

Supporting Information

Post-doping induced morphology evolution boosts Mn^{2+} luminescence in $\text{Cs}_2\text{NaBiCl}_6\text{:Mn}^{2+}$ phosphor

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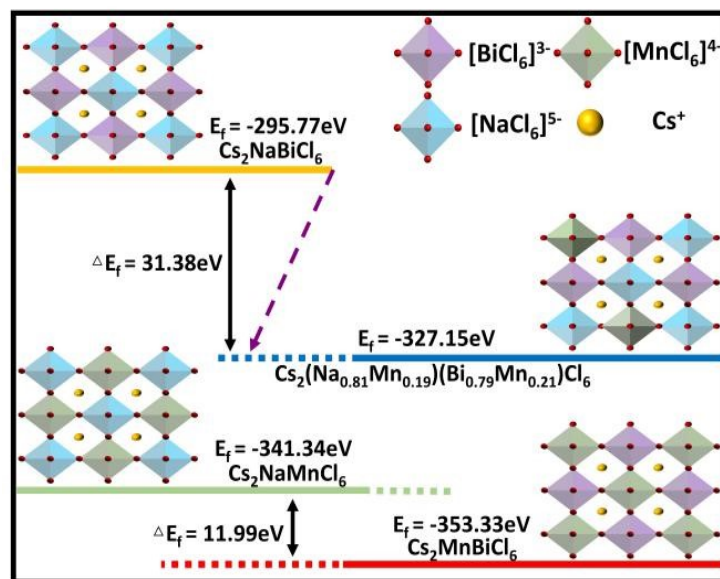


Figure S1. Scheme diagram of formation energy of $\text{Cs}_2\text{NaBiCl}_6$, $\text{Cs}_2(\text{Na}_{0.81}\text{Mn}_{0.19})(\text{Bi}_{0.79}\text{Mn}_{0.21})\text{Cl}_6$, $\text{Cs}_2\text{NaMnCl}_6$ and $\text{Cs}_2\text{MnBiCl}_6$.

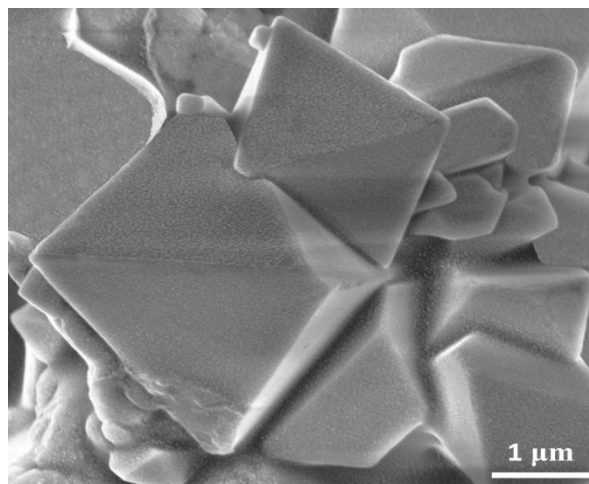


Figure S2. FE-SEM image of $\text{Cs}_2\text{NaBiCl}_6$ without Mn^{2+} doped for $60^\circ\text{C} + 10\text{min}$ stirring in the HCl .

