Supporting Information

Highly Efficient and Stable Cs_2TeCl_6:Cr^{3+} Perovskite Microcrystals for White Light Emitting Diodes

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Experimental section

Chemicals

Cesium chloride (CsCl, 99.9%), hydrochloric acid (HCl, 37 wt% in water, Sinopharm Chemical Reagent Co., Ltd.), tellurium dioxide (TeO_2, 99.99%), bismuth chloride ($BiCl_3$, 99%), manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, 99%), chromium chloride hexahydrate ($CrCl_3 \cdot 6H_2O$, 99%), cadmium chloride hemi ($CdCl_2 \cdot 5/2H_2O$, 98%), isopropyl alcohol, acetone (≥ 99.5%) and acetonitrile were purchased from Macklin. $(CH_3COO)_3Ce \cdot xH_2O$ (99.9%), $(CH_3COO)_3Sm \cdot xH_2O$ (99.9%), $(CH_3COO)_3Eu \cdot xH_2O$ (99.9%), $(CH_3COO)_3Yb \cdot 4H_2O$ (99.9%) were purchased from Sigma-Aldrich. All chemicals were used as received without any further purification.

Synthesis of Cr^{3+} doped Cs_2TeCl_6 microcrystals (MCs)

The Cs_2TeCl_6:Cr^{3+} MCs were synthesized via a solvothermal method with some modification.[1-2] 2 mmol CsCl, 1 mmol TeO_2 and a certain amount of $CrCl_3 \cdot 6H_2O$ were dissolved in 5 ml HCl and then stirred overnight at 30℃ and transferred to a polytetrafluoroethylene (PTFE) container. Subsequently, the container was placed in the oven at 180 ℃ for 12 hours, it was cooled to room temperature at 6-8 ℃/h. The products were centrifugation, washed with isopropyl alcohol, acetone and acetonitrile in sequence. Finally, the Cs_2TeCl_6:Cr^{3+} MCs were dried at 60 ℃ in a vacuum oven for 24 h before use.

Fabrication of WLEDs

The WLEDs were constructed using commercial UV LED chip (382 nm), yellow phosphor (Cs_2TeCl_6:Cr^{3+} MCs), and blue phosphor ($BaMgAl_{10}O_{17}$:Eu^{2+} MCs). The two phosphors are thoroughly mixed with epoxy resin and then coated on the UV LED chips, finally solidified at 80 °C for 1 hour to fabricate the WLEDs.

Characterization

UV-visble absorption spectra were obtained with a Shimadzu UV-1700 PC UV/Visble scanning spectrophotometer in the range from 300 nm to 1100 nm. Powder X-ray diffraction (XRD) patterns were recorded by using a Rigaku TTRIII X-ray diffractometer at 200 mA and 40 kV with Cu Kα radiation (λ = 1.5406 Å). The scan range was set from 5° to 70° with the scanning rate of 10°/min. The morphology of the products was recorded with a JEOL JSM-7500F scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) analysis and mapping. Trace-Metal Analysis was carried out using inductively coupled plasma optical emission spectrometry (ICP-OES) on a Varian720-ES ICP-optical emission spectrometer. The X-ray photoelectron spectroscopy (XPS) was performed on the Kratos Axis Ultra DLD spectrometer equipped with a monochrome Al Kα X-ray source (hν = 1486.6 eV), which was operated by a drive power of 150 W with a multichannel plate and a delay line detector under 1.0×10^{-9} Torr vacuum. Photoluminescence spectra were recorded on a Shimadzu RF-6000 spectrofluorometer. The PL decay curves were measured on a FLS 920-stm spectrometer Edinburgh Instruments and collected by PerkinElmer LS 55 fluorescence spectrometer. The PLQY of the samples were acquired using a fluorescence spectrofluorometer (FLS980, Edinburgh Instruments) equipped with an integrating sphere. All of the measurements were performed at room temperature.

Supplementary Figures and Tables:

Table S1 The data of metal ions (M) mole percent (mol %) in Cs_2TeCl_6:M MCs measured by ICP-OES.

