CHAPTER - 5

HYDROTHERMAL SYNTHESIS, UP/DOWN CONVERSION LUMINESCENCE PROPERTIES OF Ca\(_{0.5}\)Y(MO\(_4\))\(_2\)·Ln\(^{3+}\) (M = Mo, W; Ln = Pr, Sm, Eu, Tb, Dy, Yb/Er, Yb/Tm, Yb/Ho) 3D MICRO/NANO STRUCTURES

5.1. Introduction

In the current trend, the accurate architectural exploitation of inorganic nanocrystals, microcrystals and submicrocrystals with well-defined morphologies along with mono-disperse nature and accurate adjustable sizes forms a focus of research. Owing to the close relationship between physical and chemical properties of the materials exhibits unique structural factors like size, shape, surface and dimensionality [83]. The self-organization of hierarchical micro- and nanostructures requires single-crystalline morphologies, growth directions, and uniform size. This set of requirements is quite demanding, and the process of self-organization is of great interest to researchers. Rare-earth activated molybdates are excellent materials with highly uniform self-assembled three-dimensional (3D) superstructures, through the plane-to-plane combination of basic building blocks of 1D and 2D nanoparticles [84]. The systems have been observed to have control of the final sizes and morphologies have thus been studied extensively with respect to the interesting physical and chemical properties of the molybdates. The peculiar size-dependent properties of self-organized 3D micro- and nano-scale systems are distinct from those of 0D primary nanoparticles, 1D nanorods, and/or 2D nanosheets. The evolution of hierarchical architectures has permitted the development of diverse materials, resulting in noteworthy discoveries on the advancement of novel micro- and nanostructured devices. In particular, the size, dimensionality, and shape are known to be associated with the properties of a material, including the isotropy or anisotropy of behavior and region-reliant surface reactivity. This knowledge may facilitate the application in diverse research fields and has also been
established as a meaningful and expedient metric for the organization of the properties and structures in the fabrication of convoluted architectures [85].

Rare earth activated functional materials are attracted by the research community based on its applications in all the areas of science and technology. Molybdates/Tungstates with metallic elements form an essential class of phosphor materials. They belong to the scheelite family having a space group $I\overline{4}1/a$. In the tungstate family, alkaline earth based rare-earth activated double molybdates/tungstates are much more important functional materials based on their unique structural, optical properties having profound applications in technology. Alkaline rare-earth activated tungstates having a general formula $\text{ARE}(\text{MO}_4)_2$ ($A = \text{Ba, Ca, Sr} ; \text{RE} = \text{Y} ; M = \text{Mo, W}$) are considered as better luminescent hosts explored greatly for the applications as photo-catalysts, displays, etc. and possess appreciable hydrolytic and thermal stability [86].

To this point, many shapes of 3D micro- and nano-scale hierarchical structures have been reported through several wet chemistry-based techniques, including hydrothermal [87], solvothermal [88], microwave synthesis [89], the Pechini process [90], co-precipitation [91], molten salt synthesis [92], combustion [93], complex polymerization [94], polyl method [95], sonochemical [96], template-assisted methods [97]. Among these techniques, the hydrothermal route is a promising technique for the large-area production of 3D structures under practicable environments [98]. To improve the performance of rare-earth doped molybdate micro- and nanostructure-based devices, unexpected new 3D flexible morphologies have been studied that are recently reported in detail in Chapter - 2.

Currently, there is a potential research on the improvement of highly proficient phosphors with the inclusion of co-dopants of rare earth or without rare earth dopants into phosphors. The responsibility of rare earth co-dopants is in general related with the mechanism of energy transfer, cross-relaxation and up-conversion [99]. It is significant that the existence of alkali metal ions like Li$^+$, K$^+$
and Na⁺ in $A_{0.5}RE(MoO_4)_2:Eu^{3+}/A_{0.5}RE(WO_4)_2:Eu^{3+}$ matrix increases the luminescence of Eu³⁺ ions significantly. The alkali metal ions substitutions in the host would lead the distortion in the crystal field around rare-earth ions which remarkably enhance the luminescence intensity. Thus, it is important to set up a precise method to synthesize $A_{0.5}RE(MoO_4)_2:Eu^{3+},M^+/A_{0.5}RE(WO_4)_2:Eu^{3+},M^+$ red phosphors with bi-pyramid like shape with high dispersibility and narrow size distribution [87, 100]. In this crystal structure, rare-earth ions and alkali metal ions would be randomly distributed over the A site of $A_{0.5}RE(MoO_4)_2/A_{0.5}RE(WO_4)_2$ host. The arbitrary arrangement of rare earth species could induce the non-uniform broadening of optical spectra as Eu³⁺ ions were activated in the crystals and might occupy the respective positions of RE³⁺ [101]. Thus, MoO₄²⁻/WO₄²⁻ group has good absorption in UV region, hence the possible energy transfer from MoO₄²⁻/WO₄²⁻ group to rare-earth ions could readily occur, consequently improve the quantum efficiency of rare-earth ion activated materials [87, 100].

5.2. Experimental Procedure

5.2.1 Preparation of $Ca_{0.5}Y_{1-x}(MoO_4)_2:xRE^{3+}$ (RE = Eu, Pr, Sm, Tb, Dy, Yb/Er, Yb/Ho, and Yb/Tm) bi-pyramid-like architectures

All chemicals used in the syntheses were of analytical grade (99.9% purity). A similar synthesis route was followed for the preparation of trivalent rare earth-doped $Ca_{0.5}Y_{1-x}(MoO_4)_2$ using a surfactant-assisted hydrothermal route. By this synthesis method, bipyramid-like micro- and nanostructures of $Ca_{0.5}Y_{1-x}(MoO_4)_2$ were achieved. At the outset, stoichiometric quantities of $Ca(NO_3)_2.7H_2O$, $Y(NO_3)_3.7H_2O$, and $RE(NO_3)_3$ (RE = Eu, Pr, Sm, Tb, Dy, Yb, Er, Ho, and Tm) were dissolved separately in 25 mL of double-distilled water and mixed with each other. Then, water-soluble Na₂MoO₄.2H₂O was dissolved in 25 mL of double-distilled water by vigorous stirring. The mixtures of rare-earth nitrates were added drop-wise to the Na₂MoO₄.2H₂O solution until a white colloidal precipitate was obtained. The as-obtained white colloidal precipitate
was vigorously stirred for 30 min. After this, 1.5 mM of EDTA was dissolved in
20 mL double-distilled water and added to the obtained colloidal solution. The
pH value of the final product was then set to a value between of 7 and 8 by the
addition of NaOH solution. After further stirring for 30 min, the resultant solution
was transferred to a 100 mL Teflon autoclave, sealed in a stainless steel vessel.
The autoclave was maintained at 180 °C between 2 and 48 h. Following the
heat treatment, the autoclave was cooled naturally. The final product was
collected and washed with double-distilled water and absolute ethanol, and dried
at 60 °C in air for 5 h.

5.2.2 Synthesis of bi-pyramid like Ca_{0.5}Y_{1-x}(WO_4)_2:xEu^{3+} micro/nano-
architectures

For the preparation of bipyramid-like micro- and nano-structures of
Ca_{0.5}Y_{1-x}(WO_4)_2:xEu^{3+} the stoichiometric quantities of CaO, Y_2O_3, and Eu_2O_3
were converted into nitrate form using diluted HNO_3. After that water-soluble
Na_2WO_4.2H_2O was dissolved completely in 25 mL of double-distilled water by
rigorous stirring. The mixtures of rare-earth nitrates were added drop-wise to the
Na_2WO_4.2H_2O solution till the whitish colloidal precipitate was appeared. The
obtained whitish colloidal precipitate was stirred further for 30 minutes. Following
which, 1.5 mM of Na_2EDTA was kept dissolved fully in 20 mL double-distilled
water and mixed to the white colloidal solution. By adding the appropriate
amount of NaOH solution, the pH value of the obtained final product was then
adjusted to a value between 7 and 8. After stirring further for 30 min, the
resultant solution was transferred to a 100 mL Teflon autoclave which is sealed
in a stainless steel vessel. The autoclave was kept at 180°C for 24 h. Once the
heat treatment is over, the autoclave was allowed to cool normally. The final
obtained product was collected and washed with double-distilled water,
centrifuged and dried at 60°C in air for 5 h.
5.2.3 Synthesis of Ca_{0.5}Y_{1-x}(MoO_4)_2:xEu^{3+},M^+ / Ca_{0.5}Y_{1-x}(WO_4)_2:xEu^{3+},M^+ (M = Li, K and Na) bi-pyramid-like micro/nano- architectures

The stoichiometric quantities of CaO, Y_2O_3, and Eu_2O_3 along with respective alkali compounds of Na_2CO_3, K_2CO_3 and Li_2CO_3 were taken. These were converted into nitrate form using diluted HNO_3. Followed by, water-soluble Na_2MoO_4.2H_2O/Na_2WO_4.2H_2O was kept dissolved completely in 20 mL of double-distilled water by rigorous stirring. The mixtures of rare-earth nitrates along with alkali nitrates for co-doping were added gently and drop-wise to Na_2MoO_4.2H_2O/Na_2WO_4.2H_2O solution till obtaining the whitish colloidal precipitate. The obtained whitish colloidal precipitate being kept stirred further for 30 minutes. Following that, 1.5 mM of EDTA is being kept dissolved fully in 20 mL of double-distilled water which is then mixed to the white colloidal solution. By adding the appropriate amount of NaOH solution, the pH value of obtained final product was adjusted to a value between 7 and 8. Followed by stirring further for 30 min, the obtained solution was being transferred carefully to a 100 mL Teflon lined autoclave was later sealed in a stainless steel vessel. Thus, the autoclave was kept at 180ºC for 24 h. Once the heat treatment is over, the autoclave was permitted to cool to room temperature. The final product was thus collected and washed with double-distilled water, centrifuged and hence dried at 60ºC in air for 5 h.

5.2.4. Characterization techniques

The morphologies of the products were examined by field emission scanning electron microscopy (FESEM-SUPRA 55) operated at an accelerating voltage of 15-20 kV. The carbon coating was applied on both sides to minimize the damage by the electron beam. The energy loss stimulated by the K, L shell electron ionization was used for the mapping of Ca, Y, Mo, O and Eu. A high-resolution transmission electron microscope (HRTEM JEOL 3010) was used to determine the distance between two adjacent lattice planes in each product. The
phase purities and crystal structures of the as-prepared phosphors were identified and confirmed using the PANalytical X’Pert PRO Materials Research X-ray Diffractometer (Almelo, The Netherlands) equipped with CuKα radiation (λ = 0.154060 Å) at a scanning rate of 0.02 °s⁻¹ in a 2θ range of 15°–60°. Fourier transform (FT)-Raman spectroscopy studies were performed using a BRUKER RFS FT-Raman spectrophotometer. X-ray photoelectron spectroscopy (XPS) analysis was carried out using LAS-3000 surface analysis system (RIBER, France) with AlKα X-rays (1489.6 eV, width 0.5 eV). Furthermore, down-conversion PL excitation and emission studies and fluorescence decay time measurements were performed using a Cary bench-top spectrophotometer (AGILENT Instruments, USA). The up-conversion luminescence spectra in response to 980 nm near-infrared (NIR) excitation from an optical parametric oscillator and the lifetimes of the excited state energy levels were recorded using a combination of a 0.25 m monochromator (CS-260; Oriel, Rochester, NY), photomultiplier tube (70680; Oriel, Stratford, CT), lock-in amplifier, and oscilloscope. To modulate the excitation beam, a mechanical chopper was used.

