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Narrow-band red-emitting phosphor with negligible concentration quenching for hybrid white LEDs and plant growth applications[†]

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Narrow-band red-emitters are the key to solving problems encountered by the current white LED technology. In this context, a series of new red-emitting Li₃BaSrLa₃(MoO₄)₈:Eu³⁺ phosphors were synthesized and characterized through various spectroscopic methods. All phosphor compositions were crystallized in the monoclinic phase, with space group C2/c. A broad charge transfer ($O^{2-} \rightarrow Mo^{6+}$) extended up to the blue region along with strong $^{7}F_{0} \rightarrow {}^{5}L_{6}$, $^{5}D_{3}$ absorption, making them looked-for materials for warm white LED applications. The concentration quenching study reveals that there was no concentration-quenching occuring and the quantum yield of this non-concentration-quenching Li₃BaSrLa_{0.3}Eu_{2.7}(MoO₄)₈ phosphor reaches 92.6%. The Li₃BaSrLa_{0.3}Eu_{2.7}(MoO₄)₈ retain >80% of its emission intensity at 150 °C. The best red-emitting composition was integrated with near UV LED and obtained bright red emission with CIE x = 0.6647, y = 0.3357. White LED was fabricated by integrating the blue LED with yellow dye + red phosphor and white LED showed bright white light with CCT (5546 K), CIE (0.331, 0.385), and CRI (81%). In addition, the red LED spectrum is well-matched with the phytochrome (Pr) absorption spectrum and is useful for plant growth applications.

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Introduction

Energy (efficient) saving lighting technologies play a critical role in the global energy crisis and are expected to dominate energy-saving technology. Since high-performance white LEDs have begun to replace the conventional lighting sources (expected to save half of the electricity used for lightings).¹ However, the highly efficient warm white LEDs still rely on high-performance phosphor materials (an integral part in the creation of white light in solid-state lighting). The commercial white LED technology is based on yellow emitting phosphor conjugated with a blue LED chip. However, this method is not sufficient to surpass conventional lightings (low color rendering index and high color temperature), due to the lack of red component in the white LED spectrum. In order to solve this mystery, researchers have endeavoured in pursuit of new red phosphors that are suitable for excitation by blue (460-480 nm) or near UV LED (370-410 nm) chips (white LEDs based on near UV LED + trichromatic phosphor technology also need good red emitters).² It is well understood that the

warm white LEDs (for the purpose of general lightings) with improved color rendering index (CRI) and/or the luminous efficacy of radiation (LER) can be obtained by combining a broadband of yellow or green phosphor with narrow-band (narrow full-width at half maximum (FWHM)) red phosphor and a blue InGaN LED/near UV LED.³ Even though red phosphors (spectral line) contributes only one-third to the whole white spectrum, the change in red spectral lines will obviously affect the warm white LED (<4000 K of CCT) performance rather than the cool one (>5000 K of color correlation temperature (CCT)).⁴ It is also worth noting that the oxide-based red phosphor is still a bottleneck for high-performance white LEDs (since alternative nitride (including oxy-nitride) and sulfide-based phosphors suffer from the chemical stability as well as harsh synthetic conditions).⁵⁻⁷ Among all lanthanides, the trivalent europium (Eu³⁺) ion offers special spectral characteristics (both excitation and emission). It gives a narrow band red-emission ($\lambda_{\text{max}} = 610-620 \text{ nm}$), owing to the ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$ electric dipole (ED) transition with a small full width at half maximum (FWHM) (highly essential for getting for better luminous output) and the excitation lines appearing at 395 nm $({}^{7}F_{0} \rightarrow {}^{5}L_{6})$ and 465 nm $({}^{7}F_{0} \rightarrow {}^{5}D_{2})$, where the near UV or blue LED emission occurs.8 However, due to the forbidden nature of 4f-4f electronic transition of Eu³⁺ ion (near UV and blue region), the oscillator (absorption) strength is very deprived.

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This phosphor also encountered the most problematic task (light conversion energy loss) and it is imperative to decrease the loss of near UV excitation and converting it into red light. Host lattices (expected to absorb the incident photons from the LED and convert them into red emission) play a vital role in enhancing the absorption strength and overall lumine-scence efficiency of the Eu^{3+} based phosphor.

The approach could be twofold: one is to find a suitable lattice having enormous absorption in the near UV to the blue region (charge transfer band) so that it can contribute to the energy transfer progression, the second way is to find a lattice that can host rich Eu³⁺ ion concentration with zero concentration quenching (100% activation of activator ion in the lattice). Simultaneous achievement of good charge transfer band and zero concentration quenching in Eu³⁺ substituted oxide-based host lattice with non-layered structure scarcely reported.⁸ The former can be realized by having a host lattice with the MO_6/MO_4 group (M = Mo, W, good absorption in the near UV region due to metal-oxygen charge transfer (CT) band, whereas the latter can be an achieved lattice with a layered crystal structure. The scheelite-based crystal structure has shown promise for Eu³⁺ activation and potential red phosphor for white LEDs. Our group has comprehensively explored host lattices with MO_4/MO_6 where M = W/Mo with different structures like scheelites, perovskites, etc.,4,8-10 Recently, we have explored trivalent europium based red phosphor with stratified scheelite as a potential red emitter for white LEDs.^{11,12} Through continuous research efforts on trivalent europium-based narrow band emitters, we have identified the $Li_3BaSrLa_{3-x}Eu_x(MoO_4)_8$ [x = 0.3-3, in steps of 0.3] with a layered structure that showed zero concentration quenching (highly essential for high-performance white LEDs). It is worth noting that the distance between Eu-Eu is higher in different layers, which favours negligible concentration quenching in the lattice. Lastly, the red LED was fabricated by conjugating the synthesized selected red phosphor compositions with a near UV LED chip. These results revealed that the obtained Li₃BaSrLa_{0.3}Eu_{2.7}(MoO₄)₈ phosphors can be a potential red component in the white LEDs. Efforts have also been made to fabricate hybrid white LED with the amalgamation of blue LED $^{+}$ yellow organic dye +Red emitters $Li_3BaSrLa_{0.3}Eu_{2.7}(MoO_4)_8$ phosphors. These combinations showed greater color rendering and commission Internationale d'eclairage (CIE) value as compare to that of without red phosphor hybrid white LED. The currently synthesized phosphor showed outstanding quantum efficiency and reasonably favorable thermal stability and the hybrid white LEDs showed superior color quality and efficiency.

