Investigation of the Optical Absorbance, Electronic, and Photocatalytic Properties of (Cu$_{1-x}$Co$_x$)$_2$(OH)PO$_4$ Solid Solutions

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ABSTRACT: Transition metal hydroxyl phosphate compounds have attracted recent attention for catalytic and magnetic applications. Here, we present a detailed analysis on the properties of (Cu$_{1-x}$Co$_x$)$_2$(OH)PO$_4$ (0 ≤ x ≤ 1) compounds based on the mineral libethenite. Powders were synthesized using hydrothermal methods, and the photocatalytic activity was evaluated with an Fe$^{3+}$/Fe$^{2+}$ redox couple. Introduction of small fractions of Co to Cu$_2$(OH)PO$_4$ increased the photocurrent generation, but greater Co substitution caused it to decrease, with Co$_2$(OH)PO$_4$ showing the lowest photocurrent. The electronic band structure and density of states (DOS) were investigated using standard density functional theory (DFT) and hybrid functional methods. Hybrid DFT provided a better description of the electronic properties, especially the localized Cu and Co d electrons, in good agreement with the experimentally observed band gaps. The addition of Co to Cu$_2$(OH)PO$_4$ led to formation of bands within the band gap arising from Co 3d orbitals, which lowered the band gap <3 eV and changed the band-gap transition from a ligand-to-metal charge transfer (LMCT) to a metal-to-metal charge transfer (MMCT). However, higher concentrations of Co were detrimental to photocurrent generation as a result of the formation of a 3.7 eV MMCT and other electronic factors that could hinder charge separation.

1. INTRODUCTION

Recently, adamite-type compounds with the formula M$_4$(OH)XO$_6$ (M = Zn, Mn, Co, Cu, Ni, ...; X = P, As, ...) have attracted attention for their magnetic and catalytic properties. Found naturally as minerals, synthetic versions have been studied for their magnetic and catalytic behavior. For instance, Cu$_2$(OH)PO$_4$, also known by its mineral name libethenite, has shown promising activity as a catalyst for water oxidation, oxidation of olefins and alcohols, hydroxylation of phenol, and photocatalytic degradation of dyes under UV–visible and near-infrared (NIR) irradiation. For example, libethenite showed higher activity than WO$_3$ and P$_2$5 TiO$_2$ for photocatalytic degradation of organic dyes under visible and UV-irradiation. In our previous work, we studied the photoelectrochemical and electrocatalytic properties of libethenite and found that it also displays good activity for water oxidation, with turnover frequency similar to that of other common oxygen evolution reaction (OER) catalysts such as cobalt and manganese oxides. Libethenite and its related compounds have also been the focus of several magneto-structural studies. Libethenite is a spin-gap system, whereas isomorphic Co$_2$(OH)PO$_4$ showed antiferromagnetic ordering and spin-glass behavior at low temperatures and solid solutions (Cu$_{1-x}$Co$_x$)$_2$(OH)PO$_4$ are 3D antiferromagnets.

To better understand the optical and electronic properties of libethenite, there have been several descriptions of its electronic structure using density functional theory (DFT). However, here we show that standard DFT and DFT+U methods are not suitable for accurately describing the band structure of libethenite and its solid solutions with cobalt, whereas the hybrid functional method provides a better description of the electronic properties of these materials. Additionally, we use the band structure and detailed density of states (DOS) information predicted from the hybrid functional to explain the experimentally observed optical absorbance properties and photocatalytic activity for (Cu$_{1-x}$Co$_x$)$_2$(OH)PO$_4$ synthesized using hydrothermal methods. The results from this work will allow for better understanding of the properties of this class of materials for applications in photocatalysis and magnetic materials.

2. EXPERIMENTAL AND THEORETICAL METHODS

2.1. Materials Synthesis. Solid solutions of (Cu$_{1-x}$Co$_x$)$_2$(OH)PO$_4$ where x = 0, 0.2, 0.5, and 0.8, were synthesized using different ratios of Cu(NO$_3$)$_2$·5H$_2$O and Co(NO$_3$)$_2$·6H$_2$O via a hydrothermal method. In a typical experiment, 10 mmol of the metal nitrate was dissolved into 20 mL of water containing 6.7 mmol of Na$_3$PO$_4$. The solution was adjusted to pH 4–5 using NaOH or H$_3$PO$_4$ as needed. For Cu$_2$(OH)PO$_4$ (x = 0), the pH of the solution was adjusted to 6–7. The as-prepared solution was then placed in a Teflon-lined stainless-steel pressure vessel (Parr) and heated at 180 °C.