5.3. Results and Discussion

5.3.1. Ca₀.₅Y₁₋ₓ(MoO₄)₂ₓEu³⁺

5.3.1.1 Morphological progression and formation mechanism of self-assembled bi-pyramid-like Ca₀.₅Y₁₋ₓ(MoO₄)₂ₓEu³⁺ 3D micro- and nanostructures

Self-organized 3D hierarchical structures with diverse shapes and sizes were successfully synthesized by the EDTA-assisted hydrothermal route for various reaction times. By manipulating the hydrothermal reaction time interval to 0, 2, 4, 6, 9, 12, 24 and 48 h and fixing the molar concentration of the EDTA solution, temperature, and pH, self-aggregated 3D networks progressed from 2D nanoflakes and nanosheets to 3D bipyramid-like structures (Figure 5.1 - 5.3). By increasing the reaction time 0 h to 2 h, the nanoparticles became fused to form
2D nanoflakes or nanosheets with average lengths of about 200 nm and thicknesses in the range of tens of nanometers, as shown in Figure 5.1 (a) and (b). By increasing the reaction time to 4 h, the nanosheets begin stacking uniformly in common crystallographic behavior to create a lopsided morphology as shown in Figure 5.1 (c). The self-organized stacked nanosheets intertwine to begin the growth of a bipyramid-like structure as in Figure 5.1(c), as the reaction time increases to 6 h. As the hydrothermal reaction time is increased to 9 h as in Figure 5.2 (a) and then 12 h as in Figure 5.2 (b), the as-synthesized product is observed to consist of bipyramid-like microstructures with typical diameters of 1.1 μm at 6 h, which grows to 1.25 μm at the 9-h mark, and lengths of 1.0 μm at 12 h as in Figure 5.1 (d) & Figure 5.2 (b). With the further increase of reaction time to 24 h, the final product morphology consists of bipyramid-like structures with an average polar axis length of 2 – 3 μm, significantly greater than the equatorial diameter of 0.9 μm as in Figure 5.2 (c). A corresponding TEM image as shown in Figure 5.3 (a) shows a sample reacted for 24 h. It is obvious from the described time-dependent self-assembly of 3D structures that the selection of a suitable quantity of EDTA is necessary for the arrangement of such bipyramid-like structures. When the reaction time is increased to 48 h, the uniform size distribution of bipyramid-like particles appears to decrease, resulting in bipyramid-like structures with kaput edges as in Fig. 5.3 (b). This decrease in size may result from the time interval during the growth and evolution stage of 3D self-assembly, which prevails between these nanocrystals because of the high surface energies involved, as the thermal impact is flanked by the particles.

The molar concentration of EDTA in the reaction has great effect on the morphologies and size distributions of the obtained final products. The relatively low amount of EDTA used in the reaction process had a meager effect on the adsorption of metal cations, resulting in dominant anisotropic characteristics in the products. The two amine and four carboxylic groups present in EDTA are not adequate to extract a larger number of Ca$^{2+}$ or Y$^{3+}$/Eu$^{3+}$ species from the white colloidal solution. However, a higher molar concentration
of EDTA would prevent the growth of crystal nuclei. Thus, optimizing the molar concentration of EDTA used in the reaction affects the morphology and size of the final product. The metal cations are protected by the hutch-like structure of the benefactor atoms of EDTA, during the reaction between the Ca$^{2+}$ and Y$^{3+}$/Eu$^{3+}$ ions and the EDTA molecule, so that the hydrogen ions in EDTA can be replaced by the metal cations. With the increase in the reaction temperature to 180 ºC, the metal cations may be progressively released from the multifaceted transitional EDTA; these released ions react with MoO$_4^{2-}$ to slowly form Ca$_{0.5}$Y(MoO$_4$)$_2$:Eu$^{3+}$ nuclei according to the following reactions:

$$0.5[\text{Ca(NO}_3\text{)}_2.4\text{H}_2\text{O}]_\text{(s)} \rightarrow 0.5\text{Ca}^{2+}\text{(aq)} + \text{NO}_3^-\text{(aq)} + 2\text{H}_2\text{O} \quad (5.1)$$

$$0.84\text{Y(NO}_3\text{)}_3.6\text{H}_2\text{O} \_\text{(s)} \rightarrow 0.84\text{Y}^{3+}\text{(aq)} + 2.52\text{NO}_3^-\text{(aq)} + 5.04\text{H}_2\text{O} \quad (5.2)$$

$$2[\text{Na}_2\text{MoO}_4.2\text{H}_2\text{O}]_\text{(s)} \rightarrow 4\text{Na}^+\text{(aq)} + 2\text{MoO}_4^{2-}\text{(aq)} + 4\text{H}_2\text{O} \quad (5.3)$$

$$0.16[\text{Eu(NO}_3\text{)}_3.6\text{H}_2\text{O}]_\text{(s)} \rightarrow (0.16)\text{ Eu}^{3+}\text{(aq)} + (0.48)\text{ NO}_3^-\text{(aq)} + 0.96\text{H}_2\text{O} \quad (5.4)$$

$$0.5\text{Ca}^{2+}\text{(aq)} + \text{NO}_3^-\text{(aq)} + \text{Y}^{3+}\text{(aq)} + 2.52\text{NO}_3^-\text{(aq)} + 2\text{MoO}_4^{2-}\text{(aq)} + 2\text{Na}^+\text{(aq)} + 0.16\text{Eu}^{3+}\text{(aq)} + (0.48)\text{ NO}_3\text{(aq)} \xrightarrow{180^\circ C - 24 \text{h}} \text{Ca}_{0.5}\text{Y(MoO}_4\text{)}_2 + 4\text{Na(NO}_3\text{)} + 12\text{H}_2\text{O} \quad (5.5)$$

$$0.5\text{Ca}^{2+} + [\text{Y/Eu}]^{3+} + [\text{H}_2\text{L}]^{2-} \rightarrow \text{Ca}_{0.5} [\text{Y/Eu][L]}^+ + 2\text{H}^+ \quad (5.6)$$

The size of the metal ions correlates to the actual number of coordination sites. The sequestering agent EDTA acts as a quadri-dentate ligand when bonded to Ca$^{2+}$ and Y$^{3+}$/Eu$^{3+}$, forming a complex water-soluble structure. This leads to competition among the Ca$^{2+}$ and [Y$^{3+}$/Eu$^{3+}$] with [H$_2$L]$^{2-}$. The formation
reaction of the complex reaction of EDTA and metal cations proceeds as given in equation (6).

Figure 5.1: FESEM images of the $\text{Ca}_{0.5}\text{Y(MoO}_4)_2$:Eu$^{3+}$ 3D structures synthesized at different time intervals (i.e.) (a) Room Temperature (RT), (b) 2h, (c) 4h and (d) 6h with concentration of EDTA as fixed. The scale represented in figure is 1 $\mu$m.

Figure 5.2: FESEM images of the as synthesized $\text{Ca}_{0.5}\text{Y(MoO}_4)_2$:Eu$^{3+}$ 3D architectures at different time intervals (i.e.) (a) 9h, (b) 12h, (c) 24h and (d) magnified view of bi-pyramid.

In general, the actual values of coordination strongly depend on the sizes of the metal ions. At pH values greater than 6, the EDTA molecules create a multi-dentate complex with the surfaces of the metal ions. During the interaction,
the donor atoms of EDTA successfully protect the Ca$^{2+}$/Y$^{3+}$ ions. The confiscating agent EDTA acts as a quadri-dentate ligand connected with Ca$^{2+}$ and Y$^{3+}$/Eu$^{3+}$, creating the structure of a water-soluble complex. This leads to rivalry between the Ca$^{2+}$ and [Y$^{3+}$/Eu$^{3+}$] with [H$_2$L]$^2$. The detailed mechanism of formation of the EDTA complex is addressed in great detail.

Figure 5.3: (a) TEM image of the as synthesized sample at 24 h time interval, (b) FESEM image of the synthesized sample at 48 h time interval.

5.3.1.2 Powder X-ray diffraction analysis

Figure 5.4: Indexed XRD patterns of the as synthesized Ca$_{0.5}$Y(MoO$_4$)$_2$ doped with different doping [(A) host, (A$_1$) Eu$^{3+}$, (A$_2$) Pr$^{3+}$, (A$_3$) Sm$^{3+}$, (A$_4$) Tb$^{3+}$ and (A$_5$) Dy$^{3+}$], (b) [(B) Yb$^{3+}$/Er$^{3+}$, (B$_1$) Yb$^{3+}$/Ho$^{3+}$ and (B$_2$) Yb$^{3+}$/Tm$^{3+}$].

The crystallinities and phase purities of the prepared products were examined using indexed powder X-ray diffraction patterns. Figure 5.4 (a) and (b)
show the XRD patterns of the $\text{Ca}_{0.5}\text{Y}_{(1-x)}\text{(MoO}_4\text{)}_2\cdot x\text{RE}^{3+}$ (RE = Pr, Sm, Eu, Tb, Dy, Yb$^{3+}$/Er$^{3+}$, Yb$^{3+}$/Ho$^{3+}$, and Yb$^{3+}$/Tm$^{3+}$) obtained after 24 h reaction with chelating agent EDTA at 180°C and a pH of ~ 7 to 8. The compound $\text{Ca}_{0.5}\text{Y}_{(1-x)}\text{(MoO}_4\text{)}_2\cdot x\text{RE}^{3+}$ is found to crystallize in the scheelite tetragonal crystal structure with the I4$_1$/a space group [87]. The unit cell of $\text{Ca}_{0.5}\text{Y}_{(1-x)}\text{(MoO}_4\text{)}_2$ consists of $\text{[MoO}_4\text{]}^{2-}$ anions and $\text{Ca}^{2+}$ and $\text{Y}^{3+}$ cations. In this phase, the central tetrahedral sites are occupied by Mo$^{6+}$ and surrounded by four equivalent O$^{2-}$ anions. Divalent $\text{Ca}^{2+}$ and trivalent $\text{Y}^{3+}$ occupy the dodecahedral sites of the tetrahedral symmetry [87]. In the XRD pattern, all peaks are perfectly indexed, indicating a pure tetragonal phase with the scheelite crystal structure. The (1 0 1), (1 1 2), (0 0 4), (2 0 0), (2 0 4), (2 2 0), (1 1 6), and (1 3 2) planes are in perfect agreement with those of JCPDS card no. 82-2369 of $\text{NaY(MoO}_4\text{)}_2$. No other impurity peaks are observed. No peak shift is observed with doping. The strongest peak of (1 1 2) is obtained at 28.95°.

### 5.3.1.3 FT-Raman Analysis

![FT-Raman spectrum](image)

**Figure 5.5:** FT-Raman spectrum of Eu$^{3+}$ doped $\text{Ca}_{0.5}\text{Y(MoO}_4\text{)}_2$.

Figure 5.5 shows the normalized Raman scattering spectra of the $\text{Ca}_{0.5}\text{Y}_{0.84}(\text{MoO}_4)_2\cdot 0.16\text{Eu}^{3+}$ powder sample. In general, the scheelite crystal structure has $C^6_{4h}$ symmetry. Internal vibrations are caused by movements inside the $\text{MoO}_4$ molecular group. The motion of $\text{Ca}^{2+}$ and the rigid molecular
unit, designated as translational modes, are associated with lattice phonons or external vibrations. Vibrational modes are also observed within the spectra. Several peaks arising from Raman-active internal modes of the tetrahedral MoO$_4$ are $T(B_g E_g E_g)$, $v_{f.r.}(A_g)$, $v_2(A_g)$, and $v_4(B_g)$, corresponding to the locations of 102.91, 210.91, 323.20, and 397.41 cm$^{-1}$ respectively [102, 103]. The phonon energy of the Ca$_{0.5}$Y$_{(1-x)}$(MoO$_4$)$_2$:Eu$^{3+}$ is found to be maximum at 323 cm$^{-1}$, which is attributed to the symmetric bending vibrations within the [MoO$_4$]$^{2-}$ clusters [104].

