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Supporting Information

Six Metal Cations in One Double Perovskite: Exploring Complexity of Chloride Elpasolites by High-Throughput Experimentation

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Materials and Methods

A general protocol for the synthesis of "master" plates with two M^{III} species.

To enable using the same general robot-assisted synthesis protocol for the preparation of different "master" plates with two M^{III} species, a set of 14 precursor solutions was prepared for each of the M^{III} combinations. This set included eight M^{III} precursor solutions with the same total M^{III} concentration but a varied ratio of M^{III} components, the fraction of the second M^{III} component set at 1.00, 0.95, 0.90, 0.75, 0.50, 0.25, 0.10, and 0, as well as six M^{I} precursor solutions with a varied Ag/Na ratio, corresponding to a silver fraction of 0, 0.10, 0.30, 0.50, 0.80, and 1.00.

In the second step, the M^{III} precursor solutions were "multiplied" by the M^{I} precursor solutions using an automated pipetting robot yielding 8×6 arrays of perovskite samples with M^{III} varied by the X axis and M^{I} varied by the Y axis. For this, equal volumes (0.80 mL) of each of the eight M^{III} precursor solutions were transferred by the pipetting robot from precursor vials into the upper horizontal row of a 48-well Eppendorf plate (well volume of 2 mL), and this procedure was consecutively repeated for each of the next five rows. Then, equal volumes (0.80 mL) of six M^{I} stock solutions were transferred by the pipetting robot from precursor vials into the first vertical column of wells and this procedure was repeated consecutively for each of the next seven well columns. The addition of the M^{I} precursor solutions resulted in the instant precipitation of perovskite products. All manipulations were performed under intense shaking of the entire plate on the shaking station of the robotic setup to ensure homogeneous precipitation. The plate is maintained on the shaking station of the Tecan robot during the synthesis.

Preparation of six M^{I} precursor solutions. To produce M^{I} precursor solutions with a varied Ag fraction (*x*), *x* mL 1.0 M aqueous $AgNO_3$ solution, 1-*x* mL DI water, 1.15 mL 3.0 M aqueous ammonia solution, 0.25 mL 4.0 M aqueous solution of sodium acetate (NaAc), and 0.6 mL 4.0 M aqueous solution of cesium acetate (CsAc) were consecutively mixed and 5.0 mL 2-propanol added with all procedures performed under intense shaking. Proper preparation should yield transparent and colorless solutions. The volume x was set at 0, 0.10 mL, 0.30 mL, 0.50 mL, 0.80 mL, and 1.00 mL. Cesium and sodium acetates were taken in excess to ensure the preferential formation of the double perovskite phase.

Preparation of eight M^{III} precursor solutions. To produce binary M^{III} = M1+M2 precursor solutions with a varied M1 fraction (*y*), *y* mL 1.0 M aqueous $M1Cl_3$ containing 4.0 M HCl, 1-*y* mL 1.0 M aqueous $M2Cl_3$ containing 4.0 M HCl, 2.0 mL 12.0 M aqueous HCl (37 w.%) were consecutively mixed and 5.0 mL 2-propanol added with all procedures performed under intense shaking. Proper preparation should yield transparent and colorless solutions. The volume *y* was set at 0, 0.05 mL, 0.10 mL, 0.25 mL, 0.50 mL, 0.75 mL, 0.90 mL, and 1.00 mL.

Synthesis of "focus" CANBIC plate with Bi content of 0-2%.

The "focus" CANBIC plate was produced using the above-described general approach but with a different set of eight M^{III} precursor solutions. This precursor set was prepared using 0.1 M aqueous $BiCl_3$ and 0.9M $InCl_3$ stock solution containing 4.0 M HCl. The volume of this solution (*y*) was set at 0, 1.0 µL, 5 µL, 10 µL, 20 µL, 50 µL, 100 µL, and 200 µL, while the volume of the 1.0 M $InCl_3$ stock solution (1-*y*) was set at 1.00 mL, 0.999 mL, 0.995 mL, 0.990 mL, 0.980 mL, 0.950 mL, 0.900 mL, and 0.800 mL. 2.0 mL 12.0 M aqueous HCl (37 w.%) were consecutively mixed and 5.0 mL 2-propanol was added with all procedures performed under intense shaking. The set of six M^{I} precursor solutions was produced identically to the case of the "master" CANBIC plate.

A general protocol for the synthesis of "master" plates with three M^{III} species.

The universal protocol of the robot-assisted synthesis was further extended for the preparation of "master" plates with three different M^{III} species, M^{III} = M3+M1+M2 (where the metal M3 content is varied along the shorter axis of the plate). For such plates, a set of 10 precursor solutions was prepared for each of the tested sample plates. This set includes eight M^{III} precursors (M1+M2), similar to those discussed for binary M^{III} samples, as well as a separate precursor with a third M^{III} component (M3). Because the nominal Ag fraction was maintained the same for all samples in ternary plates, only one M^{I} precursor is required for all 48 samples in the plate.

To carry out the synthesis, the same volumes of each of the eight binary M^{III} precursor (M1+M2) solutions are transferred by the pipetting robot to each of six rows of the 8×6 plate (further numbered from A to F), filling with the same precursor volume every well of each of the eight well columns. Transferred volumes are 0.80 mL (A), 0.72 mL (B), 0.40 mL (C), 0.20 mL (D), 0.08 mL (E), and 0.04 mL (F). Then, equal volume of the M3 precursor is added to each of the eight wells in the row. The volume of the M3 precursor is 0 (row A), 0.08 mL (B), 0.40 mL (C), 0.60 mL (D), 0.72 mL (E), and 0.76 mL (F). Finally, 0.80 mL of the M^{I} precursor solution is added by the pipetting robot to each of the 48 wells of the plate under intense shaking (the plate is maintained on the shaking station of the Tecan robot during the synthesis).

Preparation of an M^{I} precursor solution. 0.70 mL 1.0 M aqueous $AgNO_3$ solution, 0.30 mL DI water, 1.15 mL 3.0 M aqueous ammonia solution, 0.25 mL 4.0 M aqueous solution of sodium acetate (NaAc), and 0.6 mL 4.0 M aqueous solution of cesium acetate (CsAc) were consecutively mixed and 5.0 mL 2-propanol added with all procedures performed under intense shaking. Proper preparation should yield a transparent and colorless solution. To produce the complete 48-sample plate all volumes should be magnified by a factor of 5.

Preparation of eight binary M^{III} precursor solutions. To produce M^{III} = M1+M2 precursor solutions with a varied M1 fraction (*y*), *y* mL 1.0 M aqueous $M1Cl_3$ containing 4.0 M HCl, 1-*y* mL 1.0 M aqueous $M2Cl_3$ containing 4.0 M HCl, 2.0 mL 12.0 M aqueous HCl (37 w.%) were consecutively mixed and 5.0 mL 2-propanol added with all procedures performed under intense shaking. Proper preparation should

yield transparent and colorless solutions. The volume *y* was set at 0, 0.05 mL, 0.10 mL, 0.25 mL, 0.50 mL, 0.75 mL, 0.90 mL, and 1.00 mL.

Preparation of a precursor solution of the third M^{III} component. 1.0 mL 1.0 M aqueous $M3Cl_3$ containing 4.0 M HCl and 2.0 mL 12.0 M aqueous HCl (37 w.%) were mixed with 5.0 mL 2-propanol under shaking.

A special case of $Cs_2(Ag,Na)(Fe,Bi,In)Cl_6$ plates – "master" plate.

Due to the low stability of iron(III) salts to hydrolysis the synthesis of ternary-M^{III} plates based on Fe was performed in concentrated HCl instead of a mixture of HCl with 2-propanol. As both precursor solutions and final perovskite suspensions reveal high vapor pressure of HCl, the synthesis cannot be performed by the pipetting robot. Instead, the plates were produced manually under a fume hood using an 8×6 array of vials with caps. Similar to the above-described general protocol for the automated synthesis of ternary-M^{III} perovskites, a set of 10 precursor solutions was used, including eight Bi+In precursors, the Fe precursor, and the Ag+Na precursor. The scheme of mixing and added volumes are identical to the above-described, only performed manually. Different volumes of the Bi+In precursor are distributed in the columns 8×6 vial array, filling each of eight vials in a row with a 0.80 mL (row A), 0.72 mL (B), 0.40 mL (C), 0.20 mL (D), 0.080 mL (E), and 0.04 mL (F) of the Bi+In precursor solution. Then, equal volumes of the third M^{III} precursor are added to each of the eight vials of the corresponding rows, 0 to A, 0.08 mL to B, 0.40 mL to C, 0.60 mL to D, 0.72 mL to E, and 0.76 mL to F. Finally, 0.26 mL of the Ag+Na precursor solutions are added to each of the 48 vials resulting in the precipitation of products. All manipulations are performed under intense shaking.

Preparation of an Ag+Na precursor solution. 1 mL 1.0 M aqueous $AgNO_3$ solution, 0.4 mL 13.4 M (25%) aqueous ammonia solution, 0.25 mL 4.0 M aqueous NaAc solution, and 1 mL 4.0 M aqueous CsAc solution are consecutively added under intense shaking. Proper preparation should yield a transparent and colorless solution. To produce the complete 48-sample plate all volumes should be magnified by a factor of 5. In each case, an excess of Cs+ and Na+ is present to promote the formation of the cubic perovskite $Cs_2M^IM^{III}Cl_6$ phase.

Preparation of eight binary M^{III} precursor solutions. This step is identical to that of the general robot-assisted process described above, only pure concentrated HCl is used as a solvent instead of a mixture of HCl with 2-propanol. To produce M^{III} = Bi+In precursor solutions with a varied Bi fraction (*y*), *y* mL 1.0 M aqueous $BiCl_3$ containing 4.0 M HCl, and 1-*y* mL 1.0 M aqueous $InCl_3$ containing 4.0 M HCl, were consecutively added to 7.0 mL concentrated aqueous HCl (37. w.%) under stirring. Proper preparation should yield transparent and colorless solutions. The volume *y* was set at 0, 0.05 mL, 0.10 mL, 0.25 mL, 0.50 mL, 0.75 mL, 0.90 mL, and 1.00 mL.

Preparation of a Fe precursor solution. In this special case, to prepare the precursor M3, 1.0 mL 1.0 M aqueous $FeCl_3$ containing 6.0 M HCl is mixed with 7.0 mL 12.0 M aqueous HCl (37 w.%) under stirring.

A special case of $Cs_2(Ag,Na)(Fe, Bi,In)Cl_6$ plates – "focus" plate.

The protocol for the manual synthesis of the "focus" 8×6 arrays of $Cs_2(Ag,Na)(Fe,Bi,In)Cl_6$ perovskites with iron content between 95 and 99.5% is generally similar to the above-described procedure used for the "master" plate. The Bi+In precursor is produced identically and evenly distributed to each of the eight vials forming corresponding rows, 40 µL for row A, 32 µL for B, 24 µL for C, 16 µL for D, 8 µL for E, and 4 µL for F. Then, different volumes of the Fe precursor are introduced to corresponding rows, 760.0 µL for A, 768.0 µL for B, 776.0 µL for C, 784.0 µL for D, 792.0 µL for E, and 796 µL for F. Finally, 0.26 mL of the Ag+Na precursor (the same composition as described for the "master" plate) is added to each of the vials.

