5.1 Introduction

As an active research field in modern materials chemistry, the synthesis of inorganic nanosized and nanostructured materials with different morphologies has been attracting considerable interest. These materials find various applications in catalysis, optoelectronics, microelectronics, magnetics and biology [1–5]. Out of the many inorganic materials, scheelite type (AXO$_4$, A = Ca, Sr and Ba; X = Mo and W) nanomaterials has been an active area in research due to their good thermal, chemical and luminescence properties. These nanomaterials have promising applications in photoluminescence, solid state lasers, optical fibers and scintillators due to their low vibrational frequency [6-10]. Rare-earth ion doped calcium molybdate (CaMoO$_4$) has attracted much interest due to its numerous applications in optical filters, solid state lasers, LED (light emitting diodes), scintillators, microwave dielectrics, cryogenic detectors and fluorescent lamps [11,12]. They also have other attractive features like a high melting point (1445–1480°C), high refractive index (1.98), effective average decay time (14 ms), photo electron yield (9%) and it is also chemically resistant and non-hygroscopic [13]. CaMoO$_4$ shows a broad blue and/or green luminescence emission peak in the range 350–650 nm with a peak maximum around 500 nm. This peak maximum however varies with particle size and oxygen vacancies in the lattice [14]. It is related to the electron-hole recombination after excitation through the band gap of the charge transfer (CT) from O to Mo (2p $\rightarrow$ 4d orbital) in the MoO$_4^{2-}$ complex tetrahedron cluster itself [15]. Since the emission band is very broad, it is difficult to tune the color, particularly for lighting and display applications. On the other hand, lanthanide ions have poor absorption
cross-section due to the forbidden nature of $f-f$ transitions and show poor luminescence emission [16]. To overcome this problem, materials with high absorption cross-section can be manipulated by doping ions with low absorption cross-section (e.g. lanthanide ions, $\text{Ln}^{3+} = \text{Sm}^{3+}$, $\text{Eu}^{3+}$, $\text{Tb}^{3+}$, $\text{Dy}^{3+}$ and $\text{Tm}^{3+}$). The forbidden nature of $\text{Ln}^{3+}$ ion can be relaxed by the crystal field (surroundings) when $\text{Ln}^{3+}$ ions occupy crystallographic sites of the host lattice (e.g. $\text{CaMoO}_4$). This also gives a possibility of energy transfer from host/sensitizer to the excited state of the activator by a non-radiative energy transfer mechanism [17]. This may result to a high population of photons in the excited level/levels of $\text{Ln}^{3+}$ and thereby enhanced emission of $\text{Ln}^{3+}$ may be expected.

The luminescence spectrum of the host is modified when it is doped with different rare earth ions such as $\text{Eu}^{3+}$, $\text{Tb}^{3+}$, $\text{Dy}^{3+}$ etc. due to the creation of emission centres when they are excited by UV wavelength light. Therefore $\text{Ln}^{3+}$ doped $\text{CaMoO}_4$ might emerge as promising candidates for visual display, solid state lighting etc.

Emission of white light is also one of the important areas of interest amongst the luminescent nanomaterials. A number of approaches have been reported towards the development of a long lasting solid state white-light LEDs. Lanthanide ions ($\text{Ln}^{3+}$) having emission in the primary color (red, blue and green) range can be combined together to get a white light emitter. Techniques involve utilizing a blue light-emitting $\text{InGaN}$ LED coated with cerium-doped yttrium aluminium garnet ($\text{Ce}^{3+}:\text{YAG}$) crystals, which function as a yellow phosphor [18,19]. The crystals convert some of the blue LED light to yellow light, creating a mixture of yellow and blue light that gives the appearance of white light.
Sivakumar, Veggel and Raudsepp [20] have reported that white light can easily be generated by the combination of three different lanthanide ions having red, green, and blue emissions. The Commission Internationale d’Eclairage (CIE) color coordinates are found to be $x = 0.37$ and $y = 0.32$.

Tu et al. [21] have successfully developed highly efficient white-light emission from a single polymer, using polyfluorene as a blue light-emitting component and a small amount of 1,8-naphthalimide derivative as an orange/red-light-emitting component. They found the CIE coordinates of $x = 0.32$, $y = 0.36$.

