Supporting Information

Rapid and Efficient Microwave-assisted Synthesis of Mn-doped Cesium Bromide to Phase Engineered Cesium Manganese Bromide Nanocrystals with Color-Tunable Emission

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Table S1. Optimization of reaction conditions in the MW-AT synthesis.

Sr. No.	Ratio Cs_2CO_3: $MnBr_2$	Temperature (°C)	Time (min)	Photoluminescence (PL)
1.	1:1	200	15	Blue PL, Mn^{2+}:CsBr
2.	1:1.25	200	15	Blue PL
3.	1:1.5	200	15	Blue PL
4.	1:2	180	15	No PL
5.	1:2	200	15	Green PL
6.	1:2.5	200	15	Green PL, Cs_3MnBr_5
7.	1:2	220	15	Green PL
8.	1:2	240	15	Green PL
9.	1:4	200	15	Green PL
10.	1:6	200	15	Green PL
11.	1:7	200	15	Red PL, $CsMnBr_3$
12.	1:7	220	15	Red PL
13.	1:7	240	15	Red PL
14.	1:8	200	15	Red PL
15.	1:9	200	15	Red PL

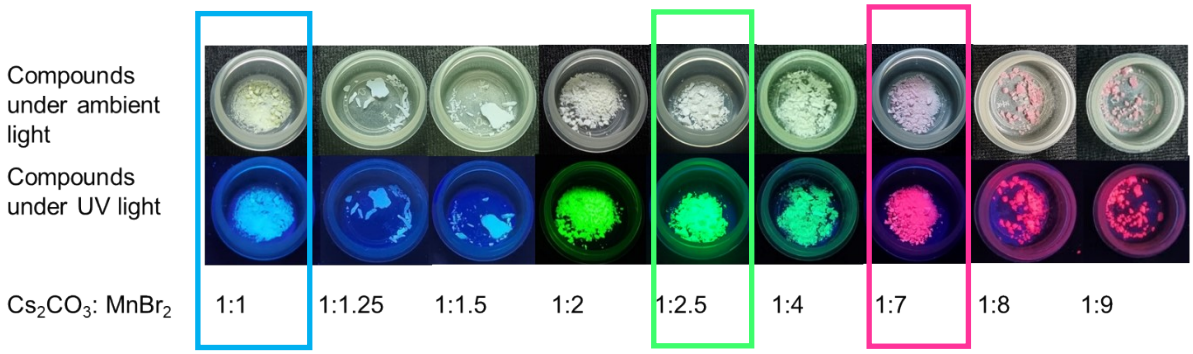


Fig. S1. Photograph of the compounds synthesised at different ratios of cesium carbonate and manganese bromide using the same reaction conditions.

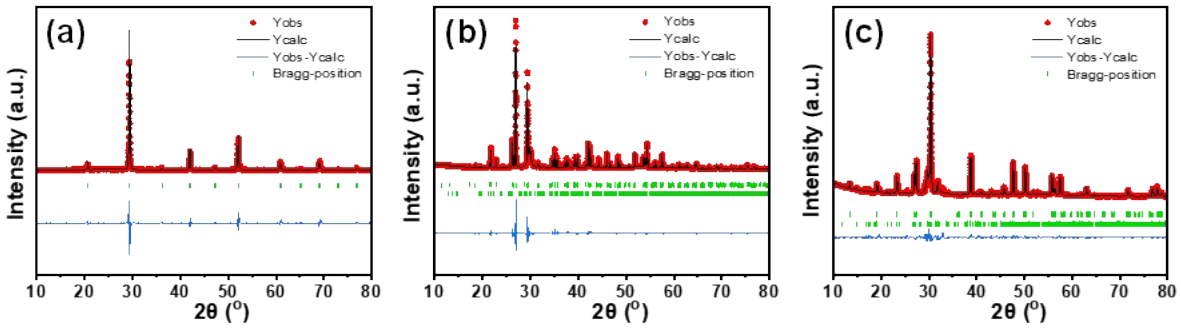


Fig. S2. Rietveld refinement of the XRD pattern of the (a) Mn^{2+}:CsBr, (b) Cs_3MnBr_5 and (c) $CsMnBr_3$.

The Rietveld refinement of the powder XRD pattern was carried out using the Fullprof suite software package. Intensities of the peaks due to Cu K-α and K-β were considered. The occupancies of the atoms were fixed to their nominal values throughout the refinement. From the refinement, it could be concluded that all the Bragg positions could be indexed and fitted with the following parameters as shown in the table below:

Table S2. Refinements parameters of all compounds.

