Comparison of the defective pyrochlore and ilmenite polymorphs of AgSbO$_3$ using GGA and hybrid DFT

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Silver antimonate, AgSbO$_3$, in both its defective pyrochlore and ilmenite structural polymorphs, has been suggested as a possible candidate mixed metal oxide for use in the photocatalytic splitting of water in visible light. In this study, we report electronic-structure calculations, using both standard and hybrid density-functional-theory approaches, on both structural forms of AgSbO$_3$ to fully characterize the band structure and composition of the valence and conduction bands. Analysis of conduction properties and optical absorption is also used to compare the predicted properties of the two materials. Results show that the valence band is dominated by O 2p and Ag 4d states, whereas the conduction band is composed mainly of Ag and Sb 5s states. Band-edge effective-mass calculations indicate the materials operate via an n-type mechanism, with conduction properties being comparable for the two materials. The fundamental and optical band gaps are also predicted to be compatible with visible light adsorption.

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I. INTRODUCTION

Over the past decade, photocatalysis has received a great deal of attention. This has mainly been in an effort to achieve an efficient use of solar radiation to help combat issues relating to both energy production, such as the formation of H$_2$ from the splitting of water, and environmental concerns, such as the degradation of organic pollutants.

The search for new or improved photocatalysts is never straightforward, as certain requirements in the electronic structure are needed. For example, a number of conditions are required for an efficient water-splitting material. Not only is the size of the band gap of importance, but also the positions of the band edges. The conduction-band minimum (CBM) must have a potential more negative than that of the H$^+/H_2$ redox potential [0 V versus normal hydrogen electrode (NHE)]. In addition, the valence-band maximum (VBM) must have a more positive potential than the redox potential of O$_2$/H$_2$O (+1.23) eV. This also provides the requirement that the very minimum theoretical band gap for a water-splitting material is 1.23 eV. To generate an effective photocatalyst that is driven by visible light, a band gap of less than 3.0 eV is also required.

The first reported semiconductor for use in solar hydrogen production was anatase TiO$_2$ and, as such, it has spawned a vast amount of research. TiO$_2$ is also highly stable and cost-effective, however, as anatase TiO$_2$ has a band gap of 3.2 eV, it cannot operate efficiently under visible light illumination.

One approach to improve the efficiency of TiO$_2$ has been through doping with nonmetallic elements, such as N and C, or metallic elements, for example Cr and V, but this approach only yields limited improvement. Although doping offers one way to enhance the properties, investigations of alternative systems can also be instructive. One such alternative is mixed metal oxides, which have been shown to possess promising photocatalytic properties.

Most mixed metal oxide photocatalysts typically contain at least two different metal cations, one of low valence (I-III) and a second of higher valence (III-VI). The higher valence metal cation possesses either $d^5$, such as Ti(IV), Nb(V), or W(VI), or $d^{10}$ electronic configurations, such as Ga(III), Sn(IV), or Sb(V). This gives rise to conduction bands (CB) that are composed mainly of $d$ or $s/p$ states, respectively. As $s/p$ electrons are less localized than $d$ electrons, they are believed to give rise to a more dispersive conduction band with higher electron mobility and higher photocatalytic activity.

The low valence cation, often an alkali or alkaline earth metal element, has little influence on the top of the valence band (VB), giving rise to an O 2p dominated VB. However, many of the mixed metal oxides with these compositions, such as Ca$_2$Nb$_2$O$_7$, NaTaO$_3$, and NaSbO$_3$, have a band gap greater than 3 eV, making them only responsive to ultraviolet (UV) rather than visible light. To make them usable as a visible light photocatalyst, some kind of modification or band engineering is required. By choosing a low valence cation that has orbitals that will mix with the O 2p states, such as Ag(I) 4d or Pb(II) 6s states, the energy of the valence band can be raised and the band gap decreased. An example of such a material is the photocatalyst AgSbO$_3$.

AgSbO$_3$ has two main polymorphs, with defective pyrochlore and ilmenite structures. The ilmenite is metastable, only forming through low-temperature ion exchange from the isostructural NaSbO$_3$, and will undergo a phase transition to the defective pyrochlore under heat treatment. The reported optical band gaps are 2.6 (Ref. 22) and 2.4–2.5 eV (Refs. 21 and 25) for the defective pyrochlore and ilmenite structures, respectively.