Post-synthesis purification of the samples.

All freshly prepared samples were kept unstirred in closed vials under paternal solutions for 12-14 h, then they were subjected to centrifugation at 1,500 rpm for 2 min, and separated from the supernatant. Afterward, 1.0 mL 2-propanol was added to each of the vials followed by shaking for 1-2 min, centrifugation in the same conditions, and separation of the supernatant. This cycle was repeated 2 times. The suspensions for the drop-casting of films were produced by adding 0.2-0.3 mL 2-propanol to purified precipitates followed by 1-2 min of intense shaking. 40-50 µL of perovskite suspension is typically drop-casted to each well to produce the films.

Preparation of stock solutions.

1.0 M aqueous $InCl_3$ solution with 4.0 M HCl: 2.21 g $InCl_3$ added to 3.3 mL 12.0 M (37 w.%) HCl, after complete dissolution DI water added to the total solution volume of 10 mL.

1.0 M aqueous $BiCl_3$ solution with 4.0 M HCl: 3.15 g $BiCl_3$ added to 3.3 mL 12.0 M (37 w.%) HCl, after complete dissolution DI water added to the total solution volume of 10 mL.

1.0 M aqueous $SbCl_3$ solution with 4.0 M HCl: 2.28 g $SbCl_3$ added to 3.3 mL 12.0 M (37 w.%) HCl, after complete dissolution DI water added to the total solution volume of 10 mL.

3.0 M aqueous ammonia solution: 0.23 mL 13.4 M (25 w.%) NH_4OH mixed with 0.77 mL DI water.

1.0 M aqueous $AgNO_3$ solution: 1.70 g $AgNO_3$ added to ca. 9 mL DI water, after complete dissolution DI water was added to the total solution volume of 10 mL.

4.0 M aqueous NaAc solution: 5.44 g $CH_3COONa×3H_2O$ added to ca. 5 mL DI water, after complete dissolution DI water was added to the total solution volume of 10 mL.

4.0 M aqueous CsAc solution: 7.68 g CH_3COOCs added to ca. 5 mL DI water, after complete dissolution DI water was added to the total solution volume of 10 mL.

1.0 M aqueous FeCl3 with 6.0 M HCl: 2.7 g $FeCl_3×6H_2O$ added to 5.0 mL 12 M (37 w.%) HCl after complete dissolution carefully diluted with DI water to the total solution volume of 10 mL.

0.1 M aqueous $BiCl_3$ in (0.9 M $InCl_3$ + 4 M HCl): 0.315 g $BiCl_3$ and 1.990 g $InCl_3$ added to 3.3 mL (37 w.%) HCl after complete dissolution DI water added to the total solution volume of 10 mL.

Evaluation of time resources necessary for the HTP synthesis

In a typical procedure, ca. 2 h is required to prepare stock solutions and a set of 14 (or 10) precursor solutions necessary for the robot-assisted synthesis. The robot-assisted preparation of a single 48-well plate typically requires 1.0 h. Totally, ca. 3.0 h is required for the synthesis of a single plate.

In the step of purification, the Eppendorf vials need to be manually closed with caps, requiring ca. 0.5 h. After centrifugation (5 min), the caps are manually removed and the supernatant solutions are separated from the precipitates (0.5 h). Afterward, 2-propanol is added by the pipetting robot and the caps are closed again (0.5 h). After centrifugation (5 min) the caps are opened (30 min) and the whole procedure is repeated for the second time. Summarily, the purification step requires ca. 3.5 h.

The final drop-casting of purified suspensions on substrates is performed by the pipetting robot, taking ca. 0.5 h. In total, ca. 7 hours are required to proceed from the preparation of stock solutions to the final drop-casted products. When several plates are produced (master and focuses), the pipetting and capping steps are multiplied by the number of the plates.

We note that the precipitation yields immediately crystalline products. However, to ensure that the crystallization is complete, the products are typically left overnight after the first capping procedure.

Instrumental methods

X-ray diffraction (XRD) patterns were registered using a Panalytical X'pert powder diffractometer with filtered Cu K_α radiation (λ = 1.54178 Å) and an X'Celerator solid-state stripe detector in the Bragg-Brentano geometry in an angle range of 2θ = 5-100° with a step rate of 0.05° per min.

The XRD patterns were subjected to a Rietveld refinement procedure using MAUD software (version 2.99). Structural CIF files were downloaded from the Crystallography Open Database (COD, https://www.crystallography.net/cod/).

Scanning electron microscopy (SEM) imaging and energy-dispersive X-ray spectroscopic (EDX) analysis were performed using a JEOL JSM-7610F Schottky field emission scanning electron microscope operating under 15-20 kV acceleration voltage and equipped with an X-Max 80 mm^2 silicon drift detector (Oxford Instruments) and AZtec nanoanalysis software. EDX spectra were collected for at least five different spots of each sample and the results were averaged.

Reflectance spectra were recorded using a BlackComet spectrometer (StellarNet Inc.) and a 75 W Xenon lamp (Thorlabs) as an excitation source. The spectra were registered with an optical Y-fiber probe in identical geometry for samples and a scattering reference (ultra-pure $BaSO_4$, Alfa-Aesar). The reflectance spectra were transformed into absorption spectra using the Kubelka-Munk formula and the reference.

Photoluminescence (PL) and PL excitation spectra were collected using a plate-reading spectrometer integrated into the Tecan pipetting robot. PL was excited at 350 nm, PLE signal registered at 600 nm.

Tables

Table S1. Composition and structural parameters of **$Cs_2(Ag,Na)(Bi,In)Cl_6$** double perovskites

Nominal ratios		Actual ratios				Lattice parameter (Å)	Bandgap E_g (eV)	PL max (eV)	PL QY (%)
Ag/M^{I}	Bi/M^{III}	Cs/M^{III}	Cl/M^{III}	Ag/M^{I}	Bi/M^{III}				
0	0	2.1	5.7	0	0	10.543	-	-	0
	0.05	2	5.5		0.06	10.559	-	-	0
	0.10	2	5.4		0.11	10.581	3.240	2.06	0
	0.25	1.95	5.1		0.24	10.620	3.265	2.02	0
	0.50	2	5.6		0.58	10.720	3.260	1.98	0
	0.75	1.95	5.4		0.83	10.800	3.265	1.95	0
	0.90	1.95	5.3		0.93	10.830	3.270	1.94	0
	1.0	1.9	5.2		1	10.856	3.250	1.93	0
0.10	0	2.1	5.1	0.1	0	10.533	3.295	2.20	0
	0.05	2	5.4	0.11	0.07	10.550	3.005	2.12	71
	0.10	2	5	0.1	0.09	10.570	2.920	2.08	57
	0.25	2	5.2	0.16	0.28	10.644	2.870	2.02	29
	0.50	2.1	5.4	0.16	0.58	10.734	2.905	1.97	22
	0.75	1.95	5.4	0.13	0.86	10.801	2.910	1.95	18
	0.90	1.9	5.2	0.11	0.95	10.821	2.915	1.94	13
	1.0	2	5.2	0.14	1	10.843	2.920	1.93	12
0.30	0	2	5.7	0.23	0	10.529	3.225	2.17	0
	0.05	2.1	5.8	0.31	0.06	10.541	2.935	2.13	84
	0.10	2	5.7	0.29	0.12	10.562	2.785	2.10	69
	0.25	2.1	5.7	0.41	0.27	10.617	2.770	2.04	35
	0.50	2.1	5.5	0.34	0.61	10.703	2.750	2.00	14
	0.75	2.1	5.3	0.3	0.8	10.769	2.760	1.97	9
	0.90	2	5.4	0.37	0.94	10.808	2.765	1.96	6
	1.0	1.9	5.2	0.3	1	10.833	2.765	1.95	6
0.50	0	1.9	5.6	0.53	0	10.514	3.175	2.17	1
	0.05	2.1	5.8	0.43	0.07	10.530	2.910	2.14	96
	0.10	2	5.6	0.41	0.11	10.541	2.870	2.12	79
	0.25	2	5.6	0.44	0.28	10.596	2.760	2.06	39
	0.50	2	5.4	0.45	0.51	10.674	2.720	2.02	13
	0.75	2	5.3	0.52	0.78	10.749	2.715	2.01	6
	0.90	1.95	5.3	0.49	0.92	10.794	2.720	2.00	4
	1.0	1.95	5.2	0.49	1	10.820	2.725	1.98	4
0.80	0	2.1	5.8	0.68	0	10.512	3.140	2.17	0
	0.05	2.1	5.9	0.59	0.06	10.523	2.900	2.15	95
	0.10	2.1	5.8	0.66	0.11	10.538	2.850	2.13	79
	0.25	2.1	5.8	0.78	0.28	10.576	2.705	2.07	32
	0.50	2	5.5	0.8	0.53	10.655	2.695	2.05	7
	0.75	1.95	5.3	0.82	0.82	10.737	2.650	2.04	3
	0.90	1.9	5.3	0.75	0.95	10.785	2.645	2.05	3
	1.0	1.95	5.3	0.74	1	10.801	2.645	2.06	3
1.00	0	2.1	6	0.71	0	10.508	3.145	2.17	0
	0.05	2.1	5.9	0.76	0.05	10.521	2.890	2.15	94
	0.10	2.2	6	0.85	0.1	10.538	2.840	2.13	78
	0.25	2	5.9	0.78	0.26	10.578	2.720	2.07	34
	0.50	2.1	5.7	0.9	0.57	10.655	2.675	2.05	6
	0.75	2	5.4	0.87	0.83	10.734	2.650	2.07	3
	0.90	1.9	5.3	0.9	0.96	10.772	2.630	2.08	3
	1.0	1.9	5.4	0.89	1	10.788	2.620	2.09	2

Notes: M^{I} = Ag+Na, M^{III} = Bi+In; E_g calculated from PL excitation spectra; PL QY measured under excitation at 365 nm. Determination accuracy is 0.001 Å, 0.005 eV, 0.01 eV, 1% for the lattice parameter, bandgap, PL maximum, and PL QY, respectively.

