Screening Mixed-Metal Sn2M(III)Ch2X3 Chalcohalides for Photovoltaic Applications

Published in:
Chemistry of Materials

DOI:
10.1021/acs.chemmater.3c01629

Published: 01/09/2023

Please cite the original version:
Screening Mixed-Metal Sn\textsubscript{2}M(III)\textsubscript{Ch,X\textsubscript{3}} Chalcohalides for Photovoltaic Applications

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ABSTRACT: Quaternary mixed-metal chalcohalides (Sn\textsubscript{2}M(III)\textsubscript{Ch,X\textsubscript{3}}) are emerging as promising lead-free, perovskite-inspired photovoltaic absorbers. Motivated by recent developments of a first Sn\textsubscript{2}SbS\textsubscript{3}I\textsubscript{3}-based device, we used density functional theory to identify lead-free Sn\textsubscript{2}M(III)\textsubscript{Ch,X\textsubscript{3}} materials that are structurally and energetically stable within Cmcm, Cmc2\textsubscript{1}, and P2\textsubscript{1}/c space groups and have a band gap in the range of 0.7–2.0 eV to cover outdoor and indoor photovoltaic applications. A total of 27 Sn\textsubscript{2}M(III)\textsubscript{Ch,X\textsubscript{3}} materials were studied, including Sn, Sb, Bi, and I for the M(III)-site, S, Se, and Te for the Ch-site, and Cl, Br, and I for the X-site. We identified 12 materials with a direct band gap that meet our requirements, namely, Sn\textsubscript{2}InS\textsubscript{3}, Sn\textsubscript{2}InS\textsubscript{3}, Sn\textsubscript{2}InSe\textsubscript{3}, Sn\textsubscript{2}InSe\textsubscript{3}, Sn\textsubscript{2}InTe\textsubscript{3}, Sn\textsubscript{2}InTe\textsubscript{3}, Sn\textsubscript{2}SbS\textsubscript{3}, Sn\textsubscript{2}SbS\textsubscript{3}, Sn\textsubscript{2}SbSe\textsubscript{3}, Sn\textsubscript{2}SbTe\textsubscript{3}, Sn\textsubscript{2}BiS\textsubscript{3}, and Sn\textsubscript{2}BiTe\textsubscript{3}. A database scan reveals that 9 of 12 are new compositions. For all 27 materials, P2\textsubscript{1}/c is the thermodynamically preferred structure, followed by Cmc2\textsubscript{1}. In Cmcm and Cmc2\textsubscript{1}, mainly direct gaps occur, whereas indirect gaps occur in P2\textsubscript{1}/c. To open up the possibility of band gap tuning in the future, we identified 12 promising Sn\textsubscript{2}M(III)\textsubscript{Ch\textsubscript{2},X\textsubscript{3}} materials, which fulfill our requirements, and an additional 69 materials by combining direct and indirect band gap compounds.

1. INTRODUCTION

Photovoltaic technologies are instrumental for the transition from conventional to green and renewable energy production. To increase the power conversion efficiency (PCE) while reducing costs and improving device longevity, new materials are continuously being explored. Lead halide perovskites (LHPs) have emerged as promising contenders due to their beneficial optoelectronic properties, defect tolerance, and cost-effective solution processing. Yet, the toxicity of lead and the moderate long-term stability in air\textsuperscript{1–4} impede the commercial viability of LHPs. Sn\textsuperscript{2+}-based perovskites and Pb\textsuperscript{2+}- and Bi\textsuperscript{3+}-based perovskite-inspired absorbers are popular low-toxicity alternatives, but they suffer from air-oxidation (Sn\textsuperscript{2+} to Sn\textsuperscript{4+}) and high defect densities.\textsuperscript{5,6} Conversely, metal chalcogenides (e.g., Pb\textsubscript{2}, Cd\textsubscript{2}, Sb-based)\textsuperscript{7–10} with tunable band gaps and high absorption cross sections have enabled highly stable solar cells with modest efficiencies. Mixed-metal chalcohalides with an M(II)\textsubscript{2}M(III)Ch\textsubscript{2},X\textsubscript{3} stoichiometry (also referred to as A\textsubscript{2}BCh\textsubscript{2},X\textsubscript{3})\textsuperscript{11} are an emerging semiconductor family combining halide perovskite and metal chalcogenide building blocks.\textsuperscript{11–13} The Ch-sites are occupied by bivalent chalcogenide anions that form strong metal–chalcogen bonds with the metal cations. Mixed-metal chalcohalides may display the intriguing optoelectronic properties of LHPs, such as dispersive valence and conduction bands, high defect tolerance due to strong dielectric screening (owing to the presence of ns\textsuperscript{2} lone pair cations), and the resultant low capture cross sections of defects,\textsuperscript{12,13} with the promise to overcome the pressing stability challenges of LHPs.\textsuperscript{4,12} In addition, the Sn–Ch bonding nature should prevent Sn\textsuperscript{2+} to Sn\textsuperscript{4+} oxidation in mixed-metal chalcohalides. Also, experimental X-ray photoelectron spectroscopy measurements suggest that synthesizing Sn\textsubscript{2}M(III)Ch\textsubscript{2},X\textsubscript{3} under reduction conditions partly suppresses Sn\textsuperscript{2+} to Sn\textsuperscript{4+} oxidation.\textsuperscript{12,13} As a result, Sn\textsubscript{2}M(III)Ch\textsubscript{2},X\textsubscript{3} films are stable even in humid environments.\textsuperscript{11,12} The photovoltaic potential of mixed-metal chalcohalides was recently demonstrated for a Sn\textsubscript{2}SbS\textsubscript{3}I\textsubscript{3}-based single-junction solar cell that achieved a PCE of 4.04\textsuperscript{12}. This is a promising start considering that the first perovskite solar cells only reached a PCE of 3.8\textsuperscript{14} in 2009 and now exceed 25\textsuperscript{15}.

