Local structure and dynamics in methylammonium, formamidinium and cesium tin(II) mixed-halide perovskites from $^{119}$Sn solid-state NMR

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Figure S2. $^1$H,$^{13}$C CP MAS NMR spectra at 11.7 T, 100 K and 12 kHz MAS of (a) MASnI$_3$, (b) MASnI$_{1.5}$Br$_{1.5}$, (c) MASnBr$_3$, (d) MASnBr$_{1.5}$Cl$_{1.5}$, (e) MASnCl$_3$, (f) MASnCl$_{1.5}$I$_{1.5}$. The well-resolved features in panels c and e correspond to distinct MA environments present in the low-symmetry low temperature phases of MASnBr$_3$ and MASnCl$_3$, respectively. The spectra of mixed-halide compositions are broader as compared to the single halide materials, consistent with the presence of halide disorder. Recycle delay: 2 s. Number of scans: 256-1024. $^1$H decoupling: 100 kHz (SPINAL-64). Contact time: 1 ms.

Figure S3. $^{14}$N MAS NMR echo-detected spectra at 11.7 T, 298 K and 5 kHz MAS of (a) MASnI$_3$, (b) FASnI$_3$, (c) MA$_{0.25}$FA$_{0.75}$SnI$_3$. The broadening of the spinning sideband manifold in the mixed-cation case (panel c) is indicative of lowering of the cuboctahedral symmetry. Recycle delay: 0.3 s. RF strength: 62.5 kHz.
Figure S4. $^{133}$Cs MAS NMR echo-detected spectra at 16.4 T, 298 K and 12 kHz MAS of (a) CsSnI$_3$, (b) CsSnBr$_3$, (c) CsSnCl$_3$. The similarity of $^{133}$Cs shift of CsSnBr$_3$ and CsSnCl$_3$ is coincidental as the compounds are cubic and monoclinic at room temperature, respectively. $^{133}$Cs resonances in 3D halide perovskites have been shown to be strongly temperature dependent and an upfield shift (to lower ppm values) is expected on increasing the temperature and symmetry in CsSnCl$_3$, consistent with previous reports. Recycle delay: (a) 120 s, (b) 40 s, (c) 40 s. RF strength: 27.8 kHz.

Figure S5. A plot of the relaxation rate $R (R = 1/T_1)$ of the variable-temperature $T_1$ relaxation data for MASnBr$_3$ at 16.4 T as a function of the square of temperature. The dependence would be linear if temperature was dominated by spin-phonon Raman scattering.

Figure S6. The effect of spinning on $^{119}$Sn NMR spectra and $T_1$ relaxation of tin(II) halide perovskites: (a) FASnI$_3$ (red: static, green: 12 kHz MAS), (b) MASnBr$_3$ (red: static, green: 1.5 kHz MAS, blue: 12 kHz MAS), (c) FASnBr$_3$ (red: static, green: 1.5 kHz MAS). The use of MAS does not lead to shortening of the $T_1$ which excludes MAS-induced heteronuclear polarization exchange as a possible relaxation mechanism in MASnBr$_3$. The slight shortening of $T_1$ on going from 1.5 to 12 kHz (panel b) is a temperature-induced effect.

Figure S7. WSolids1 (WSolids1 ver. 1.21.3, K. Eichele, Universität Tübingen, 2015) line shape simulations in the extreme narrowing regime of (a) MASnBr$_3$, (b) MASnI$_3$, (c,d) CsSnI$_3$. The relevant simulation parameters are given below the spectra. exp − experimental spectrum, sim − simulated spectrum, $J = ^{119}$Sn–X $J$-coupling, $d = ^{119}$Sn–X dipole coupling, $T_{1q}$ estimated $T_1$ relaxation of the quadrupolar nucleus. Dipolar couplings expected based on the crystal structures (Sn–X distance = 2.9-3.1 Å) are as follows: $^{119}$Sn–$^{35}$Br: $d = -410$ Hz, $^{119}$Sn–$^{81}$Br: $d = -380$ Hz, $^{119}$Sn–$^{127}$I: $d = -304$ Hz. The width of the spectrum is largely determined by the magnitude of $J$ while $d$ introduces a small asymmetry and $T_{1q}$ determines the line broadening in the extreme narrowing regime. In the case of CsSnI$_3$, the asymmetry is reproduced well with a $d$ value larger than the coupling expected based on the crystal structure (panel c). Using the coupling strength based on the crystal structure leads to a more symmetric simulated spectrum (panel d). Since the spectra are echo-acquired, we expect that the slight asymmetry may be an artifact caused by anisotropic $^{119}$Sn $T_2$ relaxation.

