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Supplementary Information for:

Erbium-Doped $CsPbI_{2.5}Br_{0.5}$ with Enhanced Crystalline Quality and Improved Carrier Lifetime for Thermally Stable All-Inorganic Perovskite Solar Cells

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Experimental Section

Chemicals and materials.

Lead iodide (PbI_2, 99.9985%, Alfa-Aesar), cesium iodide (CsI, 99.999%, Aladdin), cesium bromide (CsBr, 99.9%, Aladdin), Erbium chloride ($ErCl_3$, 99.99%, Alfa-Aesar), N,N-Dimethylformamide (DMF, 99.8%, anhydrous, Alfa-Aesar), isopropanol (99.8%, anhydrous, Aladdin), methanol (99.8%, anhydrous, Aladdin) and carbon paste (commercial conductive carbon paste). All reagents used were purchased from commercial sources without further purification unless stated otherwise.

Film preparation and device fabrication.

Firstly, the fluorine-doped tin oxide (FTO)-coated glasse substrates were etched by Zn power and 2 M HCl for desiable patterns. Then, the FTO substrates were ultrasonically cleaned with acetone, ethanol and deionized water, respectively. The first layer *c*-TiO_2 was deposited on FTO electrodes by spin-coating an ethanol solution of titanium isopropoxide (0.5 M) and diethanol amine (0.5 M) at 7000 rpm for 30 s and annealing in air at 500 °C for 2 h. Then, the *m*-TiO_2 layer was deposited on the *c*-TiO_2 layer by spin-coating a mixture of 18NR-T TiO_2 nanoparticle paste (20 nm diameter) and ethanol with the weight ratio of 1:8 at 5000 rpm for 30 s. The substrates were dried at 125 °C for 10 min and sintered at 500 °C for 30 min. Subsequntly, 1-x% mmol PbI_2 and x% mmol $ErCl_3$ are dissolved in 1mL N,N-dimethylformamide (DMF) under stirring at 80 °C for 12 h. Then, the percursor solution was spin-coated onto the FTO/*c*-TiO_2/*m*-TiO_2 layer at 1500 rpm for 40 s, followed by drying at 80 °C for 60 min. Afterwards, the prepared substrates were dippped in a methanol solution of 0.03 M CsI and 0.03 M CsBr for 10 min. After being washed with isopropanol, the substrates were annealed at 390 °C for 10 min on a hotplate in air to form the layer of $CsPbI_{2.5}Br_{0.5}$-x%-$ErCl_3$. Finally, the carbon electrodes served as both HTM and counter electrode were blade-coated on $CsPbI_{2.5}Br_{0.5}$-x%-$ErCl_3$ perovskite films, and heated at 70 °C for 60 min to form the counter electrode.

Material characterizations.

To obtain the top-surface and cross-section morphologies of $CsPbI_{2.5}Br_{0.5}$-x%-$ErCl_3$ perovskite films, scanning electron microscope (SEM) characterizations were performed with a FEI NanoSEM Nova-450 instrument. X-ray diffraction (XRD) spectra were measured by a Bruker D-8 Advance diffractometer with Cu Kα X-ray radiation. X-ray photoelectron spectroscopy (XPS) analyses on elemental binding energies and valence band maximum (VBM) positions were carried out with a PHI-5000 VersaProbe X-ray photoelectron spectrometer with Al Kα X-ray radiation. The absorbance spectra of inorganic perovskite films were measured using a Shinadzu UV-2456 spectrophotometer in the light wavelength range of 300-800 nm with an interval of 0.2 nm. The photoluminescence (PL) spectra were recorded on a home-built wide-field fluorescence microscope under the excitation wavelength of 450 nm. The current density-voltage (*J-V*) curves were measured with a Keithley 2400 Source Meter under AM 1.5G illumination. The light intensity was calibrated with a standard Si solar cell for 1 sun. Typically, in this study, the active area of the all-inorganic PSCs was 0.09 cm^2 and the scan rate was 0.1 V/s.

