

Electronic Supplementary Material

Enhancing efficiency and tuning emission band via energy transfer of Cr³⁺, Ce³⁺ co-doped CaLu₂Mg₂Si₃O₁₂ phosphors

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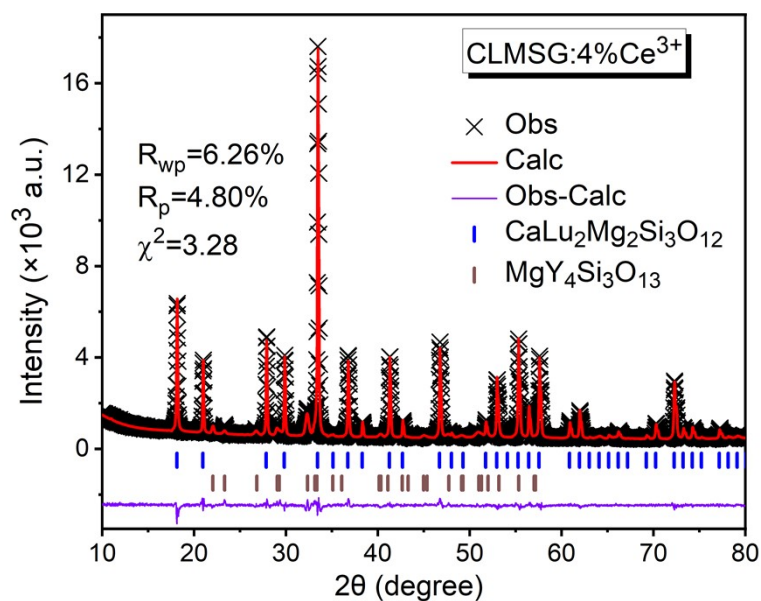


Fig. S1 Rietveld refinement results of the XRD pattern of CLMSG:4%Ce³⁺.

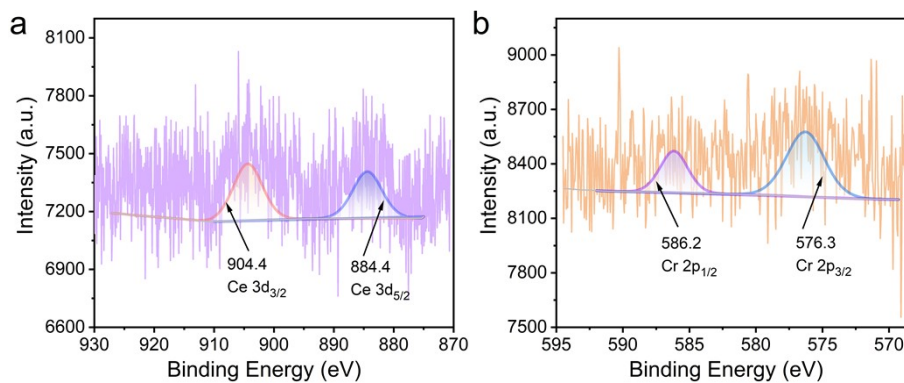


Fig. S2 XPS spectra of CLMSG:4%Ce³⁺,3%Cr³⁺ in Ce 3d and Cr 2p levels.

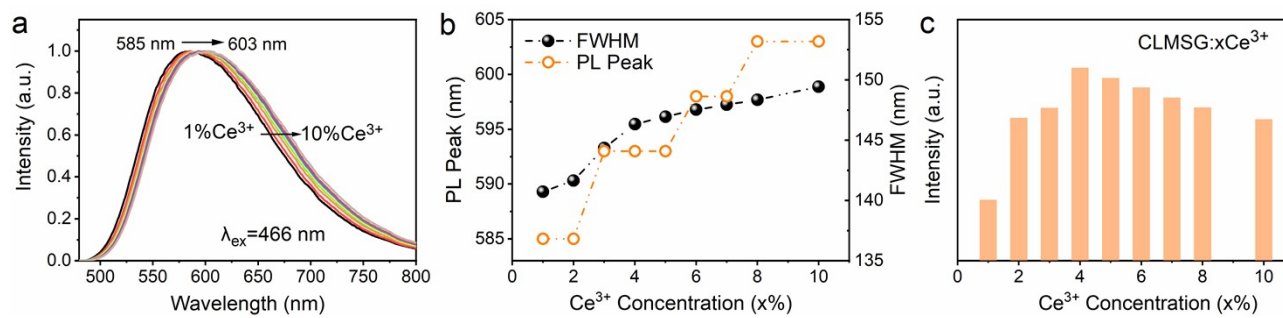


Fig. S3 (a) Normalized PL spectra, (b) PL peak and FWHM (c) intensities of CLMSG:xCe³⁺ ($x = 1\% - 10\%$).