Experimental

Intense red-emitting phosphors $Li_3BaSrLa_3(MoO_4)_8:Eu^{3+}$, where x = 0-3 (in steps of 0.3) were synthesized through a high-temperature solid-state reaction. Highly pure precursors were taken for the synthesis of the phosphors. The apposite amounts of Li₂CO₃ (99.9%, Merck), BaCO₃ (99.0% Merck), SrCO₃ (Extra pure 99.0%, HIMEDIA), La₂O₃ (minimum 99.9%, Sigma Aldrich), Eu₂O₃ (99.9% REO, Alfa Aesar) and MoO₃ (ACS Reagent >99.5%, Sigma Aldrich) were taken and ground with the help of an agate mortar and pestle, followed by transferring the same into an alumina crucible. The sample mixtures were heated at 500 °C for 6 h and reground, treated at 850 °C for 12 h. After the reaction hour, the reaction mixture was cooled to room temperature, ground again into a fine powder, and restored in vials.

Characterization

The phase formation of the phosphors was checked using a powder X-ray diffractometer (Rigaku ULTIMA IV, Japan), which utilizes CuK_{$\alpha1$} radiation (λ = 1.5418 Å) and a graphite monochromator and from 10 to 70°, resolution 2° min⁻¹ and step size 0.02°. The field emission transmission electron microscope (FE-TEM, Jeol JEM2100-F, Japan) operating at 200 kV was used for the morphological studies of synthesized phosphors. The UV-visible spectrofluorometer (PerkinElmer, UV-5400) was used to record the diffuse reflectance spectra (DRS). The Fourier transform infrared spectroscopy (FT-IR) was performed in the range of 400-4000 cm⁻¹ by using a Spectrum Two IR Spectrometer, PerkinElmer. The photoluminescence excitation and emission spectra were recorded using a JOBIN YVON spectrofluorometer; it uses a xenon lamp as the excitation source. In addition, the luminescence lifetime and absolute quantum yield measurements were taken by using Edinburg Spectrofluorometer FS-5 instruments by attaching SC-30 integrating sphere module. A pulsed xenon lamp was used as the excitation source and the signals were detected with a photomultiplier. The CIE color coordinates were calculated from the obtained spectral emission data of the phosphors by using MATLAB software. The Judd-Ofelt (J-O) intensity parameters were calculated to support the spectral emission profile, regarding the inverse symmetry of Eu³⁺ ion using classical J-O theory. All the measurements were performed at room temperature (RT). The LED (red or white LED) were fabricated by mixing an appropriate amount of phosphor in the PMMA matrix and coated on the LED chip (either near UV or blue LED).

Results and discussion

Crystal structure and X-ray diffraction (XRD) study

The purity and phase formation of the synthesized phosphors were checked by using the powder X-ray diffraction method. The diffraction patterns for $\text{Li}_3\text{BaSrLa}_{3-x}\text{Eu}_x(\text{MoO}_4)_8$, where x = 0-3 are depicted in Fig. 1a. The XRD patterns confirm the formation of a single monoclinic phase without any additional impurity peak with space group C2/c. The XRD patterns match well with the similar crystal structure of $\text{Li}_3\text{Ba}_2\text{Gd}_3(\text{MOO}_4)_8$ (Joint committee for powder diffraction system (JCPDS) card





Fig. 1 (a) Powder X-ray diffraction pattern of Li₃BaSrLa_{3-x}Eu_x(MoO₄)₈, where x = 0-3, (b) extended plot of highest intensity with 2 θ change.

number 77-0830). However, the shift was observed in the main diffraction peak shifted towards a high angle (Fig. 1a). The physical performance of the diffraction peaks was monitored along with increasing Eu^{3+} concentration in the host lattice. The plot of the highest intensity peak against the activator concentration is shown in Fig. 2b. It clearly shows the shifting of the peaks towards a higher 2θ angle, which may be due to the dissimilar ionic sizes of both the RE cations (Eu^{3+} and La^{3+}).

The affinity of a smaller Eu³⁺ ion to replace a larger La³⁺ ion within the lattice causes a slight shrink of the parent host lattice. The unit cell structure of the host lattice along with the co-ordination of the Ba and La atom with O-atom is depicted in Fig. 2a. The crystal structure of Li₃BaSrLa₃(MoO₄)₈ belongs to the layered structure, La sites are separated by LiO₆ distorted polyhedral and BaO10 polyhedra, which is shown in Fig. 2b. The layered structure favours the high concentration accommodation of Eu³⁺ ion or non-concentration quenching in the lattice. The lattice parameters are a = 5.2816 Å, b =12.8192 Å, c = 19.9946 Å, $\beta = 92.8875$ and V = 1291.305 Å³, respectively. The lattice parameters for all other compositions were also calculated and are tabulated in Table ST1.† The value of lattice parameters 'a' and 'b' constantly decreases with a higher concentration of Eu³⁺ ions in the lattice. Similarly, 'c' also follows the same trend, whereas the angle ' β ' and volume of the lattice decreases constantly but slight increases for a higher amount of Eu^{3+} (x = 3). To have a brief idea regarding the change of different lattice parameters, a plot of Eu³⁺ concentration against the lattice parameters is given in Fig. 3c for all compositions.

Morphological studies

The field emission scanning electron microscopy (FE-SEM) was used for topological studies of the presently synthesized phosphors. The SEM micrographs of $Li_3BaSrLa_{0.3}Eu_{2.7}(MoO_4)_8$ phosphors are shown in Fig. 3. The images reveal irregular shape particles with aggregation. The average particle size was found to be 3 to 5 µm. The particles are well separated from each other, implying a proper growth of the crystal. The presence of constituted phosphor elements (including europium ions) could be identified by using elemental mapping and EDX.

