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Article

# Screening Mixed-Metal Sn<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> Chalcohalides for **Photovoltaic Applications**

Pascal Henkel, Jingrui Li, G. Krishnamurthy Grandhi, Paola Vivo, and Patrick Rinke\*

Cite This: Chem. Mater. 2023, 35, 7761-7769 **Read Online** ACCESS III Metrics & More Article Recommendations Supporting Information **ABSTRACT:** Quaternary mixed-metal chalcohalides  $(Sn_2M(III)Ch_2X_3)$  are Sn<sub>2</sub>BCh<sub>2</sub>X<sub>3</sub> space energy emerging as promising lead-free, perovskite-inspired photovoltaic absorbers. Motivated by recent developments of a first Sn<sub>2</sub>SbS<sub>2</sub>I<sub>3</sub>-based device, we used optical density functional theory to identify lead-free Sn<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> materials that band gaps are structurally and energetically stable within Cmcm,  $Cmc2_1$ , and  $P2_1/c$  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<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> materials

were studied, including Sb, Bi, and In 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<sub>2</sub>InS<sub>2</sub>Br<sub>3</sub>, Sn<sub>2</sub>InS<sub>2</sub>I<sub>3</sub>, Sn<sub>2</sub>InSe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>InSe<sub>2</sub>Br<sub>3</sub>, Sn<sub>2</sub>InTe<sub>2</sub>Br<sub>3</sub>, Sn<sub>2</sub>InTe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>SbS<sub>2</sub>I<sub>3</sub>, Sn<sub>2</sub>SbSe<sub>2</sub>Cl<sub>3</sub>,



Sn<sub>2</sub>SbSe<sub>2</sub>I<sub>3</sub>, Sn<sub>2</sub>SbTe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>BiS<sub>2</sub>I<sub>3</sub>, and Sn<sub>2</sub>BiTe<sub>2</sub>Cl<sub>3</sub>. A database scan reveals that 9 of 12 are new compositions. For all 27 materials,  $P2_1/c$  is the thermodynamically preferred structure, followed by  $Cmc2_1$ . In Cmcm and  $Cmc2_1$ , mainly direct gaps occur, whereas indirect gaps occur in  $P2_1/c$ . To open up the possibility of band gap tuning in the future, we identified 12 promising Sn<sub>2</sub>M(III)<sub>1-a</sub>M(III)'<sub>a</sub>Ch<sub>2-b</sub>Ch'<sub>b</sub>X<sub>3-c</sub>X'<sub>c</sub> alloys, 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 costeffective solution processing. Yet, the toxicity of lead and the moderate long-term stability in air<sup>1-4</sup> impede the commercial viability of LHPs. Sn<sup>2+</sup>-based perovskites and Sb<sup>3+</sup>- and Bi<sup>3+</sup>based perovskite-inspired absorbers are popular low-toxicity alternatives, but they suffer from air-oxidation  $(Sn^{2+} to Sn^{4+})^{5}$ and high defect densities.<sup>6,7</sup> Conversely, metal chalcogenides (e.g., Pb-, Cd-, Sb-based)<sup>8-10</sup> 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)<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> stoichiometry (also referred to as A<sub>2</sub>BCh<sub>2</sub>X<sub>3</sub>)<sup>11</sup> are an emerging semiconductor family combining halide perovskite and metal chalcogenide building blocks.<sup>11-13</sup> 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  $ns^2$ lone pair cations), and the resultant low capture cross sections of defects,<sup>1,2,12</sup> with the promise to overcome the pressing stability challenges of LHPs.<sup>4,12</sup> In addition, the Sn-Ch bonding nature should prevent Sn<sup>2+</sup> to Sn<sup>4+</sup> oxidation in mixed-metal chalcohalides. Also, experimental X-ray photoelectron spectroscopy measurements suggest that synthesizing Sn<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> under reduction conditions partly suppresses  $Sn^{2+}$  to  $Sn^{4+}$  oxidation.<sup>12</sup> As a result,  $Sn_2M(III)Ch_2X_3$  films are stable even in humid environments.<sup>11,12</sup> The photovoltaic potential of mixed-metal chalcohalides was recently demonstrated for a Sn<sub>2</sub>SbS<sub>2</sub>I<sub>3</sub>-based single-junction solar cell that achieved a PCE of 4.04%.<sup>12</sup> This is a promising start considering that the first perovskite solar cells only reached a PCE of 3.8% in 2009<sup>14</sup> and now exceed 25%.<sup>15</sup>