Figure S8. Powder X-ray diffraction patterns of the materials reported in Figure 2 of the main text.

Figure S9. Powder X-ray diffraction patterns of the materials reported in Figure 3 of the main text. The asterisks indicate the corresponding oxidized A$_2$SnX$_6$ phase which slowly forms during the XRD measurement which is carried out in air.

Figure S10. Powder X-ray diffraction patterns of the materials reported in Figure 4a-c of the main text. The asterisks indicate the corresponding oxidized A$_2$SnX$_6$ phase which slowly forms during the XRD measurement which is carried out in air.

Figure S11. Powder X-ray diffraction patterns of the materials reported in Figure 4d-m of the main text.

Figure S12. Powder X-ray diffraction patterns of the materials reported in Figure 5 of the main text.

Table S1. Chemical shifts and peak widths of the multi-field variable-temperature $T_1$ relaxation data of MASnBr$_3$, measured using a saturation recovery sequence and a Hahn echo in the quasi-static regime: total echo duration 40 μs at 17.6 and 4.7 T, and 66.7 μs at 9.4 T. The uncertainties of the monoexponential $T_1$ fit are < 1 %.

Table S2. An Arrhenius fit of the $T_1$ relaxation data (abscissa: 1/T, ordinate: ln($T_1$/s)) to the equation: $y = a + bx$ for MASnBr$_3$. The errors of the least-squares fit are given as one standard deviation. The error of the average is given as one standard deviation of the average. $R = 8.3144598$ J/(K·mol).

Table S3. $^{119}$Sn $T_1$ values measured using a saturation-recovery sequence and fitted using a monoexponential function. The uncertainties of the fit are < 1 %.

Table S4. Acquisition and processing parameters used for the spectra in the main text.

Table S5. Summary of the degradation products of tin(II) halide perovskites detected using $^{119}$Sn MAS NMR. Note that not all possible degradation products were detected for all samples - see the discussion in the main text for details.
Synthesis of the materials

**MASnCl₂**: MACI (68 mg, 1.00 mmol), SnCl₂ (190 mg, 1.00 mmol),
**MASnBr₃**: MABr (112 mg, 1.00 mmol), SnBr₂ (279 mg, 1.00 mmol),
**MASnI₃**: MAI (159 mg, 1.00 mmol), SnI₂ (373 mg, 1.00 mmol),

**MASnCl₂Br₀.₃**: MACI (61 mg, 0.9 mmol), MABr (11 mg, 0.1 mmol), SnCl₂ (171 mg, 0.9 mmol), SnBr₂ (28 mg, 0.1 mmol)
**MASnCl₂Br₀.₅**: MACI (47 mg, 0.7 mmol), MABr (34 mg, 0.3 mmol), SnCl₂ (133 mg, 0.7 mmol), SnBr₂ (84 mg, 0.3 mmol)
**MASnCl₁₅Br₁₅**: MACI (34 mg, 0.5 mmol), MABr (56 mg, 0.5 mmol), SnCl₂ (95 mg, 0.5 mmol), SnBr₂ (139 mg, 0.5 mmol)

**MASnCl₂I₀.₃**: MACI (61 mg, 0.9 mmol), MAI (16 mg, 0.1 mmol), SnCl₂ (171 mg, 0.9 mmol), SnI₂ (37 mg, 0.1 mmol)

**MASnBr₁₉I₁₂**: MABr (34 mg, 0.3 mmol), MAI (111 mg, 0.7 mmol), SnBr₂ (84 mg, 0.3 mmol), SnI₂ (261 mg, 0.7 mmol)
**MASnBr₁₅I₁₅**: MABr (56 mg, 0.5 mmol), MAI (79 mg, 0.5 mmol), SnBr₂ (139 mg, 0.5 mmol), SnI₂ (186 mg, 0.5 mmol)
**MASnBr₂₁₆I₉**: MABr (78 mg, 0.7 mmol), MAI (48 mg, 0.3 mmol), SnBr₂ (195 mg, 0.7 mmol), SnI₂ (112 mg, 0.3 mmol)
**MASnBr₂₅I₄₅**: MABr (95 mg, 0.85 mmol), MAI (24 mg, 0.25 mmol), SnBr₂ (237 mg, 0.85 mmol), SnI₂ (56 mg, 0.25 mmol)
**MASnBr₂₇I₀.₃**: MABr (101 mg, 0.9 mmol), MAI (16 mg, 0.1 mmol), SnBr₂ (251 mg, 0.9 mmol), SnI₂ (37 mg, 0.1 mmol)

