

Supporting Information

Single Crystals of Mixed Br/Cl and Sn-Doped Formamidinium Lead Halide Perovskites via Inverse Temperature Crystallization

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Synthesis.

Synthesis of MACl. Methylammonium chloride was synthesised from the reaction of hydrochloric acid with methylamine solution. Methylamine was added to hydrochloric acid in molar ratio of 1.2:1 in an ice bath with stirring for 3 hours. The excess solvent was then evaporated and the resulting material were dried under vacuum for 2 hours at 50 °C. The white powder was then dissolved in methanol and filtered using a 0.22 µm PTFE hydrophilic filter. MACl was then recrystallized using diethyl ether and the crystals were collected and dried under vacuum at 60 °C.

Synthesis of MAPbBr₃. A one molar solution of MAPbBr₃ was prepared by dissolving equal moles of MABr and PbBr₂ in DMF. The solution was then filtered using a 0.22 µm hydrophilic PTFE filter. 2 mL of the filtrate was then added to a glass vial and the solution was added to an oil bath. The oil bath is slowly heated to 80 °C and the crystals are grown for 5 hours under ambient conditions (40-60% humidity). Single crystals were washed and then stored in DCM. Further growth of the single crystals was then achieved by carefully transferring the single crystals to a fresh growth solution as depicted in Figure S1. The growth solution was replaced three times for a total synthesise time of 20 hours.

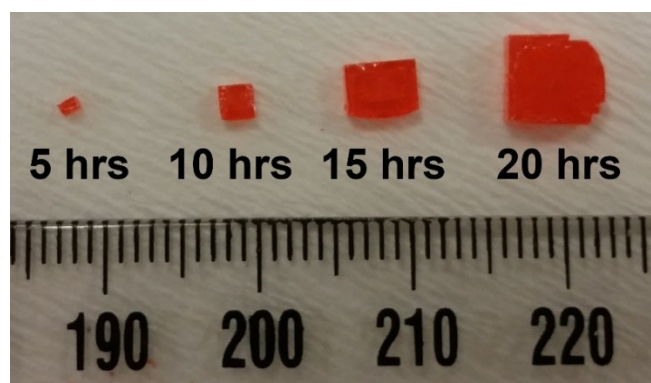


Figure S1: MAPbBr₃ crystal growth at different time intervals.

Single crystal washing. Once the crystals are removed from the oil bath the excess precursors/growth solution are discarded using a syringe. DCM (antisolvent) is then added upon which a coloured precipitate will form instantly indicating the presence of unreacted perovskite precursors. DMF is then added to the solution to dissolve the precipitate which forms a colourless solution. The excess precursors are then discarded and this process is repeated until the addition of DCM forms a colourless

solution. The single crystals are then suspended in DCM to protect the surface from alterations due to prolonged dewetting or exposure to air.

The same inverse temperature crystallisation and crystal washing technique is used to grow the following perovskites with these alterations.

Synthesis of MAPbBr_{3-x}Cl_x (nominal x=0.5). A 1M growth solution of MAPbBr_{2.5}Cl_{0.5} was prepared by dissolving MABr/PbBr₂/PbCl₂ in a 4:3:1 molar ratio in DMF. The crystals were then grown at 60 °C for 5 hours upon which the crystals are transferred to a new growth solution. The growth solution was replaced 4 times for a total synthesis time of 25 hours. The single crystals were then washed and stored in DCM.

Synthesis of MAPbBr_{3-x}Cl_x (nominal x=1). A 1M growth solution of MAPbBr₂Cl₁ was prepared by dissolving MABr/PbBr₂/PbCl₂ in a 2:1:1 molar ratio in DMF-DMSO (10:1 by volume). The crystals were grown at 65 °C for 12 hours. The growth solution was replaced 3 times for a total synthesis time of 48 hours. The single crystals were then washed and stored in DCM.

Synthesis of MAPbCl₃. A 1M growth solution of MAPbCl₃ was prepared by dissolving equal moles of MAcl and PbCl₂ in DMF-DMSO (1:1 by volume). The crystals were grown at 50 °C for 12 hours. The growth solution was replaced 3 times for a total synthesis time of 48 hours. The single crystals were then washed and stored in DCM.

Synthesis of FAPbBr₃. A 1M growth solution of FAPbBr₃ was prepared by dissolving equal moles of FABr and PbBr₂ in DMF-GBL (1:1 by volume). The crystals were grown at 60 °C for 5 hours. The growth solution was replaced 3 times for a total synthesis time of 20 hours. The single crystals were then washed and stored in DCM.

Synthesis of FAPbBr_{3-x}Cl_x (nominal x=0.5). A 1M growth solution of FAPbBr_{2.5}Cl_{0.5} was prepared by dissolving FABr/PbBr₂/PbCl₂ in a 4:3:1 molar ratio in DMF-GBL (1:1 by volume). The crystals were grown at 50 °C for 12 hours under ambient conditions. The growth solution was replaced 3 times for a total synthesis time of 48 hours. The single crystals were then washed and stored in DCM.

Synthesis of FAPbBr_{3-x}Cl_x (nominal x=1). A 0.8M growth solution of FAPbBr₂Cl₁ was prepared by dissolving FABr/PbBr₂/PbCl₂ in a 2:1:1 molar ratio in DMF-GBL (1:1 by volume). The crystals were grown at 50 °C for 12 hours. The growth solution was replaced 4 times for a total synthesis time of 60 hours. The single crystals were then washed and stored in DCM.

Synthesis of FAPbBr_{3-x}Cl_x (nominal x=1.5). A 0.5M growth solution of FAPbBr_{1.5}Cl_{1.5} was prepared by dissolving FABr/PbBr₂/PbCl₂ in a 4:1:3 molar ratio in DMF-GBL (1:1 by volume). The crystals were grown at 50 °C for 12 hours under ambient conditions. The growth solution was replaced 4 times for a total synthesis time of 60 hours. The single crystals were washed and then stored in DCM.

For the synthesis of FAPbBr_{3-x}Cl_x samples with a total synthesis time of 20 hours the growth solution was only replaced once after 12 hours.

Synthesis of MAPb_{1-x}Sn_xBr₃ (nominal x=0.25). A 1M growth solution of MAPb_{0.75}Sn_{0.25}Br₃ was prepared by dissolving MABr/PbBr₂/SnBr₂ in 4:3:1 molar ratio in DMF. The crystals were grown at 75 °C for 1 hour under ambient conditions. The temperature was then increased to 80 °C for a further 4 hours. The growth solution was replaced 2 times for a total synthesis time of 15 hours.

