Synthesis and Characterization of Color Tunable Europium(III) and Terbium(III) Co-Doped LaSrAl$_3$O$_7$ Nanocrystalline Phosphors: A Photoluminescent Synergy

Deepika Dhaterwal*, Mahesh Matoria, Annu Dalal, Surender Kumar and Sonika Singh*.

Department of Chemistry, Chaudhary Bansi Lal University, Bhiwani-127031, India

*Corresponding author: E-mail: sonikasinghdhanger@cblu.ac.in

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Color tunable La$_{0.99-x}$Eu$_{0.04}$Tb$_{0.01}$SrAl$_3$O$_7$ (x = 0.01-0.07 mol) luminous nanocrystalline materials were synthesized using an affordable, simple, streamlined and self-propagating, urea-assisted solution combustion synthesis route. The X-ray powder diffraction pattern of optimized La$_{0.99-x}$Eu$_{0.04}$Tb$_{0.01}$SrAl$_3$O$_7$ co-doped phosphor sintered at 900 ºC revealed the formation of single phased phosphor having tetragonal crystalline structure with P42/m (113) space group. The field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) micrographs revealed agglomerates featuring spherical-shaped porous nanoparticles with interconnect boundaries and smooth surface. The basic composition was determined via scrutiny of energy dispersive X-ray (EDAX) spectrum. Observations of diffuse reflectance spectroscopy were analyzed to determine the optical band gap values of synthesized Eu$^{3+}$/Tb$^{3+}$ co-doped LaSrAl$_3$O$_7$ nanocrystalline luminescent materials. To explore how dopant concentration affected the luminous intensity of phosphors, a thorough examination of the photoluminescence excitation and emission spectra of La$_{0.99-x}$Eu$_{0.04}$Tb$_{0.01}$SrAl$_3$O$_7$ (x = 0.01-0.07 mol) was executed. The analysis of luminescence spectra demonstrated that Tb$^{3+}$ efficiently sensitized the Eu$^{3+}$ ion. The critical distance (Rc) was calculated to be 5.576 Å and it emerged that non-radiant energy loss occurrence i.e. concentration quenching observed after x = 0.04 mol (Eu$^{3+}$) doping in La$_{0.99-x}$Eu$_{0.04}$Tb$_{0.01}$SrAl$_3$O$_7$ (x = 0.01-0.07 mol) co-doped phosphors was induced by the dipole-quadrupole (d-q) interactions. Moreover, colorimetric attributes including Commission International de l’Eclairage 1931 color coordinates (x, y), color purity and correlated color temperature were obtained by utilization their emission data. The derived nanophosphor materials photometric traits enable new design opportunities for upgraded luminous materials that can be utilized in field emission displays, diverse luminous sources, photonic appliances, phosphor converted light emitting diodes, full-color displays and numerous lighting devices.

Keywords: Solution combustion, Nanophosphors, Photoluminescence, Color coordinates, Tunable.

INTRODUCTION

In recent era, phosphor converted light emitting diodes (pc-LEDs), which have remarkable luminescence efficiency and an assortment of emission shades, have garnered significant attention as an accessible and environmentally sustainable source of illumination [1,2]. Multicolor emissions through a single host matrix phosphor and chip combo seem more feasible and can address the reabsorption issue as compared to ultraviolet light emitting diodes (UV-LED’s) that use diverse essential phosphor mixes [3-5]. Consequently, the need is imperative to produce the color-tunable luminescent material with single host lattice. The key benefit of single-phase color tunable emitting phosphors over multicomponent emitting devices is their ability to simultaneously improve the rendering index of illumination and produce multicolor emission at low color temperatures [6]. Owing to their superior chemical stability, prolonged emission life span, acute bandwidth, tunable illumination hue and significant luminescence efficacy, rare-earth ions doped nanophosphor materials have achieved extensive use in various areas in the recent few years, including illumination, displays, luminescence materials for biological applications, white light emitting diodes (WLEDs) as well as various kinds of sensors for analysis [7-10]. The photoluminescent materials exhibiting the required vibrant color impact could potentially be produced by changing the dopant, content of dopant and utilising rare-earth ions combos in tandem with an appropriate host [11,12]. It has been suggested that unique luminous patterns could potentially be achieved by incorporating co-dopants in single hosts as multiple energy transfer (ET) exhibits fascinating multicolor emission.
As luminosity could potentially be regulated through the energy conveyed by doped/co-doped lanthanides e.g. terbium (III) and europium(III) ions draw significant emphasis because of their extended luminescence endurance and confined emission lines inside the visible realm. The activator, Eu³⁺ is known for its red color emission correspond to the transitions ⁵Dₓ → ⁷F₂ whereas the ions Tb³⁺ exhibit green emission lines that correspond to the transitions ⁵Dₓ → ⁷F₂ [13]. The practical application of luminescent materials that contain Eu³⁺ is, however, limited by the fact that their absorption peak percentage relatively modest and slightly limited in the ultraviolet (UV) range. In phosphors, the transfer of energy is a fundamental phenomenon that could take place among doped ion pairs (sensitizer/activator) as well as from the host system to the doped ions [14]. The co-doping approach, which involves the simultaneous incorporation of various lumino-scent ions into the host lattice, has garnered significant attention in recent years. This strategy has the potential to improve the material’s luminescence properties in a synergistic manner, leading to increased color purity, increased emission intensity, and an extended wavelength range. Exploring the consequences of sensitization and the co-doping energy transfer mechanism may assist to address this issue in the future. The energy transferred from Tb³⁺ → Eu³⁺ is beneficial since Eu³⁺ absorption wavelength and Tb³⁺ emission wavelength are quite in proximity to one another.