Over the past four decades, the  $M(II)_2M(III)Ch_2X_3$  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  $Sn_2SbS_2I_3$ ,<sup>11,12,16,17</sup>  $Sn_2SbSe_2I_3$ ,<sup>18</sup>  $Sn_2BiS_2I_3$ ,<sup>19</sup>  $Pb_2SbS_2I_3$ ,<sup>20–22</sup> and  $Pb_2BiS_2I_3$ .<sup>19,22</sup> X-ray diffraction (XRD) revealed that M(II)<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> materials crystallize predominantly in an orthorhombic *Cmcm* space group.<sup>16,18-22</sup> For Sn<sub>2</sub>SbS<sub>2</sub>I<sub>3</sub>, density functional

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**Figure 1.** Visualization of the  $Sn_2M(III)Ch_2X_3$  structure in different space groups; (a) *Cmcm*, (b) *Cmc2*<sub>1</sub>, and (c) *P2*<sub>1</sub>/*c* for the example of  $Sn_2SbS_2I_3$ . The coordinating polyhedrons associated with the Sn/(A) positions are depicted in cyan, and those associated with the M(III) position are in green. The coordinates of each space group were taken from the Materials Project<sup>56</sup> and were visualized with VESTA.<sup>57</sup>

theory (DFT) calculations demonstrated that this *Cmcm* structure has to be interpreted as an average over energetically more favorable, lower symmetry *Cmc*2<sub>1</sub> configurations.<sup>11</sup> XRD measurements by Doussier et al. further found that Pb<sub>2</sub>SbS<sub>2</sub>I<sub>3</sub> changes to a monoclinic *P*2<sub>1</sub>/*c* structure below 100 K.<sup>21</sup> This *P*2<sub>1</sub>/*c* structure was then shown to be lower in energy than the *Cmcm* and *Cmc*2<sub>1</sub> phases for Sn<sub>2</sub>SbS<sub>2</sub>I<sub>3</sub> by DFT.<sup>17</sup> In addition, for Sn<sub>2</sub>SbS<sub>2</sub>I<sub>3</sub>, UV–vis absorption spectroscopy and DFT calculations revealed that the optical band gap lies below 1.5 eV.<sup>11,12,23</sup> 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).<sup>24,25</sup> 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.<sup>26</sup>

Materials' exploration can facilitate materials' discovery for targeted properties, and we apply it here to look for promising  $Sn_2M(III)Ch_2X_3$  materials. By now, many materials' databases have been compiled,<sup>27</sup> and one could search them for materials that meet specified design criteria.<sup>28–30</sup> 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.<sup>31–36</sup> 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  $\text{Sn}_2\text{M}(\text{III})\text{Ch}_2X_3$  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  $\text{Sb}^{3+}$  and  $\text{Bi}^{3+}$  ( $ns^2$  lone pair) and In(III) (with  $ns^0$  (d<sup>10</sup>) valence electron configuration). The chalcogen (Ch) site is populated by  $\text{S}^{2-}$ ,  $\text{Se}^{2-}$ , or  $\text{Te}^{2-}$  and the halogen (X) sites by Cl<sup>-</sup>, Br<sup>-</sup>, or I<sup>-</sup>, which yields altogether 27 materials. We furthermore accounted for structural diversity by including the three reported space groups (*Cmcm*, *Cmc2*<sub>1</sub>, and  $P2_1/c$ ).

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  $Sn_2M(III)_{1-a}M(III)_{a}Ch_{2-b}Ch'_{b}X_{3-c}X'_{c}$  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  $\text{Sn}_2\text{M}(\text{III})\text{Ch}_2\text{X}_3$  materials as well as for  $\text{Sn}_2\text{M}(\text{III})_{1-a}\text{M}(\text{III})'_a\text{Ch}_{2-b}\text{Ch}'_b\text{X}_{3-c}\text{X}'_c$  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.<sup>37-42</sup> For exchange and correlation (XC), we used the Perdew-Burke-Ernzerhof functional for solids (PBEsol),<sup>43,44</sup> which provides good agreement with experiment for the lattice constants of various halide perovskites at reasonable computational costs.<sup>45–47</sup> The atomic structure was relaxed with the Broyden-Fletcher-Goldfarb-Shanno algorithm and analytical stress tensor.<sup>48</sup> 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.<sup>37,49</sup> The convergence threshold for the electronic selfconsistency was set to  $1 \times 10^{-6}$  eV. The Sn<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> structures were relaxed until all forces acting on the atoms were smaller than 5  $\times$  10<sup>-3</sup> eV Å<sup>-1</sup>. 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),<sup>50-52</sup> spin orbit coupling,<sup>53</sup> and also a tier-2 basis. The latter were calculated on the basis of the linear macroscopic dielectric tensor<sup>54</sup> within the independent particle approximation.