Synthesis of MAPb_{1-x}Sn_xBr₃ (nominal x=0.5). A 1M growth solution of MAPb_{0.5}Sn_{0.5}Br₃ was prepared in a glove box under N₂ by dissolving MABr/PbBr₂/SnBr₂ in 2:1:1 molar ratio in DMF. The solution was then transferred onto a schlenk line and heated to 75° C under N₂. The temperature of the oil bath is

then increased by 5 °C every hour until 85 °C upon which the solution is left for a further 3 hours. The single crystals were then washed and stored in either DCM or in a glove box.

Synthesis of $FAPb_{1-x}Sn_xBr_3$ (nominal $x=0.25$). A 1M growth solution of $FAPb_{0.75}Sn_{0.25}Br_3$ was prepared in a glove box under N_2 by dissolving $FABr/PbBr_2/SnBr_2$ in 4:3:1 molar ratio in DMF-GBL (1:1 by volume). The solution was then transferred onto a schlenk line under N_2 and heated to 45 °C for 12 hours. The temperature of the oil bath was then increased to 50 °C for 4 hours and then 60 °C for 2 hours. The growth solution was then replaced and the above temperature profile was repeated for a total synthesis time of 36 hours. The single crystals were then washed and stored in either DCM or in a glove box.

Synthesis of $FAPb_{1-x}Sn_xBr_3$ (nominal $x=0.5$ Pb/Sn 1:1). A 1M growth solution of $FAPb_{0.5}Sn_{0.5}Br_3$ was prepared in a glove box under N_2 by dissolving $FABr/PbBr_2/SnBr_2$ in 2:1:1 molar ratio in DMF-GBL (1:1 by volume). The solution was then transferred onto a schlenk line under N_2 and heated to 50 °C for 12 hours. The temperature of the oil bath was then increased to 55 °C for 4 hours and then 60 °C for another 2 hours. The growth solution was then replaced and the above temperature profile was repeated for a total synthesis time of 36 hours. The single crystals were then washed and stored in either DCM or in a glove box under N_2 .

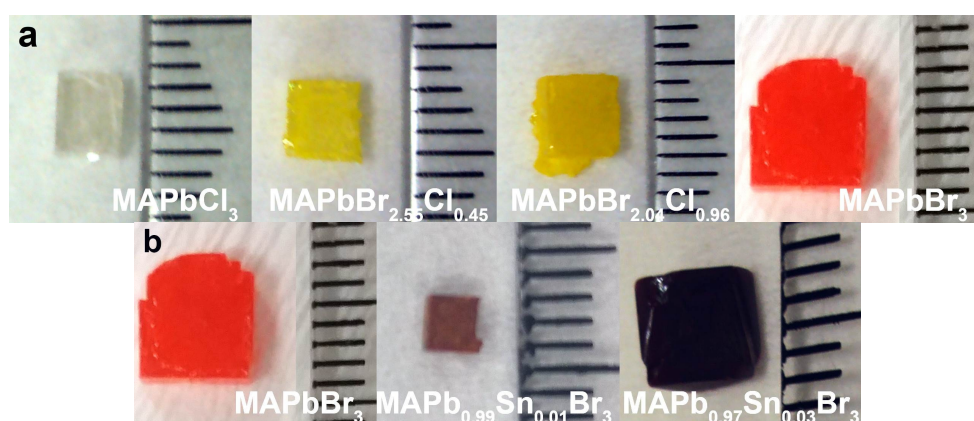


Figure S2. Photographs of $MAPbBr_{3-x}Cl_x$ and $MAPb_{1-x}Sn_xBr_3$ single crystals grown using ITC.

Table S1. Summary of optimised reaction conditions for single crystal growth

Sample	Precursor molar ratio	Solvent ratio (concentration)	Reaction conditions	Total synthesis time
$MAPbBr_3$	$MABr/PbBr_2$ 1:1	DMF (1M)	80 °C, ambient conditions	20 hours
$MAPbBr_{2.55}Cl_{0.45}$	$MABr/PbBr_2/PbCl_2$ 4:3:1	DMF (1M)	60 °C, ambient conditions	25 hours
$MAPbBr_{2.04}Cl_{0.96}$	$MABr/PbBr_2/PbCl_2$ 2:1:1	DMF/DMSO 10:1 (1M)	65 °C, ambient conditions	48 hours
$MAPbCl_3$	$MACl/PbCl_2$ 1:1	DMF/DMSO 1:1 (1M)	50 °C, ambient conditions	48 hours
$FAPbBr_3$	$FABr/PbBr_2$ 1:1	DMF/GBL 1:1 (1M)	60 °C, ambient conditions	20 hours
$FAPbBr_{2.69}Cl_{0.31}$	$FABr/PbBr_2/PbCl_2$ 4:3:1	DMF/GBL 1:1 (1M)	50 °C, ambient conditions	48 hours
$FAPbBr_{2.23}Cl_{0.77}$	$FABr/PbBr_2/PbCl_2$	DMF/GBL 1:1	50 °C, ambient	60 hours

FAPbBr _{1.33} Cl _{1.67}	2:1:1 FABr/PbBr ₂ /PbCl ₂	(0.8M) DMF/GBL 1:1	conditions 50 °C, ambient	60 hours
MAPb _{0.99} Sn _{0.01} Br ₃	4:1:3 MABr/PbBr ₂ /SnBr ₂ in 4:3:1	(0.5M) DMF (1M)	conditions 80 °C, ambient	15 hours
NAPb _{0.97} Sn _{0.03} Br ₃	2:1:1 MABr/PbBr ₂ /SnBr ₂	DMF (1M)	conditions 75 °C, under N ₂ atmosphere	6 hours
FAPb _{0.99} Sn _{0.01} Br ₃	2:1:1 FABr/PbBr ₂ /SnBr ₂	DMF/GBL 1:1 (1M)	45 °C, under N ₂ atmosphere	36 hours
FAPb _{0.97} Sn _{0.03} Br ₃	4:3:1 FABr/PbBr ₂ /SnBr ₂	DMF/GBL 1:1 (1M)	50 °C, under N ₂ atmosphere	36 hours

Powder XRD.

