Chapter III

Synthesis, Structural and Spectroscopic Characterization of Tb$_2$(MoO$_4$)$_3$ Nanophosphors

Sol-gel synthesis, structural and spectroscopic characterization along with detailed photoluminescence properties of Tb$_2$(MoO$_4$)$_3$ nanophosphors are discussed in this chapter. The structure of the phosphors was characterized by X-ray powder diffraction, Transmission Electron Microscopy, Raman spectra and Fourier transform infrared spectroscopy analysis. Detailed spectroscopic investigations were carried out using Judd–Ofelt analysis based on UV–Vis–NIR absorption spectra. The J-O intensity parameters obtained using J-O analysis was used to predict the radiative properties of Tb$^{3+}$. The Tb$_2$(MoO$_4$)$_3$ nanophosphors shows intense green emission under n-UV excitation due to the energy transfer from MoO$_4^{2-}$ to Tb$^{3+}$ ions. The CIE coordinates suggest enhanced color purity for green emission and the short fluorescence decay value propose its suitability for LED applications. These studies revealed that Tb$_2$(MoO$_4$)$_3$ phosphors can be a promising candidate for blue and n-UV excited WLEDs.
Chapter 3

3.1 Introduction

The optical properties of Tb$^{3+}$ ions in a variety of host matrices have been investigated owing to their strong green emission with proper chromaticity coordinates [1-3]. Tb$^{3+}$ based materials exhibit long spontaneous emission lifetimes, narrow spectral width and high quantum efficiency which make them an ideal choice for optical applications [4]. If the Tb$^{3+}$ ions occupy a non-centrosymmetric site in the structure, the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ emission transition at 545 nm will be dominant and can act as an efficient green phosphor with improved color purity. Moreover, the green phosphors have more significant effect on the luminous flux than the red and blue but only a few green phosphors can be excited efficiently by blue or n-UV light [5, 6]. Hence, the search for efficient green-emitting phosphor with high absorption in the n-UV region is of special attention. According to these requirements terbium molybdate nanophosphors is expected to be an ideal candidate owing to the intense and broad charge transfer band (due to the charge transfer transition from O$^{2-} \rightarrow$ Mo$^{6+}$ within the MoO$_4^{2-}$ groups) located in the n-UV region. This charge-transfer band can absorb n-UV excitation energy and efficiently transfer to Tb$^{3+}$ ions thereby producing strong green emission [7, 8].

This chapter describes the synthesis of terbium molybdate nanophosphors through sol-gel process. The detailed structural, morphological and optical characterizations were performed. The X-ray powder diffraction, Transmission electron microscopy, Raman and FTIR spectroscopy were used to analyze the structural properties. Detailed optical characterizations have been carried out through absorption, excitation, emission spectra and luminescence decay analysis of the samples. Judd-Ofelt intensity analysis, radiative properties and stimulated emission parameters of the nanophosphors were also discussed. The
energy transfer mechanism from MoO$_4^{2-}$ to Tb$^{3+}$ ions and chromaticity coordinates were also discussed.

### 3.2 Synthesis of terbium molybdate nanophosphor

Terbium molybdate nanophosphor investigated in this work was synthesized via sol–gel method. Analytical grade molybdenum trioxide (Merck Synth. 85%), terbium nitrate hexahydrate (CDH 99.9%), citric acid (CDH 99%) and Polyvinyl alcohol (CDH 99%) were used as the starting materials. In the synthesis procedure, the molar ratio of terbium to molybdenum was kept at 2:3 and that between the total metal ions, citric acid and PVA was maintained at 1:1:1. Molybdenum-citrate complex in stoichiometric ratio was prepared by dissolving molybdenum trioxide in an aqueous solution of citric acid kept at 80°C with constant stirring. Stoichiometric amount of terbium nitrate was dissolved in distilled water and added to the reaction bottle containing molybdenum-citrate complex. The resulting solution thus obtained was stirred for 1h to get a clear and homogeneous sol. Polymerization of the sol was achieved by the addition of polyvinyl alcohol and the polymerized mixture was stirred for 5h at 90°C to get a homogeneous viscous gel. The gel was then slowly heated up to 120°C for drying and then pre-fired at 450°C for 2h at a rate of 10°C/min which facilitated the pyrolysis of organic compounds and decomposed to a black-colored powder of extremely fine particle size. Finally, the samples were annealed at different temperatures 600, 700, 750, 800 and 900°C for 2h at the rate of 1°C/min.

### 3.3 Structural characterization of Tb$_2$(MoO$_4$)$_3$

The structural analysis of Tb$_2$(MoO$_4$)$_3$ nanophosphors were carried out by collecting the X-ray powder diffraction pattern on a PANalytical Xpert Pro X-ray powder Diffractometer with CuKα radiation at $\lambda = 1.54$ Å. Morphology, size, crystallinity and chemical composition of the samples
were analyzed using a JEOL, JEM-2100 High resolution transmission electron microscope (HR-TEM) equipped with energy dispersive X-ray spectrometer (EDS). Raman spectrum of the sample was recorded with HORIBA Jobin Yvon Lab Ram HR with 514.5 nm Argon ion laser as the excitation source with a spectral resolution of 0.4 cm\(^{-1}\) to analyze the vibrational modes. The FTIR spectrum of the sample was recorded using Shimadzu 8400S FTIR Spectrometer to identify the functional groups.

