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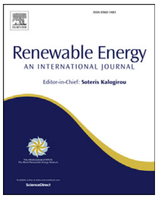

Applicability of $CuRhO_2$ as a solar energy converter

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ABSTRACT

Delafossite $CuRhO_2$ is considered as a solar radiation absorbing material for solar cells and solar-to-fuel conversion by carrying out the water splitting. The absorption features depend on the optical properties. To obtain the absorption coefficient we use the density functional theory with orbital-dependent one-electron potentials. As well as analyzing the largest contributions, the absorption coefficients have been split into different species contributions. Then, the maximum absorption efficiencies, photo-currents and photo-voltages of the sunlight conversion have been obtained using the absorption coefficients, the device thickness, and the incident spectrum as optimization criteria. Furthermore the non-radiative recombination and some voltage losses are analyzed.

1. Introduction

Materials with the Delafossite structure and with a band gap within the visible region include $CuFeO_2$, $CuRhO_2$, and β-$CuGaO_2$. These semiconductors could be suitable as absorbent of photo-electro-chemical (PEC) and/or photovoltaic (PV) solar cells. In particular Delafossite $CuRhO_2$ has been studied for water splitting under ultraviolet and visible light irradiation [1,2], and as thermoelectric material for converting waste heat into electricity [3].

The $CuRhO_2$ semiconductor crystallizes in the AMO_2 Delafossite structure ($R\overline{3}m$, space group nº 166, with lattice parameters (a,c) between (3.075,17.165) Å [4] and (3.08,17.09) Å [5]. In this structure (Fig. 1) layers of the edge-shared MO_6 octahedra alternate with O-Cu-O. The bandgap (1.9 eV [1]) and the energetic position of the conduction band (CB) and the valence band (VB) edges meets the conditions to dissociate the water molecules: $2H_2O \rightarrow 2H_2 + O_2$, with a standard potential $E^{(0)} = -1.23$ V [6,7], equivalent to Gibbs free energy $\Delta G^0 = 237.22$ kJ.mol^{-1}. Really several hundred meV of overpotential are necessary to drive the water-splitting, mainly due to anodic and cathodic overpotentials.

The photovoltaic converter either as solar cell or as part of the photoelectrochemical cell must provide the photo-voltage as the driving force for water-splitting. If this condition is satisfied then the conditions for the efficiency optimization from solar to fuel conversion are essentially the same as that of solar to electricity conversion. One significant limitation usually used to obtain the efficiencies of the photovoltaic converter to electricity or to fuel is the assumption that the semiconductor absorbs all photons with energy $E \geq E_g$. It implicitly implies that both the absorption coefficient $\alpha(E)$ and the absorptivity $a(E,w)$ as a function of the photon energy E are step functions independent of the semiconductor thickness w. However, when it is necessary to use absorber layers thinner than the photon penetration depth in the material $\alpha^{-1}(E)$ due to poor charge carrier transport, this hypothesis is not suitable. For this reason we are going to use the calculated absorption coefficient without approximations. Firstly we obtain the absorption coefficient using first principles. Both the bandgap and the absorption coefficient are in accordance with the experimental absorption spectrum of $CuRhO_2$ [1]. Secondly we obtain the different species and angular momentum contributions to the absorption coefficient. It allows analyzing the optical properties appropriately avoiding oversimplified analysis that fail for this case. Then, using the absorption coefficient previously obtained, and avoiding the approximation to a step function, we evaluate the efficiencies, photo-voltages and photo-currents as a function of the semiconductor thickness w. In addition different spectral ranges will be used in order to highlight one of the causes of discrepancies when results are compared. Finally several recombination processes causing voltage losses will be analyzed. The results obtained set an upper limit to the $CuRhO_2$ applicability for solar energy conversion. These limits can serve as a reference for experimental studies.

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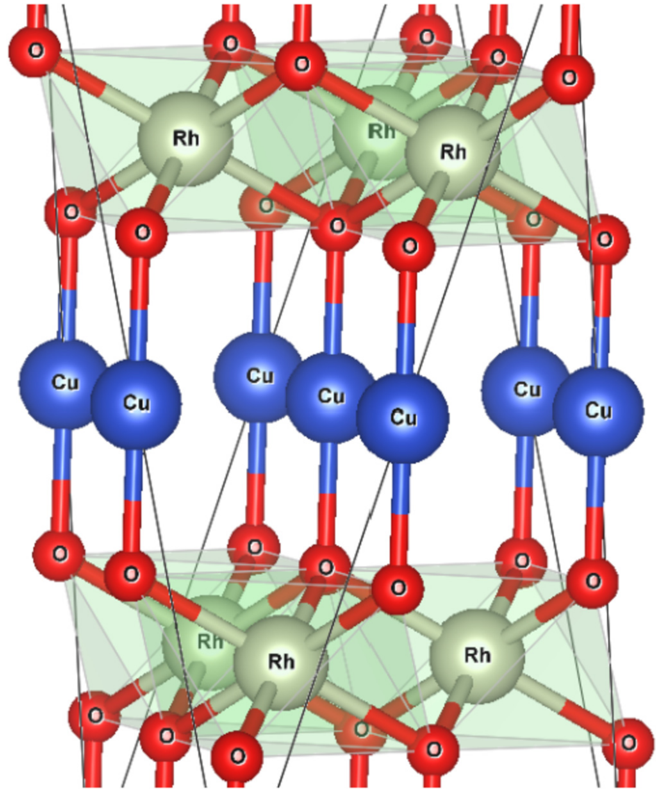

Fig. 1. Crystalline structure of the $CuRhO_2$.

