

Cite this: *Energy Environ. Sci.*, 2024, 17, 760

Substitution of lead with tin suppresses ionic transport in halide perovskite optoelectronics†

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Despite the rapid rise in the performance of a variety of perovskite optoelectronic devices with vertical charge transport, the effects of ion migration remain a common and longstanding Achilles' heel limiting the long-term operational stability of lead halide perovskite devices. However, there is still limited understanding of the impact of tin (Sn) substitution on the ion dynamics of lead (Pb) halide perovskites. Here, we employ scan-rate-dependent current–voltage measurements on Pb and mixed Pb–Sn perovskite solar cells to show that short circuit current losses at lower scan rates, which can be traced to the presence of mobile ions, are present in both kinds of perovskites. To understand the kinetics of ion migration, we carry out scan-rate-dependent hysteresis analyses and temperature-dependent impedance spectroscopy measurements, which demonstrate suppressed ion migration in Pb–Sn devices compared to their Pb-only analogues. By linking these experimental observations to first-principles calculations on mixed Pb–Sn perovskites, we reveal the key role played by Sn vacancies in increasing the iodide ion migration barrier due to local structural distortions. These results highlight the beneficial effect of Sn substitution in mitigating undesirable ion migration in halide perovskites, with potential implications for future device development.

Received 4th November 2023,
Accepted 23rd November 2023

DOI: 10.1039/d3ee03772j

rsc.li/ees

Broader context

Organic–inorganic halide perovskites are at a critical juncture in their journey towards commercialization, where limited operational stability of devices to external stressors (such as light and bias) remains the single biggest challenge that needs to be addressed. One of the key drivers of such instability is ionic migration, which is also believed to be responsible for the widely observed hysteresis in current–voltage characteristics of perovskite solar cells and partially for the efficiency roll-off at high injection currents in perovskite LEDs. While extensive studies on understanding and mitigating ion migration effects have been conducted on lead perovskite devices, similar efforts on their tin-containing counterparts are scarce. In this work, using a combination of experimental measurements on operating solar cells, we provide direct evidence for the suppressed ionic transport in mixed Pb–Sn perovskites compared to their Pb-only analogues. Furthermore, by conducting atomistic *ab initio* simulations, we attribute such observations to the presence of tin vacancies in tin-containing perovskites, which are found to increase the iodide ion migration barrier due to local structural distortion. Our work highlights the often-overlooked brighter aspects of tin in halide perovskites, which can be further leveraged for extending the operational stability of a variety of perovskite-based energy devices, including tandem solar cells, LEDs, photo- and X-ray detectors, among others.

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3ee03772j>

Introduction

Lead halide perovskites have shown a remarkable run in photovoltaic applications, with single junction solar cell efficiencies reaching close to 26% and tandem efficiencies (with Si) eclipsing 33%.¹ At the same time, external quantum efficiencies of perovskite LEDs have ascended to more than 20% for green, red and infrared emission.² In addition to their favourable optoelectronic properties, including high absorption coefficient,³ large ambipolar carrier diffusion length⁴ and facile bandgap tunability,⁵ these developments in the device performance of halide perovskites have also been aided by the relative ease of processing of these materials using inexpensive





Fig. 1 Material and device characterization. (a) XRD patterns of Pb and Pb–Sn perovskite thin films. (b) Absorption spectra (obtained from UV-visible–near-infrared spectroscopy) and photoluminescence spectra of Pb and Pb–Sn perovskite thin films. (c) Light (under AM 1.5G illumination) and dark J – V scans of a characteristic Pb perovskite solar cell (with 2PACz HTL) with a scan rate of 100 mV s^{-1} . (d) External quantum efficiency (EQE) spectra of the corresponding Pb perovskite solar cell. (e) Light (under AM 1.5G illumination) and dark J – V scans of a characteristic Pb–Sn perovskite solar cell (with PEDOT:PSS HTL) with a scan rate of 100 mV s^{-1} . (f) EQE spectra of the corresponding Pb–Sn perovskite solar cell. Here, ‘Pb’ refers to $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ and ‘Pb–Sn’ refers to $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$. Optical bandgaps of the perovskite films were calculated from the absorption spectra using the Tauc-plot method. For PL measurements, a continuous-wave 405 nm laser was used as the excitation source. All the solar cell measurements were performed in air on encapsulated devices.