**MA₂SnBr₆**: MABr (224 mg, 2.00 mmol), SnBr₄ (438 mg, 1.00 mmol),
**MA₂SnI₆**: MAI (318 mg, 2.00 mmol), SnI₄ (626 mg, 1.00 mmol),

**FASnI₃**: FAI (172 mg, 1.00 mmol), SnI₂ (373 mg, 1.00 mmol),
**FASnBr₃**: FABr (125 mg, 1.00 mmol), SnBr₂ (279 mg, 1.00 mmol),
**FASnCl₃**: FACI (81 mg, 1.00 mmol), SnCl₂ (190 mg, 1.00 mmol),
**MA₀.₅FA₀.₅SnBr₃**: MABr (56 mg, 0.5 mmol), FABr (62 mg, 0.5 mmol), SnBr₂ (279 mg, 1.00 mmol),
**MA₀.₅FA₀.₅SnCl₃**: MACI (34 mg, 0.5 mmol), FACI (40 mg, 0.5 mmol), SnCl₂ (190 mg, 1.00 mmol),
**CsSnI₃**: CsI (260 mg, 1.00 mmol), SnI₂ (373 mg, 1.00 mmol),
**CsSnBr₃**: CsBr (213 mg, 1.00 mmol), SnBr₂ (279 mg, 1.00 mmol),
**CsSnCl₃**: CsCl (168 mg, 1.00 mmol), SnCl₂ (190 mg, 1.00 mmol),
**CsSnCl₁₅Br₁₅**: CsCl (168 mg, 1.00 mmol), SnCl₂ (95 mg, 0.5 mmol), SnBr₂ (139 mg, 0.5 mmol),

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Figure S1. Echo-detected $^{119}$Sn MAS NMR spectra of MASnBr$_3$ at 4.7 T, 298 K and 12 kHz MAS using a refocusing echo period of (a) 16.7 μs (asynchronous), (b) 83.3 μs (rotor synchronized). The rotor-synchronized echo period does not lead to the appearance of spinning sidebands and its only effect is lower signal intensity due to fast transverse relaxation. Number of scans: (a) 1024, (b) 4096. Recycle delay: 50 ms.

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Figure S3. $^{14}$N MAS NMR echo-detected spectra at 11.7 T, 298 K and 5 kHz MAS of (a) MASnI$_3$, (b) FASnI$_3$, (c) MA$_{0.25}$FA$_{0.75}$SnI$_3$. The broadening of the spinning sideband manifold in the mixed-cation case (panel c) is indicative of lowering of the cubooctahedral symmetry. Recycle delay: 0.3 s. RF strength: 62.5 kHz.

Figure S4. $^{133}$Cs MAS NMR echo-detected spectra at 16.4 T, 298 K and 12 kHz MAS of (a) CsSnI$_3$, (b) CsSnBr$_3$, (c) CsSnCl$_3$. The similarity of $^{133}$Cs shift of CsSnBr$_3$ and CsSnCl$_3$ is coincidental as the compounds are cubic and monoclinic at room temperature, respectively. $^{133}$Cs resonances in 3D halide perovskites have been shown to be strongly temperature dependent and an upfield shift (to lower ppm values) is expected on increasing the temperature and symmetry in CsSnCl$_3$, consistent with previous reports.$^{1,2}$ Recycle delay: (a) 120 s, (b) 40 s, (c) 40 s. RF strength: 27.8 kHz.
Figure S5. A plot of the relaxation rate $R$ ($R=1/T_1$) of the variable-temperature $T_1$ relaxation data for $\text{MASnBr}_3$ at 16.4 T as a function of the square of temperature. The dependence would be linear if relaxation was dominated by spin-phonon Raman scattering.$^3$

