Discovering lead-free perovskite solar materials with a split-anion approach†

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Organic–inorganic hybrid perovskite solar materials, being low-cost and high-performance, are promising for large-scale deployment of the photovoltaic technology. A key challenge that remains to be addressed is the toxicity of these materials since the high-efficiency solar cells are made of lead-containing materials, in particular, CH$_3$NH$_3$PbI$_3$. Here, based on first-principles calculation, we search for lead-free perovskite materials based on the split-anion approach, where we replace Pb with non-toxic elements while introducing dual anions (i.e., splitting the anion sites) that preserve the charge neutrality. We show that CH$_3$NH$_3$BiSeI$_2$ and CH$_3$NH$_3$BiS$I_2$ exhibit improved band gaps and optical absorption over CH$_3$NH$_3$PbI$_3$. The split-anion approach could also be applied to pure inorganic perovskites, significantly enlarging the pool of candidate materials in the design of low-cost, high-performance and environmentally-friendly perovskite solar materials.

Introduction

The discovery of organic–inorganic halide perovskite materials as light absorbers to make high-efficiency solar cells*–8 has stimulated a surge of research in the past several years.9,10 The earth-abundance of the constituent elements and the low-temperature synthesis of these materials11 make them highly promising for low-cost photovoltaic applications. One of the key issues faced by the current halide perovskite materials is the use of lead (Pb) to achieve high efficiency. Both elemental Pb and its halides are well known to be highly toxic, prohibiting large-scale deployment of the Pb-based materials. A current focus of research is to replace Pb with tin (Sn).12–15 So far, the efficiency achieved by Sn-based materials has not been comparable with that by Pb-based materials. Unfortunately, for halide (or I–II–VI$_3$) perovskite materials, it appears that no other alternative elements across the periodic table can replace Pb while maintaining suitable band gaps for solar absorber application. Thus, it is of great interest to explore new perovskite materials beyond the composition of I–II–VI$_3$, e.g., chalcopyrite perovskites, which have recently been proposed as solar materials.16

Cation-splitting has been a successful approach in designing solar materials. The high-performance I–III–VI$_2$ chalcopyrite materials, e.g., CuInSe$_2$ or Cu(In,Ga)Se$_2$,17 can be considered as derived from II–VI zinc-blende structures by splitting two 2+ cations into one 1+ and one 3+ cation. The approach can be further carried out by splitting two 3+ cations into one 2+ and one 4+ cation, leading to the kesterite materials, of which Cu$_2$ZnSnSe$_4$ is a successful example.18,19 The advantage of this approach is that the crystal structure and local chemical environment of the parent materials are largely preserved, resulting in similar electronic and optical properties in the derived materials. The cation-splitting approach has also been applied to oxide perovskite materials showing promising results for photovoltaic applications.20 In contrast, anion-splitting has been rarely studied for developing new solar-cell materials. Recently, nitride-oxide perovskite materials have been synthesized for photocatalytic water splitting.21 This work shows great promise of split-anion perovskites for photovoltaic applications. The success of the halide perovskite materials, as represented by CH$_3$NH$_3$PbI$_3$, has inspired us to explore the anion-splitting approach with the aim of developing Pb-free perovskite solar materials.

Because of the high efficiency already achieved by the Pb-based materials, it is preferred to replace Pb with an element that is close to Pb in the periodic table with the hope that the desirable properties of the Pb-based materials can be preserved. Bismuth (Bi) is thus a candidate of great interest.

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Moreover, in terms of toxicity, Bi is much safer than Pb for massive use. In this paper, based on first-principles calculations, we study the Bi-based organic–inorganic perovskite materials for photovoltaic applications. Starting with CH₃NH₃PbI₃, we apply the split-anion approach by replacing one I per formula with Se or S, while replacing Pb with Bi, to satisfy the charge neutrality. In general, this approach leads to the I–III–VI–VI₂ compounds. By using hybrid functional calculations including spin–orbit coupling, we show that CH₃NH₃BiS₄I₂ and CH₃NH₃BiSeI₂ could possess a direct band gap of 1.3 to 1.4 eV, ideal for single-junction solar cells. One could also envision a large family of new compounds based on the split-anion approach, which have been largely unexplored. We will discuss one such pure inorganic compound, CsSnS₂Cl, for photovoltaic applications.

