INSIGHTS INTO THE IMPACT OF NATIVE DEFECTS ON THE CONDUCTIVITY OF CuVO₃ MATERIAL FOR PHOTOVOLTAIC APPLICATION: A FIRST-PRINCIPLES COMPUTATIONAL STUDY

MOUSSAB HARB* and LUIGI CAVALLO

KAUST Catalysis Center (KCC), Physical Sciences and Engineering Division (PSE), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

ABSTRACT: We report a theoretical study on the impact of native defects present in CuVO₃ material on its conductivity using first-principles calculations based on density functional theory. We find a low and direct band gap of 1.4 eV for the pristine cell together with relatively high solar absorption efficiency, high macroscopic dielectric constant, and delocalized orbital characters of photogenerated charge carriers. This result highlights CuVO₃ as a good candidate for photovoltaic application. Among the various explored native defects (including vacancies, interstitials, and antisites), we demonstrate that only those associated with O vacancies are shallow donors and with Cu vacancies are shallow acceptors, leading respectively to n-type and p-type conductivities under O-poor and O-rich growing conditions.

INTRODUCTION

Designing new potential absorber semiconducting materials used in photovoltaic solar cells requires the appropriate determination of different components that will be assembled in the final device. In addition to the required low band gap in the 1.1–1.5 eV range to reach the maximum solar energy efficiency, other specific intrinsic parameters directly involved in the processes must be properly tuned. They include the solar light absorption intensity, exciton binding energy, and possibility of charge carrier diffusion throughout the crystal structure to the surface.

Experimentally, previous works on semiconductors widely used in photovoltaic devices revealed that a higher dielectric constant value than 10 is enough to obtain a good ability for exciton dissociation into free holes and electrons at room temperature. Moreover, they have also shown that the delocalization orbital character of photogenerated charge carriers is required to give low effective masses and help for their good transport to the surface by minimizing the electron–hole pairs recombination.

To design and characterize new materials for solar energy conversion applications, the density functional theory (DFT) has emerged as a valuable computational tool to quantify these key intrinsic parameters because of the difficulties to their direct experimental measurement. Achieving accurate DFT computations is thus particularly relevant, and this is known to be in strong relationship with the type of the exchange–correlation functional used for describing the various electron–electron interactions.

Previous theoretical studies on largely utilized semiconducting materials in photocatalytic water splitting and photovoltaics showed that the intrinsic parameters mentioned above can be predicted with good accuracy using DFT along with the screened Coulomb hybrid Heyd–Scuseria–Ernzerhof (HSE06) functional. Following this robust computational protocol, we have recently investigated the electronic, optical, dielectric, and transport properties of the monoclinic vanadium(V) oxynitride, VON (namely, γ-phase) and the orthorhombic mixed tin(II) and tungsten(VI) oxide, pristine SnWO₄ (namely, α-phase), semiconductor crystals and predicted suitable behaviors for photovoltaic applications. A few years earlier, we have also predicted a suitable band gap of the mixed copper(I) and vanadium(V) oxide material, pristine CuVO₃, within the hexagonal crystal structure for photovoltaics.

Last, we mainly focused on deeply understanding the essential fundamental properties of CuVO₃ for solar energy conversion applications for the main reason summarized in Figure 1. By comparing the absorption intensity of pristine CuVO₃ with those acquired for VON and pristine SnWO₄ crystals, we show that the solar light absorption efficiency of CuVO₃ is the highest one in the zone covering the whole region of visible light. This result highlights this material as a very good absorber of solar energy.

Nevertheless, relevant information about the possibility for exciton separation to free electrons–holes and mobility of charge carriers using the pristine CuVO₃ needed to be clarified. Although CuVO₃ is a ternary compound and should be in strong relationship with the type of the exchange–correlation functional used for describing the various electron–electron interactions.

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be taken into consideration to fully characterize the optoelectronic properties of this compound. These fundamental aspects will be provided in detail in the present work.

