A novel Sm\(^{3+}\)-activated Li\(_3\)BaSrLn\(_3\)(MO\(_4\))\(_8\) [Ln = La, Gd, and Y; M = Mo and W] deep red-emitting phosphors for plant cultivation and white LEDs

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**ABSTRACT**

Deep red phosphor-based LEDs play a crucial role in plant growth applications, where the LED emission covers the phytochrome (Pr) absorption. In this context, a series of Sm\(^{3+}\)-activated Li\(_3\)BaSrLn\(_3\)(MO\(_4\))\(_8\):Sm\(^{3+}\) [Ln = La Gd and Y; M = Mo and W] deep red phosphors were synthesized using the solid-state method. The outcome of the PXRD patterns suggests that the synthesized phosphors were crystallized in a monoclinic structure with the space group C2/c. SEM analysis was executed to study the morphology of the phosphors, and an FT-IR study was performed to study the stretching frequency of the MO/W-O bond in the (Mo/W)O\(_4\) groups. All the Sm\(^{3+}\)-activated phosphors showed intense emission at 646 nm due to their \(4G_5/2 \rightarrow 6H_{9/2}\) transition and exhibited excellent thermal stability (> 72% at 423K). The selected phosphors showed internal quantum efficiency at around 30%. The pc-LEDs were fabricated with the combination of near-UV LED and the synthesized deep-red phosphors. Besides, the emission spectrum of the fabricated LED was compared with the phytochrome Pr absorption spectrum for plant growth application. These results suggest that the synthesized phosphor can be useful in the white LED fabrication to improve the CRI and can also be beneficial in the plant growth field.

1. Introduction

Phosphor-converted white light-emitting diodes (LEDs) are considered potential alternative candidates for conventional lighting sources, such as incandescent bulbs and fluorescent lamps, due to their advantages such as their high energy conversion efficiency, good color rendering, long-duration ability, and eco-friendly nature [1–3]. As of now, commercial white LEDs are made up of the combination of a blue LED with yellow Y\(_2\)Al\(_5\)O\(_7\):Ce\(^{3+}\) (YAG:Ce\(^{3+}\))-emitting phosphor [4]. This device lacks the red-emitting component, which accounts for its low color rendering index (CRI) and high correlated temperature (CCT) [5–7]. These issues can be resolved by utilizing the methodology of mixing near-ultraviolet (n-UV) LED chips with red-, green-, and blue-emitting phosphors. In this context, numerous commercial red phosphors have been synthesized, including Y\(_2\)O\(_2\)S:Eu\(^{3+}\) [8], Y\(_2\)O\(_3\):Eu\(^{3+}\) [9] and YVO\(_4\):Eu\(^{3+}\) [10]. However, the absorption of these phosphors is still not good enough in the n-UV region. Divalent europium-activated nitride or oxy-nitride based phosphors have also been considered potential alternatives. However, their synthetic condition and emission band restrict their usage in white LEDs.

Sm\(^{3+}\)-activated phosphors are also attracting much attention for white LEDs due to their multiple emissions at 563 nm (\(4G_5/2 \rightarrow 6H_{9/2}\)), 599 nm (\(4G_5/2 \rightarrow 6H_{7/2}\)), 646 nm (\(4G_5/2 \rightarrow 6H_{9/2}\)), and 705 nm (\(4G_5/2 \rightarrow 6H_{11/2}\)), which are expected to improve the CRI of the white LEDs and intensify their red emission at the transition. The excitation and emission of the Sm\(^{3+}\) ion correspond to the electric dipole transition, and the red luminescence intensity is greatly affected by the selection of the host lattice [11]. In recent years, transition metal oxide-based host lattices started to be seen as more attractive for getting better emission of Ln\(^{3+}\) ions, and because of its advantages such as its broad charge transfer band in the n-UV region, and its commercial support [12]. There are three kinds of transition metal oxide-based Sm\(^{3+}\)-activated red phosphors: NaKLaMO\(_5\):Sm\(^{3+}\) (M = Nb, Ta) [13], La\(_2\)MoO\(_6\):Sm\(^{3+}\), and [14] YVO\(_4\):Sm\(^{3+}\) [15]. However, these phosphors have some demerits, such as poor red color saturation, low thermal stability, and IQE. Therefore, these...
phosphors failed to improve the CRI and white LED device efficiency. To overcome these defects and thereby improve the CRI and white LED device efficiency, new host lattices that have high thermal stability and IQE must be found. The molybdate host lattice is considered a good host matrix for Ln$^{3+}$-based luminescent materials due to its high thermal quenching behavior and chemical stability [16]. Recently, the research group developed an Eu$^{3+}$-activated red phosphor with an Li$_3$BaSrLa$_3$(MoO$_4$)$_8$ host lattice. It showed a higher thermal stability, zero concentration quenching, and QY [17]. There is still no report on Sm$^{3+}$-activated Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ [Ln = La, Gd and Y; M = Mo and W] red phosphors. Thus, Sm$^{3+}$-activated Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ [Ln = La, Gd and Y; M = Mo and W] orange red phosphors were synthesized for white LED application. The synthesized phosphors showed outstanding thermal stability and decent IQE, which will greatly improve the white LED efficiency.

