J. At. Mol. Sci.
doi: 10.4208/jams.051512.060312a

Vol. **4** , No. 2 , pp. 169-175
May 2013

The first-principle study on wide-gap semiconductor material $CuYO_2$

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Received 15 May 2012; Accepted (in revised version) 3 June 2012
Published Online 28 March 2013

Abstract. Using the first-principle method within the generalized gradient approximation, this paper study the bands structure, structural parameters, and state densities of wide-gap semiconductor material $CuYO_2$. The calculated results show that, the valence band of $CuYO_2$ mainly compose of 3d of Cu, and 2p of O; while the conduction band mainly compose of 3d of Y. Through the $+U$ correction, with the increasing of the value of U, the conduction band and valence band of $CuYO_2$ become split, the peak of 3d of Y move towards high energy area, which induce to the enlarge of conduction band area and band gap; in addition, the minimum of conduction band is transfer L point into Γ point when the value of U is 2eV, which show $+U$ method mainly correct the conduction band of $CuYO_2$ so that improve the calculated value of band gap.

PACS: 31.15.A-,61.50.-f

Key words: $CuYO_2$, band structure;first-principle method

1 Introduction

Transparent conducting oxides(TCO) are technologically important material with conduction and optical properties used in in solar cells, flat panel displays, electrochromic mirrors and window, and other optoelectronic devices [1]. The most of TCO such as ZnO, Ln_2O_3, and SnO_2 have n-type conductivity and have been widely applied in industrial materials as new type TCO materials [2–5]. However, without the high merit p-type TCO, the application n-type TCO is rather restricted because the active functions of many optoelectronic elements come from p-n junction. Even so, comparing with many

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n types TCO, P-type TCO is still lack, and the conductivity of p-type TCO is significantly lower than the conductivity of n-type TCO. In order to construct the transparent p-n junctions devices, it is essential to explore new p-type TCO so that the combination of the two types of TCO can be realizable. In 1997, Kawazoe *et al.* found that transparent thin films of copper aluminium oxide $CuAlO_2$ have p-type conductivity [6]. This research result attract attentions of many researchers. $CuAlO_2$ belongs to the family $CuMO_2$, which have $CuFeO_2$ structure, the conductivity is 0.95 S/cm under the room temperature, and Seebeck value is +138(means the materials have p-type conduction) [6,7]. Although the p-type conductivity of $CuAlO_2$ is still significantly low, it still becomes a hope that constructs transparent p-n junction devices in TCO. Since then, $CuAlO_2$ has become an important material, and other $CuMO_2$(Ga, In, Sc, Y, Cr, rare earths, etc) also present p-type conductivity in the last few years [8–14]. Among all the $CuMO_2$ family, $CuYO_2$ has attracted special attentions with wide band gap, in addition, $CuYO_2$ have particular physical and chemical properties due to Y belongs to rare earth element. Extensive experiments studies have been carried out in the past to understand and improve basic properties in the $CuYO_2$ [15–18], relatively little is known regarding its band/electronic structure. In particular, we notice that an *ab initio* investigation of band gap in $CuYO_2$ is still lacking. Only Shi *et al.* [19] investigated the band structure and optoelectronic properties of $CuYO_2$. Shi *et al.* found that the indirect band gap of $CuYO_2$ is 2.63eV by the local-density approximation (LDA) method, while direct optical band gap of $CuYO_2$ is 3.3eV [19]. It is well known that conventional density-functional method such as LDA or GGA (generalized gradient approximation) underestimate the band gap of semiconductor, as a result, fail to capture the accurate band structure of $CuYO_2$ because of ground state methods. These facts, as a consequence, inhibit further understanding of $CuYO_2$. Motivated by this observation, in order to better understand band structure properties of $CuYO_2$, in this study, we modify the intraatomic Coulomb interaction through the $+U$ approaches, in which the underestimation of the intraband Coulomb interaction is corrected by the Hubbard U parameter. It is expected that the present calculated results greatly help explain the structure properties of $CuYO_2$ from a microscopic perspective and can be a guide for applications of $CuYO_2$. The remaining part of this paper is organized as follows. In section II, we present our calculation methods. Section III present and discusses our calculated formation energies and transition energy level. Finally, we summarize the conclusion in Section IV.

