

Structural, Morphological and Photoluminescence Characterization of some Rare Earth ions doped Lithium Barium Tungstate Phosphor for Photonic Applications

A Thesis Submitted

**In Partial Fulfilment of the Requirements
for the Degree of**

DOCTOR OF PHILOSOPHY

by

ANU

(2K20/PHD/AP/05)

Under the Supervision of

PROF. A.S. RAO

Professor

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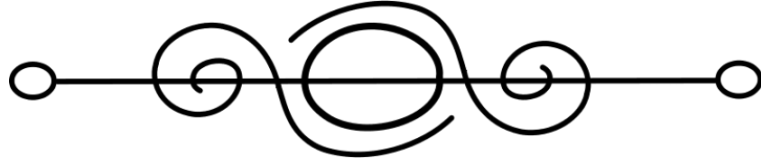
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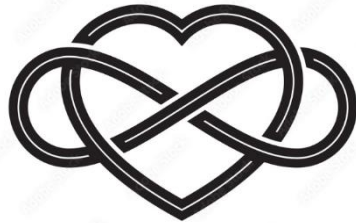
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Dedicated
To My
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CANDIDATE'S DECLARATION

I, **Anu**, hereby certify that the work which is being presented in the thesis entitled **“Structural, Morphological and Photoluminescence Characterization of some Rare Earth ions doped Lithium Barium Tungstate Phosphor for Photonic Applications”** in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy, submitted in the Department of **Applied Physics**, Delhi Technological University is an authentic record of my own work carried out during the period from **August 2020** to **December 2024** under the supervision of **Prof. A.S. Rao, Department of Applied Physics, DTU.**

The matter presented in the thesis has not been submitted by me for the award of any other degree of this or any other Institute.

Candidate's Signature

Anu

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CERTIFICATE BY THE SUPERVISOR

Certified that **Anu** (2K20/PHD/AP/05) has carried out her research work presented in this thesis entitled **“Structural, Morphological and Photoluminescence Characterization of some Rare Earth ions doped Lithium Barium Tungstate Phosphor for Photonic Applications”** for the award of **Doctor of Philosophy** from Department of Applied Physics, Delhi Technological University, Delhi, under my supervision. The thesis embodies results of original work, and studies are carried out by the student herself and the contents of the thesis do not form the basis for the award of any other degree to the candidate or to anybody else from this or any other University/Institution.

Prof. A.S. Rao

(Supervisor)

Professor and HoD

Department of Applied Physics

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Date:

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I thank one and all for helping me accomplish the successful realization of the thesis.

Thank you all!!!

Date:

(Anu)

Place: Delhi

ABSTRACT

The shift from traditional light sources like incandescent and fluorescent bulbs to solid-state lighting (SSL) is driven by the superior performance of phosphor-converted white light-emitting diodes (pc-w-LEDs), which offer extended lifetimes, high energy efficiency, fast response, and environmental benefits. pc-w-LEDs are widely used for indoor and outdoor applications, but conventional methods-such as blending red, green, and blue phosphors or using yellow phosphors on blue LEDs-face limitations, including poor color rendering index (CRI) and high correlated color temperature (CCT). These challenges can be addressed by developing single-phase phosphors doped with rare earth (RE) ions, enabling efficient white light emission via energy transfer processes, thus improving luminous efficiency, CCT, and CRI. Furthermore, phosphor materials are promising for non-contact thermometry applications due to their high selectivity, sensitivity, and precision in harsh environments. The present research focuses on synthesizing and characterizing novel, color-tunable Lithium Barium Tungstate ($\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$) phosphors doped with RE ions. These materials exhibit excellent optical properties, stability, and enhanced luminescence when doped with alkali and alkaline-earth metal ions, positioning them as advanced candidates for photonic devices and optical thermometry in next-generation SSL technologies. The present thesis spans nine chapters, encompassing morphology, structural, optical, and thermal characterizations to scale up for industrial applications.

Chapter 1 presents an introduction to the research problem, motivation, and a comprehensive review of recent literature. It highlights the technological history, advantages, and challenges associated with white light generation. Theoretical models such as Dexter theory, Dexter and Reisfeld's approximation, and the Inokuti-Hirayama (I-H) model are employed to analyze the observed spectra, ionic interactions, and energy transfer mechanisms between RE ions. The Photoluminescence (PL) emission spectra provide insights into CIE coordinates, color purity

(CP), and CCT. PL decay curves are analyzed to determine the lifetimes of activator/sensitizer ions, while temperature-dependent PL (TDPL) explores how luminescence behavior varies with temperature in optimized phosphor samples. Additionally, temperature sensing parameters such as fluorescence intensity ratio (FIR), relative sensitivity (S_r), and absolute sensitivity (S_a) are explained.

Chapter 2 focuses on the synthesis of Lithium Barium Tungstate ($\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$: LBW) phosphors doped with various RE^{3+} (Pr^{3+} , Sm^{3+} , Eu^{3+} , Dy^{3+}) ions at different concentrations using high temperature solid state reaction (SSR) method. The chapter details the experimental setup for analyzing the structural, morphological, and optical properties of the LBW phosphors. Key characterization methods include X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) spectroscopy, diffuse reflectance spectroscopy (DRS), and PL studies. The influence of temperature variation on the doped phosphors' luminescent properties, along with surface morphology observations via field effect scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDAX), are discussed.

Chapter 3 presents the structural and luminescence properties of Dy^{3+} -activated LBW phosphors, specifically for near-ultraviolet (n-UV) pumped w-LED and non-contact thermometry applications. Dy^{3+} -doped LBW phosphors were synthesized via high-temperature SSR, and their crystal structure and morphology were confirmed using XRD, Rietveld refinements, and FE-SEM with EDAX analysis. PL and XRD results validated the substitution of Ba^{2+} by Dy^{3+} , with prominent emission peaks at 493 and 583 nm corresponding to the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transitions under 368 nm excitation. The optical thermometric performance of Dy^{3+} -doped LBW phosphors was evaluated using thermal quenching in the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2, 13/2}$ transitions over a temperature range of 293-443 K. These phosphors exhibit high sensitivity, with a maximum S_r of 0.7% K^{-1} at 293 K, S_a of 4.68 K^{-1} at 443 K, and a temperature resolution of ~ 0.51 K at 443 K, demonstrating excellent potential for non-contact

thermometry. [The content of this chapter has been published in an international journal, *Sensors & Actuators: A. Physical*, 372 (2024) 115336] (I.F.= 4.1)

Chapter 4 presents the synthesis and analysis of Pr^{3+} -doped LBW phosphors, prepared using the conventional high-temperature SSR method. Structural and phase characterization was carried out via XRD, while FT-IR spectroscopy confirmed the presence of vibrational bands. The optical band gaps of both doped and undoped LBW samples were determined using DRS. Under 319 nm excitation, the Pr^{3+} -activated LBW phosphor exhibited strong blue (488 nm) and red (647 nm) emissions, corresponding to the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ and $^3\text{F}_2$ transitions. The CIE color coordinates indicated that the emissions lie in the white region, and TDPL measurements demonstrated good thermal stability. The optical sensing properties of $\text{LBW}:\text{Pr}^{3+}$ phosphors were assessed using FIR measurements, with a maximum S_r of 1.03% K^{-1} , showing promise for optical thermometry. The PL decay analysis at 647 nm exhibited a double exponential trend, with decreasing lifetime as Pr^{3+} concentration increased. Overall, Pr^{3+} -doped LBW phosphors show excellent potential for solid-state lighting and optical thermometry applications due to their emission characteristics, thermal stability, and optical sensing capabilities.

[The content of this chapter has been published in an international journal, *Optical Materials*, 145 (2023) 114476] (I.F.= 3.8)

Chapter 5 focuses on the synthesis of LBW phosphors doped with Sm^{3+} ions using a high temperature SSR. Comprehensive analyses of their structural, morphological, and photoluminescent properties were conducted. XRD confirmed the crystallinity and purity of the phosphors, with an average crystallite size of approximately 83 nm. SEM revealed irregular polyhedral shapes and mild clustering, with particle sizes in the micrometer range. FT-IR spectroscopy indicated diverse vibrational modes and molecular bonding within the host matrix. The optical bandgap (E_g) ranged from 3.74 to 3.63 eV, suggesting suitability for photonic applications. PL analysis showed three emission bands, with the strongest at 581 nm,

corresponding to the ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ transition upon 336 nm excitation. Concentration quenching was observed at a Sm^{3+} concentration of 2.0 mol%, elucidated by Dexter's dipole-dipole interaction theory. The optimized sample exhibited CIE coordinates of (0.586, 0.412), indicating a deep orange-red emission. PL decay analysis revealed a double exponential fit with decay lifetimes in the millisecond range, and thermal stability was confirmed through TDPL analysis showing high activation energy. These findings underscore the promising potential of Sm^{3+} -doped LBW phosphors for the development of advanced photonic devices, including w-LEDs. [The content of this chapter has been published in an international journal, *Journal of Fluorescence*, 34 (2024) 2391–2403] (I.F.= 2.7)

Chapter 6 presents the successful synthesis of Eu^{3+} -activated orange-red phosphors $\text{Li}_2\text{Ba}_{(5-x)}(\text{WO}_5)_3:\text{xEu}^{3+}$ ($1 \leq x \leq 9$, $\Delta x = 2$, mol%) via high-temperature SSR method. Phase identification and structural investigations were conducted through XRD and SEM, while the optical band gap was measured using DRS. PL emission spectra recorded under 322 nm and 396 nm excitation displayed strong orange-red emission at 595 nm, attributed to the ${}^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} ions, corroborated by the deep orange-red region in CIE chromaticity coordinates. PL decay profiles at $\lambda_{\text{em}} = 595$ nm and $\lambda_{\text{ex}} = 322$ nm exhibited a consistent exponential pattern, revealing decreased lifetimes with increasing Eu^{3+} concentration. To assess the thermal response, PL measurements were performed over a temperature range of 298–448 K, showing a maximum S_r of approximately $1.21\% \text{ K}^{-1}$ at 298 K, indicating enhanced sensitivity at lower temperatures. These findings suggest that the synthesized LBW: Eu^{3+} phosphors are promising candidates for non-contact optical thermometry and w-LED applications. [The content of this chapter has been published in an international journal, *Journal of Materials Science: Materials in Electronics*, 34 (2023) 2191] (I.F.= 2.8)

Chapter 7 delves into the characteristics of $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped LBW phosphors, focusing on their structural, compositional, luminescent, and temperature-dependent properties. XRD

analysis, combined with the Williamson-Hall (W-H) plot, confirmed that Dy^{3+} and Eu^{3+} ions primarily occupy Ba^{2+} lattice sites in the LBW matrix. The addition of these activator ions enabled tunable luminescence at specific excitation wavelengths, allowing color shifts from natural white to orange-red with varying Eu^{3+} concentrations, achieving warm white light emission suitable for indoor applications. Increased Eu^{3+} concentrations resulted in shorter decay times due to increase in non-radiative transitions, with a maximum energy transfer efficiency of 68.74% observed for D3E1.25 phosphors. Notably, the two emission peaks exhibited distinct temperature-dependent behaviors. A FIR model revealed a maximum sensitivity of $0.97\% \text{ K}^{-1}$ for the D3E0.75 sample at 303 K. Overall, the findings suggest that $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped LBW phosphors are promising candidates for UV-excitabile warm white LEDs with color tunability and applications in non-contact optical thermometry. [The content of this chapter has been published in an international journal, *Journal of Luminescence*, 269 (2024) 120444] (I.F.= 3.3)

Chapter 8 focuses on a series of LBW: RE^{3+} (RE = Dy, Sm) phosphors, synthesized using a high-temperature SSR method. XRD and SEM with EDAX confirmed that the crystal structure matched standard LBW, featuring small irregularly shaped particles. The DRS data was used to determine the band gaps. Fluorescence studies revealed that LBW doped with Dy^{3+} emitted blue light at 496 nm, while Sm^{3+} produced distinct emissions at 582 nm (green-yellow), 612 nm (yellow), and 669 nm (red) upon excitation with n-UV light (336 nm). Notably, energy transfer between Dy^{3+} and Sm^{3+} ions was observed, influencing the luminescence of the co-doped phosphors. Variations in activator doping concentrations altered the emission color from neutral white light to deep orange red. Additionally, decay curves indicated a decrease in luminescence lifetime with increasing Sm^{3+} concentration. The thermal degradation characteristics of the D3S5 phosphor, analyzed under 336 nm excitation, demonstrated excellent luminescence thermal stability with an activation energy of 0.16 eV. The low CCT

and favorable thermal stability suggest that the synthesized phosphors hold promise for use in warm white LED applications stimulated by UV chips. [The content of this chapter has been published in an international journal, *Journal of Physics D: Applied Physics*, 57 (2024) 315107] (I.F.= 3.1)

Chapter 9 summarized the overall research effort presented in this thesis work as well as the specific conclusions drawn from the findings. This chapter also considers how the existing research may be improved upon and used going ahead to direct new avenues of inquiry.

LIST OF PUBLICATIONS

➤ Publications in Refereed International Journals (Thesis): 06

1. **Anu**, A.S. Rao, Temperature sensing materials based on the fluorescence intensity ratio in $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Dy}^{3+}$ phosphors,
Sensors & Actuators: A. Physical 372 (2024) 115336, (I.F. = 4.1)
<https://doi.org/10.1016/j.jlumin.2024.120444>
2. **Anu**, A.S. Rao, Luminescence and optical thermometry strategy based on emission spectra of $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Pr}^{3+}$ phosphors,
Optical Materials 145 (2023) 114476,
<https://doi.org/10.1016/j.optmat.2023.114476> (I.F. = 3.8)
3. **Anu**, A.S. Rao, Synthesis, Structural and Fluorescence Investigations of Novel $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Sm}^{3+}$ Phosphors for Photonic Device Applications,
Journal of Fluorescence 34 (2024) 2391–2403,
<https://doi.org/10.1007/s10895-023-03449-z> (I.F. = 2.6)
4. **Anu**, A.S. Rao, Novel orange-red-emitting $\text{Li}_2\text{Ba}_5(\text{WO}_5)_3:\text{Eu}^{3+}$ phosphor for w-LEDs and non-contact thermometry applications,
Journal of Materials Science: Materials in Electronics 34 (2023) 2191,
<https://doi.org/10.1007/s10854-023-11602-4> (I.F. = 2.8)
5. **Anu**, Seema, A. Kumar, N. Deopa, M.K. Sahu, A. Prasad, A.S. Rao, A single phase $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphor for color tunable devices and non-contact optical thermometry,
Journal of Luminescence 269 (2024) 120444,
<https://doi.org/10.1016/j.jlumin.2024.120444>. (I.F. = 3.3)
6. **Anu**, S. Kumari, N. Deopa, A.S. Rao, Spectral studies of thermally stable $\text{Dy}^{3+}/\text{Sm}^{3+}$ co-doped $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$ phosphors for warm white LEDs,
Journal of Physics D: Applied Physics 57 (2024) 315107 (14pp)
<https://doi.org/10.1088/1361-6463/ad4566> (I.F. = 3.1)

➤ Publications in Refereed International Conferences (Thesis): 01

1. **Anu.**, N. Deopa, A.S. Rao, “Structural and luminescent properties of dysprosium ions doped tungstate phosphor for w-LEDs,” Proc. SPIE 12584, Smart Materials for Opto-Electronic Applications, 125840H (9 June 2023), doi:10.1117/12.2669275.

➤ **Publications in Refereed International Journals (Other than Thesis): 18**

1. **Anu**, N. Deopa, A.S. Rao, Structural and luminescence characteristics of thermally stable Dy³⁺ doped oxyfluoride strontium zinc borosilicate glasses for photonic device applications,
Optics & Laser Technology 154 (2022) 108328,
<https://doi.org/10.1016/j.optlastec.2022.108328> (I.F. = 4.6)
2. **Anu**, A. Kumar, Ravina, N. Deopa, A.S. Rao, Efficient tunable photoluminescence of Dy³⁺/Eu³⁺ co-doped OFSZBS glasses for warm white LEDs,
Journal of Non-Crystalline Solids 616 (2023) 122421,
<https://doi.org/10.1016/j.jnoncrysol.2023.122421> (I.F. = 3.2)
3. S. Kumari, **Anu**, A. Prasad, P. Rohilla, and A.S. Rao, Prospective applications of thermally stable Dy³⁺ doped potassium zinc strontium borate (KZSB) glasses in w-LEDs,
Journal of Materials Science: Materials in Electronics 34 (2023) 907,
<https://doi.org/10.1007/s10854-023-102726>. (I.F. = 2.8)
4. A. Kumar, **Anu**, M.K. Sahu, Ravita, S. Dahiya, N. Deopa, A. Malik, R. Punia, A.S. Rao, Spectral characteristics of Tb³⁺ doped ZnF₂-K₂O-Al₂O₃-B₂O₃ glasses for epoxy free tricolor w-LEDs and visible green laser applications,
Journal of Luminescence 244 (2022) 118676,
<https://doi.org/10.1016/j.jlumin.2021.118676> (I.F. = 3.3)
5. Manjeet, A. Kumar, **Anu**, R. Lohan, N. Deopa, A. Kumar, R.P. Chahal, S. Dahiya, R. Punia, A.S. Rao, Impact of Sm³⁺ ions on structural, thermal, optical and photoluminescence properties of ZnO-Na₂O-PbO-B₂O₃ glasses for optoelectronics device applications,
Optical Materials 139 (2023) 113778,
<https://doi.org/10.1016/j.optmat.2023.113778>. (I.F. = 3.8)
6. A. Kumar, Ravina, **Anu**, V. Kumar, N. Deopa, R. Punia, A.S. Rao, Epoxy free LED devices: Physical and optical examination of praseodymium doped borate glasses for enhanced performance,
Materials Letters: X 19 (2023) 100210,
<https://doi.org/10.1016/j.mlblux.2023.100210> (I.F. = 2.2)

7. V. Sharma, S. Maurya, **Anu**, A. Prasad, A.S. Rao, Structural, optical, and luminescence properties of Dy³⁺-activated potassium calcium silicate phosphor for white light-emitting diodes,
Luminescence (2023) 1–11, <https://doi.org/10.1002/bio.4544> (I.F. = 3.2)
8. Vidhi, Ankita, **Anu**, A.S. Rao, Spectroscopic characterizations of Dy³⁺ ions doped phosphate glasses for epoxy-free white LED applications,
Optical Materials 132 (2022) 112863,
<https://doi.org/10.1016/j.optmat.2022.112863> (I.F. = 3.8)
9. Manjeet, A. Kumar, **Anu**, Ravina, N. Deopa, A. Kumar, R.P. Chahal, S. Dahiya, R. Punia, A.S. Rao, Structural, thermal, optical and luminescence properties of Dy³⁺ ions doped Zinc Potassium Alumino Borate glasses for optoelectronics applications,
Journal of Non-Crystalline Solids 588 (2022) 121613,
<https://doi.org/10.1016/j.jnoncrysol.2022.121613>. (I.F. = 3.2)
10. A.V.S. Yeswanth, Ib Singh Deo, **Anu**, A.S. Rao, G.V. Prakash, Down-conversion and up-conversion photoluminescence studies of Er³⁺ doped calcium zinc borosilicate glass for optical fiber amplifiers,
Journal of Non-Crystalline Solids 609 (2023) 122280,
<https://doi.org/10.1016/j.jnoncrysol.2023.122280> (I.F. = 3.2)
11. Sanju, Ravina, **Anu**, A. Kumar, V. Kumar, M.K. Sahu, S. Dahiya, N. Deopa, R. Punia, A.S. Rao, Physical, structural and optical characterization of Dy³⁺ doped ZnF₂-WO₂-B₂O₃-TeO₂ glasses for opto-communication applications,
Optical Materials 114 (2021) 110937,
<https://doi.org/10.1016/j.optmat.2021.110937> (I.F. = 3.8)
12. Poonam, Shivani, **Anu**, A. Kumar, M.K. Sahu, P.R. Rani, N. Deopa, R. Punia, A.S. Rao, Judd-Ofelt Parameterization and Luminescence Characterization of Dy³⁺ Doped Oxyfluoride Lithium Zinc Borosilicate Glasses for Lasers and w-LEDs,
Journal of Non-Crystalline Solids 544 (2020) 120187,
<https://doi.org/10.1016/j.jnoncrysol.2020.120187> (I.F. = 3.2)
13. R. Lohan, A. Kumar, M.K. Sahu, **Anu**, V. Kumar, N. Deopa, and A. S. Rao, Structural, thermal, and luminescence kinetics of Sr₄Nb₂O₉ phosphor doped with Dy³⁺ ions for cool w-LED applications,
Journal of Materials Science: Materials in Electronics 34 (2023) 694,
<https://doi.org/10.1007/s10854-023-10055-z> (I.F. = 2.8)

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14. Ravina, K. Poria, Mukesh K. Sahu, A. Kumar, **Anu**, S. Dahiya, N. Deopa and A. S. Rao, Energy transfer mechanisms and color-tunable luminescence of $\text{Tm}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped $\text{Sr}_4\text{Nb}_2\text{O}_9$ phosphors for high-quality white light-emitting diodes, **RSC Advances**, 2023, 13, 33675, DOI: [10.1039/d3ra05519a](https://doi.org/10.1039/d3ra05519a). (I.F. = 3.9)
15. Ravita, A. Prasad, P. Rohilla, Rajat Bajaj, **Anu**, R. Punia, A.S. Rao, Luminescence Studies on Dy^{3+} Doped Calcium Aluminum Borosilicate (CABS) Glasses for White Light Emission and Applications in w-LEDs, **Journal of Fluorescence** 34 (2024) 1783–1792, <https://doi.org/10.1007/s10895-023-03389-8> (I.F. = 2.6)
16. A. Kumar, **Anu**, R. Lohan, U. Rani, I. Malik, N. Deopa, A.S. Rao, A. Kumar, Dysprosium Ion Concentration Variations and their Comprehensive Influence on the Physical, Structural and Optical Properties of Multi-Component Borate Glasses for Luminescence Tailoring, **Ceramics International**, <https://doi.org/10.1016/j.ceramint.2024.10.123> (I.F. = 5.1)
17. G. Yadav, J. Parashar, **Anu**, A. Prasad, A.S. Rao, Synthesis, Structural and photoluminescence characteristics of $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped CaGdSbWO_8 phosphor for warm white LEDs, **Emergent Materials** (Accepted) (I.F. = 4.8)
18. J. Parashar, G. Yadav, Seema, **Anu**, A. Prasad, A.S. Rao, Energy Transfer Studies on red emitting CaGdSbWO_8 : $\text{Sm}^{3+}/\text{Eu}^{3+}$ phosphor for w-LEDs and indoor plant growth lighting system, **Journal of Fluorescence** (Accepted) (I.F. = 2.6).

➤ International Conferences

Oral/Poster Presentations: Thesis work: 03

1. Poster presentation titled **“A comparative study of the photoluminescence properties of Dy³⁺, Sm³⁺ and Eu³⁺ ions doped tungstate phosphors”** in International Conference on Atomic, Molecular, Material, Nano and Optical Physics with Applications (ICAMNOP-2023) held at Delhi Technological University, Delhi, India during 20th -22nd December, 2023.
2. Oral presentation titled **“Photoluminescence studies of Samarium ions doped tungstate phosphors for wLEDs”** in 1st International Conference On Spectroscopy In Materials Science (ICOSIMS-2023) virtually during 20th-22nd June, 2023 organized by department of Physics, University of Aveiro, Portugal.
3. Poster presentation titled **“Structural and luminescent properties of dysprosium ions doped tungstate phosphor for w-LEDs”** in SPIE Optics and Optoelectronics Conference held from 24th-27th April, 2023 in Prague, Czech Republic.

Other than Thesis work: 02

1. Oral presentation titled **“Photoluminescence characterization of Dy³⁺ doped Borosilicate glasses for W-LEDs”** in 1st International Conference on Advances in Materials Science (ICAMS-2021) held during 22nd-24th September 2021, organized by Department of Physics, School of Applied Sciences, REVA University, Bangalore, INDIA.
2. Oral presentation titled **“Judd-Ofelt Parameterization and Luminescence Characterization of Dy³⁺ Doped Oxyfluoride Lithium Zinc Borosilicate Glasses for Lasers and w-LEDs”** in International Symposium on Materials Science and Innovation for Sustainable Society from 26th-27th August, 2020 organized by Nanomaterial Research Center, Meijo University, DCT's Dhempe College of Arts & Science and Government College of Arts, Science and Commerce, Khandola, under Cluster of Colleges for Research in Chemistry Goa.

Successful Participation: 18

1. Attended One Day National Seminar on “**RECENT ADVANCEMENTS IN SEMICONDUCTOR DEVICES AND MATERIALS (RASDM-2023)**” organized by Department of Applied Physics, Delhi Technological University (DTU) on 30th January, 2023.
2. Successfully completed the seven-day advanced instrumentation workshop “**Advanced Characterization Techniques In Condensed Matter**” (17th-23rd January, 2023) conducted by Birla Institute of Technology and Science, Pilani in association with Amity University under the auspices of Department of Science and Technology (DST) Government of India under STUTI.
3. Successfully completed the seven-day workshop “**Techniques for Advance Materials Characterization and Spectroscopy**” (10th-16th November, 2022) conducted by School of Physical Sciences, Jawaharlal Nehru University, New Delhi in association with Amity University under the auspices of Department of Science and Technology (DST) Government of India under STUTI.
4. Participated in “IP Awareness/Training program under National Intellectual Property Awareness Mission” on 26th July, 2022 organized by Intellectual Property Office, India.
5. Participated in e-workshop on “**Role of Traceable PMU in Smart Grids**” held at CSIR National Physical Laboratory, New Delhi on 29th March 2022.
6. Attending webinar on “**Luminescence Spectroscopy**” conducted on 4th February, 2022 organized by Department of Physics, Shri Ramdeobaba College of Engineering and Management (RCOEM), Nagpur, India.
7. Participated in the TENSYS2021 from 21st -22nd December 2021 International Workshop on “**Energy Technology and Sensor Systems TENSYS-2021**” organized by UNIVERSITI MALAYA and HITD&M.
8. Successfully participating in one day expert talk on the occasion of “**National Energy Conservation Day**” organized by Centre for Energy and Environment, in association with Institute Innovation Council, Delhi Technological University, Delhi, India -110042 on 14th December, 2021.
9. Participating in “**One-Day webinar on National Education Day**” organized by Human Resource Development Centre, Delhi Technological University in association with Institution Innovation Council- DTU and DTU-Innovation and Incubation Foundation held on 11th November 2021.

10. Attended the webinar “**Structured light in Material Science**” organized jointly by OSA and SPIE student chapter Manipal University and OSA student chapter MNIT Jaipur, Jaipur, India on 20th August, 2021 in Webinar Series-"Optics & Photonics: A leap for the future".
11. Participated in the online workshop “**Innovation, Ecosystem and Incubation**” conducted on 28th July, 2021 organized by THE NEW COLLEGE (AUTONOMOUS) Peters Road, Royapettah, Chennai -600014, India.
12. Participated in one day International Webinar on "**Recent Advances in Materials Science and Technology (RAMST)**" conducted jointly by Departments of Physics and Chemistry under IQAC on 12th July 2021, to pay Special tribute to Prof. J. Lakshmana Rao, Former Professor, Dept. of Physics, Sri Venkateswara University, Tirupati, A.P., India, on his 75th Birth anniversary.
13. Participated successfully in the one-day E-Workshop on "**Orientation Session for All Students & Faculties of Institute by Innovation Ambassador**" organized by the Department of Applied Physics, Delhi Technological University on 29th June, 2021.
14. Attended National Webinar cum Workshop "**LUMINESCENCE APPLICATIONS AND MATERIALS**" conducted on 25th June, 2021 organized by LUMINESCENCE SOCIETY OF INDIA Gujarat, INDIA in collaboration with SSN COLLEGE OF ENGINEERING Kalavakkam, Tamil Nadu, India.
15. Participated & completed successfully Online QIP Short Term Course on “**Advances in energy and functional materials**” from 14th-26th June 2021 at School of Minerals Metallurgical and Materials Engineering, Indian Institute of Technology Bhubaneswar.
16. Participated in Two Days National Seminar on “**Nanomaterials: Fundamentals & Applications**” (23rd -24th May, 2021) organized by Department of Physics through online mode.
17. Participated in the webinar on “**Characterization Techniques for Smart Materials**” on 15th-16th January, 2021 organized by Department of Physics, College of Basic Sciences and Humanities, CCS Haryana Agricultural University, Hisar, Haryana, India.
18. Participated in International Summit on “**Quality Indices in Higher Education - 2020**”, held during 6th-7th November, 2020 at Delhi. Technological University, Delhi.

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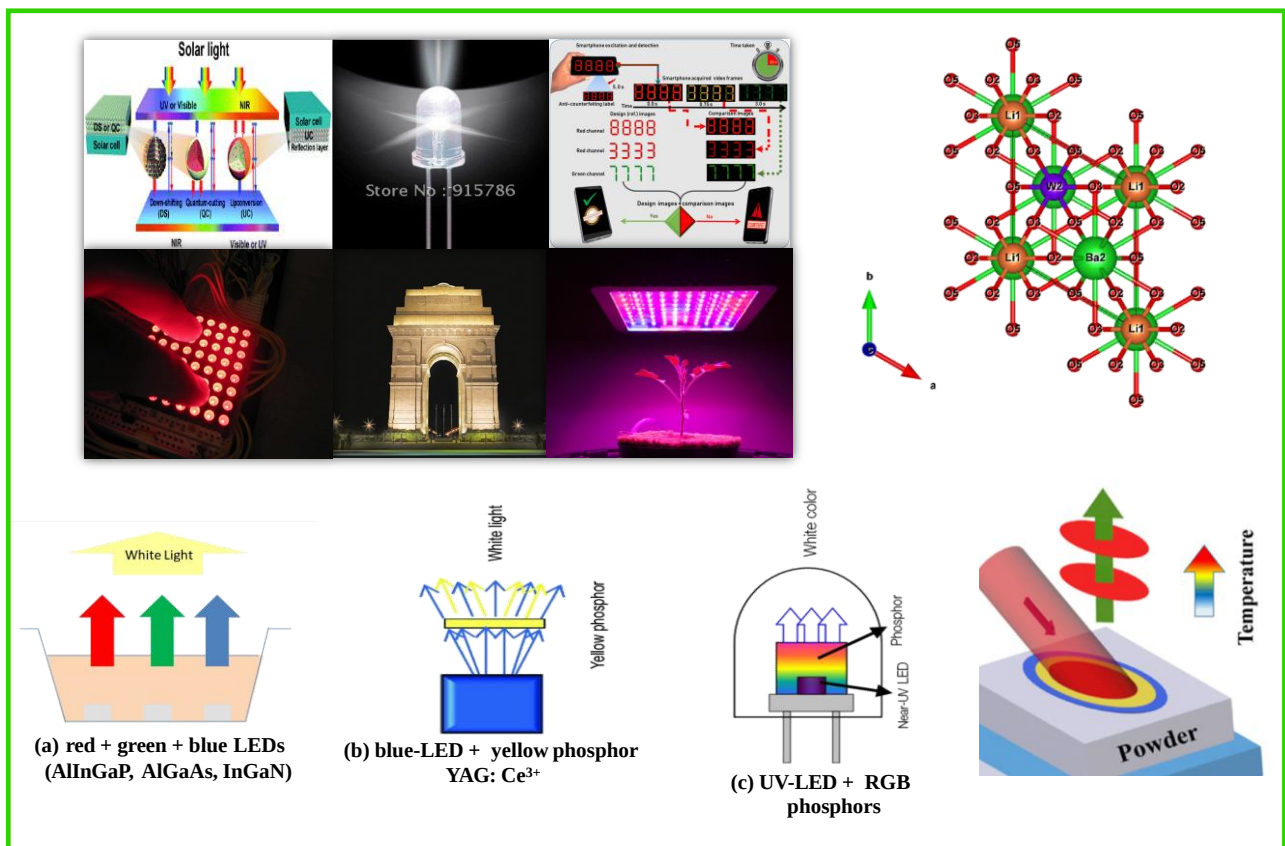
LIST OF ABBREVIATIONS

- CB- Conduction band
- CCT- Correlated color temperature
- CIE- Commission Internationale de l'Eclairage
- CP- Color purity
- CRC- Cross-relaxation channels
- CRI- Color rendering index
- DC- Down-conversion
- ED- Electric dipole
- EDAX- Energy dispersive x-ray
- ET- Energy transfer
- FE-SEM- Field emission scanning electron microscope
- FIR- Fluorescence intensity ratio
- FT-IR- Fourier transform infrared spectroscopy
- JCPDS- Joint Committee on Powder Diffraction Standard
- K-M- Kubelka-Munk
- LIR- Luminescence intensity ratio
- MD- Magnetic dipole
- NIR- Near-infrared
- n-UV- Near ultraviolet
- pc w-LEDs- Phosphor-converted white light emitting diodes
- PL- Photoluminescence
- PLE- Photoluminescence excitation
- RE- Rare-earth
- SSL- solid-state lighting
- SSR- Solid state reaction
- TCLs- Thermally coupled levels
- TDPL- Temperature Dependent Photoluminescence
- TGA- Thermogravimetric analysis
- TGPs- Thermographic phosphors
- TRPL- Time-Resolved Photoluminescence
- UC- Up-conversion
- VB- Valence band
- W-H- Williamson-Hall
- XRD- X-ray diffraction
- I-H- Inokuti-Hirayama
- S_r- Relative sensitivity
- S_a- Absolute sensitivity
- CFLS- Compact fluorescent lamps

CHAPTER 1

INTRODUCTION

In recent years, phosphor-based lighting technology has shown significant potential across a broad spectrum of applications, including w-LEDs, display technologies, horticultural illumination, and optical thermometry. This is attributed to its high luminous efficacy, enhanced chromatic performance, reduced energy consumption, and cost-effectiveness. This chapter delves into the fundamental aspects of luminescence mechanisms, phosphor materials, white light generation techniques, solid-state lighting (SSL) systems and optical thermometry. It provides a detailed discussion on the principles of photoluminescence, a comprehensive analysis of luminescent crystalline phosphors, and the critical role of activator ions in modulating their luminescence characteristics.



Rare earth (RE) elements, known for their unique optical properties and interactions, play a significant role in tuning the emission characteristics, which are governed by selection rules specific to RE ions, also discussed in detail. The theoretical frameworks used to explain energy transfer processes, including Dexter theory, Dexter and Reisfeld's approximation, and the Inokuti-Hirayama (I-H) model, provide insights into the mechanisms that drive luminescent behavior. Spectral tuning, including the analysis of CIE color coordinates, correlated color temperature (CCT), color rendering index (CRI), and Photoluminescence (PL) decay, is examined to assess how it influences the overall luminescence performance of these materials. Additionally, the research delves into non-contact optical thermometry, focusing on the fluorescence intensity ratio (FIR) method for temperature sensing. The role of thermometric parameters in improving the precision of temperature measurements is highlighted. This chapter also signifies the selection of the host lattice ($\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$). Finally, every step to accomplish the research work, such as selection of the activator and sensitizer and optimization of emission and thermal stability for direct utility in a variety of photonic devices such as w-LED and non-contact optical thermometers have been contained within this section.

1.1 LIGHT AND LUMINESCENCE

The energy that provides the sense of vision is called light. Naturally, there is a lot of light coming from the Sun that can be collected and converted in to electricity. However, none of the new technologies can depend on sunlight as a natural source of light, so artificial light must be generated. Two main phenomena which generate artificial light are luminescence and incandescence.

Incandescence involves heating a material to high temperatures, causing it to emit light due to the vibration of atoms. This process results in significant energy loss as heat [1]. Incandescent bulbs, while producing light, dissipate a considerable amount of energy as heat, making them less efficient. When tungsten filament wire in an incandescent lamp is heated by an electric current, it glows, or incandesces, to produce light.

The heat generated by the lamp causes gradual evaporation of tungsten as the filament operates. Over time, this evaporation depletes the filament's tungsten content, leading to failure either from excessive tungsten loss or breakage due to mechanical shock. Dimming incandescent lights is straightforward, and, when size and power ratings are compatible, lamps with identical bases are often interchangeable within the same fixture.

An incandescent lamp consists of several key components: a glass envelope that encases a tightly coiled tungsten filament, an exhaust tube that removes air from the bulb and fills it with inert gas, support wires to stabilize the filament, lead-in wires to conduct electric current to the filament, and a base that securely holds all components, mounts the lamp, and establishes electrical contact.

Incandescent lamps are classified as either conventional or halogen based on the type of gas and pressure within the bulb, which directly influences their efficiency, lifespan, and color output. They can operate at either low voltage or line voltage, depending on the current supplied. Incandescent lamps are further categorized as either non-reflectorized or reflectorized, depending on whether they emit light omnidirectionally or directionally. Reflectorized lamps are commonly of the halogen type, while non-reflectorized lamps are typically conventional. However, a major drawback of incandescent lights is their low efficiency, leading to higher operating costs and increased heat generation within enclosed spaces.

The term "luminescence" was first introduced in 1888. It refers to the emission of light without the need for heating the material. It occurs when a substance is exposed to certain forms of radiation like X-rays, ultraviolet (UV), or infrared radiation (IR), which excite the material's electrons, causing them to emit light.

As a result, incandescence is categorized as a hot process, while luminescence is considered as a cool process in comparison to incandescence [2]. Additionally, the lifespan of incandescent bulbs, typically around 1000 h, is considerably shorter in comparison to compact fluorescent lamps (CFLs), which last

between 8,000 and 10,000 h, and significantly shorter when compared to LEDs, which can achieve operational lifetimes of up to 50,000 h.

Examples of luminescence and incandescence are shown in Figure 1.1 and Figure 1.2, respectively.



Figure 1.1 Examples of Incandescence.

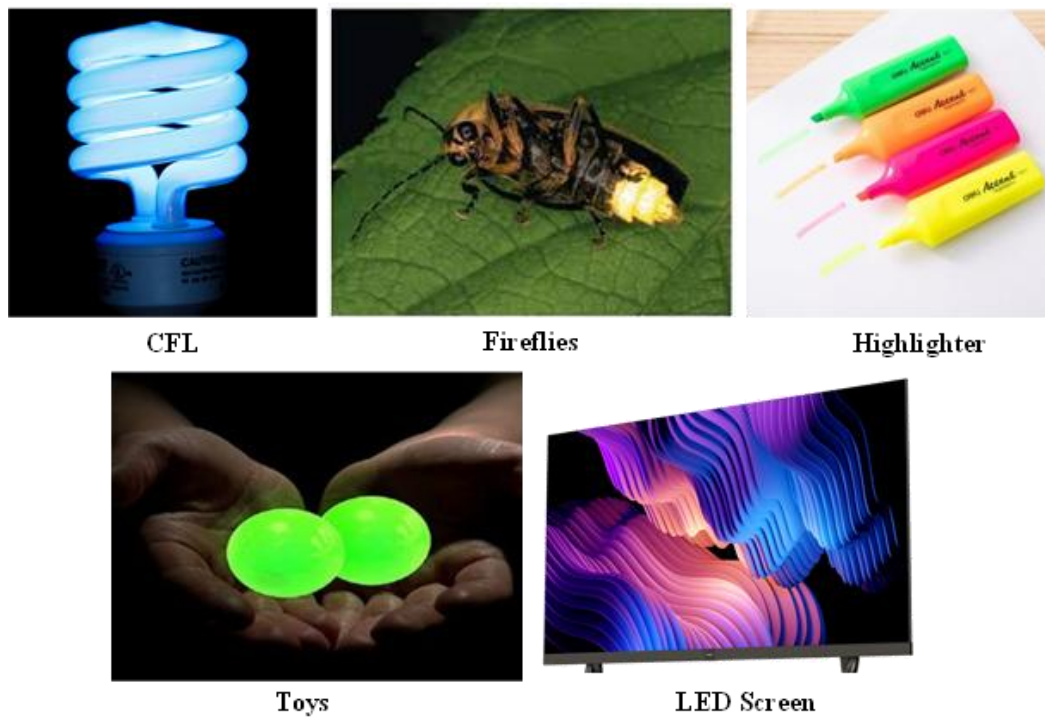


Figure 1.2 Examples of Luminescence.

The materials that experience luminescence offer greater efficiency due to its cold nature. Luminescence is an emission process that stimulates both inwardly and outwardly. The sources that are employed to excite the matter can be used to define the different luminescence processes, as listed in Table 1.1.

Table 1.1 The types of luminescence, their excitation source and applications.

Sr. No.	Luminescence Processes	Excitation source	Applications
1.	Photoluminescence	Photon	❖ Lighting sources ❖ Solar cells ❖ Display devices ❖ Lasers ❖ Sensors ❖ Highlighting paints ❖ Security ink
2.	Electroluminescence	Electric field	❖ LEDs ❖ Laser diodes ❖ EL displays ❖ EL sensors
3.	Thermoluminescence	Heat	❖ Environmental monitoring ❖ Geological dating ❖ Dosimetry of ionizing radiation
4.	Chemiluminescence	Chemical reaction	❖ Chemical analysis
5.	Cathodoluminescence	Electron beam	❖ Cathode ray oscilloscope ❖ TV screen ❖ Field emission display
6.	Bioluminescence	Bio-chemical reaction	❖ Analytical chemistry
7.	Radioluminescence	X-rays	❖ X-ray display ❖ X-ray scintillators

The current thesis/research work primarily centers on exploring and investigating the mechanisms of photoluminescence among the different classifications of luminescence mentioned earlier.

1.1.1 Photoluminescence (PL)

PL is the emission of light from a material after it absorbs photons, or electromagnetic radiation. When a material absorbs energy from light, its electrons are excited to higher energy levels. As these excited electrons return to their lower, stable energy states, they release energy in the form of light. Fluorescence and phosphorescence are two forms of PL. Both fluorescence and phosphorescence are based on the ability of a substance to absorb a light of a longer wavelength and, therefore, emit energy of a lower magnitude.

The main difference is the duration of doing so. In fluorescence, the emission is basically immediate and, therefore, generally only visible, if the light source is continuously on (such as UV lights); while a phosphorescent material can store the absorbed light energy for some time and release light later, resulting in an afterglow that persists after the light has been switched off. Depending on the material, this afterglow can last anywhere from a few seconds to hours. So, it is fluorescence if it disappears immediately and is phosphorescence if it longer. Luminescence of several types are distinguished, depending on the method of substance excitation:

1.1.1.1 *Spontaneous and stimulated emission:*

The spontaneous relaxation of excited electrons to their ground state leads to the emission of radiation. This radiative transition occurs independently for each excited electron, resulting in luminescence. Since each electron emits radiation without any phase relation to others, the emitted light is incoherent, meaning the waves are not in phase with each other, as shown in Figure 1.3. Sometimes the emission of luminescence can be stimulated by irradiation with photons of the same frequency as those of the emitted light; such stimulated transitions are used in lasers, which produce very intensive beams of coherent monochromatic light. Spontaneous luminescent emission follows an exponential law $L = L_0 \exp\left(-\frac{t}{\tau}\right)$ that expresses the rate of intensity decay and is similar to the equation for the decay of radioactivity and some chemical reactions.

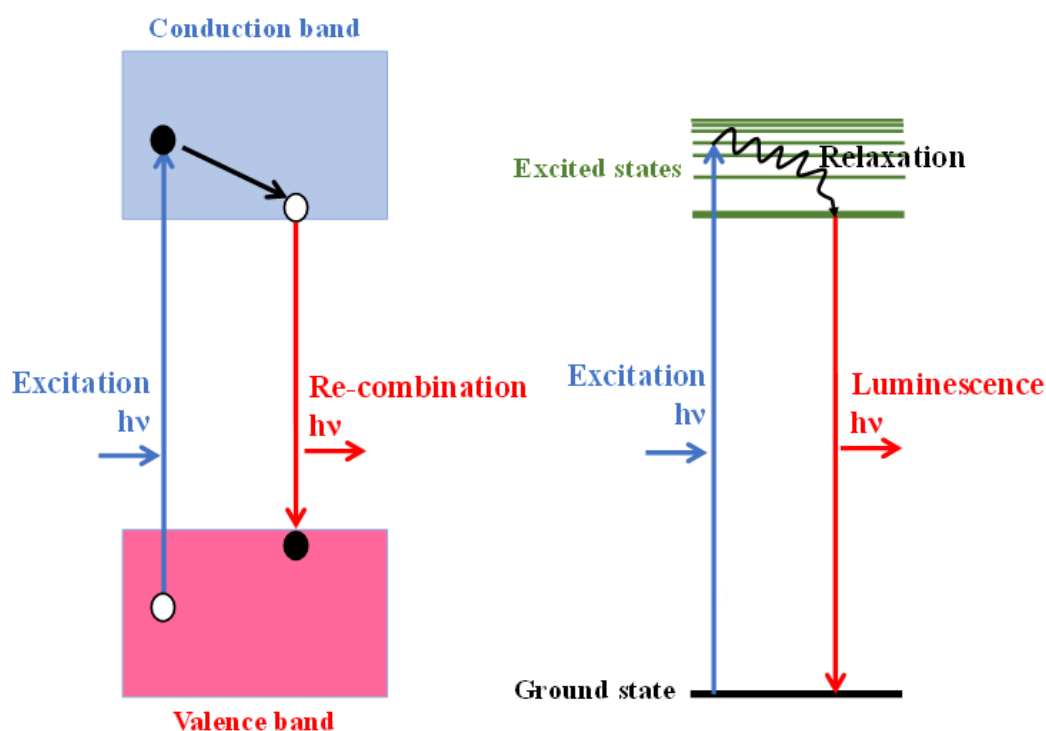


Figure 1.3 Spontaneous and stimulated emission.

1.1.1.2 Photo excitation

A fundamental requirement for PL, whether it manifests as fluorescence or phosphorescence, is the capacity of a molecule to absorb light radiation, leading to electronic excitation. When a molecule-bound electron absorbs a photon, it gains energy and becomes excited, transitioning from the ground state (S_0) to an excited state (S_n) within a timescale of approximately 10^{-15} seconds. This excitation may cause the electron to occupy various vibrational levels ($v = n$) within the excited state, contingent upon the specific wavelength of the absorbed photon. The resulting electronically excited states are inherently unstable, prompting the electrons to return to their ground state through a series of relaxation processes, which involve the dissipation of energy through various mechanisms, as shown in Figure 1.4.

Vibrational relaxation occurs on a very short timescale, ranging from 10^{-12} to 10^{-10} seconds, facilitating the rapid dissipation of energy within a single excited electronic state through vibrational modes. This

energy is subsequently transferred as heat to adjacent molecules. Since this process does not result in the emission of photons, vibrational relaxation is classified as a non-radiative transition.

Internal Conversion is a non-radiative transition that occurs iso-energetically and at a rapid timescale, typically ranging from 10^{-14} to 10^{-11} sec. This process involves the transition of an electron from one electronically excited state (S_{n+1}) to a vibrational level of a lower excited state (S_n) that possesses the same energy. An electron can entirely dissipate the energy absorbed initially through vibrational relaxation and internal conversion alone. Consequently, this relaxation pathway is fully non-radiative, resulting in the molecule not exhibiting fluorescence or phosphorescence, with all absorbed energy being released as heat. The relative probabilities of radiative events compared to fully non-radiative relaxation processes determine the quantum yield of a fluorophore, which subsequently influences its brightness.

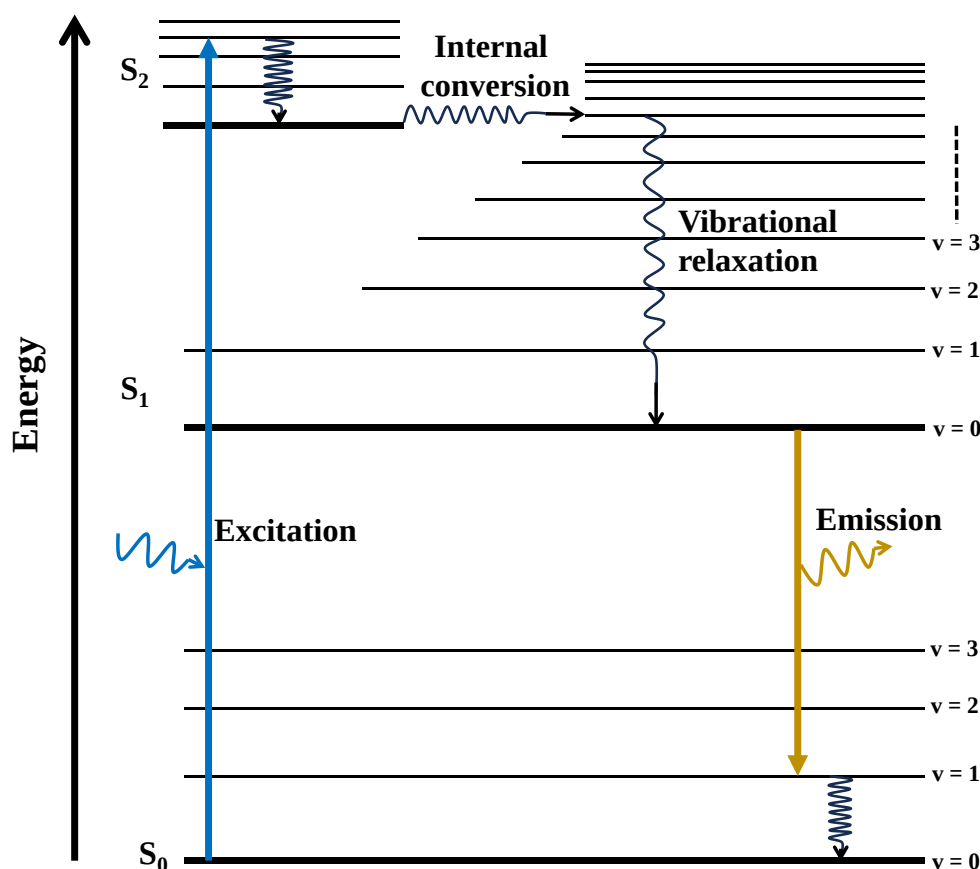


Figure 1.4 Simplified Jablonski Diagram for Fluorescence Photoluminescence.

An electron is excited upon the absorption of a photon with a specific wavelength. It subsequently relaxes to the vibrationally ground state of the lowest excited singlet state (S_1) through a series of non-radiative processes, including vibrational relaxation and internal conversion. Further relaxation to the ground state (S_0) occurs via fluorescence, leading to the emission of a photon with lower energy and a longer wavelength than the initially absorbed photon.

1.1.1.3 Fluorescence

One radiative mechanism by which excited electrons can relax is through a light-emitting transition from the lowest excited state (S_1) to the ground state (S_0) in a rapid process known as fluorescence, which occurs over a timescale of 10^{-9} to 10^{-6} seconds. The energy difference between these states is released in the form of a photon. Because the electron loses some of the initial excitation energy through vibrational relaxation, the emitted photon will have lower energy and, consequently, a longer wavelength. Similar to the excitation process, emission can have transition to various vibrational levels ($v = n$) of the ground state (S_0), resulting in a range of possible wavelengths for the emitted photon. If required, electrons can have transition from higher vibrational levels ($v = n$) to the vibrationless state ($v = 0$) through non-radiative vibrational relaxation. The emitted wavelength is generally independent of the excitation wavelength, as excited molecules typically relax to the lowest vibrational level of the lowest excited state via non-radiative processes prior to fluorescence emission. Depending on the specific molecule, non-radiative decay may account for varying proportions of the excitation energy, leading to molecule-specific shifts between excitation and emission wavelengths, a phenomenon known as the Stokes shift. Together, the potential wavelengths of photons absorbed during excitation and the emitted wavelengths-which can vary due to fluorescent decay to different vibrational levels-constitute a molecule's excitation and emission spectra. Given that the same electronic transitions are involved in both the excitation and emission processes of a fluorescent molecule, the excitation and emission spectra often exhibit a reflective similarity, a concept referred to as the mirror image rule of fluorescence. The probabilities associated with

excitation and emission events at different wavelengths ultimately define a molecule's fluorescence spectra.

1.1.1.4 Phosphorescence

The electron's spin property is crucial for understanding the distinction between fluorescence and phosphorescence. Spin is an intrinsic and invariant characteristic of an electron, representing a form of angular momentum that influences its behaviour in an electromagnetic field. An electron can possess a spin value of $\frac{1}{2}$, with possible orientations of either up or down. Consequently, the spin of an electron is denoted as $+\frac{1}{2}$ or $-\frac{1}{2}$, or equivalently as $\uparrow$ or $\downarrow$. In a single orbital, two electrons will always exhibit antiparallel spins in a singlet ground state (S_0). When one electron is promoted to an excited state, it retains its spin orientation, leading to the formation of a singlet excited state (S_1), where both spin orientations remain paired in an antiparallel configuration. All relaxation processes occurring in fluorescence are spin-neutral, ensuring that the electron's spin orientation is preserved throughout the process.

In contrast, phosphorescence involves a distinct mechanism. Rapid intersystem crossing (on the order of 10^{-11} to 10^{-6} seconds) occurs from the singlet excited state S_1 to a more energetically favourable triplet excited state T_1 , resulting in a change in electron spin orientation. Triplet excited states are defined by the parallel alignment of electron spins and exhibit metastability. Phosphorescence involves relaxation processes that lead to another electron spin inversion, culminating in photon emission. The transition back to the relaxed singlet ground state S_0 can take place after a significant delay, ranging from 10^{-3} seconds to over 100 seconds. Furthermore, during phosphorescent relaxation, a greater proportion of energy is lost through non-radiative processes compared to fluorescence. Consequently, this results in a larger energy difference between the absorbed and emitted photons, leading to a more pronounced wavelength shift. Thus, phosphorescence is characterized by a greater Stokes shift compared to fluorescence, shown in Figure 1.5. The spin of the involved electron is flipped during inter-system crossing into excited triplet state (T_1). Triplet states are metastable and relaxation by phosphorescence is delayed. The chance of

alternative relaxation by non-radiative events defines the quantum yield for both fluorescence and phosphorescence.

1.1.2 Efficiency of luminescence

The efficiency of luminescence emission should be assessed in terms of energy and quantum mechanics. When each incident photon results in the emission of a photon with identical energy (as occurs in resonance excitation, where fluorescence is induced by monochromatic light of the same wavelength as the emitted fluorescence, or in the radiation of isolated atoms in dilute gases), the luminescence efficiency reaches 100% concerning both the input energy and the number of emitted quanta. Quantum efficiency reaches 100% when the number of emitted secondary photons matches to that of the incident primary photons. However, the energy of the secondary photons is lower due to loss of some energy in the form of heat, resulting in luminescence efficiency below 100%.

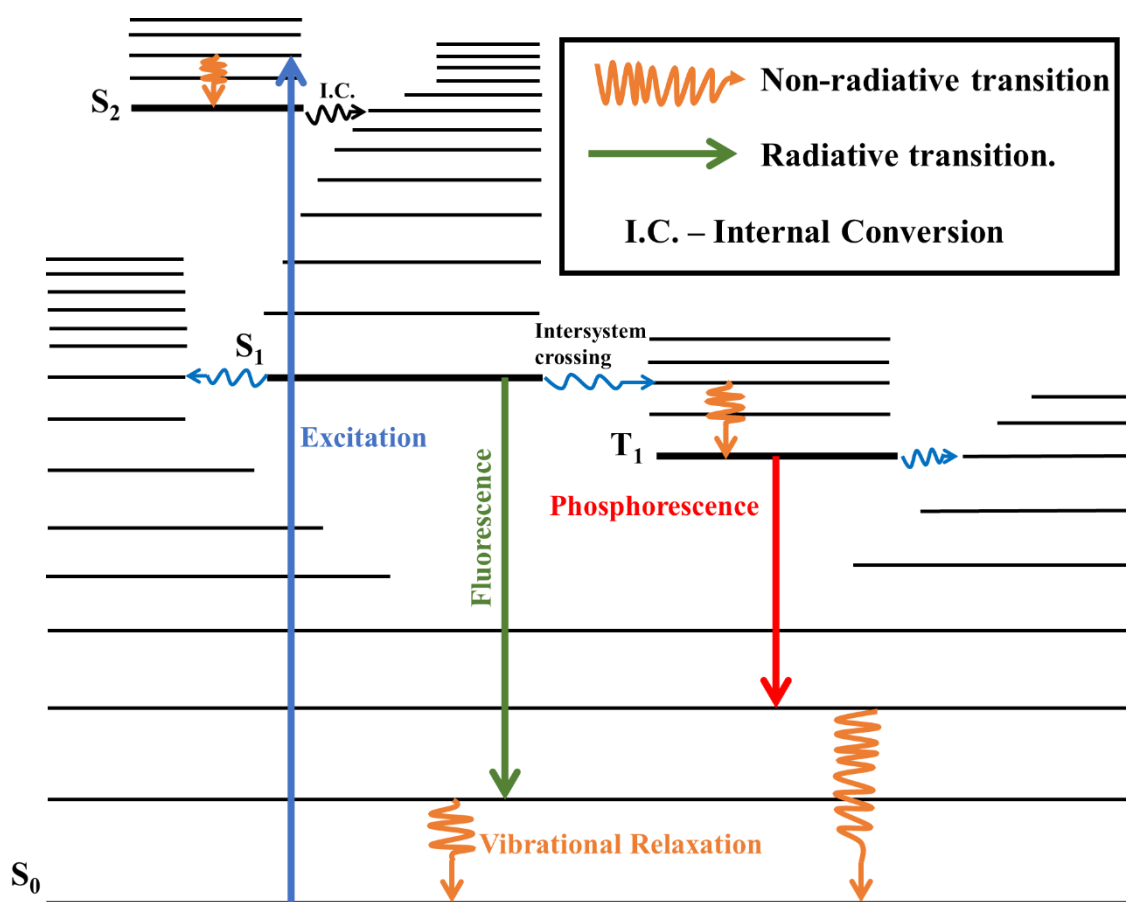


Figure 1.5 Jablonski-Diagram showing the Mechanisms of Fluorescence versus Phosphorescence.

The quantum efficiency of many luminescent materials is significantly less than 100%; for instance, zinc sulfide phosphors exhibit an efficiency of approximately 20%, while solid-state electroluminescence demonstrates an efficiency of less than 10%.

1.2 PHOSPHOR

Phosphors exhibit luminescence characteristics and are termed as luminescent materials. It is a special kind of material which emit light preferably in UV, visible or infrared region, when excited by any kind of external energy source or radiation (invisible UV, β , X-rays). Phosphors consist of a high bandgap inorganic host matrix in which some impurity ions are intentionally added called dopants (activator, sensitizer) [3].

1.2.1 Host matrix

Generally, a compound with high optical bandgap act as a host matrix for any crystalline phosphor. The inorganic host matrix holds the activator ions strongly. Sometimes host matrix may efficiently absorb the high energy ($h\nu_1$) photons and emits radiation in the visible regions with lesser energy ($h\nu_2 < h\nu_1$) as represented in Figure 1.6 (a) known as self-luminescent materials. A portion of the absorbed energy is released as phonons as a result of atomic collisions or molecular vibrations as illustrated in Figure 1.6 (b).

1.2.2 Activator

Generally, inorganic phosphor host materials are doped with small quantity of impurities or additives or quencher called as activator/dopant ions. When an ion from an activator element leaps to the excited state after absorbing excitation energy, it releases the energy as radiation while transitioning back to the ground state. As displayed in Figure 1.6 (c), the high energy ($h\nu_1$) radiation is absorbed by host lattice, subsequently transfer the energy to the activator ions and emission takes place from the activator ions. Activator ions exhibit a variety of responses within different host lattices based on their electrical configuration, structure, and solubility in the phosphor host lattices.

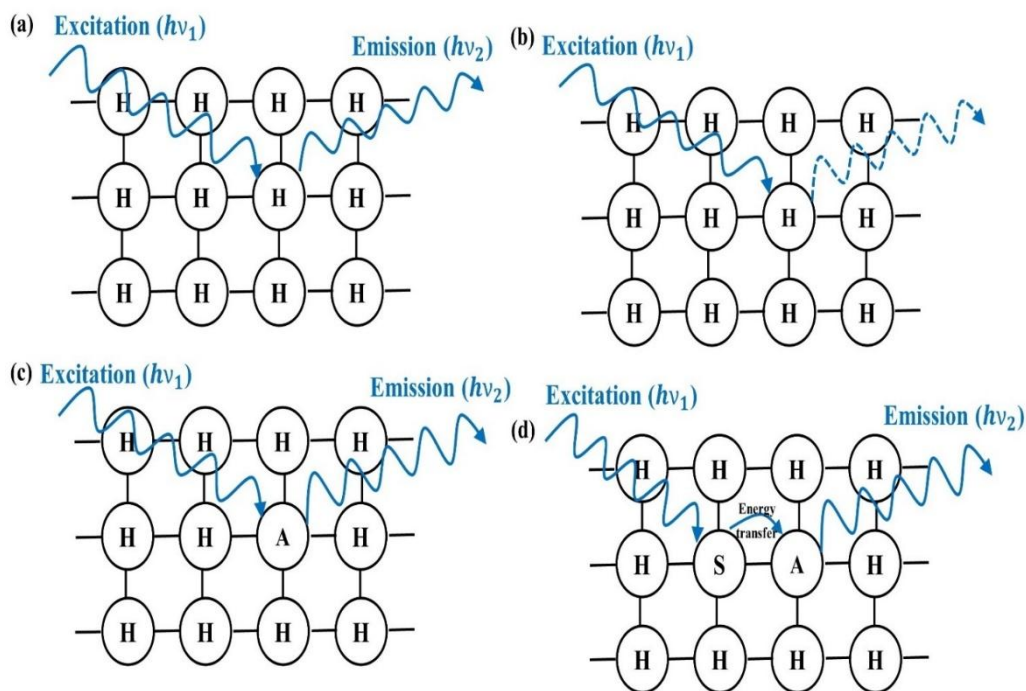


Figure 1.6 Luminescence processes involving (a), (b) host, (c) activator and (d) activator and sensitizer.

1.2.3 Sensitizers

In some cases, there is a very weak absorption by activator ions, then another kind of impurities could be added, termed as sensitizer ions. It enhances the absorption capacity and then transfers the received energy to the activator ions. Figure 1.6 (d) signifies the mechanism of luminescence involving the absorption of energy by sensitizer and transfer the part of absorbed energy to the activator ions. In general, there is a critical activator ion concentration beyond which emission intensity goes down due to concentration quenching, which is caused by cross-relaxation or energy transfer between the nearest ions [4]. Apart from the optimum activator ions concentration, there are so many various factors, such as the synthesis technique, host material, sensitizer ions, and environmental conditions, which affect the luminescence characteristics of the phosphors.

1.3 RARE EARTH ELEMENTS AND THEIR OPTICAL PROPERTIES

At the bottom of the periodic table i.e., f-block elements from ^{57}La (Lanthanum) to ^{71}Lu (Lutetium) and two other d-block elements ^{21}Sc (Scandium) and ^{39}Y (Yttrium) are considered as ‘Rare Earth (RE)’

elements. They are called rare earth as they are found in very traces in earth crust and could be obtained in purified form very recently. Thus, there are total seventeen metallic elements, in which 15 elements belong to f-block sometimes also referred to as ‘lanthanides’ and two other elements belonging to the d-block of the periodic table. Consideration of Sc and Y with RE group is totally based on their similar chemical and physical properties as possessed by other rare earths. Table 1.2 represents the symbols and electronic configurations and ground state of lanthanides alongwith their applications.

Further, the RE elements are subdivided into two distinct groups i.e., Heavy rare earths (HREs) elements and light rare earths (LREs) elements. The elements from La to Eu ($Z=57$ to 63) are LREs whereas from Gd to Lu ($Z=64$ to 71) are HREs. The lighter elements Sc and Y possess properties like HREs and therefore they are grouped in HREs.

Generally, RE elements are found in earth’s crusts and due to several identical properties, they exist together. Due to their identical properties, it is very difficult to separate them in their pure metal form. Thus, before 1945, it was difficult to get the pure form of RE metals but with the recent developments in some new chemical separation techniques, like fractional crystallization/precipitation, ion exchange and extraction of solvent etc., has been possible to separate them to a good extent [5]. Monazite, Bastnasite and Xenotime are the primary sources of collecting RE elements [6–8]. The chronological order of discovery of different rare earths and their discoverer is given in Figure 1.7.

The partially filled 4f orbitals in the RE ions result large number of energy states, with high multiplicity. This makes them special since they give photon emissions from UV, visible to n-IR and IR regions. The general electronic configuration of RE elements is $[\text{RE}]=[\text{Xe}]4f^n5d^{0,1}6s^2$; where $n = 0$ to 14 and $[\text{Xe}]$ represents the Xenon element with 54 atomic number. The RE elements do not exhibit optical emission when they are in neutral metals form. Once they are doped in a host matrix they give unique emissions from UV, Visible to near-infrared regions.

Table 1.2 Symbol and electronic configurations and ground state of lanthanides and some of their applications.

Symbol	Electronic Configuration (Ln)	Electronic Configuration (RE ³⁺)	Ground state of RE ³⁺	Some of the applications of the lanthanides
La (Z = 57)	[Xe]5d ¹ 6s ²	[Xe]	¹ S ₀	Aerospace parts, Armor alloys, modern televisions
Ce (Z = 58)	[Xe]4f ¹ 5d ¹ 6s ²	[Xe]4f ¹	² F _{5/2}	Alloys, Lasers, Glasses, polishing, petrol refining
Pr (Z = 59)	[Xe]4f ³ 6s ²	[Xe]4f ²	³ H ₄	Aircrafts engines, alloys for permanent magnets
Nd (Z = 60)	[Xe]4f ⁴ 6s ²	[Xe]4f ³	⁴ I _{9/2}	Lasers, metals, glass pigments, electronic devices
Pm (Z = 61)	[Xe]4f ⁵ 6s ²	[Xe]4f ⁴	⁵ I ₄	Atomic batteries, pacemakers guided missiles, radios, phosphors
Sm (Z = 62)	[Xe]4f ⁶ 6s ²	[Xe]4f ⁵	⁶ H _{5/2}	Infrared absorbing glasses, ceramics, lighting, lasers
Eu (Z = 63)	[Xe]4f ⁷ 6s ²	[Xe]4f ⁶	⁷ F ₀	Lasers, lighting, superconducting alloys, TV screens, fluorescent lamps
Gd (Z = 64)	[Xe]4f ⁷ 5d ¹ 6s ²	[Xe]4f ⁷	⁸ S _{7/2}	MRI, magnets, computer memory, nuclear reactors, X-ray intensifying screens
Tb (Z = 65)	[Xe]4f ⁹ 6s ²	[Xe]4f ⁸	⁷ F ₆	Solid state devices, lasers
Dy (Z = 66)	[Xe]4f ¹⁰ 6s ²	[Xe]4f ⁹	⁶ H _{15/2}	Nuclear reactors, data storage applications, hard discs
Ho (Z = 67)	[Xe]4f ¹¹ 6s ²	[Xe]4f ¹⁰	⁵ I ₈	Alloys, magnets, lasers, glass, electronic catalysts, phosphors
Er (Z = 68)	[Xe]4f ¹² 6s ²	[Xe]4f ¹¹	⁴ I _{15/2}	Lasers, fibre optics, synthetic gems, coloured glasses

Tm (Z = 69)	[Xe]4f ¹³ 6s ²	[Xe]4f ¹²	³ H ₆	X-ray devices, nuclear reactions, lasers, superconductor
Yb (Z = 70)	[Xe]4f ¹⁴ 6s ²	[Xe]4f ¹³	² F _{7/2}	Memory devices, lasers, catalysts, infrared emitting phosphors
Lu (Z = 71)	[Xe]4f ¹⁴ 5d ¹ 6s ²	[Xe]4f ¹⁴	¹ S ₀	Scintillators, PET scan detectors, magnetic bubble, memory

Sc = [Ar]3d¹4s²; Sc³⁺ = [Ar] and Y = [Kr]4d¹5s²; Y³⁺ = [Kr].

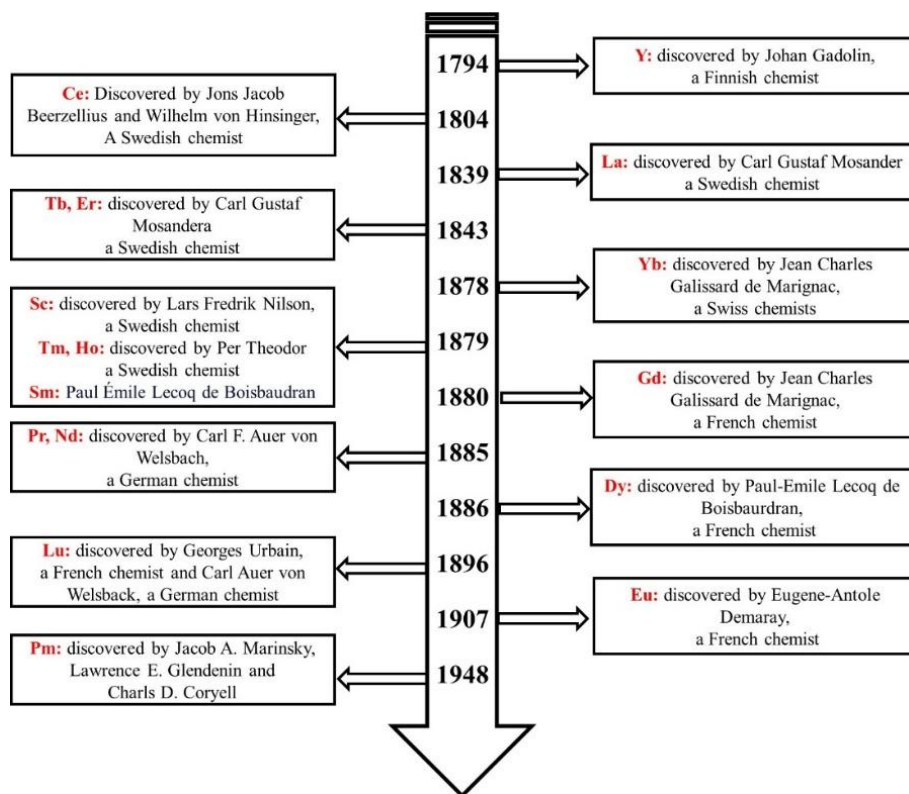


Figure 1.7 Sequential order and the chronological discovery of rare earth and their discoverer.

Among these 15 lanthanide elements, 13 elements (ions) give optical emissions. These RE ions in triply ionized state (for example. Eu³⁺, Nd³⁺, Sm³⁺, Pr³⁺, Tb³⁺, Gd³⁺, Dy³⁺, Er³⁺, Tm³⁺, Ho³⁺ and Yb³⁺) in different host matrices emit different colors covering the whole visible region. For example, Tm³⁺ emit intense (blue), Ho³⁺ (green, red), Er³⁺ (green, red), Eu³⁺ (red), Sm³⁺ (orange-red), Tb³⁺ (green), Dy³⁺ (yellow, blue), etc. Alongwith visible emission, most of the RE ions also emit intense near-infrared radiation sometimes leading to lasing.

Similarly, some of them also produce intense UV radiation (for example Gd^{3+} , Tm^{3+}). La^{3+} , Lu^{3+} , Y^{3+} and Sc^{3+} do not have upper 4f energy levels since they have either empty or filled valence orbitals. Therefore, the optical emission in visible to n-IR is not observed in these ions. They are typically taken in the choice of host materials for RE ions [9–12]. However, the 2+ and 4+ oxidation states in these viz. Eu^{2+} , Tm^{2+} , Sm^{2+} , Tb^{4+} , Ce^{4+} etc. are also found in some hosts. Most often the RE ions form 3+ oxidation state in different hosts and show the corresponding absorption and emission properties due to their 4f-4f transitions. The RE elements sharp emissions and absorptions in solid materials were discussed to some extent by JH Van Vleck in his article “*Puzzle of rare earth spectra in solid*” in 1937 which draw attention towards the RE luminescence [13]. Dieke has investigated deeply the energy levels of RE ions in trichloride host matrix [14]. Since the 4f orbital’s electrons in RE ions are shielded by external $5s^2$, $5p^6$ filled subshells and therefore a less electron-phonon coupling takes place in them. As a result of this RE^{3+} produce sharp and narrow emissions arising from f-f transitions.

1.3.1 Types of interactions in RE ions

RE ions exhibit three primary types of optical transitions: (i) characteristic transitions occurring between different 4f electronic levels, (ii) $4f^{n-1}5d^1$ transitions and (iii) charge transfer transitions. These transitions are further discussed in detail below:

(a) Intra-configurational f-f transitions: RE ion-doped materials exhibit characteristic narrow emission lines, which arise from electronic transitions between the $^{2S+1}L_J$ levels of the 4f subshell in free ions. These transitions are spin-forbidden. In the case of f-f transitions, both the excitation and emission energies remain largely unaffected by the host material in which the activator ions are embedded, due to the effective shielding provided by the 5s and 5p orbitals. As a result of this shielding, the spectra display up to 15 narrow linewidths. The interaction between the RE ions and the host matrix, upon exposure to light, gives rise to various types of electronic transitions given below:

(i) *Magnetic dipole (MD) transitions*: When the magnetic field component of incident light interacts with an RE ion via a magnetic dipole, a weakly intense transition, known as an MD transition, is observed. This occurs when charge displacement follows a rotational motion, with the direction of rotation remaining unchanged under inversion through a point. MD transitions exhibit even transformation under inversion, indicating that they have even parity, allowing transitions between states of the same parity. Consequently, MD transitions are governed by Laporte's selection rule ($|\Delta l| = \pm 1$, $|\Delta s| = 0$, $|\Delta L| \leq 0$, $|\Delta J| = 0$), where transitions involving $J = 0 \leftrightarrow 0$ are forbidden [15,16].

(ii) *Forced electric dipole (ED) transitions*: An electric dipole (ED) transition occurs when a RE ion interacts with the electric field component of incident electromagnetic radiation, causing linear charge displacement. This forced ED transition exhibits odd transformation properties under inversion, resulting in odd parity. Such transitions are typically forbidden in RE ion-doped materials because the initial and final states of $4f^n$ transitions possess the same parity, adhering to Laporte's selection rule ($|\Delta l| = \pm 1$, $|\Delta s| = 0$, $|\Delta L| \leq 6$, $|\Delta J| \leq 6$). However, non-centrosymmetric interactions between electronic states enable mixing of states with opposite parity, thus allowing the occurrence of induced ED transitions. Certain induced ED transitions, termed hypersensitive transitions, exhibit sensitivity to the local environment around RE ions and follow specific selection rules ($|\Delta S| = 0$, $|\Delta L| \leq 6$, $|\Delta J| \leq 6$). These transitions are sometimes referred to as pseudo-quadrupole transitions because they obey the same selection rules as quadrupole transitions [17].

(iii) *Electric quadrupole (EQ) transitions*: The electric quadrupole transition arises due to the displacement of quadrupole charges. It consists of four-point charges or two dipoles arranged such that the overall dipole moment is zero. It exhibits even parity. Compared to MD and induced ED transitions, EQ transitions are relatively weak [18].

(b) Inter-configurational ($4f^n5d^0-4f^{n-1}5d^1$) transitions:

The transition of 4f electrons to the 5d subshell is parity-allowed, and the intensity of such transitions is significantly influenced by the ligand field effect surrounding RE ions, resulting in high transition intensities [19]. The electronic transitions between the $4f^{n-1}5d^1$ and $4f^n5d^0$ states produce a broad spectrum of excitation and emission wavelengths, in contrast to the narrow peaks observed from transitions between 4f-4f levels. The wide range of f-d transitions can be explained by two key phenomena: the Franck-Condon principle and the lifting of degeneracy in the 4f ground state. The degeneracy of the 4f state is further lifted due to spin-orbit coupling, resulting in multiple energy levels. Additionally, the activator ion within a host crystal may experience centroid shift and/or crystal field splitting (CFS). CFS refers to the separation of the 5d energy levels of an activator ion, which occurs due to the local environment created by the host matrix in which the ion is incorporated. The extent of the CF effect is influenced by several factors, including the bond lengths between the activator ion and the surrounding ligands, the degree of overlap between molecular orbitals, the nature of the bonding (whether ionic or covalent), the characteristics of the surrounding environment, and the site symmetry of the activator ion. Notably, CFS exhibits an inverse relationship with variations in bond length or the volume of the surrounding polyhedron [20].

(c) Charge Transfer Transitions: The excitation and emission spectra can be significantly affected by charge transfer transitions occurring within the host lattice or the dopant. These transitions are typically characterized by high intensity and can overshadow the f-f transitions associated with the activator ions. Such charge transfer transitions can take place in host materials, such as vanadates or tungstates, as well as within the activator itself, for example by the charge transfer process from O^{2-} to RE^{3+} .

1.3.2 Exploring the selection rules pertaining to RE ions

An electron will not be able to jump from one energy level to any of the other existing energy levels. Any transition of a particular electron between two existing energy levels is probable in the case of fulfilment

of certain rules, which are called as selection rules. The Azimuthal quantum number (l) of 4f orbital is 3, resulting in 7 ($= 2l + 1$) orbitals, which would be able to accommodate two electrons each.

As far as ground states are concerned, the electrons are distributed in a bid to provide a maximum combined spin angular momentum (S). Combining the spin angular momentum (S) with orbital angular momentum (L), the total angular momentum (J) is arrived at $J = L - S$ (when 4f electrons < 7), $J = L + S$ (when 4f electrons is > 7).

Regarding electronic state, it is suggested $^{2S+1}L_J$, where L represents S, P, D, F, G, H, I, J, K, L, M ... which corresponds to 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10... respectively. The number $2S+1$ denotes the spin multiplicity. Several ways have been studied for interpreting the observed transitions of lanthanide ions. Such mechanisms include ED transitions, MD transitions, EQ transitions and hypersensitive transitions. An ED transition is the effect of the fundamental interaction of the lanthanide ion with the electric field vector through an ED. The formation of an ED makes a linear movement of charge. This type of transition has odd parity. However, the ED $f \rightarrow f$ transitions in free 4f ions are forbidden by the Laporte selection rule. Non-centro symmetrical interactions allow the blending of electronic states of opposite parity giving rise to weaker transitions and are called as induced ED transitions. The selection rules for the induced ED transitions are $\Delta L = \pm 1, \Delta S = 0, |\Delta L| \leq 6, |\Delta J| \leq 6, |\Delta J| = 2, 4, 6$ if $J = 0$ or $J' = 0$, where τ is equal to additional quantum number of discriminate between levels with similar S and L quantum number.

An MD transition is induced by interaction of the spectroscopic active ion with the magnetic field element of the light through a MD. The MD transition can also be regarded as a rotational displacement of charge. The rotation is not reversed under inversion through a point or inversion centre. The MD transition has even parity and allows transitions among states of equal parity. The intensity of the MD transitions is weaker (of the order of 10^{-8}) than induced ED transitions. The selection rules for the magnetic dipole transitions are $\Delta \tau = \Delta S = \Delta J = 0, \pm 1$ but $\Delta J = 0 \leftrightarrow 0$ is forbidden. The magnetic dipole transitions are not much affected by the site symmetry as they are parity allowed.

An EQ transition originates from a displacement of charges that display a quadrupole character. It pertains to four-point charges with overall zero charge and zero dipole moment. It also has even parity. These transitions are much weaker than induced ED and MD transitions. Seldom experimental evidence has existed for the occurrence of the quadrupole transitions in RE³⁺ spectra.

However, hypersensitive transitions are regarded as pseudo quadrupole transitions, because these transitions confirm the selection rules of quadrupole transitions, ($|\Delta S| = 0, |\Delta L| \leq 2$ and $|\Delta J| \leq 2$).

1.3.3 Unique properties of RE ions

RE ions exhibit the following exceptional characteristics which differentiate them from other optically active ions:

- RE ions demonstrate luminescence across various spectral regions, including the visible and near-infrared (NIR) portions of the electromagnetic spectrum.
- They possess narrow spectral lines and exhibit long emission lifetimes.
- RE ions show a significant Stokes shift upon ligand excitation, indicated by a large gap between excitation and emission wavelengths.
- The intra-configurational 4f-4f transitions in RE ions are characterized by small homogeneous linewidths.
- These ions possess multiple energy levels that are conducive to optical pumping.
- Comprehensive theoretical models exist that facilitate a systematic investigation of energy levels, transition intensities, and dynamics in excited states.

These remarkable properties of RE ions enhance their applicability in numerous fields, particularly in bio-sensing, biomedical therapies, display technologies, w-LEDs, solar energy conversion, temperature sensing, indoor horticulture and SSL [19,21–24].

1.4 THEORETICAL MODELS EXPLAINING ENERGY TRANSFER PROCESS

Typically, each phosphor demonstrates optimal luminescence output at a specific concentration of dopant ions. This optimal concentration is influenced by various factors, including the phase structure of the host matrix and the characteristics of the activator ions. The reduction in emission intensity beyond a certain dopant concentration is referred to as concentration quenching. As all activator ions share similar excited state configurations, increasing the concentration of activators within the phosphor enhances the likelihood of ET between neighbouring ions due to their proximity. ET occurs between two adjacent ions only if resonance conditions are satisfied concerning the energy differences between their ground and excited states, along with the presence of suitable interactions. ET among neighbouring activator ions typically occurs through three primary mechanisms: (i) exchange interactions, (ii) reabsorption, and (iii) multipolar interactions [18]. For radiation reabsorption to occur, there must be an overlap between the excitation and emission spectra; however, this condition is often not met in many instances. Additionally, to determine the underlying mechanisms-whether they involve exchange interactions or multipolar interactions-the critical distance (R_c) for ET needs to be evaluated, as defined by Blasse [25]:

$$R_c \approx 2 \left[\frac{3V}{4\pi X_c N} \right]^{1/3} \quad 1.1$$

where, X_c , V and N represent the optimal concentration of activator ions that yields maximum luminescence intensity, the volume of the host lattice, and the number of cations within the crystallographic unit cell, respectively. The criterion for exchange interaction stipulates that the value of R_c must be less than 5 Å [26]. If this is not the case, the final possibility for ET, attributed to a high value of R_c , occurs through multipolar interactions, which can be analyzed using Dexter's theory.

1.4.1 Dexter theory

The multipolar interactions can be categorized into three types: dipole-dipole (d-d), dipole-quadrupole (d-q), and quadrupole-quadrupole (q-q) interactions. The characterization of these interactions can be quantified using Dexter's ET equation given below [27]:

$$\log \frac{I}{x} = -\frac{Q}{3} \log x + A \quad 1.2$$

where, I denote the luminescent intensity, while x signifies the concentration of the activator ions. The parameter Q characterizes the nature of multipolar interactions, where Q = 6, 8, and 10 correspond to d-d, d-q, and q-q interactions, respectively [28]. Additionally, to determine the nature of the multipolar interactions within the sensitizer-activator system, one can utilize Dexter and Reisfeld's approximation to analyze emission spectra or apply the Inokuti-Hirayama (I-H) model to photoluminescence decay curves.

