5. SYNTHESIS AND LUMINESCENCE PROPERTIES OF CaMoO$_4$:Tb$^{3+}$

5.1 INTRODUCTION

Since, rare earth ions retain a great deal of energy levels and may undergo transfer of electrons among 4f subshells [82], its fluorescence wavelength ordinarily extend from UV to IR range. Thus, the addition of trivalent rare earth ions as luminescent center to matrices is thought-out as an exemplary method for synthesizing excellent luminescent material for lighting applications [83]. Tb$^{3+}$ activated materials have been extensively employed as the green emitting phosphor material by virtue of their strong $^5D_4 \rightarrow ^7F_5$ emission in the green spectral region. Earlier investigations have demonstrated that Tb$^{3+}$ activated aluminates and phosphates displayed almost intense absorption in the UV region and exhibit strong green emission with agreeable color purity. However, the conventional aluminate, borate and phosphate phosphor have their defects respectively [84, 85, 86]. In continuation to previous work on the red luminescent CaMoO$_4$:Eu$^{3+}$ phosphor for lighting applications [20], in the present work, Tb$^{3+}$ activated CaMoO$_4$ powder phosphors were prepared for its systematic optical characterization.

5.2 RESULTS AND DISCUSSION

5.2.1 Structural analysis

Figure. 5.1 displays XRD patterns of CaMoO$_4$:xTb$^{3+}$ (x = 0.02, 0.04, 0.06, 0.08 and 0.1mol) phosphor samples prepared by mechanochemically assisted SSM reaction route at room temperature. It can be seen that all diffraction peaks are consistent well with the respective Joint Committee on Powder Diffraction Standards (JCPDS) card No. 85-1267 of CaMoO$_4$ host.
The peaks in the XRD spectra are sharp and intense proving that a highly crystalline single-phase of tetragonal scheelite structure of CaMoO$_4$ had been successfully synthesized by mechanochemically assisted SSM reaction route at room temperature. No impurity peak was found in the XRD patterns, distinctly indicating the incorporation of Tb$^{3+}$ ions into the host material. By using, Scherrer’s equation, the almost accurate crystallite sizes of as-prepared samples was calculated as 60 nm and 65 nm for the corresponding XRD patterns.

Raman spectra of the SSM prepared CaMoO$_4$:0.08Tb$^{3+}$ phosphor material exhibits peaks referring to the Raman-active internal mode vibrations in the tetrahedral [MoO$_4$]$^{2-}$ units as shown in Figure. 5.2(a). The peaks at around 871, 843, 793, 393, 322 and 210 cm$^{-1}$ correspond to $\nu_1(A_g)$, $\nu_3(B_g)$,
\(v_3(E_g), v_4(B_g), v_2(A_g)\) and \(v_{\text{free rotation}}(A_g)\) vibrations of \(\text{Ca}_{1-x}\text{MoO}_4:x\text{ Tb}^{3+}\) [87, 88].

The FTIR spectra of \(\text{CaMoO}_4:0.08\text{ Tb}^{3+}\) phosphor is shown in Figure. 5.2(b) and it displays a very weak absorption band around 429 cm\(^{-1}\) which is associated with the bending modes of vibration of Mo-O. A very broad strong absorption band around 801 cm\(^{-1}\) is due to anti-symmetric stretching vibrations of O-Mo-O in MoO\(_4^{2-}\) tetrahedron [88]. The weak absorption band around 3418 cm\(^{-1}\) is due to O-H stretching vibration and the bands around 1630 cm\(^{-1}\) are due to H-O-H bending vibration of water absorbed from air [89].

The morphology of the crystalline \(\text{CaMoO}_4:0.08\text{ Tb}^{3+}\) particles are exhibited by SEM image, as indicated in Figure. 5.2(c). The powder particles give off an impression of being crystalline and are slightly agglomerated. However, no considerable differences were monitored in the SEM images for the powder samples with different Tb\(^{3+}\) concentrations. The average grain size of the near rounded particles is about 45 nm, which is in full agreement with the data from the XRD patterns.
Figure 5.2: (a) Raman spectra of CaMoO$_4$:0.08Tb$^{3+}$ phosphor. 
(b) FTIR spectra of CaMoO$_4$:0.08Tb$^{3+}$ phosphor. 
(c) SEM image of CaMoO$_4$:0.08Tb$^{3+}$ phosphor. 
(d) Particle size distribution of CaMoO$_4$:0.08Tb$^{3+}$ phosphor.
5.2.2 Photoluminescence properties

The excitation and emission spectra of CaMoO$_4$:0.08Tb$^{3+}$ phosphors prepared by SSM reaction route at room temperature is shown in Figure. 5.3 (a). The excitation spectrum is monitored at the emission wavelength of 547 nm. It can be observed evidently that the excitation spectrum consists of a strong and broad band from 230 to 330 nm with a maximum at about 299 nm assigned as the charge-transfer band (CTB) originated from oxygen to molybdenum within the MoO$_4^{2-}$ groups. The other sharp lines including the peaks from 350 nm to 400 nm are ascribed to the intra-configurationally f-f transition absorption of Tb$^{3+}$ ions in the host lattice [91].