We calculated each material in three crystal structures. For the #63/*Cmcm* (see Figure 1a) and #36/*Cmc2*<sub>1</sub> (see Figure 1b) phases, we used 16 atom unit cells and for the #14/*P2*<sub>1</sub>/*c* (see Figure 1c) phase, a 32 atom unit cell. In Section 2.2, we describe the three crystal structures of *Cmcm*, *Cmc2*<sub>1</sub>, and *P2*<sub>1</sub>/ *c* in more detail. A  $\Gamma$ -centered *k*-point mesh was used for the PBEsol and HSE06 calculations. For the atomic structure relaxation with PBEsol, we used a  $\Gamma$ -centered 11 × 11 × 3 *k*point mesh for the *Cmcm* and *Cmc2*<sub>1</sub> phases and a 6 × 3 × 5 mesh for *P2*<sub>1</sub>/*c*. The HSE band structure calculations were performed with  $\Gamma$ -centered 16 × 16 × 4 for *Cmcm* and *Cmc2*<sub>1</sub> and 9 × 4 × 8 for *P2*<sub>1</sub>/*c*.

Table 1. Relative	Energies of Both	Cmc2 <sub>1</sub> and P2 <sub>1</sub> /c Phase	s of Sn <sub>2</sub> SbS <sub>2</sub> I <sub>3</sub> with	Respect to the Cmcr	n Phase (Given in meV
$\operatorname{atom}^{-1})^{a}$	-			-	

	$\Delta E_{\rm form}~(Cmc2_1)$	$\Delta E_{\rm form} (P2_1/c)$	functional	$E_g$ (Cmcm)	$E_g (Cmc2_1)$	$E_g \left( P2_1/c \right)$	functional
Kavanagh et al <sup>11</sup>	-36		optB86b-vdW	1.02*	1.08		HSE06 + SOC
Nicolson et al <sup>17</sup>	-11	-71	optB86b-vdW			1.78*	HSE06 + SOC
our work	-11	-69	PBEsol	0.947*	1.007	1.686*	HSE06 + SOC
<sup>2</sup> 771		is set to 0 Duradian	DET	1 1 1 6		1 1	- for Communication

"The energy of the reference *Cmcm* phase is set to 0. Previous DFT results are included for comparison. Fundamental band gaps for *Cmcm*,  $Cmc2_1$ , and  $P2_1/c$  are given in eV. Indirect band gaps are marked with an \*.

To estimate the thermodynamic stability (at 0 K), we calculated the formation energy with respect to elemental decomposition of an individual  $Sn_2M(III)Ch_2X_3$  material as

$$E_{\text{form}}(\text{Sn}_2\text{M}(\text{III})\text{Ch}_2\text{X}_3)$$
  
=  $E_{\text{tot}}(\text{Sn}_2\text{M}(\text{III})\text{Ch}_2\text{X}_3) - \sum_i x_i\mu_i$  (1)

 $E_{tot}(Sn_2M(III)Ch_2X_3)$  denotes the (DFT-calculated) total energy of  $Sn_2M(III)Ch_2X_3$ ,  $\mu_i$  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  $\mu_i \leq E_{tot}(ith$ element), i.e., the total energy per atom in the most stable phase of the *i*th element.<sup>55</sup> We used the following elemental compounds applying analogous computational parameters (with adjusted  $\Gamma$ -centered *k*-point mesh): Sb R3m (#166), Bi R3m (#166), In I4/mmm (#139), S Fddd (#70), Se P2<sub>1</sub>/c (#14), and Te P3<sub>1</sub>21 (#152) as well as Cl, Br, and I in the gas phase as X<sub>2</sub>.

In the interest of open materials science,<sup>27</sup> all relevant data are publicly available 10.17172/NOMAD/2023.08.24–1.

**2.2.** Sn<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> Structures. Sn<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> has been reported in three different space groups: Cmcm, Cmc21, and  $P2_1/c$  (Figure 1). In the *Cmcm* phase, SnCh<sub>3</sub>X<sub>2</sub> pyramids share edges and form periodically continued [Sn<sub>2</sub>Ch<sub>2</sub>X<sub>2</sub>]<sub>n</sub> chains along the *a* axis. The 1D  $[Sn_2Ch_2X_2]_n$  chains in  $Sn_2M(III)$ - $Ch_2X_3$  Cmcm are connected by a M(III)X unit along the c axis to form a 2D  $Sn_2M(III)Ch_2X_3$  structure within the *ac* plane. These 2D planes are not connected by chemical bonds along the *b* axis (see Figure 1a). In  $Cmc2_1$  (Figure 1b), the M(III)X element exclusively bonds to a single  $[Sn_2Ch_2X_2]_n$  chain, forming a periodically linked [Sn<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub>], chain along the a axis, while the periodic connection along the c axis is interrupted. Analogous to the case for Cmcm, no linking is present along the b axis. The asymmetric location of M(III) between the chains (i.e., different from Cmcm) results in a reduction of every second square pyramidal SnCh<sub>2</sub>X<sub>3</sub> polyhedron to an SnX<sub>3</sub> tetrahedron while simultaneously forming an additional square pyramidal SnChX<sub>4</sub> polyhedron. The  $P2_1/c$  structure (Figure 1c) is characterized by  $Sn_4Ch_4X_8$ units, which are composed of four pyramids: SnChX<sub>4</sub>-SnCh<sub>3</sub>X<sub>2</sub>-SnCh<sub>3</sub>X<sub>2</sub>-SnChX<sub>4</sub>. SnChX<sub>4</sub> and SnCh<sub>3</sub>X<sub>2</sub> share faces and the two SnCh<sub>3</sub>X<sub>2</sub> units, edges. Along the c axis, two neighboring Sn<sub>4</sub>Ch<sub>4</sub>X<sub>6</sub> units are linked by two M(III) atoms, each forming a square pyramidal M(III)Ch<sub>3</sub>X<sub>2</sub>. In addition, neighboring  $Sn_4Ch_4X_6$  units share corners (X) along the b direction, thus forming a 2D  $Sn_4M(III)_2Ch_4X_6$  structure within the *bc* plane.

