Supporting Information

Lanthanide Doping Enabled Multimodal Luminescence in Layered Lead-free Double Perovskite $Cs_4MnBi_2Cl_{12}$

Jingyu Li[1], Jiawen Xiao[1,], Taifeng Lin[2], Zheng-Guang Yan[1], Xiaodong Han[1]*

[1]Institute of Microstructure and Property of Advanced Materials, Beijing Key Lab of Microstructure and Property of Advanced Materials, Faculty of Materials and Manufacturing, Beijing University of Technology, Beijing 100124, China

E-mail: xiaojw@bjut.edu.cn

[2]Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, China

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Table S1. Crystal date and structure refinement result for $Cs_4MnBi_2Cl_{12}$.

	$Cs_4MnBi_2Cl_{12}$	10% Yb
Space group	$R\bar{3}m$	$R\bar{3}m$
Crystal system	trigonal	trigonal
a(Å)	7.5426	7.5403
b(Å)	7.5426	7.5403
c(Å)	36.9150	36.9205
α(deg)	90.0000	90.0000
β(deg)	90.0000	90.0000
γ(deg)	120.0000	120.0000

Table S2.

(a) Atomic coordinates and atomic occupancies of $Cs_4MnBi_2Cl_{12}$ at room temperature.

Atom	X	Y	Z	Occupancy
Bi3	0.66670	0.33330	0.58069	0.16667
Cs4	0.33330	0.66670	0.54168	0.16667
Cs5	1.00000	1.00000	0.62477	0.16667
Cl7	0.82925	0.65850	0.54189	0.50000
Cl9	0.49142	0.50858	0.62691	0.50000
Mn1	0.33330	0.66670	0.66670	0.08333

(b) Atomic coordinates and atomic occupancies of 10% Yb doped $Cs_4MnBi_2Cl_{12}$ at room temperature.

Atom	X	Y	Z	Occupancy
Bi3	0.66670	0.33330	0.57876	0.15416
Cs4	0.33330	0.66670	0.53937	0.16667
Cs5	1.00000	1.00000	0.62512	0.16667
Cl7	0.83092	0.66184	0.53768	0.50000
Cl9	0.49142	0.50858	0.62691	0.50000
Mn1	0.33330	0.66670	0.66670	0.00812
Yb (Bi)	0.66670	0.33330	0.57876	0.01250
Yb (Mn)	0.33330	0.66670	0.66670	0.00021

Table S3. Comparisons of dopant concentrations obtained from ICP-AES analysis of the Yb^{3+} doped, Er^{3+} doped and Yb^{3+}-Er^{3+} co-doped $Cs_4MnBi_2Cl_{12}$ products.

	10% Yb	20% Yb	20% Er	20% Yb 2% Er
Mn: Bi+Ln [moral ratio]	0.44	0.48	0.4	0.46
Bi: Bi+Ln [moral ratio]	0.90	0.81	0.71	0.75
Er: Bi+Ln [moral ratio]	0	0	0.29	0.03
Yb: Bi+Ln [moral ratio]	0.10	0.19	0	0.22

Table S4. PLQYs data of Yb^{3+} doped $Cs_4MnBi_2Cl_{12}$ product.

	$Cs_4MnBi_2Cl_{12}$	5%Yb	10%Yb	20%Yb
PLQYs	1.52%	0.95%	1.41%	1.13%

Table S5. The detailed material ratio of Er^{3+} doped $Cs_4MnBi_2Cl_{12}$.

	5%Er	10% Er	20% Er
Bi_2O_3 [mmol]	0.95	0.90	0.80
Er_2O_3 [mmol]	0.05	0.10	0.20
$MnCl_2$ [mmol]	1.00	1.00	1.00
CsCl [mmol]	4.00	4.00	4.00
HCl [mL]	10	10	10

Table S6. The detailed material ratio of Yb^{3+} doped $Cs_4MnBi_2Cl_{12}$

	5%Yb	10%Yb	20%Yb
Bi_2O_3 [mmol]	0.95	0.90	0.80
Yb_2O_3 [mmol]	0.05	0.10	0.20
$MnCl_2$ [mmol]	1.00	1.00	1.00
CsCl [mmol]	4.00	4.00	4.00
HCl [mL]	10	10	10

Table S7. The detailed material ratio of Er^{3+} and Yb^{3+} doped $Cs_4MnBi_2Cl_{12}$

	10% Yb 1% Er	20% Yb 2% Er
Bi_2O_3 [mmol]	0.89	0.78
Yb_2O_3[mmol]	0.10	0.20
Er_2O_3 [mmol]	0.01	0.02
$MnCl_2$[mmol]	1.00	1.00
CsCl [mmol]	4.00	4.00
HCl [mL]	10	10

Figure S1. Scanning electron microscopy (SEM) results of dosages of undoped a), 5% b) and 10% c) Yb^{3+} doped $Cs_4MnBi_2Cl_{12}$ powder. The grain size of them is all in the order of micrometers.