Figure S6. The effect of spinning on $^{119}\text{Sn}$ NMR spectra and $T_1$ relaxation of tin(II) halide perovskites: (a) $\text{FASnI}_3$ (red: static, green: 12 kHz MAS), (b) $\text{MASnBr}_3$ (red: static, green 1.5 kHz MAS, blue: 12 kHz MAS), (c) $\text{FASnBr}_3$ (red: static, green: 1.5 kHz MAS). The use of MAS does not lead to shortening of the $T_1$ which excludes MAS-induced heteronuclear polarization exchange as a possible relaxation mechanism in $\text{MASnBr}_3$. The slight shortening of $T_1$ on going from 1.5 to 12 kHz (panel b) is a temperature-induced effect.
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**Supplementary Note 1**

It is worth noting that the CSA patterns of MASnCl$_{1.5}$Br$_{1.5}$ (fig. 2f) and MASnBr$_{2.55}$I$_{0.45}$ (fig. 3g) yield a single $^{119}$Sn peak while a sizeable CSA is expected in these cases due to asymmetric coordination of the tin(II) site. Taking a typical value of $^{119}$Sn CSA spanning 100 kHz, the dynamic process which leads to its averaging has to occur at a faster rate, i.e. with a correlation time shorter than 1/(100 kHz) = 10 μs. Since the previously determined halide hopping rates (>0.1 GHz) correspond to correlation times <10 ns, halide hopping might be the source of CSA averaging.

**Supplementary Note 2**

Estimation of the $^{119}$Sn $T_1$ minimum in the dipole-dipole relaxation mechanism for $^{119}$Sn coupled to $^{79}$Br at 4.7 T:

\[
\frac{1}{T_1} = \frac{4}{30} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_{^7S_n}^2 \gamma_{^9B_r}^2 \hbar}{r^6} S(S+1) \left( \frac{\tau}{1 + (\omega_{^7S_n} - \omega_{^9B_r})^2 \tau^2} + \frac{3\tau}{1 + \omega_{^7S_n}^2 \tau^2} + \frac{6\tau}{1 + (\omega_{^7S_n} + \omega_{^9B_r})^2 \tau^2} \right)
\]
where:
permeability of free space, \( \mu_0 = 4\pi \cdot 10^{-7} \text{ V} \cdot \text{s/(A} \cdot \text{m)} \)
Planck constant, \( \hbar = 1.054 \cdot 10^{-34} \text{ J} \cdot \text{s} \)
\(^{119}\text{Sn} \) gyromagnetic ratio, \( \gamma_{\text{Sn}} = -10.03170 \cdot 10^7 \text{ rad/(T} \cdot \text{s)} \)
\(^{79}\text{Br} \) gyromagnetic ratio, \( \gamma_{\text{Br}} = 6.72562 \cdot 10^7 \text{ rad/(T} \cdot \text{s)} \)
\(^{119}\text{Sn} - ^{79}\text{Br} \) distance in the crystal structure, \( r = 2.945 \cdot 10^{-10} \text{ m} \)
\(^{119}\text{Sn} \) Larmor frequency, \( \omega_{\text{Sn}} = 74.581 \cdot 10^6 \text{ Hz} \)
\(^{79}\text{Br} \) Larmor frequency, \( \omega_{\text{Br}} = 50.108 \cdot 10^6 \text{ Hz} \)
spin of \(^{79}\text{Br}, S = 3/2 \)
correlation time, \( \tau \) – an adjustable parameter
A \( T_1 \) minimum of 4.8 s is obtained for \( \tau = 13 \text{ ns} \).

Putting \(^{81}\text{Br} \) gyromagnetic ratio, \( \gamma_{\text{Br}} = -7.24978 \cdot 10^7 \text{ rad/(T} \cdot \text{s)} \) and \(^{81}\text{Br} \) Larmor frequency, \( \omega_{\text{Br}} = 54.0 \cdot 10^6 \text{ Hz} \), one obtains a \( T_1 \) minimum of 4.2 s for \( \tau = 13 \text{ ns} \).

