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First-principle study of native defects in $CuScO_2$ and $CuYO_2$*

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This paper studies the electronic structure and native defects in transparent conducting oxides $CuScO_2$ and $CuYO_2$ using the first-principle calculations. Some typical native copper-related and oxygen-related defects, such as vacancy, interstitials, and antisites in their relevant charge state are considered. The results of calculation show that, $CuMO_2$(M = Sc, Y) is impossible to show n-type conductivity ability. It finds that copper vacancy and oxygen interstitial have relatively low formation energy and they are the relevant defects in $CuScO_2$ and $CuYO_2$. Copper vacancy is the most efficient acceptor, and under O-rich condition oxygen antisite also becomes important acceptor and plays an important role in p-type conductivity.

Keywords: $CuMO_2$, native defects, vienna *ab-initio* simulation package (VASP)
PACC: 7125R,7155E

1. Introduction

Transparent conducting oxides (TCOs) can be used in solar cells, flat panel displays, electrochromic mirrors and windows, and other optoelectronic devices.[1] Most TCOs, including ZnO, Sn_2O and In_2O_3, have n-type conductivity and have been widely used as transparent electrodes. They are all wide-gap oxides. However, it is difficult for wide-gap oxides to be doped as p-type materials. In 1997, Kawazoe *et al*[2] found that the transparent thin films of delafossite copper aluminium oxide $CuAlO_2$ have p-type conductivity. This was an important step forward for the development of TCOs. Although the p-type conductivity of $CuAlO_2$ is significantly lower than that of many n-type conducting oxides, it still becomes a hope to construct transparent p–n junction devices in TCOs.

Since Kawazoe's discovery, there have been plenty of works[3−8] on p-type TCOs, among which delafossites $CuMO_2$(M = Al, Ga, In, Sc, Y, Cr, rare earths, etc) have attracted the most attention from researchers. Many $CuMO_2$ are wide gaps materials. For example, the optically measured direct band gaps of $CuAlO_2$, $CuGaO_2$ and $CuInO_2$ are about 3.5,[2] 3.6,[9] and 3.9 eV,[10] respectively. Some $CuMO_2$ materials have p-type conductivity without intentional doping. The properties of conductivity are mostly determined by charge carrier concentration, which is affected by charge defects and impurities. In order to control n-type and p-type conductivity, comprehensive knowledge of electronic structure and defect formation energy is required. Despite recent work on $CuMO_2$(M = Sc, Y),[11−16] there is almost no theoretical study of its defects. This paper performs a series of studies on the electronic structure and native defects of $CuMO_2$(M = Sc, Y). This study of native defects is helpful in explaining the p-type conductivity of $CuMO_2$(M = Sc, Y) and can be a guide for material preparation.

Using first-principle pseudopotential methods, we have calculated the electronic structure and native defects of $CuMO_2$ (M = Sc, Y). From our calculated band structure in Fig.1 we find that $CuScO_2$ is a direct band gap oxide and its direct band gap is at point L. But $CuYO_2$ is an indirect band gap oxide and its valance band maximum (VBM) and conduction band minimum (CBM) are at point Z and point L, respectively. Through formation energy calculation of native defects in different charge states, we explain why $CuMO_2$(M = Sc, Y) not show the n-type conductivity ability. We also find that copper vacancy and oxygen

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interstitial are the relevant defects in $CuMO_2$(M = Sc, Y) and copper vacancy is the most effective acceptor. Oxygen antisite becomes the important acceptor and plays an important role in p-type conductivity under O-rich conditions. The remaining part of this paper is organized as follows. In Section 2, we present our calculation methods. We give our results and discussion in Section 3. Finally, we present our conclusion in Section 4.

