

Supporting Information

Carbon-Modulated Reduction Synthesis of Dual-Valent Eu-Doped $\text{La}_3\text{Si}_2\text{O}_8\text{Cl}$ Phosphors: Single-Matrix White LEDs and High-Resolution Solar-Blind UV Detection

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Table S1. The second-order exponential fitting results of LSOCl:7%Eu (Eu:C = 1:0 to 1:2.4) monitored at 505 nm.

sample	A ₁	τ_1	A ₂	τ_2	$\tau_{av}(\mu s)$	R ²
Eu:C = 1:0	705	0.259	1045	1.11	0.99	0.998
Eu:C = 1:1.4	870	0.2	1083	0.981	0.87	0.999
Eu:C = 1:1.7	1111	0.26	836	1	0.81	0.999
Eu:C = 1:1.9	627	0.345	1029	1.025	0.91	0.999
Eu:C = 1:2.4	945	0.24	958	1.004	0.86	0.999

Table S2. The first-order exponential fitting results of LSOCl:7%Eu (Eu:C = 1:0 to 1:2.4) monitored at 613 nm.

sample	$\tau_1(ms)$	R ²
Eu:C = 1:0	1.49	0.99661
Eu:C = 1:1.4	1.47	0.99622
Eu:C = 1:1.7	1.47	0.99576
Eu:C = 1:1.9	1.44	0.99516
Eu:C = 1:2.4	1.46	0.99658

Table S3. The formation energy of Eu occupying different lattice sites in LSOC1

Dopants	La1 site	La2 site
Eu ³⁺	5.23 eV	5.20 eV
Eu ²⁺	1.31 eV	1.31 eV

NOTE:

We performed first-principles simulations to investigate Eu²⁺/Eu³⁺ occupancy preferences using density functional theory (DFT) implemented in the Vienna Ab initio Simulation Package (VASP)[R1]. The exchange-correlation functional was treated with the Perdew-Burke-Ernzerhof (PBE)[R3] generalized gradient approximation (GGA)[R2], employing a 700 eV plane-wave cutoff energy. A 3×5×7 Monkhorst-Pack k-mesh sampled the Brillouin zone, with structural relaxations converging to atomic forces <10⁻² eV/Å and energy differences <10⁻⁶ eV. The formation energy is calculated according to the following formula:

$$E_f = E_{doped} - E_{pure} + E_{site} - E_{atom}$$

where E_{doped} is the energy of the doped cell, E_{pure} is the energy of the initial cell, E_{site} is the energy of the replaced element, and E_{atom} is the energy of the doped element. As summarized in **Table S3**, Eu²⁺ incorporation shows equivalent formation energies (1.31 eV) at both La sites, predicting statistical distribution between La1 and La2 positions.

References

- [R1] G. Kresse, J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set[J]. Phys. Rev. B, 1996, 54(16): 11169-11186.
- [R2] G. Kresse, D. Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method[J]. Phys. Rev. B, 1999, 59(3): 1758-1775.
- [R3] P. E. Blöchl. Projector augmented-wave method[J]. Phys. Rev. B, 1994, 50(24): 17953-17979.

Table S4. CIE coordinates and offset rates of LSOC1:7%Eu Eu:C = 1:1.4

Excitation wavelength/nm	(<i>x</i>, <i>y</i>)	<i>x</i> offset rate	<i>y</i> offset rate	Total offset rate
250	(0.61,0.35)	0.00%	0.00%	0.00%
254	(0.61,0.35)	0.00%	0.00%	0.00%
260	(0.62,0.35)	1.64%	0.00%	1.64%
270	(0.61,0.35)	0.00%	0.00%	0.00%
280	(0.58,0.35)	4.92%	0.00%	4.92%
290	(0.54,0.35)	11.48%	0.00%	11.48%
300	(0.49,0.34)	19.67%	2.86%	22.53%
302	(0.47,0.34)	22.95%	2.86%	25.81%
310	(0.41,0.33)	32.79%	5.71%	38.50%
320	(0.35,0.33)	42.62%	5.71%	48.34%
330	(0.29,0.32)	52.46%	8.57%	61.03%
340	(0.27,0.33)	55.74%	5.71%	61.45%
350	(0.26,0.33)	57.38%	5.71%	63.09%
360	(0.39,0.34)	36.07%	2.86%	38.92%
365	(0.30,0.34)	50.82%	2.86%	53.68%

Table S5. CIE coordinates and offset rates under different excitation wavelengths of LSOC1:7%Eu
Eu:C = 1:1.4

Excitation wavelength/nm	(<i>x</i>, <i>y</i>)	<i>x</i> offset rate	<i>y</i> offset rate	Total offset rate
254	(0.63,0.35)	0.00%	0.00%	0.00%
254,302	(0.57,0.35)	9.52%	0.00%	9.52%
254,365	(0.55,0.34)	12.70%	2.86%	15.56%
254,302,365	(0.52,0.34)	17.46%	2.86%	20.32%