Compounds	Mn^{2+}:CsBr	Cs_3MnBr_5		$CsMnBr_3$	
		Phase 1	Phase 2	Phase 1	Phase 2
		Cs_3MnBr_5	$Cs_2MnBr_4.2H_2O$	$CsMnBr_3$	$CsMnBr_3.2H_2O$

Space group	Pm-3m	(I 4/mcm)	P-1	P63/mmc	Pcca
Crystal system	Cubic	Tetragonal	Triclinic	Hexagonal	Orthorhombic
a	4.301 Å	9.600 Å	6.022 Å	7.629 Å	9.541 Å
b	4.301 Å	9.600 Å	7.068 Å	7.629 Å	7.478 Å
c	4.301 Å	15.572 Å	7.547 Å	6.522 Å	11.964 Å
α	90°	90°	66.1 °	90°	90°
β	90°	90°	87.8 °	90°	90°
ϒ	90°	90°	83.9 °	120°	90°
Volume	79.59	1435.42	292.09	328.78	853.72
Fraction	100 %	57.98 %	42.02 %	67.25 %	32.75 %
Bragg R-factor	11.2	4.84	4.21	2.78	8.31
RF- factor	9.84	3.24	3.24	2.93	5.81
Rp	40.4	15.1		17.4	
Rwp	38.0	16.2		16.2	
Rexp	20.43	4.05		6.13	
χ2	3.4681	15.89		6.99	

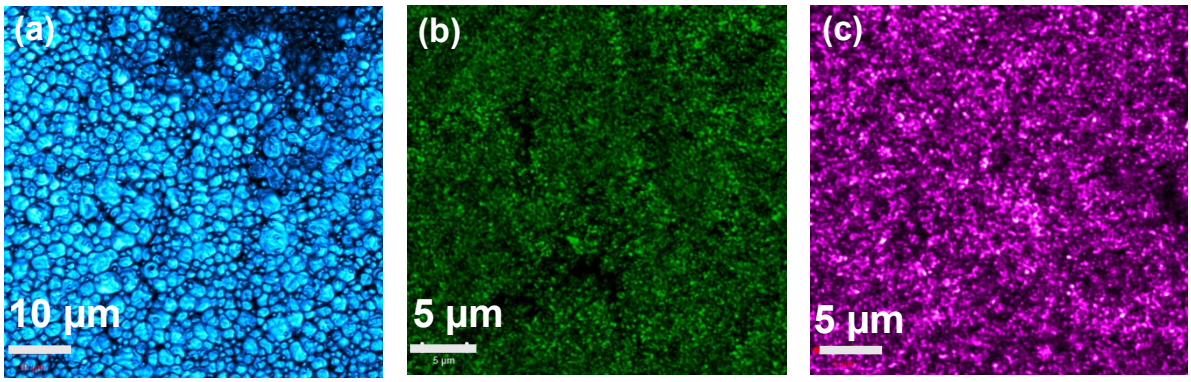


Fig. S3. Confocal microscopy reflection images of (a) Mn^{2+}:CsBr, (b) Cs_3MnBr_5 and (c) $CsMnBr_3$.

