SUMMARY AND CONCLUSION

The objective of the research work was to synthesize and characterize lanthanide ions doped molybdate and tungstate based phosphors with 3D micro/nano structures using viable techniques to enhance the luminescence properties for numerous practical applications. The major conclusion of the present study is summarized as follows.

The luminescent visible emitting phosphors of $\text{Ca}_{0.5}\text{Y(MO}_4\text{)}_2:\text{Ln}^{3+}$ ($M = \text{Mo, W}; \text{Ln} = \text{Pr, Sm, Eu, Tb, Dy, Yb/Er}$) were successfully synthesized using solid-state reaction method for the first time. Upon UV excitation, the phosphors $\text{Ca}_{0.5}\text{Y(MO}_4\text{)}_2:\text{Ln}^{3+}$ ($M = \text{Mo, W}; \text{Ln} = \text{Pr, Sm, Eu, Tb, Dy}$) show bright red, orange, red, green and yellow emissions in the visible region. The luminescence intensity enhances with an increase of $\text{Ln}^{3+}$ concentration. The presence of strong absorption bands is in agreement with near-UV and blue LED chips and could be used as visible light emitting phosphors for WLED applications. The obtained CIE color coordinate values are closer to the NTSC standard values. The concentration quenching and energy transfer process were studied. The photometric parameters such as colour coordinates, CCT, CRI, luminous efficacy of radiation, and luminescence decay time were estimated. The effect of alkali metal ions with the prepared phosphors was studied. Significantly, luminescence properties were enhanced by the presence of alkali metal ions. At the last, the photometric parameters of the phosphor suggest that the as-synthesized visible light emitting phosphors might be suitable candidates for numerous luminescence applications especially for white LEDs and solid-state lighting applications.

A facile EDTA mediated hydrothermal method was adopted for the synthesis of self-assembled bi-pyramid-shaped $\text{Ca}_{0.5}\text{Y(MO}_4\text{)}_2:\text{Ln}^{3+}$ ($M = \text{Mo, W}; \text{Ln} = \text{Pr, Sm, Eu, Tb, Dy, Yb/Er, Yb/Tm, Yb/Ho}$) 3D architectures under practical conditions. The reaction time plays a crucial role in the formation of self-aggregated bi-pyramid-like structures. By tailoring the molar concentrations of the surfactant EDTA, the size of the particles are
precisely controlled. Self-assembled, monodispersed nanoparticles were achieved at 1.5 mM EDTA concentration which is evident in FESEM and TEM analysis. Distribution of elements based on elemental mapping analysis implies the incorporation of all the elements inside the hierarchical micro/nanostructures. The indexed powder XRD patterns specifies that the samples Ca_{0.5}Y(MO_4)_{2}:Ln^{3+} (M = Mo, W; Ln = Pr, Sm, Eu, Tb, Dy, Yb/Er, Yb/Tm and Yb/HO) belongs to the scheelite-type tetragonal structure with space group I4_1/a. In that, the Mo^{6+}/W^{6+} occupies the center of tetrahedral symmetry and Ca^{2+} and Y^{3+}/Ln^{3+} are located in the dodecahedral sites of the tetrahedral symmetry.

Photoluminescence spectra clearly illustrate the visible emissions (bright-red, orange, red, green and yellow) based on UV excitations which is achieved by changing the lanthanide ions in Ca_{0.5}Y(MO_4)_{2}:Ln^{3+} (M = Mo, W). Upon 980 nm NIR laser pumping, the self-assembled 3D architectures of Ca_{0.5}Y(MoO_4)_{2} doped with Yb^{3+}/Er^{3+}, Yb^{3+}/Tm^{3+} and Yb^{3+}/Ho^{3+} exhibits strong green, blue, and yellow up-conversion luminescence, respectively. The viable energy transfer mechanisms of both down-conversion and up-conversion luminescence phosphors were studied in detail. The up-conversion mechanism indicated that, the energy is effectively transferred from sensitizer (Yb^{3+}) to the activator (Er, Tm, Ho) through multiphoton process. The as-synthesized phosphor not only exhibits down- and up-conversion visible luminescence but also exhibits the characteristic emission spectra in the near infra red region. Judd-Ofelt theory is envisaged to estimate intensity parameters, radiative emission rates, branching ratio and quantum efficiency. The as-synthesized phosphors are co-doped with alkali metal ions such as Li^{+}, K^{+} and Na^{+} and its effect on Ca_{0.5}Y_{1-x}(MoO_4)_{2}:xEu^{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. As they are having the closer ionic radius to Ca^{2+}, Na^{+} is exhibiting the remarkable charge compensation effect. Finally, the obtained results signify that the as-synthesized phosphors could stand as the suitable candidates for display applications.
Nano-sized $\text{Ca}_{0.5}\text{Y(MO}_4\text{)}_2:\text{Ln}^{3+}$ ($\text{M} = \text{Mo, W; Ln}^{3+} = \text{Eu, Tb, Dy, Yb/Er}$) thin film phosphors were deposited on quartz substrates by pulsed laser deposition technique using Nd-YAG laser source. The deposition was performed in an ultra-high vacuum (UHV) with an oxygen back pressure of 300 mTorr. Using AFM technique, the 3D surface topography, grain size distribution, roughness and rms values are obtained. The SEM images exhibited the spherical shaped phosphor particles. From SEM imaging, the average thickness of the thin film was found to be 280 nm for $\text{Ca}_{0.5}\text{Y}_{1-x}(\text{MoO}_4)_2:x\text{Eu}^{3+}$ and 270 nm for $\text{Ca}_{0.5}\text{Y}_{1-x}(\text{WO}_4)_2:x\text{Eu}^{3+}$ phosphors. XRD patterns revealed the scheelite-type crystal structure without any impurity phases. The down-conversion luminescence properties of the thin film phosphors were studied in detail. Under suitable optical excitations, Eu$^{3+}$, Tb$^{3+}$ and Dy$^{3+}$ doped samples exhibited their characteristic luminescence in red, green, yellow region due to the transitions $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$, respectively. Upon 980 nm NIR laser pumping, Yb$^{3+}$/Er$^{3+}$ doped $\text{Ca}_{0.5}\text{Y(MO}_4\text{)}_2$ thin film shows strong green due to the hypersensitive transition $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$. The nano-sized phosphor thin films could be the best materials for electro/cathodo-luminescence and display devices applications.