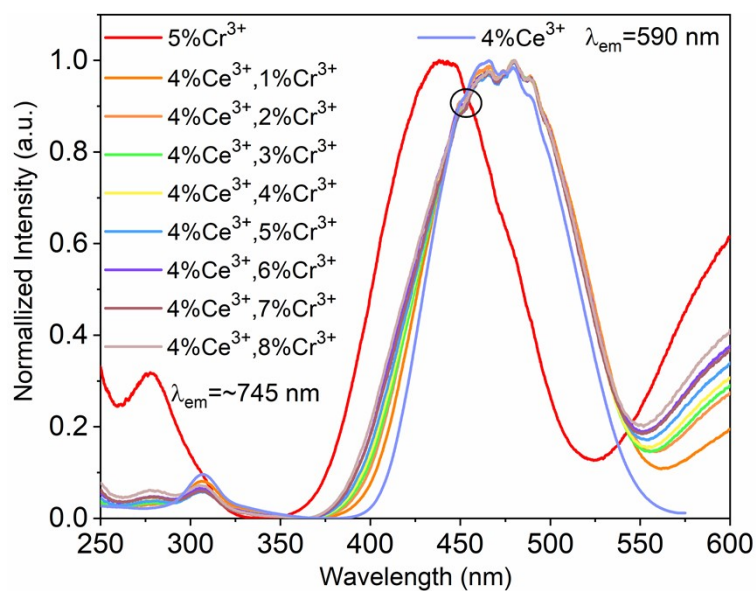


Fig. S4 Normalized PLE spectra of CLMSG:5%Cr³⁺ and CLMSG:4%Ce³⁺, yCr³⁺ (y = 0% - 8%). The cross-point of the PLE spectra is located at approximately 457 nm.

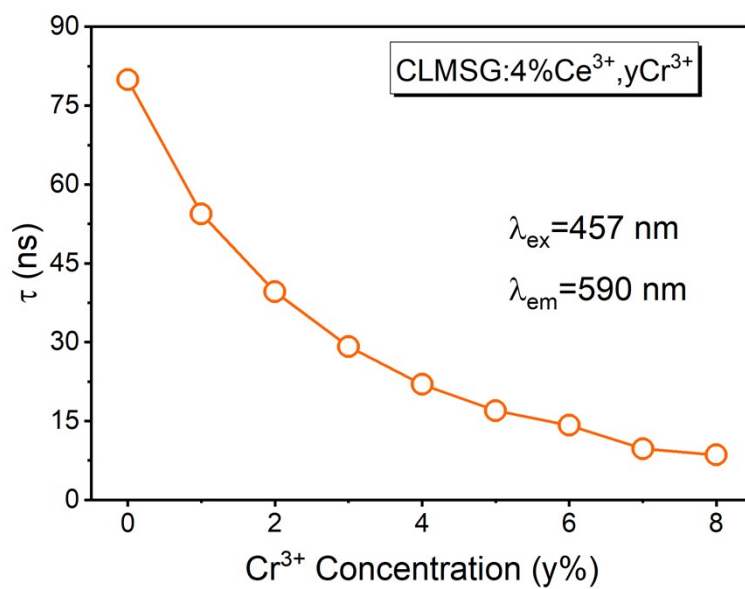


Fig. S5 Fluorescent decay times of Ce³⁺ monitored at 590 nm and excited at 457 nm in CLMSG:4%Ce³⁺, yCr³⁺ (y = 0% - 8%) recorded at RT. τ is the average lifetime, which gradually shortens from 79.9 to 8.5 ns when Cr³⁺ increases from 0 to 8%.

