

***Luminescence Study of Some Rare Earth Doped  
CaMoO<sub>4</sub> Phosphors for Lighting Application***



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# **Chapter 7**

## **Conclusion**

*“In this chapter, the overall conclusion of the research work done as a part of this thesis is summarized. The importance of our findings for lighting applications is also highlighted. The future scope and future work to be carried out are also discussed in this chapter.”*



### 7.1 Summary

The present thesis discussed interesting studies on rare-earth-doped  $\text{CaMoO}_4$  phosphors for red-green phosphors as well as single-component white light phosphors for white LED application. All phosphors were synthesized by the facilitative urea-assisted auto-combustion method. The crystal structure and phase formation were validated by Rietveld's refinement of the XRD patterns. The crystallite size and microstrain are also estimated by employing the Williamson–Hall method. SEM and TEM analysis are used to examine the morphology and estimate the average particle size of the prepared samples. The photoluminescence properties of phosphors are studied by PL excitation, emission, decay and temperature-dependent PL measurements. The phosphors studied for the present thesis are:  $\text{Eu}^{3+}/\text{Mn}^{2+}$  co-doped  $\text{CaMoO}_4$ ,  $\text{Tb}^{3+}/\text{Bi}^{3+}$  co-doped  $\text{CaMoO}_4$ ,  $\text{Dy}^{3+}/\text{Sm}^{3+}$  co-doped  $\text{CaMoO}_4$  and  $\text{Dy}^{3+}/\text{Zn}^{2+}$  doped  $\text{CaMoO}_4$ . The important points discussed in the thesis are summarized as follows-

In this thesis, the emission intensity enhancement and emission color improvement of rare-earth doped  $\text{CaMoO}_4$  red phosphors, green phosphors, and near-white emitting phosphors have been reported through co-administration of transition metals (Mn, Zn) ions, bismuth ions and rare-earth ions. Chapter 3 studies the luminescence enhancement of  $\text{Eu}^{3+}$  doped  $\text{CaMoO}_4$  red phosphors and correlates the luminescence properties with the increase in crystallite size and average particle size. All prepared red phosphors have near-UV absorption as seen in their absorption spectra. The overall emissivity of the prepared red phosphor is well within the wavelength sensitivity range of the human eye which again is beneficial for lighting. The chapter shows the enhancement of PL intensity of  $\text{Eu}^{3+}$  doped  $\text{CaMoO}_4$  phosphor with proper concentration tuning of  $\text{Mn}^{2+}$  ions. The increase in the asymmetric parameter for the 0.3%  $\text{Mn}^{2+}$  co-doped phosphor indicates that it is a better red phosphor. The  $\text{Mn}^{2+}$  co-doping affects the crystal field around the  $\text{Eu}^{3+}$  ion, thereby also

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affecting the forced electric dipole transition of the  $\text{Eu}^{3+}$  ion. As a result, an enhancement of luminescence is achieved. Thus,  $\text{Mn}^{2+}$  co-doped  $\text{CaMoO}_4:4\%\text{Eu}^{3+}$  shows a new direction as an excellent red-emitting phosphor with very low synthesis cost for white LEDs applications.

