

Supporting Information

Impact of Rubidium and Cesium Cations on the Moisture Stability of Multiple-Cation Mixed- Halide Perovskites

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EXPERIMENTAL DETAILS

Perovskite precursor solutions

The organic cation salts formamidinium iodide (FAI) and methylammonium bromide (MABr) were purchased from Dyesol, the lead halide compounds from TCI, CsI (99.9%) from Sigma-Aldrich and RbI from abcr GmbH. All chemicals were used without further purification.

FAMA: PbI_2 (508 mg, 1.1 mmol), PbBr_2 (80.7 mg, 0.22 mmol), FAI (171.97 mg, 1 mmol) and MABr (22.4 mg, 0.2 mmol) were dissolved in 800 μL of anhydrous DMF and 200 μL DMSO by heating the solution up to 100 °C. This nonstoichiometric $(\text{FA}_{0.83}\text{MA}_{0.17})\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ precursor solution contains a 10 mol% excess of PbI_2 and PbBr_2 , respectively, which was introduced to enhance device performance. The FAMA solution was filtrated through a 0.45 μm syringe filter before usage.

Cs5 and Cs10: CsI (389.7 mg, 1.5 mmol) was dissolved in 1 mL DMSO and filtrated through a 0.45 μm syringe filter, yielding an approximately 1.5 M CsI stock solution. To obtain the desired triple cation perovskite composition of approximately 5 mol% Cs, 42 μL of the CsI stock solution was added to 1 mL FAMA solution, yielding a nominal composition of $\text{Cs}_{0.05}[(\text{FA}_{0.83}\text{MA}_{0.17})]_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ for Cs5. The precursor solution for Cs10 was obtained by adding 84 μL of the CsI solution to 1 mL FAMA solution.

Rb5 and Rb10: RbI (318.5 mg, 1.5 mmol) was dissolved in 1 mL of a 4 : 1 (v/v) DMF : DMSO mixture and filtrated through a 0.45 μm syringe filter. To obtain the desired triple cation perovskite composition of 5% Rb, 42 μL of the 1.5 M RbI stock solution was added to 1 mL FAMA solution, yielding a nominal composition of $\text{Rb}_{0.05}[(\text{FA}_{0.83}\text{MA}_{0.17})]_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ for Rb5. The precursor solution for Rb10 was obtained by adding 84 μL of the RbI solution to 1 mL FAMA solution.

Rb5Cs5: To obtain the quadruple cation perovskite composition of 5% Rb and 5% Cs, 42 μL of the RbI stock solution and 42 μL of the CsI stock solution were added to 1 mL FAMA solution, yielding a nominal composition of $\text{Rb}_{0.05}\text{Cs}_{0.05}[(\text{FA}_{0.83}\text{MA}_{0.17})]_{0.9}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$.

Thin film fabrication of $\text{RbPb}(\text{I}_{1-x}\text{Br}_x)_3$

To fabricate $\text{RbPb}(\text{I}_{1-x}\text{Br}_x)_3$ films, 1 M $\text{RbPb}(\text{I}_{1-x}\text{Br}_x)_3$ solutions with different Br-contents were prepared by dissolving RbI, PbBr_2 and PbI_2 in a 4 : 1 (v/v) DMF : DMSO mixture with the corresponding stoichiometry. For 1 mL solution, the amount of RbI (212.4 mg, 1 mmol) was held constant, while the PbBr_2 : PbI_2 ratio was varied to obtain final Br-contents of approximately $x = 0.16$ (88.1 mg : 350.4 mg), $x = 0.20$ (110.1 mg : 322.7 mg) and $x = 0.25$ (137.6 mg : 288.1 mg), respectively. After dissolving the components at 100 °C, the same spin-coating procedure as for the perovskite films was conducted and the films were annealed at 100 °C for 60 min. Pale yellow films were obtained.

