Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Doped 0D Cs_4PbCl_6 Single Crystals Featuring Full-visible-region Colorful Luminescence

Yixin Qiu,[a] Zhimin Ma,[bc] Guangkuo Dai,[a] Xiaohua Fu,[a] Yunsong Wang,[c] Xinru Jia[c] and Zhiyong Ma[a]*

Prof. Z.Y. Ma, Mr. Y.X. Qiu, Mr. G.K. Dai, Mr. X.H. Fu
State Key Laboratory of Organic-Inorganic Composites, College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China. E-mail: mazhy@mail.buct.edu.cn.

Dr. Z.M. Ma
National high-tech industrial development zone in Jingdezhen, Jingdezhen, 333000, China.

Dr. Z.M. Ma, Dr. Y.S. Wang, Prof. X.R. Jia
College of Engineering, Peking University, Beijing 100871, China.

Yixin Qiu and Zhimin Ma contributed equally.

1. **Experimental Methods**

Materials. Manganese chloride tetrahydrate ($MnCl_2·4H_2O$，9.99%) and Antimony trichloride ($SbCl_3$，99.99%) were purchased from Aladdin (Shanghai, China). Lead(II) chloride ($PbCl_2$，99%), Stannous chloride dehydrate ($SnCl_2·2H_2O$，99.03%) and chloroformamidine hydrochloride ($CH_4Cl_2N_2$，97%) were purchased from Bide Pharmatech Ltd. (Shanghai, China). Zirconium tetrachloride ($ZrCl_4$，98%) and Cesium chloride (CsCl，AR) were purchased from Macklin (Shanghai, China). All chemicals were used as received without further purification.

Synthesis of doped Cs_4PbCl_6 single crystals *via* hydrothermal method. High-quality Cs_4PbCl_6:Mn^{2+} single crystals were synthesized through a hydrothermal method. The mixture of $PbCl_2$ (3 mmol), $MnCl_2·4H_2O$ (0.3 mmol), CsCl (3 g) and $CH_4Cl_2N_2$ (3 mmol) was added into a 10 ml vial with 3ml deionized water and was stirred using a glass bar. After the mixture was sufficently wetting, the vial was put into a teflon liner (25 ml). Then sealed into a steel autoclave to react at 120 ^oC for 72 hours. Finally, colorless crystals with prismatic shape were obtianed after cooling to room temperature naturally. The Cs_4PbCl_6: Sb^{3+}/Sn^{2+}/Zr^{4+} single crystals were obtained by following the synthestic method of the Cs_4PbCl_6:Mn^{2+} single crystals.

Synthesis of doped Cs_4PbCl_6 powder *via* precipitation method. In general, Cs_4PbCl_6:Mn^{2+} (2.01% as an example) powders were synthesized by a stirring precipitation method. Typical solutions were prepared by mixing $PbCl_2$ (0.5 mmol), $MnCl_2·4H_2O$ (0.01mmol), CsCl (2.224 mmol, a little bit more than stoichiometric ratio in order to avoid the formation of $CsPbCl_3$) in 3 ml anhydrous methanol in a 25 ml glass flask and then were kept stirring in an 80 ^oC silicone oil bath for 24 hours. It is worth noting that there are still some raw materials in the resulting product such as $PbCl_2$ or CsCl if the stirring time is too short. Then the mixture was purified by filtering and was

washed with anhydrous ethanol several times. Finally, colorless powders (except Cs_4PbCl_6: Sn^{2+}, light green powder) were obtained after drying in a 60 ^oC vacuum oven for 2 hours. Different doping concentration of the product can be obtained by adjusting the feeding amount of $MnCl_2 \cdot 4H_2O$. The Cs_4PbCl_6: $Sb^{3+}/Sn^{2+}/Zr^{4+}$ powders were obtained by following the synthestic method of the Cs_4PbCl_6:Mn^{2+} powders.

Structure and phase characterization. X-ray diffraction (XRD) experiments were performed on a Rigaku Ultima IV diffractometer with a 3 kW ceramic tube as the X-ray source (Cu Kα) and an X'celerator detector. X-ray photoelectron spectroscopy (XPS) experiments were performed on a ThermoFisher Scientific USA ESCALAB 250 diffractometer with a Monochromated Al Kalph (150W) as X-ray Source. ICP analysis was conducted on an ICP-AES spectrometer (Ultima2, Jobin Yvon). SEM and EDS measurements of Cs_4PbCl_6:$Mn^{2+}/Sb^{3+}/Sn^{2+}/Zr^{4+}$ single crystals were performed by using a JEOL JSM-7800F SEM equipped with a ChemiSTEM system operated at 10 kV. Acquisition time for EDS measurements was ~300 s.

Optical Spectroscopy. Samples for optical measurements were prepared by washing with ethanol several times and drying in a vacuum drying oven. Absorption spectra were measured on a SHIMADZU UV-3600 spectrometer in absorption mode using $BaSO_4$ powder as a baseline. Photoluminescence (PL) spectra and Photoluminescence excitation (PLE) spectra were recorded on the HITACHI F-7000 or Edinburgh Instruments FLS980 lifetimeequipped with a 450 W xenon lamp as excitation source and double grating monochromators. PL decay curves were obtained by time-correlated single-photon counting on the Edinburgh Instruments FLS980 lifetime and steady state spectrometer. The measurement and calculation of photoluminescence quantum yield (PLQY) was performed on the Nanolog/FluoroLog-3-2-Ihr320 combined measurement system for infrared fluorescence equipped with an integrating sphere. Photoluminescence (PL)

spectra, decay spectra and PLQY of the four doped single crystals were all acquired at the maximum excitation wavelength.

All photographs of the single crystals were taken by using a XTZ-D Binocular Stereo Microscope (Shanghai Optical Instrument One Factory) and a Huawei Mate 40 Pro without any filter.

2. **Table S1.** Integral table of ICP data and photophysical results of four doped single crystals.

Sample	ICP, mol%	PLE, nm	PL, nm	Abs, nm	PLQY, %
$Cs_4PbCl_6:Mn^{2+}$	3.08	274	616	283	14.48
$Cs_4PbCl_6:Sb^{3+}$	1.24	324	553	280	18.44
$Cs_4PbCl_6:Sn^{2+}$	6.61	315	520	282	36.79
$Cs_4PbCl_6:Zr^{4+}$	1.60	253	430	282	4.72

3. **XPS images**

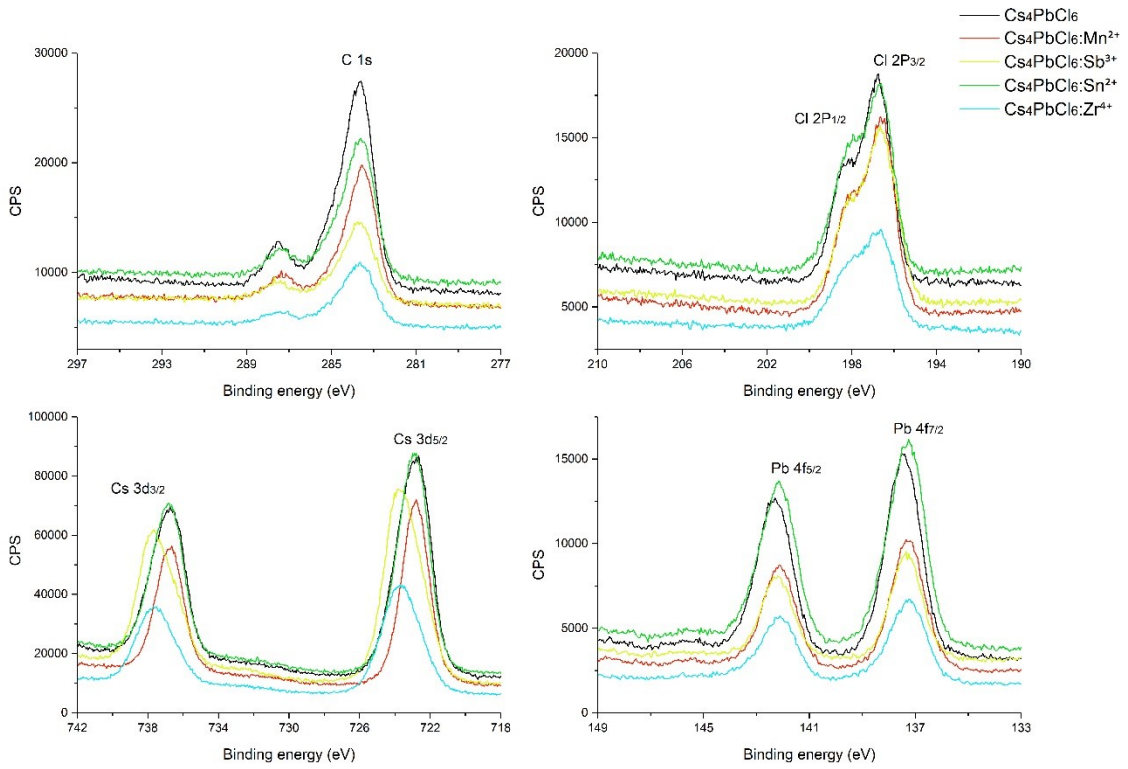


Figure S1.High-resolution XPS spectra of pure Cs_4PbCl_6, $Cs_4PbCl_6:Mn^{2+}/Sb^{3+}/Sn^{2+}/Zr^{4+}$ crystals.

4. **CIE coordinates and Photoluminescent pictures of four doped Cs_4PbCl_6 powders**

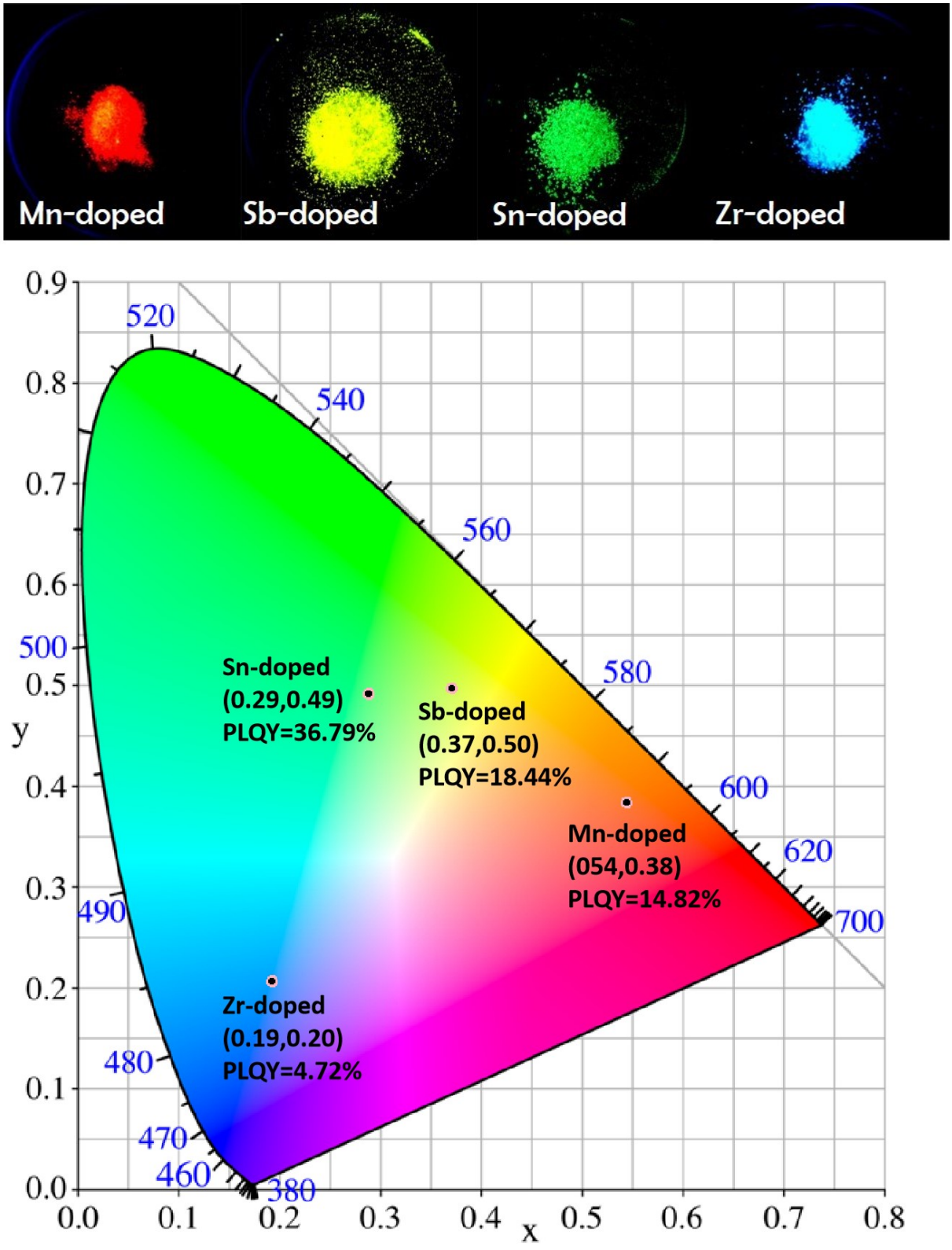


Figure S2. Photoluminescent images and corresponding CIE coordinate pictures of four crystalline powders (Cs_4PbCl_6:Mn^{2+}/Sn^{3+}/Sn^{2+}/Zr^{4+}).