We generated the initial structures of the individual  $Sn_2M(III)Ch_2X_3$  compounds from those of known materials listed in the Materials Project.<sup>56</sup> For *Cmcm* and *Cmc2*<sub>1</sub>, we adopted the  $Sn_2SbS_2I_3$  structures (ref numbers: mp-561134 and mp-1219046) and for  $P2_1/c$ , the Pb<sub>2</sub>SbS<sub>2</sub>I<sub>3</sub> 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 Sn<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> 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 chalcohalide  $Sn_2M(III)Ch_2X_3$  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 elementary decomposition computed at 0 K as expressed in eq 1. This allows us to draw first conclusions about the energetic preference of the  $Sn_2M(III)$ - $Ch_2X_3$  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<sup>24,58</sup> 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 Sn<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> 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  $Sn_2M(III)Ch_2X_3$  space have already been made or are known, we query a variety of materials' databases. The OPTIMADE python API<sup>59,60</sup> 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),<sup>61,62</sup> Alexandria, Computational materials repository (CMR), Crystallography Open Database (COD),<sup>63,64</sup> Cambridge Crystallographic Database (CCD),<sup>65</sup> Inorganic Crystal Structure Database (ICSD),66-69 Joint Automated Repository for Various Integrated Simulations (JARVIS),<sup>70</sup> Materials Cloud,<sup>71–73</sup> Materials Project,<sup>56</sup> Materials Platform for Data Science (MPDS), Novel Materials Discovery Laboratory (NOMAD),<sup>74,75</sup> Open Database of Xtals (odbx),<sup>76</sup> Open Materials Database (omdb),<sup>77</sup> Open Quantum Materials Database (OQMD),<sup>78</sup> Theoretical Crystallography Open Database (TCOD),<sup>79</sup> and 2D Materials Encyclopedia.<sup>80</sup> In addition, we also included in our search the DCGAT-3 data set by Schmidt et al., which was used to train their thirdgeneration crystal-graph attention network and includes about 3.18 million crystalline compounds, including a large number of quaternary materials.<sup>31</sup>

# 3. RESULTS AND DISCUSSION

**3.1.** Promising  $Sn_2M(III)Ch_2X_3$  Materials.  $Sn_2Sb_2I_3$  has already been studied with DFT by Kavanagh et al.<sup>11</sup> and

Nicolson et al.,<sup>17</sup> which provides us with an opportunity to validate our computational approach. Our PBEsol results for the energy differences between the  $Cmc2_1$  and  $P2_1/c$  phases and the *Cmcm* 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  $Sn_2SbS_2I_3$  agree well with the literature for all three phases; see Table 1. A direct gap is determined for  $Cmc2_1$  and indirect gaps are determined for Cmcm and  $P2_1/c$ .

In addition, Kavanagh et al. reported that the absorption edge is larger than the fundamental band gap for Sn<sub>2</sub>SbS<sub>2</sub>I<sub>3</sub>. 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 Cmcm 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.<sup>11</sup> 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  $Sn_2M(III)Ch_2X_3$  family, we calculated the absorption spectra for all 27 candidates. As an example, the absorption spectrum and the corresponding Tauc plot for  $Sn_2InS_2Br_3$  in the *Cmcm* phase are shown in Figure 2. The



**Figure 2.** Absorption spectrum normalized to 5 eV (a) and resulting Tauc plot (b) (HSE06 + SOC level of theory) for  $\text{Sn}_2\text{InS}_2\text{Br}_3$  within the *Cmcm* phase. The orange line in (a) indicates the calculated fundamental band gap of 1.617 eV and the red line in (b) the best linear fit ( $R^2 = 0.955$ ) resulting in an optical band gap of ~1.977 eV.

intensity at the fundamental band gap is weak but not zero. It then increases rapidly at  $E_{\rm g}$  + ~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<sub>2</sub>InS<sub>2</sub>Br<sub>3</sub>. The corresponding band structure is shown in Figure S1 of the Supporting Information.