Sample	M:(Te+M)	Nominal/mol%	Actual/mol%
Cr	1:200	0.5	0.03
Cr	1:50	2	0.66
Cr	1:20	5	1.34
Cr	1:10	10	3.57
Cr	3:20	15	4.89
Cr	1:5	20	6.73
Mn	3:20	15	5.12
Cd	3:20	15	4.96
Bi	3:20	15	4.77
Ce	3:20	15	2.63
Yb	3:20	15	2.84
Sm	3:20	15	2.58
Eu	3:20	15	2.71

Table S2 Atomic coordinates for Cs_2TeCl_6.

Atom	Ox	wyck	site	x/a	y/b	z/c
Te1	4	4a	m-3m	0	0	0
Cs1	1	8c	-43m	1/4	1/4	1/4
Cl1	-1	24e	4m.m	0.264	0	0

Table S3 Crystallographic data and parameters of the Rietveld refinement of Cs_2TeCl_6 and Cs_2TeCl_6:Cr^{3+} MCs.

Sample	Cs_2TeCl_6	Cs_2TeCl_6:Cr^{3+}
2θ range	$10° \leq \theta \leq 70°$	
Temperature (K)	298	
Crystal system	Cubic	
Space group	Fm3-m	
Z	4	
a = b = c (Å)	10.500	10.473
α = β = γ (deg)	90	
Volume (Å^3)	1157.798	1148.765
X-ray source	Cu Kα1	
Wavelength / Å	1.5406	
R_p (%)	6.75	6.25
R_{wp} (%)	6.12	5.68
χ^2	1.86	1.68

Table S4 Selected bond distances (Å) and angles (deg.) for Cs_2TeCl_6.

Vector	Length	Angle	Degrees
Te1-Cs1 × 8	4.53500(4)	Cl1-Te1-Cl1	90.000(0)
Te1-Cl1 × 6	2.76947(3)	Cl1-Te1-Cl1	180.000(0)
Cs1-Cs1 × 6	5.23657(6)	Cs1-Cs1-Cl1	45.048(0)
Cs1-Cl1 × 12	3.70590(3)		

Table S5 Selected bond distances (Å) and angles (deg.) for $Cs_2TeCl_6:Cr^{3+}$.

Vector	Length	Angle	Degrees
Te1-Cs1 × 8	4.54686(1)	Cl1-Te1-Cl1	90.000(0)
Te1-Cl1 × 6	2.57832(1)	Cl1-Te1-Cl1	180.000(0)
Cs1-Cs1 × 6	5.25026(2)	Cs1-Cs1-Cl1	45.005(0)
Cs1-Cl1 × 12	3.71279(1)		

Table S6 The PLQY of Cr^{3+} doped Cs_2TeCl_6 MCs.

Sample	PLQY(Vis) [%]
Cs_2TeCl_6	6.7
$Cs_2TeCl_6:Cr^{3+}$ (0.03 %)	11.2
$Cs_2TeCl_6:Cr^{3+}$ (0.66 %)	29.3
$Cs_2TeCl_6:Cr^{3+}$ (1.34 %)	55.5
$Cs_2TeCl_6:Cr^{3+}$ (3.57 %)	73.9
$Cs_2TeCl_6:Cr^{3+}$ (4.89 %)	81.5
$Cs_2TeCl_6:Cr^{3+}$ (6.73%)	53.4

Table S7 Photometric results of the WLEDs working at different drive currents.

Current(mA)	x	y	CCT (K)	R_a
5	0.3217	0.3506	5893	79.3
15	0.3208	0.3508	5779	79.9
25	0.3225	0.3503	5826	81.3
35	0.3216	0.3512	5801	81.7
45	0.3231	0.3520	5922	81.6
55	0.3209	0.3497	5703	81.8

Table S8. Summary of the optically excited WLEDs performance.

Emitters	CIE (x, y)	CCT (K)	CRI	luminous efficiency (lm/W)	Ref.
Cs_2SnCl_6:1.1%Bi^{3+}/0.2 %Te^{4+}	(0.34, 0.37)	5233	73	-	3
Cs_2SnCl_6 :Bi^{3+} /0.049% Te^{4+}	(0.33, 0.33)	5613	-	26.65	4
$Cs_2AgIn_{0.883}Bi_{0.167}Cl_6$	(0.42, 0.39)	3260	87	-	5
$CsCu_2I_3$	(0.35, 0.36)	5035	-	-	6
Cs_2(Na, Ag)$InCl_6$:7.09%Ho^{3+}	(0.39, 0.46)	-	75.4	-	7
Cs_2HfCl_6:Bi^{3+}/0.01%Te^{4+}	(0.31, 0.32)	6866	84.5	4.25	8
Cs_2ZrCl_6:1.5%Sb^{3+}	(0.32, 0.33)	5438	96	-	9
$(NH_4)_2SnCl_6$:0.5%Te^{4+}	(0.39, 0.38)	3855	83	31	10
Cs_2SnCl_6:2.75%Bi^{3+}	(0.36, 0.37)	4486	-	-	11
Cs_2TeCl_6:4.89%Cr^{3+}	(0.32, 0.35)	5826	81.3	19.34	This work

