Chapter IV

Synthesis, Structural and Spectroscopic Characterization of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ Nanophosphors

This chapter describes the synthesis of Sm$^{3+}$ activated Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ nanophosphors through sol-gel method and investigation of their structural, spectroscopic and optical properties. The structure, morphology and composition of the prepared phosphors were analyzed using XRD, TEM, Raman and FTIR analysis. The spectroscopic and laser parameters of Sm$^{3+}$ in Tb$_{2-x}$(MoO$_4$)$_3$ matrix were evaluated using Judd–Ofelt theoretical analysis. The photoluminescence excitation spectra suggest that this novel phosphor can be excited over a broad range from n-UV to blue light (300-490nm). The photoluminescence studies shows that the emission color of the phosphors can be tuned and white emission in a single composition can be obtained under host excitation due to an energy transfer from MoO$_4^{2-}$ → Sm$^{3+}$/Tb$^{3+}$ and Tb$^{3+}$ → Sm$^{3+}$. These phosphors might be a promising material for n-UV LEDs and can exhibit tricolor luminescence under single excitation wavelength.
4.1 Introduction

The development of new single component RGB phosphors for WLEDs with single excitation wavelength is one of the prime challenging targets in solid state lighting technology [1-3]. Rare earth ions are considered to be a preferable activators for phosphors since they emit over the entire spectral range. The rare earth ion, Sm$^{3+}$ shows its characteristic emissions in the orange-red region due to $^4G_{5/2} \rightarrow ^4H_{J/2}$ ($J = 5, 7, 9, 11$) transitions and are expected to possess superior red color purity [4, 5]. Moreover, Tb$^{3+}$ is one of the most frequently used green emitter possessing weak blue and intense green emissions due to $^5D_4 \rightarrow ^7F_J$ ($J = 4, 5, 6$) transitions [6, 7]. Most of the rare earth ions exhibit weak absorption in the UV region on account of the low oscillator strength. Due to this reason, it is important to choose a host that has intense and broad excitation band in the UV region in order to sensitize the rare earth ion. In this regard, molybdates are excellent candidates due to its high UV absorption efficiency and self-activated luminescence characteristics [8]. The MoO$_4^{2-}$ ligand can absorb the UV/blue radiations and efficiently transfer the energy to Ln$^{3+}$ ions thereby producing strong emission in the visible region [9]. Also, the molybdate exhibits a broad blue emission attributed to the $^1T_1 \rightarrow ^1A_1$ transition of MoO$_4^{2-}$ group. Therefore, it is desirable to produce white-emitting phosphors by the combination of RGB emissions from Sm$^{3+}$, Tb$^{3+}$ and MoO$_4^{2-}$ group. The emission from the $^5D_3$ energy level of Tb$^{3+}$ overlap well with the $^6H_{5/2}$, $^4D_{5/2}$, $^4K_{11/2}$, $^6P_{5/2}$, $^4G_{9/2}$ and $^4F_{5/2}$ transitions of Sm$^{3+}$ by which the resonant energy transfer from Tb $\rightarrow$ Sm occurs easily [10]. Here we choose Tb$_2$(MoO$_4$)$_3$ as a host, with Sm$^{3+}$ as activator ion in order to attain color-tunable emissions including white light.

The multicolor emitting Sm$^{3+}$ activated Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ nanophosphors presented in this chapter were prepared via sol-gel method.
and its structural and optical properties were investigated. X-ray powder
diffraction, TEM and EDS, Raman and FTIR spectra of the samples were
recorded and analyzed. Optical characterizations have been carried out
through absorption, excitation, emission spectra and decay profile analysis.
The Judd-Ofelt intensity parameters, radiative properties of \( ^{4}G_{5/2} \) level of
Sm\(^{3+} \) emissions were determined within the framework of Judd-Ofelt (JO)
theory. The laser characteristic parameters such as stimulated emission
cross-section, gain bandwidth and optical gain were also evaluated. The
theoretically predicted values were compared with the experimental
results. The characteristic green luminescence of Tb\(^{3+} \) ion, strong orange-
red emission of Sm\(^{3+} \) and weak broad blue band due to MoO\(_{4}^{2-} \) group
render white light emission under UV excitation as well as tunable emissions by monitoring the energy transfer from Tb\(^{3+} \) to Sm\(^{3+} \) ions.
Sensitization of Sm\(^{3+} \) is explained in terms of energy transfer through
MoO\(_{4}^{2-} \) → Tb/Sm and Tb → Sm channels. The luminescence lifetime,
chromaticity coordinates and CCT values of the samples were also
determined.

### 4.2 Synthesis of Tb\(_{2-x}\)Sm\(_{x}\)(MoO\(_{4}\))\(_{3}\) nanophosphor

The \( \text{Tb}_{2-x}\text{Sm}_{x}(\text{MoO}_{4})_{3} \) (\( x = 0.001, 0.0014, 0.002, 0.006, 0.008, 0.01 \))
nanophosphors investigated in this work were synthesized by sol-gel method.
MoO\(_{3} \) (Merck 99.9%), Tb(NO\(_{3}\))\(_{3}\).6H\(_{2}O \) (CDH, 99.9%), Sm(NO\(_{3}\))\(_{3}\).6H\(_{2}O \) (CDH,
99.9%), citric acid (CDH 99.9%) and PVA (Poly Vinyl Alcohol) of analytical
grade were used for the synthesis. The molar ratio of the rare earth ions to
molybdenum ions was kept at 2:3 and that between total metal ions (rare
earths and molybdenum), citric acid and PVA was maintained at 1:1:1. A
stoichiometric mixture of MoO\(_{3} \) and citric acid was prepared in distilled
water and kept for magnetic stirring at 80 °C. Aqueous solutions of
Tb(NO\(_{3}\))\(_{3}\).6H\(_{2}O \) and Sm(NO\(_{3}\))\(_{3}\).6H\(_{2}O \) in stoichiometric ratio were added to
the above solution to get a clear sol. The sol was subsequently polymerized by the addition of PVA and at 90 °C, it forms the gel. The gel was then slowly heated to 120 °C for further drying. The dried gels were pyrolyzed at 450 °C for 2h to get an amorphous precursor. The resulting precursor was grounded, placed in a ceramic crucible and annealed at 900 °C for 2h to get yellowish white powder of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$.

4.3 Structural characterization of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$

The crystalline nature and phase of the prepared samples were investigated using X-ray powder diffraction studies on X’Pert Pro PANalytical X-ray diffractometer. The microstructure, morphology and composition of the samples were investigated by utilizing the HRTEM, SAED and EDS spectra on a high-resolution transmission electron microscope JEOL, JEM-2100 operated at 200 kV. The FTIR spectra of the powder samples were recorded on a Shimadzu 8400S FTIR Spectrometer. Raman spectra of the sample was collected using HORIBA Jobin Yvon Lab Ram HR Raman spectrometer with Argon ion laser 514.5 nm as the excitation source.

