

Supporting Information

Trap-tuning in Afterglow Perovskite Crystals through Alkali Metal

Ion Doping

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Experimental Section

Chemicals:

Cesium chloride (CsCl, 99.9%), manganese chloride (MnCl₂, 99%), potassium chloride (KCl, 99.5%) and silver chloride (AgCl, 99.5%) were purchased from Shanghai Macklin Biochemical Co., Ltd., China. Indium chloride (InCl₃, 99.9%) was purchased from Shanghai Yien Chemical Technology Co., Ltd., China. Lithium chloride (LiCl, 99.9%) was purchased from Shanghai Aladdin Biochemical Co., Ltd., China. Hydrochloric acid (HCl, 36.0~38.0%) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd., China. All chemicals were used as received without further purification.

Synthesis of Perovskite Single Crystal.

Cs₂Li_xAg_{1-x}InCl₆:20%Mn and Cs₂K_xAg_{1-x}InCl₆:20%Mn were synthesized by hydrothermal reaction.¹ In a typical synthesis for Cs₂Li_{0.6}Ag_{0.4}InCl₆:20%Mn single crystals, 2 mmol CsCl, 1 mmol InCl₃, 0.6 mmol LiCl, 0.4 mmol AgCl, 0.2 mmol MnCl₂ and 12 ml concentrated hydrochloric acid (12 M) were loaded in a 25 ml Teflon vessel. The vessel was sealed in a steel cup and kept in muffle furnace at 180 °C for 12 hours, then slowly cooled to room temperature at a rate of 2.8 °C /h. The as-synthesized crystals were rinsed with isopropyl alcohol and dried on filter paper.

X-ray Diffraction Measurements.

Single crystals were grounded into powders before XRD measurement. Powder X-ray diffraction (XRD) patterns were collected on an X-ray diffractometer (Rigaku Ultima IV) coupled with Cu-Kα radiation ($\lambda = 1.5406 \text{ \AA}$). The scanning rate was set at 10 °/min with a step size of 0.02°.

Steady-State Measurements of Photoluminescence, Afterglow decay and PL QY.

The measurement of the PLE, PL, afterglow decay and PL QY were conducted in a spectrometer (FS5, Edinburgh Instruments) equipped with an integrated sphere of polytetrafluoroethylene (PTFE) lining.

Photoluminescence Lifetime Measurement.

The transient photoluminescence spectra of single crystals were obtained with a time-resolved spectrometer (Delta-flex, Horiba Scientific). A pulsed 355-nm LED lamp was used as the excitation source and the time window was set at 750 ms.

Optical Photographs of Single Crystals.

Optical photographs of single crystals were taken by Canon 90D camera. Exposure time for samples in daylight, 365-nm UV lamp excitation and afterglow was set at 1/6 s, 1/6 s and 3.2 s, respectively. ISO of the photographs were 1000, 6400 and 25600, respectively.

Thermoluminescence Measurement.

The crystal was excited by 365-nm UV lamp for 5 min and allowed to standby for 1 min. The sample was heated from 123 K to 473 K during which time the TL intensity was recorded by a sensitive power meter (918D-UV-OD3R, 1936-R, Newport power Meter). A temperature module (HCS421VXY, Instec, Shanghai Hengshang Precision Instrument Co., LTD) was used for accurate temperature control, and the heating rate was set at 150 °C/min.

Table S1. Elemental analysis of $\text{Cs}_2\text{K}_x\text{Ag}_{1-x}\text{InCl}_6:20\%\text{Mn}$ single crystals by EDS.

Nominal ratio of K/(K+Ag) (%)	Actual ratio of K/(K+Ag) (%)	Actual molar ratio of Mn (%)
5	13.44	1.28
10	17.79	2.54
20	21.33	2.53
40	19.89	2.24
60	24.25	2.19

Table S2. PL QY of crystals with varied K and Li doping contents. The error bars were obtained by three parallel measurements in an integrated sphere.

