THE EFFECT OF STRAIN ON ELECTRONIC AND OPTICAL PROPERTIES OF CuBO₂ (B=Y, SC) BY FIRST PRINCIPLES STUDY

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CuBO₂ (B=Y, Sc) has great interest nowadays, because it has a wide-range of application in solar cells, flat panel displays, gas sensors, biosensors and touch panels. Structural, electronic and optical properties of CuBO₂ under axial strain were investigated by using full potential linearized augmented plane-wave (FP-LAPW) method based on density functional theory (DFT) within GGA and TB-mBJ(Tran-Blaha modified Beck-johnson) functional. The computed structural lattice parameters are in good agreement with the previous simulated and experimental results. The energy band structures, density of states, charge densities, bond lengths and optical properties are calculated and analyzed with and without strain. The results show that, by increasing the tensile strain, the band gap of CuBO₂ oxide decrease as compared to unstrained copper oxide. From optical properties, it is noted that in visible energy region the CuYO₂ have more transparent behavior as compared to CuScO₂. The wide band-gap and transparent behavior for visible energy region makes it important material for transparent applications.

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1.Introduction

Transparent conducting oxides (TCOs) materials are widely used in various applications currently, such as touch screens, electrodes for optoelectronic devices, gas sensors, liquid crystal displays, solar cells, smart windows and flat panels [1]. The generally n-type TCOs are ZnO, SnO₂, In₂O₃, CdO, Cd₂SnO₄, Ga₂O₃ and p-type ternary oxides like ABO₂. Here, (A = Cu or Ag) and B belongs to either group IIIA (Al, Ga or In) or IIIB (Sc or Y) elements. The conductivity of p-type TCOs is significantly smaller than the conductivity of n-type TCOs. The importance of p-type TCOs compounds in optoelectronic devices is mainly due to their wide energy band gap (>3 eV), high transparency rate and low reflectivity in the visible energy region of the electromagnetic spectrum [2-3]

Delafossite materials have wide band gap applications [4]. Delafossite mineral group having a typical form ABO₂, the ABO₂ group differentiated through a layer of linearly directed A-cations arranged in the middle of edge shared octahedral coatings (BO₆). The ABO₂ (delafossite) structure is described over a coating of linearly coordinated A-cations fixed between

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edge-shared octahedral layers (BO6). The A-type cations are contained of Pd, Pt, Cu, or Ag ions technically in a mono-valent state. The B-type cations are contained of utmost trivalent transition metals and the rare-earth elements.

First-principles calculation within the density functional theory (DFT), holds significant importance in the study of structural, electronic and optical properties as well as in insight the defect physics of the materials owing to its excellent control characteristics. The previous calculations of ternary delafossites structures were executed within the LDA or GGA, which underestimates the band gaps. Therefore, in this research work we use a TB-mBJ(Tran-Blaha modified Beck-johnson) functional to overcome the shortcomings of LDA and GGA methods.

 $CuBO_2$ (B=Sc, Y) compounds are transparent conducting oxide p-type materials, which have a large band gap. $CuBO_2$ (B=Sc, Y) compounds are highly suitable materials for solar cell technology [4]. It is well recognized that the atomic positions and inter-atomic distances intensely effect the optical and electronic properties. Hence, these two parameters can be used to change the electronic properties with strain study through lattice mismatching. Strain is being extensively used to modify the optical and electronic properties of different materials (GaN, Si, ZnO, and SnO_2 [5]. While its effect has not been calculated in $CuBO_2$ (B=Sc, Y). Here we have focused on the strain study of these materials.

In this paper we analyze the structural, electronic and optical properties of CuBO2 (B=Sc, Y) compounds under tensile strain by using a ab initio DFT approach. We show that the TB-mBJ(Tran-Blaha modified Beck-johnson) functional effectively open the gap between VBM to CBM. The density of states, band structure and optical properties of CuBO2 (B=Sc, Y) delafossites compounds are presented in detail.

2. Methodology

The electronic, and optical properties of strained ABO_2 (A= Cu or Ag and B= Y, Sc) were determined using the full-potential linearized augmented plane waves (FLAPW) method implemented in WIEN2K. For electronic and optical properties, we have used TB-mBJ exchange correlation potential is in the form of TB-mBJ [6-8].

In present work, Muffin-tin radii (RMT) values for Cu, O, Sc (1.81, 1.56,1.96) in CuScO₂ and Cu, O, Y were (1.75,1.51,2.14) used in CuYO₂ respectively. we have optimized the RMT× K_{max} value and it is equal seven (kept constant) for all calculation in interstitial area, which converge the basis-sets functions and for Fourier expansion of charge density, Gmax is kept constant (12 au⁻¹) and 300 k-points were used for each structure to calculate the electronic and optical properties in first brillouin zone integration and total energy is converged to within 0.0001Ry.. We investigated the in-plan lattice parameter *a* in the due to strain by this formula

 $\frac{a-a_o}{a_o}$

3.Results and discussion

3.1. Structural Properties

Delafossite transparent conducting oxide $CuBO_2$ (B=Y, Sc) compounds having space-group R-3m (#166) are composed of O-Cu-O dumbbell shape in hexagonal plane separated by a BO₆ edge sharing octahedral layer having rhombohedral symmetry. The structural properties

 a_o and *a* respectively, very close to their experimental values [10].