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for 5 days. After the hydrothermal reaction, the vessel was cooled to room temperature. The precipitated powders were washed with deionized water several times and dried at 50 °C in an oven.

Co$_x$(OH)PO$_4$ ($x = 1$) was synthesized using procedures adapted from ref 22. In a typical synthesis, 0.8686 g of Co(NO$_3$)$_2$·6H$_2$O (Sigma-Aldrich), 1 mL of H$_3$PO$_4$ (85 wt %, Sigma-Aldrich), 6 mL of dimethylamine (40% in water, Sigma-Aldrich), and 1 g of 1,4-diazabicyclo[2.2.2]octane (DABCO, Sigma-Aldrich) were dissolved in 10 mL of deionized water. The pH of the mixture was adjusted to 8 using a 10 vol % solution of HCl in water. The mixture was placed in a Teflon-lined stainless-steel pressure vessel and heated at 200 °C for 4 days. After the hydrothermal reaction, the vessel was cooled to room temperature. The precipitated powders were washed with ethanol and deionized water to remove excess organic solvent. Then, the obtained powders were dried at 50 °C in an oven.

2.2. Materials Characterization. Scanning electron microscopy (SEM) was performed with an FEI XL30 field-emission scanning electron microscope. X-ray diffraction (XRD) characterization was performed with Cu Kα radiation (PANalytical Xpert Pro). Diffuse reflectance of the powders immobilized in a sample cup (Pike Technologies) was performed using an Ocean Optics USB2000 spectrometer with a deuterium–tungsten light source and a 30 mm integrating sphere.

Electrochemical measurements were performed using a Biologic SP200 potentiostat. The counter and reference electrode were Pt wire and Ag/AgCl, respectively. Photoelectrochemical tests were performed using irradiation with a 450 W Xe-arc lamp (Newport) at 300 mW/cm$^2$ light intensity with a water filter. Slurries of suspended photocatalyst powder were evaluated for photoactivity by using an Fe$^{3+}$ electron-transfer mediator (0.5 mM FeCl$_3$) and sodium acetate (0.2 M) as the electron donor. The pH was adjusted to 5 using acetic acid. The measurement was performed by applying 0.6 V between the Pt wire working electrode with a surface area of 3.6 cm$^2$ and the reference electrode and measuring the current under dark and illuminated conditions.

2.3. Density Functional Theory. The structures of M$_x$(OH)PO$_4$ (M = Cu and Co) were generated using the experimental lattice parameters obtained from Belik et al. Diamond$^{54}$ and VESTA$^{55}$ were used for visualization of crystal structures and electron-density plots. Adamite-type compounds have two crystallographically distinct sites for M, with M1 atoms arranged in MO$_4$(OH)$_2$ axially elongated octahedra and M2 in MO$_4$(OH) distorted trigonal bipyramids (Figure 1).$^{22}$ The structure of (Cu$_{1-x}$Co$_x$)$_2$(OH)PO$_4$ ($x = 0.5$) was generated with all Cu atoms residing in the M1 site for CuCo(OH)PO$_4$ or in the M2 site for CoCo(OH)PO$_4$.

Standard DFT and hybrid functional$^{56,57}$ were adopted to investigate the electronic band structures of (Cu$_{1-x}$Co$_x$)$_2$(OH)PO$_4$. The hybrid functional method has provided a better description of lattice constants and band gaps in other Cu-containing semiconductor materials.$^{26}$ In the standard DFT method with generalized gradient approximations (GGA), the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional$^{57}$ was used along with projector-augmented wave (PAW) potentials$^{58,59}$ and plane-wave basis sets. DFT plus on-site Coulomb interaction U calculations (DFT + U)$^{60}$ was also performed for Cu$_2$(OH)PO$_4$ using an effective U value of 4 eV ($U = 5$ eV, $J = 1$ eV). In the hybrid HSE06 method, the exchange-correlation functional uses a mixing parameter to incorporate the Hartree–Fock (HF) exact-exchange functional and the PBE functional. In this study, the fraction of the HF exchange was set to be the default value ($\alpha = 0.25$).