Substantial study has been put towards investigating the energy transfer process, luminescent properties and tailored full-color illuminating luminous materials co-doped with Tb³⁺ and Eu³⁺, i.e. SrLaGaO₃ [14], ZnLaBO₃ [15], Li₃La₂Te₂O₇ [16], Ca₃La₃(SiO₄)₃(PO₄)₂O₇ [17], Na₉Ca₅Si₉O₂₃ [18], Zn₉GeO₂ [19], Gd₃ZrO₄ [13], Sr₃YNb₃O₁₄F [20], LaVO₃ [21], etc. Within the field of luminous materials, research and technological advancement have been driven by search for new luminescent compounds exhibiting improved optical characteristics. So selecting an adequate host material is extremely essential for the phosphors featuring the spectacular illuminating character traits. In juxtaposed with silicates, fluorides, oxides, nitride, vanadates, oxynitride, sulfides, etc. aluminates have been revealed to be a more favourable host choice.

Rare earth elements have been incorporated into aluminates matrices to significantly alter the characteristics enabling an array of advanced applications. Due to their exceptional stability, elevated brightness, enduring after-glow, superior efficiency, and appropriate emission color, rare earth-doped aluminates have been the subject of intense research in recent years as ideal luminescent materials used in lighting and display technologies, as well as for usage in lasers, LEDs, and other photonic devices. The synthesis and structural composition of rare-earth enriched melilite families have been the subject of numerous investigation. In present investigation, La₅Sr₃Al₃O₁₀, a type of aluminates was chosen as the substrate matrix. This is one of the convoluted oxides in the huge group of rare-earth strontium aluminate with melilite structure. In literature, photoluminescence studies of La₅Sr₃Al₃O₁₀: Eu³⁺, La₅Sr₃Al₃O₁₀: Tb³⁺ doped phosphors synthesised via solution combustion method [22], La₅Sr₃Al₃O₁₀: RE³⁺ (RE = Eu, Tb) phosphors prepared using sol gel method [23] and La₅Sr₃Al₃O₁₀: 0.01Eu³⁺, xM⁺ (M = K, Na, Li) [24] phosphors obtained by solution combustion method and La₅Sr₃Al₃O₁₀: Eu³⁺ synthesized via solid-state reaction method [25] have been reported. However, the possible energy transfer process and influences of Eu³⁺/ Tb³⁺ co-doping in La₅Sr₃Al₃O₁₀ photoluminescence properties have not been reported in the literature till date.

In this work, La₀.₉₉Eu₀.₀₁Sr₃Al₃O₁₀, La₀.₉₉Tb₀.₀₁Sr₃Al₃O₁₀ and a series of La₀.₉₉₋ₓEuₓTb₀.₀₁Sr₃Al₃O₁₀ (x = 0.01-0.07 mol) co-doped nanocrystalline phosphor were prepared via simple, single step, self-propagating solution combustion method. The structural, morphological, band gap, luminescence and color-tunable characteristics were studied. Energy transfer from Tb³⁺ to Eu³⁺ ions in the host matrix was found to be effective simply adjusting the ratio of Eu³⁺/Tb³⁺ ions. Pursuant to the outcomes, the synthesized La₀.₉₉₋ₓEuₓTb₀.₀₁Sr₃Al₃O₁₀ (x = 0.01-0.07 mol) nanocrystalline luminescent materials showed emissions that could be adjusted from greenish to orange-red to a deep red. Consequently, it becomes realistic that Eu³⁺/Tb³⁺ co-doped La₅Sr₃Al₃O₁₀ can potentially be utilized as an effective illumination material in field emission displays, various light sources, photonic devices, pc-LEDs, full-color displays and other lighting fixtures.

**EXPERIMENTAL**

**Synthesis of Eu³⁺/Tb³⁺ co-doped La₅Sr₃Al₃O₁₀ crystalline nanophosphors:** An affordable, simple and self-propagating, urea-assisted solution combustion synthesis method was adopted in order to synthesize La₀.₉₉₋ₓEuₓTb₀.₀₁Sr₃Al₃O₁₀, La₀.₉₉Tb₀.₀₁Sr₃Al₃O₁₀ and a series of La₀.₉₉₋ₓEuₓTb₀.₀₁Sr₃Al₃O₁₀, co-doped phosphors where x = 0.01-0.07 mol. For combustion, the raw ingredients (metal nitrates) of high-purity i.e. La(NO₃)₃, 6H₂O, Eu(NO₃)₃, 6H₂O, Sr(NO₃)₂, Al(NO₃)₃, 9H₂O, Tb(NO₃)₃, 5H₂O as oxidants and urea (NH₂CONH₂) as fuel were used. Despite the aid of another heating origin, the process could be rapidly accelerated to extremely elevated temperatures via the energy produced by the exothermic process that occurs amid the metal nitrates and urea (fuel). Indeed, the combustion process facilitates the quick fabrication of plenty of inorganic materials sans the need for the lengthy, high-temperature sintering step [11, 26-28]. In a stoichiometric ratio, the starting ingredients (metal nitrates + fuel) were dissolved with minimum quantity of deionized water in a beaker. The resulting solution was subsequently heated on a hot plate with dynamic stirring for a maximum of two to three min to achieve a homogeneous mixture. The homogeneous solution was then inserted in a muffle furnace maintained at 500 ºC for heating for 4-6 min. A robust exothermic process results in the emergence of combustible gasses and that yields a fluffy voluminous solid material [22, 24, 26, 29].