### Method

Our first-principles calculation was based on the density functional theory (DFT) as implemented in the VASP program. The generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE) was used for the exchange–correlation functional. To better describe the interaction between the organic cation and the inorganic framework, we include the van der Waals interaction through the PBE-D3 method. A 2 × 2 × 2 supercell containing eight formula units (f.u.) of I–III–VI–VI₂ or I–III–VI–VI₃ compounds was used in our calculation. The lattice constants and the internal coordinates were obtained by performing variable-cell optimization. To ensure converged structural parameters, a cutoff energy of 544 eV for the plane-wave basis set, a 3 × 3 × 3 k-point grid, and a force criterion of 0.025 eV Å⁻¹ were used. Further details on optimizing the atomic structures are given in the ESL. Qualitative analysis of electronic structures, such as band structures and density of states, was also conducted at the PBE level. To accurately predict the band gaps, we employed the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional, as discussed below. The effect of spin–orbit coupling (SOC) was also considered when calculating the band gaps. In the HSE + SOC calculations, a cutoff energy of 340 eV and four special k-points, (0, 0, 0), (1/2, 0, 0), (0, 1/2, 0), and (1/2, 1/2, 1/2), were found to yield converged band gaps.

### Results and discussion

Fig. 1a and b illustrate the idea of the split-anion approach. Bi is the neighbor of Pb in the periodic table and has no issue with toxicity. However, simply replacing Pb in CH₃NH₃PbI₃ with Bi will introduce one extra electron per f.u. (similar to a donor) and make the material metallic. To compensate for the extra electron, we replace one I atom per f.u. with one Se atom, serving as an acceptor, so that the charge neutrality, hence the semiconductivity, can be preserved. Thus, the anion sites are split into two groups occupied by the group-VI and group-VII elements, respectively.

![Fig. 1 Atomic structures of (a) CH₃NH₃PbI₃ and (b) CH₃NH₃BiSeI₂ and a schematic illustrating the split-anion approach to replace Pb in CH₃NH₃PbI₃. (c) and (d) show the calculated band gaps of CH₃NH₃PbI₃ and CH₃NH₃BiSeI₂, respectively, using improved methods from PBE, HSE to HSE + SOC. The alignment of the band edge positions was obtained from assuming that the reference potentials from different methods are the same.](image-url)
CH$_3$NH$_3$PbI$_3$ than the experimental value if considering the SOC effect. There are two parameters in the HSE functional $\alpha$ and $\omega$ controlling, respectively, the mixing and screening of the Hartree–Fock exchange. Here we fix $\alpha$ at 0.25 following an argument based on the adiabatic connection formula, while employing a smaller $\omega$ ($0.05 \text{ Å}^{-1}$) than the standard value ($0.2 \text{ Å}^{-1}$). With the modified $\omega$, our HSE + SOC calculation yielded a band gap of 1.54 eV for CH$_3$NH$_3$PbI$_3$, in good agreement with the experiment. Below, we will use the same parameters for the Bi-based organic–inorganic perovskites.

Using the structures optimized by the PBE-D3 method, we calculated the band gap at the Brillouin zone center (Γ point) using improved methods from PBE, HSE to HSE + SOC (i.e., HSE including spin–orbit coupling). Our results show that the split-anion Bi-based perovskite materials (including the materials discussed below) also have direct band gaps at the same $\Gamma$ point of the $2 \times 2 \times 2$ supercell. Fig. 1c and d show the calculated band gaps of CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$BiSeI$_2$, where the alignment of the band edge positions was made by assuming that the reference potentials from different methods are the same. This approximation was shown to be valid for typical semiconductors because given the same atomic structure, different DFT functionals usually yield similar charge densities, which determine the average potential of the unit cell. Based on these alignments, it is shown that the HSE calculation opens up the band gap by down-shifting the valence band maximum (VBM) and up-shifting the conduction band minimum (CBM). The down-shift of the VBM is roughly two times more prominent than the up-shift of the CBM. In contrast to the effect of HSE, the SOC reduces the band gap. However, the magnitude of the down-shifting of the CBM by including the SOC effect is much more prominent than the up-shifting of the VBM because the CBM is mainly composed of the Pb or Bi 6p states (discussed below), which are more significantly affected by the SOC than the VBM (mainly Se 4p and I 5p states). The asymmetric change in the band gap by the HSE and SOC results in overall down-shifts of the band edges.