Over the past four decades, the M(II)\textsubscript{2}M(III)Ch\textsubscript{2},X\textsubscript{3} material space—lead-free as well as lead-based—has only scarcely been explored (both theoretically and experimentally), and only a few compounds are known such as Sn\textsubscript{2}SbS\textsubscript{3},\textsuperscript{11,12,16,17} Sn\textsubscript{2}SbSe\textsubscript{3},\textsuperscript{18} Sn\textsubscript{2}BiS\textsubscript{3},\textsuperscript{19} Pb\textsubscript{2}SbS\textsubscript{3},\textsuperscript{20–22} and Pb\textsubscript{2}BiS\textsubscript{3}\textsuperscript{19,22} X-ray diffraction (XRD) revealed that M(II)\textsubscript{2}M(III)Ch\textsubscript{2},X\textsubscript{3} materials crystallize predominantly in an orthorhombic Cmcm space group.\textsuperscript{16,18–22} For Sn\textsubscript{2}SbS\textsubscript{3}, density functional
theory (DFT) calculations demonstrated that this Cmcm structure has to be interpreted as an average over energetically more favorable, lower symmetry Cmc21 configurations.11 XRD measurements by Doussier et al. further found that PbSbS13 changes to a monoclinic P21/c structure below 100 K.21 This P21/c structure was then shown to be lower in energy than the Cmcm and Cmc21 phases for SnSbS13 by DFT.17 In addition, for SnSbS13, UV–vis absorption spectroscopy and DFT calculations revealed that the optical band gap lies below 1.5 eV.11,12,23 This limits its applications to single-junction solar cells as the band gap is close to the optimum value of harvesting solar radiation (1.3 eV).24,25 In contrast, materials with a wide band gap (1.6–2.5 eV) will be of interest for emerging applications such as indoor and tandem photovoltaics.36

Materials’ exploration can facilitate materials’ discovery for targeted properties, and we apply it here to look for promising SnM(III)ChX3 materials. By now, many materials’ databases have been compiled,27 and one could search them for materials that meet specified design criteria.28–30 Materials or compounds that are not expected to be catalogued in databases can be explored by means of high-throughput computational or synthesis methods, often aided by machine-learning.31–36 Higher dimensional spaces offered by, e.g., quaternary or quinary materials, still pose challenges due to their sheer size and complexity. Such high-dimensional material spaces have therefore only been explored partially.

We here add an exploration of a SnM(III)ChX3 quaternary and quinary subspace for lead-free photovoltaic devices, which is chosen such that it can still be explored with DFT. For the M(III)-site, we considered both Sb3+ and Bi3+ (ns2 lone pair) and In(III) (with ns0 (d10) valence electron configuration). The chalcogen (Ch) site is populated by S2−, Se2−, or Te2− and the halogen (X) sites by Cl−, Br−, or I−, which yields altogether 27 materials. We furthermore accounted for structural diversity by including the three reported space groups (Cmcm, Cmc21, and P21/c).

For each material and each phase, we carried out DFT calculations within the generalized gradient approximation to assess structural stability and with a hybrid functional to quantify the electronic structure. We then screened for thermodynamic stability and a suitable band gap. Promising material candidates are cross-checked against a variety of databases and data sets to assess their novelty. Lastly, we investigated the potential to tailor the band gap by exploring different SnM(III)1−xM(III)′xCh2−xCh′X3−xX′ alloys.