In other active areas where red or deep red LEDs are considered essential resources for plant growth, Sm$^{3+}$-activated phosphor-based LED could especially be effectively utilized for plant growth applications because the emission spectral band of Sm$^{3+}$-activated phosphor is well-matched with the absorption spectrum of plant pigments and overlaps well with the phytochrome Pr photoreceptor. For example, the Sm$^{3+}$-activated Sr$_8$ZnY(PO$_4$)$_7$ phosphors for plant growth application reported by Zhou et al. showed intense emission at 606 nm ($^4G_{5/2} \rightarrow ^6H_{7/2}$) [18]. Still, there was a spectral mismatch between the LED emission and the pigment absorption. To completely cover the absorption spectrum of the phytochrome Pr, the LED phosphor should have multiple emissions in the red to deep red region. The Sm$^{3+}$-activated phosphor in this study showed intense emission at 646 nm ($^4G_{5/2} \rightarrow ^6H_{5/2}$), as well as at 606 nm ($^4G_{5/2} \rightarrow ^6H_{7/2}$), which can make it a suitable choice for plant growth, since it can cover the Pr absorption more efficiently.

### 2. Experimental section

The Li$_3$BaSrLn$_3$(MoO$_4$)$_8$:Sm$^{3+}$ [Ln = La Gd and Y; M = Mo and W] phosphors were synthesized via the high-temperature solid-state route. The raw materials were purchased from Alfa Aesar. The stoichiometric amounts of Li$_2$CO$_3$, BaCO$_3$, SrCO$_3$, La$_2$O$_3$, Gd$_2$O$_3$, Y$_2$O$_3$, Sm$_2$O$_3$, MoO$_3$, and WO$_3$ were ground well in an agate mortar and pestle. These raw materials were heated at 600°C for 12 h, reground, and further heated at 800°C for another 12 h. The final product was reground and stored in vials for further use.

### 3. Results and discussion

#### 3.1. Phase conformation and crystal structure study

The powder XRD pattern of the Sm$^{3+}$-activated Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ (Ln = La Gd and Y) and Li$_3$BaSrLn$_3$(WO$_4$)$_8$ (Ln = La Gd and Y) phosphors are shown in Figures 1 and 2, respectively. As seen from the XRD pattern, all the diffraction peaks are identical with the JCPDS (Joint Committee for the Powder Diffraction System) card number 77-0830, and no impurity line was observed. The synthesized phosphors were crystallized in the monoclinic phase with the space group C2/c. Also, the Sm$^{3+}$-activated phosphors did not show any changes in the XRD patterns, which confirms the successful incorporation of Sm$^{3+}$ in the Ln$^{3+}$ sites because the identical ionic radii of the Sm$^{3+}$ ion (CN = 8) and theionic radii of the La$^{3+}$, Gd$^{3+}$ and Y$^{3+}$ (CN = 8) ions were 1.16, 1.053, and 1.019Å, respectively. Also, the ionic radii of the W$^{6+}$ (CN = 4, r = 0.42Å) was similar to the Mo$^{6+}$ (CN = 4, r = 0.41Å), so the XRD patterns of the Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ and the Li$_3$BaSrLn$_3$(WO$_4$)$_8$ were similar [19].

Figure 3 illustrates the crystal structure of the Li$_3$BaSrY$_3$(MoO$_4$)$_8$ phosphor. Site Y is shared with the Li at the proportion of 0.75:0.25, and forms a distorted Y:Li(1)O$_8$ polyhedron from its coordination with eight oxygen atoms. The adjoining Y:Li(1)O$_8$ polyhedra are associated together through mutual edges to provide a two-dimensional Y:Li(1) layer made out of six rings. The
Figure 1. Powder XRD patterns of the Li$_3$BaSrLn$_{3-x}$(MoO$_4$)$_6$$_x$Sm$^{3+}$ [Ln = (a) La, (b) Gd, and (c) Y] phosphor.

Figure 2. Powder XRD patterns of the Li$_3$BaSrLn$_{3-x}$(WO$_4$)$_6$$_x$Sm$^{3+}$ [Ln = (a) La, (b) Gd, and (c) Y] phosphor.

Ba/Sr atom is surrounded by 10 oxygen atoms and forms a distorted polyhedron. The bond distances of Ba/Sr – O range from 2.687–3.027 Å. The Li(2) atom forms a distorted octahedron by coordinating with the six oxygen atoms, and the bond distance of Li(2) – O ranges from 1.998–2.315 Å. The Ba/SrO$_{10}$ and Y:Li(1)O$_8$ polyhedra form a chain by connecting with the O(5)–O(3) and O(1)–O(7) edges, which are parallel to the Y:Li(1)O$_8$ chains. Also, the crystal structure contains two kinds of molybdate sites, Mo(1) and Mo(2), and both molybdate atoms are in the 8f site. Mo(1) is coordinated with the O(1), O(2), O(3), and O(4) atoms. Similarly, Mo(2) is coordinated with the O(5), O(6), O(7), and O(8) atoms, and the bond distances of Mo(1) – O4 and Mo(2) – O4 range from 1.740–1.765 Å and 1.721–1.784 Å, respectively. The bond distances of MoO$_4$ are the shortest pairs in the structure and stabilize the MoO$_4$ tetrahedral structure [20].

