

Electronic supplementary information

A New Zero-Dimensional (CsK₂)BiCl₆ Metal Halide: Boosting

Emission via B-Site Mn-Doping

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Experimental method

Mn²⁺:(CsK₂)BiCl₆ metal halides were synthesized by the solvent method. Taking 10%Mn²⁺ doping concentration as an example, 2 mmol CsCl, 1 mmol KCl, 1 mmol BiCl₃, and 0.1 mmol MnCl₄·H₂O and 5 ml HCl were sealed in a 25 ml Teflon liner, then heated at 160 °C for 12 h in a stainless steel autoclave, followed by slow cooling to room temperature. Transfer the reaction mixture from the lining to the centrifuge tube and put it into a high-speed centrifuge. Centrifugation at 5000 RPM for 5 min. After centrifugation, the supernatant was discarded and the sample was centrifuged at 6000 RPM for 3 minutes. Finally, the sample was washed with anhydrous ethanol 3 times and put into a drying oven and dried at 60°C for 24 hours. Different concentrations of Mn²⁺ ion doping can be adjusted according to the change of Mn/Bi feeding ratio by chemical formula.

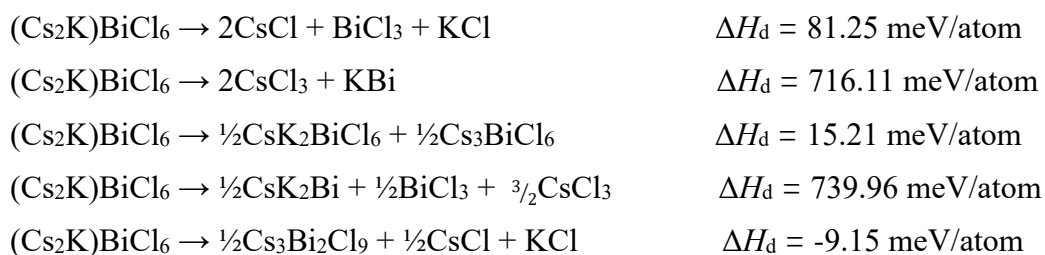
Characterizations

The Single-crystal X-ray diffraction (SCXRD) data were collected by Oxford Gemini S ultra-system with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 150 K. Powder X-ray diffraction (PXRD) data were obtained by Bruker diffractometer. The ultraviolet-visible-near infrared (UV-VIS-NIR) spectrophotometer (PerkinElmer Instruments, Lambda 750) was used to measure the absorption spectra.

The elemental composition and chemical state were identified by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi). The PL and PLE spectra, PLQY, temperature-dependent PL spectra, and PL decay were measured with a Horiba Jobin Yvon fluorolo3 spectrometer and an Edinburgh FLS 1000 fluorescence spectrometer.

The decomposition pathways and corresponding ΔH_d (unit: meV/atom) are as follows:

(Cs₂K)BiCl₆:



K₃BiCl₆:



Cs₃BiCl₆:

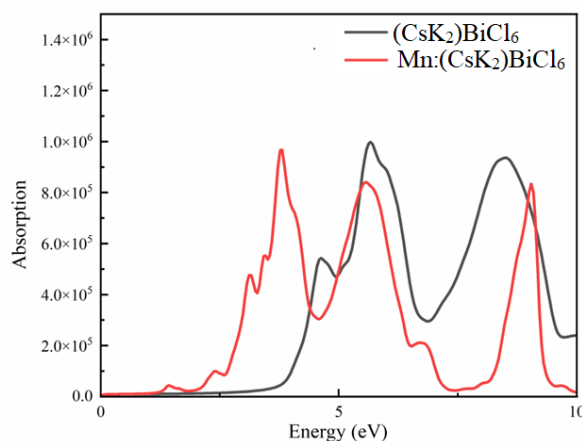


Figure S1. Absorption coefficients of Mn-doped and undoped $(\text{CsK}_2)\text{BiCl}_6$