Upon excitation at 299 nm, the obtained emission spectrum exhibits four major emission bands at 487, 547, 590 and 623 nm, corresponding to the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, and $^5D_4 \rightarrow ^7F_3$ typical transitions of Tb$^{3+}$, as shown in Figure. 5.3(b) respectively. The strongest peak appears at 547 nm is the characteristic emission of Tb$^{3+}$ with $^5D_4 \rightarrow ^7F_5$ green emission 547 nm. Compared with the emission of Tb$^{3+}$, the intrinsic emission from MoO$_4^{2-}$ groups is very feeble, signifying that an efficient energy transfer from MoO$_4^{2-}$ to Tb$^{3+}$ ions has occurred in the CaMoO$_4$:xTb$^{3+}$ (x = 0.02, 0.08 and 0.10 mol) phosphors. Only the transitions from $^5D_4$ to lower lying $^7F_J$ levels are observed at room temperature upon excitation in the UV range.

The concentration quenching occurs when the Tb$^{3+}$ concentration is beyond 8 mol%. The reason for the concentration quenching is that if the Tb$^{3+}$ concentration continues to increase, the interaction of Tb$^{3+}$-Tb$^{3+}$ also increases, consequently, the emission intensity becomes lower [88].
Figure 5.3: a) The excitation spectrum of CaMoO$_4$:0.08Tb$^{3+}$ at the emission wavelength of 545 nm.

(b) The emission spectrum of CaMoO$_4$:xTb$^{3+}$ ($x = 0.02$ (▲), 0.08 (●) and 0.1 (■) mol).
The luminescence decay of the transition at 546 nm of Tb\(^{3+}\) doped CaMoO\(_4\) phosphor sample has been studied at room temperature and is demonstrated in Figure. 5.4(a). The measured lifetime (means) for the \(^{5}D_{4} \rightarrow ^{7}F_{5}\) transition has been resolved from the decay curve which is represented by the \(I = I_{0} \cdot A \cdot e^{-t/\tau}\), where ‘A’ is the amplitude and ‘\(\tau\)’ is the fluorescence lifetime. Decay curve for CaMoO\(_4\):0.08Tb\(^{3+}\) phosphor can be fitted to a single-exponential and lifetime is calculated to be 0.51ms. The result shows that the lifetime is short enough for potential applications in displays and lights.

Figure. 5.4(b) shows the CIE chromaticity diagram for the emission spectra of CaMoO\(_4\):0.08Tb\(^{3+}\) at 299 nm excitation wavelength. The emission color was analyzed and confirmed with the help of Commission Internationale de l’Eclairage CIE chromaticity coordinates \(x, y\). The calculated CIE coordinates for the CaMoO\(_4\):0.08Tb\(^{3+}\) phosphors are found to be \(x = 0.24\), \(y = 0.69\), respectively. These coordinates are located in the green region of the CIE chromaticity coordinate diagram, as shown in Figure. 5.4(b). This indicates that CaMoO\(_4\):0.08Tb\(^{3+}\) phosphor is a promising green emitting component for fluorescent lamp applications.

**Figure. 5.4:** (a) The luminescence decay of the transition at 546 nm of 0.08 mol Tb\(^{3+}\) doped CaMoO\(_4\) phosphor sample. (b) The CIE chromaticity diagram for the as prepared CaMoO\(_4\):0.08Tb\(^{3+}\) phosphor.
5.3 CONCLUSION

A class of novel green emitting Tb$^{3+}$ doped CaMoO$_4$ phosphors was successfully prepared by mechanochemically assisted SSM reaction at room temperature. These phosphors emit intense green light dominated by 545 nm from $^5$D$_4 \rightarrow ^7$F$_5$ transition of Tb$^{3+}$ under excitation of UV light. The CIE coordinates of these phosphors located in the green area and the measured CIE coordinates were observed to be (0.24, 0.69) for CaMoO$_4$:0.08Tb$^{3+}$. All these properties indicate that these phosphors could serve as a potential green emitting phosphor for application on short ultraviolet fluorescent lamps.