Dopant concentration (mol%)		0	10	20	40	60
PL QY	K-doped crystal	1.14±0. 06	2.04±0. 27	1.83	2.33±0. 23	3.31±0.2 4
	Li-doped crystal	1.14±0. 06	2.18±0. 15	2.04±0. 11	2.04±0. 05	2.83±0.1 9

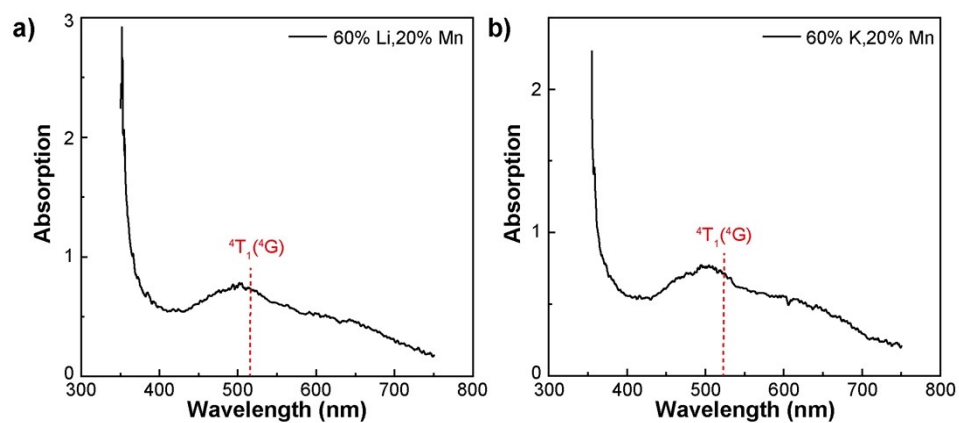


Figure S1. Absorption spectra of crystals doped with Li (a) and K (b) ions, respectively, showing a fingerprint peak of Mn²⁺ ions.

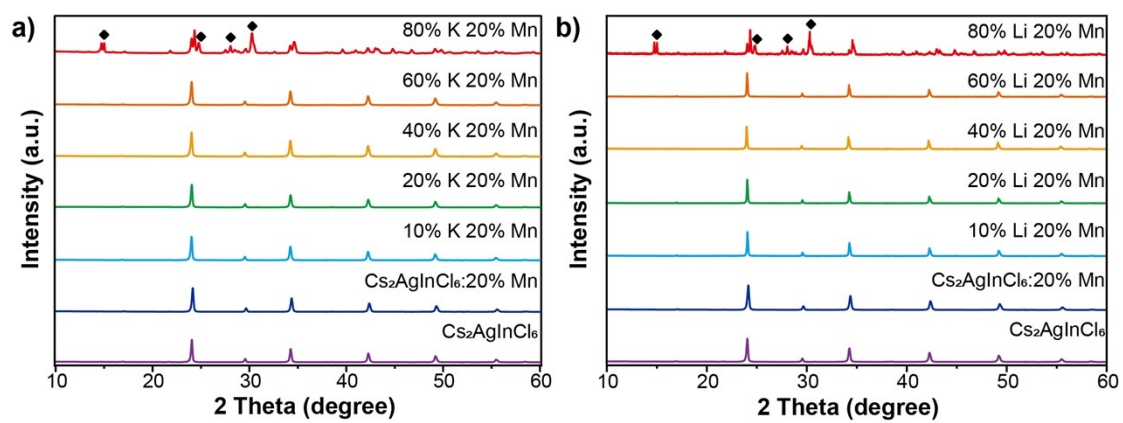


Figure S2. X-ray diffraction patterns (XRD) of (a) $\text{Cs}_2\text{K}_x\text{Ag}_{1-x}\text{InCl}_6:20\%\text{Mn}$ ($x = 0, 0.1, 0.2, 0.4, 0.6, 0.8$) and (b) $\text{Cs}_2\text{Li}_x\text{Ag}_{1-x}\text{InCl}_6:20\%\text{Mn}$ ($x = 0, 0.1, 0.2, 0.4, 0.6, 0.8$) crystals. The cubes represented the impurity phase.

