Suitability of Cu-substituted β - $\text{Mn}_2\text{V}_2\text{O}_7$ and Mn-substituted β - $\text{Cu}_2\text{V}_2\text{O}_7$ for photocatalytic water-splitting

Cite as: J. Chem. Phys. 153, 084704 (2020); doi: 10.1063/5.0019306

Submitted: 22 June 2020 • Accepted: 7 August 2020 •

Published Online: 25 August 2020

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ABSTRACT

The pyrovanadates β - $\text{Mn}_2\text{V}_2\text{O}_7$ and β - $\text{Cu}_2\text{V}_2\text{O}_7$ were previously investigated as photoanode materials for water splitting. Neither of them, however, was found to be sufficiently active. In this work, we predict the properties of these two structurally similar pyrovanadates upon Cu/Mn substitution in their corresponding lattices via density functional theory calculations to explore the suitability of their band structure for water splitting and to assess their ease of synthesis. We predict that a concentration of up to 20% Cu and Mn into β - $\text{Mn}_2\text{V}_2\text{O}_7$ and β - $\text{Cu}_2\text{V}_2\text{O}_7$, respectively, leads to a narrowing of the bandgap, which, in the former case, is experimentally confirmed by UV-vis spectroscopy. Calculations in the intermediate composition range, however, yield nearly constant bandgaps. Moreover, we predict the materials with higher substitution levels to be increasingly difficult to synthesize, implying that low substitution levels are most relevant in terms of bandgaps and ease of synthesis.

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I. INTRODUCTION

Solar water splitting is a promising strategy to convert solar energy to H_2 fuel. Photoelectrode materials used in water-splitting applications must fulfill strict criteria: they must have bandgaps small enough to absorb a large portion of the solar spectrum, their band edges must provide a sufficient overpotential for the oxygen and hydrogen evolution reactions (OER and HER on the anode and cathode, respectively), and the materials need to maintain high (electro)chemical stability under application conditions.

The two pyrovanadates, β - $\text{Mn}_2\text{V}_2\text{O}_7$ [MVO; Fig. 1(a)] and β - $\text{Cu}_2\text{V}_2\text{O}_7$ [CVO; Fig. 1(b)], as well as related stoichiometries were previously investigated as potential photoanodes.^{1–5,7} MVO has a sub-2 eV bandgap and was found to be stable under illumination in alkaline conditions. It is, however, inactive for the OER without a facile redox couple.¹ CVO, on the other hand, is OER active but has a small photoelectrocatalytic activity due to sizable excitonic effects,⁷ short carrier diffusion length, and slow water oxidation kinetics.⁸ In

addition, it has a relatively large bandgap of 2 eV.^{2,4,8} The performance of CVO can, however, be enhanced by the addition of OER catalysts.^{2,3,9}

While these two ternary pyrovanadates are thus not ideal candidates for photoanodes, improved efficiencies were previously reported for quaternary vanadates^{10–12} that can be considered to be solid solutions of ternary vanadates. Solid solutions were previously used to engineer photocatalytic activity in other materials, mostly via tuning the bandgap.^{13–18} In the case of pyrovanadates, they have so far only been investigated for thermoelectric¹⁹ and negative thermal-expansion applications.^{20,21} Structures of MVO–CVO solid solutions, in particular, were refined in the low CVO content limit and it was suggested that Cu addition can stabilize the α phase also above room temperature.²²

In the present work, we predict the effect the Cu/Mn ion substitution has on the crystal structure, electronic properties, and phase stability of the pyrovanadates β - $\text{Mn}_2\text{V}_2\text{O}_7$ and β - $\text{Cu}_2\text{V}_2\text{O}_7$ using density functional theory calculations and discuss their

FIG. 1. (a) $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ and (b) $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ have a similar crystal structure, the honey-comb geometry of the MnO_6 -octahedra in the former assuming the form of chains of CuO_5 -square pyramids in the latter.

light-harvesting properties in view of applications for solar water splitting. We show that MVO with low Cu substitution indeed shows a reduced bandgap compared to the pure material, but those bandgaps stay nearly constant for higher levels of substitution before sharply rising when approaching the CVO composition. In the case of low Cu content, these predictions are supported by experimentally determined bandgaps. Given that our calculated formation enthalpies hint at difficult synthesis of compositions far from the end members, the investigated materials at low substitution levels are thus most relevant for water-splitting applications.

