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The effects of Bi alloying in Cu delafossites: A density functional theory study

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Recently, Cu delafossites, CuMO$_2$, have received much attention as photo-catalysts for hydrogen production by water splitting due to their unique properties such as stability in most aqueous solutions and p-type conductivity with excellent hole mobility. However, due to their large optical bandgaps, they can absorb sun light only in the ultraviolet region. Hence, it is necessary to tailor their optical properties to enhance their optical absorption in the visible light regions. In this paper, we report on the effects of Bi alloying on the electronic and optical properties of Cu delafossites by density functional theory. We find that Bi alloying can lead to improved optical absorption as compared to the pristine Cu delafossites. We further find that the lone pair Bi-6s electrons create occupied delocalized anti-bonding states on the top of the valence band, leading to further improved hole mobility. © *2011 American Institute of Physics*. [doi:10.1063/1.3592149]

I. INTRODUCTION

Photoelectrochemical (PEC) splitting of water by visible spectrum of solar light is considered to be the most desirable method for hydrogen production[1,2] because of no environment unfriendly by-products. This has attracted great attention since the demonstration of water splitting by Fujishima and Honda 40 years ago using a TiO$_2$ photoanode illuminated with ultraviolet light.[3] Since then, numerous semiconductor materials have been studied as photocatalysts to split water under sunlight, but the efficiency of conversion remains very low. For a successful implementation and proliferation of PEC hydrogen production, low cost and easy to synthesize photocatalysts are needed. Such photocatalysts should satisfy some desirable electronic properties. The latter include an optimal bandgap to efficiently absorb sun light in the visible and near IR range; the positions of their band edges must be matched with the H$_2$/H$_2$O and O$_2$/H$_2$O redox potentials[4–9] and must be stable in aqueous solutions. Naturally occurring semiconductors do not satisfy all these constraints simultaneously. Therefore, new materials must be designed and synthesized to satisfy the above criteria. To achieve this goal, the electronic properties and defect physics of the studied materials must be understood.[10] Recent results also indicate that to ensure good photochemical activity the used photo-catalysts must also exhibit good carrier mobility.[11,12] To obtain efficient photocatalysts, band engineering is necessary to improve their optical absorptions.[13]

The availability of both n-type and p-type semiconductors is often desirable for photocatalysts.[14,15] Oxides, in general, are found to be n-type semiconductors. However, Cu delafossites, CuMO$_2$ (M = group III-A (13) and III-B (3) elements), exhibit p-type conductivity with excellent hole mobility and are stable in most aqueous solutions.[16–23] Cu delafossites were also found to be mechanically stable with high bulk modulus.[24] The p-type conduction in delafossites is due to the fact that their valence band maximum (VBM) is composed of hybridized Cu-d and O-p antibonding orbitals.[25,26] It has been also shown that among the delafossites, relatively higher p-type conductivity occurs when the M-O bond is found to be more covalent.[17] PEC response for some Cu delafossites has already been demonstrated.[27–30] Unfortunately, the efficiencies of these photo-conversion processes are not satisfactory, largely due to the inefficient absorption of visible light. Recent theoretical study has revealed that the poor optical absorption is due to the inversion symmetry of their special crystal structure. The absorption of photons with energy corresponds to the minimum direct gap at Γ-point is less probable due to the inversion symmetry,[13,31] an effect also observed in other oxide systems.[32] Specifically, the group IIIA (13) Cu delafossites usually have large disparity between the fundamental and the apparent optical bandgap.[31] Therefore, to improve PEC response of Cu delafossites, it is necessary to enhance the optical absorption around the fundamental bandgap in addition to optimizing the fundamental bandgap.

Previously, we have proposed to enhance the optical absorption by breaking the inversion symmetry of the delafossite materials by means of isovalent alloying group IIIA and IIIB delafossites, and improved optical absorption at the smallest direct gap was observed.[13] However, the improvement was not enough significant due to the fact that group IIIA and IIIB elements do not exhibit very large size and chemical potential mismatch. The alloying of the elements was not able to provide the global symmetry breaking. To optimize the symmetry breaking, elements with the largest mismatch with group IIIA and IIIB elements should be considered. Bi is such a candidate because of three reasons: (i) Bi is isovalent to the group-III elements, so that isovalent alloying would not create any unwanted localized defect levels in the bandgap which may act as a carrier recombination center; (ii) Bi has large size and chemical mismatch with

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group III elements; and (*iii*) Bi 6s lone pair electron will create anti-bonding sates forming more delocalized valence band maxima.[33–36] In this paper, we will report our results on the effects of Bi doping on the electronic and optical properties of copper based delafossite materials, such as $CuScO_2$, by density functional theory (DFT). We find that Bi alloying exhibit enhanced optical absorption as compared to unalloyed delafossites. We further find that the lone pair Bi-6s electrons create occupied delocalized anti-bonding states on the top of valence band, leading to further improved hole mobility. However, even with Bi doping the fundamental bandgap remained indirect in Cu delafossites.

