LUMINESCENCE STUDIES OF RARE EARTH DOPED PEROVSKITE PHOSPHORS

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TABLE OF CONTENT OF THE THESIS

1. Introduction

During the last six decades, phosphors with excellent displays of several kinds of luminescence have been widely investigated for their practical technological applications in various fields of science and technology. Phosphors doped with different luminescent activators are widely investigated for lighting devices and displays, lasers, and medical purposes [1]. As well as the production and fabrication of white light-emitting diodes (WLEDs) have attracted huge interest worldwide because of their several advantages, including low power consumption, environmental friendliness, cost-effectiveness, and high luminescence efficiency [2]. Consequently, luminescent materials, also called phosphors, with excellent luminescence displays are the key components of commercially available WLEDs. A new generation is working on the luminescence phenomenon, primarily focusing on the luminescence efficiency enhancement and low cost-effectiveness of WLEDs [3].

Rare earth elements play a crucial role in the luminescence properties of various materials. Luminescence refers to the emission of light from a substance when it absorbs energy. Rare earths are known for their unique electronic configurations, which give rise to distinct energy levels and transitions, making them excellent candidates for luminescent applications [4,5]. The electronic configuration of rare earths provides energy levels with specific quantum numbers, which determine the wavelengths of light they can absorb and emit. The transitions between these energy levels result in luminescence. Different rare earth ions exhibit specific energy level structures, leading to a broad range of colors and emission spectra [6]. Moreover, rare earth elements are widely used in phosphors, which are materials that convert absorbed energy into visible light. Phosphors doped with rare earth ions exhibit luminescence through various mechanisms, such as fluorescence, phosphorescence, and up-conversion luminescence.

In the field of luminescence investigation and its applications, many phosphors were explored for their excellent display of luminescence. In this thesis, the luminescence studies on perovskite-based luminescent phosphors and activated perovskite phosphors are discussed to functionalize them for various applications. During the initial stages of the research, a brief literature review on luminescent phosphors and rare earth-activated perovskite phosphors was carried out. As per the literature survey, several luminescent perovskites were previously reported for their diverse luminescence phenomena, such as photoluminescence, thermoluminescence, persistent luminescence, optically stimulated luminescence, up- and down-conversion luminescence, etc. This survey of literature motivates us to explore more perovskite for their practical technological applications.

2. Research methodology

After conducting an extensive review of the available literature, it becomes evident that perovskite hosts doped with rare earth ions have been the subject of numerous studies due to their remarkable luminescence properties and versatile applications in solid-state light sources, displays, temperature sensors, plasma display panels, radiation dosimetry, fluorescent lamps, optoelectronics, photonics, and more. This thesis primarily focused on the synthesis and luminescence characterization of perovskite phosphors activated by different rare earth ions. In order to fulfilment of the proposed problem, following are the steps involved and research methodology applied to accomplished the target aim.

- Synthesis of rare-earth doped perovskite phosphors using the combustion route of synthesis.
- Utilization of different characterization techniques, such as crystal structure identification using X-ray diffraction (XRD), examination of morphology using field emission scanning electron microscopy (FESEM), and functional group identification via Fourier transform infrared (FTIR) spectroscopy.
- Investigation of photoluminescence (PL) properties in several rare earth (Eu^{3+}/$Tb3^{+}$/Ho^{3+}) activated perovskite phosphors.
- Study of thermoluminescence (TL) properties in rare earth doped perovskite phosphors by irradiating them with high energy and low energy ionizing radiations, and calculation of TL parameters from the TL glow curves.

3. Results and key findings

In this study, total 23 rare earth doped double perovskite-based phosphors were synthesized via the combustion route of material synthesis. This method was chosen for its simplicity, high productivity, and cost-effectiveness. In the thesis, various characterization techniques used to examine the prepared phosphors potential, including X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Fourier-transform infrared spectroscopy (FTIR), thermoluminescence (TL), and photoluminescence (PL). Moreover, the determination of expected parameter using each characterization technique was discussed in detail.