Fourier-transform infra-red (FT-IR) spectroscopy

The FT-IR spectroscopy was performed to observe the molybspectra stretching frequency. date The FT-IR of Li₃BaSrLa₃(MoO₄)₈ host as well as doped Li₃BaSrLa_{0.3}Eu_{2.7}(MoO₄)₈ are given in Fig. 4. The strong and intense peaks at 419 cm⁻¹ and 461 cm⁻¹ are attributed to the stretching vibrations of O-Mo-O of the MoO₄ group present in the host lattice.¹² In general, the stretching vibrations of the MoO_4 group are observed below 500 cm⁻¹. Not much change was observed in the IR spectra upon the insertion of Eu³⁺ ions.



Fig. 2 (a) The unit cell structure of $Li_3BaSrLa_3(MoO_4)_8$, coordination of Ba and La with O – atom. (b) Unit cell shows the separation of La site by LiO_6 distorted polyhedral and BaO_{10} polyhedra (c) plot of $Li_3BaSrLa_{3-x}Eu_x(MoO_4)_8$ unit cell parameters as a function of Eu^{3+} concentration.

However, in the FT-IR spectrum of the Eu³⁺ activated phosphor, some extra vibration peaks were obtained at around 3000 cm⁻¹. The small stretching frequency around 1650 cm⁻¹ is attributed to O–H stretching frequency, which arises due to the presence of H_2O molecules in the air atmosphere.

Diffuse reflectance spectra (DRS) studies

The DRS spectra of $\text{Li}_3\text{BaSrLa}_{3-x}\text{Eu}_x(\text{MoO}_4)_8$ phosphors are depicted in Fig. 5. The spectra are a combination of broad absorption as well as line-like spectra. The broad absorption starting from 200 nm extended up to 340 nm is attributed to ligand (O²⁻) to metal (Eu³⁺/Mo⁶⁺) charge transfer (CT). O²⁻ has a tendency to transfer one of its non-bonding 2p electrons to the vacant 4d orbital of the Mo⁶⁺ ion. The intra-line 4f–4f transitions contribute to the line-like emission in the higher wavelength region (350 to 600 nm). The two-major lines appearing at 465 and 534 nm are corresponding to the ⁷F₀ \rightarrow ⁵D₂ and ⁷F₀ \rightarrow ⁵D₃ transition of Eu³⁺ ion, respectively. All the phosphors activated with Eu³⁺satisfie the strong absorption from the near UV to the blue region (240 to 450 nm) required for the LED application. The band gap of the phosphors was cal-

culated using Kubelka–Munk equation. The relationship between the diffuse reflectance of the sample (R_{∞}) , the absorption coefficient (K) and the scattering coefficient (S) is given by the Kubelka–Munk function $F(R_{\infty})$:

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{K}{S}$$
 (1)

The relationship between linear absorption coefficient (*a*) and band gap (E_g) is given by Tauc¹³

$$\alpha h\vartheta = C_1 \left(h\vartheta - E_g\right)^{\frac{n}{2}} \tag{2}$$

The relation between the absorption coefficient (α) and the incident photon energy ($h\nu$) can be written as:

$$\alpha h\vartheta = \mathbf{A}(h\vartheta - E_{\rm g})^n \tag{3}$$

where *A* is constant, α is the absorption coefficient and *n* depends on the type of transition involved. The value can be 1/2, 2, 3 and 3/2, the former set assigned to allow direct and indirect, while the latter one corresponding to forbidden direct or indirect transitions respectively.¹⁴ The band gap was determined from DRS spectra, extending a straight line to the *x*-axis



Fig. 3 SEM micrographs and elemental mapping (EDX) of the Li₃BaSrLa_{0.3}Eu_{2.7}(MoO₄)₈.





Fig. 5 DRS spectra of $Li_3BaSrLa_{3-x}Eu_x(MoO_4)_8$ where x = 0-3.

 $(h\nu)$ given in Fig. S1.[†] With the successful replacement of La³⁺ by Eu³⁺ in the lattice, the band gap of the samples decreases (3.75 to 3.29 eV). However, for the fully substituted (Eu-rich) composition, the band gap slightly increases (3.48 eV). The band gap (E_g) values for all the compositions are tabulated in Table ST2.[†]

PL excitation and emission spectrum of $Li_3BaSrLa_{0.3}Eu_{2.7}(MoO_4)_8$

The photoluminescence excitation and emission spectra of $Li_3BaSrLa_{0.3}Eu_{2.7}(MoO_4)_8$ phosphor is shown in Fig. 6. DRS, as well as the excitation spectrum of the sample, consist of two different spectral regions. The broad band was ascribed to overlapping of the MoO_4^{2-} group and $O^{2-} \rightarrow Eu^{3+}$ charge transfer band. The other part, which covers sharp peaks from 350 to 600 nm is related to 4f–4f electronic transitions of the trivalent Eu ion. The energy transfer process is efficient in nature, the energy absorbed by the MoO_4^{2-} moiety is successfully transferred to the Eu^{3+} ion resulting in a brightened and intense red emission.

PL excitation and emission studies of $Li_3BaSrLa_{3-x}Eu_x(MoO_4)_8$, where x = 0.3-3

PLE and PL emission spectra of the selected compositions $Li_3BaSrLa_{3-x}Eu_x(MoO_4)_8$, where x = 0.3-3, in steps of 0.3 are shown in Fig. 7a–d (all the compositions of PL and PLE spectra are given in S2–S5†). The Eu^{3+} ion having $6s^2 5d^1 4f^6$ is well shielded from the ligand environment and has a special choice towards site symmetry. The ${}^5D_0 \rightarrow {}^7F_2$ intra state transitions of Eu^{3+} ion are hypersensitive in nature, so the emission intensity is strongly prejudiced by the ligand ions in the host lattice.¹⁵ Hence, the use of Eu^{3+} ions as a structural probe in the host lattices is well-known. The pre-established selection rule does not allow the transition of Eu^{3+} ions as they are forbidden in nature. The two-major electronic transitions of

