Invited Paper

# Delafossite-alloy photoelectrodes for PEC hydrogen production: a density functional theory study

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## ABSTRACT:

Efficient photo-electrochemical (PEC) splitting of water to hydrogen usually requires photoelectrodes to have certain electronic properties. Unfortunately, at present available semiconductors do not meet all these criteria. So, a thorough understanding of band-engineering for mixed alloys is necessary to successfully design these photoelectrodes. Among the semiconductors, transition metal oxides are of particular interest due to their low cost and relatively high stability in aqueous media. Here, we will present a theoretical study of delafossite-alloys for PEC photo-electrodes. Previous studies have indicated that the group IIIA delafossite family ($CuMO_2$, M = Al, Ga, In) do not exhibit direct band gaps. Their fundamental band gaps are significantly smaller than their reported optical band gaps. On the other hand group IIIB delafossite family ($CuMO_2$, M = Sc, Y, La) in general show direct band gaps and, except for $CuLaO_2$, band gaps are above 3.00 eV. However, both of these two families exhibit p-type conductivity. We will show that by appropriate alloying of these two delafossite-families we can tune their band gaps and other opto-electronic properties. These types of alloying are desirable, as these introduce no localized impurity states in the band gap due to isovalent alloying. Also, the electronic effective masses can be lowered by selective doping of main group elements. Finally, it will be discussed that, lowering the symmetry constraints of these alloys would enhance their optical absorption properties. We'll also discuss that alloying with other 3d metal elements may decrease the band gap, but would increase the effective masses of the photo-electrons.

## I. Introduction

Photoelectrochemical (PEC) splitting of water by solar light is considered to be the most desirable "green" method for hydrogen production [1,2]. This has attracted great attention since the demonstration of water splitting using a $TiO_2$ photoanode illuminated with ultraviolet light over thirty years ago by Fujishima and Honda [3]. For a successful PEC hydrogen production by water splitting, low cost and easily obtainable photocatalysts are needed. Such photocatalysts, which are usually semiconductors, should have some desirable electronic properties; such as, for optimal use of solar energy, the visible range of the solar spectra must be absorbed by the photocatalysts. In addition, to meet the necessary energy requirements for water splitting, the desired photocatalyst must be a semiconductor of band gap around 2.0 eV,

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and the positions of its band edges must be matched with the water-splitting potentials [4,5]. Furthermore, the materials must be stable in aqueous solutions. Naturally occurring semiconductors do not satisfy all these constraints simultaneously. New methods and technology must be developed to engineer such semiconductors. So, to electronically design and achieve the suitable photoelectrode materials, its electronic properties, and how it responds to the defect formation must be understood.

It has been shown recently that, even a suitable band gap may not ensure good photocurrent activity if the electron mobility in the photo-catalysts is very poor [6,7]. In transition metal-oxides, the presence of the localized 3d metals orbitals near the band edges increase the carriers' effective masses. These 3d bands result in a very flat band structures at the conduction and/or valence band edges. So though metal oxides are sometime preferable because of their stability, these may suffer from current conduction problems. On the other hand, a conducting semiconductor with good carrier mobility does not automatically guarantee to have a better optical transition at the minimum direct gap. Due to the crystal structures, certain symmetry conditions of the crystals may prohibit an optical transition at the minimum band gap. In addition, due to doping or alloying, a direct gap material may turn into an indirect gap alloy, which is not preferable as well. To overcome these problems, a suitable band engineering approach is necessary to design a desired photoelectrode with proper band gap and to simultaneously improve the optical absorptions. Hence, while doping or alloying a photocatalyst to band engineer its gap and band edge positions, the carrier mobility and optical absorption issues need to be taken into careful considerations. In this paper, we will demonstrate these challenges in delafossite materials, such as in $CuYO_2$ by calculating the electronic properties of these materials.