**Supplementary Note 3**

The following considerations have been used to distinguish between scalar relaxation of the first and second kind:

**If the system is in the extreme narrowing limit for the \(^{79/81}\text{Br} \) \( T_{1Q} \), as the temperature increases:**

(i) \(^{79/81}\text{Br} \) \( T_{1Q} \) gets longer, \(^{119}\text{Sn} \) \( T_2 \) gets shorter (since the flipping of the quadrupole partner gets slower).

(ii) Exchange due to halide hopping gets faster. \(^{119}\text{Sn} \) \( T_2 \) gets longer (since the hopping of the quadrupole partner gets faster)

**If the system is in the slow motion limit for the \(^{79/81}\text{Br} \) \( T_{1Q} \), as the temperature increases:**

(i) \(^{79/81}\text{Br} \) \( T_{1Q} \) gets shorter, \(^{119}\text{Sn} \) \( T_2 \) gets longer (since the flipping of the quadrupole partner gets faster).

(ii) Exchange due to halide hopping gets faster. \(^{119}\text{Sn} \) \( T_2 \) gets longer (since the hopping of the quadrupole partner gets faster)

It is therefore only possible to distinguish between scalar relaxation of the first and second kind based on \(^{119}\text{Sn} \) line widths if the system is in the extreme narrowing limit. While variable-temperature relaxation measurements of \(^{79/81}\text{Br} \) \( T_{1Q} \) are impractical due to a very large quadrupole coupling constant in \( \text{MASnBr}_3 \), we corroborate that \(^{119}\text{Sn} \) \( T_1 \) is determined by halide hopping (scalar relaxation of the first kind) based on the resulting activation energy:

1. The activation energy obtained from variable-temperature \(^{119}\text{Sn} \) \( T_1 \) measurements matches well that from electrical measurements (Table 1 in the main text). The
thermally activated process which is being probed is therefore halide hopping. This
confirms that relaxation is driven by halide hopping (i.e. scalar, 1\textsuperscript{st} kind).

2. Scalar relaxation of the second kind would lead to an activation energy of the process
which drives $^{79/81}$Br $T_1\text{O}$, which is typically a Raman process related to lattice modes.
Since Raman and phonon spectra fall in the far infrared to THz range, the activation
energies corresponding to those processes are <0.03 eV, i.e. an order of magnitude
less than what is found experimentally.

**Details of NMR measurements**

Table S1. Chemical shifts and peak widths of the multi-field variable-temperature $T_1$
relaxation data of MASnBr$_3$, measured using a saturation recovery sequence and a Hahn echo
in the quasi-static regime: total echo duration 40 μs at 17.6 and 4.7 T, and 66.7 μs at 9.4 T.
The uncertainties of the monoexponential $T_1$ fit are <1 %.

| Magnetic field strength: 17.6 T |  |  |  |
|---|---|---|---|
| Temperature [K] | $^{119}$Sn chemical shift [ppm] | fwhm [kHz] | $T_1$ [ms] |
| 308 | -315 | 10.7 | 9.66 |
| 326 | -312 | 10.9 | 5.47 |
| 343 | -310 | 9.5 | 2.95 |
| 356 | -306 | 8.6 | 1.87 |
| 372 | -302 | 7.8 | 1.12 |
| 389 | -298 | 6.6 | 0.706 |
| 405 | -293 | 5.6 | 0.465 |
| 421 | -287 | 5.8 | 0.305 |
| 438 | -281 | 5.9 | 0.235 |
| 454 | -275 | 7.0 | 0.127 |
| 474 | -267 | 6.8 | 0.101 |
| 490 | -266 | 9.9 | n.d. (decomposition) |

| Magnetic field strength: 9.4 T |  |  |  |
|---|---|---|---|
| Temperature [K] | $^{119}$Sn chemical shift [ppm] | fwhm [kHz] | $T_1$ [ms] |
| 253 | -322 | 10.7 | 201 |
| 268 | -324 | 11.6 | 78 |
| 286 | -317 | 10.8 | 30 |
| 313 | -313 | 10.1 | 10 |
| 347 | -307 | 8.2 | 3.3 |

| Magnetic field strength: 4.7 T |  |  |  |
|---|---|---|---|
| Temperature [K] | $^{119}$Sn chemical shift [ppm] | fwhm [kHz] | $T_1$ [ms] |
| 317 | -334 | 10.5 | 8.271 |
| 339 | -314 | 8.7 | 4.151 |
| 347 | -310 | 7.5 | 2.426 |
| 360 | -314 | 6.9 | 1.644 |
| 368 | -310 | 6.1 | 1.138 |
| 382 | -306 | 4.7 | 0.653 |
Table S2. An Arrhenius fit of the $T_1$ relaxation data (abscissa: $1/T$, ordinate: $\ln(T_1/s)$) to the equation: $y = a + b \cdot x$ for MASnBr$_3$. The errors of the least-squares fit are given as one standard deviation. The error of the average is given as one standard deviation of the average. $R = 8.3144598 \text{ J/(K} \cdot \text{mol})$.