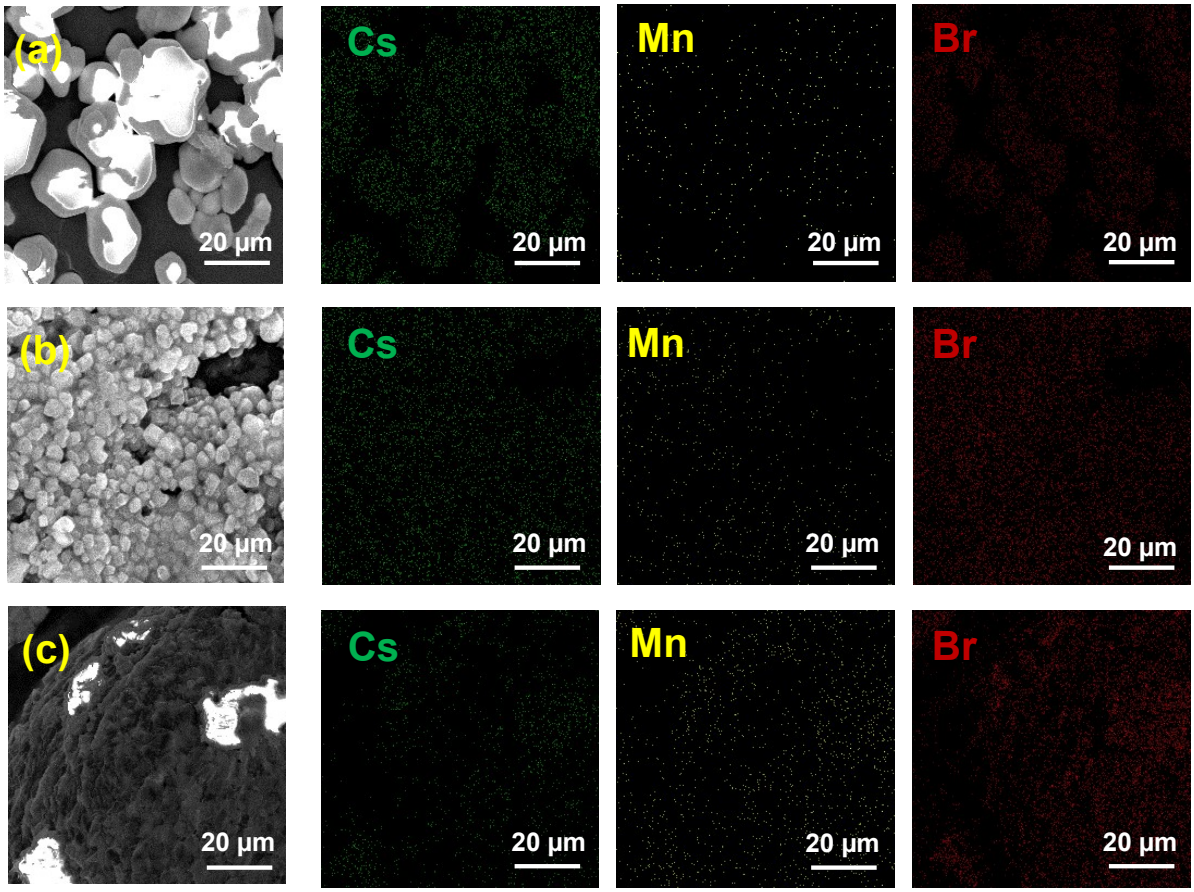
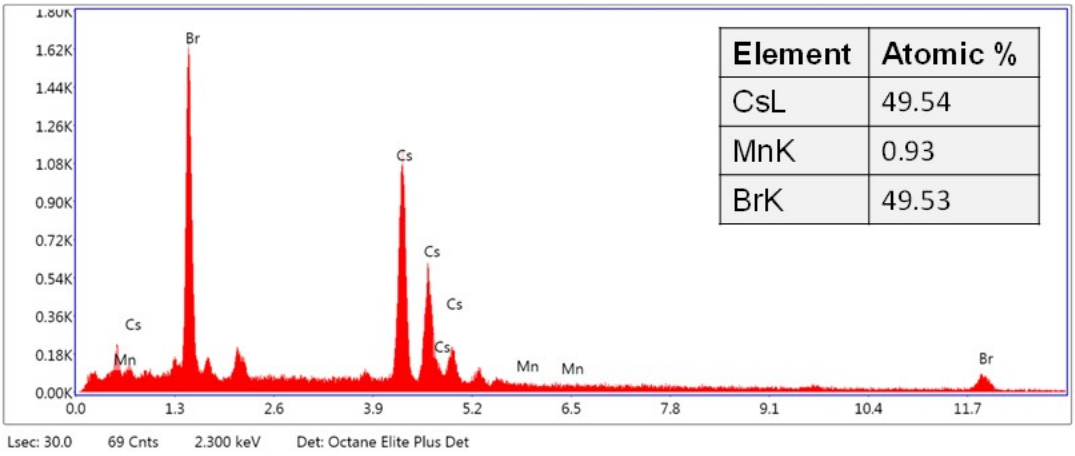


