

Narrow band dazzling red emitting (LiCaLa(MoO₄)₃:Eu³⁺) phosphor with scheelite structure for Hybrid White LEDs and LiCaLa(MoO₄)₃:Sm³⁺, Eu³⁺ Based Deep-Red LEDs for Plant Growth Applications

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Characterization

The phase formation and purity of the phosphors were analyzed using a powder X-ray diffractometer (RIGAKU, JAPAN & ULTIMA -IV) which utilizes Cu-K α 1 radiation to generate X-rays. The SEM images were taken by a JEOL JSM 6480LV scanning electron microscope. The FTIR was carried out in the range of 400 - 4000 cm⁻¹ by Perkin Elmer IRL 1600300. The PL (excitation and emission) spectra and lifetime were monitored by using Edinburg Spectrofluorometer FS-5 instruments with attaching SC-10 and SC-30 integrating sphere modules. A pulsed xenon lamp was used as the excitation source, and the signals were detected with a photomultiplier. Temperature-dependent PL spectra were measured by using Horiba Jobin-Yvon Fluorolog 3-221 spectrofluorometer having a 450W xenon lamp equipped with Janis Cryostat VPF-800. Quantum yield was measured with the attached integrating sphere. The Commission International de'Eclairage (CIE) color coordinates were calculated from CIE 1931 software. The CRI and color purity were calculated by color calculator software. All the measurements have been carried out at room temperature (RT).

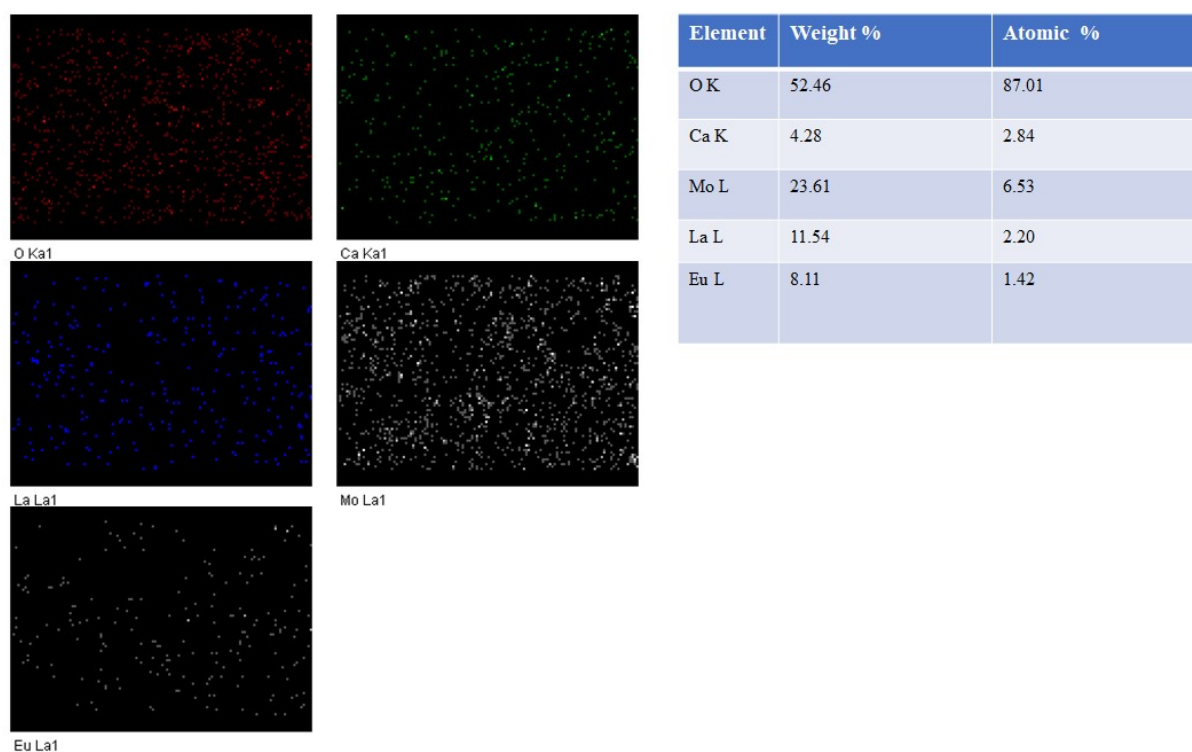


Figure. S1 Elemental mapping of the LCLM: Eu³⁺ phosphor.

