The structural properties of CuBr$_{x}$I$_{1-x}$ have been investigated in rocksalt structure by using linear combination of atomic orbitals under the density functional theory. The obtained values are in the good agreement with the available experimental and theoretical data. As the concentration changes from 0 to 1, the lattice constant varies from 6.24 to 5.92 and bulk modulus from 39.1 to 45.

Tripathi, S.N., Srivastava, V., Pawar, H. et al. First-principles investigation of structural, electronic and mechanical properties of some Dysprosium chalcogenides, DyX (X = S, Se and Te). Indian J Phys (2019). https://doi.org/10.1007/s12648-019-01564-x

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