Chapter-6

Conclusion and Future Studies

Highlights

This thesis entitled **"Luminescence Studies of Rare Earth Doped Perovskite Phosphors"** describes the synthesis and detailed luminescence investigation on some rare earth (Eu, Tb, and Ho) activated double perovskite phosphors, which are $Sr_2YNbO_6:Eu^{3+}$, $Sr_2YVO_6:Eu^{3+}$, and $Ca_3WO_6:Tb^{3+}/Ho^{3+}$. The purpose of this study is to explore the perovskite materials for its large-scale applications at domestic and industrial levels, including in lighting displays, LEDs, coloured screens, and in TL dosimetry. To fulfil the targeted aim, we have developed several rare-earth doped double perovskites with excellent luminescence display. Total 25 samples were prepared via modified two-step combustion route of synthesis, wherein, urea was taken as burning fuel. Following table shows the phosphors reported in this thesis.

Double perovskite host matrix	Dopant and doping level	Luminescence phenomena observed	Proposed application
Sr_2YNbO_6	Eu^{3+} (1-5 mol%)	PL and TL	LED phosphor
Sr_2YVO_6	Eu^{3+} (1-5 mol%)	PL and TL	Display phosphor
Ca_3WO_6	Tb^{3+} (0.5-2.5 mol%)	PL and TL	TL dosimetry
Ca_3WO_6	Ho^{3+} (1-5 mol%)	PL and TL	UV and Blue Ex. LEDs

All the phosphor under study exhibited excellent PL and TL properties, and are capable of its applications in display devices, LEDs, and in TL dosimetry. According to concerned literature survey, maybe we are the first reporting the oxide double perovskites activated with rare earth ($Sr_2YNbO_6:Eu^{3+}$, $Sr_2YVO_6:Eu^{3+}$) for their thermoluminescence properties.

This thesis is consisted of six chapters basically, including the conclusion chapter. The detailed conclusion drawn from each previously described chapter (chapter 1-5) is discussed below.

6.1 Conclusions

6.1.1 Chapter-1 Conclusion

Chapter-1 describes the brief introduction on luminescence, history of luminescence, luminescence mechanism, different kinds of luminescence and their definitions. Furthermore, it describes the introduction to perovskites and the literature survey. From the literature survey, we are motivated to explore the perovskites for their luminescence characterizations. At the end of chapter-1, the objectives are given followed by thesis layout. As a result, we achieved the objectives proposed of this thesis.

6.1.2 Chapter-2 Conclusion

This chapter of the thesis is focused on the synthesis method of the materials and different material science characterization techniques. All the sample compositions under investigation are prepared by using the combustion synthesis with urea as flux. For the phosphor synthesis, the considered method found appropriate and total 25 samples were prepared. In addition, the details of several characterization techniques, such as XRD, FESEM, EDAX, FTIR, PL, and TL were discussed in terms of their working principles and their given outputs.

6.1.3 Chapter-3 Conclusion

In the present chapter, the photoluminescence and thermoluminescence properties of Eu^{3+} activated Sr_2YNbO_6 double perovskite is discussed, wherein Eu^{3+} doping level taken from 1-5 mol%. The reported study in this chapter is mainly focused on the LED application of the material. To accomplish the aim, the combustion route synthesized materials were thoroughly examined for their structural and luminescence investigation. To study the structural and morphological aspects, the phosphor under study went through XRD and SEM characterization. The XRD results indicates highly crystalline nature of phosphor powder crystallized in pure monoclinic crystal structure with the average crystallite size of roughly 40 nm. The functional groups identified via the FTIR studies indicates standard bond formations among the neighbouring constituent elements, wherein NbO_6 octahedra's dominates the FTIR spectrum. When monitored with 614 nm emission, the phosphor under study exhibited wide range of PL excitation peaks including CTB. Among all observed PL excitation, the intra-4f transition observed at 396 nm ($^7F_0$-$^5L_6$) exhibited highest intensity followed by 467 nm peak and CTB. Taking this into account, the phosphors were excited with 274, 396, and 467 nm excitation. Under all three mentioned excitations, the phosphors exhibited standard europium emission in the orange-red spectral region at 596 nm (MD transition $^5D_0$-$^7F_1$) and 612 nm (ED transition ($^7F_0$-$^5L_2$). The phosphor containing 4 mol% of Eu^{3+} exhibited maximum PL intensity under any given excitation. Furthermore, the thermal stability of the 4 mol% Eu^{3+} containing phosphor is checked by temperature-dependent PL, and was found to the very high ~79.4%. Moreover, the TL investigation is also found interesting and shows linear dose response to beta rays. The overall results obtained from the phosphor under study provide enough evidence that the phosphor can be used as a red component phosphor in the WLEDs.