Band gap engineering is an important step in designing novel functional semiconductor materials. Widely investigated $TiO_2$ meets almost all the criteria for a suitable photoelectrodes, but its band gap is too large to absorb sunlight efficiently. Thus, band gap reduction of $TiO_2$ has been studied extensively. The most common method used for band gap reduction is the incorporation of impurities, such as C and N. However, it has been argued that although impurities can reduce the band gap, their incorporation also leads to poor photo-response because the partially occupied impurity bands can act as carrier traps for photo-generated carriers. It has been demonstrated that passive donor-acceptor co-doping may suppress the recombination and yet maintain a reduced band gap, revealing that "non-isovalent compound" alloying could be an excellent choice for band gap engineering due to the large band offsets between the compounds [8,9]. Compound alloying poses several critical problems, including choosing the appropriate host and alloying semiconductors, the alloying approach, and the alloying concentration. A thorough understanding of the non-isovalent alloying physics is necessary to pre-screen the potential alloying materials for a given purpose and hence to avoid the expensive the trial-and-error method in the lab.

The availability of both *n*-type and *p*-type semiconductors is often desirable for photocatalysts. Oxides, in general, are found to be *n*-type semiconductors because of high electronegativity of O-p orbital. For effective and sustainable p-type doping in oxides, higher valence band maximum (with respect to the vacuum) is necessary. In metal oxides, this can be achieved by selecting metals with relatively higher d-orbital position. Among the transition metals, Cu 3d has the highest energy. Hence, Cu-bases oxides are more likely to be doped with p-type carriers. However, oxides like $Cu_2O$ are not stable in aqueous solutions, though the band gap is in the right range. Recently, Cu delafossites, $CuMO_2$ ($M$ = group III-A (group 13) and III-B (group 3) elements), have received great attention due to their unique properties such as stability in most aqueous solutions and *p*-type conductivity with excellent hole mobility. The *p*-type conduction here is due to the fact that their valence band maximum (VBM) is composed of hybridized Cu-*d* and O-*p* antibonding orbitals [10]. PEC response for some Cu delafossites has already been demonstrated [11]. Unfortunately, the efficiencies of these photo-conversion processes are not very high for practical applications. In fact, recent theoretical study has revealed that due to their special crystal structure, Cu delafossites have undesirable band structures for PEC applications. Specifically, the group IIIA (with $M$ = B, Al, Ga and In) delafossites usually have large disparity between the fundamental band gaps and the measured optical band gaps [12]. The absorption of photons with energy of the minimum direct band gap at brillouin zone center is very weak due to the inversion symmetry of the delafossite structures, an effect also observed in other oxide systems. Therefore, to improve PEC responses of Cu delafossites, it is necessary to enhance the optical absorptions around the minimum direct band gaps, in addition to optimize the fundamental band gap itself. It has been shown that by breaking the symmetry of the delafossite materials by means of appropriate alloying or doping, the optical absorption can be improved at this smallest direct gap [13].

We have employed density-functional theory (DFT) to study the electronic properties of the delafossites materials. Generalized gradient approximation (GGA) to DFT and the projected augmented wave (PAW) basis as implemented in the Vienna *ab initio* simulation package (VASP) are used [14,15]. Plane-waves cut-off energy of 400 eV was used, and the ion positions were always relaxed until the force on each of them is 0.01 eV/Å or less. We have used 13×13×3 (for hexagonal cell) k-point distribution for the final energy calculations. To correct the DFT-GGA underestimation of electron correlation in the cation 3*d* bands, DFT+*U* method has been used. It should be noted that the choice of the *U* parameters cannot be determined uniquely within the present methodology. The choice of *U* for the delafossite materials has been discussed in one of our previous papers where group IIIA and IIIB delafossites have been studied in details without any doping [16]. The structural parameters and the choice of ground state crystal symmetry was found to be agreed well with the experimentally known results. In addition, it has been also shown, that while Kohn-Sham DFT did not predict the correct experimental trend for the band gaps for group IIIB delafossites, with DFT+U (with the values of U as in ref.) had been able to restore the experimental trends. Hence, in this paper we have used the same DFT+U setting. In summary, for the results reported in this paper $U_{eff}$ ($U$-$J$=7 eV) parameter was added to the DFT Hamiltonian for all the valence Cu-*d*, Sc-*d*, and Y-*d* bands. In case for $CuLaO_2$, no U has been used for La-*f* orbital.

