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Crystal structure and photophysical features of greenish perovskite type SrLa$_2$Al$_2$O$_7$:$\text{Er}^{3+}$ nanocrystals for down conversion white LEDs

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Abstract

Tetragonal phase perovskite type SrLa$_{2(1-x)}$Er$_{2x}$Al$_2$O$_7$ ($x = 1.0$–$5.0$ mol%) nanocrystals emitting green light were prepared by a facile, economical and efficient solution combustion route. Detailed analysis of their crystal structure and lattice refinement was carried out by x-ray Diffraction and Rietveld refinement, which confirmed their tetragonal phase along with 14/mmm (139) space group. Morphological investigation was done by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) which disclosed the spherical shape of nanoparticles with their average size in the range of 40–50 nm. Elemental composition of the nanophosphors was detected by Energy Dispersive x-ray Analysis (EDAX). Utilizing Diffused Reflectance Spectra (DRS), band gap value of the optimized sample i.e., SrLa$_{1.96}$Er$_0.04$Al$_2$O$_7$ was calculated as 5.01 eV. Photoluminescence studies indicated the green color emission of the synthesized nanophosphors with a prominent peak in the emission spectra at 548 nm due to $^4S_{3/2} \rightarrow \ ^4I_{15/2}$ electric-dipole transition. Optimum concentration of the Er$^{3+}$ was observed as 2.0 mol% above which concentration quenching process occurred via dipole-dipole non-radiative energy migration. Radiative lifetime value and quantum efficiency for optimized sample were determined as 0.546 ms and 68.33%, respectively. Moreover, color coordinates of the nanophosphors (0.2657, 0.6031) confirmed their emission in green region which enabled them to be a promising candidate in the phosphorescent sensors and tricolor (RedGreen-Blue) based white light emitting diodes (WLEDs).

1. Introduction

Nanotechnology has brought a revolutionary change in the lighting industry in terms of energy conservation and better lighting than the traditional lighting sources which required large amount of energy. Thus, white light emitting diodes fabricated by nanophosphors are seemed to be an effective source of illumination to meet the increasing energy demands of the expanding population [1]. Earlier, the WLEDs were synthesized via fusion of LED chips with luminescence of blue color and the YAG:Ce (Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$) phosphors with yellow luminescence [2] which proffered many drawbacks, including poor value of CRI (Color Rendition Index) i.e., 71.6, deficiency of the light in red region etc So, all these limitations were overcome by the tricolor RGB (Red, Green and Blue) based WLEDs which provide the excellent lumen outcome, long afterglow and more importantly, they are affordable (cheap) and eco-friendly with better thermal and chemical stability [3]. These tremendous properties have prompted the materials scientists to design more and more these types of novel nanophosphors which can be used to synthesize the warm WLEDs [4–8]. Regarding this, Rare earth ions (Re$^{3+}$) are considered as the most suitable dopant ions in these nanophosphors for several years. Due to the partially filled 4$f$ subshell, they give sharp lines in the visible range (400–700 nm) of their emission spectra. In this present work, trivalent erbium ion (Er$^{3+}$) was chosen because of its significant green emission in the region of longer wavelength which showed its importance in the field of laser [9, 10]. To accommodate the Er$^{3+}$ ion, the suitable
host was required. Extensive research was carried out by author for various oxide lattices out of which ternary aluminates were selected, which were identified successfully because of their extreme stable crystal structure, high chemical purity, ferroelectricity, ecofriendly nature, high thermal stability, wide energy band-gap and high value of surface area to volume ratio, enhanced lumen output in the visible region etc. Moreover, the excellency of the perovskite host matrix has been reflected by their appealing dielectric properties including adequate dielectric constant, better unloaded quality factor and ultra low temperature coefficient of resonant frequency; which enhance its utility in the microwave resonators, filters and antennas also [11]. Hence, these materials find enormous applications in the opto-electronic devices like luminescent sensors, lasers, WLEDs etc [12].