Table S2. Composition and structural parameters of **$Cs_2(Ag,Na)(Bi,Sb)Cl_6$** double perovskites

Nominal ratios		Actual ratios				Lattice parameter (Å)	Bandgap E_g (eV)
Ag/M^{I}	Sb/M^{III}	Cs/M^{III}	Cl/M^{III}	Ag/M^{I}	Sb/M^{III}		
0	1.0	1.7	4.4	0	1.0	-	2.925
	0.95	1.7	4.6		0.93	-	2.750
	0.90	1.7	4.5		0.85	-	2.765
	0.75	1.8	4.6		0.77	-	2.785
	0.50	1.9	4.7		0.52	-	2.830
	0.25	1.9	4.7		0.27	10.855	2.820
	0.10	2.0	4.8		0.13	10.855	2.825
	0	2.3	5.3		0	10.855	3.080
0.10	1.0	1.7	4.6	0.41	1.0	-	2.925
	0.95	1.7	4.6	0.38	0.90	-	2.770
	0.90	1.7	4.8	0.31	0.85	10.741	2.780
	0.75	1.7	4.8	0.32	0.75	10.757	2.800
	0.50	1.8	4.7	0.27	0.48	10.795	2.830
	0.25	2.0	5.0	0.18	0.25	10.839	2.845
	0.10	2.0	5.3	0.13	0.11	10.846	2.855
	0	2.2	5.5	0.11	0	10.845	3.120
0.30	1.0	1.9	5.2	0.65	1.0	10.718	2.860
	0.95	1.8	4.8	0.67	0.93	10.734	2.685
	0.90	1.8	4.9	0.60	0.84	10.739	2.735
	0.75	1.9	4.9	0.66	0.72	10.749	2.730
	0.50	1.9	5.0	0.54	0.48	10.778	2.780
	0.25	1.9	5.3	0.35	0.20	10.8127	2.840
	0.10	2.1	5.4	0.34	0.08	10.822	2.860
	0	2.1	5.2	0.33	0	10.832	2.960
0.50	1.0	1.9	5.2	0.79	1.0	10.717	2.845
	0.95	1.9	5.2	0.71	0.94	10.723	2.720
	0.90	1.9	5.3	0.73	0.85	10.731	2.665
	0.75	2.0	5.0	0.68	0.75	10.751	2.690
	0.50	1.9	5.2	0.76	0.52	10.768	2.735
	0.25	2.1	5.5	0.57	0.21	10.802	2.800
	0.10	2.0	5.4	0.47	0.08	10.811	2.865
	0	2.0	5.5	0.47	0	10.820	2.910
0.80	1.0	2.1	5.6	0.91	1.0	10.710	2.820
	0.95	2.0	5.6	0.77	0.94	10.715	2.600
	0.90	2.0	5.4	0.92	0.85	10.726	2.595
	0.75	2.0	5.4	0.75	0.77	10.743	2.620
	0.50	2.1	5.6	0.81	0.49	10.757	2.655
	0.25	2.0	5.4	0.80	0.24	10.777	2.695
	0.10	2.0	5.4	0.82	0.08	10.787	2.725
	0	2.0	5.3	0.83	0	10.797	2.775
1.00	1.0	2.0	5.9	0.73	1.0	10.710	2.830
	0.95	2.1	5.9	0.87	0.96	10.715	2.645
	0.90	2.1	5.9	0.82	0.86	10.721	2.575
	0.75	1.9	5.5	0.82	0.74	10.730	2.625
	0.50	1.9	5.2	0.84	0.51	10.750	2.675
	0.25	1.8	5.2	0.80	0.22	10.768	2.700
	0.10	2.0	5.4	0.77	0.09	10.783	2.745
	0	2.0	5.4	0.78	0	10.791	2.770

Notes: M^{I} = Ag+Na, M^{III} = Sb+Bi; E_g calculated from absorption spectra. Determination accuracy is 0.001 Å and 0.005 eV for the lattice parameter and the bandgap, respectively.

Table S3. Composition and structural parameters of **$Cs_2(Ag,Na)(In,Sb)Cl_6$** double perovskites

Nominal ratios		Actual ratios				Lattice parameter (Å)	Bandgap E_g (eV)
Ag/M^{I}	Sb/M^{III}	Cs/M^{III}	Cl/M^{III}	Ag/M^{I}	Sb/M^{III}		
0	1.0	1.6	4.3	0	1.0	-	2.900
	0.95	1.6	4.3		0.96	-	2.915
	0.90	1.7	4.6		0.92	-	2.930
	0.75	1.8	4.8		0.73	-	2.955
	0.50	1.9	5.4		0.48	-	2.960
	0.25	2.2	6.0		0.20	-	2.965
	0.10	2.2	5.9		0.06	-	3.395
	0	2.1	5.8		0	-	4.000
0.10	1.0	1.6	4.4	0.45	1.0	-	2.880
	0.95	1.7	4.7	0.44	0.96	-	2.950
	0.90	1.8	4.5	0.45	0.90	-	2.950
	0.75	1.8	5.0	0.34	0.72	-	2.955
	0.50	1.9	5.3	0.18	0.44	10.571	2.960
	0.25	2.1	6.0	0.15	0.23	10.563	2.965
	0.10	2.1	5.9	0.12	0.10	10.553	3.150
	0	2.2	6.0	0.12	0	10.535	4.000
0.30	1.0	1.8	4.8	0.79	1.0	10.721	2.865
	0.95	1.8	4.9	0.68	0.93	10.704	2.895
	0.90	1.7	4.9	0.66	0.89	10.684	2.900
	0.75	2.0	5.2	0.62	0.73	10.616	2.930
	0.50	2.0	5.6	0.40	0.52	10.598	2.960
	0.25	2.0	5.9	0.33	0.25	10.580	3.060
	0.10	2.0	6.0	0.33	0.09	10.545	3.090
	0	2.1	6.0	0.33	0	10.524	3.735
0.50	1.0	1.9	5.3	0.90	1.0	10.717	2.850
	0.95	1.9	5.3	0.85	0.96	10.699	2.865
	0.90	2.0	5.5	0.82	0.89	10.684	2.890
	0.75	2.0	5.6	0.71	0.74	10.646	2.935
	0.50	2.1	6.0	0.59	0.52	10.608	2.955
	0.25	2.1	6.1	0.50	0.25	10.559	3.020
	0.10	2.1	6.1	0.49	0.10	10.531	3.060
	0	2.2	6.1	0.46	0	10.514	3.715
0.80	1.0	2.1	5.6	0.84	1,0	10.716	2.820
	0.95	2.0	5.9	0.85	0.96	10.703	2.850
	0.90	2.1	5.9	0.83	0.90	10.688	2.860
	0.75	2.1	6.1	0.80	0.76	10.660	2.925
	0.50	2.1	6.1	0.68	0.50	10.604	2.960
	0.25	2.1	6.2	0.64	0.25	10.558	3.015
	0.10	2.2	6.4	0.62	0.10	10.531	3.075
	0	2.3	6.5	0.49	0	10.516	3.745
1.00	1.0	2.0	6.0	0.94	1.0	10.709	2.835
	0.95	2.1	6.1	0.93	0.97	10.700	2.835
	0.90	2.1	6.1	0.85	0.93	10.690	2.860
	0.75	2.2	6.2	0.89	0.74	10.654	2.890
	0.50	2.1	5.9	0.75	0.49	10.611	2.955
	0.25	2.2	6.3	0.64	0.26	10.560	3.010
	0.10	2.2	6.5	0.70	0.10	10.533	3.085
	0	2.2	6.6	0.62	0	10.511	3.745

Notes: M^{I} = Ag+Na, M^{III} = In+Sb; E_g calculated from absorption spectra. Determination accuracy is 0.001 Å and 0.005 eV for the lattice parameter and the bandgap, respectively.

Table S4. Composition and structural parameters of **$Cs_2(Ag,Na)(In,Bi,Sb)Cl_6$** double perovskites

Nominal ratios		Actual ratios					Lattice parameter (Å)	Bandgap E_g (eV)	ΔS_{conf}, xR (J(molK)$^{-1}$)
In/M^{III}	Bi/(Bi+Sb)	Cs/M^{III}	Cl/M^{III}	In/M^{III}	Bi/(Bi+Sb)	Ag/(Ag+Na)			
0	0	2.1	5.9	0	0	0.80	10.715	2.85	
	0.05	2.5	6.5		0.08	0.91	10.721	2.66	-
	0.10	2.2	6.5		0.11	0.89	10.725	2.63	-
	0.25	2.0	5.3		0.27	0.89	10.744	2.65	-
	0.50	1.9	5.5		0.52	0.69	10.768	2.68	-
	0.75	2.1	5.4		0.79	0.71	10.794	2.77	-
	0.90	2.1	5.6		0.92	0.63	10.806	2.82	-
	1.0	1.9	5.3		1.0	0.57	10.815	2.86	-
0.10	0	1.8	5.1	0.12	0	0.91	10.689	2.89	-
	0.05	2.0	5.7	0.07	0.06	0.67	10.690	2.73	1.23
	0.10	2.0	5.7	0.10	0.11	0.88	10.696	2.70	1.23
	0.25	1.9	5.4	0.09	0.29	0.73	10.715	2.71	1.27
	0.50	2.1	5.8	0.10	0.54	0.67	10.736	2.73	1.27
	0.75	2.2	5.6	0.11	0.80	0.64	10.762	2.77	1.29
	0.90	2.1	5.7	0.09	0.93	0.58	10.779	2.83	1.26
	1.0	2.1	5.4	0.10	1.0	0.62	10.782	2.88	1.26
0.50	0	2.3	6.1	0.55	0	0.42	10.610	2.98	-
	0.05	2.3	6.2	0.54	0.06	0.41	10.614	2.91	1.25
	0.10	2.4	6.5	0.53	0.08	0.56	10.619	2.81	1.27
	0.25	1.9	5.4	0.50	0.23	0.64	10,628	2.79	1.28
	0.50	2.1	6.1	0.50	0.54	0.57	10.646	2.77	1.28
	0.75	2.0	5.8	0.47	0.76	0.62	10.648	2.81	1.31
	0.90	2.2	6.0	0.49	0.92	0.65	10.649	2.86	1.29
	1.0	2.2	5.8	0.48	1.0	0.63	10.651	2.92	1.29
0.75	0	2.1	6.1	0.73	0	0.56	10.563	2.99	-
	0.05	2.0	5.9	0.74	0.04	0.53	10.562	2.96	1.19
	0.10	2.1	5.9	0.74	0.13	0.62	10.564	2.92	1.25
	0.25	2.2	6.2	0.75	0.29	0.60	10.564	2.89	1.27
	0.50	2.1	5.8	0.73	0.56	0.58	10.575	2.87	1.27
	0.75	2.2	6.2	0.76	0.78	0.56	10.582	2.90	1.26
	0.90	2.3	6.0	0.73	0.92	0.57	10.585	2.94	1.27
	1.0	2.3	6.1	0.73	1.0	0.50	10.589	2.98	1.26
0.90	0	2.2	6.4	0.90	0	0.51	10.533	3.10	-
	0.05	2.2	6.4	0.89	0.06	0.56	10.532	3.06	1.22
	0.10	2.1	6.2	0.89	0.13	0.50	10.531	3.04	1.21
	0.25	2.1	6.0	0.90	0.29	0.55	10.531	3.03	1.22
	0.50	2.2	6.2	0.89	0.61	0.61	10.534	3.03	1.25
	0.75	2.2	6.2	0.92	0.79	0.60	10.536	3.02	1.26
	0.90	2.0	5.7	0.89	0.89	0.56	10.540	3.03	1.24
	1.0	2.2	6.2	0.93	1.0	0.55	10.542	3.05	1.23
0.95	0	2.2	6.3	0.95	0	0.62	10.522	3.08	1.24
	0.05	2.1	6.0	0.93	0.04	0.52	10.526	3.09	-
	0.10	2.3	6.4	0.96	0.15	0.53	10.521	3.10	1.21
	0.25	2.3	6.4	0.96	0.28	0.62	10.523	3.08	1.20
	0.50	2.2	6.2	0.95	0.60	0.58	10.526	3.08	1.21
	0.75	2.3	6.1	0.94	0.77	0.63	10.527	3.08	1.22
	0.90	2.1	5.7	0.92	0.88	0.59	10.530	3.09	1.19
	1.0	2.1	6.1	0.95	1.0	0.55	10.527	3.08	1.21

Notes: M^{III} = Bi+Sb+In; E_g calculated from absorption spectra. Determination accuracy is 0.001 Å, 0.01 eV, and 0.01 J(molK)$^{-1}$ for the lattice parameter, bandgap, and configurational entropy, respectively.