The basic chemical route which prompted doped/co-doped La₅₋ₓEuₓTbₓSr₃Al₃O₁₀ crystalline phosphor was delineated as follows:

\[
(1-x-y)\text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} + \text{Sr(NO}_3\text{)}_2 + x\text{Eu(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} + y\text{Tb(NO}_3\text{)}_3 \cdot 5\text{H}_2\text{O} + \text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} + \text{NH}_2\text{CONH}_2 \rightarrow \text{La}_{1-x-y}\text{Eu}_x\text{Tb}_y\text{Sr}_3\text{Al}_3\text{O}_{10} + \text{CO}_2, \text{N}_2 \text{ and H}_2\text{O} \quad \text{(mixture of gaseous products)}
\]

Here (x = 0, y = 0.01 mol), (x = 0.01 mol, y = 0) and (x = 0.01-0.07 mol, y = 0.01 mol). After cooling the obtained volum-
inuous substances to room temperature, an agate mortar was used for grinding them into powder. Following that, the uniform powders were placed in a crucible and annealed at 900 °C for 3 h, yielding the required crystalline material and preserved in a desiccator for further analysis [30].

**Characterization of La$_{1-x}$Eu$_x$Tb$_{0.x}$SrAl$_3$O$_7$ co-doped nanocrystalline phosphors:** The crystallographic phase analysis of the synthesized Eu$^{3+}$/Tb$^{3+}$ co-doped LaSrAl$_3$O$_7$ nanomaterials were evaluated by engaging Rigaku Ultima IV X-ray powder diffractometer with Ni-filtered CuK$_\alpha$ radiations with $\lambda = 0.154056$ nm. The field emission scanning electron microscopy (FE-SEM) imaging as well as transmission electron microscopy (TEM) was employed for assessing the surface appearance and particle size of the produced co-doped phosphors. The precise elemental composition of the synthesized phosphors was determined with energy dispersive X-ray analysis (EDAX). Using BaSO$_4$ as a reference compound, Shimadzu UV-3600 plus UV-Vis-NIR spectrophotometer was used to analyze the energy band gap of the synthesized co-doped nanoparticle. A HORIBA fluorescence spectrophotometer with a xenon lamp was used to perform the photoluminescence analysis. Commission International de l’Eclairage 1931 (CIE) color coordinates $(x, y)$ and other important photometric properties of the produced La$_{1-x}$Eu$_x$Tb$_{0.x}$SrAl$_3$O$_7$ nanocrystalline luminescent samples were also determined from the exploration of their photoluminescent data. All the above mentioned characterizations were carried out at room temperature.

**RESULTS AND DISCUSSION**

**XRD studies:** The phase consistency and structural features of co-doped crystalline La$_{0.95}$Eu$_{0.04}$Tb$_{0.01}$SrAl$_3$O$_7$ nanophosphor was studied by analyzing its diffraction pattern as shown in Fig. 1. The frameworks of LaSrAl$_3$O$_7$ compounds were composed of 5-membered rings constructed with AlO$_4$ tetrahedral, Sr$^{2+}$ and La$^{3+}$ ions appear sporadically dispersed in eight coordinating positions with Cs symmetry between the layers [22]. Precise peaks in the XRD image (Fig. 1) effectively harmonized with the standard JCPDS card no. 50-1815, which revealed the formation of crystalline and pure single phase La$_{1-x}$Eu$_x$Tb$_{0.x}$SrAl$_3$O$_7$ co-doped phosphor at 900 °C. In contrast to the solid-state reaction synthesis approach, the sintering temperature has been dropped to approximately 500 °C [25,29].

The diffraction peaks of Eu$^{3+}$/Tb$^{3+}$ co-doped LaSrAl$_3$O$_7$ sintered at 900 °C (3 h) primarily belong to tetragonal crystalline structure with space group of $P4_2/m$ (113). It was evident that the nanophosphor had been successfully produced in a single phase at this temperature as no spike patterns attributable to additional phases could be spotted [23,24]. Furthermore, the lack of extra peaks in the diffraction pattern within the 10-80° scanning range demonstrated that the co-doping of Eu$^{3+}$/Tb$^{3+}$ ions within the lattice matrix did not influence LaSrAl$_3$O$_7$ basic framework [12,31].