The evolution of O$_2$, via the photocatalytic splitting of water, in the defective pyrochlore structure has been studied by Kako et al. The results of this study showed it to have a greater performance than WO$_3$, which is known to be a good photocatalyst for O$_2$ evolution in the presence of Ag(I) but inactive for H$_2$ evolution. Although the defective pyrochlore was untested for H$_2$ evolution, this suggests that it could have a possible role as a water splitter. The authors also considered its activity toward the degradation of organic molecules, through the oxidation of 2-propanol, with results...
suggested that AgSbO$_3$ in a defective pyrochlore structure has a strong enough oxidizing potential to decompose organic compounds.

Singh and Uma$^{21}$ also looked at the potential for AgSbO$_3$ to decompose organic molecules, studying both the ilmenite and defective pyrochlore polymorphs. Their results suggested that the ilmenite is superior to the defective pyrochlore for the degradation of the organic dyes and 2-chlorophenol under visible light. The defective pyrochlore structure showed either reduced activity, or, for the 2-chlorophenol, a lack of significant activity at all. However, they did suggest that this lower activity could be related to varying stoichiometries in the samples, as the work of Kako et al.$^{22}$ showed that deviations away from ideal stoichiometries had a significant effect on the reactivity, with Ag$_{1.06}$SbO$_3 >$ Ag$_{1.02}$SbO$_3 >$ Ag$_{0.99}$SbO$_3$.

The reduction in reactivity with stoichiometry for the defective pyrochlore AgSbO$_3$ suggests that any defects present in the material will cause a reduction in the photocatalytic properties. For the Ag-deficient Ag$_{0.99}$SbO$_3$, Ag vacancies are suggested to act as centers of recombination between the photogenerated holes and electrons.$^{22,27}$ in a similar manner to that observed for AgTaO$_3$. For hyperstoichiometries, Ag$_{1.02}$SbO$_3$, the silver excess is manifested as metallic silver, which Kako et al. reasoned would have a shielding effect on the surface of the material, reducing both the number of active sites for O$_2$ evolution and the amount of visible light it could adsorb.$^{22}$ Wang et al.$^{29}$ have also studied the effect of varying the Ag/Sb ratio on the photocatalytic properties. Conversely, they reported that an increase in the amount of Ag to Sb caused a reduction in the optical band gap and an increase in the photocatalytic activity, which they attributed to the formation of Sb(III) in the sample.

Kako and Ye$^{25}$ suggested that the photocatalytic properties of AgSbO$_3$ can be improved by preparing samples with mixed phases of the defective pyrochlore and ilmenite. Their results showed a greater activity than both a TiO$_2$ photocatalyst and the single-phase ilmenite material for the decomposition of acetylaldehyde to CO$_2$. They claim that the cause of this increased photocatalytic activity is a synergistic effect between the two phases, which occurs as the band edges of the ilmenite polymorph lay within those of the defective pyrochlore.

Although the primary focus on AgSbO$_3$ has been for its utilization in photocatalysis, the defective pyrochlore has also been investigated for use as an Ag(I) ion conductor,$^{30}$ an n-type thermoelectric material,$^{31,32}$ and as a transparent conducting oxide (TCO)$^{23,33}$

Density-functional-theory (DFT) calculations have been previously employed by Kako et al.$^{22}$ and Mizoguchi et al.$^{23}$ to consider the electronic structure of the defective pyrochlore form of AgSbO$_3$. Both studies showed that the composition of the VB and CB are as expected, with the top of the VB consisting of a mixture of Ag 4d and O 2p states and the bottom of the CB dominated by Ag and Sb 5s states. The composition of the VB has also been confirmed through UV photoemission spectroscopy (UPS).$^{34}$ As expected for these computational approaches, the calculated band gaps for the defective pyrochlore structures are significantly underestimated, with reported values of 0.1 (Ref. 23) and 0.4 eV.$^{22}$

The aim of this study is to provide a characterization of the electronic structures of both the defective pyrochlore and ilmenite forms using hybrid-DFT, which is expected to not only give a better structural representation but also to significantly improve the calculated band gap.$^{35-38}$ Calculations have also been carried out using the standard generalized-gradient approximation (GGA), allowing for a direct comparison to be made with the hybrid-DFT method. In addition, the calculation of band structures, optical absorption and the hole effective masses at both the VBM and CBM allows a quantification of the conduction properties of these materials. This not only allows comparisons to be made between the two different structures, but also a discussion of the suitability of the two materials for n-type water splitting.

