

Supporting Information (SI) for

Interstitial Nature of Mn²⁺ Doping in 2D Perovskites

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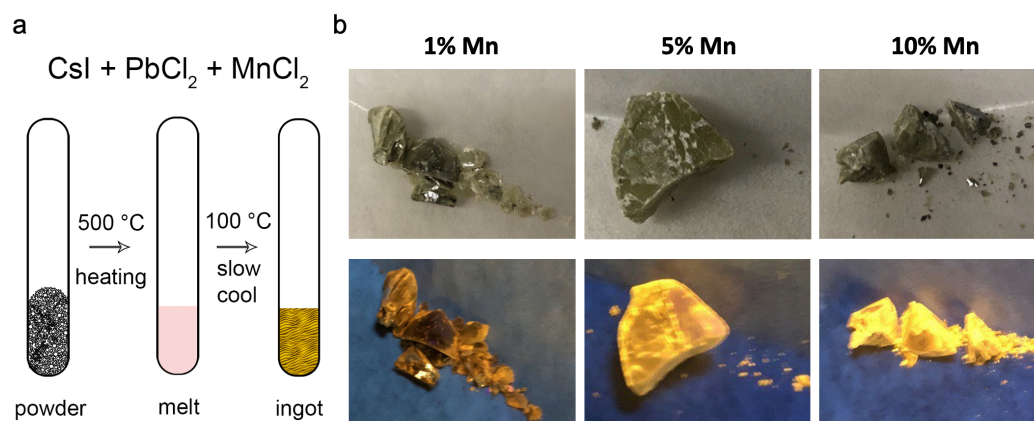
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Figure S1. (a) Synthesis schematic (b) optical images (top) and fluorescence under UV (bottom) of 1% (left), 5% (middle), 10% (left) Mn:Cs₂PbI₂Cl₂



SI Table 1. The peak characteristics after Rietveld refinement analysis of PXRD for 0-10% Mn²⁺ doped Cs₂PbI₂Cl₂ of (006) shown in Figure 1c and (110).

	Undoped		0.1% Mn		1% Mn		5% Mn		10% Mn	
	006	110	006	110	006	110	006	110	006	110
2θ (± 0.01°)	28.36	22.30	28.36	22.29	28.26	22.20	28.24	22.18	28.22	22.20
FWHM (± 0.01°)	0.30	0.22	0.34	0.22	0.32	0.26	0.40	0.33	0.42	0.33

SI Table 2. The monoexponential fitting parameters for the PL lifetime kinetics of the 2.07 eV emission peak for 0.1% Mn:Cs₂PbI₂Cl₂ shown in Figure 2c. The equation form used is $y(x) = A \cdot \exp(-x/\tau)$, where τ is the decay time constant and A is the related amplitude.

	Values
τ (μ s)	480.77
A	0.077

Figure S2. AFM height images for the single crystals of (a) undoped and (b) 0.1% Mn Cs₂PbI₂Cl₂. Scalebar is 60 nm.

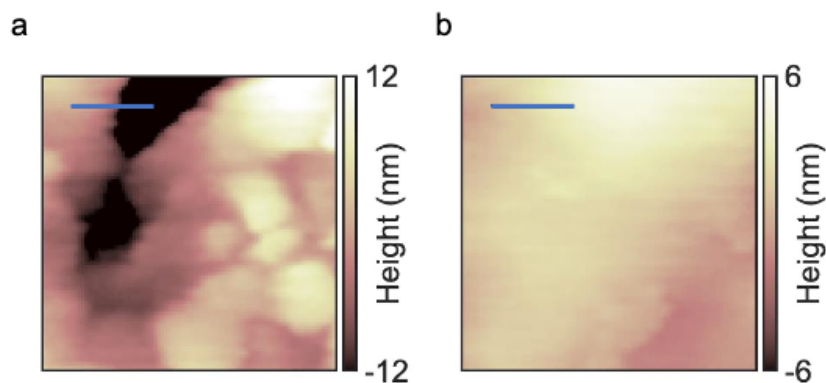


Figure S3. Example of CCD images for nanoXRD of a single Bragg peak for (a) single crystal (b) microstrain creating distortion (c) powder with many orientations. 2θ is related to the d-spacing and lattice constants of the crystal structure through Bragg's law and has a range of $20^\circ - 50^\circ$ due to instrumentation limitations. γ is related to the lattice orientation or tilt/curvature and has a range of $-5^\circ - 10^\circ$.