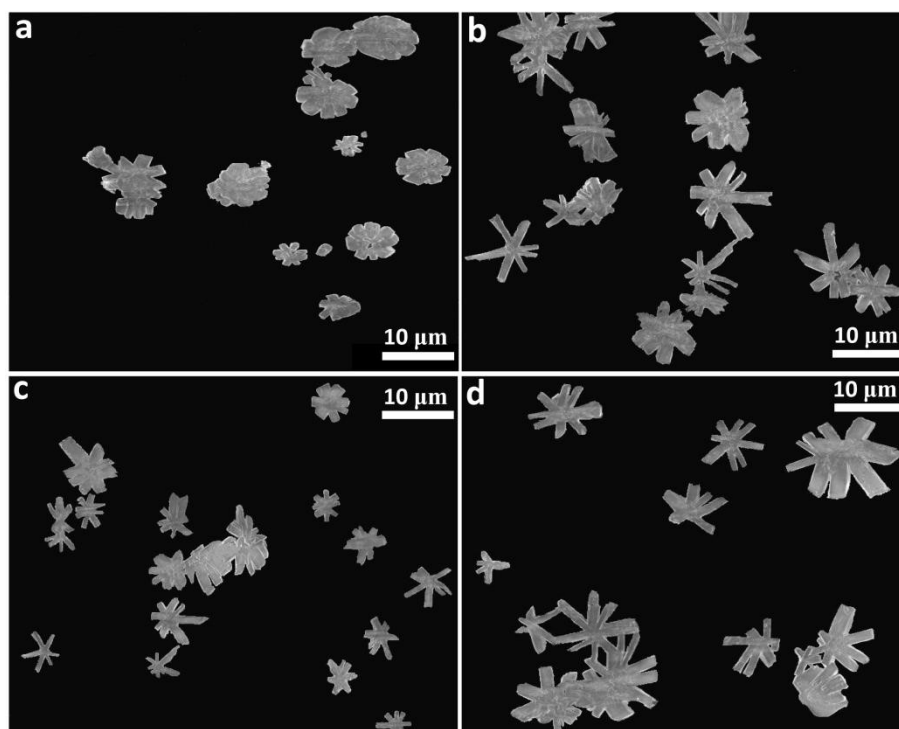


Figure S3. FE-SEM images of Mn^{2+} doped $\text{Cs}_2\text{NaBiCl}_6$ reacted at different reaction condition: a) 30°C for 10min with 0.25mol/L initial Mn^{2+} concentration. b) 50°C for 20min with 0.25mol/L initial Mn^{2+} concentration. c) 30°C for 30min with 0.35mol/L initial Mn^{2+} concentration. d) 70°C for 10min with 0.25mol/L initial Mn^{2+} concentration.

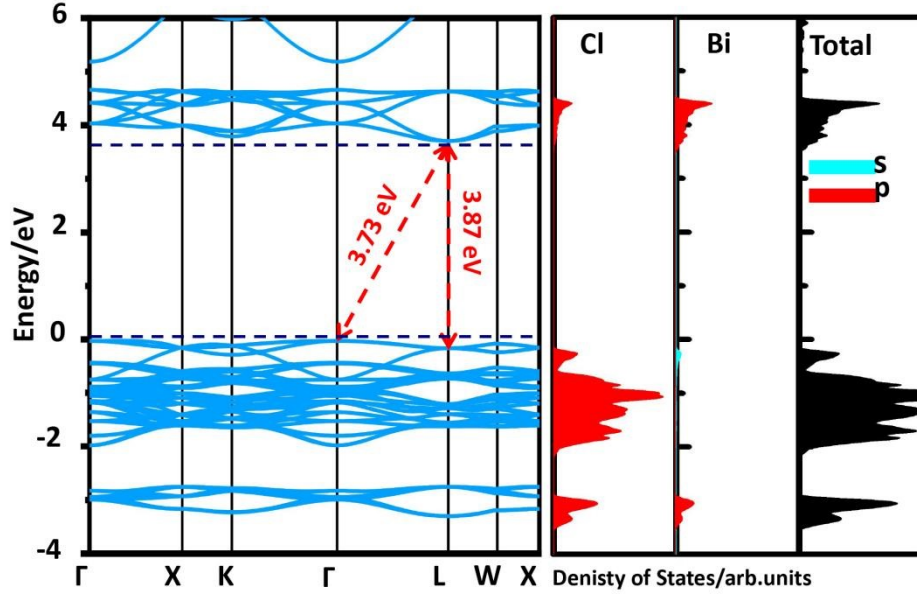


Figure S4. Calculated electronic band structures and electronic density of states (DOS) of $\text{Cs}_2\text{NaBiCl}_6$.