Thus, keeping all these points in mind, author has adopted SrLa2Al2O7 host which belongs to the class of perovskite compounds having structure of type ABnCnO3n+1 where A, B, C are alkaline earth metal ion, rare earth ion and any cation respectively while n represents the no. of octahedral units which comprise the layers of perovskite compound [13, 14]. Upon literature survey, it was found that there was reported only the crystal structure and optical analysis of Sm3+ and Dy3+ doped SrLa2Al2O7 [15, 16] but no study was accomplished up to now on the effect of Er3+ doping on the crystallographic and photophysical properties of down-converted perovskite SrLa2Al2O7 nanophosphors, which suggests the novelty of the reported research work. In this study, a facile, economic and efficient approach was opted known as Solution Combustion Synthesis (SCS) to synthesize SrLa2Al2O7:Er3+ nanophosphors. A refinement technique confirmed the tetragonal structure of the sample with 14/mmm (139) space group. Morphological analysis was carried out by SEM and TEM while elemental composition was detected by EDAX. Fourier transform infra- red (FT-IR) analysis depicted the various stretching and binding vibrations corresponding to metal-oxygen (M–O) bonds. Energy band-gap values were determined with the help of DR (diffuse reflectance) spectra while CIE 1931 (Commission International de l’Eclairage) coordinates confirmed the greenish emission of the prepared nanophosphors which authenticated the diverse applications of the perovskite type Er3+ doped SrLa2Al2O7 nanophosphors in the various opto-electronic devices like phosphorescent sensors, WLEDs etc.

2. Experimental section
2.1. Synthesis
All the powdered nanocrystals i.e., SrLa2(1–x)Er2xAl2O7 (x = 1.0–5.0 mol%) were prepared by facile, eco-friendly and efficient technique known as SCS (Solution Combustion Synthesis). Sr(NO3)2 (99.995%), La(NO3)3, 6H2O (99.999%), Er(NO3)3, 5H2O (99.999%) and Al(NO3)3, 9H2O (99.997%) were used as such in the form of oxidizers while urea (99.999%) was taken as fuel. All these precursors were then weighed in their stoichiometric ratio to form the homogenous mixture [17] which was loaded inside the preheated furnace at a temperature of 500 °C for remarkably short period i.e., 10–15 min. As a result of which exothermic reaction took place yielding the white porous product. The resultant powder was then taken out of the furnace and grinded to the fine powder form. So, the combustion method yielding the desired nanophosphors i.e., SrLa1.96Er0.04Al2O7 had undergone the following chemical reaction:

$$\text{Sr(NO}_3\text{)}_2 + 2\text{Al(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} + 1.96\text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O}$$
$$+ 0.04\text{Er(NO}_3\text{)}_3 \cdot 5\text{H}_2\text{O} + 11.67\text{NH}_3\text{CONH}_2 \rightarrow \text{SrLa}_{1.96}\text{Er}_{0.04}\text{Al}_2\text{O}_7$$
$$+ 11.67\text{CO}_2(g) + 53.30\text{H}_2\text{O(g)} + 18.67\text{N}_2(g)$$

Later on, the white powder product was allowed to undergo heat treatment at a temperature of 1350 °C for a duration of 3 h which finally resulted into the production of SrLa2Al2O7:Er3+ nanophosphors.

2.2. Phosphor characterizations
Crystal structure of the prepared nanophosphors was analysed by registering their diffraction patterns on RIGAKU ULTIMA IV x-ray Diffractometer with Cu Kα radiations having wavelength of 0.1540562 nm in the range of 20 from 10°–80° represented in figure 1. Cell parameters of crystal structure were analysed by imposing Rietveld refinement on optimized sample utilizing General Structure Analysis System (GSAS) software [18, 19]. Morphological investigation of the prepared samples was executed via JEOL JSM-6510 SEM and TECNAI G2 FEI TEM. For elemental identification, AMETEK Z2 ANALYSER EDAX was employed. FT-IR data by NICOLET iS50 FT-IR Spectrometer, was used for sample recognition by observing various peaks due to stretching and bending vibrations of the M–O bonds present in the crystal structure of nanophosphors. Band-gap studies were carried out by documenting DR spectra at room temperature. PL excitation and emission spectra were recorded via HITACHI F-7000 fluorescence spectrophotometer with xenon lamp when slits width and PMT voltage were set at 2.5 nm and 400 V respectively. Also, phosphorescence decay curves were examined by the same instrument at 5.0 nm slit width and rooting the PMT voltage at 400.
3. Results and discussion