4.3.1 X-ray powder diffraction studies

X-ray powder diffraction patterns of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ nanophosphors with varying doping concentration of Sm$^{3+}$ were recorded in the 2θ range 10-60° and are given in Figure 4.1. The crystalline nature of all the samples is revealed by sharp peaks in XRD patterns. The phase purity of the prepared
samples is confirmed by comparing the observed powder XRD patterns with the standard ICDD reference pattern. All the diffraction patterns are identical and match well with the orthorhombic phase of $\text{Tb}_2\text{(MoO}_4\text{)}_3$ having ICDD 84-0085. The doping with $\text{Sm}^{3+}$ ions does not affect the crystal structure of host lattice since $\text{Sm}^{3+}$ substitutes $\text{Tb}^{3+}$ ions owing to their similar chemical valences and comparable ionic radii ($\text{Tb}^{3+}$-1.18 Å, $\text{Sm}^{3+}$-1.22 Å). The average crystallite size calculated using Scherrer equation was found to be 35 nm.

4.3.2 Transmission electron microscopy analysis

TEM, HRTEM, SAED and EDS analysis were done to study the microstructure, morphology and composition of the prepared phosphor. The TEM images of the two representative samples of $\text{Tb}_{2-x}\text{Sm}_x\text{(MoO}_4\text{)}_3$ with $x = 0.002$ and 0.008 are shown in Figure 4.2(a) and (b) respectively. The images reveal that particles have spherical morphology with almost uniform size distribution. It is also noted that there is no significant change in the morphology and size with increase in the concentration of $\text{Sm}^{3+}$ and
the average particle size is around 30-35 nm for the respective samples. This further implies that Sm$^{3+}$ doping has little effect on the morphological features of the samples. HRTEM images exhibit clear lattice fringes without any distortion, indicating that the nanophosphors are highly crystalline in nature, as shown in Figure 4.2(c). The well-defined lattice fringes with a d spacing of 3.45 Å corresponds to the (221) crystal plane of the orthorhombic Tb$_2$(MoO$_4$)$_3$ and is marked by arrows. The calculated d spacing is in agreement with the d$_{221}$ spacing of the corresponding plane of the X-ray diffraction pattern (3.44 Å) and ICDD value (3.4654 Å). The concentric rings of bright diffraction spots in the SAED pattern confirms the polycrystalline nature of the sample and is shown in Figure 4.2(d). The EDS spectra of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ (x = 0.008) is presented in Figure 4.2(e). The spectra reveal the presence of Tb, Sm, Mo and O as constituent elements without any impurity peaks thereby confirming the purity of the material.

Figure 4.2 TEM images of (a) x = 0.002, (b) x = 0.008, (c) HRTEM (d) SAED and (e) EDS pattern of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ (x = 0.008) nanophosphor.
4.3.3 Raman spectroscopy

Raman spectra are sensitive to crystallization, structural disorder and defects in micro and nanostructures. In Raman spectra, any changes in lattice spacing and chemical environment produce shift in the vibrational frequencies of the spectra. In Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ it is expected that Sm$^{3+}$ ions replace the Tb$^{3+}$ ions and are found to crystallize in the same orthorhombic structure of Tb$_2$(MoO$_4$)$_3$. Raman spectrum of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ (x = 0.008) nanophosphor is collected in the range 50-1000 cm$^{-1}$ and is shown in Figure 4.3.

The Raman active bands are observed at 903, 850, 354 cm$^{-1}$ and both Raman and IR active bands at 960, 942 201, 327, 150, 102, 821, 746 and 388 cm$^{-1}$ respectively [11]. The symmetric stretching vibrations of MoO$_4$ tetrahedra are peaked at 960 and 942 cm$^{-1}$ with a shoulder peak at 903 cm$^{-1}$. Asymmetric stretching vibrations are observed at 746, 850 and 821 cm$^{-1}$ [12]. Asymmetric and symmetric bending vibrations of the MoO$_4^{2-}$ tetrahedra are

![Figure 4.3](image)

**Figure 4.3** Raman spectrum of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ (x = 0.008) nanophosphor.
located at 388, 354 and 327 cm\(^{-1}\), with the translational and rotational modes of the molybdate ion around 201, 150, and 102 cm\(^{-1}\). The analysis of the Raman spectra indicated that there is no significant peak shift or missing of peaks on Sm\(^{3+}\) doping when compared with pure Tb\(_2\)(MoO\(_4\))\(_3\), which means that Sm\(^{3+}\) ions are effectively incorporated into the Tb\(_2\)(MoO\(_4\))\(_3\) host.

4.3.4 Fourier transform infrared spectroscopy analysis

FTIR analysis provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. The FTIR technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. FTIR spectra of Tb\(_2\)(MoO\(_4\)) and Tb\(_{2-x}\)Sm\(_x\)(MoO\(_4\))\(_3\) (x = 0.008) nanophosphors were recorded in the range 450–4000 cm\(^{-1}\) and is shown in Figure 4.4. It is observed that even for higher doping concentrations of Sm\(^{3+}\), no change has been found in the peak positions of FTIR spectra compared to Tb\(_2\)(MoO\(_4\))\(_3\) which indicates that there are no

![Figure 4.4](image-url)

**Figure 4.4** FTIR spectra of pure Tb\(_2\)(MoO\(_4\)) and Tb\(_{2-x}\)Sm\(_x\)(MoO\(_4\))\(_3\) (x = 0.008).
Synthesis of $Tb_{2-x}Sm_x(MoO_4)_3$ Nanophosphors

structural changes in the host lattice with doping Sm$^{3+}$ ions. The bands occurring at 945 and 920 cm$^{-1}$ are due to the symmetric stretching modes of Mo–O bonds in MoO$_4$ tetrahedra. The broadband situated at 740 cm$^{-1}$ is ascribed to asymmetric stretching vibrations of Mo-O-Mo bonds in MoO$_4$ [13]. The bands at 3422, 1636, correspond to H–O–H bending and O–H stretching vibrations of water molecules present on the surface of the phosphor sample.

4.4 Optical characterization of $Tb_{2-x}Sm_x(MoO_4)_3$ nanophosphor

The optical properties of the nanophosphors were investigated using UV-Vis-NIR absorption spectra, photoluminescence excitation, emission spectra and fluorescence lifetime analysis etc. The absorption spectra were recorded with a JASCO, V-670, UV-Vis-NIR spectrophotometer. Photoluminescence measurements were performed using HORIBA, Jobin Yvon, Fluoro Max-4 spectrofluorometer with a 450-W xenon lamp as the excitation source. The fluorescence lifetime measurements were carried out on Jobin Yvon Fluorolog-3 equipped with a 150 W xenon lamp as the excitation source.