White emitting phosphors are of great interest because of their numerous applications in different forms of lighting devices. According to the principles of colorimetry (Commission Internationale d’Eclairage CIE), each colour can be matched by mixing the three primary colors viz. blue, green and red. Three primary colors can be mixed or one primary color plus a secondary color of the remaining primary colors to produce white light. There have been many reports about white light emission from materials containing more than one lanthanide ions [20,22–24]. However, such multiple doped materials have problems of self absorption, thereby reducing their performance. Therefore, single lanthanide ion doped material will be a potential candidate for this purpose. Very little investigation has been done in the field of producing white light simply by doping a single lanthanide ion. In this chapter, synthesis of white light emitting phosphor doped with a single lanthanide ion is also studied. The CIE coordinates of the samples with different $\text{RE}^{3+}$ ions are also calculated and studied.

In this chapter, we will discuss the preparation of $\text{RE}^{3+}$ doped in $\text{CaMoO}_4$ host using polyol route as the synthesis method. Efforts have been made to produce white
emission by combining single RE$^{3+}$ into the host and CIE colour coordinates for different lanthanide ions doped in the host are also calculated.

5.2 Experimental details

5.2.1 Sample preparation

Nanoparticles of CaMoO$_4$ and CaMoO$_4$ doped with RE$^{3+}$ ions (Eu$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Sm$^{3+}$) were prepared using ethylene glycol as both capping agent and reaction medium at 130°C. Calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$.4H$_2$O, AR), europium oxide (Eu$_2$O$_3$.99.99%, Aldrich), dysprosium oxide (Dy$_2$O$_3$), terbium nitrate hexahydrate (Tb(NO$_3$)$_3$.6H$_2$O, 99.99%, Aldrich), samarium nitrate (Sm(NO$_3$)$_3$. 99.99%, Aldrich) and sodium molybdate dihydrate (Na$_2$MoO$_4$.2H$_2$O, AR) were used as sources of Ca$^{2+}$, Eu$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Sm$^{3+}$ and MoO$_4^{2-}$, respectively. The synthesis procedure is followed similar to that in previous sample preparations (as described in Chapter 4) by taking stoichiometric amounts of the starting materials. The dried sample was then used for further characterization.

5.2.2 Characterization

X-ray powder diffraction (XRD) data for all the samples were recorded using PANalytical powder diffractometer (X Pert PRO) with CuKα (1.5405 Ångstrom) radiation with Ni filter. Transmission electron microscopy (TEM) was recorded using CM-200 TEM. For TEM measurement the samples were ground and dispersed in methanol. A drop of the dispersed particles was placed over the carbon coated copper
PHOTOLUMINESCENCE STUDIES OF SOME RE3+ DOPED CaMoO4 NANOPARTICLES

grid and evaporated to dryness at room temperature. Infrared spectra were recorded on a Fourier transform infrared (FT-IR) spectrophotometer of Shimadzu (model 8400S) using thin pellets with KBr. UV-vis absorption spectrum was measured on Shimadzu (model 2450) spectrophotometer. All the photoluminescence spectra and lifetime measurements of the samples were recorded using Perkin Elmer (LS-55) luminescence spectrometer in phosphorescence mode with xenon discharge lamp as the excitation source having pulse width at half height < 10 µs. For the lifetime measurements gate time was fixed at 0.05 ms and the delay time was varied starting from 0.1 ms. All the measurements were taken at room temperature.

5.3 Results and discussion

5.3.1 XRD Study

The XRD patterns of CaMoO4 doped with RE3+ ions (Eu3+, Tb3+, Dy3+, Sm3+) synthesized via EG route are shown in fig.5.1(a), (b), (c) and (d). For CaMoO4:RE3+, well-defined diffraction peaks appear and all of these peaks can be indexed to the tetragonal phase of CaMoO4 (JCPDS card No. 29-0351). No additional peaks for other phases have been found in all the patterns for CaMoO4 doped with RE3+ which indicates that RE3+ ions have been effectively doped into the CaMoO4 host lattices.

The diffraction peaks of CaMoO4:RE3+ are shifted to higher angles when compared to that of standard CaMoO4 (JCPDS No.29-0351) patterns. This shifting to higher angles is due to smaller size of Eu3+ (0.106 nm), Dy3+ (0.102 nm), Tb3+ (0.104 nm) and Sm3+.
PHOTOLUMINESCENCE STUDIES OF SOME RE3+ DOPED CaMoO4 NANOPARTICLES

(0.107 nm) than Ca$^{2+}$ (0.112 nm), for coordination number 8 in the CaMoO$_4$ host lattice [25].