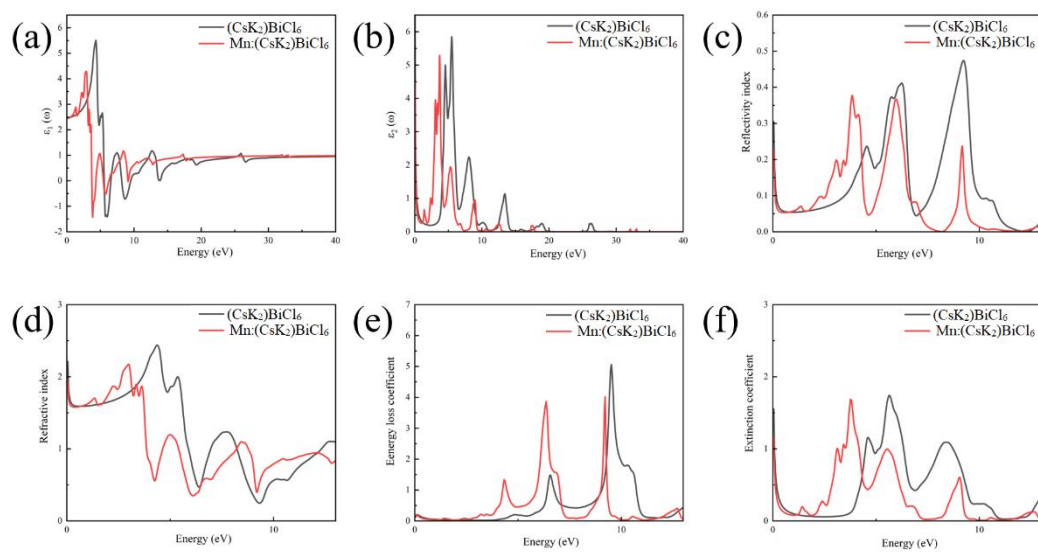


Figure S2. (a-f) Real and imaginary parts of the dielectric function, reflectivity index, refractive index, energy loss coefficient, extinction coefficient of pristine $(\text{CsK}_2)\text{BiCl}_6$ and Mn-doped $(\text{CsK}_2)\text{BiCl}_6$

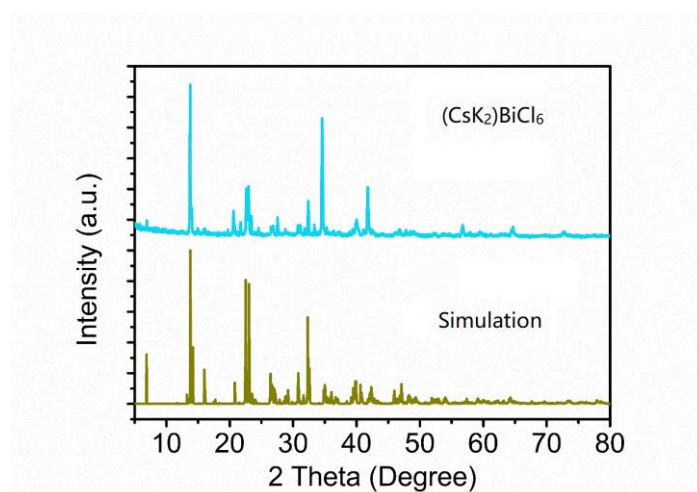


Figure S3. Experimental and calculated power XRD pattern of $(\text{CsK}_2)\text{BiCl}_6$.

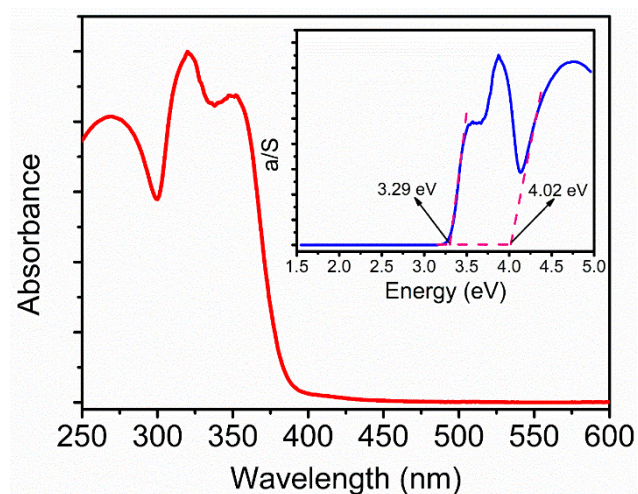


Figure S4. The absorption spectra of $(\text{CsK}_2)\text{BiCl}_6$ and corresponding Tauc spectra.