### 3.3.1 X-ray powder diffraction studies

X-ray powder diffraction studies were carried out to verify the crystallinity and to determine the structure of the synthesized samples. Powder diffraction patterns of the samples annealed at 450, 600, 700, 750, 800 and 900 °C were recorded in the 2θ range 10-60°. The diffraction patterns of the samples are given in Figure 3.1 along with relevant ICDD data for comparison.

![Figure 3.1 X-ray diffraction patterns of Tb\(_2\)(MoO\(_4\))\(_3\) samples annealed at different temperatures.](image-url)
The sample heated at 450 °C does not show any diffraction peaks owing to its amorphous nature. When annealed at 600 °C some low intensity peaks are appeared indicating the onset of crystallization and the characteristic phase of monoclinic structure is obtained at 750 °C (ICDD 25-0338). The diffraction pattern of the sample annealed at 800 °C shows peaks corresponding to both monoclinic and orthorhombic phases, indicating that a fraction of monoclinic phase has transformed into the orthorhombic phase. As the temperature is further increased to 900 °C, the pure orthorhombic phase of \( \text{Tb}_2(\text{MoO}_4)_3 \) with space group Pba2 (ICDD 84-0085) is obtained. In order to further confirm the formation of orthorhombic phase unit cell parameters are calculated using Unit Cellcalc software and are, \( a = 10.34 \, \text{Å}, \, b = 10.37 \, \text{Å}, \, \text{and} \, c = 10.64 \, \text{Å} \) with Cell volume \( V = 1142.12 \, \text{Å}^3 \). These values are in good agreement with that reported in ICDD data file (ICDD 84-0085). The crystallite size of the sample can be assessed by the Scherrer equation. The strongest diffraction peak was used to calculate the crystallite size of the prepared \( \text{Tb}_2(\text{MoO}_4)_3 \) phosphor annealed at 900 °C and is found to be 35 nm.

### 3.3.2 Transmission electron microscopy analysis

The morphology, size, crystallinity and composition of the synthesized samples were examined using TEM, HRTEM, SAED and EDS analysis. Samples for measurements were prepared by sonicating the powder samples in toluene for 20 min. A few drops of the resulting suspension were placed on a standard carbon-coated copper grid and dried before recording the micrographs. The TEM image of \( \text{Tb}_2(\text{MoO}_4)_3 \) nanophosphor shown in Figure 3.2(a) clearly indicates that the particles are well dispersed and spherically shaped with size ranging between 30-35 nm. The well-defined atomic planes in the HRTEM image shown in Figure 3.2(b) demonstrate the high crystallinity of the sample. The distance (3.46 Å)
between the adjacent lattice fringes, corresponds to the interplanar
distance from (221) crystal plane (marked by the arrows), agrees well with
the $d_{221}$ spacing of the X-ray diffraction pattern ($2\theta = 25^\circ$, 3.46 Å) and the
literature value (3.4654 Å, ICDD 84-0085). The diffused ring like diffraction
spots observed in the SAED pattern shows the polycrystalline nature of the
samples and is given in Figure 3.2(c).

The chemical composition of the nanophosphors was determined
by recording Energy dispersive spectra (EDS). Figure 3.2(d) shows the EDS
spectra of $\text{Tb}_2(\text{MoO}_4)_3$ nanophosphor. The spectra confirmed that all the
detected peaks are related to Terbium (Tb), Molybdenum (Mo) and
Oxygen (O) hence indicates chemically pure $\text{Tb}_2(\text{MoO}_4)_3$ phase. The
additional peak of Cu is due to the copper grid used during EDS analysis.

![Figure 3.2](image)

**Figure 3.2** Transmission electron micrographs and energy
dispersive spectra of $\text{Tb}_2(\text{MoO}_4)_3$ nanophosphor: (a) TEM
(b) HRTEM (c) SAED and (d) EDS spectra.
3.3.3 Raman spectroscopy

Raman spectroscopy is an excellent tool to analyze vibrational modes as well as structural disorder in metal oxide systems as it is more sensitive to metal-oxygen vibrational modes than metal-metal vibration modes [9]. Figure 3.3 presents Raman spectra of the orthorhombic Tb$_2$(MoO$_4$)$_3$ with space group Pba2 recorded in the range 50-1000 cm$^{-1}$. Out of the 12 vibrational modes of Tb$_2$(MoO$_4$)$_3$ three are purely Raman active and the rest are both Raman and IR active [10]. The peaks at 903, 850 and 354 cm$^{-1}$ correspond to the pure Raman active bands and bands observed at 960, 942, 821, 746, 388, 327, 201, 150 and 102 cm$^{-1}$ represents both Raman and IR active bands.