## II. Results and discussions

The delafossite structures can have either $P6_3/mmc$ or $R3m$ space-group symmetry. In both symmetries, O and Cu form a linear bonding structure along the *c* axis, which is considered to be the main channel for the hole transport (p-type behavior), whereas O–$M$ ($M$ = transition metal atoms) bonds form distorted octahedral (Figure 1). These octahedras

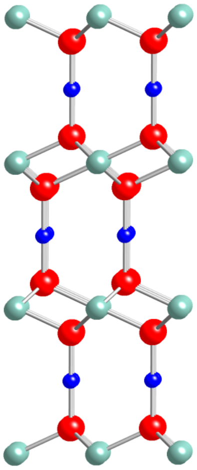

Figure 1: Hexagonal stacking of the delafossite structure is shown here. The red (large balls) and blue (small balls) are oxygen and copper atoms, respectively. The light green atoms (medium balls) are group IIIA or IIIB cations.

are connected by the linear Cu-O chains. Structurally the main difference between these hexagonal and the rhombohedral symmetries is the difference in the stacking sequence of O-*M* octahedron-layers. In general, group IIIB and IIIA delafossites prefer the hexagonal and rhombohedral symmetries, respectively. However, for a given IIIA/IIIB delafossite, the energy difference between the two symmetries is very small. For instances, for $CuYO_2$ the hexagonal structure is only 0.035eV lower in energy (per formula unit) than the corresponding rhombohedral structure. It is known that while the group IIIB delafossites have essentially direct band gaps of around 3eV, group IIIA has much lower (lower than 2eV) indirect band gaps. Also, the band gap anomalies observed in the $CuM^{IIIA}O_2$ family [12] are not found in $CuM^{IIIB}O_2$ [16]. The understanding of the band gap behaviors of these group-III cuprate-delafossites provides a unique way to design materials with the desirable band structures. Hence, in principle it is possible to band engineer the group IIB delafossites to reduce their gaps and to increase the carrier mobility. In the following, all the calculations were performed with group IIIB delafossites having the hexagonal structure.

The calculated lattice constants for both the rhombohedral and hexagonal unit cells agree well with the available experimental values. For example, for hexagonal $CuYO_2$ we found $a$ = 3.628 Å and $c$ = 11.420 Å, whereas the experimental values are $a$ = 3.521 Å and $c$ = 11.418 Å. For the conventional rhombohedral unit cell, our calculated lattice constants are $a$ = 3.521 Å and $c$ = 17.178 Å. The longer $c$ in rhombohedral unit cell corresponds to the different stacking sequence of the metal-oxide octahedron layers along the z-direction. However, when normalized to per formula unit (i.e., one stacking height), the hexagonal and rhombohedral $c$-values become $c/2$=5.710 Å and $c/3$=5.726 Å, respectively. The energy per formula unit for the hexagonal structure for $CuYO_2$ is lower by 0.034 eV than the rhombohedral structure. These differences are 0.050eV and 0.015eV per formula unit for $CuScO_2$ and $CuLaO_2$, respectively. On the other hand, the group-IIIA prefers the $R\overline{3}m$ structure. For example, the energy per formula unit for

$CuAlO_2$ structure in $R\overline{3}m$ symmetry is 0.027 eV lower than the hexagonal structure. For $CuGaO_2$ and $CuInO_2$ this difference is 0.006eV and 0.232eV, respectively. The calculated lattice constants, for example, for $CuAlO_2$, $a$ = 2.845 Å and $c$ = 17.025 Å, compares well with the previous DFT calculations and with the experimental values [8]. However, it should be pointed out that the energy differences between the rhombohedral and hexagonal structures are small except for $CuInO_2$. It is possible that the synthesized materials may exhibit either of these two symmetry groups, or a mixed symmetry structure.