Reproduction of RbPb₂I₄Br and CsPb₂I₄Br films

To reproduce the crystal phases RbPb₂I₄Br found as products of moisture-induced phase separation in Rb5 and Rb5Cs5 samples, a stoichiometric solution of RbI : PbI₂ : PbBr₂ = 1 : 1.5 : 0.5 was prepared. Therefore, RbI (106.18 mg, 0.5 mmol), PbI₂ (345.7 mg, 0.75 mmol) and PbBr₂ (91.75 mg, 0.25 mmol) were dissolved in 0.5 mL of a 4 : 1 (v/v) DMF : DMSO mixture. Then the same spin-coating procedure as for the perovskite films was conducted (without the chlorobenzene drip) and the samples were annealed at 100 °C for 10 min, yielding pale yellow films. For the reproduction of the CsPb₂I₄Br phase, RbI was replaced by CsI (129.9 mg, 0.5 mmol).

Moisture stability tests

Humidity studies on the perovskite solar cells were conducted in a glass container at a constant humidity level of 75% RH in air that was maintained by a saturated aqueous NaCl solution at the bottom of the jar. Humidity stability tests at 58% RH were performed in the same way using a NaBr solution. In order to exclude the influence of light exposure on the degradation process, the container was kept in the dark. The unencapsulated solar cells were placed onto a stage inside the sealed container being exposed to the moist air and without having direct contact with the solution. After a certain exposure time, the J - V curves of the devices were measured under ambient conditions and 1 sun illumination at a scan rate of 0.2 V s⁻¹. 24 cells were evaluated for each type of perovskite solar cell for 75% RH and 20 cells for 58% RH. The arithmetic means of the PCE and J_{sc} values extracted from the reverse J - V scans were monitored over a course of 10 days. The stability of devices under the exclusion of water was determined by measuring the PCE of 20 cells for each type of perovskites after storage in a nitrogen-filled glovebox for 5 months.

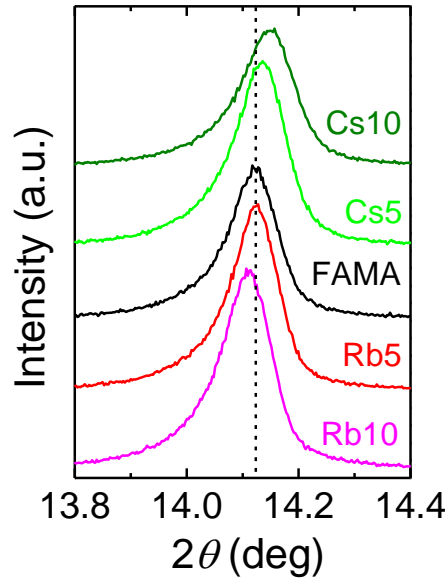


Figure S1. Magnified XRD patterns of perovskite films on FTO-glass substrates showing the peak shift for the main perovskite peak upon CsI and RbI addition. The dotted black line indicates the position of the peak maximum for FAMA. Cs-induced peak shift towards larger diffraction angles indicates lattice contraction, while Rb-induced peak shift towards smaller angles indicates lattice expansion.

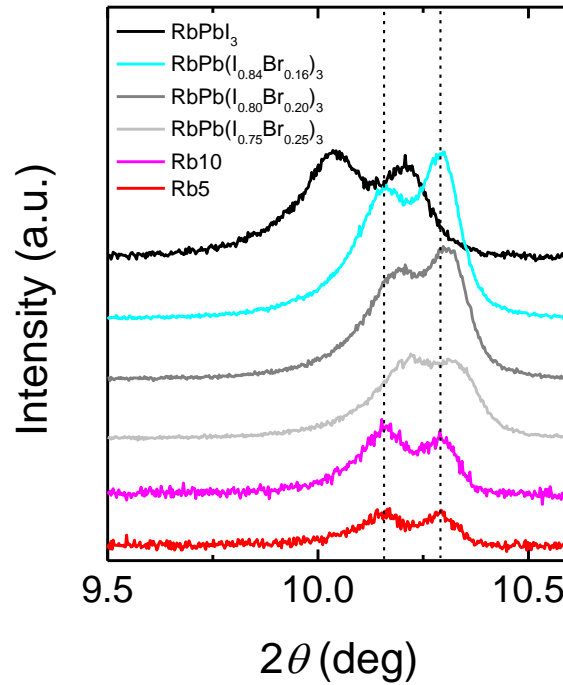


Figure S2. Magnified view on the XRD patterns of Rb5 and Rb10 compared to $\text{RbPb}(\text{I}_{1-x}\text{Br}_x)_3$ films on FTO-glass substrates. The dotted black lines indicate the positions of the peak maxima found in

Rb5 and Rb10. The peak positions for the side phase formed in Rb5 and Rb10 upon perovskite formation are in well agreement with the $\text{RbPb}(\text{I}_{0.84}\text{Br}_{0.16})_3$ compound.