The study of  $\text{Tb}^{3+}/\text{Bi}^{3+}$  co-doped  $\text{CaMoO}_4$  green phosphors for applications in lighting and display devices is covered in Chapter 4. Rietveld's refinement of the XRD pattern validates the tetragonal crystal structure of the phosphor. No impurity peak was observed in the XRD pattern indicating successful replacement of the dopant at the calcium sites. It is evident from the SEM images that the spherical shape of the particles increases with  $\text{Bi}^{3+}$  co-doping, resulting in an improvement in crystallinity. The chapter establishes a connection between structural studies and photoluminescence studies by improving crystallinity. The  $\text{Tb}^{3+}$  doped  $\text{CaMoO}_4$  phosphor, major three peaks are obtained at 489 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_6$ ), 544 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_5$ ) and 621 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_3$ ) over the host's excitation, of which 544 nm (green emission) is the most intense. After  $\text{Tb}^{3+}$  doping, an enhancement is observed in the emission spectra up to 5%  $\text{Tb}^{3+}$  doping which is further enhanced by co-doping of  $\text{Bi}^{3+}$  ions. The  $\text{Bi}^{3+}$  co-doping results in improved crystallinity in the phosphor as well as the successful transfer of energy from the  $\text{Bi}^{3+}$  excited level to the  $\text{Tb}^{3+}$  excited level, thereby enhancing the luminescence. The maximum  $\text{Tb}^{3+}$  emission intensity is achieved at 4%  $\text{Bi}^{3+}$  co-doping which gives excellent green emission, which has CIE coordinates (0.264, 0.604) in the chromaticity diagram as compared to 5%  $\text{Tb}^{3+}$  doped phosphor (0.267, 0.558) is towards the more green area. In the chapter, temperature-dependent PL is analyzed to investigate the thermal stability of superior  $\text{Tb}^{3+}/\text{Bi}^{3+}$  doped  $\text{CaMoO}_4$  phosphor and observed that it is a good thermally stable green phosphor with high activation energy (0.25 eV), which can be obtained at room temperature shows a decrease of only 24% in the emission intensity at 423 K as compared to the room temperature. Hence the loss is much

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less than that loss of the well-known  $\text{Ce}^{3+}$  doped YAG yellow phosphor (~50%) at the same temperature. No change in CIE coordinates of emission with temperature was obtained, indicating the color stability of the overall emission of the phosphor. Therefore, the 4%  $\text{Bi}^{3+}$  co-doped  $\text{CaMoO}_4:5\%\text{Tb}^{3+}$  phosphor is a promising candidate as an excellent green thermally stable phosphor for display devices and LED applications.

As we know, industrial wLED is made by depositing yellow phosphor on top of a blue chip. These depositing techniques are quite complex and expensive. Therefore, the research fraternity is focusing on developing single-component white light emitters. Since  $\text{Dy}^{3+}$  doped  $\text{CaMoO}_4$  phosphor emits near-white light due to its blue and yellow emission but has a CCT value of more than 5000 K which is not comfortable for the human eye and its emission is not perfectly white. We have studied the improvement of near white light emission of  $\text{Dy}^{3+}$  doped  $\text{CaMoO}_4$  phosphors by co-doping rare-earth and transition ions respectively in chapters 5 and 6. Chapter 5 discusses the control of the high CCT value of the white emission of  $\text{Dy}^{3+}$  doped  $\text{CaMoO}_4$  phosphors by co-doping the  $\text{Sm}^{3+}$  ion as well as the energy transfer process in  $\text{Dy}^{3+}/\text{Sm}^{3+}$   $\text{CaMoO}_4$  phosphors. The auto-combustion approach has been successfully used to produce  $\text{Dy}^{3+}/\text{Sm}^{3+}$  co-doped  $\text{CaMoO}_4$  samples. The chapter validates the tetragonal crystal structure of the phosphor using XRD and FTIR spectroscopy. PL spectroscopic studies revealed that the maximum luminescence is at 4% doping of  $\text{Dy}^{3+}$  ions, although its CCT value is higher than 5000 K due to the lack of red emission. To enhance the luminous properties of 4%  $\text{Dy}^{3+}$  doped phosphor,  $\text{Sm}^{3+}$  ions are co-doped with them. This results in the achievement of neutral white light with a controlled CCT value in  $\text{CaMoO}_4:4\%\text{Dy}^{3+}$  at 3%  $\text{Sm}^{3+}$  co-doping. The energy transfer mechanism between  $[\text{MoO}_4]^{2-}$  groups and  $\text{Dy}^{3+}/\text{Sm}^{3+}$  ions under 296 nm excitation is also covered in this chapter, as is the efficiency of energy transfer from  $\text{Dy}^{3+}$  to  $\text{Sm}^{3+}$  for a 3%  $\text{Sm}^{3+}$  co-doped phosphor. Therefore, as a single-component white light-emitting application,

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Dy<sup>3+</sup>/Sm<sup>3+</sup> co-doped CaMoO<sub>4</sub> phosphors may be a better candidate for lighting and display devices.