2. Methods

The calculations are based on density-functional theory within the local-density approximation (LDA)[17] as implemented in the vienna *ab-initio* simulation package (VASP) code[18] through the use of the projector augmented wave (PAW) pseudo potentials.[19] In our defects calculations, supercells containing 48 host atoms were used, and all atomic positions were relaxed according to the calculated Hellmann–Feynman forces. The energy cutoff for the plane-wave basis was 400 eV. The $2\times2\times2$ Monkhorst–Pack k-point set[20,21] was used to sample the Brillouin zone. In our calculation, the valence electrons include 3d and 4s of Cu, 3s, 3p, 3d and 4s of Sc, 4s, 4p, 4d and 5s of Y, 2s and 2p electrons of O. The electronic structure calculations are performed with a 4 atom unit cell, and total energy calculations are performed with a 48 atom supercell. The following defects are studied: copper vacancy (V_{Cu}), oxygen interstitial (O_i), oxygen antisite (O_{Cu}), oxygen vacancy (V_O), copper interstitial (Cu_i) and copper antisite (Cu_O), and the position of O_i and Cu_i is the same as that of Li *et al.*[22] For charged defects, a jellium background is added to keep the global charge neutrality of the periodic supercell. All the calculations use the projector augmented wave method and use the same supercell and same k-point sampling in the defect system study.

Following the conventional procedure,[23] we calculate the ionization energy by

$$\begin{aligned}\varepsilon(0/q) = &\left[E(\alpha,q)-\left(E(\alpha,0)-q\varepsilon_{\rm D}^{k}(0)\right)\right]\\ &-q\left[\varepsilon_{\rm D}^{\Gamma}(0)-\varepsilon_{\rm VBM}^{\Gamma}({\rm host})\right],\end{aligned}\tag{1}$$

where $E(\alpha,q)$ and $E(\alpha,0)$ are the total energies of the supercell at charge state q and neutral for defect α; $\varepsilon_{\rm D}^{k}(0)$ and $\varepsilon_{\rm D}^{\Gamma}(0)$ are the defect levels at the special k-points(averaged) and at the Γ-point, respectively; and $\varepsilon_{\rm VBM}^{\Gamma}({\rm host})$ is the VBM energy of the host supercell at Γ-point. The first term on the righthand side of Eq.(1) determines the U energy parameter(including both the Coulomb contribution and the atomic relaxation contribution) of the charged defects calculated at the special k-points, which is the extra cost of energy after moving $(-q)$ charge from the VBM or CBM of the host to the neutral defect level. The second term gives the single-electron defect level at the Γ-point.

According to notation of formation energy,[24,25] the defect formation energy depends sensitively on the atomic chemical potential and the electron Fermi energy. In the neutral defect system, the formation energy $\Delta H_{\rm f}(\alpha,0)$ depends on the chemical potential μ of the copper atom and the oxygen atom (defects related to Y and Sc are not considered in this work), i.e.,

$$\Delta H_{\rm f}(\alpha,0)=\Delta E(\alpha,0)+n_{\rm Cu}\mu_{\rm Cu}+n_{\rm O}\mu_{\rm O},\tag{2}$$

and

$$\begin{aligned}&\Delta E(\alpha,0)\\ &=E(\alpha,0)-E_0({\rm host})+n_{\rm Cu}\mu_{\rm Cu}^{0}+n_{\rm O}\mu_{\rm O}^{0},\end{aligned}\tag{3}$$

where $E(\alpha,0)$ is the total energy of the supercell containing the neutral defect; $E_0({\rm host})$ is the total energy of the same supercell free of any defect; $n_{\rm Cu}$ and $n_{\rm O}$ are the number of atoms transferred from the supercell to the reservoirs to form the defect cell; $\mu_{\rm Cu}^{0}$ and $\mu_{\rm O}^{0}$ are the standard chemical potentials, or the total energy of ground-state solid Cu (fcc) and O (oxygen).

In the charged defect system, the defect formation energy $\Delta H_{\rm f}(\alpha,q)$ is given by

$$\Delta H_{\rm f}(\alpha,q)=\Delta H_{\rm f}(\alpha,0)+\varepsilon(0/q)+qE_{\rm F},\tag{4}$$

where $E_{\rm F}$ is the Fermi energy measured from the VBM energy $E_{\rm VBM}$ and $E_{\rm F}$ is bound between $E_{\rm VBM}$ and $E_{\rm CBM}$.

The chemical potentials depend on the experimental growth conditions, which can be Cu-rich or O-rich (or in between). For example, for $CuYO_2$, the range of the chemical potentials is determined by the following considerations.