1.4.2 Dexter and Reisfeld's approximation

To identify the multipole-multipole interaction between the activator and sensitizer in a phosphor doped with both a sensitizer and a co-dopant activator, Dexter and Reisfeld's approximation can be applied to the emission spectra data. This approach provides a general relationship between the quantum efficiencies η_0 and η of the sensitizer in the absence and in the presence of the activator ion, respectively, as a function of the total ion concentrations (C) of both the sensitizer and activator. [29]:

$$\frac{\eta_0}{\eta} = C^{\frac{a}{3}} \quad 1.3$$

where, the variable a, which denotes the type of multipolar interaction, can assume values of 6 (for d-d interactions), 8 (for d-q interactions), and 10 (for q-q interactions). The ratio of quantum efficiencies $\left(\frac{\eta_0}{\eta}\right)$ of sensitizer ions, both in the absence and presence of an activator, can be estimated using the ratio of emission intensities $\left(\frac{I_{s0}}{I_s}\right)$. Here, I_{s0} represents the intensity of the most intense emission peak from the sensitizer without the activator, while I_s corresponds to the intensity of the same emission

peak when the activator is present. Consequently, the aforementioned relationship can be formulated as follows [30]:

$$\frac{I_{s0}}{I_s} \propto \frac{\eta_0}{\eta} = C^{\frac{a}{3}} \quad 1.4$$

The graphs of $\frac{I_{s0}}{I_s}$ versus $C^{\frac{n}{3}}$, corresponding to the value of $n = 6, 8$, and 10 are plotted. The optimal linear regression yields the value of n , which signifies the nature of the interaction involved in ET.

1.4.3 Inokuti-Hirayama (I-H) model

The ET mechanism occurring between neighbouring luminescent ions can be accurately characterized by the I-H model [31,32]. According to this model, the ET process mediated by multipolar interactions between neighbouring ions results in non-exponential decay characteristics of luminescence. Furthermore, the relationships between decay intensity and decay time can be quantitatively analysed based on this model [33,34]:

$$I_t = I_0 * \exp\left(-\frac{t}{t_0} - Q * \left(\frac{t}{t_0}\right)^{\frac{3}{s}}\right) \quad 1.5$$

here, I_t and I_0 represent the luminescence intensities measured at time ‘ t sec’ and at time ‘ 0 sec’ following excitation, respectively. The parameters $s = 6, 8$, and 10 correspond to the multipolar interactions of d-d, d-q, and q-q types, respectively, while Q denotes the ET parameter.

1.5 SPECTRAL TUNING AND THEIR INFLUENCE ON LUMINESCENCE

PERFORMANCE

It is widely known that the colour of the luminescent materials depends on the dopant ion incorporated into the host matrix via recorded PL excitation and PL emission spectra. In addition to that there are other significant parameters essentially needed to analyse the performance of the materials viz. Commission Internationale de l’Eclairage (CIE), CRI, CCT, luminescence efficiency and quantum yield [35]. The improved luminous performance with luminous parameters can be achieved by tuning the peak width and

peak position in the spectra of specific phosphor. Thus, the spectral tuning could be the efficient technique to render the excellent luminescent property and performance of RE doped phosphor material to be utilized in the SSL.

1.5.1 CIE color coordinates

It is important to extensively explore the CIE coordinates, to reveal the aptness of color array as well as the relevant application of material especially for photonic devices [36]. CIE generated color models are available to represent the tri-stimulus values of illuminated color (Red: R, Green: G, Blue: B) in the 3-dimensional color space. The standard CIE 1931 chromaticity diagram and color matching function has shown in Figure 1.8.

Since, human eye can possess three separate colors and each color produced with the combination of RGB. The color of any illuminating light can be displayed via color matching function. In color space, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ are three color matching functions and a dimensionless quantity.

$$X = \int \bar{x}(\lambda)P(\lambda)d\lambda \quad 1.6$$

$$Y = \int \bar{y}(\lambda)P(\lambda)d\lambda \quad 1.7$$

$$Z = \int \bar{z}(\lambda)P(\lambda)d\lambda \quad 1.8$$

where, tristimulus values (X, Y and Z) provide the degree of stimulus for each primary color (RGB) required to match the power spectral density $P(\lambda)$.

Moreover, the tristimulus values are employed to evaluate the chromaticity coordinates i.e. x and y, as represented in the following equations [37]:

$$x = \frac{X}{X + Y + Z} \quad 1.9$$

$$y = \frac{Y}{X + Y + Z} \quad 1.10$$

The location of the CIE chromaticity coordinates across the locus of CIE chromaticity diagram signifies the monochromaticity while multichromatic coordinates lie within the area of chromaticity diagram.

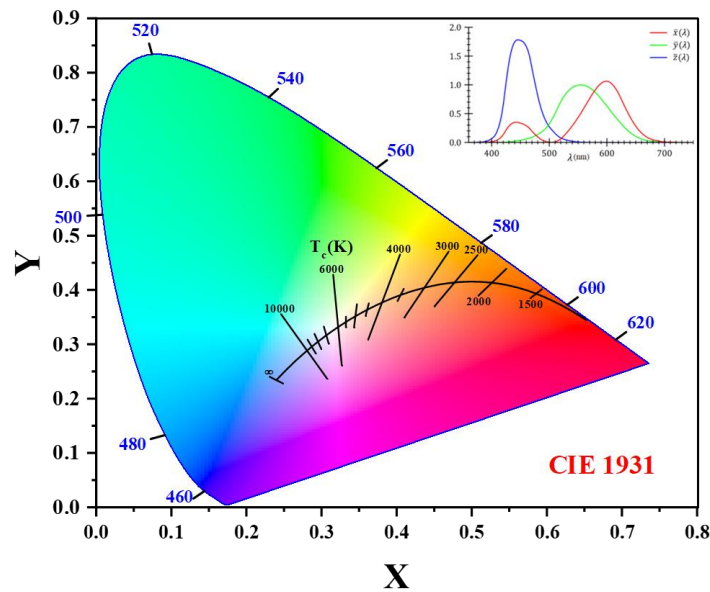


Figure 1.8 Standard CIE 1931 chromaticity plot and color matching function plot.

Thus, to quantify the monochromaticity of under investigated material using CIE coordinates, the color purity (CP) can be evaluated using formula as follows [38]:

$$CP = \frac{\sqrt{(x - x_{ee})^2 + (y - y_{ee})^2}}{\sqrt{(x_d - x_{ee})^2 + (y_d - y_{ee})^2}} \times 100\% \quad 1.11$$

where, (x, y) represent the coordinates of the phosphor, (x_{ee}, y_{ee}) denote the coordinates corresponding to the equal energy point, and (x_d, y_d) indicate the coordinates of the dominant wavelength point. The maximum attainable value for the color purity of monochromatic emitters is established at 100%.

1.5.2 Correlated color temperature (CCT)

CCT is one of the significant luminescence parameters used to measure the color temperature of focused the material and measure it in degree kelvin (K). CCT refers to the coldness and warmness of light. In general, the higher CCT (>5000 K) value denotes to the cooler light with emission of bluish light whereas lower (<5000 K) one signifies the warmer light with emission of yellow and red light [33]. Typically, CCT values has a range of 2000 to 10000 K and access in accordance to specific purpose such as indoor,

outdoor, industrial and display etc. It has been accepted commercially that the lighting source lie between 2200-6500 K range is most substantial. The CCT value of luminescent material can be estimated from the equation evaluated by McCamy as follows [39]:

$$\text{CCT} = -449 \left\{ \frac{(x - x_e)}{(y - y_e)} \right\}^3 + 3525 \left\{ \frac{(x - x_e)}{(y - y_e)} \right\}^2 - 6823.3 \left\{ \frac{(x - x_e)}{(y - y_e)} \right\} + 5520.33 \quad 1.12$$

where $\left\{ \frac{(x - x_e)}{(y - y_e)} \right\}$ represents inverse slope line and $x_e = 0.332$, $y_e = 0.186$ are the coordinates for epicentre of convergence.

1.5.3 Color rendering index (CRI)

CRI is the quantitative measure to reveal the ability of light source in terms visibility of diverse objects and compare with the natural or standard light source. The CRI is rated on the scale ranging from 0 to 100. The minimum indexing enunciates undistinguishable color whilst higher indexing refers to the “ideal” white light or daylight.

1.5.4 Photoluminescence decay

The PL decay is a nonlinear optical phenomenon characterized by the nonlinear polarization of an incident light beam. The nonlinear emission behaviour of luminescent materials reveals important aspects of excited state dynamics, such as radiative and non-radiative relaxation, intersystem crossing between singlet and triplet states, conformational changes like trans-cis isomerization, and ET mechanisms in the studied samples. In PL decay spectroscopy, the emission intensity is recorded at various time intervals after excitation, allowing for precise temporal resolution. PL decay times, obtained from decay profiles, provide critical insights into the excited state dynamics of RE ions, ET processes, molecular interactions with the surrounding environment, and the optical gain of the samples. These insights are crucial for advancing research in fields such as photonics, photosynthetic systems, nanoelectronics, and biological applications [40]. The PL decay profiles of the synthesized phosphor may be accurately modelled using either single or bi-exponential functions. At low concentrations of activator ions incorporated within the

host lattice, a single exponential decay profile is typically observed, indicating a reduced probability of ET between the ions. Conversely, a bi-exponential fit indicates a greater probability of energy transfer occurring among the activator ions. The mathematical representations for the single and bi-exponential models are as follows [41,42]:

$$I = I_0 + A \exp\left(-\frac{t}{\tau}\right) \quad 1.13$$

$$I = I_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad 1.14$$

In a single exponential decay model, τ signifies the decay time associated with the emitting level of an activator. In contrast, for a bi-exponential decay model, τ_1 and τ_2 correspond to the fast and slow components of the luminescence lifetime, respectively. The average decay time (τ_{avg}) of the emitting level can be determined from τ_1 and τ_2 using the formula provided below [42]:

$$\tau_{\text{avg}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad 1.15$$

The PL lifetime is influenced by the rates of both radiative and non-radiative relaxation processes. As the rate of non-radiative relaxations increases-often due to an increase in surface defects or the presence of quenching centers-the PL lifetime correspondingly decreases.

1.6 NON-CONTACT OPTICAL THERMOMETRY

Lanthanide-doped materials are appealing for temperature sensing purposes because the emission intensity shows temperature dependence. Non-contact temperature sensors are gaining increasing attention in optoelectronics and photonics, and can provide high spatial and temporal resolution [43]. Furthermore, temperature sensors without making contact can fulfil a need which is difficult to meet with conventional temperature sensors. For example, they can indicate ambient temperature readings in surgical therapy and can remotely measure the temperature from obscure objects in high-pressure nuclear power plants and coalfields [44]. Blackbody radiation-based devices can provide a high level of resolution over a broad temperature range and are designed for use above a few degrees Celsius. Temperature sensing has been

contemplated for decades with pronounced achievements, using microcrystalline luminescent compounds at the tip of a scanning thermal probe and an optical fibre as the primary components. Though micron-sized particles have many advantages, they also have drawbacks, such as the potential for acting as a thermal insulator and the reduction in resolution due to light scattering from their rough surfaces [45]. As a result, further research is required into optical temperature sensing, which is capable of measuring temperatures remotely over a wide temperature range and provides a quick response. Optical thermometry, focused on RE luminescence properties is attracting attention which utilises the dependence of fluorescence intensity and lifetime on temperature and excitation frequency [46,47]. FIR has gained prominence because it allows contactless temperature measurements with improved sensitivity and accuracy. In addition, advancements in RE doped luminescent materials for temperature sensing based on (up-conversion (UC), down-conversion (DC), and dual mode luminescent materials) are rapidly evolving. However, with the FIR technique, two closely spaced energy levels are combined to a single lower level for temperature monitoring. The emission intensity from the thermally coupled levels (TCLs) are proportional to the population of each energy level, so their temperature dependent ratio is independent of the source intensity. The thermally coupled fluorescence has a well-established theory which states that levels which are thermally coupled, emit fluorescence, and the population of these levels is directly proportional to the total population. As a result, any change in the total population due to changes in excitation power will have an equal impact on individual levels. In general, the FIR techniques are more sensitive than lifetime-based techniques [44,48].

1.6.1 FIR method for temperature sensing

The FIR method has been extensively used in optical sensing technologies. The FIR or sometimes called luminescence intensity ratio (LIR), technique measures temperature by comparing intensities from two closely spaced energy levels. It is well known that for energy levels separated by a few kT ($k = 200 \text{ cm}^{-1}$ at room temperature), thermal occupancies can occur above the ground state or in a

metastable excited state. Figure 1.9 depicts a schematic illustration for the FIR method using three-level system of RE ions doped phosphor.

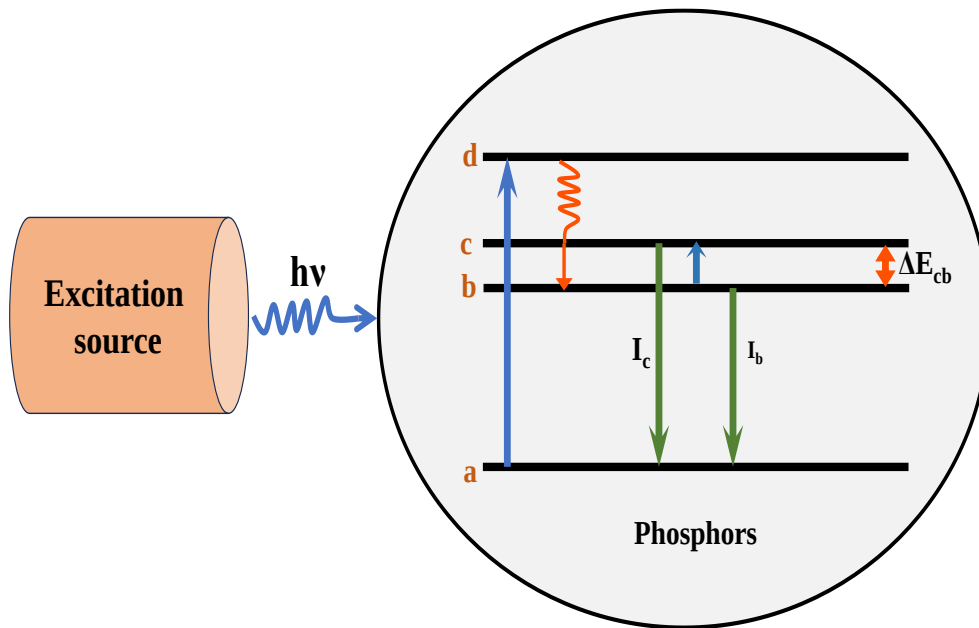


Figure 1.9 Schematic illustration of the FIR method for temperature sensing using RE doped phosphor.

Thermal coupling exists between the excited state energy levels b and c as shown in Figure 1.9. The relative population of these TCLs follows Boltzmann distribution. The atomic layouts in TCLs can be changed by adjusting the surrounding temperature of the phosphor [29]. Since the emitted intensities are in a direct relation with the population of the levels involved, the FIR ratio can be calculated by comparing the fluorescence intensity (I_c and I_b) coming from the TCLs, and is given by the relation [47,48]:

$$FIR_{TCL} = \frac{I_c}{I_b} = \frac{P(I_c)}{P(I_b)} = \frac{g_c A_c R_c w_c}{g_b A_b R_b w_b} \exp\left(-\frac{\Delta E_{cb}}{k_B T}\right) = C \times \exp\left(-\frac{\Delta E_{cb}}{k_B T}\right) \quad 1.16$$

where, I_c and I_b are the integrated intensities coming from the TCLs c and b respectively; $P(I_c)$ and $P(I_b)$ represent the population of the respective levels. R_c and R_b denotes the response of the detection at the emission angular frequencies of the w_c and w_b , respectively. The spontaneous emission rates (A), the degeneracy (g) of the levels involved, and C the amplification factor is related as shown below [49]:

$$C = \frac{g_c A_c R_c w_c}{g_b A_b R_b w_b} \quad 1.17$$

The separation (ΔE_{cb}) between the TCLs c and b is shown in Figure 1.9, k_B is the Boltzmann constant and T is the absolute temperature. ΔE_{cb} is obtained by fitting the FIR vs. temperature (T) data using the linear relation [50]:

$$\ln(\text{FIR}_{\text{TCL}}) = \ln C - \frac{\Delta E_{cb}}{k_B T} \quad 1.18$$

Factors influencing the FIR method

Important factors that determine the suitability of a material for temperature sensing includes the following considerations:

- (i) Material's availability and its cost.
- (ii) The temperature range upto which the material can withstand.
- (iii) The ease with which fluorescence can be obtained.

Much of the reported work based on FIR sensing technique is based on monitoring the TCLs of RE ions to provide the intensity ratio. For practical sensor applications, besides the energy levels to be thermally coupled, there are several other requirements which largely depend upon the host, and must meet the following prerequisites [48,49]:

- (i) The pair of TCLs should be separated by less than 2000 cm^{-1} because a larger difference tends to lower the population of upper levels.
- (ii) The separation must be more than 200 cm^{-1} to prevent overlapping of two fluorescence wavelengths.
- (iii) Radiative transitions should dominate over non-radiative transitions.
- (iv) Commonly used detectors necessitate fluorescence transitions in between 6000 to 25000 cm^{-1} .
- (v) Excitation sources (laser diodes and LEDs) must be matched and miniaturized for direct integration of the sensing material onto the optical fiber tip.

1.6.2 Thermometric parameters for temperature sensing

1.6.2.1 Sensitivity

The rate at which the FIR value changes as a function of temperature are termed as absolute sensitivity (S_a) and the relative sensitivity (S_r). Absolute sensitivity is calculated as follows [47,49]:

$$S_a = \left| \frac{dFIR_{TCL}}{dT} \right| = FIR \left(\frac{\Delta E_{cb}}{k_B T^2} \right) \quad 1.19$$

Collins *et al.* (1998) and Brites *et al.* (2012) have suggested that calculating the relative sensitivity (S_r) is more useful to compare the performance of different temperature sensors, which is expressed as [51,52]:

$$S_r = \frac{1}{FIR_{TCL}} \left| \frac{dFIR_{TCL}}{dT} \right| = \left(\frac{\Delta E_{cb}}{k_B T^2} \right) \quad 1.20$$

In general, ΔE_{cb} for different types of hosts does not differ or varies much and differs only by a few hundred cm^{-1} . Therefore, immaterial of the host, the relative sensitivities of the FIR for a specific lanthanide ion will be same. A number of studies show relative sensitivities which differ from the real values. The error may arise from measurement or poor data analysis. It can also relate to ET between the TCLs, which follow Boltzmann's redistribution, and the error given by δ [44,53]:

$$\delta(\%) = \frac{|\Delta E_{cb} - \Delta E_m|}{\Delta E_m} \times 100\% \quad 1.21$$

Where, ΔE_m stands for the “real value” of the energy difference (which can be evaluated from measured emission spectrum as a difference between respective centres of the emission band). ΔE_{cb} is the energy difference obtained from the linear fitting using equation 1.18. Lower the value of δ (%), the more accurate is the determined value of the absolute sensitivity (S_a).

1.6.2.2 Temperature uncertainty

Uncertainty during temperature measurement is defined as δT which is the tiniest detectable temperature. Published literature on a number of host materials shows the ultimate resolvable change in temperature

(δT) depends strongly on the instrumentation, sensitivity of the detector, accuracy in the data acquisition, and the signal-to-noise (S/N) ratio.

In order to determine δT , the time dependent FIR fluctuations are noted at a specific temperature taken as a reference. It is common to select (0°C) and (100°C) as two important reference points corresponding to the freezing and boiling points of water. Using equation 1.18, and the calibration curve showing a good linearity defined between the temperature span bound by ($T_{\min}$ and T_{upper}) limits, the FIR values are converted to temperature. A distribution of such FIR fluctuations converted to temperatures allow the construction of a histogram for measurements carried out within a time interval. The standard deviation of the histogram provides the value of the temperature uncertainty δT . Such an experimental procedure also provides interesting information on whether the excitation source (NIR) is used for the up-conversion process has any potential heating effects during the measurements. The elaborate measurements as described above are sometimes not possible due to experimental limitations, and in such cases an alternate way of extracting the approximate value of δT has been suggested by Baker [54] and Brite [55] as:

$$\delta T = \frac{1}{S_r} \left(\frac{\delta \text{FIR}_{\text{TCL}}}{\text{FIR}_{\text{TCL}}} \right) \quad 1.22$$

where, $\frac{\delta \text{FIR}_{\text{TCL}}}{\text{FIR}_{\text{TCL}}}$ is the relative uncertainty. When the acquisition times are longer, a low value of temperature uncertainty δT are achieved from the standard deviation.

1.6.2.3 Repeatability and reproducibility

The exactness or the accuracy in any measurement is governed by the repeatability and reproducibility of the measurement. A high level of repeatability is reflected by an insignificant variation in repeated measurements when made under the same conditions. It is preferred to use the same equipment, same geometrical distances between the sample, excitation source and the detector during the measurements. Time for sample temperature, data acquisition time at measurement become very important [55,56].

Reproducibility relates to the variations in the measurements under changed conditions of the same measurand (i.e., temperature in the present discussion). The different conditions can be due to the varying methods (thermocouples, thermometers, or other techniques), or different observers making the measurements at different times, and during these changes the error levels can undergo a change [47,53,56,57].

During the preliminary research stage experimentation, the repeatability is determined by steering (or cycling) the temperature to be measured between two pre-defined levels (say a low to high temperature, and then back to the lower temperature within a prescribed interval of time). The repeatability (R) is expressed as [47]:

$$R = 1 - \frac{\max(|FIR_c - FIR_i|)}{FIR_c} \quad 1.23$$

where, FIR_c is the mean of the FIR values [obtained from the calibration equation 1.18], and FIR_i is the instantaneous FIR ratio measured at each temperature. A minimum of 10 to 20 uninterrupted repeated cycles are considered enough for any statistical implications. Important points that need to be considered during the reliability testing of the temperature sensor include the following suggestions:

1. The measurement repeatability corresponds to computing the deviation in the temperature relative to the average value.
2. A maximum in the deviated value and the determined uncertainty must be well matched to ascertain the calibration process, and temperature uncertainty have been determined correctly.
3. For assessing reproducibility, statistical analysis is the preferred choice.
4. The stability of the calibration curve is an important factor and must be preserved to define the life and usefulness of the sensor for repeatable measurements.
5. The temperature readout should be reproducible even when the detector is changed and should provide a reliable output at different locations and under varying conditions.

1.7 IMPORTANCE OF THE PRESENT RESEARCH WORK

In the recent time, SSL is alleged to be an ultimate light source which alter the way of generating and controlling the light for distinct applications by the growing human civilization. Earlier, conventional light sources such as fire (1st generation), incandescent bulbs and fluorescent lamps (2nd and 3rd generations) were exorbitantly utilized due to lack of development of innovative technology [58]. These light sources entail high temperature, more heat dissipation and release of toxic gases which adversely affect the environment [59]. Therefore, considering the challenges about an escalating demand of energy consumption and environment problems, a substitute of conventional light source is obligatory to develop. In reference to this, SSL emerged as an alternative source of light and currently serve as 4th generation of light owing to the significant reduction of energy usage. SSL rely on the organic or inorganic based LEDs to produce light with maximum efficiency. Moreover, SSL possesses two highly enviable features includes; (i) extremely energy efficient with a great deal of potential to reduce energy usage and carbon emission and, (ii) flexible light source having several configurable characteristics such as spatial emission pattern, colour temperature, temporal modulation and control of spectrum etc. [60,61]. The introduction of LEDs over outmoded technology (incandescent and fluorescent bulbs) is to improve the quality of life and reflect benefits in performance, economy, sustainability and ecology. Thus, the current technology generates efficient white light. In general, there are three ways to generate white light as explained in Figure 1.10. The prime approach is the most common and phosphor free, in which monochromatic red (R), green (G) and blue (B) emitting LEDs are combined to attain white light. The above-mentioned RGB-LEDs are inaccessible as individual LED demands different driving currents to provide constant white light emission [62]. Further, different driving currents of each LED trigger the emission color and results unstable color temperature. Second approach is phosphor dependent and produce white light by layering yellow emitting YAG: Ce³⁺ phosphor on the top of blue emitting InGaN LED chip. This approach had proven to be advantageous over RGB LEDs due to high brightness, simple fabrication and cost-

effectiveness. Despite of these advantages and its on-going commercial practice, people are refraining to use it due to some drawbacks such as less efficiency, halo effect, low CRI (<80) and high CCT (>5000 K). The listed issues mentioned in phosphor-based LEDs are due to insufficient availability of red component and can be resolved by adopting third approach that implicates red color emitting component into the phosphor. Thus, final approach embraces two sub approaches, wherein exciting either a mixture of green and red phosphors via blue LED chip or a mixture of blue-green-red phosphors via UV/n-UV LED chip. Eventually, the final approach holds red component to produce efficient phosphor [63].

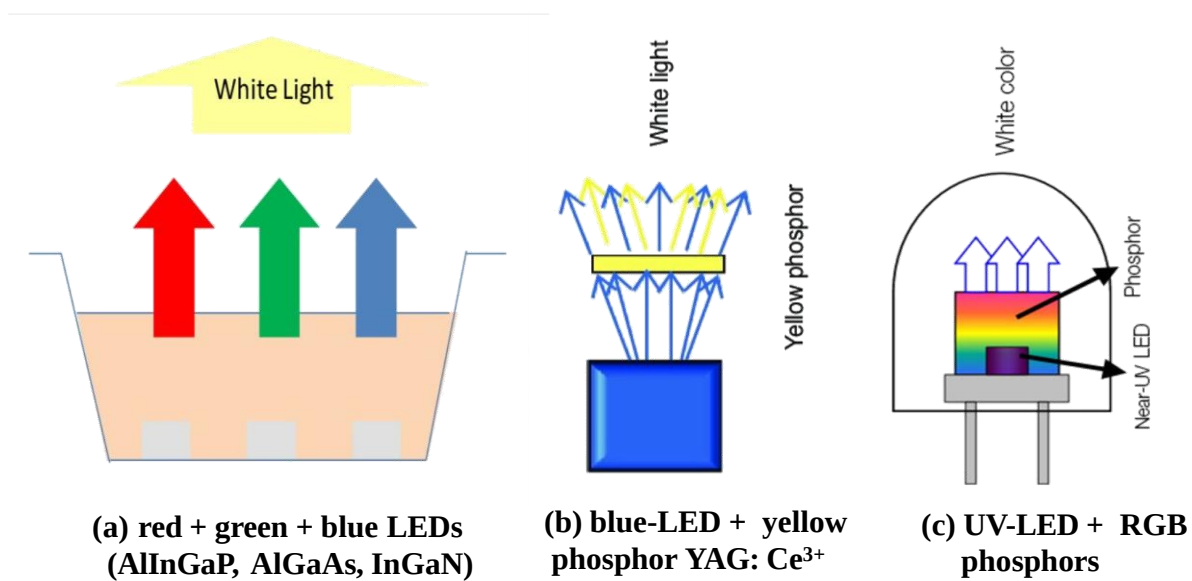


Figure 1.10 Generation of white light using phosphors.

Moreover, the prepared multiphase phosphor causes deteriorated output efficiency due to the re-absorption of blue emission through RG phosphor. Nevertheless, the deteriorated output efficiency can be improved by preparing single phase phosphor activated with double or multiple dopant ions to provide warm white light. Double or multiple dopant ions activated single phosphor yields excellent efficiency with optimum color reproducibility, suitable CCT, appropriate CRI and color tunability [64]. Additionally, phosphors have lots of applications in a wide range of fields, including scintillation, X-ray intensification, and advanced optical displays. Furthermore, RE doped phosphor has gained extra consideration due to their

high photo-stability. The parameters, PL intensity, PL lifetime and PL intensity ratio have been utilized to monitor the real time temperature of substances [65,66].

On the other hand, a photonic based thermometer using the FIR approach is seen as an advantageous method for measuring temperature because it has inherent protection from some external conflicts and high sensitivity [67–69]. Also, photonic based optical sensors have attracted a lot of attention among the many temperature sensing schemes because they have many advantages: small sensor size, which means quick response, non-contact, high precision, electromagnetic resistance, and in-situ capabilities [70–72].

Phosphors are critical components utilized in lighting, imaging, and display technologies. The development of an efficient single-phase pc w-LED heavily relies on the selection of an appropriate host material, which significantly affects the luminescent properties of the phosphor. Thus, the choice of host material is crucial. Recent studies have highlighted inorganic oxides as promising host materials due to their numerous advantages, including cost-effectiveness, ease of preparation, environmental friendliness, and exceptional stability. These materials exhibit high chemical, thermal, and photostability, making them suitable for various applications. The notable characteristics of various inorganic oxides, such as vanadates, tungstates, niobates, phosphates, aluminates, and silicates, have attracted considerable interest from researchers for further investigation [73–76]. Since tungstates have strong covalent interaction, high stability, and strong visible luminescence, they are suitable host materials for RE^{3+} ions and have potential uses in lasers, optical fibers, w-LEDs, plasma display panels, quantum electronics, phosphors, scintillators, optical thermometers and solid-state optoelectronic devices [77,78]. Also, the alkali metal ions, for instance Li^+ , Na^+ , K^+ etc. improve the luminescence emission intensity and color purity of the host matrix. A few literature [79,80] show that due to presence of Li^+ ions in the host matrix, a better luminescence property is achieved instead of other alkali ions making it a suitable modifier in the host matrix. Additionally, tungstate with alkaline earth metal ions (i.e., Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} etc.) are a fascinating group of compounds that exhibit blue or green luminescence associated with the tetrahedral WO_4 groups

[81]. These substances find extensive applications as X-ray phosphors, scintillators, laser crystals, and matrices for electron spin resonance [82].

1.8 OBJECTIVES OF THE PRESENT WORK

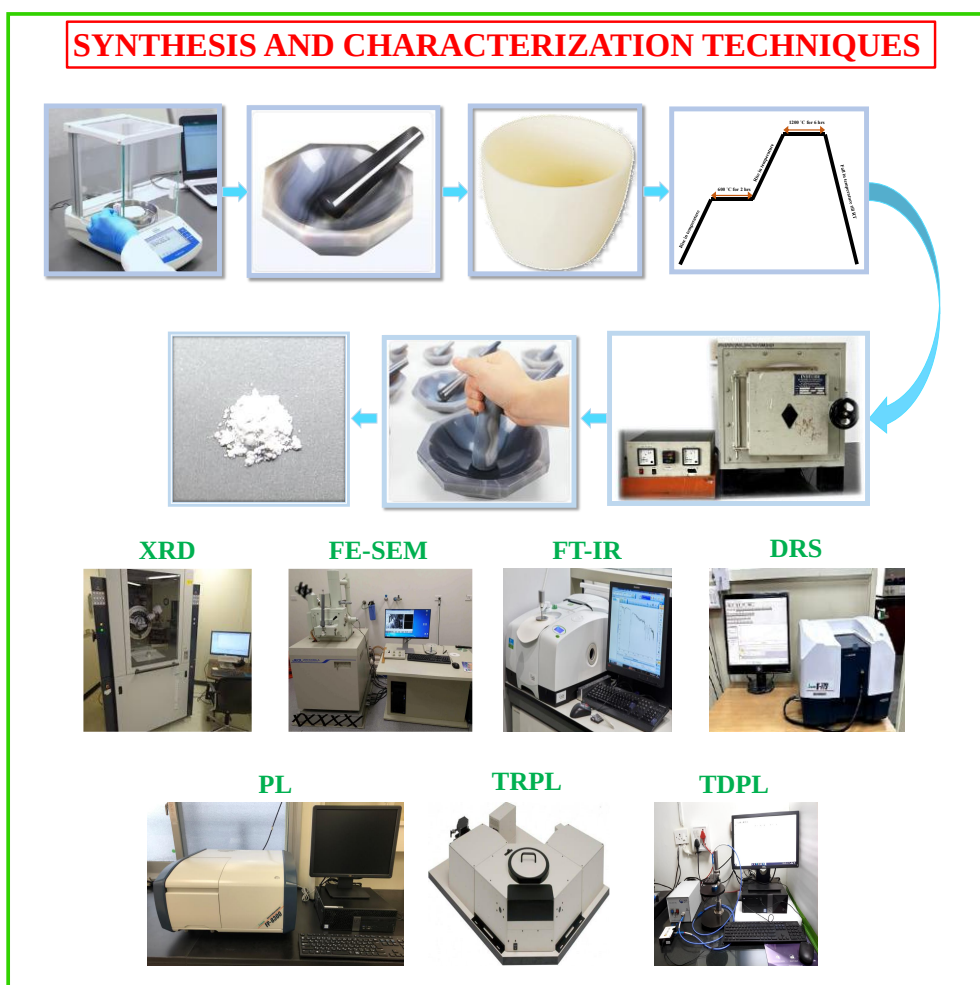
The following are the objectives of the present thesis:

- To synthesize rare earth doped phosphors with pure phase and homogeneous crystal structure.
 - To study structural, morphological and vibrational properties using XRD, SEM and FT-IR techniques.
 - To study the luminescent properties and enhanced luminescence intensity (up/down-conversion) of the as prepared phosphors by co-doping with suitable activator/sensitizer ions so as to understand the dependency of luminescence on the host as well as on the concentration of rare earth ions.
 - To assess the usability of as prepared up-converting or down-converting phosphors in w-LEDs and other photonic applications.
-

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION TECHNIQUES

The development of high-quality phosphors necessitates a thorough understanding of their synthesis methodologies and the relevant characterization techniques employed to analyze their properties. A phosphor is considered to exhibit excellent quality when its luminescent properties are reproducible. This chapter provides a detailed explanation of the experimental methods and characterization techniques employed for RE doped $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$ (LBW) phosphors.



Traditional solid state reaction methodology has been adopted to prepare various RE activated and co-activated LBW phosphor. The characteristics of RE ions doped phosphors were scrutinized via employing the numerous characterization techniques used to explore their structural, vibrational, morphological, optical and thermal characteristics for their utility in advanced photonic and optical thermometry devices. To understand the instruments better, working principles, device descriptions and operational controls of characterization tools used in the present research work are described in the current chapter.

2.1 EXPERIMENTAL WORK

The initial phase of experimental research involves the preparation and characterization of the material. This chapter provides a detailed account of the synthesis methods employed to synthesize the phosphors and the corresponding characterization methods utilized to evaluate their applicability in pc-LEDs for general illumination in w-LEDs and optical thermometry applications. This chapter deals with the detailed experimental procedure and characterization techniques used throughout the thesis work. Synthesis of RE ions doped phosphor along with the characterization techniques is described in flowchart as shown in Figure 2.1.

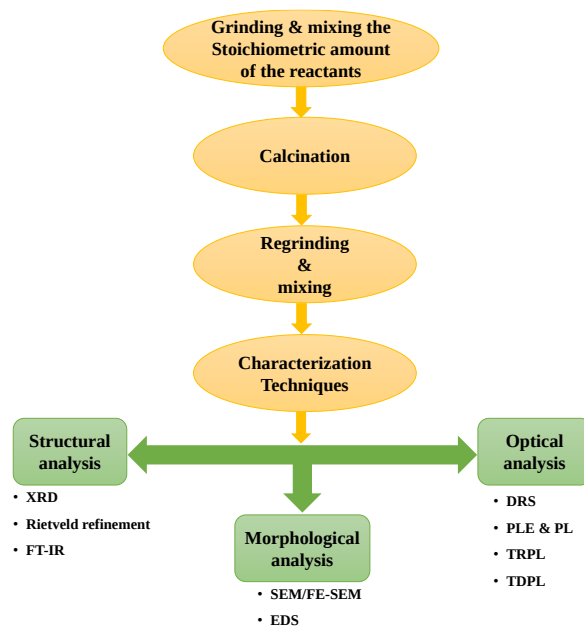


Figure 2.1 Schematic representation of phosphor synthesis and characterization techniques used for analysis.

The structural, vibrational and morphological features of the synthesized phosphors have been scrutinized via employing X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM). The spectroscopic characteristics of a phosphor was recorded by equipment like diffuse reflectance spectroscopy (DRS) and spectrofluorometer etc.

2.2 SYNTHESIS METHODOLOGY

2.2.1 Solid state reaction (SSR) method

Various synthesis techniques viz. solid-state reaction, co-precipitation, hydrothermal, spray pyrolysis, microwave and combustion methods are followed to synthesizing different phosphor materials. Among all the techniques, SSR method is conventional and ubiquitous to prepare crystalline phosphor materials. However, SSR approach is quite ordinary, but it is most promising for scaling up the production of the material. SSR approach comprises mechanical force to mix the solid constituents such as carbonates, oxides, fluorides and sulphides etc. The solid constituents are grinded for long time to allow these constituents mix together homogeneously and place this homogeneous mixture at elevated temperatures to undertake the diffusion process. In this methodology, the chemical reaction takes place at the stage where the reactants are in intimate contact with each other. Afterwards, the product layer is formed at the interface between the reactants which further proceed the reaction by the diffusion of each reactant. This process relies on various factors such as structure of product and reactants, size of the diffusion ions, presence of defects and reaction temperature. Several key points must be taken into account before begin the experimental practice for solid state reaction method such as melting temperature, vapour pressure and decomposition temperature etc. Moreover, appropriate environment needs to be provided in accordance to the requirement and stability of the reactants. Crucible selection is crucial to sinter or calcine the sample at high temperature. A chemically inert as well as thermally stabilized crucible material such as alumina (Al_2O_3) or platinum may be used and in the present work we have employed Al_2O_3 crucibles to prepare the titled phosphors [83].

Furthermore, continuous grinding of reactants may peel-off the layer formed at the interface of the product and form a contemporary layer while forming a final product. Homogeneous grinding improves the surface area and reduces the particle size as well as diffusion path. However, a non-uniform and larger size particle (usually in micrometres range) are achieved through grinding and mixing process or commonly known as solid state reaction method. There are few merits for the SSR approach which encourage the researchers to opt SSR methodology to prepare the phosphor samples.

2.2.2 Merits of SSR approach

The SSR method for synthesizing phosphors offers several merits:

- 1. Simple Process:** The SSR method is relatively simple and straightforward, involving the mixing of solid reactants followed by heating to induce chemical reactions. This simplicity makes it suitable for large-scale production.
- 2. Cost-Effectiveness:** It does not require complex equipment or solvents, therefore, the SSR method tends to be more cost-effective compared to other synthesis techniques, such as solution-based methods.
- 3. High Purity:** Solid-state reactions can often yield relatively high-purity phosphors because there are no solvent impurities introduced during the synthesis process. This high purity is essential for achieving desired optical and electronic properties.
- 4. Versatility:** This method allows for the synthesis of a wide range of phosphors with diverse compositions and properties. It can be adapted to produce phosphors for various applications, including lighting, displays, and medical imaging.
- 5. Control over Stoichiometry:** Solid-state reactions enable precise control over the stoichiometry of the phosphor composition, ensuring consistent performance and properties. This control is crucial for tailoring the phosphor's characteristics to specific application requirements.

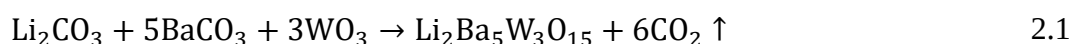
6. Environmental Friendliness: Unlike some solution-based synthesis methods that may involve hazardous solvents or generate toxic by-products, the SSR method is relatively environmentally friendly as it typically involves fewer chemicals and produces minimal waste.

7. Scalability: The SSR method is easily scalable, making it suitable for industrial-scale production. It can be carried out in batch reactors or continuously operated systems to meet the demands of large-scale production.

2.2.3 Synthesis procedure used to prepare RE doped $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$ phosphors

In the current experimental process, a series of samples with empirical formula $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$ have been synthesized through conventional SSR approach. In this, the raw materials listed as Li_2CO_3 (99.0%), BaCO_3 (99.99%), WO_3 (99.99%), and RE_2O_3 (99.99%) with high purity were taken and mixed up in the stoichiometric ratio according to chemical reaction shown in equation 2.1, as given below, in presence of acetone (dispersing medium) via manual grinding method. After continuous grinding for 1 h, the powdered sample was transferred to an alumina crucible for heat treatment. The initial heating phase involved raising the temperature to 600 °C for 2 h, followed by an increment to 1200 °C, maintained for 6 h to enhance the crystallinity of the sample. Subsequently, the sample was allowed to cool to room temperature, after which the sintered material was ground to obtain a fine powder for further analysis. The detailed process has been represented in Figure 2.2.

Chemical Reaction:



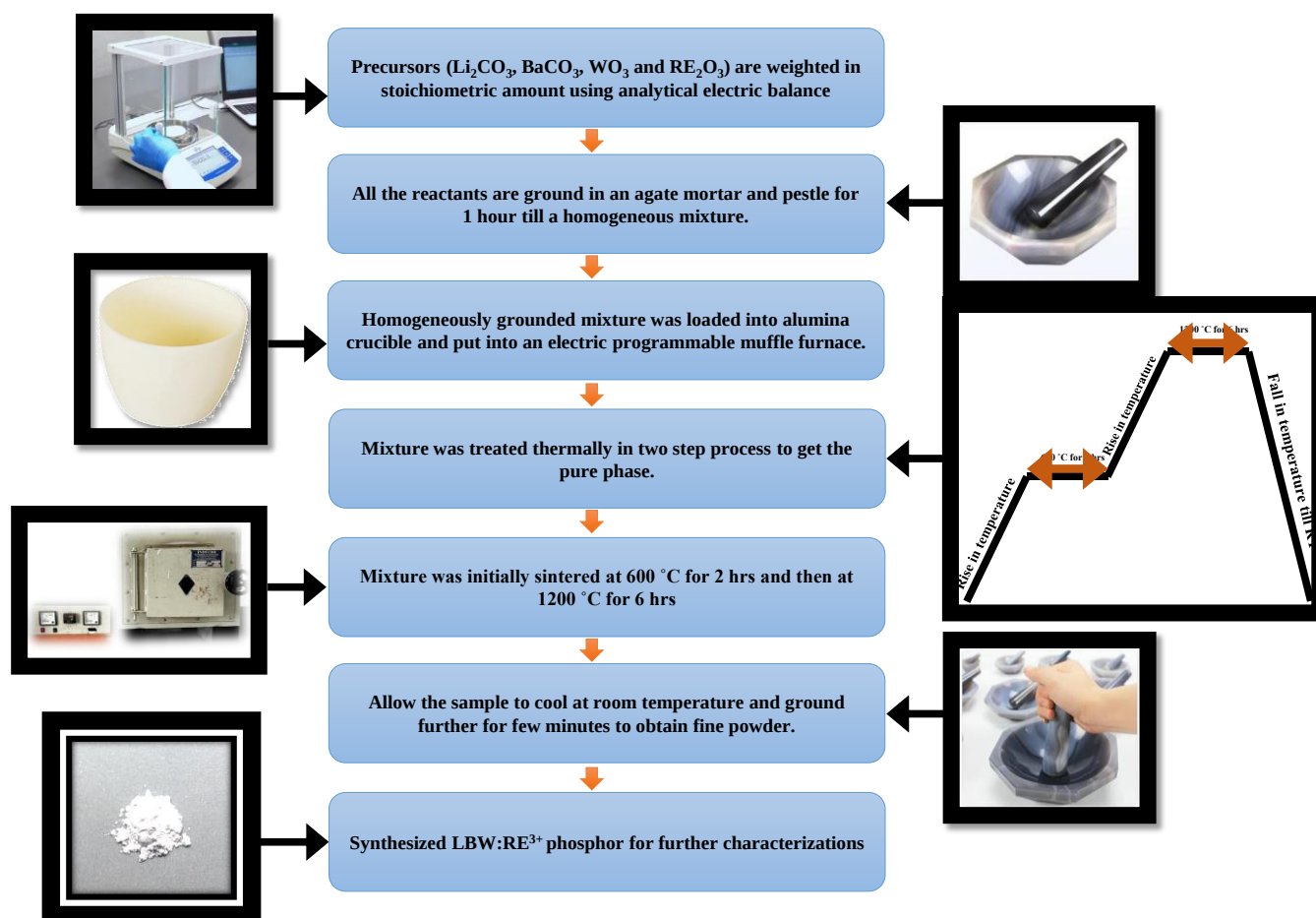


Figure 2.2 Flow chart of SSR method to synthesize LBW:RE³⁺ phosphor.

2.3 CHARACTERIZATION TECHNIQUES

The material characterization tools were very imperative part of research, which empower investigators to identify the structural characteristics, how this characteristic related with other electrical, optical, mechanical properties, and how these properties were useful in technological applications. Characterization and results are very important for the preparation and optimization of efficient phosphor for distinctive applications in the field of science and technology as well as daily life. In order to study various structural, vibrational, morphological and luminescence characteristics of the as prepared phosphor, sophisticated analytical characterization techniques were essential. Hence, the current section deeply explained about the characterization techniques and their working principle used to characterize the as-synthesized RE doped LBW phosphors.

2.3.1 Thermal analysis

In the field of physicochemical science, thermal analysis is a technique which study the behaviour of materials and quantifies in response to change in temperature. Thermal analysis is used for investigation of various other studies such as mass, enthalpy, dimension, melting temperature, cooling temperature, freezing temperature and dynamic characteristics etc. In addition, thermal analysis is widely applicable in a variety of disciplines remarkably from pharmaceutical to polymer and material sciences to understand the behaviour with respect to time and temperature[84]. In order to analyse the thermal properties of the materials, most basic thermal analytical technique is the Thermogravimetric analysis (TGA).

TGA is a technique in which the mass of sample is measured with respect to gradual increase in temperature and leads to interpret thermal events that happened during the process such as decomposition, absorption, adsorption, desorption, vaporization, sublimation, reduction and oxidation etc. The evaluation of volatile or gaseous products or by-products loss during chemical reaction for materials viz. polymer, composites, nanomaterials, fibres and thin films can be observed using TGA [85]. Figure 2.3 (a) represent the block schematic diagram of thermogravimetric instrument which is most widely used for TGA analysis and the recorded data in the form of TGA curve is known as thermogram. An alternative and complimentary representation of TGA curve with respect to temperature is the first derivative of TGA, generally known as differential thermogravimetric analysis or DTG, which clearly show the rate at which weight loss taking place. There are certain factors and conditions that are necessary to take in notice while performing the TGA analysis are as:

- (i) Mass and volume of the specimen,
- (ii) physical form of the specimen,
- (iii) shape and nature of sample holder,
- (iv) nature of atmosphere under which the analysis performed,
- (v) pressure of the atmosphere maintained in the chamber and

(vi) rate of heating as well as cooling.

Thermal analysis has been carried out using Labsys Evo instrument from Setaram, as shown in Figure 2.3 (b).

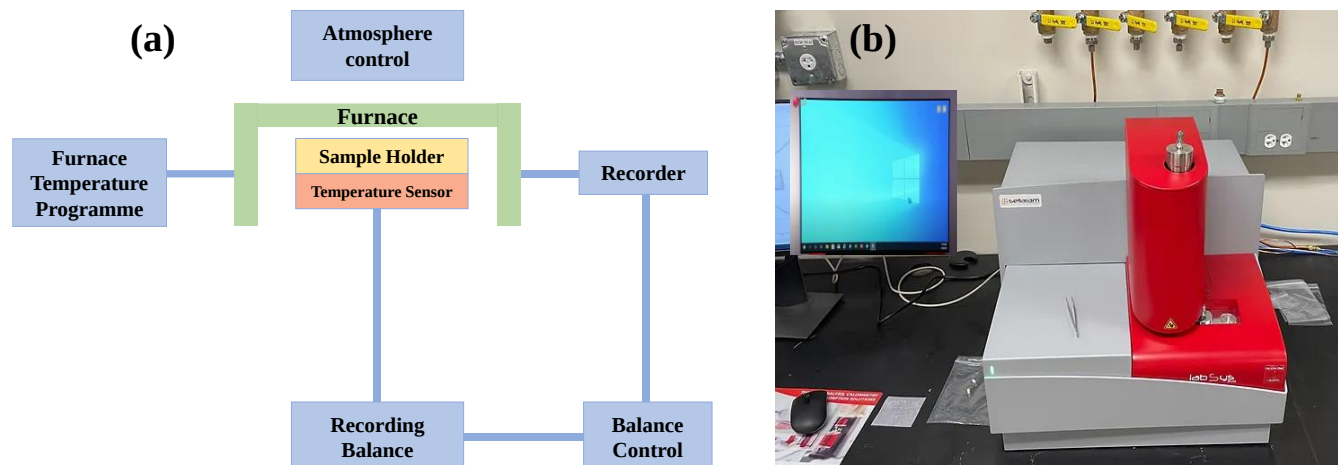


Figure 2.3 (a) Schematic diagram of thermogravimetric analysis (b) Setaram Labsys EVO TGA/DTA analysis instrument.

2.3.2 X-ray diffraction (XRD)

2.3.2.1 Basic principle

XRD is a non-destructive and versatile technique used for the identification of crystal structure, crystallite size and strain of materials employed in various institutions/industries. Diffraction technique can recognize the chemical compositions from crystal structure instead the elements [86]. XRD is a phenomenon in which an incident x-ray beam's wave interferes with one another as a result of the uniform spacing of the atoms in the crystal structure. The crystalline structure is an array of atoms ordered in a systematic pattern in 3D space known as lattice. The smallest reoccurring element of the crystal is called unit cell in which the size and shape of the unit cell are expressed by the angle between the axes as α , β , γ and the length of the three translational axes are a , b , c . In a crystal structure, based on the angles between axes, length and symmetry; seven crystal systems are categorised, which further sub-divided into 14 Bravais lattices. This technique was discovered by Von Laue in 1912 for both quantitative and qualitative investigation of polycrystalline materials. Each crystalline material has a unique diffraction

pattern, including a precise location of diffraction lines and their peak intensities. Such diffraction patterns are complicated and impossible to have similar diffraction peak profile of the materials. Thus, XRD contributes significantly to the identification of a crystalline materials as “fingerprints” [87].

2.3.2.2 Instrumentation

X-ray diffractometer is an instrument used to examine the crystal structure of single and poly crystalline samples. A spectrum for diffraction intensity versus angle between incident and diffracted beam is recorded via continuous change in the incident angle of X-ray beam. Figure 2.4 represents the geometric arrangement of diffractometer consists essentially X-ray source, sample and detector. In XRD, diffractometer is used to detect the diffracted X-rays from the materials and measure the intensity as a function of diffraction angle (2θ). The generated X-rays in the X-ray tube passes through a slit which collimate the X-ray beam and prevents the beam divergence while incident on the specimen. The specimen is in the form of flat plate which is supported by the specimen table (sample holder). The incident X-rays are diffracted from the sample and forms a convergent beam which passes through the monochromator (monochromatic filter) before entering into the detector for further record. The monochromatic filter is generally placed in the path of diffracted beam instead of incident beam in order to suppress the wavelengths other than K_{α} radiation and reduce the background radiation generated within the sample.

2.3.2.3 Bragg's law

According to Bragg's analysis, the crystal lattice planes or the atomic planes are assumed to be arranged in the layered format and these layers are separated by a distance d in the crystal. Furthermore, when a monochromatic X-ray beam incident on the crystalline solid sample, it will get diffracted by the lattice plane with the equal angle between the incident ray and the equivalent diffracted beam, as shown in Figure 2.5. In order to produce a constructive interference, the path difference must be equal to the integer multiples of the wavelength.

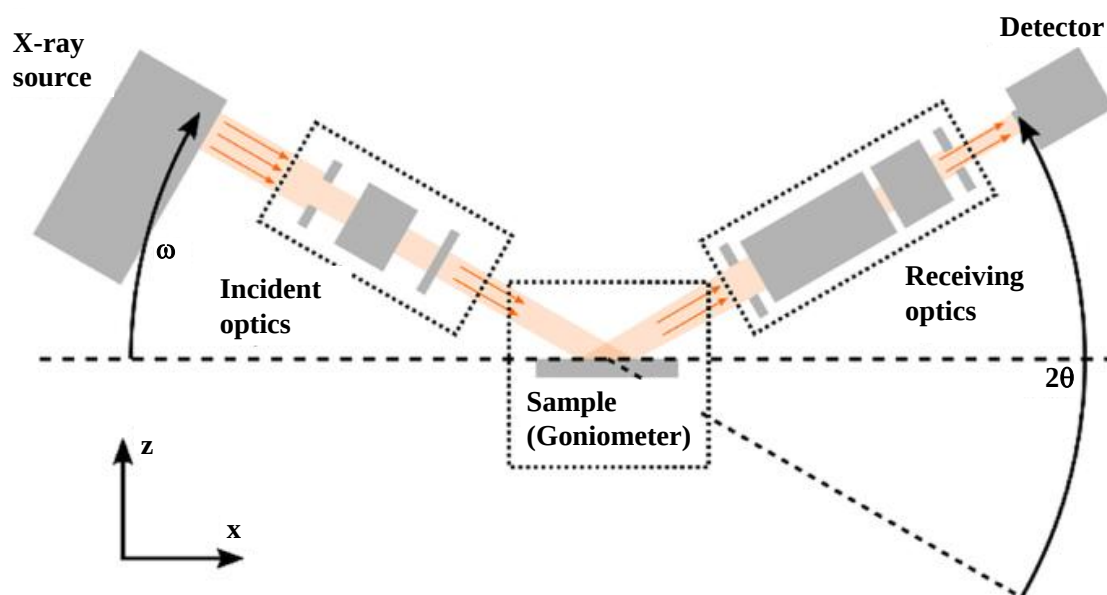


Figure 2.4 Schematic diagram of geometric arrangement of X-ray diffractometer.

The general relationship between the incident X-ray wavelength, angle of incidence and the spacing between the crystal lattice plane has been explained by the Bragg's law as mentioned below:

$$n\lambda = 2d \sin\theta \quad 2.2$$

where, n is the integer signifies the order of diffraction, λ is the wavelength of incident x-rays, d is the interplanar spacing and θ is the diffraction angle.

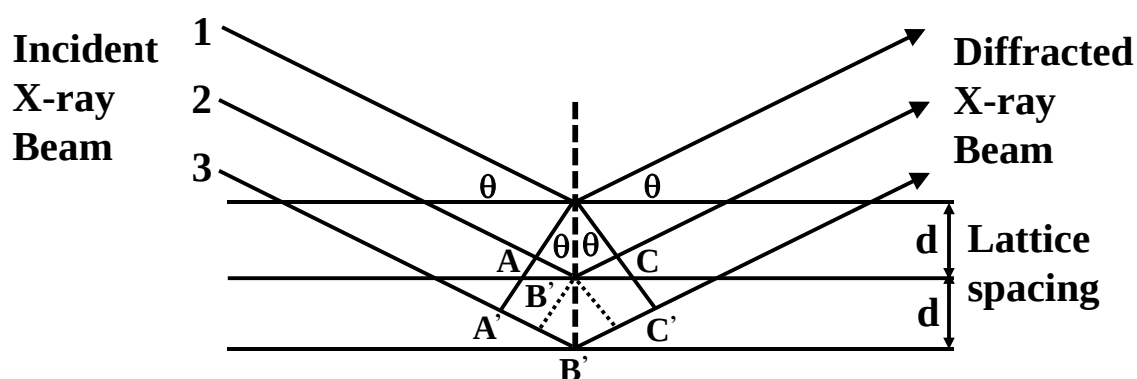


Figure 2.5 Schematic diagram of X-ray diffraction from the crystal lattice plane.

2.3.2.4 Data collection and analysis

The diffraction measurement output is obtained when a plot against XRD intensity and Bragg's angle is drawn. In general, the diffraction pattern measured in the 2θ range of 10° - 70° is sufficient to determine the phase of inorganic material. The scan time can be optimized to obtain better diffraction pattern with good intensity of diffraction peaks. In the current analysis, the obtained diffraction pattern was associated with the JCPDS (Joint Committee on Powder Diffraction Standard) database available for the reported crystalline samples. The synthesized phosphors exhibit strong and precise diffraction peaks, demonstrating their high crystallinity, which is necessary for significantly better illumination. It is also required to determine the radius percentage difference (D_r) between substituted ions and activator ions to better understand the dopant ions occupying the sites in the host lattice. The value of D_r is defined by the following expression [88]:

$$D_r = \frac{R_s(\text{CN}) - R_D(\text{CN})}{R_D(\text{CN})} \times 100\% \quad 2.3$$

The D_r is the ionic radii between the doped ion (R_D) and the substituted ion (R_s) remained within an acceptable range of up to 30 % [88]. Moreover, when assessing the size of grains, it is based on the idea that smaller grains or crystals will result in wider diffraction patterns, also referred to as peak broadening [89]. Therefore, broadening of an XRD peak indicates that a small crystallite does not have sufficient viable planes to provide fully destructive interference. Using the Debye Scherrer's equation shown below, one may determine an average crystallite size (D) of the samples:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad 2.4$$

where, k is the form factor ($=0.94$), λ ($=1.540 \text{ \AA}$) denotes the X-ray wavelength of Cu- K_α radiation used in XRD, β indicates the diffraction peak's FWHM of the corresponds to a particular angle θ . Furthermore,

the Williamson-Hall (W-H) equation was employed to calculate the crystallite size (D) and strain (ϵ) of the sample using below equation [28]:

$$\beta \cos \theta = \frac{K\lambda}{D} + 4\epsilon \sin \theta \quad 2.5$$

where K is the shape factor. The XRD pattern in the current work has been recorded using Smartlab high resolution X-ray diffractometer from Rigaku as shown in Figure 2.6 (a). The Bruker D8 Advance X-ray diffractometer (Figure 2.6 (b)) is another diffractometer used to measure the diffraction pattern. The diffractometer employs a Cu- K_α X-ray beam ($\lambda = 1.5406 \text{ \AA}$) as the radiation source. The XRD system operates at a scanning rate of 0.013° per second and covers an angular detection range of $10^\circ \leq \theta \leq 70^\circ$. The instrument is configured with an accelerating voltage of 40 kV and a current of 30 mA.



Figure 2.6 (a) Rigaku high resolution X-ray diffractometer (b) Bruker D8 Advance X-ray diffractometer.

2.3.2.5 Rietveld Refinement Study

Several phase analysis and quantitative techniques have been developed based on the XRD data. The Rietveld refinement is one of them proposed by Hugo M. Rietveld. It is extensively accepted owing to its whole-pattern fitting tactic rather than single-peak analysis. Rietveld refinement analysis technique shows the various advantages as it can effectually lessen or abolish the inaccuracies arising from preferred

particle statistics, orientation, peaks overlapping, and detection of trace phases. Under "n" iterations, the Rietveld technique performs a least square fitting analysis to adjust a hypothetical line profile to match the measured profile. A Rietveld refinement software like FullProf Suite may refine various refinement parameters like background, peak form, and lattice parameters. The pseudo-Voigt function is used to define the shape of the peaks in the XRD data, while linear interpolation between specific background points is used to determine the background or baseline level in the data. The Rietveld refinement is advantageous for quantifiable phase analysis, space group symmetry, residual stress, crystal structure and microstructural analysis.

2.3.3 Field emission scanning electron microscope (FE-SEM)

FE-SEM is a microscopic analytical technique that creates a highly magnified image based on the reflection of electrons while scanning by the electron beam produced from the mounted probe arranged to eject electrons. FE-SEM has the capability to scan the sample surface up to few microns. Following the instrumental description, FE-SEM is conducted into the vacuum chamber which holds the sample to be measured. The scanned sample's morphology is determined by the electrons that are reflected from the dark chamber after the electron is emitted from the probe to that chamber. The image captured from the FE-SEM may vary due to compositional and topographical or morphological (shape) features of the prepared samples.

2.3.3.1 Instrumentation and basic principle

Initially, the electron gun (probe) placed at the top, ejects electron beam in the vacuum chamber and follows the downward path through the electromagnetic fields. The electron beam focused onto the specimen using objective lenses fixed in the same chamber. This focused beam scans over the specific area of the specimen surface where the beam is rastered (point by point scan) across the material's surface using deflector coils, which is controlled by the scan generator. The size of the rastered region on the sample can be adjusted by the variation in magnification, as magnification controls the size of the rastered

area. When the electron beam strikes on the surface of the material, large number of signals are produced from the specimen such as electrons (secondary and backscattered) and X-rays [90]. These propagated signals are detected by the detector and converted into the signals which further produces the images (topology and morphology) of the specimen. The schematic diagram represents the principle followed to collect the FE-SEM images, as shown in Figure 2.7. Before capturing the FE-SEM image of the specimen, some pre-requisite must be followed to obtain the high-quality image. In the beginning, the applied accelerating voltages should be modulated according to the nature of the sample. The high accelerating voltage elevate the probe current which may reduce the contrast and signal to noise ratio. Indeed, high accelerating voltage may cause overcharging for conductive or non-conductive samples and reflect extreme brightness and poor image. Therefore, optimum high accelerating voltage is required to capture highly magnified image with good resolution. Moreover, non-conductive samples such as polymer, fibres, glass and ceramics are sputtered with a layer of carbon or metals such as gold/platinum/gold-palladium to prevent the sample from the cause of overcharging. The length of the line (or longitudinal area) that is scanned or “rastered” by the electron beam, as described in earlier section, directly affect the magnification (M). The magnification can be defined as the ratio of the length of the line on the screen (L) to the length of the rastered line on the material (l) and represented as $M = \frac{L}{l}$. Since, the size of the monitor is fixed, thus the variation on the length of rastered line can change the magnification of the reflected image. A wide area of scan results lower magnification whereas smaller scan area provides higher magnification. Thus, FE-SEM proved to be a versatile technique to obtain a remarkable feature of the materials such as morphology includes size, shape and organization of particles etc. [91].

In the current study, FE-SEM images were recorded using JEOL JSM-6490 scanning electron microscope, as shown in Figure 2.8. JEOL JSM-6490 is a modern field emission scanning electron microscope with 3 nm resolution, large sample chamber with advanced motorized stage and navigation supported by an

in-chamber camera. In this, high as well as low vacuum operation is possible. This microscope is equipped with additional features such as energy dispersive x-ray analysis (EDAX).

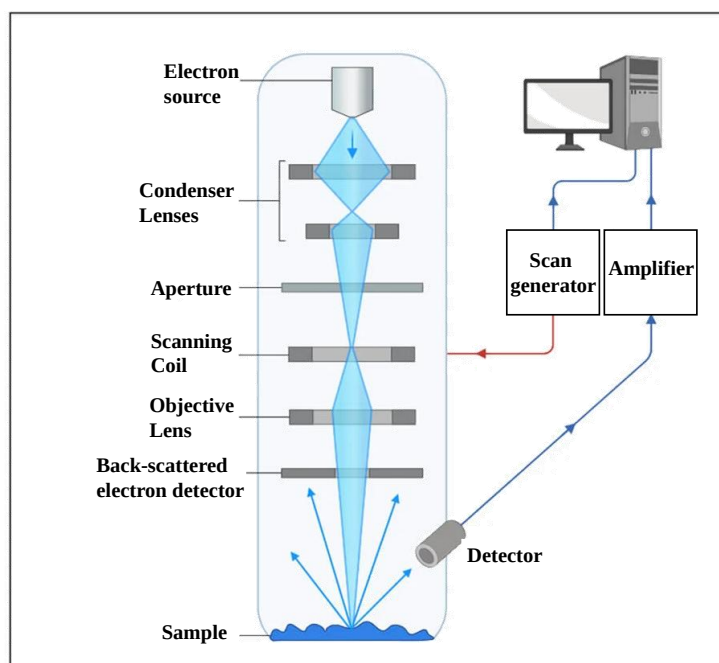


Figure 2.7 Schematic diagram of Field Emission Scanning Electron Microscope (FE-SEM).



Figure 2.8 JEOL JSM-6490 Field Emission Scanning Electron Microscope.

2.3.3.2 *Energy dispersive analysis of X-rays (EDAX)*

EDAX is a powerful technique and applied along with SEM/FE-SEM to analyse the types and quantity of the elements at the materials surface or in the vicinity of surface to provide specimen image. EDAX explained as the generation of X-rays from the sample through electron beam. Following the basic principle of EDAX technique, the X-rays are produced according to the characteristics and nature of the elements present in the material. Three principal components exist in the EDAX systems are X-ray detector, pulse processor (measure corresponding voltage of emitted X-ray) and a computer system. In the EDAX system, X-rays emitted from the sample are measured by the X-ray detector in which X-rays generate current. The small generated current further converted into voltage pulse associated with the X-rays produce by the element to accomplish the elemental analysis [82].

2.3.4 Fourier transform infrared spectroscopy (FT-IR)

2.3.4.1 *Instrumentation and basic principle*

FT-IR spectroscopy is one of the most widely used analytical techniques for the identification of functional groups in inorganic, organic and biological compounds. This versatile technique signifies the quality and consistency of the components. The IR source, interferometer, sample chamber, detector, and display screen are the main parts of the FT-IR system, which operates based on the Michelson interferometer fundamental concept. Figure 2.9 (a) represents the schematic of FT-IR spectroscopy. In the FT-IR system, interferometer contains two mirrors (movable and stationary) and one beam splitter. Initially, before reaching to the sample, the beam passes through interfere wherein the beam splits the radiation into two rays headed towards stationary and movable mirror. Once the rays reunite after travelling through different path with different mirrors, it results a signal called interferogram which consists information regarding the emitted IR radiation from the source. This information coded signals in the form of radiation strikes the sample where some part of the radiation is absorbed whilst some part is got transmitted. Further, specific signal is recollected in the detector based on the type of material and the bonds among the present

components. Since, the signal detected by the detector is difficult to read, thus it is decoded using well known mathematical tool known as Fourier transformation and the technique is called as Fourier transformation infrared spectroscopy. Figure 2.9 (b) represents the FT-IR Spectrometer (Perkin Elmer).

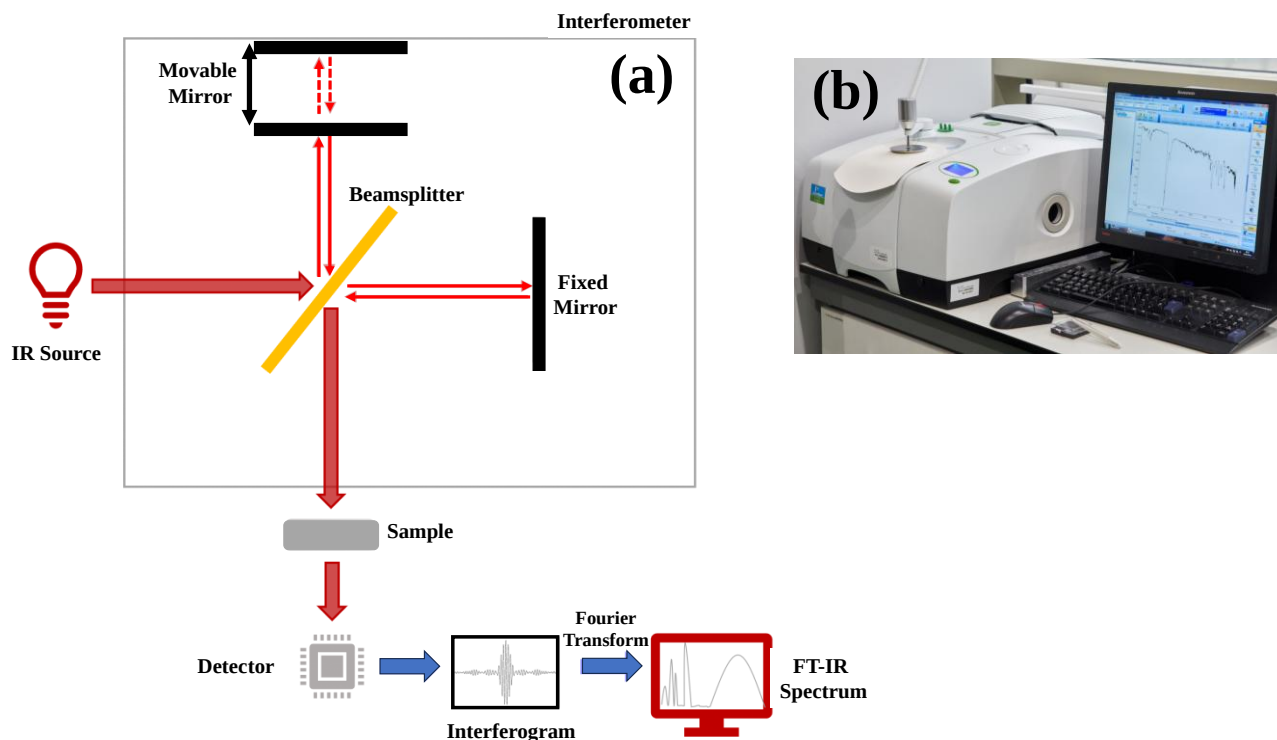


Figure 2.9 (a) Schematic diagram of FT-IR spectroscopy, (b) FT-IR Spectrometer (Perkin Elmer).

2.3.5 Diffuse reflectance spectroscopy (DRS)

2.3.5.1. Principle of DRS

DRS is one of the most crucial spectroscopic techniques based on the reflection of light in ultraviolet (UV), visible and near-infrared (NIR) regions to determine the optical band gap of the powder sample for various optoelectronic applications. In addition, the reflection of electromagnetic light generally occurs on the basis of the texture of the sample. In powder sample, the randomly oriented particles of variable sizes reflected the incident light in all angles into the hemisphere of provenance of light. Contrary to the regular (directed) reflection from the plane phase boundary, the phenomena caused by reflection, refraction, diffraction and absorption by particles oriented in all direction is known as diffuse reflection.

Figure 2.10 (a) illustrates that the incident light reflected in all directions by two types of reflection (i.e., specular and diffuse reflection) after interacting with the sample [92].

When a beam of electromagnetic radiation incident on the surface of the sample then the parts of incident light get reflected, absorbed and transmitted from the sample. The potential to reflect radiant energy is referred to as its reflectance. It is the portion of incident electromagnetic energy that is reflected at an interface and reflectance versus wavelength plot reveal the reflectance spectrum.

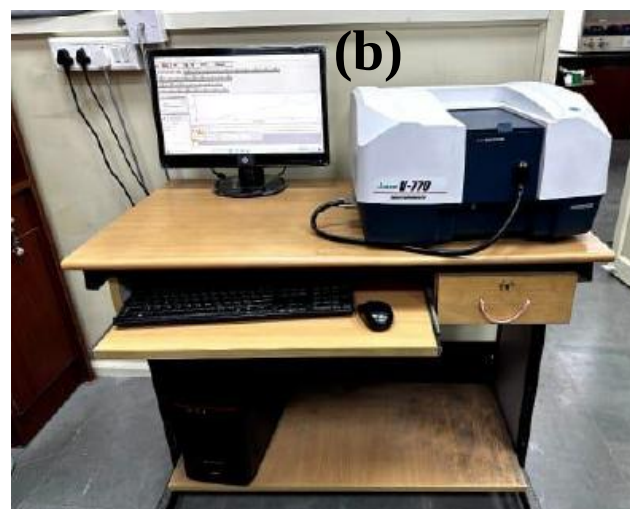
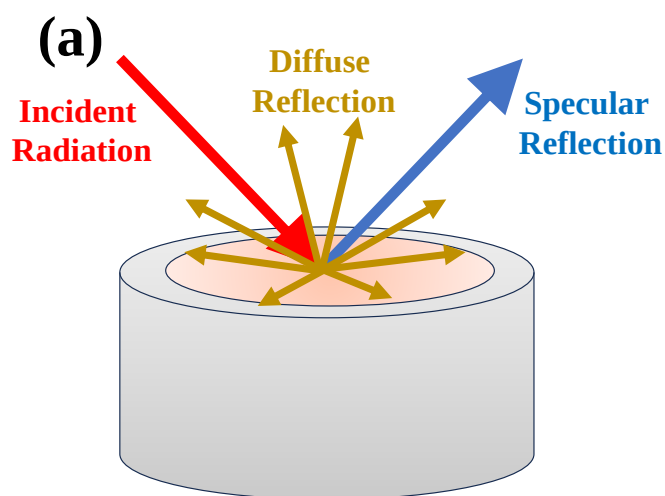


Figure 2.10 (a) Schematic diagram of reflectance from the sample (b) V-770 Jasco Spectrophotometer.

2.3.5.2. Formulation and data analysis of DRS

As expressed earlier, DRS is an essential technique used to determine the optical band gap of the powder samples. To evaluate the band gap (E_g) of the as-prepared materials, Tauc's method has been followed using the scientific relationship between E_g and α (optical absorption coefficient) as shown below:

$$\alpha h\nu = A(h\nu - E_g)^n \quad 2.6$$

where, α refers as the absorption coefficient, $h\nu$ is the energy of incident photons, A is the proportionality constant and n is the coefficient that reveals the type of electronic transition. The electronic transition depends upon the value of coefficient ' n ' expressed as the direct allowed transition for n equal to $1/2$, indirect allowed transition for n equal to 2 , direct forbidden transition for n equal to $3/2$ and indirect

forbidden transition for n equal to 3. Since, absorption is the factor essentially required to assess the Tauc's method successfully, however, the scattering component is rather acknowledgeable in case of powder samples. The recorded DR spectrum has been transformed into the equivalent absorption spectra using the function known as Kubelka-Munk (K-M) function or reemission factor $F(R_\infty)$, as given below [93]:

$$F(R_\infty) = \frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad 2.7$$

where, $R_\infty = \frac{R_{sample}}{R_{standard}}$

$$F(R) hv = B (hv - E_g)^n \quad 2.8$$

In the above equation, R_∞ denotes as the reflectance of the sample with “infinite thickness” and other parameters such as K , S and B represent absorption coefficient, scattering coefficient, and proportionality constant, respectively. The R_∞ is the ratio between the reflectance of the sample (R_{sample}) and diffuse reflectance of standard material ($R_{standard}$) where the standard material is typically being $BaSO_4$ or polytetrafluoroethylene (PTFE). Consequently, the optical band gap can be ascertained by extrapolating the linear streak to $(F(R)hv)^{\frac{1}{n}} = 0$ in $(F(R)hv)^{\frac{1}{n}}$ versus hv plot, using Equation 2.7.

The degree of disorder present in a structure is represented by Urbach's law and the following formula was used to calculate the Urbach's energy (ΔE) [94]:

$$\alpha(\nu) = C \exp\left(\frac{h\nu}{\Delta E}\right) \quad 2.9$$

where C , ΔE and ν are constant, Urbach's energy and the radiation frequency, respectively. The magnitude of Urbach's energy is calculated using the inverse of the slope of the linear section of the $\ln(\alpha)$ vs $h\nu$ (eV) graphs. In this experimental work, the diffuse reflectance measurement has been carried out at room temperature using V-770 Jasco spectrophotometer as shown in Figure 2.10 (b).

2.3.6 PL spectroscopy

Any light-sensitive substance, such as powder, liquid, glass, or thin-film samples, can have its photo-excitation and photo-emission measured using the versatile, non-destructive, and contact-free PL spectroscopy approach. PL studies have been recognized as one of the most sensitive and commonly employed tactics of exploring the optical properties of materials, such as luminescence of impurities, band structures, absorption, and point defects with high accuracy. The sample is generally subjected to various light wavelengths, resulting in the absorption of certain beams. This absorption excites the ions within the sample, leading to de-excitation processes that emit radiative transitions, ideally within the visible spectrum, alongside several non-radiative relaxation pathways [17,95]. PL spectroscopy is a powerful technique to examine transition and radiative/non-radiative recombination's of carrier ions in light influenced materials. PL spectroscopy can offer applicability in the fields of molecular electronics, environmental sciences, medical diagnostics, industries, day to day life devices and cell biology.

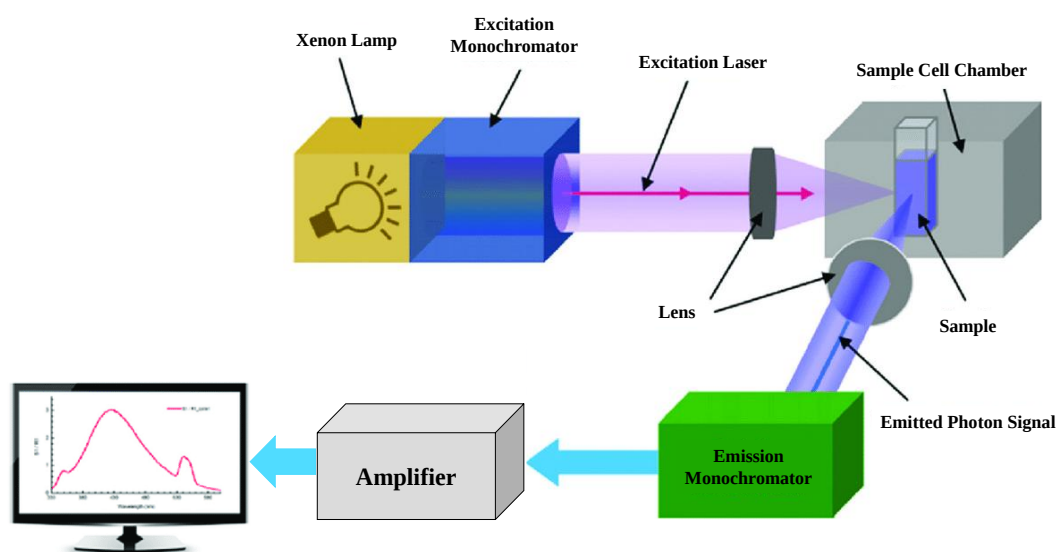


Figure 2.11 Schematic representation of PL spectrofluorometer.

The PL spectrofluorometer comprises an excitation light source, monochromator, sample cell, a number of lenses, photodetector, amplifier etc. and connected with computer, which operates and records the experiential spectrum as demonstrated in Figure 2.11. The source of excitation employed, should give continuum spectrum in the desired wavelength range. Xenon lamp can provide a moderately continuous

light output and used as light source, which emits light in 200-800 nm range. The emitted light beam is passing through the monochromator. The most common type of monochromators employs a diffraction grating. A monochromator utilizes a diffraction grating, whereby collimated light is directed onto the grating, resulting in the light emerging at varying angles based on its wavelength. The monochromator can be configured to selectively transmit specific wavelengths. The excitation monochromator serves to isolate a specific wavelength of light from the incoming beam. When the incident light interacts with the sample, a portion of it is absorbed, leading to the emission of light isotropically. Angle of 90° is chosen for emitted light and some of the light passes through the emission monochromator and reaches detector. The emitted light sensed by the photomultiplier tube as a detector. Detector can be a single-channel (senses only one wavelength at a time) or multichannel (detects all emitted wavelengths). All the components were handled and commanded with the help of dedicated software in a computer system. Finally, the detected spectrum was amplified using the photomultiplier tube, and then converted in a signal form and recorded by the computer for further investigation. The computer screen displays the recorded spectrum in terms of intensity as a function of the wavelength of emitted light.

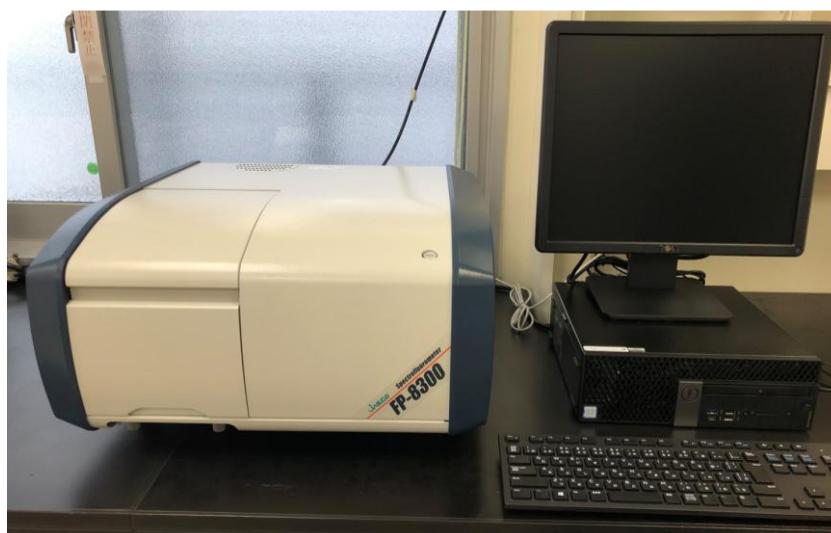


Figure 2.12 Jasco FP-8300 spectrofluorometer.

PL is the physical phenomena in which emission of light from material under the excitation of various wavelength of light sources. The PL characteristics were recorded by Jasco FP-8300 spectrofluorometer

equipped with 150-watt Xenon lamp as a source of excitation as depicted in Figure 2.12. To record the PL characteristics, initially sample holder is completely filled with prepared phosphor, placed at appropriate position in the path of incident source of excitation beam. The excitation and emission spectra were measured by selecting the appropriate emission/excitation wavelength with scan mode at a medium scan rate, slit width at 0.1 nm and high voltage photomultiplier tube (PMT) setup. The excitation profile is obtained by scanning a certain range of wavelengths while monitoring a definite and fixed emission wavelength. The emission spectra will also be recorded using the bands that were seen in the excitation spectrum. Finally, software displays the spectrum with plot between the intensity of emitted light and the wavelength.

2.3.7 Time-Resolved Photoluminescence (TRPL) Spectroscopy

TRPL is a highly effective technique for investigating both fast and slow electronic deactivation processes that lead to photon emission from specific energy levels in luminescent materials upon excitation by a particular source. This phenomenon is referred to as photoluminescence decay time or lifetime. The PL lifetime is an intrinsic property of a luminescent material, which provides the clear understanding of the material excited state dynamics. PL lifetime variations can therefore provide evidence about the local chemical environment of the materials.

The important components of TRPL are the pulsed light source (Xenon flash lamp, pulsed laser), an excitation and emission monochromators, single-photon sensitive detector, handled by computer with the dedicated software. A fast photodetector is used for recording the emission of a sample as a function of time while it is being excited by a specific pulse light source. This technique can be used to keep track of the quality of the material, identify spectral emissions with distinct emissive states, or investigate how energy is transferred from one constituent to another in mixed composites and samples. The recorded lifetime is an intrinsic characteristic of PL properties that can provide insight into the excited state dynamics [96]. The PL lifetime curve was recorded at room temperature by Edinburgh FLSP920 as seen

in Figure 2.13. Microsecond Xenon flash lamp source and single photon count PMT detector were attached with the instrument.



Figure 2.13 TRPL Edinberg FLSP920 spectrofluorometer.

The PL lifetime curves were fitted with different exponential equations. It can be observed that all the decay curves were fitted bi-exponentially with the following equation [97]:

$$I_t = I_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad 2.10$$

where I_t and I_0 denote the luminescence intensities at time t and 0, respectively. A_1 and A_2 are fitting constant. τ_1 and τ_2 represent the rapid and slow decay lifetimes. The average value of the decay time for samples was evaluated from the given formula [98]:

$$\tau_{\text{avg}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad 2.11$$

The PL lifetime for the RE ions doped luminescent materials usually ranges from a few microseconds up to milliseconds. The luminous quantum efficiency (η) is defined as the ratio of the number of the photons emitted to the number of photons absorbed. Here we define this in terms of lifetime i.e., η is the ratio of average lifetime (τ_{avg}) and radiative lifetime (τ_{rad}) and can be represented using the following equation [99]:

$$\eta = \frac{\tau_{\text{avg}}}{\tau_{\text{rad}}} \times 100\% \quad 2.12$$

Moreover, the energy transfer efficiency η_T in the context of co-doped phosphor materials is determined using the following relation [100]:

$$\eta_T = 1 - \frac{\tau_{\text{avg}}}{\tau_{\text{rad}}} \quad 2.13$$

The following given formula is employed for calculating the energy transfer probability (P_T), which quantifies the likelihood of energy transfer occurring from the donor ions to the acceptor ions [100]:

$$P_T = \frac{1}{\tau_{\text{avg}}} - \frac{1}{\tau_{\text{rad}}} \quad 2.14$$

2.3.8 Temperature Dependent Photoluminescence (TDPL) Spectroscopy

TDPL is one of the most effective, fundamental and influential optical feature investigation tools, extensively used to examine localized states, thermal stability and carrier transport in semiconductor or luminescent materials. In TDPL spectroscopy, PL spectra of the as prepared luminescent materials have been carried out at different temperatures and find out the change in PL characteristics with rise or fall in temperature. Based on the PL spectra carried out at different temperatures, a methodological theory has been established to examine the thermal stability, defects related to non-radiative transitions and carrier transport dynamics.