The spin-polarized DFT, DFT+U, and hybrid functional calculations were performed using VASP code.$^{60,61}$ The energy cutoff for the plane-wave basis set was 400.0 eV. The total energy was converged to within 0.01 meV for the self-consistent iterations. Cu/Co 3d and 4s, P 3s and 3p, O 2s and 2p, and H 1s electrons were treated as valence electrons. The partial occupancies of electron orbitals were described using Gaussian smearing with $\sigma = 0.01$ eV. The Brillouin-zone of the bulk crystal of (Cu$_{1-x}$Co$_x$)$_2$(OH)PO$_4$ was sampled at $4 \times 4 \times 4$ by using the Monkhorst–Pack meshing technique.$^{62}$

3. Results

The synthesis of adamite-type materials is facilitated by the fact that the compounds can be precipitated from aqueous solutions of the metal salts or synthesized using hydrothermal methods, similar to how the naturally occurring minerals are formed. The SEM images and XRD patterns are shown in Figure 2A,B, and photographs of the powders and corresponding UV–vis
absorbance spectra derived from the diffuse reflectance are shown in Figure 3A,B. The synthesis of pure libethenite revealed individual and agglomerated prismatic crystals about 10−20 μm in size (Figure 2A), which is similar to morphologies obtained in other reports, where particles are characterized by four {110} tetragonal prism faces, four {011} trigonal end-caps, and an elongated direction along the c axis. XRD (Figure 2B) of the product showed a match to Cu2(OH)PO4, which crystallizes in an orthorhombic structure with space group Pnmm and lattice constants a = 8.051, b = 8.378, and c = 5.880.

Although the synthesized Cu2(OH)PO4 powder was green in color (Figure 3A), changing the ratio of Cu/Co nitrate to form (Cu1−xCo)x2(OH)PO4 resulted in orchid powders that had similar prismatic microstructures (Figure 2A). XRD analysis for x = 0.2 showed a pattern very similar to that of Cu2(OH)PO4 (Figure 2B). A similar XRD pattern was also observed for x = 0.5, but the intensity of the (110) and (011) reflections at 15.2 and 18.4° was reversed compared to the patterns for x = 0 and 0.2. This is likely due to the reversal in a and b parameters as the amount of Co increases. For x = 0.8, impurity peaks corresponding to Co3(PO4)2(OH)2 were observed. Initial attempts to synthesize Co2(OH)PO4 using only Co(NO3)2 and Na3PO4 were not successful, yielding only a mixture of different products. Therefore, Co2(OH)PO4 was synthesized using a hydrothermal method with organic additives that are not incorporated into the final product. The obtained dark-purple prismatic crystals matched the XRD pattern reported with the same crystal structure as Cu2(OH)PO4 but with a = 8.042, b = 8.369, and c = 5.940. Ball-milling of Co2(OH)PO4 was used to decrease the particle size for photocatalytic testing.

The UV-vis absorbance spectra (Figure 3B) show characteristics of the transition metal ions found in the compounds. For Cu2(OH)PO4 (x = 0), three main absorption features were observed: (i) a broad band starting at ~575 nm that extends into the NIR past the measurement capabilities of the spectrometer, (ii) a peak at 433 nm (~2.86 eV), and (iii) the UV-absorption band at wavelengths below 400 nm. The first feature is characteristic of the d−d transitions for Cu2+, which has a d8 electron configuration with one unpaired electron. The Cu2+ in the axially elongated CuO4(OH)2 Cu1 site should display three optical transitions for the Jahn−Teller distorted octahedral crystal field (D4h symmetry) associated with electron

Figure 2. (A) SEM images and (B) XRD patterns of synthesized (Cu1−xCo)x2(OH)PO4 materials for x = 0, 0.2, 0.5, 0.8, and 1. The asterisks in the XRD pattern for x = 0.8 correspond to Co3(PO4)2(OH)2 side product.

Figure 3. (A) Photographs and (B) UV−vis absorbance spectra of synthesized (Cu1−xCo)x2(OH)PO4 powders.
excitation from the filled 2Eg, 2B3g and 2A1g states to the empty 2B1g state (Figure S1A). These transitions are typically found as a broad band between 575–900 nm.36–38 The transitions from Cu2+ in a trigonal bipyramid geometry (Cu2 site, D3h symmetry) associated with excitation from the 2E′ and 2E″ states to the empty 2A1′ state (Figure S1B) also likely fall in this range, as spectroscopic studies on a Cu(II) molecule with the same symmetry observed intense bands at 11 400 cm−1 (877 nm) and a weaker shoulder at 15 000 cm−1 (667 nm), attributed to transitions from the dxz/dyz orbitals to the dz2 orbital and dx2−dy2/dz2, respectively.39 Thus, the broad band (i) in the absorbance spectrum for Cu2(OH)PO4 is attributed to d−d transitions from both Cu sites in the structure, although the 2B3g → 2B1g and 2A1g → 2B3g transitions from Cu1 likely fall in the infrared region,26 outside the detection window of our spectrometer.