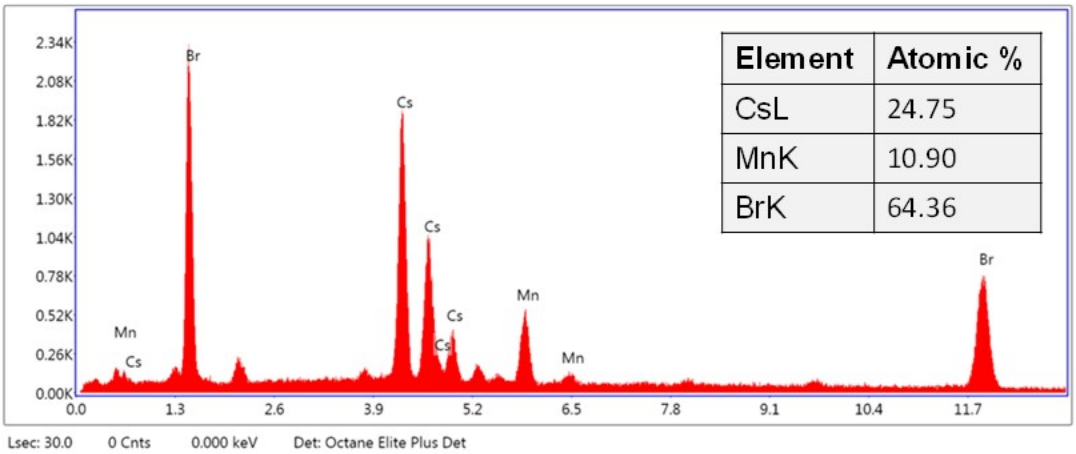
Fig. S4. FESEM image and elemental mapping of Cs, Mn and Br for the as-synthesized compounds: (a) Mn^{2+}:CsBr, (b) Cs_3MnBr_5 and (c) $CsMnBr_3$.

(a)



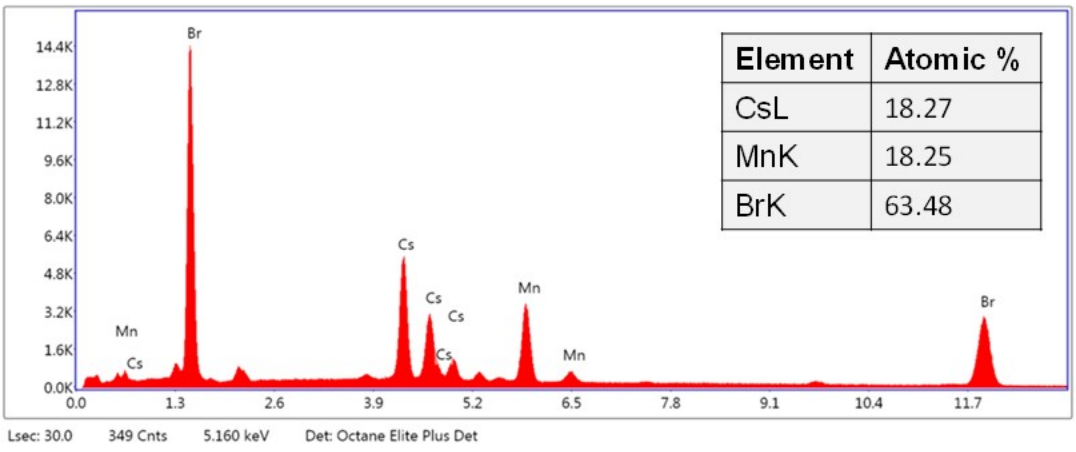
Element	Atomic %
CsL	49.54
MnK	0.93
BrK	49.53

(b)



Element	Atomic %
CsL	24.75
MnK	10.90
BrK	64.36

(c)



Element	Atomic %
CsL	18.27
MnK	18.25
BrK	63.48

Fig. S5. ESEM-EDAX and elemental atomic % of as-synthesized compounds: (a) Mn^{2+}:CsBr, (b) Cs_3MnBr_5 and (c) $CsMnBr_3$.

Table S3. XPS peak position values for the as-synthesized compounds.

Compounds	Peak position of elements (eV)					
	Cs		Mn		Br	
	$3d_{5/2}$	$3d_{3/2}$	$2p_{3/2}$ (satellite)	$2p_{1/2}$ (satellite)	$3d_{5/2}$	$3d_{3/2}$
Mn^{2+}:CsBr	724.53	738.47	641.72 (646.01)	653.29 (658.15)	68.19	69.24
Cs_3MnBr_5	725.38	739.32	642.71 (647.35)	654.18 (659.35)	69.44	70.49
$CsMnBr_3$	724.06	738.00	641.50 (645.87)	653.12 (657.83)	68.35	69.40