The outline of this article is as follows: In Section 2, we describe our computational workflow including the screening criteria and the material cross check. In Section 3, we present and discuss our results for promising SnM(III)ChX3 materials as well as for SnM(III)1−xM(II)′xCh2−xCh′X3−xX′ alloys. We conclude with a summary in Section 4.

2. COMPUTATIONAL DETAILS

2.1. DFT Calculations. We performed periodic, spin unpolarized DFT calculations with the all-electron, numeric atom-centered orbital code FHI-AIMS.37–42 For exchange and correlation (XC), we used the Perdew–Burke–Ernzerhof functional for solids (PBEsol),43,44 which provides good agreement with experiment for the lattice constants of various halide perovskites at reasonable computational costs.45–47 The atomic structure was relaxed with the Broyden–Fletcher–Goldfarb–Shanno algorithm and analytical stress tensor.38 Every structure was preoptimized using a light real-space grid setting with a tier-1 basis set and was refined with tight settings and a tier-2 basis set. We applied a Gaussian broadening of 0.01 eV to the electronic occupations, and relativistic effects were considered based on the zero-order regular approximation.39,49 The convergence threshold for the electronic self-consistency was set to 1 × 10−6 eV. The SnM(III)ChX3 structures were relaxed until all forces acting on the atoms were smaller than 5 × 10−3 eV Å−1. Following the structural optimizations with PBEsol, we performed single-point calculations for the band structure, the band gap, and the absorption spectra with the range-separated hybrid Heyd–Scuseria–Ernzerhof (HSE06) XC functional (with 25% exact exchange),50–52 spin orbit coupling,53 and also a tier-2 basis. The latter were calculated on the basis of the linear macrosopic dielectric tensor54 within the independent particle approximation.

We calculated each material in three crystal structures. For the #63/Cmcm (see Figure 1a) and #36/Cmc21 (see Figure 1b) phases, we used 16 atom unit cells and for the #14/P21/c (see Figure 1c) phase, a 32 atom unit cell. In Section 2.2, we describe the three crystal structures of Cmcm, Cmc21, and P21/c in more detail. A Γ-centered k-point mesh was used for the PBEsol and HSE06 calculations. For the atomic structure relaxation with PBEsol, we used a Γ-centered 11 × 11 × 3 k-point mesh for the Cmcm and Cmc21 phases and a 6 × 3 × 5 mesh for P21/c. The HSE band structure calculations were performed with Γ-centered 16 × 16 × 4 for Cmcm and Cmc21 and 9 × 4 × 8 for P21/c.
To estimate the thermodynamic stability (at 0 K), we calculated the formation energy with respect to elemental decomposition of an individual Sn₃M(III)Chₓ material as

\[ E_{\text{form}}(\text{Sn}_3\text{M(III)\text{Ch}x}) = E_{\text{tot}}(\text{Sn}_3\text{M(III)\text{Ch}x}) - \sum_i x_i \mu_i \]

(1)

\( E_{\text{tot}}(\text{Sn}_3\text{M(III)\text{Ch}x}) \) denotes the (DFT-calculated) total energy of \( \text{Sn}_3\text{M(III)\text{Ch}x} \), \( \mu_i \) is the chemical of the \( i \)-th element, and \( x_i \) is the corresponding number of atoms. The upper limit for the chemical potential is given by \( \mu_i \leq E_{\text{tot}}(\text{th element}) \), i.e., the total energy per atom in the most stable phase of the \( i \)-th element.\(^{55}\) We used the following elemental compounds applying analogous computational parameters (with adjusted \( \Gamma \)-centered k-point mesh): Sb R3m (#166), Bi R3m (#166), In I/mmm (#139), S Fdd2 (#70), Se P2₁/c (#14), and Te P2₃2₁ (#152) as well as Cl, Br, and I in the gas phase as \( X_i \).

In the interest of open materials science,\(^{27}\) all relevant data are publicly available 10.17172/NOMAD/2023.08.24−1.