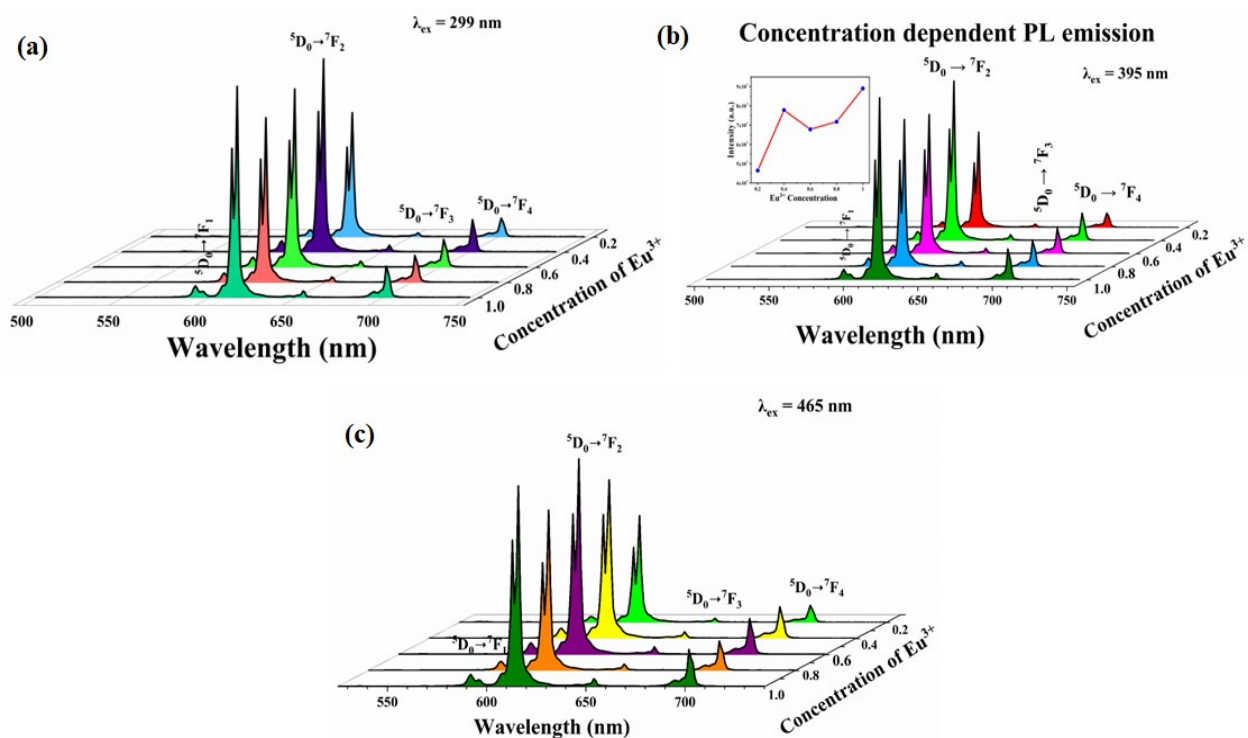


Figure. S2 PL emission spectra of LCLM: Eu³⁺ phosphor excited at (a) CT band, (b) 395 nm, (c) 465nm