The important components of TDPL spectrofluorometer are the light source (Xenon lamp, laser), monochromator, temperature-controlled sample holder, photodetector and computers with the dedicated software as represented in Figure 2.14. A Xenon lamp is used as a light source, which emits light in 200-800 nm range. The emitted beam of light is passes through the monochromator, which can select the desired wavelength of light used for excitation. The selected wavelength incident on the temperature-controlled sample holder via optical fiber.

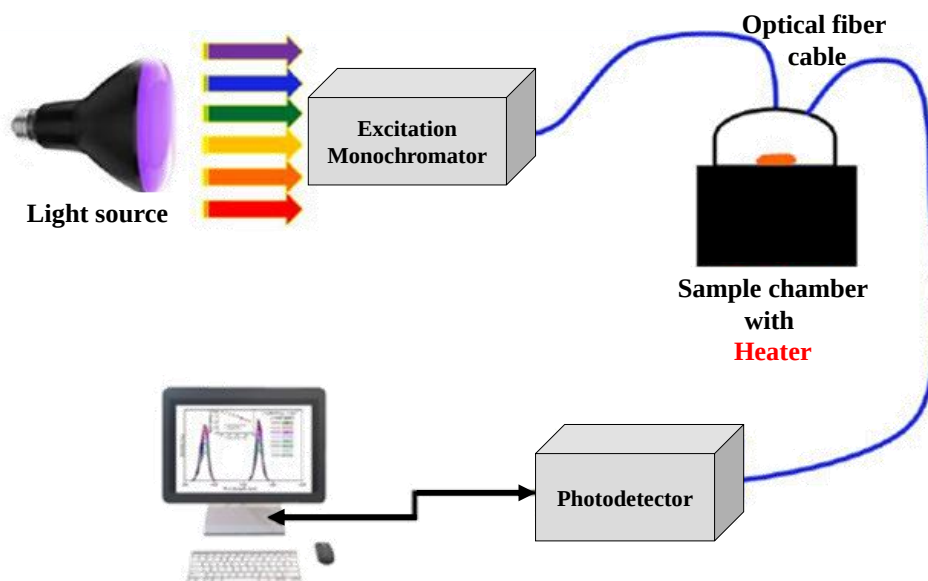


Figure 2.14 Schematic representation of TDPL spectrofluorometer.

Luminescent sample emits light under particular excitation wavelength, which can be passed through another optical fiber and detected by photodetector. Finally, the detected spectrum was recorded by computer for further process. In the current research work, the TDPL features of the as prepared phosphors are recorded by employing Ocean Optics FLAME-S-XR1-ES spectrofluorometer as demonstrated in Figure 2.15.



Figure 2.15 TDPL characterization setup with ocean Optics spectrofluorometer.

In TDPL data, the emission intensity of luminescent materials under certain source of excitation wavelength can be increased/decreased with elevated temperatures. The effect of temperature on the PL properties of phosphor materials is one of the significant features of the applicability of phosphor in many photonic and temperature sensor applications. One of the critical requirements for phosphors used in LED applications is the ability to maintain emission intensity at elevated temperatures, such as 423 K, which is the operating temperature of the LED. The temperature-dependent emission spectra illustrate the relative intensity of the phosphors under dominant excitation conditions compared to their intensity at 303 K.

Typically, a decline in intensity is observed with an increase in temperature due to the thermal quenching effect. This thermal quenching occurs as a consequence of non-radiative relaxation processes within the phosphors. The relationship between temperature and the non-radiative emission rate (R_{nr}) can be mathematically described as follows:

$$R_{nr} = K \exp\left(-\frac{\Delta E_a}{k_B T}\right) \quad 2.15$$

where, k_B denotes Boltzmann's constant, valued at 8.61733×10^{-5} eV/K ; K is a constant; and ΔE_a signifies the activation energy associated with thermal quenching. The activation energy ΔE_a represents the energy difference between the minimum energy level of the excited state parabola and the intersection point of the excited and ground state energy levels. It is clear from the Equation 2.15, that increase in temperature will increase the non-radiative relaxations rate, which leads to a decrease in emission. Changes in relative emission intensity as a function of increasing temperature can be utilized to determine the activation energy ΔE_a of the phosphor, as described by the Arrhenius equation provided below [101]:

$$I_T = \frac{I_0}{1 + \alpha \exp\left(-\frac{\Delta E_a}{k_B T}\right)} \quad 2.16$$

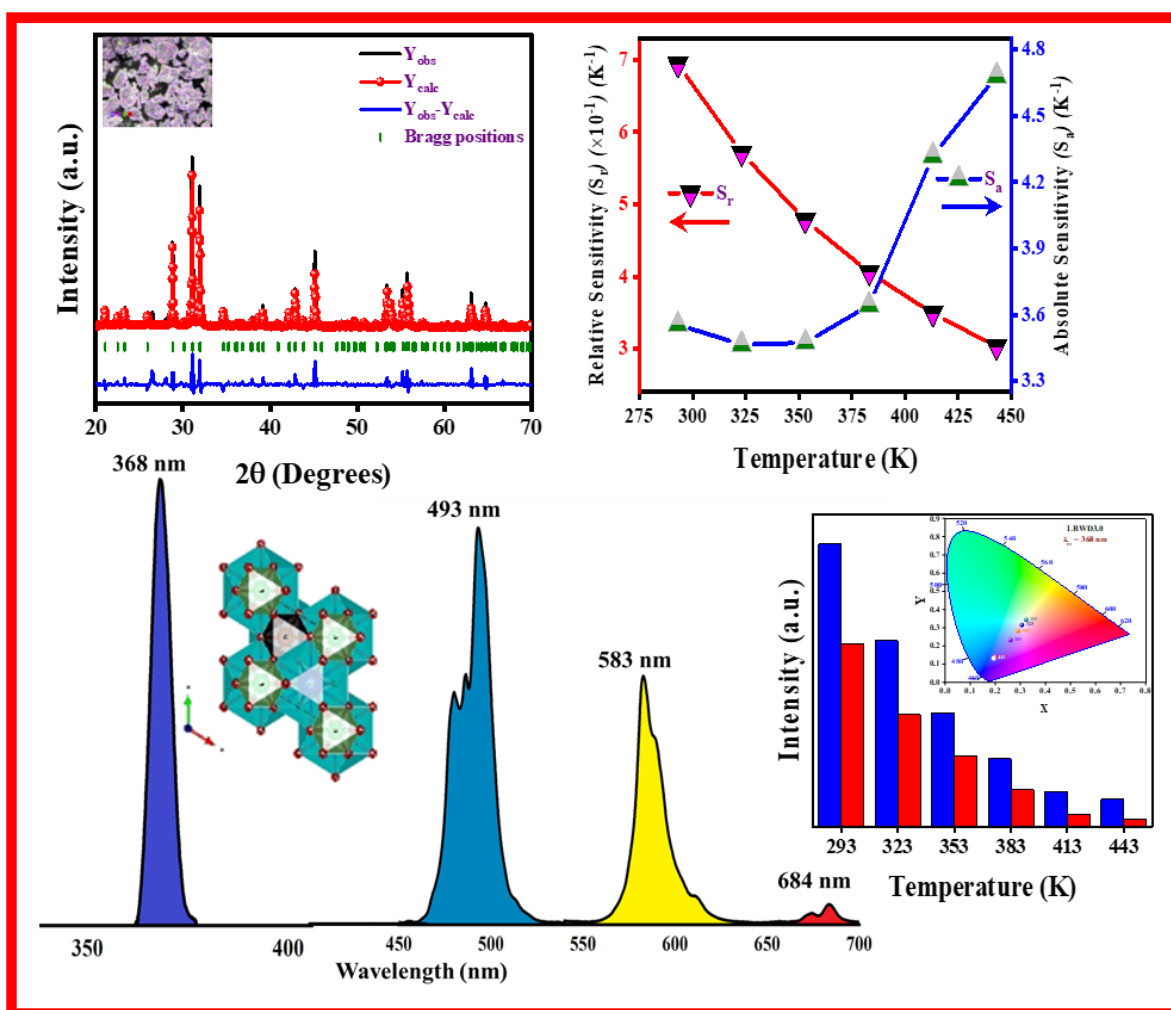
here, I_0 and I_T represent the luminescent intensities at the initial and testing temperatures, respectively, while α is a constant factor. The relationship between $\ln\left[\left(\frac{I_0}{I_T}\right) - 1\right]$ and $\left(\frac{1}{k_B T}\right)$ for the most intense emission

peak of the phosphor yields a linear graph with a specific slope, which can be used to calculate the activation energy ΔE_a . The value of ΔE_a , expressed in electron volts (eV), serves as an indicator of the thermal stability of the phosphor. A higher activation energy value correlates with improved thermal stability of the phosphor material.

The parameters related to temperature sensing were evaluated in Chapter 1, section 1.6.

CHAPTER 3

TEMPERATURE SENSING MATERIALS BASED ON THE FLUORESCENCE INTENSITY RATIO IN $\text{Li}_2\text{BA}_5\text{W}_3\text{O}_{15}:\text{DY}^{3+}$ PHOSPHORS



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3.1 INTRODUCTION

Researchers have been motivated to enhance the properties of phosphors due to the continual increase in demand and the wide range of uses for luminous materials. These luminous materials are used in a variety of industries, including sensing, solid-state lighting, lasers, sophisticated displays, optical storage, display fields, OLEDs and many more [102–105]. Since temperature is a critical and fundamental characteristic used to characterize biological, chemical, and physical processes, one of the main uses of photonic devices is to sense real-time temperature with great accuracy [106,107]. Also, with the advancement of science and technology, biological imaging and large-scale integrated (LSI) circuits created new demands for temperature measurement tolerance, high spatial resolution and remote detection [108]. Currently, there are two types of temperature measurement technologies, one is common contact temperature dimensions, and another is non-contact temperature sizes. Yet, in some unique circumstances such as electromagnetically or thermally demanding areas and organisms, using thermocouples [47] and glass liquid thermometers, the conventional contact temperature measurements are carried out [55]. The usage of contact temperature measuring instruments is challenging by virtue of the condition of contact. Therefore, the study of non-contact thermometers is very important not only from the point of view of non-contact but also from financial viability. Non-contact phosphor thermometers have been a focus of research in the field of temperature measurement because of their assets such as great selectivity, high accuracy, sensitivity and prolonged lifetime [51,109]. Further, non-contact thermometers, compared to conventional contact thermometers, are better suited to measure the temperature of inaccessible objects in environments with strong electromagnetic fields, high pressures, or corrosive conditions with high precision, high sensitivity, and a large relevant temperature range [43,47,110]. The investigation of non-contact optical thermometers has also received a great deal of attention since they have the potential to solve the shortcomings of standard thermometers, such as their slow response time and imprecision. One of the most sophisticated methods for measuring surface temperature is phosphor thermometry, which

makes use of the PL properties of materials with RE and transition metal inclusions in both crystalline and amorphous forms [111,112].

The sensitivity of the luminescence properties of RE ions doped luminous materials is the basis for temperature measurement. One of the most popular approaches in this research field is temperature measurement based on FIR, originating due to the Boltzmann distribution of two separate excitation power stages which vary with change in temperature [113]. Contrarily, the ambient factors that affect temperature measurement are unaffected by FIR temperature measuring technology and minimize or eliminate external interference. This matters for the consistency, precision, and dependability of the non-contact thermometers [114]. RE ions provide the best circumstances for their various energy levels and characteristic 4f electron structure for TCLs, which are valuable for use in the FIR temperature measurement [115]. Among all the RE ions, the TCLs of Dy^{3+} ions have the relatively high FIR temperature measuring sensitivity. Many researchers have already used Dy^{3+} ions as dopants to achieve the temperature sensor applications, given in the literature [116,117]. All the aforementioned research results prompted us to take up a comprehensive investigation on Dy^{3+} ions doped LBW phosphors to understand their usefulness in non-contact temperature sensing applications using FIR temperature statistics.

Tungstates $(\text{WO}_4)^{2-}$, which are known for their luminous qualities, offer a substantial amount of light efficiency in comparatively small volumes. They are utilized in complete gamma (γ) quanta absorption detectors, industrial and medical scanners, and X-ray detectors [118,119]. Due to its self-activating luminescence, tungstates have undergone substantial research as host materials with the doping of the RE ions [120]. The $(\text{WO}_4)^{2-}$ molecule exhibits an internal emission at around 420 nm in the luminescence graph in the literature, which is caused by the electronic transitions between tungsten and oxygen [121,122]. In this context, we report the preparation of novel $\text{Li}_2\text{Ba}_{(5-x)}\text{W}_3\text{O}_{15}:\text{x}\text{Dy}^{3+}$

($1 \leq x \leq 5$, $\Delta x = 1$ mol%) down-conversion phosphor materials. The objective of this study is to choose an inorganic phosphor that is appropriate for non-contact temperature sensor applications.

3.2 SAMPLE PREPARATION

Dysprosium ion-doped LBW phosphors were synthesized at varying concentrations of Dy^{3+} ions (0.01, 0.02, 0.03, 0.04 and 0.05 or say 1.0, 2.0, 3.0, 4.0, and 5 mol%) utilizing conventional SSR technique as discussed in section 2.2.1 and the detailed flowchart of procedure is shown in Figure 2.2 of chapter 2. The highly pure chemicals Li_2CO_3 (99.0%), BaCO_3 (99.99%), WO_3 (99.99%), and Dy_2O_3 (99.99%) have been taken as raw materials in stoichiometric ratio.

3.3 RESULTS AND DISCUSSION

3.3.1 Structural studies

3.3.1.1 X-ray diffraction analysis

XRD for all the powdered samples $\text{Li}_2\text{Ba}_{(5-x)}(\text{WO}_5)_3\text{:xDy}^{3+}$ ($1 \leq x \leq 5$, $\Delta x = 1$ mol%), annealed at 1200°C for 6 h were recorded in the 2θ range from 20° to 70° to obtain all crystalline peaks and depicted in Figure 3.1 (a). All the samples belong to a hexagonal crystal structure with $P6_3mc$ space group (186). For all the different compositions of dopant (Dy^{3+}), the crystalline single-phase hexagonal structure of LBW phosphor was formed without any second phase which is in good agreement with the JCPDS card no. 01-072-1717. Therefore, doping of Dy^{3+} into the LBW host does not distort the crystal structure, indicating that the trivalent RE ion Dy^{3+} has been correctly accumulated within the host matrix in place of the Ba^{2+} lattice position.

Using the W-H plot formalism given by equation 2.5 in section 2.3.2.4, the strain (ϵ) and crystallite size (D) for LBW:x Dy^{3+} ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors were computed [123]. As indicated by the W-H plot in Figure 3.1 (b), a graph is plotted between $\beta \cos \theta$ (along the y-axis) and $4 \sin \theta$ (along the x-axis) to

determine the values of parameters 'D' and ' ϵ ' for LBW:x Dy³⁺ ($0 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors and tabulated in Table 3.1.

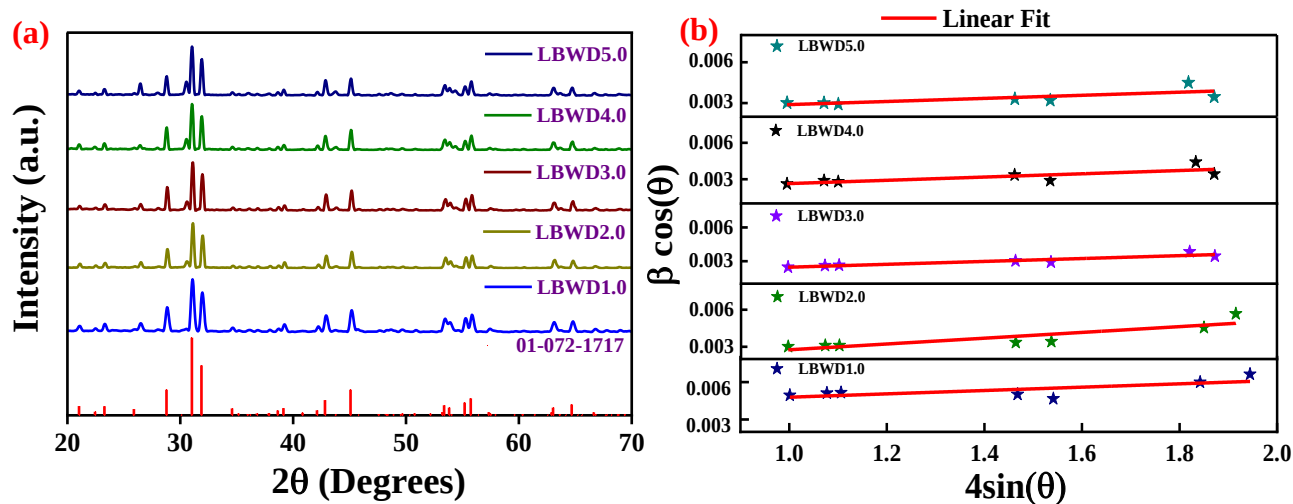


Figure 3.1 (a) The XRD patterns for LBW:x Dy³⁺ ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors, (b) A graph between $\beta \cos\theta$ and $\sin\theta$.

Table 3.1 Crystallite size D (nm) and Strain (ϵ) values for LBW:xDy³⁺ ($0 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors.

Dy ³⁺ (%)	Li ₂ Ba _(5-x) Dy _x (WO ₅) ₃	Crystallite size D (nm)	Strain (ϵ) ($\times 10^{-3}$)
0	x = 0	85	0.45
1	x = 1 mol%	80	0.41
2	x = 2 mol%	75	0.13
3	x = 3 mol%	74	0.13
4	x = 4 mol%	73	0.14
5	x = 5 mol%	70	0.34

All the compositions undergo Rietveld refinement using the FullProf Suite programme to be more thoroughly investigated structurally. The backgrounds were improved using fifteen cycles of linear interpolation, and for each composition, the pseudo-Voigt function was employed to fit the experimental data. The atomic positions of O, Li, Ba and W ions did not change significantly throughout the refining process. Figure 3.2 shows the Rietveld refinement map for an un-doped LBW and a doped (LBWD3.0)

phosphor sample. The black line in the refined map for each composition represents the observed intensity data, the red line with a circle represents the refined calculated intensity, the blue line illustrates the difference between the calculated and the observed intensities, and the green perpendicular line symbolizes the positions of Bragg's peaks. The goodness value for all refined compositions, which should fall between 1.0 and 2.0, is the most appropriate. Table 3.2 lists all the related crystal structure parameters for all the phosphor samples.

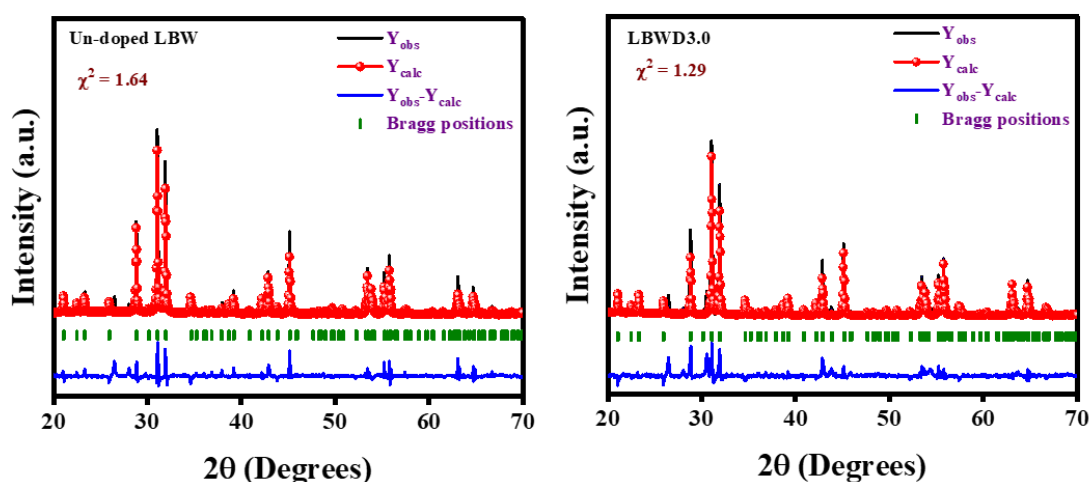


Figure 3.2 The Rietveld refinement map for an un-doped LBW and LBWD3.0 phosphor.

The VESTA software was used to analyse the crystal structure for the host lattice. The crystal structure of the host lattice contains 214 atoms, 348 bonds and 42 polyhedra including five Barium (Ba) atoms, two lithium (Li) atoms, three tungsten (W) atoms and five oxygen (O) atoms. The Li and W atoms are coordinated with six oxygen atoms and Ba is coordinated with 12 oxygen atoms. The complete crystal structure is shown in Figure 3.3.

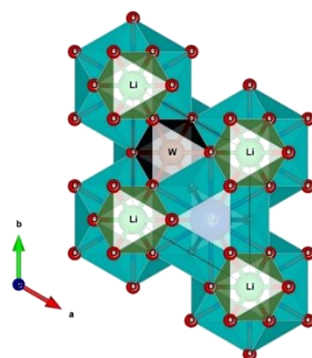


Figure 3.3 The crystal structure for LBW host lattice.

Table 3.2 Refinement parameters for LBW:xDy³⁺ (0 ≤ x ≤ 5, Δx = 1 mol%) phosphors.

Sample	JCPDS	Un-doped LBW	LBWD1.0	LBWD 2.0	LBWD 3.0	LBWD 4.0	LBWD 5.0
a = b (Å)	5.76	5.757	5.760	5.758	5.758	5.755	5.757
c (Å)	23.742	23.714	23.727	23.724	23.724	23.713	23.719
V (Å ³)	682.17	680.863	681.852	681.272	681.182	680.243	680.936
R _B	-	12.4	17.7	21.5	21.5	28.9	24.8
R _p (%)	-	30.3	33.1	35.9	38.1	37.2	41.8
R _{wp} (%)	-	33.3	38.5	39.9	42.2	42.0	46.7
R _{exp} (%)	-	11.3	16.0	14.6	15.6	17.6	17.0
χ ²	-	1.64	1.76	1.47	1.29	1.71	1.81
Density (g/cm ³)	7.264	7.387	7.270	7.274	7.275	7.285	7.278

3.3.1.2 Morphology and elemental analysis

Surface morphology for the as prepared phosphor samples were studied using FE-SEM and EDAX analysis. Figure 3.4 (a) represents the FE-SEM picture of an LBWD1.0 phosphor. As can be seen, the particle size and morphology of the phosphor are non-uniform. However, the synthesized samples exhibit an agglomeration phenomenon due to the high-temperature reaction. A histogram is plotted using ImageJ software to find the average particle size for the as-prepared LBWD1.0 phosphor sample, as shown in Figure 3.4 (b). The phosphor particles with size range in micrometers (μm) have been considered more convenient for the use in pc w-LEDs [124].

As shown in Figure 3.5 (a), the elemental composition of the as prepared LBWD1.0 phosphor was monitored by EDAX. Figure 3.5 (a) contains several sharp peaks corresponding to Ba, W, O and Dy atoms. The total element distribution map, shown in Figure 3.5 (b), demonstrates the elements' consistent distribution over the outside surface. Figure 3.5 (c-f) shows the relative element points of various colours against a dark background; blue, purple, green, and red correspond to Ba, W, O, and Dy, respectively.

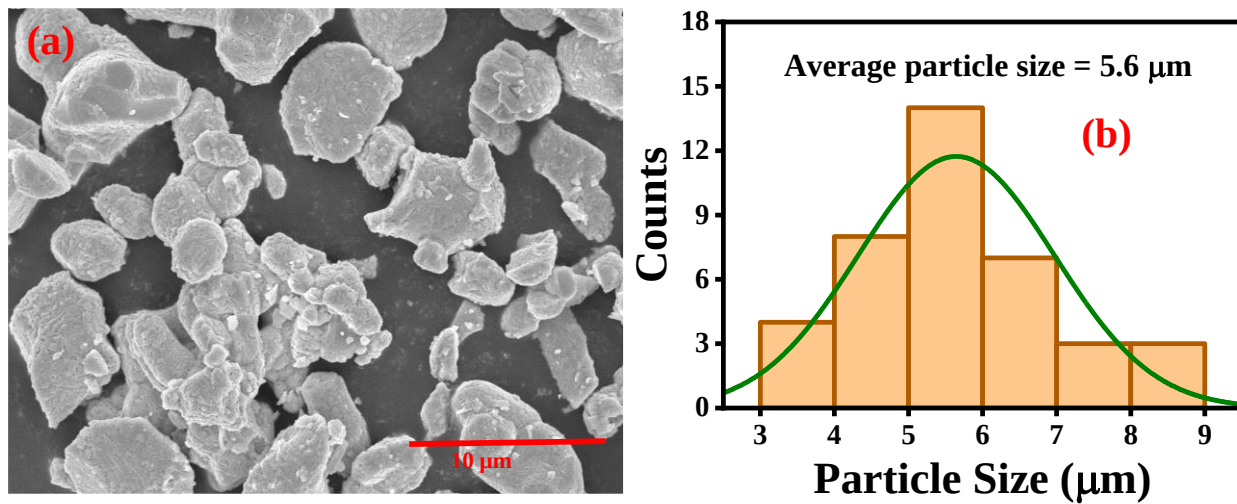


Figure 3.4 (a) The FE-SEM picture and (b) Histogram for LBWD1.0 phosphor.

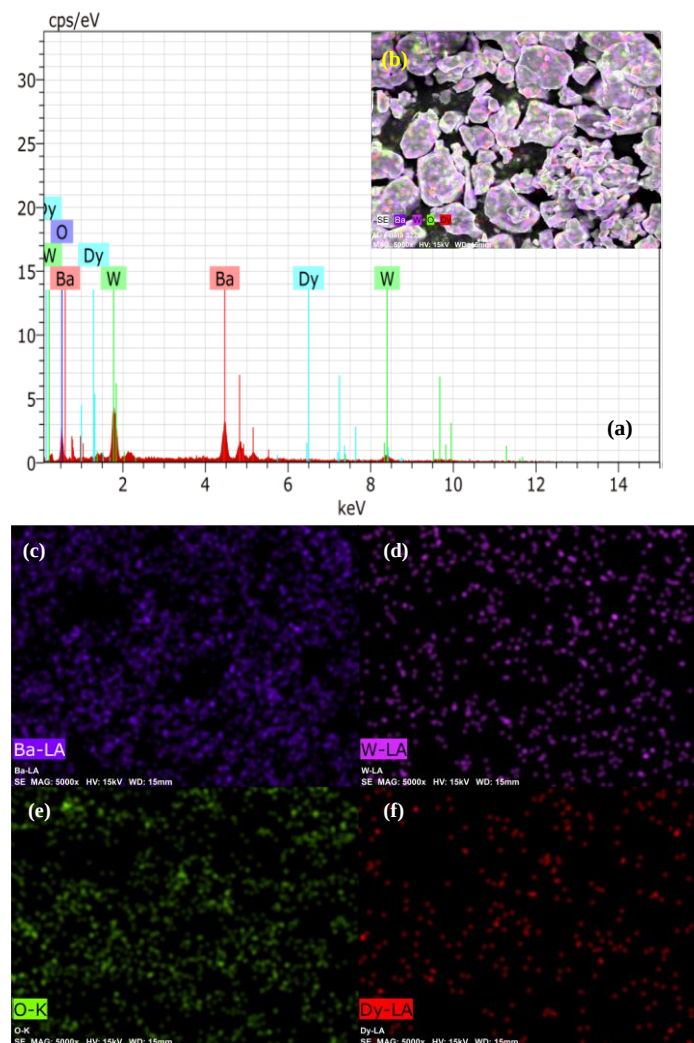


Figure 3.5 (a) The EDAX representation of the elemental composition of LBWD1.0 phosphor, (b) The total element distribution map, (c-f) shows the relative element points of various colors against a dark background; blue, purple, green, and red corresponding to Ba, W, O, and Dy elements respectively.

These findings reveal that the components of the as prepared LBWD1.0 phosphor are distributed equivalently. It is clear from the literature that light elements like Li, which have very low energy characteristic radiation, do not show any peaks in their EDAX spectrum [125].

3.3.2 Optical and photoluminescence analysis

3.3.2.1 Absorption spectral analysis

To determine how the doping of Dy^{3+} affect the absorption performance, the DRS of the LBW:xDy^{3+} ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) samples were examined and is shown in Figure 3.6. The enhanced absorption in the range of 300-400 nm is visible in DRS of both an undoped and Dy^{3+} ions-doped LBW phosphor, and is attributed to the ligand-to-metal charge transfer, or $\text{O}(2p)\text{-W}(5d)$ electronic transition [126]. Apart from the UV absorption band emerging from the host, subsequent distinctive 4f-4f absorption peaks of Dy^{3+} ions were found for all the as prepared LBW:xDy^{3+} ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors, providing additional evidence for successful incorporation of Dy^{3+} ions into LBW host lattice. These absorption peaks correspond to the transitions from the excited states ${}^6\text{F}_J$ ($J=3/2, 5/2$, and $7/2$) to the ground state ${}^6\text{H}_{15/2}$ [127,128]. The bandgap is calculated using K-M function, presented in equations 2.7-2.8 in section 2.3.5, and plotted a graph between $h\nu$ (incident energy) and $[\text{F(R)}h\nu]^2$, called Tauc's Plot for an undoped and Dy^{3+} ions doped LBW phosphor samples. By extrapolation of the linear portion of the graph to the x-axis, the bandgap values of the as prepared phosphor samples were evaluated.

The direct band is evaluated for an undoped as well as Dy^{3+} ions doped LBW phosphors and is shown in the inset of Figure 3.6. With an increase in Dy^{3+} ions concentration from 0 to 5 mol%, the E_g value slightly decreases from 3.74 to 3.62 eV, which may be due to the 4f energy level of Dy^{3+} ions [129]. On the other hand, the little decrease also suggests that the samples under consideration crystallized efficiently [127].

To learn more about how ligand ions connect to their environment, it is also important to take into consideration the nephelauxetic ratio (β) and bonding parameter (δ). The K-M function is applied to the DRS to convert it to an absorption spectrum, which is then used to calculate the β and δ parameters. The

equation provided in the reported work [130] is used to determine the values and bonding parameters and mentioned in Table 3.3.

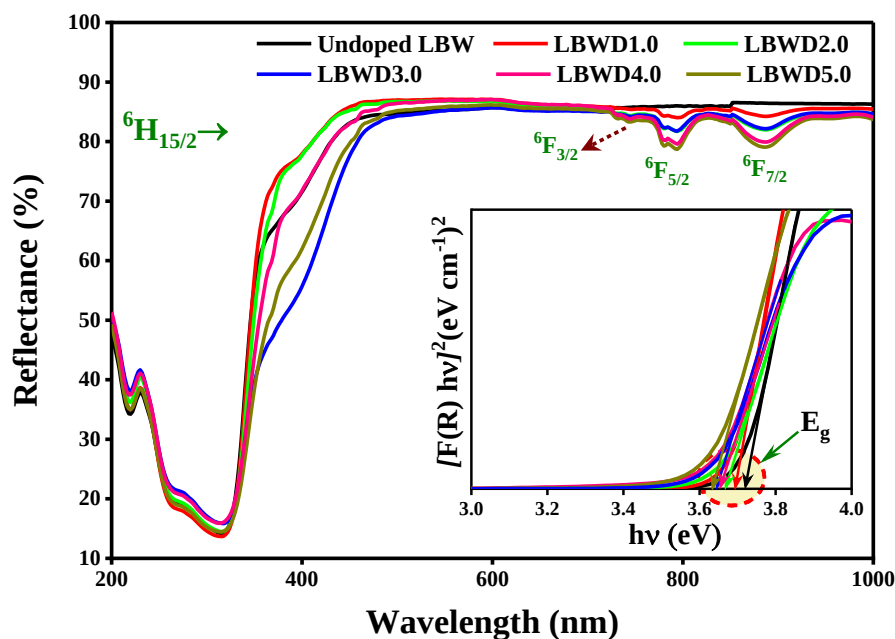


Figure 3.6 DRS of the LBW: xDy^{3+} ($0 \leq x \leq 0.05$, $\Delta x = 0.01$) phosphors [Inset shows the direct band gap for of the LBW: xDy^{3+} ($0 \leq x \leq 0.05$, $\Delta x = 0.01$) phosphors].

The nature of the Dy^{3+} ions' interactions, i.e., either covalent or ionic, with their surroundings is displayed by the sign of the bonding parameter [33]. The Dy^{3+} ions are ionic when they interact with the LBW matrix, as shown by the negative values of δ parameters.

Table 3.3 Band gap (E_g), Nephelauxetic ratio (β) and Bonding parameter (δ) for LBW: xDy^{3+} ($0 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors.

Dy^{3+} (%)	$\text{Li}_2\text{Ba}_{(5-x)}\text{Dy}_x(\text{WO}_5)_3$	Band Gap (eV)	Nephelauxetic ratio (β)	Bonding parameter (δ)
0	$x = 0$	3.74	-	-
1	$x = 1$ mol%	3.68	1.0240	-2.3437
2	$x = 2$ mol%	3.66	1.02446	-2.3874
3	$x = 3$ mol%	3.64	1.02492	-2.4311
4	$x = 4$ mol%	3.63	1.02477	-2.4175
5	$x = 5$ mol%	3.62	1.0240	-2.3437

3.3.2.2 PL excitation and emission spectroscopy

The PL excitation and PL emission spectra of LBW:xDy³⁺ ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors are well displayed by Figure 3.7 and Figure 3.8, respectively. By choosing a PL emission wavelength (λ_{em}) of 493 nm, the PLE spectra was recorded for the entire series of Dy³⁺ substituted LBW in the spectral range from 320 to 460 nm, as shown in Figure 3.7.

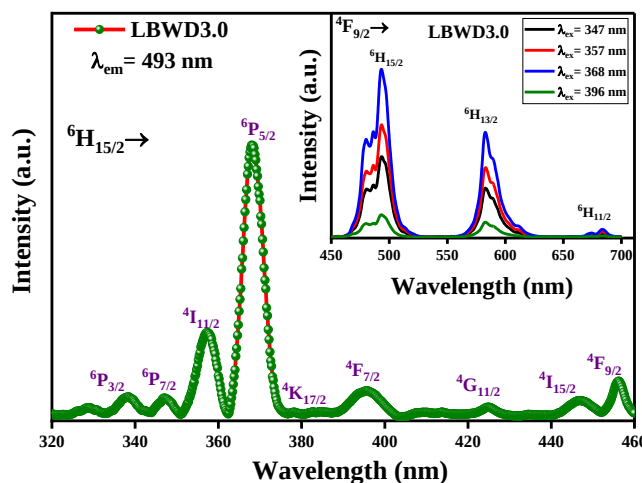


Figure 3.7 PL excitation spectrum for LBWD3.0 phosphor [Inset shows the PL emission spectra of the LBWD3.0 phosphor measured at different excitation wavelengths, i.e., 347, 357, 368 and 396 nm].

As a result nine PL excitation bands were observed from the ground state $^6H_{15/2}$ to various excited states $^6P_{3/2}$, $^6P_{7/2}$, $^4I_{13/2}$, $^6P_{5/2}$, $^4K_{17/2}$, $^4F_{7/2}$, $^4G_{11/2}$, $^4I_{15/2}$ and $^4F_{9/2}$ at 338, 347, 357, 368, 378, 396, 425, 447 and 456 nm respectively [131]. The strongest excitation band, $^6P_{5/2}$, is located around 368 nm. The PL emission spectra of LBWD3.0 phosphor were measured at different excitation wavelengths, i.e., 347, 357, 368, and 396 nm, as shown in the inset of Figure 3.7. The PL emission intensity at 368 nm excitation is regarded as optimal owing to have relatively higher PL intensity than the others, may be due to the substantially increased absorption at 368 nm wavelength. As a result, PL emission spectra for LBW:xDy³⁺ ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors were recorded monitoring the excitation wavelength (λ_{ex}) at 368 nm, as shown in Figure 3.8. Three emission peaks were visible in the PL emission spectra at wavelengths of 493 nm (blue), 583 nm (yellow), and 684 nm (red), which corresponded to the $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$ transitions, respectively [132]. The magnetic dipole (MD) transition, corresponding to $^4F_{9/2} \rightarrow ^6H_{15/2}$

at 493 nm, dominates among these transitions, while the hypersensitive (forced electric dipole (ED)) transition, corresponding to ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ at 583 nm, with ($\Delta L = 2$; $\Delta J = 2$) is relatively less intense [133].

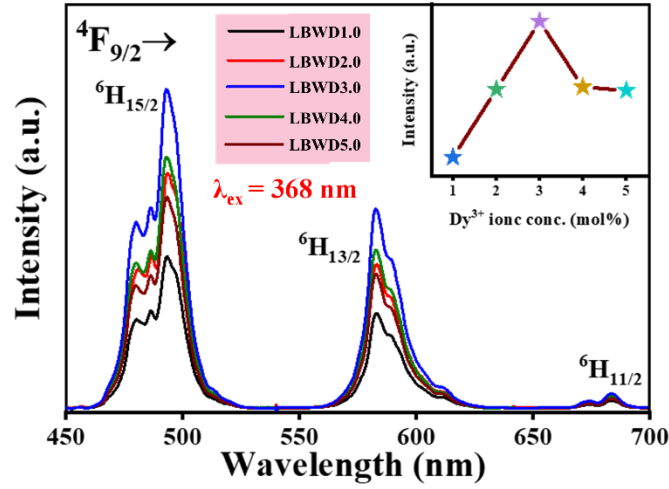


Figure 3.8 PL emission spectra of LBW:xDy³⁺ ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors at $\lambda_{ex} = 368$ nm [Inset shows the variation of PL intensity with Dy³⁺ ions concentration].

The PL emission intensities gradually increase and reached their maximum value as the concentration of Dy³⁺ ions increased from 1 to 3 mol%, and after this, PL emission intensity decreases due to concentration quenching. According to Blasse's theory, the critical distance (R_c) is estimated using formula given by equation 1.1 in section 1.4. The Dy³⁺ ions doped LBW phosphor's critical distance was found to be 27.88 Å for $X_c = 0.03$, $V = 681.182$ Å³ and $N = 2$. According to Van Uitert, the phenomenon of energy exchange, re-absorption of radiation, and numerous interactions are all related to energy transfer [134]. Amid all, the exchange interaction is responsible for the energy transfer in case of forbidden transition, and the critical distance for this should be less than 5 Å [30]. In the current investigation, $R_c = 27.88 > 5$ Å, therefore, multipolar interactions will be more significant. According to Dexter's concept, a relation between the luminous intensity (I) and mole fraction (x) of the activator ions is shown by equation 1.2 in section 1.4.1. The (s/d) value is calculated using the slope of the linear fitted curve between $\log(I/x)$ and $\log(x)$, as illustrated in Figure 3.9 (a), (b) for LBW:xDy³⁺ ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors under $\lambda_{ex} = 368$ nm for two emission wavelengths, i.e., $\lambda_{em} = 493$ and $\lambda_{em} = 583$ nm. This results the values for

"Q" parameter equal to 5.4 and 5.2, which are near to 6, therefore represents that electric d-d interaction is the cause of concentration quenching and transfer of energy between the adjacent Dy^{3+} ions.

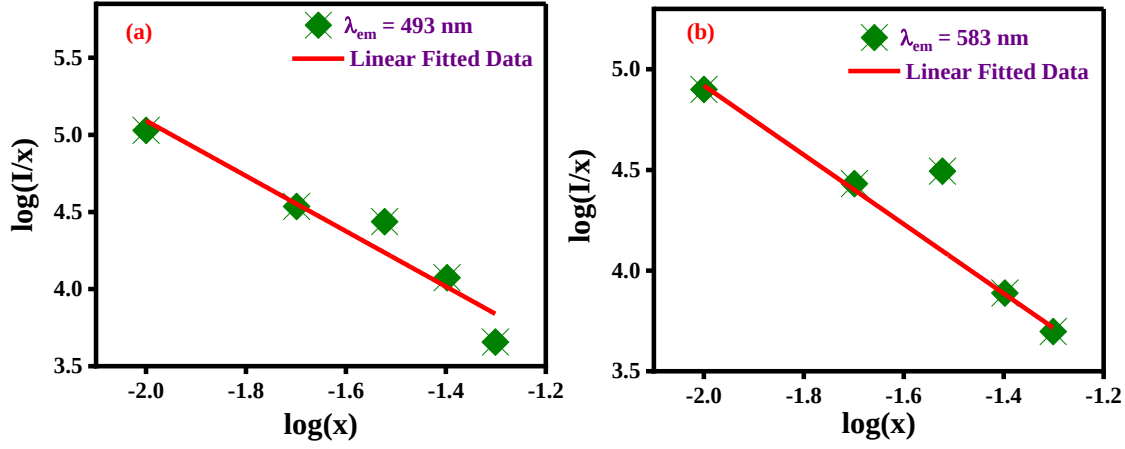
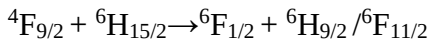
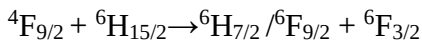
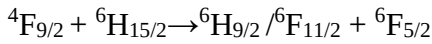


Figure 3.9. The relation between $\log(I/x)$ and $\log(x)$, for LBW:xDy³⁺ ($1 \leq x \leq 5$, $\Delta x = 1 \text{ mol\%}$) phosphors under $\lambda_{ex} = 368 \text{ nm}$ for (a) $\lambda_{em} = 493 \text{ nm}$ and (b) $\lambda_{em} = 583 \text{ nm}$.

According to the schematic energy level diagram in Figure 3.10, the radiative emission mechanism involves the first excitation of the Dy^{3+} ions to higher excited levels, followed by a rapid relaxation to the metastable state $^4\text{F}_{9/2}$ level via non-radiative and radiative transfers from the $^4\text{F}_{9/2}$ excited state to various low energy states [135]. The transition from $^4\text{F}_{9/2}$ to $^6\text{H}_J$ ($J=11/2, 13/2, 15/2$) is analogous to blue, yellow and red colors, respectively. In this illustration, Excitation and emission transitions are denoted by the upward and downward arrows, respectively.

Further, by considering the energy match rule, the following cross-relaxation channels (CRC1, CRC2 and CRC3) among Dy^{3+} ions are responsible for decrease in the population of $^4\text{F}_{9/2}$ level:



This process involves the transfer of excitation energy from a highly excited Dy^{3+} ion to an adjacent Dy^{3+} ion, elevating the latter from its ground state to a metastable state. The Dy^{3+} ions at the $^4\text{F}_{9/2}$ energy level undergo de-excitation through three specific CRCs, subsequently transferring their energy to Dy^{3+} ions

residing in the ${}^6\text{H}_{15/2}$ ground state. This energy transfer leads to the quenching of emission from ${}^4\text{F}_{9/2}$ level [135].

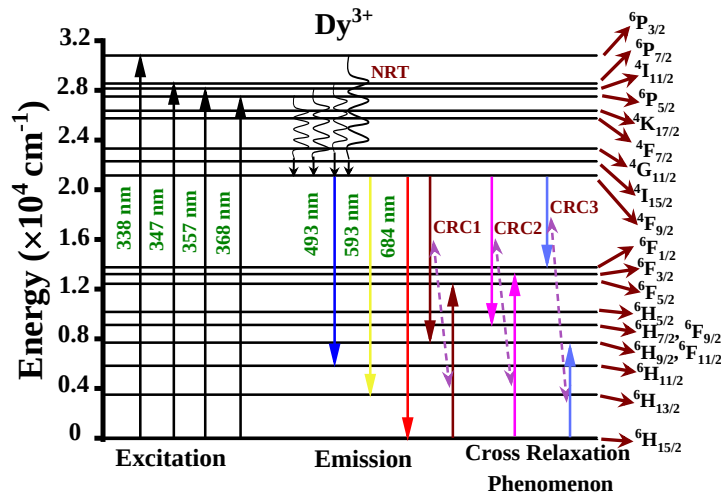


Figure 3.10 The schematic energy level diagram of Dy^{3+} ions in LBW host material.

3.3.2.3 CIE and CCT coordinates

CIE coordinates are commonly employed to describe and interpret the coloration of a phosphor material. The CIE coordinates were evaluated using the formula given in literature [30,136] and shown in equations 1.9-1.10 in section 1.5.1. CIE coordinates of all the as prepared phosphor samples fall in the white light region, ss shown in Figure 3.11.

CCT is another significant indicator for highlighting the function and significance of RE^{3+} ions doped phosphors. McCamy provides a formula for calculating the CCT values, given in section 1.5.2 and equation 1.12. The CCTs for the as-prepared LBW:xDy^{3+} phosphors were found to be significantly greater than 5000 K, signifying the production of cold white light [38].

CP is an additional significant factor in colorimetric calculations that analyze color saturation and we used the equation 1.11 given in section 1.5.1, to assess CP. The CP values, shown in the inset of Figure 3.11, lie between 14 to 16% which are extremely low, supporting the use of the as prepared phosphor materials for producing primary colours like red, blue and green. Table 3.4 includes the CIE coordinates (x, y), CCT, and CP for varied dopant concentrations.

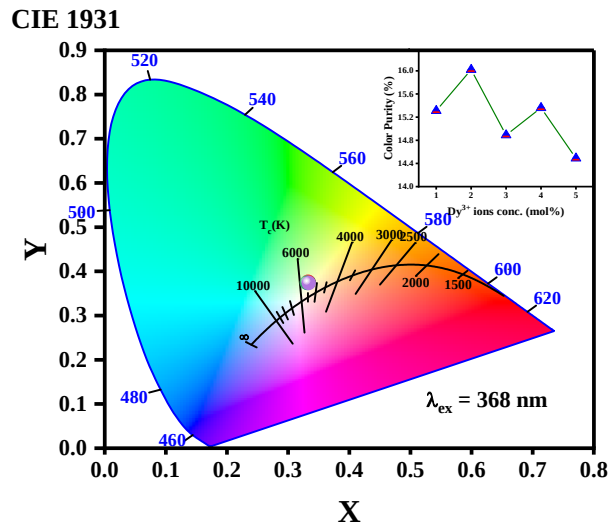


Figure 3.11 CIE chromaticity coordinates for LBW:xDy³⁺ ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors under $\lambda_{ex} = 368$ nm [Inset shows the variation of color purity values with Dy³⁺ ions concentration].

Table 3.4 CIE chromaticity coordinates, CCT (K), color purity (CP%) and average decay time (τ_{av} , μs) for LBW:xDy³⁺ ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors.

Sample Name Li ₂ Ba _(5-x) Dy _x (WO ₅) ₃	CIE		CCT (K)	CP (%)	τ_{av} (μs)
	X	Y			
x = 1 mol%	0.3356	0.3760	5392	15.31	834
x = 2 mol%	0.3348	0.3784	5425	16.02	807
x = 3 mol%	0.3328	0.3739	5495	14.89	760
x = 4 mol%	0.3319	0.3748	5526	15.36	737
x = 5 mol%	0.3348	0.3741	5423	14.49	733

3.3.2.4 TDPL studies

To examine how LBW:xDy³⁺ phosphor is used in non-contact thermometers and how stable its temperature is, the TDPL spectra of the optimised LBWD3.0 phosphor at 293 to 443 K temperature under 368 nm UV light were recorded and shown in Figure 3.12. Except their intensity, the recorded PL spectra's peak positions between 293 and 443 K temperature remain unaltered. However, when the temperature rises, non-radiative transitions of Dy³⁺ ions grow, which causes a gradual decrement in the PL intensities of the two strong PL emission bands. The variation in the PL intensities at $\lambda_{em} = 493$ & 583 nm are shown

in the inset of Figure 3.12 with the change in temperature. The PL emission intensities at both emission peaks gradually drop as the temperature rise.

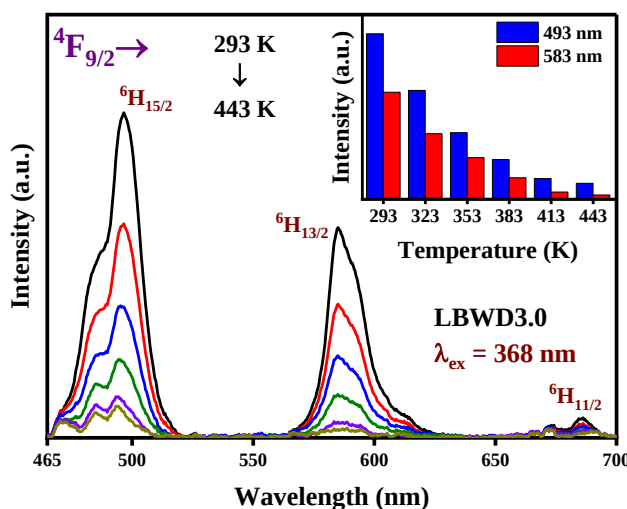


Figure 3.12 TDPL spectra of the LBWD3.0 phosphor between 293 to 443 K under 368 nm UV light [Inset shows the variation of the PL intensities of the emission peaks at 493 nm and 583 nm with temperature].

The intensity ratio of emissions from the two intense PL bands can be used to estimate the relative populations of the two levels. The integral fluorescence intensity ratio (FIR) of the two PL emission bands (at 493 and 583 nm) is fitted to form the FIR curve, which can be used to measure how well the phosphor works as a thermometer [113,137]. Moreover, the FIR curve is fitted using the equation 1.16 given in section 1.6.1. The temperature dependency of the FIR curve for LBWD3.0 phosphor is shown in Figure 3.13 (a).

Moreover, the thermal sensitivity, S_a (absolute sensitivity), is the rate at which FIR changes as a function of temperature, and is represented by the following equation 1.19 and as a result, the relative sensitivity (S_r) might be calculated using equation 1.20 given in section 1.6.2.1.

Figure 3.13 (b) represents the variation of S_a and S_r with the temperature. Throughout the whole temperature range under study, S_a values rise, and at 293 K, S_r peaks at a maximum of $0.7\% \text{ K}^{-1}$. The values, presented in Table 3.5, demonstrate good sensitivity over a broad temperature range and are comparable to the earlier reported values [113,117,138–143].

The smallest observable change in signal is known as the temperature resolution/uncertainty (ΔT), which is an important consideration when analysing a sensor, using the equation 1.22 given in section 1.6.2.2. Smaller ΔF_{IR} (evaluated using Figure 3.13 (a)), results in smaller ΔT . The calculated values of ΔT are displayed in Figure 3.13 (c), and the minimum value of ΔT is ~ 0.51 at 443 K, showing that the as prepared LBED3.0 phosphor is a suitable candidate for optical thermometry.

Table 3.5 The comparison of S_r (% K^{-1}) with some earlier reported values.

Materials	Temperature Range (K)	Temperature of S_r (K)	S_r (% K^{-1})	References
LBWDy3.0	293-443	293	0.7	Present work
CLSi: Dy ³⁺	298-548	298	0.167	[113]
CTDPSF:Dy ³⁺	303-573	473	6E-4	[117]
BYF:Dy ³⁺	550-800	800	0.2	[138]
LGT: Dy ³⁺	300-800	300	2.5E-2	[139]
YAG:Dy ³⁺	293-1700	350	7E-4	[140]
GVO4:Dy ³⁺	298-675	350	9E-3	[141]
GPO4:Dy ³⁺	290-530	290	1.55	[142]
CWO;Dy ³⁺	302-650	302	2.77	[143]

Additionally, TDPL was carried out between 293 to 443 K for 5 cycles to establish the repeatability and reliability of the as prepared phosphor sample in thermometry, as shown in Figure 3.13 (d). The potential of the as prepared phosphor in thermometers is confirmed by the nearly unaltered intensity during these processes.

The calculated CIE chromaticity coordinates using the TDPL data, also represent the temperature sensitive behaviour of the as prepared phosphor material, as shown in Figure 3.14 and presented in Table 3.6.

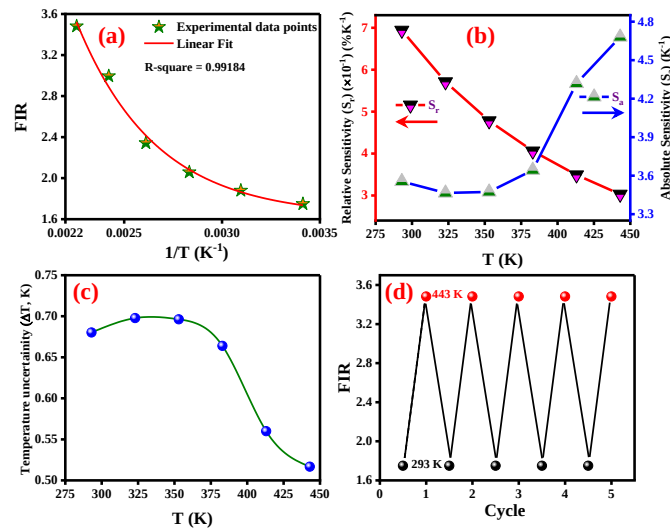


Figure 3.13 Variation of (a) FIR, (b) S_r & S_a , (c) the temperature Resolution (ΔT) with temperature and (d) the repeatability study for LBWD3.0 phosphor.

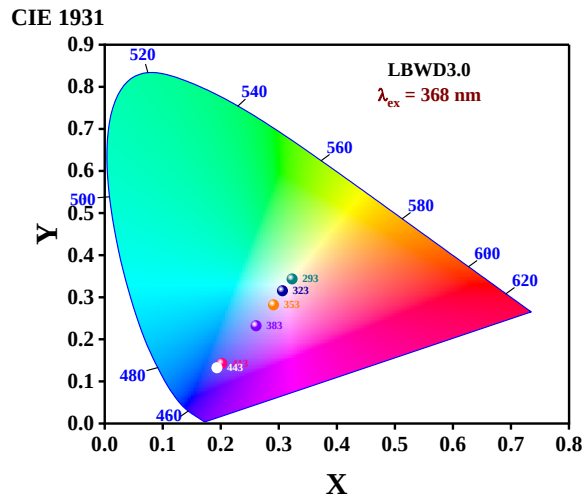


Figure 3.14 Variation of CIE chromaticity coordinates for LBWD3.0 with the change in the temperature.

Table 3.6 The Variation of CIE chromaticity coordinates for LBWD3.0 with the change in the temperature.

Sr. No.	Temperature (K)	CIE Coordinates		CCT (K)
		X	Y	
1.	293	0.29272	0.31707	5492
2.	323	0.27508	0.28141	4770
3.	353	0.25975	0.24178	4166
4.	383	0.23245	0.18998	3475
5.	413	0.1889	0.11019	2475
6.	443	0.18223	0.1018	2261

3.3.2.5 Decay spectral analysis

The double exponential equation is the best fit to the observed decay curves, can be seen from Figure 3.15. A double exponential equation can be represented by the equation 2.10 given in section 2.3.7. The PL decay curves for LBW:xDy³⁺ ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors under $\lambda_{em} = 493$ nm and $\lambda_{ex} = 368$ nm are shown in Figure 3.16. The average decay time (τ_{avg}) has been calculated using the formula given in equation 2.11, given in section 2.3.7. The values of τ_{avg} decreases with the increase in doping ions concentrations showing the possibility of transfer of energy between Dy³⁺ ions. The evaluated values of τ_{avg} presented in Table 3.4.

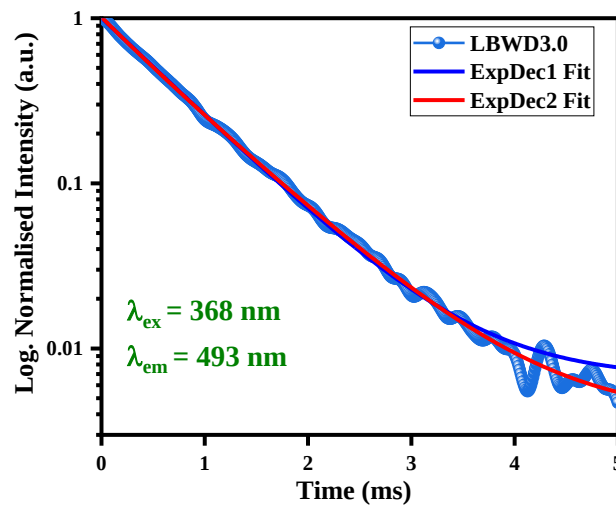


Figure 3.15 PL decay curve for the optimized LBWD3.0 phosphor for single and double exponential fitting.

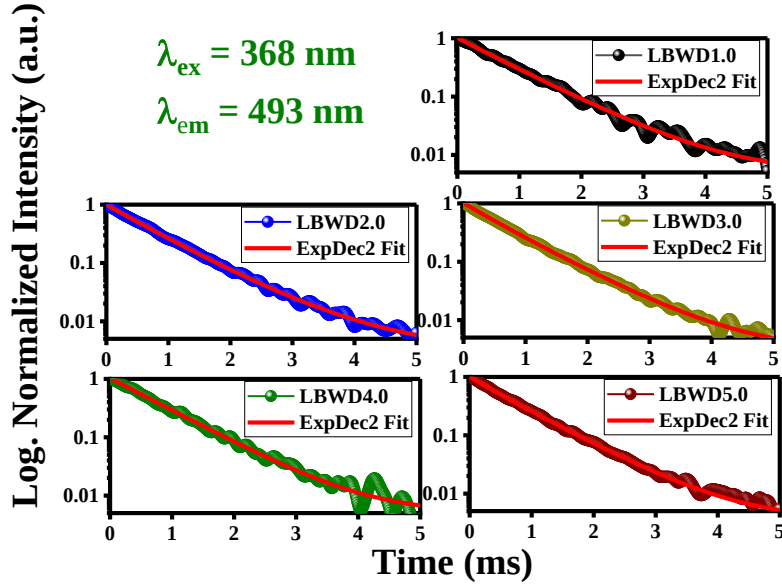


Figure 3.16 PL decay curves for LBW:xDy³⁺ ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors under $\lambda_{em} = 493$ nm and $\lambda_{ex} = 368$ nm.

3.4 CONCLUSIONS

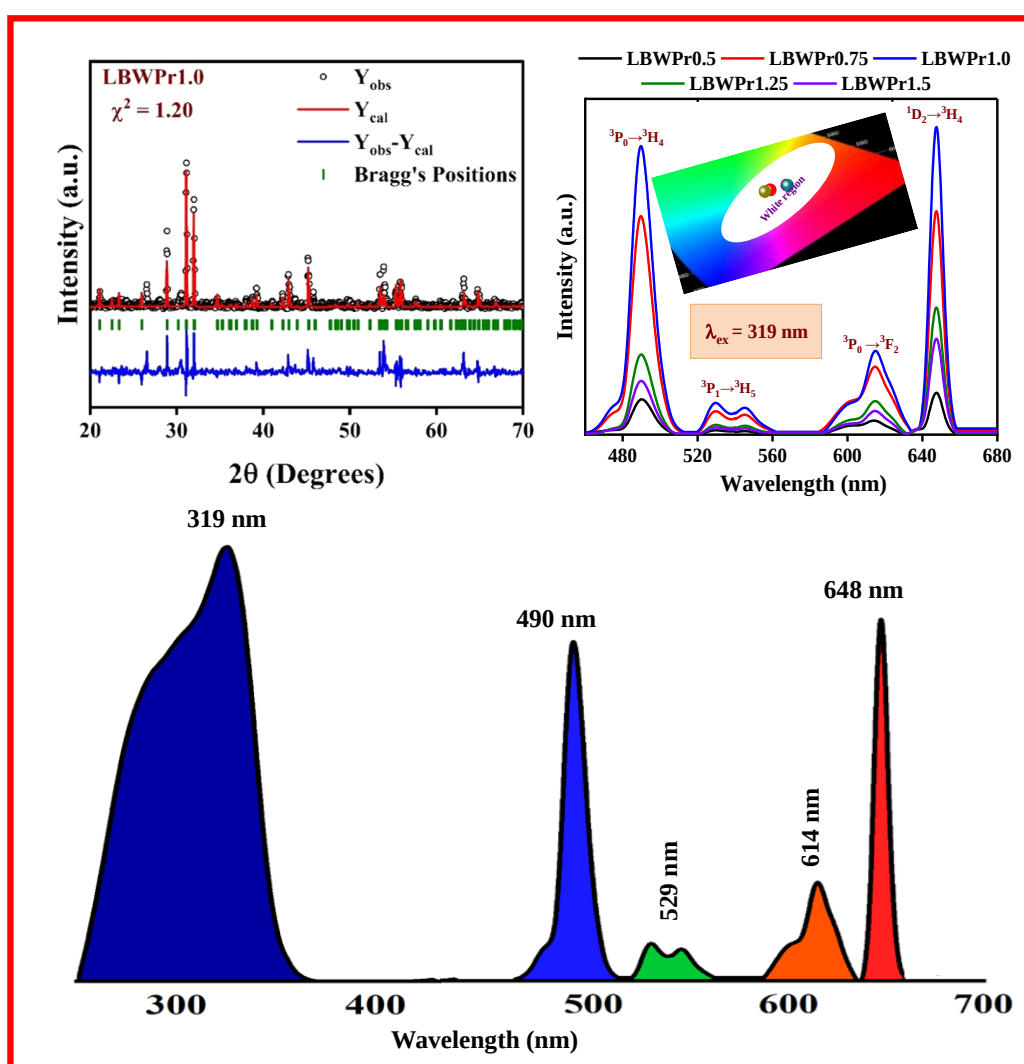
In the present study, Dy³⁺ ions doped LBW phosphors were synthesized using high-temperature SSR method. The as synthesized phosphors possess a hexagonal crystal structure with a space group of P6₃mc, as confirmed by XRD and Rietveld refinement analysis. Under 368 nm excitation, the LBW:xDy³⁺ ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors exhibit a series of emission bands attributed to specific transitions of the Dy³⁺ ions at wavelengths of 493, 583, and 684 nm. These transitions occur within the adjacent Dy³⁺ ions present in the phosphors and are responsible for the emission of light at the respective wavelengths mentioned. The optimum doping concentration of Dy³⁺ ions in the LBW lattice is determined to be 3 mol% and beyond, concentration quenching occurs. Dexter's theory reveals dipole-dipole interaction responsible for quenching and the energy transfer mechanism involved. LBWD3.0 phosphor demonstrates an S_r value of 0.7% K⁻¹ at 293 K and a S_a value of 4.68% K⁻¹ at 443 K. Also, a small value of ~ 0.51 of temperature resolution (ΔT) indicates the ability of the as prepared phosphor to accurately sense and respond to temperature changes. The above results reveal the potential of the as-prepared Li₂Ba_(5-x)(WO₅)₃:xDy³⁺ ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) phosphors for visual and highly sensitive temperature sensing applications.

CHAPTER 4

LUMINESCENCE AND OPTICAL THERMOMETRY

STRATEGY BASED ON EMISSION SPECTRA OF

$\text{Li}_2\text{BA}_5\text{W}_3\text{O}_{15}:\text{Pr}^{3+}$ PHOSPHORS



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4.1 INTRODUCTION

As discussed in Chapter 1, w-LEDs are being recognized as a highly promising alternate to the conventional incandescent and fluorescent lamps, as well as backlights due to their notable advantages such as high efficiency, extended lifespan, low energy consumption, and environmental-friendly features [144]. There are various methods to generate white light but having few drawbacks as discussed in section 1.7 in Chapter -1 [145–148]. Therefore, new red-emitting phosphors are urgently required with high efficacy, outstanding CP, and efficient absorption in the blue or UV regions. In comparison to other phosphors, oxide-based phosphors stand out for their superior chemical stability, broad UV absorption, and resistance to moisture. These characteristics make them particularly important in SSL. They have numerous uses in a variety of industries, such as the production of w-LEDs, field emission display panels, and plasma display devices [149–151]. The choice of host is also significant. Tungstates, as discussed in Chapter 1, form a part of widely recognised inorganic material that hold immense potential for applications across various fields with its unique structure and desirable qualities, such as strong covalent bonds, high stability, and intense visual luminescence [152,153]. Extensive research efforts have been dedicated to exploring RE ion-doped tungstate materials due to their luminescent properties, high covalent lattices, distinctive structures, and significant applications [154,155].

RE ions are widely utilized as luminescent centres in phosphors, making it crucial to investigate their luminescence characteristics in various host materials. Some previous researches confirm that the electrons of Pr^{3+} lanthanide ions have a relatively good tendency to be transferred than that of transition metal ions ($\text{M}^{n+} = \text{Ti}^{4+}, \text{V}^{5+}, \text{Nb}^{5+}, \text{Ti}^{5+}, \text{W}^{6+}$) with d^0 configuration [24,156] and forming an intervalence charge transfer (IVCT) state. The IVCT state provides an effective quenching channel for the $^3\text{P}_0$ state of Pr^{3+} ions. In the present work, this channel has been utilised to study the temperature dependent properties of red emission ($^1\text{D}_2 \rightarrow ^3\text{H}_4$) pertaining to Pr^{3+} ions [24]. Also, Pr^{3+} ions are particularly noteworthy due to their unique electron configuration ($4d^{10} 4f^3 5s^2 5p^6 6s^2$) and the presence of metastable multiplets

within their energy levels. The luminescence of Pr^{3+} ions is attributed to electronic transitions occurring in the 4f outermost shell, specifically in the excited states of $^3\text{P}_0$ or $^1\text{D}_2$ levels. Notably, the luminescence of Pr^{3+} ions is only minimally influenced by the main lattice field [157]. Additionally, Pr^{3+} ions are more cost-effective compared to other RE ions, allowing for the large-scale production of Pr^{3+} doped phosphors at a lower cost. Over the past few years, some Pr^{3+} ions doped phosphors, such as $\text{Lu}_2\text{MoO}_6\text{: Pr}^{3+}$ [158], $\text{SrTa}_2\text{O}_6\text{: Pr}^{3+}$ [159], $\text{Ca}_3\text{Ti}_2\text{O}_7\text{: Pr}^{3+}$ [160], $\text{Sr}_2\text{Ge}_2\text{O}_4\text{: Pr}^{3+}$ [161], and $\text{SrSnO}_3\text{: Pr}^{3+}$ [162], have been achieved by different methods. The studies have demonstrated that Pr^{3+} ions doped phosphors have the capability to convert blue or UV light into a mixture of multiple colors, resulting in the production of white light.

We conducted further research on utilizing phosphor materials for non-contact optical temperature sensors, in addition to their applications in SSL. Recent studies have indicated that the Pr^{3+} ion shows capabilities as a luminescent thermometer [163–165]. Non-contact optical thermometers, depending on specific needs, find applications in various fields including biological and medical settings for cryothermometry, as well as in other areas such as catalysis, aerospace, and surface temperature measurement [28-31]. Temperature-dependent luminescence parameters, including FIR, degradation lifetime, maximum emission position, maximum emission intensity, and emission bandwidth, can be employed to investigate changes in temperature using optical thermometers. The FIR is a versatile approach to study luminescent thermometers, as it involves comparing the intensities of two emission bands of doped ions. This ratio corresponds to the relationship between two energy levels, either TCLs or non-thermally coupled levels (NTCLs), and provides valuable insights into temperature variations [164]. The key factors determining the functional performance of a FIR thermometric material are the high S_a and high S_r . These parameters are crucial for ensuring accurate and precise temperature measurements using FIR-based thermometers.

Previous research [70,168–170], has focused on temperature sensing using both down-conversion (DC) and up-conversion (UC) processes, with a greater emphasis on the latter. UC fluorescent materials have gained significant attention due to their ability to detect the temperature of the materials by collecting far-infrared emissions from specific energy level transitions known as TCL pairs. For example, in the case of lanthanide ions like erbium (Er^{3+}), the TCL pairs, such as the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels, are commonly used for temperature sensing. This approach enables the achievement of infrared (980 nm) excited up-conversion luminescence thermometry through TCLs, employing lanthanide ions like Er^{3+} , Tm^{3+} , Ho^{3+} , etc., sensitized by ytterbium (Yb^{3+}) [171–173]. Nevertheless, the approach of utilizing TCLs for temperature sensing has limitations, including low S_a and S_r . Additionally, the narrow energy gap between TCLs can lead to overlapping emission peaks, reducing the ability to distinguish signals effectively. As a result, researchers have explored alternative strategies to achieve improved temperature sensitivity. Despite the high temperature sensitivity observed in previous studies, alternative approaches have been investigated in the literature [174–176], but these strategies only had single FIR monitoring model. Therefore, there is a need to fabricate a phosphor material that can exhibit multi-color emission to fulfil the demands of various FIR monitoring applications. Pr^{3+} ion is particularly attractive in this regard as it offers a wide range of f-f energy levels, enabling it to emit light across the spectrum from UV to NIR wavelengths. This property makes Pr^{3+} a promising choice for achieving full-color emission in phosphor materials [177,178].

In this study, we have introduced a novel thermometric phosphor named $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Pr}^{3+}$, synthesized using a high-temperature SSR method. When excited by 319 nm light, the synthesized samples exhibit four distinct emission peaks in blue, green and red regions corresponding to $^3\text{P}_0 \rightarrow ^3\text{H}_4$ (B), $^3\text{P}_1 \rightarrow ^3\text{H}_4$ (G), $^1\text{D}_2 \rightarrow ^3\text{H}_4$ (R_1) and $^3\text{P}_0 \rightarrow ^3\text{F}_2$ (R_2) transitions. These emissions display different temperature dependencies. As a result, we developed four FIR models based on the relationships between different emission peaks: (1) G/B, (2) G/ R_2 , (3) R_1 /B, and (4) R_1 / R_2 . $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Pr}1.0$ phosphor sample demonstrated high

temperature sensitivity within the range of 303–423 K for all four models. Furthermore, we have discussed in detail the underlying mechanism responsible for the different temperature dependencies of the Pr^{3+} ions. These findings suggest that $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Pr}^{3+}$ phosphor shows great potential as a high-performance and self-calibrated temperature sensing material.

4.2 EXPERIMENTAL

4.2.1 Synthesis

In this study, Pr^{3+} ion-doped LBW phosphors were synthesized at varying concentrations of Pr^{3+} ions (i.e., 0.5, 0.75, 1.0, 1.25, and 1.5 mol%) utilizing conventional SSR technique as discussed in section 2.2.1 chapter 2. The highly pure chemicals Li_2CO_3 (99.0%), BaCO_3 (99.99%), WO_3 (99.99%), and Pr_2O_3 (99.99%) have been taken as raw materials in stoichiometric ratio. Figure 4.1 represents the detailed synthesis procedure.

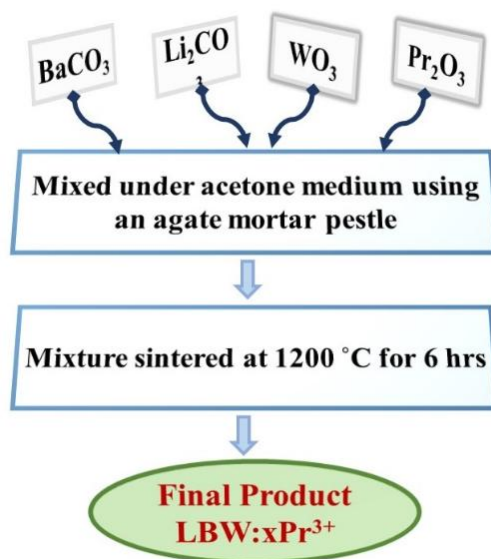


Figure 4.1 Synthesis procedure for LBW:Pr_x ($x = 0.0, 0.5, 0.75, 1.0, 1.25$, and 1.5 mol%) phosphors.

4.3 RESULTS AND DISCUSSION

4.3.1 Structural analysis

4.3.1.1 XRD analysis

XRD patterns were utilized to analyze the crystalline structure and phase purity of both the undoped and Pr^{3+} ions doped LBW phosphors. Figure 4.2 (a) presents the recorded XRD patterns alongwith the JCPDS for LBW:Pr_x ($x = 0.0, 0.5, 0.75, 1.0, 1.25, \text{ and } 1.5 \text{ mol\%}$) phosphors. The observed peaks matched well with the standard JCPDS database card No. 01-072-1717, indicating a high degree of phase purity. This confirms the successful synthesis of LBW: $x\text{Pr}^{3+}$ phosphors without any impurity phases. Furthermore, the close proximity of ionic radii between Ba^{2+} ions (ionic radius of 1.42 Å) and Pr^{3+} ions (ionic radius of 1.126 Å) allowed for the successful substitution of Ba^{2+} ions with Pr^{3+} ions. The percentage difference (D_r) in ionic radii between the doped ion (Pr^{3+}) and the substituted ion (Ba^{2+}) is evaluated using equation 2.3 and found to be equal to 20.7%, remained within an acceptable range of up to 30% [88,123]. The calculated value of D_r indicating that the Pr^{3+} ion can readily substitute the Ba^{2+} ion within the LBW lattice. The presence of strong and well-defined diffraction peaks in the XRD patterns indicates excellent crystallinity of the as synthesized phosphors, which is favourable for achieving enhanced luminescence. The peak shifting and line broadening in XRD spectral patterns are due to the existence of microstrain in the phosphors. W-H equation was used to determine the strain present in the phosphors using equation 2.5 [179]. A linear fit graph between $\beta \cos(\theta)$ (y-axis) and $4 \sin(\theta)$ (x-axis) is shown in Figure 4.2 (b). Crystallite size was determined from the intercept of the linearly fitted plot and microstrain from the slope values. The value of D and ϵ were found to be equal to 113.72 nm and 6.95×10^{-4} , respectively. In order to analyze the crystal structure and phase of the LBW phosphors, FullProf suite software is used to conduct the Rietveld refinement. The profile shape of the diffraction peaks was defined using the pseudo-Voigt function during the refinement process.

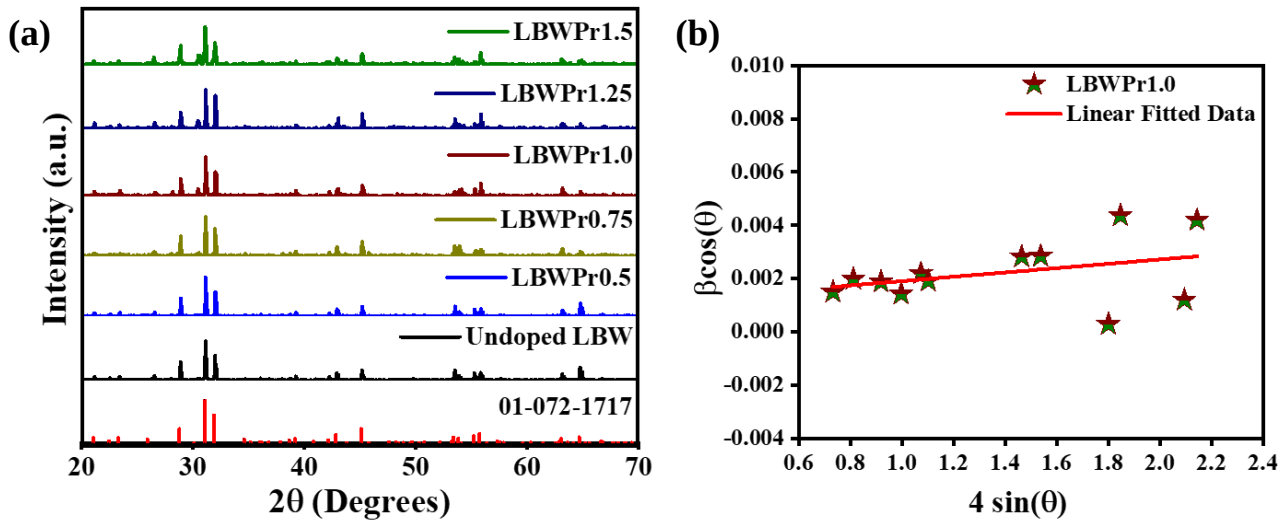


Figure 4.2 The XRD patterns for LBW:Pr_x (x = 0.0, 0.5, 0.75, 1.0, 1.25, and 1.5 mol%) phosphors, (b) A graph between $4 \sin\theta$ and $\beta\cos\theta$ for LBWPr1.0 phosphor.

Figure 4.3 illustrates the Rietveld refinement pattern of the optimized LBWPr1.0 phosphor. The various crystal structure parameters were refined and are presented in Table 4.1. The obtained goodness of fit (χ^2) was determined to be 1.20, indicated the presence of pure phase without any secondary phases in the as-prepared Pr³⁺ ions doped LBW phosphor sample with octahedral structure.

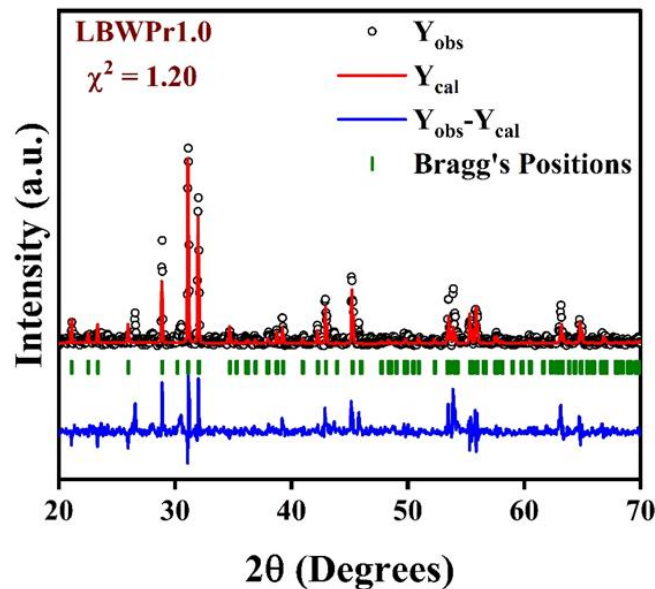


Figure 4.3 The Rietveld refinement map for LBWPr1.0 phosphor.

Table 4.1 Rietveld refinement parameters along with JCPDS data for LBWPr1.0 phosphor.

Parameters	Standard data JCPDS (01-017-1717)	LBWPr1.0
a (Å)	5.76	5.75
b (Å)	5.76	5.75
c (Å)	23.74	23.68
$\alpha = \beta$ (°)	90	90
γ (°)	120	120
χ^2	-	1.20
Cell Volume (Å ³)	682.17	678.10

4.3.1.2 FE-SEM and EDAX analysis

A key element for successful application in commercial w-LEDs is the surface morphology. Figure 4.4 (a) represents the FE-SEM picture of an LBWPr1.0 phosphor. As can be seen, the particle size and morphology of the phosphor are non-uniform. However, the as synthesised samples exhibit an agglomeration phenomenon as a result of the high-temperature reaction having an average particle size in the 1-2 μm range.

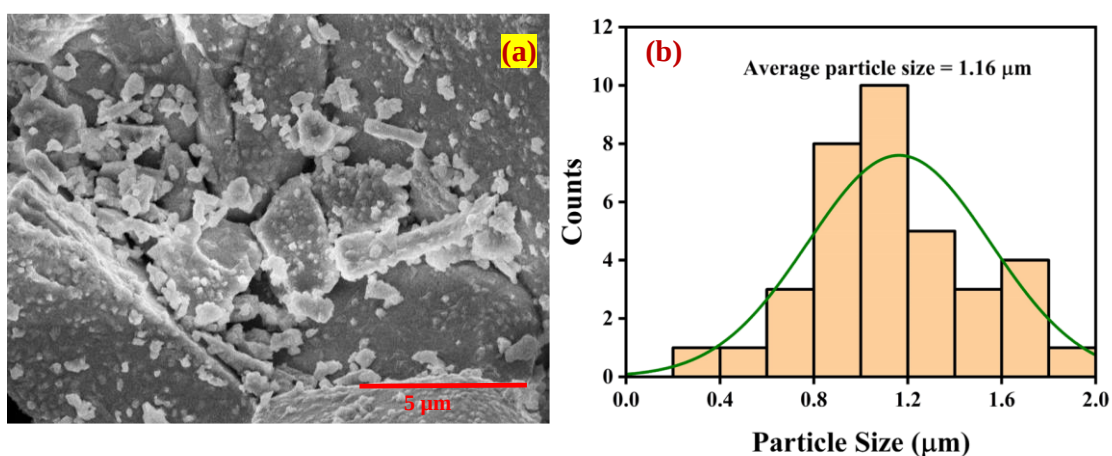


Figure 4.4 (a) The FE-SEM picture and (b) Histogram for LBWPr1.0 phosphor.

A histogram was plotted using ImageJ software to find the average particle size for the as-prepared phosphor and is shown in Figure 4.4 (b). Figure 4.5 (a) demonstrate the total element distribution map, which represents the elements' consistent distribution over the outside surface. Figure 4.5 (b-e) shows the relative element points of various colours against a dark background, i.e., green, red, yellow and purple correspond to Ba, O, W and Pr, respectively. These findings reveal that the components of the created phosphors are distributed equivalently and shows that the Pr^{3+} doped LBW phosphors are successfully prepared. It is clear from the literature that light particles like Li, which have very low energy characteristic radiation, could not be observed using EDAX [125].

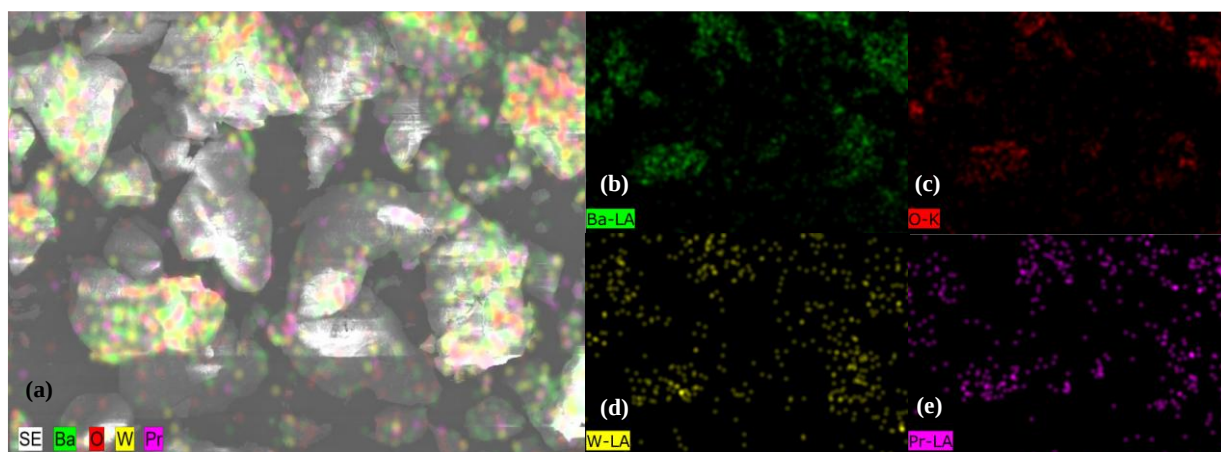


Figure 4.5 (a) The total element distribution map, (b-e) shows the relative element points of various colors against a dark background; green, red, yellow and correspond to Ba, O, W and Pr, respectively.