II. METHOD

We have employed DFT to study the electronic properties of the delafossites materials. Generalized gradient approximation (GGA)[37] to DFT and the projected augmented wave (PAW)[38,39] basis as implemented in the Vienna *ab initio* simulation package were used.[40–42] Plane-waves cut-off energy of 400 eV was used, and the ion positions and volumes were always relaxed until the force on each of them is 0.01 eV/Å or less. We have used $13 \times 13 \times 3$ (for hexagonal cell) k-point distribution for the final energy calculations. To correct the DFT-GGA underestimation of electron correlation in the cation *d* bands, $DFT + U$ method[43,44] 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] These choices of U have shown to produce better agreement with experimental bandgaps; for example, the measured[45] indirect and direct gaps for $CuAlO_2$ is 2.97 and 3.47 eV compared to our calculated gaps of 2.55 and 3.34 eV, respectively. The structural parameters and the choice of ground state crystal symmetry was found to agree 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 bandgaps for group IIIB delafossites, with $DFT + U$ (with the values of U as in Ref. 17) had been able to restore the experimental trend. 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.

III. RESULTS AND DISCUSSIONS

The delafossite structures can have either $P6_3/mmc$ (#194, hexagonal) or $R3m$ (#166, rhombohedral) 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 octahedra. These octahedras are connected by the linear Cu-O chains. Structurally, the main difference between these hexagonal and the rhombohedral symmetries is 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 instance, for $CuYO_2$ the hexagonal structure is only 0.035 eV lower in energy (per formula unit) than the corresponding rhombohedral structure. It is known that while the group IIIB delafossites have essentially direct bandgaps of around 3 eV, group IIIA has similar (3 eV) indirect bandgaps.[45] In this paper, we focus on hexagonal group IIIB delafossites.

Figure 1 shows the alloying configuration of Bi doped $CuMO_2$. Bi atoms are at the M sites with an alloying ratio of M:Bi = 1:1. Substitution of Bi at Cu site is energetically not preferable. Two configurations have been considered for the $Cu(M, Bi)O_2$ structures: M and Bi are on the same layer and M and Bi form their separate sublayers. The first structure is energetically more favorable than the second one by 0.321 eV.

The lattice constants of the Bi-alloyed delafossites were found to increase with respect to the undoped ones. For example, the lattice parameters *a* and *c* for $CuScO_2$ without any doping were 3.308 and 11.372 Å, respectively, whereas for $Cu(Sc, Bi)O_2$, these two lattice parameters became 3.449 and 11.706 Å, respectively. However, the linear O-Cu-O bond lengths did not change much, the difference being only ~0.001 Å. The distance between the octahedron layers become 5.853 Å (metal-to-metal atoms distances), whereas the corresponding distance in the pristine $CuScO_2$ was 5.685 Å. This increase of distance is mostly due to the large Bi-O distance, 2.361 Å, in the octahedron layers, which is the result of atomic size and electronegativity mismatch difference between the Sc and Bi atoms. Bi is more

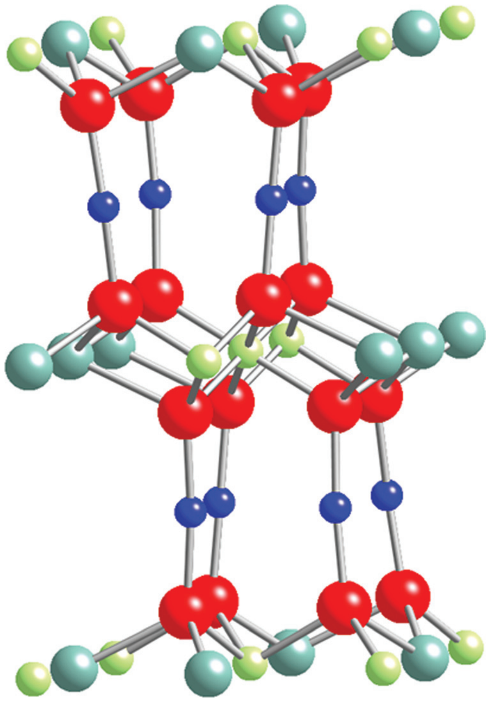

FIG. 1. (Color online) Bi doped $CuMO_2$ structure. Small blue (dark) balls are Cu atoms, large red (dark), green (gray), and light green (light gray) balls are oxygen, M and Bi atoms, respectively.