(i) The values that will cause precipitation of solid elements Cu, Y, and O, so that

$$\mu_{\rm Cu}\le 0,\quad \mu_{\rm Y}\le 0,\quad \mu_{\rm O}\le 0.\tag{5}$$

(ii) By the values that maintain a stable $CuYO_2$ compound, so that

$$\mu_{\rm Cu}+\mu_{\rm Y}+2\mu_{\rm O}=\Delta H_{\rm f}({\rm CuYO_2}),\tag{6}$$

where $\Delta H_{\rm f}({\rm CuYO_2})=-11.60$ eV is the calculated formation energy of solid $CuYO_2$. For $CuScO_2$ the calculated formation energy is $\Delta H_{\rm f}({\rm CuScO_2})=-11.63$ eV.

(iii) By the values that will cause formation of binaries, so that

$$2\mu_{\mathrm{Y}} + 3\mu_{\mathrm{O}} \leq \Delta H_{\mathrm{f}}(\mathrm{Y_2O_3}), \quad (7)$$

$$2\mu_{\mathrm{Cu}} + \mu_{\mathrm{O}} \leq \Delta H_{\mathrm{f}}(\mathrm{Cu_2O}). \quad (8)$$

Our calculated results are $\Delta H_{\mathrm{f}}(\mathrm{Y_2O_3}) = -16.04\,\mathrm{eV}$, $\Delta H_{\mathrm{f}}(\mathrm{Cu_2O}) = -1.41\,\mathrm{eV}$ and $\Delta H_{\mathrm{f}}(\mathrm{Sc_2O_3}) = -15.83\,\mathrm{eV}$.

3. Results and discussion

In the family of $CuMO_2$, Cu is a monovalent cation and M is a trivalent cation. The crystal structure of the $CuMO_2$ belongs to the space group of $R\bar{3}m$. In $CuMO_2$, each Cu atom is linearly coordinated with two oxygen atoms to form a O–Cu–O dumbbell unit placed parallel to the c-axis, and these O–Cu–O dumbbell layers in a hexagonal plane are separated by MO_6 edge-sharing octahedral layers.[3] We fully optimized the crystal lattice parameters and atomic internal parameters. The crystal lattice parameters a and c are optimized in terms of fitting total energy according to the Murnaghan equation of state,[26] and the internal atomic positions u are optimized in terms of forces applied on the atoms. For $CuYO_2$, the calculated structural parameters are $a = 0.3466(3.533)\,\mathrm{nm}$, $c = 1.6831(17.136)\,\mathrm{nm}$ and $u = 0.01060(0.1066)\,\mathrm{nm}$; for $CuScO_2$, the calculated structural parameters are $a = 0.3165(3.216)\,\mathrm{nm}$, $c = 1.6919(17.089)\,\mathrm{nm}$ and $u = 0.01064(0.1052)\,\mathrm{nm}$. The available experimental data[27,28] are in parentheses. Our calculated structural parameters have errors less than 1.9% in comparison with 0 experimental data, which may be induced by the different concentration of defects between experiment and calculation or produced by calculational precision. But this low error is allowable in theory.

Figure 1 presents the band structures of $CuMO_2(M = \mathrm{Sc, Y})$. The CBM of $CuYO_2$ is at point L and the VBM is at point Z. Thus, $CuYO_2$ has an indirect gaps of 2.75 eV, which is in good agreement with the 2.7 eV found by Mattheis.[11] $CuScO_2$ is a direct band gap oxide and the direct band gap is at point L and its width is 2.16 eV. Since LDA underestimates the band gap, $CuYO_2$ and $CuScO_2$ should have wider band gaps in practice. For the previous calculation of several similar compounds, Yanagi *et al*[4] suggested that the fundamental band gap of $CuAlO_2$ was at Γ point; Nie *et al*[3] suggested that the fundamental band gap of $CuMO_2(M = \mathrm{Ga, In})$ was at Γ point. However their calculations show that the fundamental band gap of $CuAlO_2$ is at point L instead of Γ point. Our calculations of $CuMO_2(M = \mathrm{Sc, Y})$ show that the fundamental band gaps are both at point L. For both compounds, the valance band values at points Z, L and F, and Z_{V}, L_{V}, and F_{V} are close.