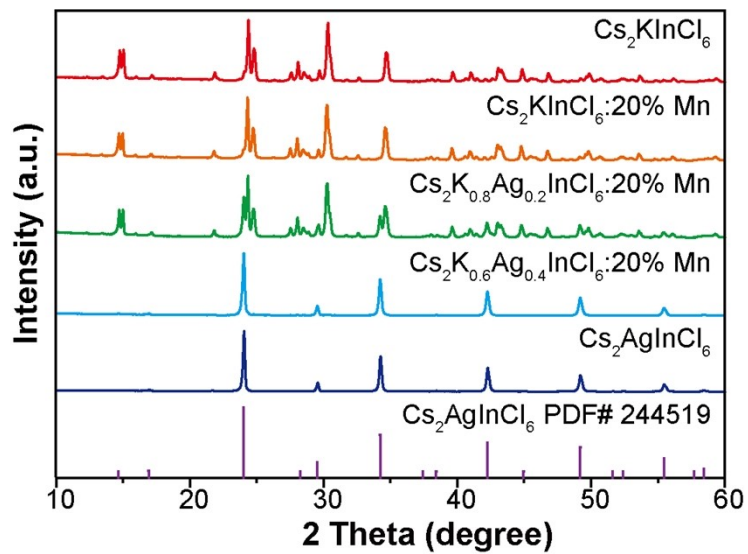


Figure S3. X-ray diffraction patterns of crystals with different doping contents, showing a clear phase separation at heavy doping level of K ions (80%).

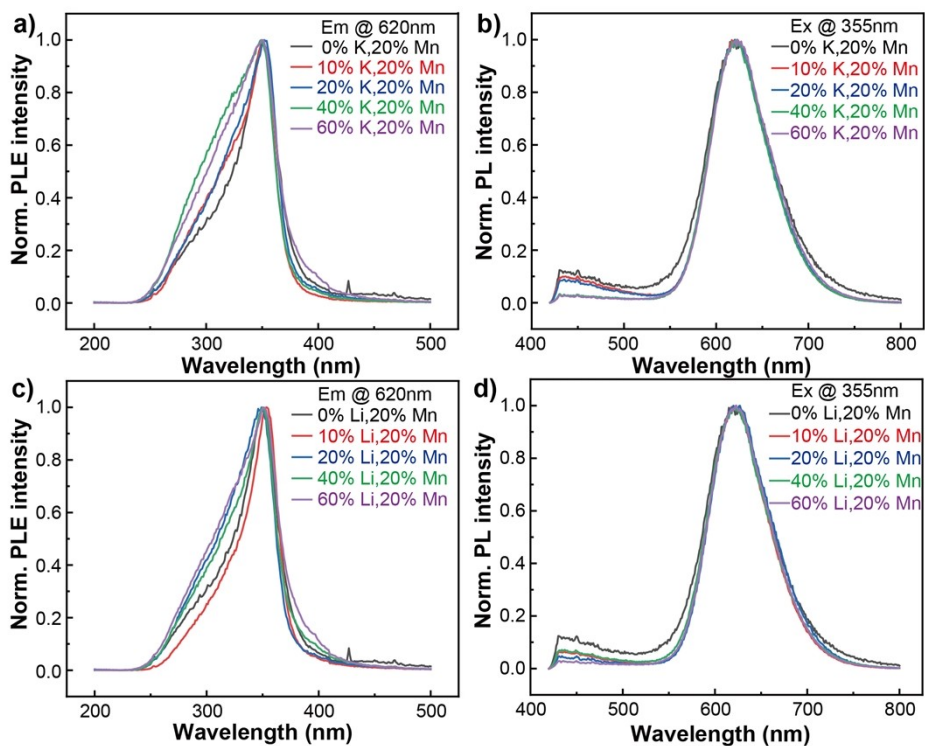


Figure S4. Normalized PLE and PL spectra of $\text{Cs}_2\text{AgInCl}_6:20\%\text{Mn}$ crystals doped with varied amount of K (a, and b) and Li ions (c, and d), respectively. It can be seen that the alkali metal ion contents did not affect the profile of PLE and PL from Mn^{2+} ions.