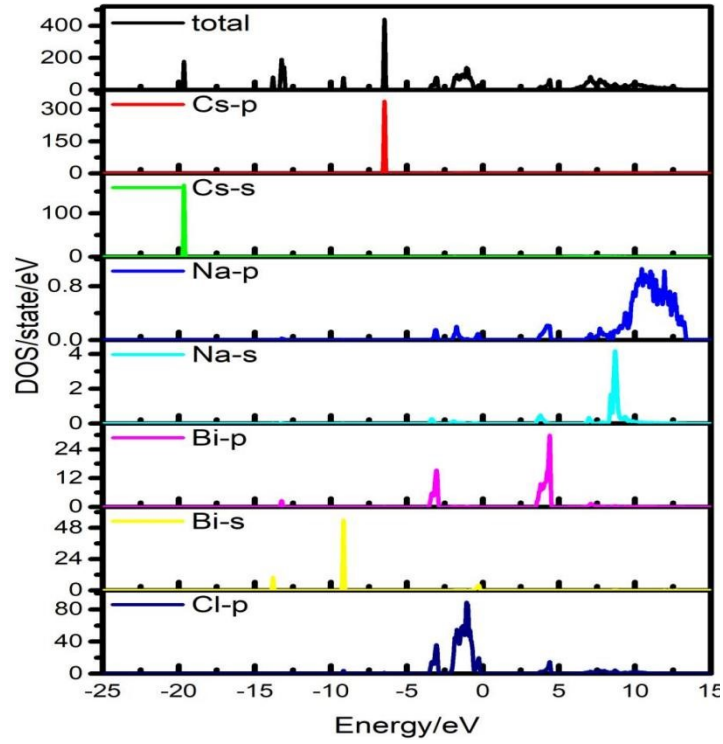


Figure S5. Calculated electronic density of states (DOS) of $\text{Cs}_2\text{NaBiCl}_6$

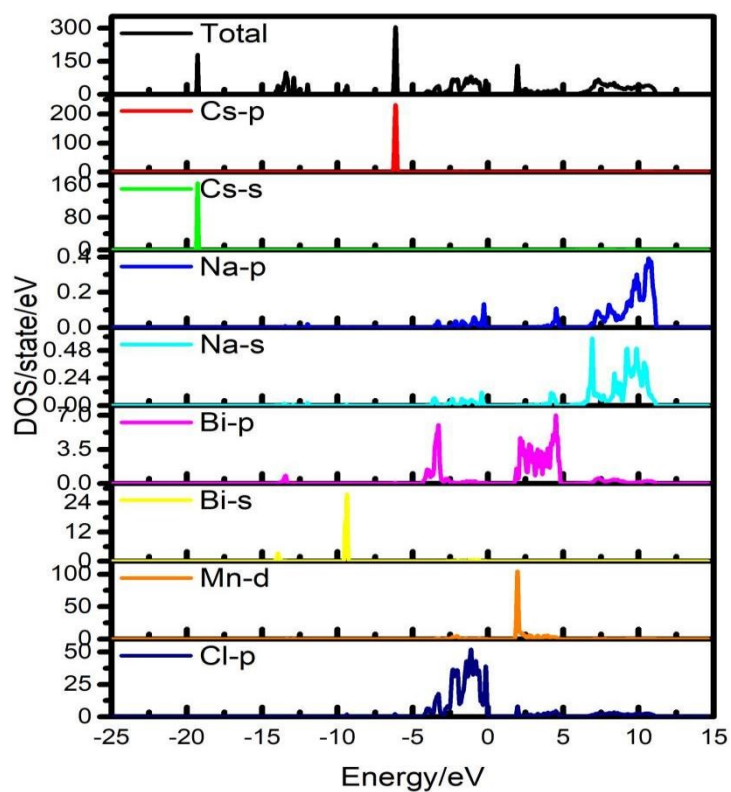


Figure S6. Calculated electronic density of states (DOS) of $\text{Cs}_2\text{Na}_{0.75}\text{Mn}_{0.25}\text{Bi}_{0.75}\text{Mn}_{0.25}\text{Cl}_6$