II. COMPUTATIONAL METHODS

The calculations described in this study were all performed using the periodic DFT code VASP$^{30,40}$ which uses a plane-wave basis set to describe the valence electrons. The projector-augmented-wave (PAW)$^{41,42}$ method was used to describe the interactions between the cores (Ag: [Kr], Sb: [Kr], and O: [He]) and valence electrons. Two methods of treating the exchange and correlation were used in this study to allow a comparison to be made of their effectiveness. The first method used the standard GGA approach with the Perdew-Burke-Ernzerhof (PBE)$^{43}$ functional. The second approach was that of Heyd, Scuseria, and Ernzerhof (HSE06)$^{44,45}$ which uses a screened hybrid functional and includes a percentage of exact Fock exchange. The HSE06 methodology is identical to that described elsewhere, where the percentage of exact nonlocal Fock exchange added to the PBE functional is 25% and the long- and short-range parts of the functional are partitioned by a screening of $\omega = 0.11$ bohr$^{-1}$. Although hybrid functionals are more computationally demanding, they are often found to give better approximations of band gaps in semiconductor systems and improved structural data.$^{35,38,47-63}$

The bulk equilibrium lattice parameters were determined by performing structural optimizations at a series of volumes. In each of these calculations, the atomic positions, lattice vectors, and cell angles were allowed to relax while the total cell volume was held fixed. The resulting energy-volume curves were then fitted to the Murnaghan equation of state to obtain the equilibrium bulk cell volume.$^{64}$ This approach avoids the problems of Pulay stress and changes in basis set that accompany volume changes in plane-wave calculations. The two polymorphs were modeled using their primitive unit cells, for which a Γ-centered $4 \times 4 \times 4$ k-point mesh was found to be sufficient for both materials. A plane-wave cutoff of 500 eV was used for the PBE calculations but reduced to 400 eV for the HSE06 due to the high computational cost.$^{46}$ For all calculations, the structures were deemed to be converged when the forces on all the atoms were less than 0.01 eV Å$^{-1}$.

The optical-absorption spectra, as well as the optical transition matrix, was calculated within the transversal approximation,$^{48,65}$ using an increased $k$-point mesh of $6 \times 6 \times 6$. This approach sums all direct VB to CB transitions to determine the optical absorption, thereby ignoring both indirect and intraband transitions.$^{66}$ As only single-particle transitions are included, any electron-hole correlations would require higher-order electronic-structure methods.$^{67,68}$
However, this approach has been shown to provide reasonable optical-absorption spectra.16,38,46,69

Structural figures have been generated using the VESTA package.70

III. RESULTS AND DISCUSSION

A. Defective pyrochlore structure

The defective cubic pyrochlore structure, space group Fd\overline{3}m, is the most common form adopted by AgSbO3. A typical cubic pyrochlore structure has a general formula of A\text{2}B\text{2}O\text{6}X, where X is typically O, F, or OH.71 The structure is composed of a corner-sharing BO\text{6} octahedra network, with the larger A cations possessing eightfold coordination, approaching a hexagonal bipyramid, to six O and two X anions. This AX\text{2} sublattice forms a channel network through the structure. The defective pyrochlore structure, exhibited by AgSbO3, differs from that of a typical cubic pyrochlore in that the X anions are absent. This gives rise to sixfold-coordinated Ag ions with a distorted octahedral geometry, approximating a flattened trigonal antiprism.72 The structure is shown in Fig. 1, with a comparison of the calculated structural parameters to the experimental structure of Mizoguchi et al.,23 provided in Table I. As can be seen, there is good agreement between the calculated and experimental structures, with the HSE06 functional providing a better fit to experiment as expected.