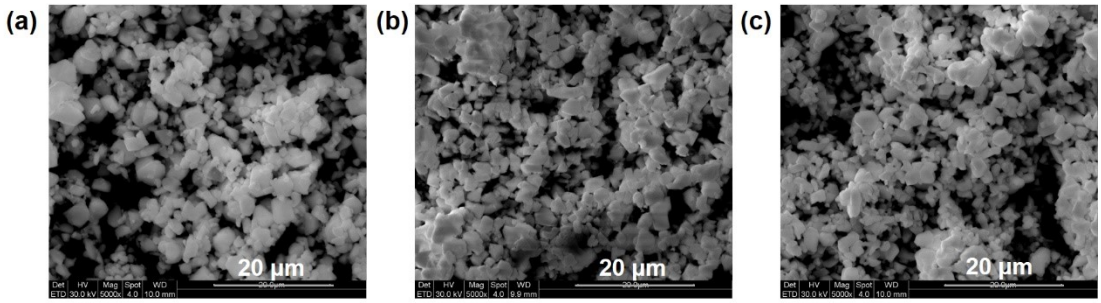


Figure S2. The XRD related Rietveld refinement results patterns of 10% Yb^{3+} doped $Cs_4MnBi_2Cl_{12}$ powder. Crosses represent the measured results, black lines are refinement results, blue lines are the difference profile between measured and refinement results, green vertical lines represent the standard diffractions.

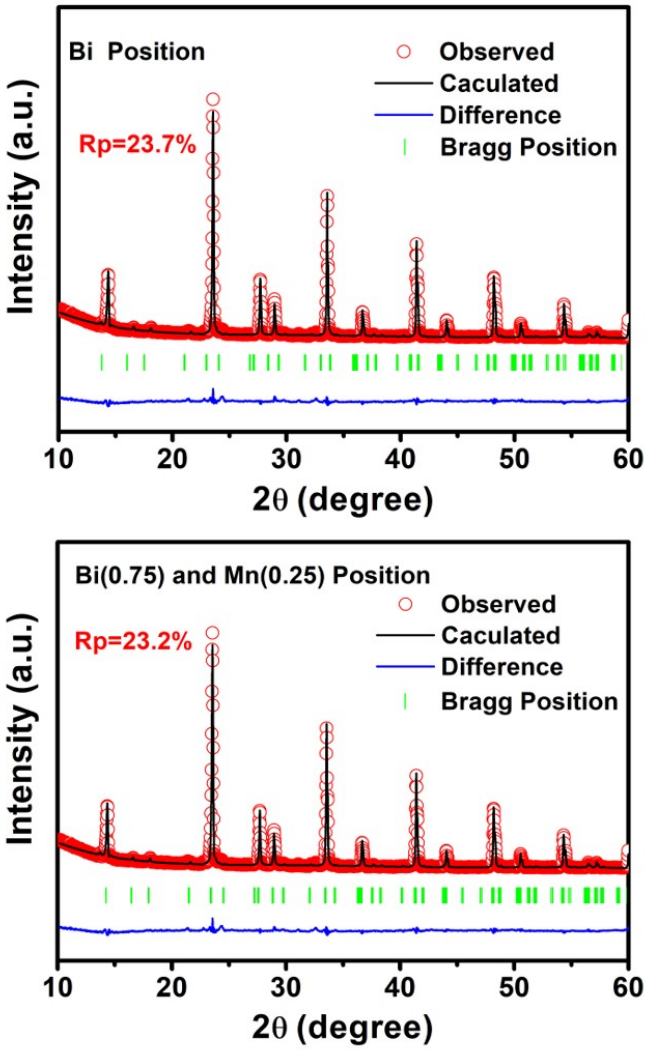


Figure S3. The XPS (X-ray photoelectron spectroscopy) survey spectrum of dosages of 10% Yb doped and undoped $Cs_4MnBi_2Cl_{12}$ powder.

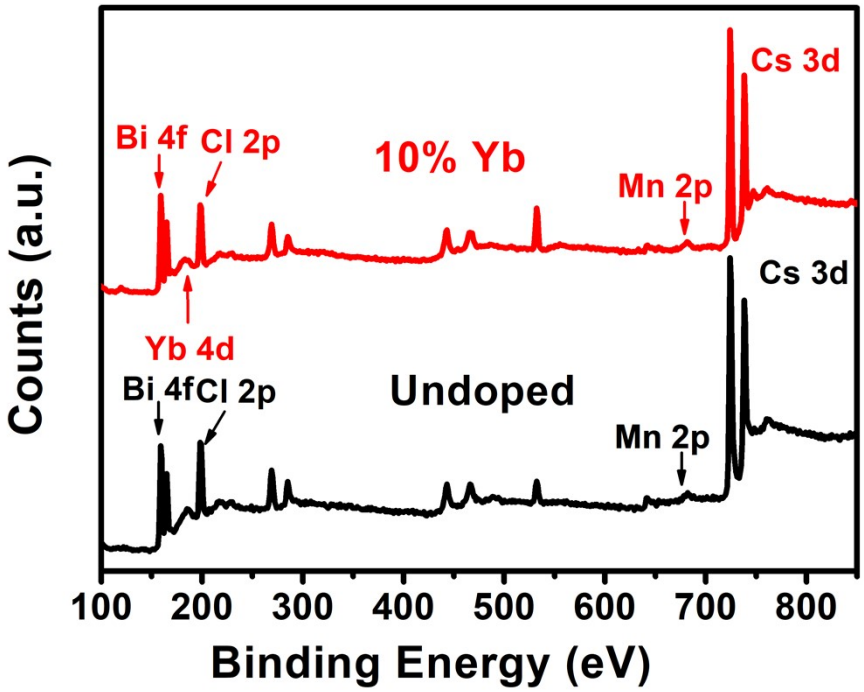


Figure S4. The XPS (X-ray photoelectron spectroscopy) survey spectrum of dosages of 10% Yb doped and undoped $Cs_4MnBi_2Cl_{12}$ powder. The high-resolution XPS spectrum of a) Cs 3d, b) Mn 2p, c) Bi 4f, d) C 1s, e) Cl 2p and f) Yb 4d.