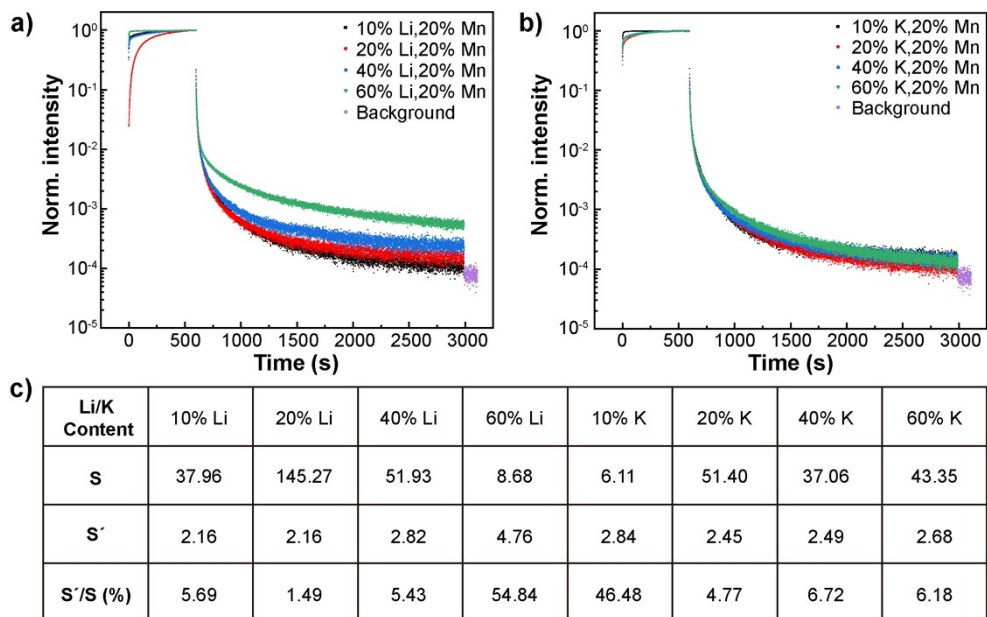


Figure S5. Afterglow profiles of (a) $\text{Cs}_2\text{Li}_x\text{Ag}_{1-x}\text{InCl}_6:20\%\text{Mn}$ ($x = 0.1, 0.2, 0.4, 0.6$) and (b) $\text{Cs}_2\text{K}_x\text{Ag}_{1-x}\text{InCl}_6:20\%\text{Mn}$ ($x = 0.1, 0.2, 0.4, 0.6$) crystals. (c) The integrated area, S and S' , and their ratio, were listed in the table.

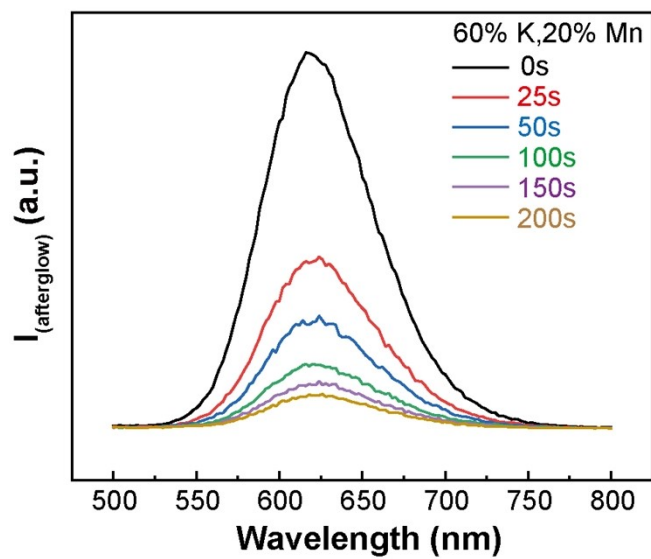


Figure S6. Afterglow emission spectra of Cs₂K_{0.6}Ag_{0.4}InCl₆:20%Mn crystals were obtained at varied delay times. Before the test, the crystals were charged by Xe lamp for 5 minutes, and the excitation wavelength was set at 355 nm.