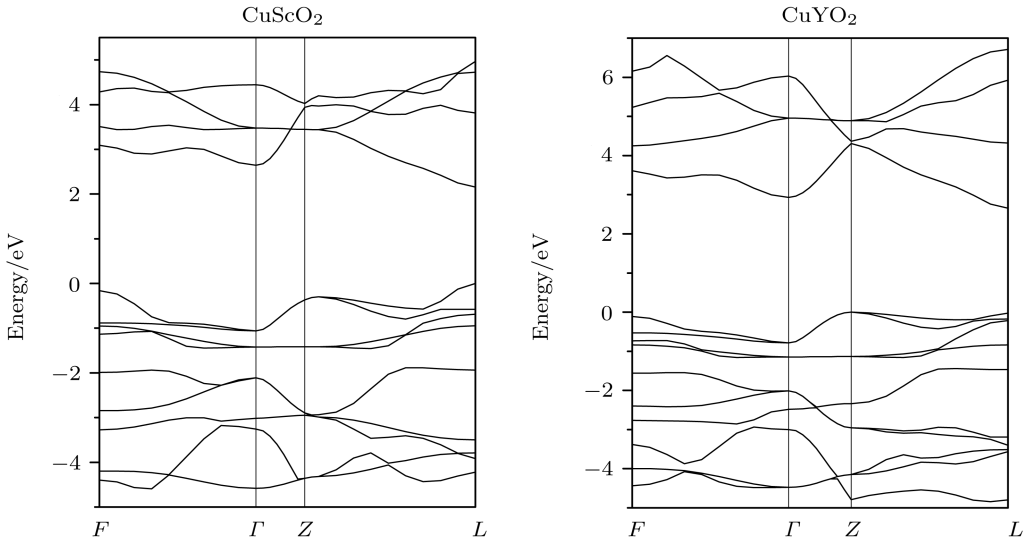


Fig.1. The band structures of $CuMO_2$ (M = Sc, Y) along the high-symmetry directions, energy zero is set to E_{VBM}.

In Fig.2, we present the density of states(DOS) of CuMO_2(M = Sc, Y). Taking $CuScO_2$ as an example, the Sc 4s, 4p and Cu 4s states hold a small proportion of the total DOS because 4s and 4p electrons of Sc and 4s electron of Cu all transfer to O 2p states and become Sc^{3+} and Cu^{1+}. O 2s electrons hold an energy level at about –17 eV lower than Fermi level, so in Fig.2 we cannot see the O 2s states. Figure 2 indicates that the VBM states are mainly composed of the Cu d states, whereas the CBM states are mainly composed of M(M = Sc, Y) atom d states.

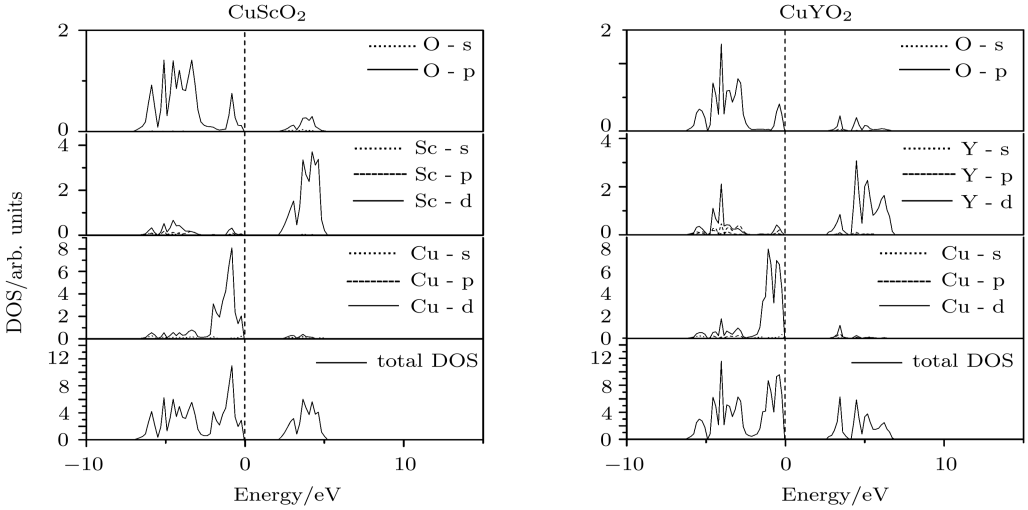


Fig.2. The density of states of CuMO_2(M = Sc, Y). Energy zero is set to $E_{\rm VBM}$. The bottom panel shows the total DOS of the CuMO_2(M = Sc, Y), others show the DOS of the s, p, or d orbital in the three component atoms.