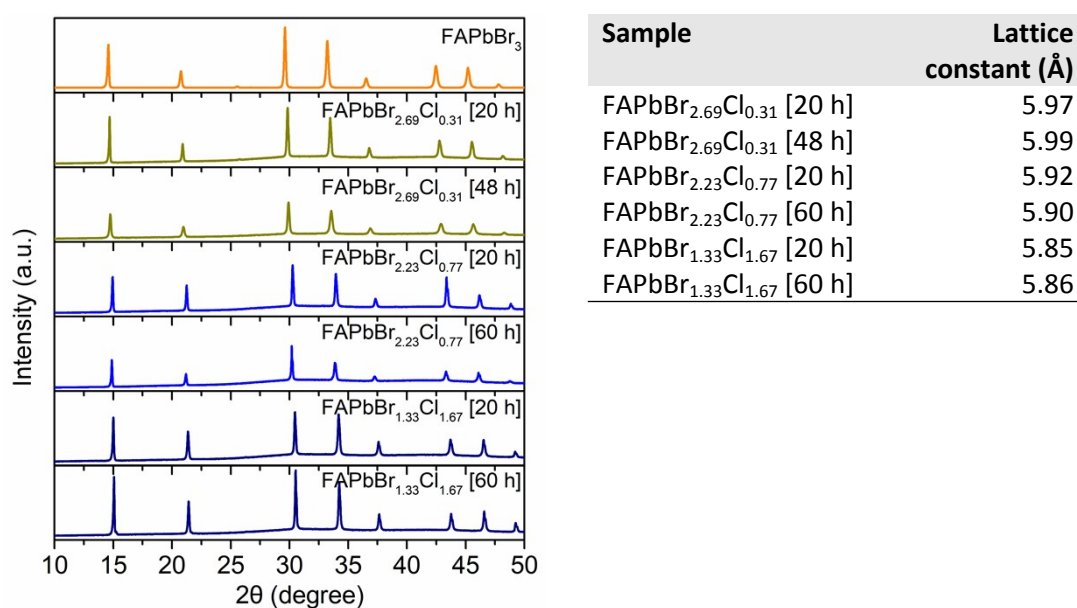


Figure S3. Comparison of powder XRD spectra and lattice constants for FAPbBr_{3-x}Cl_x based perovskites with a total synthesis time of 20 hours and > 48 hours (degraded surface).

Perovskite powder

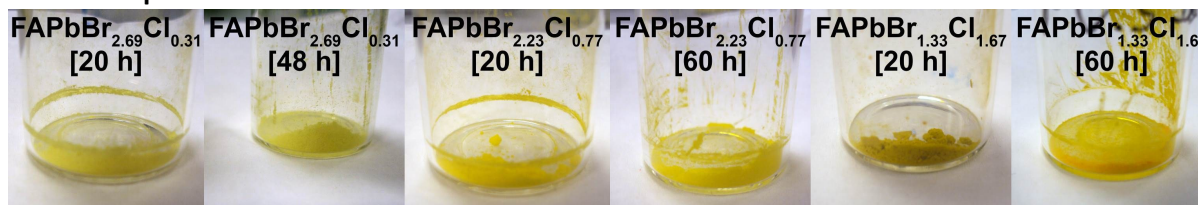


Figure S4: Photographs of FAPbBr_{3-x}Cl_x ground single crystals with different synthesis times.

Surface Degradation in Formamidinium Lead Mixed Halides.

The surface of the $\text{FAPbBr}_{3-x}\text{Cl}_x$ based perovskites appear to degrade with increasing synthesis time. Typically, single crystals are stored in dichloromethane (DCM, anti-solvent) for long term storage to prevent de-wetting of the single crystal surface. **Figure S5a** shows degraded (> 48 hour synthesis time) $\text{FAPbBr}_{3-x}\text{Cl}_x$ single crystals suspended in DCM for 4 months. It was observed that after several months in DCM the degraded single crystals appear similar to those with a total synthesis time of 20 hours. This suggests that the use of an anti-solvent can repair the degraded surface of $\text{FAPbBr}_{3-x}\text{Cl}_x$ based perovskites. In **Figure S5b**, a single crystal with significant surface degradation with a nominal Cl inclusion of 50% was suspended in chloroform for several weeks. After only 1 week a significant colour change from an initial brown/orange too yellow was observed and after 4 weeks the single crystals were observed to be a pale yellow colour and appear similar to the sample with a total synthesis time of 20 hours. Using a more polar solvent such as chloroform appears to increase the rate of the surface repair. The PL emission for the perovskite surfaces repaired using chloroform are shown in **Figure S5c**. Initially there is no PL emission. After suspending the perovskite in chloroform for 4 weeks we observe a new PL emission at 502 nm suggesting that surface of the perovskites has been altered.

