Electronic, magnetic, optical and solar energy absorption properties of the $\text{Fe}_2\text{V}_4\text{O}_{13}$ vanadate

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ABSTRACT

Keywords:

Optical properties
Photovoltaic
Solar fuel
Semiconductors
Efficiency

The iron vanadium oxide semiconductor $\text{Fe}_2\text{V}_4\text{O}_{13}$ has interesting properties as an absorbent material for the conversion of solar energy. In this work the electronic, magnetic and optical properties of $\text{Fe}_2\text{V}_4\text{O}_{13}$ have been obtained and analyzed from theoretical calculations and compared with experimental results. From the results, the main contributions to the optical properties come from the transitions between O-V states. The optical properties have been used to evaluate this compound as a solar energy converter using mono- and multi-junction configurations.

1. Introduction

Several Iron vanadium oxide semiconductors have given rise to a renewed interest in them as converters of solar energy. They have a varied crystal chemistry with several stoichiometric and nonstoichiometric ratios, and show a band gap of between ~ 1.9 – 2.3 eV (Abdi and Berglund, 2017; Mandal et al., 2016). Some of these materials may also be interesting as a possible candidate for photoelectrode materials (Abdi and Berglund, 2017) and solar energy conversion. For example, for photo-electrochemical (PEC) water splitting for the production of hydrogen.

One of the smaller bandgap metal vanadates is $\text{Fe}_2\text{V}_4\text{O}_{13}$ with an experimental bandgap of between 1.8 (Ping et al., n.d.) – 2.3 eV (Tang et al., 2016). For solar PEC water splitting the light absorbers need to meet stringent requirements: a sufficiently narrow bandgap to exploit the solar energy conversion, properly aligned band edges, and chemical and electrochemical stability. This compound exhibits the appropriate properties for use as a photoanode in a PEC cell. $\text{Fe}_2\text{V}_4\text{O}_{13}$ has also been explored for visible-light photoreduction of CO_2 (Ping et al., n.d.) and the breaking down of organic pollutants (Zhang et al., 2010). $\text{Fe}_2\text{V}_4\text{O}_{13}$ can be synthesized via a wet chemical precipitation process (Zhang et al., 2010), using a successive ion layer adsorption and reaction (SILAR) approach (Tang et al., 2016), through an orientational etching process and simultaneous nucleation and growth process (Huang et al., 2015), and hydrothermal growth (Huang et al., 2014). Moreover, the presence of Fe and V in the Earth's surface would reduce costs with respect to other compounds with less abundant elements.

The properties, the manufacturing possibilities, and the presence of reasonably abundant elements in nature are good reasons for evaluating

$\text{Fe}_2\text{V}_4\text{O}_{13}$ as a possible candidate for the conversion of solar energy. For this, first we obtain the electronic, magnetic and optical properties of this compound using theoretical calculations. These properties are analyzed and compared with results in the literature. Later, using the previously obtained optical properties, we evaluate its potential as a solar energy converter.

2. Methodology

2.1. Electronic and optical properties

For obtaining the electronic, magnetic and optical properties we carried out spin polarized calculations with periodic boundary conditions using density functional theory (DFT) (Kohn and Sham, 1965; Soler et al., 2002). The Perdew-Burke-Ernzerhof (Perdew et al., 1996) exchange-correlation functional, the Troullier-Martins (Troullier and Martins, 1991) pseudopotentials expressed in the Kleinman-Bylander (Bylander and Kleinman, 1990; Kleinman and Bylander, 1982) form, and a basis set made up of localized pseudoatomic orbitals (Sankey and Niklewski, 1989) have been used. The structural parameters were taken from the experimental $\text{Fe}_2\text{V}_4\text{O}_{13}$ values (Permer and Laligant, 1997). This compound crystallizes within the monoclinic crystal structure (space group $\text{P}2_1/\text{C}$, $n^\circ 14$), with lattice constants of $a = 8.3125 \text{ \AA}$, $b = 9.4055 \text{ \AA}$, $c = 14.5768 \text{ \AA}$, $\beta = 102.231^\circ$ (Permer and Laligant, 1997) (Fig. 1). For the calculations 75 k -points to sample the Brillouin zone have been used. In addition, for obtaining the projected density of states (shown in Fig. 2) and its integration (shown in Fig. 3) a mesh of 2000 points has been used.

