7.1 A brief summary of the research work

This chapter focuses on the important findings obtained in the previous chapters. Nanoparticles which are luminescent and capable of emitting different colours have been synthesised in the research work. Also, production of white light by combination of different primary colours has also been reported.

Chapter 3 investigates on the synthesis of nanoparticles of $\text{RE}^{3+}$ ($\text{RE}=\text{Eu}, \text{Tb}, \text{Dy}, \text{Sm}$) doped in $\text{CaWO}_4$ using different solvents. The as prepared nanoparticles are re-dispersible in polar solvents such as ethanol, methanol, water; they could also be incorporated in polymer films. XRD study revealed tetragonal phase for all the samples irrespective of the solvents used. It also confirmed the homogeneous substitution of $\text{Ca}^{2+}$ sites by dopant ions. TEM images indicate that the particles are non-agglomerated and have different morphology according to the dopant ion incorporated in the host. The crystalline nature of the nanoparticles increased with increasing annealing temperature. The luminescence intensity was also greatly affected by the solvent used. The sample prepared in EG+ water system has the highest luminescence intensity and those prepared in water has the least intensity. The luminescence intensity also increases upon heat treatment. $\text{CaWO}_4: \text{Eu}^{3+}$ also show thermoluminescence after irradiating with $\gamma$-rays. These materials could find their applications in several fields such as fluorescent lamps, optical devices and display panels.

In chapter 4, some selected rare-earth ions have been doped in $\text{CaMoO}_4$ host. The homogeneous substitution of these dopants in the host lattice was proven from XRD studies. The system also had tetragonal phase. Photoluminescence study shows the
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characteristics of the individual doped lanthanide ions. The Eu$^{3+}$ doped sample shows emission peaks at 595 nm (\(^5\)D\(_0\)-\(^7\)F\(_1\), magnetic dipole transition) and 615 nm (\(^5\)D\(_0\)-\(^7\)F\(_2\), electric dipole transition). The Dy$^{3+}$ doped sample shows emission peaks at 482 nm (\(^4\)F\(_{9/2}\)-\(^6\)H\(_{15/2}\), magnetic dipole transition) and 573 nm (\(^4\)F\(_{9/2}\)-\(^6\)H\(_{13/2}\), electric dipole transition). For Tb$^{3+}$ doped samples, emission peak at 546 nm (\(^5\)D\(_4\)-\(^7\)F\(_{5}\), magnetic dipole transition) is the most prominent; for Sm$^{3+}$ doped samples, the emission peaks are observed at 565 nm, 599 nm and 646 nm and they are assigned to \(^4\)G\(_{5/2}\rightarrow\(^6\)H\(_{5/2}\), \(^4\)G\(_{5/2}\rightarrow\(^6\)H\(_{7/2}\) (magnetic) and \(^4\)G\(_{5/2}\rightarrow\(^6\)H\(_{9/2}\) (electric dipole) transitions respectively. The CIE chromaticity coordinates of the RE$^{3+}$ doped CaMoO\(_4\) samples were calculated. The Eu$^{3+}$, Sm$^{3+}$ and Tb$^{3+}$ doped CaMoO\(_4\) samples show the CIE chromaticity coordinates around the red, orange-yellow and greenish-yellow regions. CaMoO\(_4\): Dy$^{3+}$ show CIE chromaticity coordinates (x = 0.36 and y = 0.38) which are close to reported ideal value (x = 0.33 and y = 0.33) of white light emission.

Chapter 5 is about the synthesis and luminescence studies of SrWO\(_4\):RE$^{3+}$ (RE=Eu, Tb, Dy and Sm). The prepared samples are well crystalline and exhibit tetragonal phase. The size of the particles as determined from XRD study is around 20 nm. From the excitation spectra, it is found that a broad band occurs from 230- 350 nm with peak maximum at around 240 nm which is due to oxygen-to-metal charge transfer (CTB) in WO\(_4^{2-}\). This arises from the transition of 2p electrons of O\(^2-\) to the empty 5d shells of W\(^{6+}\) ions in the WO\(_4^{2-}\) group. Other weaker bands observed from 350-450 nm are due to f-f transitions of rare-earth ions. For Eu$^{3+}$ doped samples, characteristic emission lines are observed at 595 nm and 614 nm due to \(^5\)D\(_1\)-\(^7\)F\(_1\) and \(^5\)D\(_0\)-\(^7\)F\(_2\) transitions respectively and the transition at 614 nm which corresponds to red emission is
dominant; for Tb$^{3+}$ doped samples, characteristic green emission could be observed at 546 nm due to $^5D_{4/2} \rightarrow ^7F_5$ transition; for Dy$^{3+}$ doped samples, two prominent peaks at 488 nm ($^4F_{9/2} \rightarrow ^6H_{15/2}$) and 573 nm ($^4F_{9/2} \rightarrow ^6H_{13/2}$) could be observed. The transition at $^4F_{9/2} \rightarrow ^6H_{13/2}$ (573 nm) which corresponds to yellow emission is dominant over the other transition in all the cases. For Sm$^{3+}$ doped samples, emission peaks are located at 565 nm, 599 nm and 646 nm and they are assigned to $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$ (magnetic) and $^4G_{5/2} \rightarrow ^6H_{9/2}$ (electric dipole) transitions respectively. Out of all these transitions, the transition at 646 nm dominates over other transitions and hence at all concentrations of Sm$^{3+}$, the orange emission is predominant. The luminescence intensity is again greatly influenced by the doping concentrations of the lanthanide ion, though no shift has been observed towards the higher or lower wavelength region by varying the doping concentration of dopant ion. For Eu$^{3+}$ doped samples, the optimum concentration is found to be 10 at. %; for Tb$^{3+}$ doped samples, the highest luminescence intensity is found to be 7 at. %; for Dy$^{3+}$ doped samples, the luminescence intensity is highest in 2 at. % of Dy$^{3+}$ in the host and Sm$^{3+}$ has the optimum concentration at 1 at. %. Heating the samples at higher temperatures also has pronounced effect on the luminescence intensity. Samples heated at 900°C showed the highest intensity as compared to as prepared and 500°C annealed samples. This enhancement in luminescence intensity is attributed to the increased occupancy of RE$^{3+}$ in the Sr$^{2+}$ lattice sites, the extent of reduction in the non-radiative transition with the improvement of crystallinity and decrease in the content of impurities. Change of solvents also had prominent effects on the luminescence intensity. Samples prepared in EG showed the maximum luminescence intensity with DMSO showing
moderate intensity and those prepared in water had the least intensity. This variation is due to different non-radiative transition rates.

Therefore, these selected alkaline-earth metal tungstates and molybdate could find tremendous applications in several fields such as fluorescent lamps, optical devices and display panels. These materials could also be used as potential nanophosphors for white light-emitting diodes (LEDs) applications. Their ability to disperse in different solvents like methanol, ethanol, water etc. could further expand their application in biological fields such as drug delivery.