2 Calculation methods and atomic model

The calculations are based on density-functional theory within the generalized gradient approximation(GGA) [20] as implemented in the VASP [21] code through the use of the PAW pseudo potentials [22]. In band structure calculations are performed with a four-atom unit cell, and the $4\times4\times4$ Monkhorst-Pack k-point set [23,24] has been used to sample the Brillouin zone. All atomic positions have been relaxed according to the calcu-

lated Helmann-Feynman forces. The optimization of atomic geometries is performed via a conjugate-gradient algorithm until the residual force acting on atoms is less than 0.01eV $\mathring{A}^{-1}$. The energy cutoff for the plane-wave basis is 500 eV. In this study, the valence electrons including 3d and 4s of Cu, 2s and 2p of O, 4s, 4p, 4d and 5s of Y. The crystal structure of the $CuYO_2$ belongs to the space group of $R\overline{3}m$(seen in Fig. 1). As shown in Fig. 1, one could seen that, each Cu atom is linearly coordinated with two oxygen atoms to form a O-Cu-O dumbbell unit placed parallel to the c-axis. The oxygen atoms that terminate the dumbbells are also each coordinated to three Y atoms, and the O-Cu-O dumbbell layers in a hexagonal plane are separated by YO_6 edge-sharing octahedral layer. In the primitive cell, one Cu atom is located at (0,0,0), and one Y atom is located (0,0,0.5),two O atoms are located at $\pm$ (0,0,u). According to the characters of crystal structure, in this study, we chose F(0.5,0.5,0),Γ(0,0,0),Z(0.5,0.5,0.5), and L(0,0.5,0) as the high-symmetry k points.

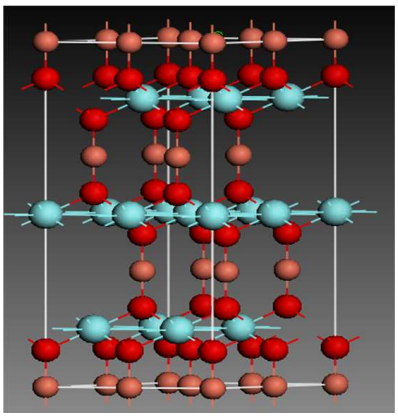

Figure 1: Crystal structures of $CuYO_2$, red atoms are O atoms, brown atoms are Cu atoms, blue atoms are Y atoms.

3 Calculated results and discussion

The structure is defined by three crystallographic parameters: two lattice parameters, a, c, and the internal parameter, u. All the lattice parameters are fitting to Murnaghan equation of state [25]. The calculated structural parameters of $CuYO_2$ and the corresponding experimental values are listed in Table I. One can see that, our calculated lattice a and c for $CuYO_2$ are 3.458Å and 16.851Å, respectively, which in agreement with corresponding experimental values [26].

In order to analyze the influence of U values on the electronic structures of $CuYO_2$, the total density of states and partial density of states in $CuYO_2$ under GGA+U methods are calculated and shown in Fig. 2. Energy zero is set to E_{VBM}. As clearly shown in Fig. 2(a), under the GGA conventional method, the dos of valence is consist of 3d state of Cu

Table 1: Calculated and experimental structural parameters of $CuYO_2$

Structural parameters	Calculated value	Experimental value
a	3.458	3.533
c	16.851	17.136
u	1.060	1.066
c/a	4.873	4.850

and 2p state of O when U is 0eV. From Fig. 2(b)- Fig. (d), we can see that, the band gap of $CuYO_2$ is enlarge with further increase of U values, which show that $+U$ method can effectively correct the problem about band gap. As shown from Fig. 2, for valence band, GGA+U method does not change the profile of 2p states of O and the width of valence band still keep 6eV; with further increase of U values, the peak of 3d of Cu become split and 3d of Cu move toward low energy area and produce three DOS peak when U is 8eV. For conduction band, take the influnces of U values into consideration, one can see that, the width of conduction band enlarge from 4eV to 5eV, in particular, with the increasing of U values, the state localization is decreasing on the whole conduction band, and the peak of 3d of Y move towards high energy area.

Table 2: The values of especial K points in $CuYO_2$ by GGA+U method

U	F_V	F_C	Γ_V	Γ_C	Z_V	Z_C	L_V	L_C	E_g(eV)
0eV	2.06	5.77	1.38	5.09	2.14	6.46	2.14	4.86	2.72
1eV	1.99	5.85	1.28	5.10	2.07	6.50	2.07	4.99	2.92
2eV	1.91	5.94	1.18	5.10	2.01	6.53	2.01	5.12	3.10
3eV	1.84	6.02	1.07	5.09	1.94	6.56	1.94	5.24	3.15
4eV	1.76	6.10	0.96	5.08	1.87	6.59	1.87	5.37	3.21
5eV	1.69	6.18	0.86	5.07	1.81	6.61	1.80	5.50	3.27
6eV	1.61	6.27	0.77	5.06	1.75	6.63	1.73	5.62	3.31
7eV	1.54	6.35	0.68	5.04	1.70	6.64	1.66	5.75	3.34
8eV	1.47	6.44	0.60	5.02	1.64	6.65	1.59	5.87	3.38