II. METHODS

A. Computational

We carried out calculations using the Quantum ESPRESSO package^{23,24} with the Perdew–Burke–Ernzerhof (PBE) gradient-corrected exchange–correlation functional.²⁵ Ultrasoft pseudopotentials²⁶ are used for all elements. The wavefunctions are expanded in plane waves with a kinetic energy cutoff of 40 Ry and a cutoff of 320 Ry for the augmented density. A Hubbard U correction was applied to improve the description of all metal $3d$ -states. We used the linear-response scheme proposed by Cococcioni²⁷ to determine the U values of 4.1 eV for Mn and 3.9 eV for V, which agree well with other theoretical studies of MVO.^{1,28} The same approach resulted in $U = 9.8$ eV for copper, which was combined with $J = 1.2$ eV, motivated by the fact that J improves the description

of the magnetic state of CuO, which is also a Cu(II) compound.²⁹ This setup differs from other CVO calculations that used either an effective $U_{\text{eff}} = U - J = 6.52$ eV^{4,30} or $U_{\text{Cu}} = 7$ eV and $J_{\text{Cu}} = 1$ eV.³¹ Despite these differences, all methods yield a qualitatively similar electronic structure. As shown in [supplementary material](#), Sec. 4.1.2, the bandgap depends on U_{Cu} . Therefore, bandgaps and band-edge positions were calculated with the HSE hybrid functional^{32,33} based on PBE+ U structures. The portion of exact exchange was fixed to 16%, so as to match the experimentally observed bandgaps of both pure compounds (see [supplementary material](#), Table S6).

We used experimental crystal structures as starting points and subsequently relaxed all lattice parameters and internal coordinates within the PBE+ U setup. The experimental MVO structure is monoclinic (space group C2/m) with $a = 6.713$ Å, $b = 8.725$ Å, $c = 4.969$ Å, and $\beta = 103.6^\circ$,³⁴ while CVO crystallizes in space group C2/c with $a = 7.689$ Å, $b = 8.029$ Å, $c = 10.106$ Å, and $\beta = 110.3^\circ$.³⁵ To obtain cells with the same number of atoms, we doubled the MVO cell along the c axis, yielding cells with 8 Cu/Mn atoms that allow for 12.5%, 25%, and 50% levels of substitution. The Brillouin zone was sampled with $6 \times 6 \times 4$ Monkhorst–Pack meshes³⁶ in all cases. Geometries were relaxed until forces converged below 0.03 eV/Å and stresses below 0.5 kbar, which for MVO and CVO resulted in deviations of 1.8% and 3.4%, respectively, from the experimental volume (see [supplementary material](#), Table S1).

The band-edge positions with respect to the normal hydrogen electrode (NHE) as a function of the copper content x were computed using the procedure outlined by Butler and Ginley³⁷ and Xu and Schoonen,³⁸ typically used in high-throughput calculations.³⁹ The valence and conduction band edges are given by

$$E_{VB,CB} = E_0 + (\chi_{\text{Cu}}^{2x} \chi_{\text{Mn}}^{2-2x} \chi_{\text{V}}^2 \chi_{\text{O}}^7)^{1/11} \pm E_{\text{gap}}/2, \quad (1)$$

where $E_0 = -4.5$ eV is the difference between the NHE and vacuum and χ is the Mulliken electronegativity of each atom in the material. Other methods for band-edge alignment include an exhaustive analysis of the materials' surfaces in contact with water⁴⁰ or in vacuum.⁴¹ This, however, goes beyond the scope of our work, which focuses on bulk properties only.

B. Experimental

The samples for the UV–vis characterization were prepared as follows. Powders of copper (I) acetate [$\text{Cu}(\text{OAc})$ 97%; Sigma-Aldrich], manganese (II) acetate [$\text{Mn}(\text{OAc})_2$ 98%; Sigma-Aldrich], and vanadium acetylacetonate [$\text{VO}(\text{acac})_2$ 98%; Sigma-Aldrich] in ratios according to the desired stoichiometry of the final product were dissolved in methanol at 70 °C. The as-prepared solutions were deposited on the quartz substrate by dip coating (rate 5 cm/min, 60 s drying, repeated for 60 cycles). The samples for X-Ray Diffraction (XRD) were prepared similarly but annealed as powders for sufficient data analysis. Details on the UV–vis and XRD experiments can be found in Ref. 7.