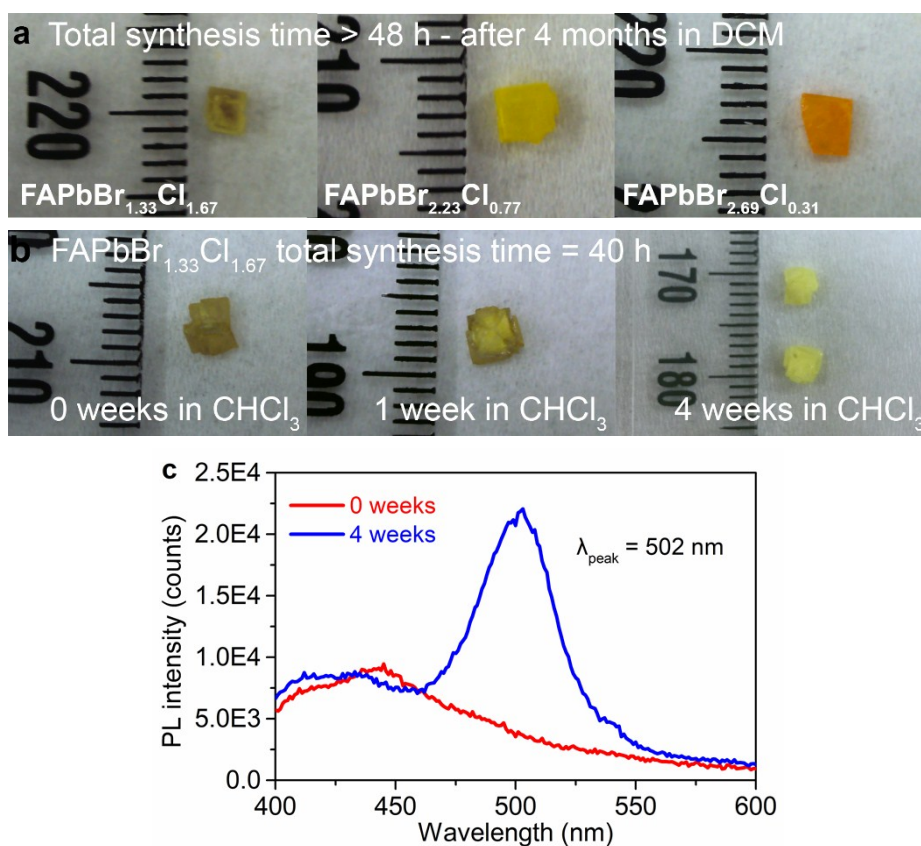


Figure S5: Surface repair of degraded $\text{FAPbBr}_{3-x}\text{Cl}_x$ perovskite single crystals. a) single crystals with a total synthesis time > 48 hours after 4 months in DCM. b) $\text{FAPbBr}_{1.33}\text{Cl}_{1.67}$ single crystal showing the surface repair after being suspended in chloroform for 1 and 4 weeks respectively. c) PL emission for $\text{FAPbBr}_{1.33}\text{Cl}_{1.67}$ single crystals with as-synthesized (degraded surface) and after 4 weeks in chloroform.

Interestingly the surface degradation is not observed for pure FAPbBr₃ or for MAPbBr_{3-x}Cl_x single crystals which were subject to similar reaction conditions and synthesis times. This suggests that a combination of both Cl and FA are responsible for the observed degradation. No changes were observed for other single crystals stored in an anti-solvent solution, so the treatment only seems to affect surfaces with significant degradation. In any case, it is apparent that the mechanism for surface degradation, and ability to be repaired, is unique to FA-based single crystals and stands in contrast to the often-reported degradation of MA-based perovskites.

EDS.

Elemental compositions are determined using SEM/EDS. An elemental map is collected at several different positions at 15 kV acceleration voltage and the average ratios are summarized in this table along with the standard deviation between all positions.

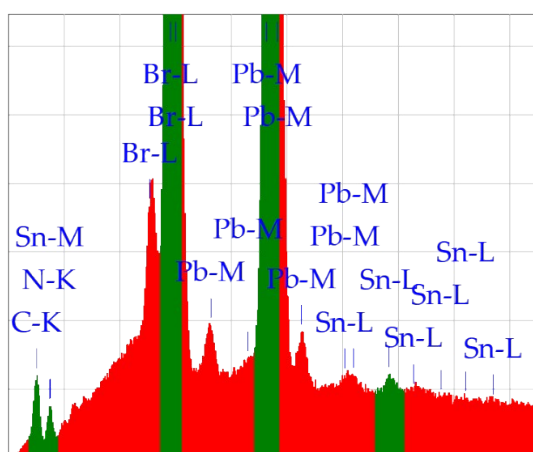


Figure S6. EDS spectrum for FAPb_{0.97}Sn_{0.03}Br₃

Table S2. Summary of elemental composition determined from SEM/EDS

Sample	Nominal Cl or Sn incorporation (in solution)	Actual Cl or Sn incorporation (EDS)	STDEV of Cl or Sn incorporation
FAPbBr _{2.69} Cl _{0.31} *	16.7 %	10.3 %	0.2 %
FAPbBr _{2.23} Cl _{0.77} *	33.3 %	25.6 %	1.7 %
FAPbBr _{1.33} Cl _{1.67} **	50.0 %	55.7 %	2.3 %
FAPbBr _{1.33} Cl _{1.67}	50.0 %	50.9 %	0.6 %
MAPbBr _{2.55} Cl _{0.45}	16.7 %	15.0 %	0.3 %
MAPbBr _{2.04} Cl _{0.96}	33.3 %	32.0 %	0.3 %
FAPb _{0.99} Sn _{0.01} Br ₃	25.0 %	1.4 %	0.2 %
FAPb _{0.97} Sn _{0.03} Br ₃	50.0 %	3.0 %	1.0 %
MAPb _{0.99} Sn _{0.01} Br ₃	25.0 %	1.0 %	0.1 %
MAPb _{0.97} Sn _{0.03} Br ₃	50.0 %	3.0 %	0.1 %

*Perovskites placed in anti-solvent (DCM) for 4 months to repair the crystal surface.

**Perovskites placed in anti-solvent (chloroform) for 1 month to repair the crystal surface

UV-vis absorption and PL emission for MA analogues.

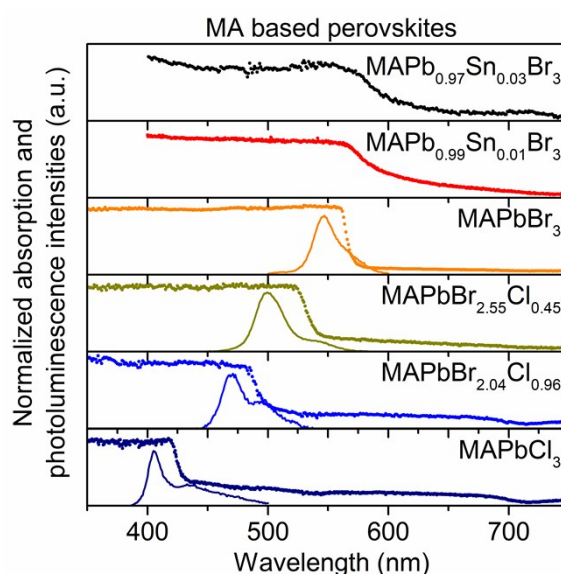


Figure S7. UV-vis absorption and PL emission for MA analogues.

Blue shifted PL peaks.

In contrast to the red shift observed in perovskite thin films, blue-shifting is observed in perovskite single crystals primarily due to the geometry used for the absorption and PL measurements. Since absorption measurements use a transmission geometry, the absorption spectra probe the entirety of the bulk crystal. Meanwhile the PL spectra are collected in a reflection geometry and are instead probing emission from the surface. In some cases, previous reports have attributed these differences to lattice deformation near the surface,¹ or from the formation of double charge surface layers which arise from defect-mediated ion migration.² However, recent reports suggest that there is no difference between the bandgaps observed, and that the discrepancy in PL emissions obtained from the surface and bulk is actually due to self-absorption/PL filtering through the single crystal.³⁻⁵ Furthermore Wengner *et al.*⁵ have shown that the sub-band gap Urbach tail is being probed when using a conventional UV-vis transmission geometry. This results in an underestimation of the actual bandgap of the single crystal material and explains the discrepancies between our observed PL emission and absorption spectra.