![Figure 3.3 Raman spectra of Tb$_2$(MoO$_4$)$_3$ nanophosphor.](image)

The two strong lines at 960 and 942 cm$^{-1}$ in the spectra with a shoulder peak at 903 cm$^{-1}$ have been assigned to the symmetric stretching vibrations and the bands at 850, 821 and 746 cm$^{-1}$ are due to asymmetric stretching vibrations of MoO$_4$ tetrahedra. Those lines at 388, 354 and 327 cm$^{-1}$ can be
attributed to the asymmetric and symmetric bending vibrations of the 
$\text{MoO}_4^{2-}$ tetrahedra. The weak Raman bands located at 201, 150 and 102 
$\text{cm}^{-1}$ arises from the rotational and translational modes of the molybdate 
ion. The observed Raman band positions and their assignments are in 
close agreement with earlier reports [11-13].

3.3.4 Fourier transform infrared spectroscopy analysis

Fourier transform infrared spectra (FTIR) of the samples were 
recorded in transmittance mode at room temperature. Figure 3.4 shows 
the FTIR spectra of the samples annealed at 450 and 900°C in the 
wavenumber range 500-4000 cm$^{-1}$. In the spectra, the prominent peaks are 
observed at 3422, 2925, 1636, 945, 920 and 740 cm$^{-1}$. The bands at 3422 and 
1636 cm$^{-1}$ are assigned to O-H stretching and H-O-H bending vibrations 
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.4}
\caption{FTIR spectra of the samples annealed at 450 and 900 °C.}
\end{figure}

of adsorbed water [14]. When annealed at 900°C, intensity of the bands at 
3422, 2925 and 1636 cm$^{-1}$ decreased considerably due to evaporation of 
adsorbed water and decomposition of organic species at high temperature.
The stretching modes of molybdates with isolated MoO$_4$ tetrahedra fall in the broad vibration frequency range 600-980 cm$^{-1}$. The bands observed in the IR spectra at 945 and 920 cm$^{-1}$ are due to the symmetric stretching of Mo–O bonds in MoO$_4$ tetrahedra. The broadband situated at 740 cm$^{-1}$ is related to the asymmetric stretching vibrations of Mo-O-Mo bonds in MoO$_4$[15].

### 3.4 Optical characterization of Tb$_2$(MoO$_4$)$_3$ nanophosphor

Optical characterization of a phosphor material is essential for suggesting it for specific practical applications. UV-Vis-NIR absorption spectra, photoluminescence excitation and emission spectra and fluorescence lifetime measurements were employed to investigate the optical properties of the prepared nanophosphors. UV-Vis-NIR absorption spectra of the samples were recorded on a JASCO V-670 UV–Vis-NIR spectrophotometer. Photoluminescence excitation and emission spectra were collected on a HORIBA Jobin Yvon, FluoroMax-4 fluorescence spectrophotometer. The fluorescence lifetime measurements were carried out on Jobin Vyon Fluorolog-3 equipped with a 150 W- Xenon lamp as the excitation source.

#### 3.4.1 UV–Vis-NIR spectroscopy

Absorption spectra of the phosphors were recorded in order to explore the energy absorption and absorption efficiency in the UV–Vis-NIR region. Figure 3.5 (a) and (b) illustrate the absorption spectra of Tb$_2$(MoO$_4$)$_3$ nanophosphors in the UV region 230–600 nm and NIR region 900-2500 nm respectively. The location and assignment of the band positions have been done according to the report of Carnall et al. [16, 17].
Chapter 3

In the UV region, a broad absorption band in the range 250-330 nm with a maximum at 290 nm is observed. This band is ascribed to the charge transfer band (CTB) due to charge transfer from O$^{2-}$ ligand to Mo$^{6+}$ ions in MoO$_4^{2-}$ groups of molybdate host lattice [18]. In this process, the electrons are excited from the lower energy band (valence band) to the higher energy band (conduction band). The bottom (lower energy region) of the conduction band is formed by the 4$d$ and 5$d$ orbitals of Mo atoms while the top (higher energy region) of the valence band is formed by the 2$p$ orbitals of the O atoms [19]. Generally, Tb-activated phosphors show 4$f$–5$d$ transition band around 200–300 nm, but this absorption band is not observed distinctly in the spectra since the strong CTB band of the molybdate host overlaps the 4$f$–5$d$ transition band of Tb$^{3+}$ [20]. In the longer wavelength region, a number of absorption peaks are observed both in the UV-Visible and NIR range. The peaks in the UV-Visible region are located at 376, 485 nm and that in NIR region are at 1884, 1991 and 2270 nm. These peaks arises due to the intra configurational f-f transitions of Tb$^{3+}$ from $7F_6 \rightarrow 5D_5$, $7F_6 \rightarrow 5D_4$, $7F_6 \rightarrow 7F_1$, $7F_6 \rightarrow 7F_2$ and

**Figure 3.5** Optical absorption spectra of Tb$_2$(MoO$_4$)$_3$ nanophosphor (a) UV–Visible region and (b) NIR region.
$^7F_6 \rightarrow ^7F_3$ transitions respectively [16]. Among these observed transitions, $^7F_6 \rightarrow ^5D_3, ^5D_4$ transition are weak and located in the visible region and the rest of the transitions $^7F_6 \rightarrow ^7F_J (J = 1, 2, 3)$ are intense and located in the near infrared region. From the absorption spectra analysis it is expected that these phosphors are excitable under n-UV and blue irradiation, owing to the strong absorption of the charge transfer band, which is one of the main prerequisites for a phosphor material in n-UV pumped WLEDs.

