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Symmetry-breaking-induced enhancement of visible light absorption in delafossite alloys

Muhammad N. Huda, Yanfa Yan, Aron Walsh, Su-Huai Wei,[a] and Mowafak M. Al-Jassim
National Renewable Energy Laboratory, Golden, Colorado 80401, USA

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Through density functional theory calculations, we demonstrate that enhancement of optical absorption and optimization of the fundamental band gap for Cu delafossites can be achieved through alloying group IIIA and IIIB delafossites. These alloys significantly improved the flexibility in designing delafossite-based photoelectrodes for application in photoelectrochemical decomposition of water by visible spectra of solar light. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3157840]

Photoelectrochemical (PEC) decomposition of water by visible light is considered as the most desirable method for hydrogen production.[1] For efficient PEC splitting of water, the electrodes must satisfy some conditions such as (i) highly stable in aqueous solution, (ii) band edge positions that match the H_2/H_2O and O_2/H_2O levels, and (iii) efficient utilization of visible light.[2,3] Beside these, the availability of both *n*-type and *p*-type semiconductors electrodes is often desirable.[4] Recently, Cu delafossites, CuMO_2 (M=group III-A and III-B 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.[5,6] The latter is due to the fact that their valence band maximum (VBM) is composed of hybridized Cu-*d* and O-*p* antibonding orbitals.[7] PEC response for some Cu delafossites has already been demonstrated.[6,8] Unfortunately, however, recent theoretical study has revealed that due to their special crystal structure, Cu delafossites have undesirable band structures for PEC applications. Specifically, they usually have large disparity between the fundamental band gap and the apparent optical band gap.[5] The absorption of photons with energy of the fundamental band gap near Γ is very weak due to the inversion symmetry of the delafossite structure,[5,9] an effect also observed in other oxide systems.[10] Therefore, to improve PEC response of Cu delafossites, it is necessary to enhance the optical absorption around the fundamental band gap and to optimize the fundamental band gap.

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. However, introducing defects can also lead to the formation of recombination centers, which are detrimental to photovoltaic and PEC devices. In this letter, we propose to enhance the optical absorption and optimize the fundamental band gap via alloying of various Cu delafossites, namely, mixing group III metal elements in delafossites. 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 (DFT) 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 $CuInO_2$.

Our DFT calculations were performed with generalized gradient approximation to DFT (Ref. 11) and the projected augmented wave basis[12] as implemented in the Vienna *ab initio* simulation package.[13] Plane-waves cutoff energy of 400 eV was used and the ion positions were always relaxed until the force on each of them was 0.01 eV/Å or less. To account for the correlation in narrow 3*d*-bands, DFT+U(U=6 eV) method has been used. It should be noted that, although a larger U parameter can open up the band gap further, it also decreases the volume. So a compromise is necessary. We have shown before that the proper choice of the U parameters restore the band gap trend in group IIIB delafossites[9] as given by the experiments.

It was found experimentally that group IIIB delafossites stabilize in hexagonal symmetry ($P6_3/mmc$), whereas the group IIIA delafossites are more stable in rhombohedral symmetry ($R\bar{3}m$). The calculated lattice constants for these delafossites agree well with the available experimental values. For example, for hexagonal $CuYO_2$ we found $a=3.628$ Å and $c=11.402$ Å, whereas the experimental values are $a=3.521$ Å and $c=11.418$ Å.[14] On the other hand, for rhombohedral $CuGaO_2$ the calculated lattice constants for the conventional cell are $a=2.973$ Å and $c=17.114$ Å. The experimental values are $a=2.980$ Å and $c=17.100$ Å.[5] The difference between these two structures is basically the different stacking sequence for the O–Cu–O linear chain and M-O octahedrons. The group III elements M determines the lattice a of the crystal structure. As has been shown in previous studies,[9] while Cu-*d* mainly contributes to the valence band, the group III atoms M determine (i) the nature of the conduction band, (ii) the symmetry of the structures, and (iii) to some extent the measure of the band gap. Hence these structures provide opportunities for tuning the electronic structure by manipulating the M metal ions.