3.2. Scanning electron microscopy (SEM)

To study the morphology of the synthesized phosphors, SEM images were collected with a scanning electron microscope. Figures 4 and 5 illustrate the SEM images of the Sm$^{3+}$-activated Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ [Ln = La, Gd and Y] and Li$_3$BaSrLn$_3$(WO$_4$)$_8$ [Ln = La, Gd and Y] phosphors, respectively. The SEM images clearly indicate that the synthesized phosphor had an irregular morphology, and the particles were aggregated. The average size of the particle ranged from 2 to 5
**Figure 3.** (a and b) Crystal structure of the Li₃BaSrY₃(MoO₄)₈ phosphor, and (c) coordination of Ba, Y/Li(1), and Li(2) with oxygen.

**Figure 4.** SEM image of the Sm³⁺-activated Li₃BaSrLn₃(MoO₄)₈ [Ln = (a and b) La, (c and d) Gd, and (e and f) Y] phosphor. Micrometers. The lower and higher magnifications of the SEM images are shown in RHS and LHS, respectively. The elemental mapping and EDX analysis of the Sm³⁺-activated Li₃BaSrLn₃(MoO₄)₈ (Ln = La, Gd and Y) and Li₃BaSrLn₃(WO₄)₈ [Ln = La, Gd and Y] phosphors are presented in Figures S1 to 6. The elemental mapping reveals the presence of all the elements and their homogeneous distribution on the surface of the phosphors.
Figure 5. SEM image of the Sm$^{3+}$-activated Li$_3$BaSrLn$_3$(WO$_4$)$_8$ [Ln = (a and b) La, (c and d) Gd, and (e and f) Y] phosphor. The homogeneous distribution of the Ln$^{3+}$ ions in the lattice can favor the luminescence characteristics of the phosphor. Also, the EDX spectrum reveals the existence of all the Ba, Sr, La, Gd, Y, Sm, Mo, W, and O elements in the phosphor composition.

3.3. FT-IR spectroscopy

Figure 6 shows the FT-IR spectrum of the Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ [Ln = La, Gd and Y; M = Mo (a) and W (b)] phosphors. All the Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ (Ln = La, Gd and Y) phosphors that show sharp peaks at
421 cm\(^{-1}\) are ascribed to the stretching vibrations of the O-Mo-O of MoO\(_4\) group in the host lattice. The MoO\(_4\) group stretching vibration are mostly observed below the 500-cm\(^{-1}\) region. Besides, the Ln-O stretching frequency can be observed in the 400- to 500-cm\(^{-1}\) region [12]. The Ln-O stretching vibrations are not visible because of the possible overlap between the MoO\(_4\) groups and the Ln-O stretching vibrations. Also, the spectra show strong bands at 834 cm\(^{-1}\), which correspond to the stretching vibrations of the Mo-O of the MoO\(_4\) groups [21].

Similar phenomena were seen with the Li\(_3\)BaSrLn\(_3\)(WO\(_4\))\(_8\) (Ln = La, Gd and Y) phosphors (Figure 6b). The sharp peak at 836 cm\(^{-1}\), which is responsible for the stretching vibrations of the W-O of the WO\(_4\) groups, is in the lattice. Another intense peak at 431 cm\(^{-1}\) is seen at the stretching vibrations of the O-W-O of the WO\(_4\) group in the host lattice. Apart from that, the Ln-O stretching frequency can be observed in the 400- to 500-cm\(^{-1}\) region, which is invisible because of the possible overlap between the MoO\(_4\) groups and the Ln-O stretching vibrations. All the FT-IR spectra that show a small peak at around the 1,700-cm\(^{-1}\) region are ascribed to the O-H stretching vibrations of the H\(_2\)O molecule, which is observed from the air atmosphere.