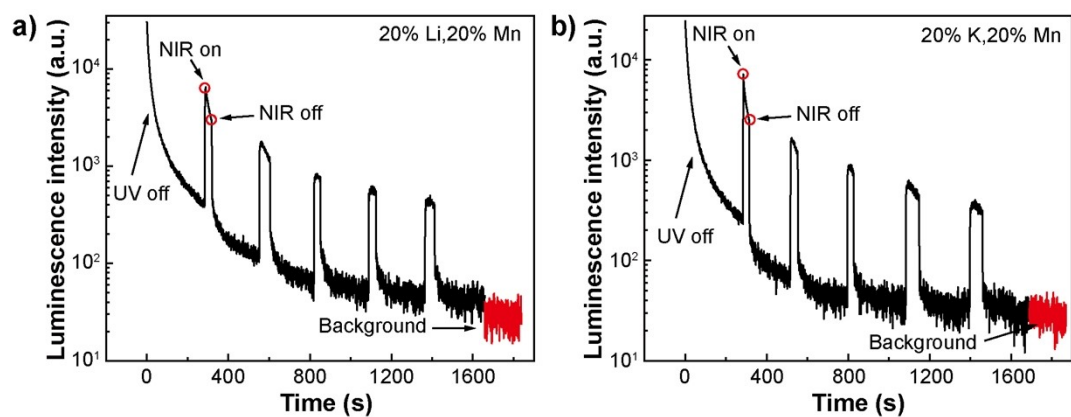


Figure S7. Photo-stimulated decay curves (by a 980-nm laser) of the $\text{Cs}_2\text{Li}_{0.2}\text{Ag}_{0.8}\text{InCl}_6:20\%\text{Mn}$ (a) and $\text{Cs}_2\text{K}_{0.2}\text{Ag}_{0.8}\text{InCl}_6:20\%\text{Mn}$ single crystals (b), respectively. The 365-nm UV lamp was used for charging for 5 min and allowed to standby for another 5 min. The stimulation was conducted by 980-nm excitation for 30 s.

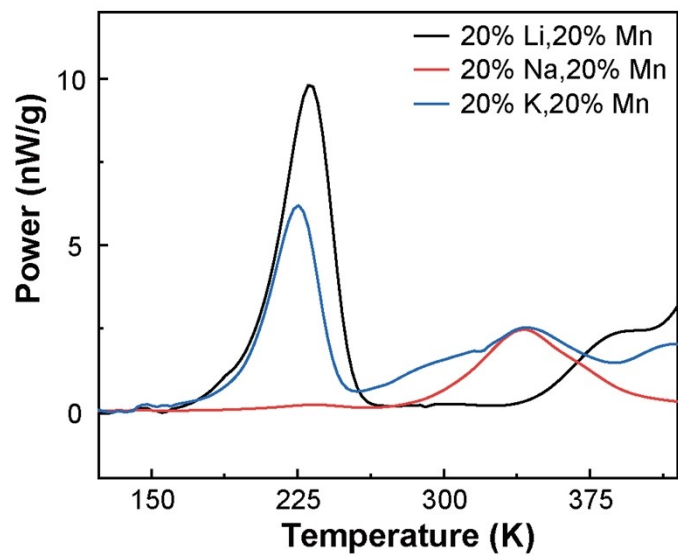


Figure S8. Thermoluminescence curves of single crystals doped with varied content of alkali metal ions. All samples were excited by 365-nm UV lamp for 5 min and allowed to standby for 1 min before measurement.

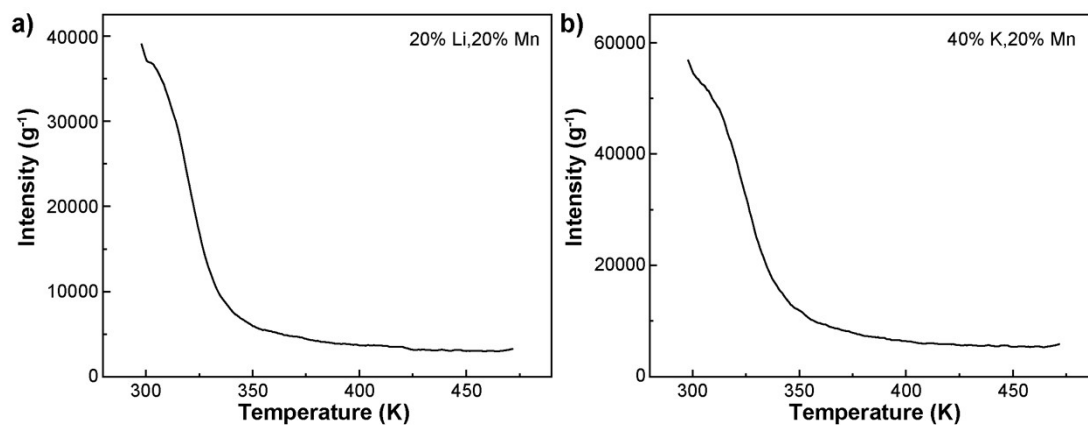


Figure S9. TL curves monitored at 620 nm emission wavelength from 298 to 470 K for Li⁺ and K⁺ doped single crystals. The crystals were pre-irradiated with a 365-nm UV lamp for 5 min.