Table S5. Composition and structural parameters of **$Cs_2(Ag,Na)(Fe,Bi,In)Cl_6$** double perovskites

Nominal ratios		Actual ratios					Lattice parameter (Å)	Bandgap E_g (eV)
Fe/M^{III}	$Bi/(Bi+In)$	Cs/M^{III}	Cl/M^{III}	Fe/M^{III}	$Bi/(Bi+In)$	$Ag/(Ag+Na)$		
0	0	2.2	6.0	0	0	0.80	10.514	3.77
	0.05	2.1	6.2		0.03	0.91	10.531	3.16
	0.10	2.4	6.4		0.07	0.89	10.542	3.12
	0.25	2.3	6.3		0.19	0.89	10.586	3.05
	0.50	2.0	5.5		0.52	0.69	10.663	2.96
	0.75	2.2	5.6		0.75	0.71	10.735	2.90
	0.90	2.1	5.6		0.90	0.63	10.773	2.88
	1.0	2.1	5.5		1.0	0.57	10.789	2.79
0.10	0	2.0	6.0	0.09	0	0.91	10.498	2.18
	0.05	2.1	5.9	0.09	0.05	0.67	10.508	2.16
	0.10	2.0	5.9	0.08	0.12	0.88	10.523	2.15
	0.25	2.0	5.9	0.08	0.27	0.73	10.564	2.09
	0.50	2.1	6.0	0.08	0.49	0.67	10.634	2.05
	0.75	2.1	5.9	0.08	0.77	0.64	10.701	2.03
	0.90	2.0	5.7	0.08	0.90	0.58	10.743	2.02
	1.0	2.1	5.6	0.08	1.0	0.62	10.766	2.01
0.50	0	2.0	5.7	0.49	0	0.42	10.420	2.13
	0.05	2.1	6.1	0.50	0.07	0.41	10.427	2.12
	0.10	2.0	6.0	0.46	0.13	0.56	10.440	2.11
	0.25	2.1	6.0	0.45	0.28	0.64	10.463	2.08
	0.50	2.0	5.9	0.47	0.52	0.45	10.513	2.06
	0.75	2.2	6.0	0.49	0.75	0.62	10.564	2.07
	0.90	2.2	5.9	0.52	0.90	0.65	10.599	2.06
	1.0	2.1	5.8	0.46	1.0	0.63	10.637	2.02
0.75	0	2.3	6.4	0.74	0	0.56	10.362	2.07
	0.05	2.1	5.8	0.70	0.08	0.53	10.366	2.05
	0.10	2.0	5.8	0.72	0.13	0.62	10.374	2.03
	0.25	2.0	5.9	0.73	0.28	0.60	10.383	2.00
	0.50	2.1	5.9	0.72	0.53	0.58	10.401	1.99
	0.75	2.2	6.1	0.77	0.77	0.56	10.430	1.97
	0.90	2.0	5.9	0.70	0.91	0.57	10.415	1.95
	1.0	2.2	6.0	0.73	1.0	0.50	10.423	1.91
0.90	0	2.0	5.9	0.87	0	0.51	10.324	2.01
	0.05	2.0	6.0	0.87	0.07	0.56	10.324	2.01
	0.10	2.0	5.7	0.91	0.14	0.50	10.320	2.00
	0.25	2.0	6.1	0.88	0.29	0.55	10.327	1.98
	0.50	2.0	5.9	0.87	0.57	0.61	10.339	1.97
	0.75	1.9	5.6	0.87	0.80	0.60	10.344	1.96
	0.90	2.0	6.0	0.89	0.87	0.56	10.342	1.94
	1.0	2.1	6.2	0.87	1.0	0.55	10.344	1.91
0.95	0	2.0	6.0	0.95	0	0.62	10.306	1.97
	0.05	2.1	6.1	0.93	0.07	0.52	10.315	1.96
	0.10	2.0	5.9	0.94	0.17	0.53	10.309	1.96
	0.25	2.0	6.0	0.92	0.32	0.62	10.313	1.94
	0.50	2.1	5.7	0.93	0.54	0.58	10.315	1.93
	0.75	2.1	6.1	0.93	0.72	0.63	10.320	1.93
	0.90	2.0	5.8	0.92	0.88	0.59	10.321	1.92
	1.0	2.0	5.9	0.94	1.0	0.55	10.323	1.91

Notes: M^{III} = Bi+In+Fe; E_g calculated from absorption spectra. Determination accuracy is 0.001 Å and 0.01 eV for the lattice parameter and the bandgap, respectively.

Figures

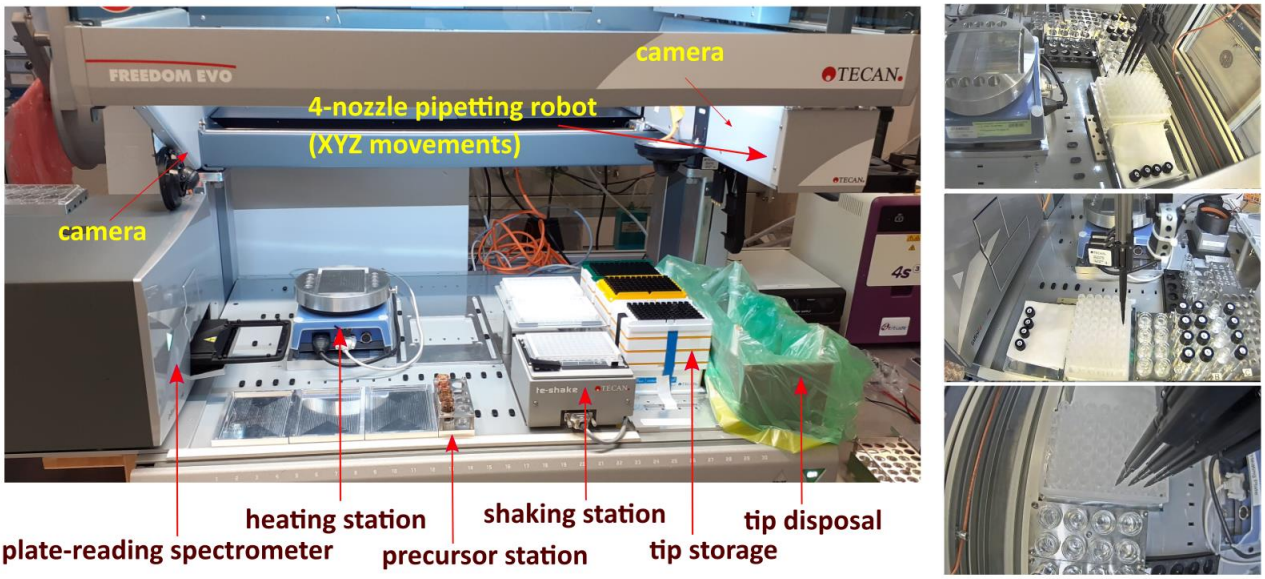

Figure S1. Schematic layout of the working area of the robotized Tecan pipetting system (left panel) and exemplary screenshots from the cameras-observers during the synthesis of a batch of perovskite samples (right panel).

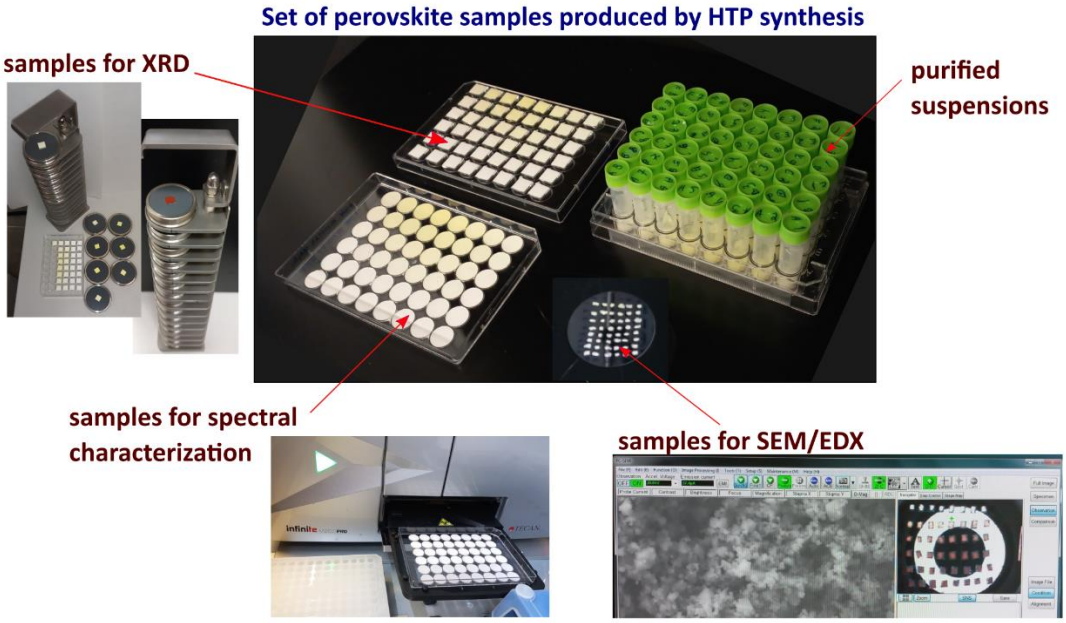

Figure S2. Perovskite samples typically produced for each compositional domain by robot-assisted high-throughput synthesis: purified suspensions in 2-propanol used for drop-casting of films; circular drop-casted films for spectral measurements; rectangular films on detachable glass plates for powder XRD; silicon plate with an array of small square samples for SEM/EDX characterization.

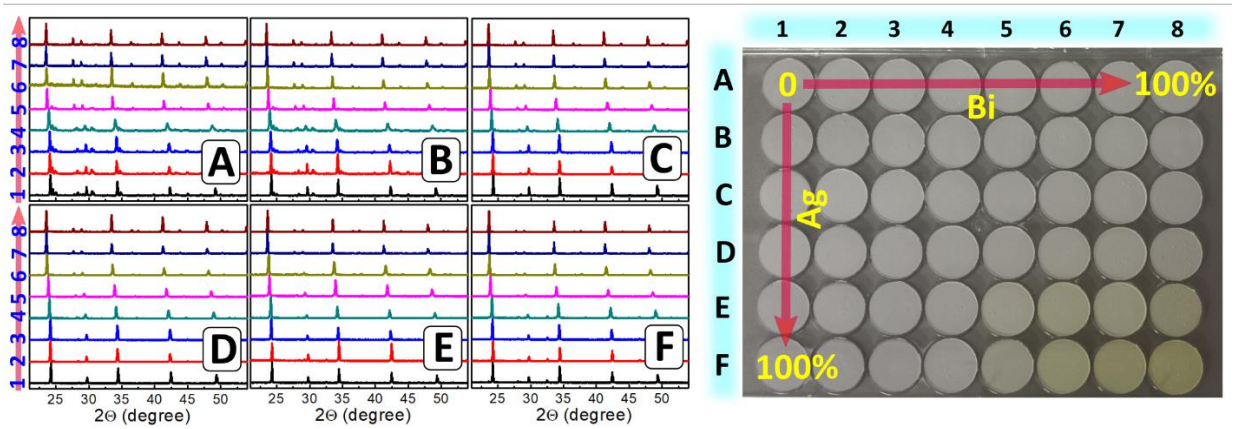

Figure S3. Collection of XRD patterns of $Cs_2(Ag,Na)(Bi,In)Cl_6$ perovskites.