The unit cell volume which is determined by calculating the cell parameters from XRD goes on decreasing with increase in the concentration of the dopant ions (Eu$^{3+}$, Tb$^{3+}$, Sm$^{3+}$, Dy$^{3+}$). Such gradual decrease in the unit cell volume is due to the incorporation of dopant ions which have smaller ionic radii than Ca$^{2+}$ in the CaMoO$_4$. This gradual decrease in unit cell volume with increase in dopant concentration suggests the quantitative substitution of the dopant ion into the lattice site of Ca$^{2+}$ in CaMoO$_4$ matrix.

The mean particle size can be roughly determined from the broadening of peaks by using the Scherrer formula, $d = 0.9\lambda / \beta \cos \theta$, where $\lambda$ is the wavelength of the X-ray and $\beta$ is the full width at half maximum (FWHM).
Fig. 5.1 XRD patterns of CaMoO₄ doped with (a) Eu³⁺, (b) Tb³⁺, (c) Dy³⁺, (d) Sm³⁺ and (e) the standard CaMoO₄ patterns.
Table 5.1. Lattice parameters, unit cell volume and crystallite sizes of Eu$^{3+}$, Tb$^{3+}$, Dy$^{3+}$ and Sm$^{3+}$ doped CaMoO$_4$

<table>
<thead>
<tr>
<th>Dopant conc. (at.%) in CaMoO$_4$</th>
<th>Lattice parameters</th>
<th>Unit cell volume (Å$^3$)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu$^{3+}$ (5 at.%)</td>
<td>$a$ (Å) 5.230</td>
<td>$c$ (Å) 11.481</td>
<td>314.067</td>
</tr>
<tr>
<td>Eu$^{3+}$ (10 at.%)</td>
<td>$a$ (Å) 5.234</td>
<td>$c$ (Å) 11.455</td>
<td>313.932</td>
</tr>
<tr>
<td>Eu$^{3+}$ (15 at.%)</td>
<td>$a$ (Å) 5.222</td>
<td>$c$ (Å) 11.452</td>
<td>312.320</td>
</tr>
<tr>
<td>Dy$^{3+}$ (1 at.%)</td>
<td>$a$ (Å) 5.218</td>
<td>$c$ (Å) 11.407</td>
<td>310.606</td>
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<tr>
<td>Dy$^{3+}$ (2 at.%)</td>
<td>$a$ (Å) 5.218</td>
<td>$c$ (Å) 11.402</td>
<td>310.549</td>
</tr>
<tr>
<td>Dy$^{3+}$ (7 at.%)</td>
<td>$a$ (Å) 5.211</td>
<td>$c$ (Å) 11.332</td>
<td>307.791</td>
</tr>
<tr>
<td>Dy$^{3+}$ (10 at.%)</td>
<td>$a$ (Å) 5.206</td>
<td>$c$ (Å) 11.301</td>
<td>306.334</td>
</tr>
<tr>
<td>Tb$^{3+}$ (5 at.%)</td>
<td>$a$ (Å) 5.285</td>
<td>$c$ (Å) 11.329</td>
<td>316.546</td>
</tr>
<tr>
<td>Tb$^{3+}$ (7 at.%)</td>
<td>$a$ (Å) 5.234</td>
<td>$c$ (Å) 11.339</td>
<td>310.712</td>
</tr>
<tr>
<td>Tb$^{3+}$ (10 at.%)</td>
<td>$a$ (Å) 5.222</td>
<td>$c$ (Å) 11.386</td>
<td>310.527</td>
</tr>
<tr>
<td>Sm$^{3+}$ (0.5 at.%)</td>
<td>$a$ (Å) 5.202</td>
<td>$c$ (Å) 11.377</td>
<td>307.929</td>
</tr>
<tr>
<td>Sm$^{3+}$ (2 at.%)</td>
<td>$a$ (Å) 5.205</td>
<td>$c$ (Å) 11.343</td>
<td>309.396</td>
</tr>
</tbody>
</table>

5.3.2 TEM study

Fig. 5.2 shows the TEM images of CaMoO$_4$ doped with different RE$^{3+}$ ions. From the images, we observe well dispersed particles with shapes depending on the RE$^{3+}$ ion doped. Fig. 5.2 (a) shows the TEM image of Dy$^{3+}$ doped in the CaMoO$_4$ host. The particles are well dispersed and are spherical as well as rice-shaped. They have length
of 20-30 nm; inset shows the SAED pattern and the rings present in the patterns reveal the crystalline nature of the prepared samples.