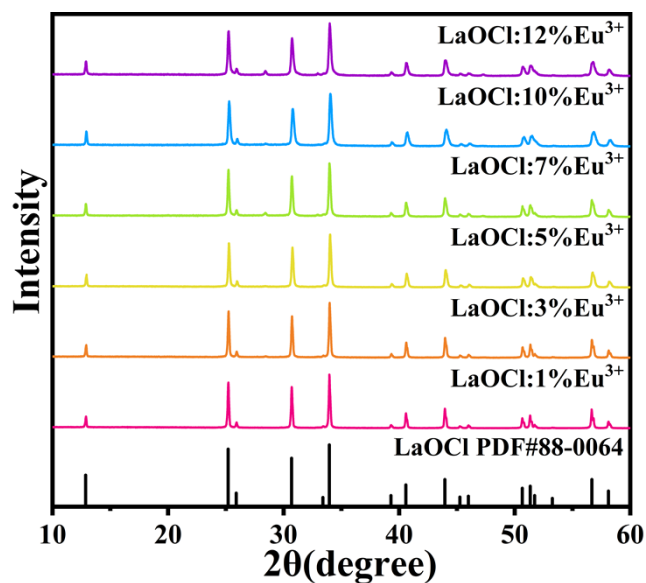


Figure S1. PXRD patterns of $\text{LaOCl}:x\%\text{Eu}^{3+}$ ($x = 1$ to 12), and standard patterns of PDF card No. 88-0064 for LaOCl as the reference.

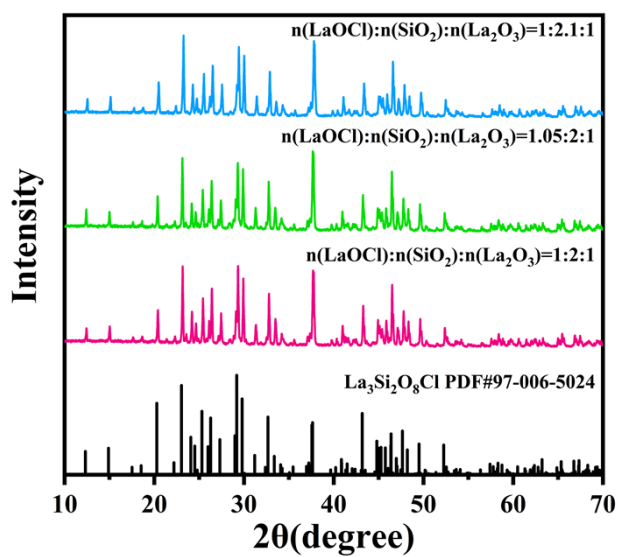


Figure S2. XRD patterns of LSOCl synthesized at different stoichiometric ratios, and standard patterns of PDF card No. 97-006-5024 for LSOCl as the reference.

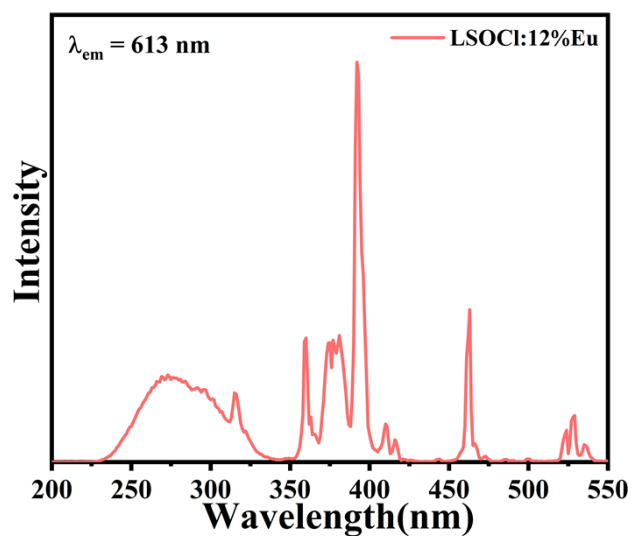


Figure S3. Excitation spectra of LSOCl:12%Eu (monitored at 613 nm).

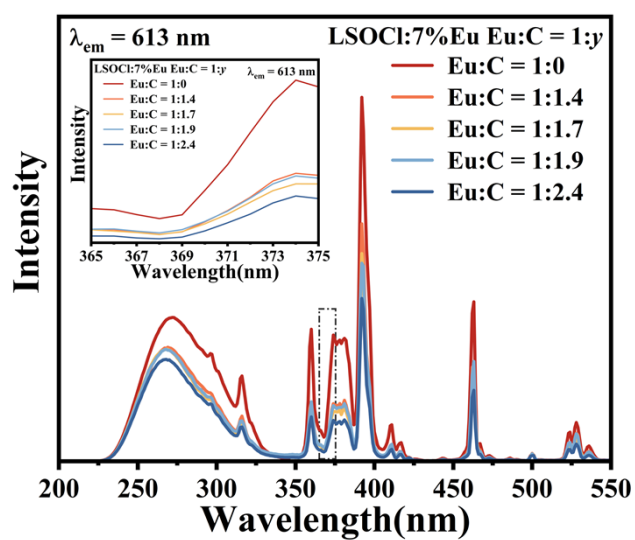


Figure S4. Excitation spectra of LSOCl:7%Eu (Eu:C = 1:0 to 1:2.4). The inset is an enlarged image of 365-375 nm.