4.4.1 UV–Vis-NIR spectroscopy

The absorption studies in UV-Vis-NIR region are widely used for the quantitative and qualitative determination of the ions present in the sample. The peaks in the absorption spectra correspond to the wavelength of radiation whose energy is equal to that required for an electronic transition. The absorption spectra of $Tb_{2-x}Sm_x(MoO_4)_3$ ($x = 0.008$) nanophosphor in the UV-Vis-NIR region is shown Figure 4.5. In the UV region spectra exhibit a broad absorption band peaked at 290 nm owing to the CTB due to electron transfer from O$^{2-}$ $\rightarrow$ Mo$^{6+}$/Sm$^{3+}$ ions and the spin allowed 4f$^5$5d transition of Tb$^{3+}$ [14-16]. The 4f$^5$5d transition of Tb$^{3+}$ from its ground state 4f$^8$ to its 4f$^5$5d$^1$ excited state and the O$^{2-}$ - Sm$^{3+}$ charge transfer
band usually found in the 250–300 nm range could not be observed distinctly due to their overlapping with the $O^{2-} \rightarrow Mo^{6+}$ charge transfer band. The absorption spectrum consists of several sharp peaks in the Vis-NIR region due to the intra configurational $f-f$ transitions of Sm$^{3+}$ from the ground state $^6H_{5/2}$ to the various excited states and are observed at 378 ($^6P_{7/2}$, $^4D_{1/2}$, $^4L_{17/2}$), 405 ($^6P_{3/2}$, $^4F_{7/2}$), 464 ($^4H_{13/2}$), 946 ($^6F_{11/2}$), 1090 ($^6F_{9/2}$), 1245 ($^6F_{7/2}$), 1400 ($^6F_{5/2}$), 1505 ($^6F_{3/2}$) and 1567 nm ($^6F_{1/2}$) \cite{17,18}. There is only one clearly visible absorption band of Tb$^{3+}$ ion is observed, which is due to the transition from the ground state $^7F_6$ to the excited state $^5D_4$ at 485 nm \cite{19,20}.

In the NIR region, spectra contain most intense $f-f$ transitions due to spin-allowed transition ($\Delta S = 0$) of Sm$^{3+}$ from the ground state $^6H_{5/2}$ to the various $^6F_J$ and $^6H_J$ levels. In the UV–Vis region the energy levels are closely spaced because of the overlap of $2s^{2}l_{J}$ energy levels \cite{21}. The absorption spectra of all the samples show similar spectral behavior (except for the variation in the intensity of $f-f$ transition). As the representative, we have chosen the sample with $x = 0.008$, for UV studies because the intensity of Sm$^{3+}$ emission was maximum for this concentration.

Figure 4.5 Optical absorption spectra of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ ($x = 0.008$) nanophosphor in the UV–Vis-NIR region.
4.4.2 Judd-Ofelt analysis

The JO analysis is a powerful tool for calculating the parity-forbidden electric-dipole radiative transition rates between the various levels of the rare earth ions [22, 23]. Through this analysis, the local environment around the metal ion and the bond covalency of metal-ligand bonds can be interpreted. Apart from this, the intensity, radiative and stimulated emission parameters of Sm$^{3+}$ ions in Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ can also be computed.

Oscillator strength and Judd-Ofelt intensity parameters

The oscillator strengths of induced electric-dipole transition between $^6H_{5/2}$ to various excited states of Sm$^{3+}$ are calculated from the absorption spectra of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ (x = 0.008) nanophosphor. The absorption transitions, peak positions, experimental and calculated oscillator strengths along with Judd-Ofelt intensity parameters are given in Table 4.1. Here the

<table>
<thead>
<tr>
<th>SI No.</th>
<th>$\text{S}'\text{L}'\text{J}'$</th>
<th>$^6H_{5/2} \rightarrow$</th>
<th>$E_{\text{exp}}$ in host ($\bar{\nu}_c$) cm$^{-1}$</th>
<th>$E_{\text{exp}}$ in aqua ($\bar{\nu}_a$) cm$^{-1}$</th>
<th>$f_{\text{exp}}$</th>
<th>$f_{\text{cal}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$^4D_{1/2}$</td>
<td>26455</td>
<td>26573</td>
<td>0.1780</td>
<td>0.0011</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$^4F_{7/2}$</td>
<td>24691</td>
<td>24775</td>
<td>0.5480</td>
<td>0.0107</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$^4I_{13/2}$</td>
<td>21551</td>
<td>21650</td>
<td>0.0606</td>
<td>0.0904</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$^4F_{11/2}$</td>
<td>10548</td>
<td>10517</td>
<td>0.0495</td>
<td>0.0832</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$^6F_{9/2}$</td>
<td>9174</td>
<td>9136</td>
<td>0.4380</td>
<td>0.4752</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$^6F_{7/2}$</td>
<td>8032</td>
<td>7977</td>
<td>0.1509</td>
<td>0.8196</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>$^6F_{5/2}$</td>
<td>7142</td>
<td>7131</td>
<td>0.9290</td>
<td>0.6160</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$^6F_{3/2}$</td>
<td>6644</td>
<td>6641</td>
<td>0.5830</td>
<td>0.6213</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>$^6F_{1/2}$</td>
<td>6381</td>
<td>6397</td>
<td>0.4690</td>
<td>0.4836</td>
<td></td>
</tr>
</tbody>
</table>

$\beta = 0.9948$, $\delta = 0.520$
low value of root mean square deviation 0.432x10^{-7} indicates a reasonable agreement between the experimentally and theoretically calculated oscillator strengths and supports the validity of JO analysis for predicting the spectral intensities of Sm^{3+} in Tb_{2-x}Sm_{x}(MoO_{4})_{3}.

The JO intensity parameters are found to be

\[ \Omega_2 = 1.244 \times 10^{-20} \]
\[ \Omega_4 = 0.786 \times 10^{-20} \]
\[ \Omega_6 = 0.460 \times 10^{-20} \]

The observed trend of JO intensity parameters \( \Omega_2 > \Omega_4 > \Omega_6 \) confirmed the covalent bond between Sm^{3+} - O^{2-} and low symmetry of the co-ordination surrounding of Sm^{3+} ions in Tb_{2}(MoO_{4})_{3} host. The magnitude of \( \Omega_2 \) indicates the possession of Sm^{3+} ion with high charge density by which it could polarize the O^{2-} anion to a much greater extent. As a result electron cloud get expanded due to large molecular orbital overlap between the f orbital of the Sm^{3+} and the p orbital of the O^{2-}, thereby producing bonds with less ionic and more covalent character [24]. Nephelauxetic ratio (\( \beta \)) and bonding parameter (\( \delta \)) are found to be 0.9948 and 0.520 respectively. The positive value of the bonding parameter indicates the covalent nature of the Sm^{3+} to ligand bond [25] and is in agreement with the result obtained from JO intensity parameter calculation.