The optical properties have been obtained by first calculating the

Fig. 1. $\text{Fe}_2\text{V}_4\text{O}_{13}$ crystal structure. The Fe, V and O atoms are represented by the colors brown, green and red respectively.

Fig. 2. PDOS on species states with more contribution to the VB and CB edges. The VB edge has been chosen as the origin of the energy. The positive/negative values correspond to the spin up/down alignments.

Fig. 3. Number of d(Fe), d(V), and p(O) states per atom as a function of the energy. The VB edge has been chosen as the origin of the energy. The two vertical lines indicate the VB and CB edges. The curves with thick/thin lines correspond to the spin up/down alignments.

imaginary part of the dielectric function as an energy photon function. Then, using the Kramers-Kronig relationships (Bassani, 1975), the rest of the optical properties have been obtained.

2.2. Evaluation as solar energy converter.

The main criterion for analyzing the potentiality of a material that absorbs solar radiation is its absorption efficiency. The efficiency η of a solar energy converter is $\eta = JV/P_{inc}$, where J and V are the photo-current and photo-voltage extracted from the converter, and P_{inc} is the irradiance of the incident sunlight spectrum. In this study we have used the AM1.5G (<http://rredc.nrel.gov/solar/spectra/am1.5/ASTMG173/ASTMG173.html>, n.d.) spectrum. If g_a is the incident spectrum photon flux density, the current produced by the absorption of photons, assuming that each photon produces an electron-hole pair, is (Green, 2003; Luque and Martí, 2003; Würfel, 2005) $J_a = q \int a(E, \alpha, w) g_a(E) dE$. Here $a(E, \alpha, w) \simeq 1 - e^{-\alpha w}$ is the absorptivity, α the absorption coefficient, w the optical thickness, and q is the electron charge. If the sunlight is concentrated with a light concentration factor X ($1 \leq X \leq 46,200$) then g_a will be multiplied by X . Thus $X = 1$ indicates the spectrum without concentration and $X = 46,200$ with the maximum concentration. There is an emission process associated with the absorption as a result of the radiative recombination with the $J_e = q \int a(E, \alpha, w) g_e(E) dE$ current in which g_e is the photon flux density emitted. It is usual to consider that the device emits radiation as a generalized Black-body at a temperature $T = 300$ K (Green, 2003; Luque and Martí, 2003; Würfel, 2005). Then $g_e(E) \sim E^2 b(E, T, qV)$ where $b(E, T, \mu) = [e^{(E-\mu)/kT} - 1]^{-1}$ is the Bose factor, k is the Boltzmann constant, V the voltage, and $\mu = qV$ is the chemical potential associated with the radiation emitted (Green, 2003; Luque and Martí, 2003; Würfel, 2005). Note that J_e depends explicitly on the voltage via the difference between the chemical potential (Fermi pseudoenergies) of the valence band (VB) and conduction band (CB) (Green, 2003; Luque and Martí, 2003; Würfel, 2005) (μ_V and μ_C respectively), i.e. on $\mu = \mu_C - \mu_V = qV$. Finally the relationship between the current-voltage is $J(V) = J_a - J_e(V)$. Therefore, in order to obtain the maximum efficiencies, it is necessary to solve a non-linear optimization problem. For a solar cell, both voltage and current are varied to reach the maximum. However, for PECs the voltage is restricted to being greater than the potential of the corresponding redox reaction plus the potential resulting from the losses. In general, this constrained efficiency will be lower than for solar cells.

From the previous description, the absorption coefficient is key to assessing the potential of an absorbing material as a solar energy converter.

3. Results and discussion

3.1. Electronic, magnetic and optical properties

Fig. 1 shows the $\text{Fe}_2\text{V}_4\text{O}_{13}$ monoclinic crystal structure. This structure is built up from isolated edge-shared Fe_2O_{10} octahedral dimers and U-shaped tetrapolyvanadate $[\text{V}_4\text{O}_{13}]^{6-}$ anions (four corner-shared tetrahedra) (Wang et al., 1998). Using the previously described methods we obtain an energy band gap of 2.15 eV. This value is within the range of values obtained experimentally (1.8 (Ping et al., n.d.) – 2.3 eV (Tang et al., 2016)) and compares reasonably well with other theoretical results in the literature (2.25–2.54 eV (Yan et al., 2017)).