| magnetic field strength [T] | a         | b         | $E_a = b \cdot R/1000$ [kJ/mol] |
|---------------------------|-----------|-----------|---------------------------------|
| 17.6                      | -18.01 ± 0.15 | 4165 ± 57 | 34.1 ± 0.5                      |
| 9.4                       | -16.75 ± 0.41 | 3811 ± 12 | 31.8 ± 0.1                      |
| 4.7                       | -20.74 ± 0.29 | 5123 ± 11 | 42.7 ± 0.1                      |
|                           | average:    |           | 36.2 ± 5.7                      |

Table S3. $^{119}$Sn $T_1$ values measured using a saturation-recovery sequence and fitted using a monoexponential function. The uncertainties of the fit are <1 %.

| compound              | $^{119}$Sn $T_1$ [s] |
|-----------------------|----------------------|
| MASnCl$_3$            | 60                   |
| MASnCl$_2$.Br$_{0.3}$ | 29.7                 |
| MASnCl$_2$.Br$_{0.9}$ | 2.59                 |
| MASnCl$_{1.3}$.Br$_{1.5}$ | 0.352            |
| MASnBr$_3$            | 0.0053               |
| MASnBr$_{2.7}$.I$_{0.3}$ | 0.0011              |
| MASnBr$_{2.1}$.I$_{0.9}$ | 0.000164         |
| MASnI$_3$             | 0.000545             |
| $\beta$-Sn            | 0.00012              |
| SnCl$_2$              | 26.4                 |
| SnBr$_2$              | 1.12                 |
| SnI$_2$               | 0.528                |
| SnBr$_4$              | 1.95                 |
| SnI$_4$               | 11.5                 |
| MA$_2$SnBr$_6$        | 9.9                  |
| MA$_2$SnI$_6$         | 0.001                |

Table S4. Acquisition and processing parameters used for the spectra in the main text.

