Crystallization Kinetics of Rapid Spray Plasma Processed Multiple Cation Perovskites in Open Air

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Figure S1: 2D WAXS plots of intensity vs time for *in situ* RSPP perovskite films with (a-c) x = 0.05, (d-f) x = 0.15, and (g-i) x = 0.25, showing consistency across each of the triplicate samples.



Figure S2: (a) Integrated intensity of (110) perovskite peak vs time along with transient intermediate for $Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(Br_{0.17}I_{0.83})_3$. (b-d) 2D WAXS plots of intensity vs time for *in situ* RSPP perovskite films with $Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(Br_{0.17}I_{0.83})_3$, showing consistency across each of the triplicate samples.



Figure S3: First derivative of (110) perovskite peak for different Cs molar fractions for x = 0.05, 0.15, and 0.25 from *in situ* WAXS of RSPP films.



Figure S4: (a) Temperature (cross: measured; dashed line: linear fit) and (b) integrated XRD peak area vs. time.



Figure S5: Temperature (cross: measured; dashed line: linear fit and integrated XRD peak area vs. time (solid line). The transition between fast and slow growth regimes is indicated by the vertical dashed line. Samples are (a) x = 0.05, (b) x = 0.15, and (c) x = 0.25.



Figure S6: Perovskite XRD peak area and fit for the (110) perovskite peak for (a) x = 0.05, (b) x = 0.15, and (c) x = 0.25.

In order scrutinize whether the change in crystallite growth rate G at time t = 0.3 s (in Figure S7, after the time axis was shifted such that crystallization starts at t = 0 s) is entirely temperaturerelated or caused by the reduction in reactive species once the plasma head has passed the volume probed with the X-rays, we follow the classic Avrami approach:

$$dV^e_{\beta} \sim G^n t^n dt.$$
 (1)

with the extended volume of the crystalline phase V_{β}^{e} and the Avrami exponent *n*.

The relation between the extended volume and the actual crystalline volume is:

$$\frac{1}{1-Y}dV_{\beta}\sim dV_{\beta}^{e},$$
 (2)

with $Y = \frac{V_{\beta}}{V}$ being the volume fraction of the perovskite crystallites, proportional to the integrated area under the dominant perovskite diffraction peak at $q = 1.0 \text{ Å}^{-1}$. From integration follows:

$$\frac{dV_{\beta}^{e}}{dt} = \frac{1}{1 - Y dt} = G^{n} t^{n}$$
(3)

We thus obtain G^n from the experimental data as

$$G^n \sim \frac{1 \quad 1 \quad dY}{t^{n_1 - Y} dt}.$$
 (4)

After its peak at roughly t = 0 s, the temperature can be approximated as linearly dependent on time

$$T(t) = at + b$$
 (5)

with the parameters a = 385.4 K and b = -10.6 K/s.

The experimental data transformed according to Equations 4 and 5 is shown in Figure S7. It is evident that the growth rate shows a very strong apparent temperature dependence. For instance, an Arrhenius like temperature dependence of G would show a $\sim 1/T$ dependence in Figure S7. Hence, the high growth rates for 382 < T/K < 385 (0 < t/s < 0.3) cannot solely be ascribed to temperature effects and are likely caused by reactive species due to the plasma.



Figure S7: G^n vs. temperature for various Avrami exponents n, obtained from the experimental XRD peak area according to Equation (4) for (a) x = 0.05, (b) x = 0.15, and (c) x = 0.25.



Figure S8: Grain size distribution analyzed from (a) the SEM images in Figure 4 as a function of Cs content and (b) as a function of MA content for RSPP perovskite films.



Figure S9: Device performance for $Cs_{0.25}FA_{0.75}Pb(Br_{0.17}I_{0.83})_3$ obtained from (a) maximum power point tracking under full spectrum illumination in ambient air and (b) J-V scans from forward to reverse bias for spin coated and RSPP perovskite films.