3.1. Structural analysis

Figure 1 reported the registered XRD patterns for as prepared nanosamples i.e., SrLa$_{2(1-x)}$Er$_{2x}$Al$_2$O$_7$ (x = 0.01–0.05) nanocrystals along with standard diffraction data of SrLa$_2$Al$_2$O$_7$ (JCPDS card no. 70–1678). This indicated the purity of tetragonal phase formed with 14/mmm (139) space group. Figure 2 showed the outputs of Rietveld analysis which was executed by operating the SrLa$_2$Al$_2$O$_7$ host file (COD No. 1536843) on the doped sample which illustrated their crystal structures and cell parameters [11]. The calculated data i.e., a = b = 3.7730 Å and c = 20.2152 Å while $\alpha = \beta = \gamma = 90^\circ$ with volume of cell (V) = 287.78 Å$^3$ fitted with the experimental data well, the comparison of which given in table 1. Thus, the little deduction in the volume of Er$^{3+}$ doped unit cell i.e., from 288.15 Å$^3$ to 287.78 Å$^3$ was observed due to the comparative less ionic size of Er$^{3+}$ ions (103 pm) than La$^{3+}$ ions (117.2 pm), which gave an idea about...
the effective doping of Er$^{3+}$ ions into the host because of their almost similar charge and size. This phenomena of replacement of host cations by dopant ions was also explained by computing the difference in percentage ($\%$) radius ($\Delta r$) whose ideal value was found to be less than 30% in order to form new solid solution [20–22]. In this case, it was calculated as [23]:

$$\Delta r = \frac{R_m(CN) - R_d(CN)}{R_m(CN)} \times 100$$

(1)

where, CN represented the coordination number, while $R_d$(CN) and $R_m$(CN) corresponded to the effective ionic radii of the dopant ions and the host cations respectively. The calculated values of $\Delta r$ for La$^{3+}$ (117.2 pm) and Er$^{3+}$ (103 pm) was 12.116% while for Al$^{3+}$ (67.5 pm) and Er$^{3+}$ was 52.593%. Since $\Delta r$ value for La$^{3+}$ and Er$^{3+}$ ions was found to be less than 30% which ascertained the replacement of La$^{3+}$ ions only by Er$^{3+}$ ions. The detailed structural analysis including the coordination environment of the cations in SrLa$_{1.96}$Er$_{0.04}$Al$_2$O$_7$ was shown in figure 3. It was clearly observed that the Er$^{3+}$ ions existed in two different environments of polyhedra with coordination number 9 and 12 while Al$^{3+}$ ions were surrounded by 6 O$^{2-}$ anions in the distorted environment of octahedral units. These different types of cation and oxygen bond distances are tabularized in table 2 and 3. Also, the crystallite size was computed by applying Scherrer equation [24]:

$$D = \frac{0.941 \lambda}{\beta \cos \theta}$$

(2)

### Table 1. Comparison of the crystal structure data of standard host lattice SrLa$_2$Al$_2$O$_7$ and the doped SrLa$_{1.96}$Er$_{0.04}$Al$_2$O$_7$.

| Formula           | SrLa$_2$Al$_2$O$_7$ | SrLa$_{1.96}$Er$_{0.04}$Al$_2$O$_7$ |
|-------------------|---------------------|-------------------------------------|
| Formula weight ($g\ mol^{-1}$) | 531.387             | 532.521                             |
| Symmetry          | Tetragonal          | Tetragonal                          |
| Space group       | 14/mmm (139)        | 14/mmm (139)                        |
| a (Å)             | 3.7756              | 3.7730                              |
| b (Å)             | 3.7756              | 3.7730                              |
| c (Å)             | 20.2140             | 20.2152                             |
| $\alpha = \beta = \gamma$ (°) | 90°                  | 90°                                 |
| Volume (Å$^3$)    | 88.15               | 287.78                              |
| Z                 | 2                   | 2                                   |
| Pearson code      | tI24                | tI24                                |
| Wyckoff sequence  | ge3ba               | ge3ba                               |

Figure 3. 3D crystal structure of the doped sample SrLa$_{1.96}$Er$_{0.04}$Al$_2$O$_7$ which is highlighting the coordinative environments of various cations present in it.
La2-O2 2.6757
O2-O1 2.7283
Al1-O2 1.8922
O2-O1 2.7292
La1 4c 4 mm 0.653 0 0 0.318 0.0000
Sr1 4e 4 mm 0.3333 0 0 1 0.0000
Al1 4e 4 mm 1.299 0 0 0.318 0.0000
Er2 2a 4 mm 0.653 0 0 0 0.318 0.0000
O3 4e 4 mm 0 0 0 0 0.0000
Er1 4e 4 mm 0.0133 0 0 0.318 0.0250