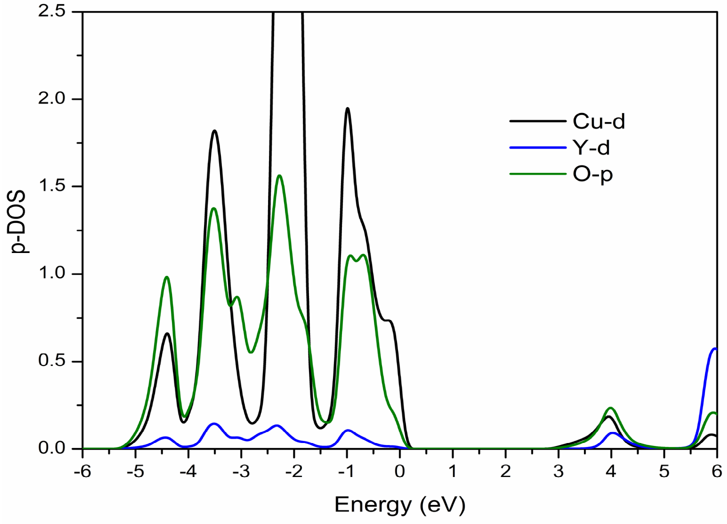

Figure 2: Partial density of states (p-DOS) plot for hexagonal $CuYO_2$.

The rhombohedral and hexagonal structures of delafossites differ only in stacking sequence and are symmetrically similar (Figure 1). So it is expected that a given delafossite in these two symmetries would have similar electronic characters. It has been reported before, in the case of Cu(I)-oxide based structure the VBM is composed of hybridized Cu-*d* and O-*p* anti-bonding [10] type band. So for the two families of delafossites in both of the two symmetries, this anti-bonding VBM is a common feature. The anti-bonding nature of the valence band edge is the main reason for the relatively higher mobility of holes, compared to the other oxides (such as ZnO). Figure 2 shows the calculated total density of states (DOS) plot for a representative delafossites: $CuYO_2$ in hexagonal symmetry. Y has one 4*d* electron, so 4*d* here is largely unoccupied. The overall features of the DOS plots are almost the same within the same group of delafossite. The electronic difference between the two groups is chemical in nature, rather than structural. For example, for both $CuAlO_2$ and $CuGaO_2$, the hexagonal and rhombohedral symmetries have similar DOS features near the top part of the valence band. In $CuAlO_2$, the unoccupied Al-*s* band lies higher in energy and Al has no -*d* electrons. On the other hand, the presence of unoccupied Ga-*s* band is seen around 6eV above the Fermi level, and a long *s*-band tail is found at the bottom of the conduction band. Very minor *d*-band contribution due to Ga in the valence band part of the DOS has almost no influence. For group IIIB, the presence of a lone 4*d* electron due to Y appears to have relatively more influence on the valence band structure for $CuYO_2$.

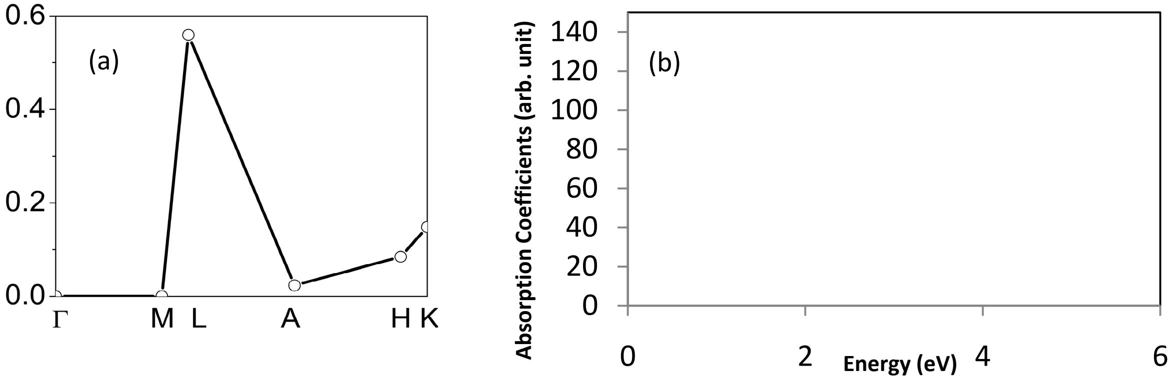

Figure 3: (a) Transition probability for a representative group IIIB delafossites, $CuYO_2$, at different symmetry points. Units in the y-axis are arbitrary. (b) The calculated optical absorption coefficients are shown for $CuYO_2$.

