

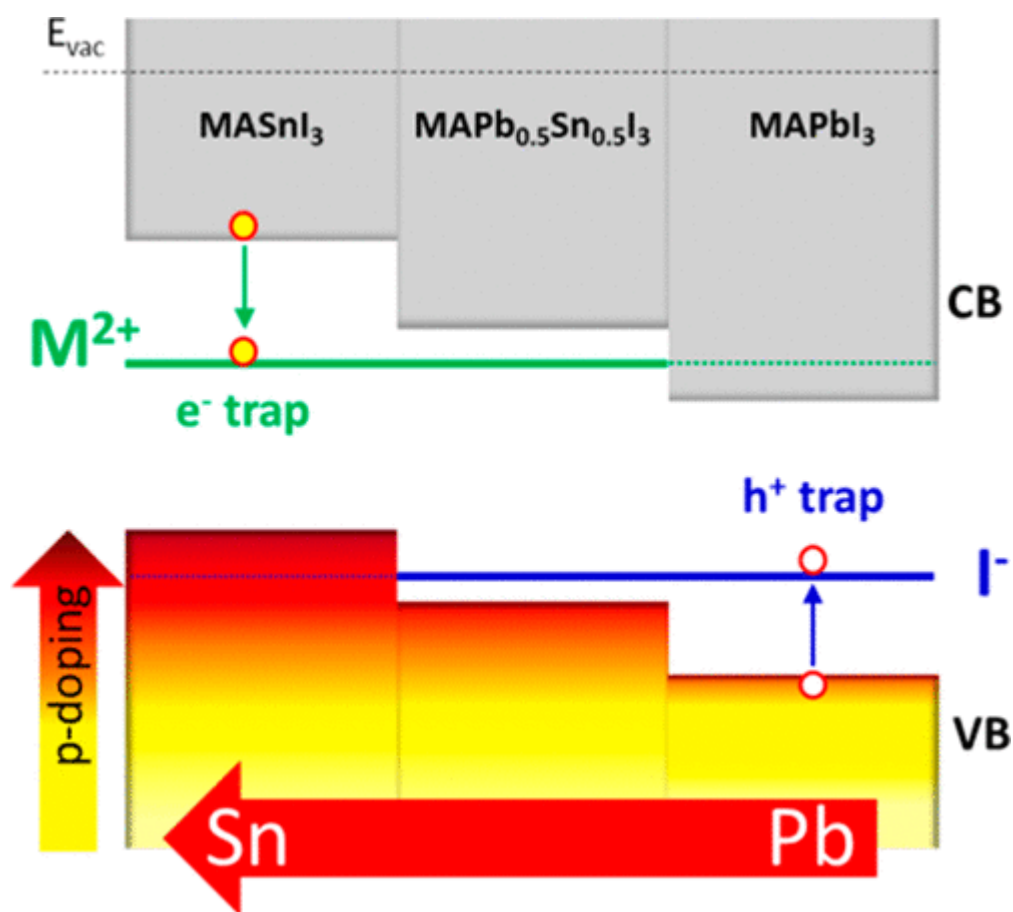
Tin versus Lead Redox Chemistry Modulates Charge Trapping and Self-Doping in Tin/Lead Iodide Perovskites

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Abstract



Tin halide perovskites make up the only lead-free material class endowed with optoelectronic properties comparable to those of lead iodide perovskites. Despite significant progress, the device efficiency and stability of tin halide perovskites are still limited by two potentially related phenomena, i.e., self-p-doping and tin oxidation. Both processes are likely related to defects; thus, understanding tin halide defect chemistry is a key step toward exploitation of this class of materials. We investigate the MASnI₃ perovskite defect chemistry, as a prototype of the entire materials class, using state-of-the-art density functional theory simulations. We show that the inherently low ionization potential of MASnI₃ is solely responsible of the high stability of tin vacancy and interstitial iodine defects, which are in turn at the origin of the material p-doping. Tin vacancies create a locally iodine-rich environment that could promote Sn(II) → Sn(IV)

oxidation. The higher band edge energies of MASnI_3 compared to those of MAPbI_3 lead to the emergence of deep electron traps associated with undercoordinated tin defects (e.g., interstitial tin) and the suppression of deep transitions associated with undercoordinated iodine defects that are typical of MAPbI_3 . Thus, while lead iodide perovskites are dominated by iodine chemistry, tin chemistry dominates tin iodide perovskite defect chemistry. Mixed tin/lead perovskites exhibit an intermediate behavior and are predicted to be potentially free of deep traps. Compositional alloying with different metals is finally explored as a strategy for mitigating defect formation and self-p-doping in tin iodide perovskites.

Lead halide perovskites (LHPs) are outstanding materials for photovoltaics due to their high absorption coefficients, long lifetimes of photogenerated carriers, and defect tolerance.^(1–6) Despite the fairly high defect density ($\sim 10^{15} \text{ cm}^{-3}$), LHP thin films have recently reached 25.2% efficiency in single-junction solar cells,⁽⁷⁾ which rivals the efficiencies of high-purity, high-quality inorganic semiconductors. The origin of the high defect tolerance of this class of materials has been widely investigated. Density functional theory (DFT) calculations showed that many native defects in LHPs have a shallow character with thermodynamic ionization levels close to or inside the band edges with a negligible impact on the optoelectronic properties of these materials.^(8,9) Subsequent studies highlighted the existence of deep traps in the prototypical MAPbI_3 (MA = methylammonium) perovskite that are associated with undercoordinated iodine atoms (e.g., interstitial iodine and lead vacancies) located in the bulk and at the surface and grain boundaries of polycrystalline thin films.^(6,10) Significantly, these defects only marginally impact the lifetime of the photogenerated charge carriers due to the existence of thermodynamic and kinetic barriers to trapping and recombination.^(6,11)

Despite the excellent properties of LHPs, concerns about lead toxicity^(12,13) have led to an increasing level of interest in replacing lead with less toxic metals.⁽¹⁴⁾ Sn(II),^(15,16) Ge(II),⁽¹⁷⁾ and combinations of I/III metals like Bi and Ag^(18–20) have been proposed as substitutes for lead in halide perovskites. Among these materials, however, only tin halide perovskites have shown significant photovoltaic properties, with device efficiencies reaching $\sim 10\%$.^(15,21–23) The use of tin in combination with lead in mixed tin/lead perovskites is so far the most effective strategy for reducing the lead content in perovskite thin films; with efficiencies of $\sim 17\%$, these mixed perovskites can be competitive with pure LHPs.⁽²⁴⁾ A further advantage of using tin and mixed tin/lead iodide perovskites is their lower and tunable band gap ($\sim 1.1\text{--}1.3 \text{ eV}$, by varying the ratio of the two metals) compared to those of typical LHPs ($\sim 1.5\text{--}1.6 \text{ eV}$), coupled to lower exciton binding energies.⁽²⁵⁾ These characteristics make mixed tin/lead perovskites appealing for the development of efficient all-perovskite tandem solar cells.⁽²²⁾