The dopant ions (Eu$^{3+}$ and Tb$^{3+}$) assumed to have substituted lanthanum (La$^{3+}$) ions in the LaSrAl$_3$O$_7$ host lattice in lieu of other (aluminum and strontium) ions because of their nearly comparable sizes and charges. The difference in percentage (%) radius (Dr) was derived in order to gain a better understanding of the substitution phenomenon in LaSrAl$_3$O$_7$ matrix by dopant ions (Eu$^{3+}$ and Tb$^{3+}$). For the formation of an adequate crystal lattice, Dr should have a value of less than 30% [32,33]. The equation used in this instance was as follows:

$$D_r(\%) = \frac{R_s(CN) - R_d(CN)}{R_d(CN)} \times 100$$  \hspace{1cm} (1)

The respective ionic radii of the host and doping ions, designated by the initials $R_s$ and $R_d$ as well as the coordination number, represented by CN in eqn 1. Considering all of the values, $D_r(\%)$ for the combos of La$^{3+}$/Tb$^{3+}$ and La$^{3+}$/Eu$^{3+}$ was determined to be 9.53% and 16%, respectively [34,35]. Privileged substitution seems generally supported to require a radius variation of less than 30% among the infused ions and host ions. It culminates in the preferential substitution of Eu$^{3+}$/Tb$^{3+}$ ions for lanthanum ions in LaSrAl$_3$O$_7$ host lattice as obtained through utilizing eqn 1.

The nanocrystalline nature of La$_{0.95}$Eu$_{0.04}$Tb$_{0.01}$SrAl$_3$O$_7$ co-doped powder sintered at 900 °C for 3 h was assessed from the average size of crystallite (D), which was obtained using Scherrer’s formula (eqn. 2) [4,13,36].

$$D = \frac{0.944\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2)
where $D$ = average grain size; $\lambda$ = X-rays wavelength of CuKα radiation (0.154056 nm); $\theta$ = Bragg’s angle of an observed X-ray diffraction peak; $\beta$ = Full width at half-maxima in radians (FWHM).

From Scherrer’s formula, the average grain size was found to be 37.55 nm. The Williamson-Hall (W-H) relation, which validates Scherrer’s approach, was also used to determine the average crystallite size of La$_{0.95}$Eu$_{0.04}$Tb$_{0.01}$SrAl$_3$O$_7$ co-doped nanocrystalline phosphor sintered at 900 °C, along with other crystallographic data including microstrain ($\varepsilon$) and dislocation density ($\delta$) [37-40] as follows:

$$\beta \cos \theta = \varepsilon (4 \sin \theta) + \frac{0.89 \lambda}{D}$$

$$\text{Dislocation density } (\delta) = \frac{1}{D^2}$$

The correlation inferred by eqn. 3 between $\beta \cos \theta$ and $4 \sin \theta$ has culminated in a straight line graph. The value of the straight-line intercept corresponds to the average crystallite size ($D$). The microstrain value was subsequently derived from the slope of the line. The strain value of 0.00208 and the crystalline size value of 63.60 nm have been retrieved from the W-H plot (Fig. 2) using the slope and Y-intercept of fit, respectively. The grain size value derived by the W-H approach was found to be marginally larger than the value derived from Scherrer’s equation because strain considered in the W-H approach not in Scherrer’s approach [41,42]. Also, dislocation density ($\delta = 0.000247 \text{ nm}^{-2}$) has been determined using eqn. 4. A comprehensive investigation of both phase analysis and crystallographic aspects disclosed the formation of single phase Eu$^{3+}$/Tb$^{3+}$ co-doped LaSrAl$_3$O$_7$ crystalline nanophosphors.

**Morphological studies:** The tailored Eu$^{3+}$/Tb$^{3+}$ co-doped LaSrAl$_3$O$_7$ sample surface morphology, nanostructure and Eu$^{3+}$/Tb$^{3+}$ ions distributions were studied through FE-SEM, TEM and EDAX techniques. The optimized La$_{0.95}$Eu$_{0.04}$Tb$_{0.01}$SrAl$_3$O$_7$ phosphor sample sintered at 900 °C revealed agglomerates featuring spherical-shaped porous particles having discrete inter-

![Fig. 3. (a) FE-SEM image and (b) TEM image of La$_{0.95}$Eu$_{0.04}$Tb$_{0.01}$SrAl$_3$O$_7$ nanophosphor synthesized via solution combustion method](image)
constituent ingredients (Tb, Eu, La, Sr, Al and O). The atomic percentage and weight percentages compositions of each component were also included as an inset [25,48]. All investigations indicated that the resulting strontium aluminum lanthanum oxide samples doped efficiently with Eu³⁺ and Tb³⁺ ions.