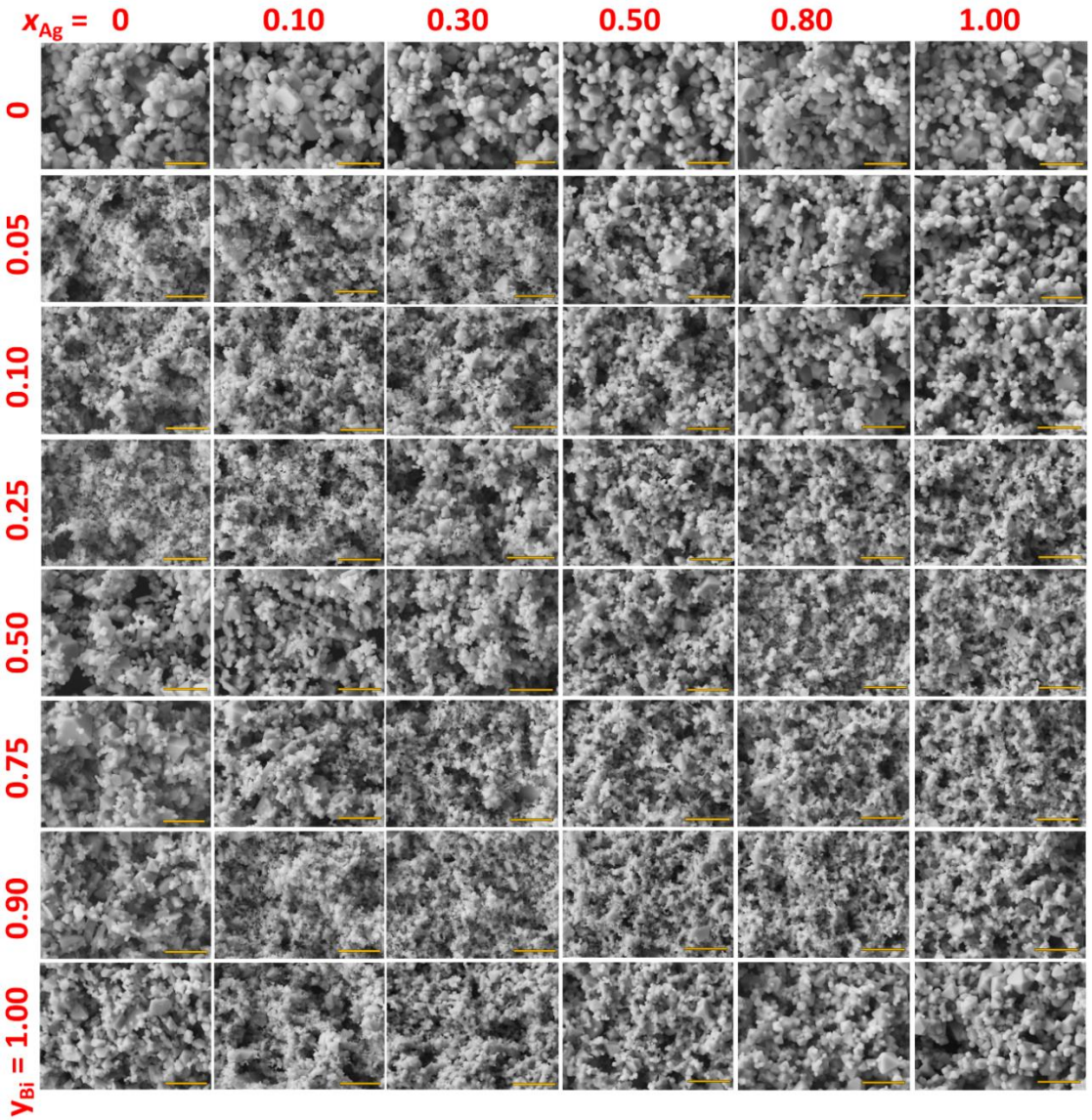

Figure S4. A collection of SEM images for the master CANBIC plate. The scale bar is 10 µm.

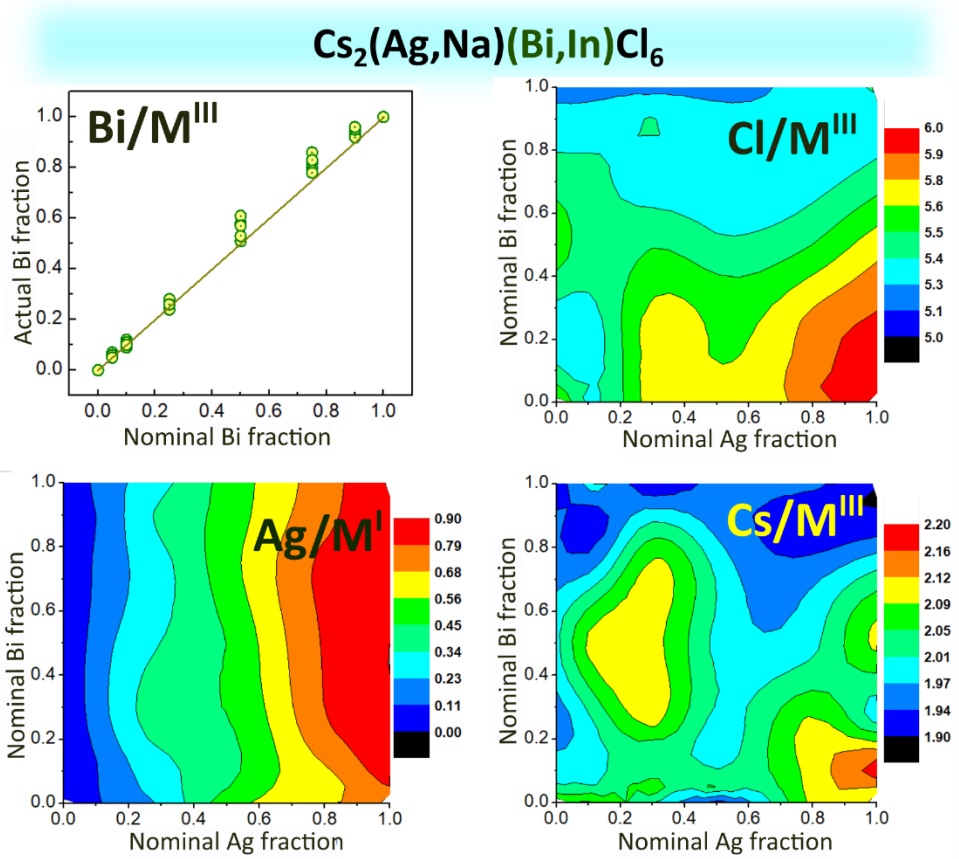

Figure S5. Summary of the EDX data for $Cs_2(Ag,Na)(Bi,In)Cl_6$ perovskites presented in Table S1: the relationship between actual (provided as the right-side multi-color scalebar) and nominal Bi/(Bi+In) fraction as well as dependencies of actual Cl/M^{III}, Ag/M^{I}, and Cs/M^{III} fractions on nominal Ag and Bi fractions. M^{I} = Ag+Na, M^{III} = Bi+In. 2D presentations were produced by interpolating and smoothing the EDX data for 48 samples. The evolution of the Cl/M^{III}, Cs/M^{III}, and Ag/M^{III} ratios is presented by colors changing from blue to red with numerical values indicated as corresponding scales.

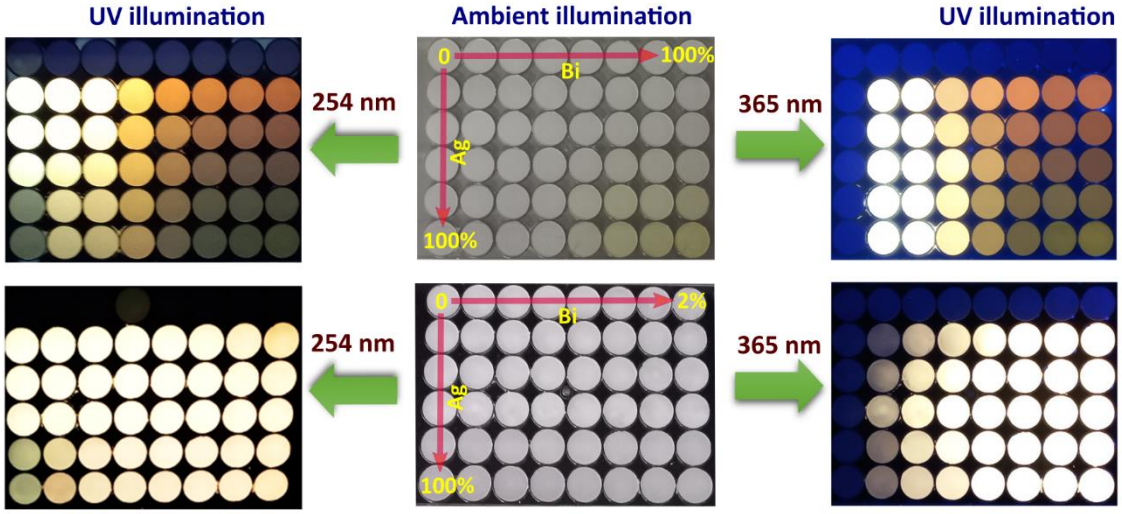

Figure S6. Photographs of CANBIC perovskite sample plates made under ambient (central section) and UV illumination (365 nm in right section, 254 nm in left section).

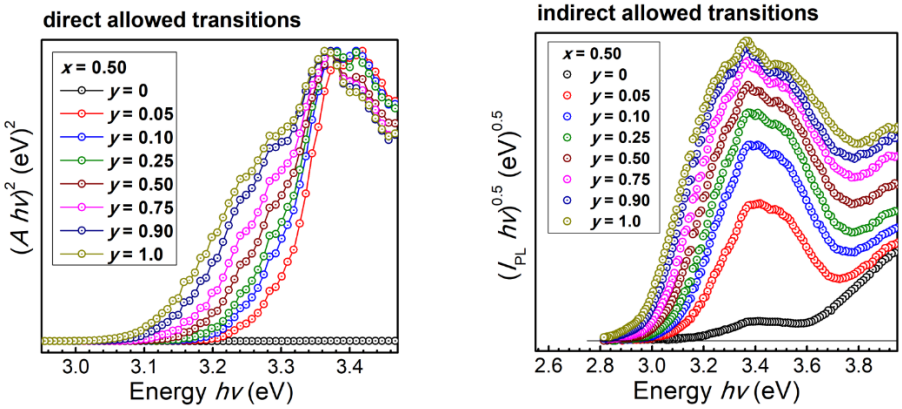

Figure S7. Exemplary normalized PL excitation spectra of $Cs_2Ag_xNa_{1-x}Bi_yIn_{1-y}Cl_6$ perovskites with x = 0.50 and a varied y plotted in the coordinates of Tauc equation for direct allowed (left section) and indirect allowed (right section) inter-band electron transitions.