 Eu^{3+} ion are electric dipole (ED) ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and magnetic dipole (MD) ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transitions. In an inorganic host lattice, in a distinct site with a center of inversion (C_i) , the ED transition is strictly forbidden whereas, without C_i, MD transitions are almost disappeared. Nevertheless, partial allowance of the selection rule of the ED transition is granted and is dominated in the host lattice, as they are hypersensitive. By monitoring the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at $\lambda_{em} = 615$ nm, the excitation spectra were recorded for all phosphors and are shown in Fig. 7a. Without any argument, the spectra contain the typical absorption line expected from the trivalent Eu ion. The lower part of the spectra is covered by a broad absorption ranging from 200 to 360 nm, while the higher part consists of several sharp spectral lines. The wide band is the result of CT occurring within the host lattice from either $Eu^{3+} \rightarrow O^{2-}$ or $O^{2-} \rightarrow Mo^{6+}$. The strength and edge of the CT band were found to enhance with an increase in the activator concentration. The Eu-rich phosphor yields a strong (broad) CT band when all La³⁺ ions residing in the lattice are completely replaced by the incoming Eu³⁺ ion. The broadening of the CT band is a result of decreasing size of Eu³⁺ sites, the shorter Eu-O bonds always facilitate the charge transfer process. The strongest line among the spectral lines centered at 394 nm is ascribed to the ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ transition of the Eu³⁺ ion. The other lines appearing at 411, 466, 527, 587 are attributed to ${}^{7}F_{0} \rightarrow {}^{5}D_{3,2,1,0}$ transitions, respectively. A modest red shift was observed for the present samples with increasing Eu content along with a slight broadening of the CT band. The presence of the strongest spectral lines at 394 and 465 nm is providing new heights for the phosphor and can be used for blue and near UV excited white LEDs.

The PL spectra of $Li_3BaSrLa_{3-x}Eu_x(MoO_4)_8$ excited with CT band, 394 and 465 nm are represented in Fig. 7b, c, and d, respectively. The spectra consist of several sharp lines like emission, which is clearly being a note in the emission spectrum. The bands originating at different wavelengths like 577,



Fig. 6 (a) Diffuse reflectance and excitation spectrum of $Li_3BaSrLa_{0.3}Eu_{2.7}(MoO_4)_8$, inset energy level diagram of Eu_3^{3+} ion, (b) emission spectrum of $Li_3BaSrLa_{0.3}Eu_{2.7}$ (MoO₄)₈ at λ_{exc} = 394 nm (inset CIE color coordinates for the phosphor, digital images under daylight/365 nm UV lamp and La coordination).



Fig. 7 PL excitation (under a. $\lambda_{em} = 615$ nm) and emission (b. at $\lambda_{exc} = CT$ band c. at $\lambda_{exc} = 394$ nm and d. at $\lambda_{exc} = 465$ nm) spectra of Li₃BaSrLa_{3-x}Eu_x(MoO₄)₈ where x = 0-3 for selected compositions.

589, 613, 652 and 700 nm are attributed to ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, ${}^{7}F_{1}$, ${}^{7}F_{2}$, ${}^{7}F_{3}$ and ${}^{7}F_{4}$ intra 4f-4f electronic transitions of Eu³⁺ ion. Among all the spectral lines, the ED transition $({}^{5}D_{0} \rightarrow {}^{7}F_{2})$ was found to be predominated in the emission spectra of xEu³⁺: Li₃BaSrLa₃(MoO₄)₈ corresponding to red emission and non centrosymmetric residence of the activator ion at an excitation wavelength (Fig. 7b-d). It was apparent that with increasing activator concentration, the intensity of the phosphor was increasing gradually. It is worth noting that among entire excitation wavelengths (CT band, 394 and 465 nm), the CT band excited emission spectrum gives signified emission intensity. This clearly indicates that the energy transfers from the host (CT band) to Eu³⁺ are efficient enough. However, the concentration of Eu³⁺ does not influence the profile and position of the emission spectra, and both remain intact. A possible explanation for this behaviour can be isolated in an electronic environment (5s and 5p), hence 4f-4f electronic transitions are least affected by ligand ions in the host lattice. The remarkable contrast in the intensity of both ED and MD transition can be noticed, the intervening ED transition elucidating the symmetry around the Eu³⁺ is low and the same deviates from the inversion centre.

The interesting observation was due to the presence of $^5D_0 \rightarrow \ ^7F_0$ spectral transition around 577 nm. The 5D_0 and

⁷F₀ states are non-degenerate in nature. So, transitions that are originating from both the non-degenerate levels will describe the number of emitting species in the host lattice. 16 Here, the ${}^5D_0\!-\!{}^7F_0$ transition is a singlet, which implies the presence of single emitting species for the presently synthesized phosphors. Several possible explanations arising from these transitions do exist. One of them is when the electronic environment is extremely low and it attains lower symmetry like Cs, C1, C2, C3, C4, etc. as per selection rule-governed for electronic transitions. Another one reported by Fujishiro et al.,^{17,18} this Judd-Ofelt as well as selection rule forbidden transition has a tendency to acquire some intensity from the 5D_0 \rightarrow 7F_2 and 7F_1 transition and $J \rightarrow J_0$ mixing is also equally responsible for this transition to be appearing. The ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions are the most sensitive transitions of the Eu³⁺ ion and taken into consideration while deciding the symmetry, whereas the remaining two transitions ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ are not falling into the category of either ED or MD transition, though it has some contribution to the emission spectra and its properties. The site symmetry of the Eu³⁺ ion within the host lattice can be regulated by crystal field splitting of ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$ transitions.