4.3.1.3 FT-IR analysis

To gain insights into the bonding nature of the as-prepared phosphor samples, IR analysis was conducted. Figure 4.6 represents the FT-IR spectra for both the un-doped LBW and LBW:Pr1.0 phosphor. The spectra cover the range of $480\text{--}4000\text{ cm}^{-1}$ and exhibits various vibrational bands close to 535, 673, 806, 1057, 1230, 1413, 2883, 2988, and 3676 cm^{-1} . Specifically, the bands within the range of $500\text{--}806\text{ cm}^{-1}$ are attributed to the symmetric and antisymmetric stretching vibrations of W-O bonds, as well as the symmetric and antisymmetric stretching deformation vibrations of O-W-O bonds in the tungstate group. These vibrational bands provide valuable information about the bonding characteristics within the LBW

sample [155]. The doping concentration of Pr^{3+} ions have a minor impact on the intensity of the peaks observed in the FT-IR spectrum. Pr^{3+} ions are known to interact with the surrounding atoms in a crystal lattice or chemical structure. When Pr^{3+} ions are introduced into a host material, they can have an impact on the local electronic and structural environment. This impact can lead to changes in the vibrational modes of nearby atoms or ions, including those of the W-O bonds. Therefore, the slight modifications in the W-O stretching vibrations at 809 and 565 cm^{-1} wavenumbers can be accredited to the variation in the local environment caused by the presence of Pr^{3+} ions. However, it is important to note that no significant changes in the structure of the phosphor were observed based on the XRD analysis. Additionally, no bonding between Pr and other constituents of the phosphor material was detected in the FT-IR spectrum. The presence of tungstate groups in the as-prepared phosphor sample is further supported by the presence of 809 and 565 cm^{-1} bands [155,180].

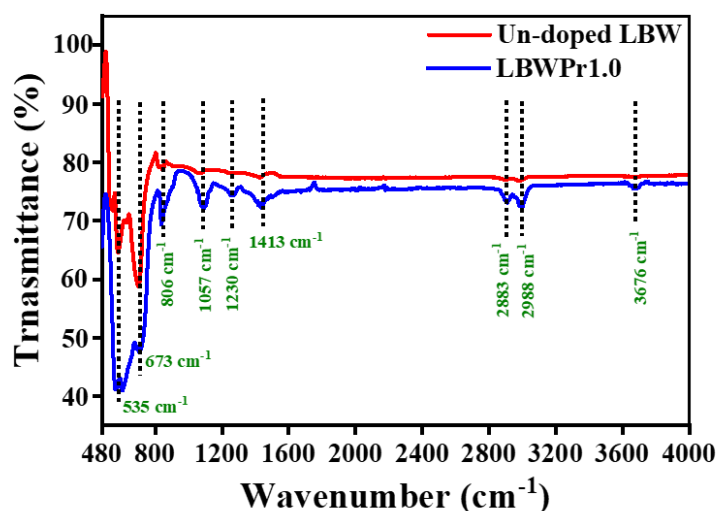


Figure 4.6 FT-IR spectrum of an un-doped LBW and LBWPr1.0 phosphor.

The peak observed at approximately 1057 and 1230 cm^{-1} in the FT-IR spectrum is attributed to the asymmetric stretching vibration of the W-O bond. On the other hand, the band at 1413 cm^{-1} can be allocated to CO_3^{2-} species present in the phosphor [155]. The band observed at 2883 cm^{-1} indicate the presence of hydroxyl radicals. Additionally, the band at 2988 cm^{-1} can be attributed to the antisymmetric stretching of adsorbed water molecules. The peak observed at 3676 cm^{-1} is due to the stretching peak of

the hydroxyl group. These spectral features provide evidence of the existence of hydroxyl groups and water molecules in the LBW phosphor [33].

4.3.2 Optical studies

4.3.2.1 DRS analysis

For the use of phosphors in w-LEDs, the optical band gap (E_g) is a crucial variable. Figure 4.7 (a) displays the detailed DRS for an un-doped LBW and LBWPr1.0 phosphor samples in the 200-2000 nm region. For the pure un-doped LBW sample, an absorption cut edge is observed near 319 nm that corresponds to its bandgap. This absorption band shows a 4 nm blue-shift with 1mol% Pr^{3+} doping that clearly indicates the decrement of the E_g with dopant ion concentrations. The five peaks were observed close to 614, 998, 1420, 1542 and 1944 nm corresponding to the transitions from $^3\text{H}_4$ to $^1\text{D}_2$, $^1\text{G}_4$, and $^3\text{F}_{4,3,2}$, respectively [181]. E_g was evaluating by modifying the DRS data into the K-M function using the equations 2.6-2.8 in section 2.3.5 and by extrapolation of the linear portion of the plotted graph between $h\nu$ (incident energy) and $[F(R)h\nu]^2$, called Tauc's Plot, for Pr^{3+} ions doped LBW phosphor samples. The un-doped LBW sample has a band gap of 3.74 eV, but when 1.0 mol% concentration of Pr^{3+} ions were added, the band gap is reduced to 3.08 eV as can be seen in Figure 4.7 (b).

The decrease in bandgap due to the dopant ions represents the efficient crystallinity of the prepared samples [127]. Also, as the bandgap decreases, the more the atoms getting excited to the upper states and thereby resulting in a stronger emission when they are falling down to the lower energy states [182]. Because of the mismatch in ionic radius and the charge compensation process, the replacement of Ba^{2+} ions by Pr^{3+} ions result in certain defect centres in the crystal. The localized states are quantum mechanically forced into the forbidden band-gap by the defects, which produce a significant potential gradient into the host matrix [183,184].

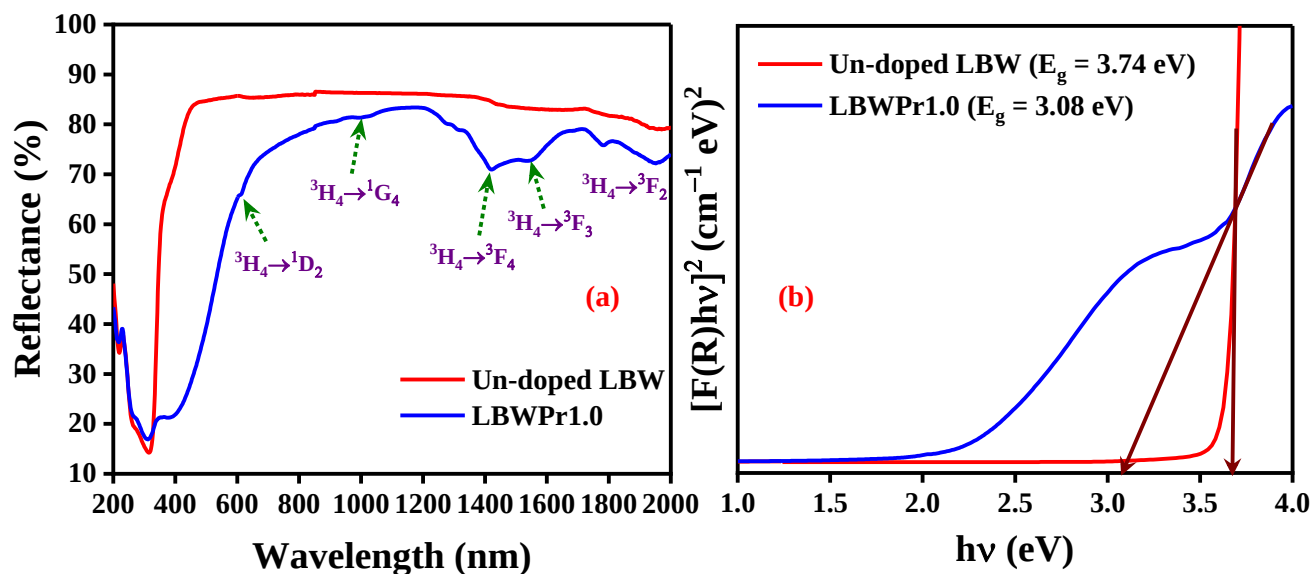


Figure 4.7 (a) DRS and (b) Direct band gap of the un-doped LBW and LBWPr1.0 phosphor samples.

4.3.2.2 PL emission spectral analysis

The PL excitation & PL emission spectrum of the un-doped LBW material is shown in Figure 4.8. The un-doped LBW sample shows a broad excitation band centered at 319 nm at 467 nm emission wavelength. Now, 319 nm excitation wavelength is used to record the PL emission spectrum of the un-doped sample. Among the two emission peaks, i.e., at 467 & 546 nm, 467 nm is relatively more intense. Now, the PL spectrum features of Pr³⁺ ions doped LBW phosphors were examined to analyze their PL characteristics.

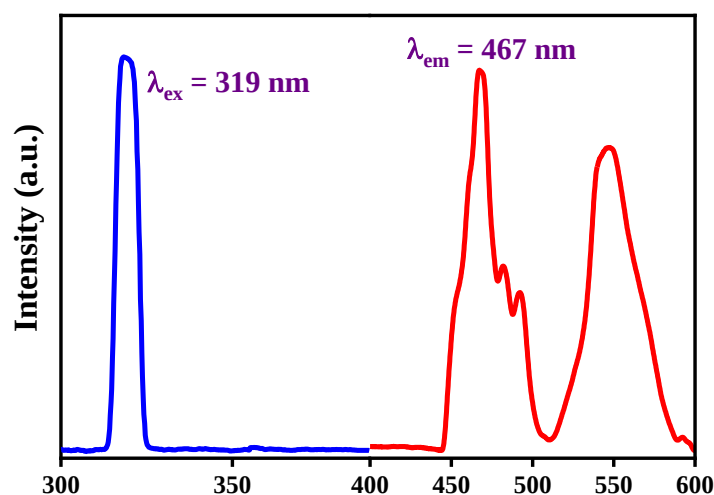


Figure 4.8 PLE & PL spectrum of an un-doped LBW sample.

Figure 4.9 displays the PL excitation spectra of the as-prepared phosphor samples at $\lambda_{em} = 647$ nm in the 250-500 nm wavelength range. In the LBW lattice, the concentration of Pr^{3+} ions range from $x = 0.50$ to 1.50 mol%, with $\Delta x = 0.25$ mol%. The spectrum is divided into two parts, the UV region having a broad charge transfer band (CTB), centered at 319 nm, and the visible region having the distinctive f-f transition peaks of the Pr^{3+} ion. The broad CTB in the UV region corresponds to the charge transfer absorption from 2p orbital of the oxygen atom to 5d orbital of tungsten [155,185]. The peaks in the visible region observed at 448, 473 and 488 nm correspond to $^3\text{H}_4 \rightarrow ^3\text{P}_{2,1,0}$ transitions, respectively [123,186]. It has been noted that the CTB of tungstate has relatively higher excitation intensity than the other characteristics bands of Pr^{3+} ions, which ensures the significant emission caused by CTB.

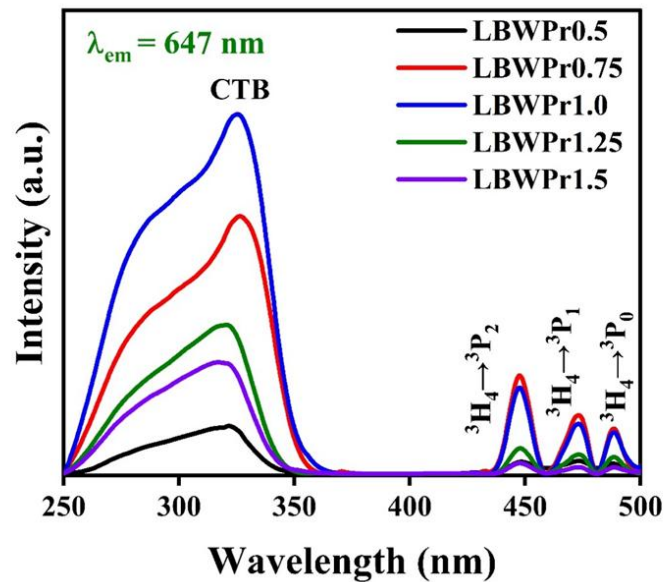


Figure 4.9 PLE spectra for LBW:Prx ($0.5 \leq x \leq 1.5$, $\Delta x = 0.25$ mol%) phosphors.

The PL emission spectra of LBW:Prx ($x = 0.0, 0.5, 0.75, 1.0, 1.25$, and 1.5 mol%) phosphors, using $\lambda_{ex} = 319$ nm, contain peaks at 490, 529, 614, and 648 nm that correspond to $^3\text{P}_0 \rightarrow ^3\text{H}_4$, $^3\text{P}_1 \rightarrow ^3\text{H}_5$, and $^3\text{P}_0 \rightarrow ^3\text{F}_2$ transitions, respectively, as shown in Figure 4.10 (a). With emission peaks in blue, green, and red spectral regions, the greatest intensity for $\lambda_{ex} = 319$ nm corresponds to 1.0 mol% of Pr^{3+} ions, and the combination of these complementary colors created white color emission from the as prepared LBW:Pr samples. The PL emission spectra of LBWPr1.0 phosphor at $\lambda_{ex} = 319$ & 448 nm, for $^3\text{P}_0 \rightarrow ^3\text{F}_2$ transition

is shown in Figure 4.10 (b). It is clear from the PL emission spectra that the emission bands associated with RE excitation (448 nm) are less intense than those associated with CTB excitation (319 nm). The energy transfer process is the cause of this anomaly. Also, some scientists predicted that the electronic states will be scattered across energy bands of few eV in width. Typically, the 5d electronic states of tungsten are admixed with some 2p electronic states of oxygen in the valence band. The conduction band of the crystal is mostly formed by tungsten's 5d electronic states. To be exact, either host absorption or the activation of W-O complexes is responsible for these CTB broad bands [187].

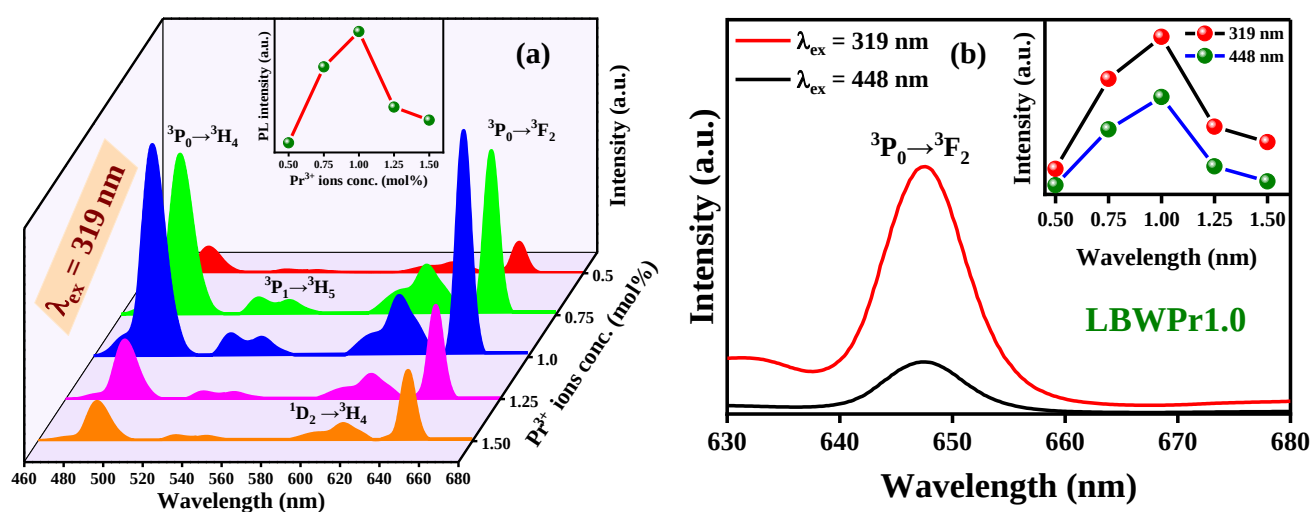


Figure 4.10 (a) PL emission spectra for LBW:Prx ($0.5 \leq x \leq 1.5$, $\Delta x = 0.25$ mol%) phosphors, (b) PL emission spectra of the LBWPr1.0 phosphor recorded at $\lambda_{\text{ex}} = 319$ and 448 nm.

The electrons are excited at 319 nm and a charge transfer state is formed due to the movement of electrons from oxygen's 2p orbitals to tungsten's 5d orbitals [155]. A fraction of this excitation energy is then transferred to the $^3\text{P}_2$ level of Pr^{3+} ions, where it undergoes a quick non-radiative relaxation. Overall, the $^3\text{P}_0$ and $^1\text{D}_2$ meta-stable states of Pr^{3+} ions are becoming more electron-rich. The different emission bands in the spectra are contributed by the radiative relaxation from meta-stable state to various lower energy states. The energy level diagram and numerous transitions of Pr^{3+} ions in LBW host lattice are shown in Figure 4.11.

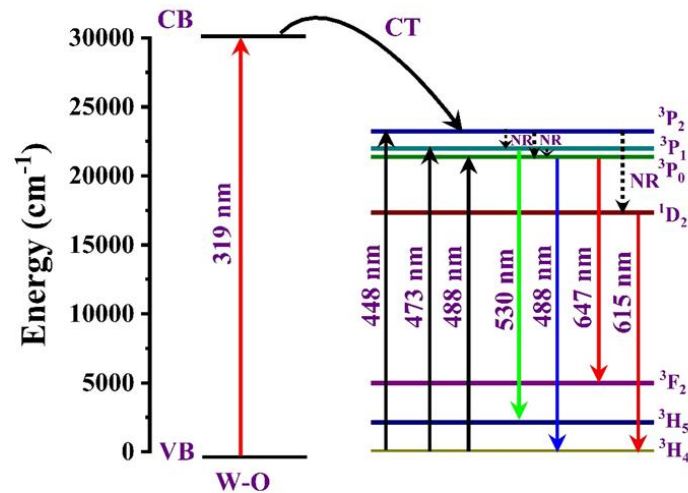


Figure 4.11 The schematic energy level diagram of Pr^{3+} ions in LBW host.

Upto 1.0 mol% of Pr^{3+} concentration, spectral intensities of the bands in the PL spectra increased, after which it started to drop. The decrement in the emission intensity is due to the energy transfer between Pr^{3+} - Pr^{3+} ions, and therefore, concentration quenching was accomplished. There may be many reasons for the concentration quenching, for instance exchange contact, multipole-multipole interaction between the activator ions and radiation reabsorption, etc. The critical distance (R_c) is evaluated using the Blesse's theory shown by equation 1.1 in section 1.4 to comprehend the kind of interaction that takes place between Pr^{3+} ions. The evaluated value of the critical distance for Pr^{3+} ions doped LBW phosphors was found to be 40.24 Å. Using Dexter's theory, it is possible to ensure that an electric multipolar interaction could be the cause of the energy transfer between the Pr^{3+} ions if the R_c value is more than 5 Å [26,188].

Dexter theory uses the relation given by equation 1.2 in section 1.4.1 to determine the type of multipolar interaction. The (s/d) value is calculated using the slope of the linear fitted curve between $\log\left(\frac{I}{x}\right)$ and $\log(x)$, as illustrated in Figure 4.12. The computed s value of 5.48, which is extremely near to 6, suggests the dipole-dipole interaction between the Pr^{3+} ions.

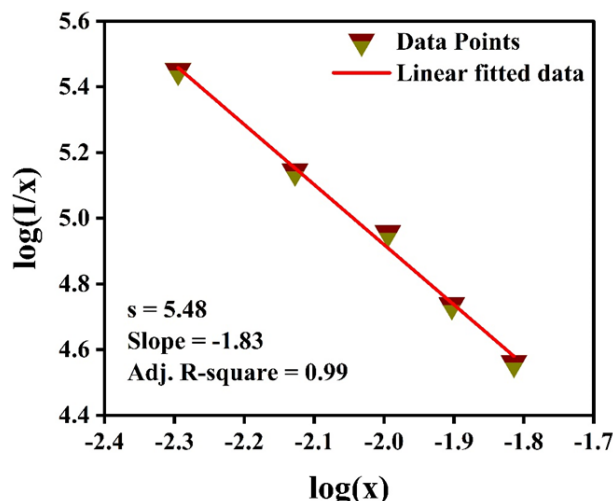


Figure 4.12 The relation between $\log(I/x)$ and $\log(x)$ for LBW:Prx ($0.5 \leq x \leq 1.5$, $\Delta x = 0.25$ mol%).

4.3.2.3 Colorimetric analysis

The CIE chromaticity coordinates are commonly employed to describe and interpret the coloration of a phosphor material. The shape or location of the emission peaks are unaffected by the variations in Pr^{3+} concentration, however the value of the PL emission intensity does. The CIE coordinates for all the as-prepared LBW:Prx ($0.5 \leq x \leq 1.5$, $\Delta x = 0.25$ mol%) phosphor samples were evaluated using the formula given in literature [30], as represented by equation 1.9-1.10, and found to be fall in the region of white light in the CIE diagram at room temperature which make the prepared phosphor samples suitable for the production of white light producing LEDs, as illustrated in Figure 4.13. CCT is another crucial parameter for illuminating the function and significance of RE^{3+} ions doped phosphor. McCamy provided a formula for calculating CCT given by equation 1.12 in section 1.5.2. For the as prepared phosphor samples, the CCT values are found to be less than 5000 K, therefore, considered as a warm white light emission [33]. In colorimetric calculations used to examine color saturation, CP is also an important consideration given by equation 1.11 in section 1.5.1. Comparative lower values of CP suggests that the as-prepared phosphor samples can be used as a single-phase white light emitting phosphor for pc-w-LEDs [155,189].

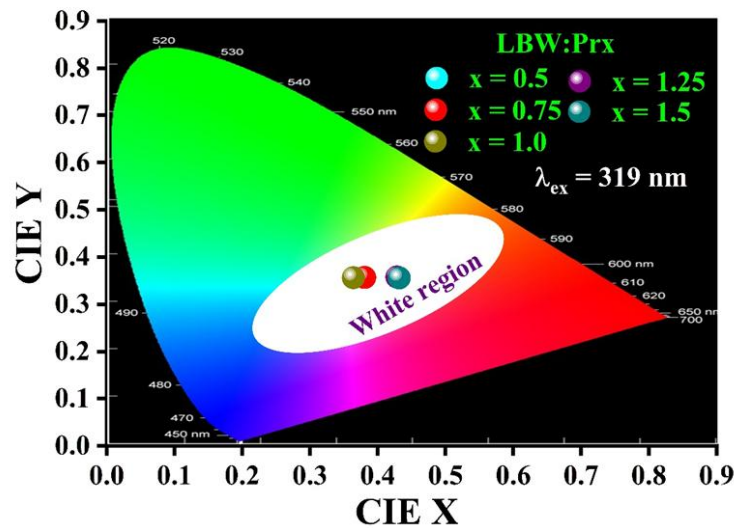


Figure 4.13 CIE chromaticity coordinates for LBW:Prx ($0.5 \leq x \leq 1.5$, $\Delta x = 0.25$ mol%) under $\lambda_{\text{ex}} = 319$ nm.

The CIE chromaticity coordinates, CCT and CP values of LBW:Prx ($0.5 \leq x \leq 1.5$, $\Delta x = 0.25$ mol%) phosphor samples are listed in Table 4.2.

Table 4.2 CIE, CCT, CP and experimental lifetime (τ_{avg} (ms)) values for as prepared LBW:Prx ($0.5 \leq x \leq 1.5$, $\Delta x = 0.25$ mol%) phosphors.

Sample	CIE		CCT (K)	CP
	X coordinate	Y coordinate		
LBWPr0.50	0.40	0.34	3158	0.20
LBWPr0.75	0.38	0.35	3858	0.18
LBWPr1.0	0.36	0.35	2734	0.13
LBWPr1.25	0.42	0.35	2655	0.30
LBWPr1.5	0.43	0.35	2738	0.27

4.3.2.4 TDPL analysis

The TDPL spectra of LBWPr1.0 phosphor were acquired at $\lambda_{\text{ex}} = 319$ nm between 303 and 423 K temperature to explore the behavior of thermal quenching. The TDPL spectra of the LBWPr1.0 phosphor revealed that, as temperature increases, PL band intensities drop without altering the peak positions, as shown in Figure 4.14 (a).

The normalized intensity of the $^1D_2 \rightarrow ^3H_4$ transition is shown as a function of temperature in Figure 4.14 (b), with 100% taken as the highest emission intensity at 303 K. The emission intensity decreases to 62% at 423 K, demonstrating a good thermal stability of LBWPr1.0 phosphor. To analyze the thermal characteristics of the as-synthesized phosphor sample, the activation energy (ΔE) was also measured using the Arrhenius equation 2.16 given in section 2.3.8. The slope of a fitted linear graph of $\ln\left(\frac{I_0}{I_T} - 1\right)$ (y-axis) and $\frac{1}{k_B T}$ (x-axis) yields the value of ΔE , as illustrated in Figure 4.14 (c), which is relatively higher than $\text{Ca}_3\text{WO}_6:0.04\text{Dy}^{3+}$ (0.105 eV) [190] and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (0.09 eV) [191] phosphors. Thus, the TDPL analysis enables us to state that the phosphor LBWPr1.0 is thermally stable and shows that it is suitable for creating visible photonic devices.

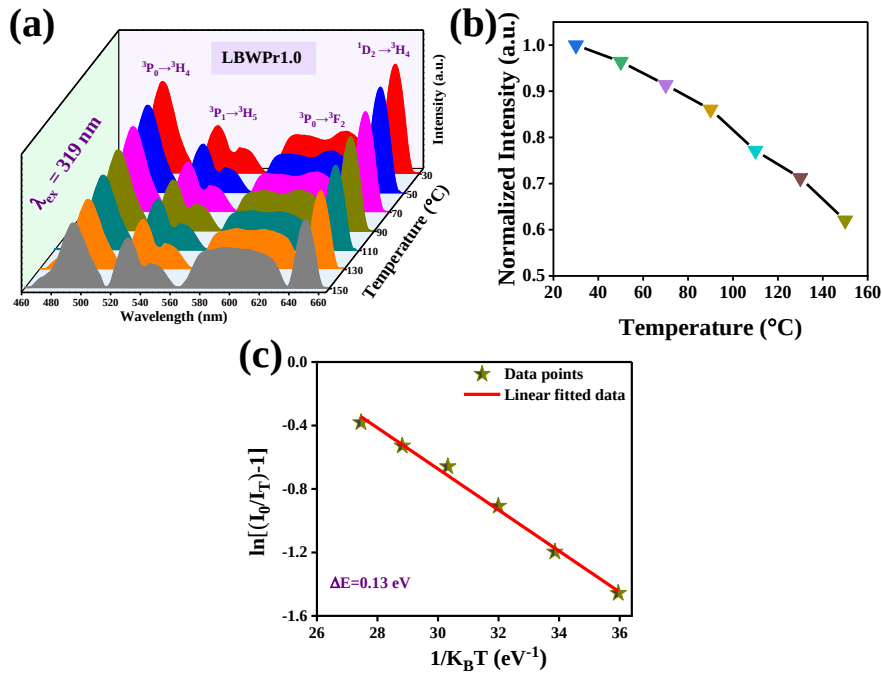


Figure 4.14 (a) TDPL spectra of the LBWPr1.0 phosphor at 303–423 K temperature, (b) The normalized intensity of the $^1D_2 \rightarrow ^3H_4$ transition as a function of temperature, (c) A graph between $\ln\left(\frac{I_0}{I_T} - 1\right)$ (y-axis) and $\frac{1}{k_B T}$ (x-axis).

4.3.2.5 Temperature sensor applications

The temperature-dependent 3D emission spectra of the LBWPr1.0 sample was recorded from 303 K to 463 K temperature as shown in Figure 4.14 (a). As the temperature rises, the intensities of $^3P_0 \rightarrow ^3H_4$ (B)

and ${}^3\text{P}_0 \rightarrow {}^3\text{F}_2$ (R_2) emissions decrease dramatically, whereas the intensities of ${}^3\text{P}_1 \rightarrow {}^3\text{H}_4$ (G) and ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ (R_1) emissions decrease to a little extent. The integrated intensities of the four emissions in Figure 4.15 (a) proved the distinction between the intensities of B and R_2 emissions, which fell faster than the intensities of G and R_1 emissions with increasing temperatures. Therefore, four FIR models, i.e., (1) G/B, (2) G/ R_2 , (3) R_1 /B, and (4) R_1 / R_2 ; are used as temperature detecting signal, due to the distinguishable temperature dependence of the four emissions. The measured plots of the four FIR models versus $1/T$ are shown in Figure 4.15 (b). It can be observed that the FIR of the four models change with increasing temperature; especially in the G/ R_2 model, the FIR monotonously decreased with the rise of $1/T$ and varied from 0.96 at 303 K to 0.43 at 423 K. The Struck and Fonger theory is used to study the luminous property of LBWPr1.0 phosphor in order to quantitatively determine the sensitivity of the four models for optical thermometry. The FIR of the four models can be calculated and represented by using the equation 1.16. Using the FIR values and equations 1.19 and 1.20, the S_a and S_r were evaluated and presented in Figure 4.15 (c) and (d), respectively.

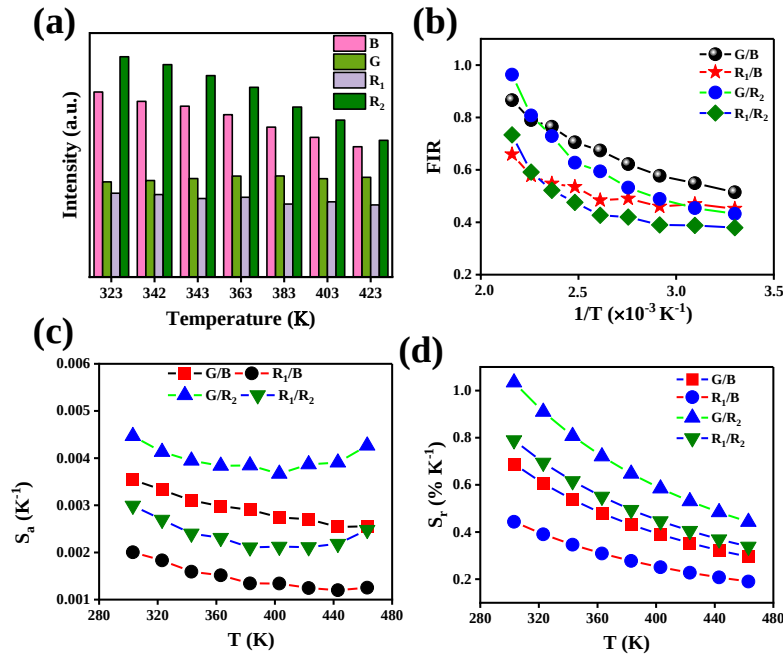


Figure 4.15 (a) Intensity variation of various peaks with temperature, (b) The temperature dependency of the FIR curve, (c) the temperature absolute sensitivity curve and (d) the temperature relative sensitivity curve for LBWPr1.0 phosphor.

The maximum values of S_a and S_r of the G/R₂ model reach as high as 0.0045 K⁻¹ and 1.03% K⁻¹, respectively. The other three models also have high temperature sensitive performance. To evaluate the temperature sensing performance of this new four models thermometer, the maximum relative sensitivities of representative temperature sensing phosphors in previous reports [123,163,192–194] are displayed in Table 4.3 with the as prepared phosphor sample. The LBW:Pr³⁺ phosphors had four models of monitored FIR. When one of the FIR models has an error, other models can be simultaneously monitored to correct the inaccuracy. So, the self-calibrated optical thermometer can be achieved by simultaneously monitoring of four models of FIR [163,195].

Table 4.3 Summary of the temperature sensitivities of Pr³⁺ ions in different host materials.

Materials	Transitions	S _r maximum (%K ⁻¹)	Temperature Range (K)	References
LMN	³ P ₀ → ³ H ₄ / ¹ D ₂ → ³ H ₄	0.71	298-523	[123]
BaNb ₂ O ₆	³ P ₁ → ³ F ₃ / ³ P ₀ → ³ F ₃	0.60	310-470	[163]
LPP	³ P ₀ → ³ H ₆ / ³ P ₀ → ³ F ₂	0.39	298-363	[192]
Lithium tellurite	³ P ₁ → ³ H ₅ / ³ P ₀ → ³ H ₅	0.97	293-473	[193]
SMO	³ P ₀ → ³ H ₄ / ¹ D ₂ → ³ H ₄	0.45	298-498	[194]
LBWPr1.0	³ P ₁ → ³ H ₅ / ³ P ₀ → ³ F ₂	1.03	303-463	Present work

4.3.2.6 TR-PL analysis

PL decay curves for LBW:Pr_x (0.5 ≤ x ≤ 1.5, Δx = 0.25 mol%) phosphors under λ_{em} = 647 nm and λ_{ex} = 319 nm are shown in Figure 4.16 (a). The bi-exponential equation 2.10 given in section 2.3.7 is the best fit to the observed decay curves. Therefore, the average decay time (τ_{avg}) is calculated by employing the equation 2.11 given in section 2.3.7 and found to be in the milliseconds range. To identify the associated energy transfer process, the I-H model has been used to the decay curves of the as-prepared Pr³⁺ ions doped LBW phosphors. The decay curves of the optimised phosphor sample LBWPr1.0 have been best fitted for s = 6 using the equation 1.5 given in section 1.4.3, indicating that the d-d interaction

is the dominant one among Pr^{3+} ions in LBW phosphor. Dexter's theory of energy transfer yielded the same conclusion.

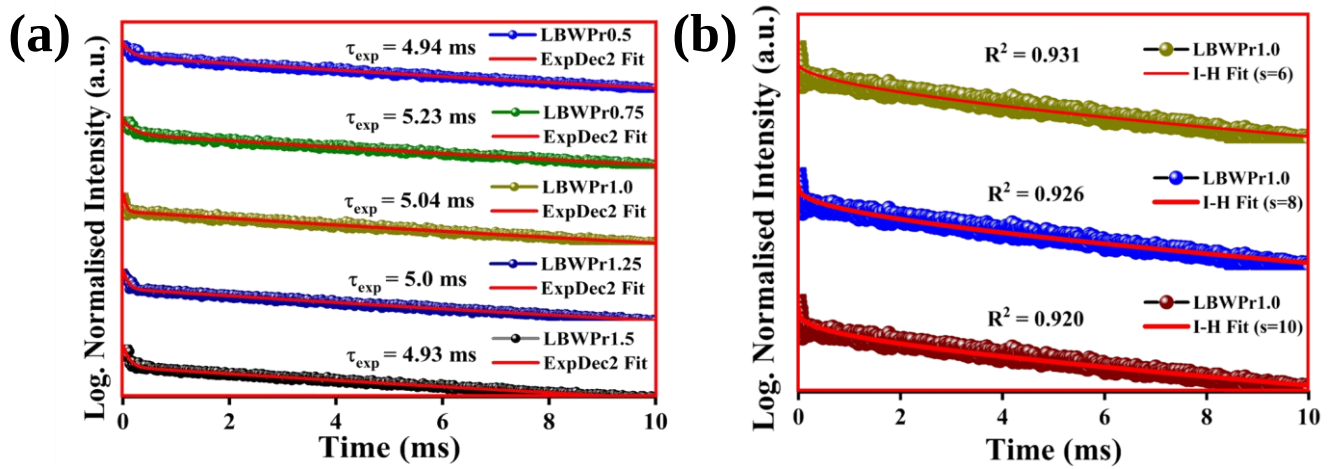


Figure 4.16 (a) PL decay curves for LBW:Prx ($0.5 \leq x \leq 1.5$, $\Delta x = 0.25$ mol%) under $\lambda_{\text{em}} = 647$ nm and $\lambda_{\text{ex}} = 319$ nm and (b) I-H fitted curves for $s = 6, 8$ and 10 for LBWPr1.0 phosphor.

4.4 CONCLUSIONS

In the present research work, a series of Pr^{3+} ions doped LBW phosphor samples was prepared using high temperature SSR method and then the structural, morphological, and PL features of the samples were examined. The XRD profile and Rietveld refinement supported the phase purity of the as-prepared phosphor samples. A variety of molecular bonds were identified by the FT-IR spectra. The band gap values for the optimized and the un-doped LBW sample was determined by the linear fitting of the Tauc's plot, which was found to be in the optical region and which make the prepared phosphor samples suitable for the photonic devices. The PL investigations show that the as-synthesised phosphors have four emission peaks, most promising at 647 nm corresponding to $^3\text{P}_0 \rightarrow ^3\text{F}_2$ transition when pumped from $\lambda_{\text{ex}} = 319$ nm. Beyond 1.0 mol% of Pr^{3+} ions, the concentration quenching occurs. The Dexter theory explains that the primary reason of concentration quenching is the dipole-dipole interaction between Pr^{3+} ions. The CIE coordinates of the as-prepared Pr^{3+} ions doped LBW phosphors fall within the white light region. The PL decay profile displays bi-exponential behavior with decreasing decay time. The decrement in the decay lifetime with increase in the Pr^{3+} ions concentration was due to the energy transfer between

Pr^{3+} - Pr^{3+} ions. Dexter theory and I-H model confirms the dipole-dipole interaction as a cause of energy transfer. The thermal stability of the optimised phosphor sample was identified by TDPL analysis. Moreover, FIR was used to analyze the optical sensing properties of the LBWPr1.0 phosphor. A maximum S_r of 1.03% K^{-1} , indicating the potential of these phosphors for optical thermometry applications. In conclusion, the emission characteristics, thermal stability, and optical sensing capabilities of the Pr^{3+} ions doped LBW phosphors demonstrate their potential for applications in SSL and optical thermometry.

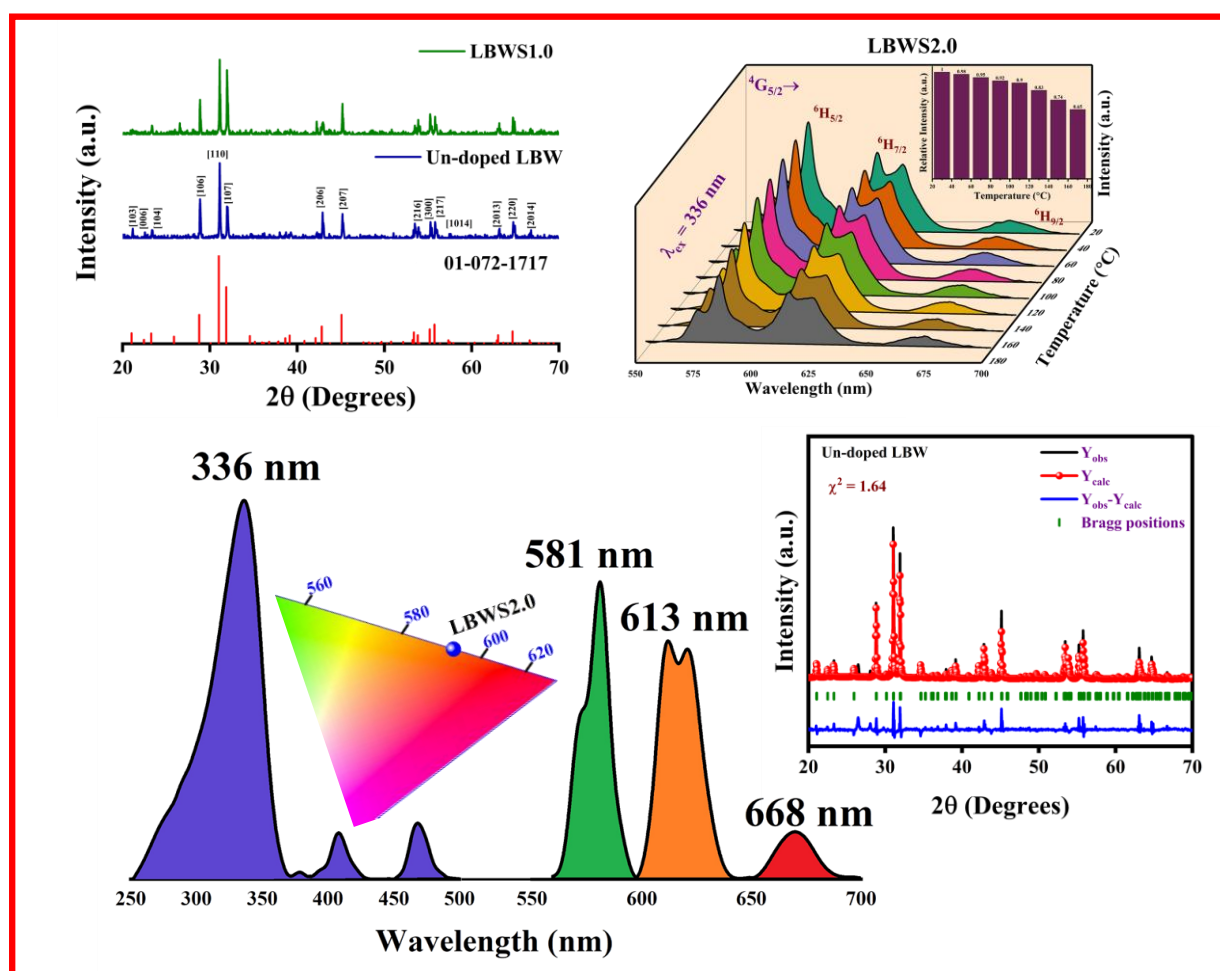
CHAPTER 5

SYNTHESIS, STRUCTURAL AND FLUORESCENCE

INVESTIGATIONS OF NOVEL $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Sm}^{3+}$

PHOSPHORS FOR PHOTONIC DEVICE

APPLICATIONS



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5.1 INTRODUCTION

As discussed in Chapter 1, w- LEDs have taken the position of traditional lighting devices in the SSL industry due to their superior qualities, especially extended durability, great brightness, sustainability, and low power consumption [196,197]. Section 1.7 of Chapter 1 highlights the methods of generating white light and significance of the present approach alongwith the choice of the host lattice. The role of RE ions in visible luminescence is crucial because of their f-f transitions which lead to luminous sharp emission when RE ions are introduced to an appropriate crystal lattice as a dopant [39,198–200]. Furthermore, these RE ions are easily energized by UV/n-UV radiation absorption, which results in the down-conversion process emitting light in the visible area. Among all the RE activator ions, Sm^{3+} ions stand out as highly effective and radiation-stable candidates, proficiently emitting red or orange-red colour and having remarkable CP [201,202]. Moreover, substances containing Sm^{3+} ions have been the subject of much research owing to their $^4\text{G}_{5/2} \rightarrow ^4\text{H}_{J/2}$ ($J = 5, 7, 9, \text{ and } 11$) emissions in the visible red region [203]. Several Sm^{3+} ions activated host matrices have already been reported, such as $\text{Sr}_3\text{Al}_2\text{O}_6$ [116], $\text{Ca}_2\text{Gd}_8\text{Si}_6\text{O}_{26}$ [204], $\text{Ba}_3\text{La}(\text{PO}_4)_3$ [205], and $\text{Ba}_5\text{Zn}_4\text{Y}_8\text{O}_{21}$ [206], BTO [207], BBiVO [208], NaGdMgTeO_6 [209], $\text{Ba}_3\text{LaNb}_3\text{O}_{12}$ [210], $\text{CaZr}_4(\text{PO}_4)_6$ [211] which results in absorption of n-UV light and emission in the intense orange-red region suitable for horticultural and w-LED applications..

To our current understanding, the utilization of Sm^{3+} ion-doped LBW phosphor was initially introduced to explore its potential uses in w-LEDs.

5.2 SAMPLE PREPARATION

Samarium ion-doped LBW phosphors were synthesized at varying concentrations of Sm^{3+} ions (i.e., 0.5, 1.0, 2.0, 3.0 and 5 mol%) utilizing conventional SSR technique as discussed in section 0 and the detailed flowchart of procedure is represented in Figure 2.2 of chapter 2. The highly pure chemicals Li_2CO_3 (99.0%), BaCO_3 (99.99%), WO_3 (99.99%), and Sm_2O_3 (99.99%) have been taken as raw materials in stoichiometric ratio.

5.3 RESULTS AND DISCUSSION

5.3.1 XRD analysis

The un-doped LBW and Sm^{3+} ions doped LBW phosphors crystalline structure and phase purity were examined using XRD patterns. The XRD patterns for un-doped LBW and LBWS1.0 phosphors are shown in Figure 5.1 (a), together with the appropriate standard JCPDS data (01-072-1717). The well-matched XRD patterns of the phosphor samples with the JCPDS database showed their high purity and therefore, enabled us to speculate the absence of any secondary or impurity phases in the as prepared phosphors even with the addition of Sm^{3+} ions. The synthesized phosphors exhibit strong and precise diffraction peaks, demonstrating their high crystallinity, which is necessary for significantly better illumination. It is also required to determine the radius percentage difference (D_r) between substituted ions and activator ions to better understand the dopant Sm^{3+} ions occupying Ba^{2+} sites in the LBW host lattice.

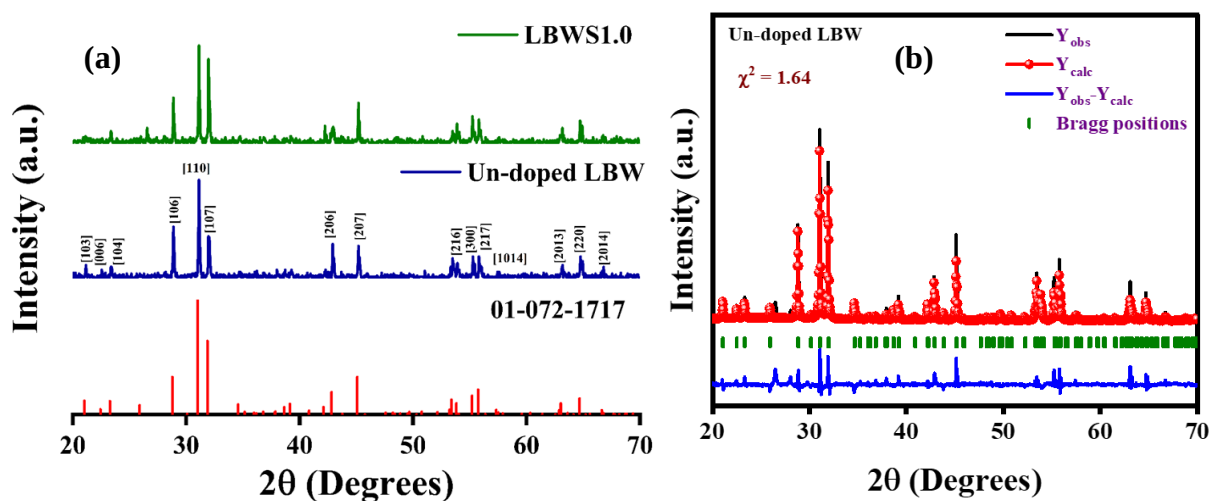


Figure 5.1 (a) The XRD patterns for un-doped LBW and LBWS1.0 phosphor, (b) Rietveld refinement of un-doped LBW sample.

The value of D_r is defined by the equation 2.3 in section 2.3.2.4. The value of D_r was determined to be 26.30%, indicating that Sm^{3+} ions could effectively replace Ba^{2+} ions' positions in LBW host lattices [88]. The well-known Debye-Scherrer formula described in equation 2.4 in section 2.3.2.4 was used to determine the crystallite size (D) while taking into consideration the primary diffraction peaks of the

recorded XRD data. The necessary values of β and θ were extracted from the XRD patterns to determine D. Using the Debye-Scherrer relation, the evaluated value of the average D for the as prepared un-doped LBW sample was found to be equal to 83 nm.

The Rietveld refinement was conducted on the as-prepared Sm^{3+} ions doped LBW phosphors using software from the Fullprof package to investigate the crystal structure and phase. The profile shape refinement has been defined using the pseudo-Voigt function. Rietveld refinement pattern of an un-doped LBW sample is shown in Figure 5.1 (b). Table 5.1 displays the improved parameters for the crystal structure. The calculated goodness of fit (χ^2) was found to be 1.64.

Table 5.1 Refinement parameters for an un-doped LBW material.

Sample	JCPDS	Un-doped LBW
a = b (Å)	5.76	5.757
c (Å)	23.742	23.714
V (Å ³)	682.17	680.863
R _B	-	12.4
R _p (%)	-	30.3
R _{wp} (%)	-	33.3
R _{exp} (%)	-	11.3
χ^2	-	1.64
Density (g/cm ³)	7.264	7.387

5.3.2 SEM: Morphological studies

The SEM metaphors of an un-doped LBW and LBWS2.0 phosphor samples were obtained to better comprehend the data pertaining to the surface morphology and the particle size. Figure 5.2 (a), (b) suggested that the as prepared LBW phosphor materials have uneven polyhedron shapes and particle sizes. Additionally, owing to the hand grinding and a very high-temperature reaction process, some phosphor

particles show low agglomeration. The bulk of commercial phosphor particles available today has a size between 2-10 μm . As a result, the samples' particle sizes are in the μm range, which makes them perfect for coating in displays and white LEDs [212].

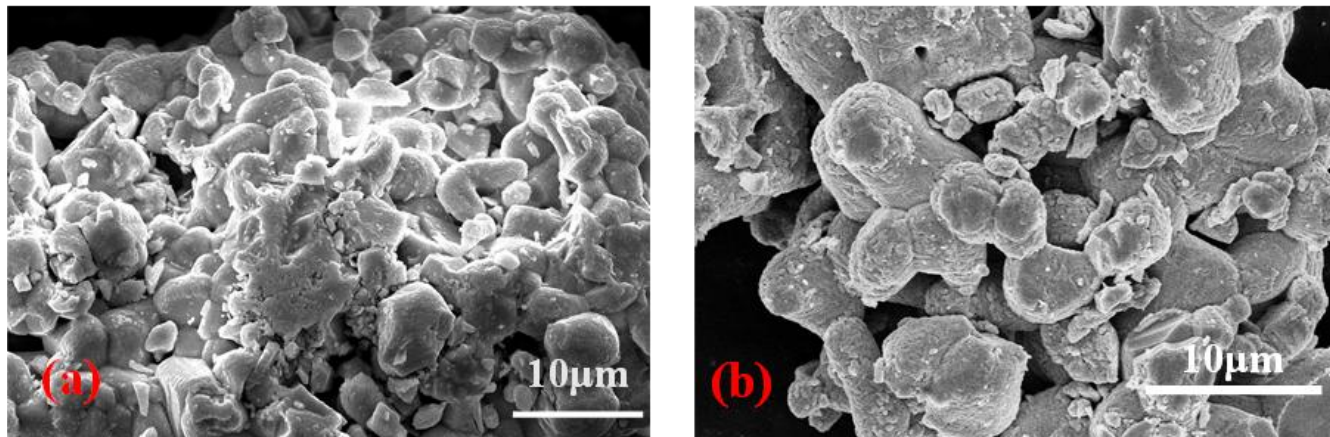


Figure 5.2 (a), (b) The SEM metaphors of an un-doped LBW and LBWS2.0 phosphor sample.

5.3.3 DRS analysis

The DR spectra for LBW:xSm^{3+} phosphors ($x = 0, 0.5, 1.0, 2.0, 3.0$ and 5.0 mol%) in the 200-1500 nm range are shown in Figure 5.3 (a). The spectra consist of a broad absorption band with a maximum nearly at $\lambda = 314$ nm. This should be attributed to the charge transfer between the 2p orbital of oxygen to 5d orbital of tungsten, causing the absorption zone in the range of 280-330 nm. At wavelengths 404, 474, 944, 1072, 1236, 1362, and 1474 nm, respectively, the spectra show transitions from the ground level $^6\text{H}_{5/2}$ to various excited levels $^4\text{F}_{7/2}$, $^4\text{I}_{11/2}$, $^6\text{F}_{11/2}$, $^6\text{F}_{9/2}$, $^6\text{F}_{7/2}$ and $^6\text{H}_{13/2}$ [213].

The bandgap is evaluated by employing the KM function using equations 2.6-2.8 in section 2.3.5 and plotted a graph between $h\nu$ (incident energy) and $[F(R)h\nu]^2$, called Tauc's Plot, as shown in Figure 5.3 (b). By extrapolation of the linear portion of the graph to the x-axis, the bandgap values for Sm^{3+} ions doped LBW phosphor samples were evaluated. The results show that the E_g decreases with increasing Sm^{3+} ions concentration, may be due to the formation of the intermediate energy levels of the Sm^{3+} ions in the LBW host matrix. The variation of bandgap values with Sm^{3+} ions concentration is presented in Table 5.2.

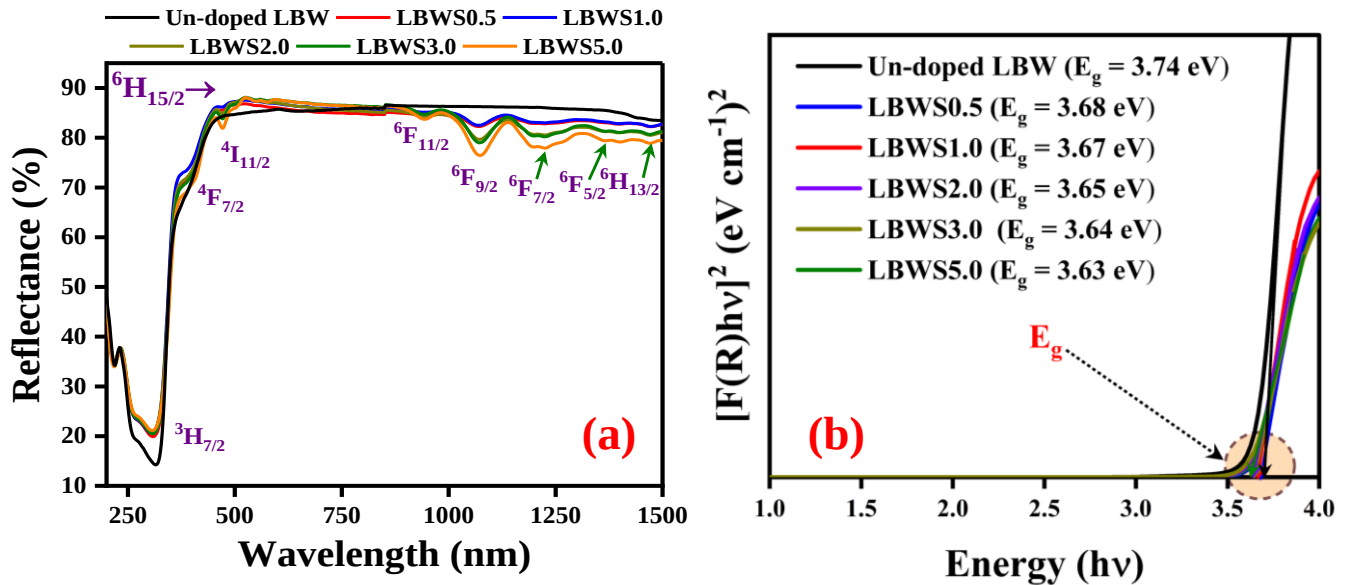


Figure 5.3 (a) DRS and (b) Direct band gap for an un-doped LBW and Sm^{3+} ions doped LBW phosphors.

Table 5.2 Band gap (E_g , eV) of an un-doped LBW and Sm^{3+} ions doped LBW phosphors.

Sm^{3+} (mol %)	System Name	Band Gap (eV)
0	Un-doped LBW	3.74
1	LBWS0.5	3.68
2	LBWS1.0	3.67
3	LBWS2.0	3.65
4	LBWS3.0	3.64
5	LBWD5.0	3.63

5.3.4 PL spectral analysis

The study of PL spectrum features at room temperature allowed us to investigate the PL characteristics of Sm^{3+} ions doped LBW phosphors. Figure 5.4 (a) displays the PL excitation spectrum of LBWS2.0 phosphor in the spectral range of 250-500 nm at $E_m = 581$ nm. Three excitation bands corresponding to the transitions from $^6\text{H}_{5/2}$ to $^6\text{P}_{7/2}$ (378 nm), $^4\text{F}_{7/2}$ (407 nm), and $^4\text{I}_{11/2}$ (467 nm), respectively, along with a charge transfer band (CTB, 336 nm) attributed to the $\text{O}^{2-}\text{-W}^{6+}$ bond comprise the PL excitation spectrum [214,215].

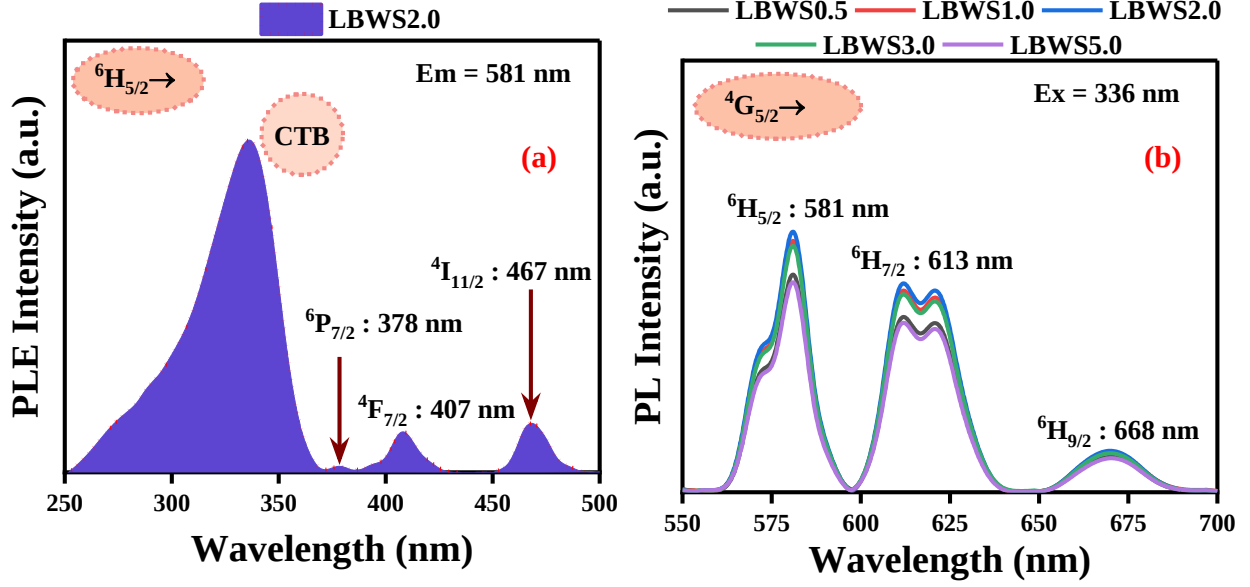


Figure 5.4 PLE spectra for LBWS2.0 phosphor and (b) PL emission spectra of the Sm³⁺ ions doped LBW phosphors at $\lambda_{ex} = 336$ nm.

The CTB is the strongest peak among all the excitation peaks, therefore, considered as the best excitation wavelength for capturing PL emission spectra. The CTB, can be seen in the excitation spectra of Sm³⁺-activated phosphors, serves as evidence for the transfer of energy from the host to the activator Sm³⁺. To address the needs of UV LEDs, the n-UV excitation range between 345 and 420 nm is quite suitable [216]. The PL emission spectra for the as-prepared phosphor LBW:xSm³⁺ (x=0.5, 1.0, 2.0, 3.0, and 5.0 mol%) at Ex = 336 nm are shown in Figure 5.4 (b). Three unique sharp peaks of Sm³⁺ ion emission in the PL emission spectra are attributed to the ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ (581 nm), ${}^6H_{7/2}$ (613 nm), and ${}^6H_{9/2}$ (668 nm) transitions, respectively, in 550-700 nm wavelength range [216]. Amid all, the peak corresponding to ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ (581 nm) transition is considerably more efficient. The splitting in the PL peaks in the PL emission spectra can be attributed to the stark splitting [217]. The PL emission peak at 668 nm, attributed to the ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition, is widely recognized as being solely an ED transition ($\Delta J \leq 6$). Conversely, the emission peak equivalent to ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ transition (at 581 nm), is exclusively an MD transition ($\Delta J = 0, \pm 1$). However, the transition corresponding to ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ (at 613 nm), exhibits a combination of both ED and MD characteristics [218]. ED transitions are not allowed in 4f-4f transitions. The ratio of ED

to MD transitions provides information about the environment of the dopant ion within the host matrix. Asymmetric nature arises from a greater ED transition, and vice versa [219]. In the examined lattice, the MD transition corresponding to the ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ transition at a wavelength of 581 nm is more prominent than the other ED transitions, indicating the high symmetry lattice position of Sm^{3+} ions. Consequently, the luminescent color emitted by the Sm^{3+} ions is expected to fall within the deep orange-red spectral region. The energy level diagram of Sm^{3+} ions in the as synthesized phosphor is presented in Figure 5.5, along with the processes for excitation, emission, ET, and CRCs. The Sm^{3+} ions are gradually promoted to a higher energy state before decaying non-radiatively to a meta-stable state (${}^4G_{5/2}$). Since a part of the energy is quickly released during non-radiative transitions which transfer Sm^{3+} ions in a ${}^4G_{5/2}$ metastable state. Through radiative decay, the Sm^{3+} ions transit from the ${}^4G_{5/2}$ energy level to the lower energy levels of ${}^6H_{5/2}$, ${}^6H_{7/2}$, and ${}^6H_{9/2}$. The reduction in intensity is attributed to resonant energy transfer (RET) interactions between the adjacent Sm^{3+} ions, which also contribute to processes like CRC and self-quenching. The probable RET channel (${}^4F_{9/2} \rightarrow {}^6H_{15/2}$) and CRC are responsible for non-radiative ET mechanisms in the prepared phosphor materials and are represented below [220]:

CRC 1: (${}^4G_{5/2} + {}^6H_{5/2} \rightarrow {}^6F_{5/2} + {}^6F_{11/2}$),

CRC 2: (${}^4G_{5/2} + {}^6H_{5/2} \rightarrow {}^6F_{7/2} + {}^6F_{9/2}$),

CRC 3: (${}^4G_{5/2} + {}^6H_{5/2} \rightarrow {}^6F_{9/2} + {}^6F_{7/2}$),

CRC 4: (${}^4G_{5/2} + {}^6H_{5/2} \rightarrow {}^6F_{11/2} + {}^6F_{5/2}$)

The PL spectral intensities of the peaks increase with Sm^{3+} ions concentration up to 2.0 mol% and after this, concentration quenching is observed due to the energy transfer between Sm^{3+} - Sm^{3+} ions. As the concentration of Sm^{3+} increases, the distance between the nearest Sm^{3+} ions decrease significantly. This proximity enhances interaction among neighbouring Sm^{3+} ions, leading to non-radiative energy transfer. The various interaction such as exchange contact, multipole-multipole interaction among the activator ions and radiation re-absorption etc. collectively contributes to concentration quenching.

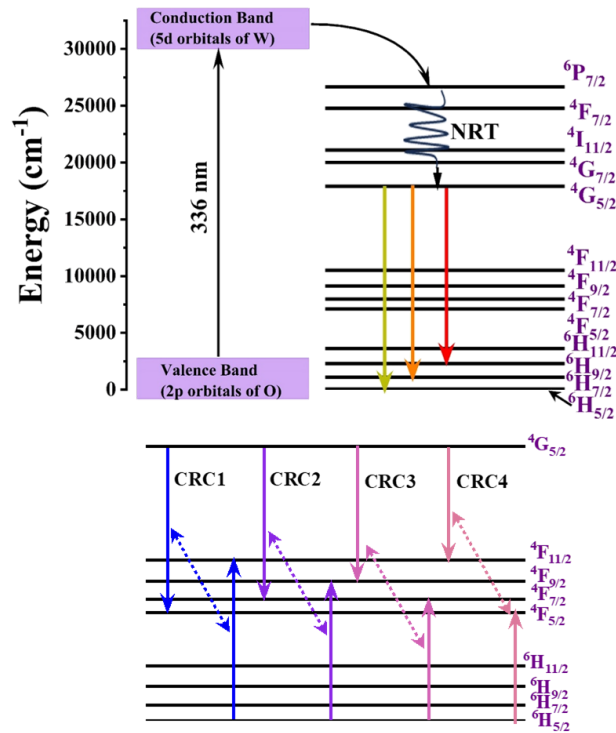


Figure 5.5 The schematic energy level diagram of Sm^{3+} ions doped LBW phosphor.

To comprehend the nature of interaction among the Sm^{3+} ions, the critical distance (R_c) is estimated using the Blasse's formula given by equation 1.1 in section 1.4. The Sm^{3+} ions doped LBW phosphor's critical distance was found to be $31.94 \text{ \AA}$. As $R_c \geq 5 \text{ \AA}$, therefore, the electric multipolar contact is responsible for energy transfer. Huang's theory gives a relation between the luminous intensity (I) and mole fraction (x) of the activator ions shown by equation 1.2 in section 1.4.1.

The $\left(\frac{s}{d}\right)$ value is calculated using the slope of the linear fitted curve between $\log\left(\frac{I}{x}\right)$ and $\log(x)$, as illustrated in Figure 5.6. The predicted s value is 5.4, which is extremely near to 6, suggests that the dipole-dipole character of the concentration quenching between the Sm^{3+} ions in LBW phosphors is the cause.

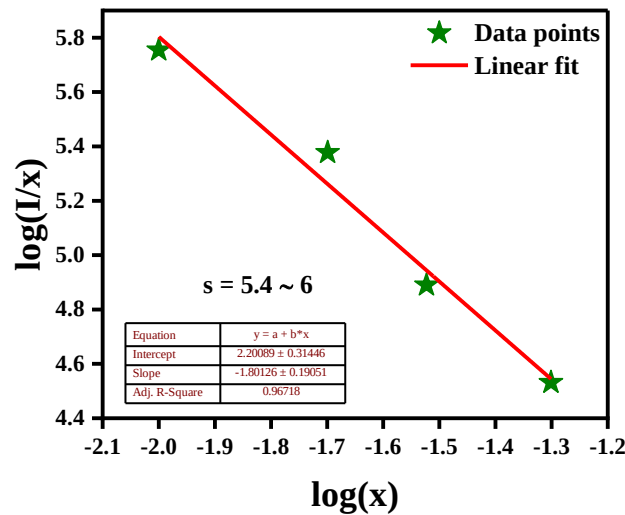


Figure 5.6 The relation between $\log(I/x)$ and $\log(x)$, for Sm^{3+} ions doped LBW phosphors under $\lambda_{\text{ex}} = 336$ nm for $\lambda_{\text{em}} = 581$ nm.

5.3.5 Colorimetric analysis

CIE coordinates are commonly used to illustrate and define the color of a phosphor. The shape or location of the PL emission peaks are unaffected by variations in Sm^{3+} concentration, however, the PL emission intensity may alter. The CIE coordinates were evaluated using the formula given in literature [30,136] and shown in equations 1.9-1.10 in section 1.5.1. All the phosphor's CIE coordinates fall in the region of deep orange-red light in the CIE diagram, as illustrated in Figure 5.7, making it suitable to produce w-LEDs. A further significant measure for highlighting the role and importance of Sm^{3+} ions doped phosphor is the colour saturation which is explained using CP which is calculated using the formula given in equation 1.11 in section 1.5.1. The CP for the optimized LBWS2.0 phosphor sample is found to be more than 80%. Another important element in colorimetric calculations used to examine the CCT. A formula for computing the CCT values is offered by McCamy given in equation 1.12 in section 1.5.2. The CCT values for the prepared Sm^{3+} ions doped LBW phosphors were found to be less than 5000 K, indicating that it can be used to produce warm white light [33].

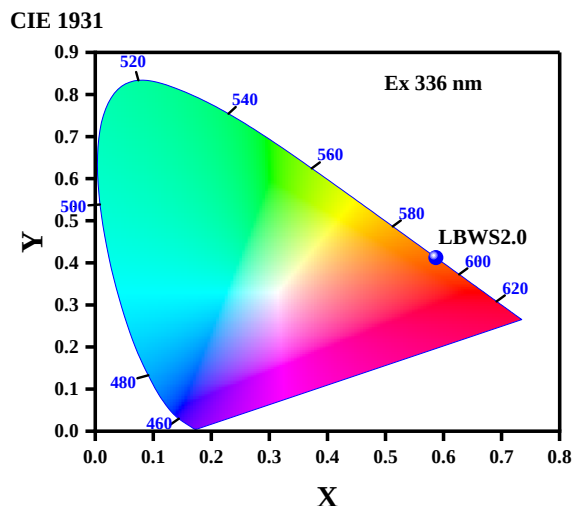


Figure 5.7 CIE chromaticity coordinates for LBWS2.0 phosphor under 336 nm excitation wavelength.

The values of CIE coordinates, CP (%) and CCT (K) values, presented in Table 5.3, demonstrate the suitability of the as-prepared Sm^{3+} ions doped LBW phosphor materials for plasma display panels and solid-state illumination as well as in n-UV or blue light excited w-LEDs.

Table 5.3 CIE chromaticity coordinates, CP (%) and CCT (K) for as prepared Sm^{3+} ions doped LBW phosphors.

System Name	CIE Coordinates		CP (%)	CCT (K)
	X	Y		
LBWS0.5	0.5845	0.4141	82	1749
LBWS1.0	0.5848	0.4138	81	1748
LBWS2.0	0.5851	0.4136	88	1747
LBWS3.0	0.5848	0.4138	83	1748
LBWD5.0	0.5849	0.4137	85	1747

5.3.6 PL decay profile analysis

The PL decay spectra for the as-prepared Sm^{3+} ions doped LBW phosphors are shown in Figure 5.8 under $\text{Ex} = 336 \text{ nm}$ and $\text{Em} = 581 \text{ nm}$ under normal conditions. The decay curves were analyzed to various exponential equations, but for all the Sm^{3+} ion concentrations, a bi-exponential equation provided the best

fit, signifying a substantial interaction between dopant ions and energy transfer from excited donor Sm^{3+} ions to unexcited acceptor Sm^{3+} ions. This exchange implies that the RE ions within the host matrix probably exist in two separate crystallographic locations. The bi-exponential fitting shown in equation 2.10 represents the best fit for the decay profile data of the prepared samples. Further the τ_{exp} values were evaluated using the equation 2.11 in section 1.5.4. The τ_{exp} values of the as-synthesized LBW: $x\text{Sm}^{3+}$ ($x = 0.5, 1.0, 2.0, 3.0$ and 5.0 mol%) phosphors were 1.73, 1.63, 1.53, 1.52 and 1.24 ms, respectively. The observed τ_{exp} values exhibited a decline as the concentration of Sm^{3+} ions increased, possibly indicating an energy transfer between adjacent Sm^{3+} - Sm^{3+} ions over shorter distances.

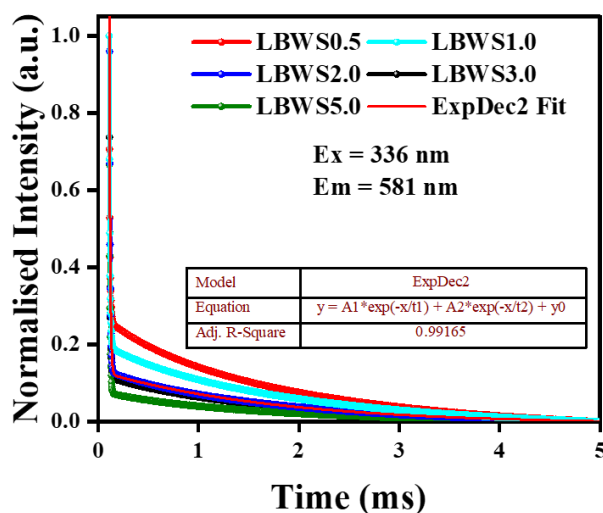


Figure 5.8 PL decay curves of Sm^{3+} ions doped LBW phosphors under $E_m = 581$ nm and $E_x = 336$ nm.

5.3.7 TDPL spectral analysis

TDPL spectra of LBWS2.0 phosphor were measured over a temperature range of 30 °C to 170 °C using $E_x = 336$ nm to study the thermal quenching characteristics. Analysis of the TDPL spectra of LBWS2.0 phosphor revealed that as the temperature increases, the intensities of the photoluminescent bands decreases while maintaining their peak positions, as illustrated in Figure 5.9 (a). The decrease in phosphor luminescence with increasing temperature can be explained by a non-radiative transition process. The inset in Figure 5.9 (a) illustrates the normalized intensity variation of the $^4G_{5/2} \rightarrow ^6H_{5/2}$ transition

concerning temperature, where the PL emission intensity is set as 100% at 30 °C. The PL emission intensity reduces to 74% at 150 °C and 65% at 170 °C, indicating the relatively high thermal stability of LBWS2.0 phosphor.

Furthermore, the assessment of thermal characteristics for the optimized LBWS2.0 phosphor included the determination of activation energy (ΔE) using the Arrhenius relation given by equation 2.16 in section 2.3.8. The value of ΔE was evaluated using the slope of a linearly fitted graph that correlates $\ln \left[\left(\frac{I_0}{I_T} \right) - 1 \right]$ (along y-axis) with $\left(\frac{1}{KT} \right)$ (along x-axis), depicted in Figure 5.9 (b). The estimated ΔE value is 0.249 eV, which is relatively higher than the values reported in prior research [221–223]; represents a comparatively better thermal stability of the as-prepared LBWS2.0 phosphor. The minimal variation in the CIE color chromaticity coordinates with the change in temperature, as illustrated in Figure 5.9 (c) and (d), further confirms the thermal stability of the LBWS2.0 phosphor sample.

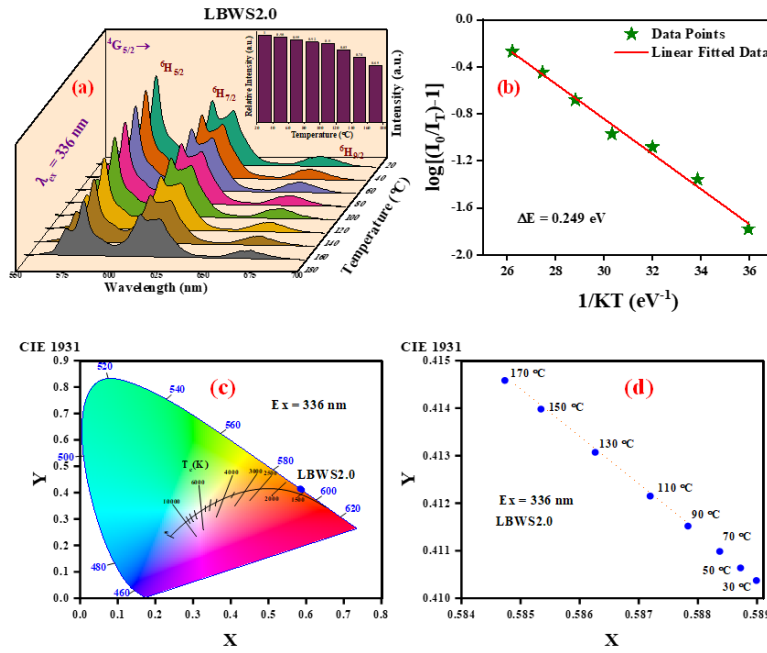


Figure 5.9 (a) TDPL spectra of LBWS2.0 phosphor at 30° to 170 °C under 336 nm UV light (Inset shows the variation of the relative PL intensities of the emission peak at 581 nm with temperature); (b) Plot between $\ln \left[\left(\frac{I_0}{I_T} \right) - 1 \right]$ versus $\left(\frac{1}{KT} \right)$ and (c) & (d) The variation in CIE color chromaticity coordinates with temperature.

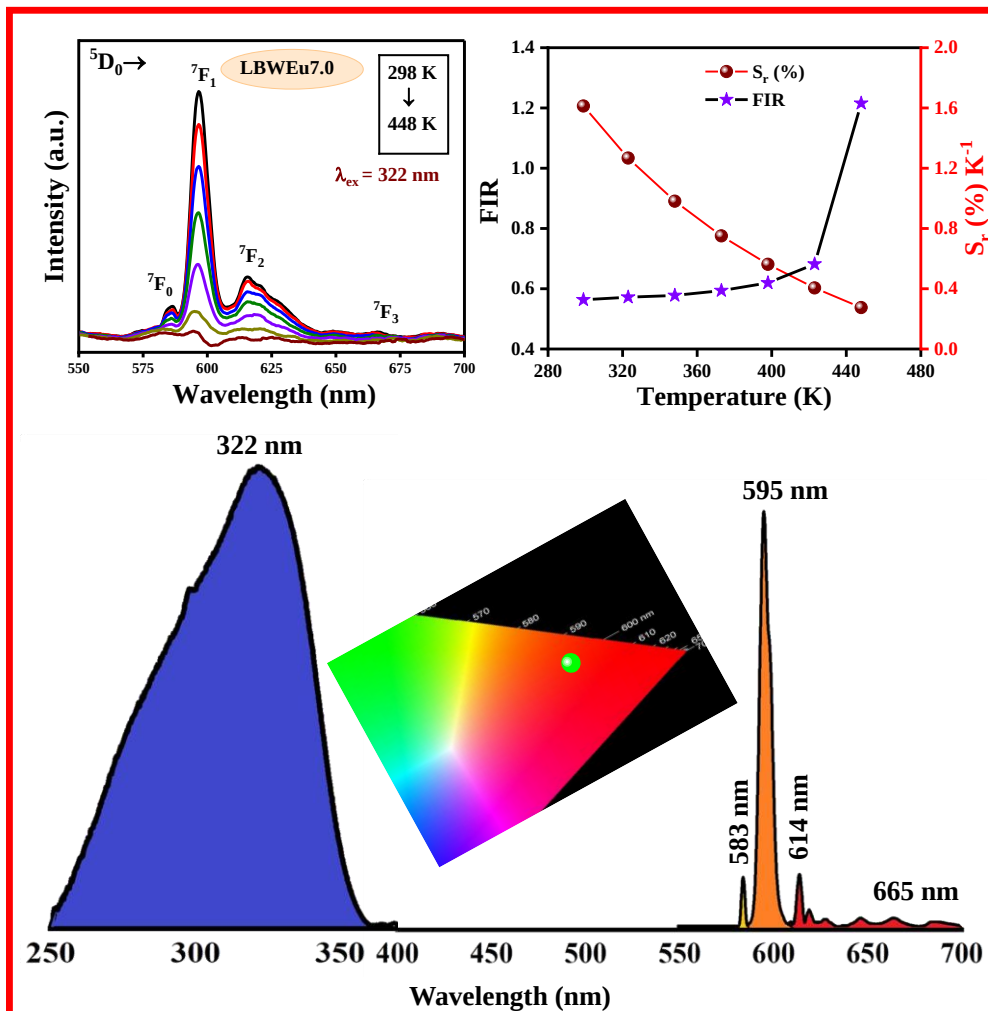
Consequently, the comprehensive TDPL analysis confirms the enhanced thermal stability of the LBWS2.0 phosphor, endorsing its suitability for the fabrication of visible photonic devices.

5.4 CONCLUSIONS

In brief, SSR method successfully synthesized a series of Sm^{3+} ions doped LBW phosphors. Various aspects of their structural, morphological, and photoluminescent properties were examined. The XRD analysis confirmed the crystallinity and purity of the as synthesized phosphors alongwith an average crystallite size of approximately 83 nm. The SEM images depicted irregular shapes with mild clustering, and the particle size fell within the μm range. The E_g values (3.74-3.63 eV) indicate the potential utility of the as-prepared phosphor samples in photonic devices. From PL analyses, the synthesized phosphors exhibited three emission bands, with the most prominent at 581 nm attributed to the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ transition upon $\text{Ex} = 336$ nm. The influence of Sm^{3+} ion concentration on the PL properties of the LBW phosphor highlighted concentration quenching at a 2.0 mol% Sm^{3+} ions concentration. The interaction between Sm^{3+} ions through dipole-dipole interaction is elucidated by employing the Dexter theory. The optimized LBWS2.0 sample exhibits CIE coordinates (0.586, 0.412) at $\text{Ex} = 336$ nm, lies in a deep orange-red region. The PL decay pattern displays a bi-exponential fitting with decay lifetimes (τ_{exp}) of millisecond (ms) range. The thermal stability of the phosphors was confirmed through TDPL analysis. Collectively, these investigations emphasize the superior potential of Sm^{3+} ion-doped LBW phosphors for the creation of photonic devices such as w-LEDs.

CHAPTER 6

NOVEL ORANGE-RED EMITTING $\text{Li}_2\text{Ba}_5(\text{WO}_5)_3:\text{Eu}^{3+}$ PHOSPHOR FOR W-LEDs AND NON-CONTACT THERMOMETRY APPLICATIONS



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<https://doi.org/10.1007/s10854-023-11602-4>*

6.1 INTRODUCTION

The basics of w-LEDs and methods of generating white light along with the significance of the host lattice is already discussed in Chapter 1. Phosphors are the substances that absorb energy and then release it as UV, visible, or IR light. They are made up of an inorganic host that has been doped with activator ions; may be transition metal or RE ions. RE-doped phosphors in particular are significant materials with numerous applications in artificial lighting, X-ray medical radiography, display technology, and high-power solid-state lasers [224]. Phosphor thermometry is a non-contact method for measuring temperature remotely using light signals. Thermographic phosphors (TGPs) are the phosphors created especially for phosphor thermometry. TGPs are resistant to oxidation in high-temperature situations and do not react with harsh chemicals, in contrast to standard techniques of monitoring temperature (thermocouples, thermistors, thermal paints). The type of RE impurity and the host, both affect the temperature-dependent changes in the TGPs' emission properties. Both the decay observations and the intensity ratio measurements serve as the foundation for phosphor thermometry. The latter has gained a lot of acceptance since it eliminates the possibility of several mistakes caused by variations in the excitation light source, temperature changes in the excitation bands, and uneven dopant concentrations [225] and has been used in the present study. It has recently been difficult to get fluorescence thermal sensing technology results for reliable temperature estimation. As a result, the need for appropriate RE-doped optical temperature-sensing materials exists. Additionally, suitable methodologies should be employed to establish the relation between temperature and fluorescence characteristics. The luminous phosphor doped with Eu^{3+} ions has a relatively high luminescence efficiency [226–228]. Moreover, energy levels of $^5\text{D}_0 \rightarrow ^4\text{F}_1$ and $^5\text{D}_0 \rightarrow ^4\text{F}_2$ of Eu^{3+} can be used as the TCLs.

Recently, many studies have been conducted on the introduction of RE^{3+} activator ions into various hosts for the usage in w-LEDs, resulting in substantial advancements. But due to a number of drawbacks, such as poor chemical and thermal stability, and poor fluorescence efficiency, orange and red phosphors still

need to be improved [229–231]. Further, due to their employment as luminous optical materials emitting in the visible and NIR regions, the absorption and emission of RE-activated crystalline hosts via f-f transition are of great interest [232]. The RE-activated inorganic materials have received significant attention due to the remarkable luminous characteristics and narrow emission bands [233,234]. Amid all the RE³⁺ ions, trivalent europium (Eu³⁺) can act as a strong activator ion [235–237].

Recently, several Eu³⁺ ions activated host matrices have already been reported, such as Parauha et al. synthesized Eu³⁺ ions doped Na₂CaSiO₄ phosphor that exhibits prominent orange and red emission bands due to the ⁵D₀→⁷F_{1,2} transitions, potentially leading to applications in lighting and display devices [88]. S. Wang and his co-workers prepared a thermally stable Y₂SiWO₈:Eu³⁺ for w-LEDs [238]. Shi et al. suggested blended phosphors for white light by combining (Gd₆WO₁₂:Eu³⁺) red and (YAG:Ce³⁺) yellow phosphors to enhance the color rendering of w-LEDs [239]. The aforementioned research work in the Eu³⁺ ions activated tungstate phosphors motivated us to explore this field.

6.2 EXPERIMENTAL STUDIES

Europium ions doped LBW phosphors at different concentrations of Eu³⁺ ions (i.e., 1, 3, 5, 7 and 9 mol%) are synthesized utilizing conventional SSR technique as discussed in section 0 and the detailed flowchart of procedure is represented in Figure 2.2 of chapter 2. The highly pure chemicals BaCO₃ (98%), Li₂CO₃ (98%), WO₃ (99.9%), Eu₂O₃ (99.9%) have been taken as raw materials in stoichiometric ratio.