The origin of peak (ii) at around 433 nm (∼2.86 eV) is not clear. This peak was not observed in the commercial libethenite we studied before,1 and it is also absent from the spectrum presented by Cho et al. in their synthesized powders.5 UV–vis absorption data recorded for TiO2 doped with Cu also had this feature in samples prepared by chemical reduction of Cu salt with NaBH4, which had the highest H2 production compared to other methods for Cu doping.41 The origin of this absorption peak and the better catalytic activity was attributed to the presence of Cu1+ or CuO in the material. This absorption peak can also be observed in Cu2O by itself.42 Hence, the presence of this peak in our libethenite may indicate the presence of Cu1+ in the sample. Finally, the absorbance in the UV region (iii) is characteristic of absorption from the valence band maximum (VBM) to the conduction band minimum (CBM), similar to that observed in conventional semiconductors and closed-shell transition metal oxides. Usually, absorption transitions in transition metals that have higher energy than the d−d transitions are due to charge transfers, such as that from a filled ligand orbital to a partially filled or empty metal d orbital (i.e., a ligand-to-metal charge transfer, LMCT). Tauc plots (Figure S2) revealed a band gap at ∼3.1 eV for both direct and indirect transitions (Table 1), with a transition at 2.1 eV associated with the absorption onset for the d−d transitions.

### Table 1. Properties from Experimental UV–Vis Absorption Data

<table>
<thead>
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<th>compound</th>
<th>UV absorption edge wavelength (nm)</th>
<th>energy (eV)</th>
<th>band gaps from Tauc plots (eV)</th>
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</thead>
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<tr>
<td></td>
<td>wavelength (nm)</td>
<td>energy (eV)</td>
<td>direct</td>
</tr>
<tr>
<td>Cu2(OH)PO4</td>
<td>412</td>
<td>3.0</td>
<td>3.15</td>
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<td>Co2(OH)PO4</td>
<td>343</td>
<td>3.6</td>
<td>3.24</td>
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</table>

Addition of Co2+ to form (Cu1−xCo)x2(OH)PO4 increased absorbance in the visible region, which progressively increased to a broad band from about 400–700 nm as the amount of cobalt increased from x = 0.2 to 1.0. The energy level diagram for Co2+ (d6 electron configuration) in a perfect octahedral (O6) and trigonal bipyramidal geometry are shown in Figure S1C–D, respectively. In an octahedral crystal field, the F ground state for Co2+ is split into the 4A2, 4T2g and 4T1g states, the latter which is further split by substantial spin–orbit coupling into the Γ suborbitals.43 The energies required for electron excitation from the 4T1g(F) ground state to the 4T1g(P) (P) and 4A2g levels are expected to occur in the visible region of light and have been assigned to absorption peaks at 545 and 647 nm, respectively, for Co2(OH)PO4.15 For Co2+ in the trigonal bipyramidal site, peaks at 510 and 633 nm were assigned to the 2E′(F) → E″(P) and 2A1′(F) → 2A1″(P) transitions, respectively, in this same study. Therefore, this visible absorption band in our samples is attributed to d−d transitions from both Co2+ sites. The first portion of a peak starting at ∼750 nm is attributed to other d−d transitions with energies in the NIR and IR region (Figure S1). Because the absorption band is similar in shape but differs in intensity for the solid-solution samples as the amount of Co changes, this suggests that Co and Cu are randomly distributed over both sites in the solid solutions. For the solid solutions x = 0.2 and 0.5, both Co and Cu d−d transitions are observed, but the Cu d−d peak is largely absent for x = 0.8. Because this sample had a significant fraction of impurity Co3+(HPO4)2(OH)2, it is possible that the amount of (Cu0.8Co0.2)2(OH)PO4 was too small to see a strong contribution from the Cu d−d transitions. Band gaps determined from the Tauc plots (Figure S2) are summarized in Table 1 for all of the synthesized compounds. Because of the relative flatness of the bands as a result of their significant d orbital character, the direct and indirect band gaps were similar in energy. The two end members Cu2(OH)PO4 and Co2(OH)PO4 had larger band gaps than the solid solutions, suggesting the formation of new bands inside the band gap for (Cu1−xCo)x2(OH)PO4.