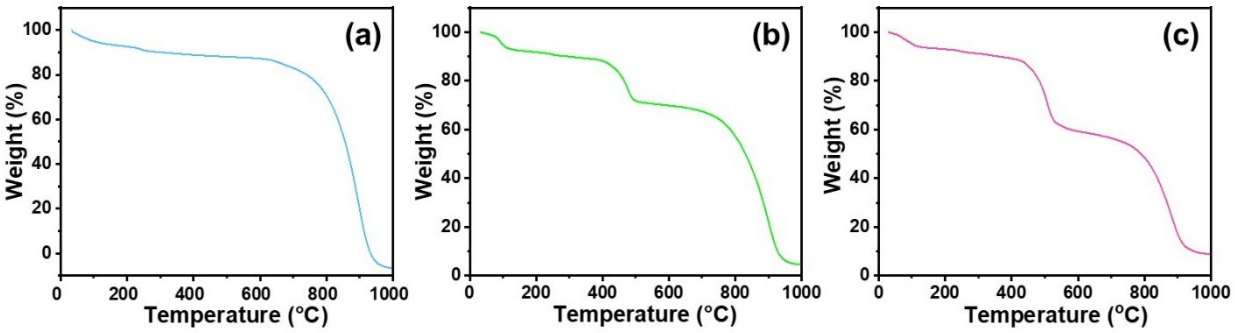


Fig. S6. TGA analysis of as-synthesized compounds: (a) Mn^{2+}:CsBr, (b) Cs_3MnBr_5 and (c) $CsMnBr_3$**.**

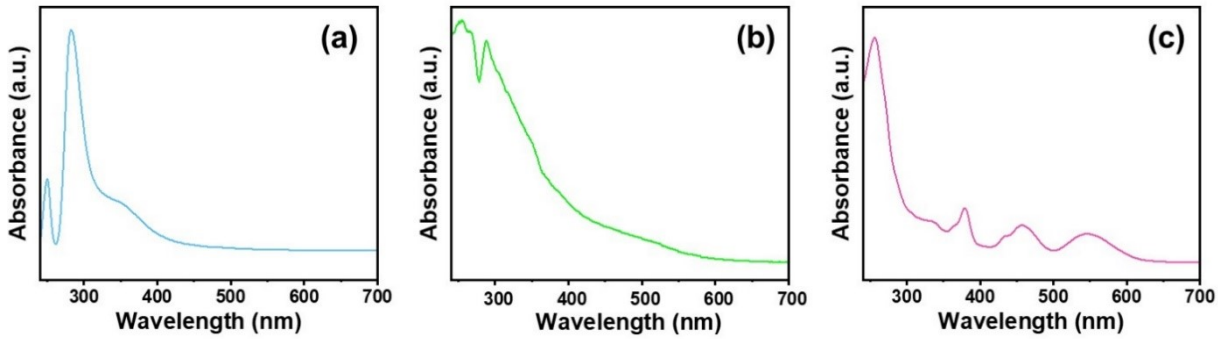


Fig. S7. UV-vis spectra of as-synthesized solid compounds: (a) Mn^{2+}:CsBr, (b) Cs_3MnBr_5 and (c) $CsMnBr_3$.

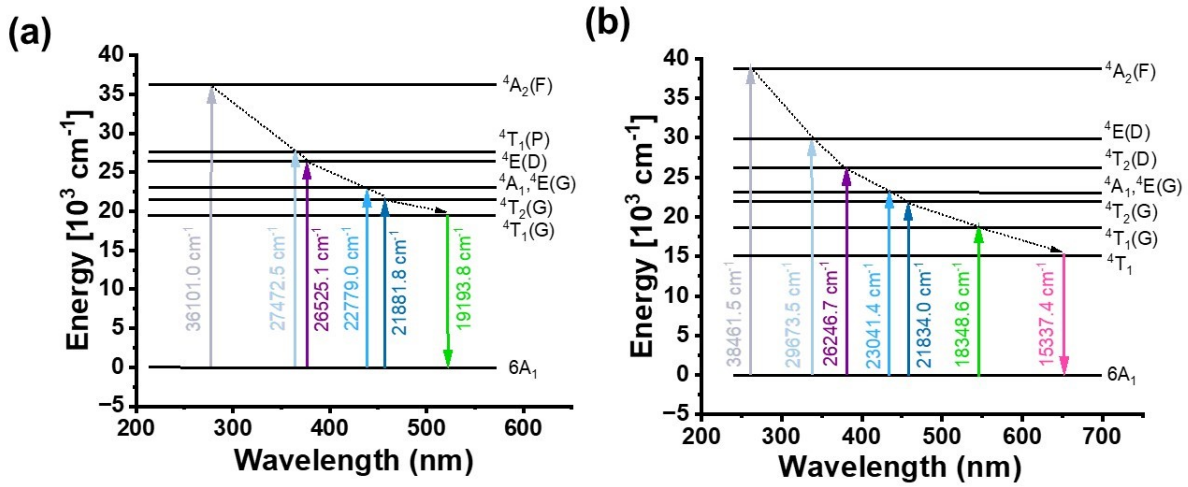


Fig. S8. Electron transition spectra of (a) Cs_3MnBr_5 and (b) $CsMnBr_3$.