Figures 3 and 4 respectively show for $CuScO_2$ and $CuYO_2$, the formation energy as functions of Fermi level for native point defects under O-rich and O-poor conditions. It is found that, most donor-type defects (dashed line) have a relatively high formation energy and a deep transition energy level. Under O-poor conditions, Cu_i has the lowest formation energy among all donors, which are about 3.04 eV and 2.19 eV for $CuScO_2$ and $CuYO_2$, respectively. And the transition energy levels of these defects are very deep. All kinds of donor-type defects seldom occur under both conditions (O-poor and O-rich). Therefore, this is not the promising donor occurred in $CuScO_2$ and $CuYO_2$. Accordingly without intentional doping, $CuScO_2$ and $CuYO_2$ have no n-type conductivity quality.

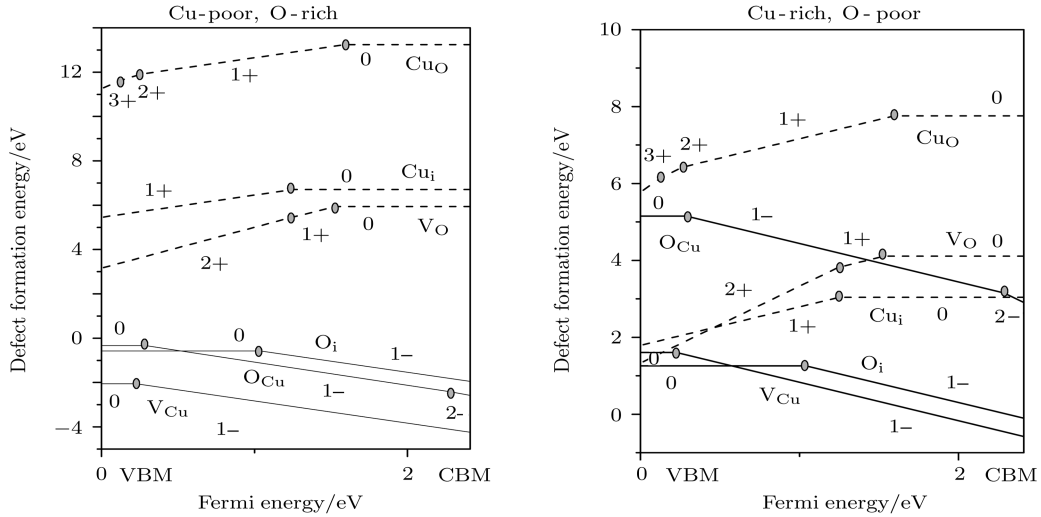


Fig.3. For $CuScO_2$, Formation energy as a function of Fermi level for native point defects under O-rich and O-poor conditions. The zero of Fermi energy is set to $E_{\rm VBM}$. Acceptors and donors are shown by solid and dashed lines, respectively. Charge state q determines the slope of each line segment. Solid dots denote values of formation energy $E_{\rm F}$ where transition between charge states occurs.