First, we prepared Sr_2YNbO_6 double perovskite by doping Eu^{3+}, and studied their luminescence properties in detail. The concentration of Eu^{3+} is taken from 1 mol% to 5 mol%. The phosphor crystallized in pure monoclinic crystal structure, that exhibited excellent PL and TL properties [7,8]. The optical properties of this phosphor were studied via the FTIR technique, wherein we found the presence of standard niobate octahedra. The results obtained

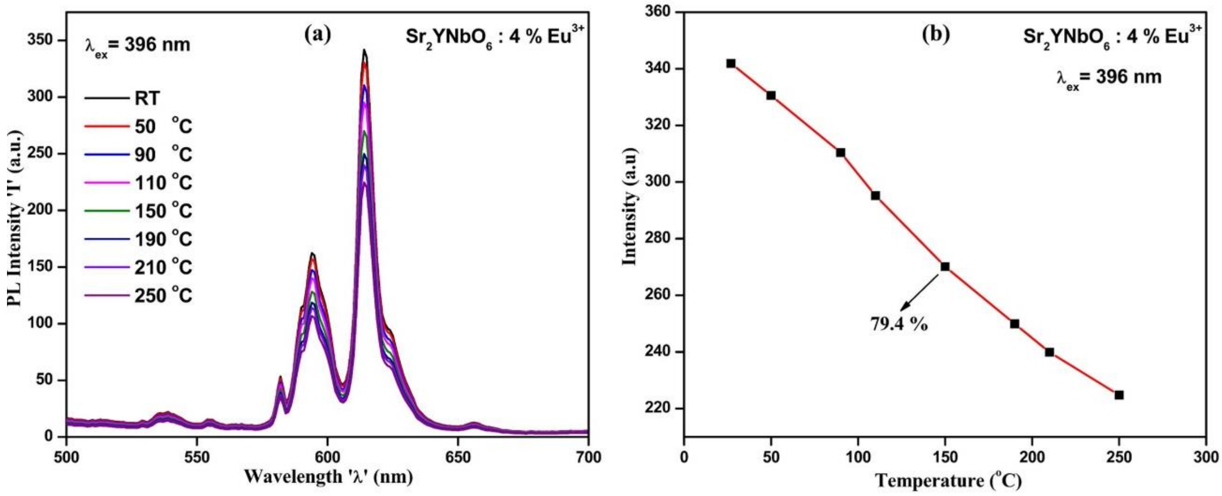

Figure 1. (a) PL emission spectra of Sr_2YNbO_6: 4 mol% Eu^{3+} at different temperatures; (b) plot of PL intensity vs. Temperature.