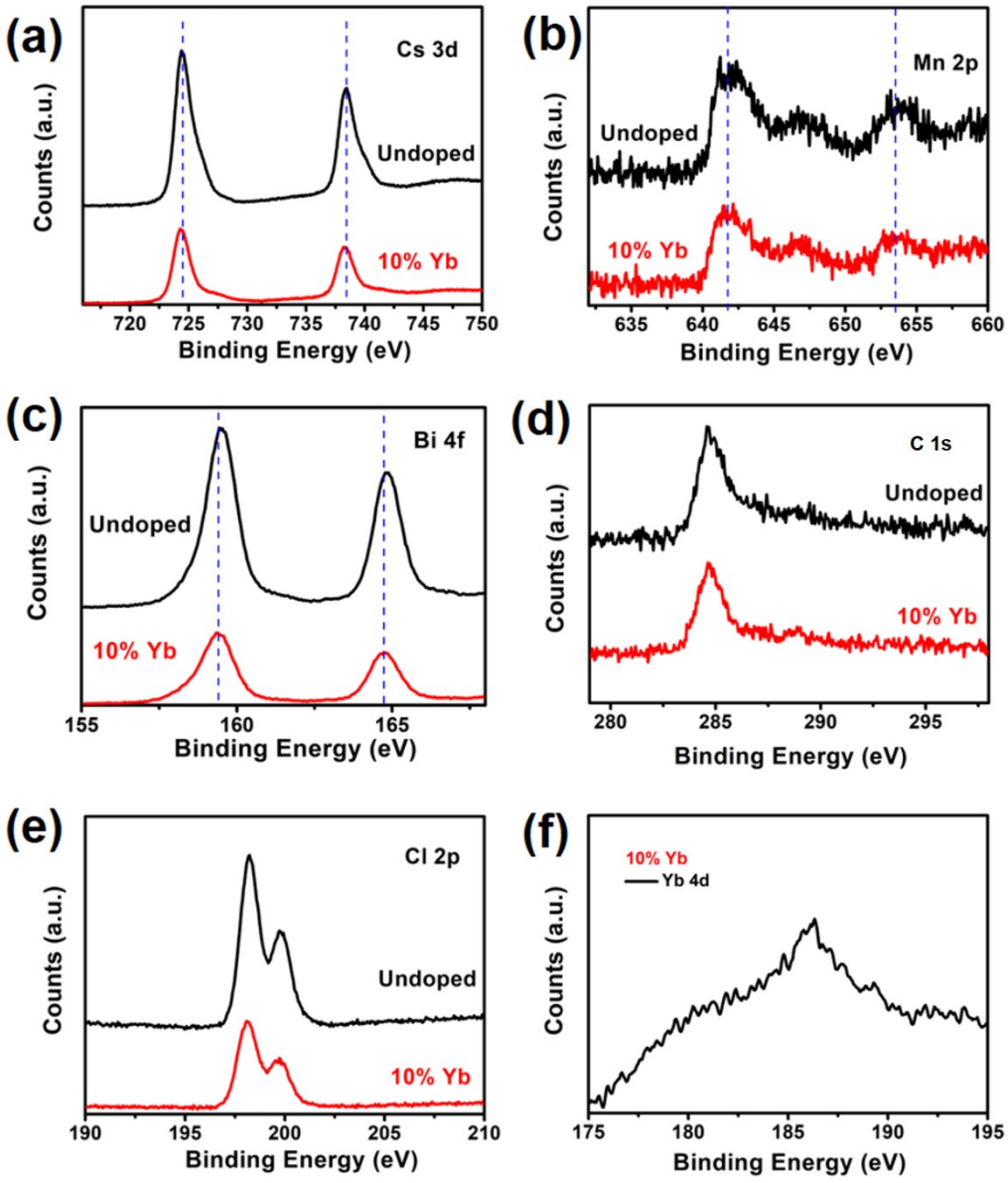
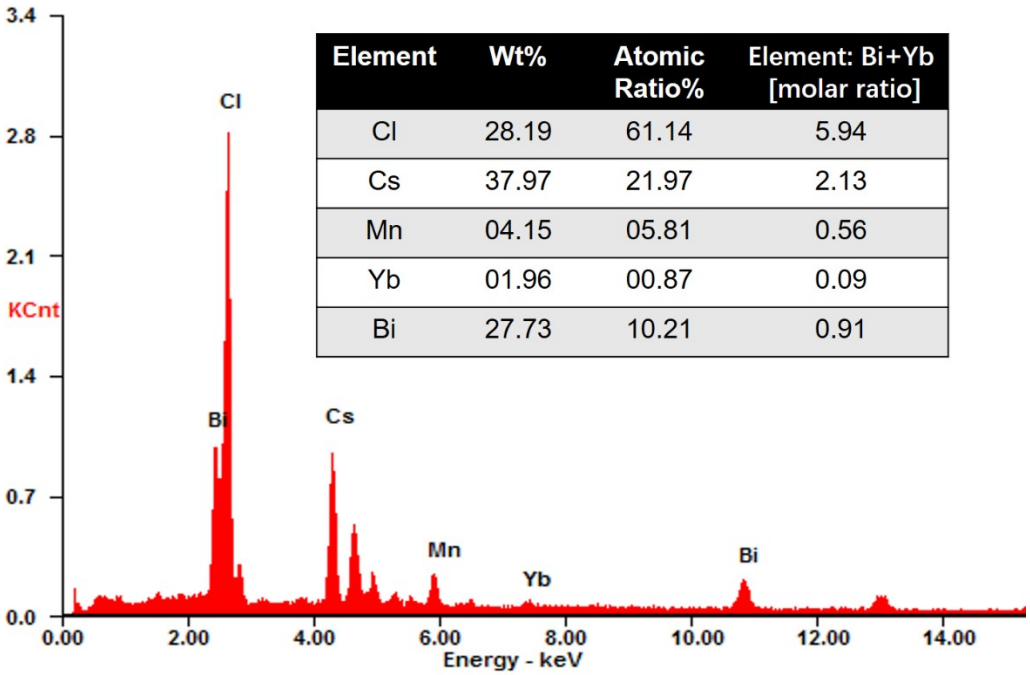