The device efficiency of tin perovskites is strongly limited by the self-p-doping characteristic of such materials that increase the background hole density to intolerable values of $\sim 10^{20} \text{ cm}^{-3}$.⁽¹⁶⁾ In fact, MASnI_3 was initially thought to be metallic due to the strong p-doping leading to unusually high conductivity.⁽²⁶⁾ Similarly, CsSnI_3 was initially proposed as a solid state hole transporter in dye-sensitized solar cells by virtue of its high p-type conductivity.⁽²⁷⁾ P-Doping increases recombination rates, reducing dramatically the lifetime and diffusion length of photogenerated charge carriers by more than an order of magnitude compared to the typical values observed in LHPs.⁽²⁵⁾

In addition to p-doping, and possibly related to it, the facile oxidation of Sn(II) to Sn(IV) limits the air stability of polycrystalline thin films,^(15,25) promoting the degradation of the perovskite to Sn(IV)-based secondary phases such as $\text{MA}_2(\text{FA}_2)\text{SnI}_6$ and SnI_4 (FA = formamidinium).^(28,29) To alleviate this issue, Shao et al. used three-dimensional (3D)/two-dimensional (2D) mixed dimensionality perovskites that stabilize the 3D FASnI_3 phase by interfacing it with a more stable 2D $\text{PEA}_2\text{FA}_{n-1}\text{SnI}_{n+1}$ phase (PEA = phenylethylammonium), possibly passivating surface defects and grain boundaries.⁽³⁰⁾ Insight into the degradation mechanisms of FASnI_3 and $\text{FAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ has been provided by Leijtens et al. through thermogravimetric analysis in air, X-ray diffraction, and ultraviolet–visible spectroscopy.⁽³¹⁾ The oxidation of FASnI_3 proceeds with release of FAI, SnO_2 , and SnI_4 , while for mixed tin/lead perovskites, release of

I₂ was also observed in addition to that of FAI, SnO₂, and PbI₂.⁽³¹⁾ While I₂ and PbI₂ are typical degradation products of LHPs, formation of PbO₂ is less likely to occur in LHPs due to the higher oxidation potential of the Pb(II)/Pb(IV) redox couple compared to that of the Sn(II)/Sn(IV) couple. As a side note, but relevant to our modeling study, the difference in lead and tin redox potentials is dictated by relativistic effects, such as spin-orbit coupling (SOC),⁽³²⁾ which are a key ingredient, together with hybrid functionals, of accurate simulations.^(10,33)

Several experimental strategies have been elaborated to reduce the level of native p-doping of tin halide perovskites. The addition of SnF₂ has been shown to effectively stabilize the metal sublattice by decreasing the background hole density and dark current.^(25,28) Milot et al. reported a 10-fold increase in the charge carrier diffusion length and lifetime for FASnI₃ by addition of an excess of a 10% molar amount of SnF₂ with respect to SnI₂ in the precursor solution, which leads to a decrease in hole density of ~2 orders of magnitude, giving a value of ~10¹⁸ cm⁻³.⁽²⁵⁾ Interestingly, although carrier dynamics in pristine and SnF₂-doped FASnI₃ is still dominated by charge recombination with background holes, a remnant contribution associated with trap-mediated recombination was also reported, indicating the existence of traps of different natures that are not (completely) passivated by SnF₂ treatment.⁽²⁵⁾ The addition of electron-donating and tin-complexing molecules was also shown to limit the Sn(II) to Sn(IV) oxidation, improving the perovskite morphology and the associated device efficiency. Lee et al. obtained homogeneous crystal grain growth with a reasonable 4.8% efficiency by using a combination of SnF₂ and pyrazine;⁽³⁴⁾ pyrazine can form a complex with SnF₂ by increasing its level of dispersion within the perovskite thin film, leading to more homogeneous films and mitigating phase separation induced by excess SnF₂. Hoshi et al. demonstrated that the addition of 5-ammonium valeric acid iodide (5-AVAI) to MASnI₃ significantly improves the stability of the material in air,⁽³⁵⁾ an effect further confirmed by Tai et al. by employing hydroxybenzenesulfonic acids.⁽³⁶⁾ Song et al. demonstrated that the use of hydrazine reducing vapors, along with SnF₂, causes a 20% decrease in the Sn(IV)/Sn(II) ratio, yielding a PCE of 3.89%.⁽³⁷⁾ The Sn(IV)/Sn(II) ratio was shown to decrease using hypophosphorous acid,⁽³⁸⁾ 5-AVAI,⁽³⁹⁾ and other bulky organic cations such as ethylenediammonium di-iodide and butylammonium iodide.⁽⁴⁰⁾ The addition of bulky cations in particular promotes the crystallization of 2D perovskites, and even for small additions in the precursors, a significant increase in the tin perovskite phase stability is reported, likely associated with the passivation of the grain surface and boundaries preventing, among other effects, the incorporation of oxygen and moisture.⁽⁴¹⁾

Due to their strong impact on the efficiency and stability of tin halide perovskites, it is essential to investigate the microscopic origin of self-p-doping and the mechanisms leading to tin oxidation to propose solutions to both issues, possibly promoting the widespread use of lead-free perovskite solar cells. In both p-doping and tin oxidation, defects are likely to play a central role, determining both the intrinsic charge carrier density and lattice instability. To quantitatively assess the role of defects in determining p-doping and instability in tin halide perovskites, we investigate the thermodynamic stability and trapping activity of native defects in the prototypical MASnI₃ system by state-of-the-art DFT calculations based on hybrid functionals and SOC. Our analysis shows that the high stability of tin vacancies, already recognized in previous studies,^(23,42,43) and interstitial iodine are responsible for the severe p-doping exhibited by MASnI₃, which we directly relate to the inherently low ionization potential of tin iodide perovskites. By comparing the electronic structure of tin and lead iodide perovskites, we show that the strong modulation of band edge energies induced by varying the tin content significantly affects the stability of metal vacancies. The higher band edge energies (lower ionization potential) of MASnI₃ compared to those of MAPbI₃ largely stabilize acceptor defects and lead to the emergence of deep electron traps associated with undercoordinated tin defects (e.g., interstitial tin) and the suppression of deep transitions associated with undercoordinated iodine defects that are active in LHPs. The shift of the band edge energies predicted upon moving from MASnI₃ to MAPbI₃⁽⁴⁴⁾ places the mixed MAPb_{0.5}Sn_{0.5}I₃ phase in an intermediate regime between the pure tin and lead phases. A high concentration of tin vacancies may also create a locally

iodine-rich environment that could promote $\text{Sn(II)} \rightarrow \text{Sn(IV)}$ oxidation through the formation of a vacancy-ordered phase similar to typical Sn(IV) phases, e.g., MA_2SnI_6 .⁽⁴³⁾ While extrinsic factors, such as exposure to oxidizing agents (O_2 or I_2), can be limited by caution in the processing conditions and encapsulation, the intrinsic instability related to the electronic structure of the material remains a critical issue that can be managed by high-quality crystal grain growth and proper surface passivation treatments. In addition, we propose a strategy for alleviating the instability of tin iodide perovskites by alloying tin with different metals.

