Defect Tolerance of Mixed B-Site Organic–Inorganic Halide Perovskites

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ABSTRACT: Further improvements in the photovoltaic performance of B-site alloyed organic−inorganic halide perovskites (OIHPs) will rely on accurate modeling of defect properties and passivation strategies. Herein, we report that B-site alloying results in defect behaviors distinct from those of pure OIHPS, a finding obtained by uniting first-principles calculations with experimental measurements. We identify from computational studies a defect-tolerant region spanning a Sn content of 30−70% in mixed Pb-Sn perovskites and experimentally observe notably longer carrier lifetimes in 50% Sn mixed perovskite films than at other Sn contents. We discuss a strategy of applying defect-tolerant 50% Pb-Sn perovskites in ideal-bandgap (1.3−1.4 eV) active layer materials which conventionally rely on 25−30% Sn compositions. The composition (FA0.75Cs0.25Pb0.5Sn0.5(I0.9Br0.1)3) achieves increased carrier lifetimes of >1 μs. This work reveals a general trend in defect tolerance for B-site alloying: a higher valence band maximum (lower conduction band minimum), along with strengthened ionic bonding, can potentially contribute to improved photovoltaic performance.

Lead-based organic−inorganic halide perovskites (OIHPs) are attractive light-absorber materials for photovoltaic (PV) applications, as seen by their rapid increase in power conversion efficiency (PCE) to 25.5%. 1 Compositional engineering at the B-site with Sn2+ and Ge2+ is an important strategy to regulate optoelectronic properties and to ease regulatory constraints related to the use of toxic Pb. B-site alloying can also provide a bandgap (Eg) as low as ∼1.2 eV in mixed Pb-Sn OIHPs relevant to all-perovskite tandems that offer routes to go beyond the Shockley–Queisser limit of single-junction solar cells. 2−4 The record certified efficiency of all-perovskite tandems has reached 26.4%, comparable to that of the best-performing silicon solar cells. 5 One remaining area for significant further improvement is the development of efficient narrow-Eg perovskites as the bottom subcell. 6−8

The ideal Eg for the maximum PCE of single-junction solar cells is 1.3−1.4 eV. 7 In order to reach this Eg, it is generally necessary to use 25−30% Sn content in mixed Pb-Sn perovskites, 10,11 resulting in PCEs that lag behind those of narrow-Eg Pb-Sn solar cells. The lagging efficiency of ideal-Eg Pb-Sn solar cells arises from high defect densities, which limits carrier lifetimes. Zhou et al. reported carrier lifetime values of 156 and 821 ns for MA0.3FA0.7Pb0.7Sn0.3I3 perovskite films without and with 12% Br. 10 Yang et al. reported a promising 50% Sn composition (MAPb0.5Sn0.5(I0.9Br0.1)3) for ideal-Eg devices, 11 a finding that motivates further study of materials in this composition.

Recent experimental work has investigated the PV performance of mixed Pb-Sn perovskites and identified a concentration range of heavy defectivity at a low Sn content of 0.5−20%. 12 This phenomenon is intriguing, especially given that the problems traceable to Sn oxidation are expected to rise with higher Sn concentration. 13 We undertook, with this in mind, a study of how B-site alloying impacts the defect properties of OIHPs.

Defect properties influence carrier density, carrier lifetime, and transport properties in semiconductors. 14 Defect physics in pure OIHPs has been studied extensively; fewer studies focus on B-site alloyed systems. 15−21 We note also the
limitations of the Perdew−Burke−Ernzerhof (PBE) method, which can lead even to incorrect trends, such as that shallow traps dominate in bulk OIHP15,16—computational studies whose trends diverge with those from experiments22−24. We therefore used hybrid functionals including a spin−orbital coupling (HSE+SOC) method to examine the defect properties.25−28

Combining computational and experimental efforts, we investigated defect properties in B-site alloyed OIHPs. We find that the HSE+SOC calculation method gives band edge trends that agree with experiments. We then identify a region (30−70% Sn content) of defect tolerance in mixed Pb-Sn perovskites, with 50% Sn mixed perovskite exhibiting notably longer carrier lifetimes than all other Sn contents. Using a defect-tolerant 50% Sn composition with 10% Br (FA0.75Cs0.25Pb0.5Sn0.5I3), we then demonstrate perovskite thin films with the same ideal Eg (1.33 eV) as conventional 30% Sn compositions, and we observe a significantly increased carrier lifetime from 304 to 1034 ns, comparable to the longest values reported to date for MA-free Pb-Sn perovskites. Our calculations also indicate the potential of alloying alkaline earth metals to improve the PV performance of Pb-Sn perovskites.