In this paper, we present a systematic first-principles computational study on native defects in CuVO₃ using DFT to understand how they can impact the conductivity of this material in direct correlation with its potential for solar energy conversion. Besides the electronic structure and the visible-light absorption coefficient spectrum of the pristine cell, we computed the imaginary and real parts of photon energy-dependent dielectric function along the three main light polarization vectors in its crystal lattice, the electronic (including local field effects) and ionic contributions to its macroscopic static dielectric tensor, and the hybridization characters of its band edges in terms of partial charge density maps to give an overall picture on its optoelectronic properties.

Then, we calculated the transition and formation energies of the various explored native defects (including vacancies, interstitials, and antisites) with different charge states together with Fermi level pinning positions. Among all of them, we found that only those corresponding to Cu vacancies are shallow acceptors and those corresponding to O vacancies are shallow donors, leading, respectively, to p-type and n-type conductivities under O-rich and O-poor/Cu-rich growing conditions.

**RESULTS AND DISCUSSION**

**Optoelectronic Properties of Pristine CuVO₃.** The crystal lattice of CuVO₃ is hexagonal (space group is rhombohedral R3) with an ordered ilmenite structure made by layers of Cu⁺ ions in octahedral O²⁻ environment. The CuO₆ octahedra are shared by edges with Cu=O bonds in between 2.02 and 2.22 Å and interconnected by corners and edges with other layers of V⁵⁺ ions in octahedral O²⁻ environment, VO₆, characterized by V=O bonds going from 1.80 to 2.06 Å (see Figure 2). The calculated lattice constants ($a = b = 4.93$ Å and $c = 13.98$ Å, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$) well reproduced the measured ones ($a = b = 4.96$ Å and $c = 14$ Å, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$).²²

Figure 3a displays the computed total and partial electronic density of states of pristine CuVO₃ using HSE06 functional. The electronic structure analysis indicates a relatively small band gap of 1.4 eV, which mainly comes from electronic excitations involving filled Cu 3d¹⁰ orbitals and unoccupied V 3d⁰ orbitals. The obtained band gap for this material is found to be either indirect from $\Gamma$ point to $\Gamma$ point in the first Brillouin zone or direct at $\Gamma$ point, as shown in Figure 3b. Interestingly, our predicted band gap of 1.4 eV for CuVO₃ is in line with the main required property for developing new and suitable semiconductors for photovoltaic devices. Note that our computed band structure using Perdew–Burke–Emzerhof (PBE) is in good agreement with that previously reported¹³ using HSE06 with only minor discrepancy. Apart from the difference in the functional, the use of more reliable model (2 $\times$ 2 $\times$ 1 supercell) together with an expanded cutoff energy (up to 600 eV) for electron wave functions as adopted here is expected to give more reliable data.

We have then studied the absorption features in pristine CuVO₃ crystal structure from the computed imaginary part of complex dielectric function in the three main incident light polarization vectors versus energy of photon using HSE06 functional. A relatively small optical anisotropy is obtained from the weak dependence on the polarization vector (see Figure 4a). If light is polarized along either (100) or (010) direction of the hexagonal lattice, the absorption edge occurs at 1.4 eV, which gives the band gap of this compound. For a
polarization of light in the (001) direction, the onset of absorption becomes slightly higher in energy.

By computing the real-part of the photon energy-dependent complex dielectric function along the three principal light polarization vectors of pristine CuVO3 crystal structure using HSE06 functional, we have examined the dielectric behavior inside the crystal lattice of this material. Figure 4b highlights (in black dots) the optical part of the dielectric tensor for this material, which was deduced from each plot at the corresponding electronic band gap energy. The dielectric analysis shows a kind of anisotropic nature related to the direction of light polarization, in particular around the electronic band gap energy zone of this material. A dielectric constant of 10 is obtained for a light polarization along either the (001) or (010) direction of the crystal lattice, while a higher value of 21 is found when the light is polarized along the (001) direction.