3.4. Photoluminescence (PL) study

The photoluminescence excitation spectra of the Sm\(^{3+}\)-activated Li\(_3\)BaSrLn\(_3\)(MoO\(_4\))\(_8\) [Ln = La, Gd and Y] and Li\(_3\)BaSrLn\(_3\)(WO\(_4\))\(_8\) [Ln = La, Gd and Y] phosphors are presented in Figures 7 and 8 (LHS), respectively. All the excitation spectra that contain a broadband in the 220- to 350-nm region can be attributed to the charge transfer transition of the O\(^2-\)-Sm\(^{3+}\) and the electronic transition from the 2p orbital of the oxygen to the 5d orbital of the Mo\(_4\) (M = Mo and W) groups. Also, the spectra consist of several sharp intense absorptions in the range of 360–500 nm, which are attributed to the 4f-4f electronic transition of the Sm\(^{3+}\) ions. The sharp peaks at 363, 376, 406, 421, and 465 nm are attributed to the \(6\)\(^{\text{H}}\)\(_{5/2}\) → \(4\)\(^{\text{L}}\)\(_{5/2}\), \(6\)\(^{\text{H}}\)\(_{5/2}\) → \(6\)\(^{\text{P}}\)\(_{7/2}\), \(6\)\(^{\text{H}}\)\(_{5/2}\) → \(4\)\(^{\text{F}}\)\(_{7/2}\), \(6\)\(^{\text{H}}\)\(_{5/2}\) → \(4\)\(^{\text{P}}\)\(_{7/2}\), and \(6\)\(^{\text{H}}\)\(_{5/2}\) → \(4\)\(^{\text{I}}\)\(_{11/2}\) electronic transitions, respectively. Among them, the peak

![Figure 7. PLE (LHS) and PL (RHS) spectra of the Li\(_3\)BaSrLn\(_3\)(MoO\(_4\))\(_8\):Sm\(^{3+}\) [Ln = (a and b) La, (c and d) Gd, and (e and f) Y] phosphor.](image-url)
Figure 8. PLE (LHS) and PL (RHS) spectra of the Li$_3$BaSrLn$_3$(WO$_4$)$_8$:Sm$^{3+}$ [Ln = (a and b) La, (c and d) Gd, and (e and f) Y] phosphor.

Figure 8. PLE (LHS) and PL (RHS) spectra of the Li$_3$BaSrLn$_3$(WO$_4$)$_8$:Sm$^{3+}$ [Ln = (a and b) La, (c and d) Gd, and (e and f) Y] phosphor.

Figure 8. PLE (LHS) and PL (RHS) spectra of the Li$_3$BaSrLn$_3$(WO$_4$)$_8$:Sm$^{3+}$ [Ln = (a and b) La, (c and d) Gd, and (e and f) Y] phosphor.

at 406 nm ($^6$H$_{5/2} \rightarrow ^4$F$_{7/2}$) is stronger than the other peaks [22].

The PL emission spectrum of the Sm$^{3+}$-activated Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ [(a) (Ln = La), (b) Gd, and (c) Y] and Li$_3$BaSrLn$_3$(WO$_4$)$_8$ [Ln = La, Gd and Y] phosphors are presented in Figures 7 and 8 (RHS), respectively, which were monitored under excitation at 406 nm. All the emission spectra exhibited a sharp red orange emission at 646 nm. All the emission spectra exhibited a sharp red orange emission at 646 nm and consisted of several sharp peaks at 563, 599, 646, and 705 nm, which are assigned to the $^4$G$_{5/2} \rightarrow ^6$H$_{5/2}$, $^4$G$_{5/2} \rightarrow ^6$H$_{7/2}$, $^4$G$_{5/2} \rightarrow ^6$H$_{9/2}$, and $^4$G$_{5/2} \rightarrow ^6$H$_{11/2}$ transitions, respectively [23]. Among these, the 646-nm ($^4$G$_{5/2} \rightarrow ^6$H$_{9/2}$) peak showed the maximum intensity. All these transitions obey the selection rule $\Delta J = \pm 1$ [24]. The major part of the $^4$G$_{5/2} \rightarrow ^6$H$_{5/2}$ transition is considered a magnetic-dipole (MD) allowed transition, and the $^4$G$_{5/2} \rightarrow ^6$H$_{7/2}$ transition is considered a partially magnetic dipole (MD) and partially electric dipole (ED) transition, whereas the $^4$G$_{5/2} \rightarrow ^6$H$_{9/2}$ transition is a completely ED transition [25]. The intensity ratio between the 646-nm ($^4$G$_{5/2} \rightarrow ^6$H$_{9/2}$) and 563-nm ($^4$G$_{5/2} \rightarrow ^6$H$_{5/2}$) regions is called R1, which can be used to measure the departure from the centrosymmetry of the sites occupied by the Sm$^{3+}$ ions. Likewise, the intensity ratio between the 604-nm ($^4$G$_{5/2} \rightarrow ^4$H$_{7/2}$) and 563-nm ($^4$G$_{5/2} \rightarrow ^6$H$_{5/2}$) regions is denoted as R2, which can be used to indicate the polarizability of the chemical environment around the Sm$^{3+}$ ion. The calculated R1 and R2 values are tabulated in Tables ST1 and ST2, and the R1 and R2 values are greater than 1. These values indicate that the Sm$^{3+}$ ion occupied the low-symmetry center in the host lattice [26].