The mixed A-site composition of FA0.75Cs0.25 in perovskites has been reported to have enhanced stability due to improved resistance to moisture and oxidation.29,30 Thus, we chose FA0.75Cs0.25Bi3 (B = Pb2+, Sn2+, Ge2+) for investigation in this work (Figure 1a). Pb-Sn alloyed systems were thermodynamically more favorable than the pure Pb and pure Sn at 300 K (Figure S3). As shown in Figure 1b, we observed the expected Eg bowing character with the minimum values (∼1.2 eV) found in the range of 50−75% Sn in FA0.75Cs0.25Pb1−xSnxI3, which can be explained by the electronic structures (Note 2 in the Supporting Information and Figure S4). It is well known that the HSE+SOC method gives Eg values more consistent with experiments than the PBE method. However, few reports discuss whether HSE+SOC band edge position predictions are consistent with experiments. Thus, we performed UV-vis-NIR absorption spectroscopy and ultraviolet photoemission spectroscopy (UPS) measurements of FA0.75Cs0.25Pb1−xSnxI3 thin films (Figure 1d and Figure S1). We observed an upshift of the valence band maximum (VBM) and conduction band minimum (CBM) with increasing Sn content, consistent with our HSE+SOC calculations (Figure 1c). We noted that the experimental VBM/CBM energy shifts are more limited compared to the calculated ones, potentially due to the antioxidant additive incorporation and imperfections of the perovskite surface in experiment and because UPS is a surface-sensitive probing technique.31

To investigate the effect of B-site alloying on the defect properties of OIHPs, we performed defect calculations in a large 4×4×4 supercell (656 atoms) using the HSE+SOC method. Charge-state transition levels (CTLs)32 are commonly used as a criterion to identify point defects as shallow or deep (see Methods section in the Supporting Information). We emphasize the importance of accurate predictions of band...
edge position on the correct evaluation of CTLs and defect formation energies. HSE+SOC predictions resulted in a downshift of both the VBM an CBM relative to the PBE results. As shown in Figure S5, we found that PBE-predicted shallow acceptors (deep donors) may become deep trap states (shallow states) in the HSE+SOC calculations (e.g., iodine interstitial (I\textsubscript{int}) for the former; Sn/Pb interstitial (Sn\textsubscript{int}/Pb\textsubscript{int}) and iodine vacancy (V\textsubscript{I}) for the latter). These results are qualitatively consistent with previous work investigating MAPbI\textsubscript{3}.\textsuperscript{25−27}

Figure 2 shows the calculated CTLs for defects in B-site alloyed perovskites. For mixed Pb-Sn perovskites, we find that the CTLs are mainly modulated by band edge positions, while their absolute values are less sensitive to the Sn content. Importantly, the 50% Sn mixed alloy exhibits enhanced defect tolerance and is free of deep traps. Some deep acceptors in pure Pb (e.g., I\textsubscript{FA} with a lower VBM become shallower in 30−70% Sn mixed alloys. We also examined the defect levels of Sn vacancies (V\textsubscript{Sn}) in 30% and 50% Sn mixed systems and find that V\textsubscript{Sn} are shallow defects in these compositions (Figure S6). Analogously, some deep donors in pure Sn (e.g., Sn\textsubscript{int}/V\textsubscript{I}) with a higher CBM also become shallower in 30−70% Sn mixed alloys. Additional discussion of the defect properties in literature is in Note 3 in the Supporting Information.

We then explored, now going beyond defect properties alone, the degradation feasibility of alloys in the presence of oxygen. Along two possible degradation pathways (eqs 1 and 2),\textsuperscript{13,33}

\begin{align*}
2\text{APb}(1-x)\text{Sn}_x\text{I}_3 + 2\text{O}_2 &\rightarrow 2(1 - x)\text{PbI}_2 + 2x\text{SnO}_2 + 2x\text{I}_2 + 2\text{AI} \quad (1) \\
4\text{CH(NH}_2)_2\text{Pb}(1-x)\text{Sn}_x\text{I}_3 + \text{O}_2 &\rightarrow 4(1 - x)\text{PbI}_2 + 4x\text{SnI}_2 + 2\text{I}_2 + 2\text{H}_2\text{O} + 4\text{CH}_4\text{N}_2 \quad (2)
\end{align*}

we calculated the reaction energies, defined as the energy difference between the reactants and products, as a function of the Sn content. From Figure S7, we found that reaction energy increased with Sn content, indicating increased energetic favorability of oxidation. This was also observed in previous experimental work.\textsuperscript{13}
Taking account of bulk defect properties along with the increased susceptibility to Sn oxidation with Sn alloying, we expected 30−70% Sn mixed perovskite films to exhibit enhanced defect tolerance. For Sn contents <30%, deep-level acceptors were expected to result in heavier defectiveness and nonradiative recombination. Taking 12.5% Sn mixed perovskite for instance, \( E_I \) induced an \( \epsilon(1+/-1+) \) CTL deep within the bandgap (0.57 eV above the VBM). However, \( E_I \) behaved differently in 50% Sn mixed perovskite, with both \( \epsilon(0/-1+) \) and \( \epsilon(0/-1-) \) near the VBM, acting as a shallow defect. For Sn contents >75%, the optoelectronic properties were expected to be limited by the deep-level donors, increased oxidation of Sn\(^{2+}\), and the subsequent heavy hole-doping.