Tauc plots.

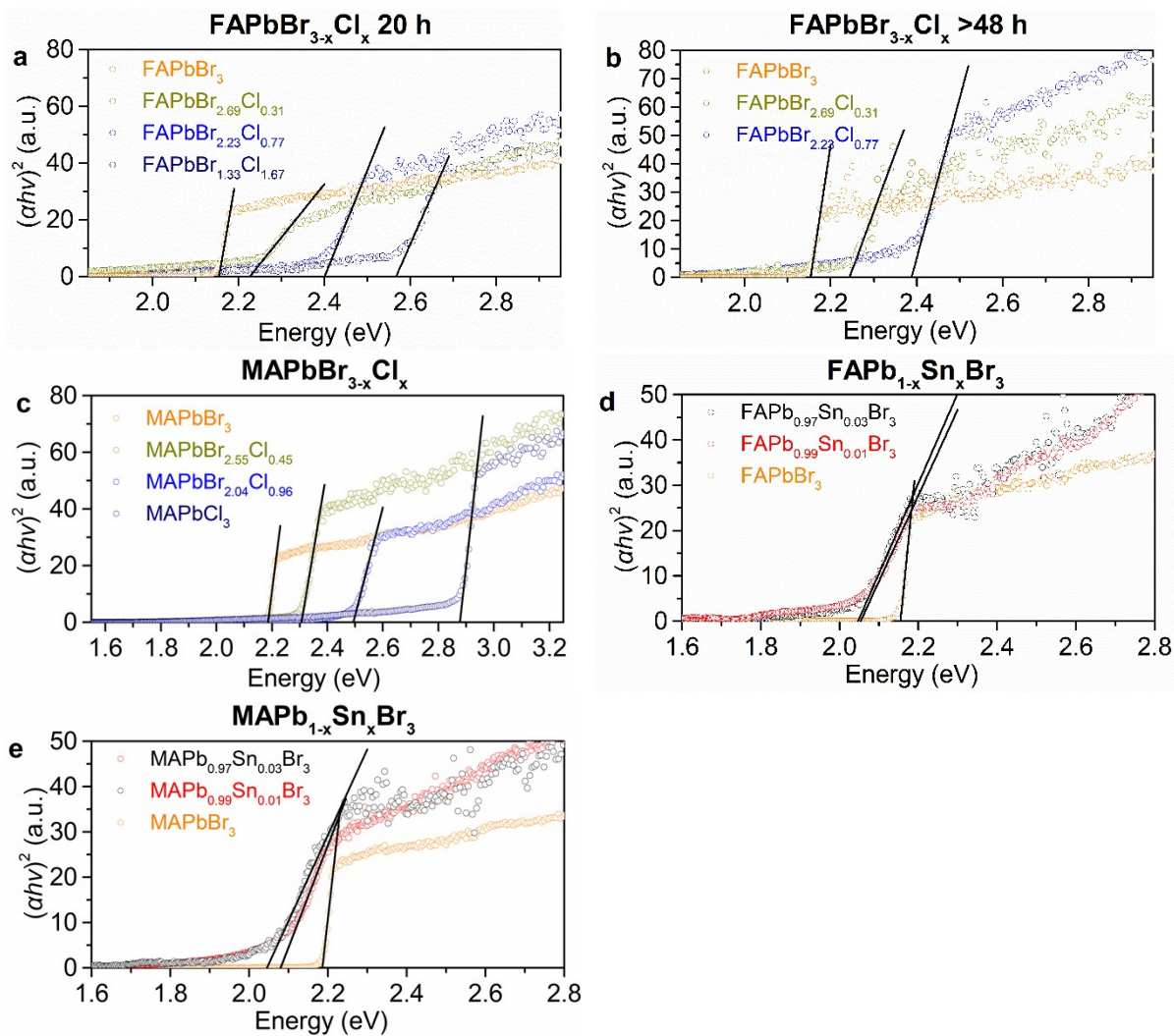


Figure S8. Tauc plot for a) $\text{FAPbBr}_{3-x}\text{Cl}_x$ perovskites with a total synthesis time of 20 hours and b) $\text{FAPbBr}_{3-x}\text{Cl}_x$ perovskites with a total synthesis time > 48 hours (degraded surface) c) $\text{MAPbBr}_{3-x}\text{Cl}_x$ perovskites d) $\text{FAPb}_{1-x}\text{Sn}_x\text{Br}_3$ perovskites e) $\text{MAPb}_{1-x}\text{Sn}_x\text{Br}_3$ perovskites.

PL Decay lifetimes

The PL decay lifetimes were investigated using time correlated single photon counting (TCSPC) spectroscopy and are shown in **Figure S9** for FAPbBr_{3-x}Cl_x based perovskites and MAPbBr_{3-x}Cl_x analogues. A bi-exponential decay was fit to the decay curves with fast (surface) and slow (bulk) decay components. The PL decay lifetimes are summarized in **Table S3**. The fast and slow decay lifetime components for FA-based perovskites are similar to those obtained for MAPbBr_{3-x}Cl_x single crystals, which are comparable to other perovskite single crystal materials (see **Supplementary Figure S11a**). Note: not all samples exhibited a strong enough emission for PL decay lifetimes to be collected. In general, it seems that a small inclusion of Cl into FAPbBr_{3-x}Cl_x based perovskites will result in a slight decrease in the PL lifetimes (**Fig. S9**), similarly for MA analogues for $x < 0.6$. Upon higher levels of Cl inclusion, the lifetimes will increase for MA analogues.

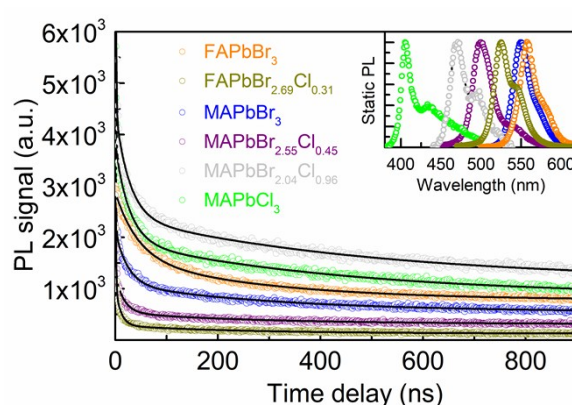


Figure S9. PL decay lifetimes for FAPbBr_{3-x}Cl_x and MAPbBr_{3-x}Cl_x based single crystals.