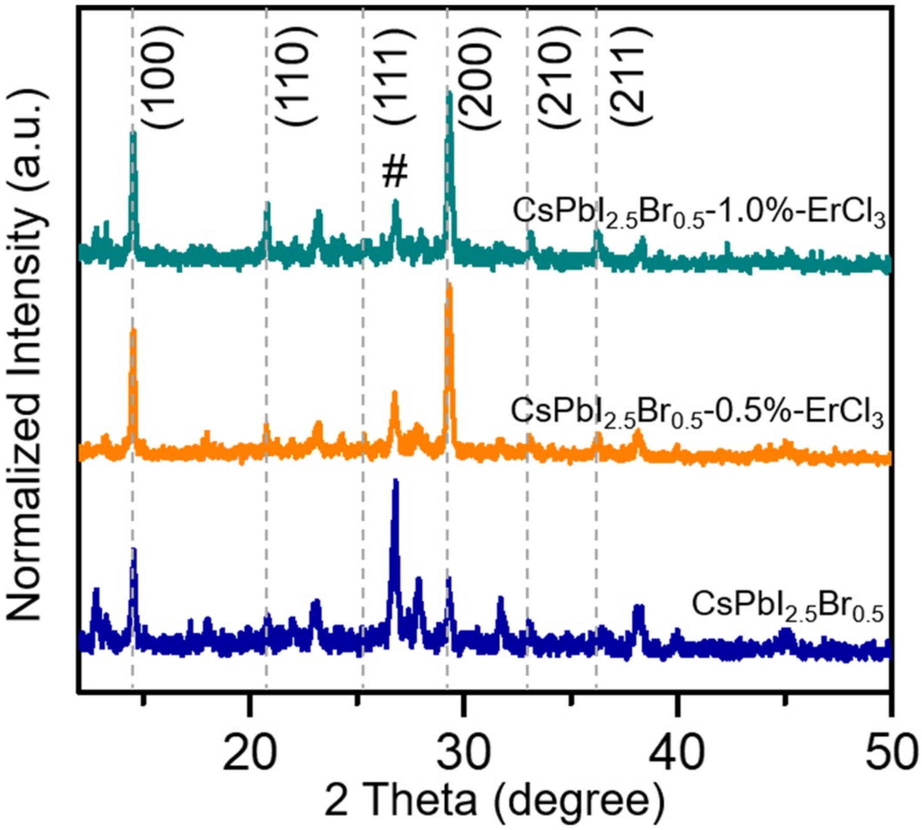

Figure S1 | XRD patterns of $CsPbI_{2.5}Br_{0.5}$-x%-$ErCl_3$ (x = 0, 0.5, 1.0) perovskite films.

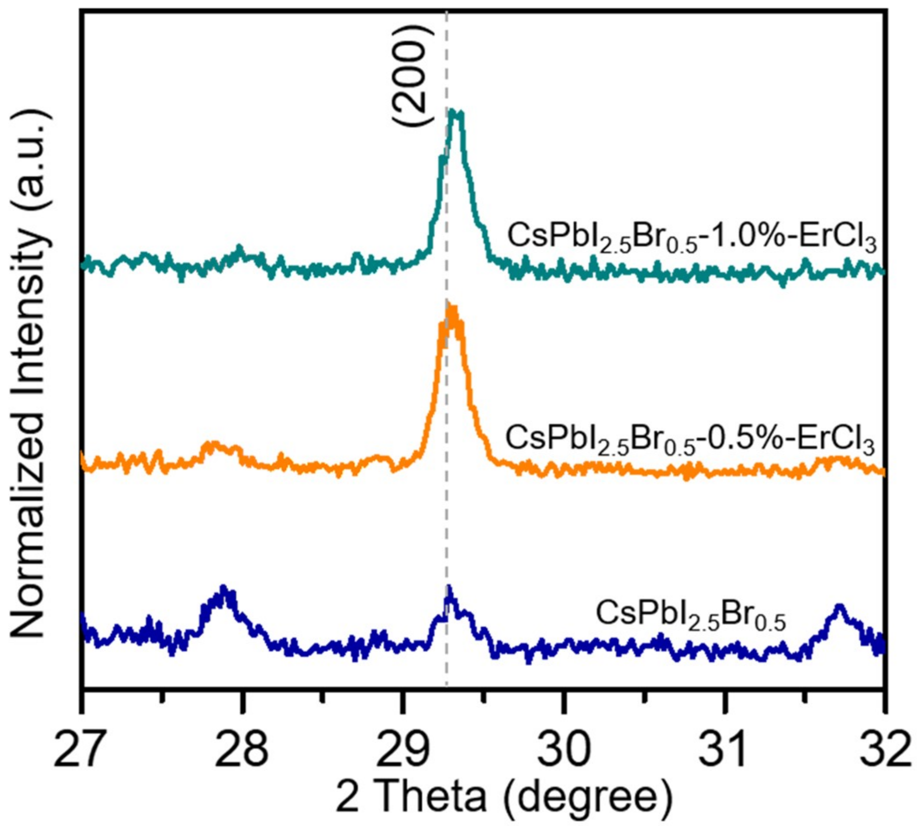

Figure S2 | Magnified (200) diffraction peaks in the XRD patterns of $CsPbI_{2.5}Br_{0.5}$-x%-$ErCl_3$ (x = 0, 0.5, 1.0) perovskite films.