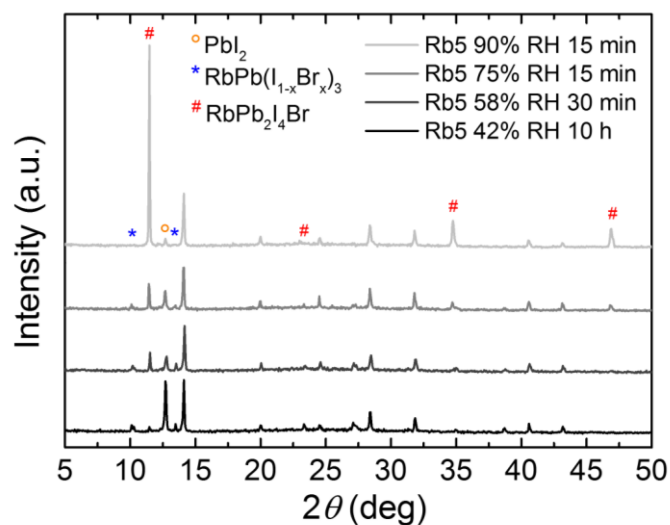


Figure S3. XRD patterns of Rb5 films on glass upon exposure to different humidity levels in air. The diffraction peaks assigned to the $\text{RbPb}_2\text{I}_4\text{Br}$ side phase appear after different exposure times.

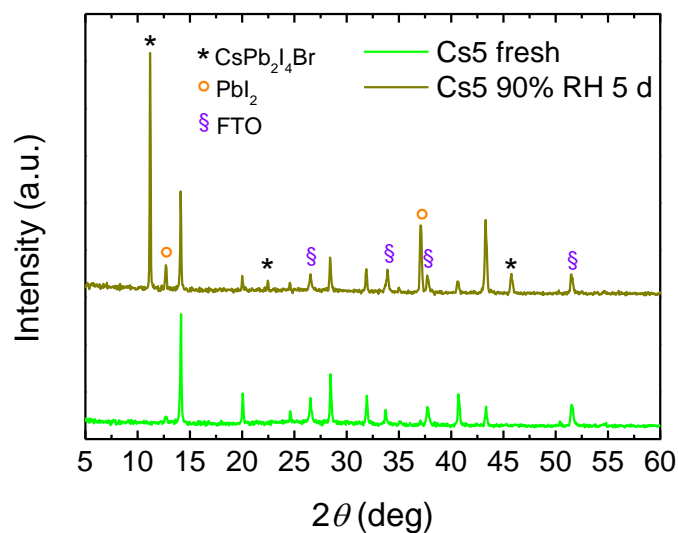


Figure S4. XRD patterns of a Cs5 perovskite film on FTO/TiO₂ before and after exposure to 90% RH for 5 days.