5.3.1.4 Down-conversion luminescence properties of Ca$_{0.5}$Y$_{(1-x)}$(MoO$_4$)$_2$:xLn$^{3+}$ (Ln = Eu, Pr, Sm, Tb, and Dy)

5.3.1.4.1 Ca$_{0.5}$Y$_{(1-x)}$(MoO$_4$)$_2$:xEu$^{3+}$

Figure 5.6 (a) depicts the room-temperature PL excitation spectrum of the Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$ (x = 0.16 M) phosphor in response to $\lambda_{em} = 395$ nm. The excitation spectrum shows two regions of a wide band and a series of sharp peaks. The wide band, located from 225 - 350 nm and centered at 296 nm, corresponds to the O$^{2-}$ to Eu$^{3+}$ ligand-to-metal-charge-transfer transition (LMCT) [105]. Above 350 nm, intense sharp peaks are located at 362 nm ($^7F_0 \rightarrow ^5D_4$), 382 nm ($^7F_0 \rightarrow ^5L_7$), 395 nm ($^7F_0 \rightarrow ^5L_6$), 416 nm ($^7F_0 \rightarrow ^5D_3$) and 465 nm ($^7F_0 \rightarrow ^5D_2$). Among these, the most intense peak is found at 395 nm. This intense peak in the UV region is suitable for exciting Eu$^{3+}$ ions. The room-temperature PL emission spectra are shown in Figure 5.6 (b) for phosphors reacted for different time intervals at 180°C. The emission spectra under 395 nm UV excitation for Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$ (x = 0.16M) shows a number of intra-configurational f-f transitions arising from the Eu$^{3+}$ $^5D_0$ excited state to the $^7F_J$ ($J = 1, 2, 3,$ and 4) ground states [106].

Under other excitation wavelengths using LMCT, no remarkable change is observed in the emission spectra. The intense emission peak at 615 nm under 395 nm UV excitation arises from the $^5D_0 \rightarrow ^7F_2$ electric-dipole transition, which shows a parity-forbidden ($\Delta J = 2$) hypersensitive red emission [107]. Two sub-
peaks arise from Stark energy splitting; that is, \((2J + 1)\) Stark components of J-degeneracy splitting [108]. The dominance of the electric-dipole transition confirms that the Eu\(^{3+}\) ions are located at sites without inversion symmetry. For a particular host lattice, \(^5\!D_0\rightarrow^7\!F_J\) emissions yield the necessary information on the site symmetry of Eu\(^{3+}\) [109]. The other transition found at 590 nm shows an orange emission and results from the magnetic-dipole transition \((^5\!D_0\rightarrow^7\!F_1)\), the last transitions at 656 nm \((^5\!D_0\rightarrow^7\!F_3)\) and 704 nm \((^5\!D_0\rightarrow^7\!F_4)\) are both relatively weak.

Figure 5.6: For Eu\(^{3+}\) doped Ca\(_{0.5}\)Y(MoO\(_4\))\(_2\) (a) PL excitation spectrum, (b) PL emission spectra at different reaction time and (c) The integrated areas of the emissions caused by the \(^5\!D_0\rightarrow^7\!F_1\) (orange) and \(^5\!D_0\rightarrow^7\!F_2\) (red) transitions as a function of the reaction time and (d) Plot of R/O ratio versus reaction time.

The PL emission intensity increases with increasing time intervals until 24 h have elapsed reaching the maximum value at 24 h because of the
continuous growth of the crystallites. The emission intensity due to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition becomes higher than the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition [110]. When the reaction time interval has reached 48 h, the PL emission intensity gets decreased suddenly because the increased time interval permits the fragmentation of the particles [111]. The integrated areas of the emissions caused by the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (orange) and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (red) transitions as a function of the reaction time interval is shown in Figure 5.6 (c) and their corresponding ratio between the red to orange emission (R/O) is shown in Figure 5.6 (d). Its maximum value is 5.2065 for the 24-h time interval. This indicates the red color purity of the prepared phosphor [112]. From this investigation, it is clear that, as Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$ possesses the scheelite tetragonal structure with C$_{3v}$ site symmetry, it could be used for display applications.

5.3.1.4.2 Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xPr$^{3+}$

Figure 5.7: For Pr$^{3+}$ doped Ca$_{0.5}$Y(MoO$_4$)$_2$ (a) PL excitation spectrum, (b) PL emission spectrum of the powder phosphor.

Figure 5.7 (a) shows the room-temperature PL excitation spectrum of bi-pyramid-like Ca$_{0.5}$Y$_{0.84}$(MoO$_4$)$_2$:0.16Pr$^{3+}$ phosphor under the monitoring wavelength of $\lambda_{em} = 653$ nm. The excitation spectrum consists of a broad peak between 220 and 350 nm with a center at 294 nm and sharp peaks of low intensity between 360 nm and 520 nm. The broad peak arises from Mo-O charge transfers (CT). The sharp peaks at 449 nm, 475 nm, and 489 nm correspond to the f-f transitions of Pr$^{3+}$ of $^3\text{H}_4 \rightarrow ^3\text{P}_2$, $^3\text{H}_4 \rightarrow ^3\text{P}_1$, and $^3\text{H}_4 \rightarrow ^3\text{P}_0$, respectively. The strongest peak is at 451 nm and may be suitable for the
excitation of Pr$^{3+}$ ions. Figure 5.7 (b) shows the room-temperature PL emission spectrum for Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xPr$^{3+}$ ($x = 0.16M$) monitored at $\lambda_{ex} = 449$ nm. The emission spectrum consists of three intense peaks at 620 nm, 653 nm, and 692 nm corresponding to $^3P_0 \rightarrow ^3H_6$, $^3P_0 \rightarrow ^3F_2$, and $^3P_0 \rightarrow ^3F_3$, respectively, from f-f intra-configurational transitions in Pr$^{3+}$. The presence of the sharp peaks indicates the high crystallinity of the as-prepared products which results in brighter luminescence bands. The most intense peaks among these transitions at 653 nm shows a characteristic deep red emission. The weak emission at 620 nm results from the $^3P_0 \rightarrow ^3H_6$, transition which is induced by the lack of inversion symmetry at the Pr$^{3+}$ sites. The narrow emission at 653 nm implies that energy is effectively transferred from the absorptions at 451 nm, 475 nm, and 489 nm [113].

5.3.1.4.3 Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xSm$^{3+}$

![Figure 5.8: For Sm$^{3+}$ doped Ca$_{0.5}$Y(MoO$_4$)$_2$ (a) PL excitation spectrum, (b) PL emission spectrum of the powder phosphor.](image)

The room-temperature PL excitation spectrum of Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xSm$^{3+}$ ($x=0.16$ M), monitored at $\lambda_{em} = 647$ nm, is shown in Figure 5.8 (a). The PLE spectrum for monitoring the $^4G_{5/2} \rightarrow ^6H_{9/2}$ emission of Sm$^{3+}$ shows a broad CT band centered at $\sim$ 283 nm owing to the O$^{2-} \rightarrow$ Sm$^{3+}$ and O$^{2-} \rightarrow$ Mo$^{6+}$ transitions;
other narrow peaks appear at 340 – 540 nm. According to molecular orbital theory, the CT band arises from the electronic transition from the 2p orbital of O\(^2\) to the 4f orbital of Sm\(^{3+}\) and the empty d orbital of Mo\(^{6+}\) in the MoO\(_4\)\(^{6-}\) groups [114]. From the appearance of the CT absorption band, it can be inferred that the energy is transferred from the host to Sm\(^{3+}\); the transfer can be judged to be stronger because of the higher intensity of the peak. In addition to this, narrow f-f transitions are observed between 340 and 540 nm. Among all f-f transitions, the strongest peak is observed at 404 nm, corresponding to the \(^6\)H\(_{5/2}\) → \(^4\)K\(_{11/2}\) transition which matches well with the wavelengths of commercial near-UV LED chips [115].

The corresponding PL emission spectrum resulting from irradiation with excitation wavelength \(\lambda_{ex} = 404\) nm is shown in Figure 5.8 (b). The emission spectra for Ca\(_{0.5}\)Y\(_{1-x}\)(MoO\(_4\))\(_2\):xSm\(^{3+}\) (x = 0.16M) monitored at \(\lambda_{ex} = 404\) nm contains three intense peaks at 554 nm (\(^4\)G\(_{5/2}\) → \(^6\)H\(_{5/2}\)), 603 nm (\(^4\)G\(_{5/2}\) → \(^6\)H\(_{7/2}\)), and 647 nm (\(^4\)G\(_{5/2}\) → \(^6\)H\(_{9/2}\)). The strongest peak at 647 nm shows a characteristic red emission. In general, the intensities of the \(^4\)G\(_{5/2}\) → \(^6\)H\(_{5/2}\) and \(^4\)G\(_{5/2}\) → \(^6\)H\(_{9/2}\) transitions depend on the local symmetry of the crystal field of the Sm\(^{3+}\) ions. The electric dipole (ED) transition \(^4\)G\(_{5/2}\) → \(^6\)H\(_{9/2}\) with \(\Delta J =2\) would be predominant and hypersensitive to the crystal field environment, as long as the Sm\(^{3+}\) ions occupy the lattice sites with no inversion centers. The magnetic dipole (MD) transition \(^4\)G\(_{5/2}\) → \(^6\)H\(_{9/2}\) is not sensitive to the site symmetry. To confirm this, the intensity ratio of ED/MD can be determined to identify the symmetry of the Sm\(^{3+}\) environment. For Ca\(_{0.5}\)Y\(_{0.84}\)(MoO\(_4\))\(_2\):0.16Sm\(^{3+}\), the ED/MD ratio is 0.67, suggesting that the Sm\(^{3+}\) ions occupy the lattice sites with no inversion centers. This is in agreement with the crystal structure of Sm\(^{3+}\) in the Y\(^{3+}\) sites having C\(_{3v}\) symmetry in the Ca\(_{0.5}\)Y(MoO\(_4\))\(_2\) host [116].