We have also calculated the electronic part of dielectric tensors of pristine CuVO3 crystal using another approach based on the self-consistent response upon the application of an external static electric field together with HSE06 functional. In principle, this method is supposed to be more accurate, as it takes into account the induced local field effects. The ionic contribution to the dielectric tensor of each material is calculated using the linear response approach through density functional perturbation theory (DFPT) with PBE functional. Table 1 reports the computed nonzero values of optical, vibrational, and total dielectric constant tensors of this material along the three principal directions. We obtained macroscopic dielectric constants of 39.2, 39.2, and 22.3 along the (100), (010), and (001) directions, respectively, with a relatively high averaged dielectric constant of 33.5. This is expected to lead to an excellent dielectric behavior using this material. The higher contribution to the macroscopic dielectric tensor in this material originates from the vibrational part (see Table 1). This is due to the important Born effective charges in the material originated from the important electronegativity of oxygen. As the computed macroscopic dielectric constant for pristine CuVO3 is notably high, the capability for photoexciton dissociation to free carriers using this material is expected to be easy. Note that the obtained electronic part of dielectric constant in the case of pristine CuVO3 is very close to that previously obtained using the independent particle approximation (see Figure 4b and Table 1). This result highlights the fact that both approaches can give reasonable optical dielectric constants of 3D semiconductors, in which the excitonic effect is relatively weak.

To understand the electron and hole mobilities tendency throughout the crystalline structure of pristine CuVO3 material, we have analyzed the hybridization character of electronic orbitals involved in the band edges of this semiconductor. Figure 5 displays the distribution of charge densities over the ac plane of the valence (left) and conduction band (right) edges of pristine CuVO3 using HSE06 functional. The valence band map indicates an important role of d-orbitals on all Cu with lower role of p-orbitals on all O (Figure 5a). The 3D delocalization of the electronic states on all Cu and O species located near each other in pristine CuVO3 could help for the migration of holes throughout its crystal structure to surface. The conduction band analysis highlights important involvements of d-orbitals on all V with minor contribution of p orbitals on all O inside the crystal lattice (Figure 5b). The delocalized character of electronic states on all V and O species spatially located close to each other tends to lead to a good ability for the excited electrons to move throughout the CuVO3 crystal structure to surface.

### Table 1. Computed Electronic ($\varepsilon^{\text{el}}$)$_{ij}$ Ion (vib)$_{ij}$ and Macroscopic ($\varepsilon^{\text{ff}}$)$_{ij}$ Dielectric Constants (Based on HSE06 and PBE Functionals) of Pristine CuVO3 Crystal along (100), (010), and (001) Directions

| Material   | Direction | ($\varepsilon^{\text{el}}$)$_{ij}$ | ($\varepsilon^{\text{vib}}$)$_{ij}$ | ($\varepsilon^{\text{ff}}$)$_{ij}$ |
|------------|-----------|------------------------------------|-------------------------------------|----------------------------------|
| CuVO3      | (100)     | 11.4                               | 27.8                                | 39.2                             |
|            | (010)     | 11.4                               | 27.8                                | 39.2                             |
|            | (001)     | 19.8                               | 2.5                                 | 22.3                             |
|            | average   | 14.2                               | 19.3                                | 33.5                             |
are reported in Table 2. Positive or negative values for donors will mean that the donor level is located below or above CBM.

Table 2. Computed Defect Energy Levels with Respect to CBM for Donors (in eV) and with Respect to VBM for Acceptors (in eV) in CuVO₃ with Various Charge States

| donors   | +1   | +2   | +3   | +4   | +5   |
|----------|------|------|------|------|------|
| Vₜₐₜ   | 0.28 | 0.43 | 0.52 | 0.66 | 0.81 |
| Vₜₐₜ   | 0.37 | 0.51 | 0.58 | 0.62 |      |
| Oₜₐₜ   | 0.21 | -0.15|      |      |      |
| acceptors | -1   | -2   | -3   | -4   | -5   |
| CuV     | 1.20 | 1.12 | 1.04 | 0.96 | 0.88 |
| Cuₐₐₜ  | 0.12 |      |      |      |      |
| Vₜₐₜ   | 0.25 | 0.28 | 0.31 | 0.34 | 0.29 |
| Oₜₐₜ   | 0.67 | 0.51 |      |      |      |