5. **UV, PLE, PL spectra of all single crystals at room temperature**

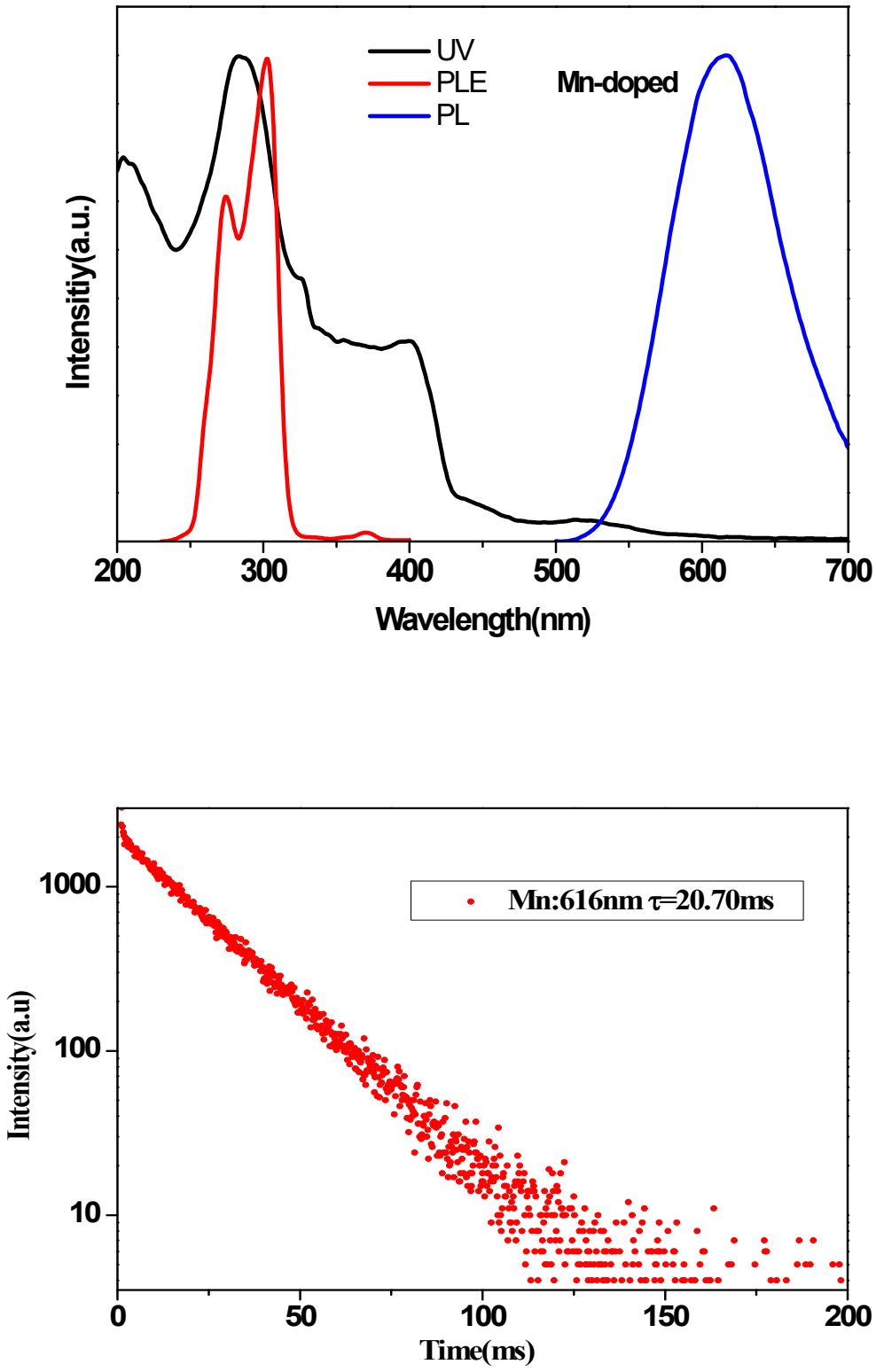


Figure S3. UV, PLE, PL and lifetime curves of $Cs_4PbCl_6:Mn^{2+}$ single crystals

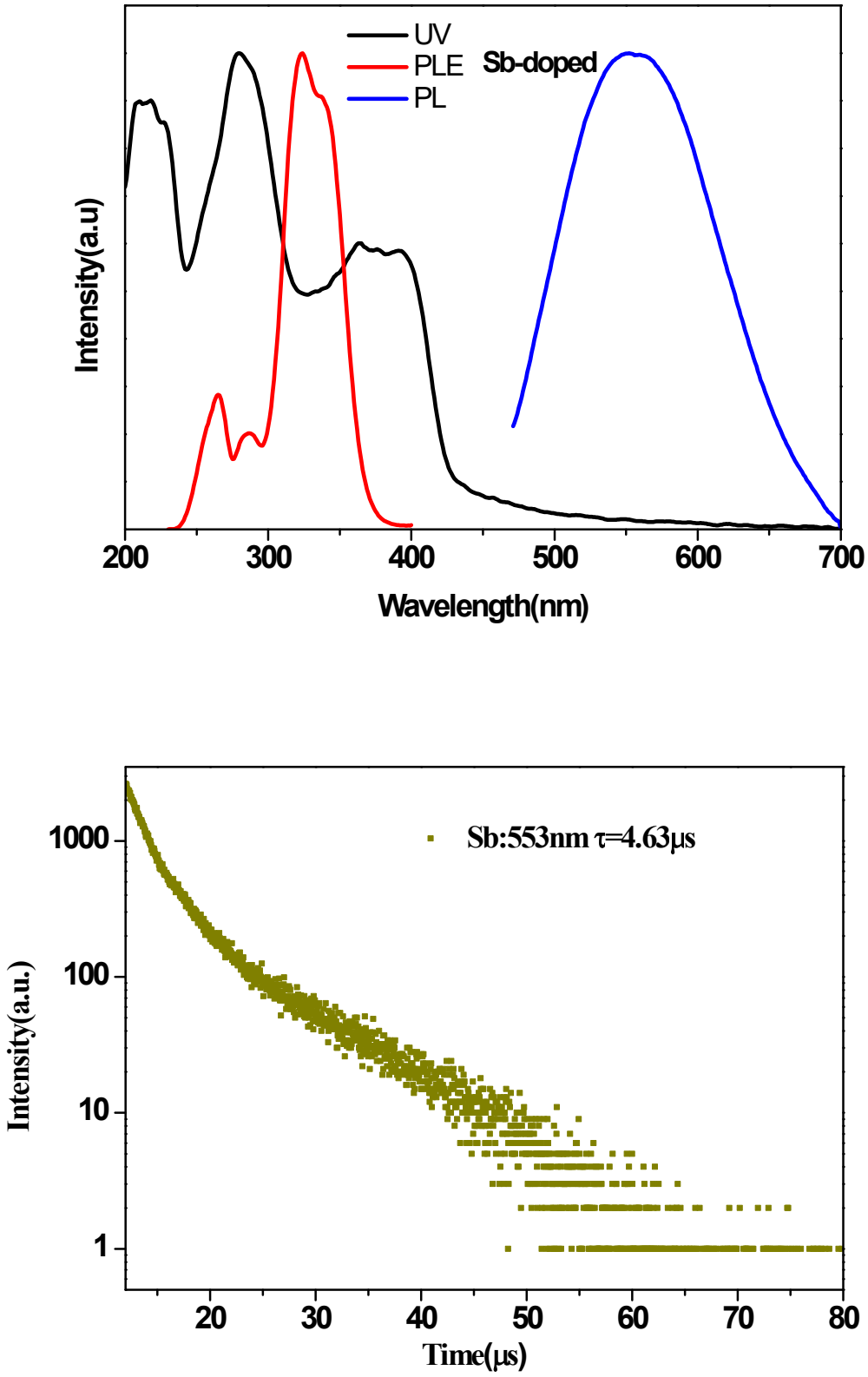


Figure S4. UV, PLE, PL and lifetime curves of $Cs_4PbCl_6:Sb^{3+}$ single crystals