5.3.1.4.4 Ca\(_{0.5}\)Y\(_{(1-x)}\)(MoO\(_4\))\(_2\):xTb\(^{3+}\)

In the Ca\(_{0.5}\)Y\(_{1-x}\)(MoO\(_4\))\(_2\):xTb\(^{3+}\) (x=0.16 M) phosphor, the PL excitation spectrum as shown in Figure 5.9 (a) monitored using 545 nm emission
wavelength contains a broad band ranging from 250 to 350 nm, peaking at ~ 282 nm. This is attributed to the LMCT transitions from O\(^{2-}\) to Mo\(^{6+}\) and O\(^{2-}\) to Tb\(^{3+}\); the other sharp band peaking between 390 and 410 nm is related to the \(^7\)F\(_6\) → \(^5\)G\(_5\) transition of Tb\(^{3+}\) [117]. The energy transfer occurs from the 4f\(^8\) to 4f\(^7\)5d configuration of Tb\(^{3+}\). Figure 5.9 (b) contains the emission spectra for Ca\(_{0.5}\)Y\(_{1-x}\)(MoO\(_4\))\(_2\):xTb\(^{3+}\) (x = 0.16M) under 296 nm UV excitation. The PL spectrum contains four bands peaking at 491 nm (\(^5\)D\(_4\) → \(^7\)F\(_6\)), 545 nm (\(^5\)D\(_4\) → \(^7\)F\(_5\)), 588 nm (\(^5\)D\(_4\) → \(^7\)F\(_4\)), and 621 nm (\(^5\)D\(_4\) → \(^7\)F\(_3\)). Among these, the most significant peak is found at 545 nm, corresponding to an emission of green light, owing to the pre-dominant transition of \(^5\)D\(_4\) → \(^7\)F\(_5\). The selection rule \(\Delta J = \pm 1\) was followed by the most intense and hypersensitive transition \(^5\)D\(_4\) → \(^7\)F\(_5\). As the energy transfer from the host populates only the \(^5\)D\(_4\) level, this predominant transition is possible. The pre-dominant emission peak shows two sub-peaks owing to Stark energy splitting [118].

![Figure 5.9](image-url)

Figure 5.9: For Tb\(^{3+}\) doped Ca\(_{0.5}\)Y(MoO\(_4\))\(_2\) (a) PL excitation spectrum, (b) PL emission spectrum of the powder phosphor.

5.3.1.4.5 Ca\(_{0.5}\)Y\(_{1-x}\)(MoO\(_4\))\(_2\):xDy\(^{3+}\)

Figure 5.10 (a) shows the room-temperature PL excitation spectrum for the phosphor Ca\(_{0.5}\)Y\(_{1-x}\)(MoO\(_4\))\(_2\):xDy\(^{3+}\) (x = 0.16 M) under 353 nm excitation. The
spectrum consists of a strong band arising from the absorption of the host, ranging from 220 to 340 nm in the UV region with a maximum at ~ 294 nm. This is designated as a charge transfer transition with sharper lines located in the longer-wavelength region. Above 340 nm, intra-configurational f-f transitions within the Dy$^{3+}$ 4f$^9$ configuration are found at 352 nm ($^6H_{15/2} \rightarrow ^6P_{7/2}$), 367 nm ($^6H_{15/2} \rightarrow ^6P_{5/2}$) and 388 nm ($^6H_{15/2} \rightarrow ^4I_{13/2}$). The most intense transition occurs at 352 nm, which may be suitable for exciting Dy$^{3+}$ ions. With the excitation wavelength fixed at 352 nm, the PL spectrum for the phosphor Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xDy$^{3+}$ ($x = 0.16$ M) is recorded as shown in Figure 5.10 (b).

The emission spectrum shows two major peaks at 485 nm, corresponding to the MD transition of $^4F_{9/2} \rightarrow ^6H_{15/2}$, and 575 nm, corresponding to the forced ED transition of $^4F_{9/2} \rightarrow ^6H_{13/2}$ [119]. The MD transition is much less sensitive to the coordination environment than typical ED transitions. The forced ED transition is allowed only in the case of Dy$^{3+}$ located at sites with non-inversion-center symmetry [120]. The blue emission centered at 485 nm is weaker in intensity than the dominant yellow emission. The yellow-to-blue line ratio is 3.5313, implying that the forced ED transition is dominant and suggesting that Dy$^{3+}$ ions are located at sites without inversion-center symmetry in the Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$ host [121].

![Figure 5.10: For Dy$^{3+}$ doped Ca$_{0.5}$Y(MoO$_4$)$_2$ (a) PL excitation spectrum, (b) PL emission spectrum of the powder phosphor.](image)
5.3.1.5 Up-conversion luminescence properties of Ca$_{0.5}$Y$_{(1-x)}$(MoO$_4$)$_2$:xYb$^{3+}$/yLn$^{3+}$ (Ln = Er, Ho, and Tm)

5.3.1.5.1 Ca$_{0.5}$Y$_{(1-x-y)}$(MoO$_4$)$_2$:xYb$^{3+}$/yEr$^{3+}$

Figure 5.11: (a) Up-conversion luminescence spectra of Yb$^{3+}$/Er$^{3+}$ doped Ca$_{0.5}$Y(MoO$_4$)$_2$ powder and thin film phosphor, (b) its corresponding NIR emission spectrum and (c) 1.53 µm IR emission spectrum.

Figure 5.11 (a) depicts the up-conversion luminescence spectra of the Ca$_{0.5}$Y$_{(1-x-y)}$(MoO$_4$)$_2$:xYb$^{3+}$/yEr$^{3+}$ (x=0.05 and y = 0.03 M) phosphors upon 980 nm excitation of the corresponding thin phosphor film as-deposited in 300mTorr. Three visible light emission peaks, located at 525 nm ($^2$H$_{11/2} \rightarrow ^4$I$_{15/2}$), 551 nm ($^4$S$_{3/2} \rightarrow ^4$I$_{15/2}$), and 654 nm ($^4$F$_{9/2} \rightarrow ^4$I$_{15/2}$), are observed in the up-conversion PL spectrum [122]. The major peak with a center at 525 nm was the most intense for all tested doping concentrations. The red emission at 654 nm was weaker because of cross-relaxation between Er$^{3+}$ ions [123]. Further, NIR and IR emissions were obtained by excitation at 980 nm and 1.53 µm, respectively.
When the phosphor is excited with an excitation wavelength of 1.53 µm, a wide emission band is observed with a center at 980 nm, as shown in Figure 5.11 (b). This results from the combination of Er$^{3+}$ and Yb$^{3+}$ emissions with the corresponding transitions of $^{4}I_{11/2} \rightarrow ^{4}I_{15/2}$ and $^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$, respectively. Upon 980 nm laser excitation, non-uniform broadening is distinctly observed at 1533 nm ($^{4}I_{13/2} \rightarrow ^{4}I_{15/2}$) as shown in Figure 5.11 (c) by the IR emission of Er$^{3+}$ ions. From the nanophosphor and thin phosphor film spectrum shown in Fig. 5.11 (a), it is observed that the splitting of the pre-dominant ~525 nm transition is uniform. No peak shift is observed for any transitions.

5.3.1.5.2 Ca$_{0.5}$Y$_{(1-x-y)}$(MoO$_4$)$_2$:xYb$^{3+}$/yTm$^{3+}$

Upon 980 nm laser irradiation, an intense up-converted visible emission spectrum is found from Ca$_{0.5}$Y$_{(1-x-y)}$(MoO$_4$)$_2$:xYb$^{3+}$/yTm$^{3+}$ (x = 0.05 and y = 0.03 M), as depicted in Figure 5.12. Three energy transfer transitions exist when Yb$^{3+}$ ions are excited by the pump light. As a result of these transitions, energy is transferred between Yb$^{3+}$ ions and Tm$^{3+}$ ions which populate the $^{1}G_{4}$ and $^{3}F_{3}$ levels [124]. The emission peak centered at 474 nm is attributed to the blue-colored emission with the transition of $^{1}G_{4} \rightarrow ^{3}H_{6}$.

Two red emission bands are observed at 649 nm ($^{1}G_{4} \rightarrow ^{3}F_{4}$) and 693 nm ($^{3}F_{3} \rightarrow ^{3}H_{6}$). It is evident from the emission spectrum that the intense sharp blue emission peak, originating from the transition of $^{1}G_{4} \rightarrow ^{3}H_{6}$ (474 nm) is higher in intensity than the other two peaks. The $^{1}D_{2}$ level of Tm$^{3+}$ cannot be populated because of the energy mismatch between Yb$^{3+}$ and Tm$^{3+}$ ions; hence, the transitions $^{1}D_{2} \rightarrow ^{3}F_{4}$ and $^{1}D_{2} \rightarrow ^{1}G_{4}$ are not observed. The $^{1}D_{2}$ level of Tm$^{3+}$ ions can be populated by increasing the doping concentration of Tm$^{3+}$ [125].

The optimal doping concentration of Tm$^{3+}$ determines the population of the $^{1}D_{2}$ level, which results from the effective cross-relaxation process between Tm$^{3+}$ ions. According to Wang et al. [126], the $^{1}D_{2}$ level of Tm$^{3+}$ can be populated by the familiar cross-relaxation processes such as $^{3}F_{2}+ ^{3}H_{4} \rightarrow ^{3}H_{6}$+
$^1D_2$ and $^1G_{4+}^3H_4 \rightarrow ^3F_{4+}^1D_2$. Hence, the up-conversion emission intensity is increased with increasing the doping concentration of Tm$^{3+}$.

![Graph showing emission spectrum with peaks at 474 nm, 649 nm, and 693 nm.]

**Figure 5.12:** Up-conversion luminescence emission spectrum of Ca$_{0.5}$Y(MoO$_4$)$_2$ doped with Yb$^{3+}$/Tm$^{3+}$.

**5.3.1.5.3 Ca$_{0.5}$Y($1-x$-$y$)(MoO$_4$)$_2$:xYb$^{3+}$/yHo$^{3+}$**

![Graph showing emission spectrum with peaks at 660 nm and 541 nm.]

**Figure 5.13:** Up-conversion luminescence emission spectrum of Ca$_{0.5}$Y(MoO$_4$)$_2$ doped with Yb$^{3+}$/Ho$^{3+}$.
Figure 5.13 shows the up-converted emission spectrum in the visible region of Ca$_{0.5}$Y$_{(1-x-y)}$(MoO$_4$)$_2$:$x$Yb$^{3+}$/yHo$^{3+}$ ($x = 0.05$ and $y = 0.03$ M) upon 980 nm laser irradiation. The emission peak in the green visible region observed at 541 nm is attributed to the $^5$S$_2$$\rightarrow$$^5$I$_8$ transition, while the red emission peaking at 660 nm may originate from the $^5$F$_5$$\rightarrow$$^5$I$_8$ transition [127]. Because of the combination of up-converted green and red emission bands, the phosphor doped with Ho$^{3+}$ (0.03 M) exhibits a yellow-colored emission. The up-converted emission peak in the red region is more intense than the green up-converted emission peak, as observed in spectrum of Ca$_{0.5}$Y(MoO$_4$)$_2$:Yb$^{3+}$/Ho$^{3+}$ [128].

5.3.1.6 Photometry and Decay-time studies

Figure 5.14: CIE diagram of Ca$_{0.5}$Y(MoO$_4$)$_2$ doped with different doping (a) [(A) Eu$^{3+}$, (B) Pr$^{3+}$, (C) Sm$^{3+}$, (D) Tb$^{3+}$ and (E) Dy$^{3+}$] and (b) [(a) Yb$^{3+}$/Er$^{3+}$, (b) Yb$^{3+}$/Ho$^{3+}$ and (c) Yb$^{3+}$/Tm$^{3+}$].

The color chromaticity co-ordinates of each phosphor were estimated using the Commission of Internationale del’ Eclairage (CIE) 1931 color matching functions [18, 129]. Fig. 5.14 (a) shows the CIE plot of Ln$^{3+}$-doped Ca$_{0.5}$Y(MoO$_4$)$_2$ (Ln = Eu, Pr, Sm, Tb, and Dy) and Fig. 5.14 (b) shows that of Yb/Er-, Yb/Ho-, and Yb/Tm-doped Ca$_{0.5}$Y(MoO$_4$)$_2$ upon 980 nm NIR excitation [15, 18].
The luminescence decay curves of RE$^{3+}$-doped Ca$_{0.5}$Y(MoO$_4$)$_2$ were fitted well with the single exponential function given by,

$$I = I_0 \exp\left(-\frac{t}{\tau}\right) \quad \text{(5.7)}$$

where $I_0$ is the intensity at time $t=0$ and the corresponding life-time is denoted as $\tau$.