Figure 1(a) shows the band structure of $CuYO_2$ and its optical transition probabilities at the special *k*-points. Figure 1(b) shows the orbital projected partial density of states (*p*-DOS) plots for the same structure. One can see that, as expected, the VBM consists of mostly contribution from Cu-*d* and O-*p* orbitals. The conduction band minimum

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[a] Electronic mail: suhuai_wei@nrel.gov.

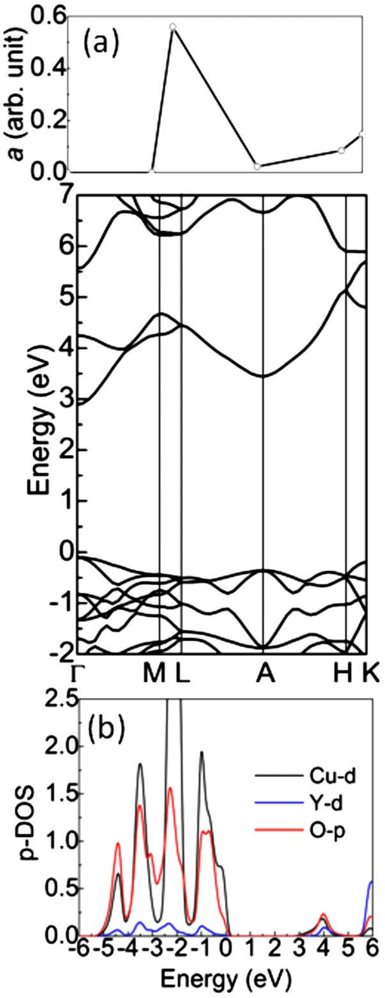

FIG. 1. (Color online) (a) Absorption probabilities a (upper panel) and band structure (lower panel) at special k-points. These clearly show that the optical absorption at smallest gap (at Γ-point) is prohibited. (b) p-DOS plot for $CuYO_2$.

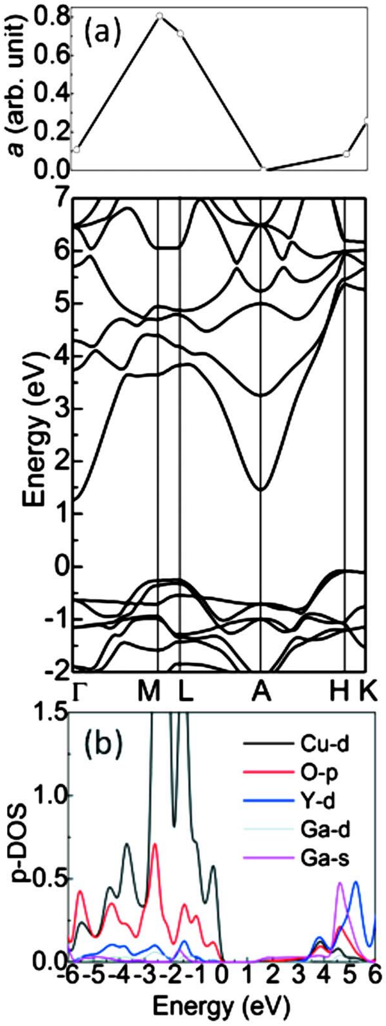

FIG. 2. (Color online) (a) Absorption probabilities a (upper panel) and band structure (lower panel) at special k-points. Here at the Γ-point the absorption probability is not zero. (b) p-DOS plot for $Cu(Y,Ga)O_2$. It indicates that the CBM has high Ga s contribution which is responsible for the lower band gap for this alloy.