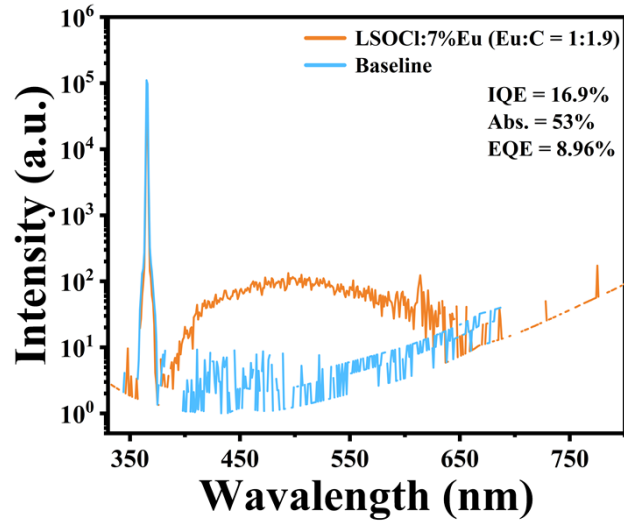


Figure S5. Measurement and spectral analysis of the internal quantum efficiency of LSOCl:7%Eu (Eu:C = 1:1.9)

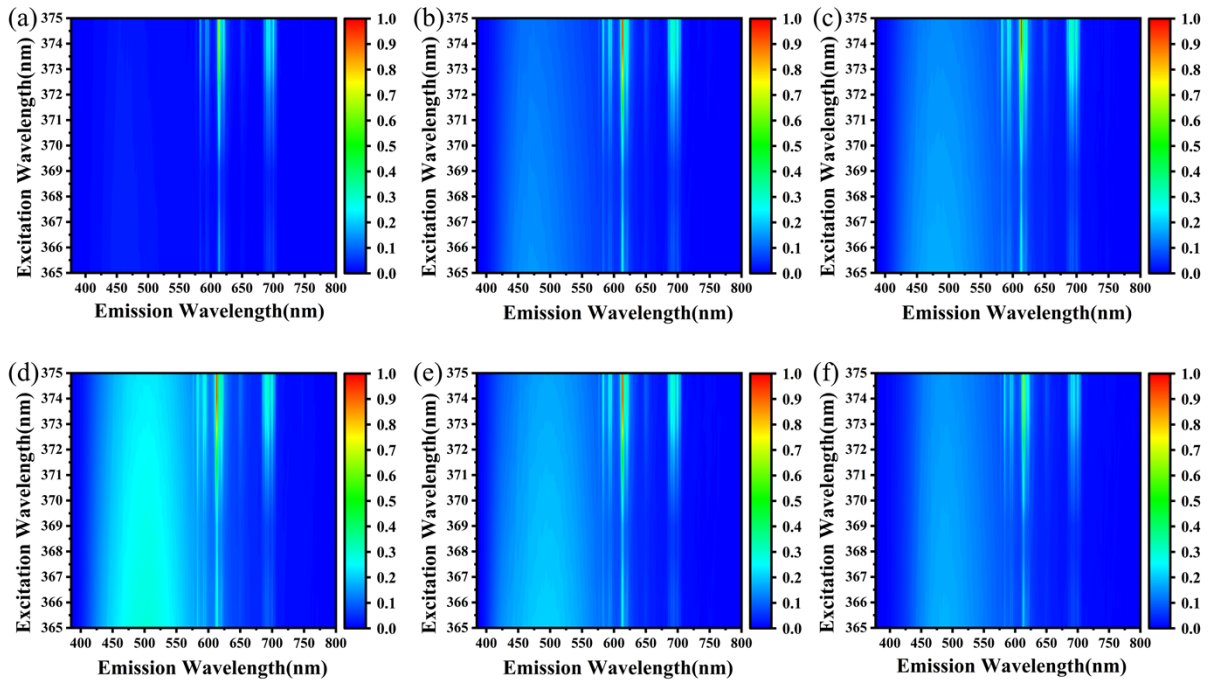


Figure S6. Excitation-dependent emission spectra of LSOCl:7%Eu Eu:C = 1:0 (a). Eu:C = 1:1.2 (b). Eu:C = 1:1.4 (c). Eu:C = 1:1.7 (d). Eu:C = 1:2.1 (e). Eu:C = 1:2.4 (f).