### 2.2. \( \text{Sn}_3\text{M(III)\text{Ch}X}_3 \) Structures

\( \text{Sn}_3\text{M(III)\text{Ch}X}_3 \) has been reported in three different space groups: \( \text{Ccmm} \), \( \text{Cmc2}_1 \), and \( \text{P2}_1/c \) (Figure 1). In the \( \text{Ccmm} \) phase, \( \text{Sn}_3\text{Ch}_3 \) pyramids share edges and form periodically continued \( \text{Sn}_3\text{Ch}_3 \) chains along the \( a \) axis. The 1D \( \text{Sn}_3\text{Ch}_3 \) chains in \( \text{Sn}_3\text{M(III)\text{Ch}X}_3 \) are connected by a M(III)X unit along the \( c \) axis to form a 2D \( \text{Sn}_3\text{M(III)\text{Ch}X}_3 \) structure within the \( ac \) plane. These 2D planes are not connected by chemical bonds along the \( b \) axis (see Figure 1a). In \( \text{Cmc2}_1 \) (Figure 1b), the M(III)X element exclusively bonds to a single \( \text{Sn}_3\text{Ch}_3 \) chain, forming a periodically linked \( \text{Sn}_3\text{M(III)\text{Ch}X}_3 \) chain along the \( a \) axis, while the periodic connection along the \( c \) axis is interrupted. Analogous to the case for \( \text{Ccmm} \), no linking is present along the \( b \) axis. The asymmetric location of M(III) between the chains (i.e., different from \( \text{Ccmm} \)) results in a reduction of every second square pyramidal \( \text{Sn}_3\text{Ch}_3 \) polyhedron to an \( \text{Sn}_3 \) tetrahedron while simultaneously forming an additional square pyramidal \( \text{Sn}_3\text{Ch}_3 \) polyhedron. The \( \text{P2}_1/c \) structure (Figure 1c) is characterized by \( \text{Sn}_3\text{Ch}_3 \) units, which are composed of four pyramids: \( \text{Sn}_3\text{Ch}_3 \text{−Sn}_3\text{Ch}_3 \text{−Sn}_3\text{Ch}_3 \text{−Sn}_3\text{Ch}_3 \). \( \text{Sn}_3\text{Ch}_3 \) and \( \text{Sn}_3\text{Ch}_3 \) share faces and the two \( \text{Sn}_3\text{Ch}_3 \) units, edges. Along the \( c \) axis, two neighboring \( \text{Sn}_3\text{Ch}_3 \) units are linked by two M(III) atoms, each forming a square pyramidal M(III)Chₓ. In addition, neighboring \( \text{Sn}_3\text{Ch}_3 \) units share corners (X) along the \( b \) direction, thus forming a 2D \( \text{Sn}_3\text{M(III)\text{Ch}X}_3 \) structure within the \( bc \) plane.

We generated the initial structures of the individual \( \text{Sn}_3\text{M(III)\text{Ch}X}_3 \) compounds from those of known materials listed in the Materials Project.\(^{56}\) For \( \text{Ccmm} \) and \( \text{Cmc2}_1 \), we adopted the \( \text{Sn}_3\text{Sb}_2\text{I}_3 \) structures (ref numbers: mp-561134 and mp-1219046) and for \( \text{P2}_1/c \), the \( \text{Pb}_3\text{Sb}_2\text{I}_3 \) structure (ref number: mp-578882). We then replaced any Pb by Sn and carried out corresponding replacements on the M(III), Ch, and X positions to generate a total of 27 \( \text{Sn}_3\text{M(III)\text{Ch}X}_3 \) compounds per space group. These were then geometry-optimized with PBEsol before we computed the electronic structure with HSE06 + SOC.

### 2.3. Screening Criteria

The aim of this study is to screen the mixed-metal chalcophile \( \text{Sn}_3\text{M(III)\text{Ch}X}_3 \) material space for compounds that are suitable for photovoltaic applications and have the potential to increase their PCE. We first consider formation energies to estimate the materials’ chemical stability. Chemical stability itself is hard to quantify because it depends on the temperature, the chemical space, the synthesis process, and the environmental conditions. To first order, we therefore approximate the chemical stability by the thermodynamic stability with respect to elemental decomposition computed at 0 K as expressed in eq 1. This allows us to draw first conclusions about the energetic preference of the \( \text{Sn}_3\text{M(III)\text{Ch}X}_3 \) compounds.

The band gap should be in the range of 1.0−1.8 eV for outdoor or 1.5−2.0 eV for indoor photovoltaics\(^{24,58}\) according to the Shockley–Queisser limit. In our DFT calculations, we observe a difference of around 0.3 eV between the fundamental and optical band gap for some \( \text{Sn}_3\text{M(III)\text{Ch}X}_3 \) materials (see the discussion in Section 3.1). We therefore set a target range of 0.7−2.0 eV to encompass indoor and outdoor photovoltaic applications and incorporate the ~0.3 eV shift.