**Radiative properties**

The emission properties of rare earth doped material can be easily determined by evaluating the radiative properties. The radiative properties for the \( ^{4}G_{5/2} \) excited state of Sm^{3+} ions are calculated using JO intensity parameters. The electric (\( S_{el} \)) and magnetic (\( S_{md} \)) dipole line strengths,
Synthesis …………Tb

2-x

Sm

x

(MoO

4

)3

Nanophosphors

91

electric (\(A_{ed}\)) and magnetic-dipole (\(A_{md}\)) transition probability, transition probability (\(A_{R}\)) and calculated branching ratio (\(\beta_{R}\)) of Sm\(^{3+}\) ion in Tb\(_{2-x}\)Sm\(_{x}\)(MoO\(_4\))\(_3\) (\(x = 0.008\)) nanophosphor is summarized in Table 4.2.

Table 4.2 Calculated radiative parameters of Sm\(^{3+}\) in Tb\(_{2-x}\)Sm\(_{x}\)(MoO\(_4\))\(_3\).

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>(S')('L')('J')</th>
<th>Energy (cm(^{-1}))</th>
<th>(S_{ed}) (10(^{-22}))</th>
<th>(S_{md}) (10(^{-22}))</th>
<th>(A_{ed}) (s(^{-1}))</th>
<th>(A_{md}) (s(^{-1}))</th>
<th>(A_{R}) (s(^{-1}))</th>
<th>(\beta_{R})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(^6)H(_5/2)</td>
<td>17724</td>
<td>0.08</td>
<td>0.58</td>
<td>3.23</td>
<td>24.71</td>
<td>27.94</td>
<td>19.79</td>
</tr>
<tr>
<td>2</td>
<td>(^6)H(_7/2)</td>
<td>16647</td>
<td>1.10</td>
<td>0.58</td>
<td>36.97</td>
<td>20.48</td>
<td>57.45</td>
<td>38.38</td>
</tr>
<tr>
<td>3</td>
<td>(^6)H(_9/2)</td>
<td>15396</td>
<td>2.03</td>
<td>0.00</td>
<td>53.93</td>
<td>0.00</td>
<td>53.93</td>
<td>36.02</td>
</tr>
<tr>
<td>4</td>
<td>(^6)H(_{11/2})</td>
<td>14025</td>
<td>0.52</td>
<td>0.00</td>
<td>10.37</td>
<td>0.00</td>
<td>10.37</td>
<td>5.88</td>
</tr>
</tbody>
</table>

The emission transitions contain both electric and magnetic dipole contributions as evident from the Table. The transition \(^6\)H\(_5/2\) is a magnetic dipole transition while \(^6\)H\(_7/2\) has both electric and magnetic dipole contributions in which the electric dipole contribution is the major component. The other two transitions \(^6\)H\(_9/2\) and \(^6\)H\(_{11/2}\) are purely electric dipole transitions since the magnetic dipole line strength is zero for both these transitions. From Table 4.2, it is observed that the calculated branching ratio \(\beta_{R}\) is maximum for \(^4\)G\(_5/2\) \(\rightarrow\) \(^6\)H\(_7/2\) transition and follows a decreasing trend for \(^6\)H\(_9/2\), \(^6\)H\(_5/2\) and \(^6\)H\(_{11/2}\) and a similar trend is expected in emission spectra.

4.4.3 Photoluminescence studies

4.4.3.1 Excitation spectra

The excitation spectra of Tb\(_{2-x}\)Sm\(_{x}\)(MoO\(_4\))\(_3\) nanophosphors by monitoring the \(^4\)G\(_5/2\) \(\rightarrow\) \(^6\)H\(_7/2\) transition of Sm\(^{3+}\) at 602 nm and \(^5\)D\(_4\) \(\rightarrow\) \(^7\)F\(_5\) transition of Tb\(^{3+}\) at 545 nm are shown in Figure 4.6(a) and (b) respectively.
In Figure 4.6(a) all the spectra exhibit a broad band ranging from 280-330 nm and sharp peaks of excitation beyond 350 nm. The broadband of excitation peaking around 290 nm is ascribed to the combined effect of the CTB of $O^{2-} \rightarrow Mo^{6+}/Sm^{3+}$ and the spin-allowed $4f^8 \rightarrow 4f^7 5d^1$ transition of $Tb^{3+}$ [26, 27]. The $O^{2-} \rightarrow Sm^{3+}$ charge transfer band and the $4f-5d$ transitions of $Tb^{3+}$ are typically not seen distinctly in the excitation spectrum since it overlaps with $O^{2-} \rightarrow Mo^{6+}$ charge transfer band. The existence of $O^{2-} \rightarrow Mo^{6+}$ charge transfer band on monitoring $Sm^{3+}$ emission at 602 nm indicates an energy transfer from $MoO_4^{2-}$ to $Sm^{3+}/Tb^{3+}$ in the $Tb_{2-x}Sm_x(MoO_4)_3$ phosphors. The intense sharp peaks observed between 350-500 nm are ascribed to intra-configurational ($f-f$) transitions of the $Tb^{3+}$ and $Sm^{3+}$ ions. The characteristic $f-f$ transition of $Tb^{3+}$ ions are due to the electronic transitions from ground state $7F_6$ to the different excited states $^5D_0$ (338 nm), $^5G_2$ (348 nm), $^5D_2$ (356 nm), $^5L_{10}$ (363 nm), $^5G_6$ (372 nm), $^5D_3$ (376 nm) and $^5D_4$ (485 nm) and that of samarium are from $^6H_{5/2}$ to $^4K_{15/2}$ (380 nm), $^6P_{3/2}$ (402 nm), ($^6P$, $^4P$)$_{5/2}$ (417 nm), $^4G_{9/2}$ (439 nm), $^4F_{5/2}$ (450 nm), $^4I_{13/2}$ (462 nm) and $^4I_{11/2}$ (470 nm) respectively [28].

![Figure 4.6](image.png)

**Figure 4.6** Excitation spectra of $Tb_{2-x}Sm_x(MoO_4)_3$ nanophosphor (a) Concentration dependent spectra monitored at 602 nm with $x = 0.0014$, 0.008 (b) monitored at 545 nm with $x = 0.008$. 
The intensity of f-f transitions of Sm$^{3+}$ is more than that of the charge transfer band and it increases with Sm$^{3+}$ doping concentration due to the more availability of Sm$^{3+}$ ions to take part in the excitation process. This further indicates the effective incorporation of Sm$^{3+}$ in Tb$_2$(MoO$_4$)$_3$ host as well as the energy transfer from the charge transfer band to the Sm$^{3+}$ levels. n-UV and blue wavelength excitations are one of the prime prerequisites for a phosphor material for use in generating white light in phosphor converted WLEDs. The intense excitation peaks observed for Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ nanophosphors between 350 - 490 nm suggests that these phosphors can be effectively excited by radiations in the n-UV and blue wavelength indicating the suitability for n-UV pumped WLED application.