We further investigated the effect of alloying Ge into mixed Pb-Sn perovskites on defect properties, to look for a more general trend in the defect tolerance in B-site alloyed OIHPs. Here we focus on \( V_I \), an important defect in perovskites. To reduce the oxidation of Sn\(^{2+}/Ge^{2+}\), we prefer to create a Sn(Ge)-rich/I-poor condition, which will promote the formation of \( V_I \). For negatively charged \( V_I^{-} \), there exist two possible configurations (\( \alpha \) and \( \beta \)), as shown in Figure 3a. The formation of the localized \( \beta \) state was determined by the competition between the energy-gain obtained by moving the electrons from the \( \alpha \) state to the \( \beta \) state (\( \Delta E_{el} \)) and the energy-loss from atomic distortion (\( \Delta E_{st} \)). Taking \( \text{Pb}_{0.5} \text{Sn}_{0.47} \text{M}_{0.03} \) (M = Zn\(^{2+}\), Cd\(^{2+}\)), \( E_I \) is located at 0.51 eV below the CBM, indicating the dominant presence of \( V_I^{-} \).
perovskites doped with alkaline earth metals (M = Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Sr\textsuperscript{2+}), while they are stable in the β configuration (\(E_\alpha > E_\beta\)) with doping of transition metals (M = Zn\textsuperscript{2+}, Cd\textsuperscript{2+}), as shown in Figure 3d. The stronger M–M or B–M bonding near the V\textsubscript{I} site in the Zn\textsuperscript{2+}/Cd\textsuperscript{2+}-doped system results in higher \(\Delta E_{\text{el}}\) energy gain; thus the β configuration will have a lower energy than the α configuration. From Figure 3e,f, we find that doping M = Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Sr\textsuperscript{2+} with the outermost electron configuration of s\textsuperscript{d} does not create deep states for V\textsubscript{I}, in contrast to M = Zn\textsuperscript{2+}, Cd\textsuperscript{2+} with the outermost electron configuration of s\textsuperscript{d}\textsuperscript{10}. Interestingly, this trend has little dependence on the atomic radii. As shown in Figure S8, we also check the CTLs of V\textsubscript{I} in Zn\textsuperscript{2+}/Cd\textsuperscript{2+}-doped perovskites with a lower doping concentration of 1.5% (Pb\textsubscript{0.95}Sn\textsubscript{0.05}M\textsubscript{0.015}) and find that V\textsubscript{I} remains deep within the bandgap. The atomic positions of the V\textsubscript{I} in doped systems are depicted in Figure S9. From Figure 3f, we can see that dopant incorporation induces a VBM downshift (0.05–0.08 eV) compared with the VBM of non-doped perovskites, which is beneficial in alleviating the detrimental hole-doping of Pb-Sn perovskites.\textsuperscript{38} In addition, Phung et al. found that incorporation of Mg\textsuperscript{2+} and Sr\textsuperscript{2+} could increase the formation energy of Pb vacancies (\(V_{\text{Pb}}\)), indicating the defect density reduction of \(V_{\text{Pb}}\).\textsuperscript{39} We offer that doping alkaline earth metals has the potential to improve PV performance in Pb-Sn perovskites.\textsuperscript{39,40}

We checked for the classification of defects as deep vs shallow, looking at the localized/delocalized wavefunction in the neutral charge state.\textsuperscript{31–43} Though \(B_{\text{int}}\)\textsuperscript{0} induced localized defect states inside the bandgap, the large atomic relaxation near \(B_{\text{int}}\)\textsuperscript{2+} from strong Coulomb interactions may cause a large reduction in its formation energy, resulting in negative-U behavior (Figure S10).\textsuperscript{34} Importantly, we found that the stronger B–X ionic bonding strength induced a higher unoccupied energy level in \(B_{\text{int}}\)\textsuperscript{2+}, with respect to the CBM,
resulting in a shallower defect CTL. As shown in Figures 2b and 3g, Ge\text{int} and Zn\text{int} create deep states within the bandgap, while other B-site interstitials (Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Sr\textsuperscript{2+}, Cd\textsuperscript{2+}) are shallow.