### 2.4. Novelty Check

To ascertain which materials in the \( \text{Sn}_3\text{M(III)\text{Ch}X}_3 \) space have already been made or are known, we query a variety of materials’ databases. The OPTIMADE python API\(^{19,60}\) provides an easy way to search a selection of databases with a single query. Our search includes the following 16 databases: Automatic FLOW for Materials Discovery (AFLOW),\(^{51,62}\) Alexandria, Computational materials repository (CMR), Crystallography Open Database (COD),\(^{63,64}\) Cambridge Crystallographic Database (CCD),\(^{65}\) Inorganic Crystal Structure Database (ICSD),\(^{66,69}\) Joint Automated Repository for Various Integrated Simulations (JARVIS),\(^{70}\) Materials Cloud,\(^{71−73}\) Materials Project,\(^{74}\) Materials Platform for Data Science (MPDS), Novel Materials Discovery Laboratory (NOMAD),\(^{74,75}\) Open Database of XtalS (odbx),\(^{76}\) Open Materials Database (omdb),\(^{77}\) Open Quantum Materials Database (OQMD),\(^{78}\) Theoretical Crystallography Open Database (TCOD),\(^{79}\) and 2D Materials Encyclopedia. In addition, we also included in our search the DCGAT-3 data set by Schmidt et al., which was used to train their third-generation crystal-graph attention network and includes about 3.18 million crystalline compounds, including a large number of quaternary materials.\(^{31}\)

### 3. RESULTS AND DISCUSSION

#### 3.1. Promising \( \text{Sn}_3\text{M(III)\text{Ch}X}_3 \) Materials

\( \text{Sn}_3\text{Sb}_2\text{I}_3 \) has already been studied with DFT by Kavanagh et al.\(^{11}\) and

<table>
<thead>
<tr>
<th>( \Delta E_{\text{form}} ) (Ccmm)</th>
<th>( \Delta E_{\text{form}} ) (P2₁/c)</th>
<th>functional</th>
<th>( E_g ) (Ccmm)</th>
<th>( E_g ) (Cmc2₁)</th>
<th>( E_g ) (P2₁/c)</th>
<th>functional</th>
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</thead>
<tbody>
<tr>
<td>Kavanagh et al(^{11})</td>
<td>−36</td>
<td>optB86b-vD</td>
<td>1.02*</td>
<td>1.08</td>
<td></td>
<td>HSE06 + SOC</td>
</tr>
<tr>
<td>Nicolson et al(^{17})</td>
<td>−11</td>
<td>−71</td>
<td>optB86b-vD</td>
<td></td>
<td></td>
<td>HSE06 + SOC</td>
</tr>
<tr>
<td>our work</td>
<td>−11</td>
<td>−69</td>
<td>PBEsol</td>
<td>0.947*</td>
<td>1.007</td>
<td>1.78*</td>
</tr>
</tbody>
</table>

*The energy of the reference Cmc2₁ phase is set to 0. Previous DFT results are included for comparison. Fundamental band gaps for Cmc2₁, Cmc2₁, and P2₁/c are given in eV. Indirect band gaps are marked with an *.\(^{24,58}\)
which provides us with an opportunity to validate our computational approach. Our PBEsol results for the energy differences between the Cmcm and $P_2_1/c$ phases and the Cmc2_1 phase are reported in Table 1 and are in good agreement with the optB86b-vdW results of Kavanagh and Nicolson.

Our band gap values calculated with HSE06 for Sn$_3$SbS$_3$I$_3$ agree well with the literature for all three phases; see Table 1. A direct gap is determined for Cmcm and indirect gaps are determined for Cmc2_1 and P2_1/c.

In addition, Kavanagh et al. reported that the absorption edge is larger than the fundamental band gap for Sn$_3$SbS$_3$I$_3$. The authors proposed two reasons: (I) a low density of states at the band edges caused by a low electronic degeneracy due to the low crystal symmetry (for Cmc2_1 and Cmc2_1) and (II) a weak transition dipole moment between the valence band maximum and the conduction band minimum due to the symmetry restrictions and a low spatial overlap. As a result, the absorption intensity is very low at the onset of absorption close to the fundamental band gap. It then rises slowly as the joint density of states increases. Appreciable absorption intensity is then only observed at some tenth of eV above the fundamental gap. To check if this behavior translates to other compounds in the Sn$_2$M(III)Ch$_3$X$_3$ family, we calculated the absorption spectra for all 27 candidates. As an example, the absorption spectrum and the corresponding Tauc plot for Sn$_3$InS$_3$Br$_3$ in the Cmc2_1 phase are shown in Figure 2. The intensity at the fundamental band gap is weak but not zero. It then increases rapidly at $E_\alpha + -0.4$, which is most evident in (b). We define this transition point as “optical gap”. From the Tauc plot, we deduce that the optical gap lies 0.36 eV above the fundamental gap for Sn$_3$InS$_3$Br$_3$. The corresponding band structure is shown in Figure S1 of the Supporting Information.