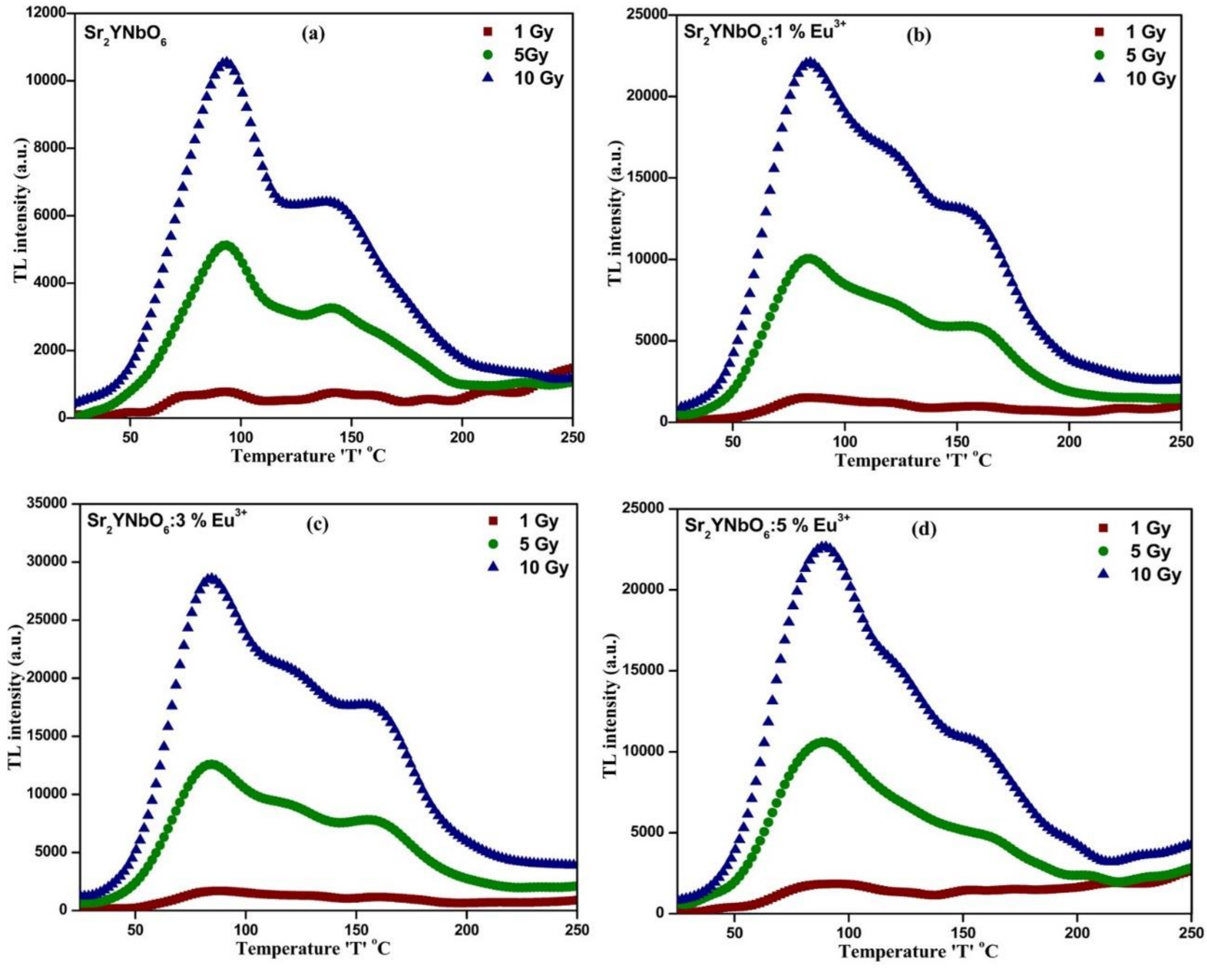

Figure 2. TL glow curves of Sr_2YNbO_6:x mol% Eu^{3+} (x=0, 1, 3, 5) phosphors at different beta doses.

from XRD and FTIR were significant and corelated. For photoluminescence studies, all samples were examined under different excitation wave length, out of which Sr_2YNbO_6: 4 mol% Eu^{3+} phosphor excited under 396 nm excitation exhibited good intense red emission, which is ascribed to standard europium emission resulting due to $^5D_0$-$^7F_2$ transition [9,10]. Furthermore, to investigate the thermal stability of Sr_2YNbO_6: 4 mol% Eu^{3+} phosphor, the PL emission spectra were measured for wide temperature range, i.e. from room temperature to 250 °C presented in Figure 1(a). The results revealed that the thermal stability could be 79.4% at LED burning temperature (150 °C), as shown in Figure 1(b), it making this phosphor promising to be used in the WLEDs as a red component phosphor [11]. Moreover, for thermoluminescence studies all samples were irradiated using beta radiation for dose the range of 1-10 Gy, then after TL glow curves were measured from room temperature to 250 °C. The effect of dose and doping concentration on TL emission was examined as well as TL kinetic parameter was calculated. The TL glow curves of Sr_2YNbO_6:x mol% Eu^{3+} (x=0, 1, 3, 5) are shown in Figure 2. The linear response of TL intensity with increasing beta dose in the range of 1-10 Gy indicate that the phosphor may also be used in the TL dosimetry [12]. The detail study of all characterizations was presented in chapter 3 of thesis.