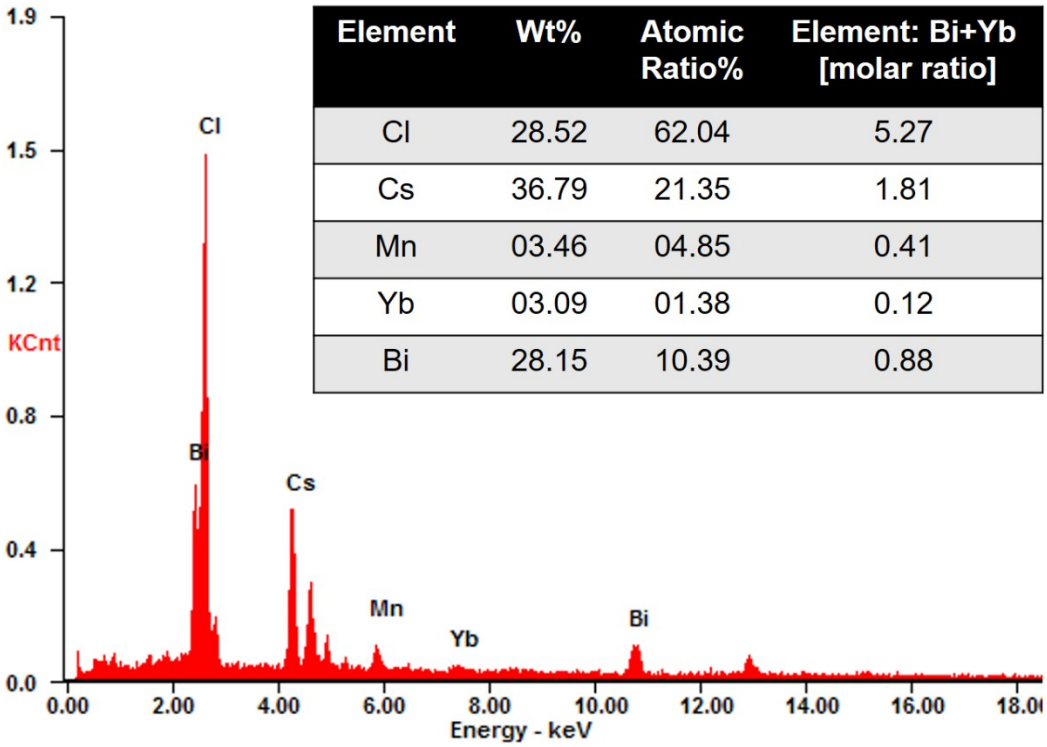