For all 27 Sn$_2$M(III)Ch$_3$X$_3$ materials, we find a larger optical gap; see Table S1 in the Supporting Information. For compounds with a direct band gap, the optical band gap lies on average 0.291 eV above the fundamental gap. This difference is space group-dependent, with $\sim 0.376$ eV for Cmc2_1 and $\sim 0.123$ eV for $P_2_1/c$. For indirect band gap materials, the optical gap is also larger than the indirect fundamental gap ($E_{\text{gind}}$). However, if we compare it to the lowest direct gap ($E_{\text{gd}}$), the difference to the optical gap is only 0.049 eV on average and nearly identical for all space groups. This is caused by an increased spatial overlap between the valence band maximum and the conduction band. Therefore, our band gap criterion considers not only the slightly different ranges for indoor and outdoor photovoltaics but also the difference between the fundamental band gap and the absorption edge (see Section 2.3).

Our DFT calculations of the Sn$_2$M(III)Ch$_3$X$_3$ materials’ space subsequently identified 12 compounds that satisfy the screening criteria of thermodynamic stability (negative formation energy at 0 K) and fundamental direct band gap (in the range of 0.7–2.0 eV): Sn$_2$InS$_3$Br$_3$, Sn$_2$InS$_3$I$_3$, Sn$_2$InSe$_2$Cl$_3$, Sn$_2$InSe$_2$Br$_3$, Sn$_2$InTe$_2$Br$_3$, Sn$_2$InTe$_2$I$_3$, Sn$_2$SbS$_3$I$_3$, Sn$_2$SbSe$_3$I$_3$, Sn$_2$SbTe$_2$I$_3$, Sn$_2$BiSe$_3$I$_3$, and Sn$_2$BiTe$_2$I$_3$. The formation energies of the 12 compounds in all three considered space groups are illustrated in Figure 3.

A detailed overview of the formation energies of all 27 Sn$_2$M(III)Ch$_3$X$_3$ compounds, as well as their lattice parameters, fundamental band, and optical band gaps, is reported in Table 1 of the Supporting Information.

All 27 Sn$_2$M(III)Ch$_3$X$_3$ structures are stable with respect to elemental decomposition (see Table S1 of the Supporting Information), but not all fall into the desired band gap range. For the 12 candidates, the most stable material is Sn$_2$InS$_3$Cl$_3$ ($-718$, $-767$, and $-765$ meV atom$^{-1}$ for Cmc2_1, Cmcm, and P2_1/c, respectively). The In-based compounds are, in most cases, significantly more stable than their Sb- and Bi-based counterparts, with the Cmcm phase being preferred. Sn$_2$InS$_3$I$_3$, in which the P2_1/c structure is the most stable, is an exception. For the Sb or Bi compounds, the P2_1/c phase is the most stable. The formation energy decreases from Sn$_2$M(III)Ch$_3$Cl$_3$ over Sn$_2$M(III)Ch$_3$Br$_3$ toward Sn$_2$M(III)Ch$_3$I$_3$, which is natural as Cl forms the strongest metal–halide bonds due to the highest electronegativity among the three halogen elements.

An analogous behavior is obtained for 15 Sn$_2$M(III)Ch$_3$X$_3$ compounds with an indirect fundamental gap (which we refer to as indirect Sn$_2$M(III)Ch$_3$X$_3$): Sn$_2$InS$_3$Cl$_3$, Sn$_2$InSe$_2$I$_3$, Sn$_2$InTe$_2$I$_3$, Sn$_2$SbS$_3$I$_3$, Sn$_2$SbSe$_3$I$_3$, Sn$_2$SbTe$_2$I$_3$, Sn$_2$BiSe$_2$I$_3$, Sn$_2$BiSe$_2$I$_3$, Sn$_2$BiTe$_2$I$_3$, and Sn$_2$BiTe$_2$I$_3$. The lowest direct gap in these 15 materials is also within the screening range of 0.7 to 2.0 eV. Their formation energies are
reported in Figure S2 and Table S1 in the Supporting Information.

Our band gap results of the 27 Sn₃M(III)ChₓXₙ materials reveal that the space group influences the nature of the gap. For example, for Sn₃InS₂Br₃, the Cmcm and Cmc2₁ structures have a direct band gap but not P2₁/c. However, replacing S with Se leads to a direct band gap for the Cmcm structure and an indirect band gap for the other two structures. Overall, it turns out that all 12 identified materials have at least one space group with an indirect band gap. In Figure 4, the direct band gaps for the 12 Sn₃M(III)ChₓXₙ materials are shown.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Direct band gaps (HSE06 + SOC level of theory) for 11 Sn₃M(III)ChₓXₙ materials of interest for Cmcm (green), Cmc2₁ (red), and P2₁/c (blue) space groups. Three structures—Sn₃SbS₂I₄, Sn₃SbSeI₃, and Sn₃BiS₂I₃—that are already known from the literature are highlighted in purple.

