Assessment of Hybrid Organic–Inorganic Antimony Sulfides for Earth-Abundant Photovoltaic Applications

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ABSTRACT: Hybrid organic–inorganic solar absorbers are currently the subject of intense interest; however, the highest-performing materials contain Pb. Here we assess the potential of three Sb-based semiconductors: (i) Sb2S3, (ii) Cs2Sb8S13, and (iii) (CH3NH3)2Sb8S13. While the crystal structure of Sb2S3 is composed of 1D chains, 2D layers are formed in the ternary cesium and hybrid methylammonium antimony sulfide compounds. In each case, a stereochemically active Sb 5s2 lone pair is found, resulting in a distorted coordination environment for the Sb cations. The bandgap of the binary sulfide is found to increase, while the ionization potential also changes, upon transition to the more complex compounds. Based on the predicted electronic structure, device configurations are suggested to be suitable for photovoltaic applications.

Since the development of silicon-based solar cells in the 1950s, there has been a search for new materials with direct bandgaps and high optical absorption coefficients that are cheap and easy to process. One recent success has been the development of lead halide perovskites, which have shown a rapid increase in light-to-electricity conversion efficiency from 3.8% in 2009 to 20.1% in 2015 with low-cost solution-based processing.1−4

An advantage of the perovskite family of compounds is that the properties are highly tunable with chemical composition. Taking the CsPbX3 (X = Cl, Br, I) series for instance, these materials have an unusual electronic structure due to the Pb2+ configuration ([Xe] 5d106s26p0). The contribution of the cation s orbital to the upper valence band results in a light hole and to provide guidance for future materials screening of hybrid semiconductors.

Crystal Structures. Sb2S3 adopts an orthorhombic crystal structure with space group Pnma, as shown in Figure 1a.17 Due to the stereochemical activity of the Sb(III) lone pair electrons, the cation sits in a distorted square pyramidal coordination environment. The (Sb2S3)2 building blocks form infinite 1D
The structural chemistry of Cs\(_2\)Sb\(_8\)S\(_{13}\) single crystals was studied several decades ago using X-ray diffraction.\(^{19,20}\) The material can be formed by the mixture of Sb\(_2\)S\(_3\) and Cs\(_2\)S. The Cs atoms are located in the apertures between Sb\(_8\)S\(_{13}\) sheets and function as cationic bridges between them. The Sb cations are present in a mixture of distorted square pyramidal (5 Sb–S bonds) and seesaw (4 Sb–S bonds) coordination environments. The [Sb\(_{13}\)]\(_n\) polyhedra share corners and edges to form infinite chains, which are linked by persulfide bonding defining the two-dimensional undulating layers. The material crystallizes in a triclinic system with the low-symmetry space group \(P\bar{1}\).

In the methylammonium antimony sulfides, a similar structure is adopted, where the organic cations CH\(_3\)NH\(_3\)\(^+\) sit within the heterorings built by the characteristic [Sb\(_3\)S\(_7\)]\(^2-\) and [Sb\(_8\)S\(_{13}\)]\(^-\) building units. The crystal is again triclinic with space group \(P\bar{1}\).\(^{21,22}\) The material can be grown hydrothermally from a mixture of Sb, S, and CH\(_3\)NH\(_2\). It should be noted that the molecular cation CH\(_3\)NH\(_3\)\(^+\) has a large intrinsic electrical dipole moment (ca. 2.2 D). Orientational disorder inside the aperture, which is also found in CH\(_3\)NH\(_3\)PbI\(_3\),\(^{23}\) could potentially result in ferroelectric or paraelectric behavior of this hybrid organic–inorganic material. Hang et al. reported a class of hybrid ferroelectrics,\(^{24}\) which also includes hybrid inorganic–organic Sb based compounds, suggesting the possibility of similar behavior in the materials discussed here. The additional structural and chemical flexibility may provide physical properties for the hybrid compounds that are distinct from the purely inorganic materials.