The optimized lattice constants of $CuBO_2$ (B=Y, Sc) structure are summarized in Table 1. The current calculated lattice constants of $CuBO_2$ (B=Y, Sc) are in good agreement with other simulated results, signifying that our lattice constants are even now reliable. After geometry optimization, calculated the B-O (Sc-O and Y-O) bond distance, the bond distance of B-O increases by increasing strain and the bond length values of Y-O are larger than Sc-O because of Y have greater atomic radius as compared to Sc. The Cu-O (bond) distance have same values by applying different strain. The calculated bond length of (CuBO₂) compounds is presented in Table 2 & 3.

Materials and structural	Experimental results	Present results
Properties		
CuYO ₂		
a (Å)	3.533 ^{a,} 3.53 ^b	3.550
c (Å)	17.136 ^a ,17.14 ^b	17.199
u	0.1066^{a}	0.1066
CuScO ₂		
a (Å)	3.216 ^c ,3.2155 ^d	3.235
c (Å)	$17.090^{\circ}, 17.089^{d}$	17.255
u	0.1103 ^c ,0.1052 ^d	0.1070

Table 1. Calculated lattice parameters and internal parameter u of CuBO₂ (B=Y,Sc).

^a Ref. [11], ^b Ref. [12], ^c Ref. [13], ^d Ref. [14].

Table 2. Calculated Bond length between d_{Cu-o} (copper oxygen bond) and d_{B-o} (Y& Sc oxygen bond).

Material	Present bond length (Å) d _{Cu-o}	Other bond length(Å) d _{Cu-o}	Present bond length (Å) d _{B-o}	Other bond length (Å) d _{B-o}	Band gap E _g
CuScO ₂	1.84629	1.83 ^a	2.13269	2.14 ^a	2.57 eV
CuYO ₂	1.83341	1.842 ^b	2.29523	2.28 ^b	2.94 eV

^a Ref. [15], ^b Ref. [16],

	Present	Present	Band gap
Material	bond length (Å)	bond length	$E_g (eV)$
	d _{Cu-o}	(Å)	
		d _{B-o}	
CuScO ₂	1.84629	2.13269	2.57
1% Strained	1.84629	2.14889	2.39
3% Strained	1.84629	2.18119	2.31
5% Strained	1.84629	2.21455	2.21
CuYO ₂	1.83341	2.29523	2.94
1% Strained	1.83341	2.31330	2.89
3% Strained	1.83341	2.35005	2.86
5% Strained	1.83341	2.38693	2.82

Table 3. Calculated Bond length with strained effect between d_{Cu-o} (copper oxygen bond)and $d_{B-o}(Y\& Sc oxygen bond)$.

3.2. Electronic Properties

3.2.1. DOSs and Energy bands

From the theoretical point of view, it is necessary to find a detailed understanding of the electronic properties of $CuBO_2$ (B=Y, Sc) before these materials can be used in the specific applications. To better understand the effect of strain on the electronic structure of $CuBO_2$ (B=Y, Sc), we have calculated and compared the electronic band structures and DOS under 1%, 3% and 5% of strain.

From Fig.1a shows the total density of state of the CuScO₂ without strain and it is observed that the lower part of valence band is in the energy range of -6.8ev to -3 eV and upper part consist in the energy range -2ev to Fermi level. Partial density of states plots Fig.1b to Fig.1d shows that from -2.0 ev to Fermi level the valance band is mostly consist of Cu-d state. The upper part (-2.5 to 6) eV of conduction band is normally formed by Y-d and O-2p state. From Fig.1e shows the total density of state of the CuScO₂ without strain and a similar behavior observed as CuYO₂. In the Fig. 1. (f-h), the partial density of density of state of CuScO₂ shows that the lower part of the valence band consists of O-2p state in the energy level (-6 to -3eV). Upper valance band (-2 to 0 eV) is composed of Cu-d state. The Sc-d state is mostly contributed in the upper part (4.5 to 8 eV) of the conduction band as compare to the Cu-d and O-p state. The valence band maxima of CuBO₂ (B= Sc, Y) are mostly composed of Cu-3d state with prominent peak located at above 2eV together with minor involvement of O-p state. The lower valence band is majorly dominated by O-2p along with small contribution of d orbitals of B atoms. In case of CuBO₂ (B=Sc, Y) the conduction band is composed of O-p and B-d states.