The calculated total and partial (ion decomposed) electronic densities of states (EDOS and PEDOS, respectively) for the defective pyrochlore structure are shown in Fig. 2. The EDOS can be broadly separated into four regions, with the VB comprising regions I–III and region IV representing the CB. The HSE06 calculation gives rise to a widening of the band gap and a small expansion of the VB in comparison to the PBE calculation, therefore giving slightly different widths for the different regions of the EDOS. However, similarities in the peak structure and composition are seen between the different methods. The O 2p states are seen throughout all regions in the EDOS for both methods, although the contributions from the cations are seen to differ between regions. The cation states in regions I and II are primarily composed of Sb 5s and 5p states, respectively, with a small amount of Sb 4d states seen in region II. Region III, however, is a mixture of Ag and Sb 4d states mixing with the O 2p, with the Ag states dominating. The CB, region IV, is comprised of Ag 5s, Sb 5s and p, and O 2p.

Agreement is seen between the calculated PEDOS and experimental photoemission spectra.34 The UPS data of Yasukawa et al. indicate four peaks in the upper valence band. Working back from the Fermi energy, the first three peaks were designated as being composed of Ag 4d and O 2p states, with the peak at the top of the VB having a significant contribution from the Ag 4d states. The fourth peak was described as consisting of mixed O 2p and cationic s and p states. This description is qualitatively similar to the calculated PEDOS, with Ag 4d and O 2p states dominating the upper valence band. The calculated PEDOS also suggests that the cationic s

![FIG. 1. (Color online) Schematic showing the optimized AgSbO3 defective pyrochlore structure. Silver, antimony, and oxygen atoms are colored blue (light gray), purple (medium gray), and red (dark gray), respectively. The antimony atoms are also shown as polyhedra in the main image. Coordination environments of the AgO\text{6} and SbO\text{6} octahedra are also shown.](image)

![FIG. 2. (Color online) Electronic density of states for AgSbO3 in a defective pyrochlore structure, split into (i) the total EDOS, (ii) Ag PEDOS, (iii) Sb PEDOS, and (iv) O PEDOS, as calculated using the (a) PBE and (b) HSE06 method. The s, p, and d states are colored blue (dot-dash), red (solid), and green (dash), respectively. Vertical dashed gray lines represent divisions between different regions in the DOS. The Fermi energy has also been set to 0 eV.](image)
form of AgSbO₃ calculated using (a) the PBE approach and (b)–(d) the HSE06 method. The HSE06-determined band structures are shown in fatband format with the contributions to the bands from the (b) Ag 4d (green), (c) Sb 5s (blue), and (d) O 2p (red) states indicated. The Fermi level is set to 0 eV, as indicated by the horizontal dashed gray line.

FIG. 3. (Color online) Band structure of the defective pyrochlore form of AgSbO₃ calculated using (a) the PBE approach and (b)–(d) the HSE06 method. The HSE06-determined band structures are shown in fatband format with the contributions to the bands from the Ag 4d (green), Sb 5s (blue), and O 2p (red) states indicated. The Fermi level is set to 0 eV, as indicated by the horizontal dashed gray line.

The calculated band structures for the defective pyrochlore, along the space group high-symmetry lines from Bradley and Cracknell,⁷³ are given in Fig. 3. The VBM is located at L and extends in the L to Γ direction for both methods, whereas the CBM is observed at the Γ point, leading to indirect band gaps of 0.08 and 2.09 eV for PBE and HSE06, respectively. The smallest direct band gaps, however, are only slightly larger at 0.09 and 2.11 eV for PBE and HSE06, respectively, and are observed at the Γ point.

For the HSE06-predicted band structure, fatband analysis has been conducted to show the contribution from the Ag 4d, Sb 5s, and O 2p states, Figs. 3(b)–3(d), respectively. As seen in the PEDOS, the top of the VB is dominated by mixed Ag 4d and O 2p states, with very little contribution from the Sb 5s states. The bottom of the CB is comprised of mainly Sb 5s and O 2p states. The contributions from Ag 5s states to the bottom of CB, not shown, are comparable to those of the O 2p states. The extent of the Sb 5s and O 2p contributions to the lowest bands in the CB are also seen to be phase-dependent. For example, at the Γ point, the primary component is seen to be from the Sb 5s states, although this is reversed at the W point, where O 2p states dominate. Although not shown, fatband analysis of the PBE-predicted band structures yields similar results. This analysis is qualitatively similar to a previous GGA study by Mizoguchi et al.,⁷³ although they report a greater mixing of Ag 5s states at the CBM with the Perdew-Wang functional.