The excitation spectra recorded by monitoring the emission peak of Tb$^{3+}$ at 545 nm is shown in Figure 4.6(b). As in the previous case the broadband observed in the shorter wavelength region is ascribed to the CTB of MoO$_4^{2-}$ and 4f $\rightarrow$ 5d transition of Tb$^{3+}$. In the longer wavelength region, the peaks corresponding to the f-f transitions of Tb$^{3+}$ are present, but excitation peaks of Sm$^{3+}$ are absent, which further indicates the absence of energy transfer from Sm$^{3+}$ to Tb$^{3+}$.

### 4.4.3.2 Emission spectra

The photoluminescence emission properties of the phosphors were studied to explore its potential as a phosphor candidate for SSL applications. The emission spectra of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ (x = 0.001, 0.0014, 0.002, 0.006, 0.008 and 0.01) nanophosphor under 290 nm excitation are given in Figure 4.7(a). At lower doping concentrations of Sm$^{3+}$, the spectra exhibits strong emission bands of Tb$^{3+}$ due to $^5$D$_4$ to $^7$F$_6$ (490 nm) and $^7$F$_5$ (545 nm) transitions together with weak emission peaks of Sm$^{3+}$ from $^4$G$_{5/2}$ to $^6$H$_{5/2}$ (564 nm), $^6$H$_{7/2}$ (602 nm), $^6$H$_{9/2}$ (650 nm) and $^6$H$_{11/2}$ (702 nm) transitions [29, 30] as shown in the inset of Figure 4.7(a). But at higher
concentrations the spectra is dominated by the emission bands of Sm$^{3+}$, while Tb$^{3+}$ emissions bands become very weak due to the enhancement of energy transfer from Tb$^{3+}$ to Sm$^{3+}$ ions as well as the more availability of Sm$^{3+}$ ions.

It is well known that lower doping concentrations of activator (Sm$^{3+}$) lead to weak luminescence while higher doping concentrations cause quenching of the luminescence of (Sm$^{3+}$) [31]. In order to understand the optimum Sm$^{3+}$ concentration for maximum intensity, a graph is plotted between emission intensity of Sm$^{3+}$ at 602 nm and the emission intensity of Tb$^{3+}$ at 545 nm for different compositions of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ nanophosphor under 290 nm excitation and is shown in Figure 4.7(b). From the figure, it is evident that an increase in Sm$^{3+}$ content results in the decrease of Tb$^{3+}$ emission intensity due to the energy transfer from Tb$^{3+}$ to Sm$^{3+}$. The emission intensity of Sm$^{3+}$ reached the maximum at $x = 0.008$, beyond which it is quenched due to concentration quenching.

The concentration quenching is mainly due to cross relaxation among two neighboring rare earth ions. As the doping concentration
reaches a certain level, the distance between Sm$^{3+}$ ions become smaller (less than a critical value) resulting an increase of cross-relaxation among Sm$^{3+}$ ions, as $\text{Sm}^{3+} (4G_{5/2}) + \text{Sm}^{3+} (6H_{5/2})/\text{Sm}^{3+} (6F_{9/2}) + \text{Sm}^{3+} (6F_{5/2})$. In Tb$_{2-x}Sm_x$(MoO$_4$)$_3$ the maximum emission intensity was observed for a relatively low doping concentration of Sm$^{3+}$ in Tb$_2$(MoO$_4$)$_3$ host matrix. The reason is, if the energy levels of the transitions $4G_{5/2} \rightarrow 6F_{9/2}$ and $6H_{5/2} \rightarrow 6F_{9/2}$ of Sm$^{3+}$ ion are approximately equal then the concentration quenching can be easily occurred [32].

**The critical distance and interaction parameter**

The non-radiative energy transfer from a sensitizer to an activator occurs either through exchange interaction or electric multipole-multipole interaction [33]. In order to understand the type of interaction involved in energy transfer, Blasse proposed an equation to find critical separation between the sensitizer (donor) and activator (acceptor, quenching site) known as the critical transfer distance ($R_c$) which the probability of the non-radiative transfer is equal to the probability of the radiative emission [34]. The critical concentration of the activator ion is estimated from the following relation [35],

$$R_c = 2\left(\frac{3V}{4\pi N_c N}\right)^{1/3}$$  \hspace{1cm} (4.1)

where $V$ is the unit cell volume, $N$ is the number of available crystallographic sites occupied by the activator ions in the unit cell and $x_c$ is the critical dopant (activator) concentration. For Tb$_{2-x}Sm_x$(MoO$_4$)$_3$ ($x = 0.008$) nanophosphor, the values of, $N$, $V$ and $x_c$ are 4, 1142.12 Å$^3$ and 0.008 respectively and the estimated $R_c$ is found to be 8.83 Å. It is well known that if non-radiative energy transfer take place via exchange interaction, the critical distance between the sensitizer and activator should
be less than 5 Å [36]. Here the calculated value of \( R_c \) is not less than 5 Å indicating that the non-radiative energy transfer in this system is governed by the electric multipole-multipole interaction with little possibility of energy transfer via the exchange interaction [37]. When the number of Sm\(^{3+}\) ions in the matrix is increased, the distance between Tb\(^{3+}\) and Sm\(^{3+}\) ions becomes shorter than 8.83 Å, the resonant energy transfer occurs. In Tb\(_2\)\(_{x}\)Sm\(_{x}\)(MoO\(_4\))\(_3\) efficient non-radiative energy transfer take place from Tb\(^{3+}\) to Sm\(^{3+}\) due to the well matching of the energy difference between \( ^{5}D_{4} \) and \( ^{7}F_{6} \) level of Tb\(^{3+}\) and \( ^{6}H_{5/2} \) and \( ^{4}G_{7/2} \) of Sm\(^{3+}\).