To obtain a more precise knowledge of the changes of band structure under GGA+U method in $CuYO_2$, furthermore, we have plotted the the band structure of $CuYO_2$(seen in Fig. 3) , and listed the values of especial K points in $CuYO_2$ under GGA+U calculation. As clearly shown in Fig. 3, in $CuYO_2$, the whole conduction band move towards high energy area and the band width enlarge when U values increasing, which means $+U$ method mainly correct the low level problem for conduction band under GGA conventional method. From the calculated results of Table 2, one can see that, $CuYO_2$ is a indirect band gap material and its width is 2.72 eV, conduction band minimum(CBM) of $CuYO_2$ is at point L and valance band maximum(VBM) is at point Z. For the previous calculation, Shi *et al.* [19] also found that the band gap of $CuYO_2$ is 2.63eV, and the CBM and VBM of $CuYO_2$ were at point L and point Z, respectively. From Table 2, one can also see that the band structure of $CuYO_2$ have some changes when take $+U$ into consideration, which means $+U$ calculation have influence on band structure. In particular, the

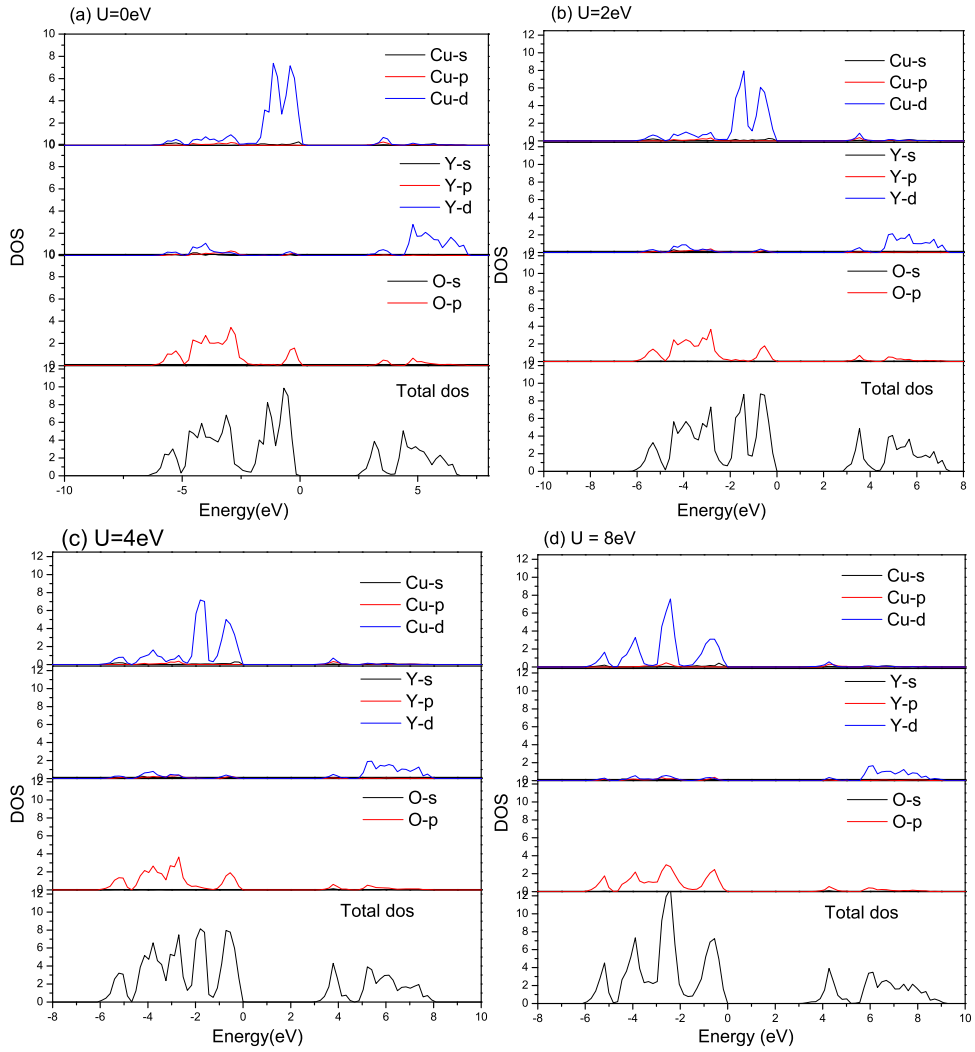

Figure 2: The total density of states and partial density of states in $CuYO_2$ under GGA+U calculation, (a)-(d) shows the density of states under U =0, 2, 4, and 8 eV, respectively.Energy zero is set to E_{VBM}.