3.5. Concentration quenching studies

Figures 9 and 10 show the emission intensity of the Sm$^{3+}$-activated Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ [(a) Ln = La, (b) Gd, and (c) Y] and Li$_3$BaSrLn$_3$(WO$_4$)$_8$ [(a) Ln = La, (b) Gd, and (c) Y] phosphors versus the Sm$^{3+}$ concentration, respectively. The optimal concentration quenching study is important for evaluating the luminescent nature of the phosphor. The optimum concentration of the Sm$^{3+}$ ion in the Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ lattice was found to have been
Figure 9. PL emission intensity of the $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition of the Li$_3$BaSrLn$_3$(MoO$_4$)$_6$:Sm$^{3+}$ [Ln = (a) La, (b) Gd, and (c) Y] phosphor; and (d) overall emission intensity of the Sm$^{3+}$-doped Li$_3$BaSrLn$_3$(MoO$_4$)$_6$ (Ln = La, Gd, and Y) phosphor.

Figure 10. PL emission intensity of the $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition of the Li$_3$BaSrLn$_3$(WO$_4$)$_6$:Sm$^{3+}$ [Ln = (a) La, (b) Gd, and (c) Y] phosphor; and (d) overall emission intensity of the Sm$^{3+}$-doped Li$_3$BaSrLn$_3$(WO$_4$)$_6$ (Ln = La, Gd, and Y) phosphor.
$x = 0.1, 0.05,$ and $0.1$ for the La, Gd, and Y host lattices, respectively. Similarly, the optimum concentration of the Sm$^{3+}$ ion in the Li$_3$BaSrLn$_3$(WO$_4$)$_8$ lattice was found to have been $x = 0.1, 0.3,$ and $0.1$ for the La, Gd, and Y host lattices, respectively. When the Sm$^{3+}$ ion concentration increased, the emission intensity also increased until it reached optimum concentration. Afterwards, the emission intensity started decreasing with the addition of the Sm$^{3+}$ ion in the host lattices. This phenomenon is called 'concentration quenching,' which mainly arises due to the cross-relaxation process among the Sm$^{3+}$ ions. In the Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ lattice, the Y$^{3+}$ host lattice showed a higher emission intensity than the other lattices (Figure 9d). Likewise, the Gd$^{3+}$-based host lattice exhibited greater emission than the other lattices in the Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ lattice (Figure 10d).

Furthermore, the concentration quenching process can be well explained by finding the critical distance ($R_c$) between the adjacent Sm$^{3+}$ ions, which was derived by Blasse. The $R_c$ energy transfer can be determined from the critical concentration of the activator ion. $R_c$ was calculated as follows [27]:

$$R_c = 2 \left( \frac{3V}{4\pi X_cN} \right)^{\frac{1}{3}}$$

Here, $R_c$ refers to the critical distance, $N$ corresponds to the number of available cationic sites in the host lattice, $V$ is the volume of the unit cell, and $X_c$ is the number of cationic sites in the host lattice. The relationship between $\log C$ and $\log (I/C)$ for the Li$_3$BaSrLn$_3$(MoO$_4$)$_8$:Sm$^{3+}$ [Ln = La, Gd, and Y; M = Mo (LHS) and W (RHS)] phosphors is shown in Figure 11.
critical concentration of the Sm$^{3+}$ ions. In this present Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ lattice, the number available cation (N) = 6, the unit cell volume (V) = 1280.373 $\text{Å}^3$, and the critical concentration quenching ($X_c$) values were 0.1, 0.05, and 0.1 for the La, Gd, and Y host lattices, respectively. The $R_c$ of both the La and Y host lattices was 15.973 Å, and that of the Gd host lattice was 20.125 Å. The Li$_3$BaSrLn$_3$(WO$_4$)$_8$ host lattice had the same N (6) and V (1280.373 $\text{Å}^3$). The $X_c$ values were 0.1, 0.3, and 0.1 for the La, Gd, and Y host lattices, respectively; of the La and Y host lattices, 15.973 Å; and of the Gd host lattice, 11.075 Å. The determined $R_c$ values were greater than 5 Å, which clearly shows that the multipolar interaction was highly responsible for the concentration quenching.

The multipolar interaction was further analyzed with the Dexter theory [28]. Through the relationship of the emission intensity (I) with the Sm$^{3+}$ ion concentration, the interaction mechanism was determined as follows.

$$I \propto a^{(1-\frac{s}{d})} \left(1 + \frac{s}{d}\right)$$ (2)

$$a = C(1 - d/s)[X_0(1 + A/)]^{d/s}$$ (3)

**Figure 12.** (a) Energy level diagram, and (b) cross-relaxation mechanism of the Sm$^{3+}$ ion in the Li$_3$BaSrLn$_3$(MO$_4$)$_8$ lattice.