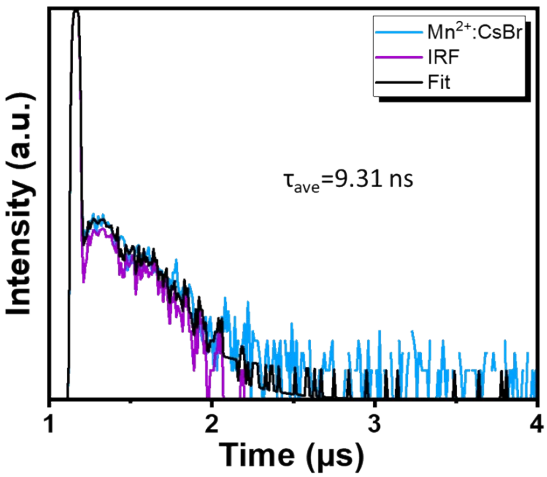


Fig. S9. Time-resolved PL decay curve: blue color represent Mn^{2+}:CsBr, purple color represents instrument response function (IRF), black color is fit curve.

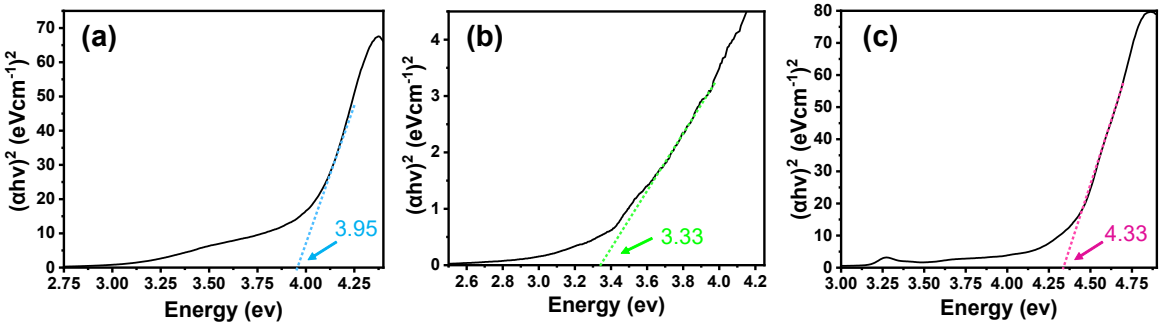


Fig. S10. Typical 'Tauc' plots for calculating optical band gaps of (a) Mn^{2+}:CsBr, (b) Cs_3MnBr_5 and (c) $CsMnBr_3$.

Table S4. Color purity of as-synthesized compounds.

Compounds	CIE coordinate of the sample emission (X, Y)	Dominant wavelength (nm)	Dominant wavelength coordinate (Xd, Yd)	CIE 1931 standard source C (*Xi, Yi*)	Color Purity (%)
Mn^{2+}:CsBr	(0.189, 0.120)	361	(0.175, 0.005)	(0.310, 0.316)	67.96
Cs_3MnBr_5	(0.198, 0.698)	521	(0.082, 0.834)		70.33
$CsMnBr_3$	(0.524, 0.281)	652	(0.727, 0.273)		51.72