The photoactivity of the synthesized powders was evaluated using an Fe2+/3+ redox electron shuttle.25 The process is shown schematically in Figure 4A, where photogenerated electrons...

![Figure 4](https://example.com/figure4.png)
from the photocatalyst are used to reduce Fe$^{3+}$ to Fe$^{2+}$. Photogenerated holes are used to oxidize sodium acetate, an electron donor, to avoid recombination. The Fe$^{2+}$ species are then reoxidized at the Pt collector (working) electrode and recorded. As shown in Figure 4B, a noticeable photocurrent was observed for each sample when the light was turned on, which decreased when the light was turned off. Each sample was illuminated until the photocurrent began to saturate. The average current generated over the total illumination time for each composition over two measurements is shown in Table S1. The photocurrent generation rate increased when going from $x = 0$ to $x = 0.2$, indicating that Co doping improved the photocatalytic activity of Cu$_2$(OH)PO$_4$. However, with addition of more Co, the photocurrent generation decreased. The rates for $x = 0.5$ and 0.8 were similar and slightly lower than that of the $x = 0$ case, and Cu$_2$(OH)PO$_4$ ($x = 1$) had the lowest photocurrent generation rate out of all of the compositions.

To better understand these observations, first-principles DFT methods were used to calculate the electronic band structure and DOS. The calculated lattice parameters and unit-cell volumes are shown in Table S2. For example, the calculated lattice constants for Cu$_2$(OH)PO$_4$ were determined to be $a = 8.131$ Å, $b = 8.526$ Å, and $c = 6.006$ Å, within 2% deviation of the experimental values.$^{10,16}$ We first considered Cu$_2$(OH)PO$_4$ and compared the spin-polarized band structures and DOS obtained using DFT-GGA with those obtained using DFT + U and the hybrid functional HSE06. The band structures obtained with standard DFT (Figure 5A) were similar to those previously reported by others,$^{1,5,17}$ showing symmetric DOS distribution around the Fermi level with spin-up and spin-down contributions arising from Cu1 and Cu2, respectively. The DFT + U method predicted two energy-degenerate configurations (Figure S3). In configuration 1 (Figure S3A), the Cu1 in the octahedral site and Cu2 in the trigonal bipyramidal site both contribute spin-down 3d states to the conduction band. A very similar band structure calculated with DFT + U was also reported by others recently.$^{7,44}$ In configuration 2 (Figure S3B), Cu1 contributes spin-up 3d orbitals to the conduction band, whereas Cu2 contributes spin-down 3d orbitals. The total energies for configurations 1 and 2 are $-201.668$ and $-201.804$ eV, respectively. The total energy difference of 0.136 eV (i.e., 0.067% with respect to their total energy) is negligible. Therefore, we claim that these are two energy-degenerate configurations.

Because the unit cell of Cu$_2$(OH)PO$_4$ contains 232 electrons, the 116 lowest spin-up and spin-down energy levels are expected to be occupied by electrons at the ground state. When using standard DFT analysis, a zero band gap was predicted between the highest occupied level (116) and the lowest unoccupied levels (117–120), as a result of the lack of accuracy in describing the localized Cu d orbitals using standard DFT. The Fermi level is shown in Figure 5A as a horizontal dashed line to highlight the zero bandgap. An energy gap of 2.55 eV was observed between the highly dispersive band (121), composed predominately of Cu 4s orbitals, and the flat band formed from hybridization of the Cu 3d and O 2p orbitals. This energy gap was previously erroneously assigned to the VBM to CBM absorption.$^{1,5}$

For the Cu$_2$(OH)PO$_4$ band structures determined using DFT + U, a direct gap of 0.83 eV was found for configuration 1. For configuration 2, the spin-up bands showed a direct gap of 1.12 eV, and the spin-down bands showed an indirect gap of 1.39 eV (Figure S3). Despite the semiempirical U value, these DFT + U-predicted band gaps are still significantly smaller than the experimental values (Table 1).