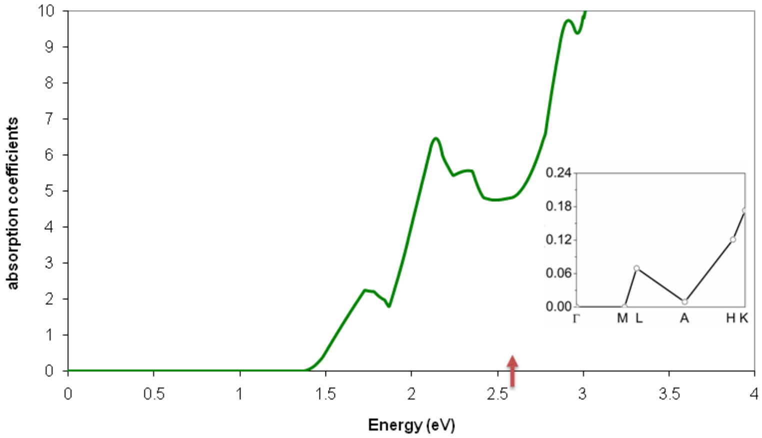

Figure 4: Calculated optical absorption coefficients for $Cu(La,Ga)O_2$. The arrow in the x-axis shows the band gap for pristine $CuLaO_2$. The reduction of optical band gap due to this isovalent alloying is clear from the figure. The inset shows that at the zone center (Γ-point) the absorption probability is zero for the pristine $CuLaO_2$.

We have also calculated the transition matrix elements between the band edges of group IIIB delafossites at the special symmetry points as shown in figure 3 (a). Figure 3(b) shows the absorption coefficients for the same delafossite. These matrix elements were calculated by the optic code as implemented in WIEN2k [17]. Here, only the diagonal components (direct gap) of the momentum matrix were calculated, because the off-diagonal elements would not contribute significantly. In all cases, the transition between VBM and CBM at Γ− point is forbidden, because of mainly *d*-character of both VBM and CBM and transition would results in parity violation. For $CuYO_2$, transition matrix elements show higher absorption at L point where the direct gaps are more than 3.5 eV. The reason for higher transition is that, at this point the CBM has higher *p*-contribution, and VBM has mainly *d*-contribution, So *p*-*d* transition is favorable here. On the other hand, $CuLaO_2$ may show different behavior because of the presence of highly localized unfilled f-band near CBM. In figure 4, we have shown the optical absorption probability for $CuLaO_2$ (at the inset). It shows higher adsorption at H and K points and the L-point transition is suppressed. So due to the lower band gap, $CuLaO_2$ has the potential to be used as a photo-electrode for PEC hydrogen production.

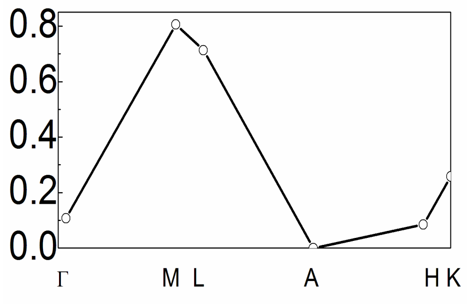

Figure 5: Transition probability for a delafossite alloy, $Cu(La,Ga)O_2$, at different symmetry points. Units in the y-axis are arbitrary.

Now, to enhance the optical absorption near the fundamental band gap, one needs to break the inversion symmetry of the delafossite structure. Alloying or introducing defects is often used to realize symmetry breaking. It should be noted, however, that introduction of defects can also lead to the formation of recombination centers, which are detrimental to the performances of photovoltaic and PEC devices. We have shown that enhancement of the optical absorption and optimization of the fundamental band gap via alloying of various Cu delafossites, namely, mixing group-IIIA metal elements in delafossites is advatageous. Such mixture of *M* elements breaks the inversion symmetry *chemically* and enhances the optical absorption corresponding to the fundamental band gap. Because the *M* elements are isovalent, the alloying would maintain the structural integrity of the delafossites and not lead to the formation of recombination centers. Furthermore, due to different positions of *s* orbitals of *M* elements, which determine the conduction band edge position of delafossites, the alloying also tunes the fundamental band gap. Our density-functional theory study shows that the enhancement of optical absorption and optimization of fundamental band gap of Cu delafossites can be achieved by alloying of $CuYO_2$ with $CuGaO_2$, and $CuInO_2$. Figure 3(b) shows the calculated absorption probabilities of such alloys, $Cu(Y,Ga)O_2$. It clearly shows non-zero absorption probability at Γ-point, where it was forbidden without the alloying. Similarly, for $Cu(La,Ga)O_2$, band gap reduction is found to be significant compared with the band gap of the pristine $CuLaO_2$ (as indicated by an arrow in the x-axis in figure 4). The optical absorption is also seen to be taken place at Γ-point which has the minimum direct gap (figure 5).