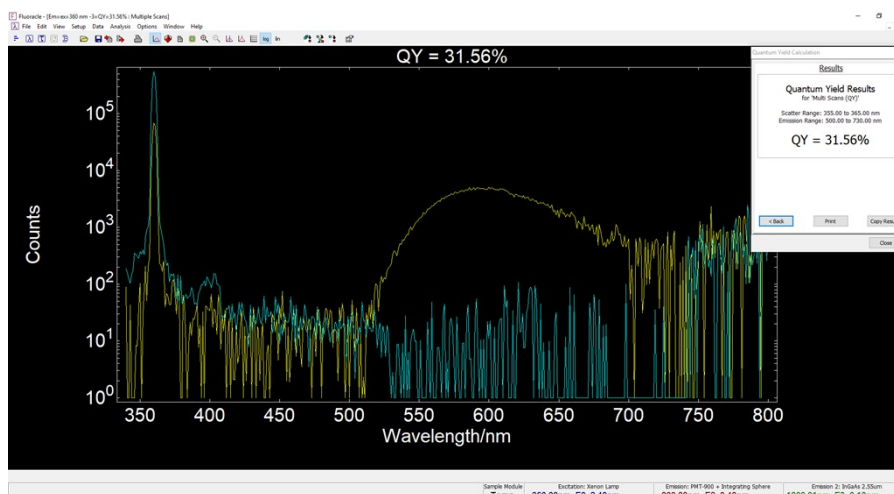


Figure S7. PLQY test results window of $\text{Cs}_2(\text{Na}_{0.81}\text{Mn}_{0.19})(\text{Bi}_{0.79}\text{Mn}_{0.21})\text{Cl}_6$.

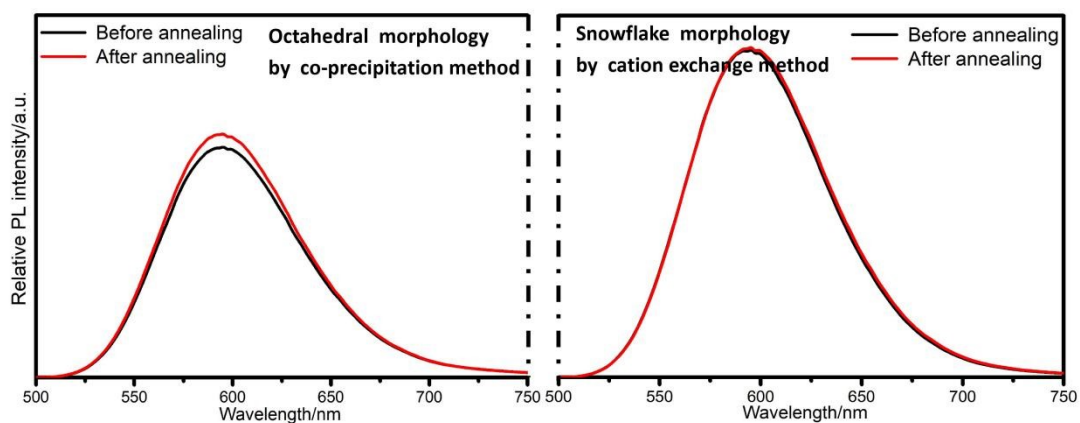


Figure S8. PL spectra of $\text{Cs}_2(\text{Na}_{0.81}\text{Mn}_{0.19})(\text{Bi}_{0.79}\text{Mn}_{0.21})\text{Cl}_6$ before and after heat treatment under 200°C for 6h