CBM of $CuYO_2$ is transfer L point into Γ point when the value of U is 2eV, while the VBM of $CuYO_2$ is still located at point Z. Combined with the analyze about Fig. 2(c)-(d) and 3, we can explain that, for conducting band, 3d states of Y have some change under $+U$ correction, which induce to the change of CBM site. In the meantime, the whole valence band move towards low energy area, while the whole conducting band move towards high energy area. It leads to the values of band gap of $CuYO_2$ from 2.72eV to 3.33eV with the U values from 0eV to 8eV, which in good agreement with optic value 3.3eV [19], and very closely the experimental values 3.5eV. This means that GGA+U method can effec-

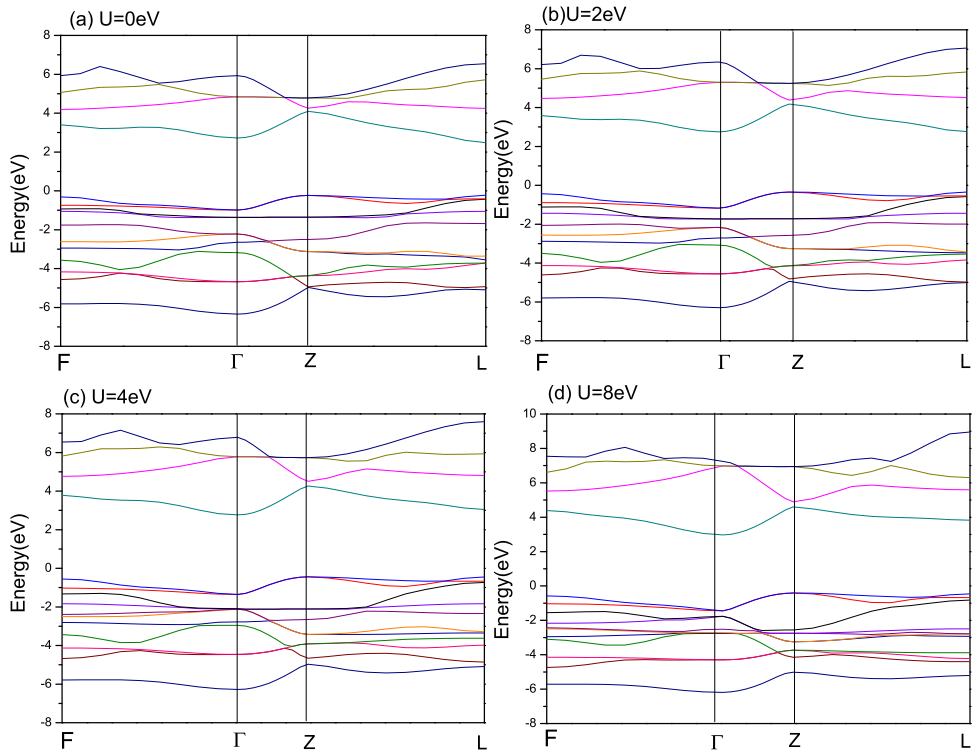

Figure 3: The band structure of $CuYO_2$ under GGA+U calculation, (a)-(d) shows the band structure under U=0, 2, 4, and 8 eV, respectively.Energy zero is set to E_{VBM}.

tively deal with the underestimation problem of band gap in $CuYO_2$. It is expected that our present calculated results will greatly help explain the various physical and chemical properties in $CuYO_2$ from a microscopic perspective and can be a theoretic guide for application of wide-gap $CuYO_2$ material.

4 Summary

In this paper, we have performed the first-principle method within the GGA+U to investigate the bands structure, structural parameters, and state densities of wide-gap semiconductor material $CuYO_2$. The calculated results show that, GGA+U method can be effectively deal with the underestimation problem of band gap in $CuYO_2$. With the increasing of U values, the area of valence band and conduction band can be produce split in band structure of $CuYO_2$. In valence band area, the peak of 3d of Cu become split and move toward to low energy area; in conduction band area, the the peak of 3d of Y move towards high energy area, which induce to the enlarge of conduction band area. In addition, CBM of $CuYO_2$ is transfer L point into Γ point when the value of U is 2eV,

which show $+U$ method mainly correct the conduction band of $CuYO_2$ so that improve the calculated value of band gap.

Acknowledgments This study is supported by National Natural Science Foundation of Chinaunder Grant No. 11147195, Guangxi Experiment Centre of Science and Technology under Grant No. LGZXKF201204, and Science plan projects of Guangxi Provincial Education Department under Grant No. 200103YB102.

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