Chapter 6 discussed the enhancement of the near-white light emission of CaMoO<sub>4</sub>:4%Dy<sup>3+</sup> by co-doping Zn<sup>2+</sup> ions and moving it to more white. This chapter shows the enhancement of luminescence by improving the crystallinity of CaMoO<sub>4</sub>:4%Dy<sup>3+</sup> phosphor with the co-doping of Zn<sup>2+</sup> ions. A red-shift in the peak broadening and absorption peak is observed by UV-vis absorption analysis of Zn<sup>2+</sup>/Dy<sup>3+</sup> doped CaMoO<sub>4</sub>. Photoluminescence studies show that in Dy<sup>3+</sup> doped CaMoO<sub>4</sub> phosphors, 4% Dy<sup>3+</sup> doped CaMoO<sub>4</sub> exhibits maximum emission. Zn<sup>2+</sup> ions are co-doped to further enhance the luminescence intensity of CaMoO<sub>4</sub>:4%Dy<sup>3+</sup> and maximum luminescence has been achieved at 0.25% Zn<sup>2+</sup> doping. The <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> transition of the Dy<sup>3+</sup> ion is a forced electric dipole transition that is affected by its chemical environment. After Zn<sup>2+</sup> co-doping, the <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> transition is affected due to the change in asymmetry around the Dy<sup>3+</sup> ions. 0.25% co-doping of Zn<sup>2+</sup> gives a 34% enhancement in the luminescence emission of 4% Dy<sup>3+</sup> doped CaMoO<sub>4</sub>. As a result, the coordinates of the CIE chromaticity diagram and the color purity of 0.25% Zn<sup>2+</sup> co-doped CaMoO<sub>4</sub>:4%Dy<sup>3+</sup> show an improvement in the overall white light emission. It is clear from the chapter that with Zn<sup>2+</sup> co-doping, the non-radiative relaxation is reduced resulting in improved white light emission of Dy<sup>3+</sup> ions. The study of the thermal stability of 0.25% Zn<sup>2+</sup> co-doped CaMoO<sub>4</sub>:4%Dy<sup>3+</sup> phosphor is presented in the chapter on temperature-dependent PL. This phosphor is presenting only a 23% reduction in emission intensity at 150 °C compared to room temperature with 0.16 eV good activation energy which makes it a better thermally stable phosphor. Thus, thermally and chemically stable single-component phosphors with excellent white light emission can be prepared at low cost for white LEDs applications.

### 7.2 Future Scope

We have successfully synthesized and studied the effect of various doping on the luminescence of rare-earth doped  $\text{CaMoO}_4$  phosphors. Further study has to be carried out to fabricate the LED device by coating prepared phosphors on the commercially available near-UV/blue chip and studying the quantum efficiency of the device, as well as we will do the necessary characterizations such as quantum yield, CRI calculations, and device characterizations. Improvement in the luminescence thermal quenching of the phosphors is still a challenge for the research community.

We have recently studied doped  $\text{CaMoO}_4$  phosphors for optical thermometry applications. The effect of doping (such as alkali metals and transition metals) on the sensitivity of the phosphor has yet to be explored. In our study, we have observed that these phosphors can affect the crystallinity of the phosphor. Therefore, it is necessary to study the change in susceptibility induced by doping concentration. The  $\text{CaMoO}_4$  phosphor has been proven to be an excellent host phosphor for rare-earth elements, so other applications such as latent fingerprints detection, IR sensitivity, and photo-catalysis can also be studied.