Asymmetric ratio and full width at half maximum (FWHM) calculations

The intensity ratio of the ED (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) to MD (${}^{5}D_{0} \rightarrow {}^{7}F_{1}$) transition is known to be the asymmetric ratio (R) and used as an important spectroscopic probe to support the site symmetry of Eu³⁺ ions within the host lattice.¹⁹ The calculated values for the presently synthesized phosphors have been tabulated in Table 3. The value state that the asymmetric ratio decreases with increasing Eu³⁺ content, hence the symmetry around the Eu³⁺ ion is decreasing. The high value of R indicates lowering the site symmetry and favours the red emission. The results are in good agreement with the emission spectra. The FWHM values were also calculated and are shown in Table 1. The phosphor to be used in white LEDs should possess FWHM < 30 nm and is considered to be the ideal phosphor. The experimentally calculated value does suggest that all the samples have an FWHM value < 10 nm and intense red emission with appropriate color purity. It is well known that the narrow emitting band red-emitting phosphor significantly enhances the overall performance of white LEDs.^{20,21}

Effect of activator concentration on luminescence profile of $Li_3BaSrLa_{3-x}Eu_x(MoO_4)_8$

The behaviour of an ideal lattice is to retain the emission properties even at higher concentrations of the activator. The change in concentration profile is directly related to the emission intensity. Hence, the Eu³⁺ concentration versus emission intensity profile is shown in Fig. 8a. The plot shows that the Eu³⁺ concentration is directly proportional to the emission intensity. In other words, the emission intensity increases with increasing activator ion concentration in the lattice and reaches and a maximum when all La³⁺ ions are substituted by Eu³⁺ ions. It also states that the energy absorbed by the host lattice has been efficiently transferred to the Eu³⁺ ion in the centre. The critical distance between two adjacent Eu³⁺ will help further to understand phenomena. Hence, a pre-established relation by Blasse²² was used to calculate the critical distance. The critical distance is when the rate of non - radiative transfer rate equals the internal decay rate (radiative rate). The equation is given by:

$$R_{\rm c} = 2 \left(\frac{3V}{4\pi X_{\rm c} N}\right)^{1/3} \tag{4}$$

where R_c is the critical distance, *V* is the volume of the lattice, *N* is the available site for dopants in the unit cell. In the present calculations, *V* is taken to 1266.653, it is mentioned earlier that the concentration quenching occurs only when all La³⁺ are fully replaced by Eu³⁺, which is when x = 3 critical concentration and N = 6. The calculated R_c value is 5.64 Å. The energy transfer process can be explained further by identifying the type of interaction involved in the energy transfer process. Blasse *et al.* have already reported that the energy transfer process is directly correlated with the mechanism of exchange interaction.²³ The emission from the ⁵D₀ level of Eu³⁺ is quenched due to the energy transfer process as well as the exchange interaction. Huang has previously established the relationship between the emission intensity and doping concentration of Eu³⁺ and has already developed a theoretical expression. To recognize the type of interaction involved in Li₃BaSrLa₃(MoO₄)₈:Eu³⁺ phosphors, we calculated these values. The relationship between emission intensity (*I*) and Eu³⁺ concentration, per Huang, is given by:

$$I \propto a^{\left(1 - \frac{s}{d}\right)} \Gamma\left(1 + \frac{s}{d}\right) \tag{5}$$

$$a = C\Gamma(1 - d/s)[X_0(1 + A/\gamma)]d/s$$
(6)

where *A* and *X*₀ are constants, and $\Gamma(1 + s/d)$ is a Γ function, γ is the intrinsic transition probability of sensitizer and *s* is the index for electric multipole, for electric dipole–dipole, electric dipole-quadrupole, and electric quadrupole-quadrupole interaction; when *s* = 6, 8, 10, correspondingly. By deriving the eqn (1) and (2), they can be rewritten as

$$\frac{I}{C} = -\frac{s}{d}\log C + \log f \tag{7}$$

where *c* is the concentration of the activator ion and *f* is independent of doping concentration. Using eqn (3), log *c* and log (I/c) values for the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition were calculated and plotted together, depicted in Fig. 8b. The values obtained were fitted using the linear fitting method and the slope was -0.7451 for -s/d, and the value is close to 1. Hence, the *s* value obtained ~ equals to 3. Thus, we concluded that the exchange interaction mechanism is dominated by the process of energy transfer process involved between two adjacent Eu³⁺ ions in Li₃BaSrLa₃(MoO₄)₈:Eu³⁺ phosphors.

The observed zero or negligible concentration quenching can be understood by looking at the crystal structure of the host lattice. The shortest distance between La^{3+} is 3.921 Å, whereas the distance varies significantly in different layers *i.e.*, the shortest distance between La^{3+} is 8.657 Å and they are isolated by MoO₄ groups (shown in Fig. 9). It is well acknowledged that the exchange interaction is more effective between the trivalent europium ion (activator) if the Eu–Eu distance is shorter than 5 Å. In the present investigation, the interaction

Table 1 Asymmetric ratio (AR) and FWHM of $Li_3BaSrLa_{3-x}Eu_x(MoO_4)_8$ where x = 0.3-3

Composition (x) in steps of 0.3	0.3	0.6	0.9	1.2	1.5	1.8	2.1	2.4	2.7	3
$AR = I_2/I_1$ FWHM in nm	11.764 5.30	10.607 6.50	8.547 6.84	9.438 6.42	14.120 7.65	9.736 7.22	13.047 8.22	10.090 6.05	9.428 5.32	8.911 7.55

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Fig. 8 (a) Eu^{3+} concentration vs. emission intensity at $\lambda_{exc} = 394$, 465 and CT band nm for $Li_3BaSrLa_{3-x}Eu_x(MoO_4)_8$ where x = 0-3. (b) The relation of the concentration of Eu^{3+} ions (log C) and the log (I/C) for the ${}^5D_0 \rightarrow {}^7F_2$ transition in $Li_3BaSrLa_3(MoO_4)_8$: Eu^{3+} phosphors $\lambda_{exc} = 394$ nm.



Fig. 9 The unit cell of Li₃BaSrLa₃(MoO₄)₈ along an *a*-axis.