For all 27 Sn<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> 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 ~0.376 eV for *Cmcm* and *Cmc*<sub>21</sub> and ~0.123 eV for *P*2<sub>1</sub>/*c*. For indirect band gap materials, the optical gap is also larger than the indirect fundamental gap ( $E_{g,ind}$ ). However, if we compare it to the lowest direct gap ( $E_{g,dir}$ ), 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<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> 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<sub>2</sub>InS<sub>2</sub>Br<sub>3</sub>, Sn<sub>2</sub>InS<sub>2</sub>I<sub>3</sub>, Sn<sub>2</sub>InSe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>InSe<sub>2</sub>Br<sub>3</sub>, Sn<sub>2</sub>InTe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>SbSe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>SbSe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>SbSe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>SbSe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>SbSe<sub>2</sub>I<sub>3</sub>, Sn<sub>2</sub>SbTe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>BiSe<sub>1</sub>Z<sub>3</sub>, and Sn<sub>2</sub>BiTe<sub>2</sub>Cl<sub>3</sub>. The formation energies of the 12 compounds in all three considered space groups are illustrated in Figure 3.



**Figure 3.** Formation energy (calculated with PBEsol) of the 12  $Sn_2M(III)Ch_2X_3$  materials of interest for *Cmcm* (green), *Cmc2*<sub>1</sub> (red), and  $P2_1/c$  (blue) space groups. Three structures— $Sn_2SbS_2I_3$ ,<sup>16</sup>  $Sn_2SbSe_2I_3$ ,<sup>18</sup> and  $Sn_2BiS_2I_3$ <sup>19</sup>—that are already known from the literature are highlighted in purple.

A detailed overview of the formation energies of all 27  $Sn_2M(III)Ch_2X_3$  compounds, as well as their lattice parameters, fundamental band, and optical band gaps, is reported in Table 1 of the Supporting Information.

All 27  $\text{Sn}_2M(\text{III})\text{Ch}_2X_3$  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  $\text{Sn}_2\text{InSe}_2\text{Cl}_3$  (-718, -767, and -765 meV atom<sup>-1</sup> for *Cmcm*, *Cmc*2<sub>1</sub>, 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 *Cmc*2<sub>1</sub> phase being preferred. Sn<sub>2</sub>InS<sub>2</sub>I<sub>3</sub>, 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<sub>2</sub>M(III)Ch<sub>2</sub>Cl<sub>3</sub> over Sn<sub>2</sub>M(III)Ch<sub>2</sub>Br<sub>3</sub> toward Sn<sub>2</sub>M(III)Ch<sub>2</sub>I<sub>3</sub>, 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  $Sn_2M(III)Ch_2X_3$ compounds with an indirect fundamental gap (which we refer to as indirect  $Sn_2M(III)Ch_2X_3$ ):  $Sn_2InS_2Cl_3$ ,  $Sn_2InSe_2I_3$ ,  $Sn_2InTe_2I_3$ ,  $Sn_2SbS_2Cl_3$ ,  $Sn_2SbSe_2Br_3$ ,  $Sn_2SbTe_2I_3$ ,  $Sn_2BiSe_2Br_3$ ,  $Sn_2BiSe_2I_3$ ,  $Sn_2BiSe_2I_3$ ,  $Sn_2BiSe_2I_3$ ,  $Sn_2BiSe_2I_3$ ,  $Sn_2BiSe_2I_3$ , and  $Sn_2BiTe_2I_3$ . 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  $\text{Sn}_2M(\text{III})\text{Ch}_2X_3$  materials reveal that the space group influences the nature of the gap. For example, for  $\text{Sn}_2\text{InS}_2\text{Br}_3$ , the *Cmcm* and *Cmc*2<sub>1</sub> structures have a direct band gap but not  $P2_1/c$ . 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  $\text{Sn}_2M(\text{III})\text{Ch}_2X_3$  materials are shown.



**Figure 4.** Direct band gaps (HSE06 + SOC level of theory) for 11  $Sn_2M(III)Ch_2X_3$  materials of interest for *Cmcm* (green), *Cmc2*<sub>1</sub> (red), and *P2*<sub>1</sub>/*c* (blue) space groups. Three structures— $Sn_2SbS_2I_3$ , <sup>16</sup>  $Sn_2SbSe_2I_3$ , <sup>18</sup> and  $Sn_2BiS_2I_3$ <sup>19</sup>—that are already known from the literature are highlighted in purple.