**Fig. 5.2** TEM images of CaMoO$_4$ doped with
(a) 5 at. % Dy$^{3+}$, (b) 10 at. % Tb$^{3+}$, (c) 5 at. % Eu$^{3+}$ and (d) 7 at. % Sm$^{3+}$ and (b) insets show their SAED patterns
Tb$^{3+}$ doped samples show spherical shaped particles with diameter of 5.5 nm to 13 nm. For Eu$^{3+}$ doped samples, we can see well dispersed, non-agglomerated cubical particles. They have length of about 48 nm and their diagonals measure about 90 nm as observed from TEM images. Fig.5.2 (d) shows the irregularly shaped Sm$^{3+}$ doped CaMoO$_4$ particles. They are dispersed and have length of 20-30 nm. Inset shows its SAED pattern and from the rings present in the pattern, the crystalline nature of the sample is confirmed.

5.3.3 FT-IR study

Fig. 5.3 shows the IR spectra of CaMoO$_4$ doped with Tb$^{3+}$ and Dy$^{3+}$. In the spectra, we observe prominent peaks at around 3320, 2980, 1676, 1388, 827 and 430 cm$^{-1}$. The bands at 3348 cm$^{-1}$ and 1636 cm$^{-1}$ are assigned to O-H stretching vibration and H-O-H bending vibration [26], respectively. The O-H group present in the sample may be from the water absorbed by the samples from atmosphere. The peak at 2980 cm$^{-1}$ is attributed to stretching vibrations of CH$_2$ groups of EG molecule [27]. A strong absorption band at 827 cm$^{-1}$ is related to O-Mo–O stretches and that at 430 cm$^{-1}$ has been attributed to the stretching vibration of Mo–O [28].
5.3.4. Luminescence study

Fig. 5.4 (a) shows the excitation spectrum of CaMoO$_4$ nanoparticles which was obtained by monitoring the emission of MoO$_4^{2-}$ group at 498 nm. A broadband is observed from 210 to 350 nm with a maximum at 277 nm. The band at 277 nm is attributed to the charge transfer absorption in MoO$_4^{2-}$ group [29-32]. Here an electron from 2$p$ orbital of oxygen atom goes into one of the empty 4$d$ orbital of Mo. Upon excitation at 277 nm, the emission spectrum of CaMoO$_4$ shows a broad band from 350 to 650 nm with a peak maximum at 498 nm as shown in fig. 5.4 (b).
Fig. 5.4 (a) Excitation and (b) emission spectra of CaMoO₄ host

Fig. 5.5 (a) and (b) shows the excitation and emission spectra of CaMoO₄: Eu³⁺ (5 at. %) nanoparticles prepared in EG. The excitation spectra were obtained by monitoring the emission of the Eu³⁺ ⁵D₀⁻⁷F₂ transition at 615 nm. The excitation spectrum shows a broad band from 230 to 350 nm with its peak maximum at 277 nm. This peak maximum corresponds to the CT absorption in the MoO₄²⁻ group.

Fig. 5.5 (a) Excitation and (b) emission spectra of CaMoO₄: Eu³⁺ (5 at. %) prepared in EG
When Eu\(^{3+}\) doped samples are irradiated with short UV light (of wavelength 277 nm), we observe the characteristic emissions of Eu\(^{3+}\). The emission spectra show peaks centred at 535 nm (\(^5\)D\(_{1}\) - \(^7\)F\(_{1}\)), 595 nm (\(^5\)D\(_{0}\) - \(^7\)F\(_{1}\), orange emission) and 614 nm (\(^5\)D\(_{0}\) - \(^7\)F\(_{2}\), red emission). The electric dipole transition which is red in colour is dominant over other transitions. To see the effect of concentration on the luminescence intensities, the emission spectra of different concentrations of Eu\(^{3+}\) in the host were recorded.

Fig. 5.6 shows the emission spectra for CaMoO\(_4\): Eu\(^{3+}\) (x at. %) excited at 275 nm. The luminescent intensity became maximal when the concentration of Eu\(^{3+}\) reached 15 at. % and intensity decreased beyond this concentration. This phenomenon is due to the concentration quenching. There is an increase in the dipole-dipole interaction with the increase in Eu\(^{3+}\) ion concentration eventually the cross- relaxation among Eu\(^{3+}\) ions increases when the mean distance between them is less than a critical value. Therefore,
the optimum concentration for the highest luminescence of Eu$^{3+}$ concentration in this study is found to be 15 at. % in CaMoO$_4$.

