Zero-concentration quenching: A Novel Eu^{3+} based red phosphor with Non-layered crystal structure for white LEDs and $NaSrY(MoO_4)_3:Sm^{3+}$ based deep-red LEDs for plant growth

Marikumar Rajendran and Sivakumar Vaidyanathan*

Department of Chemistry, National Institute of Technology Rourkela, India.

Experimental section

Eu^{3+} activated $NaSrY(MoO_4)_3$ red phosphors were synthesized by using solid-state reaction method. The highly pure starting materials were used for the synthesis procedure. The stoichiometric amounts of $SrCO_3$ (Extra pure 99.0%, HIMEDIA), Na_2CO_3 (99.9%, Merck), Y_2O_3 (99.9%, Sigma Aldrich), Eu_2O_3 (99.99% REO, Alfa Aesar), MoO_3 (ACS Reagent > 99.5%, Sigma Aldrich), were taken and ground by using an agate mortar and pestle, and were successively heated for 10 hrs at 600ºC and reground, heated at 800ºC for 10 hrs. Finally, the obtained red phosphors were ground again to form fine powder and stored in the vials for further characterization.

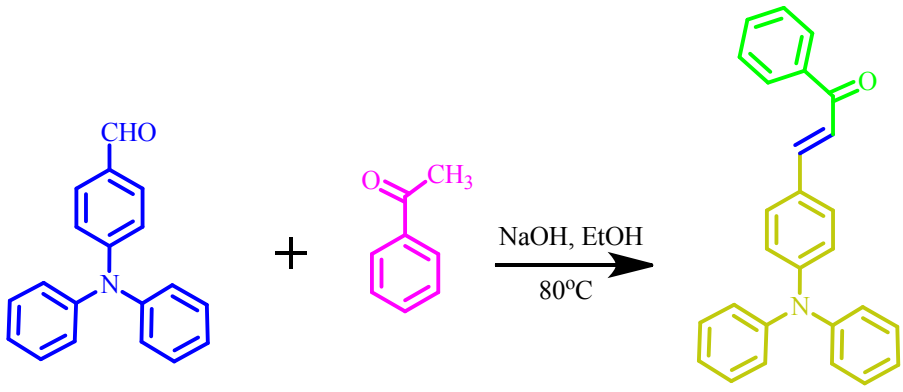
Characterization

The phase formation and purity of the phosphors were analyzed using powder X-ray diffractometer (Rigaku ULTIMA IV, Japan) which utilizes Cu-$K_{\alpha 1}$ radiation for generation of X - rays. The rietveld refinement data's were collected from Co-$K_{\alpha 1}$ radiation for generation of X - rays and the rietveld refinements were performed by using the JANA 2006 package with step width of 0.01. Crystal structure was drawn by using Diamond software. The SEM images were taken by a JEOL JSM 6480LV scanning electron microscope (SEM). The Fourier transform infrared spectroscopy (FTIR) was carried out in the range of 400 – 4000 cm^{-1} by PerkinElmer Spectrum Version 10.4.00. Diffuse reflection spectra were obtained by a scanning-type UV–visible spectrophotometer

(Shimadzu UV-3600) with $BaSO_4$ as a reference. The photoluminescence (excitation and emission) spectra, lifetime and quantum yield were monitored by using Edinburg Spectrofluorometer FS–5 instruments with attaching SC – 10 modules and SC – 30 integrating sphere module. 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 the spectrometer (Edinburgh FS5) equipped with a temperature controller. The Commission International de 'Eclairage (CIE) color coordinates were calculated from the obtained spectral emission data of the phosphors by using MATLAB software. The CRI was calculated by color calculator software.[1] All the measurements have been carried out at room temperature (RT).

Experimental section of yellow organic dye:

Aldehyde (1.831 mmol, 1 eq.) and NaOH (1.831 mmol, 1 eq.) were added into a mixture of 30 mL of water and 25 mL of ethanol, then 1-phenylethanone (3.663 mmol, 2 eq.) was added. The mixture was heated and stirred at 90 °C for 4 h. 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% and the synthetic scheme for the preparation of the yellow dye is shown below.



Scheme1. Synthesis of TPA substituted yellow organic dye.