From the projected densities of states (PDOS) plotted in Fig. 2 the VB edge states are made up mainly of p(O) states. The CB is dominated by d(V) and d(Fe) states, with a small contribution from p(O) states. The number of states $n(E)$ as an energy function can be obtained by integrating the PDOS:

$$n(E) = \int_{-\infty}^E \text{PDOS}(x) \cdot dx \quad (1)$$

In Fig. 3 the number of d(Fe), d(V), and p(O) states per atom as a function of the energy is shown for the two spin alignments. The VB and CB edges are indicated in the figure with two vertical lines. Since there are no states in the bandgap, the number of d(Fe), d(V), and p(O) states remains constant in this interval (flat curves between the vertical lines). Note that the number of states at the VB edge energy ($n(E_V)$) corresponds to the charge associated with these states. The charge associated with the p(O) states for the two spin channels is almost the same, and it is slightly different for the d(V) states. Therefore the p(O) states are almost unpolarised while the d(V) states are slightly polarized. Note that for the VB edge energy, which delimits the occupied states, and for higher energies in the CB, the number of the p(O) states for the two spin channels are almost equal. This indicates that the polarization is almost zero. It is in accordance with the V^{5+} (d^0) and O^{2-} (p^6) configurations. However the charge associated with the d(Fe) states is very different for the two spin orientations. It induces a magnetic moment $\sim 4.5\mu_B$, compatible with the $5\mu_B$ of the high-spin Fe^{3+} (d^5) configuration. This value ($5\mu_B$) is the calculated for the total magnetic moment of the cell per Fe atom. Therefore, the difference ($\sim 0.5\mu_B$) is the value of the polarization of the two vanadium atoms, i.e. $\sim 0.25\mu_B$ per V atom. It is in accordance with the charge difference between the two spin channels of the d(V) states in Fig. 3 at the VB edge energy.

From the results shown in the figure, for the spin up channel, the d(Fe) states contribute significantly to the occupied states of the VB, while their contribution to the empty states of the CB is low. The contributions of the d(Fe) states is reversed for the spin down channel.

Fig. 4 shows the magnetization around an iron atom. It is defined as the integral of the difference between the charge densities of the two spin channels ($\rho_+ - \rho_-$) in a sphere of radius r centered at $\mathbf{r}_0$:

$$M(r) = \int_{|\mathbf{q}-\mathbf{r}_0| \leq r} (\rho_+ - \rho_-) \cdot d\mathbf{q} \quad (2)$$

In the figure $\mathbf{r}_0$ corresponds to the position of an iron atom ($r = 0$). The right-hand limit of the x-axis corresponds to the position of the iron atom closest to the Fe atom chosen as the origin. The two Fe atoms (left- and right-hand limits of the x-axis) correspond to the Fe_2O_{10} octahedral dimers. The shaded regions (one region for each iron atom) delimit the r value where the magnetic moment of the Fe atom is $\sim 4.5\mu_B$. This value is $\sim 0.78 \text{ \AA}$. It matches very well with the Fe^{3+} ion radius with a 6-coordinate-octahedral arrangement of the ion's nearest neighbors, and with a high spin configuration ($0.785 \text{ \AA}$ (Shannon, 1976)).

The magnetization increases quickly in the shaded areas as a result of the high magnetization of the iron atoms. However, in the non-shaded area, where in the sphere of radius r up to 6 oxygen atoms are successively included (at 1.91, 2.04, 2.07, 2.19, 2.20, and 2.21 $\text{\AA}$), the

Fig. 4. Magnetization around the Fe atom as a function of the distance. The origin and the end of the x-axis correspond to the position of the two iron atoms of the Fe_2O_{10} octahedral dimers. The shaded regions delimit the approximate value of the ionic Fe^{3+} radii.