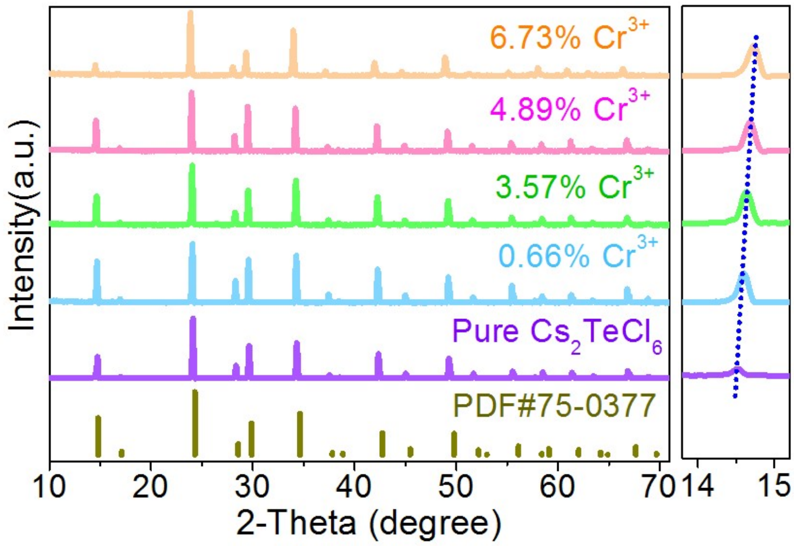

Fig. S1 XRD patterns of pure Cs_2TeCl_6 and various Cr^{3+} doped Cs_2TeCl_6 MCs.

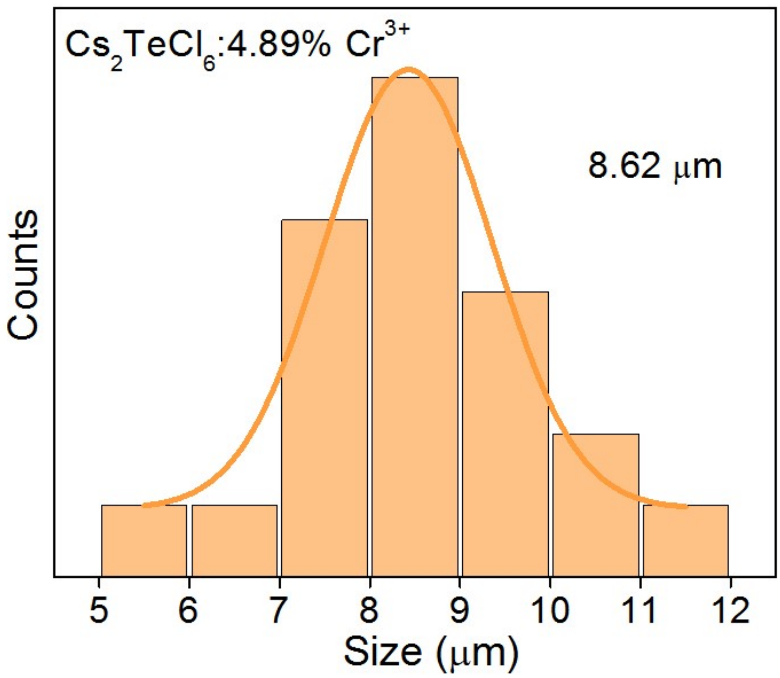

Fig. S2 Diameter distribution of Cs_2TeCl_6:Cr^{3+} (4.89 %) MCs.

