LUMINESCENCE STUDIES OF RARE EARTH DOPED PEROVSKITE PHOSPHORS

A SYNOPSIS SUBMITTED TO

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Introduction

During past few decades, 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 [1-3]. Consequently, the luminescent materials also called phosphors with excellent luminescence display are the key component of commercially available WLEDs. A new generation working on the luminescence phenomenon, majorly focusing on the luminescence efficiency enhancement and low cost-effectiveness of WLEDs [4,5]. The phosphors with excellent displays of several kinds of luminescence are 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 for medical purposes [6,7].

The word “Luminescence” comes from the Latin word “Lumen” means light, and was first introduced by the great germen scientist Eilhardt Wiedemann in 1888. In 384-322 (BC), a Greek philosopher and scientist named Aristotle observed the light that was coming out of decaying fish [8,9]. Two thousand years later, a Swiss man named Nicolas Monardes observed an extremely vivid blue color from an aqueous extract of wood called lignum nephriticum. A lot of the phenomenon of light emission was observed occurring due to natural or artificial processes. Luminescence refers to the emission of light from a substance called phosphor in absence of heat energy [10]. It is a fascinating optical phenomenon observed in several natural and artificially prepared materials. Unlike incandescent light, which is produced because of heating an object to high temperatures, luminescence emission was occurs when energy is absorbed by a material and later it will be released in the form of light. The process of luminescence involves the absorption of energy in the form of photons or any other term, by the atoms of a luminescent material. If the absorbed energy was high enough to excites the electrons within the material, it causing electrons to move in to the higher energy levels of the materials. When the excited electrons return to their original states, it releases the absorbed energy in the form of visible, ultra-violate (UV), or infrared (IR) light [11]. Based on the source of the excitation of electron, different types of luminescence were identified, including fluorescence, phosphorescence, and bioluminescence. Instant emission of light on the absorption of energy commonly defined as fluorescence emission, which ends almost instantly after the removal of source of excitation. However, phosphorescence involves a delayed emission of light even after the energy source is removed, as the excited electrons return to their original states more slowly. Bioluminescence is a particular type of luminescence found in living organisms, where chemical reactions within their bodies produce light [12].

Luminescent materials have numerous applications in various fields. They are used in lighting, displays, imaging technologies, and sensors [13-15]. For example, fluorescent dyes are employed in biological research to label and track specific molecules or cells. Phosphorescent materials find applications in glow in the dark products, such as watch dials and emergency signs. Additionally, bioluminescent organisms have provided invaluable tools for scientific research and have applications in medical diagnostics and environmental monitoring [16,17]. Overall, luminescence is an attractive phenomenon that has been attached and utilized for a wide range of practical and scientific purposes. Its study continues to advance our understanding of light and matter, leading to new discoveries and innovations in various fields.

In the field of luminescence investigation and its applications, many phosphors were explored for their excellent display of luminescence. Herein, the author of the thesis proposing luminescence studies on the perovskite based luminescent phosphors and activated perovskite phosphors to functionalized it for various applications. Present work contributes to the field of lighting devices and in radiation physics. This thesis primarily focused on the structural and luminescence characterization of perovskite phosphors activated by different rare earth ions. While some of the perovskites have been thoroughly investigated as hosts in previous research, whereas the perovskites for thermoluminescence characterization get limited attention. Consequently, this study titled "Luminescence Studies of Rare Earth Doped Perovskite Phosphors" attempts to explore the potential mechanism of thermoluminescence and photoluminescence through experiments conducted on some rare earth-doped double perovskites [18,19].

Motivation

After conducting an extensive review of the existing 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.

Objectives of the thesis

- Preparation of rare earth doped perovskite phosphors using combustion method.
- Verification of sample synthesis and analysis of crystal structure 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 determination of TL parameters from the TL glow curve.

Thesis layout:

Chapter 1. Introduction and literature survey

An overall view of the luminescence and luminescent mechanism is discussed in this chapter. The importance of the luminescent materials and different luminescence phenomenon was discussed in details.

Chapter 2. Experimental Method and Characterizations

In this study, we have used combustion method for the preparation of perovskite materials. This method was chosen for their simplicity, high productivity, and cost-effectiveness. This chapter provides a comprehensive explanation of this method. Additionally, various characterization techniques used in this research are discussed along with the corresponding equipment. The characterization techniques include X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy-dispersive spectroscopy (EDS), Fourier-transform infrared spectroscopy (FTIR), thermoluminescence (TL), and photoluminescence (PL). Moreover, the determination of expected parameter using each characterization technique were discussed in brief.

Chapter 3. Niobate based double perovskite phosphors

Present chapter describe a study on the effects of Eu^{3+} dopants on the photoluminescence thermoluminescent properties of Sr_2YNbO_6 double perovskite phosphor. The concentration of Eu^{3+} dopant was taken in the range of 1 mol% to 5 mol%. The synthesis of all the phosphor compositions was accomplished through the combustion process. The study employed various characterization techniques, including XRD, FESEM, FTIR, PL, temperature dependent PL and TL after irradiating the phosphor by UV and beta ionizing radiations. These techniques were used to confirm the compound, examine the surface morphology, analyse the internal structure, and assess the material's LED and radiation dosimetry features.