Figure 5.15: Down conversion luminescence decay profiles for Ca$_{0.5}$Y(MoO$_4$)$_2$:Ln$^{3+}$ (Ln = (a) Eu, (b) Pr, (c) Sm, (d) Tb and (e) Dy).
Figure 5.16: Up-conversion luminescence decay profiles for Ca$_{0.5}$Y(MoO$_4$)$_2$:Ln$^{3+}$ (Ln = (a)Yb/Er, (b) Yb/Tm and (c) Yb/Ho).

For Pr$^{3+}$-doped Ca$_{0.5}$Y(MoO$_4$)$_2$, the luminous decay curve is fitted by the following equation [15, 130]:

$$\tau_{\text{avg}} = \frac{\int tI(t)dt}{\int I(t)dt} \quad ... (5.8)$$

The luminous decay profiles and lifetime values for Ln$^{3+}$-doped Ca$_{0.5}$Y(MoO$_4$)$_2$ are shown in Fig. 5.15 (a-e) and 5.16 (a-c), respectively.
5.3.2 Ca\textsubscript{0.5}Y(MoO\textsubscript{4})\textsubscript{2}:Eu\textsuperscript{3+},M\textsuperscript{+} (M = Li, K and Na)

5.3.2.1 X-ray Diffraction Studies

![Indexed powder XRD patterns of the as-synthesized Ca\textsubscript{0.5}Y\textsubscript{(1-x)}(MoO\textsubscript{4})\textsubscript{2}:xEu\textsuperscript{3+},M\textsuperscript{+} (M = Li, K and Na).](image)

Figure 5.17: Indexed powder XRD patterns of the as-synthesized Ca\textsubscript{0.5}Y\textsubscript{(1-x)}(MoO\textsubscript{4})\textsubscript{2}:xEu\textsuperscript{3+},M\textsuperscript{+} (M = Li, K and Na).

The crystal structure and phase identification of the synthesized powders were analysed from indexed powder X-ray diffraction patterns. Figure 5.17 depicts the indexed XRD patterns of the Ca\textsubscript{0.5}Y\textsubscript{(1-x)}(MoO\textsubscript{4})\textsubscript{2}:xEu\textsuperscript{3+},M\textsuperscript{+} (M = Li, K and Na) obtained after 24 h reaction time. The compound is crystallized in the scheelite tetragonal crystal structure with space group of \textit{I}4\textsubscript{1}/a [15]. All diffraction peaks are properly indexed. The planes (1 0 1), (1 1 2), (0 0 4), (2 0 0), (2 0 4), (2 2 0), (1 1 6), and (1 3 2) are in well accordance with JCPDS card no. 82-2369 of NaY(MoO\textsubscript{4})\textsubscript{2} [87]. Impurity peaks are not observed. The strongest peak of (1 1 2) is obtained at 28.92°. The synthesized samples are having high phase purity as no discernible impurity or other phases are found.

5.3.2.2 Morphological Studies

To understand the surface morphology, size and mechanism of formation of the hierarchical bi-pyramid like structures, an EDTA-assisted hydrothermal
route was carried out for 24 hours reaction time. The as-synthesized products were analysed using FESEM. Figure 5.18 (a-c) shows the FESEM images of Ca$_{0.5}$Y$_{(1-x)}$(MoO$_4$)$_2$:xEu$^{3+}$,M$^+$ (M = Li, K and Na) for x = 0.16 M for 24 hours reaction time at 180°C respectively. The methodical studies of detailed evolution of morphology and formation mechanism of hierarchically self-assembled bi-pyramid like micro/nano- architectures were performed previously by the same group. The bi-pyramid like micro/nano- architectures are obtained as and when EDTA is used as a surfactant. In the present scenario also, the evolution of bi-pyramid like morphology is seen [87]. The morphology for various reaction times is not shown because there is no significant variation in the morphology. The best morphology is obtained for 24 hours reaction time. Hence, those morphologies are shown for Ca$_{0.5}$Y$_{(1-x)}$(MoO$_4$)$_2$:xEu$^{3+}$,M$^+$ (M = Li, K and Na). The previous studies suggest that Eu$^{3+}$ ions are homogeneously distributed in the crystal structure. This was confirmed by the elemental mapping associated with FESEM. As a representative, the relative distribution of various important elements such as Ca, Y, Mo, O, Eu and Na were investigated. Figure 5.19 (a-g) of elemental mapping show clearly the rare earth ions incorporation and their homogeneous distribution inside the bi-pyramid-like structure.

Figure 5.18: FESEM images of the as prepared Ca$_{0.5}$Y$_{(1-x)}$(MoO$_4$)$_2$:xEu$^{3+}$ codoped with alkali metal ions (a) Li$^+$, (b) K$^+$ and (c) Na$^+$. The scale in figure is 200 nm.
Figure 5.19: Elemental mapping of (a) Mo, (b) O, (c) Ca, (d) Y, (e) Eu, (f) Na and (g) overall distribution of elements.

5.3.2.3 X-ray photoelectron spectroscopic studies

Figure 5.20: XPS survey spectrum for Ca$_{0.5}$Y$_{(1-x)}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$.}

To investigate the chemical composition and valence states of the material, XPS technique is used. Figure 5.20 shows the representative XPS survey spectra of the Ca$_{0.5}$Y$_{(1-x)}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$. Based on the XPS analysis, it
is confirmed that the presence of core levels of Ca, Y, Mo, O, Eu and Na were present in Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$ obtained in the range of 100 – 300 eV (Eu 4d at 128 eV, Y 3d$_{5/2}$ at 156 eV, Y 3d$_{3/2}$ at 158 eV, Mo 3d$_{5/2}$ at 228 eV, Mo 3d$_{3/2}$ at 233 eV, Eu 4p at 281 eV); 300 – 600 eV(Y 3p at 311 eV, Ca 2p$_{3/2}$ at 347 eV, Ca 2p$_{1/2}$ at 352 eV, Y 3s at 392 eV, Mo 3p$_{3/2}$ at 395 eV, Mo 3p$_{1/2}$ at 413 eV, Mo 3s at 506 eV, O 1s at 530 eV) and 800 – 1200 eV (Na 1s at 1071 eV, Eu 3d$_{5/2}$ at 1125 eV, Eu 3d$_{3/2}$ at 1156 eV). The binding energy data for Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$ was calibrated using carbon (1s, 283.5 eV) as the reference. All the peaks are perfectly coincide with the literature [55].

5.3.2.4 Photoluminescence studies of Ca$_{0.5}$Y(MoO$_4$)$_2$:Eu$^{3+}$,M$^+$ (M = Li, K and Na)

Figure 5.21: (a) PLE spectra for Ca$_{0.5}$Y$_{(1-x)}$(MoO$_4$)$_2$:xEu$^{3+}$,M$^+$ (M = Li, K and Na) phosphors and (b) PL emission spectra for the different alkali metal ion co-doped phosphors Ca$_{0.5}$Y$_{(1-x)}$(MoO$_4$)$_2$:xEu$^{3+}$,M$^+$ (M = Li, K and Na).

The PL excitation spectra of the Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,M$^+$ (M = Li, K and Na) for $x = 0.16$ M as a representative is given in Figure 5.21 (a). The PLE spectra is monitored using an emission wavelength of 616 nm comprises of strong broad bands along with several sharp peaks [131-133]. The broad band ranges from 225-350 nm having a maximum at
~293 nm is designated as the charge transfer band (CTB). It might be attributed to ligand-to-Eu$^{3+}$ metal charge transfer transitions (LMCT) [134, 135]. In addition to that, sharp peaks situated at 362 nm ($^{7}F_0\rightarrow^{5}D_4$), 382 nm ($^{7}F_0\rightarrow^{5}L_7$), 395 nm ($^{7}F_0\rightarrow^{5}L_6$), 416 nm ($^{7}F_0\rightarrow^{5}D_3$), 465 nm ($^{7}F_0\rightarrow^{5}D_2$) and 535 nm ($^{7}F_0\rightarrow^{5}D_1$) are due to the 4f-4f transition of Eu$^{3+}$ ions [136]. When comparing to all the peaks, the most sharp and intense peak is found at 395 nm. The as prepared phosphor could be suitably excited by this UV region. The maximum intensity in the excitation spectra is for Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$ phosphor when compared to Li$^+$ and K$^+$ co-doped Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$. The room-temperature PL emission spectra excited at 395 nm excitation wavelength for Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,M$^+$ (M = Li, K and Na) for x = 0.16M is shown in Figure 5.21 (b) for 24 hours reaction time at 180°C. The PL spectra depicts numerous intra-configurational f-f transitions arising from Eu$^{3+}$ $^5D_0$ excited state to the $^7F_J$ ($J = 1, 2, 3, \text{ and } 4$) ground states [137, 138]. When exciting with various excitation wavelengths and LMCT, no significant variation is detected in the emission spectra. The PL emission spectra comprise of strong red emission peak at 617 nm corresponding to the $^5D_0\rightarrow^7F_2$ transition, and some weak emissions at 593 nm ($^5D_0\rightarrow^7F_1$), 656 nm ($^5D_0\rightarrow^7F_3$) and 703 nm ($^5D_0\rightarrow^7F_4$) transitions respectively. Among these two emission bands, $^5D_0\rightarrow^7F_2$ and $^5D_0\rightarrow^7F_1$ transitions are due to the characteristic emissions of Eu$^{3+}$ ions. Following the forced electric dipole (ED) transition whose selection rule ($\Delta J \leq 6$, when $J$ or $J' = 0$, $\Delta J = 2, 4, 6$), $^5D_0\rightarrow^7F_2$ transition is considered as the ED transition which comes under the category of hypersensitive transition, hence its intensity is most sensitive to crystal field [139]. In general, this characteristic emission is dominant when Eu$^{3+}$ ions occupy the sites of non-inversion centers. For the comparison, the $^5D_0\rightarrow^7F_1$ transition is attributed to magnetic dipole (MD) transition, thus the crystal field would have meager effect on its intensity. The hypersensitive red emission at 617 nm ($^5D_0\rightarrow^7F_2$) suggest that the Eu$^{3+}$ ions occupy the low symmetry sites without inversion center.
in Ca$_{0.5}$Y(MoO$_4$)$_2$ host lattice [140]. The PL emission intensity is higher for Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:$x$Eu$^{3+}$,Na$^+$ than the Li$^+$ and K$^+$ co-doped Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:$x$Eu$^{3+}$.