The thermodynamics and trapping activity of native defects are investigated by calculating the associated defect formation energies (DFEs) and thermodynamic ionization levels (TILs), $\epsilon(q/q')$, in the supercell approach^(33,45) (see [Computational Details](#)). DFEs provide information about the stability of a given defect and, thus, its thermodynamic propensity to form. TILs basically represent redox potentials associated with carrier trapping at defect sites, whereby a TIL placed (deep) in the material gap will trap a carrier; a defect with a TIL within the band edges will be essentially harmless in terms of trapping but may dope the material if its charge is not compensated by defects of the opposite charge. To provide a reliable description of defect equilibrium geometries in various charge states,⁽³³⁾ the PBE0 hybrid functional^(46,47) was used for structural relaxations, including D3 dispersion corrections.⁽⁴⁸⁾ Single-point HSE06-SOC ($\alpha = 0.43$)⁽⁴⁹⁾ calculations were performed on the PBE0-D3 optimized structures to obtain accurate band and defect energetics (see [Computational Details](#)).⁽³³⁾ All calculations have been carried out considering the respective tetragonal phases of $\text{MAPb}_x\text{Sn}_{1-x}\text{I}_3$ perovskites ($x = 0, 0.5$, and 1).

The calculated thermodynamic stability field of MASnI_3 is compared to that of MAPbI_3 in [Figure 1](#), which illustrates the range of chemical potentials of the constituent elements in which the possible phases resulting from combination of these elements are stable. MAPbI_3 is stable in a narrow region of chemical potentials, enclosed between the PbI_2 and MAI precursors, and it may exist in thermodynamic equilibrium with solid I_2 ([Figure 1a](#)). MASnI_3 is also stable in a narrow region between SnI_2 and MAI precursors, with a comparable formation enthalpy (-0.07 and -0.14 eV for MAPbI_3 and MASnI_3 , respectively). Under iodine-rich conditions ($\Delta\mu_{\text{I}} > -0.16$ eV), however, MASnI_3 is no more stable and spontaneously transforms into MA_2SnI_6 and SnI_4 phases characterized by oxidation of Sn(II) to Sn(IV) .⁽⁴³⁾ The existence of thermodynamically stable Sn(IV) phases, not existing for MAPbI_3 , represents an inherent stability limit of MASnI_3 (and in general of all tin perovskites)^(42,43) with respect to LHPs, which becomes more relevant in oxidative environments, e.g., in the presence of I_2 .

Figure 1

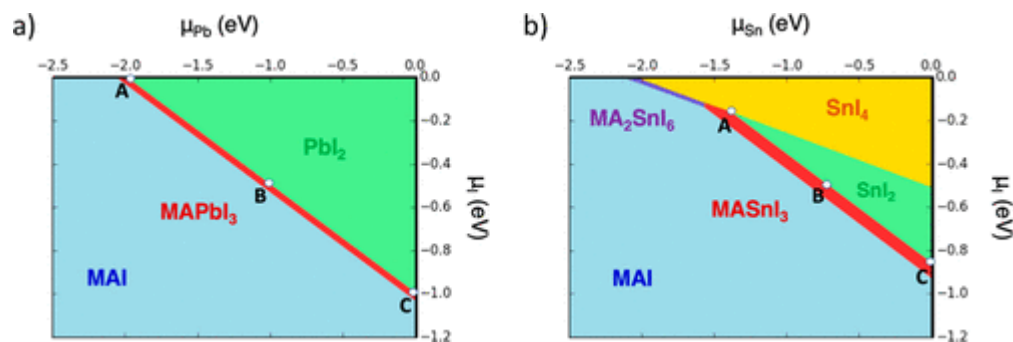


Figure 1. Phase diagrams of (a) MAPbI_3 and (b) MASnI_3 calculated at the HSE06-SOC ($\alpha = 0.43$) level of theory, including dispersion corrections. The chemical potentials of Sn, Pb, and I have been referenced to metallic Sn, metallic Pb, and solid I_2 , respectively. Three chemical potential points on the equilibrium lines between the perovskites and the relative precursors have been highlighted, indicating I-rich (point A, $\Delta\mu_{\text{I}} = 0.0$ eV and $\Delta\mu_{\text{Pb}} = -1.99$ eV for MAPbI_3 ; $\Delta\mu_{\text{I}} = -0.16$ eV and $\Delta\mu_{\text{Sn}} = -1.39$ eV for MASnI_3), I-medium (point B, $\Delta\mu_{\text{I}} = -0.50$ eV and $\Delta\mu_{\text{Pb}} = -1.00$ eV for MAPbI_3 ; $\Delta\mu_{\text{I}} = -0.51$ eV and $\Delta\mu_{\text{Sn}} = -0.70$ eV for MASnI_3), and I-poor

(point C, $\Delta\mu_i = -1.00$ eV and $\Delta\mu_{\text{Pb}} = 0.00$ eV for MAPbI_3 ; $\Delta\mu_i = -0.86$ eV and $\Delta\mu_{\text{Sn}} = 0.00$ eV for MASnI_3) conditions of perovskite growth.

DFEs calculated for MASnI_3 in I-rich, I-medium, and I-poor growth conditions (corresponding to stability points A–C in [Figure 1b](#), respectively) are reported in [Figure 2](#). A remarkable stability of acceptor defects, i.e., tin vacancies and interstitial iodine, is found under all growth conditions. Tin vacancies are stable in the 2– charge state ($\text{V}_{\text{Sn}}^{2-}$), with a 2–/– transition resonant with the top of the valence band (VB) (see [Figure 3a](#)). Upon removal of Sn from its crystal site, the lattice undergoes a limited rearrangement, leaving the vacancy site almost intact (see the optimized structures in [Figure 4a](#)). Similarly, interstitial iodine is stable in the 1– charge state (I_i^-) with the –/0 transition resonant with the top of the VB ([Figure 3a](#)). Interstitial iodine shows the typical bridge structure found for MAPbI_3 ([Figure 4b](#)).⁽¹⁰⁾

Figure 2

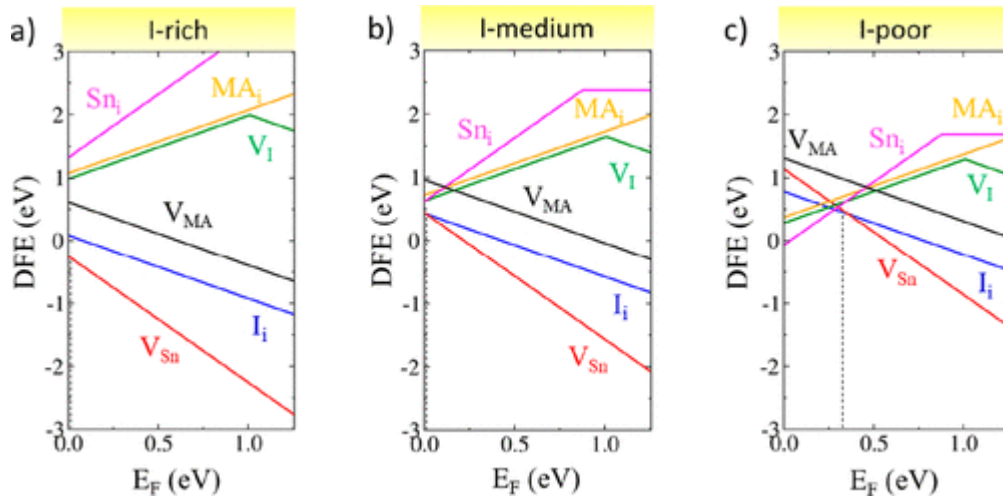


Figure 2. Defect formation energy diagrams of native defects in MASnI_3 calculated at the HSE06-SOC-D3 ($\alpha = 0.43$) level of theory for (a) I-rich, (b) I-medium, and (c) I-poor chemical conditions, i.e., points A–C in [Figure 1b](#), respectively. The vertical dashed line, overlapping with the valence band in panels a and b, indicates the native Fermi level of the system.