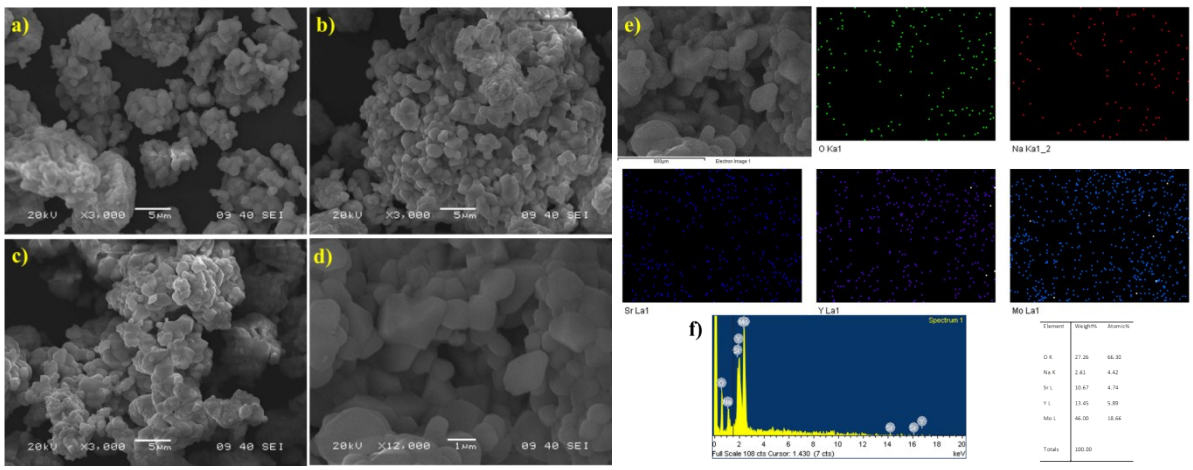


Fig. S1 (a-d) SEM images of the NSYM and NSEuM phosphors, (e and f) elemental mapping and EDX spectrum of the NSYM phosphor.

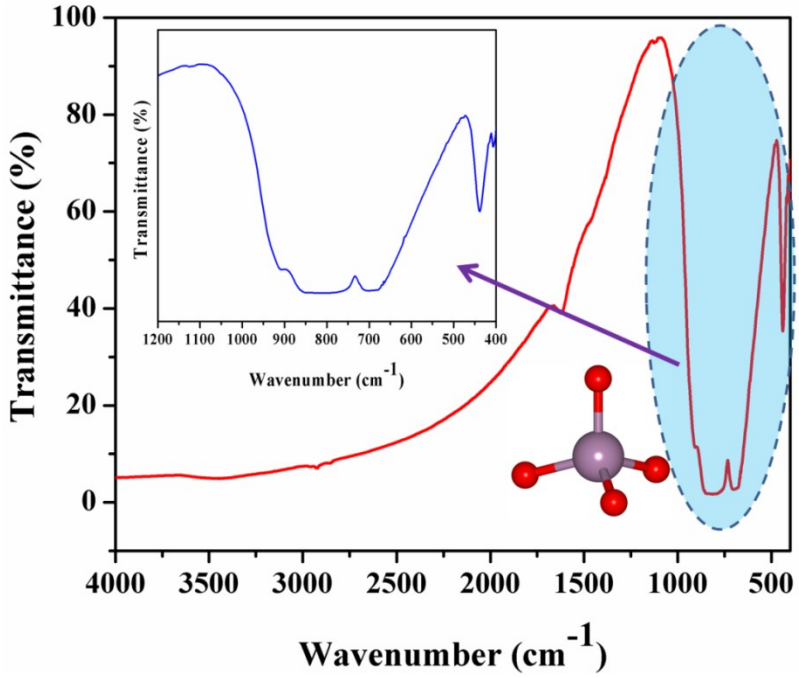


Fig. S2 FT-IR spectrum of the NSYM phosphor (inset is the enlarged region of the 400 – 1200).