5.3.2.5 Effect of alkali cations and rare earth ions on the luminescence properties of Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:$x$Eu$^{3+}$

In the existing matrix, Eu$^{3+}$ and M$^+$ co-doped in Ca$_{0.5}$Y(MoO$_4$)$_2$ would accelerate a distortion in lattice and the lattice symmetry is being lowered [19]. The co-doped Eu$^{3+}$ and M$^+$ at Ca$^{2+}$ sites in synthesized samples could play a dominant role with increased luminescence intensity. This is based on modifying the symmetry and their surroundings in the vicinity of rare earth ions by adding charge compensators of alkali metal ions [141]. Figure 5.21 (b) depicts the PL emission spectra of Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:$x$Eu$^{3+}$,M$^+$ (M = Li, K and Na) phosphors for x=0.16 M with 24 hours reaction time by the addition of alkali chlorides. The emission intensity is enormously increased for Na$^+$ ion co-doped Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:$x$Eu$^{3+}$. This could be due to the charge compensation effect and the possible mechanism is Ca$^{2+}$→2M$^+$ (M = Li$^+$, K$^+$, Na$^+$) which is described in detail in the literature [18]. Also, the ionic radius of Na$^+$ (0.97
Å) is closer to the Ca\(^{2+}\) (1.12 Å) which is comparatively better than that of K\(^{+}\) (1.33 Å) and Li\(^{+}\) (0.59 Å) [15, 18]. Hence, the Ca\(^{2+}\) ions are effectively replaced by the alkali metal ions. This is the possible mechanism for the enhanced intensity. Also, to identify the best charge compensator ion, the precursors are varied for the preparation of Na\(^{+}\), K\(^{+}\) and Li\(^{+}\) charge compensated \(\text{Ca}_{0.5}\text{Y}_{1-x}(\text{MoO}_4)_2:x\text{Eu}^{3+}\) is performed by taking the stoichiometric amounts of \(\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}\), \(\text{K}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}\) and \(\text{Li}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}\), respectively. Figure 5.22 (a) and (b) show the PL excitation and emission spectra for \(\text{Ca}_{0.5}\text{Y}_{1-x}(\text{MoO}_4)_2:x\text{Eu}^{3+},\text{M}^{+}\) (\(\text{M} = \text{Li}, \text{K}\) and Na) phosphors.

It is evident from Figure 5.22 (a-b), Na\(^{+}\) ion activated \(\text{Ca}_{0.5}\text{Y}_{1-x}(\text{MoO}_4)_2:x\text{Eu}^{3+}\) is showing the enhanced intensity. As a whole, in both the cases, by fixing the precursors along with varying the co-doping of alkali metal ions and also by varying three different precursor materials, Na\(^{+}\) ion is playing a major role in enhancing the luminescence intensity and proposed as best charge compensator. From these findings, it is suggested that these phosphors would be the appropriate red phosphor candidates for display applications.

5.3.2.6 Judd-Ofelt Theory and Spectroscopic Properties

The characteristics of the luminescence behaviour of Eu\(^{3+}\) in \(\text{Ca}_{0.5}\text{Y}_{1-x}(\text{MoO}_4)_2\) can be examined by the detailed studies of Judd-Ofelt (J-O) intensity parameters, \(\Omega_j\) (\(j = 2, 4\)) [142, 143]. The \(\Omega_2\) was dependent on the environment and are associated to the structural changes and covalency in the proximity of the Eu\(^{3+}\) ion. Thus they are greatly considered as short range effect. \(\Omega_4\) was associated with the long range effect [81].

In general, the intensity parameters would be deduced from the absorption spectra [144].Thus, Eu\(^{3+}\) has special energy level structure;
hence these intensity parameters could be estimated from the emission spectra [81, 144].

Based on the following relation between radiative emission rate and associated with intensity of the two manifolds $^5\text{D}_0$ and $^7\text{F}_J$ of the Eu$^{3+}$ ion can be calculated using the equation [144],

$$A_{0-J} = A_{0-1} \frac{I_{0-J}}{I_{0-1}} \frac{\hbar \nu_{0-1}}{\hbar \nu_{0-J}} \quad \cdots (5.9)$$

where $I_{0-J}$ and $I_{0-1}$ are integral intensities of $^5\text{D}_0 \rightarrow ^7\text{F}_J$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ attributed to magnetic dipole transition and $\hbar\nu_{0,J}$ and $\hbar\nu_{0,1}$ are their associated energies respectively [93]. The magnetic dipole radiative emission rate possesses a value of 50 s$^{-1}$ [26, 145].

The radiative emission rates $A_{0,J}$ could be associated to forced electric dipole transitions and would be expressed as a function of the J-O intensity parameters as [26],

$$A_{0-J} = \frac{64\pi^4(v_{0-J})^3 e^2}{3hC^3} \frac{1}{4\pi\epsilon_0} \chi \sum_{J=2,4} \Omega_J \left| \left\langle 5\text{D}_0 | U(J) \right| ^7\text{F}_J \right|^2 \quad \cdots (5.10)$$

where $e$ is the electric charge, $\chi$ is the Lorentz field correction factor represented as a function of refractive index of the host $\chi = \frac{n(n^2+2)^2}{9}$ [58].

The $\left\langle 5\text{D}_0 | U(J) \right| ^7\text{F}_J \right|^2$ is denoted as square reduced matrix elements and those values do not depend on the chemical environment of the Eu$^{3+}$ ion [144].

Their values are familiar and are given by $\left\langle 5\text{D}_0 | U(J) \right| ^7\text{F}_2 \right|^2 = 0.0032$ and $\left\langle 5\text{D}_0 | U(J) \right| ^7\text{F}_4 \right|^2 = 0.0023$ [58, 146]. Based on Eqs. (9) and (10), the values of $\Omega_J$ were achieved.
The estimated Judd-Ofelt parameters could be utilized to evaluate the total radiative transition probability ($A_T$) and lifetime ($\tau_{\text{rad}}$) [147, 148].

The radiative transition probability ($A_T$) was obtained using the equation below:

$$A_T = \sum_{j'} A_{0-j'} \quad \cdots (5.11)$$

The radiative lifetime $\tau_{\text{rad}}$ for an excited state is given as:

$$\tau_{\text{rad}} = \frac{1}{A_T} \quad \cdots (5.12)$$

The Judd–Ofelt intensity parameters and radiative transition probability for Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$ phosphors are given in Table 5.1. In all the cases, $\Omega_2 > \Omega_4$ suggest that forced electric dipole transition is having dominancy and possess asymmetry is higher and the covalency of Eu$^{3+}$ ions in the present hosts [81].

The branching ratio and non-radiative rate expressed by the following relations [58, 100],

$$\beta(\psi|) = \frac{A(\psi, \psi|')}{A_T(\psi|)} \quad \cdots (5.13)$$

$$A_{NR} = \frac{1}{\tau} - A_T \quad \cdots (5.14)$$

The emission quantum efficiency from the emitting $^5D_0$ level is given by [148],

$$\eta = \frac{A_T}{A_T + A_{NR}} \quad \cdots (5.15)$$

The luminescence quantum efficiency ($\eta$) values are given in Table 5.1 and these values are reasonably good for Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$.
phosphors which suggests that these phosphor candidates are good for the display applications.

Table 5.1: Judd-Ofelt intensity and radiative parameters, quantum efficiency for the phosphors Ca$_{0.5}$Y(MoO$_4$)$_2$:Eu$^{3+}$,Na$^+$. 

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>J-O intensity parameters (x$10^{-20}$ cm$^2$)</th>
<th>Transitions</th>
<th>$\Omega_2$</th>
<th>$\Omega_4$</th>
<th>$A_{0,2,4}$ (s$^{-1}$)</th>
<th>$A_{0,1}$ (s$^{-1}$)</th>
<th>$A_T$ (s$^{-1}$)</th>
<th>$\beta$ (%)</th>
<th>Quantum efficiency $\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_{0.5}$Y(MoO$_4$)$_2$:Eu$^{3+}$,Na$^+$</td>
<td>9.71 4.59</td>
<td>$^7$D$_0\rightarrow^7$F$_1$</td>
<td>—</td>
<td></td>
<td>683.00</td>
<td>50</td>
<td>966.00</td>
<td>5.18</td>
<td>70.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^5$D$_0\rightarrow^7$F$_2$</td>
<td></td>
<td></td>
<td>232.35</td>
<td>—</td>
<td>—</td>
<td>70.76</td>
<td>24.06</td>
</tr>
</tbody>
</table>

5.3.2.7 Photometric characterization and decay time analysis

Figure 5.23 illustrates the Commission Internationale de l'Eclairage (CIE) color chromaticity coordinates of the Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$ phosphor. Thus, the CIE color chromaticity coordinate of the Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$ was (0.673, 0.327). Furthermore, the CIE chromaticity coordinates of these phosphors were found nearer to the standard red light (0.675, 0.325) [100, 149, 150]. Furthermore, to know about the red emission of the Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$, the value of color purity was also deduced by the equation [100, 150],

\[
\text{Colorpurity} = \left( \frac{\sqrt{(x-x_i)^2 + (y-y_i)^2}}{\sqrt{(x_d-x_i)^2 + (y_d-y_i)^2}} \right) \times 100\% \quad \cdots (5.16)
\]

where $(x, y)$ is denoted as CIE chromaticity coordinate of the prepared sample, $(x_i, y_i)$ is the CIE white illumination, and $(x_d, y_d)$ is the CIE chromaticity coordinate of the dominant wavelength [150]. For Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$ phosphor $(x, y) = (0.673, 0.327)$, $(x_i, y_i) = (0.310, 0.316)$ and $(x_d, y_d) = (0.675, 0.325)$ [159]. Hence, the color purity of the Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$ phosphors is 99.5%. These results suggest
that Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$ phosphor with reasonable CIE chromaticity coordinate along with high color purity values might have remarkable applications in display devices and evidence as an efficient red emitting phosphor.

![CIE diagram for the as-synthesized powder phosphor Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$](image)

**Figure 5.23:** CIE diagram for the as-synthesized powder phosphor Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$. The representative PL decay curves for highest luminescence intensity emission for the phosphors Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$,Na$^+$ for $x = 0.16$ M is plotted in Figure 5.24. The values of the luminescence decay time, color chromaticity co-ordinates, and photometric parameters are estimated and are provided in Table 5.2.

**Table 5.2:** Color chromaticity co-ordinates, photometric properties, luminescence decay time and color purity for the phosphor Ca$_{0.5}$Y(MoO$_4$)$_2$:Eu$^{3+}$,Na$^+$.  

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>CCT (K)</th>
<th>CRI</th>
<th>X</th>
<th>y</th>
<th>LER (lm W$^{-1}$)</th>
<th>$\tau$ (ms)</th>
<th>Color Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_{0.5}$Y(MoO$_4$)$_2$:Eu$^{3+}$,Na$^+$</td>
<td>1020</td>
<td>25</td>
<td>0.673</td>
<td>0.327</td>
<td>290</td>
<td>0.475</td>
<td>99.5</td>
</tr>
</tbody>
</table>
Figure 5.24: Luminescence decay profiles for Na\(^+\) ion co-doped Ca\(_{0.5}\)Y\(_{(1-x)}\)(MoO\(_4\))\(_2\):xEu\(^{3+}\).

5.3.3 Ca\(_{0.5}\)Y(WO\(_4\))\(_2\):Eu\(^{3+}\)

5.3.3.1 Powder X-ray diffraction studies of Ca\(_{0.5}\)Y(WO\(_4\))\(_2\):Eu\(^{3+}\) phosphor

Figure 5.25 (a) shows the indexed powder X-ray diffraction patterns of the hydrothermally derived sample as well as thin film grown sample and Figure 5.25 (b) depicts different alkali metal ions co-doped with Ca\(_{0.5}\)Y(WO\(_4\))\(_2\):Eu\(^{3+}\). It is inferred from the figures that all diffraction peaks could be indexed to the pure tetragonal phase of Ca\(_{0.5}\)Y(WO\(_4\))\(_2\) and match well with the JCPDS card no. 48-0886. No other impurity peaks were observed.