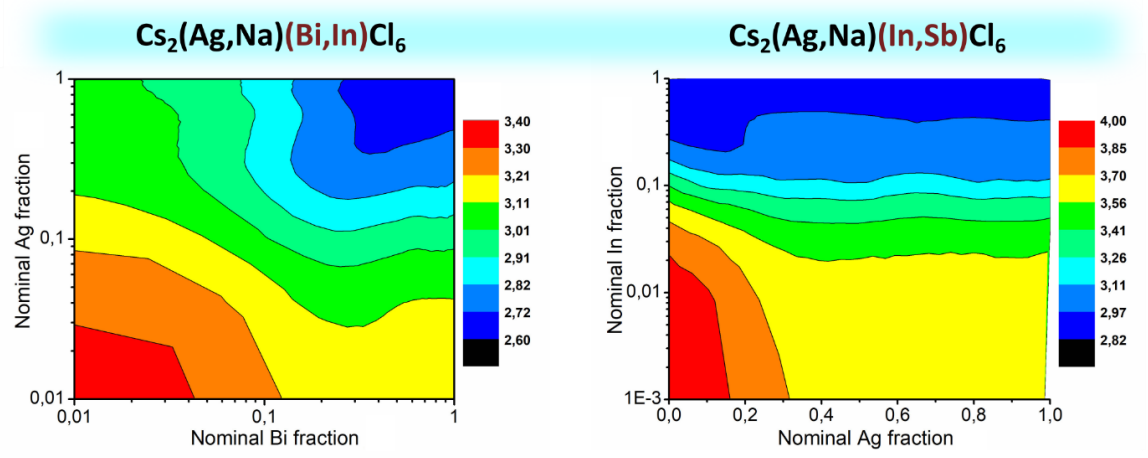

Figure S8. Bandgap of $Cs_2(Ag,Na)(Bi,In)Cl_6$ and $Cs_2(Ag,Na)(In,Sb)Cl_6$ perovskites as a function of composition (nominal fractions of Bi(In) and Ag). The bandgaps were calculated from the PL excitation spectra (CANBIC) and absorption spectra (CANISC). The evolution of bandgap is presented by colors changing from blue to red with numerical values indicated as corresponding scales.

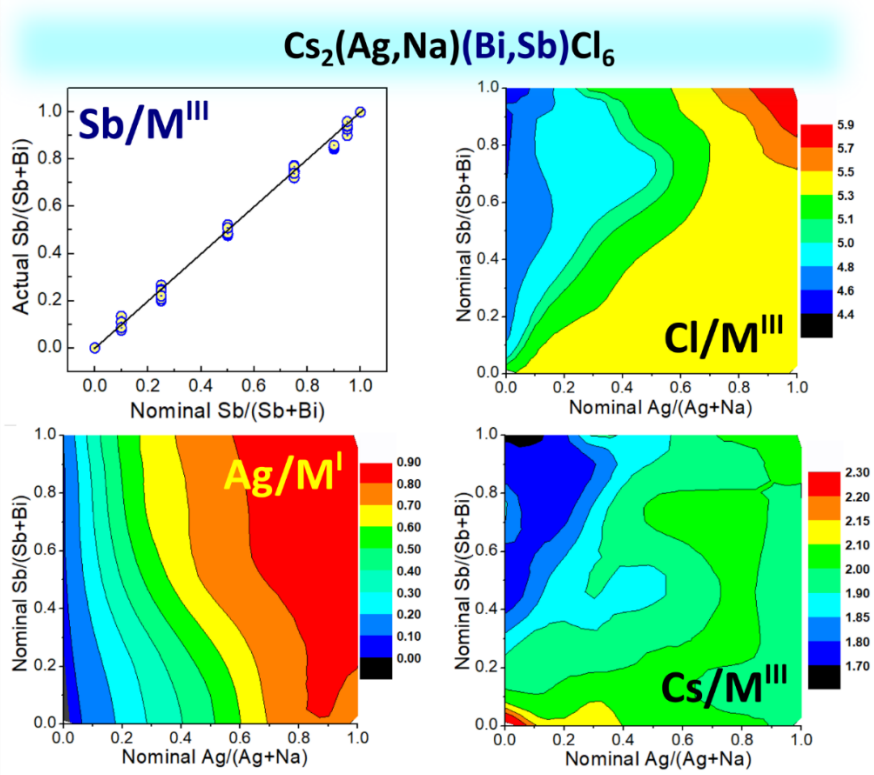

Figure S9. Summary of the EDX data for $Cs_2(Ag,Na)(Bi,Sb)Cl_6$ perovskites presented in Table S2: the relationship between actual and nominal Sb/(Sb+Bi) fraction as well as dependencies of actual Cl/M^{III}, Ag/M^{I}, and Cs/M^{III} ratios on nominal Ag and Sb ratios. M^{I} = Ag+Na, M^{III} = Sb+Bi. 2D presentations were produced by interpolating and smoothing the EDX data for 48 samples. The evolution of the Cl/M^{III}, Cs/M^{III}, and Ag/M^{III} ratios is presented by colors changing from blue to red with numerical values indicated as corresponding scales.

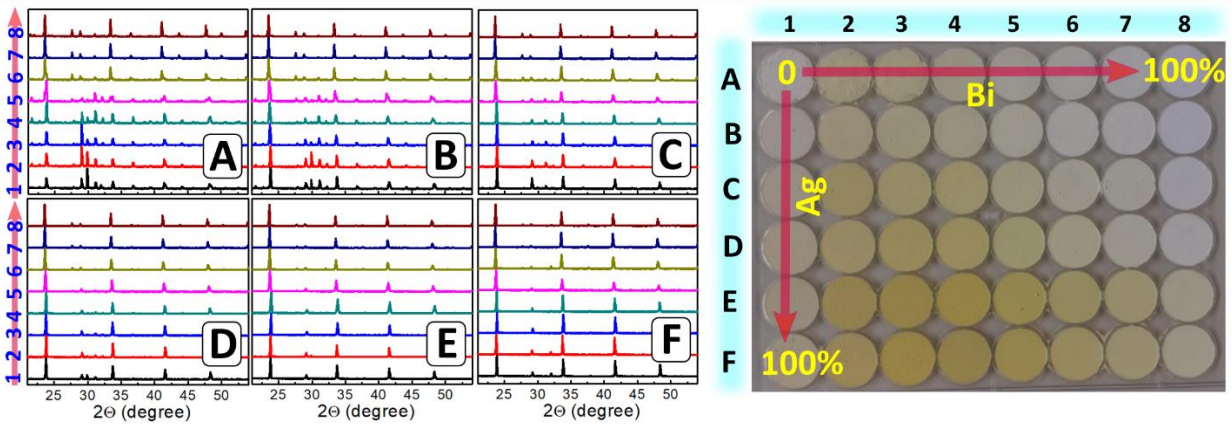

Figure S10. Collection of XRD patterns of $Cs_2(Ag,Na)(Bi,Sb)Cl_6$ perovskites.

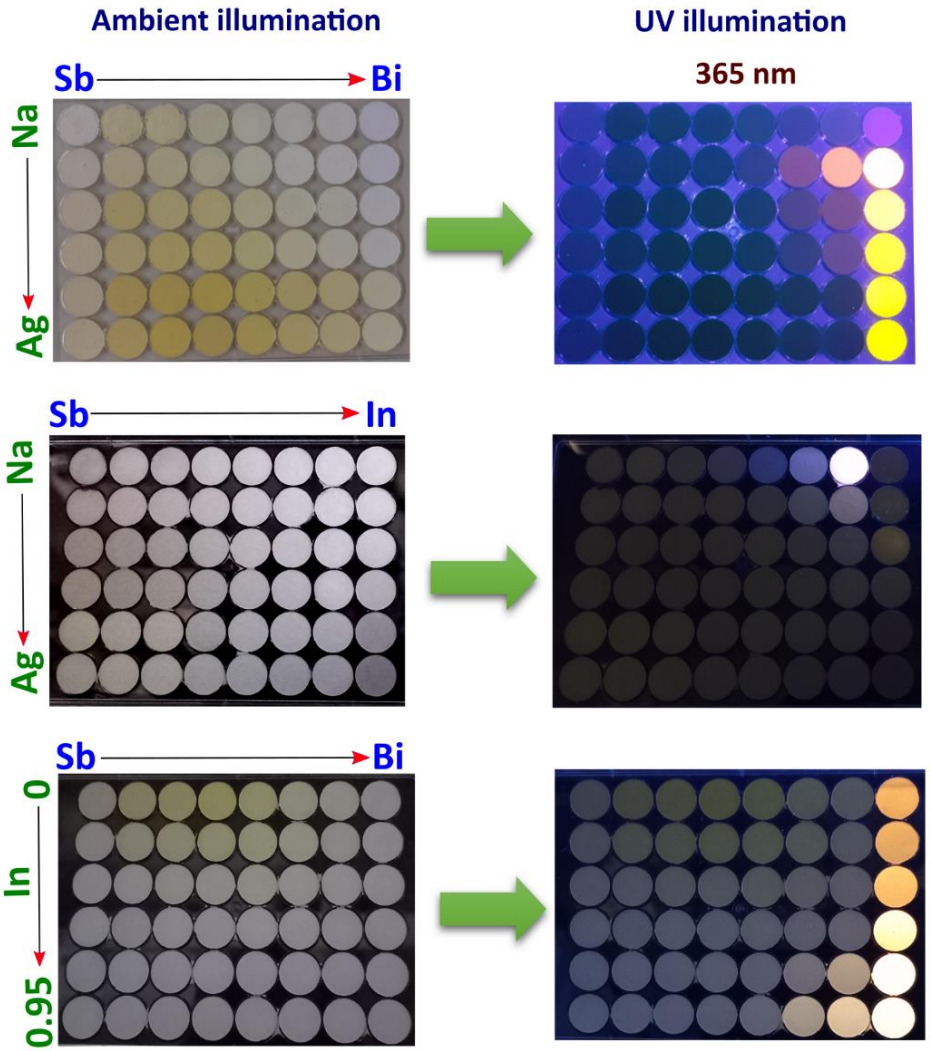

Figure S11. Photographs of $Cs_2(Ag,Na)(Bi,Sb)Cl_6$, $Cs_2(Ag,Na)(In,Sb)Cl_6$, and $Cs_2(Ag,Na)(In,Bi,Sb)Cl_6$ perovskite plates under ambient and UV llumination (365 nm).