The *Cmcm* and *Cmc*<sup>2</sup><sub>1</sub> phases tend to have direct band gaps, whereas the  $P_{2_1/c}$  structures exhibit indirect gaps. As a result, only two  $P_{2_1/c}$  compounds ( $Sn_2InTe_2Cl_3$  and  $Sn_2InTe_2Br_3$ ) fall into our targeted band gap region. Also, the band gap values depend on the space-group. Gaps of the *Cmc*<sup>2</sup><sub>1</sub> structures lie around 1 eV except for  $Sn_2InS_2Br_3$ . In contrast, *Cmcm* phases have larger band gaps of ~1.4–1.5 eV with the exception of  $Sn_2BiS_2I_3$  and  $Sn_2InSe_2Br_3$ . In general, direct band gaps are largest for  $P2_1/c$  and smallest for *Cmc*<sup>2</sup><sub>1</sub> 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  $Sn_2M(III)Ch_2X_3$  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  $Sn_2M(III)Ch_2X_3$  materials would be interesting for outdoor photovoltaics. Considering antimony's toxicity, bismuth-based  $Sn_2M(III)Ch_2X_3$  materials might be promising contenders.

Lastly, we check which  $Sn_2M(III)Ch_2X_3$  materials are already known or have appeared in databases or data sets. Our search reveals that only three materials have been reported so far:  $Sn_2SbS_2I_3$ , <sup>16</sup>  $Sn_2SbSe_2I_3$ , <sup>18</sup> and  $Sn_2BiS_2I_3$ .<sup>19</sup> For  $Sn_2SbS_2I_3$ , structures in all three space groups are known, but for the other two, only *Cmcm* and *Cmc2*<sub>1</sub> have been

reported. To the best of our knowledge, we are the first to present the nine direct band gaps materials  $(Sn_2InS_2Br_3, Sn_2InS_2I_3, Sn_2InS_2Cl_3, Sn_2InSe_2Br_3, Sn_2InTe_2Br_3, Sn_2InTe_2Cl_3, Sn_2SbSe_2Cl_3, Sn_2SbTe_2Cl_3, and Sn_2BiTe_2Cl_3) and the 15 Sn_2M(III)Ch_2X_3 indirect band gaps materials <math>(Sn_2InS_2Cl_3, Sn_2SbTe_2I_3, Sn_2SbTe_2Cl_3, Sn_2SbSe_2Br_3, Sn_2SbSe_2Cl_3, Sn_2BiSe_2Br_3, Sn_2BiSe_2Cl_3, Sn_2BiSe_2Br_3, Sn_2BiSe_2Cl_3, Sn_2BiSe_2Br_3, and Sn_2BiTe_2Br_3, and Sn_2BiTe_2Br_3, and Sn_2BiTe_2I_3).$ 

**3.2.** Promising  $\operatorname{Sn}_2 M(\operatorname{III})_{1-a} M(\operatorname{III})'_a \operatorname{Ch}_{2-b} \operatorname{Ch}'_b X_{3-c} X'_c Alloys. In this section, we extend the materials' space to possible binary <math>\operatorname{Sn}_2 M(\operatorname{III})_{1-a} M(\operatorname{III})'_a \operatorname{Ch}_{2-b} \operatorname{Ch}'_b X_{3-c} X'_c$  alloys with band gaps in the desired range. We consider alloys within the same space group for which (I) 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  $\operatorname{Sn}_2 M(\operatorname{III})_{1-a} M(\operatorname{III})'_a \operatorname{Ch}_{2-b} \operatorname{Ch}'_b X_{3-c} X'_c$  suitable alloys (see Figure 5). 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  $\operatorname{Sn}_2 M(\operatorname{III})_{1-a} M(\operatorname{III})'_a \operatorname{Ch}_{2-b} \operatorname{Ch}'_b X_{3-c} X'_c$  alloy compounds have been studied in the literature yet.

We find that the  $Cmc2_1$  space group is most prevalent, followed by Cmcm. Only a single binary alloy has the  $P2_1/c$ space group because of the phase's preference for indirect gaps. Materials in the  $Cmc2_1$  space group tend toward lower band gaps close to ~1 eV because the parent compounds have small gaps. One exception is  $Sn_2InS_{2-b}Te_bBr_3$ , which combines  $Sn_2InTe_2Br_3$  ( $E_g = 0.531 \text{ eV}$ ) and  $Sn_2InTe_2Br_3$  ( $E_g = 1.742$ eV), resulting in a broad range of 1.211 eV. For the three Cmcm alloys, we find  $Sn_2In_{1-a}Bi_aS_2I_3$  at the lower end and  $Sn_2InS_{2-b}Se_bBr_3$  and  $Sn_2InS_2Br_{3-c}$  in the middle of the range. If we drop our restriction of mixing compounds with a direct gap, we obtain an additional 69  $Sn_2M(III)_{1-a}M$ - $(III)'_aCh_{2-b}Ch'_bX_{3-c}X'_c$  alloys, reported in Figure S4 of the Supporting Information.