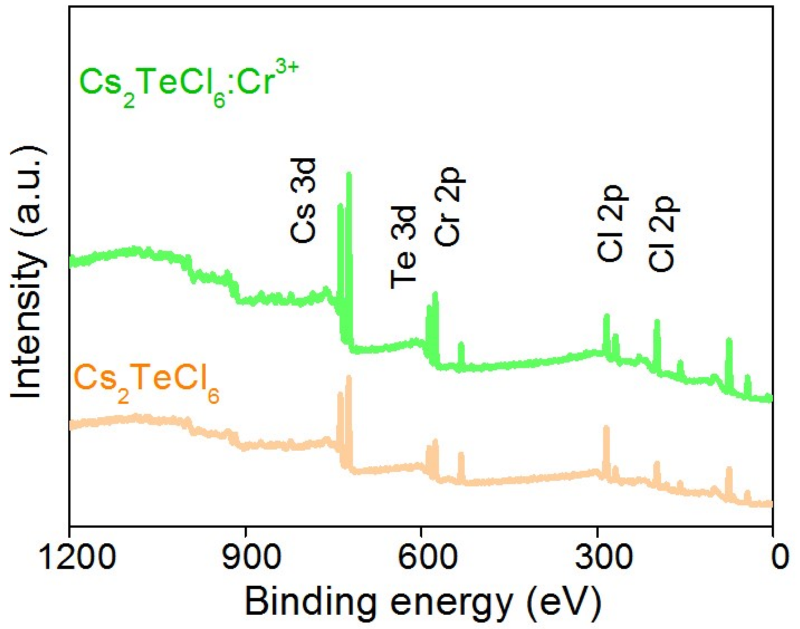

Fig. S3 High-resolution XPS analysis of pure Cs_2TeCl_6 and Cs_2TeCl_6:Cr^{3+} MCs.

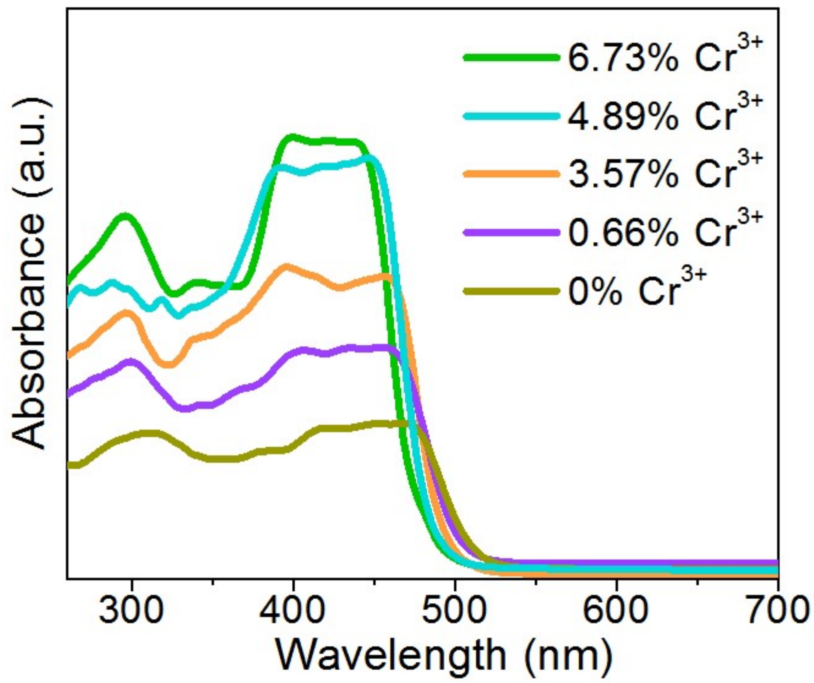

Fig. S4 Absorption spectra of various Cr^{3+} doped Cs_2TeCl_6 MCs.