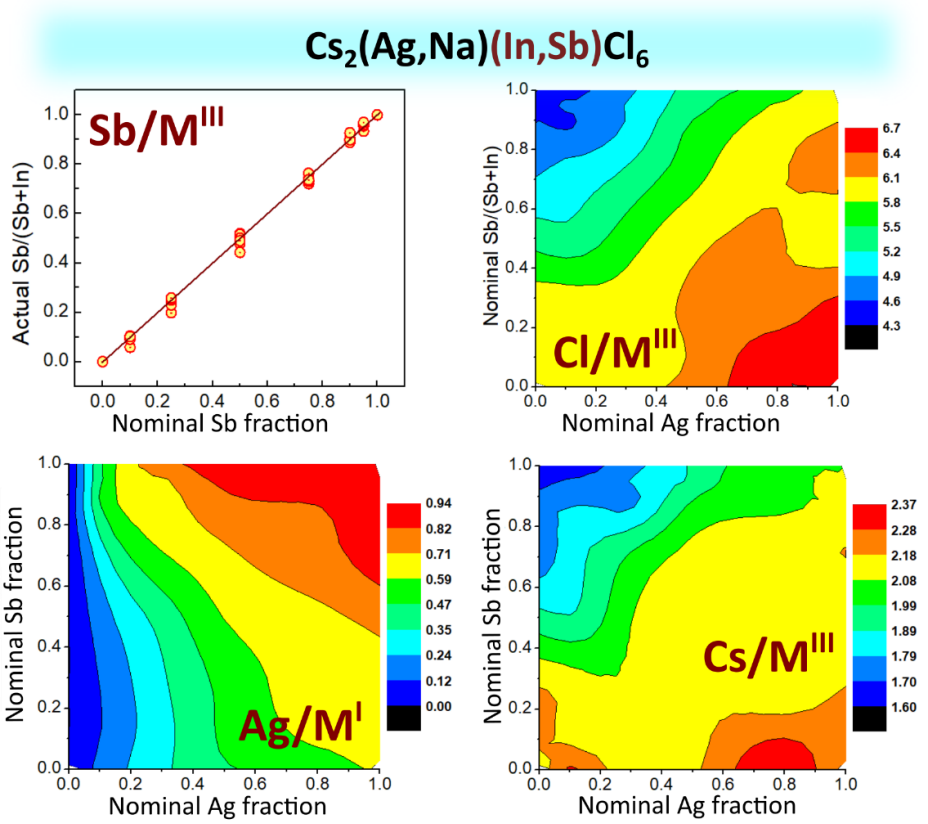

Figure S12. Summary of the EDX data for $Cs_2(Ag,Na)(In,Sb)Cl_6$ perovskites presented in Table S3: the relationship between actual and nominal Sb/(Sb+In) fraction as well as dependencies of actual Cl/M^{III}, Ag/M^{I}, and Cs/M^{III} ratios on nominal Ag and Sb ratios. M^{I} = Ag+Na, M^{III} = Sb+In. 2D presentations were produced by interpolating and smoothing the EDX data for 48 samples. The evolution of the Cl/M^{III}, Cs/M^{III}, and Ag/M^{III} ratios is presented by colors changing from blue to red with numerical values indicated as corresponding scales.

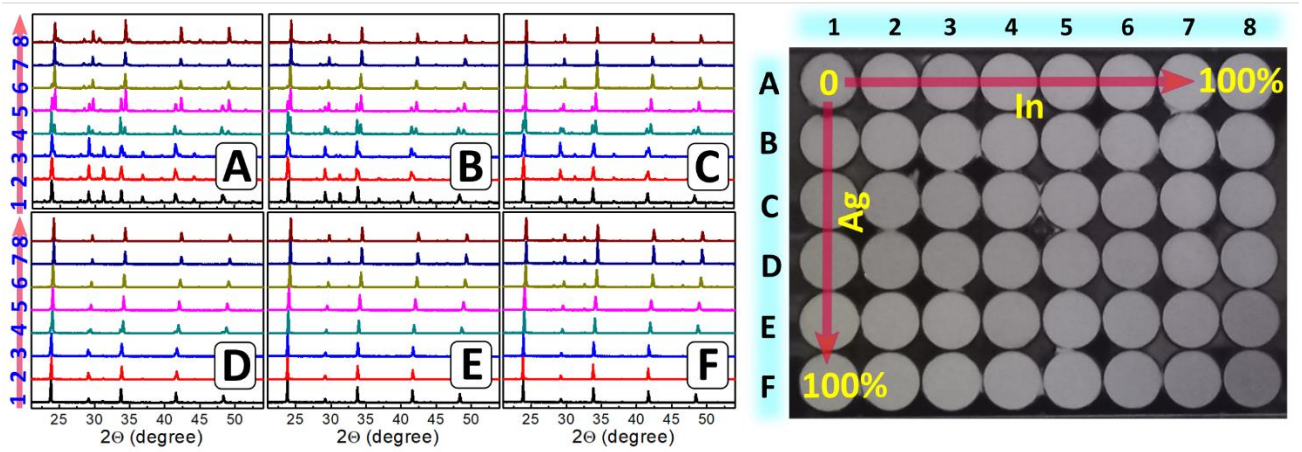

Figure S13. Collection of XRD patterns of $Cs_2(Ag,Na)(In,Sb)Cl_6$ perovskites.

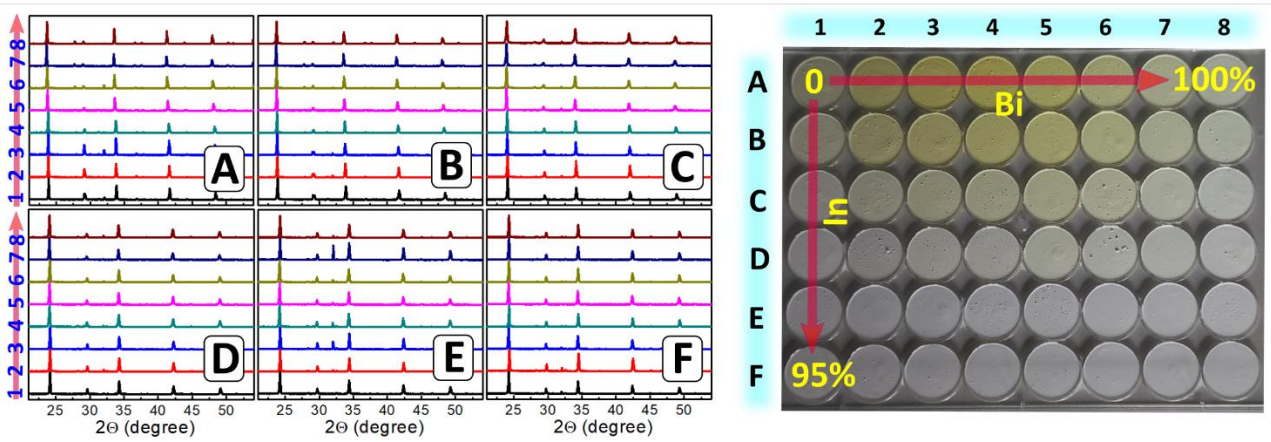

Figure S14. Collection of XRD patterns of $Cs_2(Ag,Na)(In,Bi,Sb)Cl_6$ perovskites.

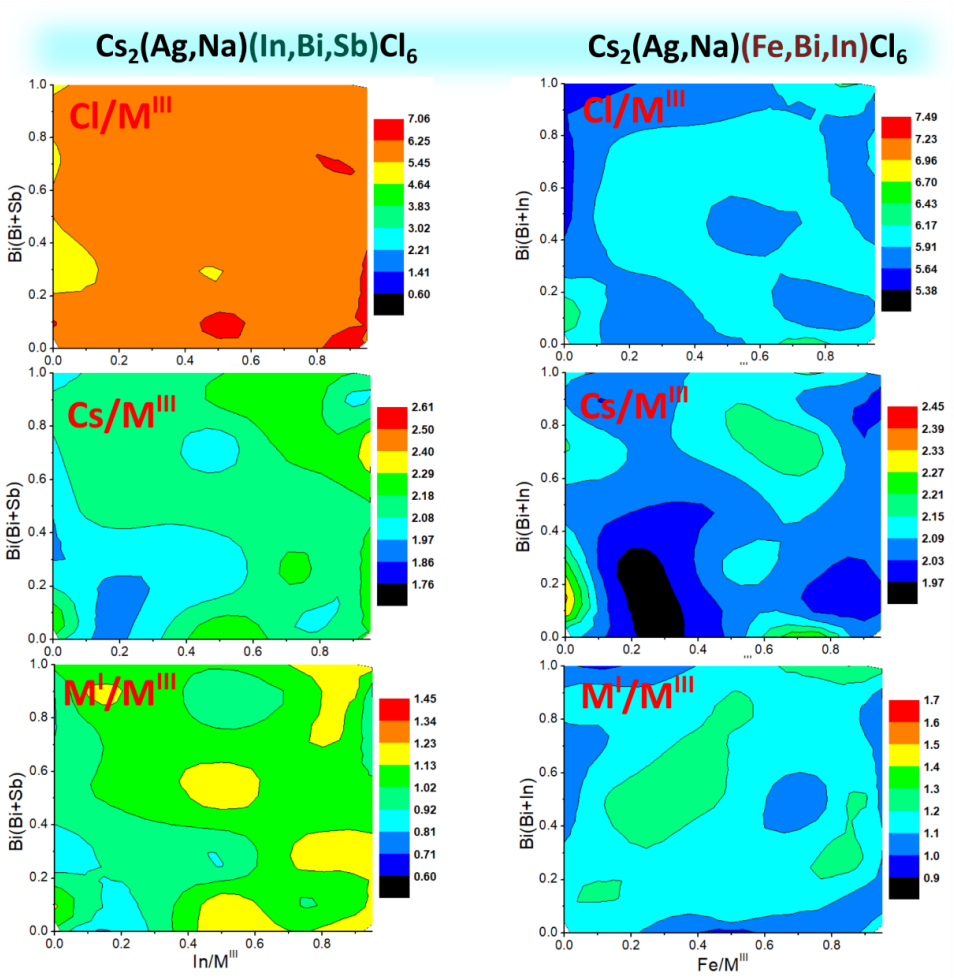

Figure S15. Summary of the EDX data for $Cs_2(Ag,Na)(In,Bi,Bi)Cl_6$ and $Cs_2(Ag,Na)(Fe,Bi,In)Cl_6$ perovskites presented in Tables S4 and S5, respectively: dependencies of actual Cl/M^{III}, Cs/M^{III}, and M^I/M^{III} ratios on nominal compositions. M^I = Ag+Na, M^{III} = In+Bi+Sb or Fe+Bi+In. 2D presentations were produced by interpolating and smoothing the EDX data for 48 samples. The evolution of the Cl/M^{III}, Cs/M^{III}, and M^I/M^{III} ratios is presented by colors changing from blue to red with numerical values indicated as corresponding scales.

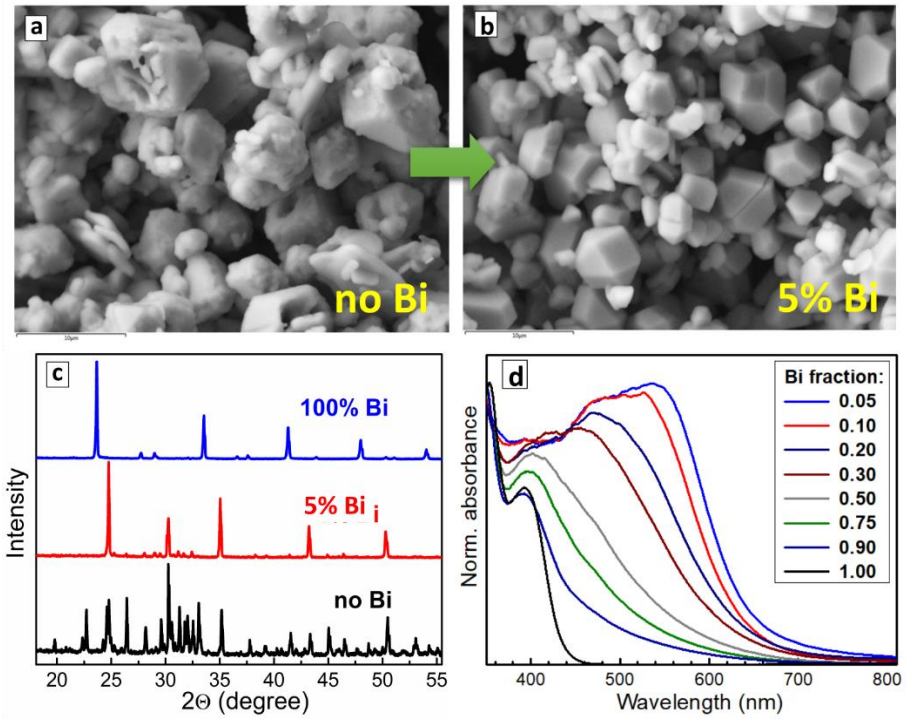

Figure S16. (a,b) SEM images of $Cs_2(Ag,Na)FeCl_6$ (a) and $Cs_2(Ag,Na)(Fe,Bi)Cl_6$, 5%Bi; (c) XRD patterns of $Cs_2(Ag,Na)FeCl_6$, $Cs_2(Ag,Na)(Fe,Bi)Cl_6$ with 5%Bi, and $Cs_2(Ag,Na)BiCl_6$; (d) Normalized absorption spectra of $Cs_2(Ag,Na)(Fe,Bi)Cl_6$ perovskites with a varied Bi content.