The calculated band structures of unstrained CuBO₂ (B=Y, Sc) are shown in Fig.2a and Fig.2b. It is noted that from the band structure, the CBM of unstrained CuBO₂ lies at gamma point and VBM of CuBO₂ lies at F point, which indicates the indirect band gap along Γ to F direction. The Fermi level is set to be zero of the energy scale.

To investigate the significance of tensile strain on the electronic properties of $CuBO_2$, we have calculated the electronic band structures and DOS under 1% ,3% and 5% of strained. From Fig. 3. (a and b), we plot the two-combined graphs of $CuBO_2$ under different strains, to carry out

the effect of strain on DOS. For valence band, under strain method the profile of 2p-O state and the width of valence band shifting toward lower energy by enhancing strain ratio. For conduction band, take the effects of strain values into account, one can see that, the value of band gap decreases by increasing strain ratio, in particular, with the increasing of strain values, the state localization is decreasing on the whole conduction band, and the peak of 3d of Y move towards lower energy area.

Fig. 4a -4f shows that the valence band maxima (VBM) lie at gamma point, while on other hand conduction band minima (CBM) lie at L point and the energy band gap is calculated along gamma to L symmetry points, it implies that $CuBO_2$ (B=Sc, Y) is a direct and indirect band gap semiconductor respectively, which are fine agreement with [4]. From table (3), we clearly seen that the calculated band gap of CuBO₂ (B=Sc, Y) with TB-mBJ is higher than PBE-GGA due to overestimation of TB-Mbj, good agreement to other simulated results mentioned in Table. 3 and less than to experimental data [4] because DFT has approximation method. While on other hand, in the presence of strain effect, the high symmetry points along which we calculated the band gap at VBM and CBM remain unchanged but the values of CuYO₂ band gap decreased upon increasing strain ratio by using GGA and TB-mBJ functional, strained band gap values also have less than as compared to unstrained values while on other hand the band gap values of $CuScO_2$ enhanced in between (1% to 3%) and more than 3% to 5% its values decreased, which clearly shown in Fig.4 (a and b), however the calculated band gap values are underestimated by DFT. It implies that the magnitudes of band gap of $CuBO_2$ (B=Sc, Y) can be varied by operating different ratio of tensile strain. From table 3, we also noted that the, by increases strain ratio, the bond length between Sc-O and Y-O also increases and corresponding its band gap values decreases.



 $\textit{Fig. 1. Calculated Total and partial density of states of \textit{CuYO}_2(a, b, c \textit{ and } d) \textit{ and }) \textit{CuScO}_2(e, f, g \textit{ and } h)}$



Fig. 2. Calculated band structure of CuYO₂(2a) and CuScO₂(2b)



Fig. 3. Calculated Total density of states for 1%,3% and 5% strain effect of (a) $CuYO_2$ and (b) $CuScO_2$



*Fig. 4. Calculated band structure for 1%, 3% and 5% strain effect of CuYO*₂ *and CuScO*₂ *a) CuYO*₂-1%, *b) CuYO*₂-3%, *c) CuYO*₂-5%, *d) CuScO*₂-1%, *e) CuScO*₂-3%, *f) CuScO*₂-5%

Material	Band Gap with PBE-GGA	Band Gap with TB-MBJ	Experimental results	Others Theoretical results
Names				
CuYO ₂	2.74 eV	2.94 eV	3.5 eV ^a	2.86 eV ^c , 2.983eV ^e , 2.63eV ^d , 2.67eV ^f
CuScO ₂	2.46 eV	2.57 eV	3.7 eV ^b	2.76 eV ^c , ,2.883 eV ^e , 2.29eV ^d , 2.17eV ^g

Table 3. Calculated band gaps of CuBO₂ (B=Y,Sc) using GGA and Tb-mBJ.

^a Ref. [17], ^b Ref. [18], ^cRef. [4], ^d Ref. [19], ^e Ref. [16], ^f Ref. [20], ^g R

Table 4. Calculated band gaps without and with Strain concentration (1%,3% and 5%).

Material	Band Gap	Band Gap with	Band Gap with	Band Gap with
Names	without	1%(Strained)	3%(Strained)	5%(Strained)(eV)
	strain (eV)	(eV)	(eV)	
CuYO ₂	2.94 eV	2.89	2.86	2.82
CuScO ₂	2.57 eV	2.39	2.31	2.21

3.2.2. Electronic Density

Electron charge density signifies the description of the bond between distinct atoms. To predict the chemical bonding in CuBO₂ (B=Y and Sc) compounds, the charge density is calculated in (100) direction plane for these compounds and have been shown in Fig 5. Valance charge density calculation is observed for CuBO₂ (B=Y and Sc) compounds. The plots show that there is strong ionic bond nature between the copper and oxygen at 0 and 1% of strain and at (3 and 5) % of strain ratios, the ionic bond nature of Cu-O decreases and covalent bonding nature increases. We also noted that from the figures, the covalent bond nature of Sc-O and Y-O increases by increase strain ratio. The ionic bonding decreases and the covalent nature increases in Sc-O and Y-O bond due to the valance charge density also increases along B-O was reported by [4].