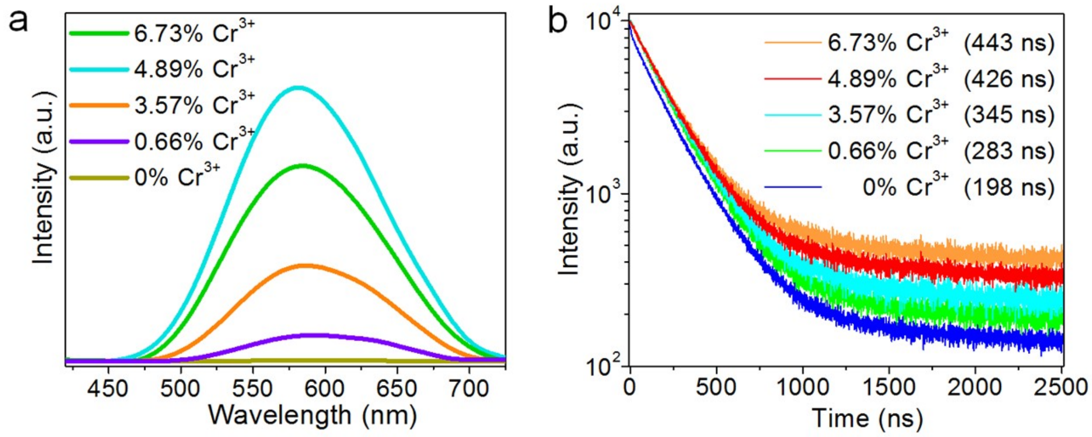

Fig. S5 (a) Emission spectra. (b) Emission dynamics of pure and various Cr^{3+} doped Cs_2TeCl_6 MCs monitored at 590 nm.

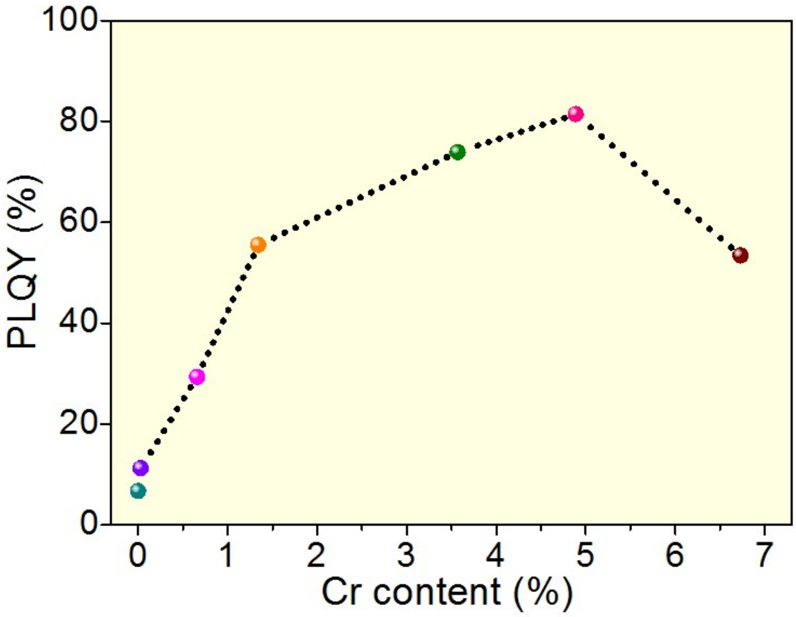

Fig. S6 PLQY of various Cr^{3+} doped Cs_2TeCl_6 MCs.

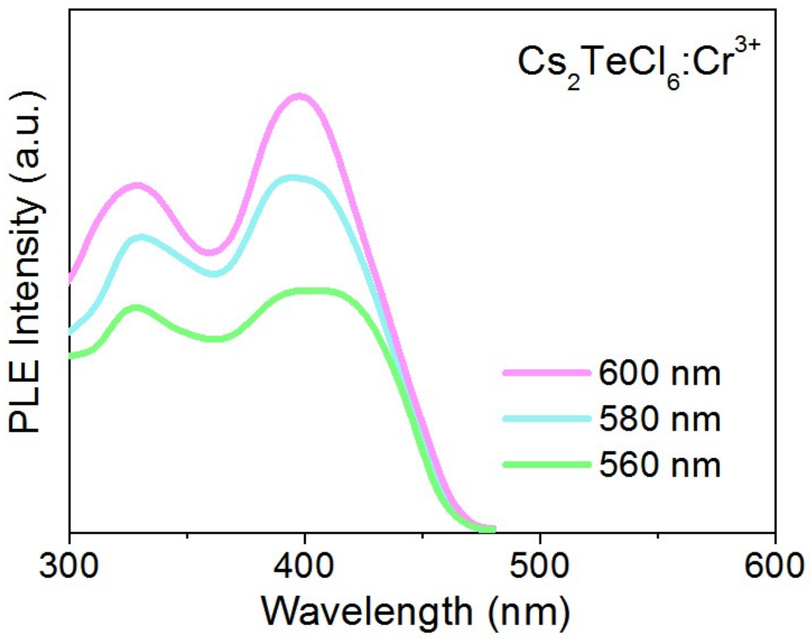

Fig. S7 The excitation spectra monitored at 560, 580, and 600 nm for $Cs_2TeCl_6:Cr^{3+}$ MCs.