### 3.4.2 Judd-Ofelt analysis

The spectroscopic studies using Judd-Ofelt (JO) analysis is an important step for the better understanding of different optical properties of rare earth ions in luminescent materials. Major optical characteristics such as fluorescence transition probabilities, radiative lifetime, branching ratio, strength of chemical bonding between RE ions and ligands, nature of the ligand bond and also the symmetry of the environment around the rare earth ion can be determined using the Judd-Ofelt analysis.

**Oscillator strength and Judd-Ofelt intensity parameters**

The oscillator strength is a measure of the relative strength of the electronic transitions within the atomic and molecular systems. The intensity of an absorption band is usually expressed in terms of the “oscillator strength”. Judd-Ofelt theory defines two types of oscillator strengths which are the experimental and calculated oscillator strengths. Experimental oscillator strengths ($f_{exp}$) are determined from the absorption spectrum, whereas the calculated oscillator strengths ($f_{cal}$) are determined using the values of JO intensity parameters.
Table 3.1 Oscillator strengths of Tb$^{3+}$ in Tb$_2$(MoO$_4$)$_3$.

<table>
<thead>
<tr>
<th>SI No.</th>
<th>S’L’J’</th>
<th>$E_{\text{exp}}$ in host (ν$_c$) cm$^{-1}$</th>
<th>$E_{\text{exp}}$ in aqua (ν$_a$) cm$^{-1}$</th>
<th>Oscillator Strengths (x 10$^{-7}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>f$_{\text{exp}}$</td>
</tr>
<tr>
<td>1</td>
<td>$^7F_6\rightarrow^7D_3$</td>
<td>26455</td>
<td>26425</td>
<td>0.6192</td>
</tr>
<tr>
<td>2</td>
<td>$^7F_6\rightarrow^7D_4$</td>
<td>20576</td>
<td>20545</td>
<td>0.2298</td>
</tr>
<tr>
<td>3</td>
<td>$^7F_6\rightarrow^7F_1$</td>
<td>5313</td>
<td>5481</td>
<td>2.1452</td>
</tr>
<tr>
<td>4</td>
<td>$^7F_6\rightarrow^7F_2$</td>
<td>5022</td>
<td>5038</td>
<td>2.1100</td>
</tr>
<tr>
<td>5</td>
<td>$^7F_6\rightarrow^7F_3$</td>
<td>4407</td>
<td>4344</td>
<td>6.2463</td>
</tr>
</tbody>
</table>

$\bar{\beta} = 0.9966$, $\delta = 0.3453$

The intensity parameters $\Omega_\lambda (\lambda = 2, 4, 6)$ are characteristics of a rare earth ion in a host matrix and are related to the radial wave functions of the 4$^N_f$ states. The values of Judd-Ofelt intensity parameters are very important for the determination of laser parameters. The three intensity parameters $\Omega_\lambda (\lambda = 2, 4, 6)$ are calculated by least square fit to Eqn.2.2. The absorption matrix elements of Tb$^{3+}$ ion used for these calculations are taken from the report by Carnall et al. [16]. The absorption transitions, peak positions, experimental and calculated oscillator strengths along with Judd-Ofelt intensity parameters are given in Table 3.1. The quality of the least square fit is expressed in terms of root mean square deviation ($\delta_{\text{r.m.s.}}$) of oscillator strengths and is calculated using Eqn.2.3. The low value of root mean square deviation, $0.026 \times 10^{-7}$ specifies good fit between experimental and calculated oscillator strengths and hence the validity of JO analysis for predicting the spectroscopic parameters.

Nephelauxetic ratio ($\beta$) and bonding parameter ($\delta$) are used to find the nature of bonding between the Tb$^{3+}$ - ligand bond and are calculated...
Synthesis \( \text{Tb}_2(\text{MoO}_4)_3 \) Nanophosphors

according to Eqn.2.4 and 2.5 respectively. The nephelauxetic effect is due to progressive overlapping of ligand wave functions with the transition electron wave functions. As a result of this nephelauxetic effect, the energy separation between the levels of \( \text{Tb}^{3+} \) ions in the host decreased compared to that of aqueous \( \text{Tb}^{3+} \) ions. Hence, we can find the nature of the bonding between the \( \text{Tb}^{3+} \)-ligand bond by calculating the nephelauxetic ratio and bonding parameter. The nephelauxetic ratio is defined as the ratio between energies of corresponding transitions in the matrix and aqueous ion. Bonding parameter value is generally used to indicate the nature of rare earth ion - ligand bond. For covalent bond, the bonding parameter gives a positive value, whereas for ionic bonding it is negative.