Table 1 Average photovoltaic parameters of Pb and Pb–Sn perovskite solar cells

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
Pb (2PACz)	1.02 ± 0.04	23.9 ± 1.0	64.5 ± 2.2	15.6 ± 1.3
Pb–Sn (PEDOT)	0.77 ± 0.04	28.9 ± 0.9	67.8 ± 4.7	14.3 ± 1.1

perovskite solution from 1.35 M to 1.8 M (device statistics in Fig. S6, ESI[†]). We have intentionally not used any defect passivating additives in the perovskite solution or as post-

deposition surface treatments in the fabricated device stacks because of their synergistic influence on ion migration. Therefore, conclusions derived from this study are applicable in general for various Sn-containing perovskite optoelectronic devices.

Ionic transport properties from scan-rate dependent measurements

Having optimized material and device fabrication, we investigated the nature and extent of the role of ion transport in solar cells comprised of Pb and Pb–Sn perovskites. We performed J – V measurements over a range of scan rates from 5 mV s^{-1} to



250 mV s^{-1} to capture any time-dependent performance changes in the devices. In these measurements, the reverse scan is followed by the forward scan at a given scan rate and then the scan rate is changed to repeat this routine. We did not lower the scan rate below 5 mV s^{-1} due to long measurement times (tens of minutes) and thus potential degradation of the devices due to bias stress, especially in dark conditions. Light J - V scans of Pb and Pb-Sn perovskite solar cells at three representative scan rates of 5 mV s^{-1} , 50 mV s^{-1} and 250 mV s^{-1} are shown in Fig. 2a and b (dark J - V scans in Fig. S7, ESI†),

with the corresponding variation in the PCE of solar cells as a function of scan rates shown in Fig. S8 (ESI†).

We display the variation of J_{sc} as a function of scan rates in the Pb and Pb-Sn cells in Fig. 2c and d, which shows an overall increase in J_{sc} (during both reverse and forward scans) with increasing scan rates from 5 mV s^{-1} to 250 mV s^{-1} for both Pb and Pb-Sn perovskite solar cells. Such a trend can be rationalized by the fact that at slow scan rates, diffusing ions have enough time to react to the changes in voltage and hence these can move their equilibrium positions from the bulk (assuming



Fig. 2 Scan-rate dependent J - V measurements. Light J - V scans of (a) Pb and (b) Pb-Sn perovskite solar cells at three scan rates: 5 mV s^{-1} , 50 mV s^{-1} and 250 mV s^{-1} . (c) J_{sc} of Pb perovskite solar cells as a function of scan rates in the reverse and forward scans. (d) J_{sc} of Pb-Sn perovskite solar cells as a function of scan rates in the reverse and forward scan. (e) Open circuit voltage of Pb and Pb-Sn perovskite solar cells as a function of scan rates in the reverse and forward scans. (f) Hysteresis index (HI) in PCE of Pb and Pb-Sn perovskite solar cells as a function of scan rates. Note that optimized 2PACz and PEDOT:PSS were used as HTLs respectively for Pb and Pb-Sn perovskite solar cells.



roughly homogenous distribution at V_{oc}) towards the interfaces with the charge transport layers. Such movement of ions causes screening of the internal built-in field at short circuit, leading to a lowering of J_{sc} .¹⁹ These observations point to the presence of mobile ions in both kinds of solar cells. Furthermore, a consistent increase in V_{oc} is also observed by lowering the scan rates (during both reverse and forward scans) for the Pb device (Fig. 2e), which may also originate from the prolonged light soaking effects on ion migration as observed by Herterich *et al.*⁴⁴ However, no such increase in V_{oc} is observed for Pb–Sn devices.

Next, we calculated the variation of hysteresis index (HI) as a function of scan rates (Fig. 2f) for both Pb and Pb–Sn perovskite solar cells, where HI in PCE is defined as $HI(PCE) = \frac{PCE(\text{reverse}) - PCE(\text{forward})}{PCE(\text{reverse})}$.⁴⁵ In the regime of scan rates $< 50 \text{ mV s}^{-1}$, we observe a significant uptick in the HI (PCE) of Pb devices, while a relatively flat response is seen for their Pb–Sn analogues. Such a phenomenon of increasing hysteresis at lower scan rates for Pb perovskites is in agreement with reported drift-diffusion modelling on p–i–n perovskite solar cells involving ionic migration effects.^{46,47}

While interface recombination and band alignment with charge transporting layers can also influence hysteresis in operating solar cells, our choice of appropriate HTLs (2PACz

for Pb perovskite devices and PEDOT:PSS for Pb–Sn perovskite devices) bring the two perovskite systems closest to their optimum performance with respect to V_{oc} (which is affected by the non-radiative recombination of carriers at the bulk and the interfaces) and FF (which is impacted by the band alignment and corresponding charge extraction at the interfaces). Thus, we argue that our scan-rate-dependent J – V hysteresis measurements are predominantly influenced by ionic migration effects, thereby indicating that the ionic transport in Pb–Sn devices is significantly slowed down as compared to that in Pb devices.