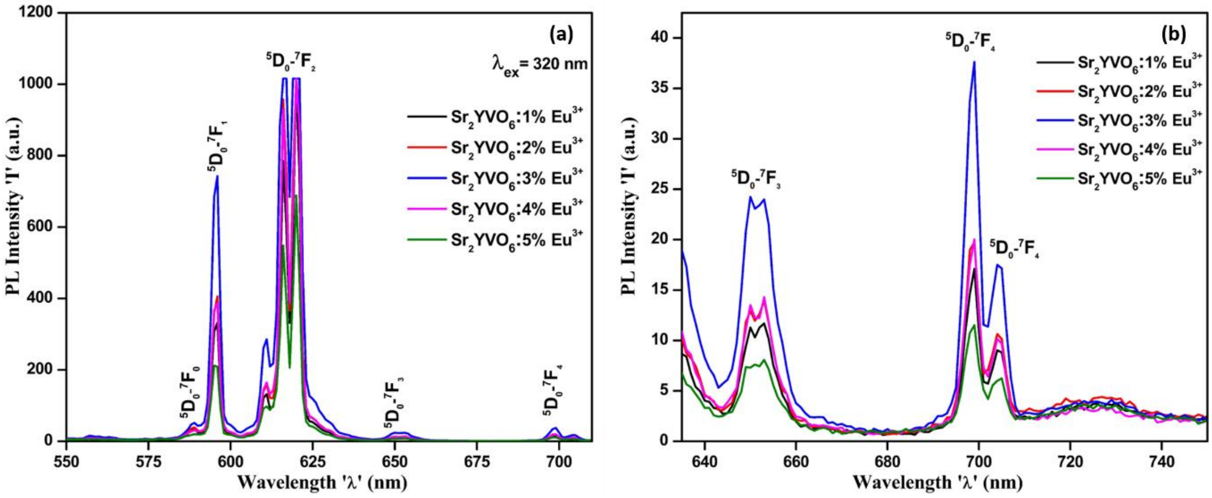

Figure 3. (a) PL emission spectra of Sr_2YVO_6: x mol% Eu^{3+} (x =1-5) phosphors monitored with 320 nm excitation wavelength; and (b) Magnified image of PL emission spectra of Sr_2YVO_6: x mol% Eu^{3+} phosphors within 630-750 nm.

In further experiments, we prepared a new double perovskite composition Sr_2YVO_6 doped with Eu^{3+}. The synthesis of this phosphors was accomplished through the combustion synthesis method, and structural analysis was performed using FESEM, EDAX, and FTIR spectroscopy. The Rietveld refinement of the XRD pattern of Sr_2YVO_6 phosphor suggests monoclinic crystal structure of all the Sr_2YVO_6 phosphor [13]. The PL properties were thoroughly examined to understand the luminescent behaviour of the phosphor, wherein we found excellent PL emission of Eu^{3+}. Figure 3(a-b) depicts the PL emission spectra of Sr_2YVO_6:x% Eu^{3+} (x=1-5) phosphor under 320 nm excitation. The red and far-red emission at 653 nm and 705 nm were observed when the 3 mol% Eu^{3+} doped phosphor excited with 320 nm excitation, which are attributed to $^5D_0$-$^7F_3$ and $^5D_0$-$^7F_4$ transitions of Eu^{3+}, respectively [14,15].