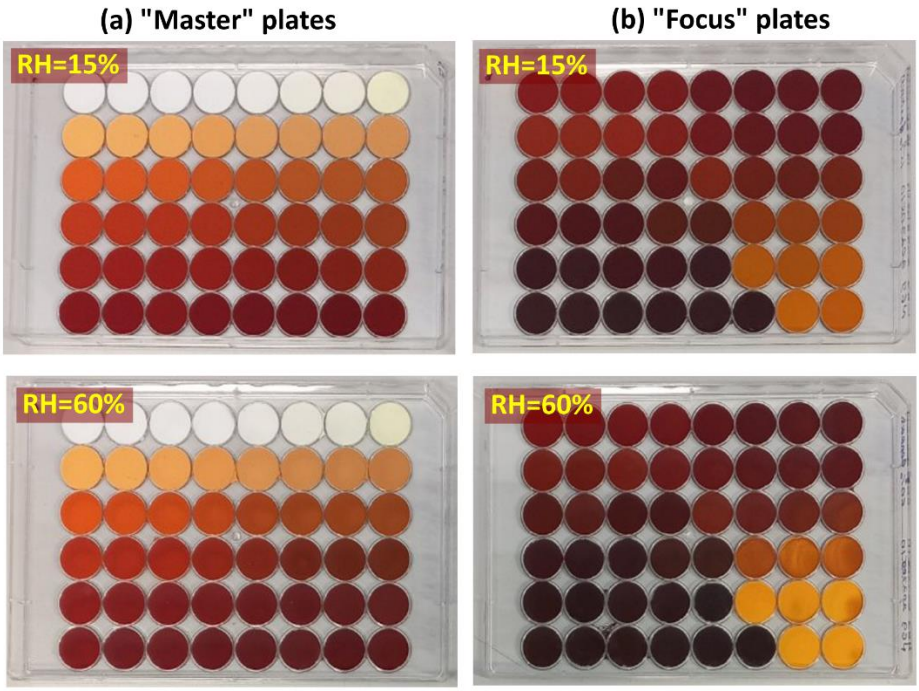

Figure S17. Photographs of $Cs_2(Ag,Na)(Fe,Bi,In)Cl_6$ "master" (a) and "focus" (b) plates produced by drop-casting and following solvent evaporation at relative humidity (RH) of 15% and 60%.

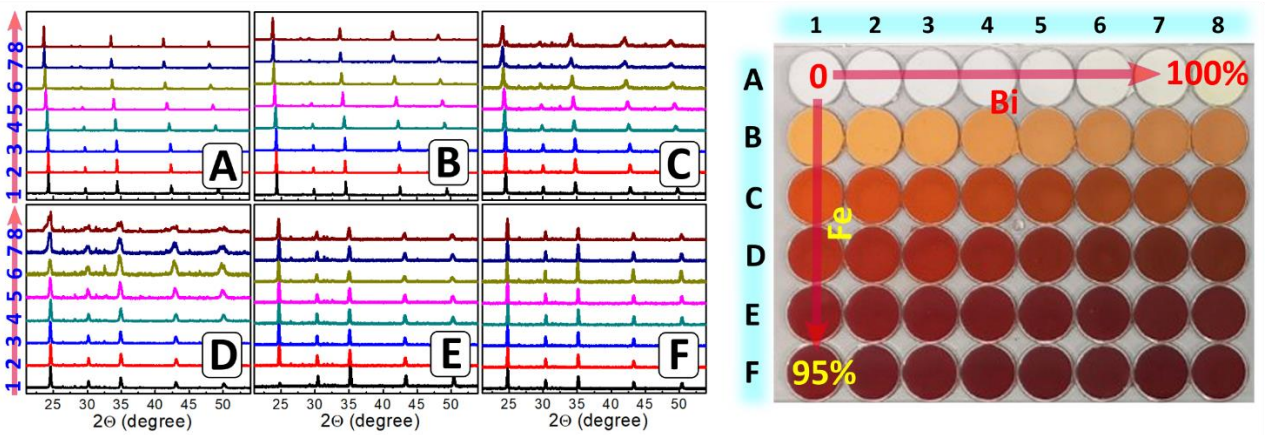

Figure S18. Collection of XRD patterns of $Cs_2(Ag,Na)(Fe,Bi,In)$ perovskites ("master" plate).

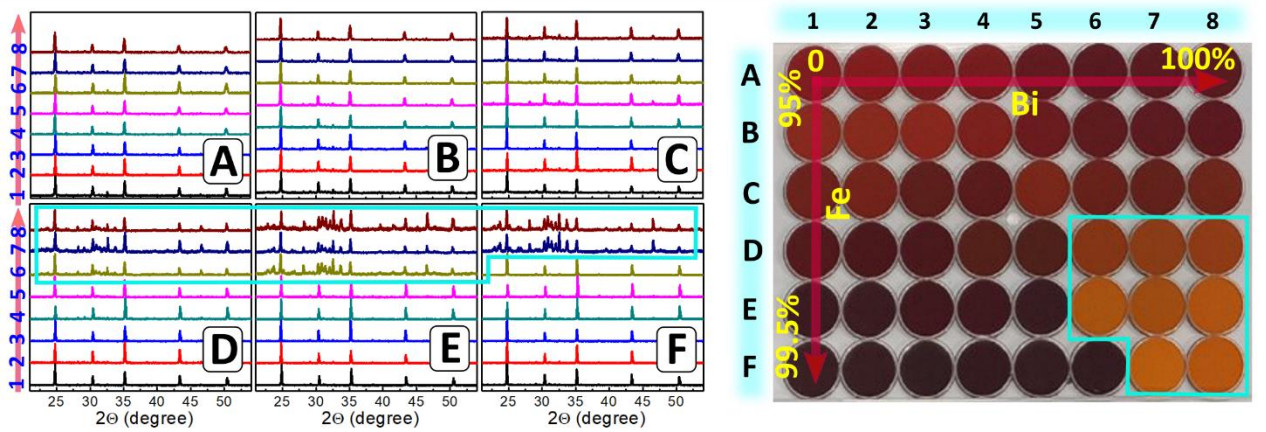

Figure S19. Collection of XRD patterns of $Cs_2(Ag,Na)(Fe,Bi,In)Cl_6$ perovskites ("master" plate).

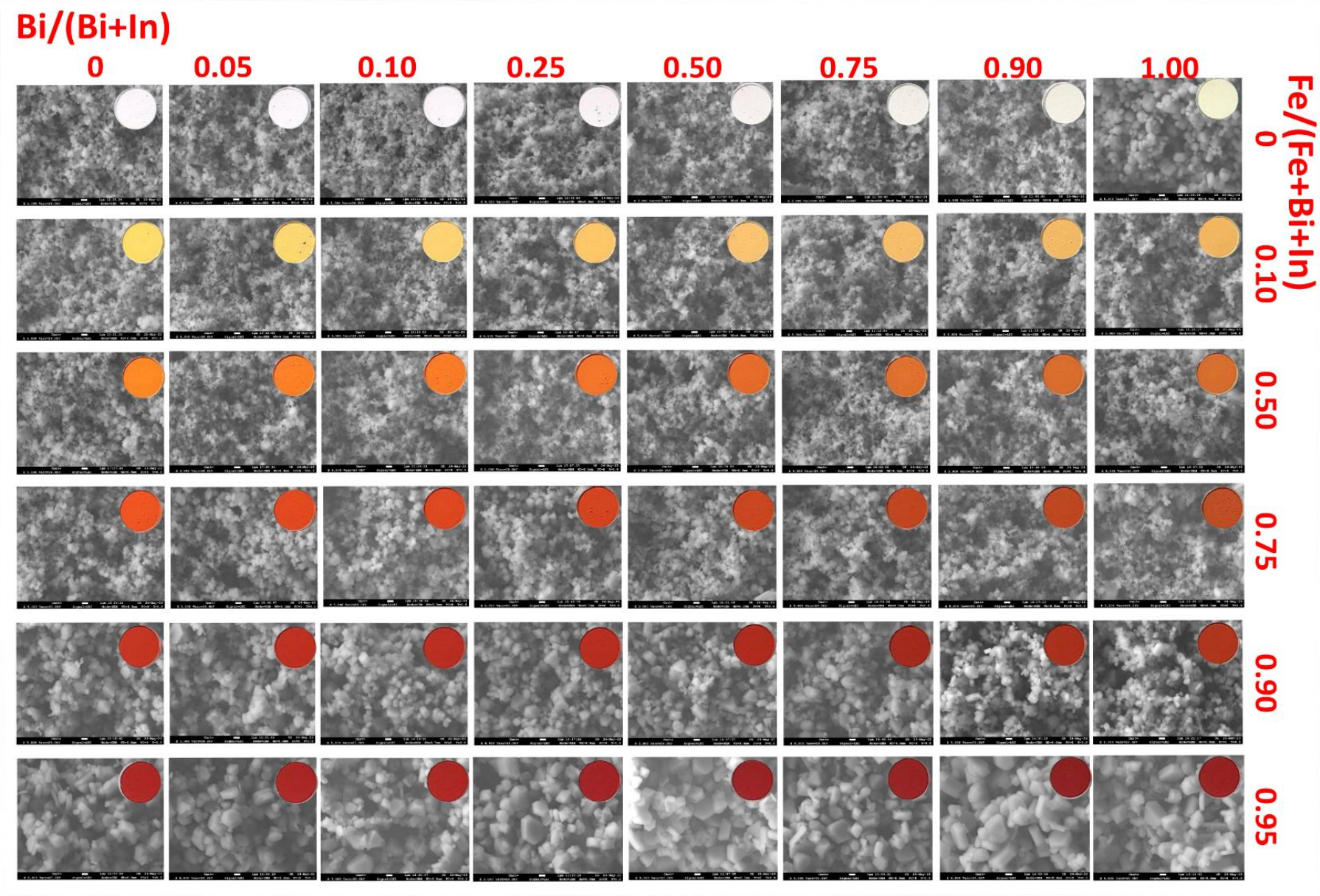

Figure S20. SEM images of $Cs_2(Ag,Na)(Fe,Bi,In)Cl_6$ perovskites. The scale bar is 1 µm.