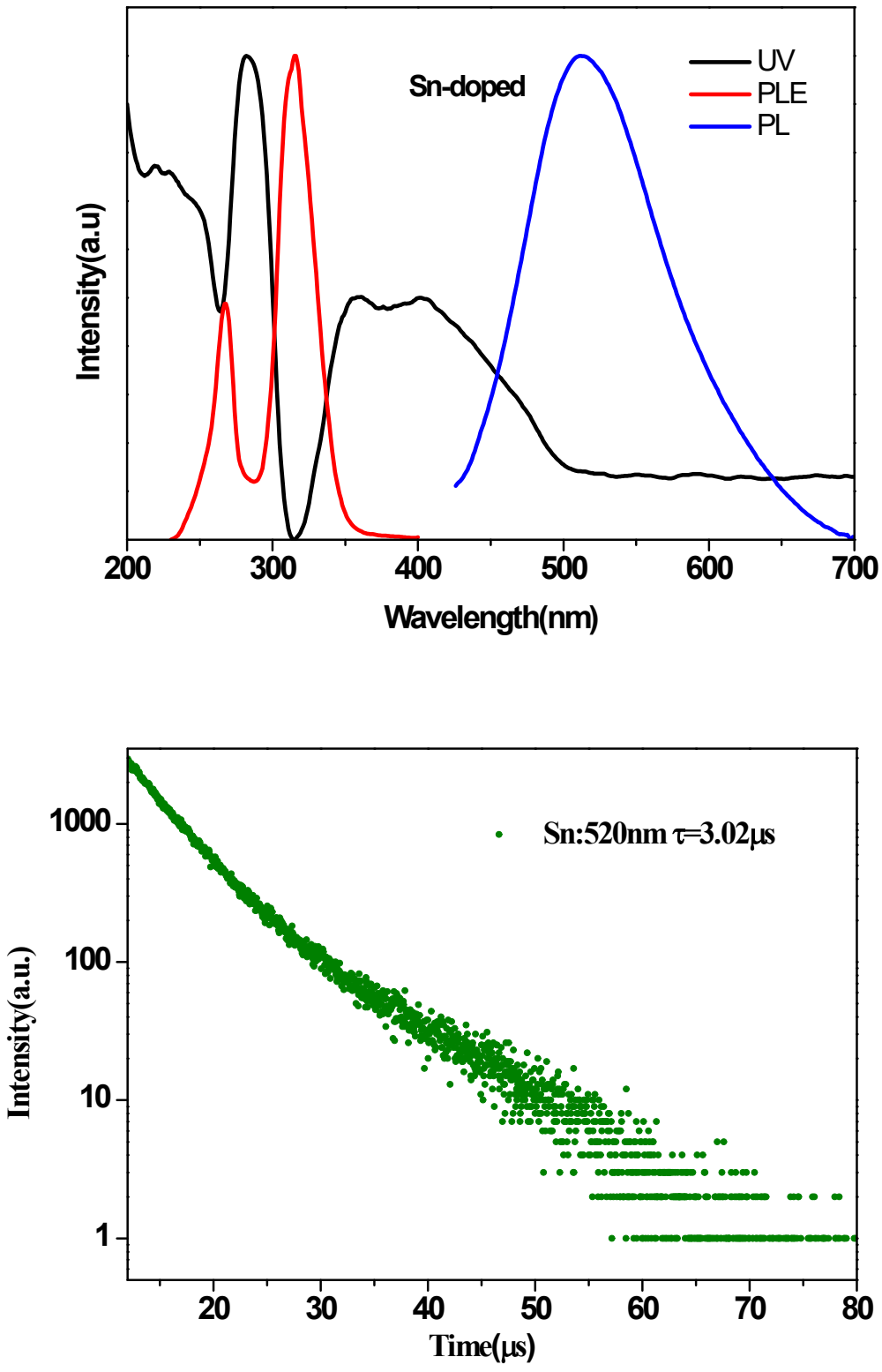


Figure S5. UV, PLE, PL and lifetime curves of Cs_4PbCl_6:Sn^{2+} single crystals

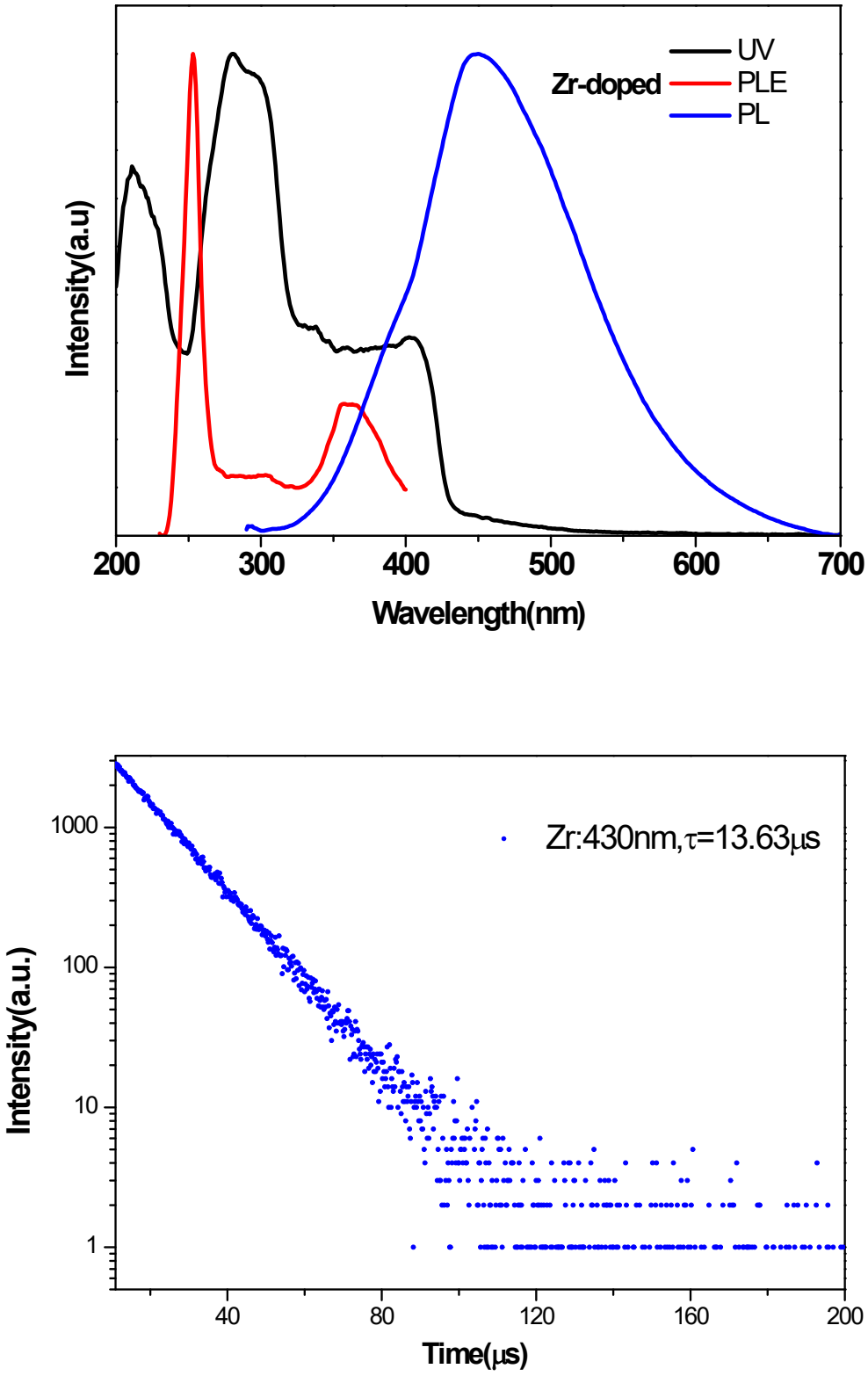


Figure S6. UV, PLE, PL and lifetime curves of Cs_4PbCl_6:Zr^{4+} single crystals.

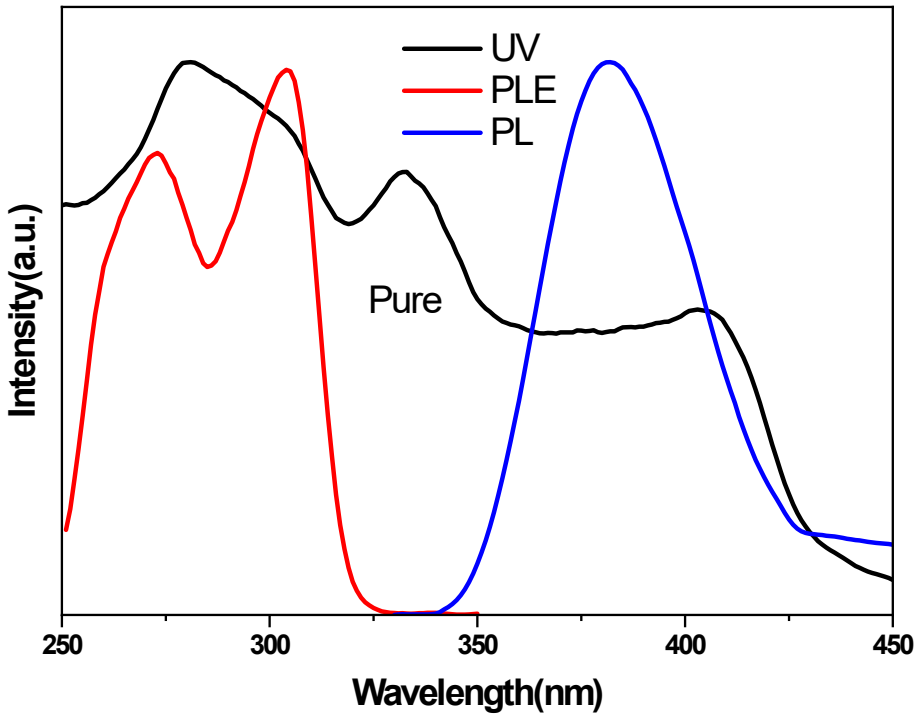


Figure S7. UV, PLE and PL spectra of pure Cs_4PbCl_6 single crystals.

6. Temperature-dependent experiments

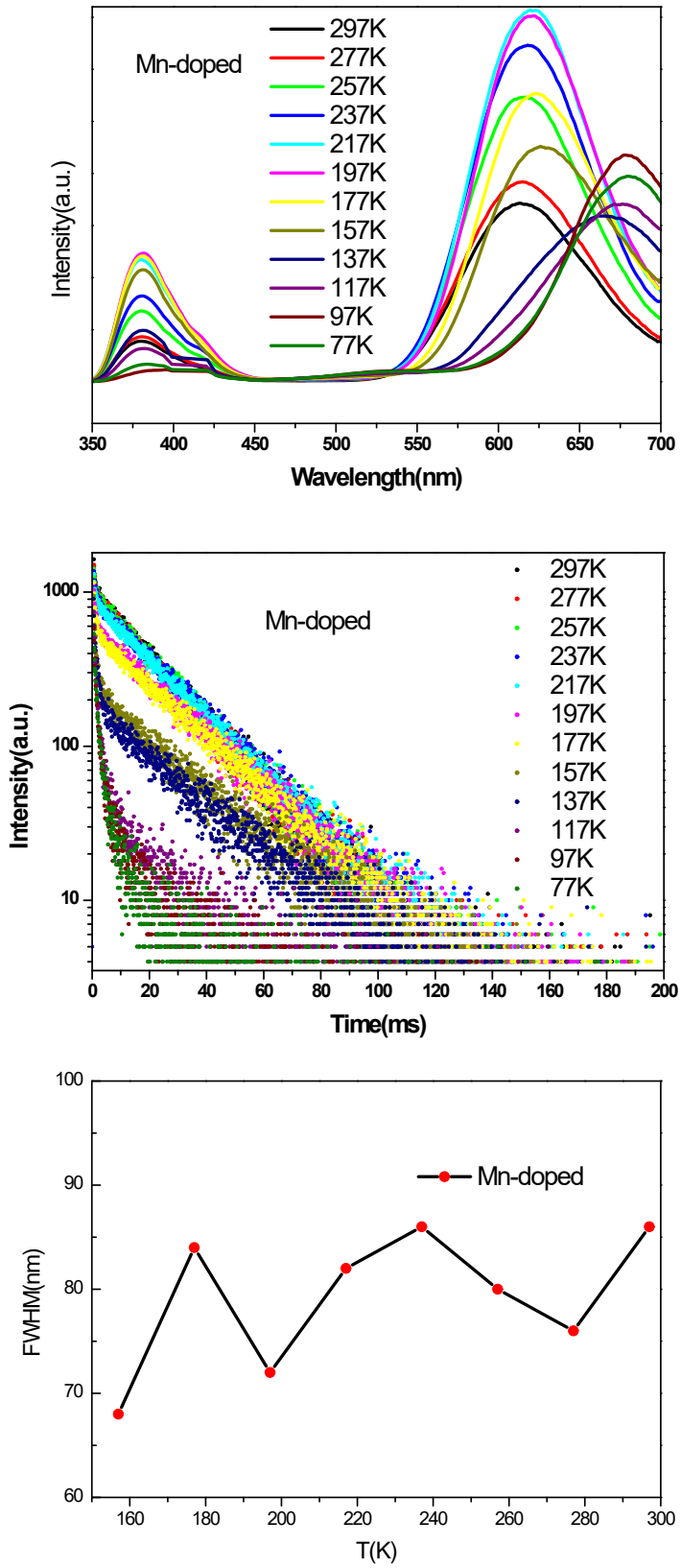


Figure S8. Temperature-dependent PL and decay spectra of Cs_4PbCl_6:Mn^{2+} single crystals.