The calculated JO intensity parameters are

\[
\begin{align*}
\Omega_2 &= 0.4358 \times 10^{-20} \\
\Omega_4 &= 0.2846 \times 10^{-20} \\
\Omega_6 &= 0.0728 \times 10^{-20}
\end{align*}
\]

The trend observed in the JO intensity parameters (\( \Omega_2 > \Omega_4 > \Omega_6 \)) for \( \text{Tb}^{3+} \) ion in \( \text{Tb}_2(\text{MoO}_4)_3 \) confirmed the asymmetry of the \( \text{Tb}^{3+} \) ion sites and covalent bonding between the \( \text{Tb}^{3+} \) ion and the surrounding \( \text{O}^{2-} \) ligand bonds. The calculated values for nephelauxetic ratios (\( \beta \)) and bonding parameters (\( \delta \)) are found to be 0.9966 and 0.3453 for respectively. The positive sign of the bonding parameter further confirms the covalent nature of the \( \text{Tb}^{3+} - \text{O}^{2-} \) ligand bond which was already predicted by the magnitude of \( \Omega_2 \) parameter [21].

Radiative Properties

Theoretical prediction of fluorescence properties of rare earth ions in a particular host is important for its practical applications especially in
developing new phosphor materials. In this context, radiative property analysis is a useful tool for determining the emission transitions of rare earth ions. Here, the fluorescence characteristics of the $^5D_4$ level of Tb$^{3+}$ in Tb$_2$(MoO$_4$)$_3$ are predicted by evaluating the radiative properties. The evaluated JO parameters are used to predict the radiative properties for the electric dipole transitions between any excited level ($|Ψ_J⟩$) to its lower-lying level ($|Ψ_{J'}⟩$). The important radiative properties such as electric dipole line strengths ($S_{ed}$), radiative transition probability ($A_R$), total radiative transition probability ($A_T$) and fluorescence branching ratio ($β_R$) for the excited state $^5D_4$ of Tb$^{3+}$ ions in Tb$_2$(MoO$_4$)$_3$ nanophosphor are calculated based on JO theory using the Eqns.2.6-2.10 and are presented in Table 3.2.

**Table 3.2** Calculated radiative parameters of Tb$^{3+}$ ion in molybdate matrix.

<table>
<thead>
<tr>
<th>Transition from $^5D_4$</th>
<th>Energy cm$^{-1}$</th>
<th>$S_{ed}$ (10$^{-23}$)</th>
<th>$A_R$ (s$^{-1}$)</th>
<th>$A_T$ (s$^{-1}$)</th>
<th>$β_R$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^7F_6$</td>
<td>20408</td>
<td>0.89</td>
<td>2.56</td>
<td></td>
<td>12.52</td>
</tr>
<tr>
<td>$^7F_5$</td>
<td>18450</td>
<td>6.93</td>
<td>14.61</td>
<td>20.44</td>
<td>71.45</td>
</tr>
<tr>
<td>$^7F_4$</td>
<td>16949</td>
<td>0.81</td>
<td>1.32</td>
<td></td>
<td>6.45</td>
</tr>
<tr>
<td>$^7F_3$</td>
<td>16129</td>
<td>1.37</td>
<td>1.95</td>
<td></td>
<td>9.55</td>
</tr>
</tbody>
</table>

The electric dipole line strength ($S_{ed}$) is determined from the intensity parameters and the reduced matrix elements, which characterizes the intensity of absorption spectrum as well as the fluorescence spectrum. The electric dipole line strengths ($S_{ed}$) corresponding to the transitions from the upper manifold state $^5D_4$ of Tb$^{3+}$ to the lower manifold states $^7F_J$ ($J = 0 - 6$) have been determined [22]. The radiative transition probability is directly dependent on electric dipole line strengths of rare
earth ion. Larger the value of $S_{ed}$, larger will be the value of radiative transition probability and more will be the possibility of corresponding radiative emission. Among the transitions, $^5D_4 \rightarrow {}^7F_5$ transition possesses the highest $S_{ed}$ and transition probability. The total radiative transition probability and radiative lifetime ($\tau_R$) of the $^5D_4$ level of Tb$^{3+}$ in Tb$_2$(MoO$_4$)$_3$ are obtained as 20.44 s$^{-1}$ and 0.48 ms respectively. Branching ratio ($\beta_R$) is a critical parameter for laser design since it describes the probability of achieving stimulated emission cross-section from any definite transition. The branching ratios of different radiative transitions were determined from the ratio of individual radiative transition probability to the total radiative transition probability. Large values obtained for the transition probabilities and branching ratios, for $^5D_4 \rightarrow {}^7F_5$ transition suggests that it can exhibit laser action. The trend of branching ratio is $^5D_4 \rightarrow {}^7F_4 > {}^7F_3 > {}^7F_6 > {}^7F_5$ and a similar pattern is expected in the emission spectra.