B. Ilmenite structure

The ilmenite structure has a rhombohedral unit cell, space group R₃₃̅, and consists of distorted octahedral AgO₆ and SbO₆ units, with the former showing the greatest distortion, exhibiting a trigonal antiprism polyhedron. The SbO₆ octahedra form edge-sharing sheets in the ab plane, as do the distorted AgO₆ octahedra, with the layers alternating between Ag and Sb in the c direction, as shown in Fig. 4. The distorted AgO₆ octahedra connect to the SbO₆ octahedra by face-sharing on one side in the c direction and corner-sharing in the other, with this arrangement alternating across the layer in the ab plane.

Comparisons between the calculated and experimental structures are given in Table II. As expected, the HSE06 method gives rise to the closest fit to experiment, with cell vectors and bond lengths within 2.1 %, whereas the PBE method predicts values within 3.0 %. However, the c lattice vector is seen to be expanded relative to the a and b vectors for both methods. This is more apparent in the HSE06-minimized structure as the PBE-calculated vectors also possess the typical overestimation seen for PBE calculations. Although the source of this expansion is not apparent, it may be a result of the failure of DFT (and hybrid-DFT) to account for van der Waals forces, as previously seen in the expansion of layered materials, such as SnO (Refs. 74 and 75) and V₂O₅.⁷⁶,⁷⁷

The calculated EDOS and PEDOS for the ilmenite structure are shown in Fig. 5. As with the defective pyrochlore structure, the EDOS can be broadly characterized by four regions, with

FIG. 4. (Color online) Schematic showing the optimized AgSbO₃ ilmenite structure. Silver, antimony, and oxygen atoms are colored blue (light gray), purple (medium gray), and red (dark gray), respectively. The antimony atoms are also shown as polyhedra in the main image. Coordination environments of the AgO₆ and SbO₆ octahedra are also shown for reference.
TABLE II. Comparison between experimental lattice constants and bond lengths for AgSbO₃ in the ilmenite structure with those calculated using PBE and HSE06 methods. Percentage changes from experiment are given in parentheses, and all values are in Å except the cell volume, which has units of Å³.

<table>
<thead>
<tr>
<th>Property</th>
<th>PBE</th>
<th>HSE06</th>
<th>Experiment²⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5.42(1.7)</td>
<td>5.35(0.4)</td>
<td>5.33</td>
</tr>
<tr>
<td>b</td>
<td>5.42(1.7)</td>
<td>5.35(0.4)</td>
<td>5.33</td>
</tr>
<tr>
<td>c</td>
<td>17.05(2.1)</td>
<td>16.99(1.7)</td>
<td>16.70</td>
</tr>
<tr>
<td>Volume</td>
<td>500.87(5.6)</td>
<td>486.30(2.5)</td>
<td>474.43</td>
</tr>
<tr>
<td>Sb-O</td>
<td>2.02(2.5)</td>
<td>1.99(1.0)</td>
<td>1.97</td>
</tr>
<tr>
<td>Ag-O</td>
<td>2.41(0.0)</td>
<td>2.41(0.0)</td>
<td>2.41</td>
</tr>
<tr>
<td>Ag-Ag</td>
<td>2.75(1.5)</td>
<td>2.75(1.5)</td>
<td>2.71</td>
</tr>
<tr>
<td>Ag-Sb</td>
<td>3.28(2.2)</td>
<td>3.24(0.9)</td>
<td>3.21</td>
</tr>
<tr>
<td>Sb-Sb</td>
<td>3.40(2.7)</td>
<td>3.38(2.1)</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>3.13(1.6)</td>
<td>3.09(0.3)</td>
<td>3.08</td>
</tr>
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</table>

The CB, region IV, is comprised of mixed Sb 5s and p with O 2p states.

Overall, the EDOS for the two different AgSbO₃ structures share a number of similarities, with the basic composition of both the VB and CB being qualitatively the same.