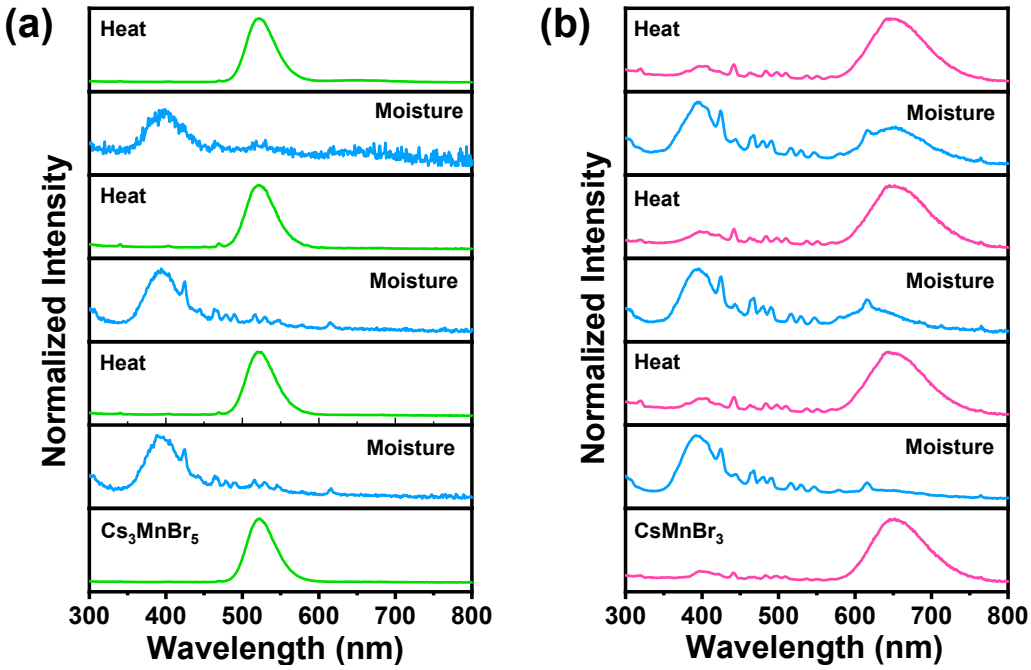


Fig. S11. PL spectra of consecutive moisture-heating process for (a) Cs_3MnBr_5 and (b) $CsMnBr_3$.

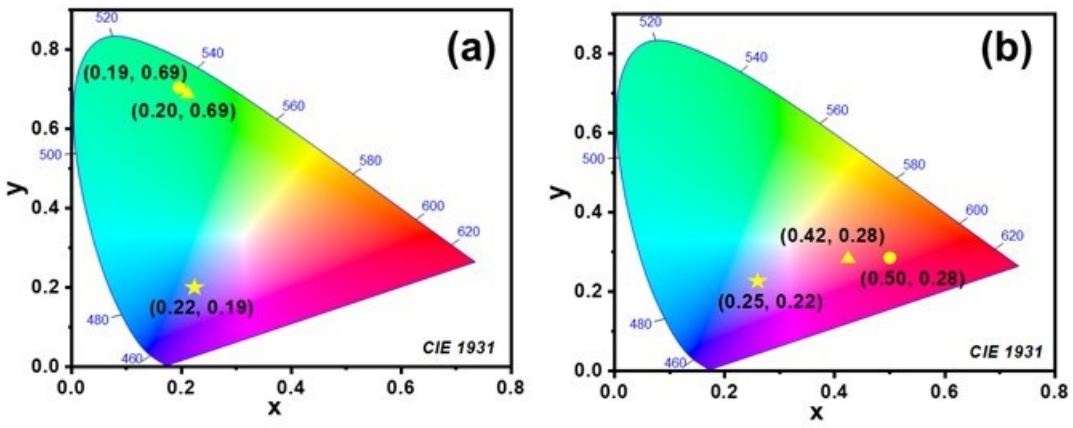


Fig. S12. CIE plots for the phase transitions of (a) Cs_3MnBr_5 and (b) $CsMnBr_3$, circle denotes as prepared, star denoted after treating in moisture, and triangle denotes after heating.

Sr. No.	Material synthesized	Lead based/ Lead free	Br sourse	Method of Synthesis, temperature (°C) & time	Excitation & emission wavelength (*as-synthesized*)	FWHM (nm)	Quantum Yield (*as-synthesized*)	Lifetime (*as-synthesized*)	Thermal stability up to (°C) (*as-synthesized*)	Reference
1.	***Mn^{2+}:CsBr***	Lead free	***$MnBr_2$***	***Microwave synthesis***, 200°C, ***15 min***	At 260 nm exc. ***Blue emission*** at 361 nm	**59**	**23.36%**	9.31 ns at 361 nm	738	This work
	Cs_3MnBr_5		-do-	-do-	At 277 nm exc. ***Green emission*** at 521 nm	**44**	**34.18%**	265.3 µs at 260 nm (fit in one component)	390	
	$CsMnBr_3$		-do-	-do-	At 260 nm exc. ***Red emission*** at 652 nm	**77**	**27.76%**	51.58 µs at 260 nm (*average life time, fit in two components*)	415 *(Air atmosphere)*	
	$Cs_2MnBr_4.2H_2O$			***Reversible phase transformation*** - Prepared by keeping Cs_3MnBr_5 or $CsMnBr_3$ in air humidity ~98-99% for ***5-10 min***	At 250 nm exc. ***Blue emission*** at 391 nm	**66**	**1.23%** * *(*prepared from Cs_3MnBr_5*)	-	-	

Table S5. Comparison of this work with previously reported literatures.