Our results indicate that  $\operatorname{Sn}_2 M(\operatorname{III})_{1-a} M(\operatorname{III})_a \operatorname{Ch}_{2-b} \operatorname{Ch}_b X_{3-c} X_c$  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,  $\operatorname{Sn}_2\operatorname{In}_{1-a}\operatorname{Bi}_a S_2 I_3$  might offer the best environmentally friendly compromise.

#### 4. CONCLUSIONS

In the pursuit of low-toxicity photovoltaic materials, we used DFT to explore the Sn<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> 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  $Sn_2M(III)Ch_2X_3$  were known previously, while the remaining nine materials, i.e., Sn<sub>2</sub>InS<sub>2</sub>Br<sub>3</sub>, Sn<sub>2</sub>InS<sub>2</sub>I<sub>3</sub>, Sn<sub>2</sub>InSe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>InTe<sub>2</sub>Br<sub>3</sub>, Sn<sub>2</sub>InTe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>SbSe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>SbTe<sub>2</sub>Cl<sub>3</sub>, Sn<sub>2</sub>BiTe<sub>2</sub>Cl<sub>3</sub> and Sn<sub>2</sub>BiTe<sub>2</sub>Cl<sub>3</sub>, are reported here for the first time. The majority of these compounds contain indium, including some of the most promising candidates such as Sn<sub>2</sub>InSe<sub>2</sub>Br<sub>3</sub> or Sn<sub>2</sub>InS<sub>2</sub>Br<sub>3</sub>. An alternative to indium- and antimony-based Sn<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> materials is bismuth-based ones, such as, e.g., Sn<sub>2</sub>BiTe<sub>2</sub>Cl<sub>3</sub>, although the band gap is smaller than its indium-based counterparts. In addition, we identified 15 previously unknown Sn<sub>2</sub>M(III)Ch<sub>2</sub>X<sub>3</sub> compounds

Table 2.	Fundar	nental and	Optical Ba	nd Gaps	$(E_{\mathrm{g,Opt}})$ [Gi	ven in eV	] of Sn <sub>2</sub> M(]	III)Ch <sub>2</sub> X <sub>3</sub> , V	Which Hav	e Been Ide	ntified as Into	eresting <sup>a</sup>			
		$Sn_2InS_2Cl_3$	$\mathrm{Sn_2InS_2Br_3}$	$\mathrm{Sn}_2\mathrm{InS}_2\mathrm{I}_3$	$\mathrm{Sn}_2\mathrm{InSe}_2\mathrm{Cl}_3$	Sn <sub>2</sub> InSe <sub>2</sub> Br <sub>3</sub>	3 Sn <sub>2</sub> InSe <sub>2</sub> I <sub>3</sub>	Sn <sub>2</sub> InTe <sub>2</sub> Cl	3 Sn <sub>2</sub> InTe <sub>2</sub> I	3r <sub>3</sub> Sn <sub>2</sub> InTe <sub>2</sub>	I <sub>3</sub> Sn <sub>2</sub> SbS <sub>2</sub> Cl <sub>3</sub>	$Sn_2SbS_2Br_3$	$Sn_2SbS_2I_3$	$\mathrm{Sn}_2\mathrm{SbSe}_2\mathrm{Cl}_3$	$\mathrm{Sn}_2\mathrm{SbSe}_2\mathrm{Br}_3$
Стст	$E_{ m g,dir}$	1.305	1.617	1.395		1.105	1.369			1.089	1.679	1.474	0.997	1.411	1.412
	$E_{\rm g,ind}$	1.251					1.299			0.994	1.611	0.883	0.947		1.330
	$E_{\rm g,opt}$	1.491	1.977	1.934		1.477	1.397			1.126	1.773	1.527	1.547	1.816	1.504
$Cmc2_1$	$E_{\rm g,dir}$	1.834	1.742	1.120	1.046	1.373		0.915		0.867	1.242	1.248	1.007	1.002	0.941
	$E_{ m g,ind}$	1.692		0.598		1.338		0.804		0.802	1.056	1.055			0.891
	$E_{\rm g,opt}$	1.887	1.783	1.187	1.684	1.396		1.011		0.964	1.288	1.344	1.506	1.261	1.044
$P2_1/c$	$E_{\rm g,dir}$		1.985			1.843	1.947	1.594	1.461	1.109			1.762		2.028
	$E_{\rm g,ind}$		1.616			1.488	1.785			1.083			1.686		1.642
	$E_{\rm g,opt}$		1.996			1.855	1.960	1.713	1.592	1.201			1.771		2.100
		$Sn_2SbSe_2I_3$	$Sn_2SbTe_2C$	Cl <sub>3</sub> Sn <sub>2</sub> Sl	oTe <sub>2</sub> Br <sub>3</sub> Sn <sub>2</sub>	SbTe <sub>2</sub> I <sub>3</sub> S	n <sub>2</sub> BiS <sub>2</sub> Cl <sub>3</sub>	Sn <sub>2</sub> BiS <sub>2</sub> Br <sub>3</sub>	Sn <sub>2</sub> BiS <sub>2</sub> I <sub>3</sub> S	in2BiSe2Cl3	Sn <sub>2</sub> BiSe <sub>2</sub> Br <sub>3</sub>	5n2BiSe2I3	$Sn_2BiTe_2Cl_3$	${\rm Sn_2BiTe_2Br_3}$	$Sn_2BiTe_2I_3\\$
Стст	$E_{\rm g,dir}$	1.057	0.943		5	0.786	1.535	1.343	0.988	1.104	0.965	1.048	0.738	0.852	
	$E_{\rm g,ind}$	0.800	1.874		1	0.465	0.986	0.956		1.096	0.666	0.769		0.715	
	$E_{\rm g,opt}$	1.056	1.997			0.795	1.548	1.434	1.390	1.124	1.063	1.141	1.059	0.854	
$Cmc2_1$	$E_{ m g,dir}$	0.962	0.950	Ι.	027		1.146	1.405	1.013	0.902	1.841	1.064	0.852	0.854	
	$E_{ m g,ind}$			0	980		1.034	1.124		0.714	0.827	0.881	0.715	0.718	
	$E_{\rm g,opt}$	1.640	1.370	Ι.	063		1.169	1.504	1.420	0.952	0.853	1.162	0.854	0.856	
$P2_1/c$	$E_{\rm g,dir}$	1.892						1.968	1.606	1.196	1.425	1.660			0.890
	$E_{\rm g,ind}$	1.672						1.717	1.490	1.076	1.118	1.474			0.256
	$E_{\rm g,opt}$	1.983						2.065	1.599	1.254	1.452	1.751			0.931
<sup>a</sup> For indire gap are bo	ect comp ld, and t	ounds, the b those with ar	and gaps of tl 1 indirect one	he lowest ( e are italic.	direct transitio	on $(E_{ m g,dir})$ as	well as of th	e lowest indir	ect transitior	ו $(E_{ m g,ind})$ are ן	orovided. Sn <sub>2</sub> M	(III)Ch <sub>2</sub> X <sub>3</sub> n	aterials with	a direct fundaı	nental band