At 28.95°, the strongest peak is observed corresponding to the (1 1 2) plane. It is well known that Ca\(_{0.5}\)Y(WO\(_4\))\(_2\) possess scheelite tetragonal crystal structure with space group C\(_{4h}\)\(^6\) in that Ca\(^{2+}\) is coordinated with eight oxygen atoms and forms S\(_4\) point symmetry with no inversion center. In this Eu\(^{3+}\) ion belongs to S\(_4\) symmetry. The acceptable percentage difference (D\(_r\)) in ionic radii between the doped (R\(_d\)) and substituted ion (R\(_s\)) should be less than 30\%. The D\(_r\) can be calculated using the equation [26],

\[
D_r = \frac{R_s - R_d}{R_s} \quad \cdots (5.17)
\]
For the present phosphor sample, it is observed to be 7.2%. Hence, Y\(^{3+}\) sites are effectively replaced by the Eu\(^{3+}\) ions without affecting the host crystal structure [26]. The crystallographic cell parameters are \(a = 5.209 \, \text{Å}\) and \(c = 11.255 \, \text{Å}\). The precursor Na\(_2\)WO\(_4\).2H\(_2\)O is being changed into (NH\(_4\))\(_6\)W\(_7\)O\(_{24}\).4H\(_2\)O and synthesized the Ca\(_{0.5}\)Y(WO\(_4\))\(_2\):Eu\(^{3+}\). From the indexed powder X-ray diffraction pattern as in Figure 5.25 (c), it is inferred that the obtained pure phase is Ca\(_{0.5}\)Y(WO\(_4\))\(_2\):Eu\(^{3+}\) and other deleterious phases are not obtained.

**Figure 5.25:** Indexed XRD patterns of the as-synthesized (a) Ca\(_{0.5}\)Y\(_{(1-x)}\)(WO\(_4\))\(_2\):xEu\(^{3+}\) phosphor and (b) Ca\(_{0.5}\)Y\(_{(1-x)}\)(WO\(_4\))\(_2\):xEu\(^{3+}\) co-doped with different alkali metal ions (A) Li\(^+\), (B) K\(^+\) and (C) Na\(^+\) and (c) Ca\(_{0.5}\)Y\(_{1-x}\)(WO\(_4\))\(_2\):xEu\(^{3+}\) phosphor using ammonium tungstate as one of the precursors.
5.3.3.2 Morphological Studies of bi-pyramid-like Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$ micro-architectures

Figure 5.26: FESEM images of the as prepared Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$ for (a) 24 h reaction time, Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$ co-doped with different alkali metal ions (b) Li$^+$, (c) K$^+$ and (d) Na$^+$. The scale represented in figure is 1 µm.
To investigate the surface morphology, formation mechanism and size of
the hierarchical bi-pyramid like structures, a Na$_2$EDTA-mediated hydrothermal
route was performed for 24 hours reaction time. The as obtained products were
characterized using FESEM. Figure 5.26 (a-d) shows the FESEM images of
$\text{Ca}_{0.5}\text{Y}_{1-x}(\text{WO}_4)_2:x\text{Eu}^{3+}$ for $x = 0.16$ M and respective alkali metal ions co-doped
$\text{Ca}_{0.5}\text{Y}_{1-x}(\text{WO}_4)_2:x\text{Eu}^{3+}$. The systematic studies of detailed morphological
evolution and possible growth mechanism of hierarchically self-assembled bi-
pyramid like micro/nano- architectures were carried out. Without using Na$_2$EDTA
as surfactant as depicted in Figure 5.27 (a) 3D micro-architectures are not
obtained. When Na$_2$EDTA is used as a surfactant, bi-pyramid like micro/nano-
architectures are achieved. In the present situation also, the evolution of bi-
pyramid like micro/nano- architectures are obtained.

Typical Ostwald ripening process could be responsible for the formation
of bi-pyramid-like microstructures from 2D nanosheets to 3D hierarchical
microstructures. As there is no remarkable variation in the morphology, the
morphologies for various reaction time is not shown. Amongst which, the best
morphology is achieved for 24 hours reaction time. Hence, the 24 hours
morphology is shown in Figure 5.26 (a). Figure 5.26 (b-d) shows different alkali
metal ions co-doped $\text{Ca}_{0.5}\text{Y}_{1-x}(\text{WO}_4)_2:x\text{Eu}^{3+}$ micro/nano- architectures. FESEM
images from Figure 5.27 (b) show the particle size of the as synthesized 3D
micro-architectures. The present motivation is to synthesize alkali metal ions co-
doped with $\text{Ca}_{0.5}\text{Y}_{1-x}(\text{WO}_4)_2:x\text{Eu}^{3+}$ phosphor.

When alkali metal ions are co-doped with $\text{Ca}_{0.5}\text{Y}_{1-x}(\text{WO}_4)_2:x\text{Eu}^{3+}$ charge
compensation takes place as a result there is an enhancement in the PL
emission intensity. Hence, the best morphologies for alkali metal ions co-doped
$\text{Ca}_{0.5}\text{Y}_{1-x}(\text{WO}_4)_2:x\text{Eu}^{3+}$ for 24 hours reaction time is shown. These self-organized micro-
structures with controllable morphology and size yield potential display
applications. The detailed description of the charge compensation mechanism is
provided in the sub-sequent sections.
Figure 5.27: FESEM image of the $\text{Ca}_{0.5}\text{Y}_{1-x}\text{(WO}_4\text{)}_2\text{xEu}^{3+}$ phosphor at (a) 24 h reaction time prepared without using the surfactant EDTA and (b) showing particle size. The scale represented in figure is 1 $\mu$m.

5.3.3.3 X-ray photoelectron spectroscopic analysis of $\text{Ca}_{0.5}\text{Y}_{1-x}\text{(WO}_4\text{)}_2\text{xEu}^{3+},\text{Na}^+$ phosphor

To investigate the valence state of the material, XPS technique is employed. Figure 5.28 shows the representative XPS survey spectrum of the $\text{Ca}_{0.5}\text{Y}_{1-x}\text{(WO}_4\text{)}_2\text{xEu}^{3+},\text{Na}^+$ obtained in the range of 0-100 eV ($W\ 4f_{5/2}$ at 33 eV); 100 – 300 eV (Eu 4d at 128 eV, Y 3d$_{5/2}$ at 156 eV, Y 3d$_{3/2}$ at 158 eV, W 4d$_{5/2}$ at 243 eV, W 4d$_{3/2}$ at 257 eV, Eu 4p at 283 eV); 300 – 600 eV (Y 3p at 311 eV, Ca 2p$_{3/2}$ at 346 eV, Ca 2p$_{1/2}$ at 352 eV, Y 3s at 393 eV, W 4p$_{1/2}$ at 490 eV, O 1s at 530 eV) and 800 – 1200 eV (Na 1s at 1072 eV, Eu 3d$_{5/2}$ at 1126 eV, Eu 3d$_{3/2}$ at
1156 eV. The data of binding energy data for Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$Na$^+$ was calibrated based on carbon (1s, 283.5 eV) as the reference. All the peaks are promptly coincided with the literature [55].

5.3.3.4 Photoluminescence properties of the as-synthesized Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$ powder phosphor

Fig. 5.29 (a) illustrates the room-temperature PL excitation spectrum of Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$ (x = 0.16 M) phosphor excited with $\lambda_{\text{ex}} = 395$ nm. The excitation spectrum comprises of two regions containing a broad band followed by a series of intense sharp peaks. The broad band located between 225 - 300 nm having a center at 240 nm, correspond to the O$^2$- to Eu$^{3+}$ and W$^{6+} - $O$^2$- charge transfer band (CTB) [95, 151]. Above 350 nm, sharp intense peaks are located at 360 nm ($^7F_0 \rightarrow ^5D_4$), 382 nm ($^7F_0 \rightarrow ^5L_7$), 395 nm ($^7F_0 \rightarrow ^5L_6$), 416 nm ($^7F_0 \rightarrow ^5D_3$), 465 nm ($^7F_0 \rightarrow ^5D_2$) and 536 nm ($^7F_0 \rightarrow ^5D_1$) [152]. Amongst which, the most intense peak in f-f electronic transition is located at 395 nm. The most intense peak lying in the UV region is appropriate for the excitation of Eu$^{3+}$ ions.

The room-temperature PL emission spectrum for powder phosphor spectrum for Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$ (x = 0.16 M) is depicted in Figure 5.29 (b). The powder phosphor is maintained at 24 hours reaction time for 180°C. The as obtained emission spectrum by exciting with 395 nm UV excitation for Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$ (x = 0.16M) shows a number of intra-configurational f-f transitions arising from the Eu$^{3+}$$^5D_0$ excited state to the $^7F_J$ ($J = 1, 2, 3, \text{and} 4$) ground states [153]. Upon exciting with other wavelengths and also by LMCT, no significant variation is seen in the emission spectra. The emission peak lying at 615 nm upon 395 nm UV excitation is owing to the $^5D_0 \rightarrow ^7F_2$ hypersensitive electric-dipole transition shows a parity-forbidden ($\Delta J = 2$) red emission in the visible region. Two sub-peaks arose from Stark energy splitting is based on (2J + 1) Stark components of J-degeneracy splitting [154]. The dominant electric-dipole transition corroborates that Eu$^{3+}$ ions are situated at sites having non-inversion symmetry. The transition lies at 590 nm gives an emission in the
orange region is due to the parity-allowed magnetic-dipole transition ($^{5}D_{0} \rightarrow ^{7}F_{1}$), while the other transitions at 656 nm ($^{5}D_{0} \rightarrow ^{7}F_{3}$) and 704 nm ($^{5}D_{0} \rightarrow ^{7}F_{4}$) are relatively weaker in intensity [155].

Figure 5.29: For Ca$_{0.5}$Y(WO$_4$)$_2$:Eu$^{3+}$ phosphor (a) PL excitation spectrum and (b) PL emission spectrum.

From Figure 5.29 (b) it is inferred that the splitting of the hypersensitive electric dipole transition is dominant for the two phosphors and no remarkable shift in peak position is observed for all the transitions. The R/O (red emission/orange emission) value for bi-pyramid-like architectures for Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$ is 6.18. This frames as a strong evidence for Eu$^{3+}$ ions which would occupy the lattice site with no inversion symmetry. The self-assembled 3D bi-pyramid-like micro-architectures would reduce the incident excitation light scattering and thus enhances the luminescence emission [156].
The intensity of various transition peaks for the thin phosphor film is closely equal to that of those for the nano powder phosphor suggests that peak intensity is associated to the reduction of particle size with the increase of homogeneity. Thus, the as-synthesized 3D powder and thin film phosphors compensate with the red components of the commercial phosphors with near UV excitation. From these investigations, it is evident that, Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$ 3D phosphors confirm the scheelite tetragonal crystal structure with S$_4$ site symmetry which might be a suitable candidate for potential display applications.

Based on the Judd-Ofelt theory, the branching ratios, non-radiative rate for $^5D_0$ level and luminescence quantum efficiency ($\eta$) are presented in Table 5.3.

5.3.3.5 Photometry studies of the Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$ powder phosphor

Figure 5.30: For the phosphor Ca$_{0.5}$Y(WO$_4$)$_2$ (a) CIE diagram and (b) luminescence decay profile.

Figure 5.30 (a) shows the CIE diagram and 5.30 (b) shows the luminescence decay curves of Eu$^{3+}$-doped Ca$_{0.5}$Y(WO$_4$)$_2$ for powder phosphor. The color purity and photometric parameters such as CIE color chromaticity co-ordinates, LER, CRI and CCT along with the luminescence decay time values are given in Table 5.4.
Table 5.3: Judd-Ofelt parameters, radiative emission rates, branching ratios and quantum efficiency for the phosphors $\text{Ca}_{0.5}\text{Y(WO}_4\text{)}_2:\text{Eu}^{3+}$ and $\text{Ca}_{0.5}\text{Y(WO}_4\text{)}_2:\text{Eu}^{3+}\text{,Na}^+$ by different methods.