The above studies showed that multipole-multipole interaction can play a major role in energy transfer process. Van Uitert have studied the energy transfer interactions between rare earth ions and proposed a relation to find the energy transfer mechanism responsible for multipolar interactions between sensitizers or between sensitizer and activator relating the emission intensity and activator concentration [38, 39]. According to this, the relation between emission intensity and doping concentration can be expressed as,

\[
\frac{I}{x} = k \left[ 1 + \beta (x)^{m/3} \right]^{-1} \tag{4.3}
\]

where \( I \) is the emission intensity, \( x \) the Sm\(^{3+}\) concentration; \( I/x \) is the emission intensity per Sm\(^{3+}\) concentration; \( k \) and \( \beta \) are constants for each interaction for a given host lattice, \( m \) represents the type of electric multipolar interaction parameter which takes values as 6, 8, or 10, corresponds to dipole–dipole (d–d), dipole–quadrupole (d–q), or quadrupole–quadrupole (q–q), interactions respectively. The above equation can be rearranged for \( \beta (x)^{m/3} \) as follows [40].
\[ \log \left( \frac{I}{x} \right) = K' - \frac{m}{3} \log x \]  \hspace{1cm} (4.3)

where \( K' = \log K - \log \beta \). From the above equation, it can be found that \( \log \left( \frac{I}{x} \right) \) acts as a linear function of \( \log x \) with a slope of \(-\frac{m}{3}\). In order to understand the electric multipolar character \( (m) \), we plotted \( \log \left( \frac{I}{x} \right) \) versus \( \log x \) and shown in Figure 4.8.

![Figure 4.8](image_url)

**Figure 4.8** The plot of \( \log \left( \frac{I}{x} \right) \) versus \( \log x \) for \( \text{Tb}_{2-x}\text{Sm}_x\text{(MoO}_4)_3 \) nanophosphor.

The dependence of \( \log \left( \frac{I}{x} \right) \) on \( \log x \) was found to be relatively linear as shown in Figure 4.8 and the slope was determined to be -1.56, when varying the doping concentration of \( \text{Sm}^{3+} \) ions \( (x = 0.001 \text{ to } 0.008) \). The calculated value of \( m \) is 4.68 which is close to 6, implying that energy transfer from \( \text{Tb}^{3+} \) to \( \text{Sm}^{3+} \) occurs via dipole-dipole mechanism in \( \text{Tb}_{2-x}\text{Sm}_x\text{(MoO}_4)_3 \) nanophosphor.

The excitation spectra analysis revealed that the samples can be effectively excited at different excitation wavelengths owing to the intense excitation peaks observed at 376, 402 and 485 nm. Hence, the samples were
subjected to different excitation wavelengths, at host excitation band (290 nm), Tb$^{3+}$ (376, 485 nm) and Sm$^{3+}$ excitation (402 nm) and the observed spectra are depicted in Figure 4.9.

![Emission spectra of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ (x = 0.008) nanophosphor under (a) 290 (b) 376 (c) 485 and (d) 402 nm excitation.](image)

Figure 4.9 Emission spectra of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ (x = 0.008) nanophosphor under (a) 290 (b) 376 (c) 485 and (d) 402 nm excitation.

The emission spectra of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ (x = 0.008) samples under 290 nm UV excitation is given in Figure 4.9(a). The spectra mainly yield the emission peaks of Sm$^{3+}$ and Tb$^{3+}$. Among the transitions, $^4G_{5/2} \rightarrow ^6H_{7/2}$ of Sm$^{3+}$ at 602 nm have the maximum intensity. The emission spectra under host excitation suggest a direct energy transfer from MoO$_4^{2-}$ to Sm$^{3+}$ and Tb$^{3+}$ and to Sm$^{3+}$ through Tb$^{3+} \rightarrow$ Sm$^{3+}$ channel. Figure 4.9 (b) and (c) represent the emission spectra of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ (x = 0.008) by exciting the transitions of Tb$^{3+}$ at 376 and 485 nm which also results in the dominated emission of Sm$^{3+}$ together with Tb$^{3+}$ emissions. This is further
indicative of energy transfer from Tb\(^{3+}\) to Sm\(^{3+}\) and is due to the resonance between the respective energy levels. Figure 4.9(d) shows the emission spectra under 402 nm excitation (\(^{6}\)H\(_{5/2}\) → \(^{6}\)P\(_{3/2}\)) of Sm\(^{3+}\). In contrast to the other emission spectra, only Sm\(^{3+}\) emission bands at 564, 602, 648 and 702 nm are obtained confirming the absence of Sm\(^{3+}\) → Tb\(^{3+}\) energy transfer.

In the emission spectra, the peak correspond to \(^{4}\)G\(_{5/2}\) → \(^{6}\)H\(_{9/2}\) transition is electric dipole allowed transition and its intensity is sensitive to the local environment around Sm\(^{3+}\) ions. Whereas \(^{4}\)G\(_{5/2}\) → \(^{6}\)H\(_{5/2}\) transition belongs to the magnetic dipole allowed and its intensity shows very little variation with the crystal field strength surrounding the Sm\(^{3+}\) ions. Therefore, the intensity ratio of electric-dipole to magnetic-dipole transition, i.e. the asymmetry ratio (R), is widely used for probing the distortion of the local environment around the Sm\(^{3+}\) ion in the lattice. The asymmetry ratios calculated for the different doping concentrations of Sm\(^{3+}\) under 290 nm excitation are listed in Table 4.3.

**Table 4.3** Asymmetric ratio of the samples.

<table>
<thead>
<tr>
<th>Tb(<em>{2-x})Sm(</em>{x})(MoO(<em>{4}))(</em>{3})</th>
<th>Asymmetric ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.001</td>
<td>1.61</td>
</tr>
<tr>
<td>x = 0.002</td>
<td>1.83</td>
</tr>
<tr>
<td>x = 0.006</td>
<td>1.89</td>
</tr>
<tr>
<td>x = 0.008</td>
<td>1.91</td>
</tr>
</tbody>
</table>

From the table, it is observed that the luminescence asymmetric ratio (R) for the samples vary from 1.61 to 1.91. This result reveals that the asymmetry of the site occupied by Sm\(^{3+}\) ion in the Tb\(_{2}\)(MoO\(_{4}\))\(_{3}\) host lattice, which was already established by the value of \(\Omega_2\) and bonding parameter...
from JO analysis [41]. Moreover, the emission peaks are observed as two or three sub-peaks due to the Stark energy splitting, indicating a low symmetry around the Sm$^{3+}$ ions [42]. The dominance of $^4G_{5/2} \rightarrow ^6H_{5/2}$ electric dipole transition compared with $^4G_{5/2} \rightarrow ^6H_{5/2}$ magnetic dipole transition also indicates a lack of inversion center for the Sm$^{3+}$ ions in the lattice thereby suggesting that the site of Tb$^{3+}$ occupied by Sm$^{3+}$ ion is not an inversion center. The analysis of the local environment of Sm$^{3+}$ ion provided by emission spectroscopy is in good agreement with structural studies.