Table S3. PL decay lifetimes for mixed Br/Cl perovskites. Relative amplitudes for fast and slow components are given in the parenthesis.

Perovskite	PL decay lifetimes (ns)	
	τ_1	τ_2
FAPbBr ₃	44 ± 2 (23%)	278 ± 5 (77%)
FAPbBr _{2.69} Cl _{0.31}	11 ± 1 (18%)	246 ± 9 (82%)
MAPbBr ₃	25 ± 1 (11%)	321 ± 8 (89%)
MAPbBr _{2.55} Cl _{0.45}	17 ± 1 (17%)	276 ± 11 (83%)
MAPbBr _{2.04} Cl _{0.96}	27 ± 1 (8%)	499 ± 8 (92%)
MAPbCl ₃	27 ± 1 (10%)	448 ± 11 (90%)

Electrical Characterization.

I-V data which can be parametrized using SCLC theory.

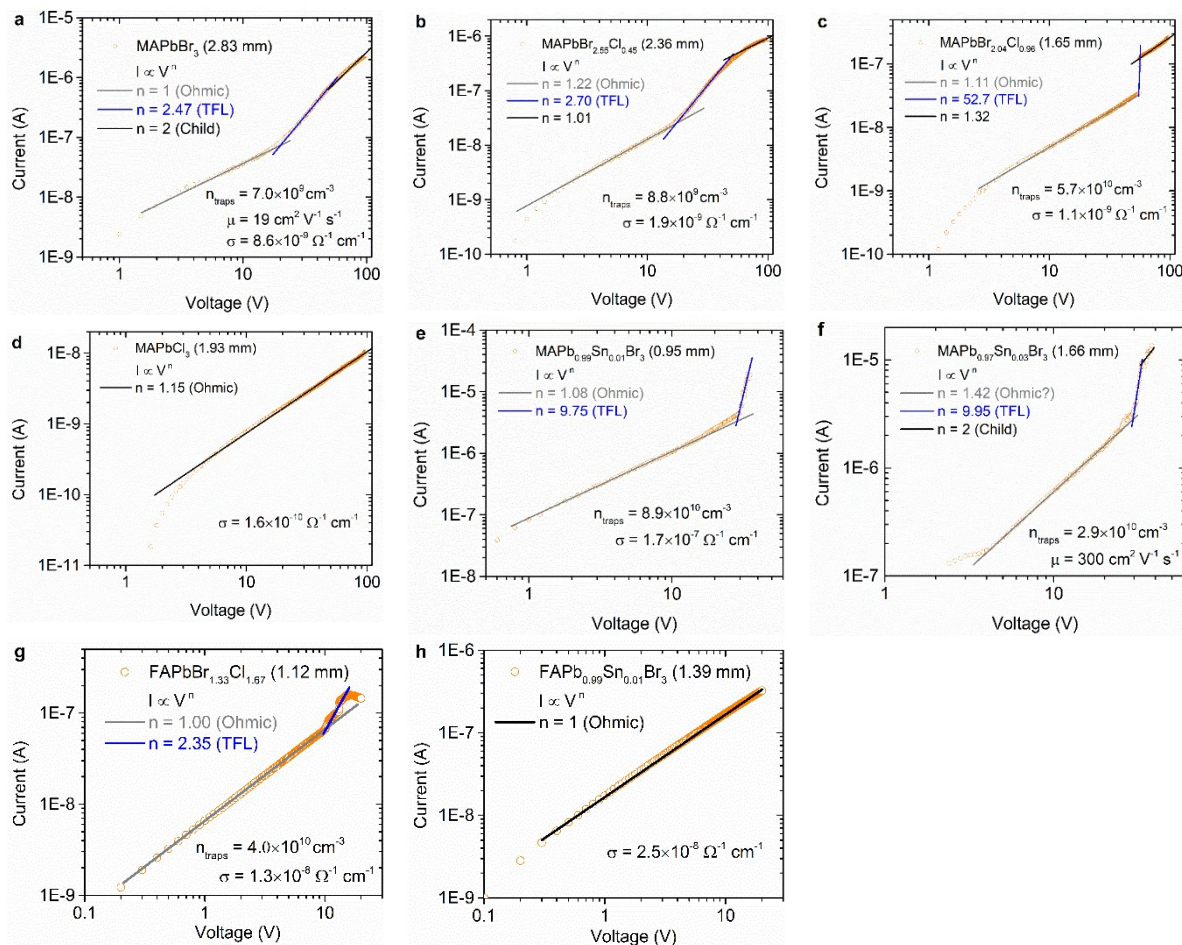


Figure S10. I-V of a) MAPbBr₃, b) MAPbBr_{2.55}Cl_{0.45}, c) MAPbBr_{2.04}Cl_{0.96}, d) MAPbCl₃, e) MAPb_{0.99}Sn_{0.01}Br₃, f) MAPb_{0.97}Sn_{0.03}Br₃ g) FAPbBr_{1.33}Cl_{1.67} and h) FAPb_{0.99}Sn_{0.01}Br₃ perovskite single crystals exhibiting regions corresponding to SCLC theory. The crystal thickness is given in the parenthesis. The conductivities are calculated from the Ohmic regime, the trap densities are calculated from the trap filled limit (TFL) and the mobilities are determined from the Child's regime.

SCLC theory and electrical properties.

The SCLC derived fits are shown in **Fig. 3** for several materials. At low voltages, a clear ohmic dependency is observed for the pure FAPbBr₃ and FAPb_{0.5}Sn_{0.5}Br₃ based perovskites, while FAPbBr₂Cl₁ exhibits a semi-ohmic region. In this linear Ohmic regime, the electrical conductivity can be estimated. As the applied bias is increased the current abruptly increases with a non-linear relationship, this corresponds to the trap filled limited (TFL) regime which occurs at V_{TFL} . From this regime the trap density, n_t , can be determined from: $n_t = 2V_{TFL}\epsilon\epsilon_0/eL^2$ where V_{TFL} is the trap filled limited voltage, ϵ is the dielectric constant, ϵ_0 is the permittivity of free space, e is the electron charge and L is the thickness of the single crystal. At high bias we have a third region in which all the traps are filled and the current-voltage properties show a quadratic relationship. This is known as the Child's regime and the current-voltage relationship can be described by Mott-Gurney's law.⁶ In this regime the mobility can be found from: $\mu = 8JL^3/9\epsilon\epsilon_0V^2$ where J is the current density.