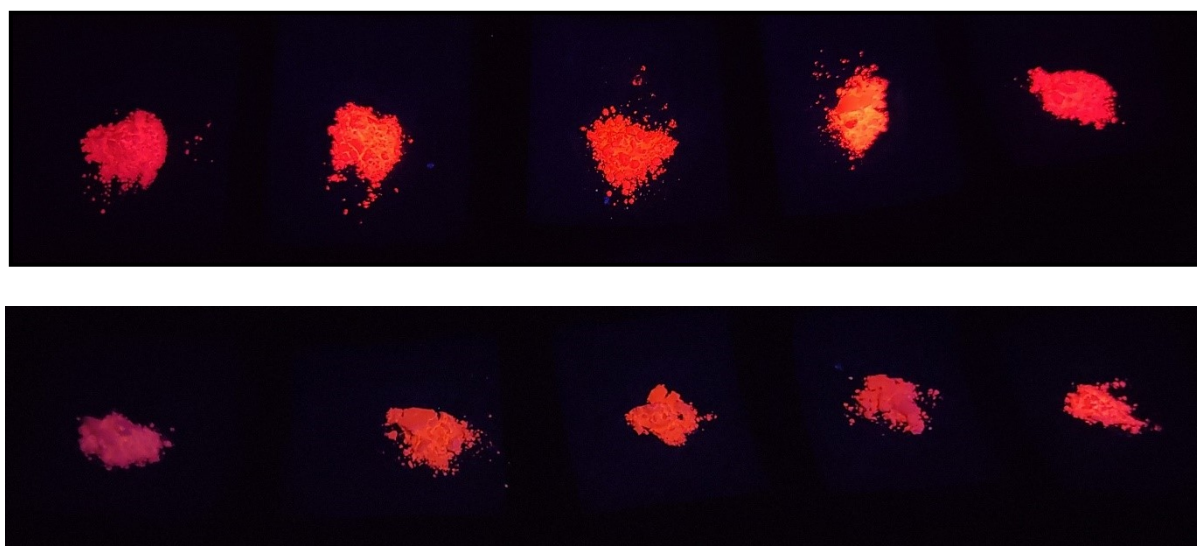


Figure S3. The digital photographs of phosphors with a) different Eu concentrations (top), b) Eu³⁺, Sm³⁺ doped (bottom), under UV lamp

Table ST1 Judd – Ofelt Parameters of LCLM: Eu³⁺ phosphor at excitation 395 nm

Concentration of Eu ³⁺	<u>Judd - Ofelt Parameter</u>		A ₀₋₁ in S ⁻¹	A ₀₋₂ in S ⁻¹	A ₀₋₄ in S ⁻¹
	Ω ₂ (10 ⁻¹⁹ cm ²)	Ω ₄ (10 ⁻²⁰ cm ²)			
0.2	1.142	4.118	50	945.570957	162.61501
0.4	1.1461	4.726	50	948.9931	186.6095
0.6	1.0327	4.541	50	858.8294	179.3121
0.8	1.0619	4.464	50	883.2060	176.4454
1.0	1.0987	4.494	50	916.4249	177.4183

Table ST2 Judd – Ofelt Parameters of LCLM: Eu³⁺ phosphor at excitation 300 nm.

Concentration of Eu ³⁺	<u>Judd - Ofelt Parameter</u>		A ₀₋₁ in S ⁻¹	A ₀₋₂ in S ⁻¹	A ₀₋₄ in S ⁻¹
	Ω ₂ (10 ⁻¹⁹ cm ²)	Ω ₄ (10 ⁻²⁰ cm ²)			
0.2	1.1413	4.137	50	945.0024713	163.361402
0.4	1.083	4.375	50	900.692474	172.769584
0.6	1.1282	4.236	50	938.3238228	167.456781
0.8	1.1007	4.369	50	918.080566	172.480643
1.0	1.1274	4.037	50	940.4017036	159.395237

Table ST3 Judd – Ofelt Parameters of LCLM: Eu³⁺ phosphor and its comparison with other reported Eu³⁺ activated molybdate phosphor.