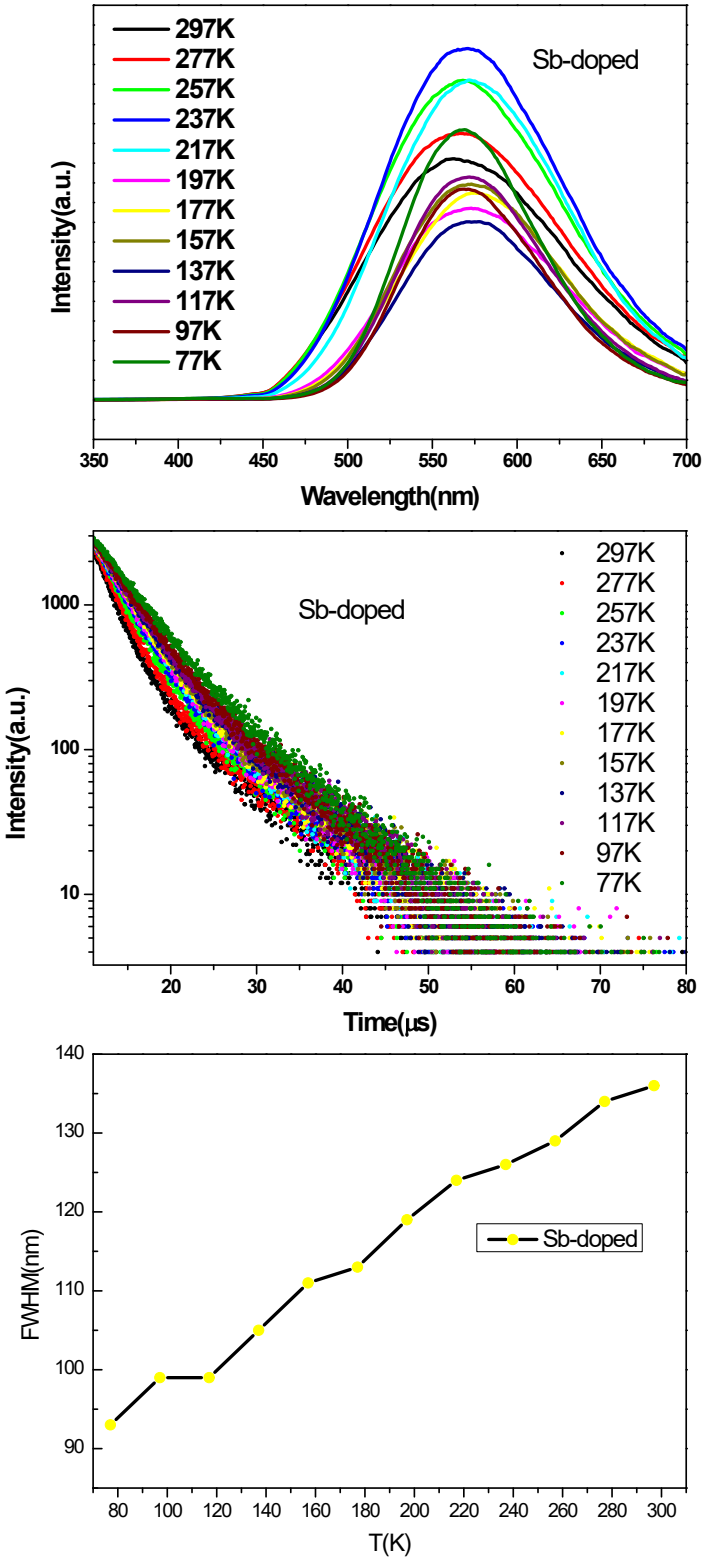


Figure S9. Temperature-dependent PL and decay spectra of Cs_4PbCl_6:Sb^{3+} single crystals.

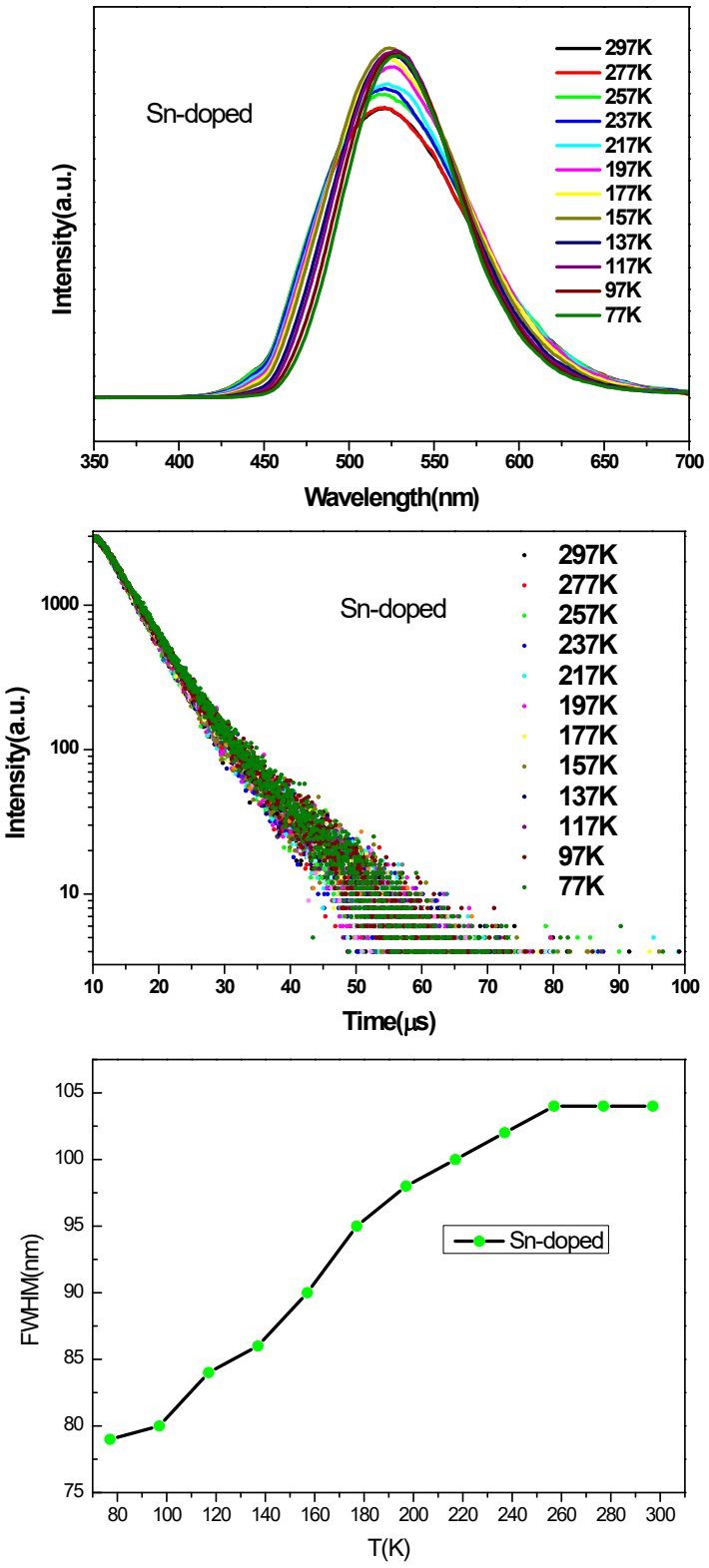
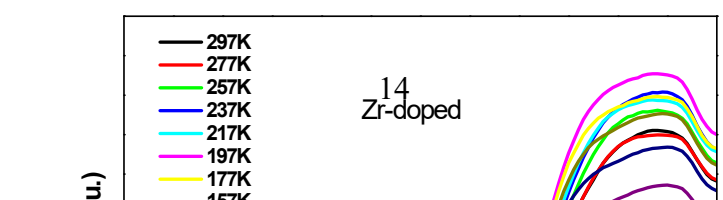


Figure S10. Temperature-dependent PL and decay spectra of Cs_4PbCl_6:Sn^{2+} single crystals.



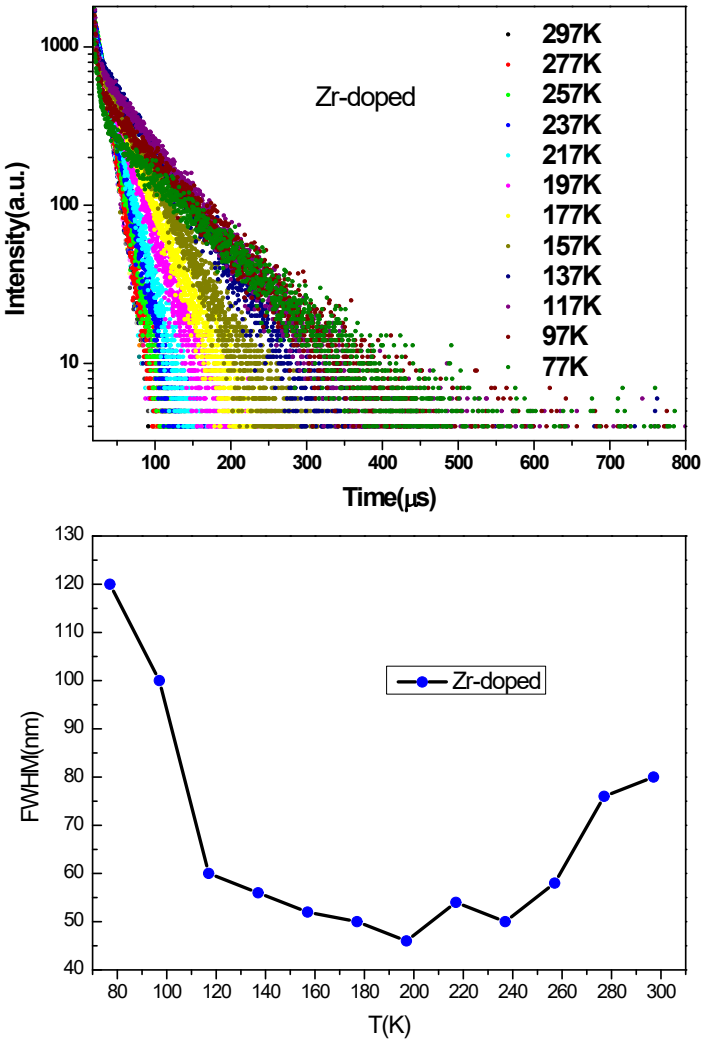


Figure S11. Temperature-dependent PL and decay spectra of Cs_4PbCl_6:Zr^{4+} single crystals.