**Figure 13.** Schematic diagram of the energy transfer from MoO$_4^{2-}$ to the Sm$^{3+}$ ion.
In the above equations, $\gamma$ represents the intrinsic transition probability of the sensitizer; $A$ and $X_0$ are constants; $\Gamma(1 + s/d)$ is a $\Gamma$ function; and $s$ refers to the index for the electric multipole, the electric dipole–dipole ($D$–$D$), the electric dipole–quadrupole ($D$–$Q$), and the electric quadrupole–quadrupole ($Q$–$Q$) interaction when $s = 6, 8, \text{and } 10$, respectively. If $s = 3$, the interaction was an exchange interaction. $d$ relates to the dimension of the sample. Here, $d = 3$, so the energy transfer that arose among the Sm$^{3+}$ ions inside the particles is considered. From Equations 2 and 3, it can be modified as:

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

where $C$ and $f$ are the concentration of the Sm$^{3+}$ ion and the independent of the doping concentration, respectively. Figure 11 shows the linear relationship between the log $C$ and log (I/C) values of the Li$_3$BaSrLn$_3$(MoO$_4$)$_8$:Sm$^{3+}$ [Ln = La, Gd and Y; M = Mo (LHS) and W (RHS)] phosphors. The obtained slope values (-s/d) of all the phosphors are close to 1. The s value was estimated from the slope as 3. Thus, the energy transfer arose between the activator (Sm$^{3+}$) ions in the Li$_3$BaSrLn$_3$(MoO$_4$)$_8$:Sm$^{3+}$ [Ln = La, Gd and Y; M = Mo and W] lattice, which prevailed through the predominant exchange interaction mechanism.

The preceding discussion revealed that the dipole–dipole interaction was responsible for the crossover relaxation between the Sm$^{3+}$ ions. Figure 12 shows the schematic energy level diagram and crossover relaxation mechanism of the Sm$^{3+}$ ion. Upon 406-nm excitation, the Sm$^{3+}$ ions were excited from the ground state ($^6H_{5/2}$) to the highest excited state ($^4K_{11/2}$), and the energy level difference between the ground state ($^6H_{5/2}$) of the Sm$^{3+}$ ion and the other excited states was significant. According to Kasha’s rule, electronic vibrational relaxation arises

![Figure 14. Decay curve of the Sm$^{3+}$-activated Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ [Ln = (a) La, (c) Gd, and (e) Y] phosphor; and (b, d, and f) lifetime values of all the phosphors.](image-url)
among the excited levels, and then fast non-radiative (NR) decay occurs via the crossover relaxation process (Figure 12b). Afterwards, the excited electrons come back from the first excited state to the $^4G_{5/2}$ to $^6H_{5/2}$ (565 nm), $^6H_{7/2}$ (606 nm), $^5H_{9/2}$ (646 nm), and $^6H_{11/2}$ (708 nm) ground states, as shown in Figure 12a [29,30].

### 3.6. Energy transfer study

Figure 13 shows the schematic energy transfer diagram of the MoO$_4^{2-}$ to Sm$^{3+}$ ions in the molybdate host lattice. Initially, upon excitation, the MoO$_4$ group absorbed energy and was excited from the $^1A_1$ ground state to the $^1T_1$ excited state, and subsequently transferred the energy to the highest excited state of the Sm$^{3+}$ ion non-radiatively. Similarly, the WO$_4$ group participated in the energy transfer process, when the electron from the WO$_4$ was excited from the $^1A_1$ ground state to the highest excited state $^1T_2$. The excited electrons fell to the first excited state ($^3T_1$) through a non-radiative process. Afterwards, the energy was transferred to the highest excited level of the Sm$^{3+}$ ion. Simultaneously, the transferred energy dropped from the highest excited state to the first excited state of $^4G_{5/2}$. As a final point, the emission arose from the $^4G_{5/2}$ level to the $^6H_J$ ($J = 5/2, 7/2, 9/2$ and $11/2$) level [31].

![Figure 15](image-url)  
Figure 15. Decay curve of the Sm$^{3+}$-activated Li$_2$BaSrLn$_3$(WO$_4$)$_8$ [Ln = (a) La, (c) Gd, and (e) Y] phosphor; and (b, d, and f) lifetime values of all the phosphors.
3.7. Decay curve analysis

Figures 14 and 15 show the decay curve profiles of the Sm$^{3+}$-activated Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ (Ln = La, Gd and Y) and Li$_3$BaSrLn$_3$(WO$_4$)$_8$ (Ln = La, Gd and Y) phosphors, respectively. The decay curve analysis was monitored under the excitation at 406 nm and the emission at 646 nm. All the decay curves of all the phosphors fit well with the single exponential function. The single exponential fitting indicates the presence of only one emissive center in the present lattice. The equation is $I(t) = I_0 e^{-t/\tau}$, where $I$ and $I_0$ represent the emission intensities at $t$ and $t = 0$, respectively, and $\tau$ signifies the lifetime. The calculated lifetime values are given in RHS in Figures 14 and 15, and the lifetime values of all the phosphors are shown in the millisecond (ms) range. When the concentration of Sm$^{3+}$ in the Li$_3$BaSrLn$_3$(MO$_4$)$_8$ [M = Mo and W] lattice was increased, the lifetime values gradually decreased because of the rapid energy transfer between the Sm$^{3+}$ ions in the host lattices as the distance between the Sm$^{3+}$ ions decreased [32,33].