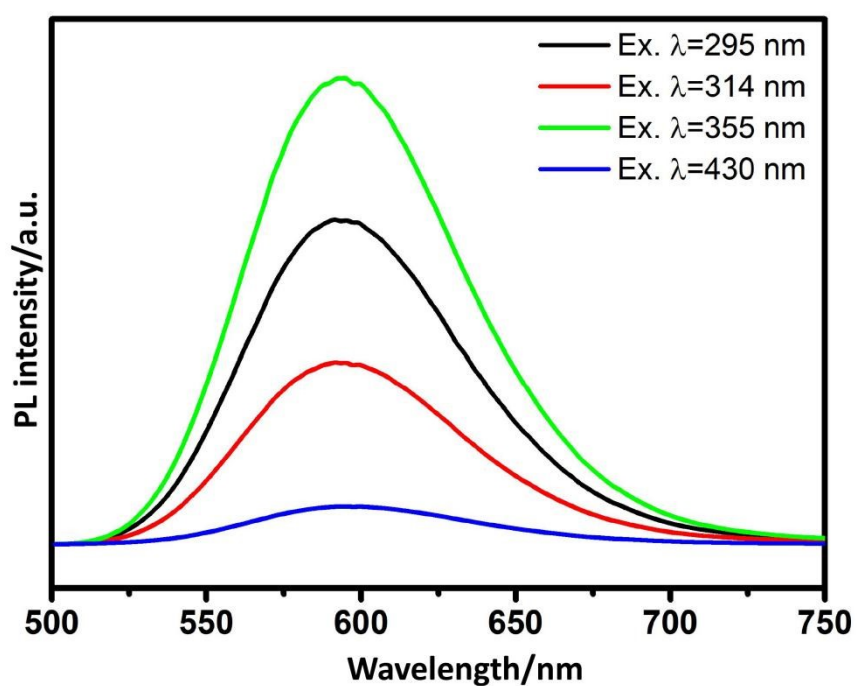


Figure S9. PL spectra of $\text{Cs}_2(\text{Na}_{0.88}\text{Mn}_{0.12})(\text{Bi}_{0.86}\text{Mn}_{0.14})\text{Cl}_6$ pumped by 295 nm, 314 nm, 355 nm and 430 nm.

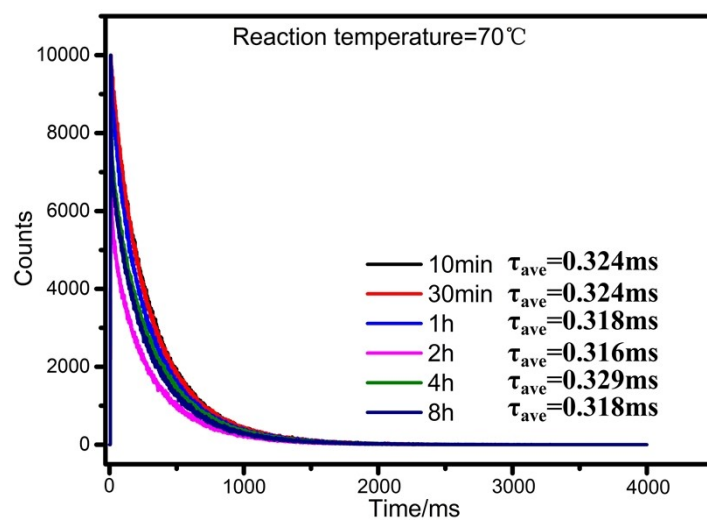


Figure S10. Room temperature decay curves under excitation at 355 nm, monitored at 592 nm.

Table. S1 Determination of $\text{Cs}_2(\text{Na}_{0.81}\text{Mn}_{0.19})(\text{Bi}_{0.79}\text{Mn}_{0.21})\text{Cl}_6$ by ICP-MS results

Reaction condition Elements	Cs (mol/L)	Na (mol/L)	Bi (mol/L)	Mn (mol/L)	Initial addition of Mn^{2+} concentration (mol/L)	η_{EX} (%)	Atomic ratio of Cs:Na:Bi:Mn
60°C for 20min	0.330	0.134	0.130	0.066	0.25	26.4	2 : 0.81 : 0.79 : 0.40

Table. S2 ICP-MS results of Mn^{2+} in different samples synthesized by various reaction conditions