Various types of interatomic bond distances (Å) in the crystal structure of SrLa1.96Er0.04Al2O7 nanophosphor.

| Bond type | Distance | Bond type | Distance |
|-----------|----------|-----------|----------|
| Al1-O1    | 1.9942 × 1 | La2/Sr1/Er2-O2 | 2.7292 × 1 |
| Al1-O1    | 1.9953 × 1 | O3-O2 | 2.8631 × 2 |
| La2/Sr1/Er2-O1 | 2.6757(9) × 4 | La1/Sr2/Er1-O3 | 2.5319 × 1 |
| O2-O1    | 2.7283 × 4 | La1/Sr2/Er1-O2 | 2.5591 × 4 |
| O2-O1    | 2.7291(10) × 4 | La1/Sr1/Er1-O3 | 2.7095(9) × 4 |
| La2/Sr1/Er2-O1 | 2.6757(9) × 4 | La1/Sr2/Er1-Al1 | 3.1673 × 4 |
| La2/Sr1/Er2-O2 | 2.7283(10) × 4 | Al1-O2 | 1.8923(2) × 4 |
| La2/Sr1/Er2-O2 | 2.7291 × 4 | Al1-O1 | 1.9953 × 1 |
| La2/Sr1/Er2-Al1 | 3.3371 × 4 | Al1-O3 | 2.1204 × 1 |
| La2/Sr1/Er2-Al1 | 3.3378 × 4 | La1/Sr2/Er1-Al1 | 3.1673 × 4 |
| All-O2   | 1.8922(2) × 2 | La2/Sr1/Er2-Al1 | 3.3378 × 4 |
| L1/Sr2/Er1-O2 | 2.5591 × 2 | All-O3 | 2.1215 × 1 |
| O2-O2    | 2.6757(9) × 4 | La1/Sr2/Er1-O3 | 2.3308 × 1 |
| O1-O2   | 2.7291(10) × 1 | La1/Sr2/Er1-O3 | 2.7095(9) × 4 |
| L2/Sr1/Er2-O2 | 2.7291 × 1 | O2-O3 | 2.8639 × 4 |
| O1-O2   | 2.7292(10) × 1 | O3-O3 | 3.2846 × 4 |

Various types of transitions observed in the spectrum of SrLa21-xErxAl2O7 (x = 1.0–5.0 mol%) nanophosphors.

| Nanophosphor | Kind of spectrum | Transitions | Wave number (cm⁻¹) | Intensity |
|--------------|-----------------|-------------|--------------------|-----------|
| SrLa21-xErxAl2O7 | Excitation | 4I15/2 → 4G7/2 | 28011 | Weak |
| (x = 1.0–5.0 mol%) | | 4I15/2 → 4G9/2 | 27397 | Medium |
| | | 4I15/2 → 4G11/2 | 26455 | Very Strong |
| | | 4I15/2 → 2F7/2 | 24691 | Weak |
| | | 4I15/2 → 2F5/2 | 22522 | Medium |
| | | 4I15/2 → 2F3/2 | 22222 | Weak |
| | | 4I15/2 → 2F1/2 | 20450 | Strong |
| | Emission | 2H9/2 → 4I15/2 | 24331 | Medium |
| | | 2H11/2 → 4I15/2 | 18975 | Weak |
| | | 4S3/2 → 4I15/2 | 18248 | Very Strong |

Table 2. Refined atomic parameters and positions for SrLa1.96Er0.04Al2O7 nanophosphor.

Table 3. Various types of interatomic bond distances (Å) in the crystal structure of SrLa1.96Er0.04Al2O7 nanophosphor.

Table 4. Various types of transitions observed in the spectrum of SrLa21-xErxAl2O7 (x = 1.0–5.0 mol%) nanophosphors.

where D denoted the average crystallite size, θ was angle of diffraction, λ was the x-ray wavelength (0.1540562 nm) whereas β symbolized the full width of the most intense peak at its half maximum i.e., FWHM in radians. On observing the XRD data, we got the output in the form of crystallite size i.e., D (2θ = 30.238°) as 42.2 nm. Crystallite size of the different amounts of nanophosphors found to increase as depicted in figure 4, which might be due to the coalescence of the crystallites [25].

