SUPPORTING INFORMATION

Thermal degradation in methylammonium-formamidinium-guanidinium lead iodide perovskites

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Supplementary Note 1: XRD data of thermally treated samples

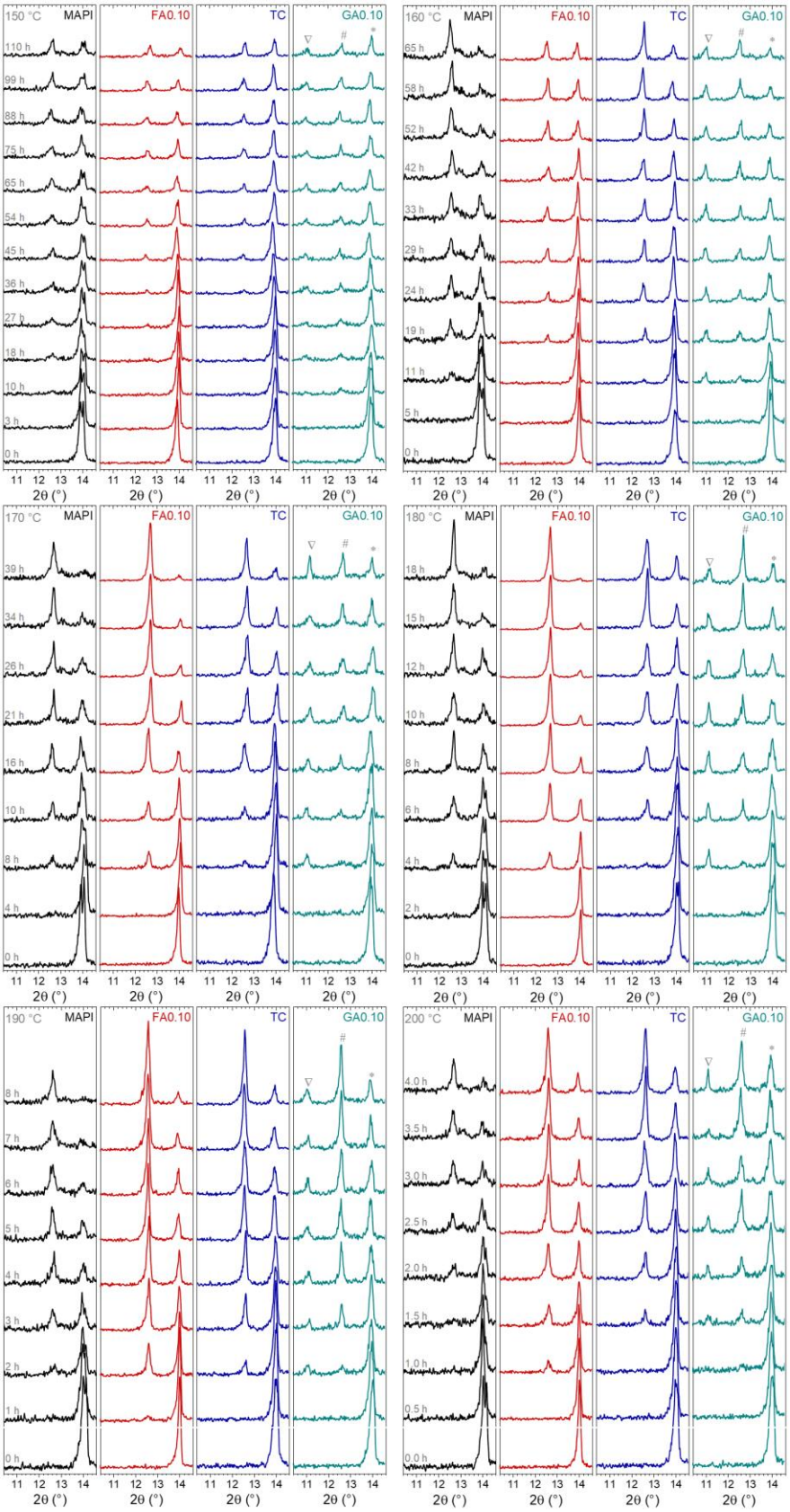

Figure S1 - X-ray diffraction of the first set of studied compositions at different times and temperatures of thermal treatment. Peak assignments are ∇: $GAPbI_3$, #: PbI_2, and *: perovskite.