7. **PLQY**

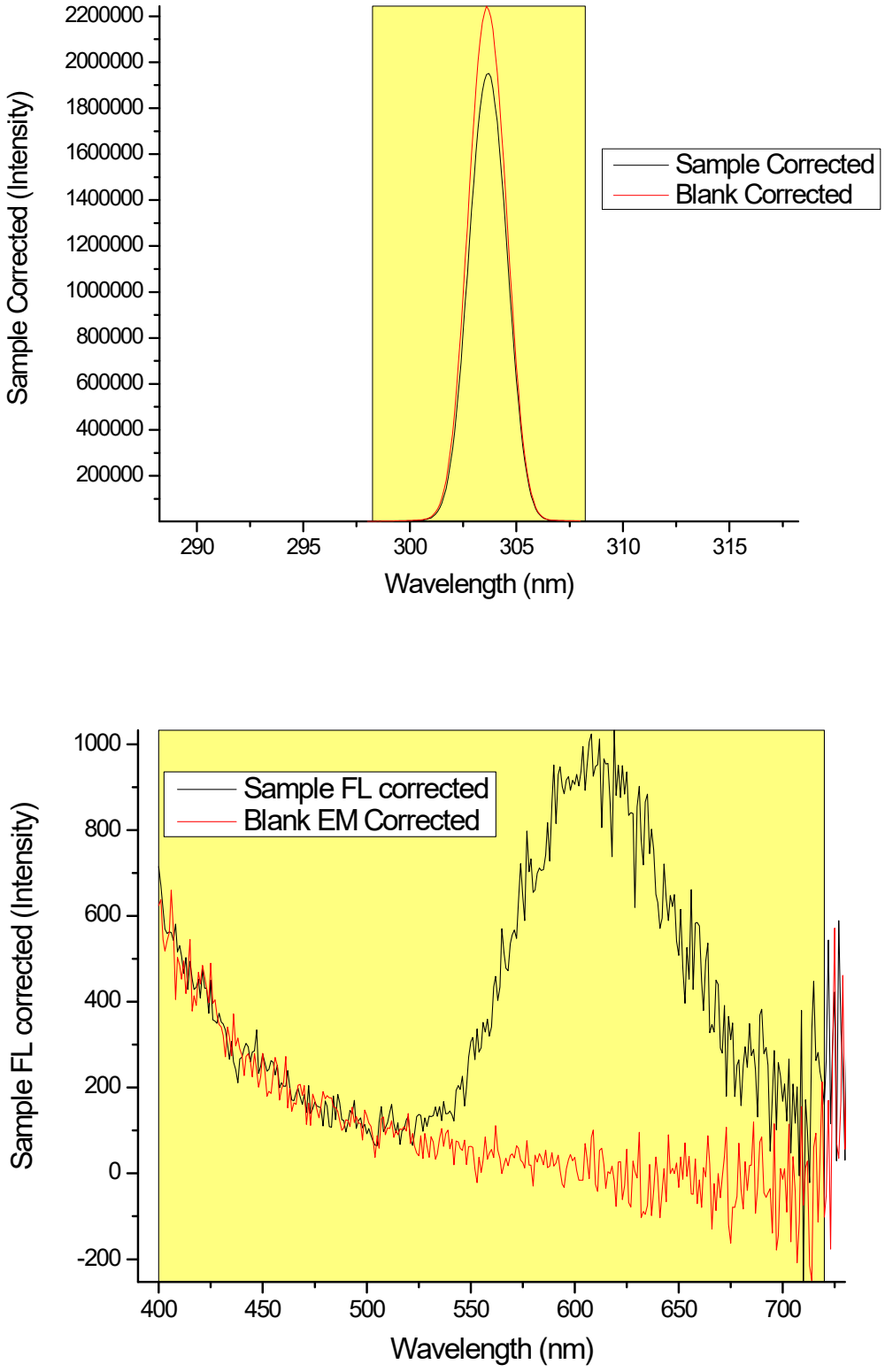


Figure S12. PLQY curves of $Cs_4PbCl_6:Mn^{2+}$ single crystals

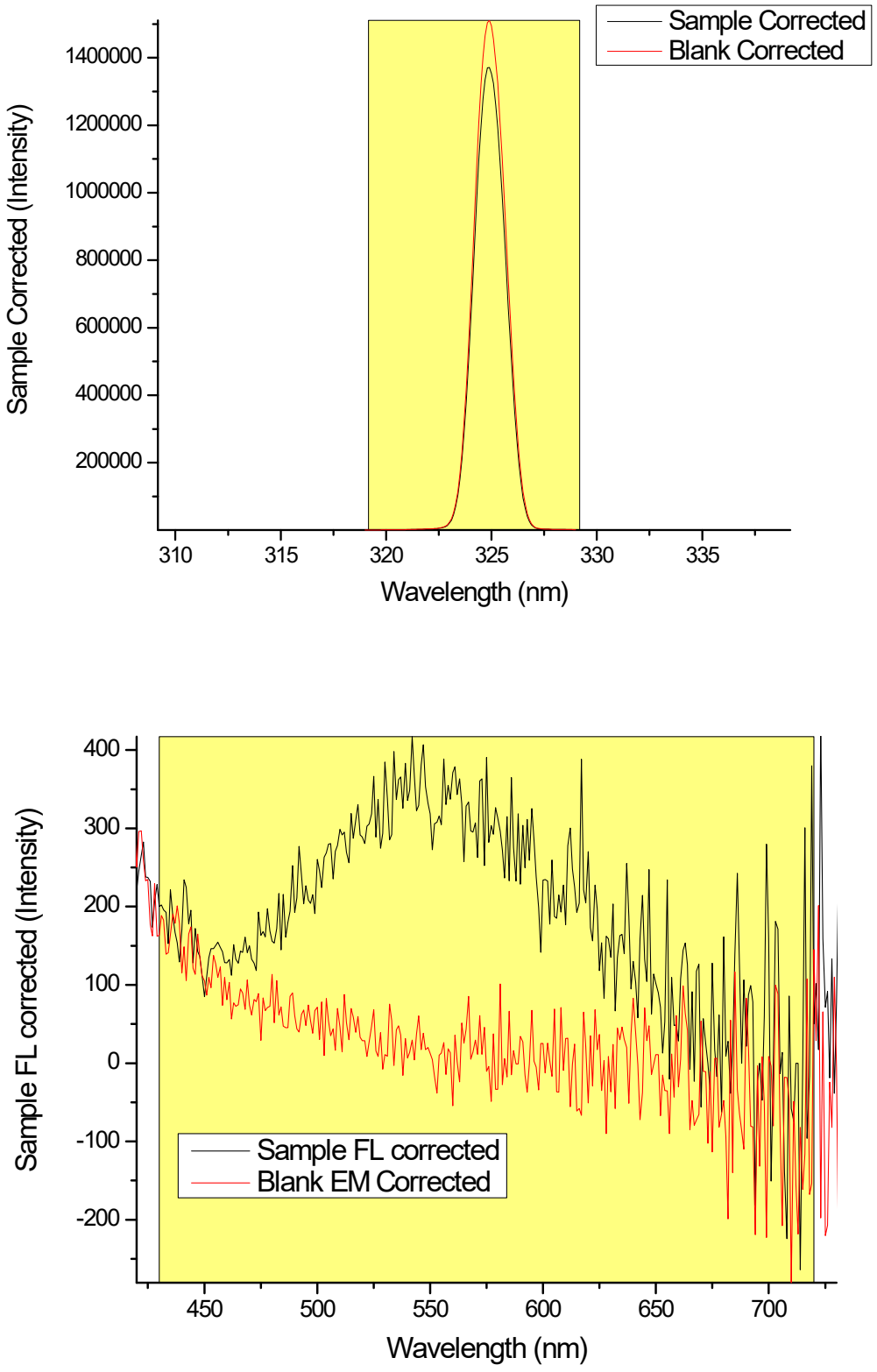


Figure S13. PLQY curves of Cs_4PbCl_6:Sb^{3+} single crystals

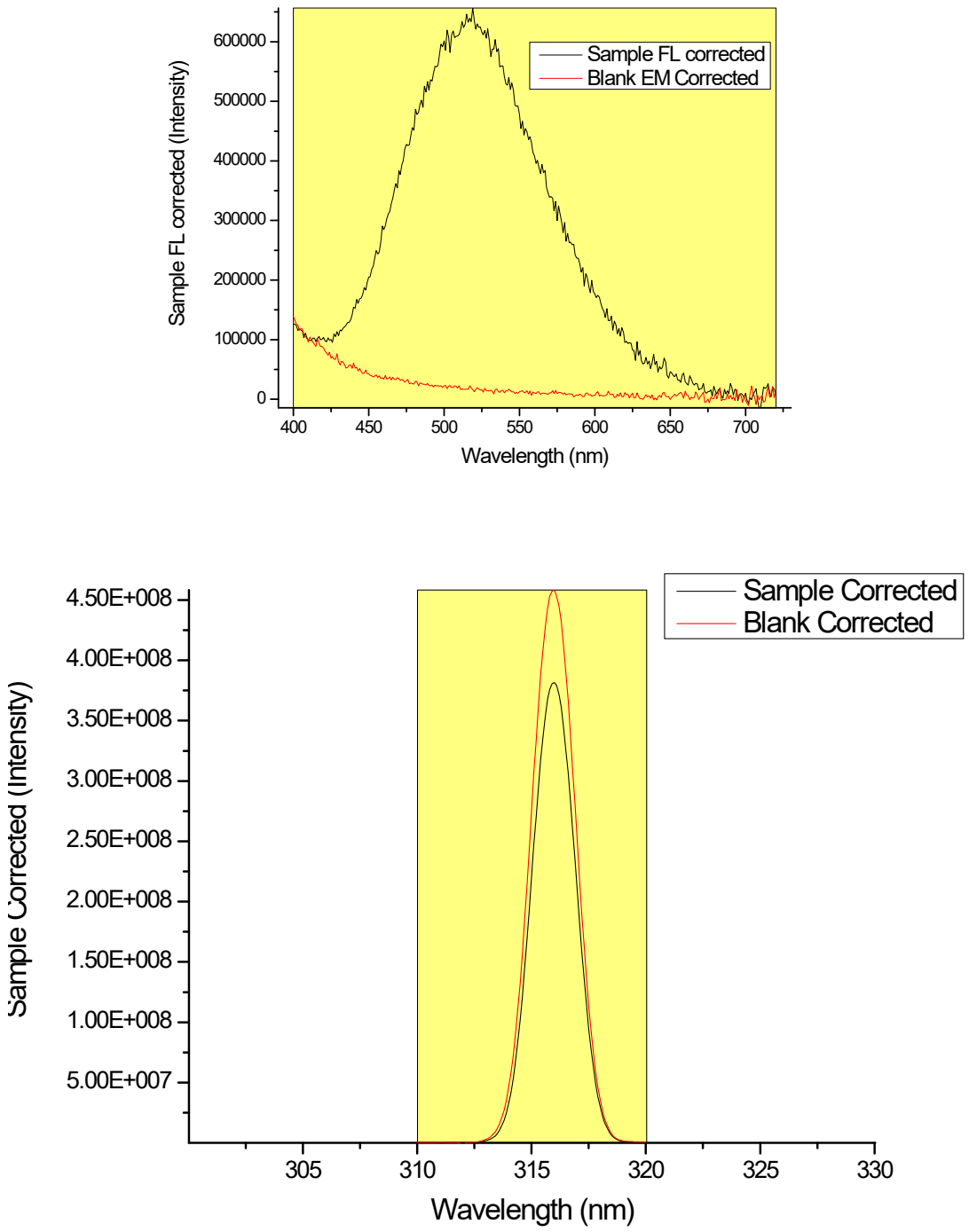


Figure S14. PLQY curves of Cs_4PbCl_6:Sn^{2+} single crystals

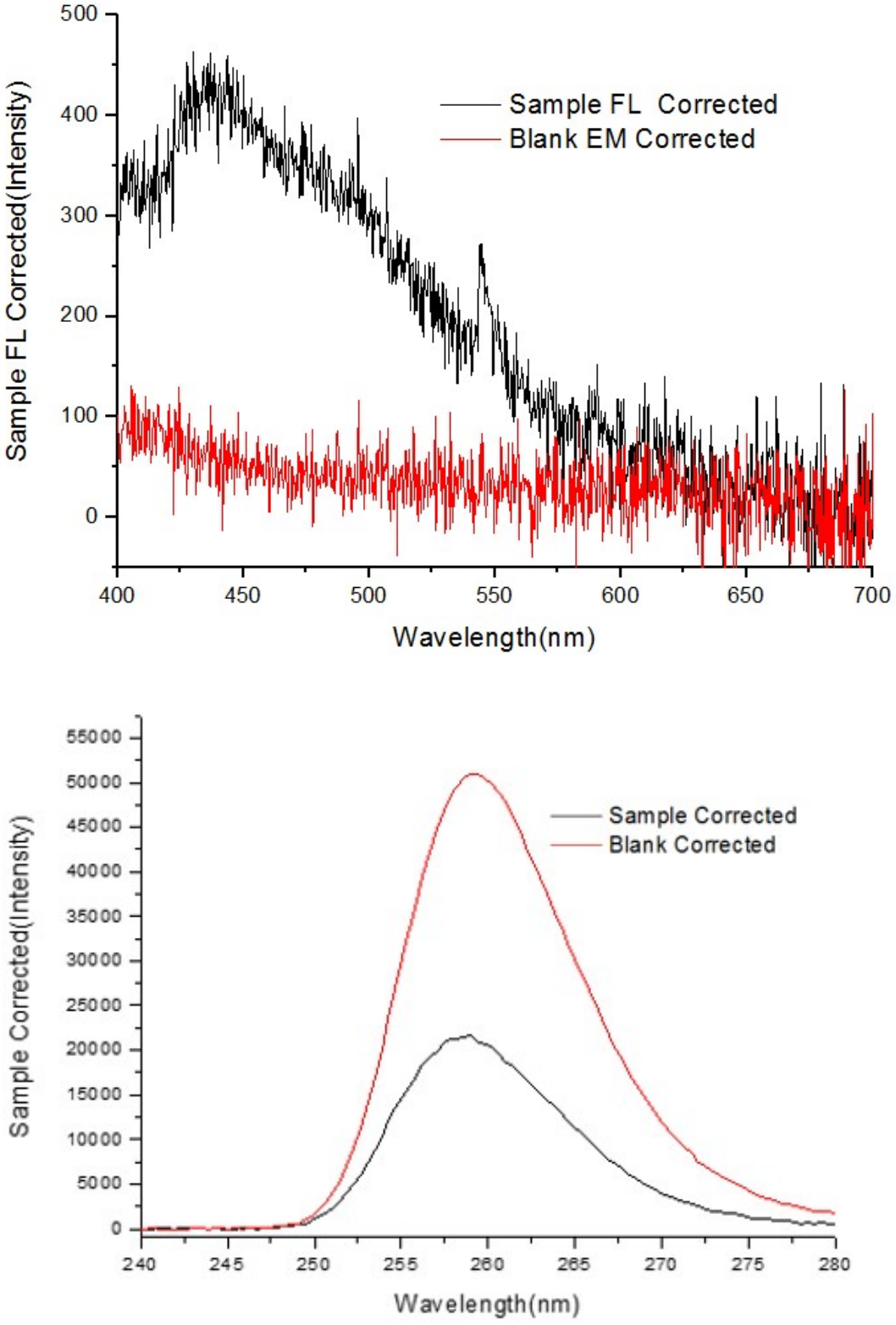


Figure S15. PLQY curves of Cs_4PbCl_6:Zr^{4+} single crystals

8. Four doped Cs_4PbCl_6 microcrystals prepared at the condition of 120 °C for 8 h

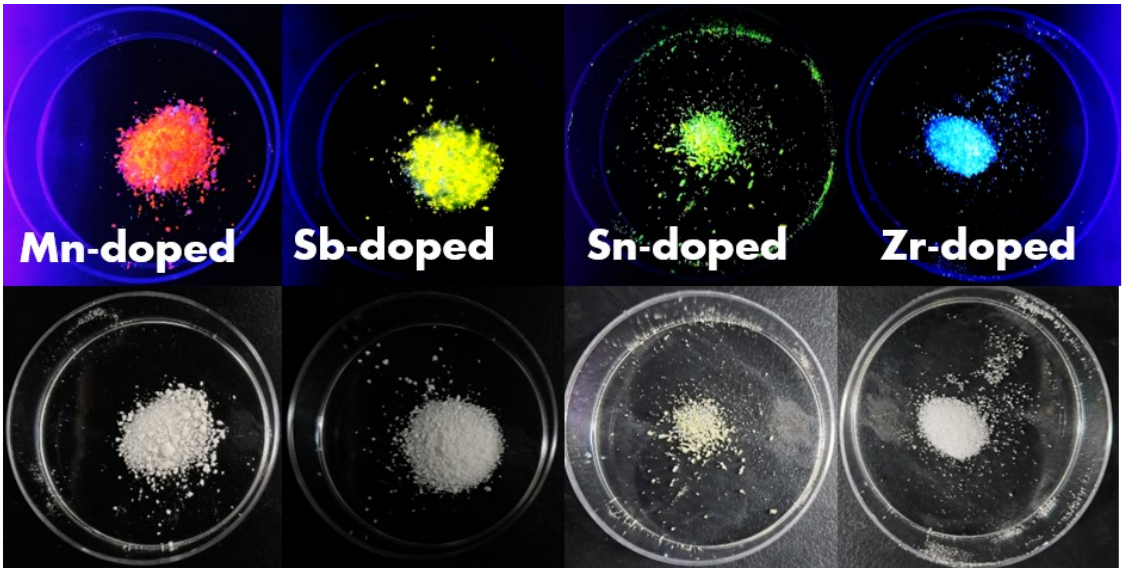


Figure S16. Optical images of four doped Cs_4PbCl_6 microcrystals prepared at the condition of 120 °C for 8 h under 254 nm UV light and room light.

8. Stability of the **four doped Cs_4PbCl_6 single crystals**

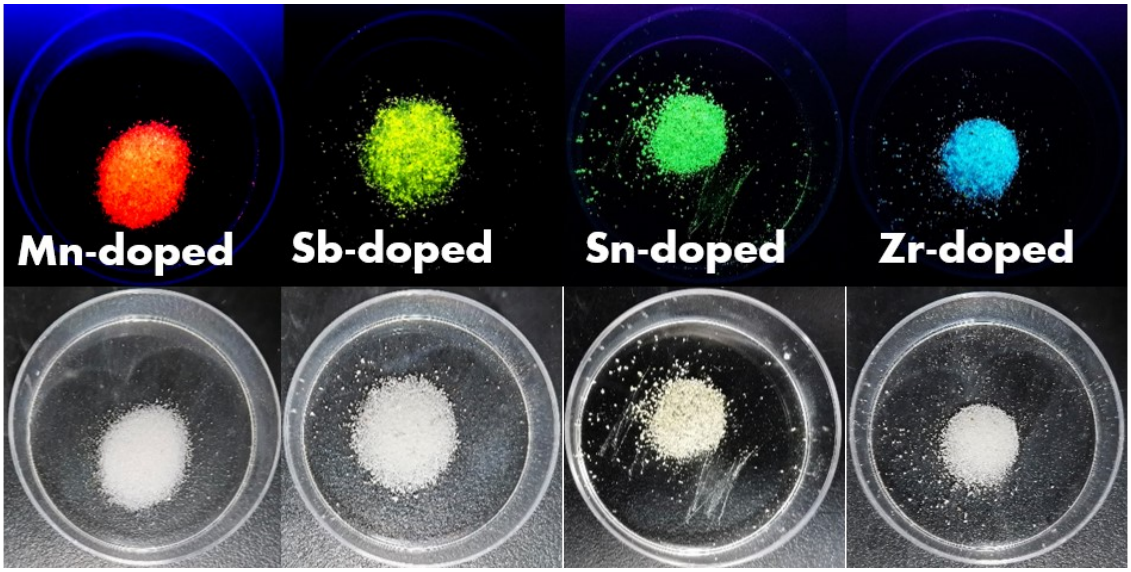


Figure S17. Optical images of four doped Cs_4PbCl_6 single crystals under 254 nm UV light and room light after being exposed to air for three months.