Similarly, positive or negative values for acceptors will mean that the acceptor level is located above or below VBM. Among the four explored donor-like defects, Cuₜₐₜ, Vₜₐₜ, Vₜₐₜ, and Oₜₐₜ, only Oₜₐₜ is found to be a shallow donor. Its (0/+2) transition energy level is even above the CBM of CuVO₃. Besides, among the four explored acceptor-like defects, CuV, Cuₐₐₜ, Vₜₐₜ, and Oₜₐₜ, only CuV is found to be a shallow acceptor. As a result, we found that the creation of a CuV does not significantly perturb the lattice upon relaxation around the Cu-vacancy site. The relaxation led to only 0.03 Å reduction on V–O bond length for V and O species located around the vacancy site. Such small relaxation is expected to make relatively small perturbation in the valence band states and therefore leads to a shallow acceptor level. A similar trend was also found in the case of Oₜₐₜ because of the small lattice relaxation around the O-vacancy site, giving relatively weak perturbation in the conduction band states. As a consequence, the formation of shallow acceptors (like Cuₐₐₜ) and shallow donors (like Oₜₐₜ) are at the origin of the p-type and n-type conductivities in this material.

In general, the conductivity of a semiconducting material is not only dependent on the donor/acceptor transition energy levels but also on their formation energies. To give rational insights into the impact of native defects on the conductivity of CuVO₃, the positions of Fermi-level pinning are needed to be addressed. Figure 6a,b displays the computed formation energies of native defects as a function of Fermi level positions under Cu-rich/O-poor and O-rich growth conditions, respectively. The results for Cuₜₐₜ are not displayed because they reveal much higher values as compared to other defect types. For CuV and Vₜₐₜ, the high formation energies can be understood by the ionic radius difference between V⁵⁺ and Cu⁺⁺. Overall, the donor formation energies are much lower under O-poor/Cu-rich condition, whereas the acceptor formation energies are much lower under O-rich condition. Under O-poor condition, the Oₜₐₜ formation energy of is the lowest one, and this means that n-type conductivity of this material can be obtained from the Oₜₐₜ formation. The Fermi level was pinned at around 0.30 eV below the CBM through the Cuₜₐₜ formation (dashed vertical line in Figure 6a). The Cuₜₐₜ formation energy was the lowest one under O-rich condition enabling for the p-type conductivity of this material. The Fermi level was pinned at around 0.40 eV above the VBM through the Oₜₐₜ formation (dashed vertical line in Figure 6b). Therefore, our calculations demonstrate that CuVO₃ needs to be prepared under O-poor/Cu-rich condition to get n-type conductivity, and it is required to be grown under O-rich condition to obtain p-type conductivity.

CONCLUSIONS

We performed a systematic first-principles computational study on native defects remaining in the CuVO₃ semiconductor material lattice using DFT to understand how they can impact the conductivity of this material in direct correlation with its potential for solar energy conversion application. First, we investigated the optoelectronic properties investigated for the pristine cell such as electronic structure, visible-light absorption coefficient spectrum, electronic and ionic contributions to its macroscopic dielectric tensor, and the hybridization characters of its band edges. Second, we calculated the transition energies and formation energies of the various explored native defects together with Fermi level pinning positions.

As for the optoelectronics of the pristine CuVO₃ material, our calculations predicted a low and direct band gap of 1.4 eV, in line with the required zone for developing new semiconductors for photovoltaic devices. In addition, we have shown that this material exhibits relatively high solar light absorption efficiency, high macroscopic dielectric constant, and delocalized orbital characters of photogenerated charge carriers throughout its crystal structure. These results highlighted CuVO₃ as a good candidate for photovoltaic application.

Regarding the various possible explored native defects (including vacancies, interstitials, and antisites), we found that only those corresponding to Cu vacancies are shallow acceptors and those corresponding to O vacancies are shallow donors, leading, respectively, to p- and n-type conductivities under O-rich and Cu-rich/O-poor growth conditions.

These data could be very useful for understanding the material properties and open good perspectives for the highly...
crystalline CuVO₃ material within a single phase to be carefully prepared and adopted as a new class of materials for solar energy conversion applications.