3.8. Temperature-dependent PL

The temperature-dependent PL emission of the Sm$^{3+}$-activated Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ (Ln = La, Gd, and Y) and Li$_3$BaSrLn$_3$(WO$_4$)$_8$ (Ln = La, Gd, and Y) phosphors are given in Figure 16. Temperature-dependent PLs of the Sm$^{3+}$-activated Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ phosphors [Ln = (a) La, (c) Gd, and (e) Y] and Arrhenius plot of the Li$_3$BaSrLn$_3$(MoO$_4$)$_8$ phosphors [Ln = (b) La, (d) Gd, and (f) Y].
shown in Figures 16 and 17 (LHS), respectively. The temperature-dependent PL emission is one of the crucial analyses to demonstrate the practical application of the synthesized phosphor. The temperature-dependent emissions of all the Sm$^{3+}$-activated phosphors were monitored under 406 nm. Figure 18 shows the intensity variations based on the temperature, and the gradual decrease in the emission intensity with increasing temperature, due to the thermal quenching effect. The optimized phosphor compositions showed excellent thermal stability at 423K, which was retained at 72.28%. This higher value of the thermal stability shows that the synthesized phosphors can be effective contenders in white LED fabrication. In comparison, the Li$_3$BaSrGd$_3$(WO$_4$)$_8$:0.3Sm$^{3+}$ phosphor showed excellent thermal stability (84.72%) compared to the other compositions. Also, the energy of activation ($E_a$) was evaluated for all the phosphors according to the Arrhenius equation, which is shown below.

$$I(T) = \frac{I_0}{1 + c \exp\left(-\frac{\Delta E}{kT}\right)}$$

Here, $I_0$ refers to the PL emission initial intensity of the phosphor at room temperature, $I(T)$ corresponds to the PL intensity at various temperatures, $c$ describes a constant for the host, $\Delta E_a$ signifies the activation energy for
Figure 18. Normalized intensity variations of the Li₃BaSrLn₃(MO₄)₈ [Ln = La, Gd, and Y; M = (a) Mo and (b) W] phosphors at different temperatures.

Figure 19. CIE images of the Sm³⁺-activated Li₃BaSrLn₃(MoO₄)₈:Sm³⁺ (Ln = La, Gd, and Y) red-orange phosphors.

Figure 20. CIE images of the Sm³⁺-activated Li₃BaSrLn₃(WO₄)₈:Sm³⁺ (Ln = La, Gd, and Y) red-orange phosphors.

thermal quenching, and k represents the Boltzmann constant at eVK⁻¹. After specific rearrangements, Equation 7 can be altered as follows.

\[
\ln \left[ \frac{(I_0/I)}{1} \right] = -\frac{\Delta E_a}{kT} + \ln c \quad (8)
\]

Ea was calculated from the plot of ln[(I₀/I) – 1] vs. 1/kT and obtained from the slope. The Arrhenius plot and the calculated respective E_a values are mentioned in their respective RHS in Figures 6.15 and 6.16. The determined E_a values are much
higher than those of the other Sm$^{3+}$-activated phosphors such as La$_6$Ba$_4$Si$_6$O$_{24}$F$_2$:0.01Sm$^{3+}$ (0.16 eV) [34] Ba$_3$Lu(PO$_4$)$_3$:0.05Sm$^{3+}$ (0.142 eV) [35] KLaSr$_3$(PO$_4$)$_3$ F:0.03Sm$^{3+}$ (0.163 eV) [36] Na$_3$GdP$_2$O$_8$:0.035Sm$^{3+}$ (0.20 eV) [37]. This outstanding result suggests that the synthesized phosphors can be a promising red-emitting component of the white LED application.

3.9. CIE color coordinates and internal quantum efficiency (IQE)

CIE is an essential parameter to identify the exact emission color of a synthesized phosphor. Figures 19 and 20 show the CIE chromaticity coordinates of the Sm$^{3+}$-activated Li$_3$BaSrLn$_3$(MO$_4$)$_8$ [Ln = (a) La, (b) Gd, and (c) Y] phosphors, which were calculated from the PL emission spectra under the 406-nm excitation. All the synthesized phosphors showed a red-orange emission with excellent CIE chromaticity coordinates. The CIE chromaticity coordinates of the Li$_3$BaSrLn$_3$(MO$_4$)$_8$:Sm$^{3+}$ phosphors were (0.623, 0.375), (0.623, 0.375), and (0.622, 0.375) for the Y, Gd, and La host lattices, respectively; and the CIE chromaticity coordinates of the Li$_3$BaSrLn$_3$(WO$_4$)$_8$:Sm$^{3+}$ phosphors were (0.616, 0.381), (0.617, 0.381), and (0.616,
Figure 22. LED emission spectrum of the fabricated red-orange-emitting LED device from the combination of InGaN LED with the (a) \( \text{Li}_3\text{BaSrLn}_3(\text{MoO}_4)_8:\text{Sm}^{3+} \) (\( \text{Ln} = \text{La, Gd, and Y} \)) and (b) \( \text{Li}_3\text{BaSrLn}_3(\text{WO}_4)_8:\text{Sm}^{3+} \) (\( \text{Ln} = \text{La, Gd, and Y} \)) phosphors.