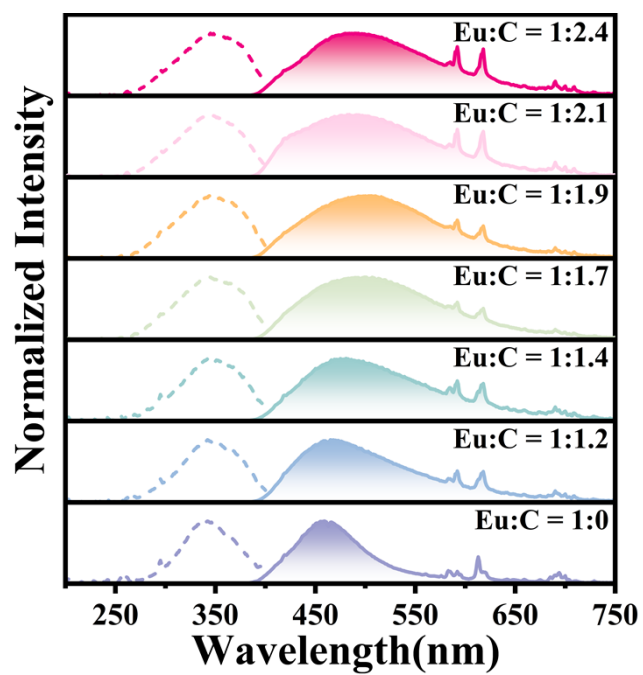


Figure S7. Excitation and emission spectra of LSOCl:7%Eu (Eu:C = 1:0 to 1:2.4) ($\lambda_{\text{ex}} = 345$ nm, $\lambda_{\text{em}} = 500$ nm).

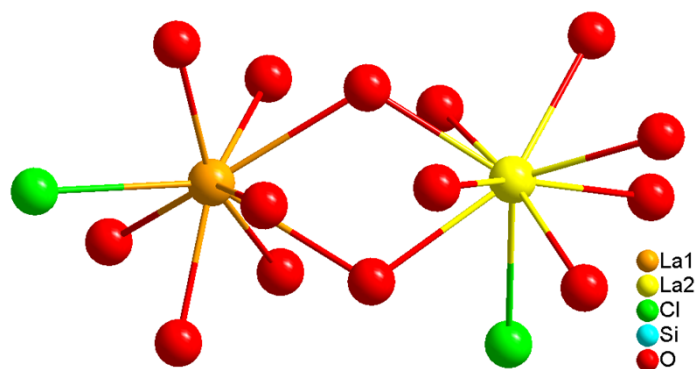


Figure S8. Coordination of La1 and La2 atoms in $\text{La}_3\text{Si}_2\text{O}_8\text{Cl}$.

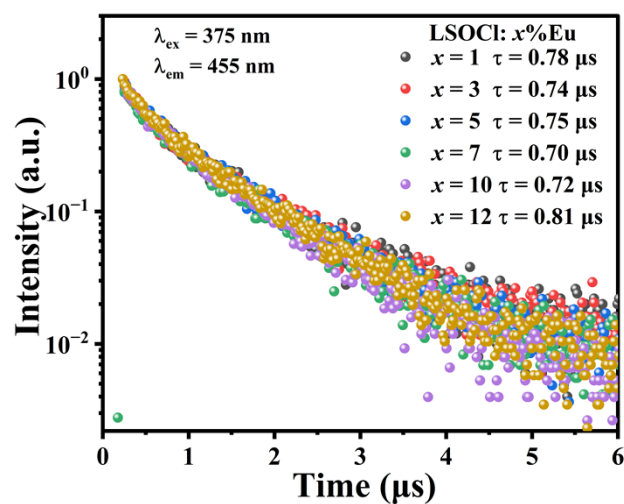


Figure S9. Luminescence decay curves of LSOCl: $x\%$ Eu ($x = 1, 3, 5, 7, 10, 12$) monitored at 455 nm.

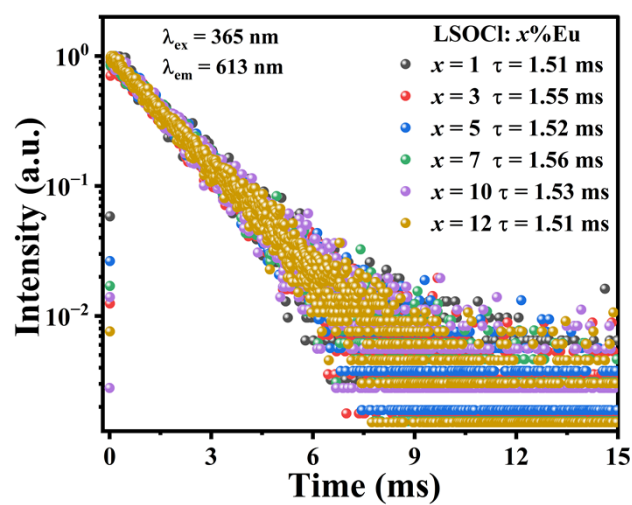


Figure S10. Luminescence decay curves of LSOCl: $x\%$ Eu ($x = 1, 3, 5, 7, 10, 12$) monitored at 613 nm.

