Supporting Information

Lattice Reconstruction of La Incorporated CsPbI₂Br with Suppressed Phase Transition for Air-Processed All-Inorganic Perovskite Solar Cells

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Table S1. Synchrotron-based grazing incidence X-ray diffraction (GIXRD) analysis of the (100) peak for $CsPb_{1-x}La_xI_2Br$ with a wavelength of 1.24 Å. Lattice constants were calculated according to Bragg's law. The wavelength of 1.5418 Å was used for the 2-theta calculations, corresponding to the Cu-K α radiation.

	(100) peak					
Samples	Q (nm ⁻¹)	2θ (deg)	Lattice constant (Å)			
CsPbI ₂ Br	10.223	14.410	6.146			
CsPb _{0.99} La _{0.01} I ₂ Br	10.230	14.421	6.142			
CsPb _{0.98} La _{0.02} I ₂ Br	10.266	14.472	6.121			
CsPb _{0.97} La _{0.03} I ₂ Br	10.177	14.346	6.174			

As the La³⁺-doping ratio increases (from x = 0 to 0.2), the lattice constant decreases, indicating that the La³⁺ doping causes shrinkage of the perovskite crystal lattice. However, when the doping concentration is 0.03 M, the lattice constant increases, indicating that excessive La³⁺ destroys the perovskite structure.



Fig. S1 Energy dispersive X-ray (EDX) spectroscopy mapping images for (a) $CsPbI_2Br$ and (b) $CsPb_{0.98}La_{0.02}I_2Br$ thin films. The scale bar is 2 μ m.



Fig. S2 XPS spectra of $CsPb_{0.98}La_{0.02}I_2Br$ film for La 3d. The XPS orbital peak of La 3d were detected.



Fig. S3 X-ray photoelectron spectroscopy (XPS) spectra of $CsPbI_2Br$ and $CsPb_{0.98}La_{0.02}I_2Br$ films at the (a) Cs 3d, (b) Pb 4f, (c) I 3d, and (d) Br 3d regions, respectively.



Fig. S4 XPS spectra of CsPbI₂Br and CsPb_{0.98}La_{0.03}I₂Br films for Pb 4f.



Fig. S5 *In situ* 1D-GIXRD patterns for (a) CsPbI₂Br and (b) CsPb_{0.98}La_{0.02}I₂Br thin films stored at different times under 55% RH condition.



Fig. S6 Top-view SEM images of fresh thin films of (a) $CsPbI_2Br$, (b) $CsPb_{0.99}La_{0.01}I_2Br$, (c) $CsPb_{0.98}La_{0.02}I_2Br$ and (d) $CsPb_{0.97}La_{0.03}I_2Br$. The scale bar is 500 nm.

As described in the SEM characterizations above, the fresh film doped with 2% La³⁺ has some pinholes compared to the undoped film. This is consistent with the fact that the efficiency of the freshly prepared 2% La-doped PSCs (5.43%) is lower than that of the undoped one (5.92%). However, after storage in humid air, the surface coverage of the doped film is significantly improved, while the coverage of the undoped film is greatly reduced.



Fig. S7 (a) UV-vis absorbance of films with varying La³⁺-ion doping concentrations. (b) Tauc plots for CsPb_{0.99}La_{0.01}I₂Br and CsPb_{0.97}La_{0.03}I₂Br calculated from the UV-vis absorbance. (c, d) Photoluminescence (PL) spectra and time-resolved PL (TRPL) decay curves for CsPb_{1-x}La_xI₂Br (x = 0-0.03) thin films spin-coated onto quartz substrate.

Table S2. TRPL decay parameters for $CsPb_{1-x}La_xI_2Br$ (x = 0-0.03) films. The TRPL decay curves are fitted with a bi-exponential function.

		CsPbI ₂ Br		CsPb _{0.99} La _{0.01} I ₂ Br		CsPb _{0.98} La _{0.02} I ₂ Br		CsPb _{0.97} La _{0.03} I ₂ Br	
		τ_1	τ_2	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2
Perov/ glass	τ (ns)	12.95	23.08	14.44	33.66	10.01	51.43	1.30	10.49
	Weight (%)	24.82	75.18	21.00	79.00	6.52	93.48	66.20	33.80
	τ _{ave} (ns)	20.57		29.62		48.73		4.41	

In the table, τ_1 and τ_2 represent the fast component of the non-radiative composite and the slow component of the effective recombination lifetime, respectively. τ_2 and weight become larger as the La³⁺-doping concentration increases; the maximum weight is 93.48% when the La³⁺-doping concentration is 0.02 M, indicating that the introduction of La³⁺ ions greatly passivate film defects and inhibit non-radiative recombination. However, when the doping concentration is 0.03 M, the average lifetime of the charge carriers is significantly reduced, indicating that the excess La³⁺ may destroy the perovskite structure, which is consistent with the GIXRD peak shift.