(CBM) have also significant Cu-d and O-p contributions as well as contribution from Y-s bands (not shown). The Y-d band does not contribute significantly to the band edges. The *fundamental* band gap is direct at the Γ-point, and has a value of 2.93 eV. The experimental *optical* band gap is at 3.5 eV. However, the calculated dipole transition probabilities show that the band edge transition probability at the Γ-point is exactly zero, whereas it has large value at the L-point, where the band gap exceeds 4.5 eV. This is consistent with the fact that the optical band gap is larger than the fundamental band gap. However, pure $CuYO_2$ should be optically transparent. From the point of view of PEC hydrogen production, using $CuYO_2$ delafossite as electrode then poses two obstacles: (1) the fundamental band gap is too large; (2) optical transition between VBM and CBM is forbidden.

The first obstacle is due to the fact that Y 5s orbital is high in energy. The second obstacle is due to the inversion symmetry of the delafossite structure. These two obstacles could be overcome when isovalent group IIIA elements with deep s orbitals, such as Ga and In, are incorporated. Previous calculation of band structures has shown that the main contrast between $CuYO_2$ and $CuGaO_2$ and $CuInO_2$ is that in the latter two cases there are larger s-band contributions in the CBM at the Γ-point due to the lower s orbital energy of Ga and In.[9,5] Hence it is expected that incorporation of Ga or In in $CuYO_2$ would increase s-band contribution at the CBM and lower the overall band gap of $CuYO_2$. Moreover, it is also expected that the ordered alloy of $CuYO_2$ and $CuGaO_2$ would break the inversion symmetry chemically, and hence the optical transition at Γ-point could become possible.

Figures 2(a) and 2(b) show the band structure and p-DOS of mixed Cu delafossite, $Cu(Y,Ga)O_2$, where Ga substituted at Y-site with a 1:1 ratio. The crystal structure (type-I) is shown in Fig. 3(a). In this case, Ga- and Y-based octahedrons are separated by the O–Cu–O chain, i.e., Ga and Y are not present in the same octahedron layers. From the band structure, the fundamental band gap is indirect with a gap of 1.340 eV, which is even lower than the band gap of $CuGaO_2$. However, at the Γ-point the direct gap is 1.880 eV. So this alloy has a direct band gap better than either of the two delafossites. From the p-DOS plot we see that at Γ-point the CBM is mainly composed of a long tail of Ga s-band with a small mixture of O-p and Cu-d band. The presence of this highly dispersive s-band at CBM is mainly responsible for the band gap reduction in the mixed alloy. Comparing the CBM of $CuYO_2$ and $Cu(Y,Ga)O_2$, we can see that the elec-