Experimentally, alloying with different anions has been commonly used to fine tune the material properties. We have considered the combinations of S, Se and Te for group-VI elements and Cl, Br and I for group-VII elements. The calculated band gaps for the nine compounds are shown in Fig. 2. It can be seen that similar to the Pb-based halide perovskites, the iodides, especially CH$_3$NH$_3$BiSI$_2$ and CH$_3$NH$_3$BiSeI$_2$, yield the optimal band gaps (1.3–1.4 eV) for solar absorbers according to the Shockley–Queisser theory. The asymmetry in the band gap by the HSE and SOC results in overall down-shifts of the band edges.

Fig. 3 compares the band structures, densities of states (DOS), and imaginary parts of the dielectric function ($\varepsilon_2$) of CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$BiSI$_2$. From the band structure in Fig. 3a, it can be seen that the bottom of the conduction band of CH$_3$NH$_3$BiSI$_2$ shows significant dispersion suggesting good electron transport properties. The top of the valence band contains one dispersive band while the other bands are less dispersive. The effective masses of electrons and holes of CH$_3$NH$_3$BiSI$_2$ are 0.32 and 0.40 $m_0$ (electron rest mass), respectively, as calculated using the PBE functional and averaged over the four directions shown in Fig. 3. It has been shown that adding SOC and quasi-particle GW correction could further reduce the effective masses. It is thus expected that the effective masses of CH$_3$NH$_3$BiSI$_2$ could be comparable with those of CH$_3$NH$_3$PbI$_3$ (0.19 and 0.25 $m_0$ for electrons and holes, respectively). From the DOS in Fig. 3b, it can be seen that the top of the valence band of CH$_3$NH$_3$BiSI$_2$ contains two main peaks. The lower peak is mainly contributed by I 5p states, while the higher peak is contributed by hybridized states between S 3p and I 5p states, which are the less-dispersive states. Similar to CH$_3$NH$_3$PbI$_3$, the bottom of the conduction band of CH$_3$NH$_3$BiSI$_2$ is contributed by the 6p states of Bi, which are responsible for the dispersive bottom conduction bands.

Fig. 3c shows a comparison of the calculated $\varepsilon_2$ of CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$BiSI$_2$. The results are obtained by using the PBE functional with a scissor operator applied to CH$_3$NH$_3$BiSI$_2$ by shifting the conduction bands up by 0.3 eV to obtain the band gap calculated by HSE + SOC. The $\varepsilon_2$ provides a direct measure of optical absorption. From this comparison, CH$_3$NH$_3$BiSI$_2$ is expected to exhibit stronger optical absorption than CH$_3$NH$_3$PbI$_3$ below 3 eV. According to the AM 1.5 solar spectrum, about 94% of the solar radiation reaching the earth surface is below 3 eV. Thus, CH$_3$NH$_3$BiSI$_2$ would be a stronger...
solar absorber than CH$_3$NH$_3$PbI$_3$. Also, given that the calculated band gap of 1.38 eV is closer to the ideal value for single-junction solar cells, CH$_3$NH$_3$BiSI$_2$ could be a promising candidate PV material.