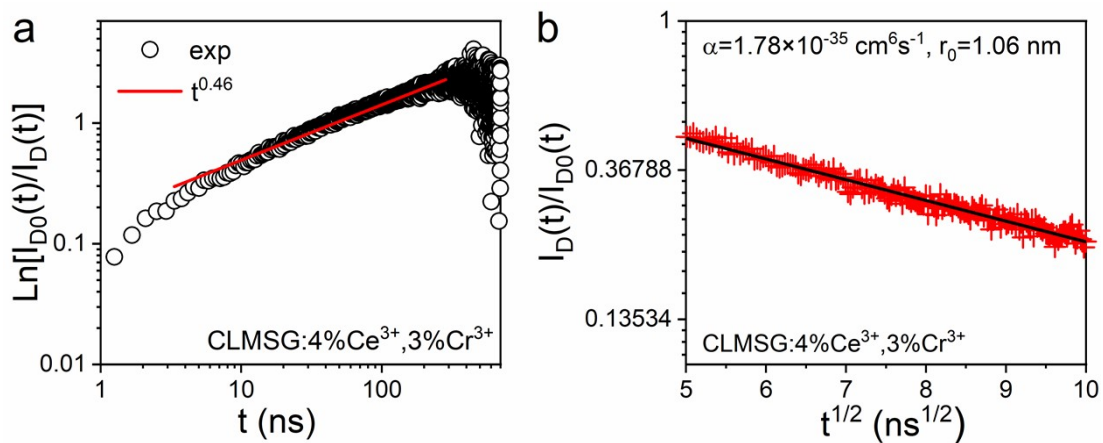


Fig. S6 (a) Log-log plot of $\ln[I_{D0}(t)/I_D(t)]$ vs t and (b) Plot of $\ln[I_D(t)/I_{D0}(t)]$ vs $t^{1/2}$ for the sample CLMSG:4%Ce³⁺,3%Cr³⁺. The solid lines indicate the fitting result.

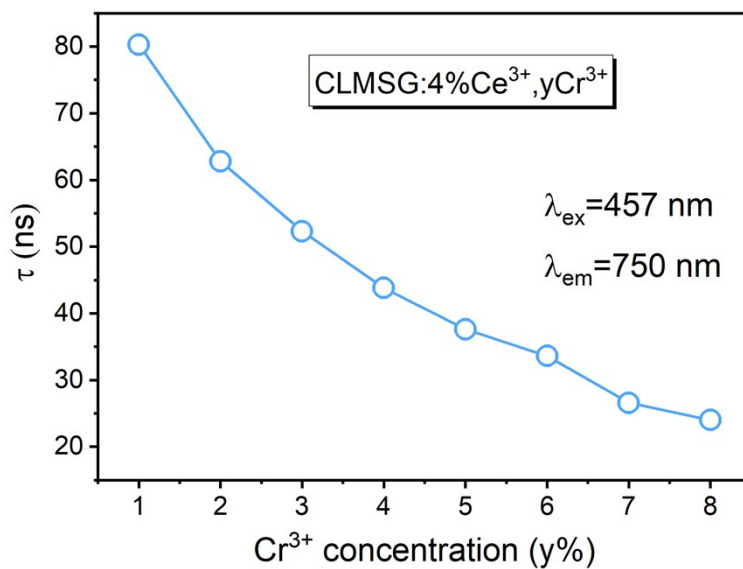


Fig. S7 Fluorescent decay times of Cr³⁺ monitored at 750 nm and excited at 457 nm in CLMSG:4%Ce³⁺, yCr³⁺ (y = 1% - 8%) recorded at RT. τ is the average lifetime, which gradually shortens from 80.3 to 24.0 ns when Cr³⁺ increases from 1% to 8%.