3.2. Morphological investigations
The surface morphology and size of the synthesized nanoparticles were investigated using SEM and TEM as represented in figures 5(a) and (b) respectively which highlighted the spherical shape of the nanosamples with their average size in the range of 40 to 50 nm which was found to be in good agreement with the size calculated from XRD data. The EDAX spectra of perovskite nanophosphors (figure 5(c)) detected the peaks corresponding
to Sr, La, Al, Er and O elements present in the optimized nanophosphor. EDAX mapping was reported in figure 5(d) which sharply pointed out the efficient doping of the Er$^{3+}$ ions into the nanosamples without any impurity and also did not provide any significant evidence for inhomogeneity in the prepared nanophosphors thus, demonstrating their better luminescence efficiency [26, 27].

3.3. FT-IR study
Fourier transform infra-red (FT-IR) spectrum of SrLa$_{1.96}$Er$_{0.04}$Al$_2$O$_7$ nanophosphor calcined at 1350 °C temperature is provided in figure 6. In the spectrum, a broad intense band with its maxima at 1103 cm$^{-1}$ was observed due to the stretching vibrations of the various Al–O bonds in the AlO$_6$ octahedra units. Moreover, bending vibrations of M–O bonds gave two short peaks of medium intensity at 625 and 395 cm$^{-1}$ [28]. It was observed that there was no peak present at 1384 cm$^{-1}$ due to the residual nitrates present in the sample. The fundamental peaks of water molecules due to O–H stretching vibration and H–O–H bending vibration at 3400 and 1600 cm$^{-1}$ respectively were completely absent which might be due to the proper calcination of the prepared samples.

3.4. Analysis of energy band-gap
To analyse the energy band-gap of the optimized sample i.e., SrLa$_{1.96}$Er$_{0.04}$Al$_2$O$_7$, DR spectra was recorded in the range from 200–500 nm wavelength on SHIMADZU 3600 UV–vis spectrophotometer as reported in the inset of figure 7 which showed the strong absorption in the region of low wavelength (upto 300 nm) while weak absorptions in the region from 300 to 500 nm due to transitions in the f subshell of Er$^{3+}$ ion. In the DR spectra, most strongly absorbed radiation was noticed at 378 nm due to $^4$I$_{15/2}$ $\rightarrow$ $^4$G$_{11/2}$ transition among Er$^{3+}$ ions (resembled well with the photoluminescence (PL) excitation spectrum as shown in figure 8(a)) which indicated the higher ability and efficiency of Er$^{3+}$ doped SrLa$_2$Al$_2$O$_7$ samples [29]. So, utilizing Kubelka-Munk (K.M.) function, value of energy band-gap was calculated in the following manner [30]:

$$ F(R_\infty) = \frac{(1 - R_\infty)2}{2 R_\infty} = \frac{K}{S} \quad (3) $$

$$ h\nu = \frac{1240}{\lambda} \quad (4) $$

where K and S were the absorption and scattering coefficients respectively, $R_\infty$ referred the reflection coefficient and $\lambda$ was wavelength taken from 200–800 nm. Thus, Kubelka-Munk function was related to photon energy by implying the following equation as [31]:

![Figure 4. Crystallite size of all the prepared Er$^{3+}$ doped nanophosphors sintered at 1350 °C.](image-url)
$[F(R_{\infty})h\nu]^n = C(h\nu - E_F)$

where $C$ represented the proportionality constant and value of $n$ (exponent) was based upon nature of electronic transitions initiated by photon absorption and equals to 0.5, 1.5, 2 and 3 owing to the indirect allowed, direct forbidden, direct allowed and indirect forbidden transition respectively. The typical graphical plot of K.M.
function of the optimized sample i.e., SrLa$_{1.96}$Er$_{0.04}$Al$_2$O$_7$ was represented in figure 7. The linear segment of the curve of $(\alpha h\nu)^2$ versus $(h\nu)$ when extrapolated to zero accorded the value of band-gap ($E_g$) energy as 5.03 eV for SrLa$_2$Al$_2$O$_7$ host matrix [15] and 5.01 eV for SrLa$_{1.96}$Er$_{0.04}$Al$_2$O$_7$ sample. Hence, doping of Er$^{3+}$ ions slightly decreased the $E_g$ value of doped sample which might be due to the formation of additional localized electronic states by Er$^{3+}$ ions within the energy band gap of the host lattice SrLa$_2$Al$_2$O$_7$ [32] which resulted into their better luminescent characteristics.