III. RESULTS AND DISCUSSION

The pure pyrovanadates MVO and CVO share a similar crystal structure with layers of edge-sharing Mn/Cu polyhedra separated

by $V_2O_7^{4-}$ layers (see Fig. 1), albeit in different space groups. The MnO_6 octahedra in MVO form a honey-comb structure, while CVO adopts a structure with chains of CuO_5 square pyramids. The different coordination is due to the Jahn–Teller effect caused by the $Cu(II)$ d^9 electron configuration, where the axial $Cu-O$ bond (2.21 Å) is longer than the equatorial ones (1.98 Å–2.02 Å). The overall metal–oxygen bond lengths appear to be shorter as compared to the $Mn-O$ bonds in MVO (2.13 Å–2.28 Å), leading to different $V-O-V$ angles of 142.9° in CVO and 179.6° in MVO, respectively. Moreover, the V_2O_7 layers are buckled, leading to alternating short and long metal–metal distances along the c -axis, which are 3.36 Å and 3.50 Å in MVO (see supplementary material, Fig. S2) as well as 3.05 Å and 3.22 Å in CVO (see supplementary material, Fig. S3). These computed structural properties agree well with the available experiments.^{34,35}

In terms of their magnetic properties, the two pyrovanadates differ. MVO is ferromagnetic (FM) in our 0 K DFT calculations, with a high-spin Mn^{2+} configuration, the lowest antiferromagnetic (AFM) state lying 4.6 meV per Mn atom higher in energy, which is in agreement with Ref. 1. CVO in contrast is AFM, the FM state lying 2.5 meV per Cu atom higher in energy, which is also in agreement with the existing studies.^{30,31,42} These lowest energy magnetic states will be kept throughout the study of the substituted models, where different magnetic arrangements were tested only on the substituted ions.

The substituted models were built from the two pure compounds, MVO and CVO, given their slightly different space group. In each case, we replaced 1/8, 1/4, and 1/2 of the parent cation and designate the substituted model $\beta-(Mn_{1-x}Cu_x)_2V_2O_7$ as $MCVO_x$ and $\beta-(Cu_{1-x}Mn_x)_2V_2O_7$ as $CMVO_x$, where x is the substitution level (0.125, 0.250, and 0.500). Such a metal exchange affects the crystal structures due to the different crystal radii of the two elements—0.97 Å for Mn and 0.79 Å for Cu.⁴³ The Cu substitution, for instance, leads to shorter bonds with oxygen atoms in the bc -plane, while those along a expand due to the Jahn–Teller effect. This is also reflected by changes in lattice constants (see supplementary material, Table S1) and a reduction in the $V-O-V$ angle from 179.6° to 167.2° , for instance, in $MCVO_{0.25}$. For substitution levels higher than $x = 0.125$, the Cu ions tend to group together (see supplementary material, Fig. S2), such clustered geometries being 0.1 eV and 0.04 eV lower in energy in $MCVO_{0.25}$ and $MCVO_{0.50}$, respectively (see supplementary material, Table S2). This can be interpreted as a less strained way of locally accommodating chains of Cu square pyramids. While the Cu spins seem to favor a FM alignment, the FM energies are very close to those of the AFM arrangement (see supplementary material, Table S2), and we will use the lowest energy in each case for further analysis. Mn ions substituted into CVO, on the other hand, show a slight preference to occupy short-couple metal sites to yield short metal–metal separation in both $CMVO_{0.25}$ and $CMVO_{0.50}$ (see supplementary material, Fig. S3 and Table S3). All Mn substitutions in CVO result in energetically similar FM and AFM states with a slight preference for the former, which we will consider for subsequent analysis. It is important to note that $CMVO_{0.50}$ and $MCVO_{0.50}$ models have different geometries, the former being 0.48 eV lower in energy. This implies that there is no unique intermediate structure, but the exact transformation mechanism based on metal diffusion is beyond the scope of the present work.

The above computational predictions agree with the fact that experimentally significant structure changes are observed in the XRD pattern already with the addition of 10% Cu (see supplementary material, Fig. S1). While reference patterns cannot be used to reliably identify a structure in such complex systems, no apparent secondary phases were identified, and we assume full incorporation of Cu into the MVO lattice at low doping levels.

Important changes also occur in the electronic structure as a function of the chemical composition of the materials. The pure compounds have very characteristic densities of states: The valence region of MVO contains Mn $3d$ and O $2p$ states, whereas in the conduction band, there are mainly V $3d$ states (see supplementary material, Figs. S5 and S9).¹ By contrast, the bandgap of CVO separates occupied O $2p$ and empty Cu $3d$ states (see supplementary material, Figs. S5 and S9).^{4,30,44} The gradual substitution of Cu with Mn entails the appearance of the occupied peaks of Mn and O states above the valence band of pure CVO, which results in a sharply narrowed bandgap (see Fig. 2 and supplementary material, Figs. S5 and S9). At higher substitution levels, these states above the valence-band edge broaden, but the gap does not change significantly. In the case of Cu substitution into pure MVO, the typical peaks of Cu $3d$ states in the conduction band appear below the V $3d$ states, which results again in a smaller bandgap for this material. The peak intensifies with increasing copper content (see supplementary material, Figs. S5 and S9).