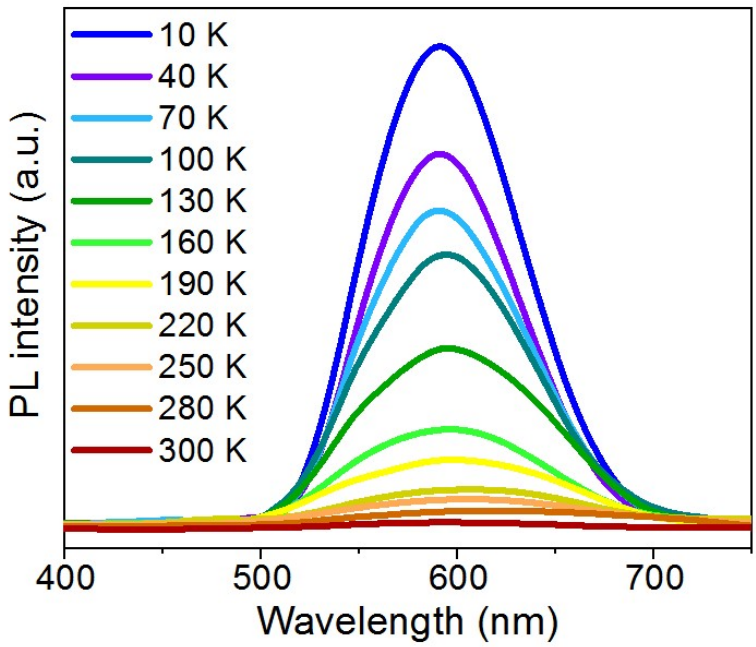

Fig. S8 Temperature-dependent PL spectra (T = 10-300 K) for Cs_2TeCl_6 MCs.

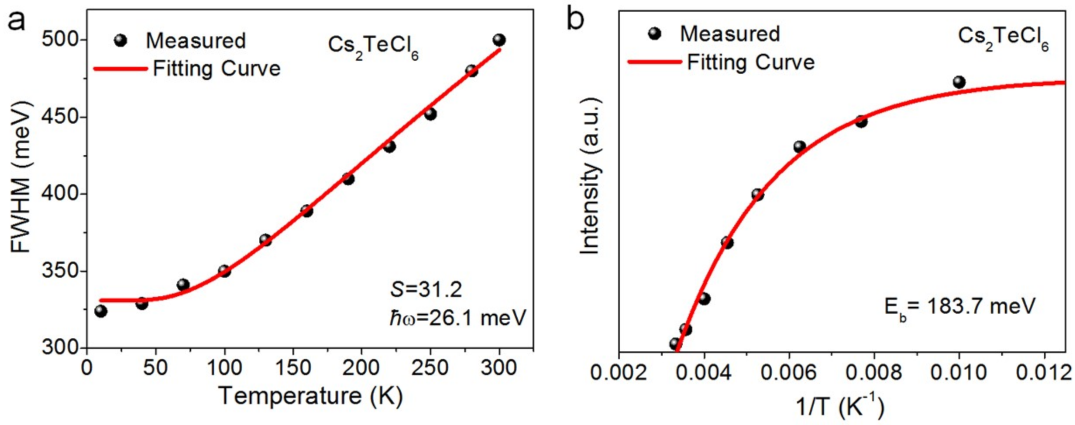

Fig. S9 (a) Fitting curve of the FWHM as a function of temperature. (b) Extracted PL intensity versus $1/T$ and the corresponding fitting result.