Using the SCLC approach, the $\text{FAPbBr}_{3-x}\text{Cl}_x$ based perovskites show an increase in the conductivity with the inclusion of Cl into pure FAPbBr_3 . The opposite trend is observed for $\text{MAPbBr}_{3-x}\text{Cl}_x$ single crystals grown using ITC, in this case the conductivity decreases with increasing Cl inclusion, with pure MAPbCl_3 having a lower conductivity than pure MAPbBr_3 . $\text{FAPbBr}_{3-x}\text{Cl}_x$ perovskite crystals have lower trap densities relative to pure FAPbBr_3 where the inclusion of Cl was observed to lead to an order of magnitude decrease in the trap density. It could be that Cl either passivates the surface, fills traps or aids in relieving strain in the crystal. In comparison $\text{MAPbBr}_{3-x}\text{Cl}_x$ based perovskites show the opposite trend, typically resulting in an increase in the trap density with Cl inclusion relative to pure MAPbBr_3 . In the case of mixed halides, there is some evidence to suggest these materials can exhibit defects due to lattice strain and disorder in local distributions of halide ions. For $\text{FAPb}_{1-x}\text{Sn}_x\text{Br}_3$ based perovskites the inclusion of only several percent of Sn has resulted in an increase in trap density by 1 order of magnitude, $\text{MAPb}_{1-x}\text{Sn}_x\text{Br}_3$ perovskites also exhibit similar trends. It is notable that some samples do not exhibit a TFL region in their I-V curves, which suggests that the V_{TFL} transition occurs at much higher voltages. This indicates that these materials would have at least an order of magnitude increase in the trap density relative to those that display TFL regimes, although surface effects can also play a role. In this work the mobility could only be determined for several perovskite single crystals, but we observed that most perovskites did not exhibit a strictly quadratic dependence at high voltages. Nevertheless SCLC is the only commonly used technique for analysing single crystals so we use it here as a means of comparison to literature.⁷⁻¹⁵ The hole mobilities for FAPbBr_3 and MAPbBr_3 were found to be $0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $19 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively. The mobility for MAPbBr_3 is comparable to previous SCLC measurements on MAPbBr_3 single crystals,^{10, 11, 13} while the mobility for FAPbBr_3 appears to be lower than that determined previously,⁹ perhaps in part related to the observed degradation at the surface of these FA based perovskites which are not seen for MA based perovskites. In the case of $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{Br}_3$ and $\text{FAPb}_{0.5}\text{Sn}_{0.5}\text{Br}_3$, we find a mobility of $300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $0.22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively. This shows a significant increase in the mobility suggesting that even a small percentage of Sn can significantly enhance the charge transport properties.

Comment on dielectric constant.

The dielectric constant for MAPbI_3 , MAPbBr_3 , and MAPbCl_3 is 28.8, 25.5 and 23.9 respectively.¹⁶ In the case of the MA containing mixed halide perovskites (Br/Cl) we used a dielectric constant similar to pure MAPbBr_3 for the calculations, as the variation between methylammonium lead halides is relatively small. Similarly, the same can be done for $\text{MAPb}_{1-x}\text{Sn}_x\text{Br}_3$ based perovskites as we only have low percentages of Sn incorporated. The dielectric constant for pure FAPbBr_3 and FAPbI_3 is 43.6 and 49.4 respectively.⁹ For our calculations we assume a similar dielectric constant to pure FAPbBr_3 for both $\text{FAPbBr}_{3-x}\text{Cl}_x$ and $\text{FAPb}_{1-x}\text{Sn}_x\text{Br}_3$ based perovskites.

Comparison with literature.