Judd-Ofelt (J-O) spectral intensity parameters

For the emission spectra of the europium-activated Li₃BaSrLa₃(MoO₄)₈ phosphors, important spectral parameters can be calculated like radiative and non-radiative lifetimes, branching ratio and quantum efficiencies, etc. The most important optical parameters that can be calculated by using the spectral emission data are Judd-Ofelt (J-O) intensity parameters. The J-O parameters are based on the classical theory developed by Judd-Ofelt.^{25,26} The detailed calculation for deriving the Ω_2 and Ω_4 parameters was explained in our previous article.¹¹ The Ω_6 parameter has not been observed. The obtained values are tabulated in Table 2. It can be observed that the Ω_2 parameter has a high value as compared to Ω_4 . The greater Ω_2 value provides necessary information regarding the covalency among the metal and ligand bond (Eu-O) as well as higher the value of Ω_2 higher is the asymmetry around the Eu³⁺ environment and greater is the emission intensity. The Ω_4 is independent of the ligand field as it is related to ${}^5D_0 \rightarrow$ ⁷F₄ transition, which is least affected by ligand environment and magnetic dipole in nature. The parameters also support

between the activator ions (Eu^{3+}) in the Li₃BaSrEu₃(MO₄)₈ lattice is two-dimensional and the interaction is also very much similar to that of the NaEuTiO₄ lattice, in which the Eu-Eu distance is 3.630 Å (interaction is also two-dimensional).²⁴ However, the shortest Eu–Eu distance was found to be longer in the present case than that in the NaEuTiO₄ lattice. Therefore, one can conclude that the exchange interaction between the activator ions is weaker in the present case and the Eu³⁺ ion can substitute completely in place of the La³⁺ site in the host lattice without diminishing the emission intensity. It is also worth noting that the La-containing polyhedra are separated by the LiO₆ distorted polyhedral and BaO₁₀ polyhedra, as shown in Fig S6.[†]

Table 2 Spectral parameters of ${\sf Eu}^{3+}{\sf substituted}\ {\sf Li}_3{\sf BaSrLa}_3({\sf MoO}_4)_8$ phosphor

	Judd–Ofelt p	arameters			
Concentration	$\Omega_2 \ (10^{-20} \ { m cm}^2)$	$\Omega_4 \ (10^{-20} \ { m cm}^2)$	$\operatorname{in}^{A_{0-1}} \mathrm{S}^{-1}$	$A_{0-2} \\ in S^{-1}$	$\frac{A_{0-4}}{\ln S^{-1}}$
0.3	3.8624	0.8334	50	366.12	33.50
0.6	4.4951	0.8148	50	374.44	32.91
0.9	4.3579	0.8354	50	427.54	33.65
1.2	4.9609	0.8258	50	413.25	33.35
1.5	5.1481	0.8351	50	363.01	33.87
1.8	4.3834	0.7554	50	321.74	30.51
2.1	5.2714	0.9992	50	440.29	40.31
2.4	3.8812	0.9048	50	322.76	36.44
2.7	5.0530	0.9623	50	419.65	38.77
3	1.8879	1.2903	50	159.07	51.98

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the information obtained from spectral emission data, the electric dipole transition is predominated in the case of presently synthesized phosphor materials. The larger Ω_2 parameter is a good sign that Eu³⁺environmental sites are distorted in the currently studied host lattice.

The Judd–Ofelt intensity parameters were utilised further to calculate other vital optical properties like transition probabilities (A_{rad} , A_{nr}), radiative lifetime (τ_{rad}), the branching ratio (β). The total radiative transition probability can be written as

$$A_{\rm rad} = \sum_{J} A_{0-J} \tag{8}$$

where A_{rad} , is the total radiative transition probabilities. The radiative lifetime of the excited state of the Eu³⁺ ion and the total radiative transition probabilities are interrelated and can be expressed as:

$$\tau_{\rm rad} = \frac{1}{A_{\rm rad}} \tag{9}$$

The fluorescence-branching ratio (β) for the transitions starting from the ⁵D₀ level can be resulting from the following equation:

$$\beta = \frac{A(0-J)}{A_{\rm rad}(0-J)} \tag{10}$$

The stimulated emission cross-section (σ_e) is also an important parameter to predict the rate of energy extraction from the material and their laser performances, which can be calculated as per the equation given below:

$$\sigma_{\rm e}(\lambda_{\rm p}) = \left[\frac{\lambda P^4}{8\pi c n^2 \Delta \lambda_{\rm eff}}\right] (A_{0-J}) \tag{11}$$

where $\lambda_{\rm p}$ is the emission peak wavelength, *c* is the velocity of light and $\Delta\lambda_{\rm eff}$ is the effective bandwidth of the emission. The calculated values of transition probabilities, radiative lifetime, branching ratios and emission cross-section are summarized in Table 3 for Li₃BaSrLa₃(MoO₄)₈:Eu³⁺ phosphors. The lifetime ($\tau_{\rm rad}$) obtained from the Judd–Ofelt parameters differ from the obtained experimental value. The possible explanation for this can be the J–O theory, which overemphasizes the radiative life-

time because of the partial insufficiency of the theory to predict the radiative properties of phosphor materials.²⁷

Temperature-dependent PL study

To use the phosphor in practical applications, it is indeed necessary to check the thermal stability of the phosphor material as it has a great influence on the light output and CRI of white LEDs and it is considered one of the most vital technical parameters. The profile of emission intensity along with temperature thermal quenching studies was executed in the temperature range of 25-200 °C under 394 nm excitation and the obtained data is shown in Fig. S7a.† Naturally, with increasing temperature, the emission intensity slowly starts degrading, but the loss is minimal. The phosphor Li₃BaSrLa_{2.7}Eu_{0.3}(MoO₄)₈ retains 60% of its emission intensity at 150 °C. The activation energy (E_g) was calculated using the Arrhenius equation. The estimated value for E_{g} for the present phosphor was found to be 0.30 eV. A plot of $\ln[(I/I_0) - 1]$ versus 1/KT is shown in Fig. S7b.† The value of E_g is comparatively higher than that of the CaS:Eu²⁺ commercial phosphor²⁸ and much higher than the other Eu³⁺ activated phosphors such as BaZrGe₃O₉:Eu³⁺ ($\Delta E = 0.175 \text{ eV}$),²⁹ LiGd₃(MoO₄)₅ ($\Delta E = 0.24$ eV)³⁰ and $Gd_2(MoO_4)_3$: Eu^{3+} ($\Delta E = 0.24 eV$) phosphors.³¹ Another advantage is that the position of peaks in the emission spectra does not change with increasing temperature. Li₃BaSrLa_{0.3}Eu_{2.7}(MoO₄)₈ phosphor showed improved thermal stability, as evidenced from the data in Fig. 10a and the corresponding E_g value is 0.24 eV. A plot of $\ln[(I/I_0) - 1]$ versus 1/KT is shown in Fig. 10b. The red phosphor Li₃BaSrLa_{0.3}Eu_{2.7}(MoO₄)₈ retain >80% of its emission intensity at 150 °C.