Figure S5. Energy Dispersive X-Ray Spectroscopy (EDS) of 5% Yb doped $Cs_4MnBi_2Cl_{12}$ powder.



Element	Wt%	Atomic Ratio%	Element: Bi+Yb [molar ratio]
Cl	28.19	61.14	5.94
Cs	37.97	21.97	2.13
Mn	04.15	05.81	0.56
Yb	01.96	00.87	0.09
Bi	27.73	10.21	0.91

Figure S6. Energy Dispersive X-Ray Spectroscopy (EDS) of 10% Yb doped $Cs_4MnBi_2Cl_{12}$ powder.



Element	Wt%	Atomic Ratio%	Element: Bi+Yb [molar ratio]
Cl	28.52	62.04	5.27
Cs	36.79	21.35	1.81
Mn	03.46	04.85	0.41
Yb	03.09	01.38	0.12
Bi	28.15	10.39	0.88

Figure S7. PL decay dynamics at 300 K for emission at 580 nm arising from dosages of 5% a) and 20% b) Yb^{3+} doped $Cs_4MnBi_2Cl_{12}$.Excitation was at 430 nm.

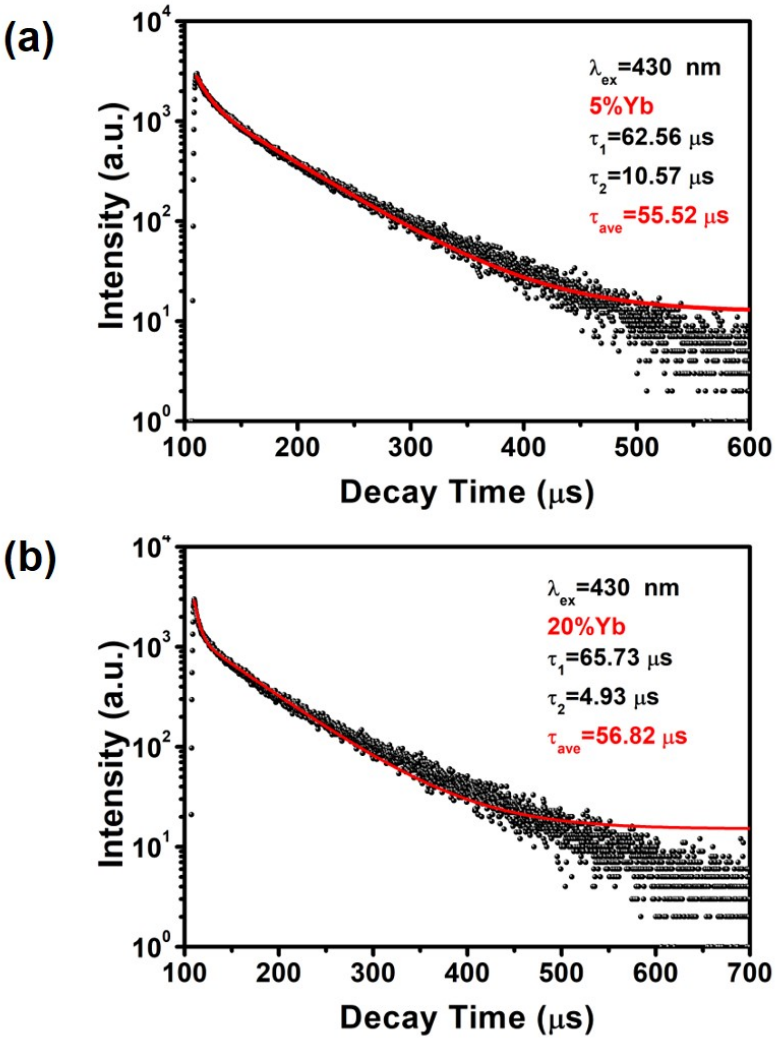


Figure S8. PL decay dynamics at 300 K for emission at 580 nm arising from dosages of 5% a) and 20% b) Yb^{3+} doped $Cs_4MnBi_2Cl_{12}$.Excitation was at 520 nm.

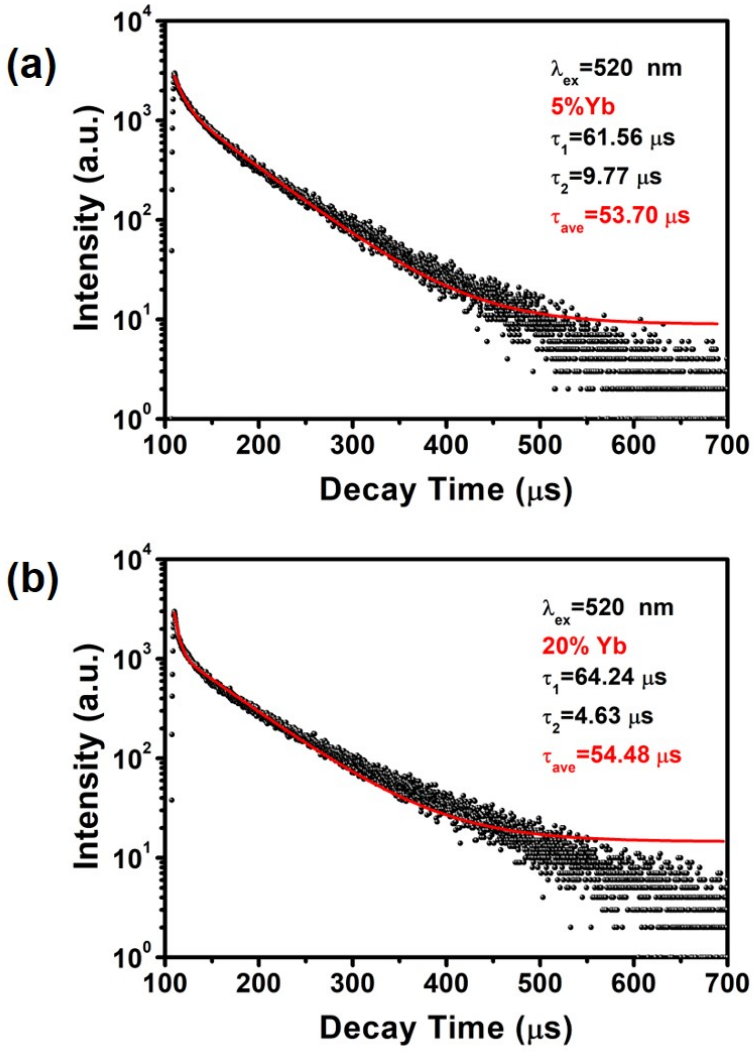


Figure S9. The PL spectra of the prepared Yb^{3+} doped and undoped $Cs_4MnBi_2Cl_{12}$ powder samples under 430 nm excitation.