6.1.4 Chapter-4 Conclusion

The following are the logical conclusions drawn from Chapter 5. In this chapter, we reported the synthesis and luminescence studies of Eu^{3+} doped vanadate double perovskite Sr_2YVO_6 prepared via combustion synthesis. For the first time, this composition of double perovskite was synthesized by doping Eu^{3+}, wherein, Eu^{3+} concentration ranged from 1-5 mol%. Herein, all the as-synthesized phosphors were first characterized by XRD studies. The Rietveld refinement of the acquired XRD patterns confirms the monoclinic crystal structure of all the phosphors under study. The sharp diffraction peaks observed in the XRD pattern revealed the highly crystalline nature of the phosphors, with an average crystallize of ~75 nm. The SEM micrographs indicated agglomerated particle cluster looks like a rise seed with an average particle size of around a few nanometres to a micrometre. The EDAX analysis confirms the presence of all the constituent elements, whereas, the elemental mapping shows an even distribution of all the constituent elements, including slightly added impurities. In PL studies, when the doped phosphors were monitored with 612 nm, a very broad absorption band within 220-350 is observed with some intra-4f excitation peaks of Eu^{3+}. The broad excitation bond observed in the spectra, is formed collectively due to the CT process between oxygen to europium and due to the absorption of vanadium tetrahedra (VO_4^{3-}). The absorption due to vanadate tetrahedra dominates the excitation spectrum in terms of intensity. The PL emission of all the phosphors under study was recorded by using 278, 320, 396, and 467 nm excitations. For all four applied excitations, a standard europium emission is observed in the red spectral region. Among all the phosphors under study, 3 mol% Eu^{3+} containing phosphor exhibited highest PL intensity. Interestingly, when the 3 mol% Eu^{3+} doped phosphor excited with 278 and 320 nm, the deep-red emission at 653 and 705 nm was detected, which is attributed to ED transitions $^5D_0$-$^7F_3$ and $^5D_0$-$^7F_4$ of Eu^{3+}. In addition, the TL studies are also found interesting in the present phosphor system when it's irradiated by beta radiation. Herein, the undoped phosphor exhibited the highest TL intensity when compared to the Eu^{3+} doped samples. The doping of Eu^{3+} charges the trapping position as well as reduces the TL glow, which may be due to the seven unpaired electrons of Eu^{3+}. The excellent linear TL dose response was observed towards high-energy beta rays. The excellent PL display at 278 and 320 nm with very high color purity shows the potential application of the phosphor under study in the display devices. Moreover, from the observed linear dose-response, it also may be useful in the TL dosimetry.

6.1.5 Chapter-5 Conclusion

This chapter of the thesis describes the photoluminescence and thermoluminescence characterization of rare earths (Tb^{3+} and Ho^{3+}) activated tungstate double perovskite Ca_3WO_6. By following the combustion route of synthesis, a total of 13 samples of Ca_3WO_6:Tb^{3+}/Ho^{3+} were prepared, including the base. The doping level of Tb^{3+} and Ho^{3+} is taken in the range of 05-2.5 mol% and 1-5 mol%, respectively. This chapter is divided into two sections, wherein, part-I describes the synthesis and luminescence properties of Ca_3WO_6:Tb^{3+} double perovskite and part-II describes the synthesis and luminescence properties of Ca_3WO_6:Ho^{3+} phosphors.