**Computational Procedure.** Starting from the crystal structures determined from X-ray diffraction as discussed above, the size, shape and internal positions of the conventional units cells were fully relaxed to their equilibrium values within three-dimensional periodic boundary conditions. The total energy was calculated within the framework of Kohn–Sham DFT using a plane-wave basis set as implemented in the code VASP.\(^{25,26}\)

The kinetic energy cutoff for the plane waves was set to 500 eV, and a \(k\)-point mesh was chosen to provide sampling of at least 25 \(k\)-points Å\(^{-1}\). The thresholds for convergence of the total energy and forces were set to \(1 \times 10^{-6}\) eV and \(1 \times 10^{-2}\) eV/Å, respectively. Electron exchange and correlation was described within the semilocal generalized gradient approx-

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**Table 1. Structural and Electronic Data for the Antimony Sulfides**\(^{48}\)

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>(a, b, c)</th>
<th>(E_{bulk})</th>
<th>(\Phi_{bulk})</th>
<th>(\Phi_{static})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb(_2)S(_3)</td>
<td>PBEsol</td>
<td>11.2, 3.8, 11.1</td>
<td>1.21 (Direct: 1.25)</td>
<td>5.56</td>
<td>5.46</td>
</tr>
<tr>
<td></td>
<td>HSE06</td>
<td></td>
<td>1.69 (Direct: 1.72)</td>
<td>5.77</td>
<td>5.78</td>
</tr>
<tr>
<td></td>
<td>Exp.</td>
<td>11.3, 3.8, 11.2</td>
<td>1.54–2.24(^{16,17})</td>
<td>5.77</td>
<td>5.78</td>
</tr>
<tr>
<td></td>
<td>LDA(^{18})</td>
<td></td>
<td>1.20 (Direct: 1.29)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>GW(^{22})</td>
<td></td>
<td>1.54 (Direct: 1.57)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs(_2)Sb(<em>8)S(</em>{13})</td>
<td>PBEsol</td>
<td>15.3, 11.3, 8.2</td>
<td>1.10 (Direct: 1.13)</td>
<td>4.90</td>
<td>4.31</td>
</tr>
<tr>
<td></td>
<td>HSE06</td>
<td></td>
<td>1.82 (Direct: 1.85)</td>
<td>5.15</td>
<td>4.75</td>
</tr>
<tr>
<td></td>
<td>Exp.(^{19})</td>
<td></td>
<td>1.54 (Direct: 1.57)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH(_3)NH(_3))(_2)Sb(<em>8)S(</em>{13})</td>
<td>PBEsol</td>
<td>15.9, 11.6, 8.1</td>
<td>1.28 (Direct: 1.34)</td>
<td>6.07</td>
<td>5.29</td>
</tr>
<tr>
<td></td>
<td>HSE06</td>
<td></td>
<td>1.99 (Direct: 2.08)</td>
<td>7.01</td>
<td>5.79</td>
</tr>
</tbody>
</table>

\(^{16}\)Lattice constants \(a, b, c\) and \(c\) are given, as well as the calculated bandgap in comparison to previous theoretical and experimental studies. The bandgap values outside the parentheses refer to indirect transitions (a change in crystal momentum). Ionization potentials of both bulk and surfaces are also shown, as defined in the text. Notice that the non-local HSE06 calculated bandgap and ionization potential are always larger than the semi-local PBEsol exchange-correlation functional. All energies are given in eV, lengths in Å.
imation using the PBEsol functional,\textsuperscript{27} which accurately describes both the crystal structure and total energies in solid-state heteropolar compounds such as these. In order to provide more quantitative electronic structure information, we used a hybrid nonlocal exchange-correlation treatment that incorporated 25\% screened Hartree–Fock exchange, the HSE06 functional.\textsuperscript{28,29} In contrast to Pb halide materials, where relativistic spin–orbit coupling (SOC) strongly affects the electronic structure,\textsuperscript{50,51} for Sb-based compounds the effect is weaker (ΔE\textsubscript{SOC} ≈ 20–60 meV for Sb\textsubscript{2}S\textsubscript{3})\textsuperscript{6,32} so only scalar-relativistic corrections are included in this study.