Fig. 5. $Fe_2V_4O_{13}$ absorption coefficient split into inter-species contributions (left y axis). The total absorption coefficient is represented in the right y axis.

magnetization varies slowly because of the almost zero magnetization of the oxygen atoms.

$Fe_2V_4O_{13}$ is attractive as a solar energy converter. The absorption coefficient, shown on the right y-axis in Fig. 5, is what determines the capacity of the absorption and subsequently the conversion of solar radiation. However, the absorption coefficient does not give us information on the main inter-species contributions. To explore the relationship of optical properties with the crystalline and atomic structure further, the absorption coefficient has been split into inter-species contributions (Crespo, 2018; Tablero, 2017). To achieve this, as the optical properties depend on the transition probabilities via the square of the momentum matrix elements, these matrix elements have been split into inter-species contributions (Crespo, 2018).

This analysis is shown in Fig. 5 (left y-axis). Note that this approach is more accurate than that based on the PDOS or on the joint-DOS (JDOS). The analysis based on the PDOS/JDOS is qualitative since it does not take into account the transition probabilities. For this reason the simplified analysis based on the PDOS/JDOS is sometimes inadequate (Crespo, 2018). Of course PDOS is appropriate for understanding electronic structures, but inappropriate for analyzing photo-excitation properties.

Nevertheless, in this compound the two analyses coincide partially. In accordance with the PDOS, the VB edge states came from the p(O) states, and the VB edge states from d(V) + d(Fe) states. Therefore, based on the PDOS, the main contributions would be the transitions $[p(O)]_{VB} \rightarrow [d(V)]_{CB}$ and $[p(O)]_{VB} \rightarrow [d(Fe)]_{CB}$. For energies close to the bandgap edge ($2.1 \text{ eV} \leq E \leq 2.5 \text{ eV}$) it is in accordance with the correct analysis (Fig. 5) where the main contributions are from O-V, O-Fe, and O-O. Moreover, in this range of energies, the three absorption coefficient contributions are similar. However, for larger energies the dominant term corresponds to the O-V transitions, i.e. to $[p(O)]_{VB} \rightarrow [d(V)]_{CB}$.

3.2. Evaluation as solar energy converter

Finally, as this material is attractive for the conversion of solar energy, we have evaluated its potential (Crespo, 2018; Tablero, 2017) as an isolated converter (Fig. 6a) or as a two-terminal device where $Fe_2V_4O_{13}$ is combined in series with another semiconductor with a bandgap E_g (Fig. 6b). In accordance with the methodology section, the efficiency and current depend on the optical thickness w of the absorbent material, which is shown in Fig. 6a for the isolated converter. With a just few micrometers of thickness, the maximum efficiencies are reached for both the AM1.5G spectra without ($X = 1$) and with maximum sunlight concentration ($X = \max = 46,200$). The efficiencies and

Fig. 6. (a) Efficiency η (%) (left y axis) and photo-voltage V (right y axis) as a function of optical thickness w using the AM1.5G spectra without ($X = 1$) and with maximum sunlight concentration ($X = \max = 46,200$). (b) Efficiency η (%), photo-current J (left y axis), and photo-voltage V (right y axis) of a solar converter made up by a single-union of $\text{Fe}_2\text{V}_4\text{O}_{13}$ with another semiconductor with a bandgap E_g . The horizontal lines indicate the values of η , J and V when E_g is equal to the $\text{Fe}_2\text{V}_4\text{O}_{13}$ bandgap (~ 2.1 eV).

voltages for $X = 1$ and $X = \max$ when $w \rightarrow \infty$ are $\eta_{X=1} = 20.69\%$, $V_{X=1} = 1.68$ V, $\eta_{X=\max} = 24.1\%$, and $V_{X=\max} = 1.96$ V respectively, and the photo-current $J/X = 12.2$ $\text{mA}\cdot\text{cm}^{-2}$.

To generate hydrogen from water electrolysis, a voltage at least equal to $V_{\text{redox}} = 1.23$ V (Abdi and Berglund, 2017; Sivula, 2016) must be supplied. In fact this voltage is higher (1.6–1.9 eV (Sivula, 2016)) as a result of energy losses. In accordance with Fig. 6a the maximum output voltage that can be obtained with maximum efficiency is between $V_{X=1} = 1.68$ V and $V_{X=\max} = 1.96$ V. Therefore this semiconductor will be self-sufficient in providing this voltage.