| $^{119}$Sn spectra |
|-------------------|-----------------|-----------------|-----------------|-----------------|
| composition       | Figure | recycle delay [s] | number of scans | acquisition time [min] | Lorentzian apodization [Hz] |
| SnCl$_2$          | 2      | 34              | 32              | 18              | 200              |
| SnBr$_2$          |        | 1.5            | 6204            | 155             | 1000             |
| MASnCl$_3$        |        | 50             | 1384            | 1153            | 500              |
| MASnCl$_2$.Br$_{0.3}$ |      | 40             | 1752            | 1168            | 500              |
| Compound                | 3          | 4          | 5          |
|------------------------|------------|------------|------------|
| MASnCl₂Br₀.₉          | 3          | 1892       | 95         | 4000       |
| MASnCl₁.₅Br₁.₅        | 0.5        | 3900       | 33         | 1000       |
| MASnBr₃               | 0.05       | 4096       | 3          | 1000       |
| SnBr₄                 | 2.5        | 2260       | 94         | 1000       |
| MA₂SnBr₆              | 13         | 680        | 147        | 2000       |
| SnI₂                  | 1          | 2224       | 37         | 2000       |
| MASnI₃               | 0.01       | 32768 ×3 offsets | 16 | 20000     |
| MASnCl₂Br₁₀.₃ (fast)  | 0.05       | 55800      | 47         | 10000      |
| MASnCl₂Br₁₀.₃ (slow)  | 50         | 2008       | 1673       | 100        |
| MASnBr₀.₉I₂.₁        | 0.01       | 3654026    | 609        | 10000      |
| MASnBr₁.₅I₁.₅        | 0.01       | 142604     | 24         | 10000      |
| MASnBr₂₁₀.₉I₀.₉      | 0.01       | 135088     | 23         | 8000       |
| MASnBr₃₅I₄₀.₄₅      | 0.001      | 81060      | 1          | 1000       |
| MASnBr₁₀.₇I₀.₃      | 0.05       | 21940      | 18         | 2000       |
| SnI₄                  | 20         | 1832       | 611        | 2000       |
| MA₂SnI₆              | 0.005      | 55980      | 5          | 1000       |
| FASnI₃               | 0.01       | 31624 ×5 offsets | 26 | 20000     |
| CsSnI₃              | 0.001      | 420560 ×3 offsets | 21 | 20000     |
| CsSnBr₃             | 0.01       | 53028      | 9          | 1000       |
| MA₀.₅FA₀.₅SnBr₃     | 0.015      | 10240      | 3          | 1000       |
| FASnBr₃            | 0.1        | 2048       | 3          | 1000       |
| MA₀.₅FA₀.₅SnCl₃     | 60         | 1240       | 1240       | 500        |
| FASnCl₃             | 60         | 964        | 964        | 500        |
| CsSnCl₃ (monoclinic) | 60         | 876        | 876        | 500        |
| CsSnCl₃ (cubic)     | 5          | 128        | 11         | 200        |
| CsSnCl₁₂Br₁₅        | 0.5        | 3300       | 28         | 100        |
| MASnBr₃ (degraded) | 13         | 4972       | 1077       | 500        |
| SnO₂                 | 12         | 128        | 26         | 100        |
| SnO₂ + 10 mol%SnBr₂ | 12         | 356        | 71         | 100        |
| FASnBr₃ (degraded at RT) | 13     | 4796       | 1039       | 1000       |
| FASnBr₃ (degraded at 250 °C) | 13  | 3300       | 715        | 500        |
| CsSnBr₃ (degraded), perovskite region | 0.01 | 53028 | 9 | 1000 |
| CsSnBr₃ (degraded), decomposition products | 13 | 968 | 210 | 2000 |
| MASnI₃ (degraded), perovskite region | 0.01 | 32768 | 5 | 10000 |
| MASnI₃ (degraded), MA₂SnI₆ region | 0.005 | 55980 | 5 | 1000 |
| Material                | Degradation conditions | Figure in the main text | Detected degradation products               |
|------------------------|------------------------|-------------------------|---------------------------------------------|
| MASnBr₃                | 1 h at 250 °C in air   | 5b                      | MA₂SnBr₆, SnO₂, (SnBr₄)                     |
| FASnBr₃                | 5 days at RT, in air   | 5f                      | FA₂SnBr₆, SnO₂,                            |
| FASnBr₃                | Same sample as above + 0.5 h at 250 °C in air | 5g                      | FA₂SnBr₆, SnO₂,                            |
| CsSnBr₃                | 0.5 h at 350 °C in air | 5i                      | Cs₂SnBr₆, SnO₂                             |
| MASnI₃                 | 1 h at 150 °C in air   | 5k                      | MA₂SnI₆, SnO₂, metallic tin                |
| FASnI₃                 | 1 h at RT in air       | 5m                      | FA₂SnI₆                                    |
| CsSnI₃                 | 3 h at 100 °C in air   | 5o                      | Cs₂SnI₆                                    |

**XRD data**

Powder X-ray diffraction patterns were recorded on an X’Pert MPD PRO (Panalytical) diffractometer equipped with a ceramic tube (Cu anode, λ = 1.54060 Å), a secondary graphite (002) monochromator and an RTMS X’Celerator (Panalytical) in an angle range of 2θ = 5° to 40°, by step scanning with a step of 0.02 degree.
Figure S8. Powder X-ray diffraction patterns of the materials reported in Figure 2 of the main text.
Figure S9. Powder X-ray diffraction patterns of the materials reported in Figure 3 of the main text. The asterisks indicate the corresponding oxidized A$_2$SnX$_6$ phase which slowly forms during the XRD measurement which is carried out in air.
Figure S10. Powder X-ray diffraction patterns of the materials reported in Figure 4a-c of the main text. The asterisks indicate the corresponding oxidized A$_2$SnX$_6$ phase which slowly forms during the XRD measurement which is carried out in air.

Figure S11. Powder X-ray diffraction patterns of the materials reported in Figure 4d-m of the main text.
Figure S12. Powder X-ray diffraction patterns of the materials reported in Figure 5 of the main text.
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