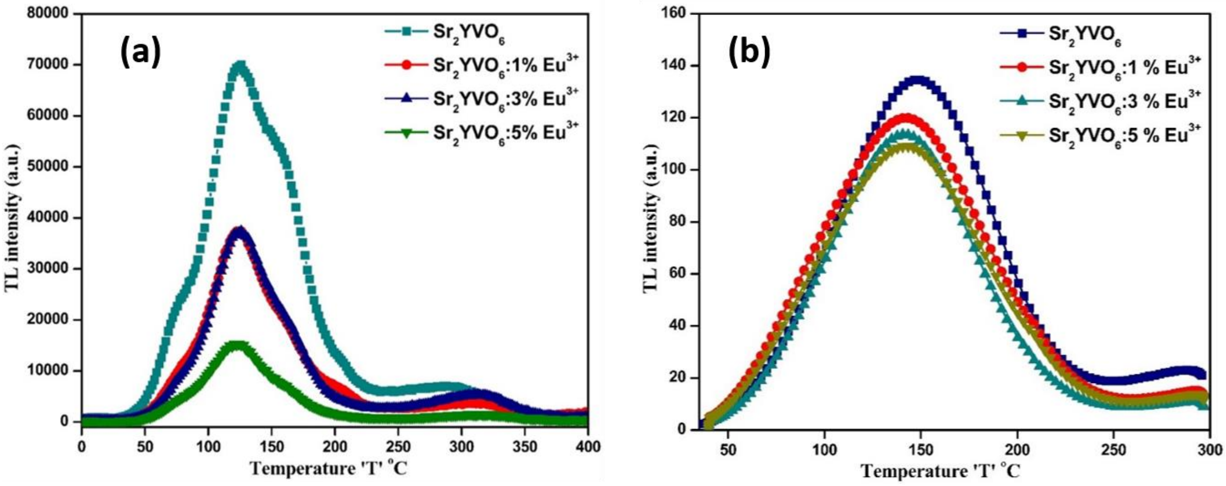

Figure 4. (a) Thermoluminescence glow curves of Sr_2YVO_6:x mol% Eu^{3+} (x=0, 1, 3, 5) phosphors after 10 Gy dose of beta irradiation; (b) TL glow curves of Sr_2YVO_6:x mol% Eu^{3+} (x=0, 1, 3, 5) phosphors under UV irradiation for 60 min.

Moreover, in TL experiments, the phosphor Sr_2YVO_6 doped with Eu^{3+} underwent irradiation using two different ionizing radiations, namely beta and UV rays, with varying radiation doses. Figure 4 (a) and (b) depicts the TL glow curves of Sr_2YVO_6:x% Eu^{3+} phosphors under fixed dose of beta and UV rays, respectively. Interestingly, the undoped phosphor under study exhibited highest TL glow under both the irradiation rays. The linear dose response towards beta rays and UV rays indicate that the phosphor may useful for the dosimetry purpose towards beta rays and UV rays [16-17]. The detail study of all characterizations was presented in chapter 4 of thesis.

Our further study aimed the perovskite exploration for the luminescence characterization. Kept this in mind, we selected a tungstate perovskite Ca_3WO_6 for luminescence study, which is doped with Tb^{3+} and Ho^{3+}. The Ca_3WO_6:Tb^{3+} (Tb^{3+}=0.5-2.5 mol%) and Ca_3WO_6:Ho^{3+} (Ho^{3+}=1-5 mol%) phosphors were prepared via the combustion route of synthesis. A study on XRD technique of all the tungstate phosphors considered for luminescence study indicated the pure monoclinic crystalline structure with a P 21/c symmetry [18-19]. A study on FTIR spectroscopy of undoped, Tb^{3+} doped and Ho^{3+} doped phosphors suggest the presence of standard tungstate bonding [20,21]. Both the phosphor series exhibited very good green spectral emission with notable intensity.

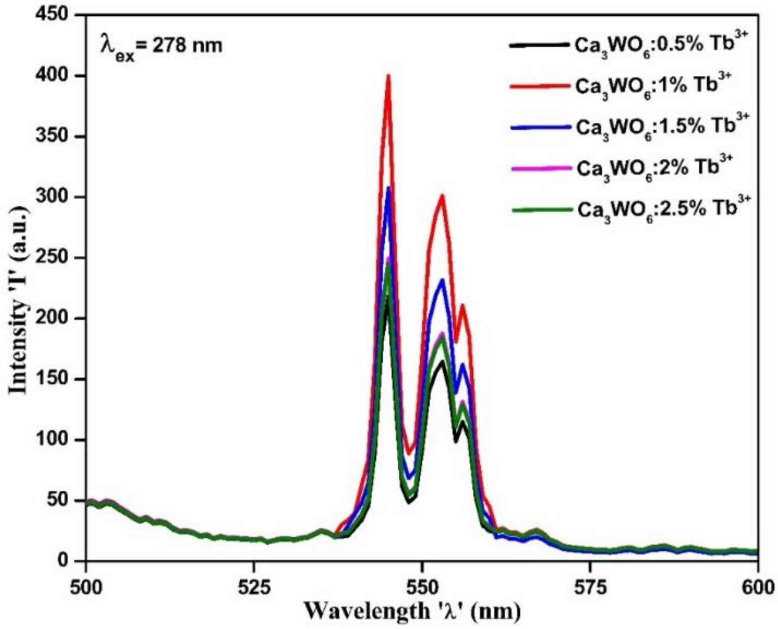

Figure 5. PL emission spectra of Ca_3WO_6: x% Tb^{3+} (x=0.5, 1, 1.5, 2, 2.5) phosphors.