**Optical band gap studies:** The optical properties of the La₀.⁹⁹Eu₀.⁰₁SrAl₃O₇, La₀.⁹⁹Tb₀.⁰₁SrAl₃O₇ and La₀.⁹₉₋ₓEuₓTb₀.⁰₁SrAl₃O₇, co-doped phosphors where (x = 0.₀₁-₀.₀₇ mol) were probed through diffuse reflectance (DR) spectroscopy. It serves as a forefront way of assessing the spectroscopic traits of solid materials, including powder or thin films. The diffuse reflectance patterns and calculated band gap values for synthesized co-doped luminescent materials are shown in Figs. 6 and 7, respectively. The La₀.⁹₉₋ₓEuₓTb₀.⁰₁SrAl₃O₇ (x = 0.₀₁-₀.₀₇ mol) luminescent materials demonstrated energy absorption in < 300 nm domain, which was analogous to photoluminescent excitation spectrum. In region ≤ 300 nm, La₀.⁹₉₋ₓEuₓTb₀.⁰₁SrAl₃O₇ (x = 0.₀₁-₀.₀₇ mol) luminescent nanomaterials showed energy absorption at 255 nm corresponding to charge transfer from O²⁻ to Eu³⁺. The minor absorption bands in > 300 nm region (Fig. 6) correlated with the 4f intra-configurational transitions of Eu³⁺ and Tb³⁺ ions [13,49,50]. The Kubelka-Munk function (eqn. 5) and Tauc’s relation (eqn. 6) were utilized to assess the probe concurrent to the DR spectra, i.e. the determination of optical band gap of La₀.⁹₉Eu₀.⁰₁SrAl₃O₇, La₀.⁹₉Eu₀.⁰₁Tb₀.⁰₁SrAl₃O₇ (x = 0.₀₁-₀.₀₇ mol) and La₀.⁹₉Tb₀.⁰₁SrAl₃O₇ nanocrystalline materials [51-56].
The optimal band gap ($E_g$) of all these phosphors were calculated [36, 57] and the values are tabulated in Table-1. With regard to Eu$^{3+}$ and Tb$^{3+}$ mono-doped LaSrAl$_3$O$_7$ phosphors, the

![Diagrams](image_url)

**Fig. 6.** Diffuse reflectance spectra of (a) La$_{0.99}$Eu$_{0.01}$SrAl$_3$O$_7$, (b-h) La$_{0.99-x}$Eu$_x$Tb$_{0.01}$SrAl$_3$O$_7$ ($x = 0.01-0.07$ mol) and (i) La$_{0.99}$Tb$_{0.01}$SrAl$_3$O$_7$ phosphors

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S}$$  \hspace{1cm} (5)

$$[F(R_\infty)h\nu]^n = C(h\nu - E_g)$$  \hspace{1cm} (6)

where $F(R_\infty) =$ Kubelka-Munk function; $h\nu = 1240/\lambda$, $R =$ sample reflection coefficient; $C =$ proportionality constant; $K =$ absorption coefficient; $S =$ scattering coefficient; and $n =$ electronic transition nature ($n = 1/2$, direct allowed transitions, $n = 2$, indirect allowed transitions, $n = 3$, indirect forbidden transitions and $n = 3/2$, direct forbidden transitions, respectively).

<table>
<thead>
<tr>
<th>Symbolization</th>
<th>Phosphor sample</th>
<th>Energy band gap (eV)</th>
<th>Refractive index ($n$)</th>
<th>Metallization criterion (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>La$<em>{0.99}$Eu$</em>{0.01}$SrAl$_3$O$_7$</td>
<td>4.00</td>
<td>2.17</td>
<td>0.447</td>
</tr>
<tr>
<td>b</td>
<td>La$<em>{0.98}$Eu$</em>{0.01}$Tb$_{0.01}$SrAl$_3$O$_7$</td>
<td>4.23</td>
<td>2.12</td>
<td>0.459</td>
</tr>
<tr>
<td>c</td>
<td>La$<em>{0.97}$Eu$</em>{0.02}$Tb$_{0.01}$SrAl$_3$O$_7$</td>
<td>4.49</td>
<td>2.08</td>
<td>0.474</td>
</tr>
<tr>
<td>d</td>
<td>La$<em>{0.96}$Eu$</em>{0.03}$Tb$_{0.01}$SrAl$_3$O$_7$</td>
<td>4.65</td>
<td>2.05</td>
<td>0.482</td>
</tr>
<tr>
<td>e</td>
<td>La$<em>{0.95}$Eu$</em>{0.04}$Tb$_{0.01}$SrAl$_3$O$_7$</td>
<td>4.74</td>
<td>2.04</td>
<td>0.486</td>
</tr>
<tr>
<td>f</td>
<td>La$<em>{0.94}$Eu$</em>{0.05}$Tb$_{0.01}$SrAl$_3$O$_7$</td>
<td>4.78</td>
<td>2.03</td>
<td>0.488</td>
</tr>
<tr>
<td>g</td>
<td>La$<em>{0.93}$Eu$</em>{0.06}$Tb$_{0.01}$SrAl$_3$O$_7$</td>
<td>5.25</td>
<td>1.96</td>
<td>0.512</td>
</tr>
<tr>
<td>h</td>
<td>La$<em>{0.92}$Eu$</em>{0.07}$Tb$_{0.01}$SrAl$_3$O$_7$</td>
<td>4.89</td>
<td>2.01</td>
<td>0.494</td>
</tr>
<tr>
<td>i</td>
<td>La$<em>{0.99}$Tb$</em>{0.01}$SrAl$_3$O$_7$</td>
<td>3.92</td>
<td>2.19</td>
<td>0.443</td>
</tr>
</tbody>
</table>
fluctuation in the $E_g$ value of Eu$^{3+}$/Tb$^{3+}$ co-doped LaSrAl$_3$O$_7$ nanomaterial reveals the accumulation of a few additional levels of energy of doped ions. As the concentration of Eu$^{3+}$ ions increased, it was observed that the $E_g$ of La$_{0.99}$Eu$_{0.01}$Tb$_{0.01}$SrAl$_3$O$_7$ nanophosphors widens attributable to the Moss effect. However, if Eu$^{3+}$ ions concentration rises further, the energy band gap shrinks, this could be due to dopant ion sublevels emerging proximal to the conduction band [49,58-62]. Also, the energy band gap values of La$_{0.99}$Eu$_{0.01}$SrAl$_3$O$_7$, La$_{0.99}$Eu$_{0.01}$Tb$_{0.01}$SrAl$_3$O$_7$ ($x = 0.01$ - 0.07 mol) and La$_{0.99}$Tb$_{0.01}$SrAl$_3$O$_7$ phosphors materials were used in eqns. 7 and 8 to determine the refractive index (n) and metallization criterion (M) of these synthesized materials.