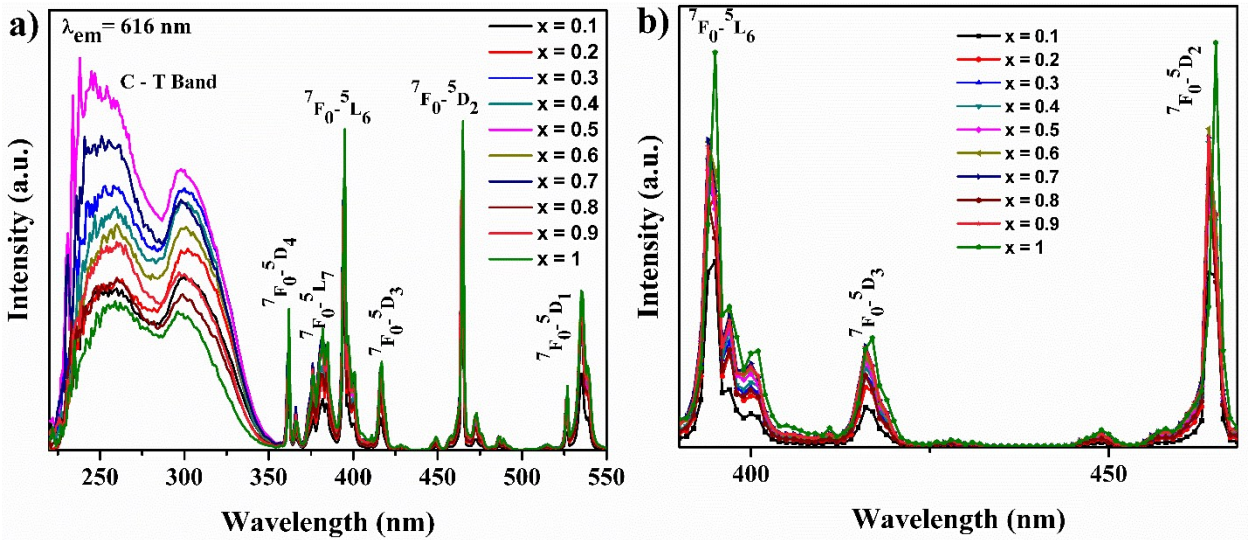


Fig. S3 a) PL excitation spectrum of Eu^{3+} activated $NaSrY(MO_4)_3$ phosphor. b) Excitation spectrum enlarged from 390-468 nm.

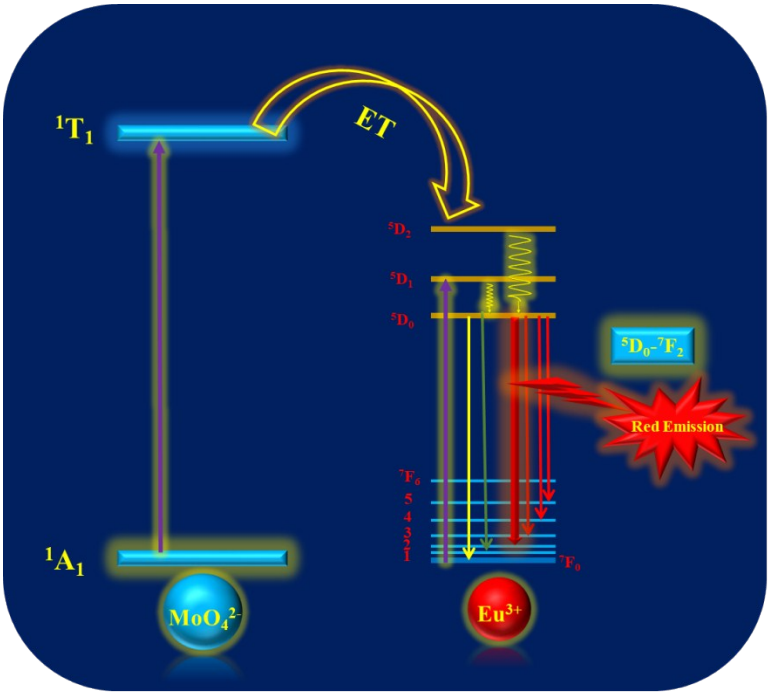


Fig. S4 Schematic energy transfer mechanism of the MoO_4^{2-} group to the Eu^{3+} ions in the NSYM host lattice.

Table ST1

Judd – Ofelt Parameters of $NaSrY(MoO_4)_3:Eu^{3+}$ phosphor.