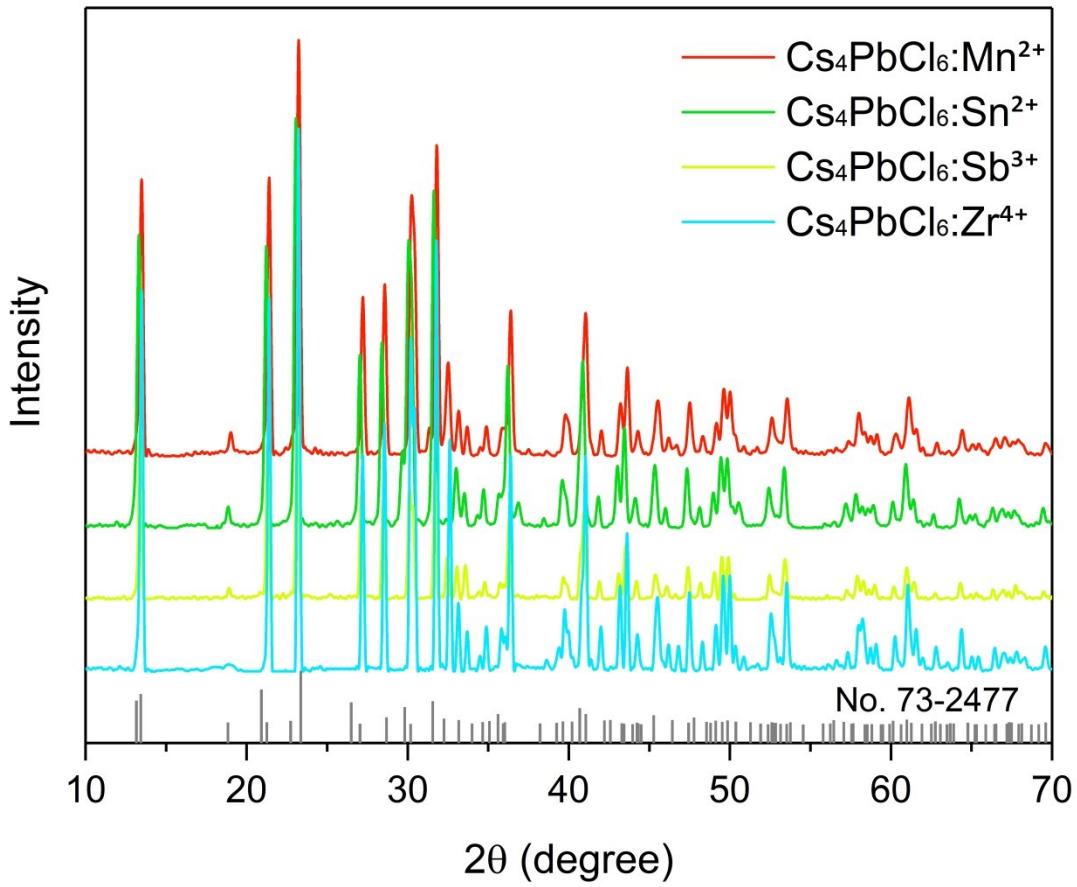


Figure S18. XRD patterns of the four doped single crystals after being exposed to air for over three months.

9. **Table S2. Table of reaction doping concentration and ICP Data of Manganese and Tin doped Cs_4PbCl_6 single crystals *via* hydrothermal method.**

Sample	Reaction,mol%	ICP,mol%	Sample	Reaction,mol%	ICP,mol%
$Cs_4PbCl_6:Mn^{2+}$ single crystals	4.62	0.01	$Cs_4PbCl_6:Sn^{2+}$ single crystals	5.40	31.07
	9.55	0.21		9.85	43.24
	16.75	4.77		17.27	30.13
	24.50	16.74		25.70	19.80

10. **Table S3. Table of reaction doping concentration and ICP Data of $Zr^{4+}/Sn^{2+}/Sb^{3+}/Mn^{2+}$-doped Cs_4PbCl_6 samples obtained by precipitation method.**

Sample	Reaction,mol%	ICP,mol%	Sample	Reaction,mol%	ICP,mol%
$Cs_4PbCl_6:Mn^{2+}$	2.01	0.68	$Cs_4PbCl_6:Sb^{3+}$	1.96	1.70
	10.92	7.99		10.71	10.40
	17.98	17.83		18.03	13.14
	25.82	24.03		25.37	23.47
$Cs_4PbCl_6:Sn^{2+}$	18.03	17.64	$Cs_4PbCl_6:Zr^{4+}$	12.61	2.13