6.3 RESULTS AND DISCUSSION

6.3.1 XRD measurements

The XRD patterns were utilized to analyze the crystalline structure and the phase purity of the as prepared phosphor samples. The XRD patterns of an un-doped LBW and optimised LBWEu9.0 phosphor samples follow the standard JCPDS data (01-072-1717), displayed in Figure 6.1 (a). The diffraction patterns for the LBW samples doped with Eu³⁺ ions are alike to standard data, indicating that the Eu³⁺ ions were

efficiently incorporated in the host material without causing any structural alterations. It is also required to determine the radius percentage difference (D_r) between substituted ions and activator ions to better understand the dopant Eu^{3+} ions occupying Ba^{2+} sites in the LBW host lattice. The value of D_r is evaluated using the expression given by equation 2.3 in section 2.3.2.4 in Chapter 2 and found to be 29.85%, indicating that Eu^{3+} could effectively replace Ba^{2+} ion positions in LBW host lattice [88,123]. Further to evaluate the crystallite size (D) using the diffraction data [240], the Debye Scherrer formula given in equation 2.4 in section 2.3.2.4 in Chapter 2 is used and evaluate to be equal to 83 nm.

Additionally, peak shifting and line broadening in XRD spectral patterns are due to the existence of microstrain in the phosphors, which was determined by using W-H equation 2.5 given in section 2.3.2.4 in Chapter 2. A linear fit graph between $\beta \cos(\theta)$ (y-axis) and $4 \sin(\theta)$ (x-axis) is shown in Figure 6.1 (b). D was determined from the intercept of the linearly fitted plot and microstrain from the slope value and were found to be nearly equal to 85 nm and 4.51×10^{-4} , respectively. The values of D computed using the above-discussed two methods varied slightly. This is because the strain component was assumed to be zero in Scherrer's formula and the apparent broadening of the XRD peaks was exclusively attributed to grain-size reduction. The VESTA software was used to analyse the hexagonal crystal structure for the host lattice, shown in Figure 6.1 (c).

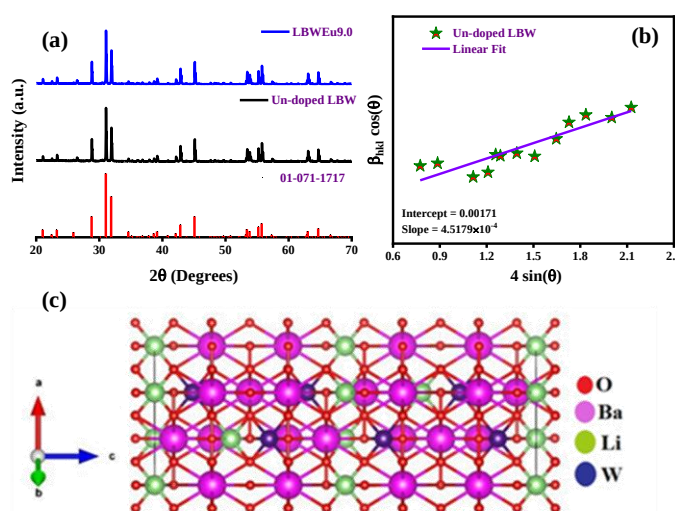


Figure 6.1 (a) The XRD patterns of an un-doped LBW and LBWEu9.0 phosphors, (b) A linear fit graph between $\beta \cos \theta$ (y-axis) and $4 \sin \theta$ (x-axis), (c) Crystal structure of an un-doped LBW sample.

6.3.2 SEM study

A key element for successful application in commercial w-LEDs is the surface morphology. The SEM and EDAX data were recorded to completely analyse the morphological behaviour of the as prepared phosphor samples. The SEM images of the as-prepared LBW: $x\text{Eu}^{3+}$ ($x = 0, 3$) phosphor samples were taken at distinct scales and resolutions to examine the morphological aspects and have been shown in Figure 6.2. Figure 6.2 (a), (c) represent the SEM images for an un-doped LBW sample and Figure 6.2 (b), (d) represent the LBWEu3.0 phosphor with different magnifications and scales, which depict different particle morphologies with irregular shapes. The particles of phosphor with a size in microns (2-4 μm) have been aggregated as a result of hand grinding and high-temperature sintering. Smaller particles with a larger surface-to-volume ratio than bulk particles are considered to be the cause behind agglomeration [241]. Smaller particles can therefore have a lot of surface energy; as a result, they tend to group together to form larger particles in order to lower this energy and to increase the stability. The phosphor particles with size ranges in micro meters (μm) have been considered more convenient for use in pc w-LEDs [42].

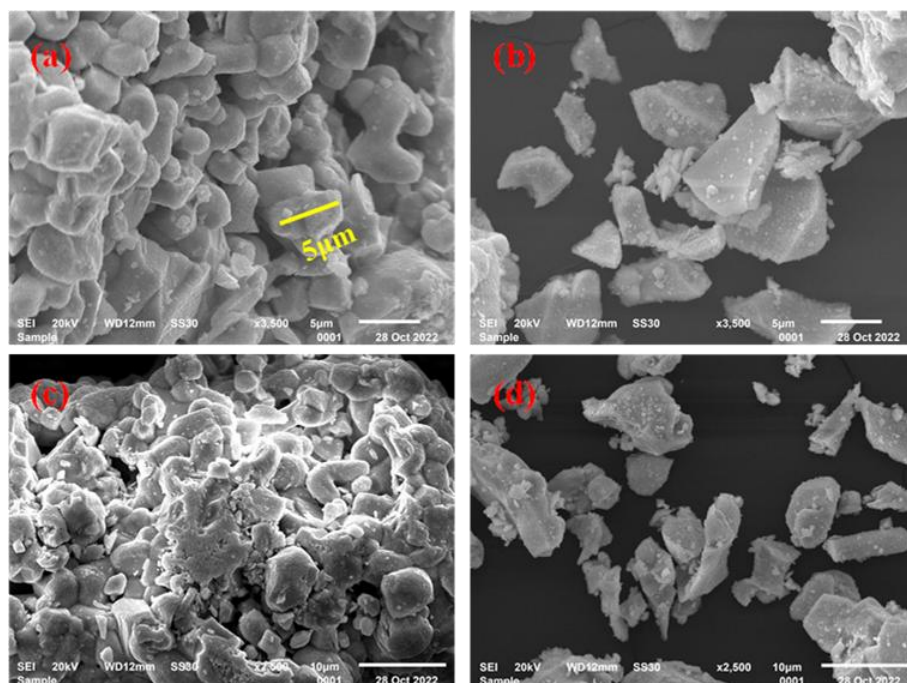


Figure 6.2 SEM images for (a), (c) an un-doped LBW sample; and (b), (d) LBWEu3.0 phosphor.

The atomic and weight percentages of the elements that are present in the LBW: $x\text{Eu}^{3+}$ ($x = 0, 3 \text{ mol\%}$) phosphors have been depicted in EDAX spectra, as shown in Figure 6.3. From Figure 6.3, it is conspicuous that, the elements such as Barium (Ba), tungsten (W), oxygen (O), and europium (Eu) are present in the as-prepared phosphor. However, the elements pertaining to Lithium (Li) is not observed in the EDAX spectra as it is a light particle. From literature it is evident that, the light particles such as Li with very low energy of characteristic radiation, does not exhibit any peak in the EDAX spectra [46].

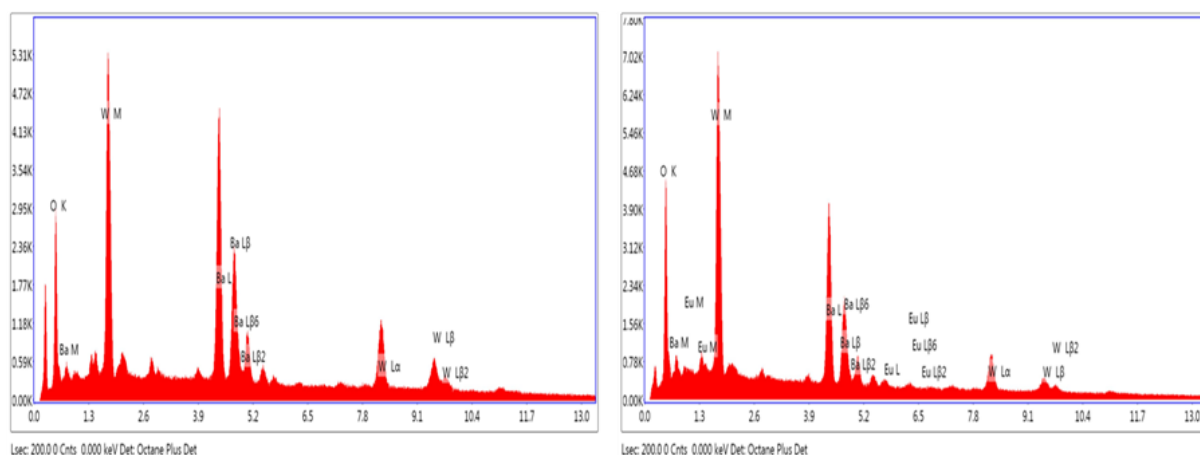


Figure 6.3 EDAX spectra for an un-doped LBW and LBWEu3.0 phosphors.

6.3.3 Thermal properties

The temperature-dependent weight loss of the as-prepared un-doped LBW material in TGA was studied to understand the thermal behavior. The TGA pattern, given in Figure 6.4, shows a total weight loss of 12.25% over a temperature range of 30 to 900°C, leaving 87.75% of the original weight. The TGA curve indicates that weight loss with temperature occurs in two stages. From 316° to 632°C, an initial weight loss of almost 3.31% was detected due to decomposition of the raw materials [242]. At temperatures between 632°C and 736°C, there was a consistent drop with 8.31% weight loss of the as-prepared LBW phosphor material was detected. The weight loss ceased and maintained a consistent trend when the temperature reached around 800°C, indicating that the calcination stage was over 800°C.

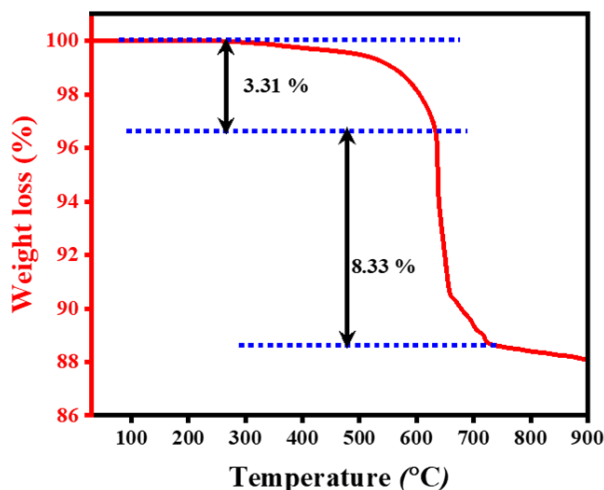


Figure 6.4 Thermogravimetric analysis (TGA) of an un-doped LBW sample.

6.3.4 DRS analysis and optical bandgap measurements

The optical band gap (E_g) evaluating from the DRS is a crucial parameter for phosphor materials used in w-LEDs. The DRS was measured for an un-doped LBW and LBWEu9.0 phosphor in between 200-1000 nm wavelength range and has been presented in Figure 6.5. This spectrum consists of a broad absorption band with a maximum absorption at nearly 306 nm wavelength. This should be attributed to the charge transfer between the 2p orbital of oxygen to 5d orbital of tungsten, causes the absorption zone in the range of 280-330 nm. LBWEu9.0 phosphor sample also shows several narrow characteristic absorption lines at 464, 530 and 596 nm, which correspond to the $^7F_0 \rightarrow ^5D_{2,1,0}$ transitions of Eu^{3+} ions, respectively (inset of Figure 6.5) [243].

The reflectance spectrum is used by employing the K-M function and using equations 2.7-2.8 and then a graph was plotted between $h\nu$ (incident energy) and $[F(R)h\nu]^2$, called Tauc Plot, for Eu^{3+} ions doped LBW phosphor samples. By extrapolation of the linear portion of the graph to the x-axis, the bandgap values of LBW:xEu^{3+} samples were evaluated, as shown in Figure 6.6.

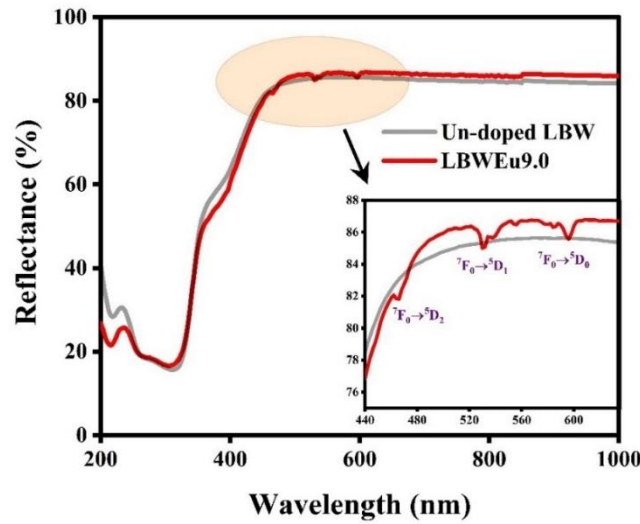


Figure 6.5 The diffuse reflectance spectrum (DRS) for an un-doped LBW and LBWEu9.0 phosphor.

The results show that the E_g values decrease with increasing Eu^{3+} ions concentration due to the formation of the intermediate energy levels of the Eu^{3+} ions in the LBW host matrix. The decrease is very less with increasing dopant ions concentration, revealing that the dopant ions do not have much effect on the structural behavior of the as-prepared LBW phosphor materials. The variation of bandgap with Eu^{3+} ions concentration is presented in Table 6.1.

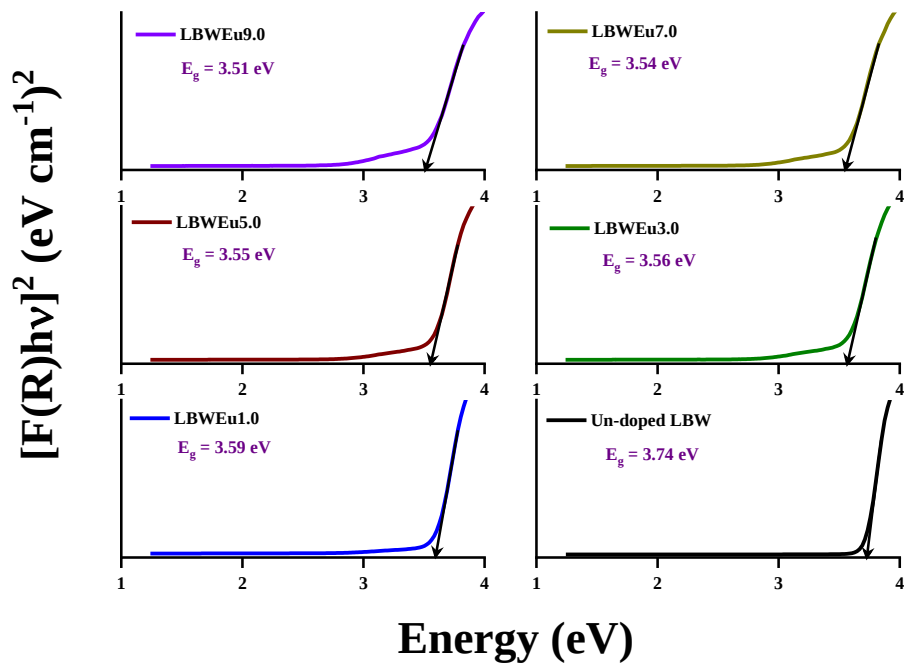


Figure 6.6 Tauc's plot for an un-doped LBW and LBW: $x\text{Eu}^{3+}$ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors.

According to calculations given in equation 2.9, the Urbach's energies for LBW: $x\text{Eu}^{3+}$ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors are 0.48, 0.36, 0.34, 0.30, and 0.24 eV, respectively, shown in Table 6.1. The Urbach's energy decreases with an increase in dopant ions concentration in the LBW phosphors indicating the decrement of defects and disorder in the host lattice with Eu^{3+} ions concentration. This means that there is relatively less chaos and lesser defects making the phosphors useful in enhancing its luminescence efficiency.

Table 6.1 Bandgap E_g (eV) and Urbach's Energy ΔE (eV) of an un-doped LBW and LBW: $x\text{Eu}^{3+}$ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors.

S. No.	System Name (LBW: $x\text{Eu}^{3+}$)	Band Gap (E_g (eV))	Urbach's Energy (ΔE (eV))
1.	$x = 0$	3.74	0.57
2.	$x = 1.0$ mol%	3.59	0.48
3.	$x = 3.0$ mol%	3.56	0.36
4.	$x = 5.0$ mol%	3.55	0.34
5.	$x = 7.0$ mol%	3.54	0.30
6.	$x = 9.0$ mol%	3.51	0.24

6.3.5 PL spectral analysis

To know more about the comprehend emission spectral features of the Eu^{3+} doped LBW phosphors, it needs to be excited with a suitable wavelength and for this an excitation spectrum need to be recorded by fixing the prominent emission band of Eu^{3+} ions. The excitation spectrum of LBWEu1.0 phosphor was recorded at $\lambda_{\text{em}} = 595$ nm in the wavelength range from 250 to 500 nm, as shown in Figure 6.7. The PL excitation spectrum containing the peaks of Eu^{3+} ions at 388, 396, 409 and 467 nm corresponding to the $^7\text{F}_0$ to $^5\text{G}_2$, $^5\text{L}_6$, $^5\text{D}_3$ and $^5\text{D}_2$ transitions, respectively [244]. A highly intense band is observed at 322 nm

corresponds to CTB suggesting that n-UV light is the best source for phosphor excitation and, therefore, is used as an excitation wavelength to study the PL emission spectrum.

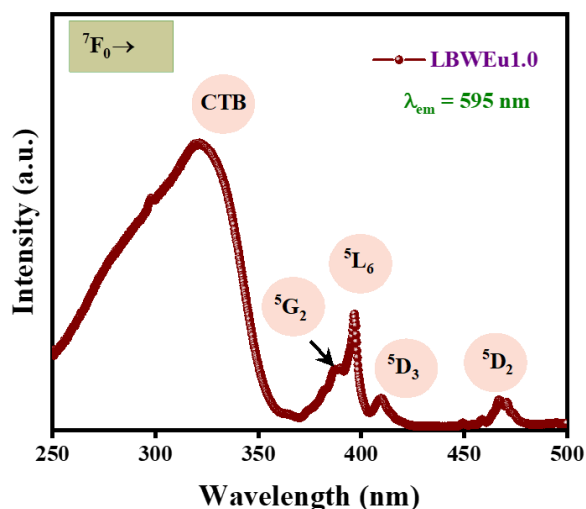


Figure 6.7 The excitation spectrum for LBWEu1.0 phosphor.

The results of the excitation-wavelength-dependent PL analysis, as displayed in Figure 6.8 (a), confirm the above finding.

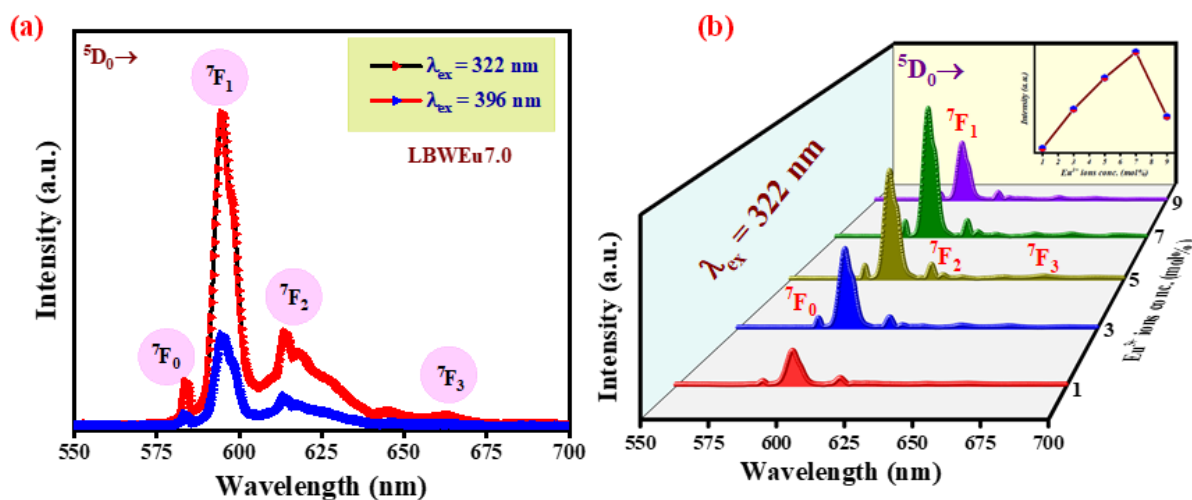


Figure 6.8 (a) Excitation-wavelength-dependent photoluminescence analysis for LBWEu7.0 phosphor, (b) The emission spectra for LBW:xEu³⁺ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors.

To determine the effect of Eu³⁺ ions on the PL intensity, the emission spectra for variable Eu³⁺ ions doped LBW phosphors were recorded. Figure 6.8 (b) illustrates the PL spectra of LBW:xEu³⁺ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors at $\lambda_{ex} = 322$ nm in 550 to 700 nm wavelength range. The spectra

contain peaks at 584, 595, 613 and 663 nm corresponding to $^5D_0 \rightarrow ^7F_0$, $^7F_1$, $^7F_2$ and $^7F_3$ electronic transitions, respectively. The $^5D_0 \rightarrow ^7F_2$ (ED) transition is highly sensitive to the surroundings of the dopant (here Eu^{3+} ions), and as a result, is hypersensitive to the distortion of the inversion symmetry, however, the $^5D_0 \rightarrow ^7F_1$ (MD) transition is independent of the environment [234]. Previous research confirmed that Eu^{3+} ions inhabit low symmetry sites without an inversion centre since the emission spectra clearly showed that the MD transition is dominant over the ED transition [88,245,246]. Ba^{2+} ions with low symmetry can be effectively replaced by Eu^{3+} ions because their ionic radii ($0.947\text{\AA}$) are lower than those of Ba^{2+} ions ($1.35\text{\AA}$), surrounded by six atoms. The positions of the peak do not change as the concentration of Eu^{3+} ions increase, and the intensity of the emission peak increases as well. For Eu^{3+} ions doped LBW phosphor, the maximum intensity is at 7 mol% concentration of Eu^{3+} ions, which is the optimum concentration. Due to the phenomenon of concentration quenching, the PL emission intensity decreases with further increase in Eu^{3+} ions concentration [247–249]. The inset of Figure 6.8 (b) illustrates the intensity variations with doping ions concentration and confirms the concentration quenching at 7 mol% of Eu^{3+} ions in LBW host lattice.

It has been observed that the concentration quenching is firmly related to the critical distance (R_c) between the Eu^{3+} ions. Blasse's theory is used to calculate R_c by applying the formula given in equation 1.1 in section 1.4 of chapter 1. The R_c is evaluated and found to be equal to $19.34\text{\AA}$ which is relatively greater than $5\text{\AA}$, confirming that the electric multipolar-multipolar interaction is the main reason for the concentration quenching in as-synthesized $\text{LBW}:\text{xEu}^{3+}$ phosphors [26,188]. According to the Dexter theory, dopant concentrations are related to luminescence emission intensity and therefore used to evaluate the multipolar-multipolar interactions, using equation 1.2 of section 1.4.1 of chapter 1.

Figure 6.9 represents the plot between $\log(I/x)$ and $\log(x)$ in $\text{LBW}:\text{xEu}^{3+}$ phosphors. The experimental data were linearly fitted and the evaluated value of Q is around 6 representing that the dipole-dipole interaction is responsible for the concentration quenching.

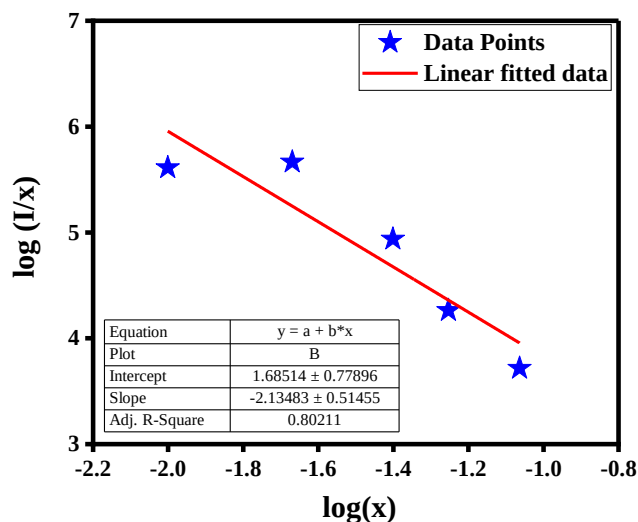


Figure 6.9 Plot between $\log(I/x)$ versus $\log(x)$ in LBW:xEu³⁺ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors.

The emission, excitation and non-radiative processes of Eu³⁺ ions in the LBW host matrix are represented in the energy level diagram, as shown in Figure 6.10. The oxygen 2p orbital electrons are excited by UV light at 322 nm excitation wavelength and move to the tungsten 5d orbital, corresponding to the valence band (VB) to conduction band (CB) transition. These electrons relax to lower energy states of tungsten through non-radiative transitions and then migrate their energies to excite Eu³⁺ ions to higher energy states. The multiphoton relaxation leads to the intensely excited electrons relaxing non-radiatively to a lower energy states and then radiatively from $^5D_0 \rightarrow ^7F_J$ ($J = 0$ to 3).

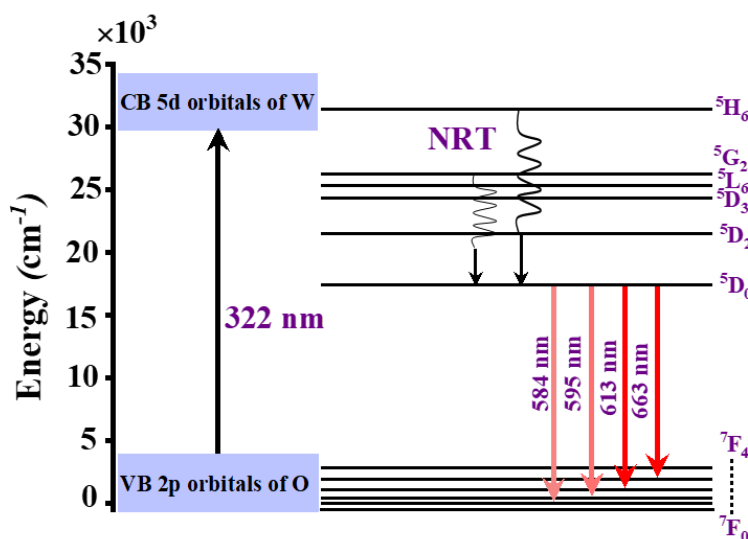


Figure 6.10 Energy Level Diagram for Eu³⁺ ions in LBW host matrix.

6.3.6 CIE and CCT analysis

For the validation of the emission color of LBW: $x\text{Eu}^{3+}$ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors, the CIE chromaticity coordinates were evaluated from the PL spectra with $\lambda_{\text{ex}} = 322$ nm using the formulae given in the literature [30] and in equation 1.9-1.10. The evaluated values of CIE coordinates are (0.6265, 0.3729), (0.6263, 0.3732), (0.6272, 0.3723), (0.6274, 0.3721) and (0.6268, 0.3727) for LBW: $x\text{Eu}^{3+}$ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors, respectively. Figure 6.11 (a) represents the CIE coordinates for LBWEu7.0 phosphor sample and lies in the orange-red region.

CCT is an additional factor which helps in assessing the efficacy of a source of light and is measured using McCamy's polynomial equation 1.12 shown in section 1.5.2 of chapter 1. The “warmness” and “coolness” of the light are commonly examined by the CCT values. The computed CCT values for different Eu^{3+} ions doped LBW phosphors are 1942, 1938, 1953, 1957, and 1946 K, respectively, and therefore, fall within the warm region [33]. The formula mentioned in the literature [250] and in equation 1.11 is used to determine the CP and found to be higher than 79% for all the as-prepared Eu^{3+} ions doped LBW phosphors under $\lambda_{\text{ex}} = 322$ nm, shown in Figure 6.11 (b). The CIE, CCT and CP values are listed in Table 6.2.

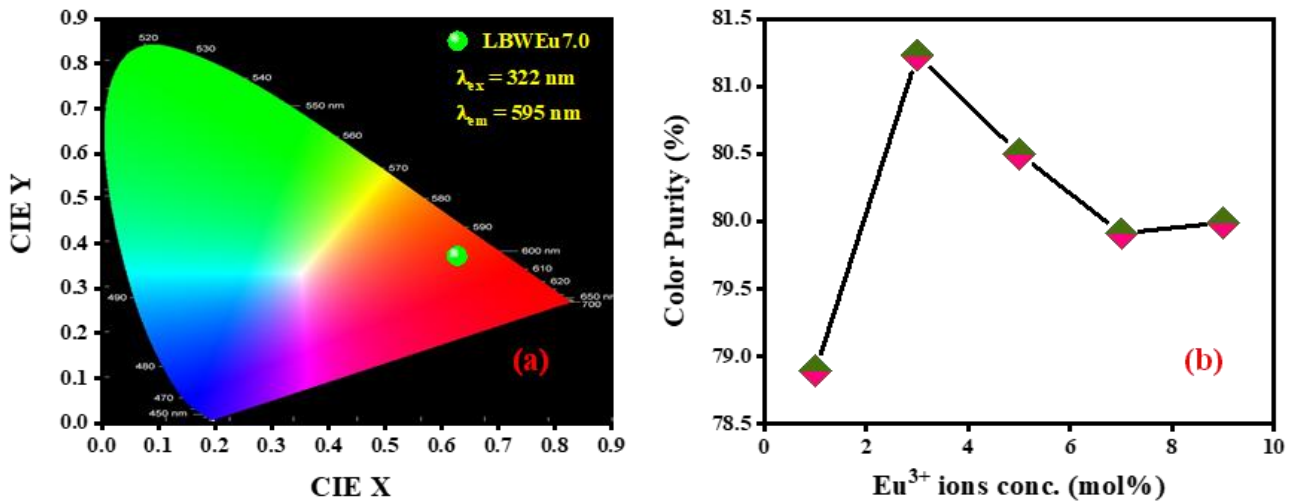


Figure 6.11 (a) CIE chromaticity coordinates for LBWEu7.0 phosphor, (b) CP for LBW: $x\text{Eu}^{3+}$ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors.

Table 6.2 CIE, CCT, CP and experimental lifetime (τ_{exp}) of as-prepared LBW:xEu³⁺ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors.

System Name LBW:xEu ³⁺	CIE Coordinates		CCT (K)	CP (%)	τ_{exp} (ms)	η (%)
	X	Y				
x = 1.0	0.626	0.373	1942	78.89	3.50	72.9
x = 3.0	0.626	0.373	1938	81.23	3.40	70.2
x = 5.0	0.627	0.372	1953	80.51	3.33	68.2
x = 7.0	0.627	0.372	1957	79.91	3.37	74.9
x = 9.0	0.626	0.373	1946	79.99	3.24	71.1

6.3.7 PL decay study

PL decay curves for LBW:xEu³⁺ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors under $\lambda_{\text{em}} = 595$ nm and $\lambda_{\text{ex}} = 322$ nm are shown in Figure 6.12 (a). The double exponential equation, shown by equation 2.10, is the best fit to the observed decay curves. The decay lifetime values decrease with an increase in Eu³⁺ ions concentration in the range of (3.50-3.24) ms, presented in Table 6.2, due to NRT of energy. The luminous quantum efficiency (η) of the as-prepared Eu³⁺ ions doped LBW phosphors are evaluated using the equation 2.12 given in section 2.3.7 of chapter 2 lie in the range 68-75% and presented in Table 6.2.

To identify the associated energy migration process, the I-H model has been used to the decay curves of all the as-prepared Eu³⁺ ions doped LBW phosphors, as shown in Figure 6.12 (b). The decay curves of LBW:xEu³⁺ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors have been best fitted for $s = 6$ using the equation 1.5 given in section 1.4.3 of chapter 1. The best I-H fit for the current samples was observed for $s = 6$, indicating that the Eu³⁺ ions' dominant interaction in LBW phosphor is d-d. Dexter's theory of energy migration yielded the same conclusion.

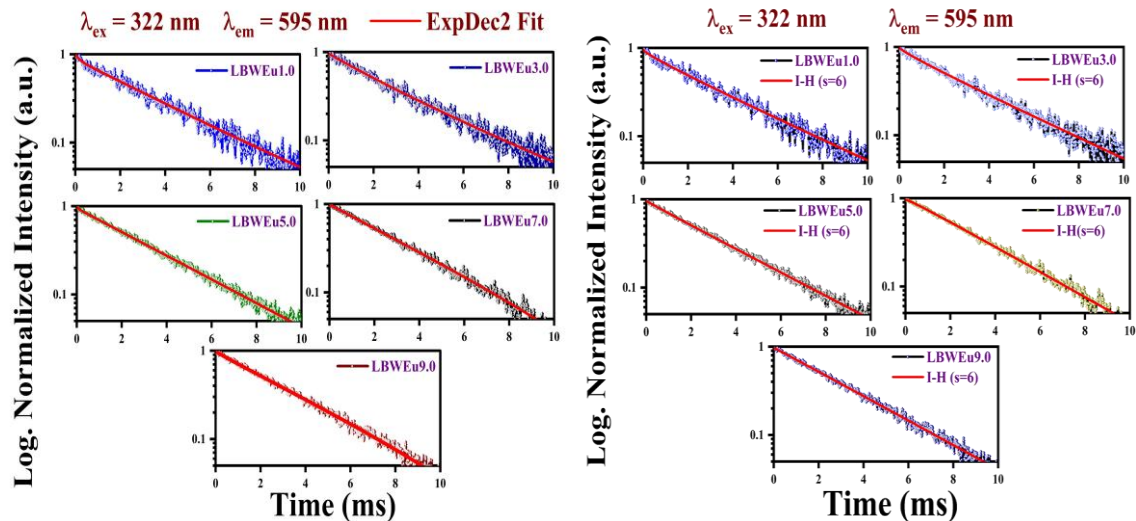


Figure 6.12 (a) PL Decay curves for LBW:xEu³⁺ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors, (b) I-H model fitted curves for LBW:xEu³⁺ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors.

6.3.8 TDPL studies

TDPL spectra of the LBWEu7.0 phosphor at $\lambda_{\text{ex}} = 322$ nm are shown in Figure 6.13 (a) in the temperature range of 298–448 K. There was a drop in the PL emission intensity of the spectra, but there was not a noticeable shift in the position of the PL emission spectra due to the temperature increase. The thermal quenching effect is responsible for the decrease in light intensity as temperature increases [251]. The intensity of PL emission vary differently for the peaks present at 595 and 615 nm with temperature, represented in Figure 6.13 (b) for LBWEu7.0 phosphor sample.

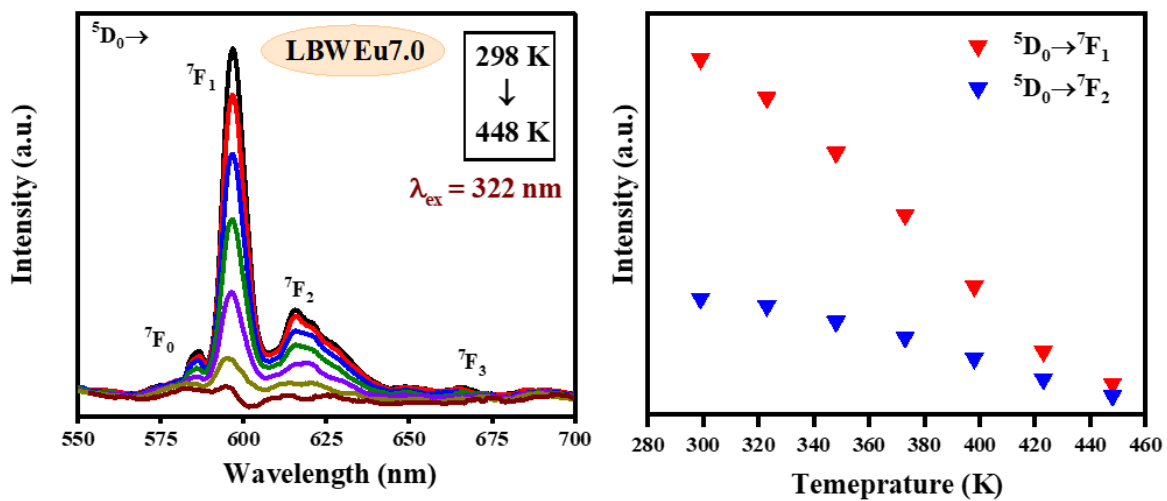


Figure 6.13 (a) TDPL spectra of the LBWEu7.0 phosphor at $\lambda_{\text{ex}} = 322$ nm, (b) Variation of the PL emission intensities of two TCLs of Eu³⁺ ions.

The temperature has an impact on the relative population of various emission levels, which follows a Boltzmann-type distribution. Using the temperature-dependent emission spectra of the LBWEu7.0 phosphor sample (Figure 6.13) under $\lambda_{\text{ex}} = 322 \text{ nm}$, the LIR theory was applied to evaluate its performance as a luminescent thermometer. Due to its simplicity, equipment requirements and most importantly, the fact that it is ratiometric and self-referenced; the LIR has undergone the most research of any luminescent temperature read-out method.

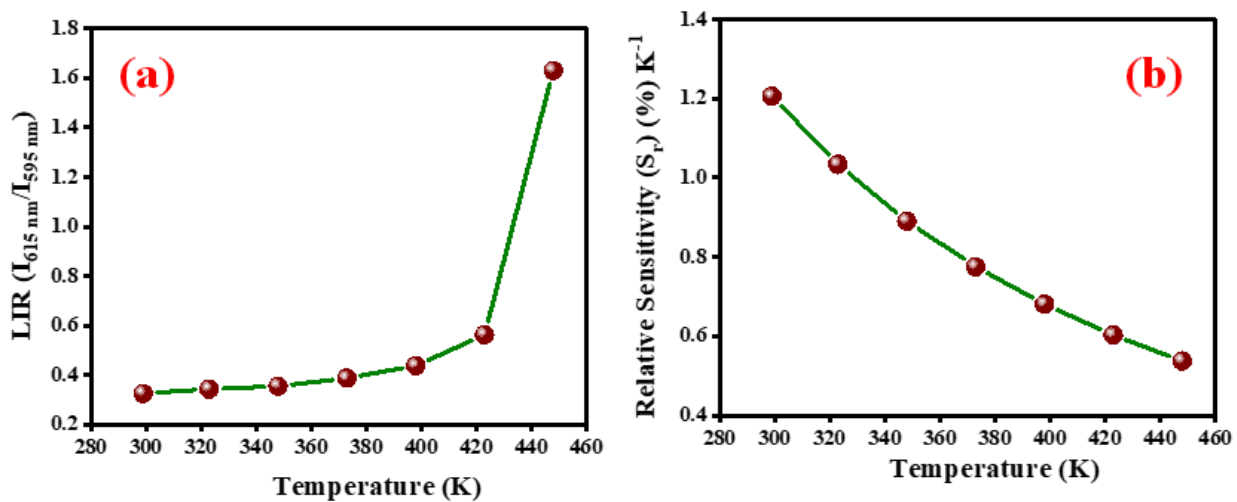


Figure 6.14 (a) Dependency of LIR of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions with the temperature, (b) S_r of LBWEu7.0 phosphor as a function of temperature.

Excitation power variations have no impact on the temperature output. RE^{3+} ions have relatively strong emission lines and a range of spectral regions, ranging from UV to NIR, making them the most desirable materials for LIR thermometry. LIR, is determined by a population distribution of the Boltzmann type and is given by the equation 1.16-1.18 shown in section 1.6.1 of chapter 1. The measured plot of LIR vs T (temperature) is nicely matched by equation 1.16, as seen in Figure 6.14 (a). For temperature control purposes, it is crucial to know the rate of change in LIR with temperature. The sensor sensitivity, which illustrates the material's sensitivity, is the rate at which the LIR changes for a specific change in temperature. S_r value, which can be computed using the equation 1.20 shown in section 1.6.2.1 of chapter 1, is used in practical applications to recognize a material's optical thermometric capability. The calculated S_r for TCLs is dependent on the absolute temperature, as shown in Figure 6.14 (b). It is evident that the

evaluated value of the S_r for prepared phosphors is $1.21\% \text{ K}^{-1}$ at 298 K and subsequently exhibits monotonic diminishing behaviour as the temperature rises. This phosphor was found to have the highest observed sensor sensitivity for the low-temperature range, which make LBWEu7.0 phosphor a top choice for optical thermometry. The estimated CIE coordinate values for LBWEu7.0 at various temperatures are shown in Figure 6.15, which confirms the tunability of the luminous colouring pattern from orange-red to yellowish-orange region.

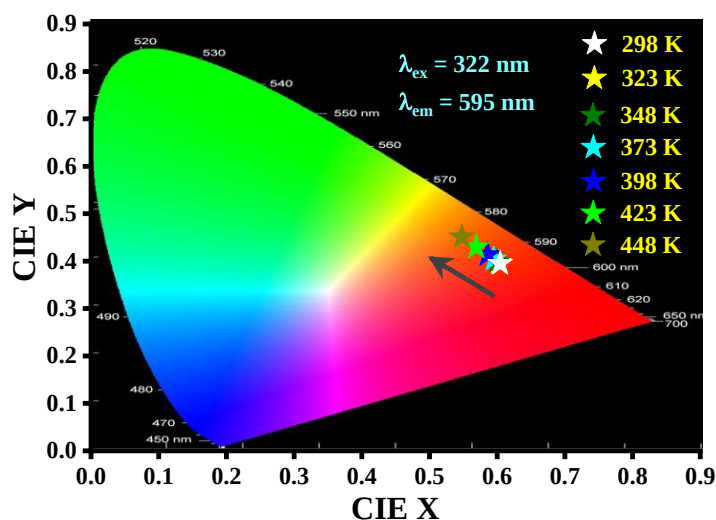


Figure 6.15 The estimated CIE coordinate values for LBWEu7.0 phosphor at various temperatures.

Table 6.3 The variation of LIR, S_r , CIE, CP and CCT of LBWEu7.0 phosphor with change in temperature (298–448 K).

Temperature (K)	LIR	S_r (%K ⁻¹)	CIE		CP (%)	CCT (K)
			X	Y		
298	0.33	1.21	0.621	0.379	79.68	1856
323	0.34	1.03	0.618	0.381	79.28	1833
348	0.36	0.89	0.616	0.383	80.14	1805
373	0.38	0.77	0.611	0.388	79.92	1763
398	0.44	0.68	0.601	0.398	80.35	1723
423	0.56	0.60	0.585	0.414	81.50	1750
448	1.63	0.53	0.563	0.435	81.90	2092

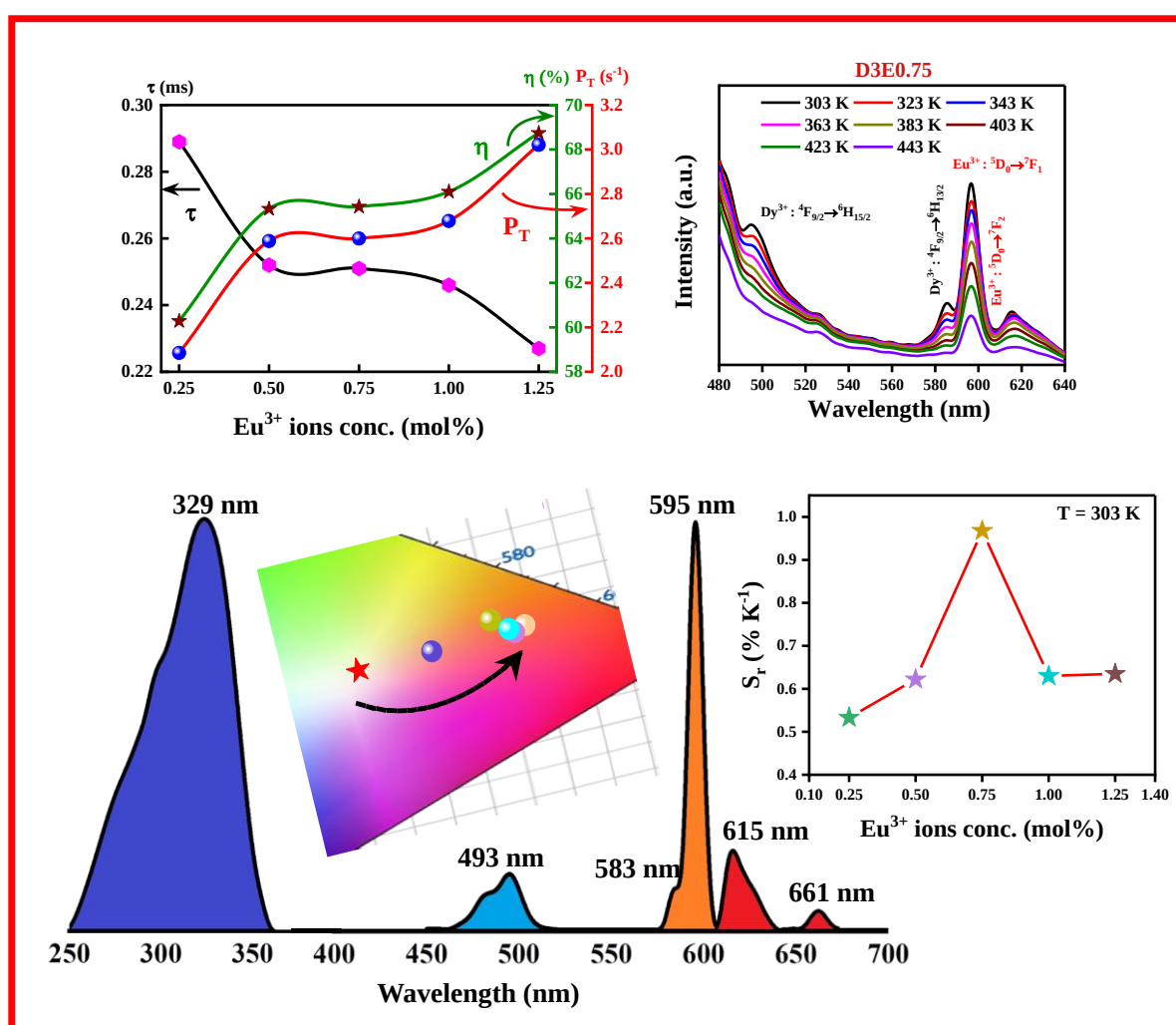
The CP values were also evaluated at various temperatures for the optimised phosphor sample. The values for all parameters, i.e., LIR, S_r , CIE, CP and CCT are presented in Table 6.3.

6.4 CONCLUSIONS

In conclusion, a series of Eu^{3+} ions doped LBW phosphors has been synthesized using the traditional SSR method and their structural, morphological and PL properties have been investigated using various characterization techniques. The XRD profile verify the phase purity of the as synthesized phosphors. The calculated values of average crystallite size using the Debye-Scherrer method and W-H plot were found to be nearly the same and equal to 83 nm and 85 nm, respectively. The SEM images display particles with irregular and non-uniform shapes, along with some mild agglomeration. The particle size is within the micrometer (μm) range, which is suitable for the production of w-LEDs. The DRS reveals the presence of 4f transitions of Eu^{3+} ions. The band gap values given by the linear fitting of the Tauc's plot and found to be in the range of 3.74-3.51 eV which illustrates the uses of synthesized phosphors in the field of optical applications. The PL investigation suggest that the as synthesized phosphors contain an intense band corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition at 595 nm when pumped with 322 nm wavelength. The concentration quenching takes place after 7 mol% concentration of Eu^{3+} ions in the host lattice. The Dexter theory as well as I-H model explain the dipole-dipole interaction as the energy transfer mechanism between the Eu^{3+} ions. The CIE coordinates of the optimized sample at $\lambda_{\text{ex}} = 322$ nm are (0.6274, 0.3721), which lie in the orange-red region. The decay profile exhibits double exponential behavior with decay lifetime values due to energy migration between Eu^{3+} - Eu^{3+} ions, with an increase in Eu^{3+} ions concentration. The TDPL measurements recorded from room temperature (298 K) to 448 K for LBWEu7.0 phosphor represented a maximum relative sensitivity of approximately $1.21\% \text{ K}^{-1}$ at 298 K, indicating its good temperature sensor ability within the studied temperature range and can be used in thermometry applications. Also, based on the optical investigations of Eu^{3+} ions doped $\text{Li}_2\text{Ba}_5(\text{WO}_5)_3$ phosphor, it can be recognised as a suitable material for fabricating photonic devices like w-LEDs and non-contact thermometry.

CHAPTER 7

A SINGLE PHASE $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Dy}^{3+}/\text{Eu}^{3+}$ PHOSPHOR FOR COLOR TUNABLE DEVICES AND NON-CONTACT OPTICAL THERMOMETRY



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7.1 INTRODUCTION

As we have already discussed in Chapter 1 about the methods of generating white light and significance of the present approach alongwith the choice of the host lattice. The significance of non-contact thermometers is also explained in the previous chapters.

RE ions provide the best circumstances to their various energy levels and characteristic 4f electron structure for TCLs, which are valuable for their use in the FIR temperature measurement [115]. The trivalent RE ions, such as Tb^{3+} ($^5\text{D}_4 \rightarrow ^7\text{F}_5$ and $^5\text{D}_3 \rightarrow ^7\text{F}_J$) [252], Sm^{3+} ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$) [253], Dy^{3+} ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$) [254], Eu^{3+} ($^5\text{D}_0 \rightarrow ^7\text{F}_J$ and $^5\text{D}_1 \rightarrow ^7\text{F}_3$) [113], Yb^{3+} ($^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$) & Tm^{3+} ($^3\text{H}_4 \rightarrow ^3\text{H}_6$) [255] and Er^{3+} ($^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) [256,257] are used frequently in this field. All the aforementioned research results prompted us for a comprehensive investigation on trivalent RE ions (in present research work, Dy^{3+} and Eu^{3+} ions) together LBW host matrix to understand their usefulness in non-contact temperature sensing applications using FIR temperature statistics.

In the present research work, we analysed the phase purity, microscopic morphology, luminescence and FIR optical thermometry properties of the warm white phosphors prepared by co-doping of Dy^{3+} and Eu^{3+} ions in the $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$ (LBW) host material.

7.2 SYNTHESIS METHOD

$\text{Dy}^{3+}/\text{Eu}^{3+}$ singly doped ($\text{LBWDy}:\text{Li}_2\text{CO}_3+(5-x)\text{BaCO}_3+3\text{WO}_3+x\text{Dy}_2\text{O}_3$; ($1 \leq x \leq 5$, $\Delta x = 1$ mol%) (already discussed in chapter 3), ($\text{LBWEu}:\text{Li}_2\text{CO}_3+(5-y)\text{BaCO}_3+3\text{WO}_3+y\text{Eu}_2\text{O}_3$ ($y = 0.01$) and $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped ($(\text{Li}_2\text{CO}_3+(5-x-y)\text{BaCO}_3+3\text{WO}_3+x\text{Dy}_2\text{O}_3+y\text{Eu}_2\text{O}_3, (x = 3, \text{ and } 0.25 \leq y \leq 1.25, \Delta x = 0.25 \text{ mol\%})$ multicomponent lithium barium tungstate phosphors (LBWDE) were prepared by utilizing conventional SSR technique as discussed in section 2.2.1 and the detailed flowchart of procedure is represented in Figure 2.2 of chapter 2. The highly pure chemicals Li_2CO_3 (99.0%), BaCO_3 (99.99%), WO_3 (99.99%), Dy_2O_3 (99.99%) and Eu_2O_3 (99.99%) have been taken as raw materials in stoichiometric ratio.

7.3 RESULTS AND THEIR DISCUSSION

7.3.1 Structural and morphological analysis

7.3.1.1 XRD analysis

The XRD patterns for all the powdered samples un-doped LBW, 3mol% concentration of Dy^{3+} (D3), 1mol% of Eu^{3+} (E1) and 3mol% of Dy^{3+} , 0.75mol% of Eu^{3+} ions co-doped (D3E0.75) LBW phosphors were recorded in the 2θ range from 20° to 70° with a step size of 0.02° to obtain all crystalline peaks and depicted in Figure 7.1 (a).

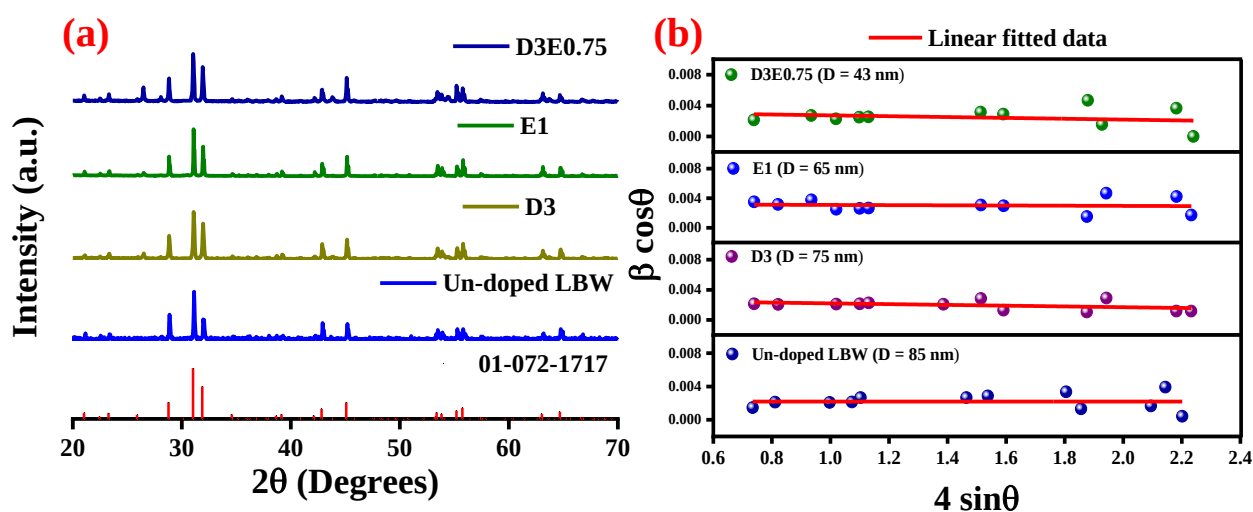


Figure 7.1 (a) The XRD patterns and (b) A graph between $\beta \cos\theta$ and $\sin\theta$ (W-H plot) for an un-doped LBW, D3, E1 and D3E0.75 phosphors.

All the samples belong to a hexagonal crystal structure with $P6_3mc$ space group (186). For all the different compositions of dopant (Dy^{3+} & Eu^{3+}) ions, the crystalline single-phase hexagonal structure of LBW phosphor was formed without any secondary phase which are in good agreement with the JCPDS card no. 01-072-1717. Therefore, doping of RE^{3+} (Dy^{3+} and Eu^{3+}) ions into LBW host lattice does not distort the crystal structure. This indicates that the dopant ions (Dy^{3+} and Eu^{3+}) has been correctly accumulated within the host matrix in place of Ba^{2+} lattice position.

Further the W-H plot formalism was used to compute the strain (ϵ) and crystallite size (D) for un-doped LBW, E1, D3 and D3E0.75 phosphors using equation 2.5 of section 2.3.2.4 of chapter 2. As indicated by

the W-H plot in Figure 7.1 (b), a graph (straight line) is produced between $\beta\cos\theta$ (along the y-axis) and $4\sin\theta$ (along the x-axis) in order to determine the values of parameters 'D' and ' ϵ ' for un-doped LBW, D3, E1 and D3E0.75 phosphors. The observed crystallite size and lattice strain values are presented in Table 7.1.

Table 7.1 Crystallite size D (nm) and Strain (ϵ) values for an un-doped LBW, E1, D3 and D3E0.75 phosphors.

Sample Name	Crystallite size D (nm)	Strain (ϵ) ($\times 10^{-3}$)
Un-doped LBW	85	0.45 ± 0.00005
D3	75	0.13 ± 0.00004
E1	65	2.70 ± 0.00040
D3E0.75	43	3.30 ± 0.00080

7.3.1.2 FE-SEM and EDAX

FE-SEM and EDAX employed to better understand the surface morphology of the prepared samples. The FE-SEM image of D3E0.75 phosphor is shown in Figure 7.2 (a). As can be observed, the phosphor's shape and particle size are not consistent. However, because of the high-temperature synthesis, the prepared materials show an agglomeration phenomenon. The FE-SEM picture displayed indicates that the average particle size of the as-prepared phosphor samples is within the range of 5 to 7 μm . As depicted in Figure 7.2 (b), EDAX analysis was employed to monitor the elemental composition of the as prepared phosphor material. In this figure, distinct peaks are evident, corresponding to Ba, W, O, Dy, and Eu, respectively. The comprehensive element distribution map, presented in Figure 7.2 (c), illustrates the uniform distribution of these elements across the external surface. Figure 7.2 (c-g) display element points in different colors against a dark background; i.e., Ba, W, O, Dy, and Eu are represented by violet, magenta, green, red, and yellow, respectively. These findings confirm that the components of the as prepared phosphors are evenly distributed, indicating the successful preparation of $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped

LBW phosphors. It is important to note that the elements with low-energy characteristic radiation, such as Li, do not exhibit any peaks in their EDAX spectrum [125].

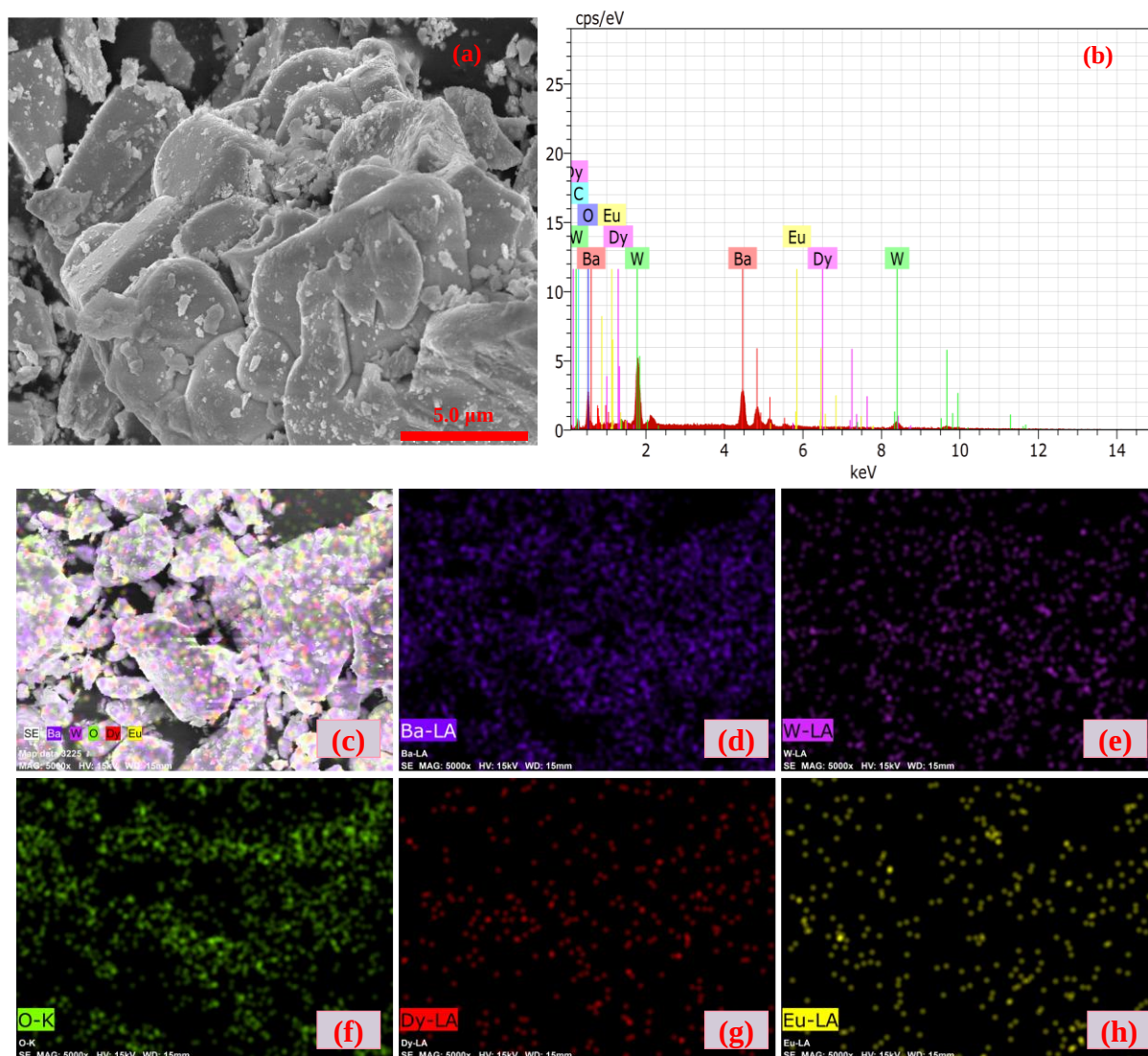


Figure 7.2 (a) The FE-SEM picture, (b) EDAX map, (c) elements' consistent distribution over the outside surface, (d-h) shows the relative element points of various colors against a dark background; blue, purple, green, and red correspond to Ba, W, O, Dy and Eu, respectively for D3E0.75 phosphor.

7.3.1.3 FT-IR spectral analysis

The IR spectroscopy analysis was conducted to gain insights into the bonding characteristics of the singly and co-doped LBW phosphor samples. Figure 7.3 shows the FT-IR spectrum of D3 and D3E0.75 phosphors in the range 4000-400 cm^{-1} , represents various vibrational bands. The FT-IR spectrum has bands near 530, 574, 680, 807, 1062, 1247, 1416, 2901, 2991 and 3673 cm^{-1} , shown in Figure 7.3. The

tungstate group's W-O symmetric and antisymmetric stretching and O-W-O symmetric and antisymmetric stretching deformation vibrations are linked to the bands between 500-807 cm^{-1} [155]. Peak intensities vary slightly depending on the doping concentration. These changes in the W-O stretching vibration at 807 and 574 cm^{-1} are related to the altered local symmetry of the Dy^{3+} ion. However, XRD study showed no change in the phosphor's geometry. The presence of tungstate groups is also indicated by the bands in the shorter wavelength range (807 and 574 cm^{-1}) [155,180].

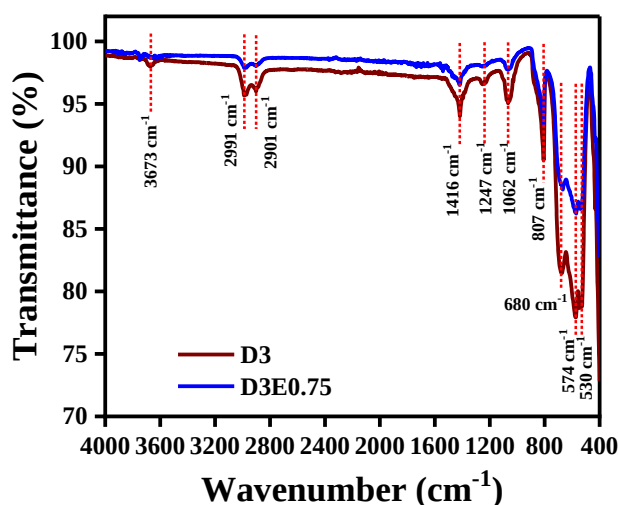


Figure 7.3 FT-IR spectra for D3 and D3E0.75 phosphors.

The W-O bond's asymmetric stretching vibration is most likely the cause of the peak seen at roughly 1062 and 1247 cm^{-1} [155]. The existence of surface CO_3^{2-} species is responsible for another band, which is situated at 1416 cm^{-1} [155]. The spectral peak at 2901 cm^{-1} analogous to the existence of hydroxyl radicals, whereas the peak at 2991 cm^{-1} represents the antisymmetric stretching of the water molecules. Lastly, the peak at 3673 cm^{-1} is associated with the stretching vibration of the hydroxyl group [33]. An increase in the OH content leads to the higher non-radiative losses, which in turn reduces the quantum efficiency of materials doped with RE elements. But as shown in Figure 7.3, the OH band have comparatively very less intensity which indicates the presence of low OH content in the as-prepared phosphor material. The distinctive bonding found in the as prepared LBW phosphors was therefore validated by the FT-IR spectra shown in Figure 7.3.

7.3.2 Optical parametric analysis

7.3.2.1 DRS analysis and band gap energy

The DRS of LBW phosphors co-doped with $\text{Dy}^{3+}/\text{Eu}^{3+}$ ions and un-doped LBW is shown in Figure 7.4 (a). At room temperature, the DRS were recorded in the 200-1600 nm range. The absorbance at 412 nm in the spectra linked to the Eu^{3+} ion's transition from $^7\text{F}_0$ to $^5\text{L}_6$ [258]. Transitions from the ground state $^6\text{H}_{15/2}$ to other excited states $^6\text{F}_{3/2}$, $^6\text{F}_{5/2}$, $^6\text{F}_{7/2}$, $^6\text{H}_{5/2}$, $^6\text{F}_{9/2}$, and $^6\text{F}_{11/2}$ are represented by the remaining peaks, related to Dy^{3+} ions [127,259].

The K-M function, which represents the optical absorption close to the band edge, can be used to solve for the band gap (E_g) given by equation 2.7-2.8. The linear part of the plot between $[\text{F(R)} \text{ } h\nu]^2$ and $h\nu$ was extrapolated to compute the band gap value as shown in Figure 7.4 (b). The optical band gap for an un-doped LBW, D3 and D3E0.75 phosphors was determined and found to be equal to 3.74, 3.64 and 3.62 eV, respectively. With the doping of RE ions, the E_g value slightly decreases from 3.74 to 3.62 eV, which may be due to the 4f energy levels of Dy^{3+} and Eu^{3+} ions [129]. On the other hand, the little decrease also suggests that the samples under consideration crystallized efficiently [127].

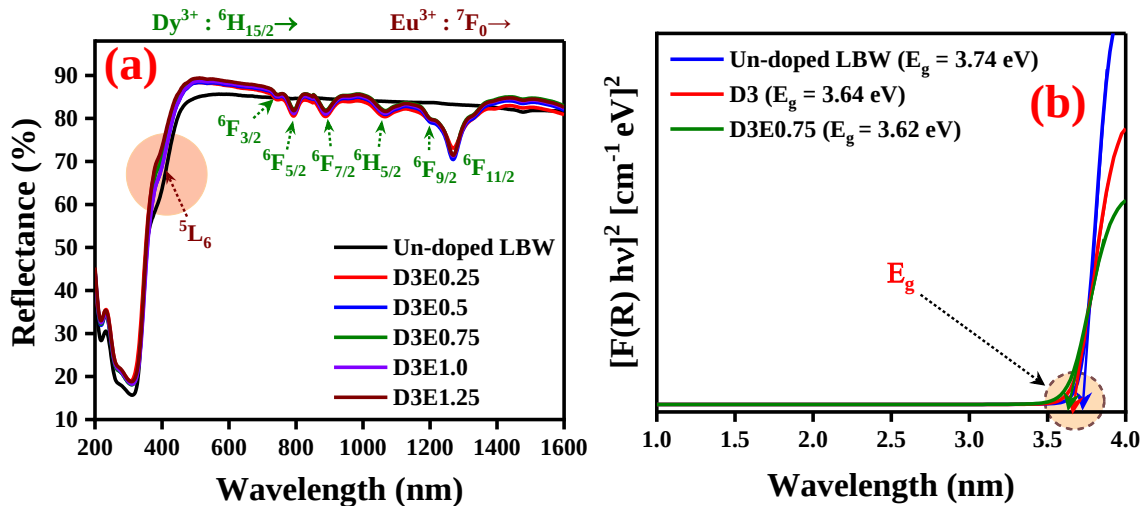


Figure 7.4 (a) DRS of the an un-doped LBW, $\text{LBW}:\text{x}\text{Dy}^{3+}/\text{yEu}^{3+}$ ($x = 3.0 \text{ mol\%}$ and $0 \leq y \leq 1.25$, $\Delta y = 0.25 \text{ mol\%}$) phosphors and (b) Band gap variations of an un-doped LBW, LBWD3, D3E0.75 phosphors.

7.3.2.2 PLE and PL properties of Dy^{3+} ions doped LBW phosphor

The PLE and PL properties of the Dy^{3+} doped LBW phosphor materials is already discussed in section 3.3.2.2 of Chapter 3.

7.3.2.3 PL properties of $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped LBW phosphor

The absence of red colour was identified in the study of phosphors doped with Dy^{3+} ions. To solve this problem, co-doping was carried out in combination with Dy^{3+} ions using Eu^{3+} , Mn^{2+} , and Mn^{4+} red-emitting ions. When exposed to the proper excitation, this co-doping technique produced white light [30]. In the present study, the host matrix LBW was altered by adding various Eu^{3+} ion concentrations in addition to the previously optimised 3.0 mol% Dy^{3+} ions concentration. The purpose of this alteration was to study the ET mechanism that exists between these two RE ions. Energy is transmitted from the ion present in a relatively high-energy state to the ion lying in a lower-energy state in RE ions, resulting in luminescence through ET-based down-conversion. Since the energy state of the Dy^{3+} ions are higher than that of the Eu^{3+} ions, the ET process is most likely to occur from Dy^{3+} to Eu^{3+} ions. The key criterion for the investigation of the ET process is the spectral overlap between the donor (Dy^{3+}) emission and the acceptor (Eu^{3+}) excitation [30]. The alignment between the excitation band of Eu^{3+} ions at 469 nm (from $^7\text{F}_0$ to $^5\text{D}_2$) and the emission band of Dy^{3+} ions at 493 nm (from $^4\text{F}_{9/2}$ to $^6\text{H}_{15/2}$) is demonstrated in Figure 7.5 (a). These discoveries prompted additional research into the ET process from Dy^{3+} to Eu^{3+} by introducing different concentrations of Eu^{3+} ions (ranging from 0.25 to 1.25 mol% in increments of 0.25 mol%) alongwith the optimal concentration of Dy^{3+} ions. Prior to conducting this study, the excitation spectra of the co-doped $\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphor samples were assessed at emission wavelengths of 583 nm for Dy^{3+} and 615 nm for Eu^{3+} ions. The obtained spectrum was then compared with those of the singly Dy^{3+} and Eu^{3+} ions doped LBW phosphors, as shown in Figure 7.5 (b). Different bands were observed in the excitation spectrum of the singly Dy^{3+} , Eu^{3+} , and $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped systems at emission wavelengths of 583 nm and 615 nm. These bands correspond to the transitions such as $^6\text{H}_{15/2}$ to $^6\text{P}_{5/2}$

(at 368 nm) and ${}^6F_{7/2}$ (at 394 nm), which are consistent with the excitation bands of Dy^{3+} ions, as well as Eu^{3+} ions bands assigned to ${}^7F_0$ to ${}^5L_6$ (394 nm), ${}^5D_3$ (410 nm), ${}^5D_2$ (466 nm), and a CTB at 329 nm. Hence, both Dy^{3+} ions (by $E_m = 583$ nm) and Eu^{3+} ions (by $E_m = 615$ nm) have the capacity to contribute towards the overall emission in as-prepared Dy^{3+}/Eu^{3+} ions co-doped LBW phosphor samples.

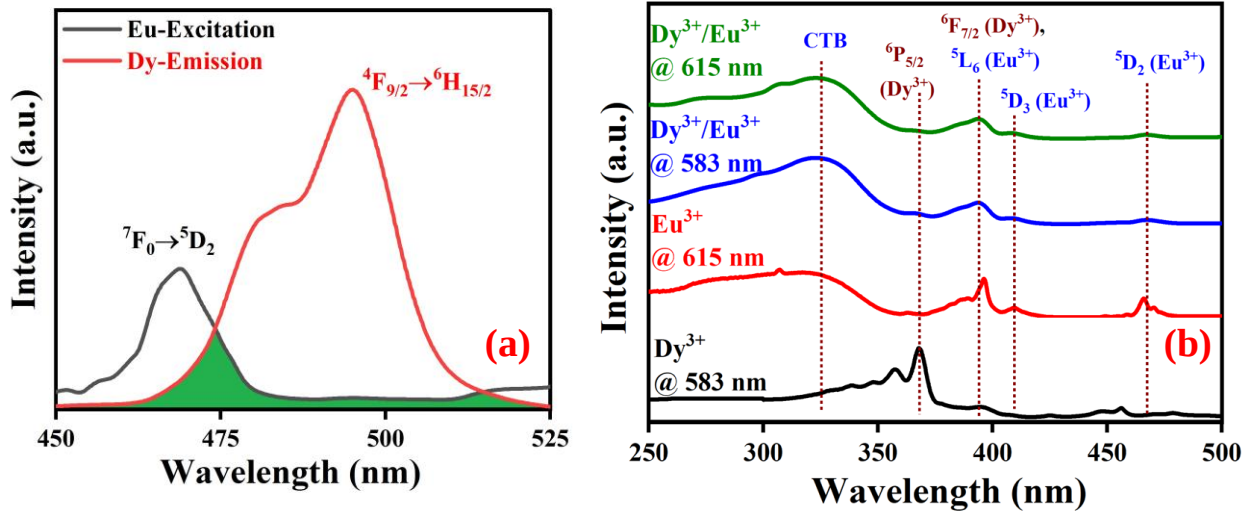


Figure 7.5 (a) The overlapped region between the Eu^{3+} excitation band and Dy^{3+} emission band, (b) The excitation spectra for the Dy^{3+}/Eu^{3+} co-doped LBW system is observed at $E_m = 583$ nm (Dy^{3+}) and 615 nm (Eu^{3+}) and correlated with the singly Dy^{3+} and Eu^{3+} doped LBW phosphors.

Based on the excitation spectra, the PL emission spectra of the Dy^{3+}/Eu^{3+} co-doped LBW phosphors were measured at two distinct excitation wavelengths ($E_x = 329$ nm and 394 nm), as shown in Figure 7.6. The PL emission spectra obtained at $E_x = 329$ nm show many strong peaks ranging from 450 to 700 nm, as shown in Figure 7.6 (a). Amid these peaks, two are ascribed to the Dy^{3+} ion transitions from ${}^4F_{9/2}$ to ${}^6H_{15/2}$ (493 nm) and ${}^6H_{13/2}$ (583 nm), however, the transitions of Eu^{3+} ions from ${}^5D_0$ to ${}^7F_1$ (595 nm), ${}^7F_2$ (615 nm), and ${}^7F_3$ (661 nm) are responsible for the remaining peaks. As the concentration of the Eu^{3+} ions rise, the change in PL emission intensity of Dy^{3+} ions indicates that energy is transferred from Dy^{3+} to Eu^{3+} ions, which causes decrement in the PL emission intensity of Dy^{3+} ions and increment in PL emission intensity of Eu^{3+} ions. Similar patterns were observed when PL emission spectra is recorded at $E_x = 394$ nm, as shown in Figure 7.6 (b). The above observations implies that Eu^{3+} ions are sensitised by Dy^{3+} ions and energy is transferred from Dy^{3+} ions to Eu^{3+} ions, leading to optical emission [30,130].

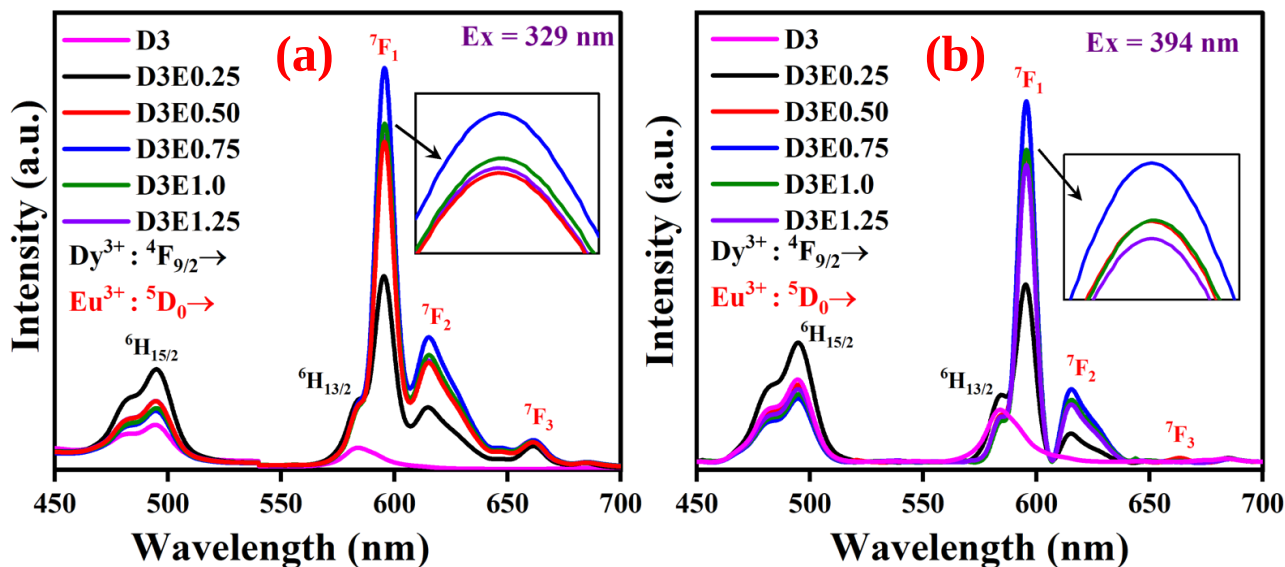


Figure 7.6 PL emission spectra for the as-prepared LBW: $x\text{Dy}^{3+}/y\text{Eu}^{3+}$ ($x = 3.0$ mol% and $0 \leq y \leq 1.25$, $\Delta y = 0.25$ mol%) phosphors at two different excitation wavelengths (a) 329 nm and (b) 394 nm.

7.3.2.4 Energy level diagram

Energy transfer can take place either between dissimilar luminescent centres or identical luminescent centres. In the scenario of involving dissimilar luminescent centres, there are two distinct centres: a sensitizer (S) and an activator (A), separated in a solid by a distance R . It is assumed that R is sufficiently short for S and A to have a non-negligible interaction. This implies that when S is in an excited state and A is in the ground state, the relaxed excited state of S can transfer its energy to A. Resonance needs to be satisfied, indicating that the energy differences between the ground and excited states must be equal, and a suitable interaction must exist for energy transfer to occur. This interaction could be an exchange interaction with wave function overlap, as shown in Figure 7.5 (a), or an electric/magnetic multipolar interaction as shown in Figure 7.8.

Dexter's formula and Reisfeld's approximation were used to determine the specific multipolar interaction mechanism present in the as prepared $\text{Dy}^{3+}/\text{Eu}^{3+}$ ions co-doped LBW phosphor samples, using the equation 1.3-1.4. With $\text{Ex} = 394$ nm, Figure 7.7 shows the variation in $\frac{I_{\text{So}}}{I_{\text{S}}}$ as a function of $C\frac{n}{3}$, where n might take values of 6, 8, or 10. The data demonstrated the best linear fit for $n = 6$, indicating that non-

radiative energy transfer via d-d interaction. Carnall's publication [213] was referenced in order to identify the energy levels for the dopant ions.

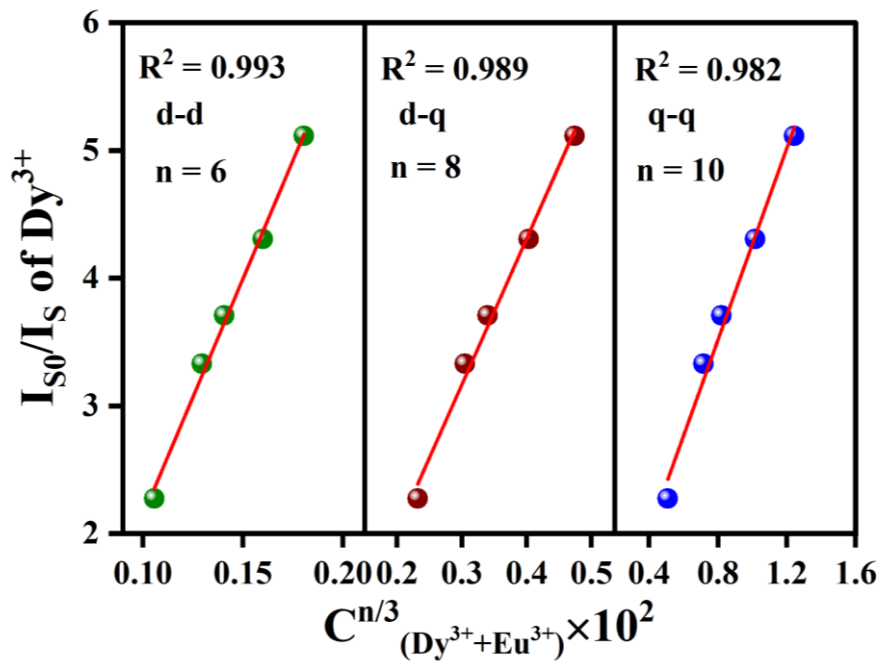


Figure 7.7 Plot between I_{S0}/I_S and $C^{n/3}$ at $\text{Ex} = 394 \text{ nm}$ with $n = 6, 8$ and 10 .

In the present case, Figure 7.8 represents the energy transfer process from Dy^{3+} ions to Eu^{3+} ions in the co-doped LBW phosphors.

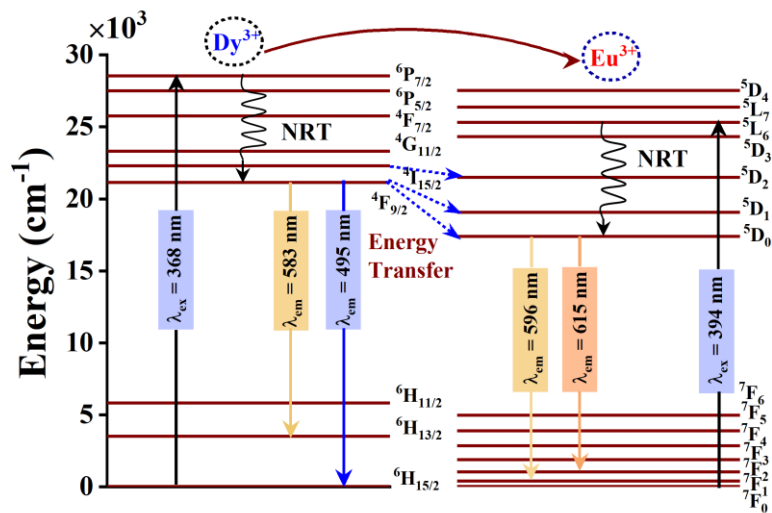


Figure 7.8 The schematic ET process between Dy^{3+} and Eu^{3+} ions in the Dy^{3+}/Eu^{3+} co-doped LBW phosphors.

During this process, a particular n-UV light source activated the as prepared phosphor samples, causing non-radiative transitions amid different energy levels of Dy^{3+} and Eu^{3+} ions. Two strong PL emission

peaks are observed at 493 and 583 nm of Dy^{3+} ions however, some of the energy is then transferred from Dy^{3+} ions to Eu^{3+} ions, causing red light emission. Figure 7.8 shows that the energy of the Dy^{3+} ions at the $^4\text{F}_{9/2}$ level is about $21,144 \text{ cm}^{-1}$, which is slightly more than the energies of the Eu^{3+} ions at the $^5\text{D}_0$ (nearly $17,393 \text{ cm}^{-1}$) and $^5\text{D}_1$ (nearly $19,077 \text{ cm}^{-1}$) levels. There is a 2067 cm^{-1} energy difference between the $^4\text{F}_{9/2}$ and $^5\text{D}_1$ levels and about 3751 cm^{-1} between the $^4\text{F}_{9/2}$ and $^5\text{D}_0$ levels. These small energy differences imply that energy transfer from Dy^{3+} to Eu^{3+} ions can be facilitated by Dy^{3+} ions acting as an effective sensitizer for Eu^{3+} ions.