Fig. 5. Calculated Valance charge density of (a) $CuScO_2$ without strain and (b to d) for 1%,3% and 5% strained effect of $CuScO_2$ respectively (e) $CuYO_2$ without strain and (f to h) for 1%,3% and 5% strained effect of $CuYO_2$ respectively.

3.3 Optical properties

The absorption spectra of unstrained CuBO₂ (B=Sc, Y) as shown in Fig.6, it shows the semiconducting character of these materials, In the energy range between 0.0eV and 3.0 eV, the absorption coefficient is almost zero because in this range medium and incident photon have lack of interaction. In visible region (1.7 to 3.3) eV, the material CuYO₂ have more absorption rate as compared to CuScO₂, it implies that CuYO₂ has more transparent than to CuScO₂. It has two peaks at 4.0 eV and the other at 5.0 eV also having a shoulder at lower energy. These materials occupy good absorption coefficient near 4 eV and 5eV energy range. To explore the effect of tensile strain on the absorption spectrum, we have calculated and compared the absorption coefficient of CuYO₂ and CuScO₂ under 1%, 3% and 5% of tensile strain. From Fig. 7 (a,b) it is observed that as tensile strain increase, the absorption coefficient starts decreasing. It is observed that absorption coefficient decreases almost linearly with the increase of magnitude of tensile strain, and reaches maximum up to energy around 4eV. This energy range exist in the ultraviolet range of the light

spectrum and thinks that the medium takes up maximum photons in the ultraviolet range. The transparency for the visible-region of light-spectrum and absorbance of photons in the ultraviolet region makes it suitable for flat-panel displays and window layer in solar-cells.

The real and imaginary part of dielectric function of both materials without strain are plotted in Fig.8. (a and b), The energy transition of the computed imaginary spectra occurs at 2.4 eV for CuScO₂ and 2.8 eV for CuYO₂, it means that energy transition of CuScO₂ is less than to CuYO₂. These calculated threshold energies are related to electronic transition, for pure CuBO₂ (B= Y, Sc) case, we noticed that a main sharp peak around the photon energy 3.0 eV for CuScO₂ and 4.0 eV for CuYO₂. This peak of CuBO₂ (B= Y, Sc) are caused by the direct transitions from the O 2p states near VBM to the empty orbitals in the conduction band. It is noted that in Fig.8 (a and b), the threshold-energy of both materials decreases by applying the tensile strain, at 1%, 3% and 5%, the values of peak of CuYO₂ are 2.8 eV, 2.6eV and 2.4eV and for CuScO₂ are 2.3 eV, 2.1eV and 1.9 eV respectively in both cases. The imaginary part of dielectric-function displays a red shift traffic with the increase of tensile strain.

Fig.9 (a), illustrated the real-part of di-electric function of $CuBO_2$ (B= Y, Sc) with and without strain, the static di-electric constant value of $CuScO_2$ is 4.6 eV and for $CuYO_2$ is 3.8 eV. It means that at static level, the value of di-electric constant of $CuScO_2$ is higher than that of $CuYO_2$. The values of dielectric constant almost remained same after applying different values of strain. For comparative study of the real part of dielectric function of $CuBO_2$ (B= Y, Sc) for strain ratio (1%, 3% and 5%), it is noted that the static di-electric constant value of $CuScO_2$ is greater than $CuYO_2$.



Fig. 6. Absorption of CuYO₂ and CuScO₂



Fig. 7 Absorption of 1%,3% and 5% strain effect of CuYO₂(a) and CuScO₂(b)



Fig. 8. (a) Real and (b) Imaginary parts of dielectric function of CuYO₂ and CuScO₂



Fig. 9. Real (a, b) and imaginary (c, d) parts of dielectric function of 1%,3% and 5% strain effect of CuYO₂ and CuScO₂

4. Conclusion

In this research work, carried out the structural, electronic, optical and comparative study of $CuBO_2$ (B= Y, SC) under tensile strain (1%, 3% and 5%) by using FP-LAPW method. The band structure information, lattice parameters and its optical properties were calculated and discussed. The bond lengths values of Sc-O and Y-O increases by increases strain ratio, band gap values decreased as compared to unstrained. From DOS results, noted that, the valence band of CuYO₂ and CuScO₂ mainly compose of 3d state of Cu, and 2p state of O, while the conduction band mainly compose of 3d of Sc state.

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