Supplementary Note 2: Determination of rate constants

For first-order reaction kinetics, the differential kinetics law is expressed as:

$$\frac{dn}{dt} = -kn$$

where n a quantity-related property, such as mass, volume, number of moles, etc. In our approach, the basic assumption was to consider n as being proportional to the quantity of crystalline perovskite phase, related to the area A of the perovskite peaks in the respective diffractograms. Hence, it can be implied that:

$$\frac{dA}{dt} = -kA$$

Through integration from A_0 at t = 0 to $A(t)$ at a given t, it follows that:

$$A(t) = A_0 \exp(-kt)$$

Then, defining the extent of degradation $\alpha(t) = 1 - A(t)/A_0$, it results in:

$$\frac{A(t)}{A_0} = 1 - \alpha(t) = \exp(-kt)$$

from where we obtain:

$$\alpha(t) = 1 - \exp(-kt) \rightarrow 1 - \alpha(t) = \exp(-kt)$$

which is used in its linearized form:

$$\ln[(1 - \alpha(t)] = -kt$$

where the slope $= -k$ of respective linear fits to experimental data gives the rate constant.

Now, for second-order reaction kinetics, using the same assumptions, the differential kinetics law can be expressed as:

$$\frac{dn}{dt} = -kn^2 \rightarrow \frac{dA}{dt} = -kA^2$$

Through integration, it follows that:

$$\frac{1}{A(t)} = \frac{1}{A_0} + kt$$

and then, as $\alpha = 1 - A(t)/A_0$, simple algebra leads to:

$$\frac{A(t)}{A_0} = \frac{1}{1 + A_0 kt} \rightarrow 1 - \alpha(t) = \frac{1}{1 + kt}$$

Finally, we used the above equation in its linearized form:

$$\frac{1}{1 - \alpha(t)} = 1 + kt$$

from where the slope $= k$ of respective linear fits to experimental data gives the rate constant.

Using the above equations, we plotted the experimental data in the respective linear forms (Figure S2) and obtained the kinetic constants of each composition in the studied temperatures. The results are given in Table S1.