3.4.3 Photoluminescence studies
3.4.3.1 Excitation spectra

The excitation spectra of the samples were recorded in the wavelength range 250-530 nm. Figure 3.6 represents the excitation spectra of the samples annealed at different temperatures, fixing the emission wavelength at 545 nm corresponding to $^5D_4 \rightarrow {}^7F_5$ transition of Tb$^{3+}$. The broadband observed in the range 270-340 nm with a maximum at 290 nm is attributed to the CTB due to O$^{2-}$ to Mo$^{6+}$ ions in MoO$_4^{2-}$ group (an electron from 2$p$ orbital of oxygen atom goes into one of the empty 4$d$ or 5$d$ orbital of molybdenum) [23]. The Tb$^{3+}$ ion exhibits several transitions between 270-310 nm originating from $4f^8-4f^55d^1$ transitions and are hardly be detected because of their weak intensity [24]. Thus, the broadband observed in the excitation spectra is attributed to the combinations of the CTB of molybdate and the $4f-5d$ transition of Tb$^{3+}$ ions. All the spectra
consist of many intense sharp lines between 350–500 nm, ascribed to the intra-configurational $f$-$f$ transitions of the Tb$^{3+}$ ions arise due to the transition from $^7F_6$ to $^5D_0$ (338 nm), $^5G_2$ (348 nm), $^5D_2$ (356 nm), $^5L_{10}$ (363 nm), $^5G_6$ (372 nm), $^5D_3$ (376 nm) and $^5D_4$ (385 nm) respectively [22].

The presence of CTB of MoO$_4^{2-}$ group in the excitation spectra on monitoring the Tb$^{3+}$ emission at 545 nm clearly indicates that there exists an energy transfer from MoO$_4^{2-}$ group to Tb$^{3+}$. This charge transfer band is relatively high for the orthorhombic Tb$_2$(MoO$_4$)$_3$ samples compared with monoclinic structure. This implies that multiphonon-assisted energy dissipation prevails in the monoclinic samples and consequently high amount of excitation energy is dissipated before it can be trapped by Tb$^{3+}$ ions. The excitation spectra analysis suggests that the Tb$^{3+}$ ions in the Tb$_2$(MoO$_4$)$_3$ could be activated through two channels by sensitizing the charge transfer band of MoO$_4^{2-}$ and subsequent energy transfer to Tb$^{3+}$ or by directly exciting Tb$^{3+}$ via $f$-$f$ transitions.

![Figure 3.6](image-url)  

**Figure 3.6** Excitation spectra of Tb$_2$(MoO$_4$)$_3$ nanophosphor at different temperatures.
3.4.3.2 Emission spectra

Emission spectra of the samples were recorded in the wavelength range 400-650 nm in order to study the structure dependent luminescence properties. Figure 3.7 shows the emission spectra of the prepared sample annealed at different temperature under 290 nm (CTB) excitation. All the spectra exhibit characteristic emission peaks of Tb$^{3+}$ expect for their variation in luminescence intensities. The emission peaks are located at 490, 545, 600, 619 nm and are due to the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ transitions respectively [25]. Usually, Tb$^{3+}$ ions exhibit emission from $^5D_3$ and $^5D_4$ levels and here the emissions from the $^5D_3$ level are weak due to the low phonon energies of the sample. Also emission from the $^5D_3$ level has been quenched because of the cross-relaxation process, as described by Tb$^{3+}$ ($^5D_3$) + Tb$^{3+}$ ($^7F_6$) → Tb$^{3+}$ ($^5D_4$) + Tb$^{3+}$ ($^7F_0$), results in the strong emission from $^5D_4$ to the $^7F_J$ levels [26]. When compared with the emission of Tb$^{3+}$, the intrinsic blue emission from MoO$_4^{2-}$ is weak, suggesting efficient energy transfer from MoO$_4^{2-}$ to Tb$^{3+}$.

![Emission spectra of Tb$_2$(MoO$_4$)$_3$ nanophosphor prepared at different temperatures. Inset figure shows dependence of emission intensity of $^5D_4 \rightarrow ^7F_5$ transition at 545 nm on the annealing temperature.](image)
Chapter 3

The inset of Figure 3.7 shows the plot of luminescence intensity of the samples at different temperature for the $^5D_4 \rightarrow ^7F_5$ transition with an excitation wavelength of 290 nm. The luminescence intensity of samples is increased with annealing temperature and reached a maximum at 900°C when the orthorhombic phase is formed. This confirms that orthorhombic structure has better luminescence properties than monoclinic structure. Accordingly, the orthorhombic samples are a better candidate for the luminescence of Tb$^{3+}$.

Direct excitation of $^7F_6 \rightarrow ^5D_3$ and $^7F_6 \rightarrow ^5D_4$ transition of Tb$^{3+}$ at 376 and 485 nm yields the similar spectrum resembling as that of the CTB excited, where the $f$-$f$ transitions of Tb$^{3+}$ is dominated by the green emission of $^5D_4 \rightarrow ^7F_5$ transition at 545 nm as shown in Figure 3.8.

![Emission spectra of Tb(MoO$_4$)$_3$ nanophosphor upon excitation into the $f$-$f$ transition of Tb$^{3+}$.](image)

**Figure 3.8** Emission spectra of Tb(MoO$_4$)$_3$ nanophosphor upon excitation into the $f$-$f$ transition of Tb$^{3+}$.