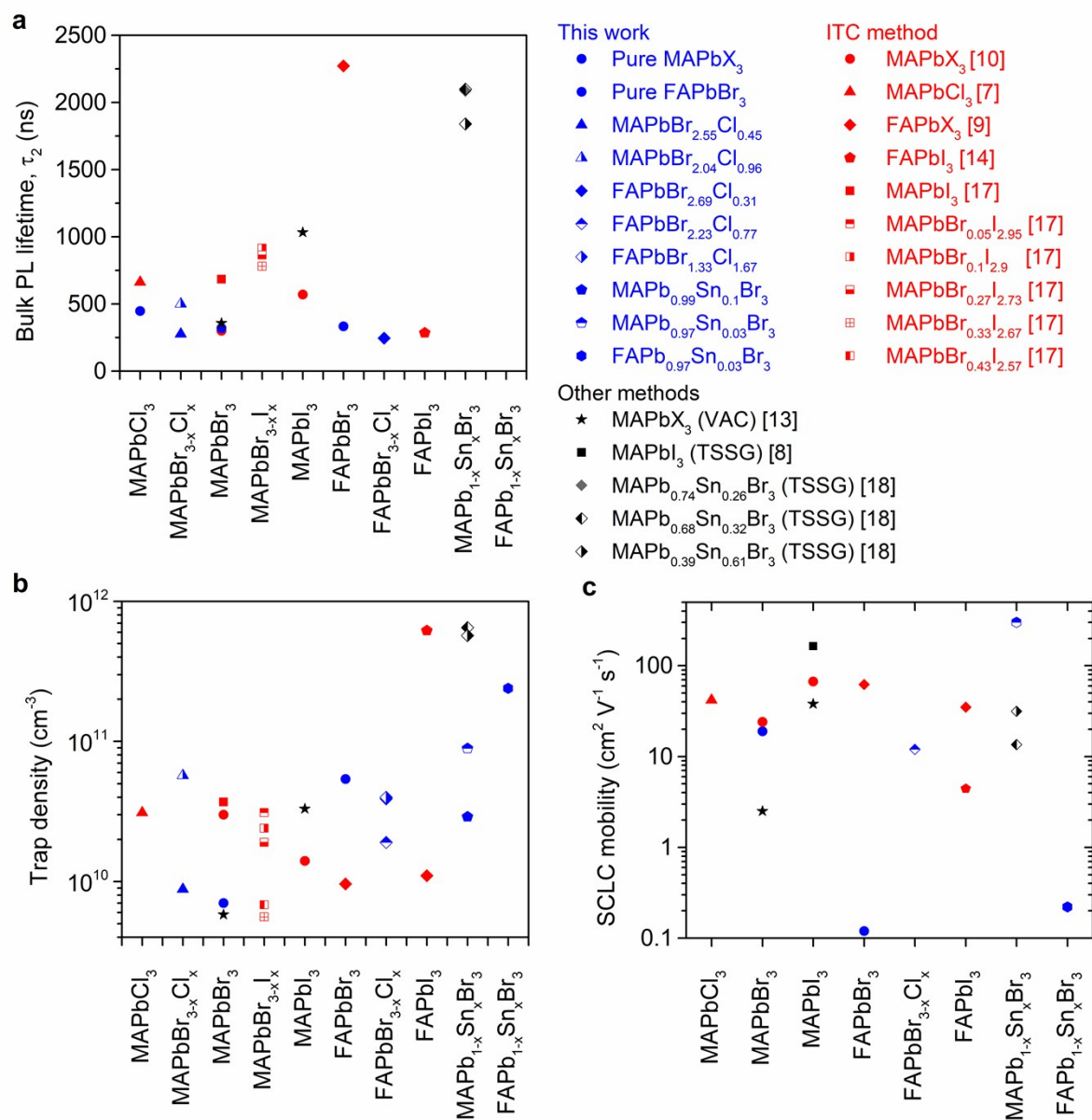


Figure S11. Comparison of extracted bulk a) PL life times, b) trap density and sc) mobility for single crystal perovskites grown using ITC method,^{7,9,10,14,17} vapour assisted crystallization (VAC)¹³ and top seeded solution growth (TSSG).^{8,18}

Table S4. Summary of parameters extracted during this work using SCLC theory as well as literature reports for single crystals

Perovskite	Conductivity (S cm ⁻¹)	Trap density (cm ⁻³)	Mobility (cm ² V ⁻¹ s ⁻¹)	Reference
MAPb _{0.99} Sn _{0.01} Br ₃	2.1 × 10 ⁻⁷	8.9 × 10 ¹⁰	---	this work
MAPb _{0.97} Sn _{0.03} Br ₃	---	2.9 × 10 ¹⁰	300	this work
MAPbBr ₃	8.6 × 10 ⁻⁹	7.0 × 10 ⁹	19	this work
MAPbBr _{2.55} Cl _{0.45}	1.9 × 10 ⁻⁹	8.8 × 10 ⁹	---	this work
MAPbBr _{2.04} Cl _{0.96}	1.1 × 10 ⁻⁹	5.7 × 10 ¹⁰	---	this work
MAPbCl ₃	1.6 × 10 ⁻¹⁰	---	---	this work
FAPb _{0.99} Sn _{0.01} Br ₃	2.5 × 10 ⁻⁸	---	---	this work
FAPb _{0.97} Sn _{0.03} Br ₃	2.6 × 10 ⁻⁹	2.4 × 10 ¹¹	0.22	this work
FAPbBr ₃	2.0 × 10 ⁻¹⁰	5.4 × 10 ¹⁰	0.12	this work
FAPbBr _{2.69} Cl _{0.31} *	--	3.9 × 10 ¹⁰	---	this work
FAPbBr _{2.23} Cl _{0.77} *	8.5 × 10 ⁻¹⁰	1.9 × 10 ¹⁰	12	this work
FAPbBr _{1.33} Cl _{1.67} *	1.3 × 10 ⁻⁸	4.0 × 10 ¹⁰	---	this work
MAPbI ₃	---	1.4 × 10 ¹⁰	67	10
MAPbI ₃	1 × 10 ⁻⁸	3.3 × 10 ¹⁰	2.5	13
MAPbI ₃	---	3.6 × 10 ¹⁰	164	8
MAPbBr ₃	---	3 × 10 ¹⁰	24	10
MAPbBr ₃	---	5.8 × 10 ⁹	38	13
MAPbBr ₃	---	1.5 × 10 ¹¹	27	11
MAPbCl ₃	2.7 × 10 ⁻⁸	3.1 × 10 ¹⁰	42	7
FAPbBr ₃	1.5 × 10 ⁻⁸	9.6 × 10 ⁹	62	9
FAPbI ₃	2.2 × 10 ⁻⁸	1.1 × 10 ¹⁰	35	9
FAPbI ₃	1.1 × 10 ⁻⁷	6.2 × 10 ¹¹	4.4	14
MAPb _{0.68} Sn _{0.32} Br ₃	---	6.5 × 10 ¹¹	13.5	18
MAPb _{0.39} Sn _{0.61} Br ₃	---	5.8 × 10 ¹¹	30.8	18
MAPbI ₃	---	3.7 × 10 ¹⁰	---	17
MAPbBr _{0.05} I _{2.95}	---	3.1 × 10 ¹⁰	---	17
MAPbBr _{0.10} I _{2.90}	---	2.4 × 10 ¹⁰	---	17
MAPbBr _{0.27} I _{2.73}	---	1.9 × 10 ¹⁰	---	17
MAPbBr _{0.33} I _{2.67}	---	5.6 × 10 ⁹	---	17
MAPbBr _{0.43} I _{2.57}	---	6.8 × 10 ⁹	---	17

*Perovskites placed in anti-solvent (DCM) for 4 months to repair the crystal surface. Note: Data for some perovskites could not be extracted, as the corresponding regime were not observed using the SCLC approach.

Our materials exhibit comparable PL lifetimes to other reported materials as shown in **Figure S11a**. However, some materials like pure FAPbBr₃ exhibit significantly higher lifetimes, most likely due to polishing of the surfaces prior to PL measurements which was not done for our materials. Overall the trap density of our materials is significantly low and comparable to other reported single crystals materials, which are shown in **Figure S11b**. Interestingly for our materials synthesized using ITC the MAPbBr_{3-x}Cl_x based perovskites exhibited an increase in the trap density with increasing Cl inclusion, while FAPbBr_{3-x}Cl_x based perovskites exhibited the opposite trend with a decrease in the trap density with Cl inclusion. The mobilities extracted using SCLC are summarized **Figure S11c** along with a comparison to literature. We can see for pure MAPbBr₃ and MAPbI₃ there is a large variation in the reported mobilities, highlighting the difficulties of extracting electrical properties with this approach. Nevertheless, our materials exhibit comparable mobilities to those reported in the literature. Remarkable, for only 3% incorporation of Sn in MAPb_{1-x}Sn_xBr₃ based perovskites we can get an

exceptional 2 orders of increase in the mobility. Highlighting the viability to increase the charge transport properties of perovskite materials with only dopant level concentration of Sn.

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