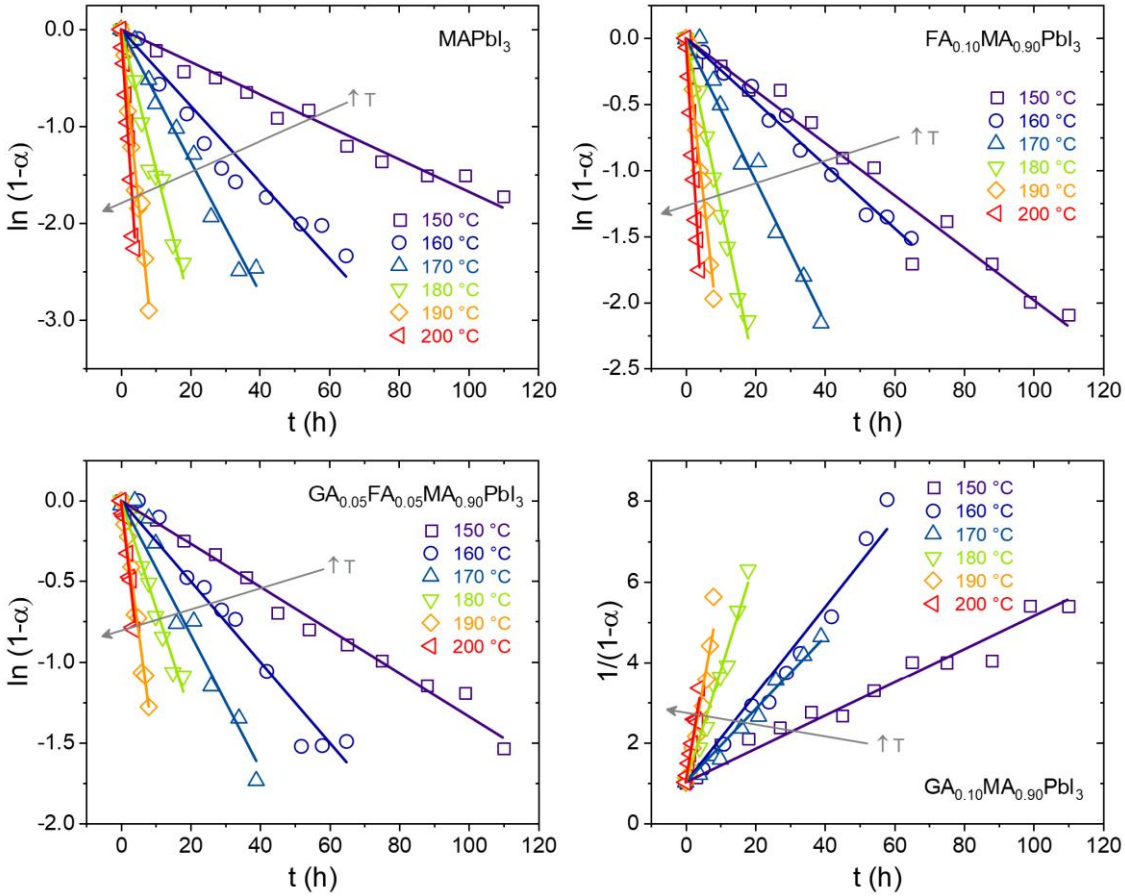

Figure S2 - Experimental data and linear fits at different temperatures for MAPI, FA0.10, TC, and GA0.10.

Table S1 - Calculated rate constants from the linear fits of Figure S2.

T (°C)	MAPI	FA0.10	TC	GA0.10
150	0.0168 ± 0.0005	0.0198 ± 0.0007	0.0134 ± 0.0003	0.041 ± 0.001
160	0.039 ± 0.002	0.0240 ± 0.0005	0.0250 ± 0.0009	0.109 ± 0.004
170	0.068 ± 0.002	0.054 ± 0.002	0.041 ± 0.002	0.090 ± 0.003
180	0.143 ± 0.005	0.126 ± 0.003	0.066 ± 0.003	0.276 ± 0.009
190	0.35 ± 0.01	0.236 ± 0.007	0.160 ± 0.005	0.48 ± 0.03
200	0.54 ± 0.02	0.43 ± 0.01	0.19 ± 0.01	0.52 ± 0.03