Ionic transport properties from impedance spectroscopy

To further understand the extent and impact of ionic diffusion, we employ impedance spectroscopy, which is a powerful technique to disentangle the ionic and electronic response in perovskite device stacks due to the characteristically different time scales of the two phenomena.^{48–50} We carried out temperature-controlled impedance spectroscopy on Pb and Pb–Sn perovskite solar cells at open circuit under illumination with a blue 470 nm LED (Fig. 3). To ensure the cells were stable during the measurements, they were loaded in a gas-tight device holder in a N_2 glovebox and also measured under nitrogen. Furthermore, to eliminate any complexity in the impedance response arising due to different HTLs, we used



Fig. 3 Impedance spectroscopy measurements. (a) Nyquist plot of a Pb perovskite solar cell measured under illumination with a 470 nm LED at open circuit, while the cell was held at 25 °C throughout the measurement. (b) Plots of the imaginary impedance against frequency for the corresponding Pb perovskite solar cell within a range of temperatures (21–40 °C). (c) Nyquist plot of a Pb–Sn perovskite solar cell measured under illumination at open circuit, while the cell was held at 25 °C throughout the measurement. (d) Plots of the imaginary impedance against frequency for the corresponding Pb–Sn perovskite solar cell within a range of temperatures (21–40 °C). All data were assessed through a Kramers–Kronig transformation which shows that the measured data are valid within these frequencies (Fig. S11, ESI†).





Fig. 4 Ion migration pathways through atomistic *ab initio* simulations. (a)–(c) Inequivalent iodide migration paths (A, B and C) in $\text{FAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ involving the SnI_2 Schottky-type defect comprised of a Sn vacancy and two I vacancies. Here, yellow, olive, pink, turquoise, blue and white spheres represent lead, tin, iodine, carbon, nitrogen and hydrogen atoms respectively. The red arrows point to the direction of iodide migration in the lattice. (d) Energy profiles for iodide ion migration via paths A, B and C in $\text{FAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$.

Table 2 Rate-limiting ion migration energies for long-range iodide ion transport in different model perovskite systems

Perovskite system	Ion migration energy (eV)
FAPbI_3	0.45
FASnI_3 (without Sn vacancies)	0.36
FASnI_3 (in presence of Sn vacancies)	1.12
$\text{FAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ (without Sn vacancies)	0.47
$\text{FAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ (in presence of Sn vacancies)	1.45

examined three distinct iodide ion migration pathways labelled A, B, and C (more details in Supplementary Note 3 in ESI†) in Fig. 4a–c, and their energy profiles are shown in Fig. 4d. For $\text{FAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$, these A, B and C pathways involve different sequences of equatorial-axial type hops leading to energy barriers greater than 0.9 eV and to a rate-limiting ion migration energy for long-range diffusion of 1.45 eV. Following similar migration paths in FASnI_3 , we again find energy barriers for iodide ion migration greater than 0.9 eV and to a rate-limiting migration energy for long-range diffusion of 1.12 eV (Fig. S15, ESI†).

Table 2 summarises the rate-limiting migration barriers for iodide ions in the different model perovskite systems with and without the presence of Sn vacancies. Thus, our simulations clearly suggest that iodide migration near Sn vacancy defects in $\text{FAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ and FASnI_3 face high energy barriers (>1.1 eV) compared to <0.5 eV for Pb perovskites due to severe local structural distortion, thereby reducing the mobility of halide ions. It is, however, important to note that due to the nature of *ab initio* simulations adopted in this study (*i.e.*, single crystal-like behaviour of model perovskite systems without the influence of effects such as grain boundaries or dynamic effects related to the ambient operational conditions of real devices), these differences in activation energy of iodide ions need to be understood in a qualitative manner for valuable comparison with the trends found from the experimental results. Moreover, first-principles calculations by Meggiolaro *et al.* suggests similar values of formation energy (and hence the density) of iodide vacancies irrespective of the choice of B-site metal.⁶² Therefore, the reduced migration of iodide ions in the presence of Sn may also correspondingly result in lower ionic conductivity.