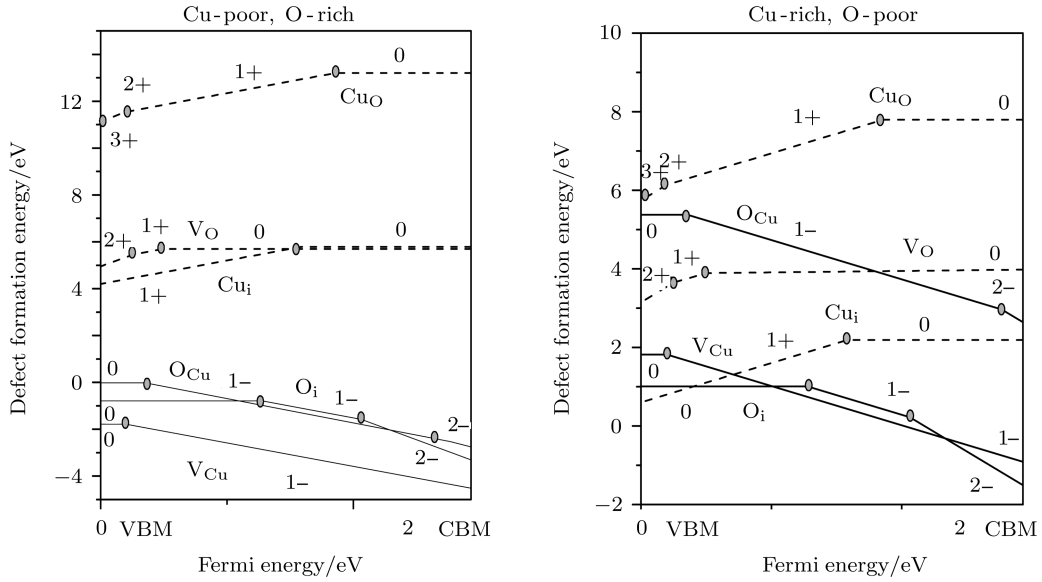


Fig.4. For $CuYO_2$, Formation energy as a function of Fermi level for native point defects under O-rich and O-poor conditions. The zero of Fermi energy is set to E_{VBM}. Acceptors and donors are shown by solid and dashed lines, respectively. Charge state q determines the slope of each line segment. Solid dots denote values of formation energy E_{F} where transition between charge states occurs.

Whereas all the acceptor-type defects have relatively low formation energy, the formation energies of O_i, O_{Cu}, and V_{Cu} are always negative within the energy gap under O-rich conditions, which means that these defects can be formed spontaneously under O-rich conditions. For interstitial oxygen O_i, the defect transition energies are $\epsilon_\alpha(-/0) = E_v + 1.28\,\mathrm{eV}$ and $\epsilon_\alpha(-/0) = E_v + 1.04\,\mathrm{eV}$ for $CuYO_2$ and $CuScO_2$, respectively, where E_v is the VBM energy. These transition energy levels belong to deep levels and will form localized states. Therefore interstitial oxygen O_i can not reach high hole concentration at room temperature, namely, O_i does not offer too much carrier in the p-type conductivity. Under O-poor conditions the formation energy of O_{Cu} is much higher, so it is difficult for O_{Cu} to emerge. But under O-rich conditions O_{Cu} has a lower formation energy, as shown in Figs.3(a) and 3(c), and the defect transition level belongs to shallow level. Thus, we can conclude that O_{Cu} plays a positive role in the p-type conductivity under O-rich conditions.

For vacancy copper V_{Cu}, under O-poor conditions, the formation energy of V_{Cu} decreases as E_F moves toward CBM and becomes negative, it means that, V_{Cu} can be formed spontaneously. The defect transition level of V_{Cu} are $\epsilon_\alpha(-/0) = E_v + 0.199\,\mathrm{eV}$. Therefore V_{Cu} belongs to a shallow single acceptor. For $CuScO_2$, the V_{Cu} defect transition level is $\epsilon_\alpha(-/0) = E_v + 0.227\,\mathrm{eV}$, and V_{Cu} also belongs to a shallow acceptor. Under O-rich conditions both V^0_{Cu} and V^-_{Cu} have lower energy than that of O-poor condition. These results indicate that copper vacancy can be an important acceptor in $CuMO_2$ (M = Sc, Y) under both O-poor and O-rich conditions. Our results indicate that under both O-rich and O-poor conditions V_{Cu} can easily come into being so V_{Cu} is an ideal acceptor. Under O-rich condition O_{Cu} also has a low formation energy and a shallow transition level and can be formed easily in the crystal growth process. By controlling the copper and oxygen pressure during the thermal non-equilibrium pulsed laser deposition (PLD) or molecular beam epitaxy (MBE) crystal growth, we can acquire desired acceptor defects to realize p-type conductivity in $CuScO_2$ and $CuYO_2$.

4. Conclusion

In summary, we study the electronic structure and native defects in $CuScO_2$ and $CuYO_2$ through the first-principles calculations. Our calculations show that, the direct band gap of $CuScO_2$ is 2.16 eV, and the indirect band gap of $CuYO_2$ is 2.75 eV. We have found that copper vacancy and oxygen interstitial have relatively low formation energy in $CuScO_2$ and $CuYO_2$. The transition energy level of copper vacancy

is close to VBM, thus copper vacancy is the most efficient acceptor in $CuScO_2$ and $CuYO_2$, under O-rich condition, oxygen antisite has low formation energy and also becomes important acceptor .

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