However, the advanced hybrid functional HSE06 provides a better description of the localized d electrons in transition metals and their band gaps. Analysis of the Cu$_2$(OH)PO$_4$ band structure within HSE06 (Figure 5B) shows an energy gap of 3.36 eV for the spin-up bands and 3.23 eV for the spin-down bands between the 116th (occupied) and 117th (unoccupied) energy levels, with the latter levels forming a flat conduction band edge separated from the dispersive band (121) by about 1.8 eV. The total DOS for Cu$_2$(OH)PO$_4$ within standard DFT, DFT + U, and HSE06 are compared in Figure S3C. The DFT-GGA and hybrid DFT band structures were also compared for Co$_2$(OH)PO$_4$ and solid solutions with composition (Cu$_{0.5}$Co$_{0.5}$)$_2$(OH)PO$_4$ where CuCo(OH)PO$_4$ contains all of the Cu atoms in the M1 distorted octahedral site and Co in the M2 trigonal bipyramidal site, and vice versa for CoCu(OH)PO$_4$. The addition of Co to Cu$_2$(OH)PO$_4$ led to formation of new spin-down bands. The band structures obtained using DFT-GGA approximation (Figure S4) all showed zero band gaps and were similar to those obtained using the local density approximation (LDA) of DFT.$^{17}$ In contrast, the HSE06-predicted band structures in Figure 6 showed appropriate energy gaps and discrete flat spin-down bands. The VBM, CBM, and band gap energies from the hybrid HSE06 band structures are given in Tables 2 (for spin-up bands) and 3 (spin-down). From these data, we can see that standard DFT severely underestimates the band gaps of these compounds and does not give an accurate representation of the band structure, whereas the band gaps described with the

![Figure 5. Spin-polarized band structure and total density of states (DOS) of Cu$_2$(OH)PO$_4$ within (A) DFT-GGA and (B) hybrid functional HSE06. Horizontal dashed line at zero corresponds to the Fermi level.](image)
hybrid functional are similar in value and follow the same trends as the experimental observations (Table 1).

The total DOS and projected DOS (PDOS) for the HSE06 band structures are shown in Figure S5, with the PDOS overlaid close to the Fermi level shown in Figure 7. For Cu2(OH)PO4, the PDOS reveals that the Cu 3d orbitals from the octahedral sites (Cu1) comprise the conduction band for the spin-up polarization (Figure 7A), whereas the Cu 3d orbitals from the trigonal bipyramids (Cu2) form the conduction band for the spin-down (Figure 7B). In both cases, the valence band is predominately composed of O 2p orbitals. Specifically, the spin-up valence band is dominated by the p_y orbitals from the O atoms that form bonds with Cu1, whereas the spin-down valence band is mostly comprised of the p_x orbitals from the O atoms that form bonds with Cu2. Hence, absorption of light with energy 3.23 eV or greater (λ < 384 nm) will result in excitation of electrons from the occupied O 2p orbitals to the unoccupied Cu 3d orbitals, which is considered a ligand-to-metal charge transfer (LMCT).

Using hybrid DFT to look at the Co-containing compounds reveals that discrete levels arising from the Co 3d orbitals are formed below the Co 4s and above the O 2p orbitals. For Co2(OH)PO4, these orbitals are clearly seen in the spin-down bands in the total DOS (Figure S5D) which make up the top of the valence band and the bottom of the conduction band. Inspection of the PDOS (Figure 7D) shows that the highest occupied Co 3d orbital in the valence band comes from the Co2+ in the trigonal bipyramid (Co2), whereas the lowest unoccupied orbital is from Co2+ in the octahedral site (Co1). Therefore, light absorption will result in a metal-to-metal charge transfer (MMCT) between the d orbitals on the two different Co sites. The calculated band gap for this absorption process was 3.7 eV. From these results, we can see that the M2 → OH → M1 transition is associated with the VBM to CBM transition for Co2(OH)PO4 but not Cu2(OH)PO4.

The band structures and DOS for the mixed compounds CuCo(OH)PO4 and CoCu(OH)PO4 looked very similar to each other. The PDOS for CuCo(OH)PO4 is shown in Figure 7C. The highest occupied band is from Co 3d orbitals, and the conduction band consists of two bands of lower energy from Cu 3d orbitals and three bands of higher energy from Co 3d orbitals. These discrete bands form in between the occupied O 2p orbitals and the hybridized Co and Cu 4s orbitals, resulting in smaller band gaps for the solid solutions compared to those of the pure Cu and Co end members. Furthermore, the band gap transition of ~2.3 eV is a MMCT from Co 3d to Cu 3d-orbitals.