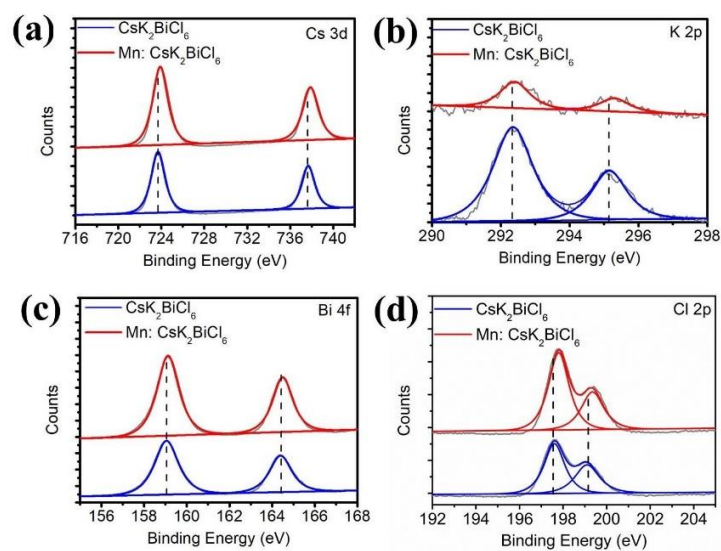


Figure S5. the high-resolution XPS spectra of Cs, K, Bi and Cl in the 10%Mn: $(\text{CsK}_2)\text{BiCl}_6$

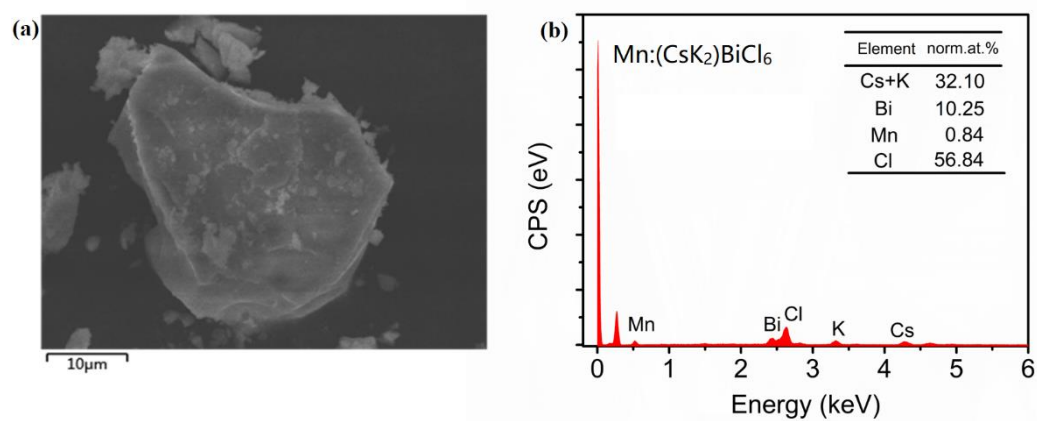


Figure S6. (a)The SEM characterization of 10% $\text{Mn}:(\text{CsK}_2)\text{BiCl}_6$. (b) the corresponding EDS spectrum.