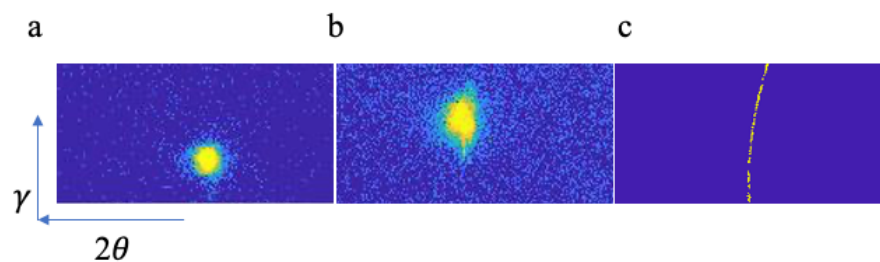


Figure S4. Further 2D mapping of nanoXRD of undoped (left) and 0.1% Mn^{2+} (right) $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ across $1\mu\text{m} \times 1\mu\text{m}$ region (a) total intensity (b) high 2θ ROI intensity (c) spectrums of four different 5×5 pixel regions where the solid line denotes the ROI split

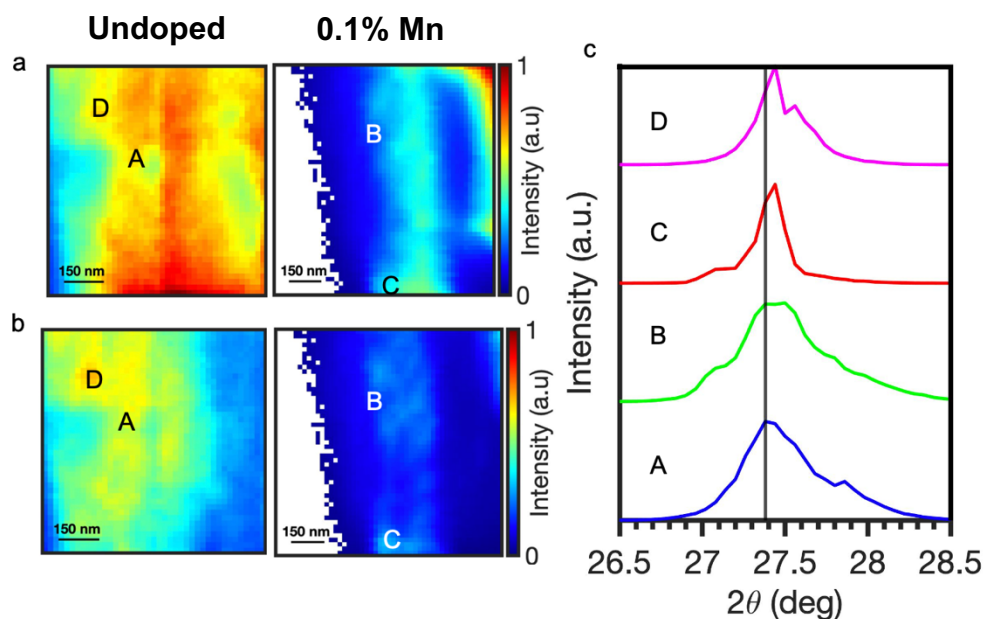


Figure S5. Further 2D mapping of nanoXRF of undoped (left) 0.1% Mn^{2+} (right) $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ across a $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$ region (a) lead (b) cesium. Scalebar is 150 nm.