Within periodic boundary conditions the electrostatic potential of a crystal is not defined with respect to an external vacuum level, so that the absolute electronic energy levels (eigenvalues) from different calculations cannot be compared.\textsuperscript{53} To overcome this limitation, we have generated surface terminations for each of the three materials: the well-studied (001) surface of Sb\textsubscript{2}S\textsubscript{3} and the (100) surfaces of Cs\textsubscript{2}Sb\textsubscript{8}S\textsubscript{13} and (CH\textsubscript{3}NH\textsubscript{3})\textsubscript{2}Sb\textsubscript{8}S\textsubscript{13}. Using the package MacroDensity,\textsuperscript{54} the Kohn–Sham eigenvalues of the upper valence band (ε\textsubscript{VB}) were aligned with respect to an external vacuum level (VL), with the surface ionization potential (Φ\textsubscript{surf}) calculated according to

\[
\Phi_{\text{surf}} = \epsilon_{\text{VB}}^{KS} - \text{VL}
\]  

(1)

The effect of the surface states was removed by aligning bulk and surface calculations using core-level eigenvalues (ε\textsubscript{core} and ε\textsubscript{surf}), yielding a bulk ionization potential:

\[
\Phi_{\text{bulk}} = \epsilon_{\text{VB}}^{KS} - (\epsilon_{\text{core}}^{\text{bulk}} - \epsilon_{\text{core}}^{\text{surf}}) - \text{VL}
\]  

(2)

This procedure accounts for surface states created due to the under-coordination of atoms at the crystal termination.

**Electronic Structure.** The equilibrium crystal structures are in good agreement (within 2\%) with the finite-temperature structures previously determined from X-ray diffraction (see Table 1). The calculated electronic band structures are presented in Figure 2. Multiple valleys are found in the conduction band of each material with the minimum falling away from the high-symmetry k-points. The fundamental bandgaps are indirect in each case, and there are small differences between the direct and indirect bandgaps (E\textsubscript{g}\textsuperscript{direct} − E\textsubscript{g}\textsuperscript{indirect} < 0.1 eV).

The predicted direct bandgaps of Sb\textsubscript{2}S\textsubscript{3}, Cs\textsubscript{2}Sb\textsubscript{8}S\textsubscript{13} and (CH\textsubscript{3}NH\textsubscript{3})\textsubscript{2}Sb\textsubscript{8}S\textsubscript{13} are 1.72, 1.85, and 2.08 eV, respectively. Both the conduction and valence bands of Sb\textsubscript{2}S\textsubscript{3} show high dispersion in reciprocal space, which is associated with light electron and hole effective masses. The range of reported optical bandgaps of Sb\textsubscript{2}S\textsubscript{3} is 1.54–2.24 eV,\textsuperscript{41–45} with differences due to data fitting procedures and sample variation, thus our calculations are at least consistent with experimental results. For the multicomponent materials, there is an increase in the magnitude of the bandgap by 0.1 and 0.3 eV for Cs\textsubscript{2}Sb\textsubscript{8}S\textsubscript{13} and (CH\textsubscript{3}NH\textsubscript{3})\textsubscript{2}Sb\textsubscript{8}S\textsubscript{13}, respectively. While in Cs\textsubscript{2}Sb\textsubscript{8}S\textsubscript{13} and (CH\textsubscript{3}NH\textsubscript{3})\textsubscript{2}Sb\textsubscript{8}S\textsubscript{13} the valence band is relatively flat, the conduction band still exhibits large dispersion, thus we would expect enhanced n-type conductivity in these materials. The strong bonding within the (011) layers in real space can result in favorable electron transport pathways.