7.3.2.5 Evaluation of CIE chromaticity coordinates

CIE color chromaticity coordinates for the as-prepared $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped LBW phosphors were evaluated using the PL emission spectra under $\text{Ex} = 394 \text{ nm}$ and presented in Table 7.2 and shown in Figure 7.9 (a), by employing the formula given in equation 1.9-1.10. The evaluated CIE color coordinates were lie in red region and shows a color tunability with the varying concentration of Eu^{3+} ions. The color coordinates were shifted from white to red region in co-doped LBW phosphors as the Eu^{3+} ions concentration changes from 0 to 1.25 mol%. Thus, $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped LBW phosphors may be a suitable choice for red emitters and therefore, useful to fabricate n-UV driven w-LEDs. In Figure 7.9 (b), CIE X shows a noticeable variation, however, CIE Y remains nearly constant. Therefore, the overall variation of the color chromaticity coordinates with the variation of the Eu^{3+} ions confirm the color tunability of the as prepared co-doped phosphors.

Moreover, the McCamy relation, represented by equation 1.12 is employed to evaluate the CCT, which is an essential measure for characterising white light [260]. The addition of Eu^{3+} ions caused the computed CCT values in the as prepared phosphor samples to change from a colder to a warmer white light. This suggests that when excited by n-UV LEDs, these phosphors can potentially rely on to generate warm white light and making the as prepared co-doped phosphor samples suitable for indoor lighting applications.

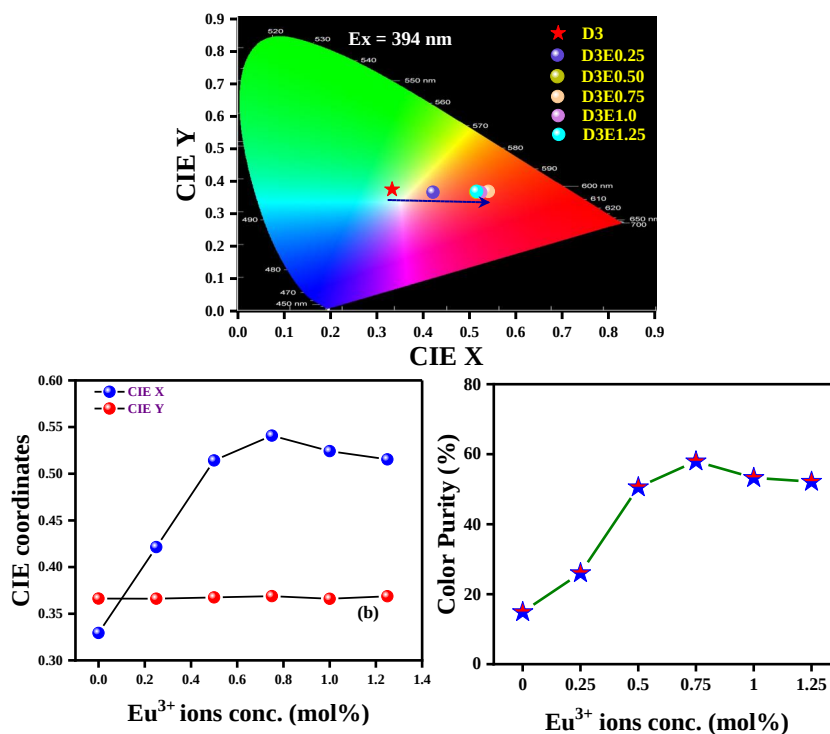


Figure 7.9 (a) CIE color coordinates, (b) the variation of CIE X & CIE Y and (c) the variation of CP values with Eu^{3+} ions in $\text{LBW}:\text{x}\text{Dy}^{3+}/\text{y}\text{Eu}^{3+}$ ($x = 3.0$ and $0 \leq y \leq 1.25$, $\Delta y = 0.25$ mol%) phosphors.

Another important parameter to further investigate the as prepared $\text{LBW}:\text{x}\text{Dy}^{3+}/\text{y}\text{Eu}^{3+}$ ($x = 3.0$ mol% and $0 \leq y \leq 1.25$, $\Delta y = 0.25$ mol%) phosphors is the CP, calculated using the equation 1.11. Figure 7.9 (c) represents the variation of CP values with the co-dopant Eu^{3+} ions. The evaluated CIE chromaticity coordinates, CCT (K) and CP (%) values are presented in Table 7.2.

Table 7.2 CIE chromaticity coordinates, CCT and CP values of as-prepared $\text{LBW}:\text{x}\text{Dy}^{3+}/\text{y}\text{Eu}^{3+}$ ($x = 3.0$ mol% and $0 \leq y \leq 1.25$, $\Delta y = 0.25$ mol%) phosphors.

System	CIE		CCT (K)	CP (%)
	X	Y		
D3	0.332	0.373	5392	14.89
D3E0.25	0.421	0.366	2955	26.02
D3E0.50	0.514	0.367	1824	50.57
D3E0.75	0.540	0.368	1734	57.96
D3E1.0	0.524	0.366	1772	53.25
D3E1.25	0.515	0.368	1824	52.15

7.3.2.6 PL decay analysis and exponential fitting

A greater understanding of the energy transfer mechanism was obtained by studying the PL decay. As shown in Figure 7.10 (a), the decay curves for all the prepared LBW phosphor samples co-doped with Dy^{3+} and Eu^{3+} were measured at $\text{Ex} = 394 \text{ nm}$ and $\text{Em} = 596 \text{ nm}$. The decay curves were seen to have non-exponential behaviour, specifically the bi-exponential, represented by equation 2.10 provides the best fitting. The average lifetime (τ), which ranges from 0.289 ms to 0.227 ms, decreases as the concentration of Eu^{3+} ions increase. The reduction in τ as the concentration of Eu^{3+} increases offer additional evidence of the energy transfer from Dy^{3+} to Eu^{3+} ions. Moreover, the increase in energy transfer efficiency (η), evaluated using the equation 2.13, with the concentrations of Eu^{3+} ions is attributed to non-radiative energy transfer rates. The energy transfer probability (P_T) is also evaluated using the equation 2.14. provides an overview of all the evaluated parameters, and Figure 7.10 (b) shows the variation of τ , η and P_T with the concentration of Eu^{3+} ions.

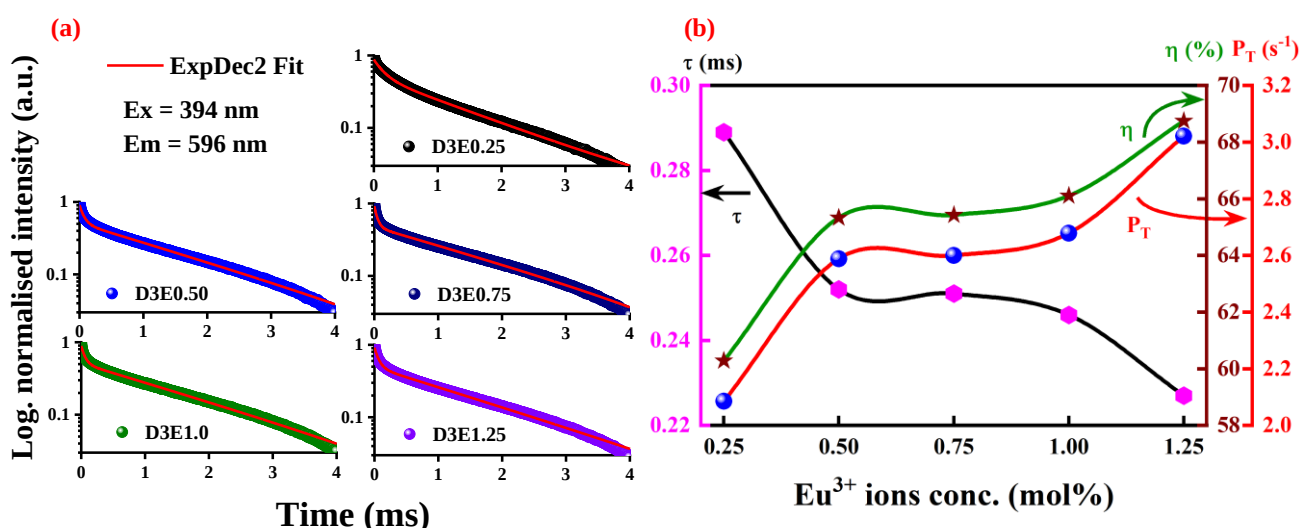


Figure 7.10 (a) The decay curves at $\text{Em} = 596 \text{ nm}$ & $\text{Ex} = 394 \text{ nm}$, (b) variation of τ , η and P_T with the Eu^{3+} ions concentration for all the as-prepared $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped LBW phosphor samples.

The observed pattern of η provides additional evidence in favour of the theory that energy is transferred from donors (Dy^{3+}) to acceptors (Eu^{3+}) ions. Interestingly, the sample labelled D3E1.25 has an η value

more than 68%, which is comparatively higher than the previous studies [261–264] and presented in

Table 7.4

Table 7.3 Variation of lifetime τ (ms), energy transfer efficiency (η) (%) and energy transfer probability (P_T) (s^{-1}) for Dy^{3+}/Eu^{3+} co-doped LBW phosphors.

Sample	τ (ms)	η (%)	$P_T (s^{-1})$
D3E0.25	0.289	60.28	2.08
D3E0.50	0.252	65.33	2.58
D3E0.75	0.251	65.42	2.59
D3E1.0	0.246	66.10	2.67
D3E1.25	0.227	68.74	3.02

Table 7.4 Comparison of energy transfer efficiency (η) of the optimized phosphor sample with some previously reported literature.

Sample	η (%)	References
D3E1.25	68.74	This work
D2E7	39.6	[261]
D9E15	51.0	[262]
D5E3	51.2	[263]
D5E20	60.1	[264]

7.3.2.7 TDPL studies

As temperature rises, UV/blue LED chips lose optical performance. Consequently, TDPL tests were conducted, as seen in Figure 7.11, for all as-prepared phosphor samples at $\lambda_{ex} = 394$ nm in order to examine their temperature sensitivity by adjusting the temperature from room temperature (303 K) to 443 K.

The relative emission intensities with the variation of temperature for the $^4F_{9/2} \rightarrow ^6H_{15/2}$ (495 nm), $^6H_{13/2}$ (585 nm), and $^5D_0 \rightarrow ^7F_1$ (596 nm), $^7F_2$ (615 nm) transitions is shown in Figure 7.12, with the greatest

integrated emission intensity being 100% at room temperature. Due to the increase in non-radiative transitions with rise in temperature, the emission peak intensity appears to be decreased [265].

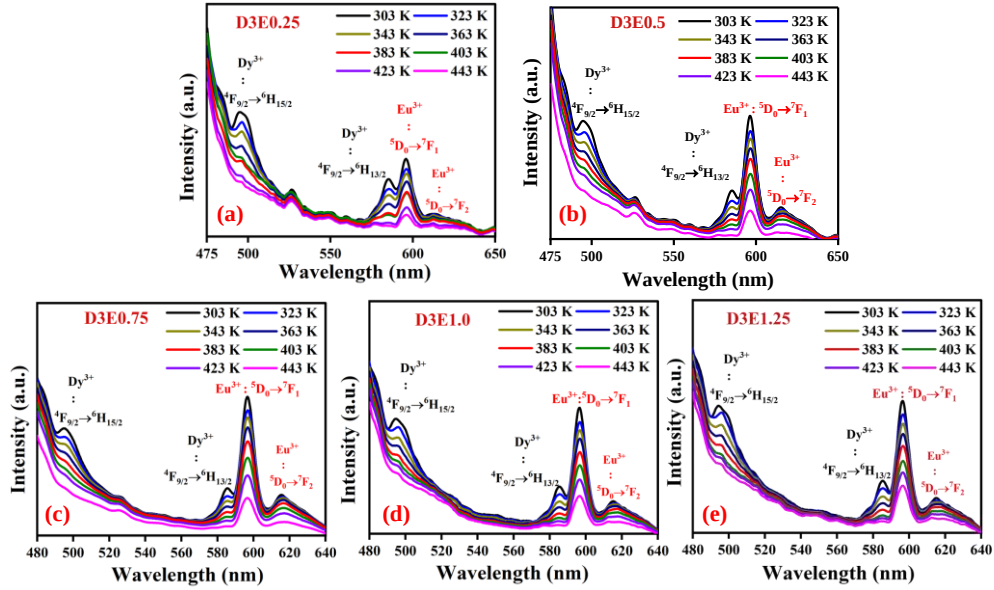


Figure 7.11 The TDPL emission spectra of LBW: $x\text{Dy}^{3+}/y\text{Eu}^{3+}$ ($x = 3.0$, $0.25 \leq y \leq 1.25$, $\Delta y = 0.25$ mol%) phosphors.

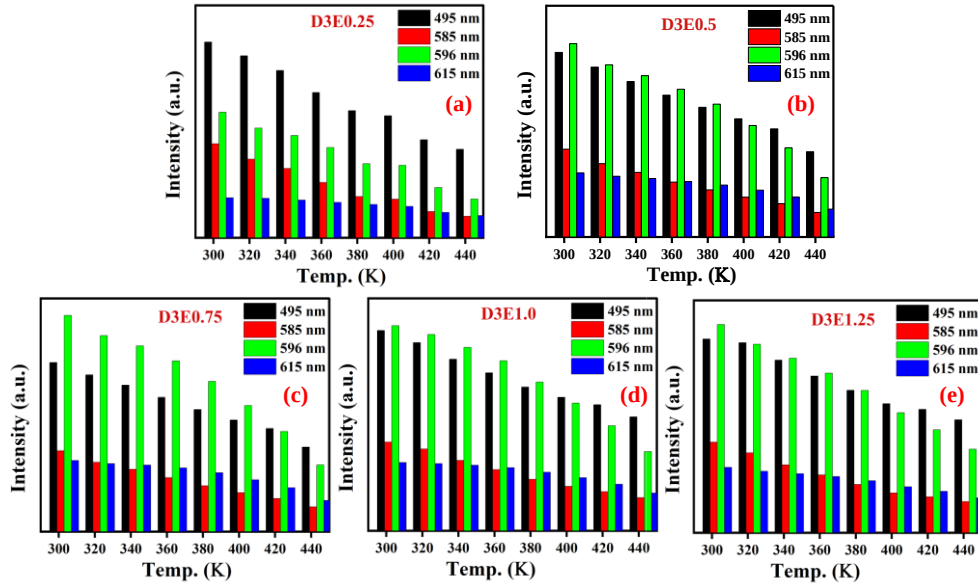


Figure 7.12 The variation of PL intensities of various peaks of LBW: $x\text{Dy}^{3+}/y\text{Eu}^{3+}$ ($x = 3.0$, $0.25 \leq y \leq 1.25$, $\Delta y = 0.25$ mol%) phosphors with temperature.

However, with the rise in temperature, there is a little decrement in the PL emission intensities of ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions, whereas the PL emission intensities of ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transitions decrease dramatically, can be seen in Figure 7.12. Temperature has an impact on the

relative population of various emission levels, which follows a Boltzmann-type distribution. Using the TDPL spectra of all the prepared phosphors (Figure 7.11) under $\text{Ex} = 394 \text{ nm}$, the FIR theory was applied to evaluate their performance as luminescent thermometer. The ratio of the population between the two energy levels, FIR, is determined by a population distribution of the Boltzmann type and is given by the equation 1.16-1.18. The measured plot of FIR vs T is nicely matched by equation 1.16, as shown in Figure 7.13 (a). For temperature control purposes, it is crucial to know the rate of change in FIR with temperature. The sensor sensitivity, which illustrates the material's sensitivity, is the rate at which the FIR changes for a specific change in temperature.

S_r value is used in practical applications to recognize the thermometric capability of a phosphor sample, which can be computed using the equation 1.20. Figure 7.13 (b) represents the values of S_r for all the as prepared phosphors having maximum value at 303 K and subsequently exhibits monotonic diminishing behaviour as the temperature rises. It is evident that the evaluated value of the S_r is maximum with a value of $0.97\% \text{ K}^{-1}$ at 303 K, for D3E0.75 phosphor amid all the as prepared samples, shown in Figure 7.13 (c). The values of FIR, S_r parameters for D3E0.75 phosphor with variation of temperature are presented in Table 7.5.

Table 7.5 The variation of FIR and S_r values of D3E0.75 with change in temperature (298-448 K).

Temperature (K)	FIR	$S_r (\% \text{ K}^{-1})$
303	0.81	0.97
323	0.98	0.85
343	1.07	0.75
363	1.18	0.67
383	1.28	0.61
403	1.33	0.55
423	1.43	0.50
443	1.52	0.45

D3E0.75 phosphor was found to have the highest observed sensor sensitivity for the low-temperature range, when compared with the previous literature [66,227,266–268], presented in Table 7.6.

Table 7.6 Optical parameters comparison of the as prepared optimised D3E0.75 phosphor sample with previously reported temperature sensing materials.

Sensing material	Temperature range (K)	S_r (% K ⁻¹)	References
Tb _{0.99} Eu _{0.01} (BDC) _{1.5} (H ₂ O ₂)	300–320	0.37	[266]
CYSO:Bi ³⁺ /Eu ³⁺	298–523	0.95	[227]
SYF:Er ³⁺ glass ceramic	300–500	0.62	[66]
LaOBr:Ce ³⁺ /Tb ³⁺ phosphor	293–433	0.42	[267]
NLF:Ho ³⁺ /Yb ³⁺ phosphor	360–780	0.83	[268]
D3E0.75 phosphor	298–443	0.97	Present work

The estimated CIE coordinate values for D3E0.75 phosphor at various temperatures, taking $\lambda_{\text{ex}} = 394$ nm, are shown in Figure 7.13 (d), confirm the tunability of the luminous colouring pattern from orange-red to yellowish-orange region.

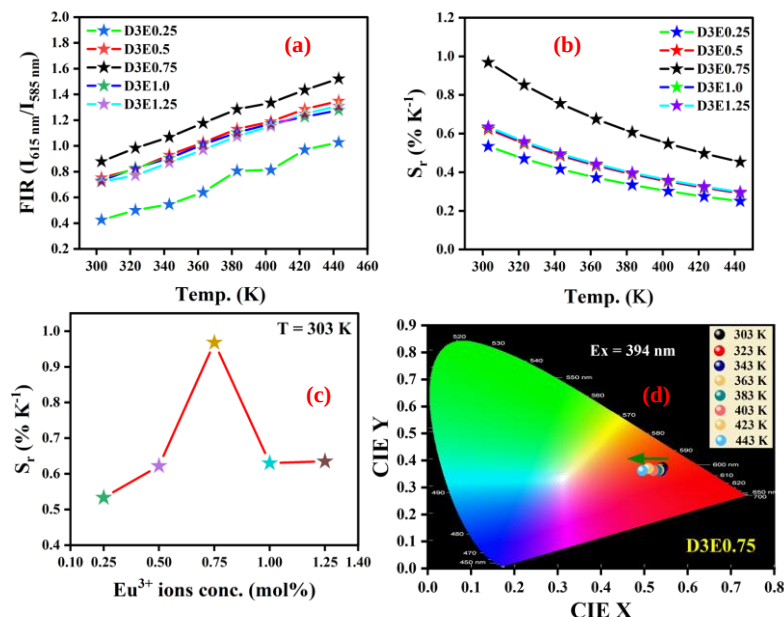


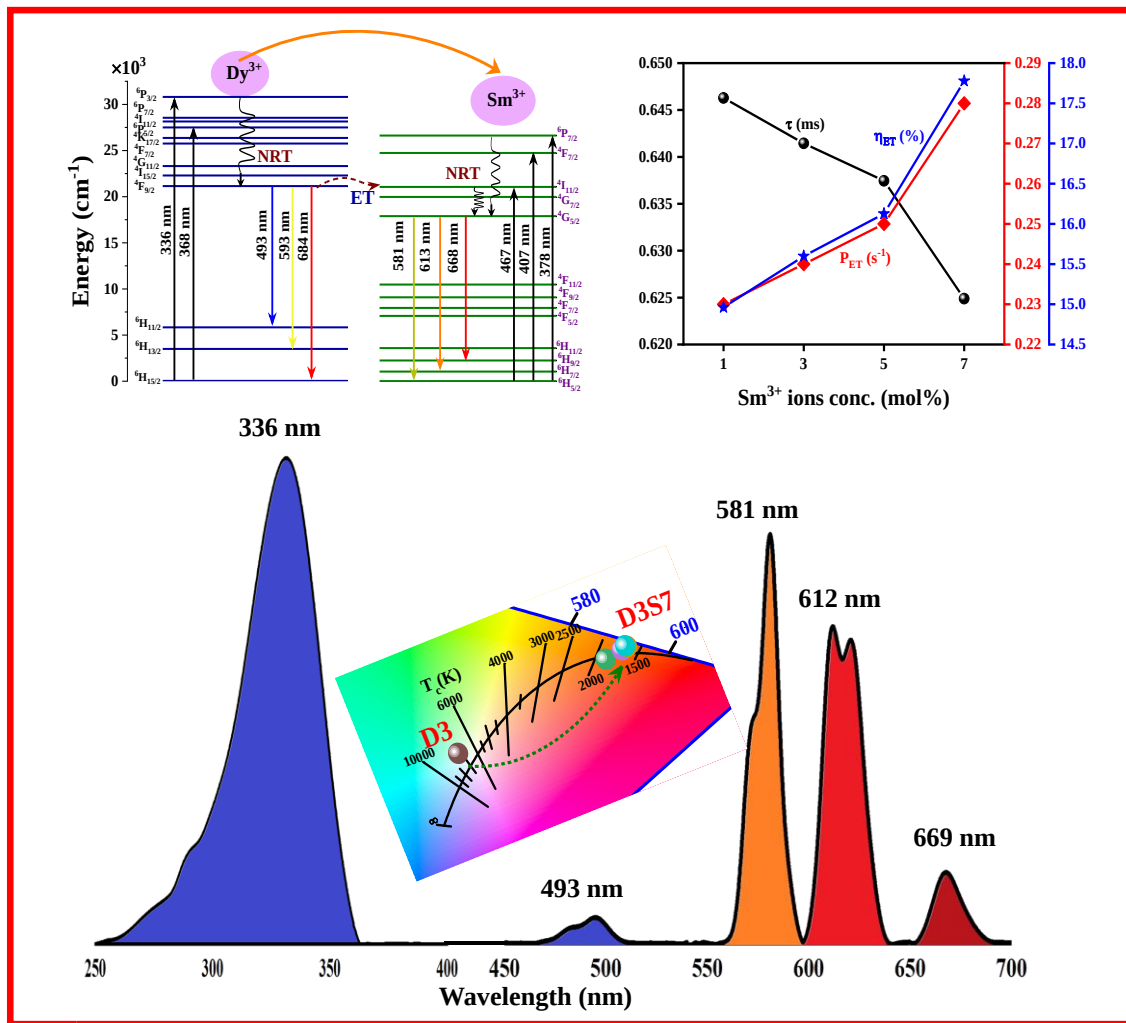
Figure 7.13 (a) The temperature dependency of the FIR curve and (b) the temperature sensitivity curves and (c) Variation of S_r (% K⁻¹) with Eu³⁺ ions concentration at 303 K temperature for LBW:xDy³⁺/yEu³⁺ ($x = 3.0$, $0.25 \leq y \leq 1.25$, $\Delta y = 0.25$ mol%) phosphors and (d) variation of CIE color coordinates with temperature for D3E0.75 phosphor.

7.4 CONCLUSIONS

In summary, the crystal $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$ has been employed as a host material for integrating lanthanide activator ions (i.e., Dy^{3+} and Eu^{3+} ions). XRD analysis, in combination with W-H plot, demonstrated that Dy^{3+} and Eu^{3+} ions primarily occupy the Ba^{2+} lattice sites within the LBW host lattice. The little variation of bandgap with the dopant ions in the host matrix indicated the incorporation of dopant ($\text{Dy}^{3+}/\text{Eu}^{3+}$) ions in the LBW host without causing any excessive crystal defects. A luminescence spectroscopy study was conducted on $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped LBW samples. The incorporation of Dy^{3+} and Eu^{3+} activator ions into the LBW host allowed for adjustable luminescent performance at a specific excitation wavelength, resulting in the emission of multiple colors. By simply varying the concentration of Eu^{3+} , the luminescent colors could be shifted from natural white to orange-red, achieving warm white light emission with a low CCT, making it suitable for indoor lighting applications. The Reisfeld approximation suggested that energy transfer from Dy^{3+} to Eu^{3+} ions occur through dipole-dipole interactions. As the concentration of Eu^{3+} ions increase, the decay time also decrease due to an increase in the non-radiative transitions which further revealed the energy transfer from Dy^{3+} to Eu^{3+} ions with a maximum energy transfer efficiency of 68.74% for D3E1.25 phosphors. Furthermore, by adjusting the $\text{Dy}^{3+}/\text{Eu}^{3+}$ ions concentrations and excitation wavelengths, the CIE chromaticity coordinates, CCTs and energy transfer efficiency (η) can be effectively modified. Finally, using TDPL analysis, a FIR model was established, yielding a maximum S_r of $0.97\% \text{ K}^{-1}$ for the D3E0.75 phosphor sample at 303 K. Therefore, all the experimental results indicated that the as prepared $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped LBW phosphors can be a suitable choice for UV excitable warm white lighting devices with color tunability and non-contact optical thermometry measurements.

CHAPTER 8

SPECTRAL STUDIES OF THERMALLY STABLE DY³⁺/SM³⁺ CO-DOPED LI₂BA₅W₃O₁₅ PHOSPHORS FOR WARM WHITE LEDS



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8.1 INTRODUCTION

As discussed in Chapter 1, n-UV/blue LEDs have become increasingly popular because of their many benefits over other SSL sources, including their long lifespan, stability, high efficiency, and environmental friendliness [269–272]. Section 1.7 of Chapter 1 highlights the methods of generating white light and significance of the present approach alongwith the choice of the host lattice. As an alternative, the use of RGB phosphors and UV or n-UV LED chips is becoming more common because of their high CRI values [273,274]. It is possible to produce white light with more uniformity and stable emission using this technology, since the output of the white LEDs produced depends on the quality of light emitted from the phosphors [275]. Recent reports have indicated that a number of RGB phosphors, such as $\text{KSrPO}_4\text{:Eu}^{2+}$ [276], $\text{BaAl}_2\text{S}_4\text{:Eu}^{2+}$ [277], and $\text{CaAlSiN}_3\text{:Eu}^{2+}$ [278], decrease blue emission efficiency by partially absorbing blue light. To increase the effectiveness of w-LEDs, it is important to investigate novel UV or n-UV excitable phosphors [279]. Warm white lighting is great for areas like living rooms, bedrooms, and hallways as it creates a cozy and enjoyable lighting ambiance [273]. Studies have demonstrated that certain transitions of Dy^{3+} : $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ [280], Sm^{3+} : $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ [281], can cause PL emission of $\text{Dy}^{3+}/\text{Sm}^{3+}$ ions co-doped phosphors [282,283] or glasses [284,285] in the warm white light range. All the aforementioned scientific patronages offered by the constituent chemical species prompted us to prepare a series of Dy^{3+} and Sm^{3+} ions co-doped $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$ (LBW) phosphor materials and analysed their phase purity, microscopic morphology, PL and TDPL properties.

8.2 SAMPLE PREPARATION

Multicomponent lithium barium tungstate phosphors, co-doped with Dy^{3+} and Sm^{3+} ($(\text{Li}_2\text{CO}_3 + (5-x-y)\text{BaCO}_3 + 3\text{WO}_3 + x\text{Dy}_2\text{O}_3 + y\text{Sm}_2\text{O}_3$, where $x = 3$ and $1 \leq y \leq 7$, $\Delta y = 2$ mol% or say $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$), were synthesized in the present study utilizing conventional SSR technique as discussed in section 2.2.3 and the detailed flowchart of procedure is represented in Figure 2.2

of chapter 2. The highly pure chemicals Li_2CO_3 (99.0%), BaCO_3 (99.99%), WO_3 (99.99%), Dy_2O_3 (99.99%) and Sm_2O_3 (99.99%) have been taken as raw materials in stoichiometric ratio.

8.3 RESULTS AND DISCUSSION

8.3.1 Structural and morphological investigations

8.3.1.1 XRD study: structural investigations

XRD analysis were conducted on all the as prepared powdered samples, including both un-doped LBW and co-doped LBW ($\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$; where $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$). The measurements were performed in $20^\circ \leq 2\theta \leq 70^\circ$ range and the results were illustrated in Figure 8.1 (a). The diffraction patterns align closely with the JCPDS database file no. 01-072-1717. The host's crystal structure and the emergence of an impurity phase do not seem to be affected by increasing doping concentrations, suggesting that the activator ions (Dy^{3+} and Sm^{3+}) have been efficiently integrated into the host matrix to take the position of the Ba^{2+} in the lattice structure. W-H plot, by employing the equation 2.5, was utilized for the un-doped LBW sample and $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$) phosphors to calculate the strain (ϵ) and the average crystallite size (D). The graph (straight line) between $\beta \cos \theta$ and $4 \sin \theta$ is drawn to calculate the values of “D” and “ ϵ ”, as shown by Figure 8.1 (b).

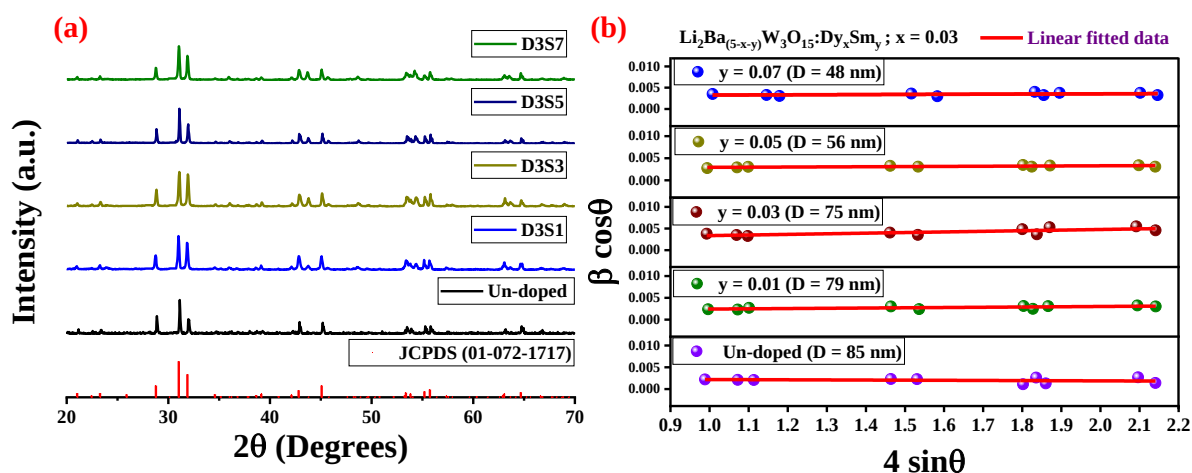


Figure 8.1 (a) XRD patterns and (b) A graph between $\beta \cos \theta$ and $4 \sin \theta$ for un-doped LBW and $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$) phosphors.

8.3.1.2 SEM and EDAX studies: morphological investigations

The surface morphology of the as prepared phosphor sample was analysed using SEM and EDAX. The SEM image in Figure 8.2 (a) depicts the surface of a $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $y = 0.05$) phosphor.

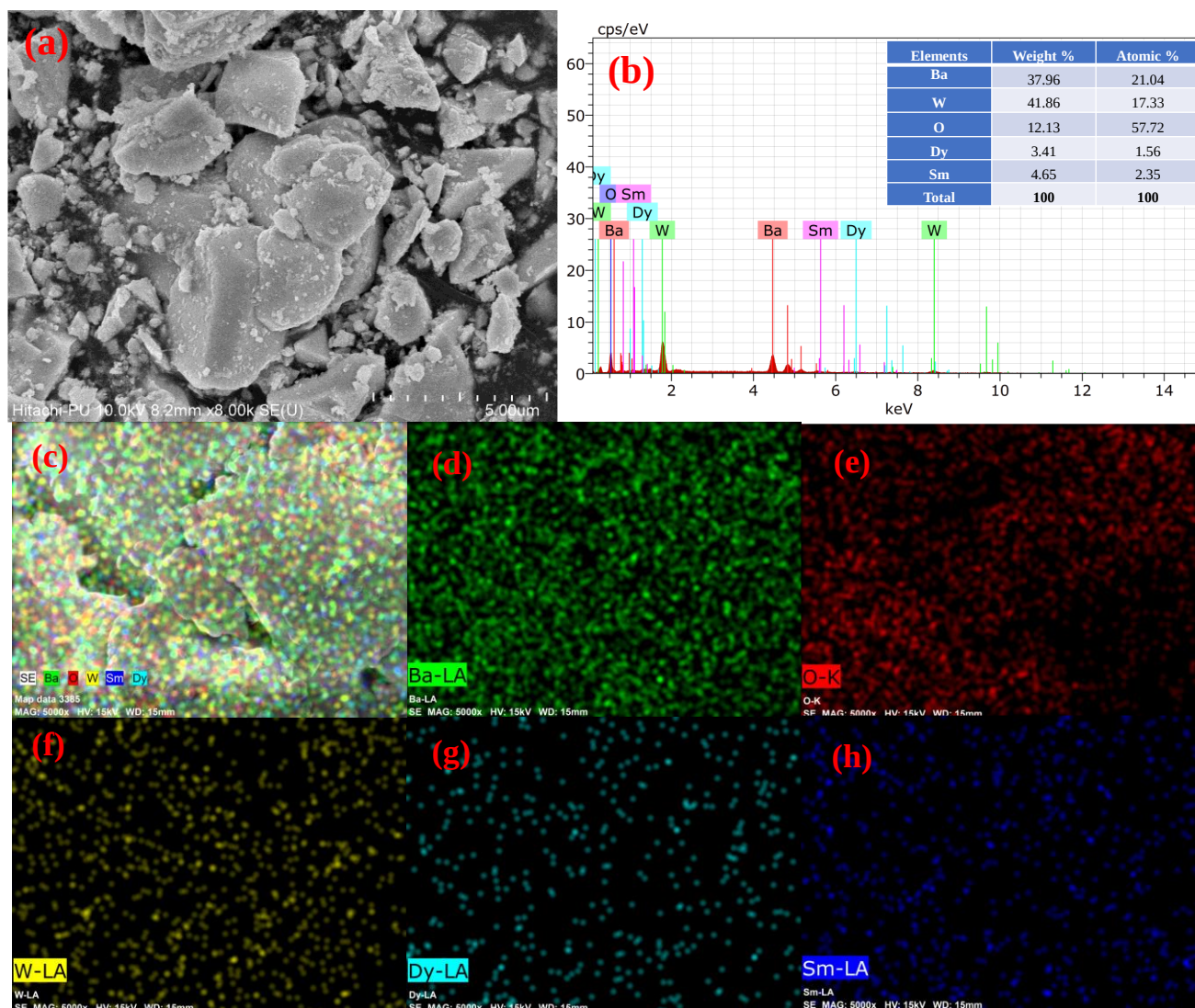


Figure 8.2 (a) The SEM picture, (b) EDAX pattern (Insert figure show the weight% and atomic% of individual atoms present in the phosphor) and (c)-(h) elemental distribution (Ba, W, O, Dy and Sm) for $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $y = 0.05$) phosphor.

It is evident that there is inconsistency in both the shape and size of the particles. This variability is attributed to the agglomeration phenomenon observed in the as prepared material, likely due to the high-

temperature synthesis process and hand-grinding. The whole consists of irregular micron-sized particles, which play a pivotal role in enhancing the luminous intensity in SSL devices [286]. As shown in Figure 8.2 (b), the EDAX analysis was utilized for the confirmation of the elements present in the as prepared phosphor material. Clear peaks corresponding to Ba, O, W, Dy, and Sm are observed in the EDAX spectrum, validating the uniform distribution of these components in the as prepared phosphors. This confirms the synthesis of LBW:Dy³⁺/Sm³⁺ phosphors, as further illustrated in Figure 8.2 (c)-(h). Notably, elements with low energy, like Li, show no peaks in the EDAX spectra, which is consistent with observations found in the literature [125].

8.3.2 Optical studies

8.3.2.1 DRS and band gap (E_g) energy evaluation

Figure 8.3 represents the DRS of an un-doped LBW and Dy³⁺/Sm³⁺ ions co-doped LBW phosphors in the 200-1600 nm range. The peaks corresponding to 472, 946, 1072, 1272, 1378, 1474 and 1530 nm wavelength shows the transition from the ground state, i.e., ⁶H_{5/2} to the various excited states ⁴I_{11/2}, ⁶F_{11/2}, ⁶F_{9/2}, ⁶F_{7/2}, ⁶F_{5/2}, ⁶H_{13/2} and ⁶H_{11/2}, related to Sm³⁺ ions [287], however, the transitions corresponding to ⁶F_{3/2}, ⁶F_{5/2} and ⁶F_{7/2} excited states from the ground state ⁶H_{15/2}, represented by the remaining peaks at 736, 792 and 888 nm, were related to Dy³⁺ ions [127,259].

The optical absorption near the band edge is represented by the K-M function, using equation 2.7-2.8 in section 2.3.5, which can be utilised to address the band gap energy (E_g). The inset in Figure 8.3 shows the band gap value, which was determined by extrapolating the linear section of the plot between $[F(R)h\nu]^2$ and $h\nu$ and found to be equal to 3.74, 3.64 and 3.61 eV for the un-doped LBW, Li₂Ba_(5-x-y)W₃O₁₅:Dy_xSm_y (where x = 0.03 and y = 0, y = 0.05) phosphors. The 4f energy level of Dy³⁺ and Sm³⁺ ions may be the cause of insignificant fall in the E_g values from 3.74 to 3.61 eV with the doping ions concentration. Conversely, the slight decline also implies that the studied materials crystallized effectively [127].

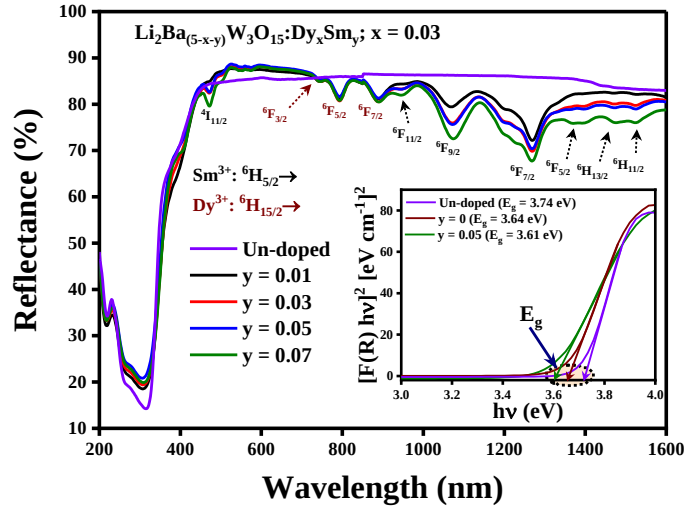


Figure 8.3 DRS of an un-doped LBW and $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$). [Inset shows the band gap variations of un-doped LBW and $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $y = 0, y = 0.05$) phosphors].

8.3.2.2 Study of PL excitation and PL emission spectra of $\text{LBW}:\text{Dy}^{3+}$ phosphors

The PLE and PL properties of the Dy^{3+} doped LBW phosphor materials is already discussed in section 3.3.2.2 in Chapter 3.

8.3.2.3 Effect of co-doping of Sm^{3+} ions on $\text{LBW}:\text{Dy}^{3+}$ phosphor

In the pursuit of synthesising single-phase warm white phosphors, we utilized $\text{Li}_2\text{Ba}_{(5-x)}\text{W}_3\text{O}_{15}:\text{Dy}_x$ ($x = 0.03$) phosphors co-doped with the varying concentrations of Sm^{3+} ions. Another objective of this modification was to explore the ET mechanism between the two RE^{3+} ions. In RE^{3+} ions, the down-conversion through ET involves the transfer of energy from a high-energy RE^{3+} ion to a low-energy state RE^{3+} ion resulting in luminescence.

It is much more probable that the ET process will go from Dy^{3+} to Sm^{3+} ions due to the higher energy state of the Dy^{3+} ions as compare to the Sm^{3+} ions. The spectrum overlap between the acceptor (Sm^{3+}) excitation and the donor (Dy^{3+}) emission is the primary requirement for the ET process analysis [30]. Figure 8.4 shows the alignment of the PL emission peak of Dy^{3+} ions at 495 nm (from ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$) with the PL excitation peak of Sm^{3+} ions at 468 nm (from ${}^6\text{H}_{5/2} \rightarrow {}^4\text{I}_{11/2}$). These findings inspired us for further

investigation into the ET process from Dy^{3+} to Sm^{3+} by combining the ideal concentration of Dy^{3+} ions with various concentration levels of Sm^{3+} ions (from 1 to 7 mol% in increments of 2 mol%).

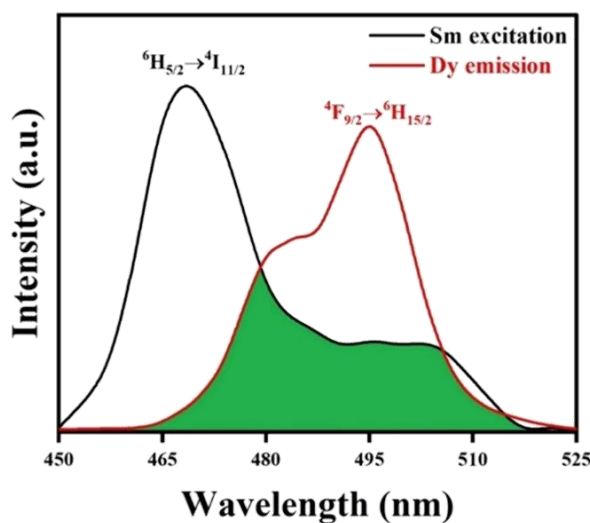


Figure 8.4 The overlapped region between the Sm^{3+} excitation band and Dy^{3+} emission band.

Before commencing this investigation, the PL excitation spectrum of solely Dy^{3+} (3 mol% doping of Dy^{3+} -D3) and Sm^{3+} (1 mol% doping of Sm^{3+} -S1) ions doped phosphors can be observed at $\lambda_{\text{Ex}} = 336$ nm, as depicted in Figure 8.5 (a).

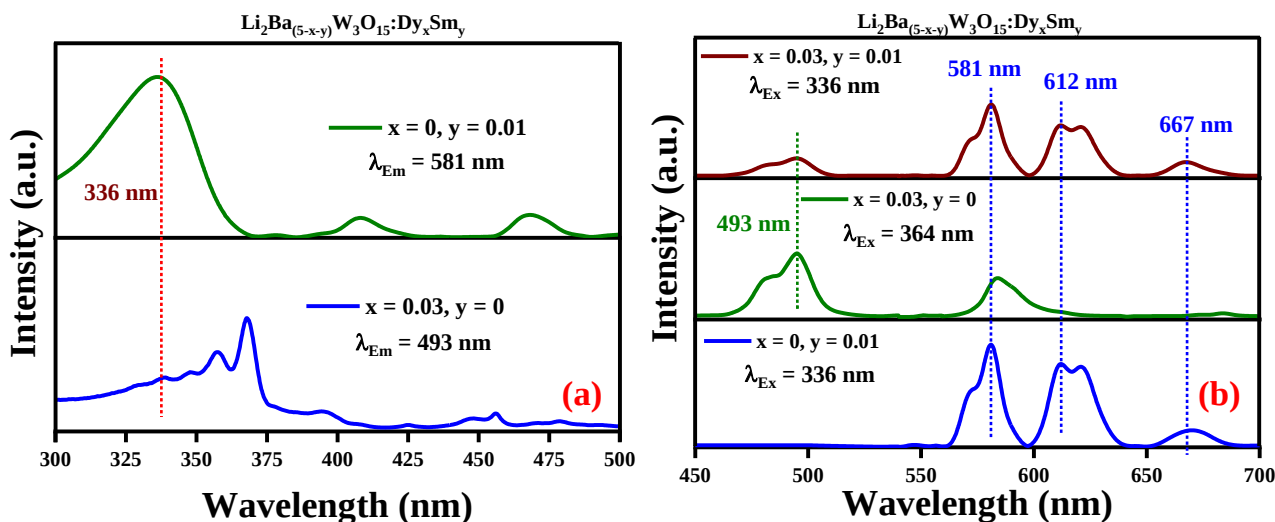


Figure 8.5 (a) PL excitation spectrum of $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03, y = 0$ & $x = 0, y = 0.01$) phosphors, (b) PL emission spectrum of $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0, y = 0.01$; $x = 0.03, y = 0$ and $x = 0.03, y = 0.01$) phosphors.

Figure 8.5 (b) displays the PL emission spectra of three samples individually doped with 3 mol% Dy^{3+} (D3); 1 mol% Sm^{3+} (S1) ions and 3 mol% Dy^{3+} , 1% mol Sm^{3+} (D3S1) ions co-doped. Under $\lambda_{\text{Ex}} = 336$ nm, the D3S1 samples exhibit characteristic emission peaks from both Dy^{3+} and Sm^{3+} ions. These include an emission peak at 495 nm for Dy^{3+} ions and emission peaks at 581, 612, and 667 nm corresponding to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$, $^6\text{H}_{7/2}$, and $^6\text{H}_{9/2}$ transitions for Sm^{3+} ions [42,286]. It is evident from the literature that the commercial LED has its excitation wavelength from n-UV to UV region [288]. $\lambda_{\text{Ex}} = 336$ used in the present work is near to UV region, therefore, the commercial LEDs can be used practically to excite the phosphors studied in the present work. In Figure 8.6 (a), the intensity of PL emission peaks of Sm^{3+} at 581, 612, and 669 nm significantly increases by about 3-4 times when doped with Dy^{3+} , as compared to single doped with Sm^{3+} ions. This suggests the effective ET from Dy^{3+} to Sm^{3+} under $\lambda_{\text{Ex}} = 336$ nm. Figure 8.6 (b) displays the PL emission spectra of $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$) phosphors. Under $\lambda_{\text{Ex}} = 336$ nm excitation, both characteristic peaks of Sm^{3+} and Dy^{3+} are simultaneously visible.

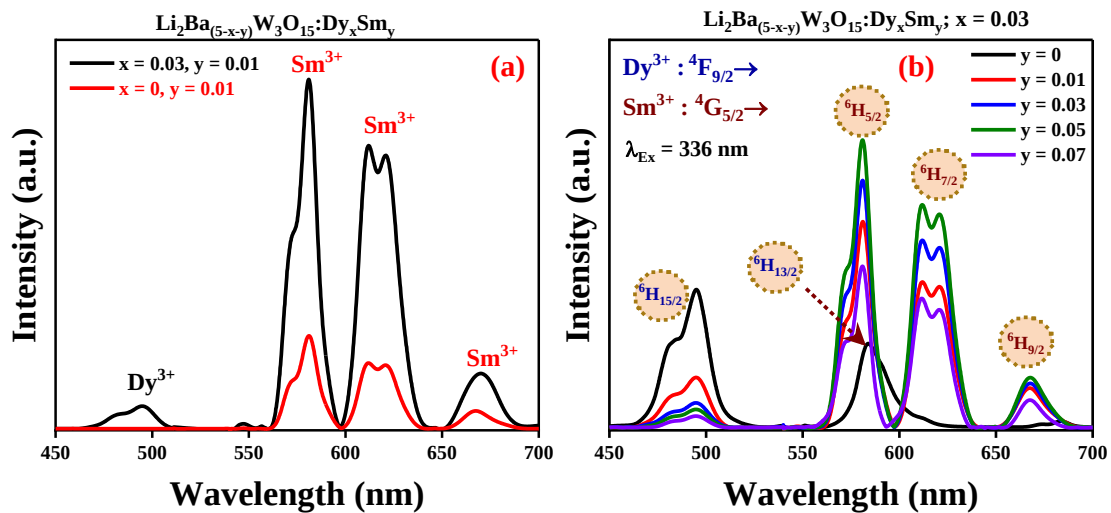


Figure 8.6 (a) PL emission spectra comparison of $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ ($x = 0.03$, $y = 0.01$ & $x = 0$, $y = 0.01$) at 336 nm excitation, (b) PL emission spectra for LBW, $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$) phosphors.

Specifically, the peaks at 493 nm (blue light) and 583 nm (yellow light) correspond to the characteristic transitions of $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^6\text{H}_{13/2}$ for Dy^{3+} , respectively. Meanwhile, the peaks at 581 nm (yellow light),

612 nm (orange-red light) and 669 nm (red light) correspond to the characteristic transitions of $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^6H_{7/2}$, and $^6H_{9/2}$ for Sm^{3+} ions. The luminous intensity of Dy^{3+} ions gradually diminish with an increase in the concentration of Sm^{3+} ions taking Dy^{3+} ions concentration constant which approves the ET between Dy^{3+} and Sm^{3+} ions. After 5 mol% doping concentration of Sm^{3+} ions, the PL emission intensity of various peaks subsequently decrease due to concentration quenching.

8.3.2.4 Energy transfer calculation

Figure 8.7 (a) illustrates the schematic representation of the ET mechanism from Dy^{3+} to Sm^{3+} within the LBW host material. The excited state of Dy^{3+} ($^4F_{9/2}$) ions is slightly higher than those of Sm^{3+} ($^4I_{19/2}$) ions, suggested that the non-radiative mechanisms are primarily responsible for the ET from Dy^{3+} to Sm^{3+} ions. These non-radiative ET mechanisms involve radiation reabsorption, exchange interaction, and electric multipole interaction [282]. The multipole-multipole interaction has a higher chance of causing ET amid all the interactions, in the present study. Reisfeld's approximation, shown by equation 1.3-1.4, was utilized to identify the precise interaction mechanism that exists in the as prepared Dy^{3+}/Sm^{3+} co-doped phosphor samples. Figure 8.7 (b) illustrates the changes in the ratio $\frac{I_{s0}}{I_s}$ as a function of $C^{a/3}$. For, $a = 6$, the data showed the strongest linear fit, suggesting non-radiative ET through d-d interaction. The energy levels for the dopant ions were determined by referring to Carnall's paper [287].

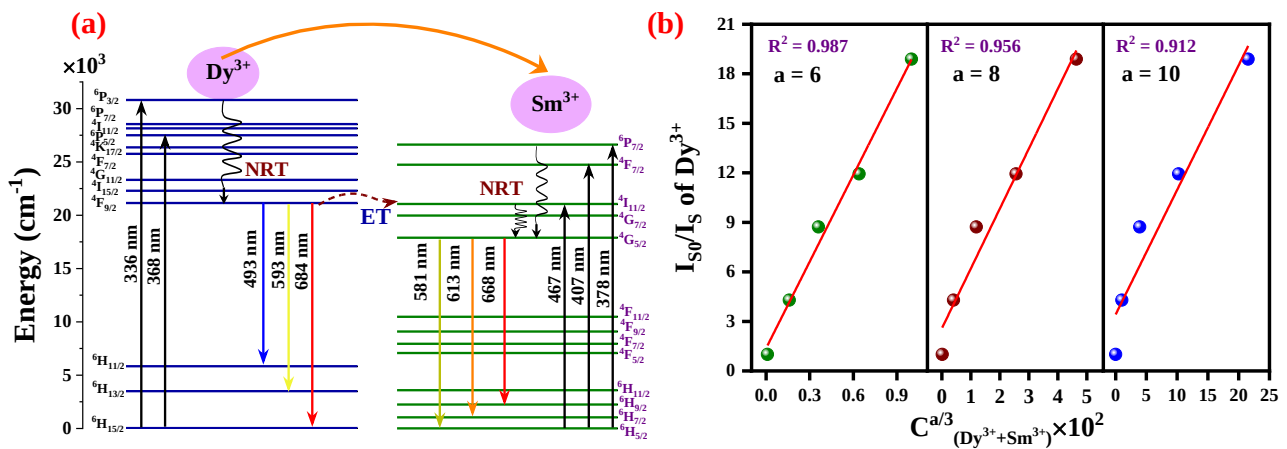


Figure 8.7 (a) Schematic diagram of energy transfer from Dy^{3+} to Sm^{3+} in LBW host material, (b) The variation in the ratio I_{s0}/I_s as a function of $C^{a/3}$.

8.3.2.5 Study of TRPL analysis

Figure 8.8 (a) shows the decay curves for $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$) co-doped phosphors when the excitation and emission wavelengths are fixed at 336 nm and 581 nm, respectively. This allows for a deeper exploration of the ET process between Dy^{3+} and Sm^{3+} ions. Single exponential fitting is not appropriate for the measured data; however, double exponential fitting, given by equation 2.10 provides a useful assessment method. Using the double exponential fitting and by applying the formula given in equation 2.11, the average value of decay lifetime (τ) for the as-prepared $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$) co-doped phosphor samples is computed and found to be 0.646 ms, 0.641 ms, 0.637 ms, and 0.624 ms, respectively. The energy transfer efficiency (ETE; η_{ET}) and energy transfer probability (P_{ET}) are evaluated using the using the equations 2.13-2.14 and therefore τ , η_{ET} and P_{ET} plotted against the Sm^{3+} ions concentration in Figure 8.8 (b). As seen in Figure 8.8 (b), adding more Sm^{3+} ions, shortens the luminescence lifetime values, indicating the possibility of ET from $\text{Dy}^{3+} \rightarrow \text{Sm}^{3+}$. When $y = 0.07$, the maximum η_{ET} increases to 18%. Table 8.1 provides an overview of the above evaluated parameters.

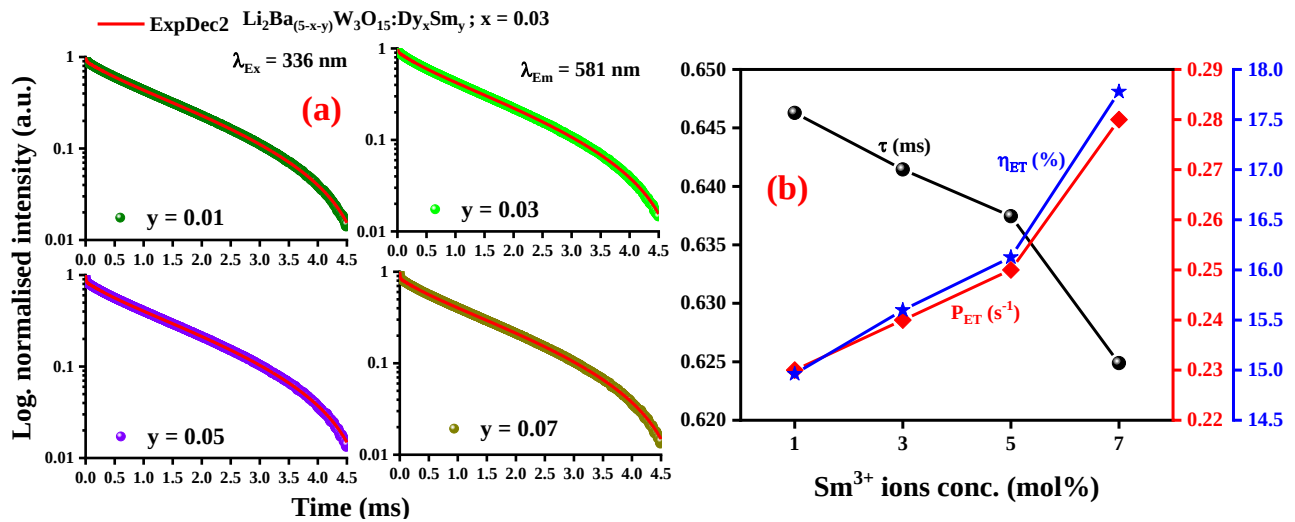


Figure 8.8 (a) The decay curves of $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$) phosphors at $\lambda_{\text{Em}} = 581$ nm & $\lambda_{\text{Ex}} = 336$ nm and (b) variation of τ , η_{ET} and P_{ET} with the Sm^{3+} ions concentration.

Table 8.1 The average value of decay lifetime (τ , ms), energy transfer efficiency (η_{ET}) and energy transfer probability (P_{ET}) of $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$) co-doped phosphors.

System Name	τ (ms)	η_{ET} (%)	P_{ET} (s^{-1})
D3S1	0.646	14.96	0.23
D3S3	0.641	15.60	0.24
D3S5	0.637	16.12	0.25
D3S7	0.624	17.78	0.28

8.3.2.6 Evaluation of CIE color coordinates

The chromaticity coordinate diagram for Dy^{3+} single ions doped and $\text{Dy}^{3+}/\text{Sm}^{3+}$ ions co-doped LBW phosphors, designed by the Commission International de l'éclairage (CIE) in 1931, evaluated using the formula given in literature [30,132] and shown in Figure 8.9 (a). CIE of D3 sample lie in yellowish-white region, but when Sm^{3+} ions are co-doped with D3 phosphors, the emission gradually moves towards the warm white light region. Table 8.2 represents the CIE chromaticity coordinates, CCT and emission light color information for the as prepared $\text{Dy}^{3+}/\text{Sm}^{3+}$ ions co-doped LBW phosphor samples.

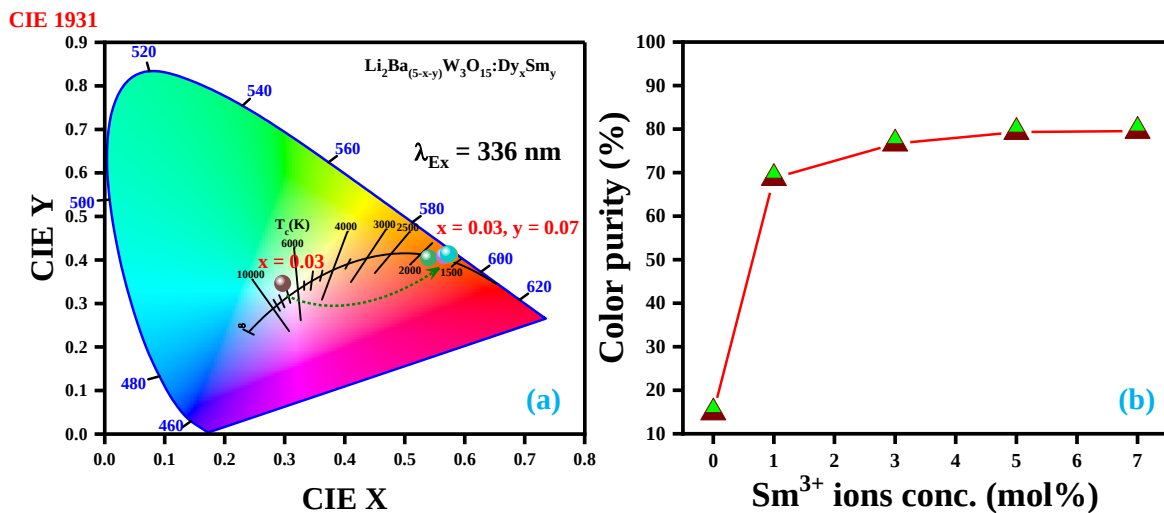


Figure 8.9 (a) CIE chromaticity coordinates, (b) CP values for $\text{Li}_2\text{Ba}_{(5-x)}\text{W}_3\text{O}_{15}:\text{Dy}_x$ (where $x = 0.03$) and $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$) phosphors.

Table 8.2 The CIE chromaticity coordinates, CCT (K), emission color and CP (%) of the $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$) phosphor samples.

System Name	CIE		CCT (K)	Emission color	CP (%)
	X	Y			
D3	0.3328	0.3739	5495	Neutral white	14.89
D3S1	0.5397	0.4047	1882	Warm white	68.73
D3S3	0.5655	0.4101	1791	Warm white	76.64
D3S5	0.5746	0.4120	1768	Warm white	79.31
D3S7	0.5726	0.4143	1782	Warm white	79.57

The CCT values are determined using the Mc-Camy equation 1.12. Table 8.2 illustrate that the introduction of a specific quantity of Sm^{3+} doping into the D3 host leads to a notable decrease in color temperature, shifting the emission from the yellow-white sunlight region to the warmer white light region. While the D3 phosphor itself, emitting cold white light, achieves white light emission through blue and yellow light emissions, however, the absence of red light can cause prolonged discomfort such as eye strain, fatigue, and piercing sensations.

Table 8.3 Comparison of CCT value of the optimized phosphor $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$, $y = 0.05$ (D3S5)) sample with previously reported literature.

Material	CCT (K)	References
$\text{NaY}(\text{MoO}_4)_2:\text{Dy}10\text{Sm}15$	3705	[282]
$\text{CYN}:\text{Dy}5\text{Sm}7$	3241	[286]
$\text{NYF}:\text{Dy}1\text{Sm}1.6$	4174	[289]
$\text{CaLaTiO}_3:\text{Dy}4\text{Sm}1$	2591	[290]
D3S5	1768	This work

Consequently, a phosphor incorporating a three-color mixture is developed to emit warm white light, thereby reducing the detrimental effects of blue light on human eyes and significantly cutting costs. Hence, the as synthesized $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$ and $0.01 \leq y \leq 0.07$, $\Delta y = 0.02$) co-doped phosphors, owing to its low CCT value and emission of warm white light, holds promise as a potential

candidate for indoor and ambient lighting applications, alleviating eye fatigue. Table 8.3 shows the comparison of CCT of the optimised phosphor $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$, $y = 0.05$) sample with previously reported literature [282,286,289,290].

CP, an additional significant factor in colorimetric calculations that analyse the color saturation, is evaluated using equation 1.11 given in section 1.5.1. The CP values, shown in the Figure 8.9 (b), increases from 15% to nearly 80%, which are relatively high, indicate the use of the as prepared phosphor material as a reddish-orange emitting element in w-LEDs when excited by n-UV or blue light and are presented in Table 8.2.

8.3.2.7 Study of TDPL spectra

The thermal stability of the phosphor samples prepared can be well understood using the TDPL studies. TDPL studies have been recorded in the present work for the co-doped LBW phosphors. It is well known that, temperature has a significant effect on w-LED performance, as UV/blue LED chips lose optical performance as the temperatures rises. Thus, for the optimized phosphor sample $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$, $y = 0.05$) at $\lambda_{\text{Ex}} = 336$ nm, TDPL experiments were performed, as shown in Figure 8.10, to investigate its thermal behavior by raising the temperature from ambient temperature to 443 K. As seen in Figure 8.10 (a), the PL emission peak intensity seems to be slightly decreasing as the temperature increases from 298 K to 443 K, however, the peak position remains unchanged. Figure 8.10 (b) displays the shift of CIE chromaticity coordinates with temperature ranges from 293 K to 443 K. The CIE chromaticity coordinates are almost unchanged for $\Delta x < 0.001$ and $\Delta y < 0.006$, although the temperature rises from 298 K to 443 K.

The activation energy (ΔE) must be investigated in order to better understand the thermal quenching effect, and it can be estimated using the Arrhenius equation 2.16. The ΔE value can be obtained using the relationship between $\ln \left[\left(\frac{I_0}{I_T} \right) - 1 \right]$ and $\frac{1}{KT}$, as seen in Figure 8.10 (c). Consequently, following the linear

fitting for these sites, ΔE was calculated to be 0.16 eV, exceeding earlier researches [289,291–294], presented in Table 8.4.

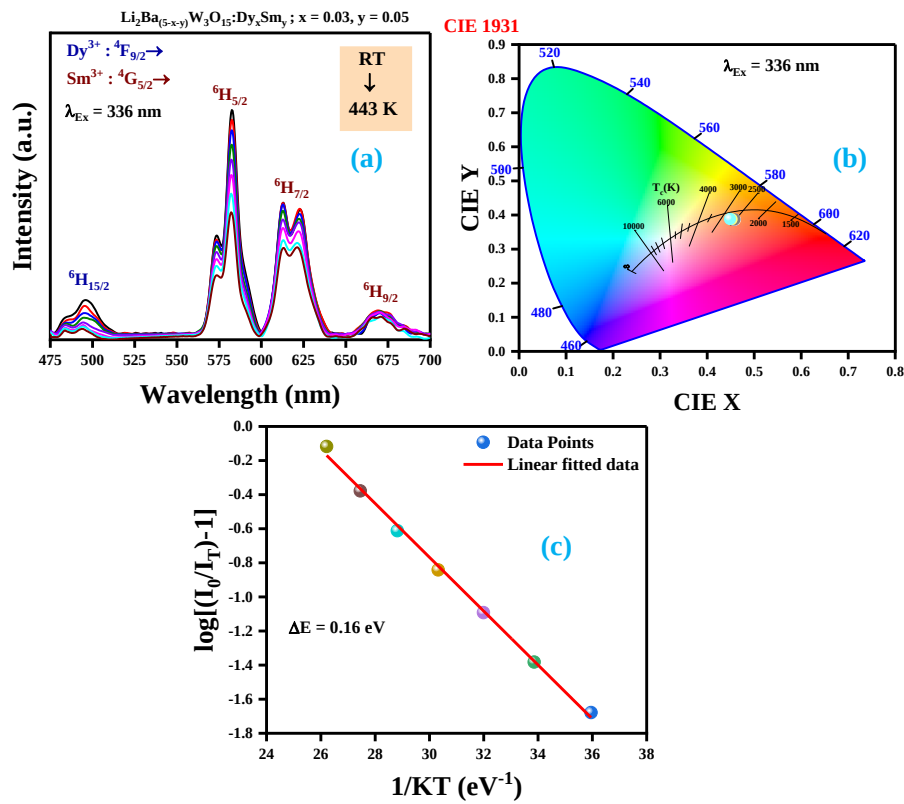


Figure 8.10 (a) TDPL, (b) CIE color chromaticity coordinates and (c) The linear fitting curve of $\log \left[\left(\frac{I_0}{I_T} \right) - 1 \right]$ against $\frac{1}{KT}$ for $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$, $y = 0.05$) phosphor sample.

Table 8.4 Comparison of the ΔE value for the as prepared $\text{Li}_2\text{Ba}_{(5-x-y)}\text{W}_3\text{O}_{15}:\text{Dy}_x\text{Sm}_y$ (where $x = 0.03$, $y = 0.05$ (D3S5)) phosphor with some previously reported samples.

Sensing material	ΔE (eV)	References
Na5Y9F32:Dy1Sm0.8	0.14	[289]
CLGP:Dy0.20	0.09	[291]
Li0.97NbO3: Dy2Sm1	0.15	[292]
Na5Y9F32:Dy1Sm2.4	0.15	[293]
Lu1.93Ge2O5:Bi6Sm1	0.11	[294]
D3S5	0.16	This work

8.4 CONCLUSIONS

In conclusion, the high-temperature SSR technique was used to synthesize a series of $\text{Dy}^{3+}/\text{Sm}^{3+}$ co-doped warm white LBW phosphors. The addition of dopant ($\text{Dy}^{3+}/\text{Sm}^{3+}$) ions in the LBW host lattice without inducing structural changes was shown by the slight shift in bandgap with the change in its concentration. Warm white light emission with a low CCT (1768 K) value can be achieved by simply changing the concentration of Sm^{3+} which makes the light emission appropriate for indoor lighting applications. Co-doping of LBW:Dy^{3+} phosphors with Sm^{3+} ions allow for the modification of the luminescent colors from the neutral white to orange-red region. The concentration quenching of $\text{Dy}^{3+}/\text{Sm}^{3+}$ co-doped LBW phosphors is caused by d-d interaction, suggested by Reisfeld approximation. In this study, the maximum η_{ET} was determined to be 17.78%. The optimised phosphor sample's activation energy of 0.16 eV was discovered to be higher than that of previously reported phosphors, indicating the better thermal stability of the as prepared phosphor. According to our findings, the $\text{Dy}^{3+}/\text{Sm}^{3+}$ co-doped LBW phosphor has a wide range of potential applications in the warm light w-LED technological advances due to their superior solubility for RE^{3+} ions, high thermal stability and high luminous efficiency.

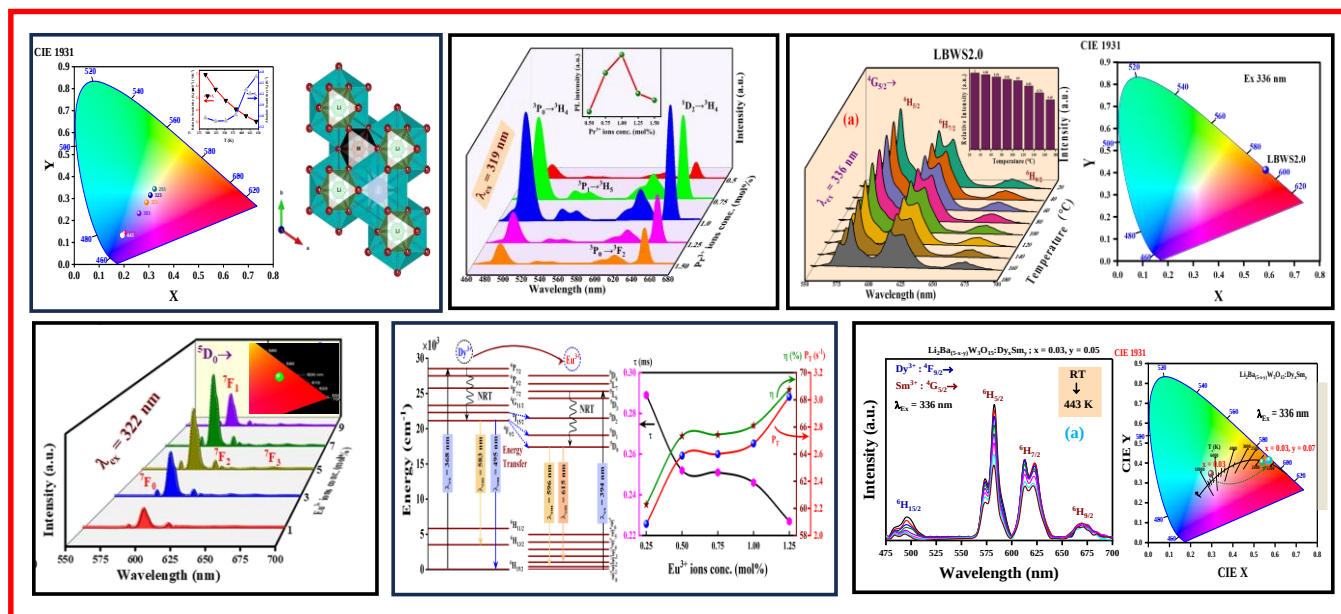
CHAPTER 9

CONCLUDING REMARKS

AND

FUTURE RESEARCH SCOPE

This chapter provides concluding remarks on the research presented in this thesis and outlines future perspectives. The primary goal of this thesis study is to synthesize and analyse RE doped $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$ (LBW) phosphors for the use in general illumination for solid state lighting applications and non-contact optical thermometry. By adding Dy^{3+} , Pr^{3+} , Sm^{3+} and Eu^{3+} ions as RE dopants, multicolour emitting pure phase LBW phosphors were successfully synthesized using SSR method. Significant emphasis has been paid to improving emission qualities by altering the dopant RE ion concentrations and co-doping of the RE ions.



9.1 SUMMARY OF THE PRESENT RESEARCH WORK

Firstly, we introduce the research problem, motivation, and recent literature, emphasizing the history, advantages, and challenges of white light generation. The theoretical models like Dexter theory, Dexter and Reisfeld's approximation, and the Inokuti-Hirayama model were explained to analyze the spectral data, ionic interactions, and energy transfer between RE ions. The PL emission spectra are used to evaluate CIE coordinates, CP, CCT, and activator/sensitizer ion lifetimes. The TDPL and temperature sensing parameters, such as FIR and sensitivities (relative and absolute), are also discussed.

Further, we focus on synthesizing Lithium Barium Tungstate ($\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$: LBW) phosphors doped with RE ions (Pr^{3+} , Sm^{3+} , Eu^{3+} , Dy^{3+}) using the high-temperature SSR method. The structural, morphological, and optical properties are characterized through XRD, FT-IR, DRS, and PL studies. Additionally, the effects of temperature on luminescent properties, with morphological analysis using SEM and EDAX were explained.

Firstly, we prepared a series of Dy^{3+} ions doped LBW phosphors using SSR method, exhibiting a hexagonal structure (space group $P6_3mc$) confirmed by XRD and Rietveld analysis. Under 368 nm excitation, these phosphors emit light at 493, 583, and 684 nm due to specific Dy^{3+} ion transitions. The optimal doping concentration was determined to be 3 mol%, beyond which concentration quenching occurs via dipole-dipole interactions, as explained by Dexter's theory. Additionally, the phosphors demonstrated non-contact temperature sensing capabilities through FIR ($I_{493\text{nm}}/I_{583\text{nm}}$) measurements, with a S_r of 0.7% K^{-1} at 293 K and S_a of 4.68% K^{-1} at 443 K. The temperature resolution (~ 0.51) highlights the material's ability for precise thermal sensing. These findings indicate the phosphors' potential for applications in w-LEDs and highly sensitive temperature detection.

Subsequently, a series of Pr^{3+} ions doped LBW phosphor was successfully synthesized via the high-temperature SSR method and analyzed for structural, optical, and thermal properties. XRD and Rietveld refinement confirmed phase purity. The band gap, determined from Tauc's plot, is suitable for photonic

applications. PL studies revealed four emission peaks, with a prominent 647 nm peak ($^3P_0 \rightarrow ^3F_2$ transition) under 319 nm excitation. Optimal doping occurred at 1.0 mol%, with concentration quenching caused by dipole-dipole interactions, as explained by Dexter's theory. The phosphors exhibit white light emission (confirmed by CIE coordinates), bi-exponential decay profiles, and energy transfer between Pr^{3+} ions with increasing concentration. Thermal stability was validated through TDPL analysis, and the phosphors showed strong optical thermometry capabilities with a maximum S_r of $1.03\% \text{ K}^{-1}$. These characteristics make Pr^{3+} -doped LBW phosphors suitable for SSL and optical thermometry applications.

To search a thermally stable phosphor sample, we further prepared a series of Sm^{3+} doped LBW phosphors using the high-temperature SSR method, and their structural, morphological, and PL properties were analyzed. XRD confirmed high crystallinity and purity with an average crystallite size of ~ 83 nm, while SEM images showed irregular polyhedron shapes with mild clustering and micro-sized particles. The band gap values (3.74–3.63 eV) suggested suitability for photonic applications. PL analysis showed three emission bands, with the most prominent at 581 nm ($^4G_{5/2} \rightarrow ^6H_{5/2}$ transition) under 336 nm excitation. Optimal performance was observed at 2.0 mol% Sm^{3+} , with concentration quenching attributed to dipole-dipole interactions, as per Dexter's theory. The optimized sample's CIE coordinates (0.586, 0.412) indicate deep orange-red emission. Double exponential PL decay with millisecond lifetimes and high thermal stability, confirmed by TDPL analysis, demonstrate the material's robustness. These results establish Sm^{3+} ions doped LBW phosphors as promising candidates for photonic devices, particularly w-LEDs.

In the next chapter, Eu^{3+} -activated $\text{Li}_2\text{Ba}_{5-x}(\text{WO}_5)_3:\text{xEu}^{3+}$ ($1 \leq x \leq 9$, $\Delta x = 2$ mol%) phosphors were synthesized via the SSR method, and their structural, morphological, and PL properties were studied. XRD confirmed phase purity, and the average crystallite size, calculated using the Debye-Scherrer method and W-H plot, was ~ 83 –85 nm. SEM images revealed irregular, non-uniform particles with mild agglomeration and micro-range sizes suitable for white LEDs. The band gap values (3.74–3.51 eV) suggest optical suitability. The PL analysis showed a prominent orange-red emission at 595 nm ($^5D_0 \rightarrow ^7F_1$

transition) under 322 nm excitation. Optimal Eu^{3+} concentration was 7 mol%, beyond which concentration quenching occurred due to dipole-dipole interactions, as explained by Dexter theory and the I-H model. The optimized sample exhibited orange-red emission with CIE coordinates (0.6274, 0.3721). TDPL properties were evaluated using the LIR method, with the LBW:Eu7.0 phosphor showing a maximum S_r of 1.21% K^{-1} at 298 K, demonstrating its potential for non-contact temperature sensing. These findings establish Eu^{3+} -doped $\text{Li}_2\text{Ba}_5(\text{WO}_5)_3$ as a promising material for photonic applications, including w-LEDs and optical thermometry.

To understand the ET processes in co-doped phosphors, we synthesized $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped LBW phosphors and analyzed for their structural, compositional, and luminescent properties, including temperature-dependent behavior, using techniques such as XRD, FE-SEM, EDAX, FT-IR, PL, PL decay, and TDPL. XRD with W-H plots confirmed that Dy^{3+} and Eu^{3+} ions replace Ba^{2+} sites in the LBW lattice without significant crystal defects. The phosphors exhibit tunable luminescence, enabling color shifts from natural white to orange-red by varying Eu^{3+} concentrations, achieving warm white light suitable for indoor lighting due to low CCT. Energy transfer from Dy^{3+} to Eu^{3+} ions, facilitated by dipole-dipole interactions, was confirmed with a maximum efficiency of 68.74% for D3E1.25 phosphors. Increasing Eu^{3+} concentration reduced decay times due to enhanced non-radiative transitions. A FIR model revealed temperature-dependent emission trends, with a maximum S_r of 0.97% K^{-1} at 303 K for D3E0.75 phosphors. These findings highlight the potential of $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped LBW phosphors for UV-excitable warm white lighting applications with tunable colors and optical thermometry capabilities.

Finally, a series of LBW phosphors doped with Dy^{3+} and Sm^{3+} ions were synthesized via a high-temperature SSR method. XRD and SEM-EDAX analyses confirmed the retention of the LBW crystal structure and revealed small, irregularly shaped particles. The incorporation of Dy^{3+} and Sm^{3+} ions caused minor bandgap shifts without altering the crystal structure. The Sm^{3+} concentration significantly influenced the emission color, enabling warm white light with a low CCT of 1768 K, suitable for indoor

lighting. Co-doping with Sm^{3+} modified luminescent colors from neutral white to orange-red. Concentration quenching, attributed to d-d interactions, was analyzed using Dexter theory and the Reisfeld approximation, with an energy transfer efficiency (η_{ET}) of 17.78%. The optimized phosphor exhibited superior thermal stability with an activation energy of 0.16 eV, surpassing previously reported phosphors. These findings highlight the $\text{LBW:Dy}^{3+}/\text{Sm}^{3+}$ phosphor's potential for warm white LED applications due to its high luminous efficiency, thermal stability, and excellent RE^{3+} ion solubility.

9.2 FUTURE RESEARCH SCOPE

- ✚ To carry out a further literature survey on the aforementioned topic for thorough knowledge and understanding.
- ✚ Try to synthesize the phosphors with other chemical routes also like Co-precipitation, Hydrothermal to obtain a homogeneous and pure crystalline phase so that it can improve the particle morphology, and reduce the particle size which in turn further improves the luminescence properties.
- ✚ To enhance the luminescence properties of $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$ phosphor by using other suitable dopants/co-dopants (for ex: Yb^{3+} may act as a sensitizer for Ho^{3+} , Tm^{3+} and Tb^{3+}) so that we can explore our application part in other down-conversion/up-conversion applications.
- ✚ To project these phosphors in device fabrication and other photonic applications.
- ✚ To make the prepared phosphor usable for optical thermometry at high temperature range.

REFERENCES

- [1] D. MacIsaac, G. Kanner, G. Anderson, Basic physics of the incandescent lamp (lightbulb), *Phys. Teach.* 37 (1999) 520–525. <https://doi.org/10.1119/1.880392>.
- [2] B. Valeur, M.N. Berberan-Santos, A Brief History of Fluorescence and Phosphorescence before the Emergence of Quantum Theory, *J. Chem. Educ.* 88 (2011) 731–738. <https://doi.org/10.1021/ed100182h>.
- [3] N. Deopa, A.S. Rao, Photoluminescence and energy transfer studies of Dy³⁺ ions doped lithium lead alumino borate glasses for w-LED and laser applications, *J. Lumin.* 192 (2017) 832–841. <https://doi.org/10.1016/J.Lumin.2017.07.052>.
- [4] S. Gai, C. Li, P. Yang, J. Lin, Recent Progress in Rare Earth Micro/Nanocrystals: Soft Chemical Synthesis, Luminescent Properties, and Biomedical Applications, *Chem. Rev.* 114 (2014) 2343–2389. <https://doi.org/10.1021/cr4001594>.
- [5] Z. Chen, Z. Li, J. Chen, P. Kallem, F. Banat, H. Qiu, Recent advances in selective separation technologies of rare earth elements: a review, *J. Environ. Chem. Eng.* 10 (2022) 107104. <https://doi.org/10.1016/j.jece.2021.107104>.
- [6] S.C. Chelgani, M. Rudolph, T. Leistner, J. Gutzmer, U.A. Peuker, A review of rare earth minerals flotation: Monazite and xenotime, *Int. J. Min. Sci. Technol.* 25 (2015) 877–883. <https://doi.org/10.1016/j.ijmst.2015.09.002>.
- [7] N. Haque, A. Hughes, S. Lim, C. Vernon, Rare Earth Elements: Overview of Mining, Mineralogy, Uses, Sustainability and Environmental Impact, *Resources.* 3 (2014) 614–635. <https://doi.org/10.3390/resources3040614>.
- [8] A. Kumari, R. Panda, M.K. Jha, J.R. Kumar, J.Y. Lee, Process development to recover rare earth metals from monazite mineral: A review, *Miner. Eng.* 79 (2015) 102–115. <https://doi.org/10.1016/j.mineng.2015.05.003>.
- [9] T.-L. Phan, M.-H. Phan, N. Vu, T.-K. Anh, S.-C. Yu, Luminescent properties of Eu-doped Y₂O₃ nanophosphors, *Phys. Status Solidi.* 201 (2004) 2170–2174. <https://doi.org/10.1002/pssa.200406825>.
- [10] H. Liu, L. Wang, S. Chen, Effect of Yb³⁺ concentration on the upconversion of Er³⁺ ion doped La₂O₃ nanocrystals under 980 nm excitation, *Mater. Lett.* 61 (2007) 3629–3631. <https://doi.org/10.1016/j.matlet.2006.12.018>.
- [11] L. Li, X. Cao, Y. ZHANG, C. GUO, Synthesis and upconversion luminescence of Lu₂O₃:Yb³⁺, Tm³⁺ nanocrystals, *Trans. Nonferrous Met. Soc. China.* 22 (2012) 373–379. [https://doi.org/10.1016/S1003-6326\(11\)61186-2](https://doi.org/10.1016/S1003-6326(11)61186-2).
- [12] C. Zhang, Q. Jiang, X. Wang, J. Liu, Y. Xiao, C. Li, H. Lin, F. Zeng, Z. Su, A novel scheme to acquire enhanced up-conversion emissions of Ho³⁺ and Yb³⁺ co-doped Sc₂O₃, *Curr. Appl. Phys.* 20 (2020) 82–88. <https://doi.org/10.1016/j.cap.2019.10.002>.
- [13] J.H.V. Vleck, The Puzzle of Rare-earth Spectra in Solids., *J. Phys. Chem.* 41 (1937) 67–80. <https://doi.org/10.1021/j150379a006>.
- [14] G.H. Dieke, R.A. Satten, Spectra and Energy Levels of Rare Earth Ions in Crystals, *Am. J. Phys.* 38 (1970) 399–400. <https://doi.org/10.1119/1.1976350>.
- [15] M. Hatanaka, S. Yabushita, Mechanisms of f–f hypersensitive transition intensities of lanthanide trihalide molecules: a spin–orbit configuration interaction study, *Theor. Chem. Acc.* 133 (2014) 1517. <https://doi.org/10.1007/s00214-014-1517-2>.
- [16] J. Sucher, Magnetic dipole transitions in atomic and particle physics: ions and psions, *Reports Prog. Phys.* 41 (1978) 1781–1838. <https://doi.org/10.1088/0034-4885/41/11/002>.