To better visualize the VB to CB transitions, the electron density within 0.5 eV of the VBM and CBM are shown in Figure 8. From the contour plots, we can clearly see that for Cu2(OH)PO4, the VB is composed of O orbitals, whereas the CB is from the orbitals from both Cu sites (Figure 8A). For CuCo(OH)PO4, the VB has contributions from the Co in the M2 (trigonal bipyramidal) sites, and the CB is from the Cu in the M1 octahedral sites (Figure 8B). The VB and CB electron density extends to the bridging hydroxyl group, confirming that the transition is of the form M2 → OH → M1. For CoCu(OH)PO4, the VB is still composed of Co orbitals, but from the M1 site, with additional contribution from the O orbitals (Figure 8C). Similarly, the CB has contributions from the Cu in the M2 site. For Co2(OH)PO4, both metal sites and O contribute to the VB, whereas the CB is predominately from the octahedral Co1.
4. DISCUSSION

The optical absorption features for the \((\text{Cu}_{1-x}\text{Co}_x)_2(\text{OH})\text{PO}_4\) compounds in the visible to NIR region agree well with those predicted from ligand field theory for \(d\rightarrow d\) transitions in transition-metal complexes. However, to fully understand the electron transitions under light irradiation, appropriate analysis with the correct band structures is required, particularly because the absorption features at higher energies cannot be explained by \(d\rightarrow d\) transitions. Using hybrid DFT, we show that the VB to CB absorption in \(\text{Cu}_2(\text{OH})\text{PO}_4\) is a LMCT with energy of 3.23 eV; this is in very close agreement with the direct band gap of 3.15 eV determined from the experimental UV absorption region in the Tauc plot. We note that when using the band structure generated by configuration 1 of DFT + \(U\), the nature of the VBM to CBM absorption can be erroneously attributed to other transitions, such as \(d\rightarrow d\) transitions in the NIR associated with excitation from \(\text{Cu}_2\) to \(\text{Cu}_1\) through the hydroxyl bridge, as a result of the underestimated band gap energy. However, with the hybrid DFT band structure, the VBM to CBM transition is described more accurately as a LMCT between \(\text{O}\) and \(\text{Cu}_1\) for spin-up and \(\text{O}\) and \(\text{Cu}_2\) for spin-down bands. Because of the different spins in the octahedral \(\text{Cu}\) versus trigonal bipyramid \(\text{Cu}\), the \(\text{Cu}_2 \rightarrow \text{OH} \rightarrow \text{Cu}_1\) transition is not feasible. Rather, internal \(d\rightarrow d\) transitions within the \(\text{Cu}_1\) or \(\text{Cu}_2\) 3d orbitals are possible after UV excitation and relaxation to the \(d\) bands. Hence, we show that identification of the correct functional is important for obtaining a better understanding of the absorption spectra and the origin of UV–vis and NIR photocatalytic activity in \(\text{Cu}_2(\text{OH})\text{PO}_4\).

Addition of Co results in formation of a new valence band consisting of Co 3d orbitals, as shown schematically in Figure 9. This not only reduces the band gap and increase the visible light absorption but also changes the band gap transition to a MMCT from the Co sites to the Cu via the bridging hydroxyl group. Dispersed bimetallic complexes such as \(\text{Ti}--\text{O}--\text{Cu}\) and \(\text{Zr}--\text{O}--\text{Co}\) also operate as MMCT photocatalysts and have attracted much attention recently for \(\text{CO}_2\) photoreduction and solar water splitting. The presence of the second metal center linked via the oxo bridge is proposed to suppress electron–hole recombination, resulting in higher photocatalytic activity than in complexes with one metal center and LMCT transitions. Indeed, the hydroxyl bridge between the M1 and M2 sites in the adamite-type (Figure 1C) structures is reminiscent of the oxo-bridged heterobinuclear units in the \(\text{M}--\text{O}--\text{M}\) complexes. For instance, the \(\text{Ti}--\text{O}--\text{Mn}\) complex consists of \(\text{Ti}\) in a pentahedral coordination with an oxo bridge to \(\text{Mn}\) in a distorted octahedral coordination, similar to the \(\text{M}2\) and \(\text{M}1\) sites in the adamite-based compounds. However, according to the band structure calculations, the MMCT between two Co polyhedra requires close to 4 eV (Figure 7D). Thus, as the concentration of Co in the material increases and there are fewer \(\text{Co} \rightarrow \text{OH} \rightarrow \text{Cu}\) transitions and more \(\text{Co} \rightarrow \text{OH} \rightarrow \text{Co}\) transitions, higher energy UV light is required for photoexcitation between the VBM and the CBM. At low fractions of Co, the presence of predominately \(\text{O} \rightarrow \text{Cu}\) and \(\text{Co} \rightarrow \text{OH} \rightarrow \text{Cu}\) transitions, which require lower energy wavelengths for excitation, result in a higher photocurrent value. From these results, we can understand why the photocurrent observed from the slurry photocatalysts increases upon doping with small fractions of Co then decreases at higher Co compositions.