$$n^2 - 1 = n^2 + 2 \left(1 - \frac{E_g}{20}\right)$$  \hspace{1cm} (7)

$$M = 1 - \frac{n^2 - 1}{n^2 + 2} = \sqrt{\frac{E_g}{20}}$$  \hspace{1cm} (8)

The theoretically calculated metallization criterion ($M < 1$) by Dimitrov and Sakka’s expression (eqn. 8) validating the non-metallic character of co-doped La$_{0.99-x}$Eu$_x$Tb$_{0.01}$SrAl$_3$O$_7$ ($x = 0.01$-0.07 mol) nanosamples [58,63,64].

**Luminescence studies:** The photoluminescence excitation (PLE) and photoluminescence emission (PL) spectra of La$_{0.99}$Eu$_{0.01}$SrAl$_3$O$_7$ observed at 617 nm and 255 nm, respectively are shown in Fig. 8. The PLE spectrum of doped La$_{0.99}$Eu$_{0.01}$SrAl$_3$O$_7$ nanophosphor monitored at $\lambda_{em} = 617$ nm corresponding to the $^5D_{0} \rightarrow ^7F_{2}$ transition (Eu$^{3+}$) shown in Fig. 8(left) exhibited five excitations bands due to the charge transfer band (CTB) of O$^{2-}$-Eu$^{3+}$ bond (255 nm), $^7F_{0} \rightarrow ^5H_{5}$ (321 nm), $^7F_{0} \rightarrow ^5D_{4}$ (360 nm), $^7F_{0} \rightarrow ^5L_{6}$ (392 nm) and $^7F_{0} \rightarrow ^5D_{2}$ (464 nm) transitions [23,65,66]. The emission spectrum of La$_{0.99}$Eu$_{0.01}$SrAl$_3$O$_7$ phosphor monitoring at $\lambda_{ex} = 255$ nm exhibited emission bands corresponding to $^5D_{0} \rightarrow ^7F_{1}$ (589 nm), $^3D_{0} \rightarrow ^7F_{2}$ (612, 617 nm) and $^3D_{0} \rightarrow ^7F_{3}$ (655 nm) transitions (Table-2). The emission spectra revealed non-centrosymmetric arrangement of Eu$^{3+}$ ions in
LaSrAlO₇ host lattice as evident by much greater red-light emission intensity corresponding to the electric dipole transition (⁴D₀ → ⁷F₁) than the orange-red emission corresponding to the magnetic dipole transition (⁴D₀ → ⁷F₃) [22,67-69].

The PLE spectrum (Fig. 9) of La₀.99Tb₀.01SrAlO₇ phosphor nanosample monitored at λ_em = 544 nm, exhibited a prominent band 235 nm generated from spin-allowed 4f⁶ → 4f⁵5d¹ transition and some other bands at 318 (⁴F₀ → ⁴D₁), 339 (⁴F₀ → ⁴G₂), 366 (⁴F₀ → ⁴D₃), and 376 (⁴F₀ → ⁴L₉) nm that were attributed to 4f⁶-4f⁵ intraconfigurational transitions of Tb³⁺ ion in LaSrAlO₇ host matrix. The emission spectrum (Fig. 9, right) of La₀.99Tb₀.01SrAlO₇ nanophosphor monitored at λ_ex = 235 nm exhibited by the six emission bands in 400-650 nm region corresponding to ⁴D₁ → ⁷F₃ (415 nm), ⁴D₁ → ⁷F₁ (439 nm), ⁴D₁ → ⁷F₃ (485 nm), ⁴D₁ → ⁷F₁ (544 nm), ⁴D₁ → ⁷F₁ (593 nm) and ⁴D₁ → ⁷F₁ (622 nm) transitions of Tb³⁺ ions [15,22,70].