0.382) for the Y, Gd, and La host lattices, respectively. All these CIE values of the \( \text{Li}_3\text{BaSrLn}_3(\text{MoO}_4)_8:\text{Sm}^{3+} \) are close to the CIE chromaticity coordinates of the commercial \( \text{Y}_2\text{O}_3 \) red phosphor (0.644, 0.357).

The internal quantum efficiency (IQE) was determined for the optimized composition of the \( \text{Sm}^{3+} \)-activated \( \text{Li}_3\text{BaSrLn}_3(\text{MoO}_4)_8 \) (\( \text{Ln} = \text{La, Gd, and Y}; \text{M} = \text{Mo and W} \)) phosphors, which were monitored under 406 nm. The IQE was calculated according to the following equation.

\[
\eta = \frac{\int L_S}{\int E_R - \int E_S}
\]

In the above equation, \( \eta \) denotes the IQE; \( L_S \) corresponds to the emission spectrum of the synthesized red phosphor; and \( E_R \) and \( E_S \) are the excitation lights without and with the existence of the deep red phosphors, respectively. The calculated IQE is mentioned in Figure 21, and all the phosphors show a greater IQE than the other reported \( \text{Sm}^{3+} \)-activated phosphors such as \( \text{NaKL}a_{0.97}\text{Sm}_{0.03}\text{NbO}_5 \) (8.5%) [13], \( \text{Bi}_{0.97}\text{Sm}_{0.03}\text{OCl} \) (2.12%) [38], and \( \text{NaLa}_{0.98}\text{Sm}_{0.02}\text{MgWO}_6 \) (11.9%) [39]. These outcomes show that the \( \text{Sm}^{3+} \)-doped \( \text{Li}_3\text{BaSrLn}_3(\text{MoO}_4)_8 \) phosphor can be a potential red-emitting phosphor for WLED application.

3.10. LED fabrication and plant growth study

To assess the commercial application of the synthesized \( \text{Sm}^{3+} \)-activated \( \text{Li}_3\text{BaSrLn}_3(\text{MoO}_4)_8 \) [\( \text{Ln} = \text{La, Gd, and Y}; \text{M} = \text{Mo and W} \)] phosphors, the red-orange LEDs were fabricated for the synthesized phosphors with the combination of the nUV and LED chips. Figure 22 shows the LED emission spectrum of the fabricated deep red LEDs. All the LEDs show a red-orange emission in the spectrum, and the \( \text{Sm}^{3+} \) ion emission dominates the nUV-LED emission. With these results, it can be concluded that the synthesized phosphor can be a potential red-orange emitting component of WLED fabrication.

To prove the efficiency of the fabricated LEDs for plant growth application, the LED emission spectrum (\( \text{Li}_3\text{BaSrY}_3(\text{WO}_4)_8:\text{Sm}^{3+} \)) was compared with the absorption spectrum of the phytochrome Pr (Figure 23). The phytochrome Pr is an essential photoreceptor for plant growth application. The LED emission spectrum consists of two dominant emissions at around 394 nm, which belongs to the n-UV LED emission, and the other peaks at 580, 604, 646, and 704 nm correspond to the emission of the \( \text{Sm}^{3+} \) ion. The emission at 646 nm is higher than the other emissions in the spectrum, which is highly attractive in covering the full range of the phytochrome Pr absorption spectrum. Likewise, the absorption spectrum of phytochrome Pr contains two
emissions in the n-UV and red regions. The n-UV LED emission of the fabricated LED was well-matched with the n-UV region absorption of phytochrome Pr, and the rest of the Sm$^{3+}$ emissions precisely overlapped with the red region absorption band of phytochrome Pr. These excellent outputs indicate that the presently synthesized phosphors could be applicable in plant growth LED applications.

4. Conclusion
A series of Sm$^{3+}$-activated Li$_3$BaSrLn$_3$(MO$_4$)$_8$ (Ln = La, Gd, and Y; M = Mo and W) deep red emitting phosphors was synthesized, and their optical properties were systematically studied. The PL emission revealed that all the phosphors showed intense red emissions at 646 nm due to the $^{4}G_{5/2} \rightarrow ^{6}H_{9/2}$ transition. The energy transfer mechanism was also studied systematically. Temperature-dependent PL emission and IQE were performed to analyze the practical application of the synthesized phosphor, and the optimized phosphor compositions exhibited the highest thermal stability and IQE. The deep red LEDs were fabricated by combining the optimized red phosphors with n-UV LED, and all the LEDs showed intense red emissions at 646 nm. The fabricated deep red LED emission spectrum matched well the absorption spectrum of phytochrome Pr. These results show that the studied phosphor can be a potential red component of white LEDs, and a resource for plant growth application.

Disclosure statement
No potential conflict of interest was reported by the author(s).

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