**Figure 5.** Band gap ranges (HSE06 + SOC level of theory) for the 12  $Sn_2M(III)_{1-a}M(III)'_aCh_{2-b}Ch'_bX_{3-c}X'_c$  binary alloys of interest for *Cmcm* (green), *Cmc2*<sub>1</sub> (red), and *P2*<sub>1</sub>/*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  $\text{Sn}_2M(\text{III})_{1-a}M(\text{III})'_a\text{Ch}_{2-b}\text{Ch}'_bX_{3-c}X'_c$  alloys. In total, 12  $\text{Sn}_2M(\text{III})_{1-a}M(\text{III})'_a\text{Ch}_{2-b}\text{Ch}'_bX_{3-c}X'_c$  alloys were identified by alloying within the same phase and considering only structures with direct gaps. For example, the fundamental gap of  $\text{SnIn}_{1-a}\text{Bi}_a\text{S}_2\text{Br}_3$  can be tuned between 0.988 and 1.395 eV. Furthermore, we identified additional 69  $\text{Sn}_2M(\text{III})_{1-a}M(\text{III})'_a\text{Ch}_{2-b}\text{Ch}'_bX_{3-c}X'_c$  alloys by dropping our requirement to use only direct band gap  $\text{Sn}_2M(\text{III})\text{Ch}_2X_3$  end structures, which significantly broadens the  $\text{Sn}_2M(\text{III})_{1-a}M(\text{III})'_a\text{Ch}_{2-b}\text{Ch}'_bX_{3-c}X'_c$  spectra.

Our findings highlight the relevance of materials' design and theoretical explorations, and the identified  $Sn_2M(III)Ch_2X_3$  materials, and  $Sn_2M(III)_{1-a}M(III)'_aCh_{2-b}Ch'_bX_{3-c}X'_c$  alloys encourage the synthesis and the use of highly stable materials in various optoelectronic devices.

# ASSOCIATED CONTENT

# **3** Supporting Information

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

Band structure for  $Sn_2InS_2Br_3$  (*Cmcm*); lattice parameters, formation energies, and fundamental (direct and indirect) and optical gaps for all  $Sn_2M(III)Ch_2X_3$  materials; formation energies of indirect  $Sn_2M(III)-Ch_2X_3$  materials; band gaps for all  $Sn_2M(III)Ch_2X_3$  materials; and  $Sn_2M(III)_{1-a}M(III)'_aCh_{2-b}Ch'_bX_{3-c}X'_c$  alloys (PDF)

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#### Notes

The authors declare no competing financial interest.

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