11. **EDS maps of doped Cs_4PbCl_6 powder obtained by precipitation method**

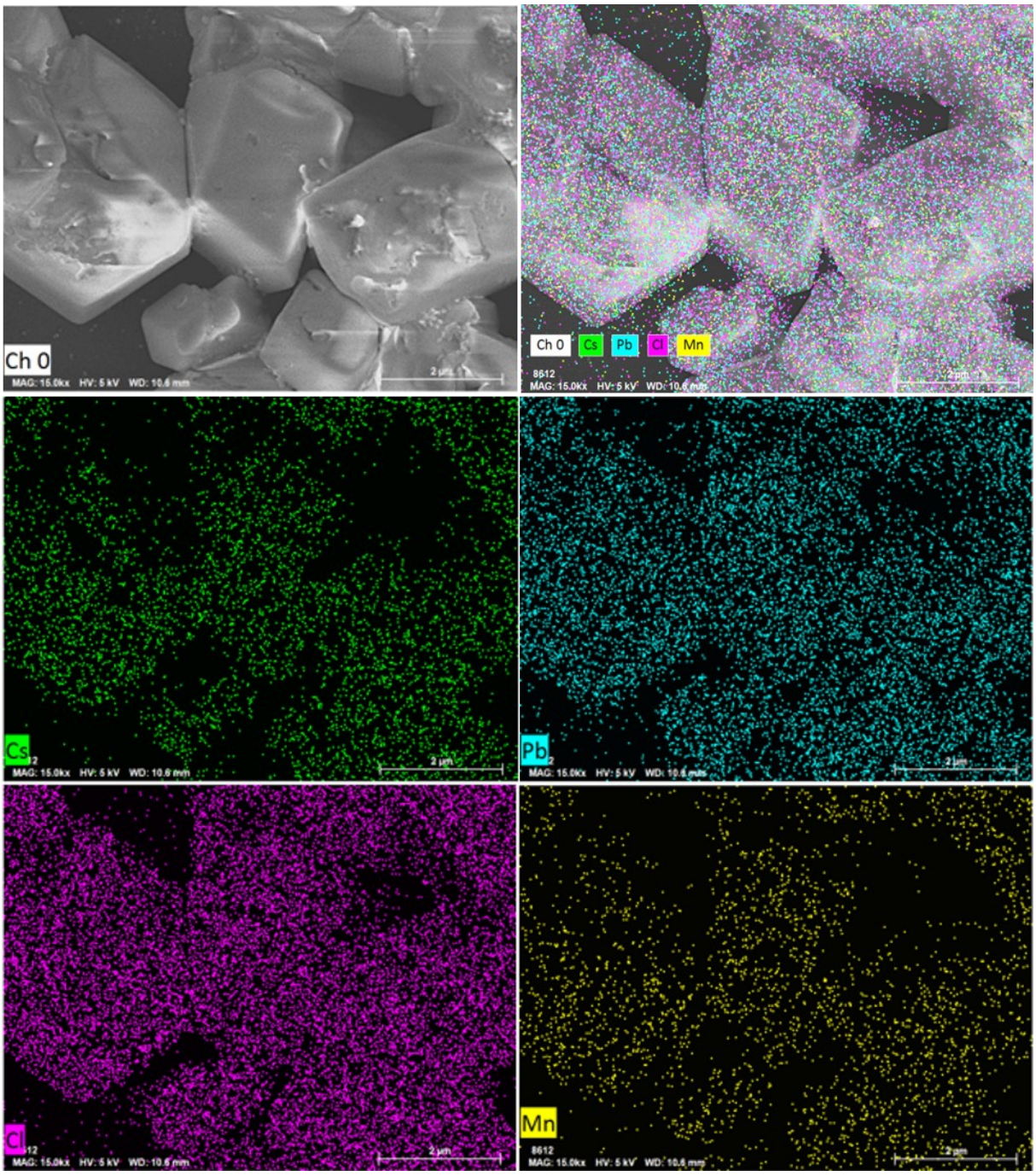


Figure S19. EDS map of Cs_4PbCl_6:7.99%Mn obtained by precipitation method.

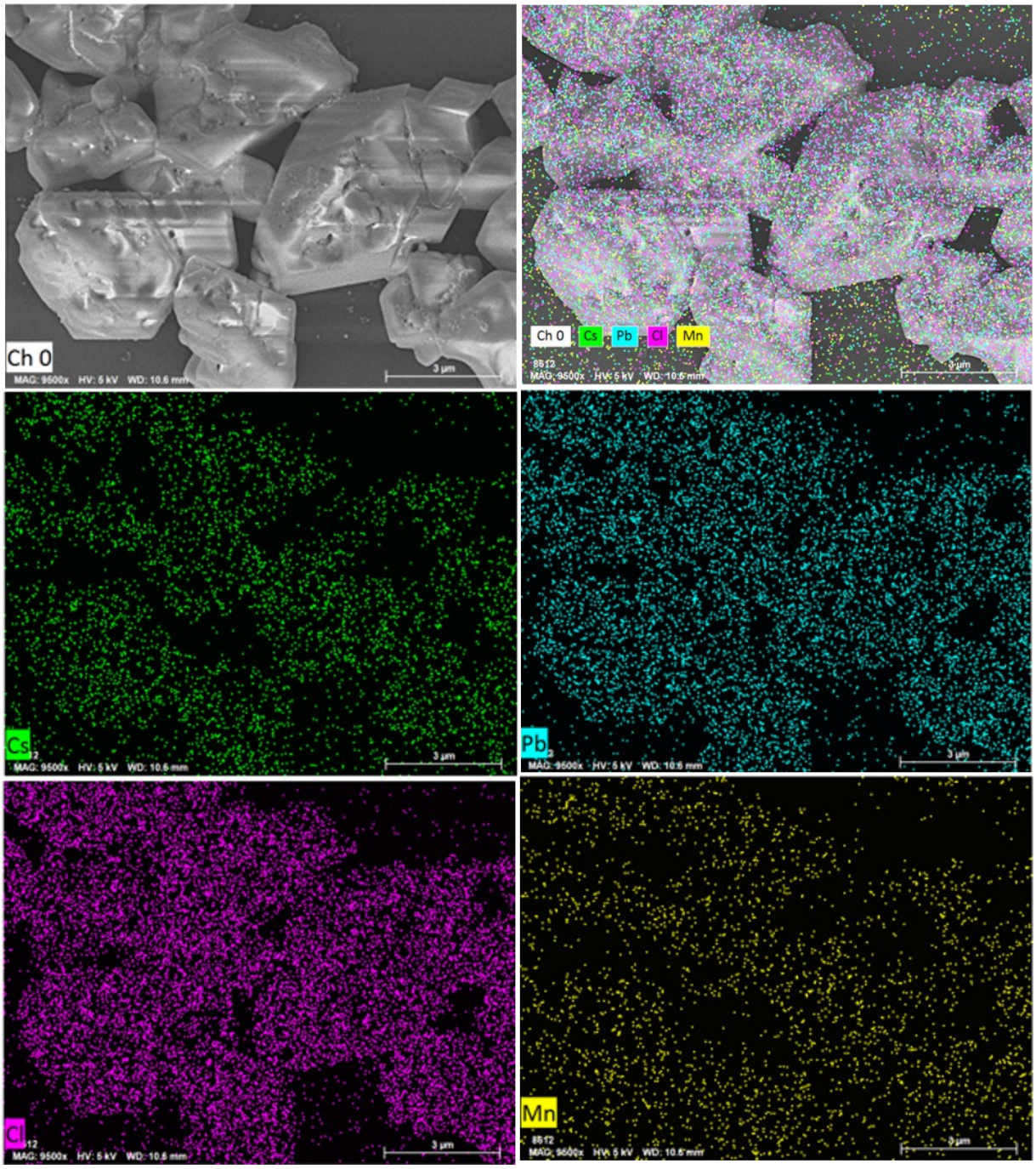


Figure S20. EDS map of Cs_4PbCl_6:17.83%Mn obtained by precipitation method.

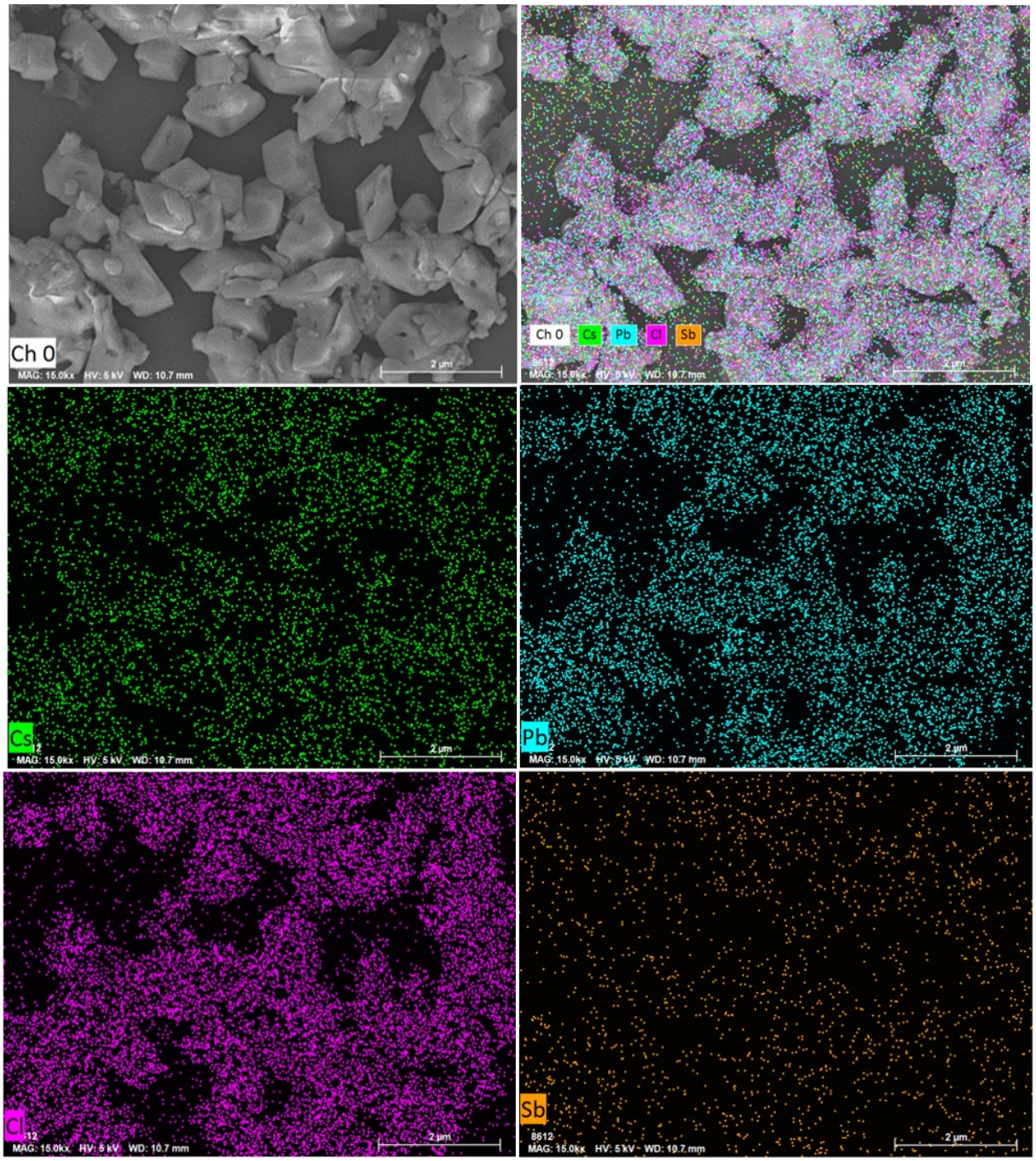


Figure S21. EDS map of Cs_4PbCl_6:10.40%Sb obtained by precipitation method.