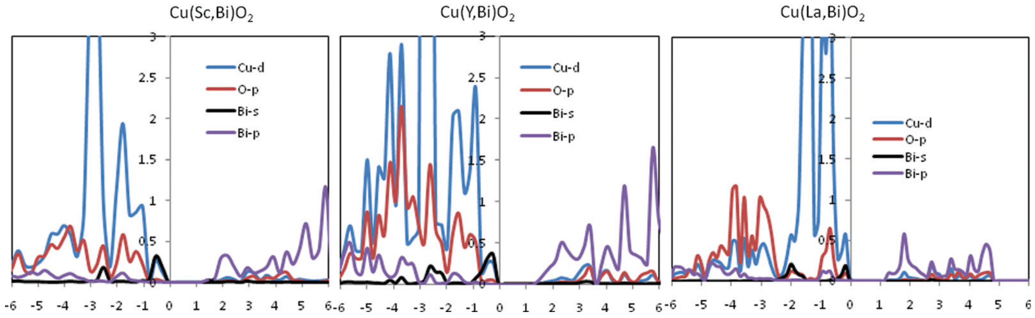

FIG. 2. (Color online) Partial density of state (p-DOS) of Bi alloyed (a) $CuScO_2$, (b) $CuYO_2$, and (c) $CuLaO_2$.

electronegative than Sc. Similar trends were found for $Cu(Y,Bi)O_2$ and $Cu(La,Bi)O_2$. In addition, the distance between the Cu atoms and the Sc (or Bi) atoms increases by about 0.150 Å due to doping.

Figure 2 shows the partial density of states (p-DOS) plots for Bi doped group IIIB delafossites with M:Bi ratio of 1:1. It is seen that Bi-s bands are located near the Fermi level (E_F), and overlap with Cu-d bands. For $CuScO_2$ and $CuYO_2$, the contributions from Bi-s and Cu-d near E_F are almost equal; the contribution of O-p near E_F is rather low. For $CuLaO_2$, Cu-d overshadows Bi-s, while O-p and Bi-s have almost equal contributions. The contributions of Bi-s and Cu-d band near the Fermi level indicate anti-bonding. On the other hand, conduction band minimum (CBM) is dominated by Bi-p band with a very small contribution from Cu-d. In CBM, the Bi-p band moves downward with respect to E_F from $CuScO_2 \rightarrow CuYO_2 \rightarrow CuLaO_2$. The width of Bi-p band becomes narrower in $CuLaO_2$. La 4f band does not show up near the CBM, its first noticeable presence occurs at more than 3 eV above the Fermi level. Overall, due to the presence of delocalized Bi-s and -p bands, the alloyed delafossites are expected to have smaller optical bandgap and smaller electron and hole effective masses. Bi alloying should enhance the p-type conductivity.

Now, as a next step, it is essential to examine the nature of the bandgap for this Bi-doped delafossites. Host group IIIB delafossites are direct gap semiconductors which are desirable for high optical absorption. However, Bi doping could alter this feature. To understand this issue, we have calculated band structures for two delafossites ($M = $ Sc and Y) with Bi alloying as shown in Fig. 3. For comparison purpose, the band structures of pristine delafossites, which have been discussed in details elsewhere,[17] are also shown. We have previously studied group-IIIA elements doped group-IIIB delafossites for optimizing the bandgaps and optical absorption properties of these semiconductors.[13] Though these dopings did reduce the bandgap and enhanced the optical absorption properties, they however did not influence the VBM considerably so that the doped delafossites remained predominantly of Cu-d characters. It is now expected that Bi alloying in these delafossite would enhance the hole transport properties by introducing more delocalized Bi 6s antibonding states. It is clearly evident that after Bi alloying the fundamental bandgaps are no longer direct. For $CuScO_2$, the fundamental bandgaps before and after doping are 3.05 and 1.44 eV, whereas for $CuYO_2$ bandgaps are 2.95 and 1.24 eV, respectively. The minimum direct bandgap occurred at A-point which is 2.543 and 2.348 eV for $Cu(Sc,Bi)O_2$ and $Cu(Y,Bi)O_2$, respectively. In addition, VBM at both Γ- and A-points are dominated by Cu-d band. In fact, two highly localized d-like bands are visible in between Γ- and A-points about 1 eV below the Fermi level. In the undoped delafossites, optical transition at Γ-points point was forbidden due to inversion symmetry related selection rule. Bi doping would partially reduce the inversion symmetry, and hence the optical absorption would be enhanced at Γ-point. In both cases, VBM occurs at H point in the Brillouin zone, and has significant Bi-s character. On the other hand, CBM occurs at two places: at Γ- and A- point. Unlike Ga or In doping where CBM has long tail of s-band,[13] here the CBM has major