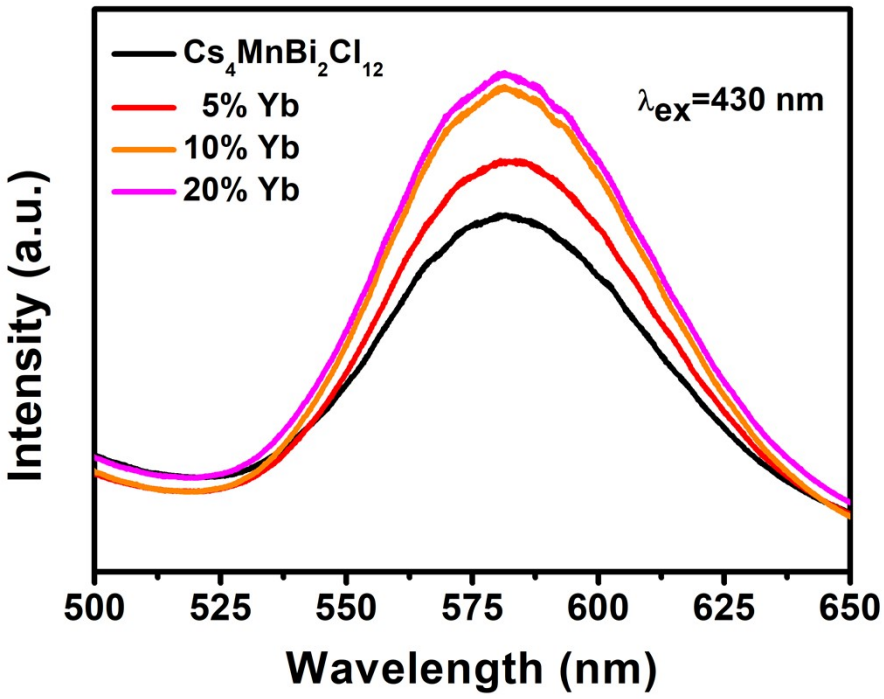


Figure S10. The PL spectra of the prepared 10% Yb^{3+} doped $Cs_4MnBi_2Cl_{12}$ and $Cs_4CdBi_2Cl_{12}$ powder samples under 360 nm excitation.

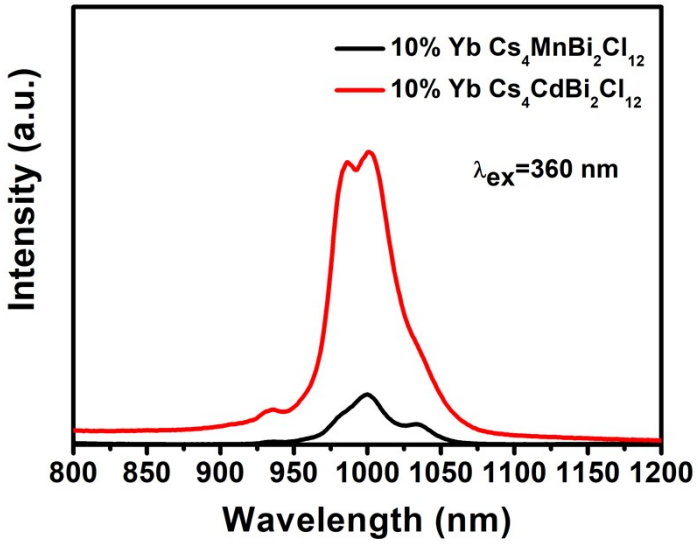


Figure S11. The PL spectra of the prepared 10% Yb^{3+} doped $Cs_4MnBi_2Cl_{12}$ powder sample. Excited by the 980 nm laser at 80K.

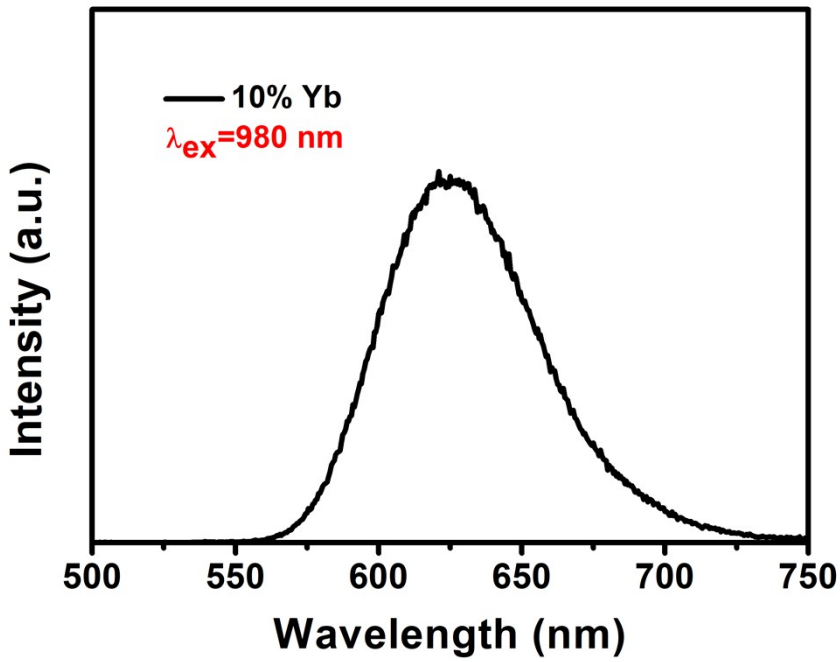


Figure S12. The PL spectra of the prepared 10% Yb^{3+} doped $Cs_4MnBi_2Cl_{12}$ powder sample. The results are excited by the 980 nm diode laser with the power from 180 mW to 1190 mW.