Material	Judd - Ofelt Parameter		Asymmetry ratio	References
	Ω_2 (10 ⁻¹⁹ cm ²)	Ω_4 (10 ⁻²⁰ cm ²)		
LCLM:Eu ³⁺	1.1461	4.726	18.27	This work
La ₂ (MoO ₄) ₃ :Eu ³⁺	0.962	1.56	6.55	(26)
CaGd(WO ₄) ₃ :Eu ³⁺	0.679	0.79	6.75	(27)
Sr ₂ ZnW _{1-x} MoxO ₆ :Eu ³⁺ ,Li ⁺	0.514	0.12	4.75	(28)

Table ST4 CIE coordinates, Color purity and Asymmetry ratio of LCLM: Eu³⁺ phosphor calculated at ED transition.

Eu ³⁺ Concentration	CIE coordinates (x, y)	Color purity	Asymmetry ratio
0.2	0.6617, 0.3376	95.2%	18.20
0.4	0.6657, 0.3338	96.2%	18.27
0.6	0.6672, 0.3323	96.6%	16.56
0.8	0.6685, 0.3311	96.9%	17.05
1.0	0.6690, 0.3306	97.1%	17.68

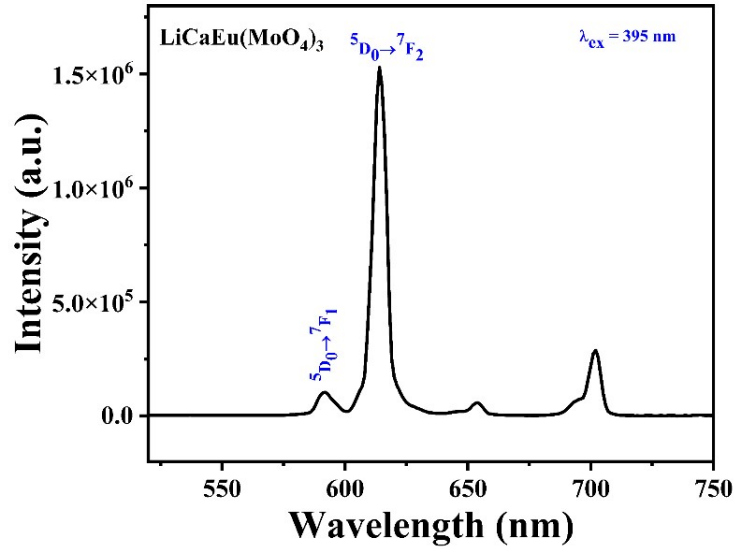


Figure S4. Quantum yield calculation for fully doped Eu^{3+} phosphor

Table ST5. The reported phosphors with their activation energy

S.No	Phosphor compositions	Activation energy ΔE_a (eV)	Reference
1	$\text{CaB}_2\text{Si}_2\text{O}_8$	0.195	1
2	$\text{Ba}_2\text{LiGa}(\text{P}_2\text{O}_7)_2$	0.238	2
3	$\text{Li}_3\text{Ba}_2\text{La}_3(\text{WO}_4)_8$	0.24	3
4	$\text{Li}_3\text{BaSrY}_{0.3}\text{Eu}_{2.7}(\text{MoO}_4)_8$	0.35	4a
5	$\text{LiCaEu}(\text{MoO}_4)_3$	0.40	This work