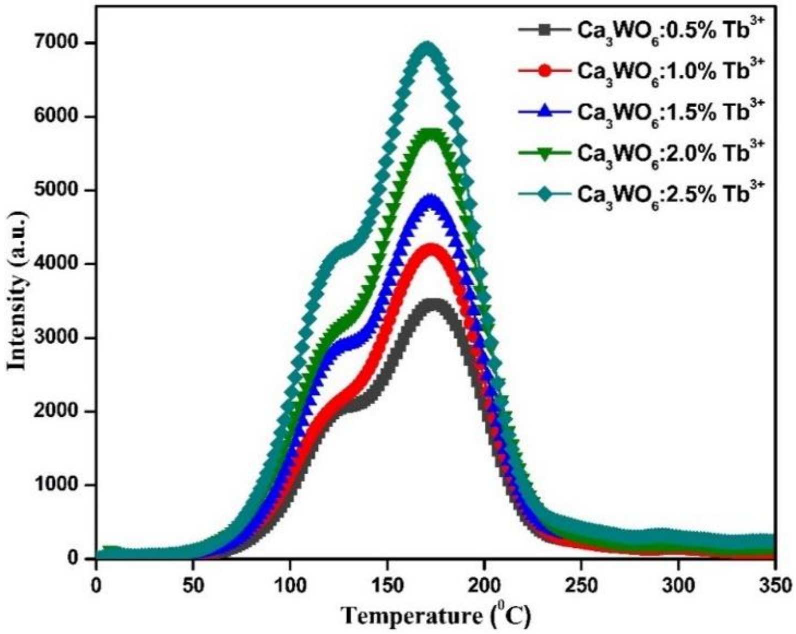

Figure 6. TL glow curves of Ca_3WO_6:x% Tb^{3+} (x=0.5-2.5) phosphors after 50 Gy dose of beta irradiation.

When Ca_3WO_6:Tb^{3+} phosphor excited with 278 nm, it shows green emission at 545 nm, which is standard terbium emission occurs from $^5D_4$-$^7F_5$ transition, shown in Figure 5 [22,23]. When the phosphor is doped with 1 mol% of Tb^{3+}, it exhibited highest PL intensity. Later, for higher doping concentration of Tb^{3+}, the PL intensity found quenched. Moreover, a high intense TL is observed from $Ca_3WO_6:Tb^{3+}$ phosphors after beta irradiation, shown in Figure 6. After 50 Gy dose of beta irradiation, the Ca_3WO_6:x% Tb^{3+} (x=0.5-2.5) phosphors exhibited most intense TL glow maximum at 170 °C with a small hump on the lower temperature side. The excellent linear dose response with increasing beta dose, and less TL fading making Ca_3WO_6:2.5%Tb^{3+} phosphor promising candidate to be used in TL dosimetry [24,25].