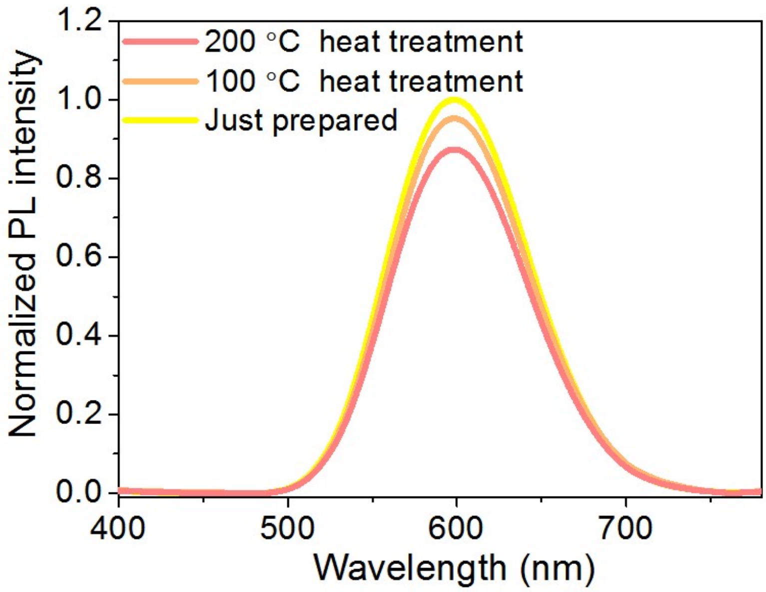

Fig.S10 Normalized PL spectra of just-prepared and heat-treated Cs_2TeCl_6:4.89%Cr^{3+} samples.

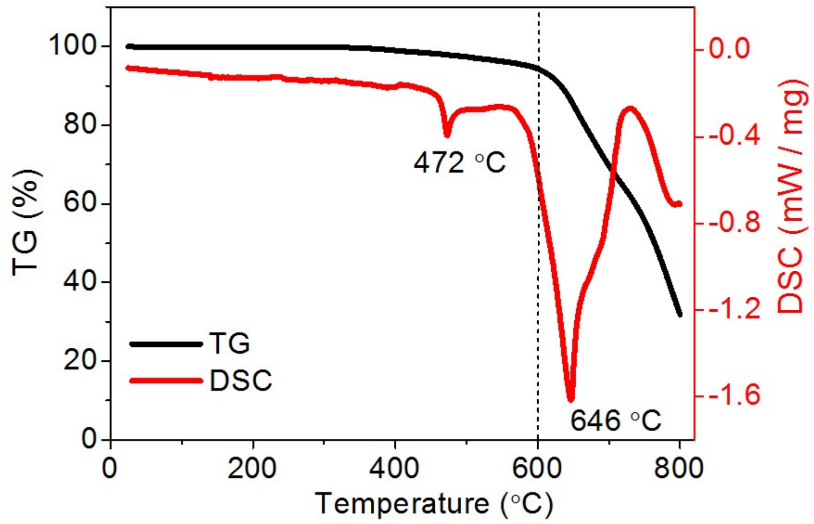

Fig.S11 TG and DSC curves of Cs_2TeCl_6:4.89%Cr^{3+} MCs.

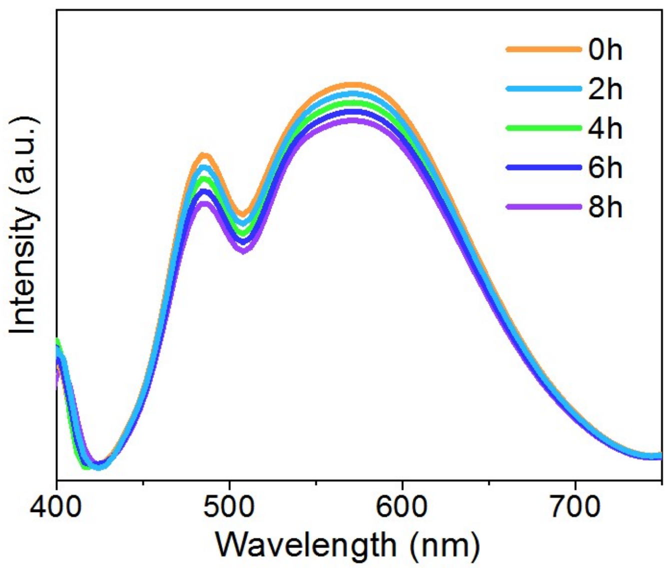

Fig. S12 EL spectra of the WLEDs at different operating times driven the current of 25 mA.

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