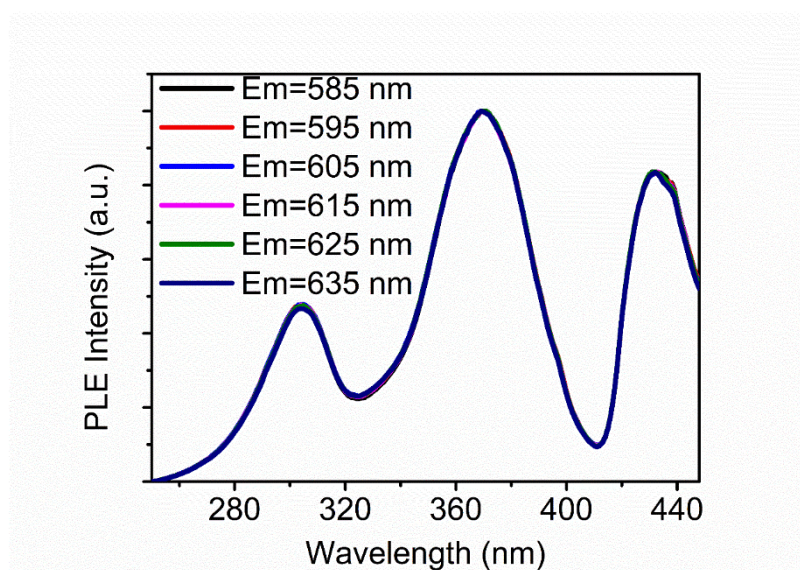


Figure S7. The PLE spectra for different PL positions of $\text{Mn}:(\text{CsK}_2)\text{BiCl}_6$ (Mn/Bi=0.1).

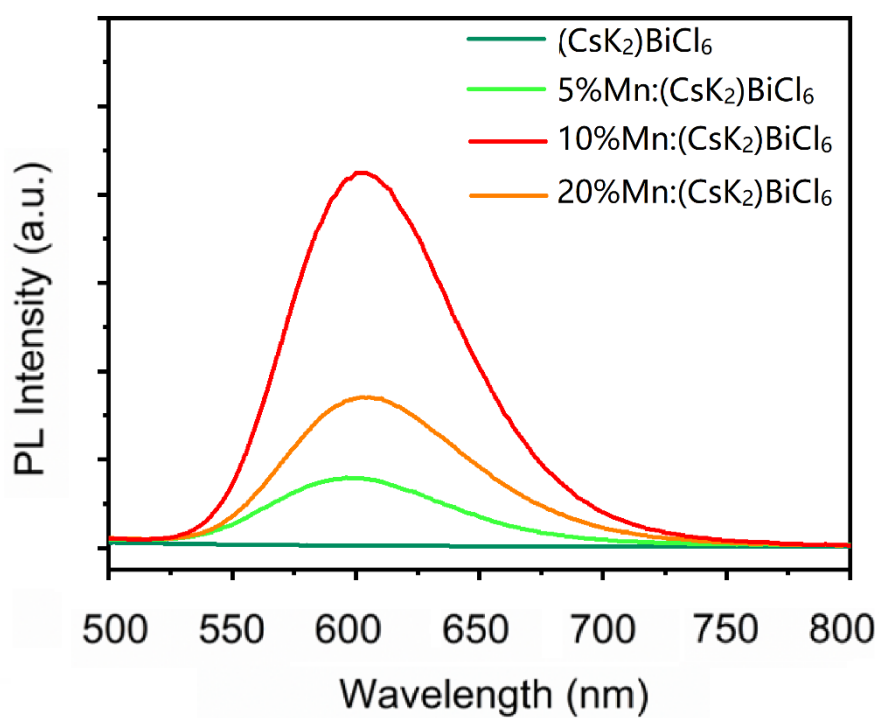


Figure S8. The PL spectra of $\text{Mn}:(\text{CsK}_2)\text{BiCl}_6$ with different Mn^{2+} doping concentrations.