Figure 3

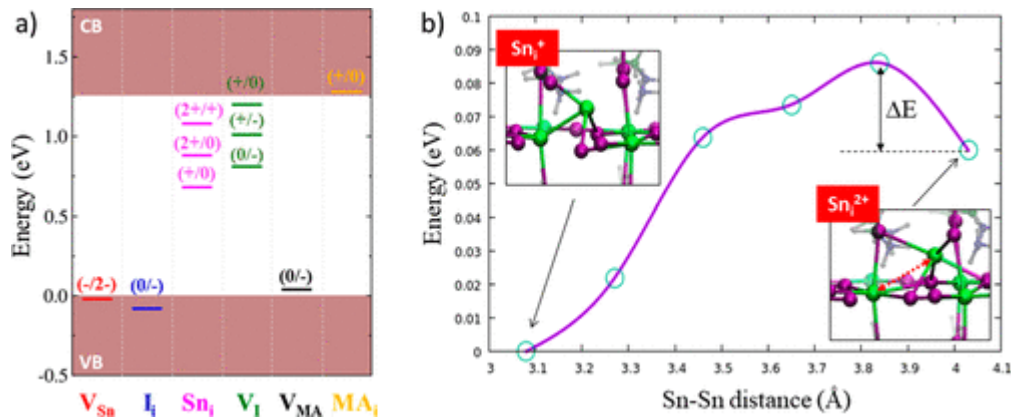


Figure 3. (a) Thermodynamic ionization levels of native defects in MASnI_3 calculated at the HSE06-SOC-D3 ($\alpha = 0.43$) level of theory. (b) Simulated path for electron trapping at the Sn_i^{2+} defect. Tin ions are unbound in the Sn_i^{2+} defect (right), while they are bonded to form a dimer in the Sn_i^{+} equilibrium configuration (left). The calculated barrier ΔE is 0.03 and 0.10 eV at the PBE and HSE06-SOC levels of theory, respectively.

Figure 4

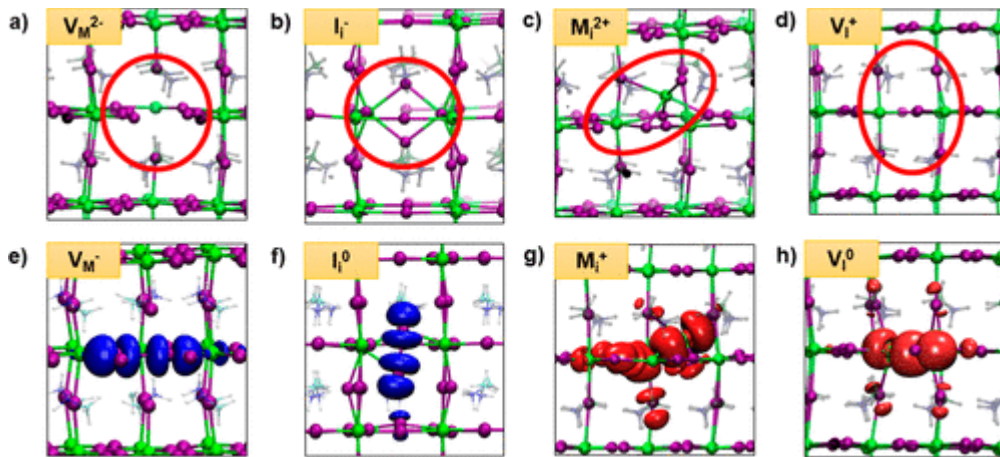


Figure 4. (a–d) Optimized structures of the main defects in MASnI₃ and MAPbI₃ (green for metal and purple for iodine). Sn and Pb are both denoted as M. (e–f) Plot of the orbital associated to the trapped charge on the V_M^- and I_i^0 defects in MAPbI₃. (g–h) Plot of the orbital associated to the trapped electron on the M_i^+ and V_i^0 defects in MASnI₃.

MASnI₃ p-doping is thus promoted by the formation of both defects, following the reactions



In [reaction 1](#), the reduction of Sn(II) to Sn metal (Sn_{bulk}) leads to the oxidation of the lattice by release of two holes. This process formally leads to the loss of the metal from the perovskite to form a Sn-rich phase, in agreement with experiments reporting the formation of Sn-rich clusters in mixed tin/lead perovskites with the concomitant formation of subgap trap states.[\(22\)](#) Similarly, in [reaction 2](#), the incorporation of iodine to form I_i^- introduces one charge hole into the VB. It is clear that these processes are in general facilitated by a high VB energy, i.e., by a low ionization potential, which stabilizes the charge holes produced by the perovskite to compensate the negative charge of the native defects.

The lack of compensating defects with a positive charge under I-rich and I-medium conditions places the native Fermi level at the top of the VB, indicating that MASnI₃ tends to grow intrinsically p-doped, with estimated hole densities of $\sim 10^{19} \text{ cm}^{-3}$ under I-medium perovskite growth conditions, in fairly good agreement with experiments.[\(21\)](#) Notice that our simulations refer to perfect bulk crystals, so that higher defect (and hole) densities are expected in polycrystalline thin films due to lower DFEs typically associated with surfaces and grain boundaries.[\(50\)](#)

Donor defects, such as iodine vacancies (V_i^+) and interstitial tin (Sn_i^{2+}), are less stable than acceptor defects under I-rich and I-medium conditions ([Figure 2a,b](#)), while they show stability comparable to that of tin vacancies under I-poor conditions for which Sn_i^{2+} is the most stable defect ([Figure 2c](#)). Via introduction of a stable (i.e., of low DFE) positively charged defect compensating for the negative charge of V_{Sn}^{2-} and I_i^- , the native Fermi level rises at $\sim 0.3 \text{ eV}$ above the VB maximum. Our analysis shows that under I-poor (or Sn-

rich) conditions self-p-doping can be limited by formation of $\text{Sn}_i^{2+}/\text{V}_{\text{Sn}}^{2-}$ Frenkel pairs, whose formation energy in the limit of non-interacting defects is comparable to that computed for MAPbI_3 .⁽⁵¹⁾

In the stable 2+ charge state, interstitial tin (Sn_i^{2+}) shows a distorted octahedral configuration, with a shortest Sn–Sn distance of 4.08 Å (Figures 3b and 4c). Addition of electrons to form Sn_i^+ and Sn_i^0 leads to a decrease in the Sn–Sn distance to 3.08 and 2.94 Å, respectively, indicating the formation of a new bond between lattice and interstitial Sn ions (Figures 3b and 4g). The corresponding 2+/+ and 2+/0 TILs are placed 1.08 and 0.88 eV above the VB maximum, respectively, over a calculated band gap of 1.26 eV (Figure 3a). The thermodynamically stable Sn_i^{2+} defect can thus trap electrons through the 2+/+ transition calculated at 0.18 eV below the conduction band (CB) minimum, promoting nonradiative recombination. This is likely the defect observed by Milot et al. leading to a remnant bimolecular recombination in FASnI_3 .⁽²⁵⁾ Figure 4g shows a plot of the orbital associated with the defect-trapped electron of Sn_i^+ . Because in the 2+ charge state no such orbital is observed in the band gap, a barrier to electron trapping at this defect is likely to occur, possibly limiting its trapping activity. To estimate the electron trapping barrier at this defect, a linear transit between the Sn_i^{2+} and Sn_i^+ geometrical configurations in the 1+ state of charge was carried out (see Computational Details). The calculated path confirms the existence of a small barrier to electron trapping on the Sn_i^{2+} defect of 0.1 eV at the HSE06-SOC level (see Figure 3b). This highlights the fact that electron trapping at interstitial tin may be kinetically hindered, potentially limiting the trapping activity of this defect.