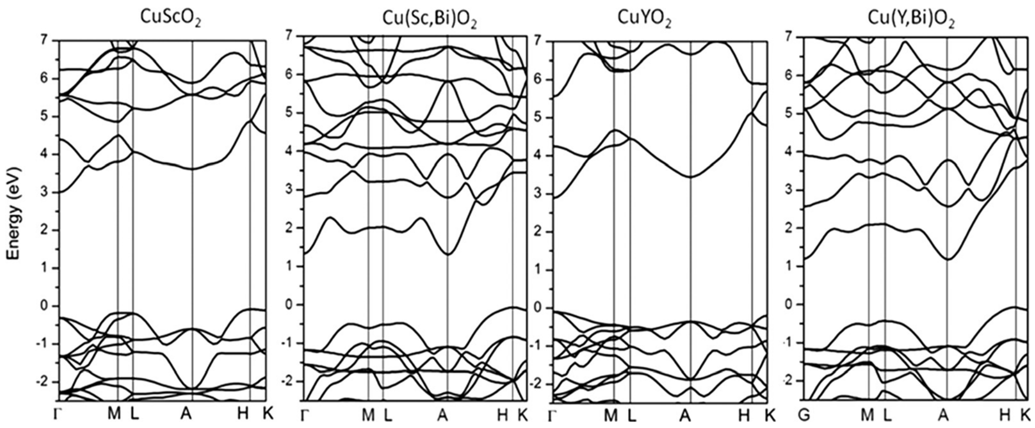

FIG. 3. Band structures of (a) $CuScO_2$, (b) $Cu(Sc,Bi)O_2$, (c) $CuYO_2$, and (d) $Cu(Y,Bi)O_2$.

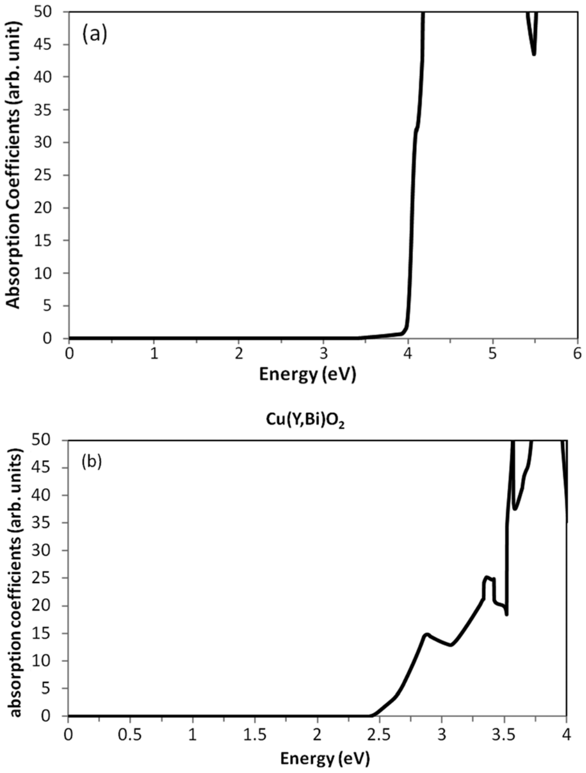

FIG. 4. Optical absorption coefficients for (a) $CuYO_2$ and (b) $Cu(Y, Bi)O_2$.

contribution from the Bi-p bands. From the dispersion of the band at CBM it can be inferred that the electron effective mass will be reduced. Therefore, from carrier mobility point of view, Bi alloyed delafossites should be better PEC photocatalysts as compared to group-IIIA and III-B alloyed delafossites.

Figure 4 shows the optical absorption coefficient plot for Bi doped $CuYO_2$. Optical absorption coefficients are calculated from the imaginary part of the dielectric function, ε_2. This ε_2 is calculated from the frequency dependent dielectric matrix after the electronic ground state has been determined. Details of the method as applicable to PAW formalisms were explained by Gajdoscaron *et al.*[46] The onset of the absorption curve for $Cu(Y, Bi)O_2$ is at about 2.350 eV. Comparing this with the band structures of Fig. 3(d), we can argue that this energy corresponds to optical transition at either Γ-point or A-point, and the nature of transition is d-p transition. Compared to the transition for $Cu(Y, Ga)O_2$ where it was mainly a d-s transition,[13] d-p transitions is more favorable. Also, comparing to Fig. 4(a), the effective optical bandgap reduction is about 1.152 eV.