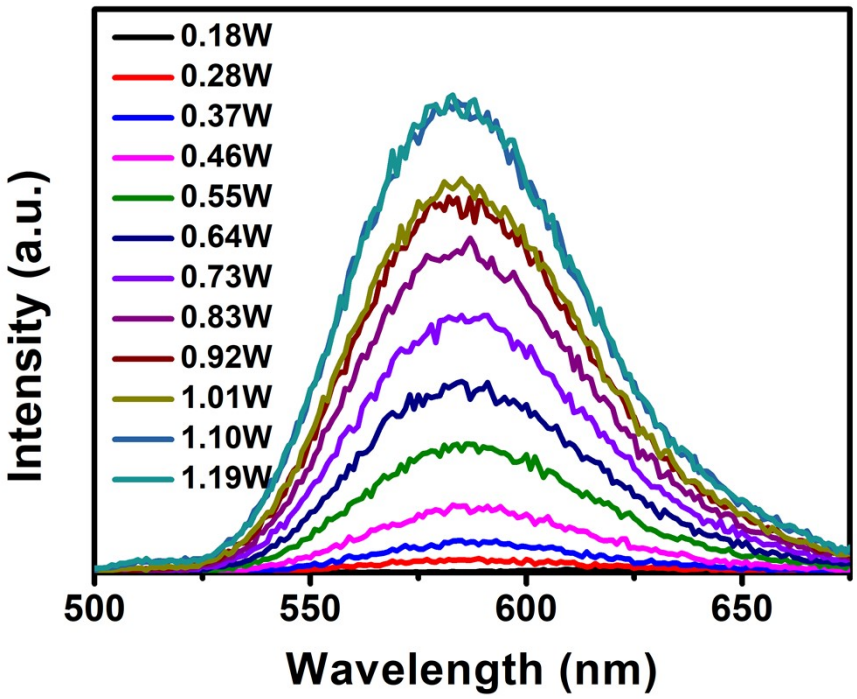


Figure S13. XRD patterns of Er^{3+} and Nd^{3+} ions doped $Cs_4MnBi_2Cl_{12}$.

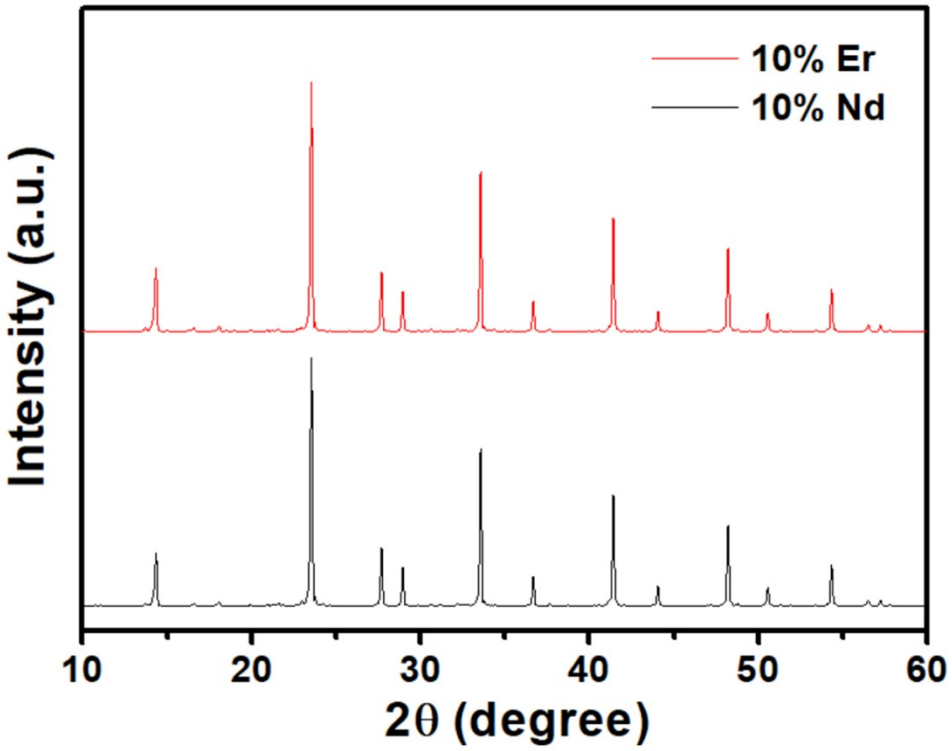


Figure S14. The PL spectra of the prepared 10% $Cs_4MnBi_2Cl_{12}$ samples doped with Er^{3+} and Nd^{3+} ions. Excited by the 360 nm laser at 300K.