Iodine vacancies are stable in the positive (V_i^+) and negative (V_i^-) charge states along the Fermi level. In the positively charged state, the two undercoordinated tin atoms are at distances of ~6 Å, with minimal geometrical rearrangement compared to the pristine structure (Figure 4d). Like the case for interstitial tin, addition of electrons to V_i^+ leads to the formation of a Sn–Sn bonded dimer, with intermetal distances of 3.48 and 3.24 Å for the neutral and negative states, respectively (Figure 4h). The density plot of the trapped electron on the neutral V_i^0 , reported in Figure 4h, highlights the charge localization on the defect center. The calculated +/0 and +/- TILs are found 1.20 and 1.01 eV above the VB maximum, respectively; thus, electron trapping on the V_i^+ centers is only slightly favored, with a TIL lying 0.06 eV below the CB minimum. Defects associated with the cation sublattice such as V_{MA}^- and MA_i^+ , on the other hand, do not introduce deep levels in the band gap; thus, they are not active in trapping processes.

Our quantitative analysis of MASnI_3 defect chemistry highlights two main factors possibly limiting the material optoelectronic quality: (i) the self-p-doping caused by the high stability of tin vacancy and interstitial iodine defects, which increases the level of monomolecular radiative recombination, and (ii) the existence of nonradiative recombination centers associated with undercoordinated tin centers in the form of tin interstitials and iodine vacancies.

The defect chemistry of tin perovskites appears thus to be profoundly different from that of MAPbI_3 and analogous LHPs. Self-p-doping is not observed in MAPbI_3 , and iodine vacancies and lead interstitials, which are possible electron traps, are not active in LHPs because their TILs are resonant with the CB^(6,33) (Figure 5d). It is interesting to further compare the defect properties of MASnI_3 and MAPbI_3 to those of the mixed $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ perovskite (Figure 5). Besides the different metal, the stability and trapping activity of defects in their different states of charge are largely influenced by the electronic structure of the host, particularly by the absolute energy positions of the VBM and CBM.

Figure 5

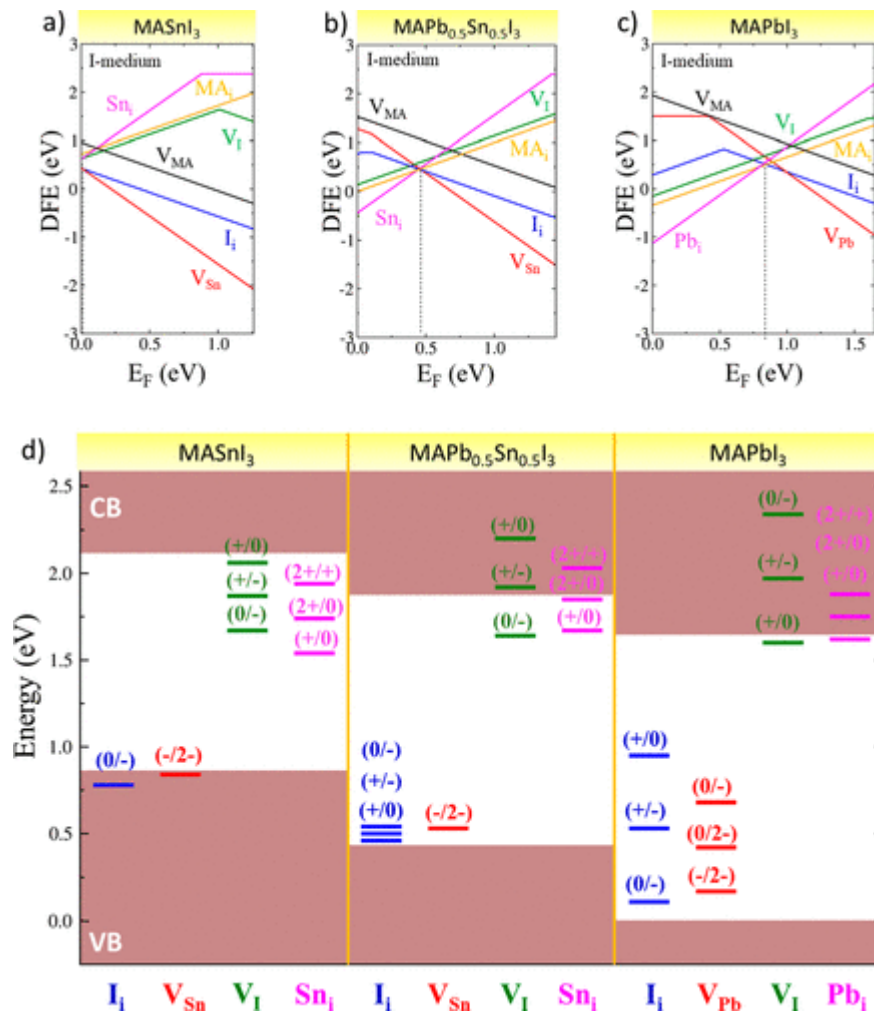


Figure 5. Defect formation energies computed at the HSE06-SOC-D3 ($\alpha = 0.43$) level of theory for I-medium conditions of (a) MASnI₃, (b) MAPb_{0.5}Sn_{0.5}I₃, and (c) MAPbI₃ perovskites. (d) Thermodynamic ionization levels (TILs) of MASnI₃, MAPb_{0.5}Sn_{0.5}I₃, and MAPbI₃ at the same level of theory. The zero of the energy scale in panel d is placed at the VB of MAPbI₃.

The VB energy (ϵ_{VB} in [eq 3](#) in [Computational Details](#)) associated with the oxidation potential of the pristine material (ionization potential) defines the electronic energy associated with the exchange of charges between the defect and the Fermi level of the bulk (see [Computational Details](#)). Because an almost monotonic increase in the VB energy is predicted moving from MAPbI₃ to MAPb_{0.5}Sn_{0.5}I₃ and MASnI₃ perovskites, we anticipate a significantly different DFE for the three perovskites, with the mixed tin/lead material showing somehow intermediate properties.