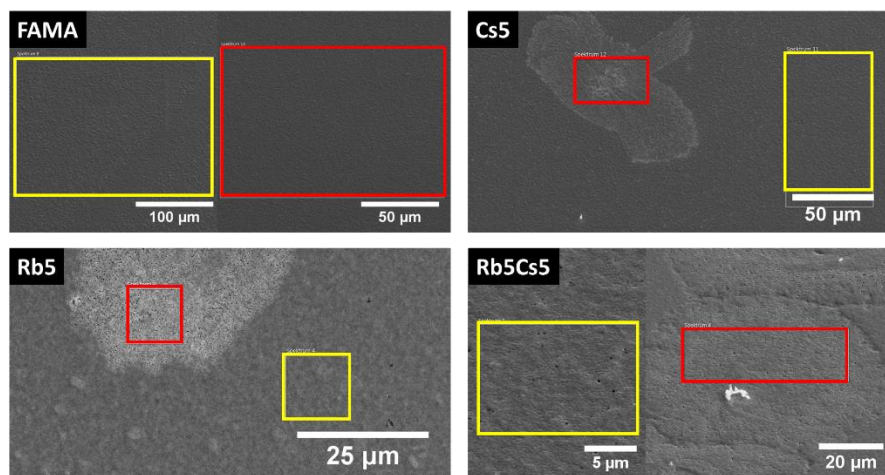


Figure S5. SEM top-view images of FAMA, Cs5, Rb5 and RbCs5 perovskite films and the evaluated areas for EDX elemental analysis of the intact (yellow) and degraded (red) areas.

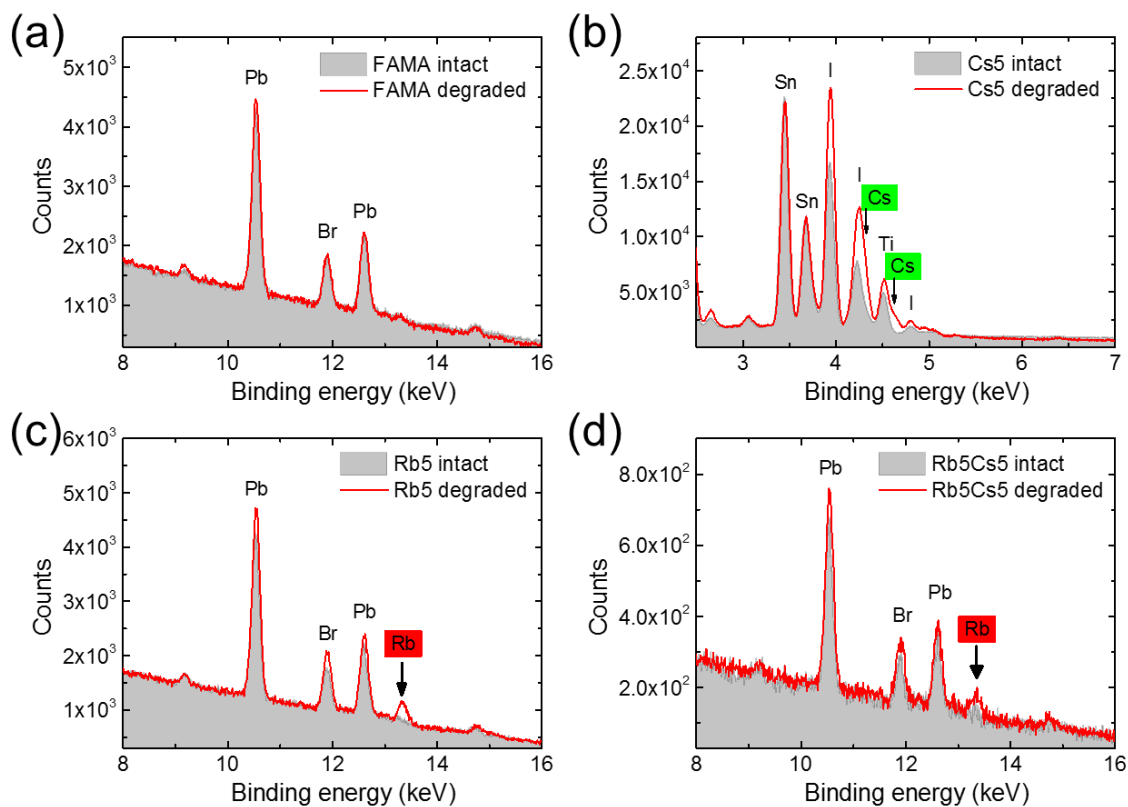


Figure S6. EDX spectra of the intact and degraded areas for (a) FAMA, (b) Cs5, (c) Rb5 and (d) Rb5Cs5 films after exposure to 90% RH.