The Cmcm and Cmc2₁ phases tend to have direct band gaps, whereas the P2₁/c structures exhibit indirect gaps. As a result, only two P2₁/c compounds (Sn₃InTe₂Cl₃ and Sn₃InTe₂Br₃) fall into our targeted band gap region. Also, the band gap values depend on the space-group. Gaps of the Cmc2₁ structures lie around 1 eV except for Sn₃InS₂Br₃. In contrast, Cmcm phases have larger band gaps of ~1.4–1.5 eV with the exception of Sn₃BiS₂I₃ and Sn₃InSe₂Br₃. In general, direct band gaps are largest for P2₁/c and smallest for Cmc2₁ with Cmcm in between (see also Table 2). A similar picture emerges for the lowest direct band gaps in indirect gap materials (see Table S2 and Figure S3 of the Supporting Information).

In summary, our results indicate that the band gaps of indium-based Sn₃M(III)ChₓXₙ compounds lie in the middle and upper regions of our screening range, making them interesting for both indoor and outdoor photovoltaics. However, the scarcity of indium becomes a cost factor, whereby a number of efforts are underway to ensure the long-term supply of indium through significant changes in processing and recycling. With band gaps of around 1 eV, antimony- and bismuth-based Sn₃M(III)ChₓXₙ materials would be interesting for outdoor photovoltaics. Considering antimony’s toxicity, bismuth-based Sn₃M(III)ChₓXₙ materials might be promising contenders.

Lastly, we check which Sn₃M(III)ChₓXₙ materials are already known or have appeared in databases or data sets. Our search reveals that only three materials have been reported so far: Sn₃SbS₂I₄, Sn₃SbSeI₃, and Sn₃BiS₂I₃ For Sn₃SbS₂I₄, structures in all three space groups are known, but for the other two, only Cmcm and Cmc2₁ have been reported. To the best of our knowledge, we are the first to present the nine direct band gaps materials (Sn₃InS₂Br₃, Sn₃InS₂I₄, Sn₃InSe₂Cl₃, Sn₃InSe₂Br₃, Sn₃InTe₂Br₃, Sn₃InTe₂Cl₃, Sn₃SbSe₂Cl₃, Sn₃SbSe₂Br₃, and Sn₃BiTe₂Cl₃) and the 15 Sn₃M(III)Chₓ indirect band gaps materials (Sn₃InS₂Cl₃, Sn₃InSe₂Cl₃, Sn₃InTe₂Cl₃, Sn₃SbS₂Br₃, Sn₃SbSe₂Br₃, Sn₃SbSe₂Cl₃, Sn₃BiS₂Cl₃, Sn₃BiS₂Br₃, Sn₃BiSe₂Cl₃, Sn₃BiSe₂Br₃, Sn₃BiTe₂Cl₃, and Sn₃BiTe₂Br₃).

3.2. Promising Sn₃M(III)₁₋ₓM(III)ₓCh₂₋ₓCh’ₓXₙ₋ₓ’x’ Alloys.

In this section, we extend the materials’ space to possible binary Sn₃M(III)₁₋ₓM(III)ₓCh₂₋ₓCh’ₓXₙ₋ₓ’x’ alloys with band gaps in the desired range. We consider alloys within the same space group for which (1) at least one compound has a direct band gap in the target range or (II) one compound has a direct band gap below 0.7 eV and the another above 2 eV. We identified 12 Sn₃M(III)₁₋ₓM(III)ₓCh₂₋ₓCh’ₓXₙ₋ₓ’x’ suitable alloys (see Figure S5). We expect direct band gaps in at least some of the compositions. With such alloys, the band gap can be tuned for specific optoelectronic applications. To the best of our knowledge, none of these binary Sn₃M(III)₁₋ₓM(III)ₓCh₂₋ₓCh’ₓXₙ₋ₓ’x’ alloy compounds have been studied in the literature yet.

We find that the Cmc2₁ space group is most prevalent, followed by Cmcm. Only a single binary alloy has the P2₁/c space group because of the phase’s preference for indirect gaps. Materials in the Cmc2₁ space group tend toward lower band gaps close to 1 eV because the parent compounds have small gaps. One exception is Sn₃InS₂–₂Te₃Br₅, which combines Sn₃InTe₂Br₃ (E₁ ≈ 0.531 eV) and Sn₃InTe₂Br₃ (E₂ ≈ 1.742 eV), resulting in a broad range of 1.211 eV. For the three Cmcm alloys, we find Sn₃In₁₋ₓBiₓS₂I₄ at the lower end and Sn₃In₁₋ₓSe₂Br₃ and Sn₃InₓSe₂Br₃ in the middle of the range. If we drop our restriction of mixing compounds with a direct gap, we obtain an additional 69 Sn₃M(III)₁₋ₓ–M(III)ₓCh₂₋ₓCh’ₓXₙ₋ₓ’x’ alloys, reported in Figure S4 of the Supporting Information.