Finally, effects of the alloying concentrations on the electronic structures have been considered. We have also considered low Bi concentration with Y:Bi ratio of 11:1. Figure 5 shows the calculated p-DOS of the system with low Bi concentration. It is seen that the bandgap reduction is not significant, 2.87 eV, whereas without Bi the bandgap for $CuYO_2$ was 2.95 eV. At CBM, the contribution from the Bi-p orbital is larger, but the width of the Bi-p band near the gap is much narrower as compared to the high Bi alloying case [Fig. 3(b)]. This suggests that electron mobility enhancement would be lower for lower Bi concentration. In one of our previous studies[13] we have shown that doping of Ga in $CuScO_2$ or $CuYO_2$ can significantly reduce both the bandgap and the electron's effective mass due to the presence of the Ga-s band at the lower part of the conduction band. To study the effect of Ga doping in low concentration Bi doped $CuScO_2$ we have constructed a $CuScO_2$ supercell with Ga and Bi co-doping at the concentrations of Sc:Ga:Bi = 10:1:1. Two different configurations have been considered: (i) Ga and Bi are on the same layer, (ii) Ga and Bi are on different layers. The first one is more stable by 0.32 eV than the second one. Figure 6 shows the band structures of Ga and Bi co-doped $CuScO_2$. It is seen that the fundamental bandgap is still indirect, 2.35 (between Γ and M-point), while the minimum direct gap is 2.73 eV at the H-point. DOS plot (not shown here) revealed that Bi-6s contribution at VBM is significant, whereas Ga-s contribution at CBM is not significant, because Ga-s band is much higher in energy than Bi-p band.

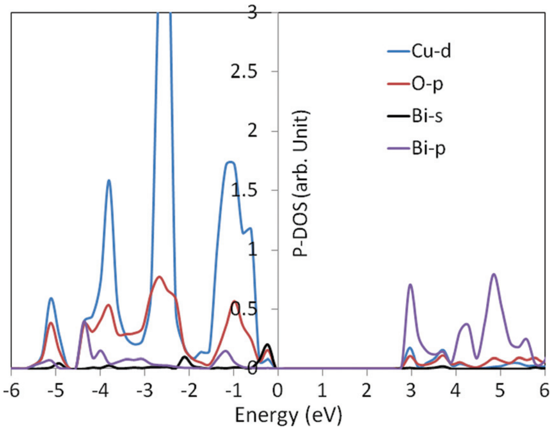

FIG. 5. (Color online) p-DOS for Bi doped $CuYO_2$ with Y:Bi = 11:1.

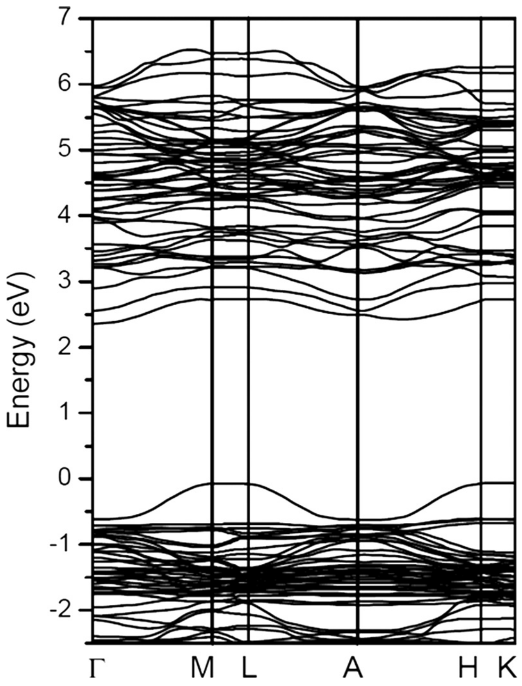

FIG. 6. Band structure of $Cu(Sc, Ga, Bi)O_2$ with Sc:Ga:Bi ratio of 10:1:1.

IV. CONCLUSIONS

We have studied Bi alloying in Cu-based delafossites to band-engineer their electronic and optical properties for photocatalytic applications to produce hydrogen by water splitting. The alloying at high concentration reduces the bandgaps, which lead to enhanced optical absorptions in the visible wavelength range. The presence of Bi-s and Bi-p band at the VBM and CBM, respectively, are responsible for higher dispersion at the band edges, which lowers the carriers' effective masses. It also raises the VBM with respect to the parent delafossite materials due to the contribution from Bi-s anti-bonding bands. This feature would enhance the p-type conductivity of the alloyed delafossites. Overall, the Bi alloying should lead to improved p-type conductivity and optical absorption for Cu delafossites.

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