The electronic structures of tin and lead perovskites share many similarities. In both cases, the VB is composed by iodine p orbitals and metal s orbitals, while the CB is mainly derived from metal p orbitals ([Figure S1](#)). In the case of tin, the contribution of tin s orbitals to the VB is slightly larger than in the lead perovskite.⁽⁵²⁾ The different metal strongly affects the absolute position of the band edges in the two perovskites and thus the defect properties in terms of both DFEs and TILs. The calculated DFEs under I-medium growth conditions and the aligned band edges with the calculated TILs of the main defects for MASnI₃, MAPb_{0.5}Sn_{0.5}I₃, and MAPbI₃ are compared in [Figure 5](#). As one may notice, the absolute VBM and CBM energies of MASnI₃ are higher, i.e., closer to the vacuum level, by 0.86 and 0.48 eV, respectively, than in MAPbI₃. The mixed MAPb_{0.5}Sn_{0.5}I₃ perovskite shows intermediate band energies between those of the full lead and full tin perovskites, with an almost linear change in the electronic structure moving between

the two limiting compositions. The calculated band offsets are slightly higher than those measured by UPS experiments,⁽⁵³⁾ likely due to the pinning of the VBM energies caused by the different chemical compositions of the surfaces in polycrystalline thin films probed by photoemission spectroscopy.⁽⁵⁴⁾ It is apparent at first glance that the higher energy of VBM in MASnI₃ with respect to that of MAPbI₃ is indicative of a stronger propensity of the tin perovskite to oxidize compared to those of MAPbI₃ and MAPb_{0.5}Sn_{0.5}I₃.

Upon examination of the DFEs in panels b and c of [Figure 5](#), the most stable defects in MAPbI₃ and MAPb_{0.5}Sn_{0.5}I₃ are both donors and acceptors in the form of MA and iodine interstitials. Other defects such as V_{Pb} (V_{Sn}) and Pb_i (Sn_i) are also stable at the native Fermi level. Overall, a progressive stabilization (destabilization) of acceptor (donor) defects is reported moving from MAPbI₃ to MASnI₃ caused by the VBM upshift. The calculated DFEs show a monotonic shift moving from MAPbI₃ to MAPb_{0.5}Sn_{0.5}I₃ to MASnI₃, following the shift of the electronic band edges of the pristine phases. As an example, DFEs calculated in MASnI₃ at the VBM show values comparable to those calculated at an E_F of 0.86 eV in MAPbI₃, i.e., at the Fermi level corresponding to the position of the aligned VBM of MASnI₃. The MAPb_{0.5}Sn_{0.5}I₃ phase shows intermediate defect properties between those of full tin and lead perovskites. This points out that contributions due to the different nature of the metal–halide bond to defect formation are rather similar and the differences in DFEs mainly stem from the different electronic structure of the pristine phases. Interestingly, native defects pin the Fermi levels ~ 0.8 , ~ 0.4 , and ~ 0 eV above the VBM in MAPbI₃, MAPb_{0.5}Sn_{0.5}I₃, and MASnI₃, respectively. Self-p-doping in MASnI₃ (not observed in MAPbI₃) is thus intimately related to the electronic band edge energies, whereby an increasingly intrinsic behavior can be expected upon alloying MASnI₃ with larger amounts of lead.

An interesting consequence of this behavior is that in the p-doped region of MAPbI₃ I_i and V_{Pb} are stable in their oxidized forms, i.e., I_i⁺ and V_{Pb}⁰, leading to the formation of iodine trimers whereby iodine is oxidized to a form similar to I₃[−].^(6,33) ([Figure S2](#)). Interstitial iodine and lead vacancies introduce thermodynamic ionization levels deep in the band gap and are active recombination centers in MAPbI₃ ([Figure 5d](#)).^(6,33) The trapping of electrons and/or holes on these centers leads to the formation of intermediate radical states, i.e., I_i⁰ and V_{Pb}[−], where two iodine atoms are bonded to form dimers at distances of 3.20–3.30 Å (see panels e and f of [Figure 4](#) for plots of the localized orbitals of these defects).^(6,33) Similar defect structures also exist in MASnI₃ but are less stable than the I_i[−] and V_{Pb}^{2−} defects with one and two holes delocalized in the VB, respectively; thus, the associated TILs occur deep in the VB of MASnI₃. The higher VB energy of MASnI₃ thus prevents their formation, by favoring only the reduced forms of these defects, i.e., I_i[−] and V_{Sn}^{2−}, in the Fermi level range spanned by the band gap.

On the other hand, donor defects such as V_I and Pb_i are stable only in the respective oxidized forms in MAPbI₃, i.e., Pb_i²⁺ and V_I⁺. In MASnI₃, a progressive destabilization of these defects is reported at the VBM. The higher energy of the VBM and CBM in MASnI₃ compared to those of MAPbI₃ stabilizes the reduced forms of these defects, i.e., V_I[−] and Sn_i⁰, in the n region of the DFE diagram, thus favoring the formation of bonded Sn dimers. Notably, similar structures for V_I[−] and Pb_i⁰ are obtained in MAPbI₃ at the PBE and PBE0 levels of theory,⁽⁵⁵⁾ but the inclusion of SOC strongly destabilizes the respective Pb dimer-bonded forms, making them unstable.⁽³³⁾ As a result, the associated TILs that have a shallow character in MAPbI₃ become deep in the band gap of MASnI₃. The energy upshift of both the VBM and the CBM in MASnI₃ with respect to MAPbI₃ leads to the suppression of deep hole traps associated with I_i and V_{Pb} and to the emergence of deep electron traps associated with undercoordinated tin centers, i.e., V_I and Sn_i. Nonradiative recombination processes in MAPbI₃ and MASnI₃ are thus ruled by iodine and tin chemistry, respectively. Interestingly, the band edge energies in the mixed MAPb_{0.5}Sn_{0.5}I₃ phase, intermediate between those of MAPbI₃ and MASnI₃, lead to the concomitant suppression of both deep hole and electron traps associated with undercoordinated iodine and tin centers, respectively. Hence, Pb alloying is useful both in limiting self-p-doping and in reducing the density of recombination centers compared to that of MASnI₃.

Our analysis highlights the fact that MAPbI₃, MAPb_{0.5}Sn_{0.5}I₃, and MASnI₃ share a similar defect chemistry, but the different band edge energies modulate the relative stability of defects with transitions in the perovskite band gap. The inherent low ionization energy, promoting the formation of tin vacancies and p-doping, thus represents the critical factor limiting the efficiencies of tin perovskites in solar cells with respect to the mixed and full lead perovskites.

The beneficial role of Sn-rich conditions of growth in the efficiencies of tin perovskites, such as the addition of SnF₂,^(21,25,28,37,56–59) can be interpreted as a strategy that aims to increase the chemical potential of tin, hindering the formation of tin vacancies.⁽²⁵⁾ As reported in [Figure 2c](#), Sn-rich (I-poor) conditions increase the DFE of V_{Sn}²⁻ by ~0.7 eV in MASnI₃ compared to stoichiometric growth conditions (I-medium). Under such conditions, the heavy p-doping of MASnI₃ is mitigated by the upshifting of the native Fermi level at ~0.3 eV above the VBM due to the formation of tin Frenkel couples in the lattice. According to our predictions, a potential decrease in the hole density from 10¹⁹ to 10¹⁵ cm⁻³ may be achieved by using strong Sn-rich conditions. The use of Sn-rich environments, on the other hand, may favor the formation of Sn_i and V_i electron traps, potentially enhancing trap-assisted recombination in the tin perovskite. The presence of a thermodynamic barrier to electron trapping on these defects, however, may attenuate their detrimental impact on the solar cell efficiency.