Additionally, there are numerous potentials of tunable light manifestations that may originate via the union of two or more trivalent lanthanides ions as dopants in a host system, comprising solid-state lighting, colored light emitting diodes, display devices etc. Emission lines typically distinctive features of specific rare earth ions. The mixing of different trivalent rare earth ions into the phosphors material will culminate in customizable luminous capabilities [54,71-73]. Pursuant to the Dexter theory, there needs to be a coincidence between the PL spectrum of Tb³⁺ ions and the PLE spectrum of Eu³⁺ ions for effective energy transfer. The preliminary desire for energy transfer has been fulfilled, as shown by Fig. 10, revealing that the PLE spectrum of Eu³⁺ ions and the PL spectrum of Tb³⁺ ions in LaSrAlO₇ matrix barely overlapped in 400-500 nm region [74,75]. The phonons spectrum could assist transfer of energy from Tb³⁺ → Eu³⁺, according to the literature evidence especially in scenarios if there is a slight spectral crossover. Thus, it could be concluded that energy transfer from Tb³⁺ → Eu³⁺ ions in selected lattice may occur in the context of co-doping of Tb³⁺ and Eu³⁺ ions [67,76,77].

For additional insight regarding the intriguing luminescence aspects of La₀.99₋ₓEuₓTb₀.01SrAlO₇ (x = 0.01-0.07 mol) nanocrystalline phosphor materials, the PLE and PL spectra of these co-doped nanophosphors were examined. The PLE and PL spectra of La₀.99₋ₓEuₓTb₀.01SrAlO₇ (x = 0.01-0.07 mol) phosphors, obtained at monitoring λ_em = 617 and λ_ex = 255 nm depicted in Figs. 11 and 12, respectively. The combined PLE spectra of La₀.99₋ₓEuₓTb₀.01SrAlO₇ (x = 0.01-0.07 mol) phosphors showed a striking resemblance to PLE spectrum of La₀.99Eu₀.01SrAlO₇ phosphor (Fig. 8). The excitation band attributed to Tb³⁺ ions appeared significantly overlaid by Eu³⁺ ions
excitation bands, presumably because the intensity associated with the Tb$^{3+}$ ions transitions was significantly lower than that of the Eu$^{3+}$ ions transitions [12,78,79].

Also, emission peak corresponding to Eu$^{3+}$ ions along with relatively low intensity Tb$^{3+}$ ions emission peak (at 544 nm) were clearly visible in the combined PL spectra (Fig. 12) of La$_{0.99-x}$Eu$_x$Tb$_{0.01}$SrAl$_3$O$_7$ ($x = 0.01-0.07$ mol) nanosamples [80]. It seems vital to investigate how concentration of Eu$^{3+}$ ions influences the co-doped phosphors emission intensity in order to ascertain the optimum Eu$^{3+}$ ion concentration as well as the energy transfer mechanism [81,82]. As the concentration of Eu$^{3+}$ ions ($x$) raised, lumen intensity of Tb$^{3+}$ ions peak ($^7$D$_4$ $\rightarrow$ $^7$F$_5$, 544 nm) gradually diminished while lumen intensity of Eu$^{3+}$ ions peak ($^5$D$_0$ $\rightarrow$ $^7$F$_2$, 617 nm) increased. The critical distance (Rc) value should be less than 5 Å, otherwise, the multipolar interactions were significant [15]. For the study of the non-radiative energy transfer mechanism i.e. concentration quenching, the critical distance ($R_c$) can be calculated using eqn. 9 as follows [86-88]:
The correlated graphical representation (Fig. 15) of \( I_0/I \) versus \( (C_{Eu^{3+}} + Tb^{3+})^{n/3} \) for Eu\(^{3+}/Tb^{3+}\) co-doped LaSrAl\(_3\)O\(_7\) phosphors was utilized to approximate the value of \( \eta_0/\eta \) ratio adopting Reisfeld’s approximation. Here, \( I \) and \( I_0 \) signify luminescence intensities corresponding to dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) interactions, respectively.

The ratio of photoluminescence intensity (\( I_0/I \)) can be utilized to approximate the value of \( \eta_0/\eta \) ratio adopting Reisfeld’s approximation. Here, \( I \) and \( I_0 \) signify luminescence intensities of sensitizer (Tb\(^{3+}\)) with and devoid of activator (Eu\(^{3+}\)), respectively. The correlated graphical representation (Fig. 15) of \( I_0/I \) versus \( C^{n/3} \) demonstrated an optimal linear tandem at \( n = 8 \), which are correlate to the dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) interactions between dopant ions in selected LaSrAl\(_3\)O\(_7\) matrix.

\[
R_c = 2\left(\frac{3V}{4\pi c N}\right)^{1/3}
\]  
(9)

where \( V = \) unit cell volume (325.48 Å\(^3\)); \( c = \) critical concentration of dopant Tb\(^{3+}\) and Eu\(^{3+}\) ions (0.05 mol); \( N = \) available locations for dopants in unit cell \( N = 2 \).