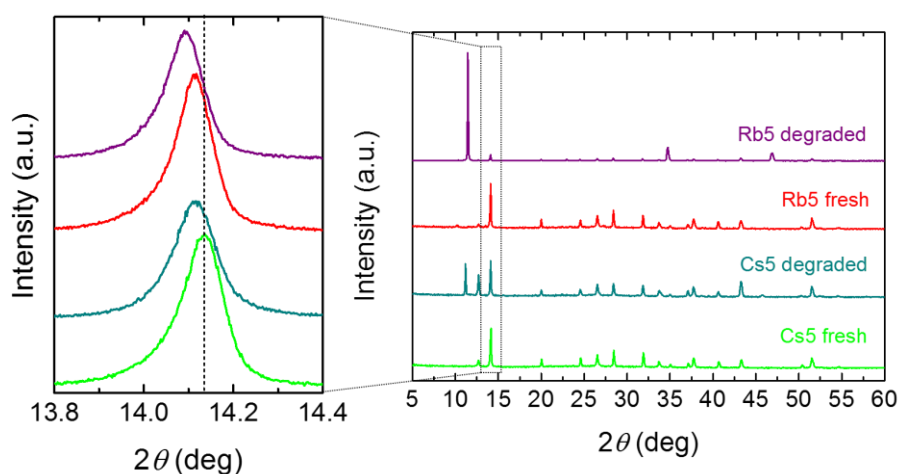


Figure S7. XRD patterns of fresh Cs5 and Rb5 samples compared to degraded samples after exposure to 90% RH. The magnified view shows the peak shift towards smaller diffraction angles for the perovskite main peak in both samples upon moisture-induced phase segregation. The dotted black line indicates the position of the peak maximum for a fresh Cs5 sample.

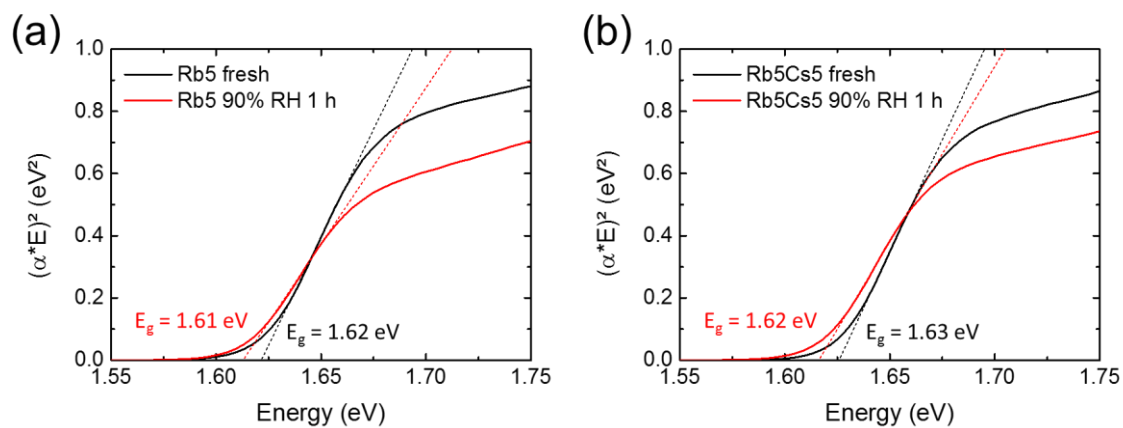


Figure S8. Tauc plots for (a) Rb5 and (b) Rb5Cs5 films on glass before and after exposure to 90% RH for 1 h.