![Excitation spectra and emission spectra for CaMoO$_4$: Tb$^{3+}$ nanoparticles prepared in EG](image)

Fig. 5.7 (a) Excitation spectra and (b) emission spectra for CaMoO$_4$: Tb$^{3+}$ nanoparticles prepared in EG

Fig. 5.7 (a) and (b) shows the excitation and emission spectra for Tb$^{3+}$ doped samples. The excitation spectrum is obtained by monitoring the emission of the Tb$^{3+}$ $5D_4$-$7F_5$ transition at 546 nm. Similar to the earlier case, we can observe that the excitation spectrum consists of a strong and broad band from 200 to 350 nm with a maximum at about 273 nm which corresponds to the charge-transfer transitions within the MoO$_4^{2-}$ groups (as described above).

The $f$-$f$ transitions within the Tb$^{3+}$ $4f^6$ configuration can hardly be detected because of their weak intensity. The presence of the excitation band of the MoO$_4^{2-}$ groups in the excitation spectrum of Tb$^{3+}$ indicates that there is an energy transfer from the MoO$_4^{2-}$ groups to Tb$^{3+}$ ions in the CaMoO$_4$: Tb$^{3+}$ nanoparticles. Upon excitation into the MoO$_4^{2-}$ at 273 nm, the obtained emission spectrum contains the characteristic emission of Tb$^{3+}$ with $5D_4$-$7F_5$ green emission (546 nm) as the most prominent group. Other emissions
PHOTOLUMINESCENCE STUDIES OF SOME RE3+ DOPED CaMoO4 NANOPARTICLES

are located at 439, 491, 590 and 621 nm and they have been ascribed to the transitions of \( ^5\text{D}_3 \rightarrow ^7\text{F}_4, ^5\text{D}_4 \rightarrow ^7\text{F}_6, ^5\text{D}_4 \rightarrow ^7\text{F}_4 \) and \( ^5\text{D}_4 \rightarrow ^7\text{F}_3 \), respectively. It is also evident from fig. 4.7 (b) that the optimum \( \text{Tb}^{3+} \) concentration for maximum luminescent intensity is 10 at. %. Above this particular concentration, the emission intensity decreases and this is due to concentration quenching effect as mentioned in earlier cases.

**Fig.5.8** Excitation spectra of \( \text{CaMoO}_4: \text{Dy}^{3+} \) and inset shows the expanded region of f-f transition

For the \( \text{CaMoO}_4: \text{Dy}^{3+} \) nanoparticles too, the excitation spectrum consists of a broad band from 230 nm to 320 nm (shown in fig.5.8), with a maximum at around 277 nm, which corresponds to the charge-transfer transitions within the \( \text{MoO}_4^{2-} \) group.

In addition to the absorption peaks of \( \text{MoO}_4^{2-} \) groups, some weak intensity peaks in the excitation spectra are also present. These weaker peaks in the longer wavelength region indicate the \( f-f \) transitions within the \( \text{Dy}^{3+} 4f^0 \) electronic configuration. The expanded region of 350-450 nm in the excitation spectra of \( \text{CaMoO}_4 \) doped with \( \text{Dy}^{3+} \) is shown in inset of fig.5.8 and the excitation peaks are observed at around 354 nm \( ^6\text{H}_{15/2} \)
PHOTOLUMINESCENCE STUDIES OF SOME RE3+ DOPED CaMoO4 NANOPARTICLES

$\rightarrow^4M_{15/2}+^6P_{7/2}$, 367 nm ($^6H_{15/2}\rightarrow^4I_{11/2}$), 390 nm ($^6H_{15/2}\rightarrow^4M_{19/2}+^4M_{21/2}$) and 440 nm ($^6H_{15/2}\rightarrow^4G_{11/2}$) [33].

The presence of the excitation band of MoO$_4^{2-}$ groups in the excitation spectrum of Dy$^{3+}$ indicates the existence of energy transfer from MoO$_4^{2-}$ groups to the lanthanide ion in Dy$^{3+}$ doped CaMoO$_4$ nanoparticles.

Fig. 5.9 (a) shows the emission spectra of different at. % Dy$^{3+}$ doped CaMoO$_4$ nanoparticles which were obtained by exciting at 273 nm. The transition band at $^4F_{9/2}^\rightarrow^6H_{15/2}$ (488 nm) is due to magnetic dipole transition whereas that at $^4F_{9/2}^\rightarrow^6H_{13/2}$ (573 nm) is due to electric dipole transition. The transition at $^4F_{9/2}^\rightarrow^6H_{13/2}$ (573 nm) which is yellow in colour is dominant over other transitions in all the cases. The luminescence intensity is greatly influenced by the doping concentrations of the lanthanide ion, however, no shift has been observed towards the higher or lower wavelength region by
varying the doping concentration of dopant ion. The photoluminescence intensity increased from 2 at. % till it reaches 7 at. % of Dy\(^{3+}\), further increase in dopant concentration resulted in decrease of photoluminescence intensity. This phenomenon is due to the concentration quenching. There is an increase in the dipole-dipole interaction with the increase in Dy\(^{3+}\) ion concentration eventually the cross-relaxation among Dy\(^{3+}\) ions increases when the mean distance between them is less than a critical value. Therefore, the optimum concentration for the highest luminescence of Dy\(^{3+}\) concentration is found to be 7 at. %.