$$I(T) = \frac{I_0}{I + A \exp\left(\frac{E}{kT}\right)} \tag{12}$$

PL decay analysis

The luminescence decay lifetime (τ) of Eu³⁺ in Li₃BaSrLa₃(MoO₄)₈ host was measured by monitoring ⁵D₀ \rightarrow ⁷F₂ transition at different excitation wavelengths (CT band, 394 and 465 nm). A plot of the intensity of the emission and time

Table 3	Spectral parameters of Eu^{3+} substituted $Li_3BaSrLa_3(MoO_4)_8$ phosphor	
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		$\tau_{\rm rad} ({\rm ms})$	Branching	ratios		Emission area of cross – section $(10^{-3}) \text{ cm}^2$		
Composition	$A_{\rm rad} \left({\rm s}^{-1} \right)$		β_1	β_2	β_4	σ_1	σ_2	σ_4
0.3	449.62	2.22	11.12	81.42	7.45	0.542	2.723	0.429
0.6	457.35	2.19	10.93	81.87	7.19	0.566	2.707	0.461
0.9	511.19	1.96	9.78	83.63	6.58	0.624	2.447	0.514
1.2	496.6	2.01	10.06	83.21	6.71	0.578	2.795	0.508
1.5	446.88	2.24	11.18	81.23	7.57	0.686	1.785	0.630
1.8	402.25	2.49	12.43	79.98	7.58	0.769	1.670	0.680
2.1	530.6	1.88	9.42	82.97	7.59	0.720	1.944	0.852
2.4	409.2	2.44	12.21	78.87	8.90	0.549	2.458	0.567
2.7	508.42	1.97	9.83	82.54	7.62	0.811	1.662	0.960
3	267.05	3.74	18.72	59.56	19.46	0.721	0.773	0.629



Fig. 10 (a) Temperature dependence profile of emission intensity at λ_{exc} = 394 nm from 298 K to 473 K, (b) plot of ln(I/I_0) – 1 versus 1/KT for Li₃BaSrLa_{0.3}Eu_{2.7}(MoO₄)₈ phosphor.

at $\lambda_{\rm exc}$ of 394 nm is given in Fig. 11, while the other two are shown in Fig. S8 and S9.† The same values are tabulated in Table ST3.† The decay curves observed are stripper for higher Eu³⁺ concentration. All the spectral data were fitted using a single exponential decay function given by:

$$I(t) = I_0 e^{-\frac{t}{\tau}} \tag{13}$$

where I(t) is the intensity at a given time t, I_0 is the initial intensity, and τ is the lifetime. In general, a longer value of fluorescence lifetime (τ) is obtained when the environment around Eu³⁺ is highly symmetric as a result of which the 4f–4f transition becomes more forbidden in nature. Whereas, the shorter value indicates the increase of disorders around Eu³⁺ and relaxation of transition selection rules.¹⁵ For the presently studied phosphor, the unit cell structural data confirm the



Fig. 11 PL lifetime for $Li_3BaSrLa_{2.7}Eu_{0.3}(WO_4)_8$ phosphors with different concentrations under 394 nm excitation.

presence of a Eu³⁺ ion in an 8-coordinated site, with increasing concentration of Eu ion in the lattice, no significant changes were noticed in the τ value. The results conclude that the Eu³⁺ ion is residing in the more distorted site (noncentrosymmetric) in the host lattice, as a result of this, an increased ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition was observed.

CIE chromaticity coordinates

The colorimetric technique is a good tool for commenting on the color purity of the phosphor samples. The Commission International de 'Eclairage (CIE) chromaticity for the Li₃BaSrLa₃(MoO₄)₈:Eu³⁺ activated phosphors (selected composition) is shown in Fig. 12a. The calculation was performed using the spectral emission data by using MATLAB software as an imperative mathematical tool. The National Television Standard Committee (NTSC) value for a red color is x = 0.67and y = 0.32. In the case of the presently synthesized phosphors, the chromaticity coordinates move to an intense red region with increasing Eu³⁺ concentration. The calculated values for all compositions with different excitation wavelengths (394 and 465 nm), including CT band excitation are being tabulated in Table ST4.[†] All the samples exhibit x and y values close to the NTSC standard. The CIE x and y values are also compared with commercial CaS:Eu and the same given in Fig. 12b. Furthermore, the color purity of $Li_3BaSrLa_{3-x}Eu_x(MoO_4)_8$, where x = 0.3-3 phosphors were calculated³² and are presented in Fig. 12c, S9 and S10.† The color purity can be determined using the following equation:

Color purity =
$$\frac{\sqrt{(x - x_i)^2 + (y - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}}$$
 (14)

In the above equation, (x, y) denotes the CIE chromaticity coordinates of Li₃BaSrLa₃(MoO₄)₈:Eu³⁺ phosphor. (x_i, y_i) represents the CIE white light illumination $(x_i = 0.310, y_i = 0.316)$, and the (x_d, y_d) refer to the chromaticity coordinates dominant



Fig. 12 (a) CIE color coordinates of selected compositions, inset the image of phosphor under day light and UV irradiation, (b) fragment of CIE 1931 color diagram with color points of $Li_3BaSrLa_{3-x}Eu_x(MOO_4)_8$ where x = 0.3-3 phosphors as a function of Eu^{3+} concentration, (c) color purity percentage of the $Li_3BaSrLa_{3-x}Eu_x(MOO_4)_8$ phosphors ($\lambda_{ex} = 394$ nm).

wavelength points ($x_d = 0.682, y_d = 0.317$). In the present study, the obtained CIE values for the Li₃BaSrLa_{0.3}Eu_{2.7}(MoO₄)₈ phosphor are x = 0.651, y = 0.348, and thus the color purity was found to be 92.32%. Fig. 11c, S8 and S9[†] illustrate the color purity of all the red phosphors, all of them exhibit color purity greater than 92%. The presently-studied Li₃BaSrLa_{0.3}Eu_{2.7}(MoO₄)₈ phosphor exhibited excellent color purity than that shown by other reputed red phosphors (NaSrY $(MoO_4)_3$: Eu^{3+} (93.6%),³³ KBaGd $(MoO_4)_3$: Eu^{3+} (94%)³⁴ and SrMoO₄: Eu^{3+} (85.8%)).³⁵ This result suggests that the Li₃BaSrLa₃(MoO₄)₈:Eu³⁺ red phosphor shows superior color coordinates with greater color purity, which indicates that the phosphor can perform as a suitable red component in the white LEDs.

