Study of Luminescence Properties of doped $SrMoO_4$ and $Zn_3(VO_4)_2$ Phosphors for wLED and Optical Thermometry

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Chapter 8
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 and optical thermometry applications is also highlighted. The future scope and future work to be carried out are also discussed in this chapter.

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8.1 Summary

The present thesis discusses interesting studies on red and greenish-yellow phosphors for white LED application, rare-earth doped phosphors for tunable light emitting sources, and optical thermometry application. The phosphors were synthesized by facile urea-assisted auto-combustion and citrate sol-gel method. The crystal structure and phase formation were validated by the Rietveld refinement of the XRD patterns. The estimation of the crystallite size and microstrain is also done by employing the Williamson-Hall method. The SEM analysis is used to examine the morphology and estimation of the average particle size of the prepared samples. The photoluminescence properties of the phosphors are studied by the PL excitation, emission, decay, and temperature-dependent PL measurements. The phosphors studied for the present thesis are Sm^{3+}/Bi^{3+} co-doped $SrMoO_4$, Sm^{3+}/Zn^{2+} co-doped $SrMoO_4$, Dy^{3+}/Eu^{3+} co-doped $SrMoO_4$, Bi^{3+} doped $Zn_3(VO_4)_2$, and Li^{+} doped $Zn_3(VO_4)_2$. The important points discussed in the thesis can be summarised as-

The study of luminescence enhancement of the Sm^{3+} doped $SrMoO_4$ phosphor via Bi^{3+} and Zn^{2+} co-doping and co-relating the luminescence properties with the augmentation in the crystallite size and average particle size has been carried out. All the prepared red phosphors have near-UV absorption as seen in their absorption spectra. The excitation (404 nm) of the prepared red phosphors matches well with the emission of the commercially available InGaN or GaN blue chip and therefore phosphors can be coupled with the chip for the realization of white light. The overall emission of the prepared red phosphors lies well within the human eye wavelength sensitivity range which again is beneficial for lighting application. In the Sm^{3+}/Bi^{3+} co-doped $SrMoO_4$ phosphors the possibility of the energy transfer from Bi^{3+} to Sm^{3+} is also studied by recording the emission spectra monitored at excitation wavelength corresponding to the Bi^{3+} transitions (308 nm). Amongst all the prepared red phosphors, the 1% Zn^{2+} co-doped $SrMoO_4$:4Sm^{3+} phosphor

has the best emission. The thermal stability of the luminescence of the best prepared red phosphor has been carried out by the temperature-dependent PL analysis. The calculated activation energy was 0.17 eV and the loss of emission intensity at 423 K was 31% of the emission at room temperature. The mechanism behind the loss of emission intensity with temperature is also discussed with the help of a configurational coordinate diagram. Further, the PL lifetime measurements have been carried out to validate the effect of improved crystallinity and average particle size on the emission of the red phosphors. The other advantages such as cost-effective synthesis, environmental friendliness, and good chemical stability also favor the scope of the prepared red phosphors in the field of white LEDs.

The study of Dy^{3+}/Eu^{3+} co-doped $SrMoO_4$ phosphors for tunable light sources and optical thermometry applications is included in chapter 4. The Rietveld refinement of the XRD patterns validates the tetragonal crystal structure of the phosphors. The red-shift in the absorption peak as a consequence of the Dy^{3+} and Eu^{3+} doping is observed, which is attributed to the defect energy levels formed within the bandgap of the host phosphor. The PL excitation spectra show the presence of LMCT and CTB broadband with some characteristic peaks of Dy^{3+} and Eu^{3+} ions. The color tunability is studied by observing the PL emission at different wavelengths and by controlling the dopant concentration. It is observed that the energy transfer from energy levels of the Dy^{3+} to Eu^{3+} is very weak which results in weak emission lines of the Eu^{3+} ion when excited with 352 nm. Whereas, the energy transfer from $[MoO_4]^{2-}$ LMCT band to Dy^{3+} and Eu^{3+} energy levels is efficient, resulting in the greater intensity of emission peaks of both Dy^{3+} and Eu^{3+} ions. This feature enables the applicability of the Dy^{3+}/Eu^{3+} co-doped $SrMoO_4$ phosphors for tunable light sources. The emitting color of the co-doped samples can be adjusted from white to greenish-yellow and greenish-yellow to reddish-orange. Furthermore, the temperature-

dependent PL emission of the phosphors is also utilized to probe the temperature sensing property of the phosphors. It is observed that with an increase in the temperature and setting the excitation wavelength to 297 nm, the intensity of all the emission lines corresponding to the Dy^{3+} ions increases. Whereas, when the excitation wavelength was shifted to 352 nm, the usual thermal quenching is observed in the emission of the Dy^{3+} ions. The anti-thermal quenching in the PL emission of the Dy^{3+} ions is the result of energy transfer from the $[MoO_4]^{2-}$ excited band lying close to the Dy^{3+} energy levels. This energy transfer prompts extra electrons to the excited energy levels of Dy^{3+}, resulting in an anti-thermal quenching phenomenon. However, the usual thermal quenching is observed in the emission of Eu^{3+} ion at 297 nm. Therefore, we have exploited the contrasting nature of Dy^{3+} and Eu^{3+} PL emission with temperature and for 297 nm excitation to probe the temperature sensing property of the phosphor. Based on FIR mode, the S_r value for 4% Eu^{3+} co-doped $SrMoO_4$:4Dy^{3+} phosphor is 1.46% K^{-1} at 300 K.