3.4.4 The stimulated emission parameters

The stimulated emission parameters such as stimulated emission cross section ($\sigma_e$), branching ratio ($\beta_R$) and radiative lifetime ($\tau_R$) provides information about the potential laser performance of a material which are
important to select good laser host. The stimulated emission parameters are determined using Eqn.2.12. The values of stimulated emission cross-section ($\sigma_e$) indicate the rate of energy extraction from the lasing material and the products $\sigma_e \times \Delta \lambda_{\text{eff}}$ and $\sigma_e \times \tau_r$ signify gain band width and optical gain of the material respectively. The experimental branching ratio ($\beta_{\text{exp}}$) was found by integrating the area under the peaks corresponding to different transitions in the luminescence spectra. Table 3.3 shows the stimulated emission parameters along with comparison between the experimental ($\beta_{\text{exp}}$) and predicted branching ratio ($\beta_R$). The most potential laser transitions possess large values for stimulated emission parameters [27]. From Table 3.3 it may be noted that $^5D_4 \rightarrow ^7F_5$ transition of Tb$^{3+}$ at 545 nm possesses highest value for stimulated emission cross-section, optical bandwidth and optical gain as $0.4999 \times 10^{-23}$, $0.5036 \times 10^{-30}$ cm$^3$ and $0.2441 \times 10^{-26}$ cm$^2$S respectively. Such high values are adequate to attain favorable lasing action, high bandwidth and optical gain for amplifiers. The experimental and calculated branching ratios are in good agreement and follow a decreasing trend for transitions from $^5D_4 \rightarrow ^7F_5$, $^7F_6$ and $^7F_4$. These results indicate that the green luminescence in Tb$_2$(MoO$_4$)$_3$ is more stable and sustainable for its applications in display devices and green luminescent optoelectronic materials.

**Table 3.3** Stimulated emission cross-section ($\sigma_e$), gain band width ($\sigma_e \times \Delta \lambda_{\text{eff}}$), optical gain ($\sigma_e \times \tau_r$), experimental and calculated branching ratios for the $^5D_4$ transition Tb$^{3+}$ in Tb$_2$(MoO$_4$)$_3$ nanophosphor.

<table>
<thead>
<tr>
<th>$^5D_4 \rightarrow$</th>
<th>Energy (cm$^{-1}$)</th>
<th>$\Delta \lambda_{\text{eff}}$ (nm)</th>
<th>$\sigma_e$ ($10^{-23}$ cm$^2$)</th>
<th>$\sigma_e \times \Delta \lambda_{\text{eff}}$ ($10^{-30}$ cm$^3$)</th>
<th>$\sigma_e \times \tau_r$ ($10^{-26}$ cm$^2$S)</th>
<th>$\beta_{\text{exp}}$</th>
<th>$\beta_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^7F_6$</td>
<td>20408</td>
<td>8.491</td>
<td>0.0676</td>
<td>0.0575</td>
<td>0.033</td>
<td>30.63</td>
<td>12.52</td>
</tr>
<tr>
<td>$^7F_5$</td>
<td>18450</td>
<td>10.075</td>
<td>0.4999</td>
<td>0.5036</td>
<td>0.244</td>
<td>60.72</td>
<td>71.45</td>
</tr>
<tr>
<td>$^7F_4$</td>
<td>16949</td>
<td>17.021</td>
<td>0.0360</td>
<td>0.0613</td>
<td>0.017</td>
<td>8.64</td>
<td>6.46</td>
</tr>
</tbody>
</table>
Chapter 3

3.4.5 Luminescence decay analysis

Decay curve for the emission of Tb\(_2\)(MoO\(_4\))\(_3\) nanophosphor were recorded for \(5\text{D}_4 \rightarrow 7\text{F}_5\) (545 nm) transition of Tb\(^{3+}\) under 290 nm excitation and is given in Figure 3.9. The decay curves can be fitted well with single exponential function Eqn.2.17. The lifetime is found to be 0.38 ms which is close to the calculated radiative lifetime (\(\tau_R\)) from JO analysis. On the basis of the experimental and predicted lifetime values, the quantum efficiency (\(\eta\)) of the \(5\text{D}_4\) emitting level of Tb\(^{3+}\) ion can be determined. For rare earth ions, emission quantum efficiency (\(\eta\)) is equal to the ratio of the experimental fluorescence lifetime to the predicted lifetime given by Eqn.2.22 [28]. The quantum efficiency for \(5\text{D}_4 \rightarrow 7\text{F}_5\) transition of Tb\(_2\)(MoO\(_4\))\(_3\) nanophosphor is found to be 77% and this reasonably high value indicates its utility for green luminescence at 545 nm.