VB energy tuning through a change in the chemical composition may be the guideline for improving the intrinsic performance of tin-based perovskites. As discussed above, metal alloying with Pb is a satisfactory strategy for increasing the ionization potential of MASnI₃ yielding more tolerable p-doping and better stability, without dramatic effects on the perovskite band gap. Notably, according to our calculations, the mixing of MASnI₃ and MAPbI₃ to give MAPb_{0.5}Sn_{0.5}I₃ is thermodynamically slightly disfavored by 0.04 eV, highlighting a tendency of this phase to disproportionate. This limitation can be alleviated by using tailored doping strategies, as discussed by Bowman et al., which showed that incorporation of Zn in mixed tin/lead perovskites induces a more controllable p-doping and an enhancement of the lattice stability.⁽⁶⁰⁾ Alternative strategies may rely on alkaline and transition metal doping, which have been extensively investigated in LHPs.^(61–63) It has been reported that Sr doping of FASnI₃ improves the material thermal stability and morphology, also leading to increased solar cell performances.^(61–63) Like metal doping, the alloying with more electronegative halides, such as bromide, may be beneficial to increase the efficiency of tin perovskites, as shown for MASnI₃ and FASnI₃.^(64,65)

To investigate the potential effects of tin alloying with metals different from lead, we modeled MASnI₃ doped with various concentrations of Cd, Sr, Zn, and Ca as substitutions for Sn. We monitored the shift of the band edge energies with respect to the pristine MASnI₃ for doping concentrations from ~3% to 25% (see the results in [Table S1](#) and [Figure S3](#)). To provide a more accurate estimate of the VB shift, we refined calculations for the lowest dopant density of ~3% at the HSE06-SOC-D3 level of theory in [Table 1](#).

Table 1. Energy Shifts of the VB, CB, and Band Gaps of MASnI₃ Doped with ~3% Cd, Sr, Zn, and Ca as Substitutions for Tin; Estimated Variations of the Energy of Formation of the Tin Vacancy (V_{Sn}²⁻ DFE) Based on the Shifts of the VB; and Calculated Exchange Energies of the Dopants as Substitutions for Tin^a

| metal | VB shift | CB shift | band gap shift | V _{Sn} ²⁻ DFE shift | exchange energy |
|-------|----------|----------|----------------|---|-----------------|
| Cd | -0.07 | +0.08 | +0.15 | +0.14 | -0.01 |
| Sr | -0.06 | +0.04 | +0.10 | +0.12 | 0.03 |
| Zn | -0.05 | +0.10 | +0.15 | +0.10 | 0.01 |
| Ca | -0.06 | +0.05 | +0.11 | +0.12 | -0.01 |

^aEnergy shifts of the VB and CB relative to the band edges of the pristine MASnI_3 have been calculated after aligning the inner 4s levels of tin in the perfect and doped supercells. All values (electronvolts) are calculated at the HSE06-SOC-D3 level of theory.

As one may notice, the series of considered alloying metals confirm a decrease (increase) in the VB (CB) energy compared to that of pristine MASnI_3 and an overall band gap increase. Results in [Table 1](#) are consistent with an increase in the DFE of $V_{\text{Sn}^{2-}}$ of ~ 2 times the VB shift (cf. [eq 3](#) and the [Supporting Information](#)), i.e., to an increase in the $V_{\text{Sn}^{2-}}$ DFE from 0.44 eV in the pristine material to $0.44 + 0.10/0.14$ eV. At the simulated 3% doping densities, a reduction in the hole density of ~ 2 orders of magnitude is accordingly predicted (from $\sim 10^{19}$ to $\sim 10^{17}$); thus, these doping elements may contribute to alleviating the self-p-doping in tin/iodine perovskites. The energetics of metal exchange, however, are only slightly favored in the case of Cd and Ca substitution. The small exchange reaction energies suggest that a significant excess of metal is required to induce its incorporation into the bulk, in agreement with the results of Adjokatse et al., who found a PL blue-shift, corresponding to the signature of incorporation of Sr into the bulk, only at a Sr precursor concentration of $>15\%$.[\(66\)](#) In line with these observations, we also predict an increase in the band gap upon incorporation of Sr into bulk MASnI_3 .

We investigated by state-of-the-art DFT methods the defect chemistry of tin iodide perovskite by focusing on the trapping activity of native defects in this system and the origin of the self-p-doping. The emergence of self-p-doping in MASnI_3 , not observed in lead-based perovskites, is ascribed to the high stability of tin vacancies, which originated in the high valence band energy. Our defect analysis confirms many similarities in defect chemistry among MASnI_3 , $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$, and MAPbI_3 . The relative stability of defects in these systems is significantly modulated by the different VB energies. This feature remarkably affects the charge trap chemistries, dominated by iodine in MAPbI_3 and tin in MASnI_3 . Interestingly, the intermediate value of the valence band in the mixed $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ phase leads to the parallel suppression of deep hole and electron traps found in the full metal perovskites. Overall, these results show that strategies for increasing the efficiencies of tin perovskites should focus on increasing the inherent low ionization potential of the tin perovskite, responsible for the p-doping. In this regard, changes in the chemical compositions, such as alloying of tin with different metals, among which we identify cadmium as a good candidate, may represent a promising route toward the exploitation of these materials in lead-free solar cells.

Computational Details

Defects have been modeled in the $2 \times 2 \times 2$ supercells of tetragonal MASnI_3 , $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$, and MAPbI_3 phases using the supercell approach. Equilibrium structures have been found by relaxing ion positions in the defect supercells by using the PBE0 functional[\(46,47\)](#) and including dispersion corrections through the DFT-D3 scheme.[\(48\)](#) In all cases, the cell parameters were fixed to the experimental values: for MASnI_3 , $a = b = 8.758$ Å and $c = 12.429$ Å; for $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$, $a = b = 8.855$ Å and $c = 12.535$ Å; for MAPbI_3 , $a = b = 8.849$ Å and $c = 12.642$ Å.[\(2\)](#)

Hybrid functional PBE0 calculations have been performed by using the freely available CP2K suite of codes,[\(67\)](#) keeping the fraction of Fock exchange α at its original value (0.25), and by including van der Waals interactions through the DFT-D3 scheme.[\(48\)](#) Calculations have been carried out with Goedecker–Teter–Hutter pseudopotentials,[\(68\)](#) double- ζ polarized basis sets for the wave functions,[\(69\)](#) and a cutoff of 300 Ry for the expansion of the electron density in plane waves. We used the auxiliary density matrix method with the cFIT auxiliary basis set to accelerate the hybrid functional calculations.[\(70\)](#)

The energies of all calculated structures have been thus refined by using the HSE06 functional[\(49\)](#) by including SOC and DFT-D3 dispersions[\(48\)](#) by using the Quantum Espresso package.[\(71\)](#) We used full relativistic norm-conserving pseudopotentials (Pb, 22 electrons, $5s^2$, $5p^6$, $5d^{10}$, $6s^2$, $6p^2$; Sn, 22 electrons, $4s^2$, $4p^6$, $4d^{10}$, $5s^2$, $5p^2$; I, 7 electrons, $5s^2$, $5p^5$; C, 4 electrons, $2s^2$, $2p^2$; N, 5 electrons, $2s^2$, $2p^3$; H, 1 electron, $1s^1$) with a cutoff on the wave functions of 40 Ry and 80 Ry on the Fock grid, sampling the Brillouin zone at the

gamma point. An increased fraction of exact exchange has been included in the HSE06 functional ($\alpha = 0.43$). Such a value has been shown to provide accurate electronic properties of lead perovskites, in good agreement with experiments and state-of-the-art G_0W_0 -SOC calculations.^(10,33,52) Band gaps of 1.26, 1.45, and 1.65 eV were obtained by this approach for MASnI_3 , $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$, and MAPbI_3 , respectively.