Fig. S8 Kinetics of the GSB probed at 1.97 ± 0.01 eV for (a) CsPbI₂Br and (b) CsPb_{0.98}La_{0.02}I₂Br films at different pump excitation density. (c) The maximum value of ground state bleaching signal is fitted linearly with excitation intensity.

	T ₀ (ps)	σ (ps)	D_1	τ_1 (ps)	D ₂	τ_2 (ps)	D ₃	τ_3 (ps)
CsPbI ₂ Br								
130 μJ cm ⁻²	0.7525	0.2	0.0761	0.3578	-0.0785	232.944	-0.1241	3055.28
177 μJ cm ⁻²	0.7525	0.2	0.1214	0.6189	-0.1128	126.854	-0.1997	1642.94
265 μJ cm ⁻²	0.7525	0.2	0.2045	0.5906	-0.1914	118.263	-0.2237	1500.63
354 μJ cm ⁻²	0.7524	0.2	0.2703	0.6785	-0.2495	84.7335	-0.2946	1217.07
531 μJ cm ⁻²	0.7524	0.2	0.3751	0.6728	-0.3347	61.3667	-0.3834	1001.91
CsPb _{0.98} La _{0.02} I ₂ Br								
130 μJ cm ⁻²	0.7410	0.2	0.1034	0.5153	-0.1253	304.261	-0.1652	3993.43
177 μJ cm ⁻²	0.7421	0.2	0.1525	0.7425	-0.1558	164.640	-0.2363	1827.39
265 μJ cm ⁻²	0.742	0.2	0.2537	0.6745	-0.2373	121.007	-0.2956	1462.99
354 μJ cm ⁻²	0.742	0.2	0.3247	0.7627	-0.3150	102.150	-0.3338	1323.90
531 μJ cm ⁻²	0.742	0.2	0.4297	0.7632	-0.4204	76.424	-0.4015	1077.12

Table S3. Parameters obtained from the fitting of the kinetics of the GSB probed at 1.97 ± 0.01 eV for CsPbI₂Br and CsPb_{0.98}La_{0.02}I₂Br films.

The kinetics of the GSB probed at 1.97 ± 0.01 eV for CsPbI₂Br and CsPb_{0.98}La_{0.02}I₂Br films can be expressed as:¹

$$g(t) = \left\{ D_1 \operatorname{erfc}(\frac{\sigma}{\sqrt{2}\tau_1} - \frac{t}{\sqrt{2}\sigma}) \exp(-\frac{t}{\tau_1}) + D_2 \operatorname{erfc}(\frac{\sigma}{\sqrt{2}\tau_2} - \frac{t}{\sqrt{2}\sigma}) \exp(-\frac{t}{\tau_2}) + D_3 \operatorname{erfc}(\frac{\sigma}{\sqrt{2}\tau_3} - \frac{t}{\sqrt{2}\sigma}) \exp(-\frac{t}{\tau_3}) \right\}$$

where D_1 , D_2 and D_3 are the relative amplitudes, "erfc" represents the integral error function, and σ is the laser pulse duration.



Fig. S9 Current density-voltage (*J-V*) curves of $CsPb_{1-x}La_xI_2Br$ -based (x = 0-0.03) PSCs after a period of storage in air.

As the La³⁺-doping concentration increases, the power conversion efficiency of the PSCs is significantly improved due to the optimized carrier lifetime and surface coverage. The photovoltaic performance of the PSCs decreases when the doping concentration is above 3%, which can be attributed to the destruction of the CsPbI₂Br perovskite lattice.



Fig. S10 One of the best CsPb_{0.98}La_{0.02}I₂Br-based PSCs measured with a scan rate of 200 mV s⁻¹.



Fig. S11 *J-V* curves of the newly prepared $C_{sPb_{1-x}}La_{x}I_{2}Br$ -based (x = 0-0.03) PSCs.

Table S4. Photovoltaic performance parameters of the newly prepared PSCs with different La³⁺ concentrations.

Perovskite	$V_{OC}\left(\mathbf{V}\right)$	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
CsPbI ₂ Br	0.95	11.39	54.27	5.92
$CsPb_{0.99}La_{0.01}I_2Br$	0.99	10.47	51.81	5.39
$CsPb_{0.98}La_{0.02}I_2Br$	1.01	11.49	46.94	5.43
$CsPb_{0.97}La_{0.03}I_2Br$	0.82	9.18	33.15	2.50

Perovskite	$V_{OC}(\mathbf{V})$	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
CsPbI ₂ Br	0.98	11.53	55.74	6.31
$CsPb_{0.99}La_{0.01}I_2Br$	1.05	11.28	56.05	6.66
$CsPb_{0.98}La_{0.02}I_2Br$	1.12	11.66	61.24	8.03
CsPb _{0.97} La _{0.03} I ₂ Br	0.94	10.27	54.32	5.23

Table S5. Photovoltaic performance parameters of PSCs doped with different La^{3+} concentrations after a period of storage in air.

Notes and references

1 R. P. Prasankumar and A. J. Taylor, *Optical techniques for solid-state materials characterization*, CRC Press, 2016.