In a similar fashion, we have tried other 3d metal to alloy the $CuYO_2$ delafossites. For example, substitutional alloying of Mn or Cr (both can be iso-valent to Y) does reduce the optical band gap of $CuYO_2$ significantly; however, the

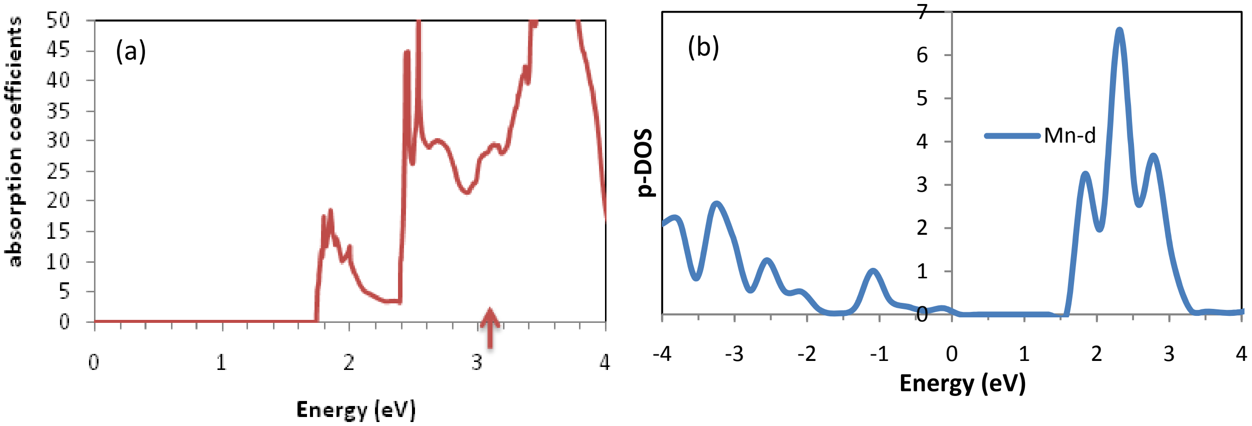

Figure 6: (a) Optical absorption probability of Mn alloyed $CuYO_2$. The small arrow in the x-axis indicates the band gap for $CuYO_2$ before alloying. (b) p-DOS plot of Mn 3d band in $Cu(Y,Mn)O_2$.

dominant presence of the 3d band at the bottom of the conduction band would significantly enhance the photo-excited electron's effective masses. Figure 6(a) and (b) shows the optical absorption coefficients of $Cu(Y,Mn)O_2$ alloy and the p-DOS plot for Mn-d band in this alloy. In addition, due to multiple ionization states of these metal atoms, unwanted defect level may also exist in the band gap. Hence such type of doping would not be suitable for designing PEC photo-electrodes.

## III. Conclusions

In conclusion, an alloying scheme to electronically design the photoelectrodes has been discussed here with density functional theory by considering high band gap group-IIIB delafossites as an example. It has been discussed here that for band engineering by doping or alloying, electronically suitable elements needs to be selected so that the resulting alloy has the desirable band gap and band edge characters. The later is important for the better electron and hole mobility. Furthermore, this alloying should also enhance the optical absorption processes. Our theoretical studies have shown that here isovalent and iso-structural alloying, such as $Cu(Y,Ga)O_2$, can be a suitable pathway for achieving desirable photoelectrodes for water splitting. We have shown here that this type of alloying not only reduced the band gap, but also enhance the optical absorption at the minimum direct gap where, before the alloying, the absorption probability was zero. We have also discussed that, 3d transition metal alloying with the delafossite materials would add a significant d-band contribution to the conduction band which would effectively reduce the electron mobility by increasing its' effcetive mass. These predictions from the theoretical studies can help expedite the experimental search for the better photoelectrodes.

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