3.5. Luminescent properties
Figures 8(a) and (b) represented the excitation spectrum of SrLa$_{2(1-x)}$Er$_{2x}$Al$_2$O$_7$ ($x$ = 1.0–5.0 mol%) nanocrystals and the optimized sample, monitored at 548 nm, in the range from 200–500 nm due to $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition respectively [33]. This spectrum was comprised of various sharp peaks beyond 351 nm due to f–f transitions within Er$^{3+}$ ions and were observed at 357 nm, 365 nm, 378 nm, 405 nm, 444 nm, 450 nm and 489 nm due to the $^4I_{15/2} \rightarrow ^4G_{7/2}, ^4I_{15/2} \rightarrow ^4G_{9/2}, ^4I_{15/2} \rightarrow ^4G_{11/2}, ^4I_{15/2} \rightarrow ^4G_{9/2}, ^4I_{15/2} \rightarrow ^4F_{3/2}, ^4I_{15/2} \rightarrow ^4F_{5/2}$ and $^4I_{15/2} \rightarrow ^4F_{7/2}$ transitions respectively [34]. Out of these, the most intense

![Image](https://via.placeholder.com/150)
peak was situated at 378 nm due to $^4I_{15/2} \rightarrow ^4G_{11/2}$ transition. The photoluminescence emission spectra of all the prepared nanophosphors, noted in the range of 400–700 nm upon excitation at 378 nm is presented in figure 8(c) which exposed the 3 main emission peaks (cleaving into few shoulder peaks) at 411 nm, 527 nm and 548 nm subjected to $^5H_{9/2} \rightarrow ^4I_{15/2}$, $^3H_{11/2} \rightarrow ^4I_{15/2}$ and $^5S_{3/2} \rightarrow ^4I_{15/2}$ transition respectively [35, 36]. Among these, the dominant peak was observed at 548 nm because of $^5S_{3/2} \rightarrow ^4I_{15/2}$, which was electric dipole transition having value of $\Delta J = 6$ [37]. Figure 8(d) revealed the various kinds of excitation and emission transitions (provided in table 4 also) in the detailed energy level diagram for SrLa$_2$Al$_2$O$_7$:Er$^{3+}$ nanophosphors. Effect of the variation in the concentration of Er$^{3+}$ on the intensities of emission at 548 nm wavelength was studied in detail (figure 8(e)) and noted an enhancement in the intensity upto 2.0 mol% which later on started to fall off due to the phenomenon of quenching of concentration which might occur due to non-radiative migration of energy.
It was found that the non-radiative energy migration was possible due to the phenomena of exchange interaction, radiation reabsorption and multipolar interactions process. Since there was no overlapping type of PL spectrum observed so the chances of route of radiative reabsorption were obviated. While exchange interaction mechanism was applicable only if value of $R_c$ (critical distance) was less than 4 Å. So, the possible path which caused the quenching process was followed by using the Blasse’s relation which derived the value of $R_c$ as:

$$R_c = \left( \frac{3V}{4\pi XN} \right)^{1/3}$$

where $X$ signified the optimal concentration of dopant ions, $V$ denoted the volume of unit cell and $N$ was the no. of the cations existing in the host unit cell [41]. Utilizing the crystallographic data, we assessed $V = 287.78$ Å³, $N = 4$, $X = 0.02$ and the $R_c$ value was obtained as 18.590 Å. Since, the calculated $R_c$ value was much greater than 4 Å so the quenching mechanism of exchange interactions was also ruled out. Thus, the outputs decided the electric multipolar interactions as the actual route of quenching phenomenon. Although this concluded route was further divided into three types; d-d (dipole-dipole), d-q (dipole-quadrupole) and q-q (quadrupole-quadrupole) transitions. Accordingly, the actual possible mechanism for quenching behaviour was electric multi-polar interactions that could be determined by Dexter’s formula:

$$\log \frac{I}{x} = -\frac{s}{d} \log(x) + \log(f)$$

where $I/x$ implied the ratio of emission intensity to concentration of dopant ions, $x$ defined as the concentration of dopant ions higher than optimal one, $d$ was the sample dimension and $s$ was the constant having value of 6, 8 and 10 for d-d (dipole-dipole), d-q (dipole-quadrupole) and q-q (quadrupole-quadrupole) interactions respectively. The plot of $\log(I/x)$ versus $\log(x)$ yielded the slope value as $-2.157$ with the help of which value of $s$.