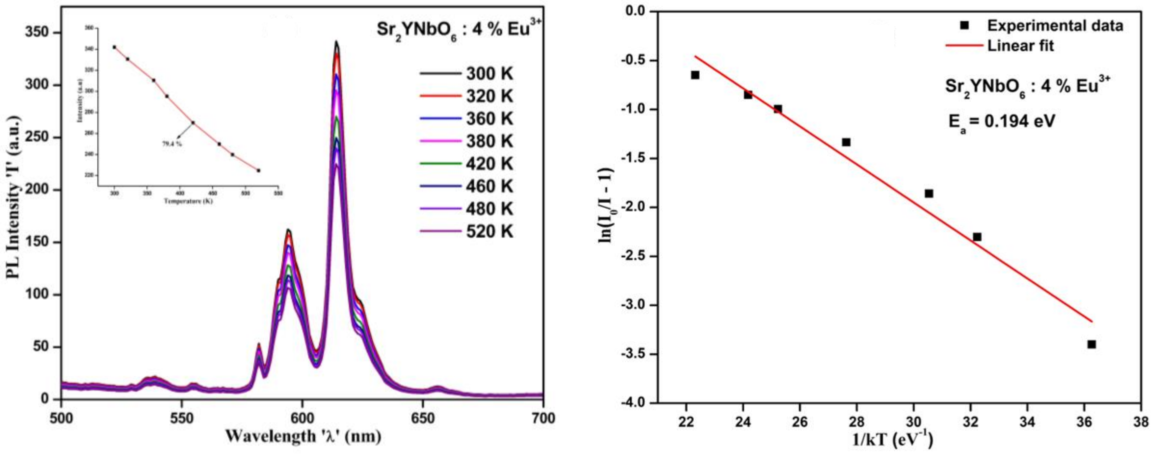

Figure 1. Thermal stability check of the phosphor for LED application

Chapter 4. Vanadate based double perovskite phosphors

This chapter presents an investigation on a vanadate double perovskite Sr_2YVO_6 phosphor doped with Eu^{3+}. The synthesis of this phosphor was carried out using the combustion synthesis method. To determine the phase and confirm the crystal structure, XRD was used. Additionally, structural analysis was performed using FESEM, EDAX and FTIR spectroscopy. 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. The PL properties were thoroughly examined to gain a comprehensive understanding of the phosphor's characteristics. In further analysis, the CIE study was utilized to calculate the chromaticity coordinates and color temperature, exploring the potential application of the phosphor displays. Overall obtained results give enough evidence to the phosphor under study to be incorporated for displays and TLD applications.

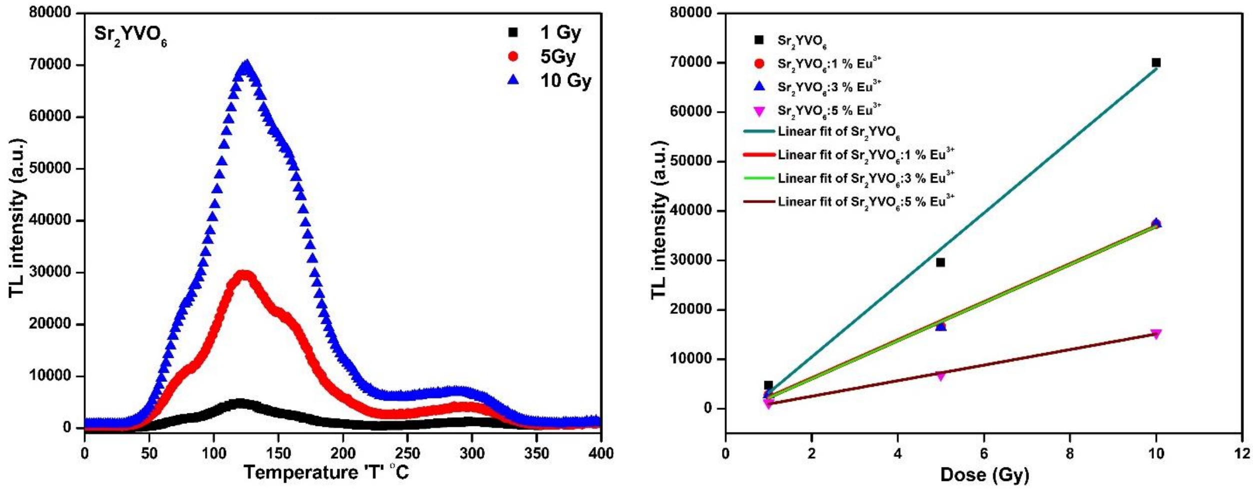

Figure 2. Dose response of phosphor to beta rays for low dose TLD application.