- [17] J.-C.G. Bünzli, S. V. Eliseeva, Basics of Lanthanide Photophysics, in: 2010: pp. 1–45. https://doi.org/10.1007/4243_2010_3.
- [18] S. V. Eliseeva, J.-C.G. Bünzli, Lanthanide luminescence for functional materials and bio-sciences, *Chem. Soc. Rev.* 39 (2010) 189–227. <https://doi.org/10.1039/B905604C>.
- [19] J. McKittrick, M.E. Hannah, A. Piquette, J.K. Han, J.I. Choi, M. Anc, M. Galvez, H. Lugauer, J.B. Talbot, K.C. Mishra, Phosphor Selection Considerations for Near-UV LED Solid State Lighting, *ECS J. Solid State Sci. Technol.* 2 (2013) R3119–R3131. <https://doi.org/10.1149/2.017302jss>.
- [20] N.C. George, K.A. Denault, R. Seshadri, Phosphors for Solid-State White Lighting, *Annu. Rev. Mater. Res.* 43 (2013) 481–501. <https://doi.org/10.1146/annurev-matsci-073012-125702>.
- [21] L. Yang, Y. Wan, Y. Huang, C. Chen, H.J. Seo, Development of $\text{YK}_3\text{B}_6\text{O}_{12}:\text{RE}$ ($\text{RE} = \text{Eu}^{3+}$, Tb^{3+} , Ce^{3+}) tricolor phosphors under near-UV light excitation, *J. Alloys Compd.* 684 (2016) 40–46. <https://doi.org/10.1016/j.jallcom.2016.04.052>.
- [22] B. Tian, B. Chen, Y. Tian, X. Li, J. Zhang, J. Sun, H. Zhong, L. Cheng, S. Fu, H. Zhong, Y. Wang, X. Zhang, H. Xia, R. Hua, Excitation pathway and temperature dependent luminescence in color tunable $\text{Ba}_5\text{Gd}_8\text{Zn}_4\text{O}_{21}:\text{Eu}^{3+}$ phosphors, *J. Mater. Chem. C.* 1 (2013) 2338. <https://doi.org/10.1039/c3tc00915g>.
- [23] J.-C.G. Bünzli, C. Piguet, Taking advantage of luminescent lanthanide ions, *Chem. Soc. Rev.* 34 (2005) 1048. <https://doi.org/10.1039/b406082m>.
- [24] S. Yuan, S. Zhao, L. Lou, D. Zhu, Z. Mu, F. Wu, Fluorescence intensity ratio optical thermometer $\text{YNbO}_4: \text{Pr}^{3+}, \text{Tb}^{3+}$ based on intervalence charge transfer, *Powder Technol.* 395 (2022) 83–92. <https://doi.org/10.1016/j.powtec.2021.09.053>.
- [25] Y. Hua, S.K. Hussain, J.S. Yu, Eu^{3+} -activated double perovskite Sr_3MoO_6 phosphors with excellent color purity for high CRI WLEDs and flexible display film, *Ceram. Int.* 45 (2019) 18604–18613. <https://doi.org/10.1016/j.ceramint.2019.06.084>.
- [26] X. Geng, Y. Xie, Y. Ma, Y. Liu, J. Luo, J. Wang, R. Yu, B. Deng, W. Zhou, Abnormal thermal quenching and application for w-LEDs: Double perovskite $\text{Ca}_2\text{InSbO}_6:\text{Eu}^{3+}$ red-emitting phosphor, *J. Alloys Compd.* 847 (2020) 156249. <https://doi.org/10.1016/j.jallcom.2020.156249>.
- [27] P. Rohilla, A.S. Rao, Synthesis optimisation and efficiency enhancement in Eu^{3+} doped barium molybdenum titanate phosphors for w-LED applications, *Mater. Res. Bull.* 150 (2022) 111753. <https://doi.org/10.1016/j.materresbull.2022.111753>.
- [28] Anu, A.S. Rao, Novel orange-red-emitting $\text{Li}_2\text{Ba}_5(\text{WO}_5)_3:\text{Eu}^{3+}$ phosphor for w-LEDs and non-contact thermometry applications, *J. Mater. Sci. Mater. Electron.* 34 (2023). <https://doi.org/10.1007/s10854-023-11602-4>.
- [29] Anu, Seema, A. Kumar, N. Deopa, M.K. Sahu, A. Prasad, A.S. Rao, A single phase $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphor for color tunable devices and non-contact optical thermometry, *J. Lumin.* 269 (2024) 120444. <https://doi.org/10.1016/j.jlumin.2024.120444>.
- [30] Anu, A. Kumar, Ravina, N. Deopa, A.S. Rao, Efficient tunable photoluminescence of $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped OFSZBS glasses for warm white LEDs, *J. Non. Cryst. Solids.* 616 (2023) 122421. <https://doi.org/10.1016/j.jnoncrsol.2023.122421>.
- [31] H. Yu, D. Deng, D. Zhou, W. Yuan, Q. Zhao, Y. Hua, S. Zhao, L. Huang, S. Xu, $\text{Ba}_2\text{Ca}(\text{PO}_4)_2:\text{Eu}^{2+}$ emission-tunable phosphor for solid-state lighting: luminescent properties and application as white light emitting diodes, *J. Mater. Chem. C.* 1 (2013) 5577. <https://doi.org/10.1039/c3tc30998c>.
- [32] Y. Chang, C. Liang, S. Yan, Y. Chang, Synthesis and Photoluminescence Characteristics of High Color Purity and Brightness, 3 (2010) 3645–3652.
- [33] Anu, N. Deopa, A.S. Rao, Structural and luminescence characteristics of thermally stable Dy^{3+} doped oxyfluoride strontium zinc borosilicate glasses for photonic device applications, *Opt. Laser Technol.* 154 (2022) 108328. <https://doi.org/10.1016/j.optlastec.2022.108328>.

- [34] V. Uma, K. Maheshvaran, K. Marimuthu, G. Muralidharan, Structural and optical investigations on Dy^{3+} doped lithium tellurofluoroborate glasses for white light applications, *J. Lumin.* 176 (2016) 15–24. <https://doi.org/10.1016/j.jlumin.2016.03.016>.
- [35] M. Dhanalakshmi, R.B. Basavaraj, G.P. Darshan, S.C. Sharma, H. Nagabhushana, Pivotal role of fluxes in $\text{BaTiO}_3:\text{Eu}^{3+}$ nano probes for visualization of latent fingerprints on multifaceted substrates and anti-counterfeiting applications, *Microchem. J.* 145 (2019) 226–234. <https://doi.org/10.1016/j.microc.2018.10.020>.
- [36] H. Wu, Z. Sun, S. Gan, L. Li, Effects of alkali metal as charge compensator on the luminescence properties of $\text{ZnWO}_4:\text{Eu}^{3+}$ phosphors synthesized by solid-state reaction, *J. Photochem. Photobiol. A Chem.* 368 (2019) 258–262. <https://doi.org/10.1016/j.jphotochem.2018.09.048>.
- [37] C. Ronda, Challenges in application of luminescent materials, a tutorial overview (Invited Review), *Prog. Electromagn. Res.* 147 (2014) 81–93. <https://doi.org/10.2528/PIER14051103>.
- [38] Anu, A.S. Rao, Luminescence and optical thermometry strategy based on emission spectra of $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Pr}^{3+}$ phosphors, *Opt. Mater. (Amst)*. 145 (2023) 114476. <https://doi.org/10.1016/j.optmat.2023.114476>.
- [39] K. Siva Rama Krishna Reddy, K. Swapna, S. Mahamuda, M. Venkateswarlu, A.S. Rao, G. Vijaya Prakash, Investigation on structural and luminescence features of Dy^{3+} ions doped alkaline-earth boro tellurite glasses for optoelectronic devices, *Opt. Mater. (Amst)*. 85 (2018) 200–210. <https://doi.org/10.1016/j.optmat.2018.08.057>.
- [40] H. Xu, Q. Sun, Z. An, Y. Wei, X. Liu, Electroluminescence from europium(III) complexes, *Coord. Chem. Rev.* 293–294 (2015) 228–249. <https://doi.org/10.1016/j.ccr.2015.02.018>.
- [41] Z.-H. Ju, R.-P. Wei, J.-X. Ma, C.-R. Pang, W.-S. Liu, A novel orange emissive phosphor $\text{SrWO}_4:\text{Sm}^{3+}$ for white light-emitting diodes, *J. Alloys Compd.* 507 (2010) 133–136. <https://doi.org/10.1016/j.jallcom.2010.07.138>.
- [42] Anu, A.S. Rao, Synthesis, Structural and Fluorescence Investigations of Novel- $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Sm}^{3+}$ Phosphors for Photonic Device Applications, *J. Fluoresc.* (2023). <https://doi.org/10.1007/s10895-023-03449-z>.
- [43] J. Zhong, D. Chen, Y. Peng, Y. Lu, X. Chen, X. Li, Z. Ji, A review on nanostructured glass ceramics for promising application in optical thermometry, *J. Alloys Compd.* 763 (2018) 34–48. <https://doi.org/10.1016/j.jallcom.2018.05.348>.
- [44] X. Wang, Q. Liu, Y. Bu, C.-S. Liu, T. Liu, X. Yan, Optical temperature sensing of rare-earth ion doped phosphors, *RSC Adv.* 5 (2015) 86219–86236. <https://doi.org/10.1039/C5RA16986K>.
- [45] A. Nexha, J.J. Carvajal, M.C. Pujol, F. Díaz, M. Aguiló, Lanthanide doped luminescence nanothermometers in the biological windows: strategies and applications, *Nanoscale*. 13 (2021) 7913–7987. <https://doi.org/10.1039/D0NR09150B>.
- [46] C.D.S. Brites, P.P. Lima, N.J.O. Silva, A. Millán, V.S. Amaral, F. Palacio, L.D. Carlos, Lanthanide-based luminescent molecular thermometers, *New J. Chem.* 35 (2011) 1177. <https://doi.org/10.1039/c0nj01010c>.
- [47] C.D.S. Brites, S. Balabhadra, L.D. Carlos, Lanthanide-Based Thermometers: At the Cutting-Edge of Luminescence Thermometry, *Adv. Opt. Mater.* 7 (2019). <https://doi.org/10.1002/adom.201801239>.
- [48] Y. Zhao, X. Wang, Y. Zhang, Y. Li, X. Yao, Optical temperature sensing of up-conversion luminescent materials: Fundamentals and progress, *J. Alloys Compd.* 817 (2020) 152691. <https://doi.org/10.1016/j.jallcom.2019.152691>.
- [49] S.A. Wade, S.F. Collins, G.W. Baxter, Fluorescence intensity ratio technique for optical fiber point temperature sensing, *J. Appl. Phys.* 94 (2003) 4743–4756. <https://doi.org/10.1063/1.1606526>.

-
- [50] A.A. Ansari, A.K. Parchur, M.K. Nazeeruddin, M.M. Tavakoli, Luminescent lanthanide nanocomposites in thermometry: Chemistry of dopant ions and host matrices, *Coord. Chem. Rev.* 444 (2021) 214040. <https://doi.org/10.1016/j.ccr.2021.214040>.
- [51] S.F. Collins, G.W. Baxter, S.A. Wade, T. Sun, K.T. V. Grattan, Z.Y. Zhang, A.W. Palmer, Comparison of fluorescence-based temperature sensor schemes: Theoretical analysis and experimental validation, *J. Appl. Phys.* 84 (1998) 4649–4654. <https://doi.org/10.1063/1.368705>.
- [52] C.D.S. Brites, P.P. Lima, N.J.O. Silva, A. Millán, V.S. Amaral, F. Palacio, L.D. Carlos, Thermometry at the nanoscale, *Nanoscale*. 4 (2012) 4799. <https://doi.org/10.1039/c2nr30663h>.
- [53] M.D. Dramićanin, Sensing temperature via downshifting emissions of lanthanide-doped metal oxides and salts. A review, *Methods Appl. Fluoresc.* 4 (2016) 042001. <https://doi.org/10.1088/2050-6120/4/4/042001>.
- [54] S.N. Baker, T.M. McCleskey, G.A. Baker, An Ionic Liquid-Based Optical Thermometer, in: 2005: pp. 171–181. <https://doi.org/10.1021/bk-2005-0902.ch014>.
- [55] C.D.S. Brites, A. Millán, L.D. Carlos, Lanthanides in Luminescent Thermometry, in: 2016: pp. 339–427. <https://doi.org/10.1016/bs.hpcr.2016.03.005>.
- [56] J.W. Bartlett, C. Frost, Reliability, repeatability and reproducibility: Analysis of measurement errors in continuous variables, *Ultrasound Obstet. Gynecol.* 31 (2008) 466–475. <https://doi.org/10.1002/uog.5256>.
- [57] M. Haase, H. Schäfer, Upconverting Nanoparticles, *Angew. Chemie Int. Ed.* 50 (2011) 5808–5829. <https://doi.org/10.1002/anie.201005159>.
- [58] E.F. Schubert, J.K. Kim, H. Luo, J.-Q. Xi, Solid-state lighting-a benevolent technology, *Reports Prog. Phys.* 69 (2006) 3069–3099. <https://doi.org/10.1088/0034-4885/69/12/R01>.
- [59] M. Cao, Y. Xu, P. Li, Q. Zhong, D. Yang, Q. Zhang, Recent advances and perspectives on light emitting diodes fabricated from halide metal perovskite nanocrystals, *J. Mater. Chem. C*. 7 (2019) 14412–14440. <https://doi.org/10.1039/C9TC03978C>.
- [60] M. Loi, A. Villani, F. Paciolla, G. Mulè, C. Paciolla, Challenges and Opportunities of Light-Emitting Diode (LED) as Key to Modulate Antioxidant Compounds in Plants. A Review, *Antioxidants*. 10 (2020) 42. <https://doi.org/10.3390/antiox10010042>.
- [61] T.H. Kim, W. Wang, Q. Li, Advancement in materials for energy-saving lighting devices, *Front. Chem. Sci. Eng.* 6 (2012) 13–26. <https://doi.org/10.1007/s11705-011-1168-y>.
- [62] A.G. Bispo-Jr, L.F. Saraiva, S.A.M. Lima, A.M. Pires, M.R. Davolos, Recent prospects on phosphor-converted LEDs for lighting, displays, phototherapy, and indoor farming, *J. Lumin.* 237 (2021) 118167. <https://doi.org/10.1016/j.jlumin.2021.118167>.
- [63] C.C. Lin, A. Meijerink, R.-S. Liu, Critical Red Components for Next-Generation White LEDs, *J. Phys. Chem. Lett.* 7 (2016) 495–503. <https://doi.org/10.1021/acs.jpcllett.5b02433>.
- [64] J. Cho, J.H. Park, J.K. Kim, E.F. Schubert, White light-emitting diodes: History, progress, and future, *Laser Photon. Rev.* 11 (2017). <https://doi.org/10.1002/lpor.201600147>.
- [65] S. Liu, J. Cui, J. Jia, J. Fu, W. You, Q. Zeng, Y. Yang, X. Ye, High sensitive $\text{Ln}^{3+}/\text{Tm}^{3+}/\text{Yb}^{3+}$ ($\text{Ln}^{3+} = \text{Ho}^{3+}, \text{Er}^{3+}$) tri-doped $\text{Ba}_3\text{Y}_4\text{O}_9$ upconverting optical thermometric materials based on diverse thermal response from non-thermally coupled energy levels, *Ceram. Int.* 45 (2019) 1–10. <https://doi.org/10.1016/j.ceramint.2018.09.162>.
- [66] X. Li, J. Cao, Y. Wei, Z. Yang, H. Guo, Optical Thermometry Based on Up-Conversion Luminescence Behavior of Er^{3+} -Doped Transparent Sr_2YbF_7 Glass-Ceramics, *J. Am. Ceram. Soc.* 98 (2015) 3824–3830. <https://doi.org/10.1111/jace.13804>.

- [67] J. Cao, X. Li, Z. Wang, Y. Wei, L. Chen, H. Guo, Optical thermometry based on up-conversion luminescence behavior of self-crystallized $\text{K}_3\text{YF}_6:\text{Er}^{3+}$ glass ceramics, *Sensors Actuators B Chem.* 224 (2016) 507–513. <https://doi.org/10.1016/j.snb.2015.10.087>.
- [68] I.E. Kolesnikov, E.V. Golyeva, M.A. Kurochkin, E. Lähderanta, M.D. Mikhailov, Nd^{3+} -doped YVO_4 nanoparticles for luminescence nanothermometry in the first and second biological windows, *Sensors Actuators B Chem.* 235 (2016) 287–293. <https://doi.org/10.1016/j.snb.2016.05.095>.
- [69] A.F. Silva, F. Elan, E.L. Falcão-Filho, L.J.Q. Maia, C.B. de Araújo, Thermal sensitivity of frequency upconversion in $\text{Al}_4\text{B}_2\text{O}_9:\text{Yb}^{3+}/\text{Nd}^{3+}$ nanoparticles, *J. Mater. Chem. C* 5 (2017) 1240–1246. <https://doi.org/10.1039/C6TC04630D>.
- [70] W. Ran, H.M. Noh, S.H. Park, B.R. Lee, J.H. Kim, J.H. Jeong, J. Shi, Er^{3+} -Activated NaLaMgWO_6 double perovskite phosphors and their bifunctional application in solid-state lighting and non-contact optical thermometry, *Dalt. Trans.* 48 (2019) 4405–4412. <https://doi.org/10.1039/C9DT00315K>.
- [71] H. Zhou, N. An, K. Zhu, J. Qiu, L. Yue, L.-G. Wang, L. Ye, Optical temperature sensing properties of $\text{Tm}^{3+}/\text{Yb}^{3+}$ co-doped LuAG polycrystalline phosphor based on up-conversion luminescence, *J. Lumin.* 229 (2021) 117656. <https://doi.org/10.1016/j.jlumin.2020.117656>.
- [72] A. Pandey, V.K. Rai, V. Kumar, V. Kumar, H.C. Swart, Upconversion based temperature sensing ability of $\text{Er}^{3+}-\text{Yb}^{3+}$ codoped SrWO_4 : An optical heating phosphor, *Sensors Actuators B Chem.* 209 (2015) 352–358. <https://doi.org/10.1016/j.snb.2014.11.126>.
- [73] X. Tian, S. Lian, C. Ji, Z. Huang, J. Wen, Z. Chen, H. Peng, S. Wang, J. Li, J. Hu, Y. Peng, Enhanced photoluminescence and ultrahigh temperature sensitivity from NaF flux assisted $\text{CaTiO}_3:\text{Pr}^{3+}$ red emitting phosphor, *J. Alloys Compd.* 784 (2019) 628–640. <https://doi.org/10.1016/j.jallcom.2019.01.087>.
- [74] H. Liu, H. Liang, W. Zhang, Q. Zeng, D. Wen, Improving the thermal stability and luminescent efficiency of $(\text{Ba},\text{Sr})_3\text{SiO}_5:\text{Eu}^{2+}$ phosphors by structure, bandgap engineering and soft chemistry synthesis method, *Chem. Eng. J.* 410 (2021) 128367. <https://doi.org/10.1016/j.cej.2020.128367>.
- [75] Q. Cheng, F. Ren, Q. Lin, H. Tong, X. Miao, High quantum efficiency red emitting α -phase $\text{La}_2\text{W}_2\text{O}_9:\text{Eu}^{3+}$ phosphor, *J. Alloys Compd.* 772 (2019) 905–911. <https://doi.org/10.1016/j.jallcom.2018.08.320>.
- [76] Y. Zheng, Z. Wang, D. Yang, Z. Fang, Y. Xiang, T. Yang, S. Yang, Y. Mao, K. Xiong, J. Zhu, Highly thermostable white-emitting $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7:\text{Ce}^{3+}, \text{Dy}^{3+}$ single-phase phosphor with tunable photoluminescence and energy transfer, *Dalt. Trans.* 51 (2022) 2770–2781. <https://doi.org/10.1039/D1DT04124J>.
- [77] J. Liao, B. Qiu, H. Lai, Synthesis and luminescence properties of $\text{Tb}^{3+}:\text{NaGd}(\text{WO}_4)_2$ novel green phosphors, *J. Lumin.* 129 (2009) 668–671. <https://doi.org/10.1016/j.jlumin.2009.01.016>.
- [78] S.A. Yan, Y.S. Chang, J.W. Wang, W.S. Hwang, Y.H. Chang, Synthesis and luminescence properties of color-tunable $\text{Ba}_{1-y}\text{Sr}_y\text{La}_{4-x}\text{Tb}_x(\text{WO}_4)_7$ ($x = 0.02-1.2$, $y = 0-0.4$) phosphors, *Mater. Res. Bull.* 46 (2011) 1231–1236. <https://doi.org/10.1016/j.materresbull.2011.04.010>.
- [79] H. Zhu, C. Liang, W. Huang, Crystal structure and luminescent properties of Li^+ ions doped double tungstate $\text{KEu}(\text{WO}_4)_2$ red emitting phosphors, *Phys. B Condens. Matter.* 582 (2020) 411999. <https://doi.org/10.1016/j.physb.2020.411999>.
- [80] Y. Liu, Y. Wang, L. Wang, Y.-Y. Gu, S.-H. Yu, Z.-G. Lu, R. Sun, General synthesis of $\text{LiLn}(\text{MO}_4)_2:\text{Eu}^{3+}$ ($\text{Ln} = \text{La}, \text{Eu}, \text{Gd}, \text{Y}$; $\text{M} = \text{W}, \text{Mo}$) nanophosphors for near UV-type LEDs, *RSC Adv.* 4 (2014) 4754–4762. <https://doi.org/10.1039/C3RA46224B>.
- [81] B.S. Barros, A.C. de Lima, Z.R. da Silva, D.M.A. Melo, S. Alves-Jr, Synthesis and photoluminescent behavior of Eu^{3+} -doped alkaline-earth tungstates, *J. Phys. Chem. Solids.* 73 (2012) 635–640. <https://doi.org/10.1016/j.jpcs.2011.12.026>.

-
- [82] J.S. Thorp, E.A.E. Ammar, Spin-lattice relaxation in gadolinium-doped calcium tungstate, *J. Mater. Sci.* 11 (1976) 1215–1219. <https://doi.org/10.1007/BF00545138>.
- [83] R. Vajtai, ed., *Springer Handbook of Nanomaterials*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2013. <https://doi.org/10.1007/978-3-642-20595-8>.
- [84] M.S.H. Akash, K. Rehman, *Essentials of Pharmaceutical Analysis*, Springer Nature Singapore, Singapore, 2020. <https://doi.org/10.1007/978-981-15-1547-7>.
- [85] A.W. Coats, J.P. Redfern, Thermogravimetric analysis. A review, *Analyst.* 88 (1963) 906. <https://doi.org/10.1039/an9638800906>.
- [86] M. Shiraishi, M. Inagaki, X-ray Diffraction Methods to Study Crystallite Size and Lattice Constants of Carbon Materials, in: *Carbon Alloy.*, Elsevier, 2003: pp. 161–173. <https://doi.org/10.1016/B978-008044163-4/50010-3>.
- [87] J. Martin, M. Beauparlant, J. Lesage, H. Van Tra, Development of a quantification method for quartz in various bulk materials by X-ray diffraction and the Rietveld method, *Powder Diffr.* 27 (2012) 12–19. <https://doi.org/10.1017/S0885715612000036>.
- [88] Y.R. Parauha, D.K. Halwar, S.J. Dhoble, Photoluminescence properties of Eu^{3+} -doped $\text{Na}_2\text{CaSiO}_4$ phosphor prepared by wet-chemical synthesis route, *Displays.* 75 (2022) 102304. <https://doi.org/10.1016/j.displa.2022.102304>.
- [89] L. Henriksen, Electron diffraction, *Radiat. Eff.* 11 (1971) 59–59. <https://doi.org/10.1080/00337577108230469>.
- [90] A. Popelka, S. Zavahir, S. Habib, Morphology analysis, in: *Polym. Sci. Innov. Appl.*, Elsevier, 2020: pp. 21–68. <https://doi.org/10.1016/B978-0-12-816808-0.00002-0>.
- [91] L. Kumari, W.Z. Li, C.H. Vannoy, R.M. Leblanc, D.Z. Wang, Zinc oxide micro- and nanoparticles: Synthesis, structure and optical properties, *Mater. Res. Bull.* 45 (2010) 190–196. <https://doi.org/10.1016/j.materresbull.2009.09.021>.
- [92] A. Escobedo-Morales, I.I. Ruiz-López, M. deL. Ruiz-Peralta, L. Tepech-Carrillo, M. Sánchez-Cantú, J.E. Moreno-Orea, Automated method for the determination of the band gap energy of pure and mixed powder samples using diffuse reflectance spectroscopy, *Heliyon.* 5 (2019) e01505. <https://doi.org/10.1016/j.heliyon.2019.e01505>.
- [93] C. Cao, S. Wei, Y. Zhu, T. Liu, A. Xie, H.M. Noh, J.H. Jeong, Synthesis, optical properties, and packaging of Dy^{3+} doped Y_2WO_6 , $\text{Y}_2\text{W}_3\text{O}_{12}$, and Y_6WO_{12} phosphors, *Mater. Res. Bull.* 126 (2020) 110846. <https://doi.org/10.1016/j.materresbull.2020.110846>.
- [94] Z. Xia, Y. Zhang, M.S. Molokeev, V. V. Atuchin, Structural and Luminescence Properties of Yellow-Emitting $\text{NaScSi}_2\text{O}_6:\text{Eu}^{2+}$ Phosphors: Eu^{2+} Site Preference Analysis and Generation of Red Emission by Codoping Mn^{2+} for White-Light-Emitting Diode Applications, *J. Phys. Chem. C.* 117 (2013) 20847–20854. <https://doi.org/10.1021/jp4062225>.
- [95] S. Shionoya, Photoluminescence, in: *Lumin. Solids*, Springer US, Boston, MA, 1998: pp. 95–133. https://doi.org/10.1007/978-1-4615-5361-8_3.
- [96] K. Wakabayashi, Y. Yamaguchi, T. Sekiya, S. Kurita, Time-resolved luminescence spectra in colorless anatase TiO_2 single crystal, *J. Lumin.* 112 (2005) 50–53. <https://doi.org/10.1016/j.jlumin.2004.09.080>.
- [97] K. Li, X. Liu, Y. Zhang, X. Li, H. Lian, J. Lin, Host-Sensitized Luminescence Properties in $\text{CaNb}_2\text{O}_6:\text{Ln}^{3+}$ ($\text{Ln}^{3+} = \text{Eu}^{3+}/\text{Tb}^{3+}/\text{Dy}^{3+}/\text{Sm}^{3+}$) Phosphors with Abundant Colors, (2015).
- [98] J. Sun, X. Zhang, Z. Xia, H. Du, Synthesis and luminescence properties of novel $\text{LiSrPO}_4:\text{Dy}^{3+}$ phosphor, *Mater. Res. Bull.* 46 (2011) 2179–2182. <https://doi.org/10.1016/j.materresbull.2011.07.033>.
- [99] R. Lohan, A. Kumar, M.K. Sahu, A. Mor, V. Kumar, N. Deopa, A.S. Rao, Structural, thermal, and luminescence kinetics of $\text{Sr}_4\text{Nb}_2\text{O}_9$ phosphor doped with Dy^{3+} ions for cool w-LED applications, *J. Mater. Sci. Mater. Electron.* 34 (2023). <https://doi.org/10.1007/s10854-023-10055-z>.

- [100] Ravita, A.S. Rao, Effective sensitization of Eu^{3+} visible red emission by Sm^{3+} in thermally stable potassium zinc alumino borosilicate glasses for photonic device applications, *J. Lumin.* 244 (2022) 118689. <https://doi.org/10.1016/j.jlumin.2021.118689>.
- [101] Y. Zhang, D. Geng, X. Li, J. Fan, K. Li, H. Lian, M. Shang, J. Lin, Wide-Band Excited $\text{YTiTaO}_6 : \text{Eu}^{3+}/\text{Er}^{3+}$ Phosphors: Structure Refinement, Luminescence Properties, and Energy Transfer Mechanisms, *J. Phys. Chem. C*. 118 (2014) 17983–17991. <https://doi.org/10.1021/jp504437f>.
- [102] C. Zhang, J. Lin, Defect-related luminescent materials: synthesis, emission properties and applications, *Chem. Soc. Rev.* 41 (2012) 7938. <https://doi.org/10.1039/c2cs35215j>.
- [103] P. Dhankhar, R. Devi, S. Devi, S. Chahar, M. Dalal, V.B. Taxak, S.P. Khatkar, P. Boora, Synthesis and photoluminescent performance of novel europium (III) carboxylates with heterocyclic ancillary ligands, *Rare Met.* 41 (2022) 1342–1352. <https://doi.org/10.1007/s12598-019-01261-y>.
- [104] S. Hau, G. Stanciu, D. Avram, L. Gheorghe, C. Gheorghe, Energy transfer and luminescent properties of Tb^{3+} and Tb^{3+} , Yb^{3+} doped CNGG phosphors, *J. Rare Earths*. 40 (2022) 1445–1453. <https://doi.org/10.1016/j.jre.2021.09.008>.
- [105] Y.-H. Ma, X. Gao, W.-T. Zhang, Z.-R. Yang, Z. Zhao, C. Qu, Enhanced red luminescence of $\text{Ca}_3\text{Si}_{2-x}\text{M}_x\text{O}_7:\text{Eu}^{3+}$ ($\text{M} = \text{Al}, \text{P}$) phosphors via partial substitution of Si^{4+} for applications in white light-emitting diodes, *Rare Met.* 43 (2024) 736–748. <https://doi.org/10.1007/s12598-023-02334-9>.
- [106] Z. Feng, L. Lin, Z. Wang, Z. Zheng, Highly efficient and wide range low temperature sensing of upconversion luminescence of $\text{NaYF}_4:\text{Er}^{3+}$ nanoparticles: Effects of concentration of active or sensitive ions, excitation power and particle size on temperature sensing sensitivity, *Opt. Commun.* 491 (2021) 126942. <https://doi.org/10.1016/j.optcom.2021.126942>.
- [107] B. Hou, M. Jia, P. Li, G. Liu, Z. Sun, Z. Fu, Multifunctional Optical Thermometry Based on the Rare-Earth-Ions-Doped Up-/Down-Conversion $\text{Ba}_2\text{TiGe}_2\text{O}_8:\text{Ln}$ ($\text{Ln} = \text{Eu}^{3+}/\text{Er}^{3+}/\text{Ho}^{3+}/\text{Yb}^{3+}$) Phosphors, *Inorg. Chem.* 58 (2019) 7939–7946. <https://doi.org/10.1021/acs.inorgchem.9b00646>.
- [108] X. Wang, O.S. Wolfbeis, R.J. Meier, Luminescent probes and sensors for temperature, *Chem. Soc. Rev.* 42 (2013) 7834. <https://doi.org/10.1039/c3cs60102a>.
- [109] S.W. Allison, G.T. Gillies, Remote thermometry with thermographic phosphors: Instrumentation and applications, *Rev. Sci. Instrum.* 68 (1997) 2615–2650. <https://doi.org/10.1063/1.1148174>.
- [110] W. Xu, Y. Hu, L. Zheng, Z. Zhang, W. Cao, H. Liu, X. Wu, Enhanced NIR-NIR luminescence from $\text{CaWO}_4:\text{Nd}^{3+}/\text{Yb}^{3+}$ phosphors by Li^{+} codoping for thermometry and optical heating, *J. Lumin.* 208 (2019) 415–423. <https://doi.org/10.1016/j.jlumin.2019.01.005>.
- [111] D. Chen, Z. Wan, Y. Zhou, X. Zhou, Y. Yu, J. Zhong, M. Ding, Z. Ji, Dual-Phase Glass Ceramic: Structure, Dual-Modal Luminescence, and Temperature Sensing Behaviors, *ACS Appl. Mater. Interfaces*. 7 (2015) 19484–19493. <https://doi.org/10.1021/acsami.5b06036>.
- [112] R. Ao, L. Xing, W. Yang, A high-brightness phosphor based on $\text{Yb}^{3+}/\text{Er}^{3+}$ codoped Y_2O_3 micro-crystals and controllable temperature sensing sensitivity via rare earth ions, *Opt. Commun.* 492 (2021) 126967. <https://doi.org/10.1016/j.optcom.2021.126967>.
- [113] Q. Liu, M. Wu, B. Chen, X. Huang, M. Liu, Y. Liu, K. Su, X. Min, R. Mi, Z. Huang, Optical thermometry based on fluorescence intensity ratio of Dy^{3+} -Doped oxysilicate apatite warm white phosphor, *Ceram. Int.* 49 (2023) 4971–4978. <https://doi.org/10.1016/j.ceramint.2022.10.012>.
- [114] S. Zhou, S. Jiang, X. Wei, Y. Chen, C. Duan, M. Yin, Optical thermometry based on upconversion luminescence in $\text{Yb}^{3+}/\text{Ho}^{3+}$ co-doped NaLuF_4 , *J. Alloys Compd.* 588 (2014) 654–657. <https://doi.org/10.1016/j.jallcom.2013.11.132>.
- [115] M. Que, Z. Ci, Y. Wang, G. Zhu, Y. Shi, S. Xin, Synthesis and luminescent properties of $\text{Ca}_2\text{La}_8(\text{GeO}_4)_6\text{O}_2:\text{RE}^{3+}$ ($\text{RE}^{3+} = \text{Eu}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Sm}^{3+}, \text{Tm}^{3+}$) phosphors, *J. Lumin.* 144 (2013) 64–68. <https://doi.org/10.1016/j.jlumin.2013.06.052>.

-
- [116] Y. Yang, H. Pan, L. Guan, D. Wang, J. Zhao, J. Yang, Z. Yang, X. Li, Electronic structure and luminescent properties of $\text{Sr}_3\text{Al}_2\text{O}_6\text{:Sm}^{3+}$ orange phosphor prepared by hydrothermal method, *J. Mater. Res. Technol.* 9 (2020) 3847–3855. <https://doi.org/10.1016/j.jmrt.2020.02.011>.
- [117] J. Zhang, L. Mei, Y. Zhang, Q. Guo, L. Liao, H. Liu, Influence of dysprosium concentration on sensitivity of luminescent thermometers of phosphors $\text{Ca}_9\text{Tb}(\text{PO}_4)_5(\text{SiO}_4)\text{F}_2$, *J. Rare Earths.* 39 (2021) 946–951. <https://doi.org/10.1016/j.jre.2020.08.013>.
- [118] V. V. Bakovets, I. V. Yushina, O. V. Antonova, E.S. Zolotova, Bandgap-width correction for luminophores CaMoO_4 and CaWO_4 , *Opt. Spectrosc.* 123 (2017) 399–403. <https://doi.org/10.1134/S0030400X17090053>.
- [119] M. Türemiş, İ.Ç. Keskin, M.İ. Katı, A. Çetin, K. Ay, R. Kibar, Comprehensive study on structural, thermal, morphological and luminescence (RL, PL, TL) properties of $\text{CaLa}_2(\text{WO}_4)_4\text{: Tb}^{3+}, \text{Dy}^{3+}$ phosphors synthesized via sol-gel method, *Ceram. Int.* 47 (2021) 25708–25720. <https://doi.org/10.1016/j.ceramint.2021.05.297>.
- [120] J. Zhang, Y. Wang, Z. Zhai, G. Chen, Investigations on morphology, photoluminescence and cathodoluminescence of SrWO_4 and $\text{SrWO}_4\text{: Tb}^{3+}$, 38 (2014) 126–130. <https://doi.org/10.1016/j.optmat.2014.10.013>.
- [121] H. Xu, D. Ying, A. Lu, X. Wang, J. Hu, Surfactant-assistant solvothermal synthesis of $\text{CaWO}_4\text{:Eu}^{3+}$ phosphors and luminescence, *Superlattices Microstruct.* 83 (2015) 668–675. <https://doi.org/10.1016/j.spmi.2015.04.011>.
- [122] Y. Tian, Y. Liu, R. Hua, L. Na, B. Chen, Synthesis and luminescent properties of spindle-like $\text{CaWO}_4\text{: Sm}^{3+}$ phosphors, *Mater. Res. Bull.* 47 (2012) 59–62. <https://doi.org/10.1016/j.materresbull.2011.10.007>.
- [123] S. Jana, A. Mondal, J. Manam, S. Das, Pr^{3+} doped BaNb_2O_6 reddish orange emitting phosphor for solid state lighting and optical thermometry applications, *J. Alloys Compd.* 821 (2020) 153342. <https://doi.org/10.1016/j.jallcom.2019.153342>.
- [124] V. Sharma, S. Maurya, Anu, A. Prasad, A.S. Rao, Structural, Optical and Luminescent Properties of Dy^{3+} activated KCS phosphor for white light emitting diodes, *Luminescence.* (2023). <https://doi.org/10.1002/bio.4544>.
- [125] C. Kumari, A. Kumar, S.K. Sharma, J. Manam, $\text{Sr}_3\text{LiSbO}_6\text{: Er}^{3+}$ phosphors for green LEDs and solar cell applications, *Vacuum.* 207 (2023) 111599. <https://doi.org/10.1016/j.vacuum.2022.111599>.
- [126] H. Huang, L. Liu, N. Tian, Y. Zhang, Structure, optical properties, and magnetism of $\text{Zn}_{1-x}\text{Ni}_x\text{WO}_4$ ($0 \leq x \leq 1$) solid solution, *J. Alloys Compd.* 637 (2015) 471–475. <https://doi.org/10.1016/j.jallcom.2015.02.224>.
- [127] Y. Xiang, Y. Zheng, L. Yang, M. Li, Y. Mao, J. Zhu, Exploring a new Dy^{3+} -activated borotellurate phosphor with thermally stable photoluminescence, *J. Alloys Compd.* 919 (2022) 165837. <https://doi.org/10.1016/j.jallcom.2022.165837>.
- [128] Y. Che, Y. Zheng, D. Yang, Z. Fang, C. Li, J. Zhu, Investigation into the surface chemical analysis and luminescent properties of $\text{La}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2\text{:Dy}$ phosphor, *Ceram. Int.* 46 (2020) 8483–8489. <https://doi.org/10.1016/j.ceramint.2019.11.243>.
- [129] V. V. Shanbhag, S.C. Prashantha, T.R.S. Shekhar, H. Nagabhushana, R. Naik, K.M. Girish, S. Ashwini, D. Rangappa, D.S. Prasanna, Enhanced photoluminescence of SiO_2 coated $\text{CaTiO}_3\text{:Dy}^{3+}, \text{Li}^+$ nanophosphors for white light emitting diodes, *Ceram. Int.* 47 (2021) 10346–10354. <https://doi.org/10.1016/j.ceramint.2020.11.077>.
- [130] N. Deopa, M.K. Sahu, P.R. Rani, R. Punia, A.S. Rao, Realization of warm white light and energy transfer studies of $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped $\text{Li}_2\text{O-PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses for lighting applications, *J. Lumin.* 222 (2020) 117166. <https://doi.org/10.1016/j.jlumin.2020.117166>.

- [131] W.T. Carnall, P.R. Fields, K. Rajnak, Electronic Energy Levels of the Trivalent Lanthanide Aquo Ions. III. Tb^{3+} , *J. Chem. Phys.* 49 (1968) 4447–4449. <https://doi.org/10.1063/1.1669895>.
- [132] S. Kaur, A.S. Rao, M. Jayasimhadri, Color tunability and energy transfer studies of $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped calcium aluminosilicate phosphor for lighting applications, *Mater. Res. Bull.* 116 (2019) 79–88. <https://doi.org/10.1016/j.materresbull.2019.04.022>.
- [133] G.H. Dieke, H.M. Crosswhite, Absorption Spectrum and Magnetic Properties of Ytterbium Chloride*, *J. Opt. Soc. Am.* 46 (1956) 885. <https://doi.org/10.1364/JOSA.46.000885>.
- [134] L.G. Van Uitert, J.E. Soc, I.G. Van Uitert, Characterization of Energy Transfer Interactions between Rare Earth Ions Characterization of Energy Transfer Interactions between Rare Earth Ions, 114 (1967) 1048–1053. <https://doi.org/10.1149/1.2424184>.
- [135] S. Dutta, S. Som, S.K. Sharma, Luminescence and photometric characterization of K^{+} compensated $\text{CaMoO}_4:\text{Dy}^{3+}$ nanophosphors, *Dalt. Trans.* 42 (2013) 9654. <https://doi.org/10.1039/c3dt50780g>.
- [136] N. Deopa, S. Kaur, A. Prasad, B. Joshi, A.S. Rao, Spectral studies of Eu^{3+} doped lithium lead alumino borate glasses for visible photonic applications, *Opt. Laser Technol.* 108 (2018) 434–440. <https://doi.org/10.1016/j.optlastec.2018.07.010>.
- [137] S. Čulubrk, V. Lojpur, S.P. Ahrenkiel, J.M. Nedeljković, M.D. Dramićanin, Non-contact thermometry with Dy^{3+} doped $\text{Gd}_2\text{Ti}_2\text{O}_7$ nano-powders, *J. Lumin.* 170 (2016) 395–400. <https://doi.org/10.1016/j.jlumin.2015.06.006>.
- [138] W.B. Dai, K. Huang, H. Li, Y.M. Fan, Y. Chen, M. Xu, Study on the structure and optical properties of phosphor $\text{Ca}_3\text{La}_3(\text{BO}_3)_5:\text{Dy}^{3+}$ for potential application in temperature sensing, *J. Lumin.* 227 (2020) 117529. <https://doi.org/10.1016/j.jlumin.2020.117529>.
- [139] J. Komar, R. Lisiecki, M. Głowacki, M. Berkowski, M. Suszyńska, W. Ryba-Romanowski, Spectroscopic properties of Dy^{3+} ions in $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ single crystal, *J. Lumin.* 220 (2020) 116989. <https://doi.org/10.1016/j.jlumin.2019.116989>.
- [140] E. Hertle, L. Chepyga, M. Batentschuk, S. Will, L. Zigan, Temperature-dependent luminescence characteristics of Dy^{3+} doped in various crystalline hosts, *J. Lumin.* 204 (2018) 64–74. <https://doi.org/10.1016/j.jlumin.2018.07.032>.
- [141] M.G. Nikolić, D.J. Jovanović, M.D. Dramićanin, Temperature dependence of emission and lifetime in Eu^{3+} - and Dy^{3+} -doped GdVO_4 , *Appl. Opt.* 52 (2013) 1716. <https://doi.org/10.1364/AO.52.001716>.
- [142] M.T. Abbas, S.A. Khan, J. Mao, N.Z. Khan, L. Qiu, J. Ahmed, X. Wei, Y. Chen, S.M. Alshehri, S. Agathopoulos, Optical thermometry based on the luminescence intensity ratio of Dy^{3+} -doped GdPO_4 phosphors, *J. Therm. Anal. Calorim.* 147 (2022) 11769–11775. <https://doi.org/10.1007/s10973-022-11415-3>.
- [143] Z. Liao, B. Cao, L. Li, Y. Cong, Y. He, B. Dong, Exploring the excitation spectrum behavior of Dy in CaWO_4 for a new excited-state-based ratiometric thermometry, *Appl. Mater. Today.* 31 (2023) 101765. <https://doi.org/10.1016/j.apmt.2023.101765>.
- [144] Anu, N. Deopa, A.S. Rao, Structural and luminescent properties of dysprosium ions-doped tungstate phosphor for w-LEDs, in: I. Rendina, L. Petti, D. Sagnelli, G. Nenna (Eds.), *Smart Mater. Opto-Electronic Appl.*, SPIE, 2023: p. 43. <https://doi.org/10.1117/12.2669275>.
- [145] S. Kaur, N. Deopa, A. Prasad, R. Bajaj, A.S. Rao, Intense green emission from Tb^{3+} ions doped zinc lead alumino borate glasses for laser and w-LEDs applications, *Opt. Mater. (Amst).* 84 (2018) 318–323. <https://doi.org/10.1016/J.OPTMAT.2018.07.020>.
- [146] Y. Liu, Z. Lu, Y. Gu, W. Li, Hydrothermal-assisted ion exchange synthesis and photoluminescence of Li^{+} and Eu^{3+} co-doped $\text{NaLa}(\text{WO}_4)_2$ as near-UV type red phosphors, *J. Lumin.* 132 (2012) 1220–1225. <https://doi.org/10.1016/j.jlumin.2011.12.069>.

- [147] D. Huang, Y. Zhou, W. Xu, Z. Yang, M. Hong, J. Yu, Synthesis and luminescent properties of $\text{Na}_5\text{La}_{1-x}\text{Eu}_x(\text{WO}_4)_4$ red phosphors, 132 (2012) 2788–2793. <https://doi.org/10.1016/j.jlumin.2012.05.022>.
- [148] J. Huang, B. Hou, H. Ling, J. Liu, X. Yu, Crystal Structure, Electronic Structure, and Photoluminescence Properties of $\text{La}_3\text{BW}_{1-x}\text{Mo}_x\text{O}_9 : \text{Eu}^{3+}$ Red Phosphor, (2014) 3–9.
- [149] H. Shih, K. Liu, L. Teoh, L. Wei, Y. Chang, Microelectronic Engineering Synthesis and photoluminescence properties of (La, Pr) co-doped, MEE. 148 (2015) 10–13. <https://doi.org/10.1016/j.mee.2015.07.007>.
- [150] A. Durairajan, D. Thangaraju, S.M. Babu, M.A. Valente, Luminescence characterization of sol-gel derived Pr^{3+} doped $\text{NaGd}(\text{WO}_4)_2$ phosphors for solid state lighting applications, Mater. Chem. Phys. 179 (2016) 295–303. <https://doi.org/10.1016/j.matchemphys.2016.05.042>.
- [151] H. Shih, Y. Tsai, K. Liu, Y. Liao, Y. Chang, The luminescent properties of Pr^{3+} ion-doped BaY_2ZnO_5 phosphor under blue light irradiation, Opt. Mater. (Amst). 35 (2013) 2654–2657. <https://doi.org/10.1016/j.optmat.2013.08.007>.
- [152] L. Li, H. Wu, Host composition dependent tuneable morphology and luminescent property of the $\text{Ca}_x\text{Sr}_y\text{Ba}_{1-x-y}\text{WO}_4 : \text{RE}^{3+}$ (RE = Pr, Ho, and Er) phosphors, 702 (2017) 106–119. <https://doi.org/10.1016/j.jallcom.2017.01.255>.
- [153] E. Sreeja, S. Gopi, V. Vidyadharan, P. Remya Mohan, C. Joseph, N. V. Unnikrishnan, P.R. Biju, Luminescence properties and charge transfer mechanism of host sensitized $\text{Ba}_2\text{CaWO}_6:\text{Eu}^{3+}$ phosphor, Powder Technol. 323 (2018) 445–453. <https://doi.org/10.1016/J.POWTEC.2017.09.036>.
- [154] X. Jiang, J. Ma, Y. Yao, Y. Sun, Z. Liu, Y. Ren, J. Liu, B. Lin, Low-temperature synthesis of SrWO_4 nano-particles by a molten salt method, Ceram. Int. 35 (2009) 3525–3528. <https://doi.org/10.1016/j.ceramint.2009.05.015>.
- [155] E. Sreeja, V. Vidyadharan, S.K. Jose, A. George, C. Joseph, N. V. Unnikrishnan, P.R. Biju, A single-phase white light emitting Pr^{3+} doped Ba_2CaWO_6 phosphor: synthesis, photoluminescence and optical properties, Opt. Mater. (Amst). 78 (2018) 52–62. <https://doi.org/10.1016/j.optmat.2018.02.003>.
- [156] P. Boutinaud, R. Mahiou, E. Cavalli, M. Bettinelli, Red luminescence induced by intervalence charge transfer in Pr^{3+} -doped compounds, J. Lumin. 122–123 (2007) 430–433. <https://doi.org/10.1016/j.jlumin.2006.01.198>.
- [157] N. Zhang, X. Jiang, Y. Wang, X. Pan, Y. Zhang, B. Liu, Y. Yang, X. Wang, Synthesis, structure and luminescence characteristics of $\text{La}_3\text{Ga}_5\text{SiO}_{14}:\text{Pr}^{3+}$ phosphors, J. Alloys Compd. 932 (2023) 167626. <https://doi.org/10.1016/j.jallcom.2022.167626>.
- [158] L.L. Noto, M.Y.A. Yagoub, O.M. Ntwaeaborwa, H.C. Swart, Persistent photoluminescence emission from $\text{SrTa}_2\text{O}_6:\text{Pr}^{3+}$ phosphor prepared at different temperatures, Ceram. Int. 41 (2015) 8828–8836. <https://doi.org/10.1016/j.ceramint.2015.03.112>.
- [159] B. Wang, H. Lin, J. Xu, H. Chen, Z. Lin, F. Huang, Y. Wang, Design, Preparation, and Characterization of a Novel Red Long-Persistent Perovskite Phosphor: $\text{Ca}_3\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$, Inorg. Chem. 54 (2015) 11299–11306. <https://doi.org/10.1021/acs.inorgchem.5b01894>.
- [160] K. Fiaczyk, S. Omagari, A. Meijerink, E. Zych, Temperature dependence of $4f^{n-15}d^1 \rightarrow 4f^n$ luminescence of Ce^{3+} and Pr^{3+} ions in Sr_2GeO_4 host, J. Lumin. 198 (2018) 163–170. <https://doi.org/10.1016/j.jlumin.2018.02.034>.
- [161] T. Raghu Raman, Y.C. Ratnakaram, B. Deva Prasad Raju, Synthesis and spectroscopic investigations on Pr^{3+} -doped LiPbB_5O_9 phosphor: A blue converting red phosphor for white LEDs, Optik (Stuttg). 225 (2021) 165758. <https://doi.org/10.1016/j.ijleo.2020.165758>.
- [162] M. Wei, S. Feng, X. Tian, C. Ji, Z. Huang, J. Wen, X. Liu, F. Luo, C. Li, J. Li, Y. Peng, Albumin assisted sol-gel synthesized $\text{SrSnO}_3 : \text{Pr}^{3+}$ red persistent phosphors for temperature sensing, J. Lumin. 239 (2021) 118328. <https://doi.org/10.1016/j.jlumin.2021.118328>.

- [163] H. Zhang, Z. Gao, G. Li, Y. Zhu, S. Liu, K. Li, Y. Liang, A ratiometric optical thermometer with multi-color emission and high sensitivity based on double perovskite $\text{LaMg}_{0.402}\text{Nb}_{0.598}\text{O}_3$: Pr^{3+} thermochromic phosphors, *Chem. Eng. J.* 380 (2020) 122491. <https://doi.org/10.1016/j.cej.2019.122491>.
- [164] P. Bolek, J. Zeler, C.D.S. Brites, J. Trojan-Piegza, L.D. Carlos, E. Zych, Ga-modified $\text{YAG}:\text{Pr}^{3+}$ dual-mode tunable luminescence thermometers, *Chem. Eng. J.* 421 (2021) 129764. <https://doi.org/10.1016/j.cej.2021.129764>.
- [165] C. Gheorghe, S. Hau, G. Stanciu, D. Avram, A. Broasca, L. Gheorghe, Novel optical temperature sensors based on the emission of the Pr^{3+} ions doped $\text{Ca}_3(\text{M},\text{Ga})_5\text{O}_{12}$ ($\text{M}^{5+} = \text{Nb}, \text{Ta}$) garnet phosphors, *J. Alloys Compd.* 922 (2022) 166178. <https://doi.org/10.1016/j.jallcom.2022.166178>.
- [166] M.D. Dramićanin, Trends in luminescence thermometry, *J. Appl. Phys.* 128 (2020) 040902. <https://doi.org/10.1063/5.0014825>.
- [167] S.W. Allison, D.L. Beshears, M.R. Cates, M.B. Scudiere, D.W. Shaw, A.D. Ellis, Luminescence of $\text{YAG}:\text{Dy}$ and $\text{YAG}:\text{Dy},\text{Er}$ crystals to 1700 °C, *Meas. Sci. Technol.* 31 (2020) 044001. <https://doi.org/10.1088/1361-6501/ab4ebd>.
- [168] L. Li, F. Qin, L. Li, H. Gao, Z. Zhang, Highly sensitive optical ratiometric thermal sensing based on the three-photon upconversion luminescence of $\text{Y}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nano-thermometers, *J. Mater. Chem. C* 7 (2019) 7378–7385. <https://doi.org/10.1039/C9TC01276A>.
- [169] D. Zhang, Y. Xu, Q. Liu, Z. Xia, Encapsulation of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskite Quantum Dots in MOF-5 Microcrystals as a Stable Platform for Temperature and Aqueous Heavy Metal Ion Detection, *Inorg. Chem.* 57 (2018) 4613–4619. <https://doi.org/10.1021/acs.inorgchem.8b00355>.
- [170] Y. Zhang, S. Xu, X. Li, J. Zhang, J. Sun, H. Xia, R. Hua, B. Chen, Fabrication, photothermal conversion and temperature sensing of novel nanoplatform-hybrid nanocomposite of $\text{NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}@\text{NaYF}_4$ and Au nanorods for photothermal therapy, *Mater. Res. Bull.* 114 (2019) 148–155. <https://doi.org/10.1016/j.materresbull.2019.03.003>.
- [171] Z. Zhao, K. Li, C. Liu, Q. Yin, J. Han, J. Heo, Intense up-conversion emission from $\text{Er}^{3+}/\text{Yb}^{3+}$ ion co-doped transparent oxyfluoride glass-ceramics containing $\text{Y}_5\text{O}_4\text{F}_7$ nanorods for optical thermometry, *J. Mater. Chem. C* 7 (2019) 6134–6143. <https://doi.org/10.1039/C9TC00280D>.
- [172] N. Zhang, M.S. Molokeev, Q. Liu, Z. Xia, Pure red upconversion luminescence and optical thermometry of Er^{3+} doped sensitizer-rich SrYbInO_4 phosphors, *J. Mater. Chem. C* 6 (2018) 7361–7366. <https://doi.org/10.1039/C8TC02565G>.
- [173] A.M. Kaczmarek, M.K. Kaczmarek, R. Van Deun, Er^{3+} -to- Yb^{3+} and Pr^{3+} -to- Yb^{3+} energy transfer for highly efficient near-infrared cryogenic optical temperature sensing, *Nanoscale* 11 (2019) 833–837. <https://doi.org/10.1039/C8NR08348G>.
- [174] R. Shi, L. Ning, Y. Huang, Y. Tao, L. Zheng, Z. Li, H. Liang, $\text{Li}_4\text{SrCa}(\text{SiO}_4)_2:\text{Eu}^{2+}$: A Potential Temperature Sensor with Unique Optical Thermometric Properties, *ACS Appl. Mater. Interfaces* 11 (2019) 9691–9695. <https://doi.org/10.1021/acsami.8b22754>.
- [175] Y. Pan, X. Xie, Q. Huang, C. Gao, Y. Wang, L. Wang, B. Yang, H. Su, L. Huang, W. Huang, Inherently $\text{Eu}^{2+}/\text{Eu}^{3+}$ Codoped Sc_2O_3 Nanoparticles as High-Performance Nanothermometers, *Adv. Mater.* 30 (2018) 1705256. <https://doi.org/10.1002/adma.201705256>.
- [176] L. Xu, J. Liu, L. Pei, Y. Xu, Z. Xia, Enhanced up-conversion luminescence and optical temperature sensing in graphitic C_3N_4 quantum dots grafted with $\text{BaWO}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ phosphors, *J. Mater. Chem. C* 7 (2019) 6112–6119. <https://doi.org/10.1039/C9TC01351B>.
- [177] H. Zhang, G. Li, Y. Zhu, S. Liu, K. Li, Y. Liang, Color tuning and white light emission in a single-phased $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}, \text{Tb}^{3+}$ phosphor, *J. Alloys Compd.* 798 (2019) 800–809. <https://doi.org/10.1016/j.jallcom.2019.05.306>.

- [178] Z. Chen, W. Wang, S. Kang, W. Cui, H. Zhang, G. Yu, T. Wang, G. Dong, C. Jiang, S. Zhou, J. Qiu, Tailorable Upconversion White Light Emission from Pr^{3+} Single-Doped Glass Ceramics via Simultaneous Dual-Lasers Excitation, *Adv. Opt. Mater.* 6 (2018) 1700787. <https://doi.org/10.1002/adom.201700787>.
- [179] P. Kumar, S. Singh, I. Gupta, K. Nehra, V. Kumar, D. Singh, Structural and luminescent behaviour of Dy(III) activated $\text{Gd}_3\text{Al}_5\text{O}_{12}$ nanophosphors for white-LEDs applications, *Mater. Chem. Phys.* (2022) 127035. <https://doi.org/10.1016/j.matchemphys.2022.127035>.
- [180] S.K. Hussain, J.S. Yu, Citrate-based sol-gel synthesis of blue- and green-emitting $\text{BaLa}_2\text{WO}_7\text{:Tm}^{3+}$ or Er^{3+} phosphors and their luminescence properties, *Mater. Res. Bull.* (2017). <https://doi.org/10.1016/j.materresbull.2017.07.031>.
- [181] W.T. Carnall, P.R. Fields, K. Rajnak, Electronic Energy Levels in the Trivalent Lanthanide Aquo Ions. I. Pr^{3+} , Nd^{3+} , Pm^{3+} , Sm^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , and Tm^{3+} , 4424 (1968). <https://doi.org/10.1063/1.1669893>.
- [182] P. Rohilla, A.S. Rao, Energy transfer induced colour tunable photoluminescence performance of thermally stable $\text{Sm}^{3+}/\text{Eu}^{3+}$ co-doped $\text{Ba}_3\text{MoTiO}_8$ phosphors for white LED applications, *J. Mater. Sci. Mater. Electron.* 34 (2023) 1–19. <https://doi.org/10.1007/s10854-023-11025-1>.
- [183] D. Fields, D.R. Pure, A. Added, A. Added, Effect of Defect Fields on the Optical Absorption Edge, 130 (1963) 1962–1964.
- [184] A.S. Hassanien, A.A. Akl, Influence of composition on optical and dispersion parameters of thermally evaporated non-crystalline $\text{Cd}_{50}\text{S}_{50-x}\text{Se}_x$ thin films, *J. Alloys Compd.* (2015). <https://doi.org/10.1016/j.jallcom.2015.06.231>.
- [185] H. Zhu, M. Fang, Z. Huang, K. Chen, X. Min, Y. Mao, M. Wang, Photoluminescence properties of $\text{Li}_2\text{Mg}_2(\text{WO}_4)_3\text{:Eu}^{3+}$ red phosphor with high color purity for white LEDs applications, *J. Lumin.* 172 (2016) 180–184. <https://doi.org/10.1016/j.jlumin.2015.12.021>.
- [186] X. Yang, F. Huang, Z. Huang, F. Cao, J. Zhang, Small-size and Monodispersed Red-Emitting Pr^{3+} doped Barium Molybdate Nanocrystals with Ultrahigh Color Purity Xuyong, (2016). <https://doi.org/10.1039/C6RA14222B>.
- [187] Z. Mu, Y. Hu, L. Chen, X. Wang, G. Ju, Z. Yang, Y. Jin, A single-phase, color-tunable, broadband-excited white light-emitting phosphor $\text{Y}_2\text{WO}_6\text{:Sm}^{3+}$, *J. Lumin.* 146 (2014) 33–36. <https://doi.org/10.1016/j.jlumin.2013.09.043>.
- [188] G.V. Kanmani, V. Ponnusamy, G. Rajkumar, M.T. Jose, Development of novel $\text{Na}_2\text{Mg}_3\text{Zn}_2\text{Si}_{12}\text{O}_{30}\text{:Eu}^{3+}$ red phosphor for white light emitting diodes, *Opt. Mater. (Amst.)* 96 (2019) 109350. <https://doi.org/10.1016/j.optmat.2019.109350>.
- [189] S. Arunkumar, G. Venkataiah, K. Marimuthu, Spectroscopic and energy transfer behavior of Dy^{3+} ions in $\text{B}_2\text{O}_3\text{TeO}_2\text{PbOPbF}_2\text{Bi}_2\text{O}_3\text{CdO}$ glasses for laser and WLED applications, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 136 (2015) 1684–1697. <https://doi.org/10.1016/j.saa.2014.10.067>.
- [190] D. Xu, Z. Yang, J. Sun, X. Gao, J. Du, Synthesis and luminescence properties of double-perovskite white emitting phosphor $\text{Ca}_3\text{WO}_6\text{:Dy}^{3+}$, *J. Mater. Sci. Mater. Electron.* 27 (2016) 8370–8377. <https://doi.org/10.1007/s10854-016-4848-z>.
- [191] Y. Shi, Y. Wang, Y. Wen, Z. Zhao, B. Liu, Z. Yang, Tunable luminescence $\text{Y}_3\text{Al}_5\text{O}_{12}\text{:006Ce}^{3+}$, $x\text{Mn}^{2+}$ phosphors with different charge compensators for warm white light emitting diodes, *Opt. Express.* 20 (2012) 21656. <https://doi.org/10.1364/OE.20.021656>.
- [192] S. Gharouel, L. Labrador-Páez, P. Haro-González, K. Horchani-Naifer, M. Férid, Fluorescence intensity ratio and lifetime thermometry of praseodymium phosphates for temperature sensing, *J. Lumin.* 201 (2018) 372–383. <https://doi.org/10.1016/j.jlumin.2018.04.035>.
- [193] V.K. Rai, S.B. Rai, A comparative study of FIR and FL based temperature sensing schemes: an example of Pr^{3+} , *Appl. Phys. B.* 87 (2007) 323–325. <https://doi.org/10.1007/s00340-007-2592-z>.

- [194] L. Li, P. Yang, W. Xia, Y. Wang, F. Ling, Z. Cao, S. Jiang, G. Xiang, X. Zhou, Y. Wang, Luminescence and optical thermometry strategy based on emission and excitation spectra of Pr^{3+} doped SrMoO_4 phosphors, *Ceram. Int.* 47 (2021) 769–775. <https://doi.org/10.1016/j.ceramint.2020.08.187>.
- [195] Y. Wu, H. Suo, X. Zhao, Z. Zhou, C. Guo, Self-calibrated optical thermometer $\text{LuNbO}_4:\text{Pr}^{3+}/\text{Tb}^{3+}$ based on intervalence charge transfer transitions, *Inorg. Chem. Front.* 5 (2018) 2456–2461. <https://doi.org/10.1039/C8QI00755A>.
- [196] C. Sumalatha, R. Doddaji, M. Venkateswarlu, P.R. Rani, K. Swapna, S. Mahamuda, A.S. Rao, White light emission from Dy^{3+} -doped $\text{ZnO} + \text{Bi}_2\text{O}_3 + \text{BaF}_2 + \text{B}_2\text{O}_3 + \text{TeO}_2$ glasses: Structural and spectroscopic properties, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 240 (2020) 118568. <https://doi.org/10.1016/j.saa.2020.118568>.
- [197] N. Deopa, S. Saini, S. Kaur, A. Prasad, A.S. Rao, Spectroscopic investigations on Dy^{3+} ions doped zinc lead alumino borate glasses for photonic device applications, *J. Rare Earths.* 37 (2019) 52–59. <https://doi.org/10.1016/J.JRE.2018.04.013>.
- [198] G.B. Nair, H.C. Swart, S.J. Dhoble, A review on the advancements in phosphor-converted light emitting diodes (pc-LEDs): Phosphor synthesis, device fabrication and characterization, *Prog. Mater. Sci.* 109 (2020) 100622. <https://doi.org/10.1016/j.pmatsci.2019.100622>.
- [199] V. Balaram, Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact, *Geosci. Front.* 10 (2019) 1285–1303. <https://doi.org/10.1016/j.gsf.2018.12.005>.
- [200] D. Halmurat, T. Yusufu, Q. ling Wang, J. He, A. Sidike, Rare earth ion Tb^{3+} doped natural sodium feldspar ($\text{NaAlSi}_3\text{O}_8$) Luminescent properties and energy transfer, *Sci. Rep.* 9 (2019) 1–8. <https://doi.org/10.1038/s41598-019-51171-3>.
- [201] X. Jin, Y. Xie, R. Tang, X. Geng, J. Che, L. Lou, W. Chen, B. Deng, R. Yu, Novel double perovskite $\text{Sr}_3\text{WO}_6:\text{Sm}^{3+}$, Na^+ orange-red emitting phosphors with high thermal stability for white LEDs, *J. Alloys Compd.* 899 (2022) 162739. <https://doi.org/10.1016/j.jallcom.2021.162739>.
- [202] L. Zhang, J. Che, Y. Ma, J. Wang, R. Kang, B. Deng, R. Yu, H. Geng, Luminescent and thermal properties of novel orange-red emitting $\text{Ca}_2\text{MgTeO}_6:\text{Sm}^{3+}$ phosphors for white LEDs, *J. Lumin.* 225 (2020) 117374. <https://doi.org/10.1016/j.jlumin.2020.117374>.
- [203] Z. Qin, L. Dong, G. Zhang, Y. Liu, G. Zhao, Y. Fang, J. Hou, Hetero-valent substitution design of high thermal stability reddish-orange $\text{Sr}_3\text{Ga}_2\text{Sn}_{1.5}\text{Si}_{2.5}\text{O}_{14}:\text{Sm}^{3+}$ phosphor for healthy lighting white-light-emitting-diodes applications, *Opt. Mater. (Amst)*. 131 (2022) 112640. <https://doi.org/10.1016/j.optmat.2022.112640>.
- [204] G. Seeta Rama Raju, J.S. Yu, J.Y. Park, H.C. Jung, B.K. Moon, Photoluminescence and Cathodoluminescence Properties of Nanocrystalline $\text{Ca}_2\text{Gd}_8\text{Si}_6\text{O}_{26}:\text{Sm}^{3+}$ Phosphors, *J. Am. Ceram. Soc.* 95 (2012) 238–242. <https://doi.org/10.1111/j.1551-2916.2011.04762.x>.
- [205] W. Zhou, M. Gu, Y. Ou, C. Zhang, X. Zhang, L. Zhou, H. Liang, Concentration-Driven Selectivity of Energy Transfer Channels and Color Tunability in $\text{Ba}_3\text{La}(\text{PO}_4)_3:\text{Tb}^{3+}$, Sm^{3+} for Warm White LEDs, *Inorg. Chem.* 56 (2017) 7433–7442. <https://doi.org/10.1021/acs.inorgchem.7b00737>.
- [206] S. Devi, A. Khatkar, V.B. Taxak, M. Dalal, S. Chahar, J. Dalal, S.P. Khatkar, Optical properties of trivalent samarium-doped $\text{Ba}_5\text{Zn}_4\text{Y}_8\text{O}_{21}$ nanodiametric rods excitable by NUV light, *J. Alloys Compd.* 767 (2018) 409–418. <https://doi.org/10.1016/j.jallcom.2018.07.127>.
- [207] M.K. Ekmekçi, M. İlhan, A.S. Başak, S. Deniz, Structural and Luminescence Properties of Sm^{3+} Doped TTB -Type BaTa_2O_6 Ceramic Phosphors, *J. Fluoresc.* 25 (2015) 1757–1762. <https://doi.org/10.1007/s10895-015-1663-5>.

- [208] P. Devi, P. Sehrawat, M. Sheoran, H. Dalal, N. Sehrawat, R.K. Malik, Crystal Chemistry and Photoluminescent Aspects of Bright Orange Light Emitting Sm^{3+} -Activated $\text{Ba}_2\text{BiV}_3\text{O}_{11}$ Nanomaterials for Advanced Illuminating Applications, *J. Fluoresc.* (2023). <https://doi.org/10.1007/s10895-023-03275-3>.
- [209] L. Zhou, H. Su, C. Li, R. Yang, Y. Shang, C. Wang, J. Lian, S. Xie, X. Ji, R. Yu, Synthesis and photoluminescence properties of a novel double perovskite $\text{NaGdMgTeO}_6\text{:Sm}^{3+}$ red-emitting phosphor for plant growth LEDs and w-LEDs, *Ceram. Int.* 49 (2023) 28246–28255. <https://doi.org/10.1016/j.ceramint.2023.06.079>.
- [210] J. Li, J. Liu, Q. Ni, Q. Zhu, Z. Zeng, J. Huo, C. Long, Q. Wang, Key Role Effect of Samarium in Realizing Zero Thermal Quenching and Achieving a Moisture-Resistant Reddish-Orange Emission in $\text{Ba}_3\text{LaNb}_3\text{O}_{12}\text{:Sm}^{3+}$, *Inorg. Chem.* 61 (2022) 17883–17892. <https://doi.org/10.1021/acs.inorgchem.2c03231>.
- [211] G.B. Nair, S.J. Dhoble, Photoluminescence properties of $\text{Eu}^{3+}/\text{Sm}^{3+}$ activated $\text{CaZr}_4(\text{PO}_4)_6$ phosphors, *J. Fluoresc.* 26 (2016) 1865–1873. <https://doi.org/10.1007/s10895-016-1880-6>.
- [212] L. Shi, Y. jie Han, H. xin Wang, D. chen Shi, X. yu Geng, Z. wei Zhang, High-efficiency and thermally stable far-red emission of Mn^{4+} in double cubic perovskite $\text{Sr}_9\text{Y}_2\text{W}_4\text{O}_{24}$ for plant cultivation, *J. Lumin.* 208 (2019) 307–312. <https://doi.org/10.1016/j.jlumin.2018.12.065>.
- [213] W.T. Carnall, P.R. Fields, K. Rajnak, Electronic Energy Levels of the Trivalent Lanthanide Aquo Ions. IV. Eu^{3+} , *J. Chem. Phys.* 49 (1968) 4450–4455. <https://doi.org/10.1063/1.1669896>.
- [214] L. Zhou, L. Liu, R. Yang, J. Kong, Y. Li, Y. Zhao, Y. Du, C. Li, Z. Zou, B. Deng, R. Yu, A novel yellow-emitting $\text{CaGdSbWO}_8\text{:Dy}^{3+}$ single-phase phosphor with high thermal stability and application in w-LEDs, *Inorg. Chem. Commun.* 148 (2023) 110316. <https://doi.org/10.1016/j.inoche.2022.110316>.
- [215] A. Zhang, Z. Sun, M. Jia, Z. Fu, B.C. Choi, J.H. Jeong, S.H. Park, Sm^{3+} -doped niobate orange-red phosphors with a double-perovskite structure for plant cultivation and temperature sensing, *J. Alloys Compd.* 889 (2021) 161671. <https://doi.org/10.1016/j.jallcom.2021.161671>.
- [216] J. Wu, S. Shi, X. Wang, J. Li, R. Zong, W. Chen, Controlled synthesis and optimum luminescence of Sm^{3+} -activated nano/submicroscale ceria particles by a facile approach, *J. Mater. Chem. C.* 2 (2014) 2786–2792. <https://doi.org/10.1039/C3TC32424A>.
- [217] K. Nanda, R.S. Kundu, I. Pal, R. Punia, N. Kishore, Concentration dependence of intensity parameters and radiative properties of Sm^{3+} ions doped in $\text{BaO-ZnO-B}_2\text{O}_3$ glasses, *J. Alloys Compd.* 676 (2016) 521–526. <https://doi.org/10.1016/j.jallcom.2016.03.112>.
- [218] I. Kumar, A.K. Gathania, Photoluminescence and quenching study of the Sm^{3+} -doped LiBaPO_4 phosphor, *J. Mater. Sci. Mater. Electron.* 33 (2022) 328–341. <https://doi.org/10.1007/s10854-021-07301-7>.
- [219] R. Yu, Y. Guo, L. Wang, H.M. Noh, B.K. Moon, B.C. Choi, J.H. Jeong, Characterizations and optical properties of orange-red emitting Sm^{3+} -doped Y_6WO_{12} phosphors, *J. Lumin.* 155 (2014) 317–321. <https://doi.org/10.1016/j.jlumin.2014.06.041>.
- [220] S. Kaur, A.S. Rao, M. Jayasimhadri, Spectroscopic and photoluminescence characteristics of Sm^{3+} doped calcium aluminozincate phosphor for applications in w-LED, *Ceram. Int.* 43 (2017) 7401–7407. <https://doi.org/10.1016/J.CERAMINT.2017.02.129>.
- [221] G. Zhu, Z. Li, F. Zhou, C. Wang, S. Xin, A novel temperature sensitive Sm^{3+} doped niobate orange-red phosphor : The synthesis and characteristic luminescent property investigation, *J. Lumin.* 196 (2018) 32–35. <https://doi.org/10.1016/j.jlumin.2017.12.014>.
- [222] Q. Li, S. Zhang, W. Lin, W. Li, Y. Li, Z. Mu, F. Wu, Spectrochimica Acta Part A : Molecular and Biomolecular Spectroscopy phosphors by energy transfer of Bi^{3+} -sensitized $\text{Eu}^{3+}/\text{Sm}^{3+}$, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* (2019) 117755. <https://doi.org/10.1016/j.saa.2019.117755>.

- [223] L. Wu, Y. Bai, L. Wu, H. Yi, Y. Kong, Y. Zhang, J. Xu, Sm^{3+} and Eu^{3+} codoped $\text{SrBi}_2\text{B}_2\text{O}_7$: A red-emitting phosphor with improved thermal stability, *RSC Adv.* 7 (2017) 1146–1153. <https://doi.org/10.1039/c6ra26752a>.
- [224] L.R. Đačanin, M.D. Dramićanin, S.R. Lukić-Petrović, D.M. Petrović, M.G. Nikolić, Eu^{3+} doped YNbO_4 phosphor properties for fluorescence thermometry, *Radiat. Meas.* 56 (2013) 143–146. <https://doi.org/10.1016/j.radmeas.2013.01.038>.
- [225] A.H. Khalid, K. Kontis, Thermographic Phosphors for High Temperature Measurements: Principles, Current State of the Art and Recent Applications, (2008) 5673–5744. <https://doi.org/10.3390/s8095673>.
- [226] S.K. Sharma, T. Köhler, J. Beyer, M. Fuchs, R. Gloaguen, J. Heitmann, Extending the temperature sensing range using Eu^{3+} luminescence up to 865 K in a single crystal of EuPO 4, *Phys. Chem. Chem. Phys.* 21 (2019) 16329–16336. <https://doi.org/10.1039/C9CP03501J>.
- [227] K. Li, R. Van Deun, Site- Bi^{3+} and Eu^{3+} dual emissions in color-tunable $\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2:\text{Bi}^{3+}$, Eu^{3+} phosphors prepared via sol-gel synthesis for potentially ratiometric temperature sensing, *J. Alloys Compd.* 787 (2019) 86–95. <https://doi.org/10.1016/j.jallcom.2019.02.087>.
- [228] A.M. Kaczmarek, $\text{Eu}^{3+}/\text{Tb}^{3+}$ and Dy^{3+} POM@MOFs and 2D coordination polymers based on pyridine-2,6-dicarboxylic acid for ratiometric optical temperature sensing, *J. Mater. Chem. C.* 6 (2018) 5916–5925. <https://doi.org/10.1039/C8TC01062E>.
- [229] P. Chen, W. Hu, D. Yang, J. Zhu, J. Zhang, Y. Wu, $\text{Ba}_2\text{ZnWO}_6:\text{Sm}^{3+}$ as promising orange-red emitting phosphors: Photoluminescence properties and energy transfer process, *Phys. B Condens. Matter.* 530 (2018) 127–132. <https://doi.org/10.1016/j.physb.2017.11.012>.
- [230] H. Nagabhushana, D. V. Sunitha, S.C. Sharma, B. Daruka Prasad, B.M. Nagabhushana, R.P.S. Chakradhar, Enhanced luminescence by monovalent alkali metal ions in $\text{Sr}_2\text{SiO}_4:\text{Eu}^{3+}$ nanophosphor prepared by low temperature solution combustion method, *J. Alloys Compd.* 595 (2014) 192–199. <https://doi.org/10.1016/j.jallcom.2014.01.094>.
- [231] Y. Li, X. Liu, Energy transfer and luminescence properties of $\text{Ba}_2\text{CaMoO}_6:\text{Eu}^{3+}$ phosphors prepared by sol-gel method, *Opt. Mater. (Amst.)* 42 (2015) 303–308. <https://doi.org/10.1016/j.optmat.2015.01.018>.
- [232] S. Sailaja, S.J. Dhoble, B. Sudhakar Reddy, Synthesis and photoluminescence properties of Sm^{3+} and Dy^{3+} ions activated $\text{Ca}_2\text{Gd}_2\text{W}_3\text{O}_{14}$ phosphors, *J. Mol. Struct.* 1003 (2011) 115–120. <https://doi.org/10.1016/j.molstruc.2011.07.048>.
- [233] F.B. Dejene, Thermoluminescence study of beta irradiated $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ phosphor synthesized using solution-combustion process, *J. Lumin.* 199 (2018) 433–441. <https://doi.org/10.1016/j.jlumin.2018.03.067>.
- [234] J. Liang, L. Sun, G. Annadurai, B. Devakumar, S. Wang, Q. Sun, J. Qiao, H. Guo, B. Li, X. Huang, Synthesis and photoluminescence characteristics of high color purity $\text{Ba}_3\text{Y}_4\text{O}_9:\text{Eu}^{3+}$ red-emitting phosphors with excellent thermal stability for warm W-LED application, *RSC Adv.* 8 (2018) 32111–32118. <https://doi.org/10.1039/c8ra06129g>.
- [235] Y. Zhang, Y. Li, Y. Yin, Red photoluminescence and morphology of Eu^{3+} doped $\text{Ca}_3\text{La}_3(\text{BO}_3)_5$ phosphors, *J. Alloys Compd.* 400 (2005) 222–226. <https://doi.org/10.1016/j.jallcom.2005.04.001>.
- [236] X. Huang, H. Guo, B. Li, Eu^{3+} -activated $\text{Na}_2\text{Gd}(\text{PO}_4)(\text{MoO}_4)$: A novel high-brightness red-emitting phosphor with high color purity and quantum efficiency for white light-emitting diodes, *J. Alloys Compd.* 720 (2017) 29–38. <https://doi.org/10.1016/j.jallcom.2017.05.251>.
- [237] B. Li, X. Huang, H. Guo, Y. Zeng, Energy transfer and tunable photoluminescence of $\text{LaBWO}_6:\text{Tb}^{3+}$, Eu^{3+} phosphors for near-UV white LEDs, *Dye. Pigment.* 150 (2018) 67–72. <https://doi.org/10.1016/j.dyepig.2017.11.003>.

- [238] S. Wang, C. Xu, X. Qiao, High thermal stability and color purity of red-emitting phosphor Y_2SiWO_8 : Eu^{3+} for w-LEDs: Synthesis and photoluminescence properties, *Ceram. Int.* 47 (2021) 1063–1075. <https://doi.org/10.1016/j.ceramint.2020.08.222>.
- [239] W. Shi, A. Feng, H. Tang, Z. Ding, Y. Ma, M. Wu, G. Li, Preparation, characterization, and luminescence of Eu^{3+} -doped gadolinium tungstate, $\text{Y}_3\text{Al}_5\text{O}_{12}$:Ce phosphor, and their mixtures, *Opt. Mater. (Amst.)* 35 (2013) 609–616. <https://doi.org/10.1016/j.optmat.2012.10.038>.
- [240] L. Alexander, H.P. Klug, Determination of Crystallite Size with the X-Ray Spectrometer, *J. Appl. Phys.* 21 (1950) 137–142. <https://doi.org/10.1063/1.1699612>.
- [241] A.K. Bedyal, A.K. Kunti, V. Kumar, H.C. Swart, Effects of cationic substitution on the luminescence behavior of Dy^{3+} doped orthophosphate phosphor, *J. Alloys Compd.* 806 (2019) 1127–1137. <https://doi.org/10.1016/j.jallcom.2019.07.305>.
- [242] I. Tseng, M. Tsai, T. Hsu, C. Lin, S. Lin, C. Huang, Tunable luminescence properties of GeO_2 - Doped $\text{Li}_2\text{ZnTi}_3\text{O}_8$: Mn^{4+} red phosphor, *Opt. Laser Technol.* 157 (2023) 108777. <https://doi.org/10.1016/j.optlastec.2022.108777>.
- [243] S. Shisina, S. Das, S. Som, S. Ahmad, V. Vinduja, P. Merin, K.G. Nishanth, P. Kumari, M.K. Pandey, Structure and optoelectronic properties of palmierite structured $\text{Ba}_2\text{Y}_{0.67}\text{Sr}_{0.33}\text{V}_2\text{O}_8$: Eu^{3+} red phosphors for n-UV and blue diode based warm white light systems, *J. Alloys Compd.* 802 (2019) 723–732. <https://doi.org/10.1016/j.jallcom.2019.05.355>.
- [244] B. Vasanthi, N. Gopakumar, P.S. Anjana, Structural, optical and luminescence properties of $\text{BaLaGa}_3\text{O}_7$: x Eu^{3+} ceramic phosphors, *J. Lumin.* 241 (2022) 118486. <https://doi.org/10.1016/j.jlumin.2021.118486>.
- [245] K.N. Shinde, S.J. Dhoble, A. Kumar, Combustion synthesis of Ce^{3+} , Eu^{3+} and Dy^{3+} activated NaCaPO_4 phosphors, *J. Rare Earths.* 29 (2011) 527–535. [https://doi.org/10.1016/S1002-0721\(10\)60492-9](https://doi.org/10.1016/S1002-0721(10)60492-9).
- [246] V. Dubey, J. Kaur, S. Agrawal, N.S. Suryanarayana, K.V.R. Murthy, Effect of Eu^{3+} concentration on photoluminescence and thermoluminescence behavior of YBO_3 : Eu^{3+} phosphor, *Superlattices Microstruct.* 67 (2014) 156–171. <https://doi.org/10.1016/j.spmi.2013.12.026>.
- [247] S.R. Bargat, Y.R. Parauha, G.C. Mishra, S.J. Dhoble, Combustion synthesis and spectroscopic investigation of $\text{CaNa}_2(\text{SO}_4)_2$: Eu^{3+} phosphor, *J. Mol. Struct.* 1221 (2020) 128838. <https://doi.org/10.1016/j.molstruc.2020.128838>.
- [248] Y.R. Parauha, V. Chopra, S.J. Dhoble, Synthesis and luminescence properties of RE^{3+} ($\text{RE} = \text{Eu}^{3+}$, Dy^{3+}) activated $\text{CaSr}_2(\text{PO}_4)_2$ phosphors for lighting and dosimetric applications, *Mater. Res. Bull.* 131 (2020) 110971. <https://doi.org/10.1016/j.materresbull.2020.110971>.
- [249] Y.R. Parauha, S.J. Dhoble, Synthesis and luminescence characterization of Eu^{3+} -doped $\text{Ca}_7\text{Mg}_2(\text{PO}_4)_6$ phosphor for eco-friendly white light-emitting diodes and thermoluminescence dosimetric applications, *Luminescence.* 36 (2021) 1837–1846. <https://doi.org/10.1002/bio.3900>.
- [250] G. Zhu, Z. Li, C. Wang, X. Wang, F. Zhou, M. Gao, S. Xin, Y. Wang, Highly Eu^{3+} ions doped novel red emission solid solution phosphors $\text{Ca}_{18}\text{Li}_3(\text{Bi},\text{Eu})(\text{PO}_4)_{14}$: structure design, characteristic luminescence and abnormal thermal quenching behavior investigation, *Dalt. Trans.* 48 (2019) 1624–1632. <https://doi.org/10.1039/C8DT04047H>.
- [251] S.N. Menon, S.Y. Kadam, D.K. Koul, Thermal quenching studies in LiMgPO_4 based OSL phosphors, *J. Lumin.* 216 (2019) 116716. <https://doi.org/10.1016/j.jlumin.2019.116716>.
- [252] N. Pasberg, D. den Engelsen, G.R. Fern, P.G. Harris, T.G. Ireland, J. Silver, Structure and luminescence analyses of simultaneously synthesised $(\text{Lu}_{1-x}\text{Gd}_x)_2\text{O}_2\text{S}:\text{Tb}^{3+}$ and $(\text{Lu}_{1-x}\text{Gd}_x)_2\text{O}_3:\text{Tb}^{3+}$, *Dalt. Trans.* 46 (2017) 7693–7707. <https://doi.org/10.1039/C7DT00862G>.