Figure 8. (a) Schematic 3-dimensional PL excitation spectra of SrLa$_{2-x}$Er$_{x}$Al$_2$O$_7$ $(x = 0.01–0.05)$ nanophosphors observed by recording green emission at 548 nm. (b) Excitation spectrum of the optimized sample depicting the various energy transitions. (c) A 3D representation of PL emission spectrum of the SrLa$_{2-x}$Er$_{x}$Al$_2$O$_7$ $(x = 0.01–0.05$) nanophosphors recorded at 378 nm excitation wavelength. (d) A detailed energy level diagram which comprises the different emission and excitation transitions for Er$^{3+}$ doped SrLa$_2$Al$_2$O$_7$ host matrix. (e) Variation in the intensity of PL emission wavelength with different composition of dopant ions. (f) Linear fitting graph of $\log(I/x(\text{Er}^{3+}))$ versus $\log(x(\text{Er}^{3+}))$. (g) Luminescence decay curves of SrLa$_{2-x}$Er$_{x}$Al$_2$O$_7$ $(x = 0.01–0.05)$ nanophosphors while the inset shows the decay curve of optimized sample, subjected to emission at 548 nm ($^4I_{15/2} \rightarrow ^2G_{11/2}$) and excitation wavelength at 378 nm ($^4I_{15/2} \rightarrow ^2I_{13/2}$). (h) Auzel fit curve of the Auzel’s model showing dependence of decay life time on concentration of Er$^{3+}$ ions.
came out to be 6.471 (shown in figure 8) which clearly pointed out the dipole-dipole interactions as the most probable mechanism for the concentration quenching process.

Figure 8 demonstrated phosphorescence decay curves recorded at 378 nm excitation wavelength and 548 nm emission wavelength of the prepared samples i.e., SrLa$_{2(1-x)}$Er$_{2x}$Al$_2$O$_7$ ($x = 1.0$–$5.0$ mol\% which were calcined at 1350 °C. The obtained curves had mono-exponential character which was depicted by given formula [43]:

$$I = I_0 \exp (-t/\tau)$$

(8)

where $\tau$ manifested radiative-decay time, $I$ and $I_0$ symbolised the glow powers at time t and 0 respectively. Following this equation, radiative life-time ($\tau$) values for prepared nanocrystals i.e., SrLa$_{2(1-x)}$Er$_{2x}$Al$_2$O$_7$ ($x = 1.0$–$5.0$ mol\%) were calculated (reported in table 5) and showed a decline in their values i.e., from 0.657 ms to 0.394 ms with the intensification of Er$^{3+}$ concentration. Moreover, the normalized PL intensities of

| SrLa$_{2(1-x)}$Er$_{2x}$Al$_2$O$_7$ (mol\%) | Lifetime (ms) | Quantum efficiency (%) | CIE coordinates (x,y) |
|------------------------------------------|---------------|------------------------|-----------------------|
| 1.0                                      | 0.657         | 82.22                  | 0.2671, 0.5150        |
| 2.0                                      | 0.546         | 68.33                  | 0.2637, 0.6031        |
| 3.0                                      | 0.447         | 55.94                  | 0.2504, 0.5904        |
| 4.0                                      | 0.413         | 51.68                  | 0.2458, 0.5739        |
| 5.0                                      | 0.394         | 49.31                  | 0.2512, 0.5249        |
SrLa$_{1.96}$Er$_{0.04}$Al$_2$O$_7$ versus time were plotted on a logarithmic scale (recorded in the inset of figure 8). Thus, phosphorescence life-time value ($\tau$) for the optimized nanophosphor i.e., SrLa$_{1.96}$Er$_{0.04}$Al$_2$O$_7$ was calculated as 0.546 ms which documented the presence of migration of energy in a non-radiative manner.