2.	Cs_3MnBr_5	Lead free	**Trimethylbromosilane** (TMSBr)	Hot injection, 200 °C, **1 hour,** under **nitrogen atmosphere**	At 280 nm exc. ***dual emission*** at 520 nm & 660 nm (***as prepared***), after treatment with isopropanol for 5.5 hours, green emission at 520 nm	43	**6%** (***as prepared***) 48% (after treatment with isopropanol)	At 520 nm Average lifetime 31.4 µs, at 660 nm 121.06 µs	-	(1)
	$CsMnBr_3$		-do-	-do-	At 260 nm exc. red emission at 660 nm	91	11%	133.6 µs	-	
	$Cs_2MnBr_4.2H_2O$			***Irreversible phase transformation***** - Prepared by keeping Cs_3MnBr_5 or $CsMnBr_3$ in air humidity of 99% for ***several hours*** ** $Cs_2MnBr_4{\cdot}2H_2O$ phase transformed into the mixture of $CsMnBr_3$ and Cs_3MnBr_5 phase, during the dehydration step	Blue emission at 440 nm	81	0.47% (from $CsMnBr_3$) 1.29 % (prepared from Cs_3MnBr_5)	1.51 ns	-	
3.	Cs_3MnBr_5	Lead free	Trimethylbromosilane (TMSBr)	One-pot sonication method at room temperature	Green emission at 522 nm	-	82 ± 5 %	236 µs	425 °C *(air atmosphere)*	(2)
	$CsMnBr_3$				Red emission at 655 nm		11%	9.546 µs		
4.	$CsMnBr_3$	Lead free	benzoyl bromide	Colloidal hot-injection method, 170 °C, 4-5 hours under nitrogen atmosphere	Red emission at 643 nm	78	54% (nanocrystal) 6.7% (single crystal)	600 ps (nanocrystal) 550 ps (single crystal)	590 °C	(3)

5.	$CsMnBr_3$ $CsMnBr_3$: Pb doped $CsMnBr_3$: Sb doped	Lead free Lead based Lead free	Trimethylbromosilane (TMSBr)	Modified hot injection method, 90°C to completely dissolved the precursors then adjusted 25-100 °C	Pink emission at 666 nm Red emission at 663 nm Red emission at 656 nm	74 76 74	3.67% 41.5% 15.8%	273.8µs 180.6 µs 306.3 µs	-	(4)
6.	Cs_3MnBr_5 $CsMnBr_3$	Lead free	benzoyl bromide	Hot injection, degassed at room temp for 30 min then increased up to 210 °C to make clear solution under nitrogen atmosphere	Green emission at 522 nm Red emission at 661 nm	-	33 ± 4 % 33 ± 4 %	170 µs 235 µs	-	(5)
7.	Cs_3MnBr_5	Lead free	$MnBr_2$	evaporative crystallization (evaporative heating of a 200 nm syringe-filtered solution at 150 °C for 2 hours)	Green emission at 520 nm	38	66.3%	0.34 ms	-	(6)
8.	$CsMnX_3$ (X = Cl, Br, and I) embedded glass samples	Lead free	Sodium bromide	High temperature solid-state chemistry method; at 1150 °C for 15 min	Red emission at 649 nm	130	65.1%	6.37 µs (average)	-	(7)
9.	Cs_3MnBr_5	Lead free	$MnBr_2$	high-energy ball milling at air atmosphere conditions	Green emission at 520 nm	44	11.4%	101.1 µs (average)	-	(8)

10.	Cs_3MnBr_5 $CsMnBr_3$	Lead free	$MnBr_2$	Water-based solution method. 100°C, 1 hour	Green emission at 514 nm Red emission at 651 nm	40 65	82% 20.3%	245 ms 193 ms	-	(9)
11.	Cs_3MnBr_5 Zn^{2+}doped Cs_3MnBr_5	Lead free	HBr	Evaporative crystallization method	Green emission at 520 nm	42 -	49%	0.29 ms 0.30 ms	-	(10)
12.	$CsPbX_3$ (X = Cl, Br, I)	Lead based	PbX_2 (X = Cl, Br, I)	Microwave, 160°C, 5 min	410 nm - 694 nm (by changing the anion concentration)	17	75% (nanocubes)	-	-	(11)

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