Table ST6. The reported phosphors with their color purity

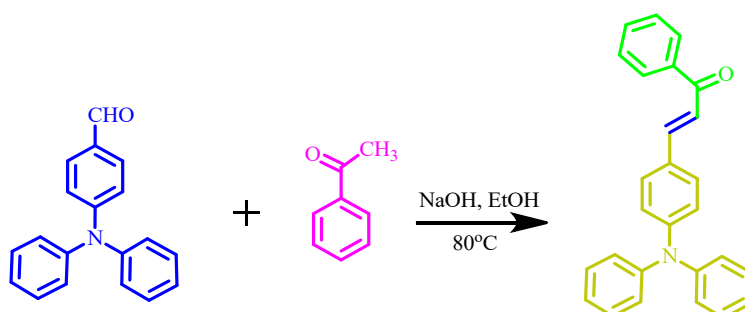
S.No	Phosphor compositions	Color purity (%)	Reference
1	$\text{NaSrY}(\text{MoO}_4)_3:\text{Eu}^{3+}$	93.6	4b
2	$\text{KBaGd}(\text{MoO}_4)_3:\text{Eu}^{3+}$	94	5
3	$\text{SrMoO}_4:\text{Eu}^{3+}$	85.8	6
4	$\text{CaMo}_{0.6}\text{W}_{0.4}\text{O}_4:\text{Eu}^{3+}$	93.8	7
5	$\text{NaBiF}_4:\text{Eu}^{3+}$	90.2	8
6	$\text{Li}_3\text{BaSrY}_{0.3}\text{Eu}_{2.7}(\text{MoO}_4)_8$	95.7	4a
7	$\text{LiCaEu}(\text{MoO}_4)_3$	97	This work

Table ST7. The reported red phosphors emission peaking wavelength and FWHM

S. No	Red phosphors	Emission peaking wavelength (nm)	CIE color coordinates (x,y)	FWHM (nm)	Ref
1	CaS:Eu ²⁺	647.8	(0.689, 0.311)	74.2	9
2	SrS:Eu ²⁺	609	(0.608, 0.391)	82	10-12
3	Sr ₂ Si ₅ N ₈ :Eu ²⁺	617.8	(0.619, 0.301)	94.2	13-19
4	CaAlSiN ₃ :Eu ²⁺	650	(0.664, 0.336)	92.4	20-24
5	(Sr,Ca)AlSiN ₃ :Eu ²⁺	659	(0.648, 0.352)	126	25
6	Li ₃ BaSrY _{0.3} Eu _{2.7} (MoO ₄) ₈	615	(0.660, 0.339)	6.24	4a
7	LiCaEu(MoO ₄) ₃	615	(0.670,0.331)	6	This work

Experimental section of yellow organic dye:

Aldehyde (1.831 mmol, 1 eq.) and NaOH (1.831 mmol, 1 eq.) were added to a mixture of 30 mL of water and 25 mL of ethanol, and then 1-phenylethanone (3.663 mmol, 2 eq.) was added. The mixture was heated and stirred at 90 °C for 4 hours. After cooling, the mixture was filtered and washed with plenty of water and then dried at RT to produce a yellow powder with a yield of 80%. The synthetic scheme for the preparation of the yellow dye is shown below.



Scheme 1. Synthesis of TPA substituted yellow organic dye.

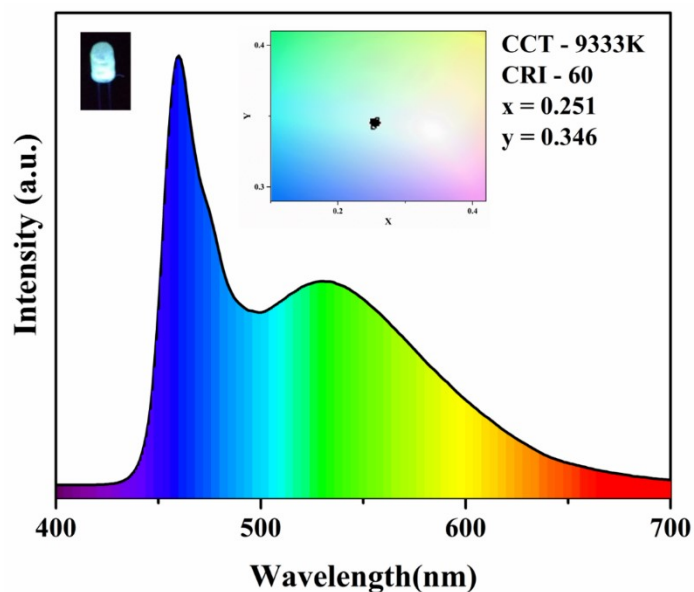


Fig. S5 EL spectrum of white LED by using blue LED with yellow organic dye.

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