Concentration of Eu^{3+}	Judd – Oflet Parameters		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)			
0.1	1.0817	3.7185	50	886.9574	148.0641
0.2	1.0787	4.59932	50	884.5231	183.1366
0.3	1.1003	4.30121	50	902.1725	171.2665
0.4	1.1091	4.5727	50	909.4422	182.8588
0.5	1.1116	4.4588	50	911.4722	177.5420
0.6	1.1359	4.1227	50	931.3967	164.8648
0.7	1.1276	4.4377	50	924.5509	176.7040
0.8	1.1493	4.2786	50	942.3662	170.3667
0.9	1.1833	4.4862	50	970.2736	179.4011
1	1.1951	4.2631	50	979.9528	170.4764

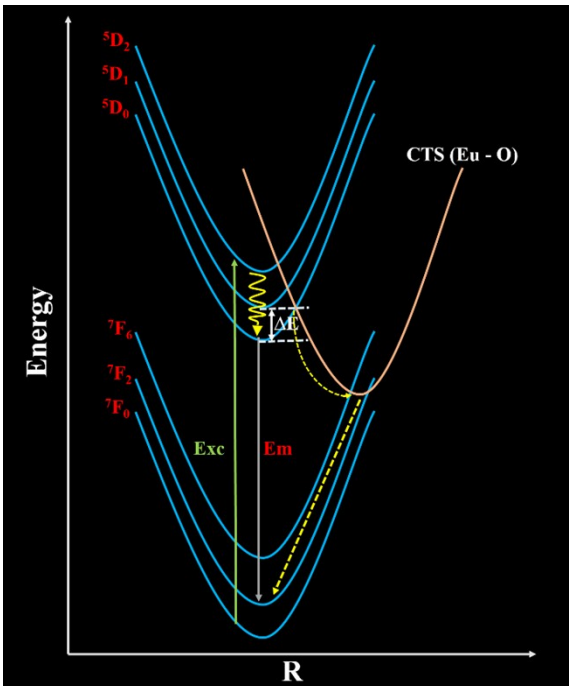


Fig. S5. A schematic configuration diagram for the crossover relaxation.

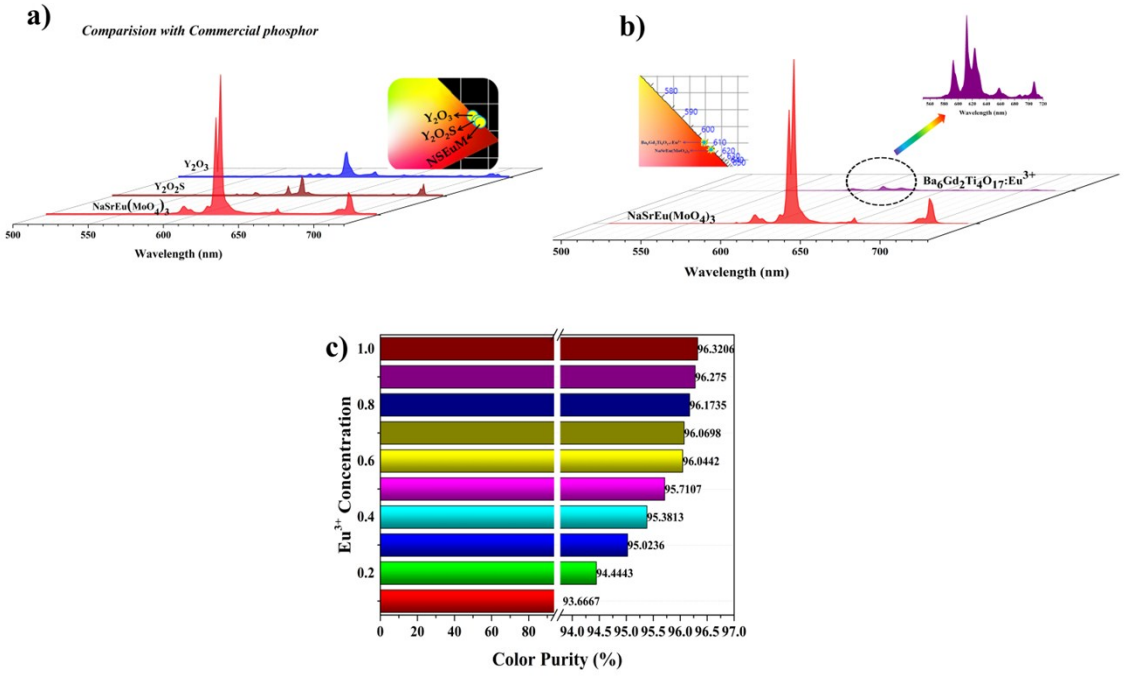


Fig. S6 a) Comparison with commercial phosphors (Y_2O_3 and Y_2O_2S under 395 nm excitation). b) Comparison with Eu^{3+} activated Layered $Ba_6Gd_2Ti_4O_{17}$ structure. C) Color purity of the NSYM:Eu^{3+} red phosphors.