In chapters 6 and 7 we discuss the PL emission enhancement of $Zn_3(VO_4)_2$ phosphors as a result of Bi^{3+} and Li^+ doping. The PL emission is improved by a factor of 11 after Bi^{3+} doping, which is much greater than the improvement compared to Li^+ doped phosphor. The role of Bi^{3+} and Li^+ ions in enhancing the PL intensity is discussed in detail. The doping of Bi^{3+} and Li^+ ions creates variation in the crystal lattice field surrounding the $(VO_4)^{3-}$ groups owing to the difference in ionic radius of Zn^{2+} and dopant ions. This may consequently influence the spin-orbit coupling and distort VO_4 tetrahedron even more from the ideal thereby increasing the luminescence in Bi^{3+} and Li^+ doped $Zn_3(VO_4)_2$. The improved crystallinity and average particle size also plays role in improving the emission. Apart from these reasons, the Bi^{3+} ion forms a metal-metal charge transfer band because of the transitions between $Bi^{3+}(6s^2) – V^{5+}(3d^0)$ and $Bi^{4+}(6s^1) – V^{4+}(3d^1)$ configurations. This again helps in improving the absorption, thereby improving the PL emission of the host phosphor.

The thermal stability of the Li^+ doped $Zn_3(VO_4)_2$ phosphor is then checked by examining the temperature-dependent PL spectra. The calculated activation energy of the Li^+ doped $Zn_3(VO_4)_2$ is 0.29 eV, validating the good thermal stability of the phosphor. Moreover, there is a 44% loss of emission intensity at 150 ℃. In conclusion, the near UV excitation, greenish-yellow emission, good thermal stability, and cost-efficient synthesis process, make Bi^{3+} and Li^+ doped $Zn_3(VO_4)_2$ phosphor an excellent material for near UV-based white LEDs and other optoelectronic devices.

Finally we have summaried the highlights of the work done in Table 8.1 and compared it with the reported work.

Table 8.1 Some major highlights of the work done and its comparison with reported work.

Compound studied	Major Highlights	Comparison with reported work
Zn^{2+}/Sm^{3+} co-doped $SrMoO_4$	• The phosphors were synthesized by the lucrative urea-assisted solution combustion process. • Enhancement in emission intensity by 87.80% after 1% Zn^{2+} co-doping in $SrMoO_4$:4Sm^{3+} for 404 nm excitation wavelength. • Therefore, there is a 31% loss of emission intensity as compared to room temperature emission. • The obtained value of activation energy is around 0.17eV	• Some of the other reported phosphors have a significant part of the emitted light of these phosphors lying outside the human eye spectral sensitivity range (i.e. beyond 700 nm), which limits their use in the wLED application. • The activation energy of our phosphor is higher than many other previously reported Sm^{3+} doped red phosphors such as $CaLa_2(MoO_4)_4$, $Ca_9La(PO_4)_7$,$KLaSr_3(PO_4)_3$, $Ca_2Y_8(SiO_4)_6O_2$ [2,156,158].
Dy^{3+}/Eu^{3+} co-doped $SrMoO_4$	• Color tuning by precisely controlling the contents of Dy^{3+} and Eu^{3+} ions in the host phosphor and by modulation of excitation wavelength is discussed. • The phenomenon of anti-thermal quenching in the Dy^{3+} doped $SrMoO_4$ phosphors is discussed. • The high value of relative sensitivity (1.46% K^{-1}) is obtained.	• The relative sensitivity is fairly large than many previously reported works on dual-mode optical thermometry[164,180,186,188,189,243].
Li^+ and Bi^{3+} doped $Zn_3(VO_4)_2$	• Phosphors were prepared by the facile urea-assisted solution combustion process. • The PL emission is enhanced by the factor of 11 after 1% Bi^{3+} doping in $Zn_3(VO_4)_2$. • The high activation energy of Li^+ doped $Zn_3(VO_4)_2$ confirms the thermal stability of the phosphor.	• The phosphors were prepared at a lower calcination temperature which makes the synthesis process cost-effective. • Better thermal stability compared to other vanadates such as $Ca_2KZn_2(VO_4)_3$, $Ca_3LiMgV_3O_{12}$, $LiCa_3MV_3O_{12}$ (M = Zn and Mg), and $Rb_3RV_2O_8$ (R = Y, Lu) [240,242,244].

8.2 Future Scope of the study

We have successfully synthesized and studied the effect of doping on the red and greenish-yellow luminescence of $SrMoO_4$ and $Zn_3(VO_4)_2$ phosphors, respectively. Further study has to be carried out to fabricate the LED device by coating prepared phosphors on the commercially available blue chip and studying the quantum efficiency of the device. Improvement in the luminescence thermal quenching of the phosphors is still a challenge for the research community. Therefore, there is scope in improving the thermal stability of Sm^{3+} doped $SrMoO_4$ and $Zn_3(VO_4)_2$ phosphors.

We have also studied the doped $SrMoO_4$ phosphors for optical thermometry application. The effect of doping (such as alkali metals and transition metals) on the sensitivity of phosphor is yet to be explored. In our study, we have observed that these phosphors can affect the crystallinity of the phosphors. Therefore, it is required to study the change in sensitivity induced by doping concentration. The $SrMoO_4$ phosphor has proven to be an excellent host phosphor for rare-earth elements, therefore, other applications such as anti-counterfeiting can also be explored.