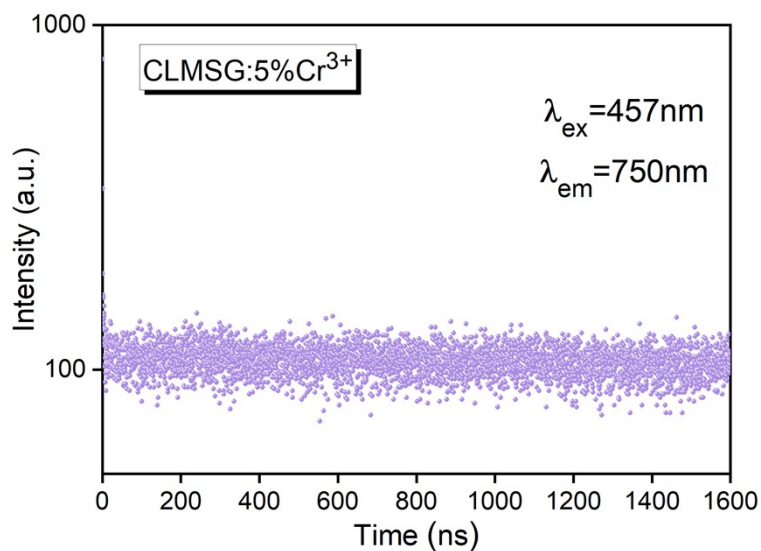


Fig. S8 Decay curves of Cr³⁺ ($\lambda_{\text{ex}}=457\text{ nm}$, $\lambda_{\text{em}}=750\text{ nm}$) of CLMSG:5%Cr³⁺. There is no decay in CLMSG:5%Cr³⁺.

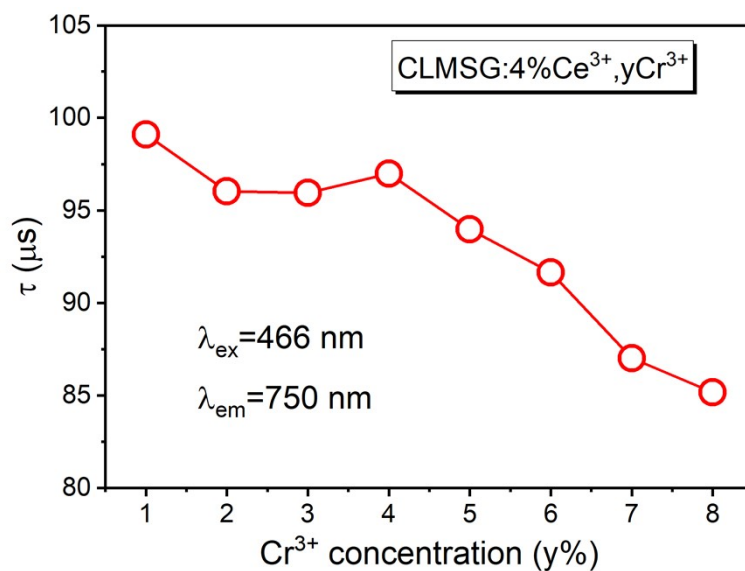


Fig. S9 Fluorescent decay times of Cr³⁺ monitored at 750 nm and excited at 466 nm in CLMSG:4%Ce³⁺, yCr³⁺ ($y=1\% - 8\%$) recorded at RT. τ is the average lifetime, which gradually shortens from 99.1 to 85.2 μs when Cr³⁺ increases from 1% to 8%.