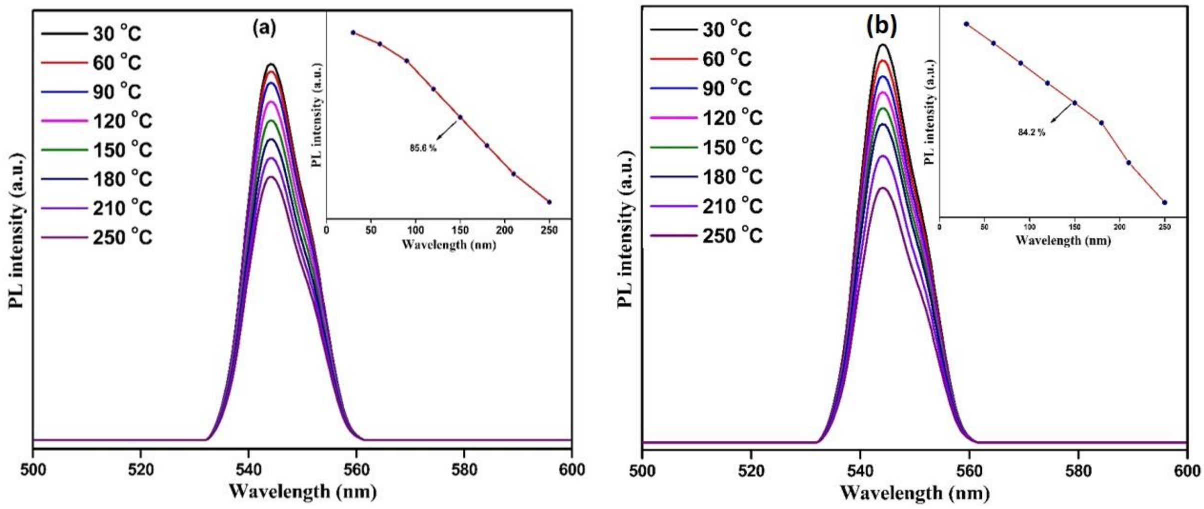

Figure 7. (a) Temperature dependent PL of Ca_3WO_6:1 mol% Ho^{3+} phosphor monitored with 454 nm; (b) Temperature dependent PL of Ca_3WO_6:1 mol% Ho^{3+} phosphor monitored with 362 nm.

In the case of $Ca_3WO_6:Ho^{3+}$ phosphor series, we found admirable PL display with notable emission intensity. When the $Ca_3WO_6:Ho^{3+}$ phosphor is excited at 362 nm, and 454 nm, it exhibited standard holmium emission, which is resulted due to $^5F_4$-$^5I_8$ transition of Ho^{3+} [26,27]. The thermal stability of the phosphor $Ca_3WO_6:Ho^{3+}$ phosphor was checked by taking the PL emission at various temperatures, starting from RT to 300 °C. Figure 7 (a) and (b) shows the temperature dependent PL emission spectra of Ca_3WO_6:1%Ho^{3+} phosphor under 454 nm and 362 nm excitations. The phosphor under study shows very high thermally stable PL emission at 150 °C (LED burning temperature) with PL intensity of 85.6% when excited at 454 nm, and 84.2% when excited at 362 nm, when compared to intensity observed at RT. The excellent thermal stability of $Ca_3WO_6:Ho^{3+}$ phosphor making it very promising for its applications in UV and blue excited LEDs [28]. The detail study of all characterizations was presented in chapter 5 of thesis.

4. Conclusion and future study

Herein, several rare earths (Eu^{3+}, Tb^{3+} and Ho^{3+}) activated double perovskite phosphors were synthesized via the combustion synthesis and studied for their luminescence characterizations. As a result, we found multi-purpose materials for their applications in the field of lighting devices and radiation detection. First, we have prepared the Sr_2YNbO_6 double perovskite doped with various concentrations of Eu^{3+}. Wherein, we have found highly thermally stable materials with the thermal stability of the order of ~79.4%. Moreover, the TL investigation is also found interesting and shows linear dose response to beta rays within the dose range of 1-10 Gy. The overall results obtained from the Sr_2YNbO_6 phosphor under study provide enough evidence that the phosphor can be used as a red component phosphor in the WLEDs. Later, by replacing the Nb^{5+} site with V^{5+} in the Sr_2YNbO_6 double perovskite, we have prepared new double perovskite Sr_2YVO_6 by doping Eu^{3+}. As a result, we found deep red PL emission in addition to the orange-red PL emission. Moreover, these phosphors also exhibited excellent TL response after beta irradiation. 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.

In the next experiment, we have taken a tungstate based double perovskite Ca_3WO_6 and doped with various concentrations of Tb^{3+} and Ho^{3+}. When the Ca_3WO_6:Tb^{3+} 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. Additionally, after beta irradiation, all the Tb^{3+} doped Ca_3WO_6 phosphors exhibited excellent TL response. 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. Moreover, the bright green emission under 278 nm excitation reviled potential application of the phosphor in the display materials. In the second tungstate-based phosphor series doped with Ho^{3+}, we have found highly intense single-peak wavelength green emission under UV (362 nm) and blue (454 nm) excitations. A study on temperature dependent PL shows highly thermally stable material, which has ability to emit bright green emission even after reaching LED burning temperature. In addition, all the Ho^{3+} doped tungstate phosphors displayed good TL response after beta irradiation. Wherein, 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.

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.

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