We have also modelled the migration of Sn^{2+} cations through the available Sn vacancies in FASnI_3 (Fig. S16, ESI†) and obtained a high migration barrier of 1.53 eV, which is even higher than the corresponding rate-limiting migration barrier of iodide ions. Therefore, similar to our previous work on MAPbI_3 ,⁸ we find that the migration of B-site metal cations (Sn in this case) is associated with a large activation energy and hence unlikely to meaningfully contribute to the current–voltage hysteresis in solar cells.

Overall, we highlight the important role of Sn vacancies in arresting the migration of iodide ions in Sn-containing perovskites, in good accordance with our experimental observations of much slower ion diffusion in mixed Pb–Sn devices.

Conclusion

The impact of substituting Pb with Sn on the ion migration properties of halide perovskite optoelectronic devices has been



investigated using a combination of experimental and computational techniques. Short circuit current loss obtained at lower scan rates ($<50 \text{ mV s}^{-1}$) indicates the prevalence of ion migration in both Pb and Pb–Sn perovskite solar cells, but the kinetics of ion transport are suppressed in mixed Pb–Sn systems as inferred from scan-rate dependent hysteresis measurements. These results are further corroborated by temperature-dependent impedance spectroscopy measurements performed on the fabricated devices at open circuit and under light illumination, which suggest a substantial lowering of ionic diffusion with the partial substitution of Pb with Sn. In addition, atomistic *ab initio* simulations highlight the role of Sn vacancies in increasing the iodide ion migration barriers ($>1.1 \text{ eV}$) in Sn-containing perovskites due to severe local structural distortion, which corroborates and rationalises our experimental observations of much slower ion diffusion in mixed Pb–Sn perovskite solar cells. Overall, our findings can be generalized for a variety of Pb halide perovskite optoelectronic devices, where the benefit of Sn substitution in suppressing ionic migration effects may lead to enhanced operational stability and improved device architectures.

Author contributions

K. D. conceived the idea and designed the experimental plan with supervision from S. D. S., M. S. I. and P. J. C.; K. D. optimized the processing of perovskite films and transport layers and accordingly fabricated all the devices for electrical characterization. K. D. performed and analyzed UV-Vis, XRD and PL measurements on the perovskite films. K. D. also carried out and analyzed standard and scan-rate dependent *J–V* measurements on perovskite solar cells. D. G. conducted DFT calculations on the migration barrier of iodides in different perovskite systems with assistance from P. D. and interpreted the results with M. S. I.; M. P. and S. R. P. measured impedance spectroscopy on perovskite solar cells and analyzed the data with P. J. C.; B. R. measured the top-view SEM of the perovskite films. S. P. S. provided useful inputs on the understanding of ionic migration in perovskite devices. K. D. interpreted all the data and wrote the first draft of the manuscript with detailed contributions from all the authors.

Conflicts of interest

S. D. S. is a cofounder of Swift Solar. The remaining authors declare no competing interests.

Acknowledgements

K. D. acknowledges the support of the Cambridge Trust for the Cambridge India Ramanujan Scholarship and Cambridge Philosophical Society for the research studentship. This work received funding from the European Research Council under the European Union's Horizon 2020 research and innovation programme (HYPERION, grant agreement no. 756962). M. S. I.

and D. G. acknowledge ARCHER2 supercomputer resources *via* membership of the HEC Materials Chemistry Consortium funded by the EPSRC (EP/R029431). D. G. acknowledges the IIT Delhi SEED Grant (PLN12/04MS), the Science and Engineering Research Board (SERB), Department of Science and Technology (DST), India for Start-up Research Grant SRG/2022/001234 and the IIT Delhi HPC facility for computational resources. P. J. C. and M. P. thank the EPSRC Centre for Doctoral Training in New and Sustainable Photovoltaics (EP/L01551X/2) for funding. S. P. S. acknowledges funding support from SERB (SRG/2020/001641 and IPA/2021/000096). S. D. S. acknowledges support from the Royal Society and Tata Group (UF150033). The authors acknowledge the Engineering and Physical Sciences Research Council (EPSRC) for funding (EP/R023980/1, EP/T02030X/1, EP/V012932/1). For the purpose of open access, the authors have applied a Creative Commons Attribution (CC BY) licence to any Author Accepted Manuscript version arising from this submission.

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