4.4.4 The stimulated emission parameters

The stimulated emission cross-section provides useful information about the potential laser performance of a material and it signifies the rate of energy extracted from the lasing material. The stimulated emission cross-section $\sigma_e$, gain bandwidth $\sigma_e \times \Delta \lambda_{eff}$, optical gain $\sigma_e \times \tau_r$ and experimental branching ratios ($\beta_{exp}$) for all the transitions of Sm$^{3+}$ in Tb$_2$(MoO$_4$)$_3$ are summarized in Table 4.4. From the table it is noted that the values of $\sigma_e$ for the $^4G_{5/2}$ emission transition of Sm$^{3+}$ are in the order $^6H_{7/2} > ^6H_{9/2} > ^6H_{5/2} > ^6H_{11/2}$ and a similar pattern is observed in the photoluminescence spectra under 290 nm excitation. Among the transitions

**Table 4.4** Stimulated emission cross-section ($\sigma_e$), gain band width ($\sigma_e \times \Delta \lambda_{eff}$), optical gain ($\sigma_e \times \tau_r$), experimental and calculated branching ratios for the $^4G_{5/2}$ transition of Sm$^{3+}$ in Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ (x= 0.008) nanophosphor.

<table>
<thead>
<tr>
<th>$^4G_{5/2}$</th>
<th>Energy (cm$^{-1}$)</th>
<th>$\Delta \lambda_{eff}$ (nm)</th>
<th>$\sigma_e$ (10$^{-23}$)</th>
<th>$\sigma_e \times \Delta \lambda_{eff}$ (10$^{-30}$) cm$^3$</th>
<th>$\sigma_e \times \tau_r$ (10$^{-25}$) cm$^2$S</th>
<th>$\beta_{exp}$</th>
<th>$\beta_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6H_{5/2}$</td>
<td>17724</td>
<td>8.86</td>
<td>6.912</td>
<td>0.6142</td>
<td>0.4624</td>
<td>13.39</td>
<td>19.79</td>
</tr>
<tr>
<td>$^6H_{7/2}$</td>
<td>16647</td>
<td>9.68</td>
<td>25.48</td>
<td>2.4675</td>
<td>1.7066</td>
<td>52.91</td>
<td>38.38</td>
</tr>
<tr>
<td>$^6H_{9/2}$</td>
<td>15396</td>
<td>15.52</td>
<td>11.79</td>
<td>1.8305</td>
<td>0.7898</td>
<td>25.84</td>
<td>36.02</td>
</tr>
<tr>
<td>$^6H_{11/2}$</td>
<td>14025</td>
<td>118.9</td>
<td>5.585</td>
<td>6.6416</td>
<td>0.3740</td>
<td>3.81</td>
<td>5.88</td>
</tr>
</tbody>
</table>
the $^{4}\text{G}_{5/2} \rightarrow ^{6}\text{H}_{7/2}$ exhibits relatively higher value for branching ratio and stimulated emission cross-section as compared to other transitions. For laser materials, it is highly desirable to have large emission cross-section to provide high gain. From the high value of gain bandwidth and optical gain ($2.4675 \times 10^{-30} \text{ cm}^3$ and $1.7066 \times 10^{-25} \text{ cm}^2 \text{ S}$) corresponding to $^{4}\text{G}_{5/2} \rightarrow ^{6}\text{H}_{7/2}$ transition, it may be concluded that $\text{Tb}_{2-x}\text{Sm}_x(\text{MoO}_4)_3$ ($x = 0.008$) is a promising material for optical application and its emission at 602 nm, can provide high gain bandwidth and optical gain for amplifiers.

4.4.5 Luminescence decay analysis and energy transfer efficiency

The luminescence decay is an important parameter that reflects the energy levels and energy transfer mechanism in a system. The existence of the energy transfer from $\text{Tb}^{3+}$ to $\text{Sm}^{3+}$ in $\text{Tb}_{2-x}\text{Sm}_x(\text{MoO}_4)_3$ is further confirmed by the dependence of the lifetime values of $^5\text{D}_4$ level of $\text{Tb}^{3+}$ on $\text{Sm}^{3+}$ doping. Figure 4.10(a) shows the decay profiles for $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of $\text{Tb}^{3+}$ in $\text{Tb}_{2-x}\text{Sm}_x(\text{MoO}_4)_3$ ($x = 0.002, 0.008$) nanophosphor under 290 nm excitation. The decay curves exhibit non-exponential nature and can be well fitted by a double-exponential function (Eqn.2.19). The double-exponential decay behavior of the activator is often observed when the excitation energy is transferred from the donor ($\text{Tb}^{3+}$) to acceptor ($\text{Sm}^{3+}$) [43]. On doping it is expected that $\text{Tb}^{3+}$ ions are replaced by the $\text{Sm}^{3+}$ in the matrix and the lifetime of the $^5\text{D}_4$ state of $\text{Tb}^{3+}$ should increase accordingly. But here the $^5\text{D}_4$ state of $\text{Tb}^{3+}$ shows fast fluorescence decay with $\text{Sm}^{3+}$ concentration and the lifetime was measured to be 0.18 and 0.01 ms for $x = 0.002$ and $x = 0.008$ of $\text{Sm}^{3+}$ respectively. This faster decay is a consequence of a non-radiative energy transfer from $\text{Tb}^{3+}$ to $\text{Sm}^{3+}$ [44]. In order to avoid fluorescence scintillating, the lifetime of phosphors used for LEDs should
be short. It can be seen that the lifetime of the present samples are much shorter and can find potential application in the above mentioned field.

![Figure 4.10](image-url)

**Figure 4.10** Decay curves of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ under excitation at 290 nm monitoring (a) $^5$D$_4 \rightarrow ^7$F$_5$ transition of Tb$^{3+}$ ($x = 0.002, 0.008$), (b) $^4$G$_{5/2} \rightarrow ^6$H$_{7/2}$ transition of Sm$^{3+}$ ($x = 0.008, 0.1$).

Figure 4.10(b) shows the decay curves of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ nanophosphors under 290 nm excitation, monitoring the $^4$G$_{5/2} \rightarrow ^6$H$_{7/2}$ transition of Sm$^{3+}$ at 602 nm and the lifetime observed is 0.51 ms for $x = 0.008$ sample. No considerable variation in the lifetime was noticed for Sm$^{3+}$ emission level even at a higher concentration of $x = 0.1$, which yields the lifetime value of 0.47 ms and is due to energy transfer among the nearest neighbor activator (Sm$^{3+}$). This also demonstrates the evidence for the absence of energy transfer from Sm$^{3+}$ to Tb$^{3+}$.

Energy transfer probability ($W$) is calculated using lifetime value of donor, in the presence and absence of acceptor and the energy transfer efficiency of Tb$^{3+} \rightarrow$ Sm$^{3+}$ ($E_T$) is given by the relations [45].

\[ W = \frac{I}{\tau(Tb : Sm)} - \frac{I}{\tau(Tb)} \]  

\[ E_T = 1 - \frac{\tau(Tb : Sm)}{\tau(Tb)} \]  

(4.4)  

(4.5)
The energy transfer probability and efficiency are found to be 2.92 and 52% respectively for $x = 0.002$ and are increased to 97.36 and 97% when the concentration is increased to $x = 0.008$.