Defect formation energies (DFE) and thermodynamic ionization levels (TIL) were calculated according to the following equations:^(33,45)

$$\text{DFE} [X^q] = E [X^q] - E [\text{perf}] - \sum_i n_i \mu_i + q (\varepsilon_{\text{VB}} + \varepsilon_{\text{F}}) + E_{\text{corr}}^q \quad (3)$$

$$\varepsilon (q/q') = \frac{E [X^q] - E [X^{q'}]}{q' - q} + \frac{E_{\text{corr}}^q - E_{\text{corr}}^{q'}}{q' - q} - \varepsilon_{\text{VB}} \quad (4)$$

where $E[X^q]$ is the energy of the supercell with defect X in charge state q , $E(\text{perf})$ is the energy of the perfect (nondefective) supercell, n and μ are the number and the chemical potentials of the species added to or subtracted from the nondefective system, respectively, and ε_{VB} is the valence band energy. The last two terms of [eq 3](#) represent the energy due to the exchange of electrons with the Fermi level of the system (ε_{F}) and corrections due to periodic charges. Due to the high ionic dielectric constants of the simulated perovskites and the shallow nature of many defects, only the electrostatic potential correction has been included in the E_{corr}^q term of the equations.

The chemical potentials of $\text{MAPb}_x\text{Sn}_{1-x}\text{I}_3$ ($x = 0, 0.5$, or 1) constituents were set by considering the thermodynamic equilibrium between the perovskite and the relative metal precursors (SnI_2 and PbI_2)

$$\mu (\text{MA}) + x\mu (\text{Pb}) + (1 - x)\mu (\text{Sn}) + 3\mu (\text{I}) = \mu (\text{MAPb}_x\text{Sn}_{1-x}\text{I}_3) \quad (5)$$

$$\mu (\text{Pb}) + 2\mu (\text{I}) = \mu (\text{PbI}_2) \quad (6)$$

$$\mu (\text{Sn}) + 2\mu (\text{I}) = \mu (\text{SnI}_2) \quad (7)$$

Three different chemical conditions of growth were simulated, i.e., iodine-rich, iodine-medium, and iodine-poor (points A–C in [Figure 1](#), respectively). I-Rich conditions were simulated by setting the chemical potentials of iodine to the value of solid I_2 for MAPbI_3 [$\mu(\text{I}) = 1/2\mu(\text{I}_2^{\text{sol}})$], while due to the instability of MASnI_3 under such conditions, the chemical potentials of the species of MASnI_3 under I-rich conditions have been calculated by considering the equilibrium among the MASnI_3 , SnI_4 , and SnI_2 phases (see [Figure 1b](#)).^(72–74) I-Poor conditions were simulated by setting the chemical potentials of Pb and Sn to the values in the respective metal bulk phases [$\mu(\text{Pb}) = \mu(\text{Pb}_{\text{bulk}})$, and $\mu(\text{Sn}) = \mu(\text{Sn}_{\text{bulk}})$]. For the mixed $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ phase, the same chemical potential ranges calculated for Sn and I in MASnI_3 have been used. Band edge energies and TILs of MASnI_3 , $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$, and MAPbI_3 reported in [Figure 5d](#) have been aligned to the inner 5s and 4s levels of Pb and Sn, included in the norm-conserving pseudopotentials used in hybrid SOC calculations.

The barrier to electron trapping on the Sn_i^{2+} defect has been calculated by performing a linear transit between the equilibrium configurations of the defect in the 2+ and 1+ charge states, by fixing the charge of the supercell to 1+, i.e., simulating trapping of one electron on Sn_i^{2+} . In the linear transit, the Sn–Sn distance between the tin interstitial and a tin of the lattice represents the reaction coordinate to the electron trapping process. The energy profile was calculated by using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional⁽⁷⁵⁾ in the $2 \times 2 \times 2$ supercell by constraining Sn–Sn distances to values between 3.08 and 4.03 Å (representing the Sn–Sn equilibrium distances in Sn_i^+ and Sn_i^{2+} , respectively, at the PBE level) and relaxing ion positions. PBE calculations were performed using ultrasoft pseudopotentials (Sn, 14 electrons, $4d^{10}$, $5s^2$, $5p^2$; I, 7 electrons, $5s^2$, $5p^5$; C, 4 electrons, $2s^2$, $2p^2$; N, 5 electrons, $2s^2$, $2p^3$; H, 1 electron, $1s^1$) and the plane-wave basis set. A cutoff on the wave function of 25 Ry and on the charge density of 200 Ryd was used, sampling the Brillouin zone at the gamma point. The calculated barrier at the PBE level was thus refined by performing single-point hybrid calculations using the HSE06-SOC functional ($\alpha = 0.43$).

DFT calculations of doped MASnI_3 have been performed in the $2 \times 2 \times 2$ supercell by simulating a doping percentage increasing from 3% to 25%, by substituting from 1 to 8 tin ions in the pristine supercells (32 formula units). Equilibrium structures were computed using the PBE functional,⁽⁷⁵⁾ relaxing ion positions until forces on atoms were $<0.001 \text{ Ry } \text{\AA}^{-1}$ and fixing cell parameters to the experimental values. To quantitatively estimate defect properties, DFEs and electronic properties of singly substituted dopant supercells were refined by using the HSE06⁽⁴⁹⁾ hybrid functional ($\alpha = 0.43$), including SOC, and applying dispersion corrections a posteriori through the DFT-D3 scheme of Grimme.⁽⁴⁸⁾

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcclett.0c00725>.

- Projected density of states (PDOS) computed at the HSE06-SOC level of MAPbI_3 and MASnI_3 ; structures of the reduced and oxidized forms of defects in MASnI_3 and MAPbI_3 ; calculated band edge energy shifts (ΔVB and ΔCB), band gaps (E_g), exchange energies, and variation of the DFEs of $\text{V}_{\text{Sn}}^{2-}$ of MASnI_3 doped with Cd, Sr, Zn, and Ca as substitutions for tin (PBE level); diagram reporting the relative variation of the tin vacancy $\text{V}_{\text{Sn}}^{2-}$ DFE (PBE) and 2^*VB with respect to the pristine MASnI_3 for increasing dopant densities; converged structures and energies of the phases used throughout the work (Table S2); the converged $2 \times 2 \times 2$ supercell structures of MAPbI_3 , MASnI_3 , and $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ (Table S3); and iodine interstitials I_i^+ , I_i^0 , and I_i^- in MAPbI_3 and tin interstitial Sn_i^{2+} , Sn_i^+ , and Sn_i^0 in MASnI_3 [\(PDF\)](#)

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• Notes

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