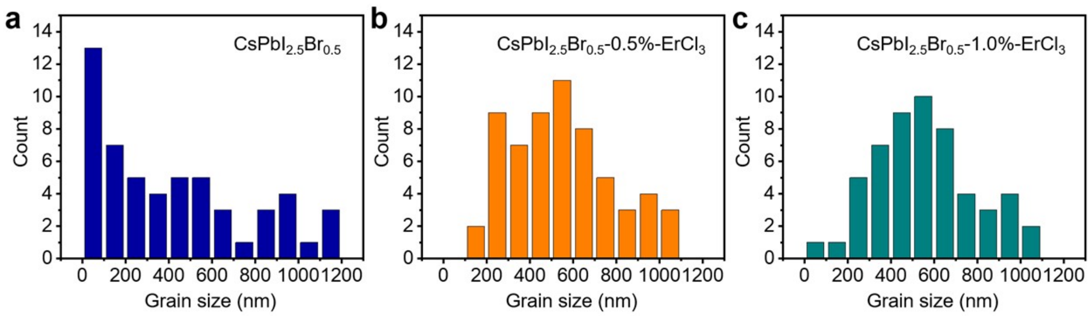

Figure S3 | Grain size distribution histograms of as-prepared $CsPbI_{2.5}Br_{0.5}$-x%-$ErCl_3$ thin films.

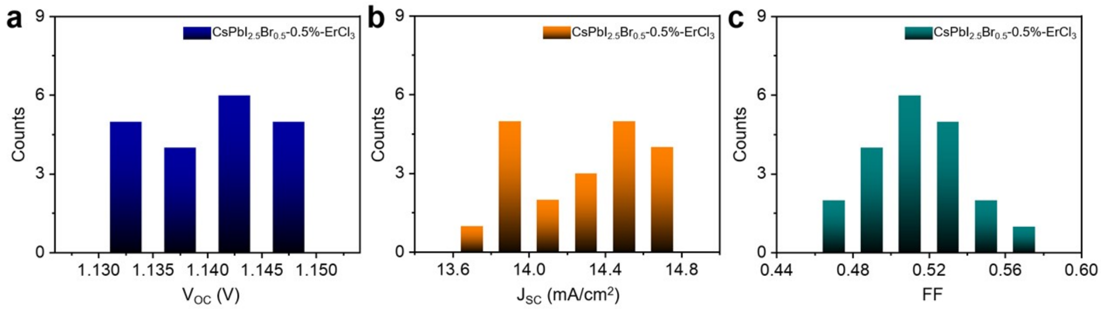

Figure S4 | Statistical histograms of (a) V_{OC}, (b) J_{SC}, and (c) FF distributions of 20 individual $CsPbI_{2.5}Br_{0.5}$-0.5%-$ErCl_3$ based AIPSCs.

Extended Table S1 | XPS binding energies of different elements measured from the as-prepared $CsPbI_{2.5}Br_{0.5}$-x%-$ErCl_3$ (x = 0, 0.5, 1.0) perovskite films.

Binding energy (eV)	C 1s	Cs $3d_{5/2}$	Cs $3d_{3/2}$	Pb $4f_{7/2}$	Pb $4f_{5/2}$	I $3d_{5/2}$	I $3d_{3/2}$
$CsPbI_{2.5}Br_{0.5}$-0%-$ErCl_3$	284.8	724.5	738.4	138.0	142.9	618.9	630.4
$CsPbI_{2.5}Br_{0.5}$-0.5%-$ErCl_3$	284.8	724.6	738.5	138.1	143.0	619.0	630.5
$CsPbI_{2.5}Br_{0.5}$-1.0%-$ErCl_3$	284.8	724.7	738.6	138.1	143.0	619.1	630.5

Binding energy (eV)	Br $3d_{5/2}$	Br $3d_{3/2}$	Er 4d	Cl $2p_{3/2}$	Cl $2p_{1/2}$
$CsPbI_{2.5}Br_{0.5}$-0%-$ErCl_3$	68.5	69.5	--	--	--
$CsPbI_{2.5}Br_{0.5}$-0.5%-$ErCl_3$	68.5	69.7	169.3	198.2	199.5
$CsPbI_{2.5}Br_{0.5}$-1.0%-$ErCl_3$	68.7	69.7	169.3	198.3	199.5

Extended Table S2 | Photovoltaic parameters of the as-assembled $CsPbI_{2.5}Br_{0.5}$-x%-$ErCl_3$ (x = 0, 0.5, 1.0) based AIPSCs.