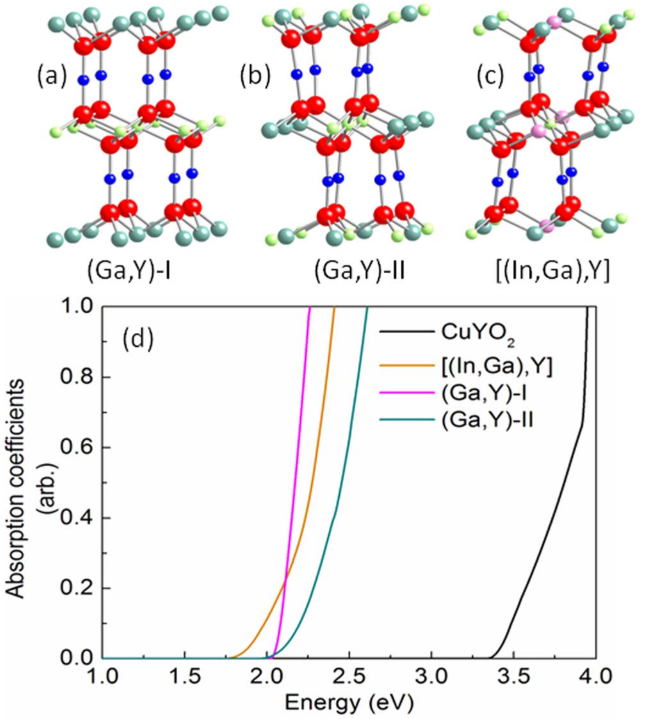

FIG. 3. (Color online) Mixed Cu(Y,Ga)O$_2$ delafossite, where Y and Ga atoms (a) are in different plane and (b) share the same plane. (c) Mixed Cu(Y,Ga,In)O$_2$ structure, where the ratio of Y:Ga:In is 2:1:1. Finally, (d) absorption coefficients for different alloys are shown and compared with that of undoped CuYO$_2$.

tron effective mass in the alloy is much smaller. Furthermore, the lower energy of the new CBM would facilitate the *n*-type doping[15] in Cu(Y,Ga)O$_2$. Though delafossites are generally found as *p*-type semiconductors, the bipolar nature of these alloys may facilitate their versatile use such as in tandem cell or multiple-junction devices. The effect of alloying on the VBM is small because the VBM has very little group III component.

From the calculated dipole transition matrix elements [Fig. 2(a), upper panel], we see that for Cu(Y,Ga)O$_2$ alloy, the absorption probability at Γ-point is no longer zero. This can be explained as follows. In CuYO$_2$ and CuGaO$_2$, the band edge transition probability is zero at Γ-point, because the band edge states have the same even parity, thus the electrical dipole transition is forbidden. For Cu(Y,Ga)O$_2$ alloy the system no longer has inversion symmetry, thus the wave function has no definite parity. Furthermore, orbital nature of CBM at Γ-point has changed significantly from CuYO$_2$ due to the presence of large Ga *s*-contribution. Due to this mixed nature of the CBM, the transition matrix element is no longer zero. However, the matrix element is still not very large because for this isovalent alloy, the wave function mixing is relatively small. Nevertheless, the breakdown of the inversion symmetry should help to improve the near-band edge absorption. The 50%-50% alloy, however, has an indirect band gap with its VBM away from Γ, which may not be desirable for PEC application. However, this can be remedied by further band engineering approach, e.g., by reducing the Ga concentration.

To show the ordering effect, we constructed in Fig. 3(b) a new mixed Cu(Y,Ga)O$_2$ alloy (type-II) where both Y- and Ga-based octahedrons share the same plane. The atomic relaxation in this new structure is clearly seen due to the size mismatch of the Y and Ga atoms. The relaxation is mainly reflected by the asymmetric bending of the O–Cu–O chain. We find that due to better accommodation of the strain, this new structure is 0.422 eV/formula unit more stable than the layered structure [Fig. 3(a)]. In Fig. 3(d) we plot optical absorption coefficients for both the type-I (pink line) and type-II (light green line) structures. The absorption onset of the type-II alloy is slightly lower in energy, however, the absorption increase is faster for the type-I layer structure, and both show remarkable improvements over bulk CuYO$_2$.

To explore the symmetry breaking effect further, we have tested a more complex Cu(Y,Ga,In)O$_2$ alloy, where Y:Ga:In ratio is 2:1:1. The obtained absorption curve is also shown in Fig. 3(d). The direct band gap at Γ-point is 1.725 eV. Close inspection of the absorption curve [Fig. 3(d)] also shows the onset of absorption at the same energy. This indicates that first, the band gap is reduced further from the previous alloy, and second, the absorption at Γ-point is not suppressed.

In conclusion, we have shown that significant band gap modification can be achieved by isovalent alloying of Cu-based delafossites. This alloying significantly improves the optical absorption at lower energy because it reduces the crystal symmetry, thus lifts the parity forbidden transition near the band edge, which exists in the pure delafossite compounds. Moreover, the band gap of the quaternary delafossites alloy can be further tuned through alloy composition and ordering, thus improving the flexibility in designing delafossite-based PEC photoelectrodes.

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