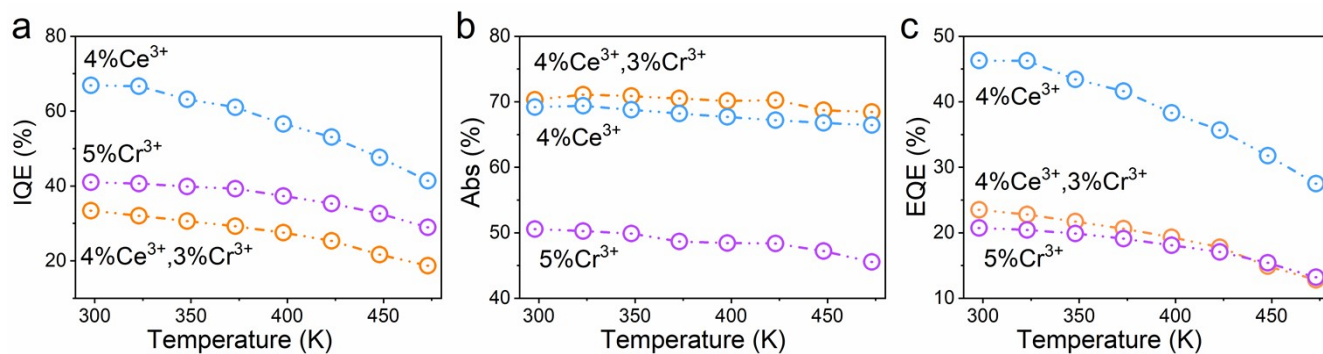


Fig. S10 (a) IQE, (b) Abs and (c) EQE of CLMSG:5%Cr³⁺, CLMSG:4%Ce³⁺ and CLMSG:4%Ce³⁺, 3%Cr³⁺ dependent on temperatures from RT to 473 K.

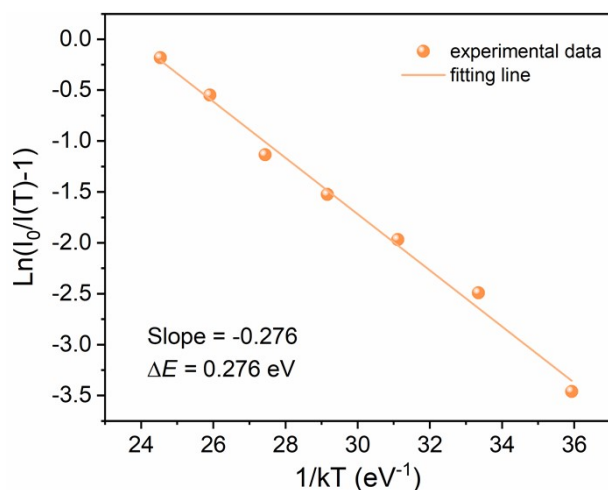


Fig. S11 Relationship between $1/kT$ and $\ln[(I_0/I(T))-1]$ of CLMSG:4%Ce³⁺, 3%Cr³⁺.

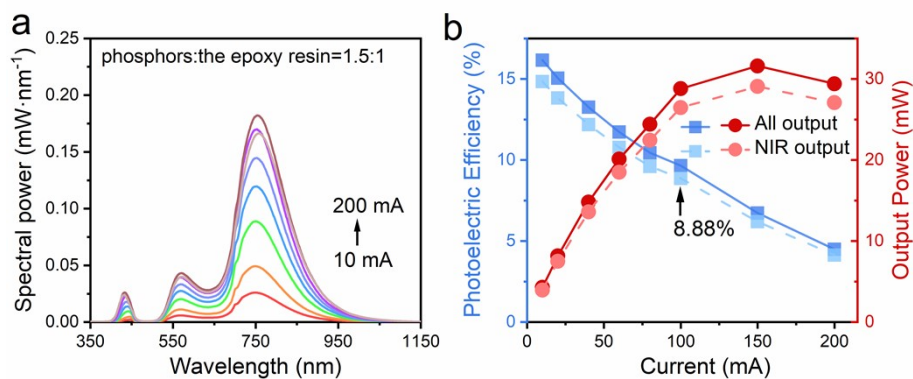


Fig. S12 The EL spectra (a), output NIR power and photoelectrical conversion efficiency (b) of NIR pc-LED with phosphor-to-epoxy ratios of 1.5:1 dependent on driven current (10 - 200 mA).

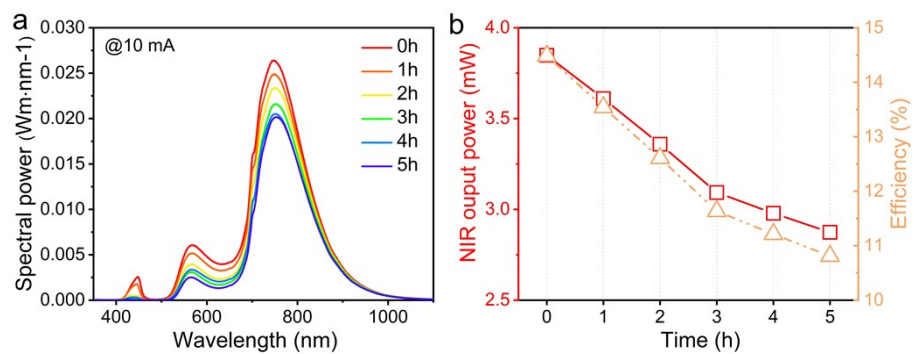


Fig. S13 The EL spectra (a), NIR output power and photoelectrical conversion efficiency (b) of the NIR pc-LED device with a 1:1 phosphor-to-epoxy ratio, measured under continuous operation at 10 mA for 5 hours.