**COMPUTATIONAL METHODS**

The hexagonal crystalline phase of copper vanadate, CuVO₃, was considered for structural modeling based on the experimental determination and refinement by full-matrix least-squares procedures using automatic diffractometer data. To examine the various possible native defects in pristine CuVO₃, we considered the 2 × 2 × 1 supercell model of the hexagonal structure of pristine CuVO₃, which consists of two unit cells stacked both along the a- and b-axes (24 functional units Cu₃V₂O₇ or 120 atoms). All crystal structures considered in this work were fully optimized by means of the spin-polarized DFT with the PBE exchange–correlation functional and the frozen-core projector augmented-wave approach using VASP software. The configurations of valence electrons taken explicitly into account in our calculations are 3d¹⁰4s¹ for Cu, 3p⁶3d⁴4s¹ for V, and 2s²2p⁴ for O. In all cases, the default value of 0.2 Å for range separation. The optical PBE was taken into account at short range interaction with the standard mixture of 25% Hartree–Fock and 75% PBE exchange–correlation energy. This contribution directly correlated with the electron density of states.

The electronic structure of each material was optimized by DFT through VASP package using the HSE06 functional where the standard mixture of 25% Hartree–Fock and 75% PBE was taken into account at short range interaction with the default value of 0.2 Å for range separation. The optical dielectric tensor ε(ω) of pristine CuVO₃ was determined using the HSE06 functional with VASP, either from the real part of the dielectric function ε₁(ω) or by investigating the self-consistent interaction of the material with an external electric field, which includes the local field effects. The use of HSE06 functional is needed to more accurately describe ε(ω) based on the good description of the obtained band gap energy. This contribution directly correlated with the electron density polarizability of the material. The ionic dielectric tensor εᵢ(ω) was acquired using the linear response approach with the PBE functional through DFPT. This contribution is directly dependent on the polarization induced by the softest vibrational frequencies. The macroscopic dielectric tensor ε(ω) was quantified through the summation of both parts.

The steady production of CuVO₃ under thermal equilibrium growth conditions is given by the following expression:

\[
\mu_{\text{Cu}} + \mu_{V} + 3\mu_{O} = \Delta H_f(\text{CuVO}_3) \tag{1}
\]

where \(\mu_{\text{Cu}}, \mu_{V}, \) and \(\mu_{O}\) are the Cu, V, and O chemical potentials, respectively. \(\Delta H_f\) is the enthalpy of formation for CuVO₃ per functional unit.

For native defects formation energy calculation, we followed the mixing scheme taking into account the benefits of specific k-point and Γ-point approach that has been successfully applied to a large variety of semiconductors. For a native defect \(\delta\) with a charge \(q\), the enthalpy of formation \(\Delta H_f(\delta q)\) is dependent on the relative Fermi-level position \((E_F)\) to the VBM, on the transition level \(\epsilon(0/q)\), as well as on the chemical potential \(\mu\), as follows:

\[
\Delta H_f(\delta q) = \Delta H_f(\delta, 0) - q\epsilon(0/q) + qE_F \tag{2}
\]

where \(\Delta H_f(\delta, 0)\) is given by

\[
\Delta H_f(\delta, 0) = E(\delta, 0) - E(\text{bulk, 0}) + \sum_i n_i(E_i + \mu_i) \tag{3}
\]

The steady production of CuVO₃ under thermal equilibrium growth conditions is given by the following expression:

\[
\epsilon(0/q) = \left[ \epsilon_{\text{CBM}}^f(\text{bulk, 0}) - \epsilon_{\text{VBM}}^f(\text{bulk, 0}) \right] + \left[ E(\delta, 0) - |E(\delta, 0) - q\epsilon_{\delta}(\delta, 0)| \right]/(q) \tag{4}
\]

As displayed in eqs 2 and 3, the computed formation energies for charged native defects are dependent on \(\mu_{\text{Cu}}, \mu_{V}, \) and \(\mu_{O}\) values as well as on the Fermi-level positions. We presented here results under two representative growing conditions such as Cu-rich/O-poor and O-rich.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: moussab.harb@kaust.edu.sa. Phone: +966.12.808.07.88.*

**ORCID**

Moussab Harb: 0000-0001-5540-9792
Luigi Cavillo: 0000-0002-1398-338X

**Notes**

The authors declare no competing financial interest.

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