The band structures of the ilmenite form of AgSbO₃, using both PBE and HSE06 methods, are given in Fig. 6. Although both methods give rise to a similar band structure, the major difference is in the opening up of the band gap with the HSE06 method. The positions of both the VBM and CBM are the same for both methods, located at the Γ point, with direct band gaps of 0.13 and 1.92 eV for the PBE and HSE06 methods, respectively.

The HSE06-predicted band structure is shown in a fatband format, displaying the contributions from the Ag 4d, Sb 5s, and O 2p states in Figs. 6(b)–6(d), respectively. As expected from the PEDOS, the top of the VB is dominated by mixed Ag 4d and O 2p states, with little contribution from the Sb 5s states. The bottom of the CB, however, is comprised of mainly Sb 5s and O 2p states. The contribution of the Ag 5s states, not shown, to the lowest-energy band is similar to those seen for the Sb 5s states. A phase-dependent mixing of the Sb 5s and O 2p states is observed in the lowest bands in the CB. For the lowest energy band, the O 2p contribution is seen to decrease significantly on approaching the Γ point, whereas for the second lowest energy band in the CB, a similar case is seen for the Sb 5s contribution around the Z point. Although not
shown, fatband analysis of the PBE-predicted band structures yields similar results.

C. Optical absorption

As the experimental optical band gaps of 2.6 and 2.5 eV for the defective pyrochlore and ilmenite structures, respectively, are determined by optical absorption, it is instructive to compare these directly to the calculated optical absorption, rather than the fundamental band gaps. The Tauc relation states that $E_g \propto \alpha^2$, therefore, by extrapolating $\alpha^2$, we can determine the value of the optical band gap. Figure 7 shows the plots of optical absorption (in terms of $\alpha^2$) for both AgSbO$_3$ structures calculated using HSE06, with comparison to experiment.21,22 The calculated optical band gaps for the defective pyrochlore and ilmenite forms are seen to be equal to 2.44 and 2.24 eV, respectively. Both the magnitudes and the relative order are consistent with experiment. The calculated optical band gaps, however, are larger than the fundamental band gaps of 2.09 and 1.92 eV for the defective pyrochlore and ilmenite, respectively.

For both materials, adsorption between the VBM and CBM at the $\Gamma$ point is forbidden, which is the location of the direct fundamental band gap. The onset of adsorption for the defective pyrochlore is therefore seen along the $\Gamma$-$X$ high-symmetry line, and along $\Gamma$-$Z$ for the ilmenite structure. This observation is also noted for a range of oxide materials that show a symmetry-forbidden fundamental band gap, such as CuBO$_2$, SrCu$_2$O$_4$, In$_2$O$_3$, and Cu$_2$O.

D. Band-edge effective masses

To allow a comparison of the electronic conductivity of the two structures, the electron and hole effective masses at the CBM and VBM, respectively, can be determined. The effective mass ($m^*$) is calculated by

$$\frac{1}{m^*(E)} = \frac{1}{\hbar^2} \frac{dE}{dk},$$

where $E(k)$ is the band-edge energy as a function of wave vector $k$, obtained directly from the calculation.81 The bands at the top of the VB for both structures are clearly not parabolic, therefore AgSbO$_3$ is not expected to be well described under a typical semiconductor effective-mass approximation. However, as the bottom CB bands for the two structures are seen to be more parabolic in nature, the calculated electron effective masses should have a higher degree of accuracy than the hole effective masses. However, the calculated effective masses will serve as an approximate guide allowing comparisons to be drawn, as has been previously done for Cu$_2$O$_3$ (where $M$ = Al, Sc, Y, Cr, and B),82 (Cu$_2$S$_2$)(Sr$_3$Sc$_2$O$_9$),83 and In$_2$O$_3$,83 indicating the relative abilities of the two structures for $n$- or $p$-type conductivity. The calculated effective masses at the VBM and CBM for the defective pyrochlore and ilmenite structures are given in Table III. Effective masses have been calculated in the [001], [010], and [100] directions, as well as along the special directions shown in the previously mentioned band structures.