Fig. 5.9 (b) shows the emission spectra of CaMoO\(_4\) doped with different concentrations of Sm\(^{3+}\). The emission spectra were obtained by exciting at 273 nm. The emission peaks are observed at 565 nm, 599 nm and 646 nm and they are assigned to \(4G_{5/2} \rightarrow 6H_{5/2}\), \(4G_{5/2} \rightarrow 6H_{7/2}\) (magnetic) and \(4G_{5/2} \rightarrow 6H_{9/2}\) (electric dipole) transitions respectively. Out of all these transitions, the transition at 646 nm dominates over other transitions and hence at higher concentrations of Sm\(^{3+}\), the orange emission is predominant. But at lower concentrations of Sm\(^{3+}\) (0.5 and 2 at. %), the bluish green emission of MoO\(_4^{2-}\) dominates over orange emission. The emission intensity at 646 nm is further increased with increasing Sm\(^{3+}\) ion concentration and attains maximum intensity at 5 at. % and it decreases with further increase of Sm\(^{3+}\) ion concentration as a result of concentration quenching effect.

The luminescence study could therefore be summarized as follows:

An efficient energy transfer occurs from MoO\(_4^{2-}\) to Ln\(^{3+}\). The energy transfer from MoO\(_4^{2-}\) to the Ln\(^{3+}\) activator ions can occur through an exchange interaction and/or dipole-dipole interaction in CaMoO\(_4\):Ln\(^{3+}\) nanofibers like YVO\(_4\):Ln\(^{3+}\)[34,35] and
The whole excitation and emission process of CaMoO$_4$:Ln$^{3+}$ under UV radiation is supposed to take place in three major steps.

(i) The first one is absorption of UV radiation by MoO$_4^{2-}$,

(ii) The second step is the excited energy is subsequently transferred to Ln$^{3+}$ ions by resonance interactions, and

(iii) The final one is the de-excitation process of excited Ln$^{3+}$, which yields their characteristic emissions.

5.3.5 Lifetime study

The kinetic decay curves for the emission of CaMoO$_4$:RE$^{3+}$ were measured. Fig. 5.10 shows the luminescence decay curves with their typical fitting for Dy$^{3+}$ (5 at. %) doped in CaMoO$_4$ nanoparticles. All the luminescence decay data are fitted with bi-exponential decay equation,

\[
I_t = I_1 e^{-\frac{t}{\tau_1}} + I_2 e^{-\frac{t}{\tau_2}}
\]

(1)

And the average lifetime values were calculated using,

\[
\tau_{av} = \frac{I_1 \tau_1^2 + I_2 \tau_2^2}{I_1 \tau_1 + I_2 \tau_2}
\]

(2)

$I_1$ and $I_2$ are intensities at two different interval times, $\tau_1$ and $\tau_2$ are their corresponding decay times.

The average lifetime values for Dy$^{3+}$ doped in CaMoO$_4$ are found to be 195, 246, 287 and 250 $\mu$s for 2, 5, 7 and 10 at. % Dy$^{3+}$, respectively. The reported lifetime values for
CaMoO$_4$: 5 mol % Dy$^{3+}$ is 0.0705 ms [38]. For Dy$^{3+}$ doped in CaMoO$_4$ host, the average lifetime values increased with increasing concentration from 2 at. % to 7 at % of the dopant ion. The lifetime value decreased when the concentration of Dy$^{3+}$ increased beyond 7 at % (shown in Table 5.2). The bi-exponential decay behaviour of the activator is frequently observed when the excitation energy is transferred from the donor and in this case we can say that there is an energy transfer from MoO$_4^{2-}$ to the activator ion (Dy$^{3+}$).