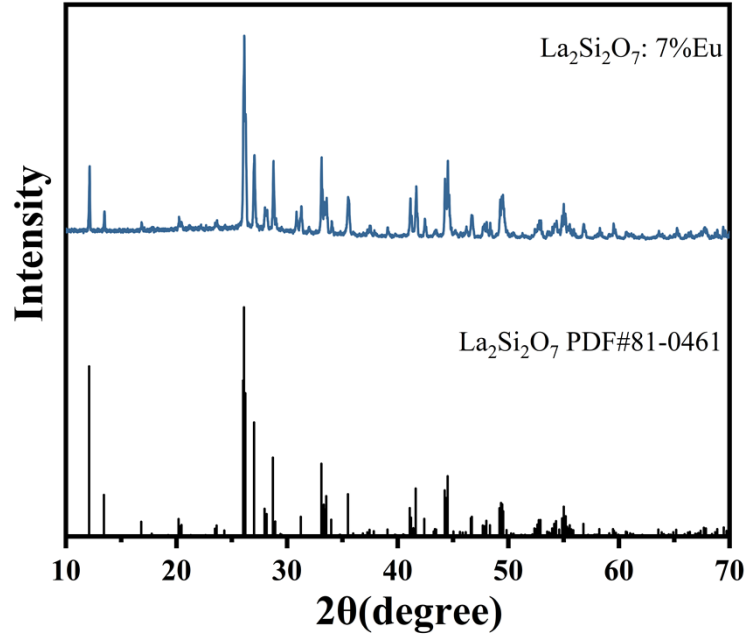


Figure S11. PXRD patterns of $\text{La}_2\text{Si}_2\text{O}_7:7\%\text{Eu}$ phosphor, and standard patterns of PDF card No. 81-0461 for $\text{La}_2\text{Si}_2\text{O}_7$ as the reference.

(**Note :** The raw materials used include La_2O_3 , SiO_2 and Eu_2O_3 . The samples were prepared by two rounds of sintering. The first round of sintering was carried out in an air atmosphere. The raw materials were placed in a muffle furnace, heated to 1350 °C for 1300 min, and held for 360 min to obtain $\text{La}_2\text{Si}_2\text{O}_7:7\%\text{Eu}^{3+}$ sample. The second round of sintering was carried out in a reducing atmosphere created by carbon powder. Similarly, in a muffle furnace, after 400 min heating up to 1350 °C and holding for 360 min, the $\text{La}_2\text{Si}_2\text{O}_7:7\%\text{Eu}$ samples were finally obtained.)

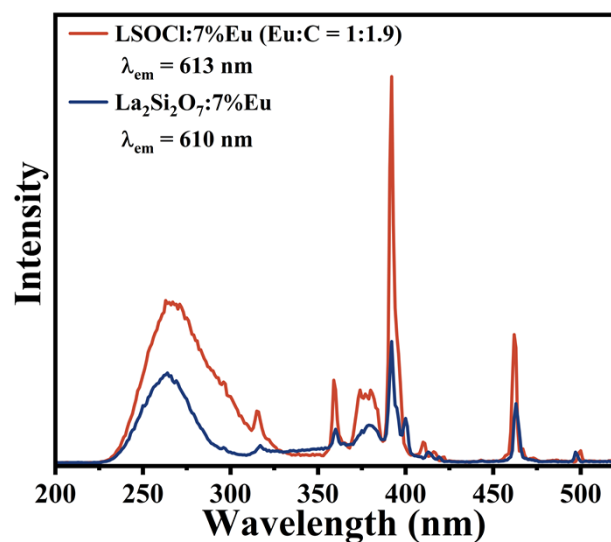


Figure S12. Excitation spectra of $\text{La}_2\text{Si}_2\text{O}_7$:7%Eu and $\text{La}_3\text{Si}_2\text{O}_8\text{Cl}$:7%Eu (Eu:C=1:9).

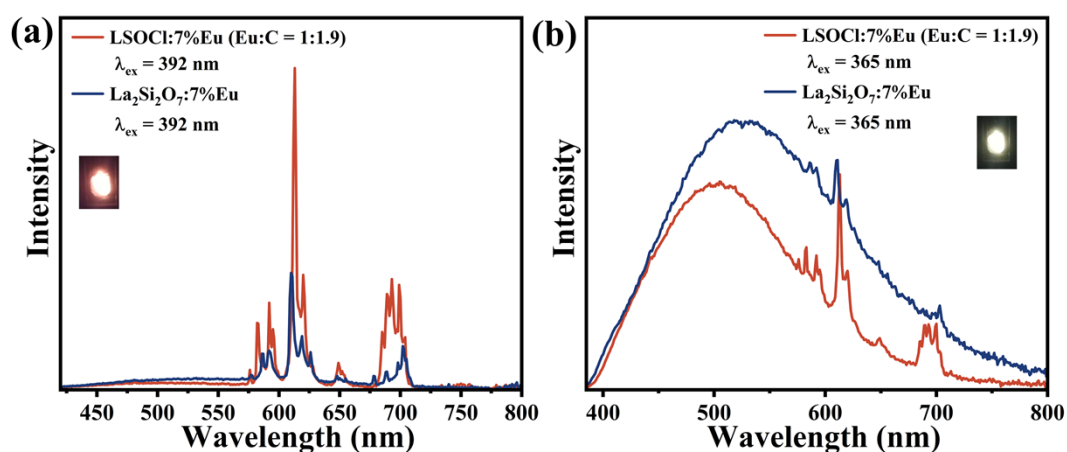


Figure S13. Photo luminescence spectra of $\text{La}_2\text{Si}_2\text{O}_7$:7%Eu and $\text{La}_3\text{Si}_2\text{O}_8\text{Cl}$:7%Eu (Eu:C=1:9) excited at 392 nm (a) and 365 nm (b).