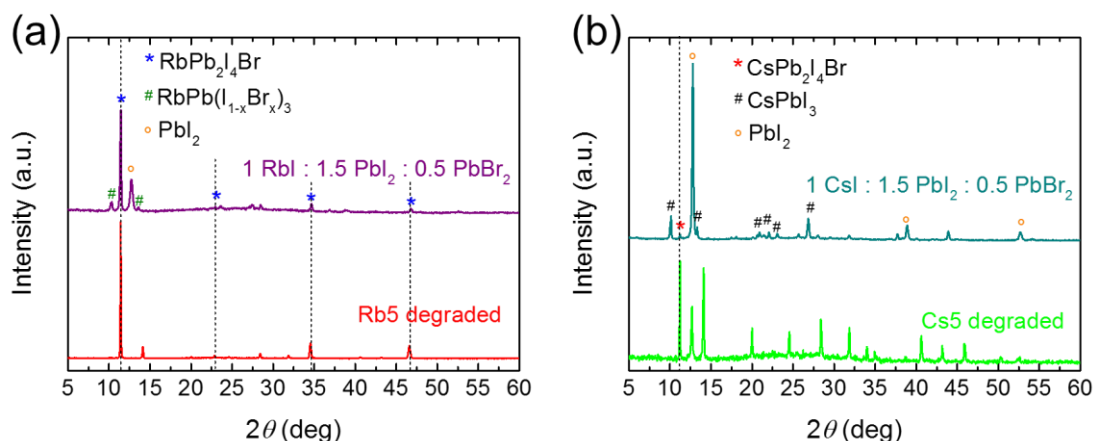


Figure S9. (a) XRD patterns of a degraded Rb5 film showing moisture-induced phase segregation compared to a film obtained from a precursor solution with $\text{RbI} : \text{PbI}_2 : \text{PbBr}_2$ in a molar stoichiometry of 1 : 1.5 : 0.5. (b) XRD patterns of a degraded Cs5 film compared to a film obtained from a solution with $\text{CsI} : \text{PbI}_2 : \text{PbBr}_2 = 1 : 1.5 : 0.5$. The dotted black lines indicates the peak positions of $\text{RbPb}_2\text{I}_4\text{Br}$ in (a) and $\text{CsPb}_2\text{I}_4\text{Br}$ in (b), respectively.

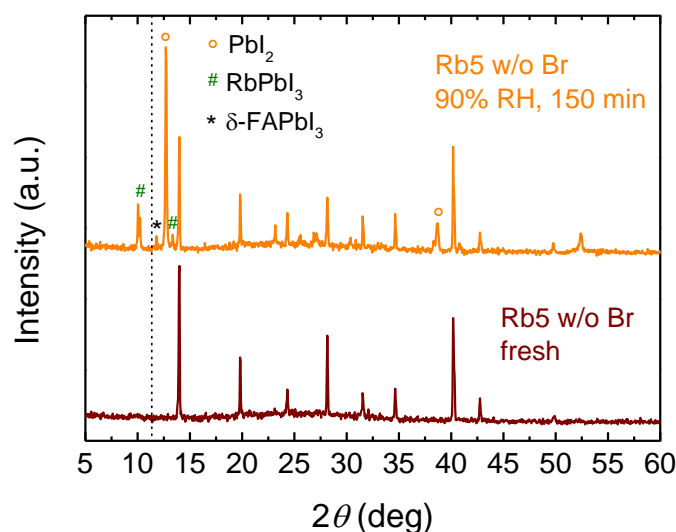


Figure S10. XRD patterns of iodide-only Rb5 perovskite films without bromide in the precursor solution before and after exposure to 90% RH. The dotted black line indicates the peak position of the $\text{RbPb}_2\text{I}_4\text{Br}$ phase. No $\text{RbPb}_2\text{I}_4\text{Br}$ is formed in the absence of bromide in the Rb5 precursor solution.