We have considered above the I–III–VI–VII$_2$ compounds to demonstrate the split-anion approach. Other possible split-anion compounds could also have chemical compositions of II–II–VI–VII$_2$, I–IV–VI$_2$–VII, and II–III–VI$_2$–VII. The split-anion approach thus significantly enlarges the pool of elements for the design of new perovskite materials, not only for the organic–inorganic hybrid perovskites, but also for pure-inorganic perovskites. Currently, lead-free perovskite solar materials are mainly based on the replacement of Pb by Sn. In such materials, Sn is in the 2+ oxidation state (Sn$^{II}$), part of which could be oxidized to the 4+ state (Sn$^{IV}$) under ambient conditions. The Sn$^{IV}$ defects in the Sn$^{II}$ compounds could be detrimental to the device performance.$^{12,13}$ The split-anion approach provides a possibility of designing all Sn$^{IV}$-based perovskite solar materials to avoid further oxidation.

Taking CsSnI$_3$ as an example, which has a nearly ideal band gap of 1.3 eV and has been used to make dye-sensitized solar cells with an efficiency up to 8%,$^{37}$ we now demonstrate the design of Sn$^{IV}$-based perovskite solar materials. We note that, while Cs is used here for the A-site cation as an example, other 1+ cations could also be considered as candidates. Similar to Fig. 2, we considered nine combinations of the anions. It was found that CsSnS$_2$Cl possesses a suitable band gap as a solar absorber, while the band gaps of other materials are smaller than 1 eV.

Fig. 4a and b show the structure of CsSnS$_2$Cl in the distorted perovskite phase, which has the symmetry of the I4/mcm space group, i.e., the symmetry of CH$_3$NH$_3$PbI$_3$ at room temperature. Fig. 4c and d show the Brillouin zone and the band structure calculated using the standard hybrid HSE functional (i.e., $\alpha = 0.25$ and $\omega = 0.2$). Here we used the quasi-particle GW method$^{38}$ to calibrate the hybrid functional and found that the standard HSE functional already yielded a band gap in agreement with the GW calculation within 0.01 eV (see the ESI†). CsSnS$_2$Cl is an indirect-gap material with the CBM located at the $\Gamma$ point and the VBM at about one-third distance from $\Gamma$ to M. The HSE band gap is 0.98 eV. It is worthwhile to note that an indirect gap may not necessarily be a disadvantage for solar absorber materials since indirect-gap materials have a weaker
radiative recombination than direct-gap materials, which could improve the carrier lifetime in the regime where defect-mediated (or non-radiative) recombination is weak.

While having an indirect band gap, CsSnS2Cl shows different behaviors in optical absorption from typical indirect-gap solar materials, such as Si. Fig. 4e compares the calculated $e_2$ of CsSnS2Cl, CsSnI3 and Si. It can be seen that Si, as is well known, exhibits a slow increase in $e_2$ until about 3 eV. In contrast, CsSnS2Cl exhibits a sharp increase when the photon energy is greater than the band gap. This is because the direct band gap of CsSnS2Cl at the $\Gamma$ point is 1.11 eV. In comparison, the direct gap of Si at the $\Gamma$ point is 3.34 eV based on our HSE calculation. According to Fig. 4e, CsSnS2Cl could have even better optical absorption than the direct-gap CsSnI3 below 3 eV. This is partly because of the relatively large density of states near the top of the valence bands due to the presence of dual anions, similar to the case of CH$_3$NH$_3$BiSI$_2$ shown in Fig. 3b.

**Conclusions**

In summary, we have explored the split-anion approach to search for lead-free perovskite solar absorber materials. Starting from the high-performance organic-inorganic hybrid perovskite CH$_3$NH$_3$PbI$_3$, we replace Pb with non-toxic Bi while splitting the three I per f.u. into two I and one Se or S. The resulting materials, CH$_3$NH$_3$BiSI$_2$ and CH$_3$NH$_3$BiSeI$_2$, are shown to preserve or even improve the properties of CH$_3$NH$_3$PbI$_3$, as solar absorber materials. The split-anion approach could also be applied to pure inorganic perovskite materials. As an exploratory example, we studied CsSnS$_2$Cl, which has an indirect band gap of about 1 eV according to our hybrid functional calculation, but promising optical absorption even higher than CsSnI$_3$. The split-anion approach with possible compositions of I–III–VI–VII$_2$, II–II–VI–VII$_2$, I–IV–VI–VII, or II–III–VI–VII significantly enlarges the pool of elements for the design of environmentally benign and high-performance solar absorber materials.

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