Although the visible light absorption increases in \(\text{Co}_x(\text{OH})\text{PO}_4\), this absorption band arises from internal \(d\rightarrow d\) transitions. In a study on \(\text{Co}^{2+}\) doped \(\text{ZnO}\), internal \(d\rightarrow d\) transitions from tetrahedral Co were not found to contribute greatly to the photocatalytic activity of the material under visible light absorption. It has also been proposed that the \(\Gamma\) Co 3d suborbitals, formed by splitting due to spin–orbit coupling, can act as nonradiative recombination centers.
which could also explain the lower photocurrent as the fraction of Co is increased. Recent pump−
dyn

probe carrier dynamics studies on Co3O4 showed that LMCTs and MMCTs could quickly convert to d−
d excitations through electron−phonon coupling; this indicates that the d−d excitations act as
recombination centers.53 However, recombination of the d−d excitations back to the ground state was found to be a long-
lived process (∼ nanoseconds), suggesting that these transitions could indeed be exploited for photocatalysis in
compounds containing transition metals. In fact, Cu2(OH)PO4 has already been reported to have activity as an NIR
photocatalyst,7 presumably with the activity originating from these excited d−d states. Hence, further investigation of the

Co-based adamite compounds could perhaps lead to interesting photocatalytic properties in the NIR region of light, even if the activity in the UV and visible regions is lower than that observed for Cu3(OH)PO4 and Cu2(OH)PO4 with low levels of Co substitution.

In summary, the optical, electronic, and photocatalytic properties of the cobalt-substituted libethenite series
(CuxCo1−x)2(OH)PO4 (0 ≤ x ≤ 1) were investigated in powders prepared using hydrothermal synthesis. The absorption
spectra showed characteristics consistent with d−d transitions for Cu and Co in distorted octahedral and trigonal
bipyramid environments and band gap transitions associated with LMCT for Cu2(OH)PO4 and MMCT for the Co/Cu
solid solutions and Co2(OH)PO4. Substitution of small fractions of Cu with Co resulted in higher photocatalytic
activity as a result of a decrease in band gap. However, higher concentrations of Co were detrimental to photocurrent
generation because of the higher-energy MMCT and other electronic factors that could hinder charge separation.

Importantly, we show that hybrid functional HSE06 can more accurately describe the band structure of these
compounds compared to standard DFT and DFT + U methods and can calculate band gaps that are in close
agreement with experimental values. The band structures and DOS obtained within hybrid DFT were used to understand
the photocatalytic activity and should also aid further understanding regarding the other properties, such as magnetism and
spin-exchange interactions, of this family of materials.

ASSOCIATED CONTENT

S Supporting Information

Table of photocurrent generated with photocatalysts; table of DFT calculated lattice constants and unit cell volume;
schematic of term system diagrams for different Cu2+ and Co2+ ligand field geometries; Tauc plots for experimental UV−vis
absorption data; band structure and DOS for Cu2(OH)PO4 within DFT + U; band structure for CuCo(OH)PO4,
CoCu(OH)PO4, and Co2(OH)PO4 within DFT-GGA; and total and projected DOS within HSE06. This material is
available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

M.L. performed the experimental tasks and characterization. X.P. performed the computational tasks. All authors partici-
pated in data analysis and discussion. The manuscript was written by C.K.C. with contributions from M.L. and X.P. All

Figure 8. Electron-density contour plots for (A) Cu2(OH)PO4, (B) CuCo(OH)PO4, (C) CoCu(OH)PO4, and (D) Co2(OH)PO4 within
0.5 eV of the valence band (pink clouds) and conduction band (yellow clouds) edges.

Figure 9. Schematic of energy band diagrams for (A) Cu2(OH)PO4, (B) (Cu1−xCo2x)2(OH)PO4, and (C) Co2(OH)PO4.
authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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REFERENCES


(38) Bale, S.; Rahman, S. EPR and Optical Absorption Spectral Investigations of Cu$^{2+}$ in Bi$_2$O$_3$-ZnO-B$_2$O$_3$-Li$_2$O Glasses. ISRN Spectrosc. 2012, 583015.