For other nanoparticles doped with other RE$^{3+}$ ions (Eu$^{3+}$, Sm$^{3+}$, Tb$^{3+}$) in CaMoO$_4$ host, the decay curves could also be fitted with bi-exponential equation. Fig.4.11 shows the decay curve for Tb$^{3+}$ doped samples and the solid line indicates the bi-exponential fitting. The bi-exponential behaviour is dependent on the number of luminescent centres created by the dopant, energy transfer from the donor to the activator and defects present in the host [39].
Table 5.2. Average lifetime values of CaMoO$_4$:RE$^{3+}$ nanoparticles

<table>
<thead>
<tr>
<th>Concentration of RE$^{3+}$ (at. %)</th>
<th>Average lifetime (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Dy$^{3+}$) 2</td>
<td>195</td>
</tr>
<tr>
<td>(Dy$^{3+}$) 5</td>
<td>246</td>
</tr>
<tr>
<td>(Dy$^{3+}$) 7</td>
<td>287</td>
</tr>
<tr>
<td>(Dy$^{3+}$) 10</td>
<td>250</td>
</tr>
<tr>
<td>Eu$^{3+}$ (5)</td>
<td>321</td>
</tr>
<tr>
<td>Eu$^{3+}$ (10)</td>
<td>695</td>
</tr>
<tr>
<td>Eu$^{3+}$ (15)</td>
<td>1680</td>
</tr>
<tr>
<td>Eu$^{3+}$ (20)</td>
<td>121</td>
</tr>
<tr>
<td>Tb$^{3+}$ (2)</td>
<td>339</td>
</tr>
<tr>
<td>Tb$^{3+}$ (5)</td>
<td>541</td>
</tr>
<tr>
<td>Tb$^{3+}$ (10)</td>
<td>809</td>
</tr>
<tr>
<td>Tb$^{3+}$ (15)</td>
<td>291</td>
</tr>
<tr>
<td>Sm$^{3+}$ (2)</td>
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</tr>
<tr>
<td>Sm$^{3+}$ (5)</td>
<td>1190</td>
</tr>
<tr>
<td>Sm$^{3+}$ (7)</td>
<td>252</td>
</tr>
</tbody>
</table>

The average lifetime values for 5 at. % Eu$^{3+}$, Tb$^{3+}$ and Sm$^{3+}$ doped in CaMoO$_4$ is 0.321, 0.541 and 1.19 ms, respectively. The average lifetime decreases after reaching a certain concentration of the rare earth ion (as shown in Table 5.2). This is attributed to the...
concentration quenching effect. As the concentration of RE$^{3+}$ ion increases, the cross-relaxation taking place among RE$^{3+}$-RE$^{3+}$ increases and this in turn decreases their lifetimes.

5.3.6 CIE chromaticity coordinates and white emission study

The Commission Internationale de l'Eclairage (CIE) chromaticity coordinates of a phosphor are very important certification for photoluminescence applications [40]. In Fig. 5.12 (a), dots marked with A, B and C correspond to positions of the CIE color coordinates for as prepared CaMoO$_4$:Eu$^{3+}$, Tb$^{3+}$ and Sm$^{3+}$ samples, respectively. In Fig. 4.1b, the point marked as ‘A’ represents the CIE color coordinates for un doped host samples and point B shows the coordinates for CaMoO$_4$: Dy$^{3+}$. The calculated CIE colour coordinates for all the analyzed samples are summarized in Table 5.3. From Figure 5.12 b, we can observe that the chromaticity coordinates for the un-doped CaMoO$_4$ is x=0.18 y = 0.36 (marked as point A) falls in blue-green cross region of the CIE chromaticity diagram. The CIE coordinates change from x =0.18, y = 0.36 for CaMoO$_4$ to x=0.36, y = 0.38 for CaMoO$_4$:7 at. % Dy$^{3+}$ (marked as point B). This clearly shows that the blue-green colour emitted from the host calcium molybdate mixed with the yellow colour emitted from the dopant Dy$^{3+}$ results in white colour. Hence, the single lanthanide ion, Dy$^{3+}$ doped CaMoO$_4$ shows emission in the white region of CIE co-ordinates.
Table 5.3. CIE color coordinates of the samples with the corresponding colours

<table>
<thead>
<tr>
<th>Sample</th>
<th>CIE chromaticity coordinates</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaMoO₄</td>
<td>0.18 0.36</td>
<td>Bluish green</td>
</tr>
<tr>
<td>Eu³⁺ (5 at. %)</td>
<td>0.51 0.33</td>
<td>Red</td>
</tr>
<tr>
<td>Eu³⁺ (15 at. %)</td>
<td>0.51 0.33</td>
<td>Pinkish red</td>
</tr>
<tr>
<td>Tb⁺⁺ (10 at. %)</td>
<td>0.28 0.44</td>
<td>Greenish yellow</td>
</tr>
<tr>
<td>Tb⁺⁺ (7 at. %)</td>
<td>0.26 0.44</td>
<td>Greenish yellow</td>
</tr>
<tr>
<td>Sm³⁺ (5 at. %)</td>
<td>0.52 0.36</td>
<td>Orange-yellow</td>
</tr>
<tr>
<td>Dy³⁺ (7 at. %)</td>
<td>0.36 0.38</td>
<td>White</td>
</tr>
</tbody>
</table>