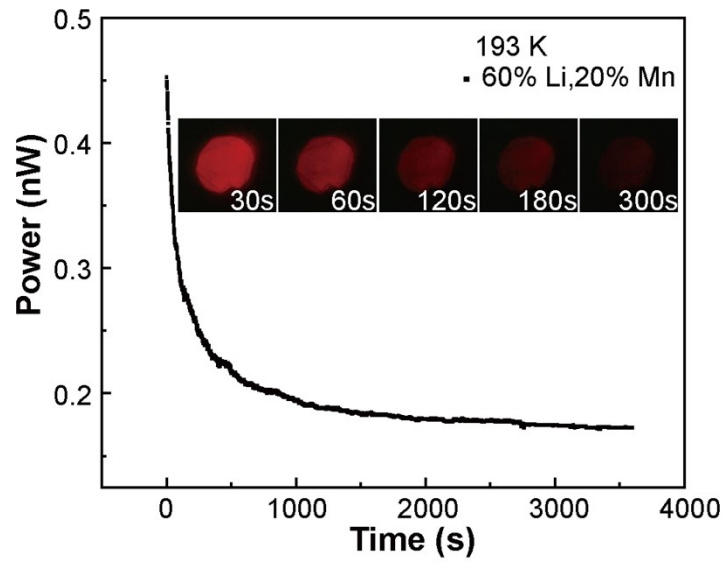


Figure S10. The afterglow decay curve of $\text{Cs}_2\text{Li}_{0.6}\text{Ag}_{0.4}\text{InCl}_6: 20\%\text{Mn}$ crystals at 193 K. The inset showed the crystals photographs at different decay times.

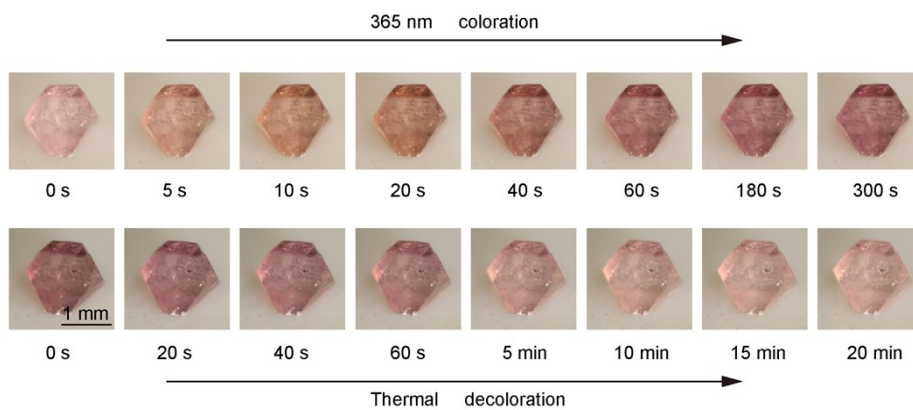


Figure S11. Under the irradiation of 365-nm ultraviolet lamp (3 mW/cm^2), the $\text{Cs}_2\text{Li}_{0.4}\text{Ag}_{0.6}\text{InCl}_6:20\%\text{Mn}$ crystal had obvious photochromism, the color was from light pink to dark purple. When heated on a 423 K hot plate, the crystal became lighter again. The exposure time and ISO of optical photographs were 1/4 s and 640, respectively.

Reference:

1. W. Zheng, X. Li, N. Liu, S. Yan, X. Wang, X. Zhang, Y. Liu, Y. Liang, Y. Zhang and H. Liu, *Angew. Chem. Int. Ed.*, 2021, **60**, 24450-24455.