Chapter 5. Tungstate based double perovskite phosphors

Part-I

This section discusses the structural and luminescence optimization in terbium activated tungstate double perovskite Ca_3WO_6. A detailed structural study of the phosphor under study were carried out in terms of XRD, SEM, and FTIR characterization techniques. The PL study's findings suggesting an efficient green emitting perovskite phosphor with excellent CIE color coordinates. Moreover, in TL, the phosphor explored for their wide investigation aspects, such as effect of doping concentration, effect of radiation dose and most important fading effect.

Part-II

In this section, a detail on the a Ho^{3+} single doped Ca_3WO_6 double perovskite investigation is discussed. The phosphor studied extensively for their structural characterization, including XRD, SEM, EDAX and FTIR and were prepared using combustion synthesis. An interesting phenomenon of up-conversion luminescence was observed in addition with down-conversion luminescence from single Ho^{3+} doped Ca_3WO_6 phosphor. A high thermal stability of the phosphor was obtained from temperature dependent PL. Moreover, the TL display is also found to be quite interesting between undoped and doped Ca_3WO_6. In TL, effect of doping, effect of ionizing dose and effect of different heating rates on TL intensity was discussed in detail.

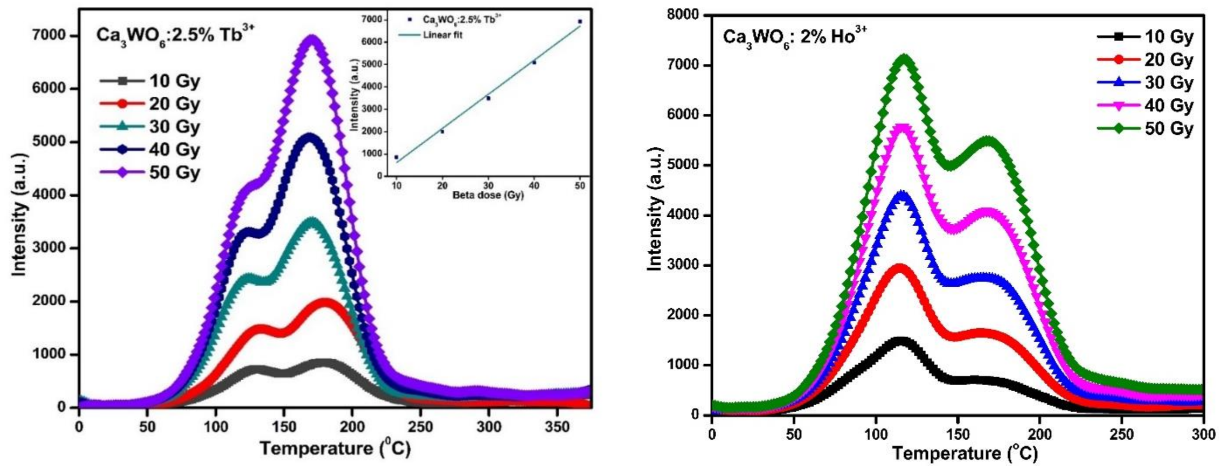

Figure 3. Dose response of phosphor to beta rays for high dose TLD application.

Chapter 6. Summary and Conclusion

In summary, the work presented in this thesis were summarized and future aspects was discussed. Also, the future scope of such kind of work is discussed.

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List of Publications

Publications in Peer-Reviewed Journals

1. **Europium doped Sr_2YNbO_6 double perovskite phosphor for photoluminescence and thermoluminescence properties**
   Naresh Degda, Nimesh Patel, Vishwnath Verma, Mangalampalli Srinivas, Kota Venkata Ramana Murthy, Divi Haranath, Luminescence 38, 176 (2023).

2. **Photoluminescence and thermoluminescence kinetic features of Eu^{3+} doped Sr_2YVO_6 double perovskite phosphor**
   Naresh Degda, Nimesh Patel, Vishwnath Verma, M. Srinivas, Kota Venkata Ramana Murthy, Naveen Chauhan, Malika Singhal, M. Srinivas, Opt. Mater. 142, 114019 (2023).

Publications in Proceedings of the National Conferences

1. **Photoluminescence Study of Eu^{3+} Activated Ca_2CeNbO_6: Red Emitting Double Perovskite Phosphor for LED Application**
   Naresh Degda, Nimesh Patel, Vishwnath Verma, M. Srinivas, K. V. R. Murthy, 65, 307 (2021) ISBN- 81-8372-085-4.
2. **Photoluminescence Studies of Eu^{3+} Activated Sr_2CeNbO_6 Double Perovskite**
   Naresh Degda, Nimesh Patel, Vishwnath Verma, M. Srinivas, K. V. R. Murthy, 66, xxx (2022). (In production)

Achievements

1. Participated and gave an oral presentation in international conference on luminescence and its applications (ICLA-2023), on " Luminescence Optimization of Eu^{3+} Activated Novel Double Perovskite for Display and TLD Applications", **won Best Oral Presentation Award.**
2. Participated and gave an oral presentation in international seminar on advanced materials and its applications (ISAMA-2022), on " Photoluminescence of Eu^{3+} Activated Multipurpose Far-red Emitting Double Perovskite: Phosphor for UV-LED and Plant Cultivation", **won third prize in oral presentation.**