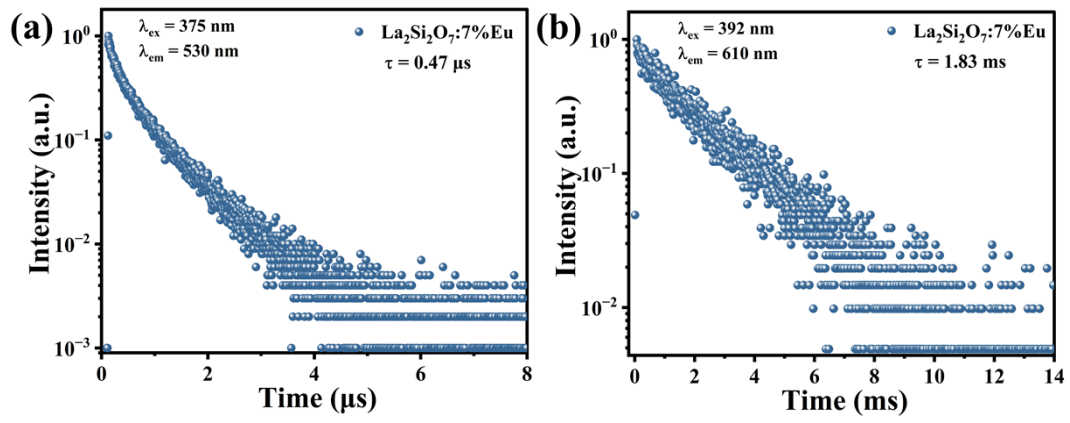


Figure S14. Photo luminescence spectra of $\text{La}_2\text{Si}_2\text{O}_7:7\%\text{Eu}$ and $\text{La}_3\text{Si}_2\text{O}_8\text{Cl}:7\%\text{Eu}$ (Eu:C=1:9) excited at 392 nm (a) and 365 nm (b).

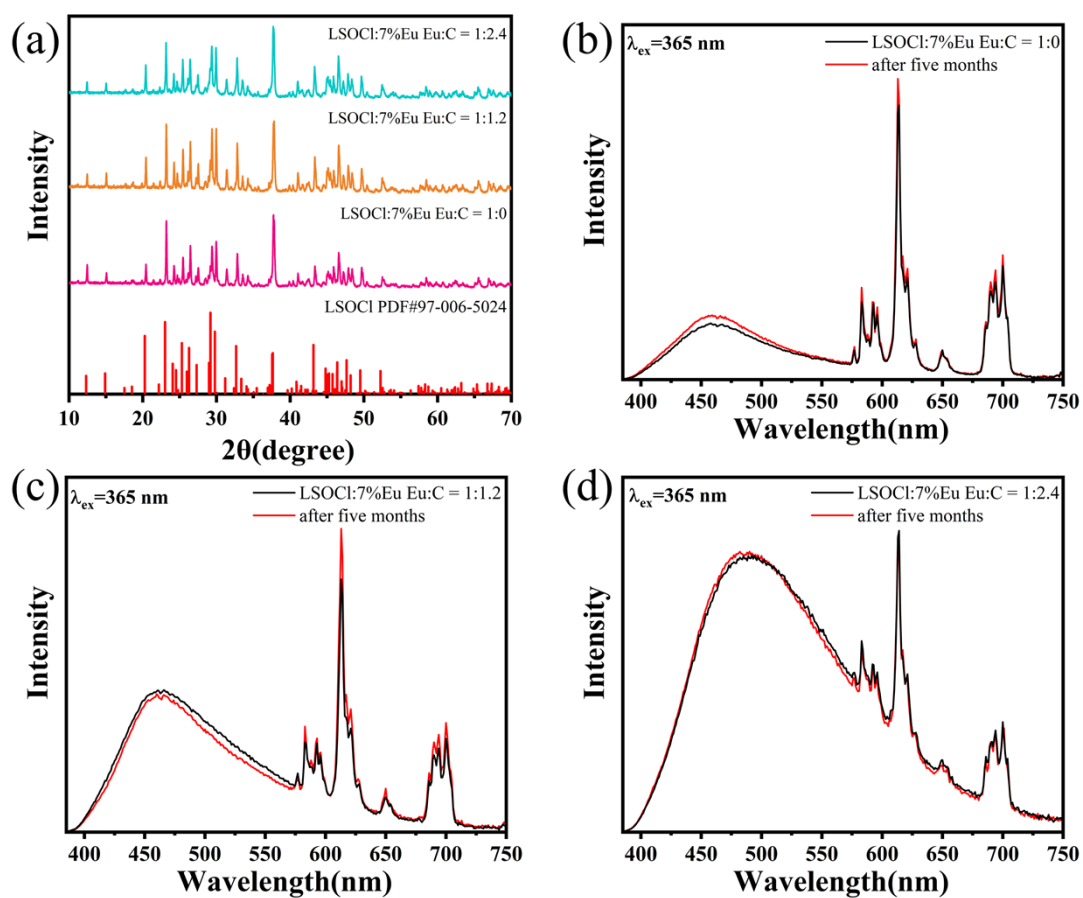


Figure S15. PXRD patterns of LSOC1:7%Eu (Eu:C = 1:0, 1:1.2, and 1:2.4) (a) emission spectra (b-d) after being exposed in ambient air for five months.