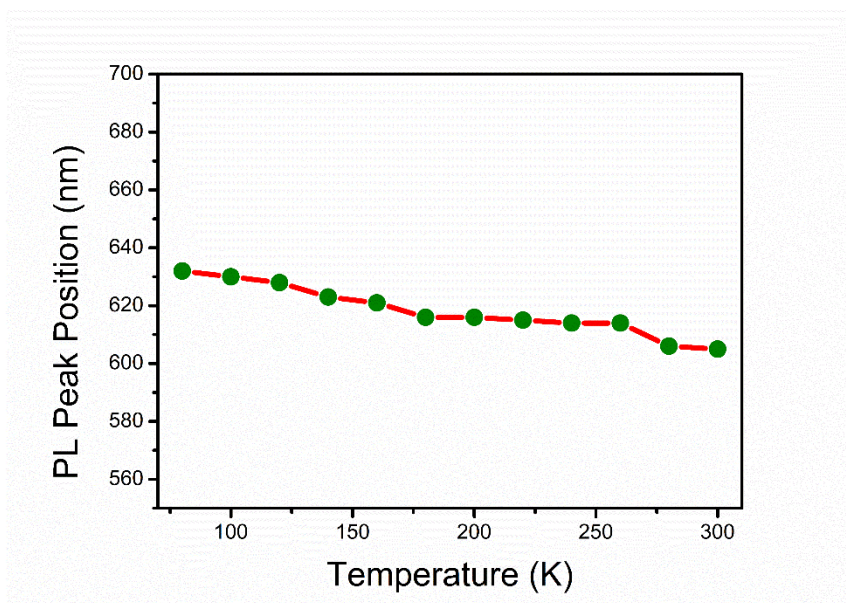


Figure S9. Dot plot of PL peak position as a function of temperature.

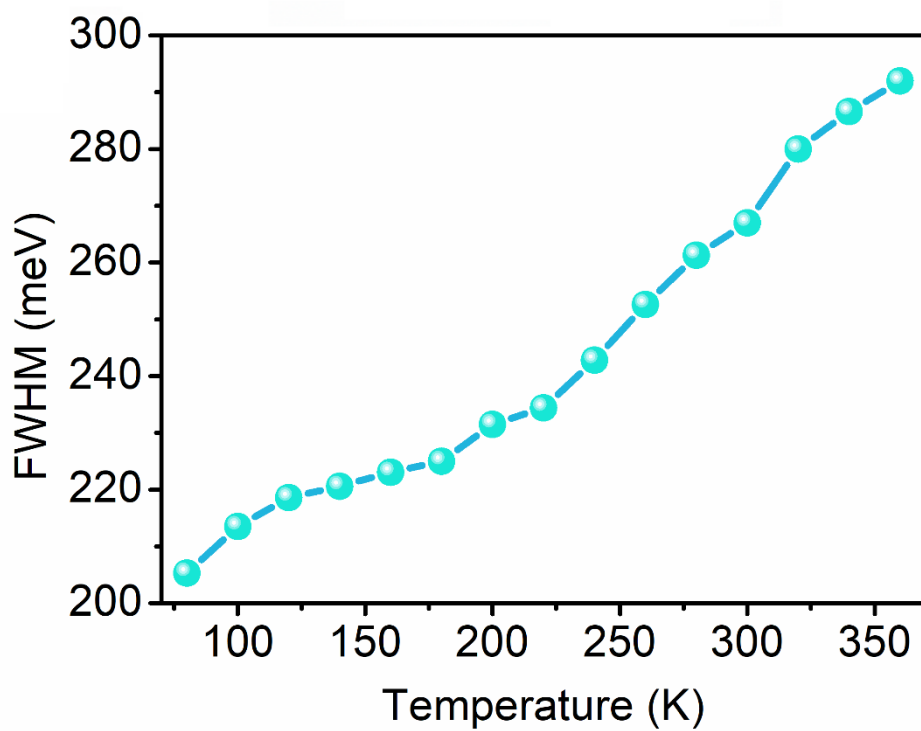


Figure S10. The relationship between FWHM and temperature.

Table S1 The PL lifetime fitting result of $(\text{CsK}_2)\text{BiCl}_6$ with different Mn concentration.

Mn concentration	A_1	τ_1 (ms)	A_2	τ_2 (ms)	τ_{ave} (ms)
5%	0.2977	0.0612	0.9579	0.0123	0.0419
10%	0.2671	0.0964	0.8282	0.0198	0.0666
20%	0.1174	0.1379	0.9293	0.0239	0.0819