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>J-O intensity parameters (x10^{-20} cm^2)</th>
<th>Transitions</th>
<th>$A_{0-2,4}$ (s^{-1})</th>
<th>$A_{0-1}$ (s^{-1})</th>
<th>$A_T$ (s^{-1})</th>
<th>$A_{NR}$ (s^{-1})</th>
<th>$\beta$ (%)</th>
<th>Quantum efficiency $\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ca}_{0.5}\text{Y(WO}_4\text{)}_2:\text{Eu}^{3+}$ (Bulk)</td>
<td>8.28 5.71</td>
<td>$^{5}\text{D}_0\rightarrow^{7}\text{F}_1$</td>
<td>582.00</td>
<td>50</td>
<td>921.00</td>
<td>289.00</td>
<td>5.43</td>
<td>63.21 69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{5}\text{D}_0\rightarrow^{7}\text{F}_2$</td>
<td>288.91</td>
<td>50</td>
<td>288.91</td>
<td>289.00</td>
<td>31.36</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{5}\text{D}_0\rightarrow^{7}\text{F}_4$</td>
<td>921.00</td>
<td>50</td>
<td>921.00</td>
<td>289.00</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>$\text{Ca}_{0.5}\text{Y(WO}_4\text{)}_2:\text{Eu}^{3+},\text{Na}^+$ (Bulk)</td>
<td>8.56 5.27</td>
<td>$^{5}\text{D}_0\rightarrow^{7}\text{F}_1$</td>
<td>602.00</td>
<td>50</td>
<td>918.00</td>
<td>266.00</td>
<td>5.44</td>
<td>65.55 71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{5}\text{D}_0\rightarrow^{7}\text{F}_2$</td>
<td>602.00</td>
<td>50</td>
<td>918.00</td>
<td>266.00</td>
<td>65.55</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{5}\text{D}_0\rightarrow^{7}\text{F}_4$</td>
<td>602.00</td>
<td>50</td>
<td>918.00</td>
<td>266.00</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>$\text{Ca}_{0.5}\text{Y(WO}_4\text{)}_2:\text{Eu}^{3+}$ (Nano)</td>
<td>6.67 5.72</td>
<td>$^{5}\text{D}_0\rightarrow^{7}\text{F}_1$</td>
<td>266.40</td>
<td>50</td>
<td>812.00</td>
<td>291.00</td>
<td>58.08</td>
<td>58.08 64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{5}\text{D}_0\rightarrow^{7}\text{F}_2$</td>
<td>266.40</td>
<td>50</td>
<td>812.00</td>
<td>291.00</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{5}\text{D}_0\rightarrow^{7}\text{F}_4$</td>
<td>266.40</td>
<td>50</td>
<td>812.00</td>
<td>291.00</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>$\text{Ca}_{0.5}\text{Y(WO}_4\text{)}_2:\text{Eu}^{3+},\text{Na}^+$ (Nano)</td>
<td>7.30 5.82</td>
<td>$^{5}\text{D}_0\rightarrow^{7}\text{F}_1$</td>
<td>516.00</td>
<td>50</td>
<td>862.00</td>
<td>296.00</td>
<td>58.08</td>
<td>58.08 66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{5}\text{D}_0\rightarrow^{7}\text{F}_2$</td>
<td>516.00</td>
<td>50</td>
<td>862.00</td>
<td>296.00</td>
<td>66</td>
<td></td>
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<td></td>
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<td>$^{5}\text{D}_0\rightarrow^{7}\text{F}_4$</td>
<td>516.00</td>
<td>50</td>
<td>862.00</td>
<td>296.00</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>$^{5}\text{D}_0\rightarrow^{7}\text{F}_4$</td>
<td>516.00</td>
<td>50</td>
<td>862.00</td>
<td>296.00</td>
<td>66</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.4: Photometric characterization and luminescence decay time of the phosphors Ca\textsubscript{0.5}Y(WO\textsubscript{4})\textsubscript{2}:Eu\textsuperscript{3+}, Ca\textsubscript{0.5}Y(WO\textsubscript{4})\textsubscript{2}:Eu\textsuperscript{3+},Na\textsuperscript{+}.

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Different methods</th>
<th>CCT (K)</th>
<th>CRI</th>
<th>X</th>
<th>Y</th>
<th>LER (lm W\textsuperscript{-1})</th>
<th>(\tau) (ms)</th>
<th>Color Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca\textsubscript{0.5}Y(WO\textsubscript{4})\textsubscript{2}:Eu\textsuperscript{3+}</td>
<td>Nano</td>
<td>&lt;1000</td>
<td>23</td>
<td>0.650</td>
<td>0.349</td>
<td>305</td>
<td>0.535</td>
<td>93.6</td>
</tr>
<tr>
<td>Ca\textsubscript{0.5}Y(WO\textsubscript{4})\textsubscript{2}:Eu\textsuperscript{3+},Na\textsuperscript{+}</td>
<td>Alkali from Nano</td>
<td>1043</td>
<td>23</td>
<td>0.655</td>
<td>0.345</td>
<td>305</td>
<td>0.548</td>
<td>94.8</td>
</tr>
</tbody>
</table>

5.3.3.6 Enhancement of PL emission due to co-doping of alkali metal ions

![PL emission spectra](image)

Figure 5.31: PL emission spectra of Ca\textsubscript{0.5}Y(WO\textsubscript{4})\textsubscript{2}:Eu\textsuperscript{3+} phosphor doped with various alkali metal ions.

Based on the reduction of the phonon energy and by changing the symmetry of the coordination of Eu\textsuperscript{3+}, the intensity of red emission is improved in scheelite based molybdate phosphors, as indicated by Wang et al. Following these results, as a representative study, the co-doping of Li\textsuperscript{+}, K\textsuperscript{+} and Na\textsuperscript{+} metal ions is performed to the Ca\textsubscript{0.5}Y\textsubscript{1-x}(WO\textsubscript{4})\textsubscript{2}:xEu\textsuperscript{3+}. Figure 5.31 shows the
photoluminescence emission spectra for Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$,M$^+$ (M = Li, K and Na) for $x=0.16$ M with 24 hours reaction time. The corresponding decay profile and CIE diagram for Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$,Na$^+$ is given in Figure 5.32 (a) & (b). The emission intensity is drastically enhanced in the case of Na$^+$ co-doped to Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$. The improvement of the intensity could be attributed to the charge compensation effect [157].

Figure 5.32: (a) Luminescence decay profile for Ca$_{0.5}$Y(WO$_4$)$_2$:Eu$^{3+}$,Na$^+$ phosphor and (b) CIE diagram of Ca$_{0.5}$Y(WO$_4$)$_2$:Eu$^{3+}$, Na$^+$. 

Earlier works suggested that alkali metal ions added into the rare-earth-doped materials show significant enhancement in the luminescent intensities. This could be due to the alteration of the local symmetry and the surroundings near the rare earth ions by adding charge compensator of alkali metal ions [157]. The R/O value for Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$,Na$^+$ is 6.49.

Following Ghaderi et al. [158], two types of charge compensating patterns are being proposed. One is hump shaped (type I) and flat (type II), for Eu$^{3+}$ substitution in Ca$^{2+}$ via the following pathways: $2$Ca$^{2+} = $ Eu$^{3+} + $ Na$^+$ for type I and $3$Ca$^{2+} = 2$Eu$^{3+} +$ (where is a Ca site vacancy) for type II. It is noticed that formation of oxygen defects or cation vacancies must yield long-lasting luminescence. Following the lifetime values in milliseconds, type II charge
compensating pattern is ruled out. The existing charge compensating pattern is type I.

Following type I, for the studying case, the charge compensation pattern is \(0.5\text{Ca}^{2+} + \text{Y}^{3+} = \text{Eu}^{3+} + \text{Na}^{+}\). This leads to charge balance and a reduction in \(\text{Ca}^{2+}\) vacancy concentration. The \(\text{Eu}^{3+}\) and \(\text{Na}^{+}\) co-doped in \(\text{Ca}_{0.5}\text{Y(WO}_4)_{2}\) lattice induce a lattice distortion and a lowered lattice symmetry [159]. While comparing all the charge compensator, the ionic radius of \(\text{Na}^{+}\) (0.97 Å) is most similar to the ionic radius of \(\text{Ca}^{2+}\) (1.12 Å) compared to \(\text{Li}^{+}\) (0.59 Å) and \(\text{K}^{+}\) (1.33 Å) [157]. This forms the basis for the enhanced intensity. Hence, these phosphors play a vital role in the field of display applications.

### 5.4 Conclusion

In summary, rare-earth activated phosphors \(\text{Ca}_{0.5}\text{Y}_{1-x}(\text{MoO}_4)_2:x\text{Ln}^{3+}\) (\(\text{Ln} = \text{Eu, Pr, Sm, Tb, Dy, Yb/Er, Yb/Ho, and Yb/Tm}\)), scheelite structured \(\text{Ca}_{0.5}\text{Y}_{1-x}(\text{MoO}_4)_2:x\text{Eu}^{3+},M^{+}\) (\(M = \text{Li, K and Na}\)) and \(\text{Ca}_{0.5}\text{Y}_{1-x}(\text{WO}_4)_2:x\text{Eu}^{3+}\) and with the co-doping of alkali metal ions were successfully synthesized using a surfactant-mediated hydrothermal method. The FESEM images exhibited the bi-pyramid-like structures of the prepared phosphors. XRD patterns and FT-Raman spectra revealed the scheelite-type crystal structure without any impurity phases. The compositional analysis by x-ray photoelectron spectroscopy confirms the presence of all the elements \(\text{Ca, Y, Mo/W, O, Eu and Na}\). The down-conversion properties of the powders were studied in detail. Upon optical excitation, \(\text{Eu-}, \text{Pr-}, \text{Sm-}, \text{Tb-}, \text{and Dy-doped Ca}_{0.5}\text{Y}_{1-x}(\text{MoO}_4)_2\) powder phosphors showed characteristic emissions in the red, bright-red, orange-red, green, and yellow regions, respectively. Based on the up-conversion studies, it is indicated that \(\text{Yb}^{3+}/\text{Er}^{3+}, \text{Yb}^{3+}/\text{Ho}^{3+}, \text{and Yb}^{3+}/\text{Tm}^{3+}\)-doped \(\text{Ca}_{0.5}\text{Y}_{1-x}(\text{MoO}_4)_2\) exhibited emissions in the visible regions of green, yellow, and blue regions, respectively. Judd-Ofelt theory is envisaged to estimate intensity parameters, radiative emission rates, branching ratio and quantum efficiency. The effect of alkali cations (\(\text{Li}^{+}, \text{K}^{+} \text{and Na}^{+}\)) on \(\text{Ca}_{0.5}\text{Y}_{1-x}(\text{MoO}_4)_2:x\text{Eu}^{3+}\) and
Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$ were analysed in detail. From the results, it is evident that the red emission peak intensity of Ca$_{0.5}$Y$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$ and Ca$_{0.5}$Y$_{1-x}$(WO$_4$)$_2$:xEu$^{3+}$ using Na$^+$ ions as charge compensator is greater than that of Li$^+$ and K$^+$ ions and Na$^+$ ions has the remarkable charge compensation effect. From the CIE chromaticity diagram and by the obtained results, it is suggested that the as-synthesized powder phosphors could serve as efficient materials for displays and electro-luminescence applications.