Quantum yield measurement and comparison with Y_2O_2S and $Y_2O_3:Eu^{3+}$

The absolute quantum yield (QY) of the selected compositions was measured to support the efficiency of the samples for versatile applications. The absolute QY of Li₃BaSrLa_{0.3}Eu_{2.7}(MoO₄)₈ phosphor was found to be 92.6% (Fig. S11†). The calculated value of QY for Y₂O₃:Eu³⁺ can be 90% under the excitation of ~270 nm. However, QY is near about ~9.6% with excitation at 396 nm, which is previously reported by Long *et al.*³⁶ The emission intensity of the Y₂O₂S, Y₂O₃:Eu³⁺ commercial red phosphor was compared with our sample. The result (Fig. 13) shows that the currently synthesized Li₃BaSrLa_{0.3}Eu_{2.7}(MoO₄)₈ phosphor shows more than



Fig. 13 Comparison of emission intensity with $Y_2O_2S,\,Y_2O_3\colon Eu^{3+}$ with $Li_3BaSrLa_{0.3}Eu_{2.7}(MoO_4)_{B.}$

4 times higher emission intensity. The color purity and high QY of the samples are favorable for white applications. It is noteworthy that the quantum efficiency of redemitting phosphor $\mathrm{Sr_2Si_5N_8:Eu^{2+}}$ is ~64% under 450 nm excitation.^{37,38}

Fabrication of red and white LED (based on near UV/blue LED chip)

The best composition $Li_3BaSrLa_{0.3}Eu_{2.7}(MoO_4)_8$ red-emitting phosphor is integrated with near UV LED (InGaN, 395 nm). The emission spectrum of the fabricated LED shows a red emission at 20 mA forward bias (Fig. 14a) and their CIE color coordinates, as well as the diagram, are shown as an inset. In

order to increase the emission intensity of the phosphor, the concentration of the red phosphor is increased in the polymethyl methacrylate (PMMA) matrix. The digital image of the LED is given in the inset Fig. 14a. In addition, efforts have also been made to fabricate white LED based on blue LED chips. The white LED was fabricated by using yellow organic dye (experimental details for the synthesis of yellow dye are given in Scheme S1[†])³⁹ and red phosphor integrated with blue LED chip and for comparison, the white LED spectrum integrated with yellow dye with blue LED chip is shown in Fig. S13.[†] The corresponding white LED spectrum is shown in Fig. 14b and the color coordinate CIE, CCT, CRI and the digital image are shown as insets. It is also worth noting that the recently reported non-concentration red borate Ca₃Eu₂B₄O₁₂ phosphorbased white LED showed yellowish-white (CIE x = 0.3823, y =0.3683). However, the presently investigated red phosphorbased hybrid white LED showed pure white light emission.⁴⁰ It is worth noting that the endorsed CRI values depend on the application environment; though, CRI of >80 is recommended for most applications. In addition, the luminous efficiency of the radiation (LER) was also calculated for the hybrid white LEDs, which describes how bright the radiation is perceived by the average human eye in lumen per watt (lm per W).⁴¹ Luminous efficiency of the radiation (LER) for hybrid white LED is ~322 lm per W. The LER value for the red LED was also calculated and the values are 184, 238, 271 lm per W for the ratio (PMMA: Phosphor) 1:10, 1:20 at 1:30, respectively.

In addition, it is also worth noting that the presently synthesized selected compositions based on the red LED emission spectra have emerged with Pr absorption and both the near UV LED emission as well as the electric dipole transition at 615 nm red LED emission is covering the Pr absorption (Fig. 15). The results are promising and this LED could be potential use in plant growth applications.



Fig. 14 (a) Comparison of emission intensity with different ratios of Li₃BaSrLa_{0.3}Eu_{2.7}(MoO₄)₈ phosphor with PMMA, inset corresponding CIE color co-ordinates and a digital photograph. (b) White LED spectrum of fabricated white LED.



Fig. 15 The spectral overlap between the red LED and Phytochrome (Pr) absorption.

Conclusions

Zero concentration quenching red Li₃BaSrLa_{3-x}Eu_x(MoO₄)₈ phosphors were synthesised and their optical properties systematically investigated. All the compositions showed a narrowband red emission, due to electric dipole transitions and concentration quenching was not observed until x = 2.7 (clearly indicates that the phosphor having zero concentration quenching). The excitation and emission properties were similar for all compositions, however, the increase in the emission intensity was observed while moving from low to high concentration (0.3–3) of the Eu³⁺ ions. The ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ED transition dominated all over the emission spectra. The chromaticity coordinates and Judd-Ofelt parameter support the emission profile of the phosphors. The high value of emission intensity, color purity and quantum yield (92.6%) makes the phosphor potential for white LEDs. The fabricated LED with the best compositions show red emission with CIE values are located in the deep-red region. The phosphor can be efficiently excited by either blue rays or near UV excitation, and are budding contenders for white LED applications. White LED fabricated by using blue LED in conjugation with yellow organic dye + red phosphor and the LED is shown as CCT (5546 K), CIE (0.331, 0.385), and CRI (81%). The fabricated red LED spectral lines are well-matched with the phytochrome (Pr) absorption and this clearly indicates that this red LED could find prospective application in plant growth.

Conflicts of interest

There are no conflicts to declare.

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