If more voltage were necessary because of losses in the water electrolysis or for another type of solar fuel, the $\text{Fe}_2\text{V}_4\text{O}_{13}$ semiconductor could be connected in series or multi-junction with another semiconductor. The main characteristics of this configuration are shown in Fig. 6b. Note that in this figure E_g refers to the other semiconductor bandgap. For this single-junction the maximum efficiency without light concentration ($\eta_{X=1}^{(2)} \sim 35\%$) would be reached when the other semiconductor had a bandgap of around 1.6 eV. Then the output voltage would be approximately 2.9 V. Note that the voltage increases almost linearly as E_g increases. This does not happen with efficiency or with current. In fact when the other semiconductor has E_g almost equal to the $\text{Fe}_2\text{V}_4\text{O}_{13}$ bandgap, the voltage is double, the current is half, and the efficiency is the same (horizontal lines to the corresponding axes in the Fig. 6b) as the isolated $\text{Fe}_2\text{V}_4\text{O}_{13}$ semiconductor (Fig. 6a): $\eta_{X=1}^{(2)} = \eta_{X=1} = 20.69\%$, $V_{X=1}^{(2)} = 2 \cdot V_{X=1} = 3.36$ V, and $J_{X=1}^{(2)} = J_{X=1}/2 = 6.1$ $\text{mA}\cdot\text{cm}^{-2}$. The large efficiency fluctuation in the Fig. 6b reflects the problem of multi-union solar cells where the bandgaps must be adjusted with precision. Otherwise the efficiencies vary sharply.

Fig. 7. Same legend as that of Fig. 6, but for a fraction of the radiative recombination $\rho = 10^{-3}$.

So far only radiative recombination has been considered. However, there are other loss mechanisms that reduce the efficiency (non-radiative recombination, surface recombination, etc). These effects can be modeled by multiplying the emission current by $1/\rho$ (Baruch et al., 1995; Crespo, 2018; Ross and Collins, 1980). The factor ρ represents the fraction of radiative recombination with respect to the total losses (radiative recombination, non-radiative, etc.). If k_R and k_L are the rates of the radiative and other recombination losses respectively, then $\rho = k_R/(k_R + k_L)$.

When the non-radiative recombination and other losses are considered, the efficiency and voltage decrease. In the absence of specific data, it is assumed that k_L is the same for all cases in order to illustrate the losses. In Fig. 7 the equivalent of Fig. 6 ($\rho = 1$) is shown but with a fraction of the radiative recombination $\rho = 10^{-3}$ ($k_L/k_R = 999 \sim 10^3$). Comparing the (a) panels in Figs. 6 and 7 the efficiency and voltage decrease from $\eta_{X=1} = 20.69\% \rightarrow 18.50\%$, $V_{X=1} = 1.68$ V $\rightarrow 1.51$ V, $\eta_{X=\max} = 24.1\% \rightarrow 22.33\%$, and $V_{X=\max} = 1.96$ V $\rightarrow 1.79$ V.

4. Conclusions

An analysis of the electronic, magnetic and optical properties of $\text{Fe}_2\text{V}_4\text{O}_{13}$ has been carried out in this work from theoretical calculations. Our results of bandgap, magnetic moments, and ionic radii compare well with experimental results in the literature. An in-depth study reveals that the contributions to the absorption coefficient of p(O)-d(V) and p(O)-d(Fe) transitions are similar for energies close to the bandgap. However, for larger energies the p(O)-d(V) is the main contribution.

Several solar energy converters configurations have been evaluated using the previously calculated absorption coefficients. $\text{Fe}_2\text{V}_4\text{O}_{13}$ is self-sufficient in supplying the voltage for water electrolysis if there are no voltage losses caused by non-radiative recombination or by other causes. Otherwise, it would be necessary to increase the solar

concentration or use a multi-junction configuration.

Acknowledgments

This work has been supported by the National Spanish projects MADRID-PV (S2013/MAE-2780, FEDER FUNDS) and INVENTA-PV (TEC2015-64189-C3-1-R, MINECO/FEDER).

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