Supplementary Note 3: Differences between exposed and non-exposed surfaces

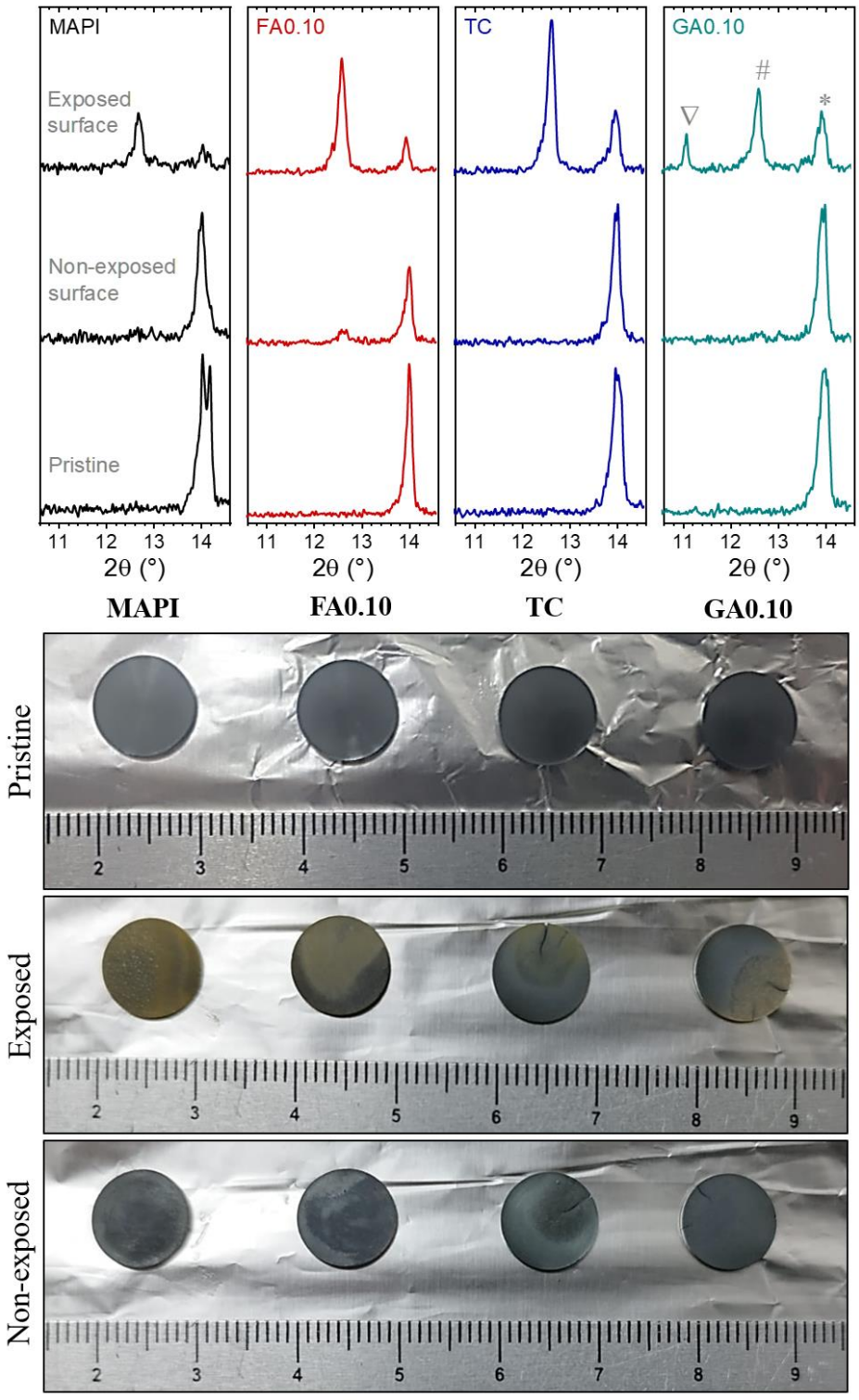

Figure S3 - Results of XRD (top) and visual aspect of samples (down) in pristine and after thermal treatment at 200 °C for 4 h conditions in the exposed and non-exposed surfaces. Peak assignments are ∇: $GAPbI_3$, #: PbI_2, and *: perovskite. Yellowing of the exposed surfaces are due to formation of PbI_2, which was barely formed at the non-exposed surfaces of the same samples.