Thus, the non-radiative energy deportation had been estimated via Auzel’s expression given below [15, 16]:

$$\tau(c) = \frac{\tau_R}{1 + \frac{c}{c_0} e^{-N/\delta}}$$

(9)

where decay lifetime at 'c' concentration was denoted by $\tau(c)$, $N$ was phonon number while $c_0$ symbolised concentration constant. Fitted curve of decay lifetimes of the fabricated phosphors was displayed in figure 8(h). For $^4S_{3/2}$ state of Er$^{3+}$ ions, $\tau_R$ (intrinsic radiative life time) was reckoned as 0.799 ms. Following this value, the quantum (photoluminescence) efficiencies (\(\phi\)) of the as-developed nanosamples were simply derived as:

$$\phi = \frac{\tau_0}{\tau_R}$$

(10)

where $\tau_0$ referred the observed life time of $^4S_{3/2}$ (excited state) of Er$^{3+}$ ions. Consequently, the absolutely high values of quantum efficiency of the fabricated nanomaterials were achieved (tabularized in table 5) which ensured their successful implementation in the white light emitting diodes for illumination.

Figure 9. (a) and (b) shows the photograph of the optimized nanophosphor in the shorter and longer wavelength under UV lamp respectively while (c) depicts CIE chromaticity diagram of the synthesized nanophosphors i.e., SrLa$_{2-x}$Er$_x$Al$_2$O$_7$ ($x = 0.01−0.05$).
3.6. CIE 1931 studies

CIE 1931 studies basically, revealed the chromatic performance of the prepared SrLa$_{2+x-0.6}$Er$_{0.6}$Al$_2$O$_7$ (x = 1.0–5.0 mol%) nanophosphors by examining their chromaticity coordinates via MATLAB software which were obtained as (0.2671, 0.5150), (0.2657, 0.6031), (0.2504, 0.5904), (0.2458, 0.5739) and (0.2512, 0.5249) by utilizing their emission spectra and listed in table 5. Figures 9(a) and (b) shows the photograph of the optimized nanophosphor in the shorter and longer wavelength under UV lamp respectively and the color coordinates of all the synthesized nanosamples were plotted on the chromaticity diagram (portrayed in figure 9(c)) and thus, the color coordinates of the optimized sample (SrLa$_{1.96}$Er$_{0.04}$Al$_2$O$_7$) i.e., (0.2657, 0.6031) were found to be identical with the European Broadcasting Unit (EBU: green illuminant = 0.29, 0.60) and other green nanophosphors reported earlier i.e., ZnS:Cu, Al [44] and Zn$_2$SiO$_4$:Tb [45] which possessed the values of color coordinates as (0.284, 0.605) and (0.287, 0.554) respectively. In this way, the obtained color coordinates disclosed the greenish emission of synthesized nanophosphors in a well efficient manner.

4. Conclusions

In summary, novel nanocrystalline Er$^{3+}$ doped perovskite type SrLa$_2$Al$_2$O$_7$ nanophosphors with greenish emission were synthesized via facile, economical and efficient SCS technique. Crystallographic studies were carried out in detail which confirmed the tetragonal phase of the prepared nanophosphors. Morphological analysis disclosed the spherical morphology of the nanoparticles with the average size in the range of 40–50 nm. FT-IR data showed the peaks corresponding to the stretching and bending vibrations of the M–O bonds present in the structure of nanosamples. Band-gap value for the optimized sample i.e., SrLa$_{1.96}$Er$_{0.04}$Al$_2$O$_7$ was calculated as 5.01 eV by recording the DR spectra. Greenish emission was observed in the PL spectra of the nanophosphors which were recorded upon near UV excitation of 378 nm. In the emission spectrum, most prominent peak showing green emission was situated at 548 nm due to $^5$S$_{3/2}$ $\rightarrow$ $^4$I$_{15/2}$ which was electric dipole transition having value of $\Delta J = 6$. The optimum amount of the dopant ions was found to be 2.0 mol% above which concentration quenching took place via dipole-dipole interactions. Further, intrinsic life time and quantum efficiency of optimized sample was found to be 0.546 ms and 68.33%, respectively. CIE coordinates of the SrLa$_{1.96}$Er$_{0.04}$Al$_2$O$_7$ sample were computed as (0.2657, 0.6031) which justified the emission in the green region graphically, thus proved the prepared nanophosphors as the promising candidate in the phosphorescent sensors and RGB based WLEDs [46–51].

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Conflicts of interest

The author has no conflict of interest to declare regarding this research work.

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