The Eu³⁺, Sm³⁺ and Tb³⁺ doped CaMoO₄ samples show the CIE chromaticity coordinates around the red, orange-yellow and greenish-yellow regions. Therefore, based on the Commission Internationale d’Eclairage (CIE) coordinates calculations, only Dy³⁺ doped CaMoO₄ samples have CIE coordinates close to the ideal white light values amongst the samples. The coordinates fit well in the white region of CIE chromaticity diagram [41].

These materials could be used as potential nanophosphors for white light-emitting diodes (LEDs) applications.
5.4 Conclusion

CaMoO$_4$:RE$^{3+}$ (RE$^{3+} = \text{Eu}^{3+}, \text{Dy}^{3+}, \text{Tb}^{3+}, \text{Sm}^{3+}$) nanophosphors have been synthesized using ethylene glycol as the reaction medium. It also serves as capping agent. The synthesised nanophosphors show the tetragonal phase. Substitution of the lanthanide ion in CaMoO$_4$ gives a slight variation of the unit cell volume with negligible change in their particle size. This indicates that strains do not develop after doping with lanthanide ions. This is because of the similar ionic size of the lanthanide ion, Eu$^{3+} = 1.06$ Å, Dy$^{3+} = 1.02$ Å, Sm$^{3+} = 1.07$ Å and Tb$^{3+} = 1.04$ Å with the Ca$^{2+}$ ion (1.12 Å).

From FTIR studies, vibrations of CH$_2$ group from EG, O-Mo–O and Mo-O vibrations are found to be at 2980, 827 and 430 cm$^{-1}$ respectively. From TEM study, the particle shapes were found to differ with the doped rare-earth ion. Eu$^{3+}$ doped samples have
cubical particles, Tb$^{3+}$ doped samples show spherical shaped particles, Sm$^{3+}$ doped samples are irregularly shaped whereas those doped with Dy$^{3+}$ have spherical as well as rice-shaped particles. Photoluminescence study shows the excitation peaks of $4f$–$4f$ transition of the lanthanide ions and Mo–O charge transfer. Intensity of Mo–O charge transfer is significantly more than that of the lanthanide ions indicating strong energy transfer from Mo–O to lanthanide ions. Emission study shows the characteristics of the individual doped lanthanide ions. The Eu$^{3+}$ doped sample shows emission peaks at 595 nm ($^5D_{0}→^7F_1$, magnetic dipole transition) and 614 nm ($^5D_{0}→^7F_2$, electric dipole transition). The Dy$^{3+}$ doped sample shows emission peaks at 482 nm ($^4F_{9/2}→^6H_{15/2}$, magnetic dipole transition) and 573 nm ($^4F_{9/2}→^6H_{13/2}$, electric dipole transition). For Tb$^{3+}$ doped samples, emission peak at 546 nm ($^5D_{4}→^7F_5$, magnetic dipole transition) is the most prominent; other emissions are located at 439, 491, 590 and 621 nm and they have been ascribed to the transitions of $^5D_3→^7F_4$, $^5D_4→^7F_6$, $^5D_4→^7F_4$ and $^5D_4→^7F_3$, respectively. For Sm$^{3+}$ doped samples, the emission peaks are observed at 565 nm, 599 nm and 646 nm and they are assigned to $^4G_{5/2}→^6H_{5/2}$, $^4G_{5/2}→^6H_{7/2}$ (magnetic) and $^4G_{5/2}→^6H_{9/2}$ (electric dipole) transitions respectively. The Eu$^{3+}$, Sm$^{3+}$ and Tb$^{3+}$ doped CaMoO$_4$ samples show the CIE chromaticity coordinates around the red, orange-yellow and greenish-yellow regions. CaMoO$_4$: Dy$^{3+}$ show CIE chromaticity coordinates (x = 0.36 and y = 0.38) which are close to reported ideal value (x = 0.33 and y = 0.33) of white light emission. These materials could be used as potential nanophosphors for white light-emitting diodes (LEDs) applications.
References