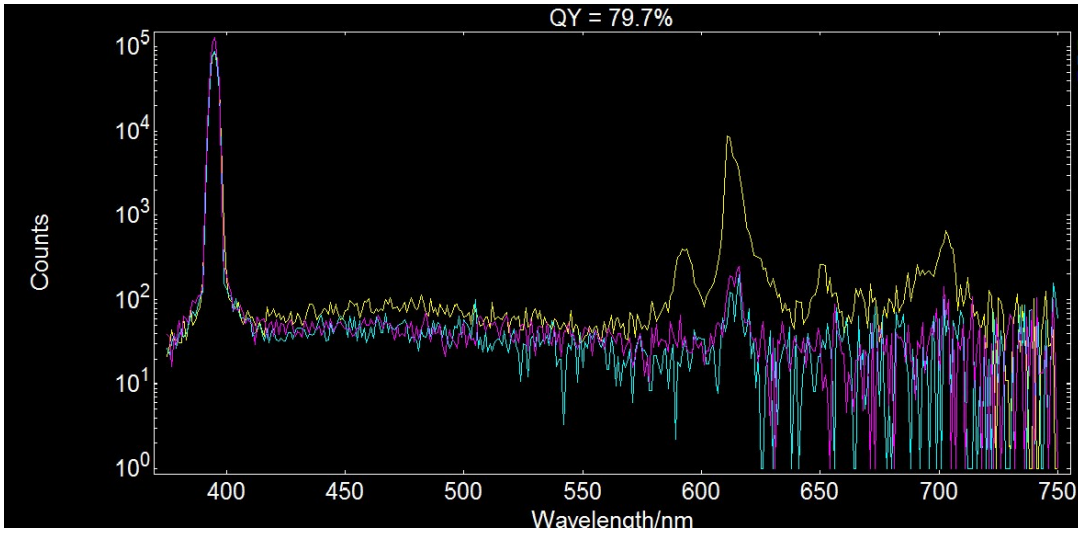


Fig. S7. Quantum yield of the NSEuM phosphor.

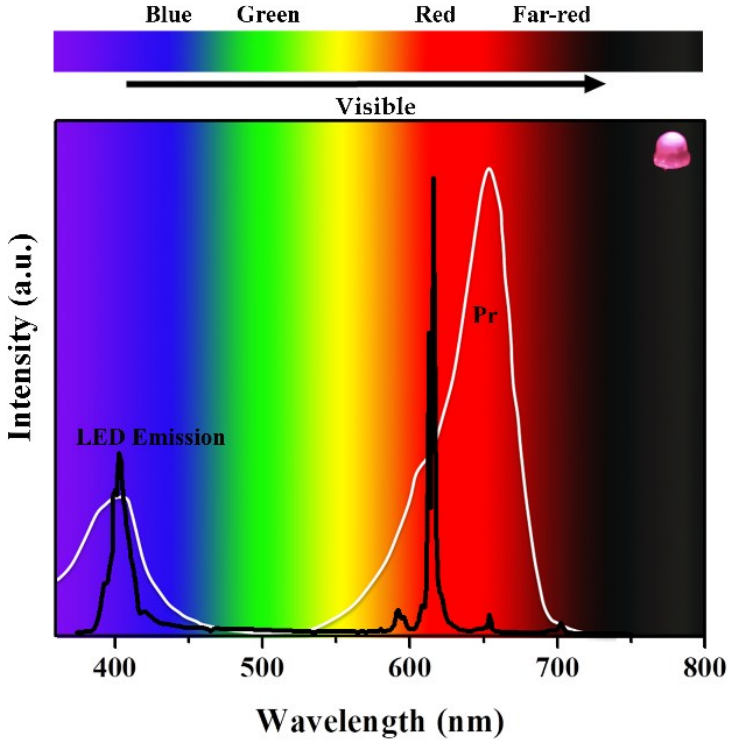


Fig. S8. EL spectrum of the red LED (NSEuM) and absorption of spectra of Phytochrome (Pr) (inset red LED image).

Reference:

1. Osram LED color calculator, https://www.osram.us/cb/tools-and-resources/applications /led-colorcalculator/index.jsp.