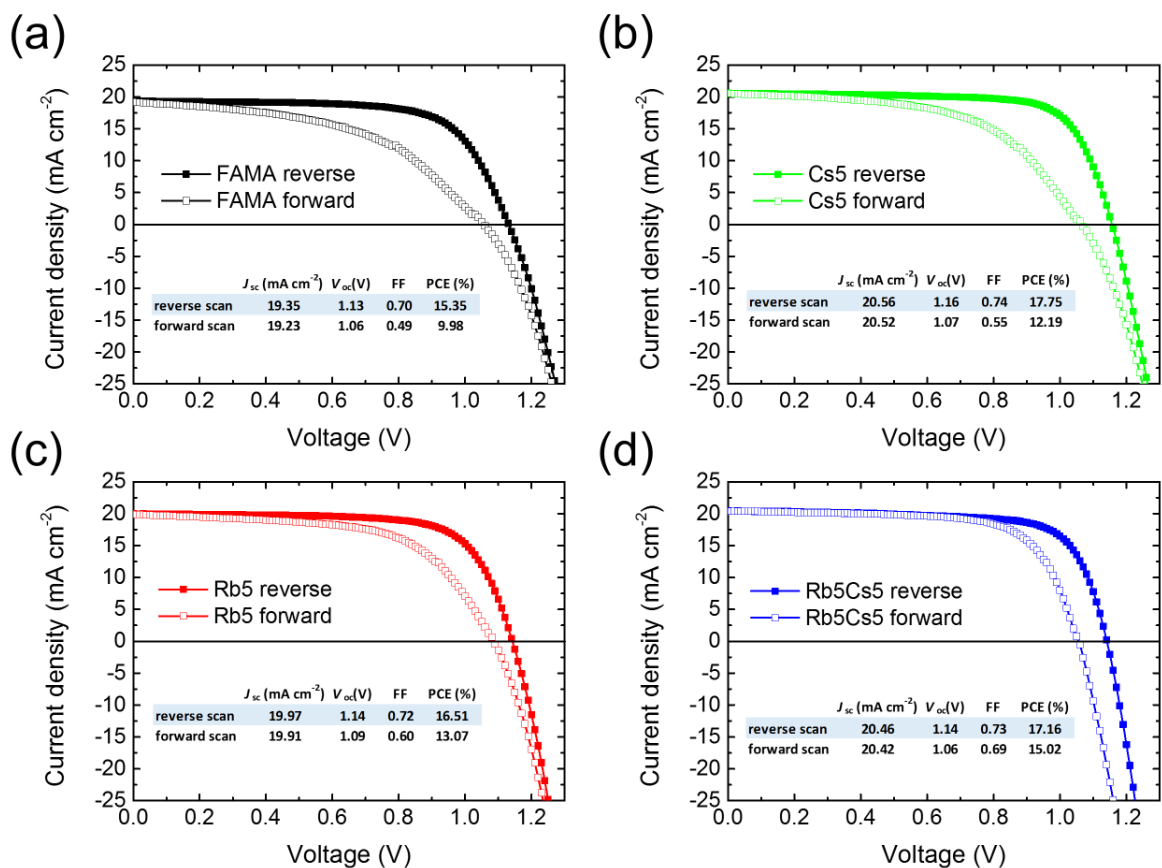


Figure S11. J - V curves for (a) FAMA, (b) Cs5, (c) Rb5 and (d) Rb5Cs5 champion devices under 1 sun illumination, recorded at a scan rate of 0.1 V s^{-1} .

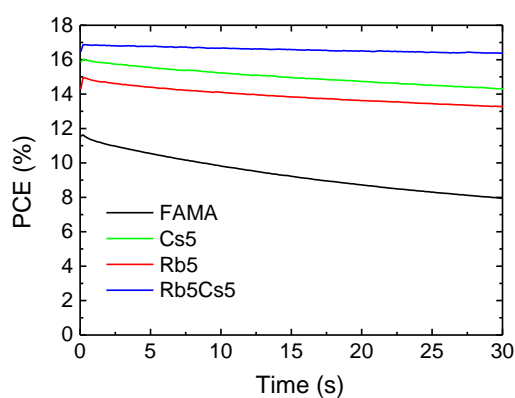


Figure S12. Maximum power point tracking for the champion perovskite solar cells with the device architecture glass/FTO/compact TiO_2 /perovskite/spiro-OMeTAD/Au under 1 sun illumination in air.