6.1.5.1 Part-I Luminescence Studies of Ca_3WO_6:Tb^{3+}

From the Rietveld refinement of the acquired XRD pattern of pure Ca_3WO_6 material, the monoclinic crystal structure of the phosphor is confirmed. Because of the very small amount of Tb^{3+} impurities added, we did not observe any notable change in the XRD patterns of the Tb^{3+} containing tungstate phosphors. This indicated the Tb^{3+} is incorporated without disturbing the parent crystal structure, as we found similar XRD patterns in the doped samples. The FESEM micrographs depict particle clusters, wherein the average particle size ranges between 500 nm to a few micrometres. However, the EDAX analysis and mapping of constituent elements show an even distribution of all constituent elements throughout the material. Through the FTIR study, the standard tungstate functional groups were identified. When the phosphor under study was excited at 278 nm, it exhibited excellent green emission at 545, 553, and 567 nm, with the highest intensity at 545 nm ($^5D_4$-$^7F_5$ transition of Tb^{3+}). The highest PL intensity was observed from the phosphor containing 1 mol% of Tb^{3+}, however, further increment in doping level leads to intensity quenching, for which multipolar interaction is the responsible phenomenon.

Furthermore, high-intensity TL was observed from Ca_3WO_6:Tb^{3+} phosphors after beta irradiation. For the first time, Ca_3WO_6:Tb^{3+} underwent the TL studies after beta, and we found excellent results. The effect of Tb^{3+} concentration and the effect of beta dose on TL intensity are two major aspects that have been investigated in detail. When the doping level is increased, the TL intensity increased, and is found maximum for the phosphor containing 2.5 mol% of Tb^{3+}. Excellent linear dose response in TL intensity was observed with raising dose beta rays in the dose range of 10-50 Gy. Moreover, the Ca_3WO_6:2.5 mol% Tb^{3+} phosphor was studied for its fading phenomenon in order to examine the dose storage capability. In addition, the trapping parameters were calculated via the PSM and GCD. The excellent linear dose-response and the very low fading of the order of ~12% indicate that the Ca_3WO_6:2.5 mol% Tb^{3+} phosphor can be a good candidate to be used in TL dosimeters.

6.1.5.2 Part-II Luminescence Studies of $Ca_3WO_6:Ho^{3+}$

After the Rietveld refinement studies of the host lattice, the monoclinic structure of the phosphor under study is discovered, as mentioned in section 6.1.5.1. Later, the effect of holmium doping on crystal structure was discussed in detail. From the FTIR study, it is found the phosphor under study shows standard tungstate bond vibrations. When the phosphors underwent PL studies and were monitored with 545 nm, they exhibited standard PL excitation peaks of Ho^{3+} in addition to a broad charge transfer band. Including the Ho^{3+} characteristic excitation and the CTB, we found a new excitation peak at 722 nm, which indicates that the phosphor under study may able to emit the up-conversion luminescence. The PL emission was recorded after several excitations, including 275, 303, 362, 422, 454, 488, and 722 nm. Under all the applied excitations, phosphor exhibited excellent PL emission in the green spectral region at 545 nm. It should be mentioned that the phosphor under study also shows the up-conversion luminescence when excited with 722 nm. Later, the Ca_3WO_6:1 mol% Ho^{3+} phosphor, the phosphor with the highest PL intensity at 362 and 454 nm excitation, was examined for the temperature-dependent PL studies, to assess its application in UV (362 nm) and blue (454 nm) excited LEDs. Under both the applied excitation, we found excellent PL response at higher temperatures, wherein, the PL intensity remained 85.6% for the excitation of 454 nm, and 84.2% for the excitation of 362 nm when compared to the PL intensity observed at RT. The TL studies of beta-irradiated Ca_3WO_6 phosphors were examined in order to evaluate the intrinsic nature of electron traps. In this study, the effect of Ho^{3+} concentration and different doses of beta radiation were studied and discussed. Among all studied samples, Ca_3WO_6:2% Ho^{3+} was found more promising for TL characteristics. An exceptional linear dose-response was observed from the phosphor within the dose range of 10-50 Gy. Besides, the effect of heating rate on the TL glow curve was studied, which indicates negligible thermal quenching from the phosphor under study. Finally, the linear dose response and lower thermal quenching features make phosphor a good candidate to be used for dosimetry applications. The exceptionally high thermal stability at 362 and 454 nm excitation, makes phosphor promising to be used in UV- and blue-excited LEDs.

6.2 Future Studies

In this thesis, we reported the rare-earth activated double perovskites, which are prepared via the combustion route of synthesis. In future, we would like to explore the rare-earth free perovskites as well as rare-earth doped perovskites for their PL and TL characterization. Also, we want to explore the perovskite nanoparticles, that can be prepared by using the hydrothermal method of material synthesis.