No.	Synthetic method	Morphology	Temperature (°C)	Time (min)	Initial Mn^{2+} (mol/L)	Actual Mn^{2+} (mol/L)
1	co-precipitation	octahedron	70	30	0.15	0.0086
2	cation exchange	sheet	30	30	0.05	0.0086

3	cation exchange	flower-like	50	20	0.05	0.0085
4	cation exchange	snowflake	60	10	0.05	0.0086

Table. S3 ICP-MS results and calculations with various reaction temperature of Mn^{2+}
exchange for 5 min

Temperature Elements	Cs (mol/L)	Na (mol/L)	Bi (mol/L)	Mn (mol/L)	Initial addition of Mn^{2+} concentration (mol/L)	η_{EX} (%)	Atomic ratio of Cs:Na:Bi:Mn
30°C	0.399	0.190	0.178	0.0323	0.25	12.92	2 : 0.95 : 0.89 : 0.16
40°C	0.396	0.186	0.174	0.0365	0.25	14.60	2 : 0.94 : 0.88 : 0.18
50°C	0.385	0.173	0.171	0.0412	0.25	16.48	2 : 0.90 : 0.89 : 0.21
60°C	0.340	0.150	0.148	0.0432	0.25	17.28	2 : 0.88 : 0.87 : 0.25
70°C	0.348	0.153	0.150	0.0451	0.25	18.04	2 : 0.88 : 0.86 : 0.26
80°C	0.352	0.151	0.146	0.0545	0.25	21.80	2 : 0.86 : 0.83 : 0.31
90°C	0.338	0.144	0.137	0.0574	0.25	22.96	2 : 0.85 : 0.81 : 0.34

Table. S4 ICP-MS results and calculations with various reaction time of Mn^{2+}
exchange under 30°C

Mn^{2+} exchange time Elements	Cs (mol/L)	Na (mol/L)	Bi (mol/L)	Mn (mol/L)	Initial addition of Mn^{2+} concentration (mol/L)	η_{EX} (%)	Atomic ratio of Cs:Na:Bi:Mn
10min	0.395	0.186	0.178	0.0324	0.25	12.96	2 : 0.94 : 0.90 : 0.16
30min	0.391	0.172	0.170	0.0489	0.25	19.56	2 : 0.88 : 0.87 : 0.25
60min	0.371	0.161	0.156	0.0538	0.25	21.52	2 : 0.87 : 0.84 : 0.29
120min	0.323	0.132	0.128	0.0629	0.25	25.16	2 : 0.82 : 0.79 : 0.39
240min	0.303	0.120	0.117	0.0667	0.25	26.68	2 : 0.79 : 0.77 : 0.44
480min	0.306	0.121	0.119	0.0658	0.25	26.32	2 : 0.79 : 0.78 : 0.43

Table. S5 ICP-MS results and calculations with various addition concentration of Mn^{2+} under 30°C for 5 min

Addition of Mn^{2+} Elements	Cs (mol/L)	Na (mol/L)	Bi (mol/L)	Mn (mol/L)	Initial addition of Mn^{2+} concentration (mol/L)	η_{EX} (%)	Atomic ratio of Cs:Na:Bi:Mn
0.15mol/L	0.381	0.185	0.183	0.0125	0.15	8.33	2 : 0.97 : 0.96 : 0.07
0.20mol/L	0.390	0.187	0.183	0.0193	0.20	9.65	2 : 0.96 : 0.94 : 0.10
0.25mol/L	0.399	0.190	0.178	0.0323	0.25	12.92	2 : 0.95 : 0.89 : 0.16
0.30mol/L	0.470	0.216	0.207	0.047	0.30	15.67	2 : 0.92 : 0.88 : 0.20
0.35mol/L	0.50	0.223	0.218	0.060	0.35	17.14	2 : 0.89 : 0.87 : 0.24
0.40mol/L	0.521	0.230	0.219	0.073	0.40	18.25	2 : 0.88 : 0.84 : 0.28