![Luminescence decay curve of Tb\(^{3+}\) in Tb\(_2\)(MoO\(_4\))\(_3\) nanophosphor.](image)

3.4.6 Energy transfer mechanism in Tb\(_2\)(MoO\(_4\))\(_3\) nanophosphor

Energy transfer study is a useful tool to understand the luminescence process associated with rare earth ions in any host. In
Tb$_2$(MoO$_4$)$_3$ the excitation and emission process involves absorption of UV radiation by MoO$_4^{2-}$, then the excitation energy is subsequently transferred to Tb$^{3+}$ ions by resonance interactions, and de-excitation process of Tb$^{3+}$, which yields their characteristic emissions. A summary of the emission and energy transfer process in Tb$_2$(MoO$_4$)$_3$ is schematically given in Figure 3.10. The energy levels of Tb$_2$(MoO$_4$)$_3$ are composed by oxygen 2$p$ state and molybdenum 4$d$ state [29]. Upon 290 nm UV excitation, an electron in the oxygen 2$p$ state (1$A_1$) (4$d$/5$d^2$–Mo$^{6+}$/2$p^6$ – O$^{2-}$ state) is excited into the 1$T_2$ level of molybdenum 4$d$ state in MoO$_4^{2-}$. The excited electron either relaxes to its lowest excited 1$T_1$ (4$d$/5$d^1$–M$^{5+}$/2$p^5$ – O$^-$ state) level of MoO$_4^{2-}$, producing emission by the transition to the 1$A_1$ level, or the excitation energy transfers to 7$D$ levels of Tb$^{3+}$ by resonance process.

The excitation energy of MoO$_4^{2-}$ is mostly transferred to 5$D_3$ or to the higher levels 7$D_1$ (4$f^6$5$d$) and 9$D_1$ (4$f^6$5$d$). The relaxation originates from 7$D_1$ (4$f^6$5$d$) and 9$D_1$ (4$f^6$5$d$) levels to the lowest excited state 5$D_4$ through multiphonon relaxation and thereby enhances the population of the 5$D_4$ level, resulting the enrichment of luminescence intensity. On the other hand, relaxation from 5$D_3$ to 5$D_4$ cannot happen by a multiphonon relaxation process due to the large energy difference between these two levels. But the relaxation occurs due to the resonance between the excited and the ground states of two Tb$^{3+}$ ions, which can be described as the cross relaxation process 5$D_3 + 7F_6 → 5D_4 + 7F_0$. High Tb$^{3+}$ concentrations shorten the distance between Tb$^{3+}$ ions and promotes the cross relaxation from 5$D_3$ to 5$D_4$ energy level. As a result, the emission peaks originating from 5$D_3$ level almost vanish and the green emission becomes intense.
3.4.7 CIE chromaticity coordinate analysis

The color purity of the luminescence emissions is commonly characterized by the Commission Internationale de l’Eclairage (CIE) coordinates. The CIE coordinates for the emission spectra of Tb$_2$(MoO$_4$)$_3$ with different excitation wavelengths are resolved as, $x = 0.3362$, $y = 0.5004$ at 290 nm (a) and $x = 0.3127$, $y = 0.5538$ at 376 nm (b) and are shown in Figure 3.11. The small difference in the values is due to the contribution of self-activated broad emission band of molybdate on exciting the CTB of MoO$_4^{2-}$ (290 nm), which is absent in direct excitation of $f$-$f$ transition (376 nm). They all spot in the yellowish green and green region due to the combination of blue emission from MoO$_4^{2-}$ and $^5D_4 \rightarrow ^7F_6$ of Tb$^{3+}$ at 490 nm, green emission from $^5D_4 \rightarrow ^7F_5$ of Tb$^{3+}$ at 545 nm, orange to red light from $^5D_4 \rightarrow ^7F_4$ at 586 nm and $^5D_4 \rightarrow ^7F_3$ at 619 nm of Tb$^{3+}$. The digital photographs of the samples under 290 and 376 nm excitation using UV lamp are shown in the inset Figure 3.11, which is in concurrence with the result of CIE hue diagram.
Terbium molybdate nanophosphors were prepared by the conventional sol-gel method. The X-ray diffraction studies revealed that the samples crystallize in monoclinic and orthorhombic phase depending on the annealing temperature. TEM analysis revealed that the nanophosphors are spherically shaped with uniform size around 35 nm. Raman and FTIR analysis confirmed the vibrational modes as well as the functional groups associated with the sample. Using the JO theory, the intensity parameters, spontaneous emission probabilities and radiative lifetimes of Tb$^{3+}$ ions in Tb$_2$(MoO$_4$)$_3$ were determined. JO intensity parameters were found to be in the order $\Omega_2 > \Omega_4 > \Omega_6$. The higher value of $\Omega_2$ and positive value of bonding parameter is an indication of the dominant covalent nature between Tb$^{3+}$ - O$^2$ ligand bond. The high value
of stimulated emission cross-section and branching ratio for the $^5D_4 \rightarrow ^7F_5$ transition with reasonably high quantum efficiency suggests its potential application in various photonic devices. The energy transfer, as well as luminescence intensity in orthorhombic phase, was found to be more efficient than monoclinic phase when sensitizing the host lattice. The activation of Tb$^{3+}$ ion through sensitizing MoO$_4^{2-}$ groups in the host lattices and sensitizing Tb$^{3+}$ ions directly via the $f-f$ transitions are discussed. The decay curves exhibit single exponential nature and fluorescence lifetime values are found to be shorter which are favorable for LED application. The chromaticity color coordinates confirmed the feasibility to generate green light under UV excitation. We conclude that the Tb$_2$(MoO$_4$)$_3$ is a stable, efficient, and potential green phosphor for future SSL devices.

References