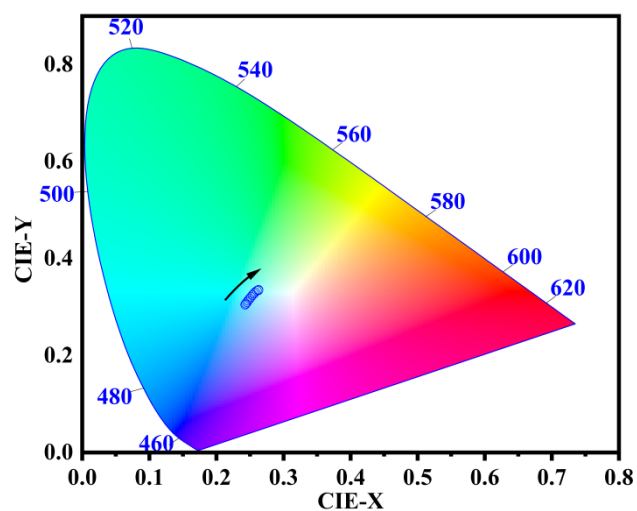


Figure S16. Temperature-dependent CIE color coordinates of LSOC1:7%Eu (Eu:C = 1:1.9) at temperature ranges of 80-300 K.

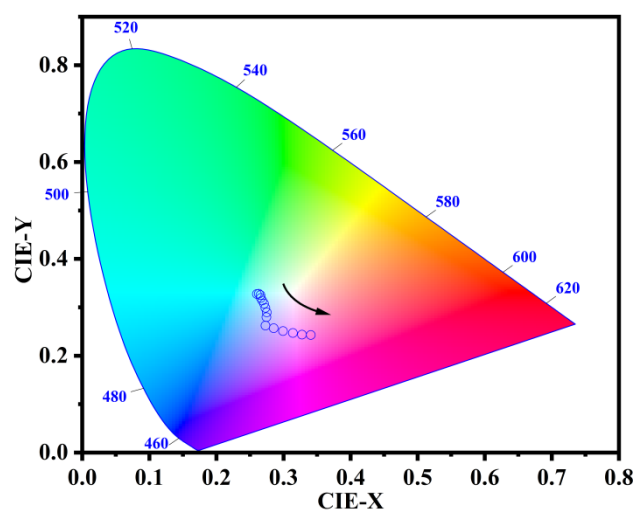


Figure S17. Temperature-dependent CIE color coordinates of LSOC1:7%Eu (Eu:C = 1:1.9) at temperature ranges of 300-578 K.

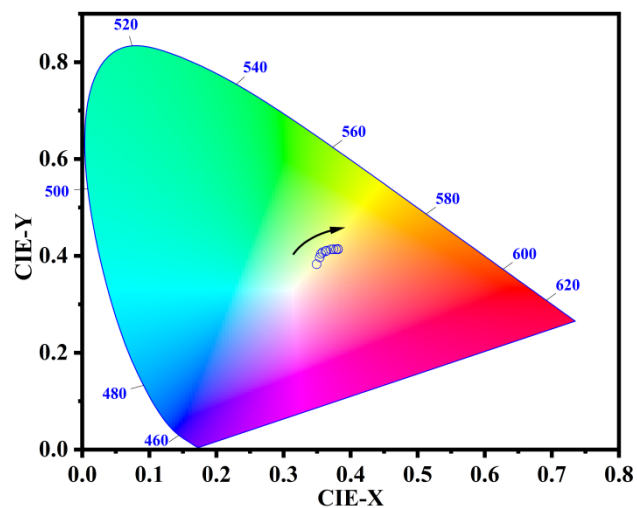


Figure S18. Current-dependent CIE color coordinates of the WLED based on LSOCl:7\%Eu ($\text{Eu:C} = 1:1.9$)

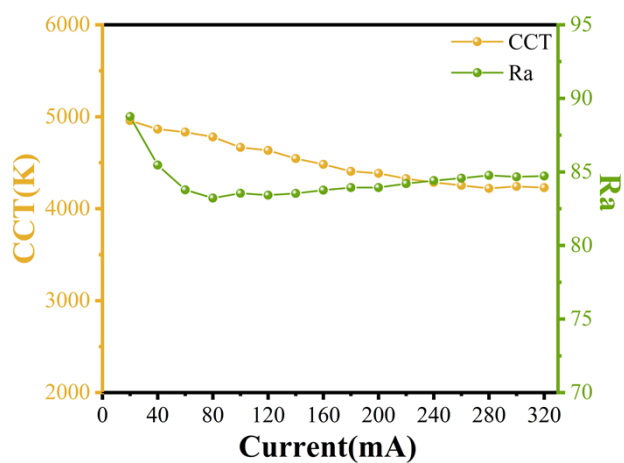


Figure S19. CCT and Ra of the WLED based on LSOCl:7\%Eu ($\text{Eu:C} = 1:1.9$) under different applied current.