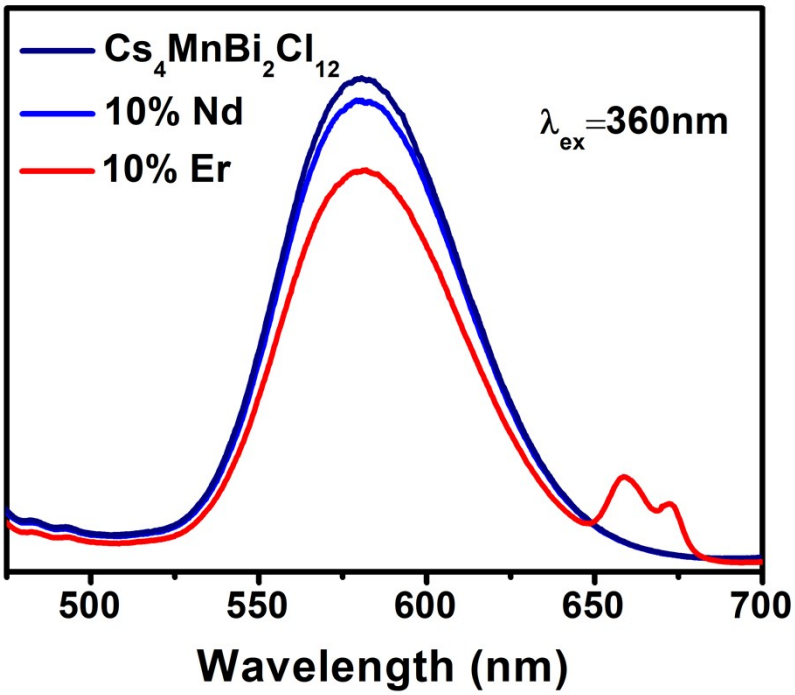


Figure S15. Absorption spectra of doped $Cs_4MnBi_2Cl_{12}$ with 5%, 10% and 20% Yb^{3+} dosages and undoped $Cs_4MnBi_2Cl_{12}$ powders.

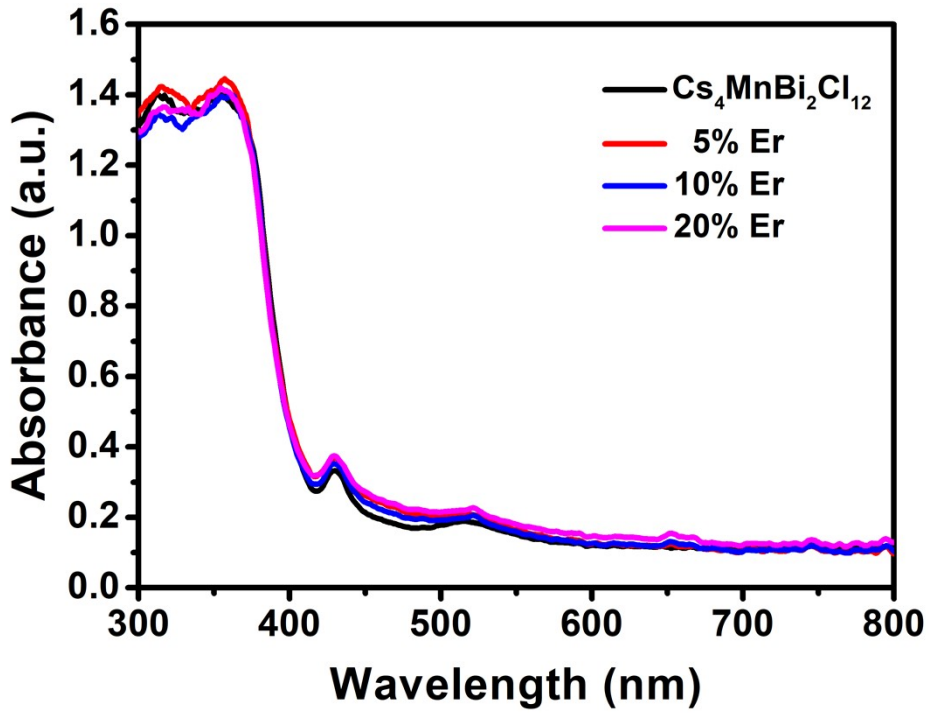


Figure S16. Near infrared PL spectra of Er^{3+} powder sample excited by different wavelength laser. The results are excited by the 360 nm,430 nm and 520 nm diode laser at 300K.

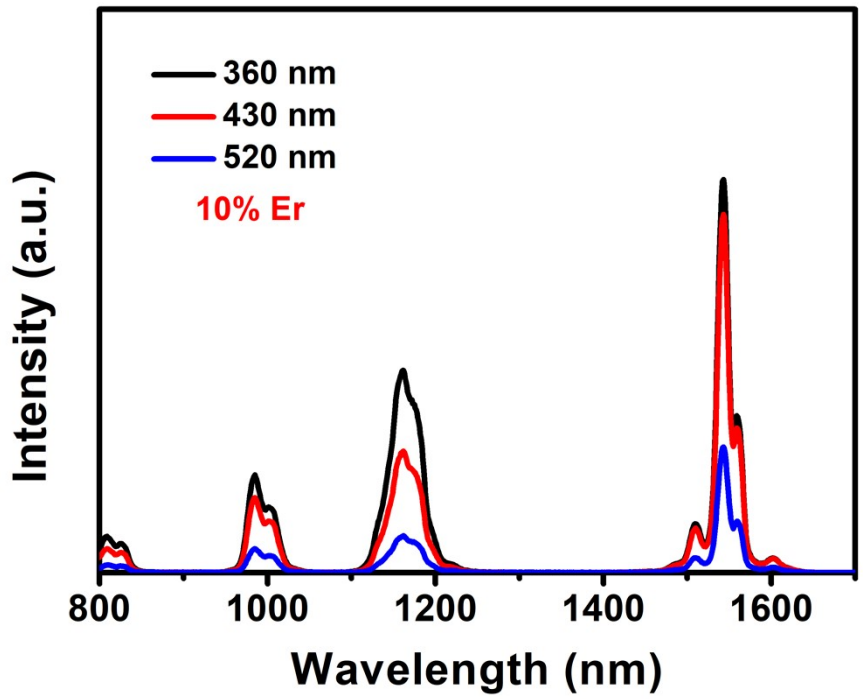


Figure S17. The PL spectra of the prepared $Cs_4MnBi_2Cl_{12}$ samples co-doped with Yb^{3+} -Er^{3+} ions. Excited by the 360 nm laser at 300K.