Analysis of the electronic density of states shows that the upper valence band of Sb\textsubscript{2}S\textsubscript{3} is mainly formed by Sb 5s and partially by the S 3p orbitals, while the lower conduction band consists of mainly Sb 5p as well as minor contribution from the S 3p orbitals. The lone electron pair of Sb leads to an asymmetric electronic density at the upper valence band of Sb\textsubscript{2}S\textsubscript{3}. The same characteristic is also observed in antimony oxides,\textsuperscript{46} chalcogenides\textsuperscript{47} and even persists in the amorphous state.\textsuperscript{58}

The multivalley electronic structure of Sb\textsubscript{2}S\textsubscript{3}, Cs\textsubscript{2}Sb\textsubscript{8}S\textsubscript{13} and (CH\textsubscript{3}NH\textsubscript{3})\textsubscript{2}Sb\textsubscript{8}S\textsubscript{13} can be regarded as a favorable characteristic for photovoltaic absorber layers, corresponding to the coexistence of strong optical absorption and slow recombination of electrons and holes.\textsuperscript{49,50} The multivalleys provide a high electronic density of states, while maintaining band dispersion at each stationary point. There will be an associated energy loss due to thermalisation of hot carriers; however, this is balanced by the separation of electrons and holes to different wavevectors that suppresses bimolecular recombination processes. Similar band structure features are found for other lone pair materials with low symmetry crystal structures such as SnS and CuSbS\textsubscript{2}.\textsuperscript{53–54} A kinetic model of electron transport and recombination in these unconventional (non-tetrahedral) semiconductors is required to provide quantitative insights into their photophysical behavior.

**Absolute Electron Energies.** In addition to the bulk electron distributions, the absolute electron energies are critical for application of these materials in photovoltaic devices. In particular, work function matching is required for effective
electron and hole extraction from the absorber layer and to minimize resistive losses at the interfaces.

In order to calculate the ionization potential, we have cut nonpolar surface terminations and aligned the Kohn–Sham electronic eigenvalues to the vacuum (using eqs 1 and 2). The ionization potentials of the three materials are compared in Figure 3. For Sb$_2$S$_3$, the ionization potential is calculated to be 5.77 and 5.78 eV for the bulk and (001) surface, respectively. The negligible difference indicates a chemically smooth termination without sub-bandgap surface states. The cleaved planes are weakly bound and held together by van der Waals interactions between the Sb lone pairs.

As the crystal structure gets more complex, the change of the ionization potential between the bulk and the surface increases, with 4.90 and 4.31 eV for bulk and (100) surface of Cs$_2$Sb$_8$S$_{13}$ and 6.07 and 5.29 eV for the bulk and (100) surface of (CH$_3$NH$_3$)$_2$Sb$_8$S$_{13}$. The greater difference between surface and bulk values indicates the presence of more surface states than in stibnite due to the complex chemical environment and greater amount of bond cleavage at the interface, especially for the hybrid (CH$_3$NH$_3$)$_2$Sb$_8$S$_{13}$ material. While we have confirmed there is no macroscopic dipole—the electrostatic potential plateau to the same vacuum level on each side of the slab—the electrostatic fluctuations toward the surface are significant. This highlights a potential problem in working with low symmetry multicomponent crystals: surface and interface dipoles may be challenging to control and could require chemical passivation or modification layers in order to avoid undesirable photovoltage losses.

The ionization potential of Sb$_2$S$_3$ is similar to that of CH$_3$NH$_3$PbI$_3$, which has been calculated to be 5.7 eV. In conclusion, we have used first-principles techniques to investigate the structure and electronic properties of Sb$_2$S$_3$, Cs$_2$Sb$_8$S$_{13}$, and the hybrid compound (CH$_3$NH$_3$)$_2$Sb$_8$S$_{13}$. Each of these materials has been successfully synthesized in the past; however, their physical properties were hitherto unknown. The equilibrium crystal structure and the bandgap of Sb$_2$S$_3$ is consistent with previous experimental studies. Both Cs$_2$Sb$_8$S$_{13}$ and (CH$_3$NH$_3$)$_2$Sb$_8$S$_{13}$ show suitable bandgaps and structures for solar energy applications, and demonstrate that the bandgap can be tuned by changing the cation. The work function of the three materials has also been reported, which varies more than the bandgap, indicating the role of surface states and polarization for the multicomponent systems. A number of possible contact materials are suggested for testing photovoltaic activity.

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**Notes**

The authors declare no competing financial interest.

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**Corresponding Author**

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