Our results indicate that Sn₃M(III)₁₋ₓ–M(III)ₓCh₂₋ₓCh’ₓXₙ₋ₓ’x’ alloys with indium and iodine offer the most flexibility (i.e., widest tuning ranges). However, considering the scarcity of indium and the relatively high toxicity of antimony, alloys with bismuth would be favored. Since we could not identify a suitable bismuth alloy, Sn₃Inₓ–ₓBiₓS₂I₄ might offer the best environmentally friendly compromise.

4. CONCLUSIONS

In the pursuit of low-toxicity photovoltaic materials, we used DFT to explore the Sn₃M(III)ChₓXₙ material space. We identified 12 absorbers that fulfill our requirements by being lead-free, thermodynamically stable, and with a direct band gap in the screening range of 0.7–2.0 eV. Three of these Sn₃M(III)ChₓXₙ were known previously, while the remaining nine materials, i.e., Sn₃InS₂Br₃, Sn₃InS₂I₄, Sn₃InSe₂Cl₃, Sn₃InTe₂Br₃, Sn₃InTe₂Cl₃, Sn₃SbSe₂Cl₃, Sn₃SbSe₂Br₃, Sn₃BiTe₂Cl₃, and Sn₃BiTe₂Br₃ are reported here for the first time. The majority of these compounds contain indium, including some of the most promising candidates such as Sn₃InSe₂Br₃ or Sn₃InS₂Br₃. An alternative to indium- and antimony-based Sn₃M(III)ChₓXₙ materials is bismuth-based ones, such as, e.g., Sn₃BiTe₂Cl₃ although the band gap is smaller than its indium-based counterparts. In addition, we identified 15 previously unknown Sn₃M(III)ChₓXₙ compounds
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For indirect compounds, the band gaps of the lowest direct transition (E_{g,dir}) as well as of the lowest indirect transition (E_{g,ind}) are provided. Sn_{2}M(III)Cl_{3} materials with a direct fundamental band gap are bold, and those with an indirect one are italic.
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Notes
The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

The authors thank Milica Todorović and Armi Tiihonen for fruitful discussions. This study was supported by the Academy of Finland through Project no. 334532 and the National Natural Science Foundation of China (Grant no. 62281330404). P.H., J.L., and P.R. further acknowledge the CSC-IT Center for Science, Finland, the Aalto Science-IT project, Xi’an Jiaotong University’s HPC platform, and the Hefei Advanced Computing Center of China for generous computational resources. P.V. acknowledges the financial support of Academy of Finland, Decision no. 347772. This work is part of the Academy of Finland Flagship Programme, Photonics Research and Innovation (PREIN), Decision no. 320165. G.K.G. acknowledges Tampere Institute for Advanced Study for postdoctoral funding.

# REFERENCES


ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.chemmater.3c01629.

Band structure for Sn2InS2Br3 (Cmcm); lattice parameters, formation energies, and fundamental (direct and indirect) and optical gaps for all Sn2M(III)ChX3 materials; formation energies of indirect Sn2M(III)ChX3 materials; band gaps for all Sn2M(III)ChX3 materials; and Sn2M(III)ChX3 alloys (PDF)

ASSOCIATED CONTENT

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Figure 5. Band gap ranges (HSE06 + SOC level of theory) for the 12 Sn2M(III)1−M(III)′Ch2−Ch′X3−X′ binary alloys of interest for Cmcm (green), Cmc21 (red), and P21/c (blue) space groups.

with indirect band gaps, which have the lowest direct band gap within the screening range.

We investigated the potential to tune the band gap by exploring Sn2M(III)1−M(III)′Ch2−Ch′X3−X′ alloys. In total, 12 Sn2M(III)1−M(III)′Ch2−Ch′X3−X′ alloys were identified by alloying within the same phase and considering only structures with direct gaps. For example, the fundamental gap of SnIn1−BiS2Br3 can be tuned between 0.988 and 1.395 eV. Furthermore, we identified additional 69 Sn2M(III)1−M(III)′Ch2−Ch′X3−X′ alloys by dropping our requirement to use only direct band gap Sn2M(III)ChX3 end structures, which significantly broadens the Sn2M(III)1−M(III)′Ch2−Ch′X3−X′ spectra.

Our findings highlight the relevance of materials’ design and theoretical explorations, and the identified Sn2M(III)ChX3 materials, and Sn2M(III)1−M(III)′Ch2−Ch′X3−X′ alloys encourage the synthesis and the use of highly stable materials in various optoelectronic devices.