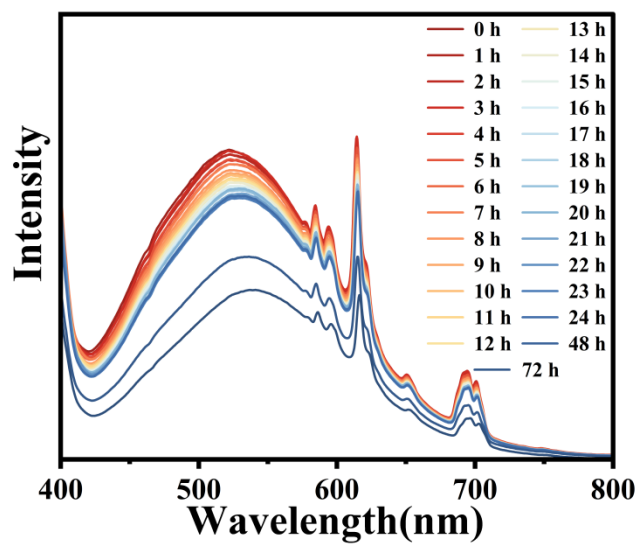


Figure S20. The emission spectra of the WLED based on LSOCl:7%Eu (Eu:C = 1:1.9) under seventy-two hours of continuous operation.

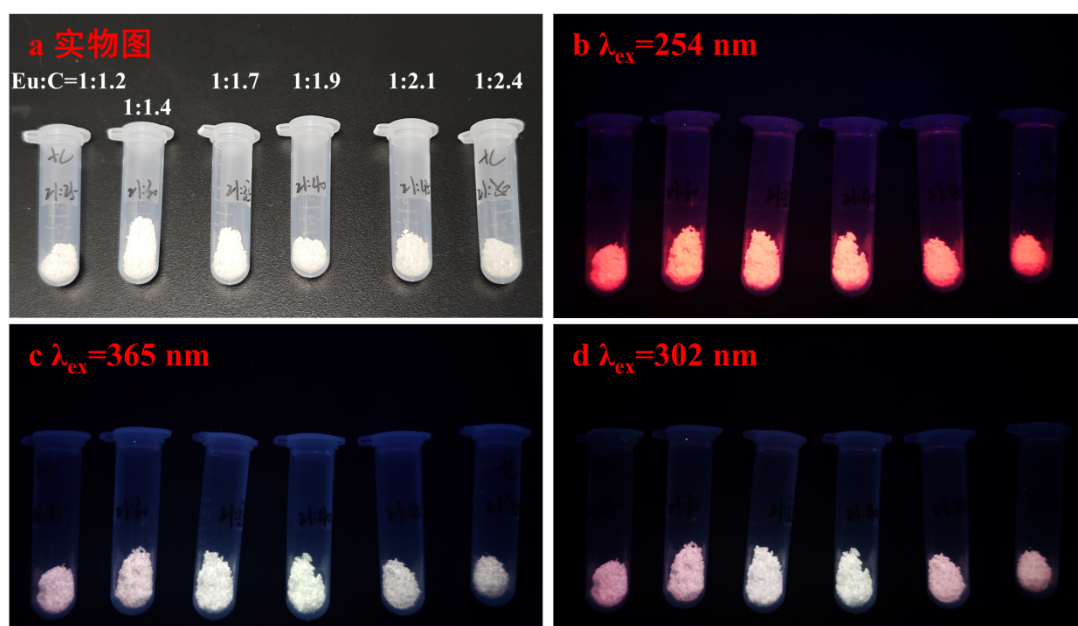


Figure S21. Photograph of LSOCl:7%Eu (Eu:C = 1:0 to 1:2.4)

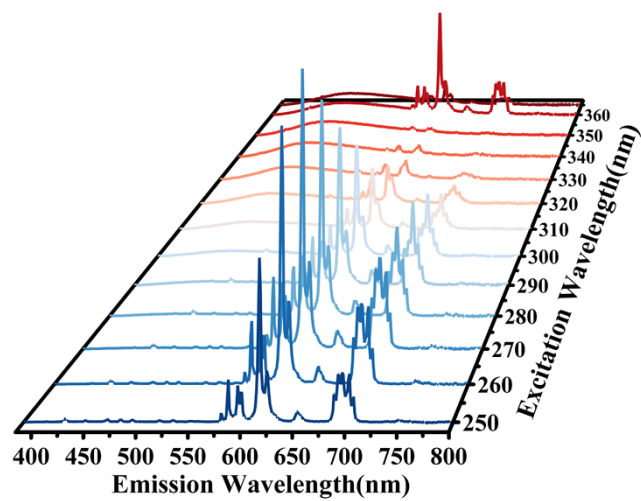


Figure S22. Excitation-dependent emission spectra of LSOC1:7%Eu Eu:C = 1:1.4 ($\lambda_{\text{ex}} = 250\text{-}365$ nm).