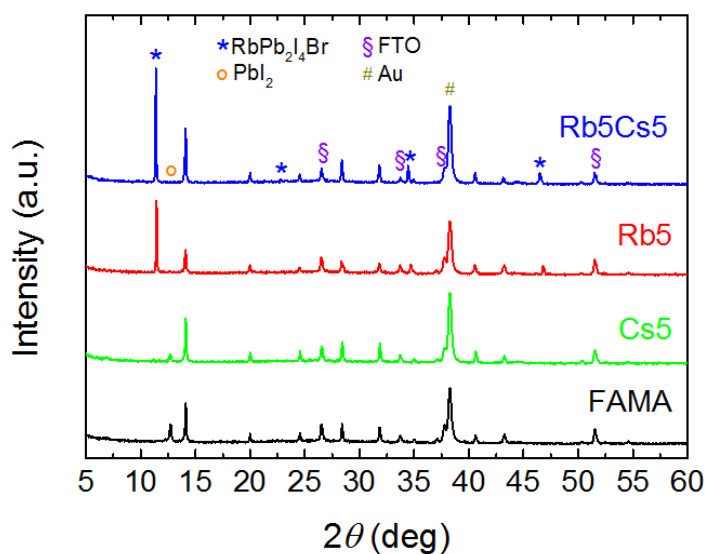


Figure S13. XRD patterns of unencapsulated perovskite solar cells after 1 day exposure to 75% RH at room temperature in the dark.

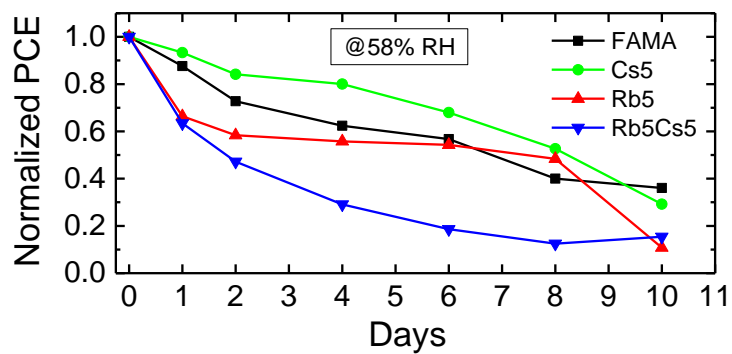


Figure S14. Monitoring the efficiency of unencapsulated perovskite solar cells upon exposure to 58% RH at room temperature in the dark. The reverse J - V scans of 20 cells under 1 sun illumination were evaluated for each type of perovskite and the arithmetic mean of the PCE values were determined over a course of 10 days. Scan rate: 0.2 V s^{-1} .

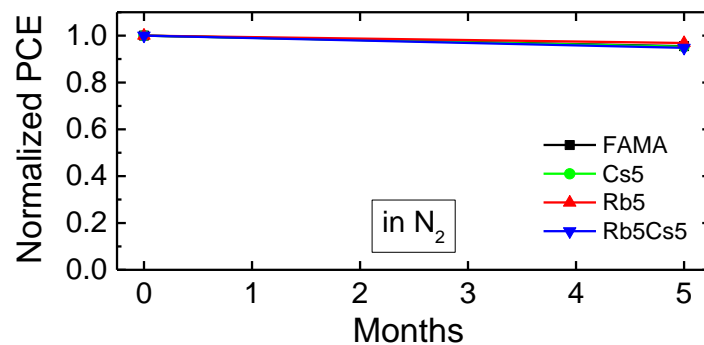


Figure S15. Monitoring the efficiency of unencapsulated perovskite solar cells stored in a nitrogen-filled glovebox under exclusion of moisture at room temperature for 5 months. The reverse J - V scans of 20 cells under 1 sun illumination were evaluated for each type of perovskite and the arithmetic mean of the PCE values were determined. Scan rate: 0.2 V s^{-1} .

Table S1. SEM-EDX elemental analysis of intact and phase separated areas of FAMA, Cs5, Rb5 and Rb5Cs5 perovskite films on FTO/TiO₂. The films were exposed to 90% RH in air at room temperature in the dark. The elemental composition is given in atomic % (at%).

sample	Cs [at%]	Rb [at%]	Pb [at%]	I [at%]	Br [at%]
FAMA intact	-	-	26	61	13
FAMA degraded	-	-	26	61	13
Cs5 intact	2	-	25	60	13
Cs5 degraded	10	-	25	50	14
Rb5 intact	-	0	25	63	12
Rb5 degraded	-	14	24	50	12
Rb5Cs5 intact	2	0	24	61	13
Rb5Cs5 degraded	3	12	24	48	13