Supplementary Note 4: Mass spectra at different thermal treatment times

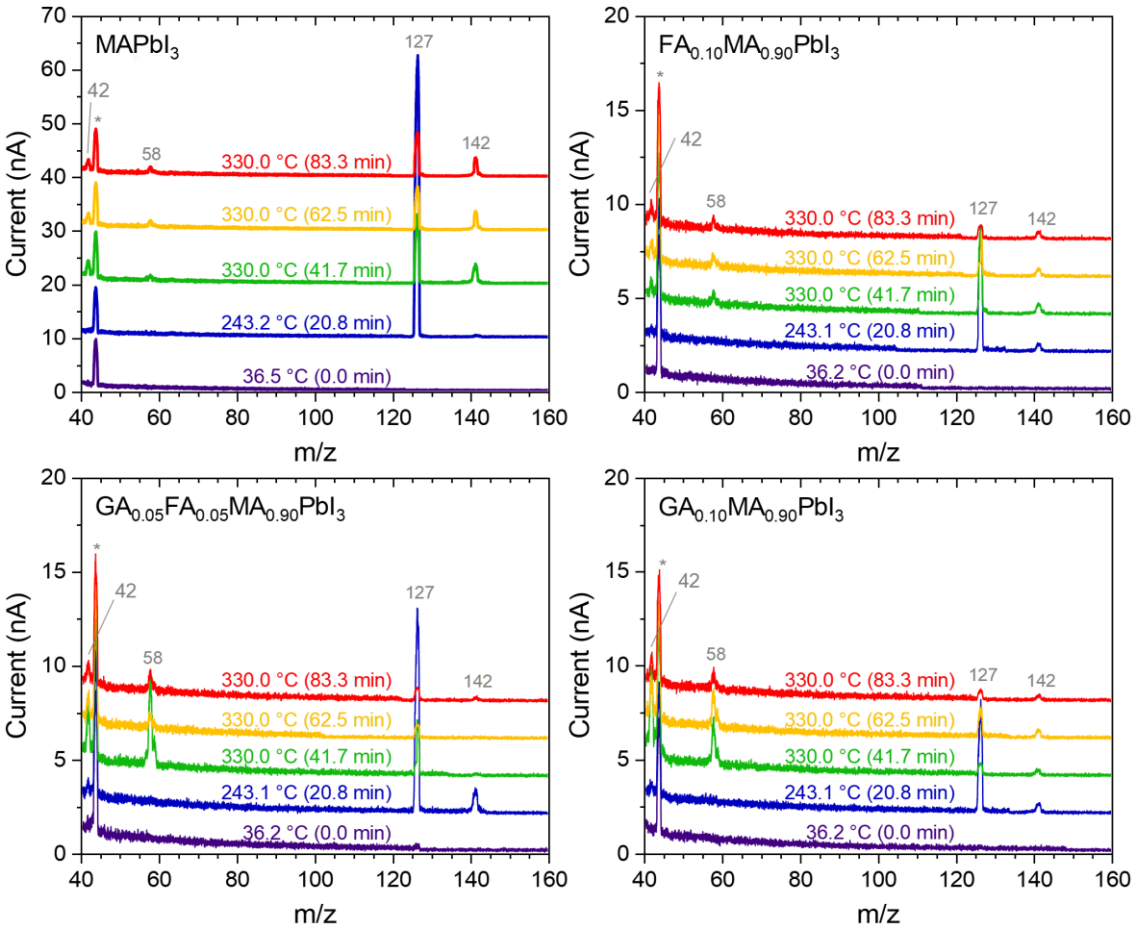

Figure S4 - Instant mass spectra in the *m*/*z* range from 40 to 160 collected at different times. The peak at *m*/*z* = 44 (*) is due to the pulsed CO_2 injections used for calibration. Vertical shifts between spectra were made intentionally for better visualization of results.

Supplementary Note 5: Thermal degradation of $GA_xFA_yMA_{1-x-y}PbI_3$ perovskites