4.4.6 Energy transfer mechanism in $\text{Tb}_{2-x}\text{Sm}_x(\text{MoO}_4)_3$ nanophosphor

The energy transfer from $\text{MoO}_4^{2-}$ to $\text{Sm}^{3+}$ occurs by two channels. Under UV excitation the excited $\text{MoO}_4^{2-}$ directly transfers energy to $\text{Sm}^{3+}$ and $\text{Tb}^{3+}$ higher levels by resonance process [46]. The $\text{Sm}^{3+}$ ions were also excited by the energy transfer from the excited $\text{Tb}^{3+}$ due to the spectral overlap of the energy levels of $\text{Sm}^{3+}$ and $\text{Tb}^{3+}$ ions. A summary of the emission and energy transfer process in $\text{Tb}_{2-x}\text{Sm}_x(\text{MoO}_4)_3$ is shown schematically in Figure 4.11.

When excited by 290 nm UV, the electrons in the ground state ($^1\text{A}_1$) are excited into the $^1\text{T}_2$ level of $\text{MoO}_4^{2-}$. The electron either relaxes to its lowest excited $^1\text{T}_1$ level of $\text{MoO}_4^{2-}$ or $^6\text{P}_{7/2}$ levels of $\text{Sm}^{3+}$ ion and its higher levels by a resonance process. The transition from $^1\text{T}_1$ to the ground state $^1\text{A}_1$ causes the blue emission of the $\text{MoO}_4^{2-}$ [47]. The numerous closely
spaced intermediate energy levels between the $^6P_{7/2}$ and $^4G_{5/2}$ level of Sm$^{3+}$ ion boosts the nonradiative relaxation and leads to the population of the $^4G_{5/2}$ state, from which the relaxation occurs to the ground state to give Sm$^{3+}$ emissions. The excitation of Tb$^{3+}$ is by the energy transfer from MoO$_4^{2-}$ to the $^5D_3$ or higher levels of Tb$^{3+}$. The relaxation from $^5D_3$ to $^5D_4$ level of Tb$^{3+}$ is due to cross-relaxation. From $^5D_4$ the energy transfers either to higher energy levels of Sm$^{3+}$ or to its own ground state to produce the Tb$^{3+}$ emissions.

4.4.7 CIE chromaticity coordinate and CCT analysis

The CIE chromaticity coordinates and CCT values of a phosphor are a very important certification for photoluminescence applications. CIE chromaticity diagram for the emission spectra of the Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ (x = 0.001, 0.0014, 0.002, 0.006, 0.008) nanophosphor as a function of the Sm$^{3+}$ concentration is shown in Figure 4.12. Due to different energy transfer

![Figure 4.12 CIE chromaticity diagram for the emission spectra of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ samples and inset digital photograph of the emission from samples.](image-url)
efficiencies at different Sm$^{3+}$ doping concentrations the luminescence color can be tuned from green to orange-red by changing the doping concentration of Sm$^{3+}$ ions. The inset of Figure 4.12 shows the digital photographs of phosphors emitting different colors under 290 nm UV excitation, which is in good agreement with the result of the CIE hue diagram. When the concentration of Sm$^{3+}$ is $x = 0.0014$, white light emission can be realized. The CCT values of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ nanophosphor samples were calculated from the CIE chromaticity coordinates using McCamy’s approximate formula Eqn.2.28 and are tabulated in Table 4.5 [48]. The CCT values show cool white close to the chromaticity coordinates of white light. From the table, it is also observed that on increasing the Sm$^{3+}$ concentration, the red component could decrease the correlated color temperature by which CCT values in the cool region can be tuned to warm CCT region. In addition, phosphors with lower CCT values as 4394, 2717 and 2168 K find potential application in WLEDs.

**Table 4.5** CIE Coordinates ($x, y$) and CCT values for the emission Spectra of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ nanophosphors under 290 nm excitation.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Concentration</th>
<th>CIE chromaticity coordinates</th>
<th>CCT (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>$x = 0.001$</td>
<td>0.34, 0.49</td>
<td>5343</td>
</tr>
<tr>
<td>b</td>
<td>$x = 0.0014$</td>
<td>0.32, 0.34</td>
<td>6072</td>
</tr>
<tr>
<td>c</td>
<td>$x = 0.002$</td>
<td>0.36, 0.34</td>
<td>4394</td>
</tr>
<tr>
<td>d</td>
<td>$x = 0.006$</td>
<td>0.43, 0.36</td>
<td>2717</td>
</tr>
<tr>
<td>e</td>
<td>$x = 0.008$</td>
<td>0.48, 0.38</td>
<td>2168</td>
</tr>
</tbody>
</table>
4.5 Conclusions

Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ nanophosphors with varying doping concentration of Sm$^{3+}$ were synthesized by sol-gel route. The prepared samples were structurally and optically characterized using various techniques. The X-ray diffraction studies confirmed the orthorhombic phase of the nanophosphor. TEM analysis revealed that the prepared phosphors exhibit uniform particle size distribution having an average size of 35 nm. Raman and FTIR spectroscopy were employed to analyze vibrational modes and functional groups associated with the samples. Judd-Ofelt analysis for Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ (x = 0.008) nanophosphor has been carried out and intensity parameters were evaluated and found to be in the order $\Omega_2 > \Omega_4 > \Omega_6$. The radiative properties were predicted on the basis of the JO theory which shows good agreement with the observed emission spectrum. The higher value of stimulated emission cross-section of the $^4G_{5/2} \rightarrow ^4H_{7/2}$ transition is favorable for low threshold and high gain to obtain continuous wave laser action. Detailed luminescence studies were carried out by analyzing the variations in the fluorescence spectra with different doping concentrations of Sm$^{3+}$ and excitation wavelength. The excitation spectra of Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ phosphors indicate two types of energy transfer processes, MoO$_4^{2-} \rightarrow$ Sm$^{3+}$/Tb$^{3+}$ and Tb$^{3+} \rightarrow$ Sm$^{3+}$. Due to different energy transfer schemes, Tb$_{2-x}$Sm$_x$(MoO$_4$)$_3$ phosphor shows the characteristic emissions of Sm$^{3+}$ and Tb$^{3+}$ ions upon excitation at 290, 376 and 485 nm. The non-radiative nature of the Tb$^{3+} \rightarrow$ Sm$^{3+}$ energy transfer is confirmed by the fast non-radiative decay of the Tb$^{3+}$ emission. The efficient energy transfer process from Tb$^{3+}$ to Sm$^{3+}$ occurs via the dipole–dipole mechanism and the critical distance for Tb$^{3+}$ to Sm$^{3+}$ is calculated to be to 8.83 Å. The CIE chromaticity coordinate implies the feasibility to produce multicolor emission in the prepared phosphors. The CCT values of the phosphors can
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