In terms of their bandgap type, MVO is experimentally determined to have a direct bandgap.¹ Computational studies have, however, found a 0.02 eV narrower indirect bandgap.¹ Our PBE+ U

FIG. 2. Total density of states (TDOS) of the MVO and CVO obtained with the HSE functional as a function of their chemical composition and level of substitution. A Gaussian broadening of 0.01 eV was used.

findings are similar not only for MVO but also for all MVO-derived substituted models (see [supplementary material](#), Sec. S4.1.1). Indeed, the indirect and direct bandgaps differ by about 0.01 eV–0.02 eV, and in the case of $\text{MCVO}_{0.50}$, they even have the same energy as a result of the rather flat conduction band coming from the Cu-states. CVO, on the other hand, is reported to be an indirect bandgap semiconductor.^{4,30} This is maintained upon Mn substitution, while the energy difference with respect to the direct bandgap increases in a pronounced way for $\text{CMVO}_{0.25}$ (by 0.13 eV) and $\text{CMVO}_{0.50}$ (by 0.09 eV) as shown in [supplementary material](#), Sec. S4.1.1.

The theoretical predictions are supported by experimental UV–vis spectroscopy [see [Fig. 3\(b\)](#)] that points to a bandgap reduction slightly larger than 0.1 eV going from MVO to $\text{MCVO}_{0.1}$, followed by a significantly larger bandgap of over 2 eV for CVO. These results suggest that MVO could benefit from a $\approx 10\%$ Cu substitution to

FIG. 3. (a) HSE band-edge positions and (b) Tauc plots from UV–vis experiments assuming direct bandgap.

FIG. 4. Phase diagram for the ternary subsystems with a chemical potential of $\mu_{\text{O}} = -0.65$ eV, corresponding to a temperature of 600 K under 0.21 atm pressure. The unstable compounds are presented in red.

absorb a larger fraction of solar light, while CVO will have to be substituted with $>20\%$ Mn to significantly lower the bandgap. Under all considered substitution levels, the band-edge positions and, in particular, the valence band-edge remains in a suitable position to provide a sufficiently high overpotential for the OER that is catalyzed on these photoanode materials [see [Fig. 3\(a\)](#)]. CVO band edges are in good agreement with the experimental findings for CVO.^{2,8}

It was not possible to synthesize solid-solutions with Cu content higher than 10%, as also reported in previous experimental work.²² This is in agreement with our theoretical prediction that such materials are unstable with respect to the pure pyrovanadates (see [supplementary material](#), Sec. S5 for details), the instability getting more pronounced further from the end members. Changing the experimental conditions by varying the pressure and/or temperature affects the value of the oxygen chemical potential but does not render the substituted models stable as shown by the unstable red phases in the phase diagram (see [Fig. 4](#)). Low substitution levels in these materials are thus obtained as potentially metastable or entropy stabilized phases. In addition, given the low concentration of the substituted metal, we do not expect such systems to deviate significantly from the parent material in terms of their stability in water.^{1,45}

IV. CONCLUSIONS

We investigated Cu/Mn substitution in $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ and $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ with the aim to evaluate their suitability for water-splitting applications. Our results show that up to 20% Cu incorporation into $\beta\text{-Mn}_2\text{V}_2\text{O}_7$ leads to an about 0.3 eV reduction in bandgap, while the incorporation of Mn into $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ is predicted by our calculations to lead to a marked reduction in bandgap of about 1 eV. In the intermediate composition range, bandgaps remain roughly constant. Our calculations predict that all substituted models are metastable, with higher substitution levels being increasingly more difficult to form. This suggests that the light-harvesting properties of

both β - $\text{Mn}_2\text{V}_2\text{O}_7$ and β - $\text{Cu}_2\text{V}_2\text{O}_7$ end members could be enhanced by low-level substitution with Cu and Mn, respectively. Further studies are required to assess if these materials are able to overcome the limitations inherent to pure β - $\text{Cu}_2\text{V}_2\text{O}_7$.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for additional computed and XRD structural information, detailed PBE+*U* and HSE electronic structure data, and the method used to compute the phase diagram.

ACKNOWLEDGMENTS

This research was funded by the SNF Professorship (Grant No. PP00P2_157615). Calculations were performed on UBELIX (<http://www.id.unibe.ch/hpc>), the HPC cluster at the University of Bern. M.S. acknowledges the H2020 Marie Curie Individual Fellowship (Grant Agreement No. 753124).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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