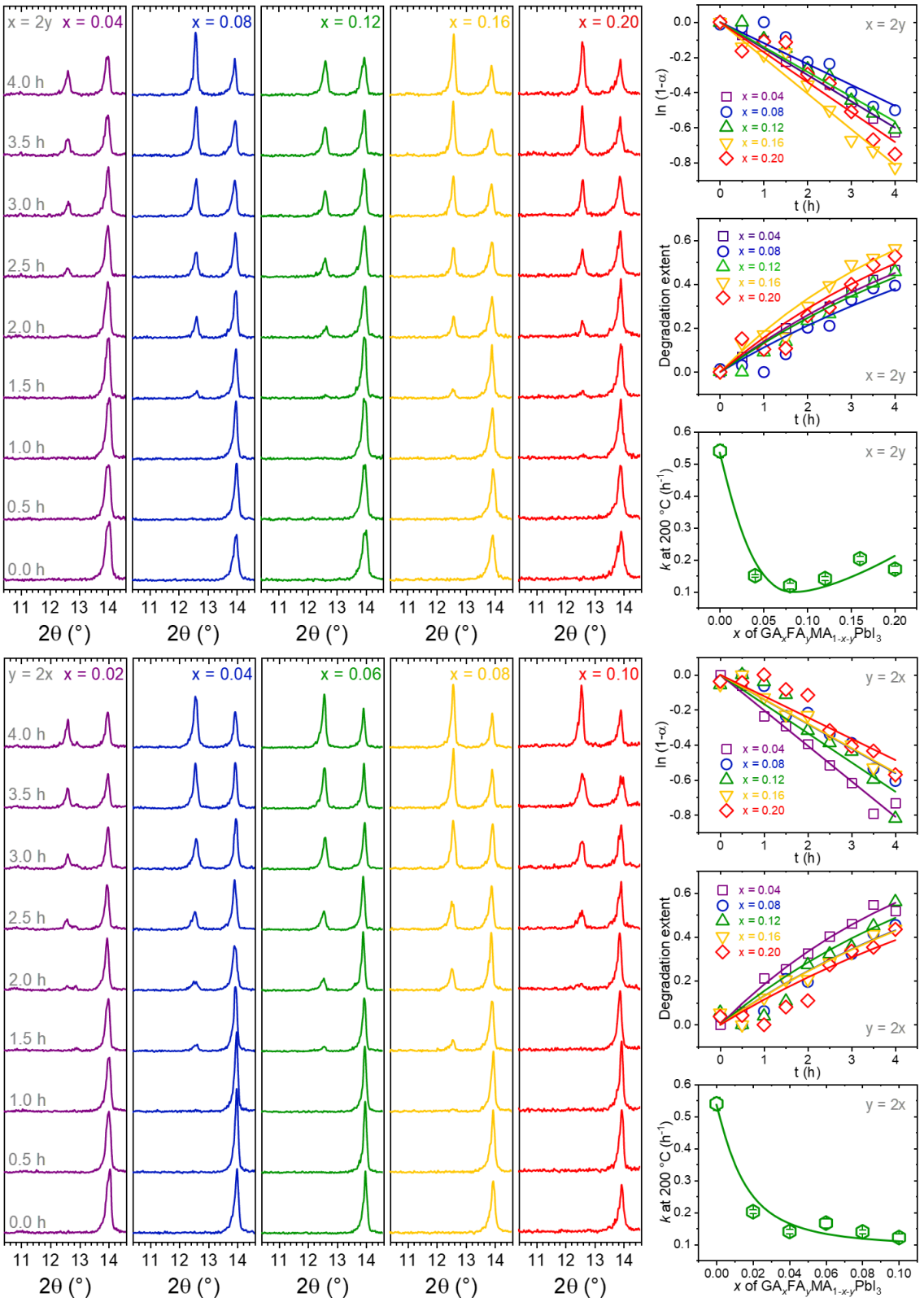

Figure S5 - Thermal degradation data and results of $GA_xFA_yMA_{1-x-y}PbI_3$ perovskites for the set of compositions $x = 2y$ (top) and $y = 2x$ (bottom).