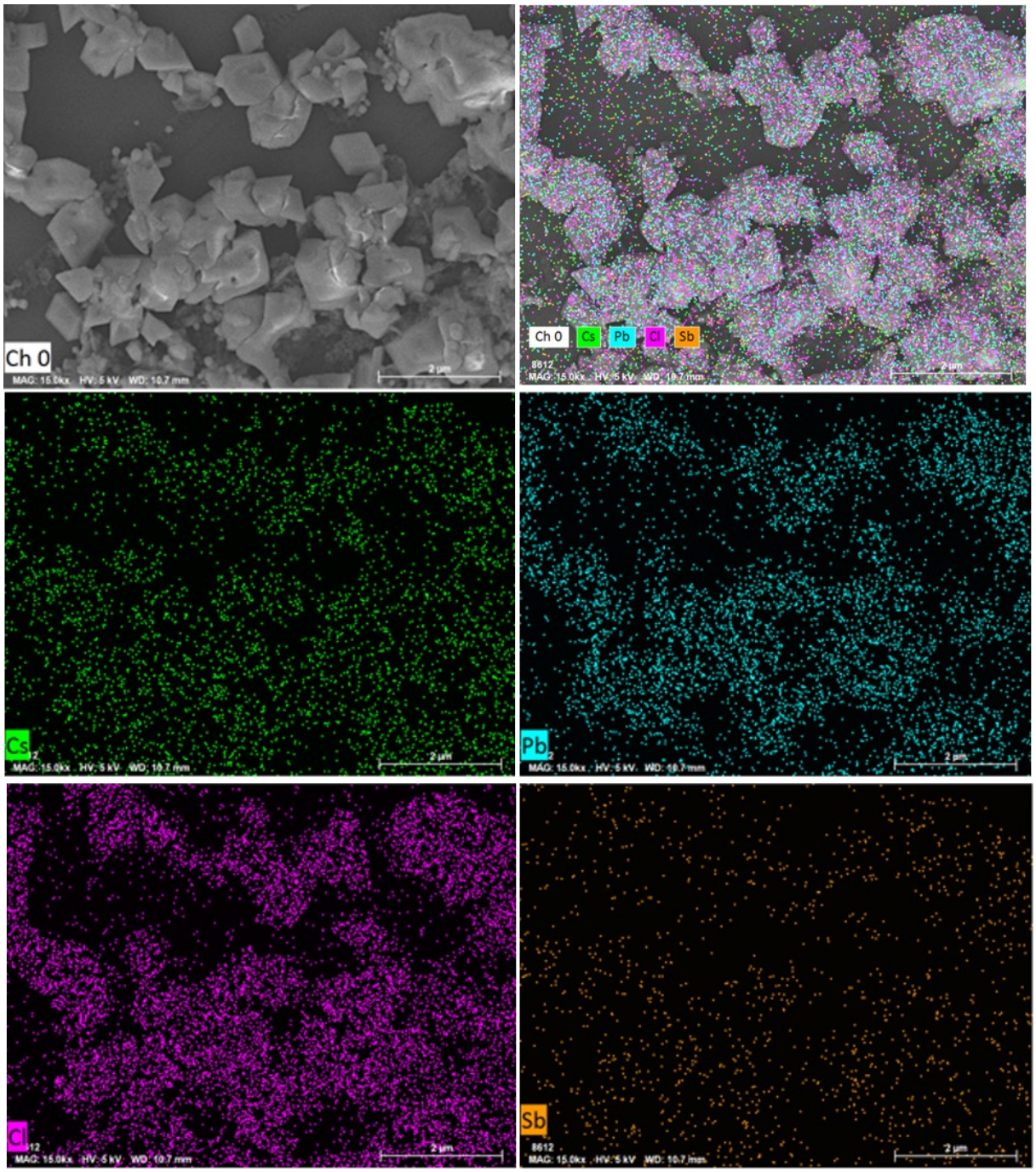


Figure S22. EDS map of Cs_4PbCl_6:13.14%Sb obtained by precipitation method.

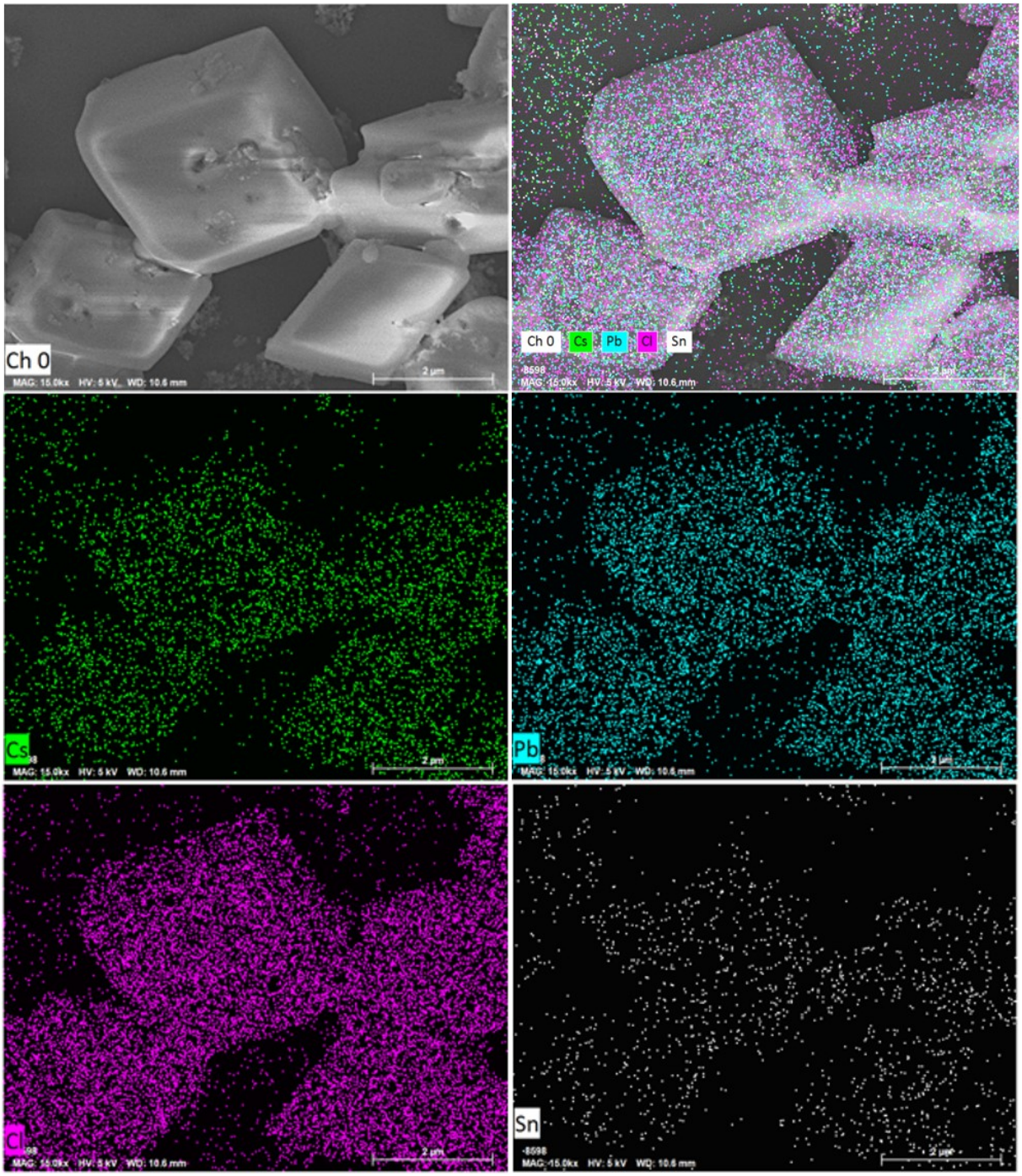


Figure S23. EDS map of Cs_4PbCl_6:17.64%Sn obtained by precipitation method.

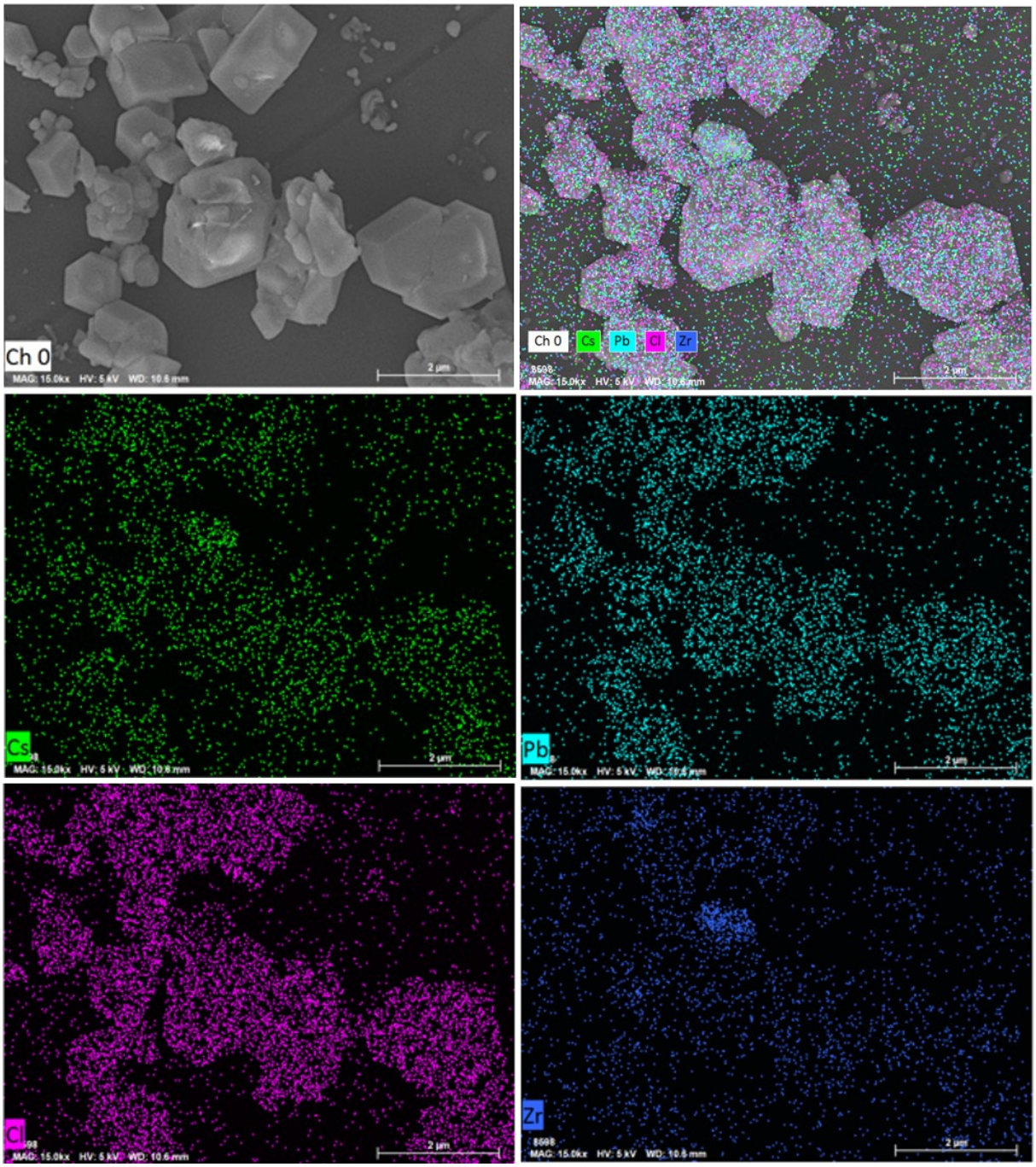


Figure S24. EDS map of Cs_4PbCl_6:2.13%Zr obtained by precipitation method.

12. **PL spectra of $Cs_4PbCl_6:Sn^{2+}$ and $Cs_4PbCl_6:Zr^{4+}$ obtained by precipitation method.**

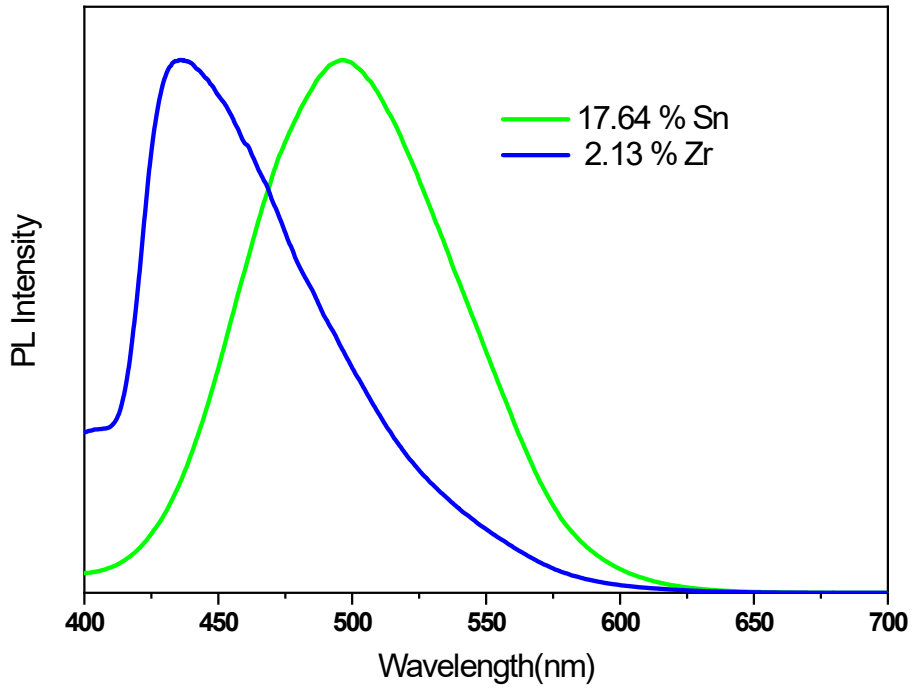


Figure S25.PL curves of 17.64%Sn and 2.13%Zr obtained by precipitation method.