Overall, we find that the band edge positions and coordination environment (short-range orbital hybridization and long-range electrostatic interaction) determine the defect properties in B-site alloyed systems. We conclude two general trends of enhanced defect tolerance in OIHPs via B-site alloying: (i) A higher VBM (lower CBM) is beneficial for the suppression of deep acceptors (donors). (ii) Stronger B–X ionic bonding and weaker B–B covalent bonding yield shallower defects.

Finally, we carried out experimental measurements to explore further the property of defect tolerance. We observed a decrease in PCE of mixed Pb-Sn perovskite solar cells when alloying Ge at the B-site (Table S2). We then turned our focus to measuring the optoelectronic properties of mixed Pb-Sn perovskites with varying Sn content. We first performed steady-state photoluminescence (PL) measurements on FA\textsubscript{0.75}Cs\textsubscript{0.25}Pb\textsubscript{1−x}Sn\textsubscript{x}I\textsubscript{3} perovskite films. As shown in Figure 4a, the general trend of PL peak shifts agrees well with the optical $E_g$ of the films measured using UV-vis-NIR spectroscopy (Figure S1). Interestingly, we found that the PL intensities were enhanced noticeably for Sn content of 50% or higher (Figure 4b). We then employed time-resolved photoluminescence (TRPL) to study the carrier dynamics of the Pb-Sn perovskites. As shown in Figure 4c, both Sn-poor (<30%) and Sn-rich (>75%) mixed Pb-Sn perovskites exhibited much shorter PL lifetimes, indicative of their highly defective nature. However, the carrier lifetimes were significantly improved to 754 ns at 50% Sn, implying suppressed non-radiative recombination.

Since 50% Sn mixed perovskites are significantly more defect tolerant, as we have shown theoretically and experimentally, we sought to determine whether the defect-tolerant nature of 50% Sn mixed Pb-Sn perovskites could be applied beyond narrow-$E_g$ perovskites to ideal-$E_g$ single-junction solar cells. Using a 10% Br composition of FA\textsubscript{0.75}Cs\textsubscript{0.25}Pb\textsubscript{0.5}Sn\textsubscript{0.5}(I\textsubscript{0.9}Br\textsubscript{0.1})\textsubscript{3}, we achieved the same ideal $E_g$ as with Br-free 30% Sn thin films (1.33 eV) and observed a significantly increased carrier lifetime from 304 to 1034 ns (Figure 4c and Figure S11), among the longest carrier lifetimes reported for MA-free Pb-Sn perovskites. This can be partly attributed to the stronger B–X (X = Br) bonding than when X = I. Our calculations also confirm that both I\textsubscript{int} and Br\textsubscript{int} are shallow defects in this composition (Figure S12).

In summary, we have combined advanced first-principles defect calculations, UV-vis-NIR, UPS, steady-state PL, and TRPL measurements to investigate the effects of B-site alloying on the optoelectronic properties of OIHPs. We identified a region of enhanced defect tolerance spanning Sn contents of 30–70% in mixed Pb-Sn perovskites. In particular, 50% Sn alloyed perovskite with a $E_g$ of 1.25 eV exhibited notably longer carrier lifetimes than all other Sn contents. Importantly, we demonstrate an ideal-$E_g$ (1.33 eV) perovskite composition using the defect-tolerant 50% Sn content (FA\textsubscript{0.75}Cs\textsubscript{0.25}Pb\textsubscript{0.5}Sn\textsubscript{0.5}(I\textsubscript{0.9}Br\textsubscript{0.1})\textsubscript{3}) with a much-improved carrier lifetime of >1 μs, offering a direction for efficient ideal-bandgap solar cells. Our calculations also indicate the potential of alloying alkaline earth metals for improving the PV performance of Pb-Sn perovskites. This work reveals a general trend of defect tolerance for B-site alloying in OIHPs: a higher VBM (lower CBM) along with stronger ionic bonding potentially leads to enhanced defect tolerance.

■ ASSOCIATED CONTENT

 Supporting Information

 The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsenergylett.1c02105.

 DFT calculation methods (calculation details, mixing thermodynamics, defect thermodynamics); experimental methods (materials preparation, perovskite precursor solution, perovskite film fabrication and characterization); UPS calculations; free energy and enthalpy of mixing; origin of the bandgap bowing; projected band structures; PBE-calculated CTLs of intrinsic defects; CTLs of $V_{\text{int}}$ calculated relative reaction energies; calculated $\Delta$values for $V_{\text{int}}$; CTLs of $V_{\text{int}}$ in different doping concentrations; local atomic structures of $V_{\text{int}}$ in doped systems; single particle energy levels; PV performance of perovskite solar cells and UV-vis-NIR; and CTLs of I\textsubscript{int}/Br\textsubscript{int} including Figures S1–S12 and Tables S1 and S2 (PDF)

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 J.X. and A.M. contributed equally to this paper.

 Notes

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