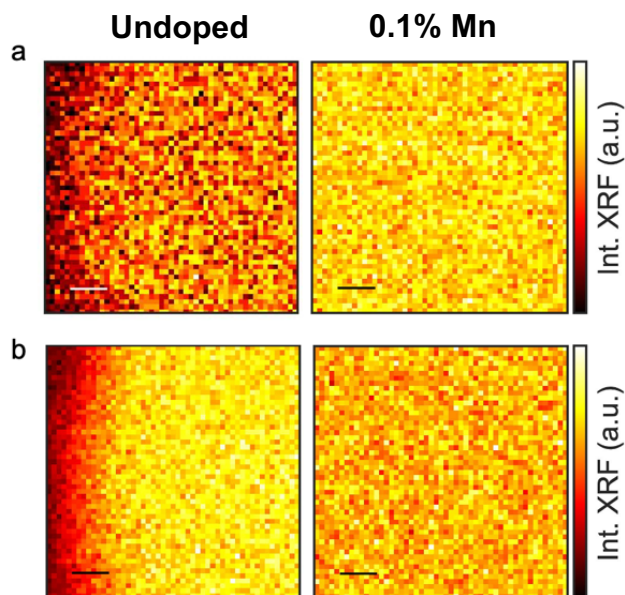


Table S3. Lattice constants (in Å) and lattice constant changes (relative to the pristine perovskite) for Mn^{2+} substitutional and interstitial doped $\text{Cs}_2\text{PbI}_2\text{Cl}_2$. Note that the values for the supercells must be considered as multiples of the primitive unit cell.

	Doping density	a_x	a_y	a_z	Δa_x	Δa_y	Δa_z
Substitutional	0.79%	17.140	17.140	19.327	-0.42%	-0.42%	-0.004%
	0.44%	22.907	22.907	19.303	-0.18%	-0.18%	-0.13%
Interstitial	0.79%	17.289	17.266	19.330	0.45%	0.31%	0.01%
	0.44%	23.029	23.001	19.329	0.34%	0.22%	0.004%

Figure S6. DFT analysis of an undoped $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ $4\times 4\times 1$ supercell for (a) pristine crystal structure. PBE exchange-correlation function analysis for (b) band structure (c) PDOS. For crystal structure, colors denote Pb-black, Cs-mint green, I-purple, Cl-green.

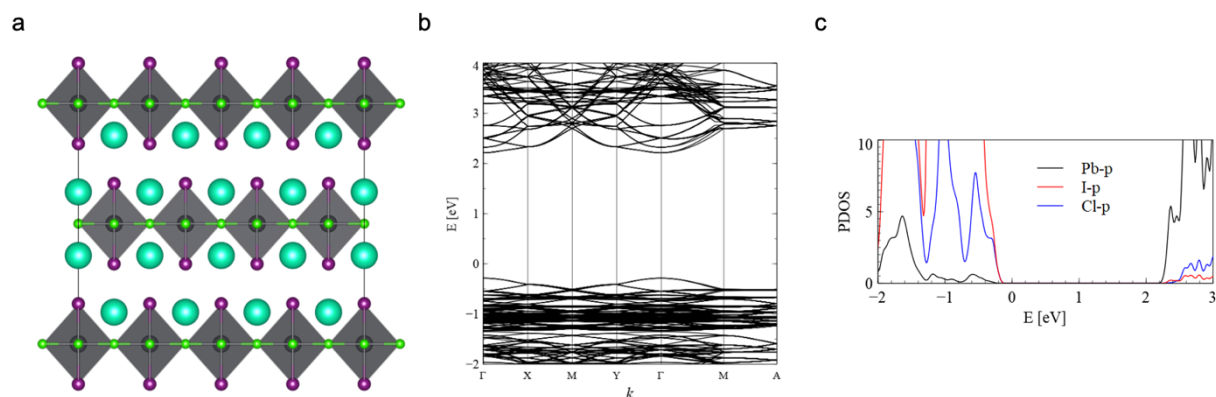


Figure S7. Crystal structure of a double Mn-doped 2D $\text{Cs}_2\text{PbI}_2\text{Cl}_2$, where colors denote Pb-black, Cs-mint green, I-purple, Cl-green, Mn-red.