2. Methodology

2.1. Electronic properties

In order to obtain the optical properties, density functional theory (DFT) [8,9] calculations were carried out with orbital-dependent one-electron U potentials (DFT + U method [10–15]) using the formalism described in Refs. [12,13]. The exchange-correlation effects were described through the generalized gradient approximation within the Perdew-Burke-Ernzerhof [16] approach. The Troullier–Martins [17] pseudopotentials expressed in Kleinman–Bylander [18,19] form, a localized pseudoatomic orbital basis set [20] for the valence wave functions, and periodic boundary conditions to approximate the infinite solid were used. The U parameter has been set to reproduce the experimental gap. Using U = 5 eV for the d (Rh) and d (Cu) states gives the best agreement with the experimental band gap (~2.0 eV).

2.2. Optical properties

The optical properties have been obtained by previously calculating the transition probabilities proportional to the square of the momentum matrix elements $p_{\mu\lambda}$ between all the bands at k points in the Brillouin zone. Later, with these transition probabilities together with band energies $E_{\lambda,\mathbf{k}}$ and occupations $f_{\lambda,\mathbf{k}}$, the complex dielectric function e_2 has been evaluated:

$$e_2(E) \sim C\frac{1}{E^2}\sum_{\lambda>\mu}\int d\mathbf{k}\left[f_{\mu,\mathbf{k}}-f_{\lambda,\mathbf{k}}\right]\left|p_{\mu\lambda}\right|^2\delta\left(E_{\lambda,\mathbf{k}}-E_{\mu,\mathbf{k}}-E\right) \tag{1}$$

The other optical properties have been obtained from the complex dielectric function using the Kramers-Kronig relationships [21]. Note that both the absorption and stimulated emission are considered [22,23]. Omitting the k point index to simplify the notation, the rate of absorption from μ to λ states induced by photons is proportional to $r_a = f_\mu(1-f_\lambda)\left|p_{\mu\lambda}\right|^2$, whereas the rate of stimulated emission is proportional to $r_e = f_\lambda(1-f_\mu)\left|p_{\lambda\mu}\right|^2$. Therefore, as the momentum operator and the associate matrix are hermitic, the net absorption rate $(r_a - r_e)$ which defines the absorption coefficient is proportional to $(f_\mu - f_\lambda)\left|p_{\mu\lambda}\right|^2$.

To carry out a more in-depth analysis, the optical properties have been split into atomic species and into angular momentum contributions [24]. To succeed the momentum matrix elements $p_{\mu\lambda}$ have been split as $p_{\mu\lambda} = \sum_A\sum_B p_{\mu\lambda}^{AB}$ and $p_{\mu\lambda}^{AB} = \sum_{l_A\in A}\sum_{l_B\in B}(p_{\mu\lambda}^{AB})_{l_Al_B}$ where $p_{\mu\lambda}^{AB}$ is the inter-species component that couples the basis set functions on different species atoms A and B (it represents an intra-species component if A = B), and $(p_{\mu\lambda}^{AB})_{l_Al_B}$ is the contribution to the transition between the l_A shell-states located at the A atoms and the l_B shell-states located at the B atoms. As usual we use the notation *s*, *p*, *d*, etc for $l = 0, 1, 2$, etc. The complex dielectric function and other optical properties depend on the square of the momentum operator matrix elements involving terms $\left|(p_{\mu\lambda}^{AB})_{l_Al_B}\right|\left|(p_{\mu\lambda}^{CD})_{l_Cl_D}\right|$. Therefore it can be split as a many-species expansion depending on the number of different species involved. In particular for the absorption coefficient: $\alpha = \alpha(S) + T$, where $\alpha(S) = \sum_{A,l_A\in A}\sum_{B,l_B\in B}\alpha_{l_Al_B}^{AB}$ include terms with one or two atomic species (C = A and D = B) and T represents the terms including three and four different non-equivalent species. In general the absorption coefficient can be approximated by $\alpha \approx \alpha(S)$ because $\alpha(S) \gg T$.

2.3. Photo-currents and photo-voltages

In order to determine the conversion efficiency we have used initially the usual standard approximations [22,25,26]: an ideal system without non-radiative recombination, without ohmic losses, and with ideal contacts. With these approximations the photo-current J is the difference between the current J_a generated by the sunlight absorption and the emitted J_e due to radiative recombination ($J = J_a - J_e$). These currents are obtained as $J_\zeta = q\int a(E,\alpha,w)g_\zeta(E)dE$ ($\zeta = a,e$ for absorption and emission respectively), where $a(E,\alpha,w)$ is the absorptivity, α the absorption coefficient, w the thickness of the absorbent material, q is the electron charge, g_a is the incident spectrum photon flux density, and g_e is the photon flux density emitted as a result of the radiative recombination. For the emitted spectrum we have used the standard approach considering that the device emits radiation as a Black-body at a temperature T = 300 K [22,25,26] ($g_e(E) \sim E^2 b_{BE}(E,T,qV)$, where $b_{BE}(E,T,\mu) = [e^{(E-\mu)/kT} - 1]^{-1}$, k is the Boltzmann constant and $\mu = qV$ is the chemical potential associated with the radiation emitted [22,25,26]. With the previous approximations the results are independent on the architecture and on the energy band alignment structure. Of course, when some of these effects are considered the efficiencies will decrease with respect to the optimum value. It will be discussed later. Nevertheless, this maximum efficiency conversion is an upper limit and represents a first filter: if the absorption efficiency is small then the absorbent material will be not suitable for any solar energy converter.

Note that the procedure for obtaining the maximum efficiency, and the current and voltage corresponding to this maximum power point, for any given thickness of the sample, does not consist solely