The energy transfer between the dopant ions should be regulated by the electric multipolar interaction in synthesized co-doped nanocrystalline phosphor as \( R_c \) was calculated to be 5.576 Å \([15,89]\). The Dexter energy transfer equation of multipolar interaction (eqn. 10) was applied to grasp the possible mechanism for multipolar interactions between dopant ions in a synthesized LaSrAl\(_3\)O\(_7\) matrix.

\[
\frac{\eta}{\eta_0} = \left(C^{n/3}\right)
\]  
(10)

where \( \eta_0 = \) sensitizor (Tb\(^{3+}\)) quantum efficiency in absence of activator; \( \eta = \) sensitizor (Tb\(^{3+}\)) quantum efficiency in presence of activator (Eu\(^{3+}\)); \( C = \) content quantity of sensitizor (Tb\(^{3+}\)) and activator (Eu\(^{3+}\)); \( n = 6, 8 \) and 10, which are correlate to the dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) interactions, respectively.

The CIE chromaticity coordinates (\( x, y \)) were calculated to be \((0.353, 0.554)\) and \((0.643, 0.357)\) which were lying in greenish and deep red zone, respectively. It is also significant that color-tunable phosphor essences ranging from greenish to orange-red to a deep red could be achieved by merging Tb\(^{3+}\) and Eu\(^{3+}\) ions in LaSrAl\(_3\)O\(_7\) substrate lattice as shown in Fig. 16. Consequently, it appears evident that pigment emission can be tailored to a desired color range merely only altering the concentration of co-dopants (Tb\(^{3+}\) and Eu\(^{3+}\)). Further, the color purity (CP) of the produced nanosamples was ascertained using eqn. 11 by utilizing their CIE color coordinates to gauge their luminous attributes \([12,92,93]\).

\[
\text{Color purity (CP)} = \frac{\sqrt{(x-x')^2 + (y-y')^2}}{\sqrt{(x_d-x')^2 + (y_d-y')^2}} \times 100
\]  
(11)

The resulting co-doped luminous materials revealed high color purity (80-90% assortment), signifying potential utili-
zation of these materials in solid state lighting technologies. Also, the CCT is a key criterion for figuring out the chromatic aspects of the produced illumination in Kelvin (K). The McCamy formula (eqn. 12) was used to probe the CCT of radiance stemming by La\textsubscript{0.99-x}Eu\textsubscript{x}Tb\textsubscript{0.01}SrAl\textsubscript{3}O\textsubscript{7} (x = 0.01-0.07 mol) co-doped nanocrystalline luminous materials [94-96].

\[
\text{CCT} = -437n^1 + 3601n^2 - 6861n + 5514.3 \quad (12)
\]

where \( n = (x - x_e)/(y - y_e) \) with chromaticity epicentre \( x_e = 0.332 \) and \( y_e = 0.186 \).

The following computations were engaged in the conversion of chroma \((x, y)\) to \(u', v'\) for calculating CCT values [12,97]:

\[
u' = \frac{4x}{-2x + 12y + 3}; \quad v' = \frac{9y}{-2x + 12y + 3} \quad (13)
\]

The insights observed for all La\textsubscript{0.99-x}Eu\textsubscript{x}Tb\textsubscript{0.01}SrAl\textsubscript{3}O\textsubscript{7} (x = 0.01-0.07 mol) co-doped nanoluminescent sample pursuant to investigation validate their potential as the platform for sophisticated displays, diverse luminous sources, photonic appliances and numerous lighting devices [11,27,98,99].

**Conclusion**

In present work, La\textsubscript{0.99-x}Eu\textsubscript{x}Tb\textsubscript{0.01}SrAl\textsubscript{3}O\textsubscript{7} (x = 0.01-0.07 mol) color tunable luminous nanocrystalline materials were synthesized using a simple, cost effective, less time consuming, self-propagating solution combustion synthesis route. The XRD pattern of synthesized La\textsubscript{0.99-x}Eu\textsubscript{x}Tb\textsubscript{0.01}SrAl\textsubscript{3}O\textsubscript{7} co-doped phosphor revealed the formation of crystalline and pure single phase at 900 °C. The synthesized co-doped phosphor sample illustrated the loosely organized bunches of spherical shaped nanoscale particles. The EDAX spectrum shows that Tb, Eu, La, Sr, Al and O elements were present in Eu\textsuperscript{3+}/Tb\textsuperscript{3+} co-doped LaSrAl\textsubscript{3}O\textsubscript{7} nanophosphor. Moreover, the DR spectroscopy revealed that the band gap energy of Eu\textsuperscript{3+}, Tb\textsuperscript{3+} co-doped LaSrAl\textsubscript{3}O\textsubscript{7} nanophosphors lay within the range of inorganic semiconductor substances, which strengthened their potency. With altering the contrast ratio of Tb\textsuperscript{3+} and Eu\textsuperscript{3+}, specific emission based on energy transfer (ET) from Tb\textsuperscript{3+} \( \rightarrow \) Eu\textsuperscript{3+} was also feasible to be altered ranging from greenish to orange-red to a deep red. Under 255 nm excitation it emerged that the energy transfer was caused by a dipole-quadrupole (d-q) interaction. The observed color-tunable emission for La\textsubscript{0.99-x}Eu\textsubscript{x}Tb\textsubscript{0.01}SrAl\textsubscript{3}O\textsubscript{7} (x = 0.01-0.07 mol) co-doped nanoluminescent demonstrates their future use as a foundation for sophisticated displays, diverse luminous sources, photonic appliances, pc-LEDs, full-color displays and numerous lighting devices.

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**CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this article.

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