Absorber layer	Band gap (eV)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
$CsPbI_{2.5}Br_{0.5}$-0%-$ErCl_3$	1.81	13.29	1.08	0.49	7.05
$CsPbI_{2.5}Br_{0.5}$-0.5%-$ErCl_3$	1.80	14.71	1.15	0.55	9.22
$CsPbI_{2.5}Br_{0.5}$-1.0%-$ErCl_3$	1.79	12.63	1.13	0.55	7.85

Extended Table S3 | Photovoltaic performance comparison of existing AIPSCs with Cs-based inorganic perovskite absorbers and carbon-based counter electrodes.

Ref.	Cell configuration	E_g (eV)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
This work	**FTO/*c*-TiO_2/*m*-TiO_2/$CsPbI_{2.5}Br_{0.5}$-0.5%-$ErCl_3$/Carbon**	**1.80**	**14.71**	**1.15**	**0.55**	**9.22**
[38]	FTO/*c*-TiO_2/*m*-TiO_2/$CsPb_{0.97}Sm_{0.03}Br_3$/Carbon	--	7.48	1.59	0.85	10.14
[45]	FTO/TiO_2/CsBr/$CsPbIBr_2$/Carbon	2.04	11.80	1.26	0.72	10.71
[46]	FTO/*c*-TiO_2/$CsPbIBr_2$/Carbon	2.05	10.66	1.25	0.69	9.16
[47]	FTO/*c*-TiO_2/$CsPbIBr_2$/Carbon	2.05	11.17	1.28	0.60	8.60
[48]	ITO/passivated SnO_2/$CsPbIBr_2$/Carbon	2.03	8.50	1.23	0.67	7.00
[49]	FTO/*c*-TiO_2/$CsPbIBr_2$/Carbon	2.05	9.11	1.14	0.63	6.55
[18]	FTO/*c*-TiO_2/*m*-TiO_2/$CsPbIBr_2$/Carbon	1.90	12.32	1.08	0.62	8.25
[18]	FTO/*c*-TiO_2/*m*-TiO_2/$CsPb_{0.9}Sn_{0.1}IBr_2$/Carbon	1.79	14.30	1.26	0.63	11.33
[19]	FTO/*c*-TiO_2/*m*-TiO_2/$CsPb_{0.995}Mn_{0.005}I_{1.01}Br_{1.99}$/Carbon	1.85	13.15	0.99	0.57	7.36
[50]	FTO/TiO_2/$CsPbBr_3$/Carbon	1.83	5.30	1.20	0.64	3.90
[51]	FTO/TiO_2/α-$CsPbI_3$/Carbon	1.68	18.5	0.79	0.65	9.50
[52]	FTO/*c*-TiO_2/$CsPbBr_3$/Carbon	2.30	6.46	1.34	0.68	3.60
[53]	ITO/SnO_2/$CsPbI_2Br$/Carbon	1.91	13.68	1.20	0.69	11.34
[54]	FTO/c-TiO_2/$CsPbI_2Br$/Carbon	1.91	13.54	1.15	0.64	10.00
[55]	ITO/PEDOT:PSS/$CsPbI_2Br$/SnPc/Carbon	1.91	13.69	1.24	0.67	11.39
[56]	FTO/c-TiO_2/$CsPbI_2Br$/Carbon	1.91	13.36	1.14	0.62	9.38
[57]	ITO/SnO_2/$CsPbI_2Br$/Carbon	1.92	14.20	1.27	0.62	11.20
[58]	ITO/SnO_2/$CsPbI_2Br$/Carbon	1.85	12.06	1.20	0.72	10.42
[59]	ITO/SnO_2/$CsPbI_2Br$/Co_3O_4/Carbon	1.82	13.09	1.19	0.72	11.21

Extended Table S4 | Photovoltaic parameters of as-assembled 20 individual $CsPbI_{2.5}Br_{0.5}$-0.5%-$ErCl_3$ based AIPSCs.

Device No.	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)	Device No.	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
1	14.71	1.15	0.54	9.22	**11**	14.65	1.09	0.52	8.28
2	14.84	1.15	0.53	9.09	**12**	12.77	1.12	0.58	8.26
3	14.82	1.15	0.52	8.86	**13**	13.76	1.16	0.51	8.21
4	14.68	1.14	0.53	8.81	**14**	12.66	1.16	0.56	8.18
5	14.17	1.12	0.55	8.70	**15**	13.99	1.15	0.50	8.04
6	13.18	1.17	0.56	8.66	**16**	13.00	1.06	0.58	7.98
7	13.74	1.15	0.54	8.52	**17**	14.10	1.02	0.55	7.92
8	13.17	1.17	0.55	8.51	**18**	13.15	1.12	0.53	7.82
9	13.71	1.19	0.52	8.48	**19**	12.71	1.10	0.55	7.70
10	12.24	1.17	0.58	8.45	**20**	10.73	1.16	0.58	7.33