As can be seen, the results show that in terms of the $n$-type conductivity, both structures have very similar properties. The electron effective masses of the CBM are also smaller than the hole effective masses of the VBM for both structure types, indicating that the $n$-type ability of the materials will be greater than the $p$-type ability. The $p$-type properties differ between the structure types though, with the VBM hole effective masses suggesting that the defective pyrochlore structure will possess better $p$-type properties. However, neither material is predicted to exhibit strong $p$-type properties.

Effective-mass calculations have been used recently to describe In$_2$O$_3$, which is an industrial standard $n$-type TCO.83 The effective masses at the VBM and CBM were calculated as being 16$m_e$ and 0.24$m_e$, respectively, and can be considered as being indicative of poor $p$-type and good $n$-type ability. The CBM electron effective masses of both AgSbO$_3$ polymorphs are comparable to In$_2$O$_3$, albeit slightly larger, suggesting that AgSbO$_3$ has strong $n$-type properties. Although the calculated hole effective masses of the VB are more approximate, due to its nonparabolic nature, the $p$-type properties will also be...
significantly better than $\text{In}_2\text{O}_3$. $\text{Cu}_2\text{O}$ is the parent compound of a range of $p$-type delafossite TCO’s with general formula $\text{CuM}_2\text{O}_4$, where $\text{M}$ is typically a group 3 or 13 metal. The experimental hole effective mass of the VB of $\text{Cu}_2\text{O}$ is $0.56\ m_e^{\ast}$, whereas the calculated value for the delafossite $\text{CuBO}_2$ is $0.45\ m_e^{\ast}$. In comparison, our calculated VBM hole effective masses suggests that the defective pyrochlore may also exhibit reasonable $p$-type properties.

**IV. CONCLUSION**

In conclusion, this study has used both PBE and HSE06 DFT approaches to model the electronic structure of the defective pyrochlore and ilmenite forms of $\text{AgSbO}_3$. As expected, the HSE06 method affords a structure that has a much better fit to experiment, in terms of both the unit-cell dimensions and the bond lengths.

Despite the different structures, the orbital composition of the density of states and band structures for the two materials is similar, with orbital contributions to the bands in agreement with experiment and previous calculation. The top of the VB is composed primarily of $\text{Ag}\ 4d$ and $\text{O}\ 2p$ states. For the ilmenite polymorph, the $\text{O}\ 2p$ states in the uppermost bands are slightly diminished, with respect to the defective pyrochlore, which may give rise to the increased dispersion in these bands. For the bottom of the CB, the composition is seen to be mainly mixed $\text{Ag}\ 5s$, $\text{Sb}\ 5p$, and $\text{O}\ 2p$ states. However, there is a difference in the phase dependence of contributions to the lowest-energy conduction band. Both materials show a reduction in the $\text{O}\ 2p$ states at the CBM, which increases in directions away from this point. For the defective pyrochlore, the $\text{Sb}\ 5p$ contribution also has an inversely proportional relationship to those of the $\text{O}\ 2p$, reaching a maximum at the CBM.

Agreement between experiment and the HSE06-calculated band gaps is also seen. For the defective pyrochlore (ilmenite) structure, the HSE06 approach predicts an indirect (direct) fundamental band gap of $2.09\ eV$ (1.92 eV) and an optical band gap of $2.44\ eV$ (2.24 eV), which compares well with the experimental value of $2.6\ eV$ (Refs. 22 and 25). The calculated band gaps are also consistent with their use in photocatalytic splitting of water in visible light, which requires a band gap of between 1.23 and 3.00 eV. The magnitudes of these optical band gaps, however, exclude the use of $\text{AgSbO}_3$ as a TCO, which previous studies have suggested.

The two materials are also seen to have comparable effective masses for the CB, which would give rise to similar $n$-type properties. As the values of the effective masses are only slightly bigger than those calculated for $\text{In}_2\text{O}_3$, their $n$-type properties are predicted to be good, which is a consequence of the strong dispersion seen at the bottom of the CB due to $\text{Sb}\ 5s$ and $\text{O}\ 2p$ interactions. In contrast to these results, experiment has suggested different reactivities for the two polymorphs. However, this has been linked to differing stoichiometries rather than an inherent property of the pure materials. The defective pyrochlore is predicted to have better $p$-type ability than the ilmenite, and, while neither polymorph is predicted to be a strong $p$-type material, the defective pyrochlore may show reasonable $p$-type properties.

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