Supplementary Note 6: Thermal degradation of $FA_yMA_{1-y}PbI_3$ perovskites

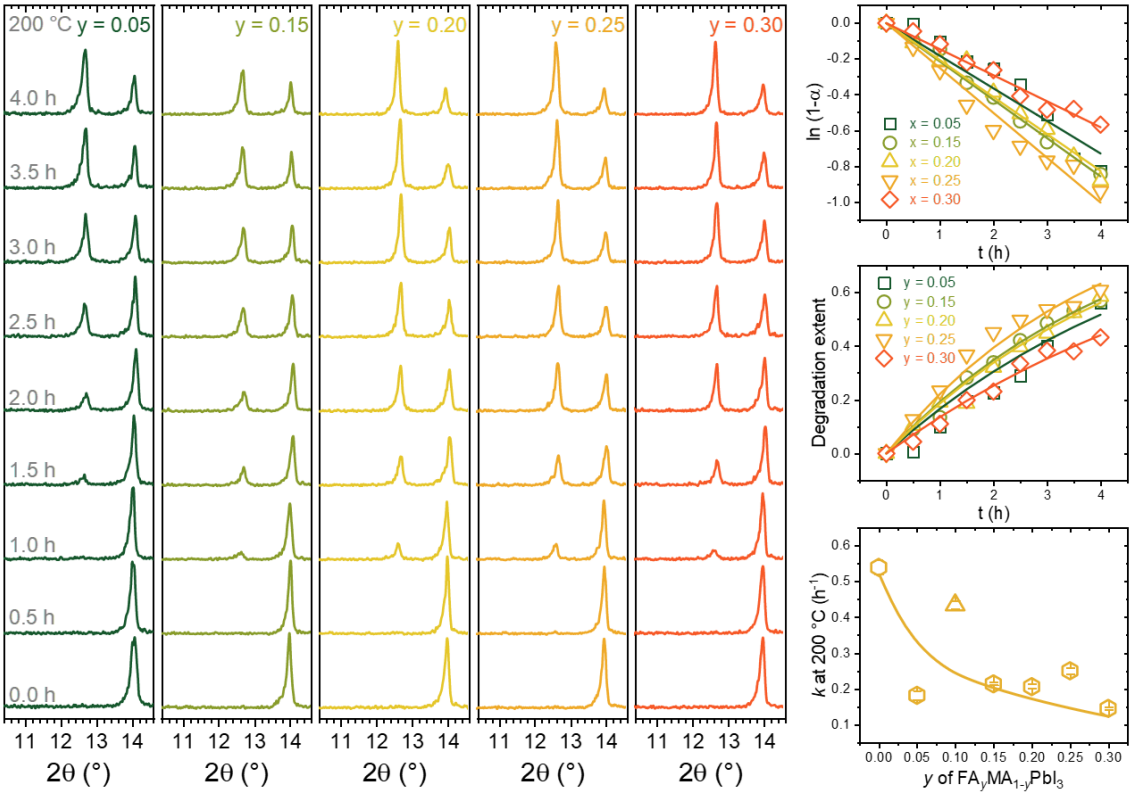

Figure S6 - Thermal degradation data and results of $FA_yMA_{1-y}PbI_3$ perovskites.

Supplementary Note 7: Degradation rate constants at 200 °C

Table S2 - Summary of experimental rate constants at 200 °C of all compositions studied.

x (GA^+)	y (FA^+)	1-x-y (MA^+)	k (h^{-1})	R^2
0.00	0.00	1.00	0.54 ± 0.02	0.96
0.00	0.05	0.95	0.18 ± 0.01	0.91
0.00	0.10	0.90	0.43 ± 0.01	0.98
0.00	0.15	0.85	0.214 ± 0.004	0.99
0.00	0.20	0.80	0.206 ± 0.006	0.98
0.00	0.25	0.75	0.251 ± 0.009	0.96
0.00	0.30	0.70	0.146 ± 0.004	0.98
0.02	0.04	0.94	0.150 ± 0.004	0.99
0.04	0.08	0.88	0.119 ± 0.009	0.89
0.06	0.12	0.82	0.141 ± 0.006	0.96
0.08	0.16	0.76	0.203 ± 0.008	0.96
0.10	0.20	0.70	0.17 ± 0.01	0.91
0.03	0.03	0.94	0.26 ± 0.01	0.97
0.05	0.05	0.90	0.19 ± 0.01	0.91
0.06	0.06	0.88	0.26 ± 0.02	0.93
0.09	0.09	0.82	0.155 ± 0.009	0.95
0.12	0.12	0.76	0.162 ± 0.008	0.96
0.15	0.15	0.70	0.150 ± 0.007	0.96
0.04	0.02	0.94	0.202 ± 0.006	0.97
0.08	0.04	0.88	0.140 ± 0.007	0.94
0.12	0.06	0.82	0.17 ± 0.01	0.90
0.16	0.08	0.76	0.139 ± 0.006	0.96
0.20	0.10	0.70	0.12 ± 0.01	0.88
0.02	0.00	0.98	0.37 ± 0.01	0.97
0.04	0.00	0.96	0.225 ± 0.006	0.98
0.06	0.00	0.94	0.246 ± 0.005	0.99
0.08	0.00	0.92	0.24 ± 0.01	0.94
0.10	0.00	0.90	0.52 ± 0.03	0.94
0.15	0.00	0.85	0.67 ± 0.03	0.98
0.20	0.00	0.80	0.69 ± 0.03	0.97