Table S1 Atomic coordinates and site occupancy fraction (SOF) for CaLu₂Mg₂Si₃O₁₂:4%Ce³⁺,3%Cr³⁺ phosphor.

Atom	x	y	z	SOF	U _{iso}
Ca1	0.1250	0.0000	0.2500	0.4000	0.0080
Lu1	0.1250	0.0000	0.2500	0.5717	0.0083
Mg2	0.1250	0.0000	0.2500	0.0150	0.0250
Mg1	0.0000	0.0000	0.0000	0.9850	0.0120
Cr1	0.0000	0.0000	0.0000	0.0150	0.0250
Ce1	0.1250	0.0000	0.2500	0.0133	0.0250
Si1	0.3750	0.0000	0.2500	1.0000	0.0100
O1	0.0351	0.0538	0.6578	1.0000	0.0217

Table S2 Rietveld refined crystallographic data for the CLMSG:5%Cr³⁺, CLMSG:4%Ce³⁺, and CLMSG:4%Ce³⁺, 3%Cr³⁺.

Formula	CLMSG:5%Cr ³⁺	CLMSG:4%Ce ³⁺	CLMSG:4%Ce ³⁺ , 3%Cr ³⁺
Crystal system		Cubic	
Space group		Ia $\bar{3}$ d	
$\alpha = \beta = \gamma(^{\circ})$		90.000	
a = b = c(Å)	11.9753	11.9776	11.9668
Volume (Å ³)	1717.367	1718.35	1713.68

Table S3 Thermal stability of some reported NIR phosphors.

NIR phosphor	I _{150 °C} (%)	ref
Ca ₃ Sc ₂ Si ₃ O ₁₂ :0.06Ce ³⁺ ,0.03Cr ³⁺	78	1
Ca ₂ LuHf ₂ Al ₃ O ₁₂ : 0.03Ce ³⁺ ,0.03Cr ³⁺	58	2
Ca ₃ Sc ₂ Ge ₃ O ₁₂ :0.14Ce ³⁺ ,0.16Cr ³⁺	79@373K	3
Ca ₂ YHf ₂ Al ₃ O ₁₂ :0.04Ce ³⁺ , 0.02Cr ³⁺	58	4
CaY ₂ Mg ₂ Ge ₃ O ₁₂ :0.02Ce ³⁺ ,0.02Cr ³⁺	36.3	5
CaY ₂ ScZrAl ₃ O ₁₂ :0.11Cr ³⁺ ,0.03Ce ³⁺	60@373K	6
CaLu ₂ Mg ₂ Si ₃ O ₁₂ : 0.04Ce ³⁺ ,0.03Cr ³⁺	75.7	This work

Table S4 NIR pc-LED performance of CLMSG:Ce³⁺,Cr³⁺ compared with the reported.

NIR phosphor	Photoelectronic conversion Efficiency@ drive current	Ref.
Ga ₄ GeO ₈ :Cr ³⁺	8.0%@100 mA	7
LiGaP ₂ O ₇ :Cr ³⁺	~9.2%@100 mA	8
BaO(Al ₂ O ₃) ₄ (ZnAl ₂ O ₄):Cr ³⁺	7.98%@100 mA	9
Ca ₃ Sc ₂ Ge ₃ O ₁₂ :0.14Ce ³⁺ ,0.16Cr ³⁺	11.2%@100 mA	5
CaY ₂ ScZrAl ₃ O ₁₂ :0.11Cr ³⁺ ,0.01Ce ³⁺	16.4%@100mA	6
CaLu ₂ Mg ₂ Si ₃ O ₁₂ : 0.04Ce ³⁺ ,0.03Cr ³⁺	8.97%@100 mA	This work

References

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