- [253] Q. Wang, M. Liao, Q. Lin, M. Xiong, Z. Mu, F. Wu, A review on fluorescence intensity ratio thermometer based on rare-earth and transition metal ions doped inorganic luminescent materials, *J. Alloys Compd.* 850 (2021) 156744. <https://doi.org/10.1016/j.jallcom.2020.156744>.
- [254] Z. Li, X. Geng, Y. Wang, Y. Chen, Synthesis and luminescence properties of $\text{NaBaPO}_4\text{:Tm}^{3+}$, Dy^{3+} white-light emitting phosphors with enhanced brightness by Li^+ co-doping, *J. Lumin.* 240 (2021) 118428. <https://doi.org/10.1016/j.jlumin.2021.118428>.
- [255] M. Runowski, P. Woźny, N. Stopikowska, I.R. Martín, V. Lavín, S. Lis, Luminescent Nanothermometer Operating at Very High Temperature-Sensing up to 1000 K with Upconverting Nanoparticles ($\text{Yb}^{3+}/\text{Tm}^{3+}$), *ACS Appl. Mater. Interfaces.* 12 (2020) 43933–43941. <https://doi.org/10.1021/acsami.0c13011>.
- [256] T. Zheng, M. Runowski, P. Woźny, B. Barszcz, S. Lis, M. Vega, J. Llanos, K. Soler-Carracedo, I.R. Martín, Boltzmann vs. non-Boltzmann (non-linear) thermometry - Yb^{3+} - Er^{3+} activated dual-mode thermometer and phase transition sensor via second harmonic generation, *J. Alloys Compd.* 906 (2022) 164329. <https://doi.org/10.1016/j.jallcom.2022.164329>.
- [257] M. Runowski, P. Woźny, S. Lis, V. Lavín, I.R. Martín, Optical Vacuum Sensor Based on Lanthanide Upconversion-Luminescence Thermometry as a Tool for Ultralow Pressure Sensing, *Adv. Mater. Technol.* 5 (2020) 1901091. <https://doi.org/10.1002/admt.201901091>.
- [258] D. Jiang, L. Geng, S. Zhou, Y. Wang, Photoluminescence properties and energy transfer in the Sm^{3+} and Eu^{3+} co-doped $\text{Ca}_3\text{Bi}(\text{PO}_4)_3$ red phosphor, *Inorg. Chem. Commun.* 142 (2022). <https://doi.org/10.1016/j.inoche.2022.109668>.
- [259] Z.P. Ning Liu, Lefu Mei, Jianxiong Bin, Ze Zhang, Effect of anionic group $[\text{SiO}_4]^{4-}/[\text{PO}_4]^{3-}$ on the luminescence properties of Dy^{3+} -doped tungstate structural compounds, (2021) 843–851.
- [260] S. Kumari, Anu, A. Prasad, P. Rohilla, A.S. Rao, Prospective applications of thermally stable Dy^{3+} doped potassium zinc strontium borate (KZSB) glasses in w-LEDs, *J. Mater. Sci. Mater. Electron.* 34 (2023) 1–17. <https://doi.org/10.1007/s10854-023-10272-6>.
- [261] A. Kumar, J. Manam, Color tunable emission and temperature dependent photoluminescence properties of Eu^{3+} co-doped $\text{Gd}_2\text{Zr}_2\text{O}_7\text{:Dy}^{3+}$ phosphors, *Opt. Mater. (Amst).* 96 (2019) 109373. <https://doi.org/10.1016/j.optmat.2019.109373>.
- [262] E.A. Rathnakumari, S.M.M. Kennedy, Photoluminescence properties of certain trivalent RE ions ($\text{Dy}/\text{Sm}/\text{Eu}$) activated $\text{NaSrBi}_2(\text{PO}_4)_3$ phosphors and cool to warm white color tuning in Dy^{3+} - Sm^{3+} and Dy^{3+} - Eu^{3+} codoped $\text{NaSrBi}_2(\text{PO}_4)_3$ phosphors for indoor lighting applications, *J. Lumin.* 235 (2021) 118018. <https://doi.org/10.1016/j.jlumin.2021.118018>.
- [263] S.K. Hussain, H.S. Go, J.J. Han, H. Patnam, G. Nagaraju, J.S. Yu, Energy transfer mechanism and tunable emissions from $\text{K}_3\text{La}(\text{VO}_4)_2\text{:Dy}^{3+}/\text{Eu}^{3+}$ phosphors and soft-PDMS-based composite films for multifunctional applications, *J. Alloys Compd.* 805 (2019) 1271–1281. <https://doi.org/10.1016/j.jallcom.2019.07.116>.
- [264] W. Wang, J. Li, Z. Zhang, Z. Liu, The synthesis and luminescent properties of Dy/Re ($\text{Re} = \text{Tb}$ or Eu) co-doped $\text{Gd}_2(\text{WO}_4)_3$ phosphor with tunable color via energy transfer, *J. Lumin.* 207 (2019) 114–122. <https://doi.org/10.1016/j.jlumin.2018.10.122>.
- [265] J.A. Jiménez, Temperature Dependent Spectroscopic Properties of Cu^+ and Dy^{3+} Co-Doped Phosphate Glass: Band Gap Analysis and Cu Nanocluster-Enhanced Dy^{3+} Luminescence, *ChemPhysChem.* (2018) 399–404. <https://doi.org/10.1002/cphc.201800971>.
- [266] A. Cadiau, C.D.S. Brites, P.M.F.J. Costa, R.A.S. Ferreira, J. Rocha, L.D. Carlos, Ratiometric Nanothermometer Based on an Emissive Ln^{3+} -Organic Framework, *ACS Nano.* 7 (2013) 7213–7218. <https://doi.org/10.1021/nn402608w>.
- [267] X. Zhang, Y. Huang, M. Gong, Dual-emitting Ce^{3+} , Tb^{3+} co-doped LaOBr phosphor: Luminescence, energy transfer and ratiometric temperature sensing, *Chem. Eng. J.* 307 (2017) 291–299. <https://doi.org/10.1016/j.cej.2016.08.087>.

- [268] X. Chen, Z. Zheng, L. Teng, R. Wei, F. Hu, H. Guo, Self-calibrated optical thermometer based on luminescence from $\text{SrLu}_2\text{O}_4:\text{Bi}^{3+}$, Eu^{3+} phosphors, *RSC Adv.* 8 (2018) 35422–35428. <https://doi.org/10.1039/C8RA06358C>.
- [269] J. Wang, J. Guo, Q. Lv, Z. Ma, X. Feng, Y. Lu, J. Gao, W. Chen, B. Deng, R. Yu, Spectroscopic investigation of the novel orange-red phosphor $\text{Ca}_3\text{La}_2\text{W}_2\text{O}_{12}:\text{Sm}^{3+}$ with the high color purity for w-LED applications, *J. Lumin.* 241 (2022) 118459. <https://doi.org/10.1016/j.jlumin.2021.118459>.
- [270] Q. Wu, Y. Li, Y. Wang, H. Liu, S. Ye, L. Zhao, J. Ding, J. Zhou, A novel narrow-band blue-emitting phosphor of Bi^{3+} -activated $\text{Sr}_3\text{Lu}_2\text{Ge}_3\text{O}_{12}$ based on a highly symmetrical crystal structure used for WLEDs and FEDs, *Chem. Eng. J.* 401 (2020) 126130. <https://doi.org/10.1016/j.cej.2020.126130>.
- [271] H. Gao, M. Wang, Y. Mao, Q. Zhao, C. Zhang, L. Jin, Y. Xia, W. Li, K. Zhang, H. Zeng, Intramolecular-Catalyzed Vitrimers with White-Light Emission for Light-Emitting Diode Encapsulation, *Adv. Mater.* 35 (2023). <https://doi.org/10.1002/adma.202300616>.
- [272] Xin Zhang, Ruirui Cui, Jun Zhang, Gaofeng Yuan, X. Qi, Structural and photoluminescence properties of a novel $\text{Ba}_2\text{GdNbO}_6:\text{Sm}^{3+}$ phosphor, *Optik* 245 (2021) 167646. <https://doi.org/10.1016/j.ijleo.2021.167646>.
- [273] L. Sun, B. Devakumar, J. Liang, S. Wang, Q. Sun, X. Huang, A broadband cyan-emitting $\text{Ca}_2\text{LuZr}_2(\text{AlO}_4)_3:\text{Ce}^{3+}$ garnet phosphor for near-ultraviolet-pumped warm-white light-emitting diodes with an improved color rendering index, *J. Mater. Chem. C* 8 (2020) 1095–1103. <https://doi.org/10.1039/C9TC04952E>.
- [274] C. Ta, H. Wen, Z. Mo, Y. Huo, Z. Mu, E.A. Dawi, L. Luo, D.A. Hakeem, Preparation and luminescence investigations of garnet-based $\text{Y}_2\text{Ca}_2\text{Ga}_3\text{VO}_{12}:\text{RE}$ ($\text{RE} = \text{Eu}^{3+}$, Sm^{3+} , and Dy^{3+}) phosphors, *Mater. Res. Bull.* 164 (2023) 112254. <https://doi.org/10.1016/j.materresbull.2023.112254>.
- [275] J. Meyer, F. Tappe, Photoluminescent Materials for Solid-State Lighting: State of the Art and Future Challenges, *Adv. Opt. Mater.* 3 (2015) 424–430. <https://doi.org/10.1002/adom.201400511>.
- [276] Y.-K. Su, Y.-M. Peng, R.-Y. Yang, J.-L. Chen, Effects of NaCl flux on microstructure and luminescent characteristics of $\text{KSrPO}_4:\text{Eu}^{2+}$ phosphors, *Opt. Mater. (Amst)*. 34 (2012) 1598–1602. <https://doi.org/10.1016/j.optmat.2012.03.019>.
- [277] R. Yu, H. Mi Noh, B.K. Moon, B.C. Choi, J.H. Jeong, K. Jang, H.S. Lee, S.S. Yi, Enhanced photoluminescence of $\text{BaAl}_2\text{S}_4:\text{Eu}^{2+}$ phosphor by Mg^{2+} ions doping, *Ceram. Int.* 39 (2013) 9709–9713. <https://doi.org/10.1016/j.ceramint.2013.04.041>.
- [278] H. Wang, Y. Liu, X. Zhu, L. Wei, X. Jiang, Y. Chen, L. Li, Preparation of $\text{CaAlSiN}_3:\text{Eu}^{2+}$ red-emitting phosphor by a two-step method for solid-state lighting applications, *Ceram. Int.* 46 (2020) 23035–23040. <https://doi.org/10.1016/j.ceramint.2020.06.080>.
- [279] D.S. Jo, Y. Luo, K. Senthil, K. Toda, B.S. Kim, T. Masaki, D.H. Yoon, Synthesis and photoluminescence properties of new $\text{NaAlSiO}_4:\text{Eu}^{2+}$ phosphors for near-UV white LED applications, *Opt. Mater. (Amst)*. 34 (2012) 696–699. <https://doi.org/10.1016/j.optmat.2011.10.004>.
- [280] J. Long, F. Chu, Y. Wang, C. Zhao, W. Dong, X. Yuan, C. Ma, Z. Wen, R. Ma, M. Du, Y. Cao, $\text{M}_8\text{MgSc}(\text{PO}_4)_7 : x \text{Dy}^{3+}$ ($\text{M} = \text{Ca/Sr}$) Single-Phase Full-Color Phosphor with High Thermal Emission Stability, *Inorg. Chem.* 56 (2017) 10381–10386. <https://doi.org/10.1021/acs.inorgchem.7b01268>.
- [281] X. Sun, Z. Huang, X. Fu, L. Xu, K. Liu, H. Yuan, Generation of warm white light by doping Sm^{3+} in $\text{Ca}_3\text{TeO}_6:\text{Dy}^{3+}$ fluorescent powders, *Ceram. Int.* 46 (2020) 14252–14256. <https://doi.org/10.1016/j.ceramint.2020.02.058>.

- [282] B. Mu, J. Huang, R. Song, Y. Dong, B. Qi, Optical analysis of $\text{Dy}^{3+}/\text{Sm}^{3+}$ co-doped $\text{NaY}(\text{MoO}_4)_2$ phosphors for warm white LED, *J. Alloys Compd.* 945 (2023) 168916. <https://doi.org/10.1016/j.jallcom.2023.168916>.
- [283] G. Ouertani, K. Maciejewska, W. Piotrowski, K. Horchani-Naifer, L. Marciniak, M. Ferhi, High thermal stability of warm white emitting single phase GdPO_4 : $\text{Dy}^{3+}/\text{Sm}^{3+}$ phosphor for UV excited wLEDs, *J. Lumin.* 265 (2024) 120228. <https://doi.org/10.1016/j.jlumin.2023.120228>.
- [284] M. Vijayakumar, K. Marimuthu, Effective role of Co-dopants (Dy^{3+} , Sm^{3+}) on Tunable multicolour emission of Tb^{3+} doped telluroborate glasses for Natural White light applications, *J. Non. Cryst. Solids.* 620 (2023) 122591. <https://doi.org/10.1016/j.jnoncrysol.2023.122591>.
- [285] E. Malchukova, RE-codoping effect on emission ability of Sm,Gd- and Sm,Eu-codoped complex borosilicate glasses, *Mater. Res. Bull.* 152 (2022) 111847. <https://doi.org/10.1016/j.materresbull.2022.111847>.
- [286] Y. Shi, R. Cui, X. Liu, L. Yang, Y. Li, J. Zhang, C. Deng, Ca_2YNbO_6 : Dy^{3+} , $\text{Sm}^{3+}/\text{Eu}^{3+}$ warm white phosphors with tunable light color and FIR optical temperature measurement characteristics, *Opt. Mater. (Amst.)* 136 (2023). <https://doi.org/10.1016/j.optmat.2023.113495>.
- [287] W.T. Carnall, P.R. Fields, K. Rajnak, Spectral Intensities of the Trivalent Lanthanides and Actinides in Solution. II. Pm^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , and Ho^{3+} , *J. Chem. Phys.* 49 (1968) 4412–4423. <https://doi.org/10.1063/1.1669892>.
- [288] V. Bachmann, C. Ronda, A. Meijerink, Temperature Quenching of Yellow Ce^{3+} Luminescence in $\text{YAG}:\text{Ce}$, *Chem. Mater.* 21 (2009) 2077–2084. <https://doi.org/10.1021/cm8030768>.
- [289] F. Xu, X. Zhou, H. Xia, H. Song, B. Chen, Highly thermally stable $\text{Dy}^{3+}/\text{Sm}^{3+}$ co-doped $\text{Na}_5\text{Y}_9\text{F}_{32}$ single crystals for warm white LED, *J. Phys. Chem. Solids.* 158 (2021) 110240. <https://doi.org/10.1016/j.jpcs.2021.110240>.
- [290] S. Fu, L. Tian, Tunable cool to warm white emission in $\text{Ca}_{1-x}\text{La}_{2x/3}\text{TiO}_3$ coped with Dy^{3+} and Sm^{3+} for white LED application, *Optik (Stuttg.)* 219 (2020) 165305. <https://doi.org/10.1016/j.ijleo.2020.165305>.
- [291] S. Liu, S. Liu, J. Wang, P. Sun, Y. Zhong, J.H. Jeong, B. Deng, R. Yu, Preparation and investigation of Dy^{3+} -doped $\text{Ca}_9\text{LiGd}_{2/3}(\text{PO}_4)_7$ single-phase full-color phosphor, *Mater. Res. Bull.* 108 (2018) 275–280. <https://doi.org/10.1016/j.materresbull.2018.08.026>.
- [292] Z. Min, Q. Zeng, S. Chen, Y. Qin, C. Yao, Tunable photoluminescence of LiNbO_3 : RE^{3+} ($\text{RE}^{3+} = \text{Dy}^{3+}$, Sm^{3+} , $\text{Dy}^{3+}/\text{Sm}^{3+}$) single-phase phosphors for warm white LEDs, *J. Alloys Compd.* 924 (2022) 166497. <https://doi.org/10.1016/j.jallcom.2022.166497>.
- [293] C. Chen, C. Yu, F. Xu, Q. Li, Y. Zhang, High energy transfer in $\text{Dy}^{3+}/\text{Sm}^{3+}$ co-doped transparent borosilicate glass-ceramics containing novel $\text{Na}_5\text{Y}_9\text{F}_{32}$ nanocrystals for w-LEDs applications, *Ceram. Int.* 47 (2021) 1–9. <https://doi.org/10.1016/j.ceramint.2020.08.190>.
- [294] Q. Li, S. Zhang, W. Lin, W. Li, Y. Li, Z. Mu, F. Wu, A warm white emission of $\text{Bi}^{3+}\text{-Eu}^{3+}$ and $\text{Bi}^{3+}\text{-Sm}^{3+}$ codoping $\text{Lu}_2\text{Ge}_2\text{O}_7$ phosphors by energy transfer of Bi^{3+} -sensitized $\text{Eu}^{3+}/\text{Sm}^{3+}$, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 228 (2020) 117755. <https://doi.org/10.1016/j.saa.2019.117755>.



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Education

Program	Institution	Division	Year
<i>Doctorate of Philosophy</i> (Ph.D.) (Applied Physics)	Delhi Technological University	-	Submitted
<i>Masters of Science</i> (M.Sc.) (Physics)	Kurukshetra University	First with Distinction	2017
<i>Bachelor of Science (B.Sc.)</i> (Physics, Chemistry, Mathematics)	Kurukshetra University	First	2015

National/State level Achievements

- Qualified CSIR-UGC NET-JRF Physical Sciences (Dec. 2018)
- Qualified GATE Physical Sciences (2018)

Awards/Honors

- **BEST STUDENT PAPER AWARD** for the paper “**Structural and luminescent properties of dysprosium ions-doped tungstate phosphor for w-LEDs [12584-43]**” presented at Smart Materials for Opto-Electronic Applications in SPIE Optics and Optoelectronics Conference 24th -27th April 2023 Prague, Czech Republic.
- Received two consecutive **Commendable Research Awards** in 2023 & 2024, from Delhi Technological University, Delhi, India.

- **Best oral presentation award** in “1st International Conference on Advances in Materials Science (ICAMS-2021)” held during 22nd-24th September 2021, organized by Department of Physics, School of Applied Sciences, REVA University, Bangalore, India.

Research Publications/Patents:

2020- till date

(International Journal: 24 /Conference Proceeding: 01/ Patent: 01)

- **Optics & Laser Technology: 01 (I.F. = 4.6)**
- **Journal of Luminescence: 02 (I.F. = 3.3)**
- **Sensors & Actuators: A. Physical: 01 (I.F. = 4.1)**
- **Ceramic International: 01 (I.F. = 5.1)**
- **Emergent Materials: 01 (I.F. = 4.8)**
- **Optical Materials: 04 (I.F. = 3.8)**
- **RSC Advances: 01 (I.F. = 3.9)**
- **Journal of Non-Crystalline Solids: 04 (I.F. = 3.2)**
- **Journal of Physics D: Applied Physics: 01 (I.F. = 3.1)**
- **Journal of Material Science: Materials in Electronics: 03 (I.F. = 2.8)**
- **Journal of Fluorescence: 03 (I.F. = 2.6)**
- **Materials Letters: X: 01 (I.F. = 2.2)**
- **Luminescence: 01 (I.F. = 3.2)**
- **Indian Patent (Govt. of India): 01 (364481)**

International/National Conferences:

2020 - till date

- Presentation in National/International Conferences/workshops: **05 (03 oral, 02 poster)**
- Participated in National/International Conferences/workshops: **18**

Publications:

- [1] **Anu**, A.S. Rao, Temperature sensing materials based on the fluorescence intensity ratio in $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Dy}^{3+}$ phosphors, Sensors & Actuators: A. Physical, 372 (2024) 115336, <https://doi.org/10.1016/j.sna.2024.115336>
- [2] **Anu**, Sheetal Kumari, Nisha Deopa and A S Rao, Spectral studies of thermally stable $\text{Dy}^{3+}/\text{Sm}^{3+}$ co-doped $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$ phosphors for warm white LEDs, Journal of Physics D: Applied Physics, 57 (2024) 315107 (14pp), DOI 10.1088/1361-6463/ad4566

-
- [3] **Anu**, A.S. Rao, Novel orange-red-emitting $\text{Li}_2\text{Ba}_5(\text{WO}_5)_3\text{Eu}^{3+}$ phosphor for w-LEDs and non-contact thermometry applications, *Journal of Materials Science: Materials in Electronics*, 34 (2023) 2191, <https://doi.org/10.1007/s10854-023-11602-4>
- [4] **Anu**, A.S. Rao, Luminescence and optical thermometry strategy based on emission spectra of $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Pr}^{3+}$ phosphors, *Optical Materials*, 145 (2023) 114476, <https://doi.org/10.1016/j.optmat.2023.114476>
- [5] **Anu**, A.S. Rao, Synthesis, Structural and Fluorescence Investigations of Novel $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Sm}^{3+}$ Phosphors for Photonic Device Applications, *Journal of Fluorescence*, 34 (2024) 2391–2403, <https://doi.org/10.1007/s10895-023-03449-z>.
- [6] **Anu**, Seema, A. Kumar, Nisha Deopa, Mukesh K. Sahu, Aman Prasad, A.S. Rao, A single phase $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphor for color tunable devices and non-contact optical thermometry, *Journal of Luminescence*, 269 (2024) 120444, <https://doi.org/10.1016/j.jlumin.2024.120444>
- [7] **Anu**, A. Kumar, Ravina, N. Deopa, A.S. Rao, Efficient tunable photoluminescence of $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped OFSZBS glasses for warm white LEDs, *Journal of Non-Crystalline Solids*, 616 (2023) 122421, <https://doi.org/10.1016/j.jnoncrysol.2023.122421>
- [8] **Anu**, Nisha Deopa, A.S. Rao, Structural and luminescence characteristics of thermally stable Dy^{3+} doped oxyfluoride strontium zinc borosilicate glasses for photonic device applications, *Optics & Laser Technology*, 154 (2022) 108328, <https://doi.org/10.1016/j.optlastec.2022.108328>
- [9] Amit Kumar, **Anu**, Ravina Lohan, Usha Rani, Isha Malik, Nisha Deopa, A.S. Rao, Anand Kumar, Dysprosium Ion Concentration Variations and their Comprehensive Influence on the Physical, Structural and Optical Properties of Multi-Component Borate Glasses for Luminescence Tailoring, *Ceramics International*, <https://doi.org/10.1016/j.ceramint.2024.10.123>
- [10] Ravina, Kanishk Poria, M.K. Sahu, A. Kumar, **Anu**, Sajjan Dahiya, Nisha Deopa and A. S. Rao, Energy transfer mechanisms and color-tunable luminescence of $\text{Tm}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped $\text{Sr}_4\text{Nb}_2\text{O}_9$ phosphors for high-quality white light-emitting diodes, *RSC Advances*, 13 (2023) 33675, DOI: 10.1039/d3ra05519a.

-
- [11] Ravita, Aman Prasad, Pooja Rohilla, Rajat Bajaj, **Anu**, Rajesh Punia, A.S. Rao, Luminescence Studies on Dy³⁺ Doped Calcium Aluminum Borosilicate (CABS) Glasses for White Light Emission and Applications in w-LEDs, *Journal of Fluorescence* 34 (2024) 1783–1792, <https://doi.org/10.1007/s10895-023-03389-8>
- [12] Amit Kumar, Ravina, **Anu**, V. Kumar, Nisha Deopa, R. Punia, A.S. Rao, Epoxy free LED devices: Physical and optical examination of praseodymium doped borate glasses for enhanced performance, *Materials Letters: X* 19 (2023) 100210, <https://doi.org/10.1016/j.mlblux.2023.100210>
- [13] Vibha Sharma, Shreya Maurya, **Anu**, Aman Prasad, A.S. Rao, Structural, optical, and luminescence properties of Dy³⁺-activated potassium calcium silicate phosphor for white light-emitting diodes, *Luminescence* (2023) 1–11, DOI: 10.1002/bio.4544.
- [14] Manjeet, A. Kumar, **Anu**, Ravina Lohan, Nisha Deopa, Anand Kumar, R.P. Chahal, S. Dahiya, R. Punia, A.S. Rao, Impact of Sm³⁺ ions on structural, thermal, optical and photoluminescence properties of ZnO-Na₂O-PbO-B₂O₃ glasses for optoelectronics device applications, *Optical Materials*, 139 (2023) 113778, <https://doi.org/10.1016/j.optmat.2023.113778>
- [15] Sheetal Kumari, **Anu**, Aman Prasad, Pooja Rohilla, and A.S. Rao, Prospective applications of thermally stable Dy³⁺ doped potassium zinc strontium borate (KZSB) glasses in w-LEDs, *Journal of Materials Science: Materials in Electronics* 34 (2023) 907, <https://doi.org/10.1007/s10854-023-10272-6>
- [16] A.V.S. Yeswanth, Ib Singh Deo, **Anu**, A.S. Rao, G. Vijaya Prakash, Down-conversion and up-conversion photoluminescence studies of Er³⁺ doped calcium zinc borosilicate glass for optical fiber amplifiers, *Journal of Non-Crystalline Solids*, 609 (2023) 122280, <https://doi.org/10.1016/j.jnoncrysol.2023.122280>
- [17] Ravina Lohan, A. Kumar, Mukesh K. Sahu, **Anu**, V. Kumar, Nisha Deopa, and A.S. Rao, Structural, thermal, and luminescence kinetics of Sr₄Nb₂O₉ phosphor doped with Dy³⁺ ions for cool w-LED applications *Journal of Materials Science: Materials in Electronics*, 34 (2023) 694, <https://doi.org/10.1007/s10854-023-10055-z>
- [18] Vidhi, Ankita, **Anu**, A.S. Rao, Spectroscopic characterizations of Dy³⁺ ions doped phosphate glasses for epoxy-free white LED applications, *Optical Materials*, 132 (2022) 112863, <https://doi.org/10.1016/j.optmat.2022.112863>

-
- [19] Manjeet, A. Kumar, **Anu**, Ravina, Nisha Deopa, Anand Kumar, R.P. Chahal, S. Dahiya, R. Punia, A.S. Rao, Structural, thermal, optical and luminescence properties of Dy³⁺ ions doped Zinc Potassium Alumino Borate glasses for optoelectronics applications, *Journal of Non-Crystalline Solids*, 588 (2022) 121613, <https://doi.org/10.1016/j.jnoncrysol.2022.121613>
- [20] A. Kumar, **Anu**, M.K. Sahu, Ravita, S. Dahiya, Nisha Deopa, Anand Malik, R. Punia, A.S. Rao, Spectral characteristics of Tb³⁺ doped ZnF₂-K₂O-Al₂O₃-B₂O₃ glasses for epoxy free tricolor w-LEDs and visible green laser applications, *Journal of Luminescence*, 244 (2022) 118676, <https://doi.org/10.1016/j.jlumin.2021.118676>
- [21] Sanju, Ravina, **Anu**, A. Kumar, V. Kumar, M.K. Sahu, S. Dahiya, N. Deopa, R. Punia, A.S. Rao, Physical, structural and optical characterization of Dy³⁺ doped ZnF₂-WO₂-B₂O₃-TeO₂ glasses for opto-communication applications, *Optical Materials*, 114 (2021) 110937, <https://doi.org/10.1016/j.optmat.2021.110937>
- [22] Poonam, Shivani, **Anu**, A. Kumar, M.K. Sahu, P.R. Rani, Nisha Deopa, R. Punia, A.S. Rao, Judd-Ofelt Parameterization and Luminescence Characterization of Dy³⁺ Doped Oxyfluoride Lithium Zinc Borosilicate Glasses for Lasers and w-LEDs, *Journal of Non-Crystalline Solids*, 544 (2020) 120187, <https://doi.org/10.1016/j.jnoncrysol.2020.120187>
- [23] **Anu.**, Nisha Deopa, A.S. Rao, " Structural and luminescent properties of dysprosium ions-doped tungstate phosphor for w-LEDs," *Proc. SPIE 12584, Smart Materials for Opto-Electronic Applications*, 125840H (9 June 2023), [doi:10.1117/12.2669275](https://doi.org/10.1117/12.2669275).
- [24] Gaurank Yadav, Jatin Parashar, **Anu**, Aman Prasad, A.S. Rao, Synthesis, Structural and photoluminescence characteristics of Dy³⁺/Eu³⁺ co-doped CaGdSbWO₈ phosphor for warm white LEDs, *Emergent Materials* (Accepted).
- [25] Jatin Parashar, Gaurank Yadav, Seema, **Anu**, Aman Prasad, AS Rao, Energy Transfer Studies on red emitting CaGdSbWO₈: Sm³⁺/Eu³⁺ phosphor for w-LEDs and indoor plant growth lighting system, *Journal of Fluorescence* (Accepted).

Workshops/Seminars/Conferences

Oral/Poster Presentations:

1. Poster presentation titled "A comparative study of the photoluminescence properties of Dy^{3+} , Sm^{3+} and Eu^{3+} ions doped tungstate phosphors" in International Conference on Atomic, Molecular, Material, Nano and Optical Physics with Applications (ICAMNOP-2023) held at Delhi Technological University, Delhi, India during 20th -22nd December, 2023.
2. Oral presentation titled "**Photoluminescence studies of Samarium ions doped tungstate phosphors for wLEDs**" in 1st International Conference On Spectroscopy In Materials Science (ICOSIMS-2023) virtually during 20th-22nd June 2023 organized by department of Physics, University of Aveiro, Portugal.
3. Poster presentation titled "**Structural and luminescent properties of dysprosium ions-doped tungstate phosphor for w-LEDs**" in SPIE Optics and Optoelectronics Conference held from 24th-27th April 2023 in Prague, Czech Republic.
4. Oral presentation titled "**Photoluminescence characterization of Dy^{3+} doped Borosilicate glasses for W-LEDs**" in 1st International Conference on Advances in Materials Science (ICAMS-2021) held during 22nd-24th September 2021, organized by Department of Physics, School of Applied Sciences, REVA University, Bangalore, INDIA.
5. Oral presentation titled "**Judd-Ofelt Parameterization and Luminescence Characterization of Dy^{3+} Doped Oxyfluoride Lithium Zinc Borosilicate Glasses for Lasers and w-LEDs**" in International Symposium on Materials Science and Innovation for Sustainable Society from 26th-27th August, 2020 organized by Nanomaterial Research Center, Meijo University, DCT's Dhempe College of Arts & Science and Government College of Arts, Science and Commerce, Khandola, under Cluster of Colleges for Research in Chemistry Goa.

Successful Participation:

1. Attended One Day National Seminar on "RECENT ADVANCEMENTS IN SEMICONDUCTOR DEVICES AND MATERIALS (RASDM-2023)" organized by Department of Applied Physics, Delhi Technological University (DTU) on January 30, 2023.

2. Successfully completed the seven-day advanced instrumentation workshop “Advanced Characterization Techniques In Condensed Matter” (17th -23rd January, 2023) conducted by Birla Institute of Technology and Science, Pilani in association with Amity University under the auspices of Department of Science and Technology (DST) Government of India under STUTI.
3. Successfully completed the seven-day workshop “Techniques for Advance Materials Characterization and Spectroscopy” (10th -16th November, 2022) conducted by School of Physical Sciences, Jawaharlal Nehru University, New Delhi in association with Amity University under the auspices of Department of Science and Technology (DST) Government of India under STUTI.
4. Participated in IP Awareness/Training program under National Intellectual Property Awareness Mission on July 26,2022 organized by Intellectual Property Office, India.
5. Participated in e-workshop on Role of Traceable PMU in Smart Grids” held at CSIR National Physical Laboratory, New Delhi on 29th March 2022.
6. Attending webinar on "Luminescence Spectroscopy" conducted on 4th February 2022 organized by Department of Physics, Shri Ramdeobaba College of Engineering and Management (RCOEM), Nagpur, India.
7. Participated in the TENSYS2021 from 21st-22nd December 2021 International Workshop on Energy Technology and Sensor Systems TENSYS-2021 organized by UNIVERSITI MALAYA and HITD&M.
8. Successfully participating in one day expert talk on the occasion of "National Energy Conservation Day" organized by Centre for Energy and Environment, in association with Institute Innovation Council, Delhi Technological University, Delhi, India -110042 on 14th December, 2021.
9. Participating in "One-Day webinar on National Education Day organized by Human Resource Development Centre, Delhi Technological University in association with Institution Innovation Council- DTU and DTU-Innovation and Incubation Foundation held on 11th November 2021.
10. Attended the webinar “Structured light in Material Science” organized jointly by OSA and SPIE student chapter Manipal University and OSA student chapter MNIT Jaipur, Jaipur, India on 20th August, 2021 in Webinar Series-"Optics & Photonics: A leap for the future".
11. Participated in the online workshop “Innovation, Ecosystem and Incubation” conducted on 28th July, 2021 organized by THE NEW COLLEGE (AUTONOMOUS) Peters Road, Royapettah, Chennai -600014, India.

12. Participated in one day International Webinar on "Recent Advances in Materials Science and Technology (RAMST)" conducted jointly by Departments of Physics and Chemistry under IQAC on 12th July 2021, to pay Special tribute to Prof. J. Lakshmana Rao, Former Professor, Dept. of Physics, Sri Venkateswara University, Tirupati, A.P., India, on his 75th Birth anniversary.
13. Participated successfully in the one-day E-Workshop on "Orientation Session for All Students & Faculties of Institute by Innovation Ambassador" organized by the Department of Applied Physics, Delhi Technological University on 29th June, 2021.
14. National Webinar cum Workshop "LUMINESCENCE APPLICATIONS AND MATERIALS" conducted on 25th June, 2021 organized by LUMINESCENCE SOCIETY OF INDIA Gujarat, INDIA in collaboration with SSN COLLEGE OF ENGINEERING Kalavakkam, Tamilnadu, India.
15. Participated & completed successfully Online QIP Short Term Course on Advances in energy and functional materials from 14th-26th June 2021 at School of Minerals Metallurgical and Materials Engineering, Indian Institute of Technology Bhubaneswar.
16. Participated in Two Days National Seminar on "Nanomaterials: Fundamentals & Applications" (23rd-24th May, 2021) organized by Department of Physics through online mode.
17. Participated in the webinar on "Characterization Techniques for Smart Materials" on 15th-16th January, 2021 organized by Department of Physics, College of Basic Sciences and Humanities, CCS Haryana Agricultural University, Hisar, Haryana, India.
18. Participated in International Summit on Quality Indices in Higher Education - 2020, held during 6th -7th November, 2020 at Delhi. Technological University, Delhi.

Academic/Research Experience

- Worked as Assistant Professor in Department of Physics in CRSU, Jind Haryana from 2019-20.
- Worked as Assistant Professor in Department of Applied Physics in DCRUST, Murthal, Haryana in 2019.
- Worked as Assistant Professor in Department of Physics in Indus Degree College, Jind, Haryana from 2018-19.

- Worked as a member of student organizing committee of the "International Conference on Atomic, Molecular, Material, Nano and Optical Physics with Applications (ICAMNOP-2023)" held at Delhi Technological University, Delhi, India during 20th-22nd December, 2023.
- Worked as Research Scholar Faculty in B.Tech. Labs from Jan. 2021 to till date.

Technical Skills

- **Operating System:** Windows
- **Tools:** Microsoft Office
- **Software Skill:**
 - Origin
 - Mendeley
 - VESTA software
 - X'pert Highscore
- **Instruments handling capability in:**
 - High temperature Muffle Furnace
 - UV-Vis-NIR spectrophotometer of JASCO model V-770
 - JASCO FP-8300 spectrofluorometer
 - Bruker Model D8 Advance XRD instrument
 - Electronic analytical balance
 - FLAME-S-XR1-ES having an ocean optics spectrometer

Others

- **Hobbies:** Travelling, Cricket, Meditation, Badminton
- **Languages:** English, Hindi

Declaration

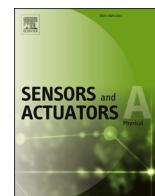
I do hereby declare that all the details furnished above are true to the best of my knowledge and belief.

Place: Delhi, (India)

Date:

(Anu)

Publications in Refereed International Journals
(Thesis)



Temperature sensing materials based on the fluorescence intensity ratio in $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Dy}^{3+}$ phosphors

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ABSTRACT

One of the interesting uses of phosphors is the development of non-contact thermometers apart from their usage as visible photonic devices. A series of Dy^{3+} -doped $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$ (LBW) phosphors were successfully synthesized using high temperature solid-state reaction process. The crystal structure and morphology of $\text{LBW}:\text{x}\text{Dy}^{3+}$ phosphors were studied using X-ray diffraction (XRD), Rietveld refinements and field effect scanning electron microscopy (FE-SEM) with energy dispersive x-ray (EDX) analysis. The XRD and photoluminescence (PL) analyses validated the effective substitution of Ba^{2+} ions with Dy^{3+} ions. Two prominent emission peaks were found at 493 and 583 nm corresponding to $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transitions respectively under 368 nm excitation wavelength. A comprehensive analysis has been carried out on the usage of the Dy^{3+} doped LBW phosphors in fluorescence intensity ratio (FIR) thermometry. The optical temperature measurement performance of the $\text{LBW}:\text{x}\text{Dy}^{3+}$ phosphor was achieved by utilizing distinct thermal quenching transitions, specifically on $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2,13/2}$, at temperatures ranging from 293 to 443 K. The as-prepared phosphors demonstrate excellent performance as optical thermometers, with a maximum relative sensitivity (S_r) of $0.7\% \text{ K}^{-1}$ at 293 K, an absolute sensitivity (S_a) of 4.68 K^{-1} at 443 K and a temperature resolution of ~ 0.51 at 443 K. These values indicate that the phosphors are highly responsive to changes in temperature, making them suitable for non-contact thermometry applications.

1. Introduction

Researchers have been motivated to enhance the properties of phosphors due to the continual increase in demand and the wide range of uses for luminous materials. These luminous materials are used in a variety of industries, including sensing, solid-state lighting, lasers, sophisticated displays, optical storage, display fields, OLEDs and many more [1–4]. Since temperature is a critical and fundamental characteristic used to characterize biological, chemical, and physical processes, one of the main uses of photonic devices is to sense real-time temperature with great accuracy [5,6]. Also, with the advancement of science and technology, biological imaging and large-scale integrated circuits (LSI) created new demands for temperature measurement tolerance, high spatial resolution and remote detection [7]. Currently, there are two types of temperature measurement technologies, one is common contact temperature dimensions and another is non-contact temperature sizes. Yet, in some unique circumstances such as electromagnetically or thermally demanding areas and organisms, using thermocouples [8] and glass liquid thermometers, the conventional contact temperature

measurements are carried out [9]. The usage of contact temperature measuring instruments is challenging by virtue of the condition of contact. Therefore, the study of non-contact thermometers is very important not only from the point of view of non-contact but also from financial viability. Non-contact phosphor thermometers have been a focus of research in the field of temperature measurement because of their assets such as great selectivity, high accuracy, sensitivity and prolonged lifetime [10,11]. Further, non-contact thermometers, compared to conventional contact thermometers, are better suited to measure the temperature of inaccessible objects in environments with strong electromagnetic fields, high pressures, or corrosive conditions with high precision, high sensitivity, and a large relevant temperature range [8,12,13]. The investigation of non-contact optical thermometers has also received a great deal of attention since they have the potential to solve the shortcomings of standard thermometers, such as their slow response time and imprecision. One of the most sophisticated methods for measuring surface temperature is phosphor thermometry, which makes use of the photoluminescence properties of materials with rare earth and transition metal inclusions in both crystalline and amorphous

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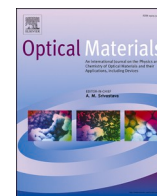
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Research Article

Luminescence and optical thermometry strategy based on emission spectra of $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Pr}^{3+}$ phosphors

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ABSTRACT

In this study, a series of Pr^{3+} ions doped Lithium Barium Tungstate ($\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$) was synthesized using the conventional high-temperature solid state method. The structure and phase of the phosphors were analysed using X-ray diffraction (XRD) patterns. Fourier Transform Infrared (FT-IR) spectroscopy was used to examine the different vibrational bands present. The optical band gap values of the optimized LBW phosphor and the undoped LBW sample were measured using diffuse reflectance spectra (DRS). Under 319 nm excitation, the photoluminescence (PL) spectra of the Pr^{3+} -activated LBW phosphor exhibited strong visible blue and reddish emissions at 488 nm and 647 nm respectively corresponding to the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ and $^3\text{F}_2$ transitions of the Pr^{3+} ions. The evaluated CIE color chromaticity coordinates of the as-prepared $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Pr}^{3+}$ phosphors lie within the white region. The temperature-dependent PL (TDPL) measurement demonstrated relatively good thermal stability for the synthesized phosphor. Moreover, the fluorescence intensity ratio (FIR) was used to analyze the optical sensing properties of the $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Pr}^{3+}$ phosphor. A maximum relative sensitivity (S_r) of 1.03 % K^{-1} indicated the potential of these phosphors for optical thermometry applications. A double exponential trend with decreasing lifetime was observed in the PL decay data at 647 nm emission (λ_{em}) under 319 nm excitation (λ_{ex}), with an increase in the Pr^{3+} ions concentration in the host matrix. In conclusion, the investigations conducted demonstrate that the Pr^{3+} ions doped LBW phosphors show great potential for applications in solid-state lighting and optical thermometry. Its emission characteristics, thermal stability, and optical sensing capabilities establish it as a suitable candidate for these applications.

1. Introduction

White light-emitting diodes (w-LEDs) are being recognised as a highly promising alternative to conventional incandescent and fluorescent lamps, as well as backlights. This is due to their notable advantages such as high efficiency, extended lifespan, low energy consumption, and environmentally-friendly features [1]. The most common method of producing white LEDs is by combining a blue-emitting InGaN-based LED chip with a yellow-emitting $(\text{Y,Gd})_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) phosphor, which emits yellow light. However, there are several challenges associated with these white LEDs. These challenges include a low color-rendering index (CRI), which affects the ability to accurately reproduce colors, as well as difficulties in achieving consistent color reproduction and low luminous efficiency [2]. An alternative method to create white LEDs is by using near-UV (360–410 nm) InGaN-based LEDs to excite tricolour phosphors consisting of blue, green, and red components. This approach has the potential to achieve superior color

rendering properties. However, when it comes to red phosphors activated by Eu^{3+} ions, there are still certain drawbacks. These include lower luminous efficiency and a reduced color rendering index, which can affect the overall performance of white LED lighting systems [3–5]. Investigating new red-emitting phosphors with high efficacy, outstanding color purity, and efficient absorption in the blue or UV regions is therefore urgently needed. In comparison to other phosphors, oxide-based phosphors stand out for their superior chemical stability, broad UV absorption, and resistance to moisture. These characteristics make them particularly important in solid-state lighting. They have numerous uses in a variety of industries, such as the production of white light LEDs, field emission display panels, and plasma display devices [6–8]. Tungstates form a part of widely recognised inorganic materials that hold immense potential for applications across various fields [9]. Because of their unique structure and desirable qualities, such as strong covalent bonds, high stability, and intense visual luminescence, tungstates have been recognised as suitable host material for luminescence

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Synthesis, Structural and Fluorescence Investigations of Novel $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Sm}^{3+}$ Phosphors for Photonic Device Applications

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Abstract

In the current study, Sm^{3+} ions doped Lithium Barium Tungstate ($\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$) (LBW) phosphors with the ability to emit orange-red light were made using the traditional high-temperature solid-state reaction technique. The structure and phase of the as-synthesized phosphor samples were examined via X-ray diffraction (XRD) patterns. The diffraction peaks of the undoped LBW and Sm^{3+} ions doped LBW phosphors closely resemble those of the Joint Committee on Powder Diffraction Standards (JCPDS) pattern with card number 01–072–1717. Scanning electron microscopy (SEM) was employed for the analysis of the morphological characteristics of the synthesized phosphor material. Fourier Transform Infrared (FT-IR) spectroscopy was used to study several vibrational and molecular bands present in the host matrix. Using diffuse reflectance spectra (DRS), the optical band gap values (E_g) were evaluated by applying Tauc's method. The photoluminescence (PL) spectra characteristics at $\lambda_{\text{ex}} = 336$ nm indicate the emission of dopant ions (Sm^{3+}) in the deep orange-red region corresponding to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ transition (at 581 nm) with concentration quenching after 2 mol % of Sm^{3+} ions. Using the PL spectra, the CIE chromaticity coordinates of LBWS2.0 phosphor were estimated and found in the deep visible orange-red area, indicating the potential use of the prepared phosphor material for phosphor-converted white light emitting diodes (w-LEDs) applications. Double exponential behaviour can be seen in the PL decay spectral profiles obtained under $\lambda_{\text{em}} = 581$ nm and $\lambda_{\text{ex}} = 336$ nm. The experimental lifetimes (τ_{exp}) decrease as the concentration of Sm^{3+} ions rise. The temperature-dependent PL (TDPL) and activation energy results show that the as-synthesized phosphor has considerably superior thermal stability. The results of the current research contemplate us the applicability of Sm^{3+} ions doped LBW phosphor for photonic devices such as w-LEDs.

Keywords Sm^{3+} · Rietveld, scanning electron microscopy (SEM) · Bi-exponential · TDPL

Introduction

White light-emitting diodes (w-LEDs) have taken the position of traditional lighting devices in the SSL industry due to their superior qualities, especially extended durability, great brightness, sustainability, and low power consumption [1, 2]. Commercial w-LEDs built on a InGaN chip with a $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) phosphor have high correlated colour temperatures (CCT) and poor colour rendering indices (R_a) due to the lack of red element in the visible light region, which restricts their further growth [3, 4]. Another alternate technique for creating w-LEDs involves coating

an InGaN chip with trichromatic phosphors (phosphors that emit blue, green, and red light). Excellent red phosphors like nitride are produced under extreme conditions (high pressures and high temperatures). To address the demand for high-performance w-LEDs, it is crucial to create red-emitting phosphors that can be efficiently activated by ultraviolet (UV) or near ultraviolet (n-UV) light. Rare-earth (RE) ions are renowned for their exceptional efficacy as dopant ions within host lattices. The role of RE ions in visible luminescence is crucial because of f-f transitions. These f-f transitions lead to luminous sharp emission when RE ions are introduced as a dopant to an appropriate crystal lattice [5–8]. Furthermore, these RE ions are easily energized by UV/n-UV radiation absorption, which results in the down-conversion process releasing light in the visible area. Among all the RE activator ions, Sm^{3+} ions stand out as highly effective and radiation-stable candidates, proficiently emitting red or

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Novel orange-red-emitting $\text{Li}_2\text{Ba}_5(\text{WO}_5)_3:\text{Eu}^{3+}$ phosphor for w-LEDs and non-contact thermometry applications

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ABSTRACT

Novel Eu^{3+} -activated orange-red phosphors $\text{Li}_2\text{Ba}_{(5-x)}(\text{WO}_5)_3:\text{xEu}^{3+}$ (LBW: xEu^{3+}) (here, $1 \leq x \leq 9$, $\Delta x = 2$, and x is the mol%) were successfully prepared via high-temperature solid-phase reaction. The X-ray diffraction (XRD) patterns were recorded for structural analysis and phase identification of the synthesized phosphors. Morphological analysis was done using scanning electron microscopy (SEM). The optical bandgap value has been measured using diffuse reflectance spectra (DRS). The photoluminescence (PL) emission spectra recorded for the LBW: xEu^{3+} phosphors under 322 and 396 nm excitation reveal strong visible orange-red emission at 595 nm corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition of Eu^{3+} ions. The CIE chromaticity coordinates were estimated for all the phosphors and were found to be in the deep orange-red region. The PL decay spectral profiles recorded at 595 nm emission when excited with 322 nm light showed a consistent exponential pattern. The experimental lifetimes were observed to decrease as the concentration of Eu^{3+} ions increased. In order to study the luminescence intensity ratio (LIR) of the paired emissions lines of Eu^{3+} as a function of temperature, PL measurements were carried out in the temperature range of 298–448 K. With a maximum sensitivity of nearly $1.21\% \text{ K}^{-1}$ at 298 K, the synthesized phosphors are relatively more sensitive at low temperatures. The aforementioned results represent that the synthesized LBW: Eu^{3+} phosphor samples can be employed in non-contact optical thermometry as well as in w-LED applications.

1 Introduction

Phosphors are substances which absorb energy and then release it as UV, visible, or IR light. They are made up of an inorganic host that has been doped with activator ions; these ions are usually found in transition metals or rare earths (RE). RE-doped phosphors in particular are significant materials with numerous

applications in artificial lighting, X-ray medical radiography, display technology, and high-power solid-state lasers [1]. Phosphor thermometry is a non-contact method for measuring temperature remotely using light signals. Thermographic phosphors (TGP) are phosphors created especially for phosphor thermometry. TGP are resistant to oxidation in high-temperature situations and do not react with harsh chemicals,

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Full Length Article

A single phase $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphor for color tunable devices and non-contact optical thermometryAnu^a, Seema^{a,b}, A. Kumar^c, Nisha Deopa^c, Mukesh K. Sahu^d, Aman Prasad^e, A.S. Rao^{a,*}^a Department of Applied Physics, Delhi Technological University, Bawana Road, New Delhi, 110 042, India^b Department of Physics, Govt. College Nagina, Nuh, Haryana, 122108, India^c Department of Physics, Chaudhary Ranbir Singh University, Rohtak Bypass Road, Jind, Haryana, 126102, India^d Department of Electronics and Communication Engineering, GLA University, Mathura UP 281406, India^e Department of Physics and Computer Science, Dayalbagh Educational Institute (DEI), Deemed University, Agra UP 282005, India

ARTICLE INFO

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Reisfeld approximation

Color tunability

Energy transfer

ABSTRACT

A set of warm white phosphor samples $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}(\text{LBW}):\text{x}\text{Dy}^{3+}, \text{y}\text{Eu}^{3+}$ were prepared via a high-temperature solid-state process. Field emission scanning electron microscopy (FE-SEM) and Energy-dispersive X-ray analysis (EDX) with X-ray diffraction (XRD) are the structural analyses that show the incorporation of Dy^{3+} and Eu^{3+} ions into the LBW host matrix, without causing any damage to the lattice structure. Fourier Transform Infrared Spectroscopy (FT-IR) approves the presence of distinct vibrational characteristics of the proposed phosphors. The band gaps of the prepared phosphor samples were determined using diffused reflectance spectral (DRS) data. The energy transfer between Dy^{3+} and Eu^{3+} ions was observed, contributing to the adjustable luminescence of the $\text{LBW}:\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphors. By varying the activator doping levels while keeping the excitation wavelength constant, the emission colors of $\text{LBW}:\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphors shift from natural white with negligible color purity to a relatively pure orange-red region. The decay curves follow the bi-exponential behavior of decreasing lifetime with increasing concentration of the activator ions. A temperature measurement model using fluorescence intensity ratio (FIR) was developed using D3E0.75 phosphor demonstrating excellent optical temperature measurement properties, with a maximum value of $S_T (=0.97\% \text{ K}^{-1})$. Therefore, all the experimental results indicate that the prepared $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped LBW phosphors can be a suitable choice for UV-excitable warm white lighting devices with color tunability and non-contact optical thermometry measurements.

1. Introduction

Photonic devices based on rare earth or transition metal induced luminous materials are currently rapidly expanding and have made huge advancements all over the world. To meet the demands of the necessary applications, this worldwide innovation generates an ever-increasing demand for transformative photonic devices [1,2]. The use of photonic devices is widespread in all fields, from cutting-edge science and technology to many industries and activities of daily life. Researchers have been motivated to enhance the properties of phosphors due to the continual increase in demand and the wide range of uses for luminous materials. These luminous materials are used in a variety of industries, including sensing, solid-state lighting, lasers, sophisticated displays, optical storage, and many more [3]. The temperature has a critical and fundamental characteristic use for biological, chemical, and physical

processes. One of the main uses of photonic devices is to sense the real-time temperature with great accuracy [4,5]. Also, with the advancement of science and technology, biological imaging and large-scale integrated circuits (LSI) created new demands for temperature measurement tolerance, high spatial resolution and remote detection [6]. Currently, there are two types of temperature measurement technologies, one is common contact temperature dimensions and another is non-contact. Yet, in some unique circumstances such as electromagnetically or thermally demanding areas and organisms, the conventional contact temperature measurements are carried out [7,8]. The usage of contact temperature measuring instruments are challenging by virtue of its condition of contact. Therefore, the study of non-contact thermometers is very important not only from the point of view of non-contact but also from financial viability. Non-contact phosphor thermometers have been a focus of research in the field of

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Spectral studies of thermally stable $\text{Dy}^{3+}/\text{Sm}^{3+}$ co-doped $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}$ phosphors for warm white LEDs

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Abstract

In the current study, a series of $\text{Li}_2\text{Ba}_5\text{W}_3\text{O}_{15}:\text{RE}^{3+}$ ($\text{RE} = \text{Dy}, \text{Sm}$) [$\text{LBW}:\text{Dy}^{3+}/\text{Sm}^{3+}$] phosphors were prepared using a high-temperature solid-state method. X-ray diffraction, Scanning electron microscopy with energy-dispersive x-ray analysis scans showed that the crystal form was consistent with the standard LBW and comprised small irregularly shaped particles. Diffuse reflectance spectral (DRS) data was utilized to calculate the band gaps. Fluorescence study shows that LBW material doped with Dy^{3+} and Sm^{3+} yield distinct colors at 496 nm (blue) for Dy^{3+} and 582 nm (green-yellow), 612 nm (yellow), and 669 nm (red) for Sm^{3+} when excited by near-ultraviolet (336 nm) light. The observation of energy transfer between Dy^{3+} and Sm^{3+} ions play a role in modifying the luminescence of $\text{LBW}:\text{Dy}^{3+}/\text{Sm}^{3+}$ co-doped phosphors. With a constant excitation wavelength (λ_{Ex}), different levels of activator doping lead to a change in the emission colors from their neutral white light to a deep orange-red region for $\text{LBW}:\text{Dy}^{3+}/\text{Sm}^{3+}$ phosphors. The decay curves demonstrate a decrease in lifetime with an increase in the concentration of activator ions (Sm^{3+}). For D3S5 phosphor, the temperature-dependent photoluminescence characteristics were analyzed under $\lambda_{\text{Ex}} = 336$ nm excitation. The results indicate excellent luminescence thermal stability with an activation energy of 0.16 eV at $\lambda_{\text{Ex}} = 336$ nm. With its low color-correlated temperature and good thermal stability, the prepared phosphor sample shows potential as a solid-state emitting phosphor that can be used with UV chip stimulation for warm white LED applications.

Keywords: $\text{Dy}^{3+}/\text{Sm}^{3+}$, warm white, Reisfeld approximation, CIE, TDPL

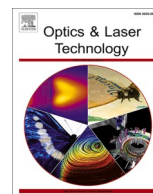
1. Introduction

Nowadays near-ultraviolet (n-UV)/blue light-emitting diodes (LEDs) have become increasingly popular because of their many benefits over other solid-state lighting sources, including their long lifespan, stability, high efficiency, and environmental friendliness [1–4]. Commercial LED technology was first introduced in 1960, and with the 1997 release

of the InGaN blue LED, research interest in white LEDs strengthened. White light is produced by combining three primary Color combinations: the LED chips emit red, green, and blue (RGB); the $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ ($\text{YAG}:\text{Ce}^{3+}$) phosphor combines blue and yellow color to provide a blue hue; and the UV or n-UV LED excitable phosphors emit a mixture of RGB hues [5]. RGB LED combinations for creating white light are less common due to their complex production and use, as well as their varied rates of deterioration and fluctuating driving current [6]. Therefore, the use of phosphor materials excitable by LED chips is encouraged to overcome these

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Publications in Refereed International Journals
(Other than Thesis)



Structural and luminescence characteristics of thermally stable Dy³⁺ doped oxyfluoride strontium zinc borosilicate glasses for photonic device applications

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ABSTRACT

Structural, thermal, and photoluminescence (PL) characteristics of a series of Dy³⁺ doped Oxyfluoride Strontium Zinc Borosilicate (OFSZBS) glasses have been investigated. The XRD of 1.0 mol% Dy³⁺ ions doped OFSZBS glass and FT-IR investigations conducted on an un-doped as well as all the Dy³⁺ ions doped OFSZBS glasses confirm the non-crystalline nature and distinct functional groups present in it respectively. The Differential Scanning Calorimetry (DSC) thermogram recorded for an un-doped OFSZBS glass reveals thermal stability (ΔT) and transition temperature (T_g). The optical band gaps were computed using the Tau's method. Under 348 nm pumping wavelengths, the Photoluminescence (PL) spectra of the as-synthesized OFSZBSDy glass samples exhibit blue (450 nm), yellow (575 nm), and red (650 nm) color transitions. The PL intensity increases with Dy³⁺ ions concentration up to 1 mol% and after that intensity decreases due to the concentration quenching effect. The PL decay profiles reported at higher concentrations were best fitted to the Inokuti-Hirayama (I-H) model for $s = 6$, indicating the energy transfer process as dipole-dipole in nature. The result obtained from the I-H model is in consonance with that of Dexter's theory. At 448 K, the PL intensity is up to 85% of room temperature, indicating that the as-synthesized glasses have exceptional thermal stability. Relatively higher values of quantum efficiency (η), emission cross-sectional area (σ_{se}), and probability of radiative transition (A_R) observed for 1 mol% Dy³⁺ ions doped OFSZBS glasses declare their suitability in photonic devices under n-UV/blue pumping wavelength.

1. Introduction

Lanthanides (Ln³⁺) activated substances have fascinated researchers' attention in the modern world due to their superior luminescent properties in applications, for instance, lasers, white light-emitting diodes (w-LEDs), fiber transmission and bright displays waveguides, etc. [1,2]. Further, Ln³⁺ activated glasses are superior to crystalline materials because of their exceptional features such as high transparency, fabrication in many ways, show an unmistakable light emission, corrosion resistance, and high durability [3,4]. Currently, w-LEDs are being produced by combining a blue-/n-UV semiconducting chip covered with an epoxy whose inner side is coated with one or more suitable phosphors. The epoxy resin is fabricated by a polymer substance and the w-LED emission is heavily impacted by the thickness of the polymer material and the phosphor concentration. The strength of epoxy resin is diminished when the material is exposed to extremely

high temperatures or powerful energy sources. Therefore, Ln³⁺ actuated glasses are ideal substitutes for phosphors, filament-based light bulbs, and standard CFLs owing to their high durability and illuminated intensity [5]. The PL properties of Ln³⁺ doped glasses can be strongly influenced by the host phonon energies and the ligand's environment. Generally, a low phonon energy glass composition can improve radiative emission, therefore enhancing the performance of the luminescence device [6,7]. Oxide glasses are superior to fluoride glasses due to their high chemical durability. However, oxide glasses lag due to their relatively high phonon energy [8]. Of all the traditional glass formers, borates (B₂O₃) are well-known due to their flexible properties such as a suitable host for alkali and alkaline earth elements, minor fusion heat, stronger covalent B-O bonds, and small size of cation. When compared to other glass formers, B₂O₃ is considered as a friendly retainer of Ln³⁺ ions doping for the reasons stated above [9].

In addition, the introduction of silica to the borate glasses

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Efficient tunable photoluminescence of Dy³⁺/Eu³⁺ co-doped OFSZBS glasses for warm white LEDs

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Reisfeld approximation

Inokuti-Hirayama (I-H) model

Correlated Color Temperature (CCT)

CIE

ABSTRACT

A series of oxyfluoride strontium zinc borosilicate (OSZBS) glasses co-doped with Dy³⁺/Eu³⁺ ions was prepared via melt quench method. The structural properties were examined using XRD and scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) on DE2.0 and undoped OFSZBS glasses, respectively. UV–Vis absorption spectroscopy was used to evaluate the direct & indirect energy band gaps. At different excitations (348, 362, 385 and 393 nm), the photoluminescence (PL) spectra were observed with tuned light. Warm white light was generated through the Dy³⁺ (⁴F_{9/2}→⁶H_{15/2}, ⁶H_{13/2}) and Eu³⁺ (⁵D₀→⁷F₂) transitions. Dexter Reisfeld approximation applied to PL data revealed a dipole-dipole (d-d) mechanism accountable for the energy transfer (non-radiative) between sensitizer (Dy³⁺) and activator (Eu³⁺) ions. The energy transfer efficiency in the co-doped glass samples was found between 8% to 50%, depending on the doping. The Inokuti-Hirayama (I-H) fitting of PL decay profiles also confirm the energy transfer mechanism. The CIE chromaticity color coordinates observed for OFSZBSDE2.0 glass also confirm the color tunability. The above findings reveal the applications of as-prepared Dy³⁺/Eu³⁺ co-doped OFSZBS glasses excited using n-UV light for warm white LEDs and tuned devices.

1. Introduction

Recently, researchers from all over the world have been working hard to enhance luminescent-based devices to address a variety of challenges with high-power lighting appliances like street lights, spot-lights, pole lights, emergency lights and decorative lighting. Optical materials, doped or co-doped with trivalent rare-earth (RE³⁺) like phosphors, crystals, and glasses have drawn the attention of numerous materials science researchers over the past few decades because of their wide range of applications in different areas like solid-state lighting (SSL) [1], fiber amplifiers, solar cells, temperature sensing devices [2,3] etc. The devices based on luminescence make use of luminescent materials that produce high-power visible light when integrated with UV/blue light-emitting diodes (LEDs) [4,5]. The three commonly used methods to prepare white light: in the first method, an electronic system is used to combine light from RGB LEDs. Another way is to fabricate yellow phosphor associated with a blue LED chip. The third process involves combining blue and yellow or RGB phosphors with a UV light source. The best alternative is to combine a UV LED chip with a single multi-chromatic phosphor [6]. The significant disadvantage of these

approaches is the thermal deterioration of phosphor-captured polymer resin, which results in a loss in efficiency as well as a change in color properties. As a result, the UV-LED chip combined with a white light-emitting glassy world is a good choice for making w-LED lamps because of its many advantages, including improved thermal stability, endurance and fluorescence intensity [7].

Human health has been negatively affected by the increased usage of lights and luminous devices such as phones and laptops, as well as the reduced exposure of humans to sun radiation, as a result of mankind's advancement into the industrial age [8]. Furthermore, lightning is used in optical fiber transmission also. This drew interest in the development of a bright material with color-balancing properties [9]. The 5s and 5p shells which lie outer protects the 4f shell of RE caused sharp fluorescence in the ultraviolet and infrared areas [10]. Amid all the glasses, B₂O₃ is the superior glass former system because of its great transparency, excellent durability, and high thermal and mechanical characteristics [11]. Due to the oxidation state +3 of boron, a strong covalent bond is formed in the as-prepared glass structure, which explains its great thermal stability. B-O-B links may be found in BO₃ triangles and BO₄ pyramids in these glasses [12]. The addition of SiO₂ to borate

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Prospective applications of thermally stable Dy³⁺ doped potassium zinc strontium borate (KZSB) glasses in w-LEDs

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ABSTRACT

In this present work, Dysprosium (Dy³⁺) ions doped potassium zinc strontium borate (KZSB) glasses were synthesized via the melt-quench method. X-ray diffraction (XRD) study of the prepared glasses shows a broad hump and confirms the amorphous nature of the glasses. Various vibrational shoulders were seen in the Fourier transform infrared (FT-IR) spectrum. Thermo gravimetric analysis–differential scanning calorimetry (TGA–DSC) was carried out to check the thermal stability and corresponding weight loss behavior of the undoped sample. Absorption spectra were recorded for undoped as well as doped glasses in the UV–VIS–NIR region, and the corresponding optical band gap was calculated. The photoluminescence (PL) spectra of as-prepared Dy³⁺ doped KZSB glasses under 350 nm excitation show three peaks at 482, 575 and 665 nm corresponding to the transitions $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$. Commission Internationale de l’Eclairage (CIE) chromaticity coordinates calculated from the emission data lie in the white region. The photometric analysis of prepared glasses under UV lamp with 365 nm excitation also shows white emission. Temperature-dependent PL (TDPL) investigation demonstrates the superiority in thermal stability of the as-prepared glasses, with an activation energy of 0.232 eV estimated for 0.5 mol% (optimized concentration of rare earth ion) of Dy³⁺ ions. After analyzing the results of all studies, we propose to use these borate glasses doped with Dy³⁺ ions for white light-emitting diodes (w-LEDs) fabrication and other solid state lighting (SSL) applications.

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Spectral characteristics of Tb³⁺ doped ZnF₂-K₂O-Al₂O₃-B₂O₃ glasses for epoxy free tricolor w-LEDs and visible green laser applications

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ABSTRACT

In the current work, a series of Zinc Potassium Alumino fluoroborate (ZKAIFB) glasses doped with different concentrations of Terbium ions (Tb³⁺) were synthesized by employing the melt-quench technique. The spectroscopic properties of the as-prepared glass samples were examined using characterization techniques like XRD, FT-IR, DSC, UV-vis-NIR absorption and emission to unlock their utility in photonic devices. Absorption spectral information was used to determine the nature of bonding between Tb³⁺ ions and its surrounding ligands. FT-IR spectral information recorded for an undoped glass has been used to understand various functional groups present in the as-prepared ZKAIFB glass. The DSC thermogram was used to estimate glass thermal stability (ΔT) and transition temperature (T_g) of the as-prepared ZKAIFB glass. The Judd-Ofelt (J-O) intensity parameters estimated from absorption spectral data are correlated with the emission spectral profiles to estimate radiative properties. The photoluminescence (PL) intensity of the as-prepared ZKAIFBTb glasses is found to be maximum for 1 mol% of Tb³⁺ ions and beyond decreases showing concentration quenching. Using PL spectral data, the CIE color coordinates, and Correlated Color Temperature (CCT) values were evaluated to understand the suitability of the as-prepared glasses for green color emitting photonic devices. The experimental lifetime values estimated from the decay profiles are decreasing with elevation in Tb³⁺ ion concentration due to energy transfer through the cross-relaxation process. Quantum efficiency (η), emission cross-section (σ_{se}), CIE and CCT values obtained for 1 mol% Tb³⁺ ions doped ZKAIFB glass demonstrates its superiority in fabricating epoxy free tricolor w-LEDs and visible green lasers.

1. Introduction

The development of inorganic lighting technology has gained widespread consideration for the rare earth (RE) doped glasses that act as a leading idea in the construction of photonic devices, and their luminescence properties play a significant role in fabricating w-LEDs and color displays [1–5]. Further, the RE ions in glasses are optically active that can reveal diverse properties of massive significance in the field of science and technology.

[6]. The exclusive features that discriminate RE ions from other ions (transition metal ions) are their electronic enrich arrangement, which shows the shielding of 4f shell by external 5s and 5p sub-shells and in turn expedite them as optically active, revealing longer lifetime and narrow emissions [7,8]. Furthermore, RE ions activated glasses have received more attention over crystals and ceramics due to their wide in-homogeneous bandwidths, cheap production cost and high quantum efficiency [2]. They possess various auspicious applications such as optical fibers, display devices, w-LEDs, lasers, memory devices, sensors,

and waveguides [3–5].

Recently, the w-LEDs have been used globally in every household, restaurant and office owing to their excellent characteristics such as environmental friendliness, longer lifespan, lower fabrication cost and higher reliability [9,10]. The w-LEDs can be fabricated by combining blue color emitting LED InGaN chip with yellow color emitting YAG: Ce³⁺ phosphor. This popular technique of producing w-LEDs is deprived of poor color rendering index (CRI) and halo-effect [11,12]. To resolve the aforesaid problems, RGB phosphors are pumped with n-UV LEDs that support in reducing the halo effect and refining the CRI value. However, both techniques provide encapsulated phosphors in an epoxy region that can deteriorate at intense excitation & temperatures, causing a decrease in its output progressively [13,14]. Therefore, glasses doped with RE ions might be considered the probable aspirants and alternatives for devising w-LEDs due to the absence of epoxy region.

The selection of the host matrix is generally known to be a critical challenge in studying the luminescence behavior of materials. Among the various oxide glass formers such as borate, borosilicate, germanate,

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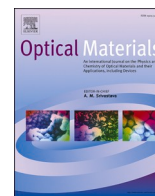
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Research Article

Impact of Sm^{3+} ions on structural, thermal, optical and photoluminescence properties of $\text{ZnO-Na}_2\text{O-PbO-B}_2\text{O}_3$ glasses for optoelectronics device applications

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Lead
Raman
DSC
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ABSTRACT

This work describes the impact of trivalent samarium (Sm^{3+}) ions concentrations on the thermal, structural, physical, optical and photoluminescence (PL) characteristics in Zinc Sodium Lead Borate (ZnNaPbB) glasses with configuration $(70-x) \text{B}_2\text{O}_3-10\text{PbO}-10\text{ZnO}-10\text{Na}_2\text{CO}_3-x\text{Sm}_2\text{O}_3$, (where $x = 0.1-2.0 \text{ mol\%}$). The glass samples were synthesized using a traditional melt-quench technique and characterized by various spectroscopic methods such as X-ray diffraction (XRD), Raman spectroscopy, Fourier Transform Infrared (FT-IR), UV-Vis-NIR spectra, Differential scanning calorimetry (DSC) and PL emission-excitation spectra to illuminate their photonic applications. The broad band perceived in the XRD diffractogram confirmed the amorphous nature of an un-doped ZnNaPbB glass. The physical properties including thickness, density, molar volume, dielectric constant, rare earth (RE) ion concentration, field strength and molecular electronic polarizability, etc. were calculated from the standard formulae. The FT-IR spectra identify the presence of stretching vibration in BO_3 and BO_4 units with some additional structural and functional groups with their bond nature. The observed DSC data was used to estimate the glass transition temperature (T_g). The absorption spectra presented all the probable transitions of Sm^{3+} ion-doped ZnNaPbB glass and the optical band gaps were computed using Tauc's method. All the glass samples depicted band gap values over 3 eV, proving that the material is insulating. The absorption spectra were utilized to evaluate Judd-Ofelt (J-O) parameters which were further used in different radiative parameters calculations to find the luminous levels of Sm^{3+} ions doped ZnNaPbB glasses. The PL emission spectra of the present ZnNaPbBSm glasses parade four bands parallel to the transitions $^4\text{G}_{5/2}$ to $^6\text{H}_{5/2}$ (563 nm), $^6\text{H}_{7/2}$ (599 nm), $^6\text{H}_{9/2}$ (646 nm) and $^6\text{H}_{11/2}$ (706 nm), respectively. Additionally, the evaluated values of the emission cross-section and branching ratios describe the suitability of the present ZnNaPbBSm glasses for optoelectronic applications. Further, the colorimetric parameters such as CIE coordinates (x, y) and correlated color temperature (CCT) were evaluated using PL emission data and the measured CIE coordinates are found in the reddish-orange region for the present glasses. The time decay profiles of as-prepared glasses were used to evaluate the experimental lifetime, energy transfer parameter and type of donor-acceptor interaction. The Dexter theory and Inokuti-Hirayama (I-H) fitting are used to recognize the type of interaction in non-radiative energy transfer which is responsible for the concentration quenching. The result demonstrates that the as-prepared ZnNaPbBSm glasses are applicable for optoelectronics device applications.

1. Introduction

For the last few decades, researchers have been meticulousness

interested to elaborate glasses as they have a broad range of commercial applications in the field of solid-state lighting (SSL) such as liquid crystal displays (LCD), white light-emitting diodes (w-LEDs), traffic signals,

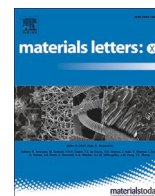
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Epoxy free LED devices: Physical and optical examination of praseodymium doped borate glasses for enhanced performance

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ARTICLE INFO

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Judd Ofelt theory
Band gap
Density
Glass

ABSTRACT

Borate glass doped with Praseodymium (Pr^{3+}) having different concentration were synthesized via melt quenching method. The density of the glass is proven to enhance with the abundance of the Pr^{3+} ions resulting in structural compactness of the glass. Variation of the dielectric constant, reflection loss, molar refraction and polaron radius has been analyzed with the concentration of Pr^{3+} ions. Absorption spectra were recorded in the range of 200 nm–1800 nm and seven peaks were observed. Band gap is evaluated using Tauc plot. Absorption spectra are used to assess the bonding parameter and Judd-Ofelt intensity parameter. The results of the Judd Ofelt theory are consistent with the bonding parameters. Variation of the Urbach energy with the band gap has been analyzed. The known result affirms the glasses potential as a green component in reddish orange luminescent devices.

Introduction

Incorporating Rare Earth (RE) ions in Solid-State Lighting (SSL) technology set a new benchmark in this modern era of technology. Increased usage of light-emitting diodes (LEDs) not only helps in energy saving but also helps in reducing the carbon footprint, which is a priority for many industrialised and emerging nations to be environmentally friendly [1]. Currently, LEDs are fabricated using phosphor-coated excitation sources. Its properties like high efficiency, higher lifespan and compact size output are strongly affected by the concentration and epoxy region that binds with phosphor. Despite all these properties, the sealant of pc converted LEDs deteriorates at high power and high temperature, resulting in a low colour rendering index, and relatively limited lifespan of LEDs. To conquer this problem rare earth doped glassy matrix is a worthy substitute due to its properties like low production costs, simple manufacturing processes and exceptional thermal and chemical stability [2].

The host composition strongly affects the radiative properties of RE ions doped glass matrix as it affects the phonon energy. Higher the phonon energy lower will be the quantum efficiency. Glass hosts prefer borate glass because of its outstanding RE ions transparency, strong thermal stability and comparatively low melting temperature [3]. When

ZnF_2 is added to borate glass, the OH ligand is removed, reducing phonon energy and non-radiative losses while increasing radiative emission [4]. Strontium carbonate works as a network modifier to make the glass network more stable and reduce its expansion coefficient. It also improves the bio-activity of the glass. The addition of lithium oxide reduces the hygroscopic nature of the glass matrix and provides more stability by generating non-bridging oxygen (NBO).

Experimental

Synthesis

The present Pr^{3+} ions activated ZSLFB glass samples have been prepared by employing melt quench technique with composition $10\text{ZnF}_2-(10-x)\text{SrO}-15\text{Li}_2\text{O}-65\text{H}_3\text{BO}_3-x\text{Pr}_2\text{O}_3$ (where $x = 0.1, 0.5, 1.0, 1.5$ and 2.0) and assigns their names according to the concentration of Pr^{3+} ions as mentioned in Table 1. Initially weighing of chemicals according to batch calculation has been performed according to mol percent taking initial chemicals ZnF_2 , SrCO_3 , Li_2CO_3 and Pr_2O_3 with 99.99% purity. Then all the chemicals was crushed to a homogenous state with the help of agate mortar and put in an alumina crucible. In an electric furnace, obtained mixture is melted at 1275°C temperature with three time slots

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RESEARCH ARTICLE

Structural, optical, and luminescence properties of Dy³⁺-activated potassium calcium silicate phosphor for white light-emitting diodes

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Abstract

A dysprosium (Dy³⁺)-activated potassium calcium silicate (K₄CaSi₃O₉) phosphor was prepared using a solid-state synthesis route. The phosphor had a cubic structure with the space group Pa $\bar{3}$ as confirmed using X-ray diffraction (XRD) measurements. Details of surface morphology and elemental composition of the as-synthesized undoped KCS phosphor was obtained using scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy. The chemical structure as well as the vibrational modes present in the as-prepared KCS phosphor was analyzed using Fourier transform infrared (FT-IR) spectroscopy. Diffuse reflectance spectra (DRS) were used to determine the optical bandgap of the phosphors and were found to be in the optical range 3.52–3.71 eV. Photoluminescence (PL) spectra showed intense yellow emission corresponding to the ⁴F_{9/2}→⁶H_{13/2} transition under 350 nm excitation. Commission International de l'Eclairage colour chromaticity coordinates were evaluated using the PL spectral data lie within the white region. Dexter theory and the Inokuti-Hirayama (I-H) model were applied to study the nature of the energy transfer mechanism in the as-prepared phosphors. The relatively high activation energy of the phosphors was evaluated using temperature-dependent PL (TDPL) data and confirmed the high thermal stability of the titled phosphor. The abovementioned results indicated that the as-prepared KCS:Dy³⁺ phosphor was a promising candidate for n-UV-based white light-emitting diodes.

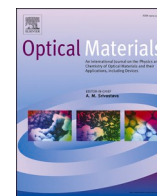
KEYWORDS

activation energy, I-H model, luminescence, phosphor, w-LEDs

1 | INTRODUCTION

In this modern era of digitization, in many areas affecting social and economic development, energy is crucial. The constant demand for energy results in permanent changes to our environment. A significant portion of the total energy generated across industries is used for both indoor and outdoor lighting. Typical incandescent and fluorescence lighting uses either gas discharge or heat. Due to the high

temperatures involved, both phenomena are linked to significant energy losses [1, 2]. Along with energy efficiency, it is crucial to guarantee that the lighting technology is environmental friendly. There is no prominent option compared with solid-state lighting if all of these requirements must be met. It is based on light-emitting diodes, which are essentially semiconductor chips with p-n junctions that are forward biased to emit light. Luminous efficacy, low power dissipation, persistence, environmental friendliness, and a lasting operative



Research Article

Spectroscopic characterizations of Dy³⁺ ions doped phosphate glasses for epoxy-free white LED applicationsVidhi, Ankita, Anu, A.S. Rao^{*}

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ABSTRACT

The present work illustrates a detailed spectroscopic analysis carried out on dysprosium ions doped Zinc Aluminosodium Phosphate (ZnAlNaP) glasses with chemical composition of (10-x)ZnO–20Al₂O₃–10Na₂O–60P₂O₅–xDy₂O₃ (x = 0.1–2.0 mol%). The XRD spectra verified for an un-doped and Dy³⁺ ions doped ZnAlNaP glasses demonstrate an enormous hump confirming its amorphous behavior. The FT-IR and Raman spectrum recorded for an un-doped ZnAlNaP and ZnAlNaPDy1.0 glass elucidates various functional groups and vibrational modes involved, respectively. The DSC & TGA studies conducted on an un-doped ZnAlNaP glass revealed its thermal stability and overall weight loss. The absorption spectra were used to calculate the optical bandgap for the as-synthesized glasses and were found to be in the range of 2.9 eV–4.7 eV. Photoluminescence (PL) excitation, emission and decay spectral analysis were done to investigate the suitability of the as-synthesized glasses for epoxy-free solid-state lighting (SSL) devices. The PL emission recorded under 350 nm excitation show two significant bands in blue and yellow regions. Temperature-dependent PL studies conducted on ZnAlNaPDy1.0 glass revealed activation energy of 0.212 eV with a 25.6% loss in PL intensity. The CIE color chromaticity coordinates and correlated color temperature (CCT) were calculated from the PL spectral characteristics. All the spectroscopic investigations conducted on the as-synthesized ZnAlNaPDy glasses finally reveal their superior nature for fabricating epoxy-free white-light emitting diodes (w-LEDs).

1. Introduction

One of the most remarkable innovations of the twentieth century was light emitting diodes (LEDs) which are a great source of artificial lighting and at the same time eco-friendly. Today, white-LEDs (w-LEDs) have become fourth-generation solid-state lighting (SSL) gadgets due to the wide range of benefits, such as higher dependability, brilliant productivity, luminous efficiency, low power consumption, good reliability and exceptional low-temperature performance [1]. The w-LEDs are now made with optical excitation sources that have a single or many layers of phosphors [2]. The concentration of epoxy resin placed on the phosphor has a significant impact on the emission of phosphor converted (pc) w-LEDs. The sealant used in pc w-LEDs gets degraded at high temperatures, which considerably affects its characteristics such as luminous efficiency and color rendering index [3–6]. The research in rare earth (RE) doped luminescent materials has taken a quantum leap due to impressive advancements in SSL technologies [1] and in optical fibre waveguide lasers and optical amplifiers [7]. RE doped glasses have proven to be more advantageous than phosphors due to their unique

properties including broader non-homogeneous bandwidths, large doping capacity and improved thermal stability and these RE doped glasses are possible only if it is chemically & thermally stable, have relatively minimal phonon energies and have better RE³⁺ solubility with excellent transparency. The host glass's structure and ligand field environment affect the bandwidths of emission bands and therefore decide the photoluminescence (PL) adequacy of RE³⁺ ions. Thus, selecting a host material with relatively lower phonon energies is very important [6,8]. Phosphate glasses, in contrast to commonly used glass formers such as silicates, borates, aluminates etc., have relatively good mechanical and thermal stability, excellent transparency, better RE³⁺ ions solubility, good optical properties, isotropic refractive index, low melting temperature, improved chemical stability and good mechanical properties [1,9,10]. The morphology of glass is decided by two main components, the network former and the network modifier. A network former is considered to be an integral component in the construction of any glass matrix. It modifies its internal structure and simultaneously builds an integrated environment for the RE³⁺ ions, allowing them to maintain a high luminescence efficiency [11]. Aluminium oxide (Al₂O₃)

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Structural, thermal, optical and luminescence properties of Dy^{3+} ions doped Zinc Potassium Alumino Borate glasses for optoelectronics applications

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ABSTRACT

Zinc Potassium Alumino Borate (ZnKAlB) glasses doped with dysprosium (Dy^{3+}) ions of different concentrations were synthesized through the process of melt quenching which is commonly used in solid-state lighting (SSL) and laser systems, to comprehend their viability. This article evaluates and analyzes the physical, structural, thermal and optical properties of Dy^{3+} ions doped glasses by X-ray diffraction (XRD), Infrared Fourier Transform (FT-IR), differential scanning calorimetry (DSC), UV absorption and photoluminescence (PL) spectra to explain their utilization in optoelectronic devices such as lasers and white light-emitting diodes (w-LEDs). The physical parameters viz. density, refractive index, inter-ionic distance, molar volume, polaron radius, field strength, optical electronegativity, dielectric constant, reflection loss and metallization were computed by following the expressions reported in the literature. Glasses are non-crystalline materials and the non-crystallinity of an un-doped Zinc Potassium Alumino Borate glass was proven by the absence of high-pitched peaks in the XRD spectra. FT-IR spectroscopy was used to identify the presence of different functional groups and their bond nature in Dy^{3+} ions doped ZnKAlB glasses. The transition temperature (T_g), melting temperature (T_m) and thermal stability was calculated by monitoring DSC thermograms of all glasses. Further, the bonding parameters (δ) and nephelauxetic ratio (β) were estimated to explore the bonding nature of Dy^{3+} ions in its neighborhoods by using UV-absorption data. The optical direct-indirect band gap energy (E_{opt}) and Urbach's energy (ΔE) were enumerated from the absorption spectrum to elaborate electrical properties of as-prepared glasses. Judd-Ofelt theory was employed to find oscillator strengths from absorption spectra and for further calculation of radiative parameters such as the radiative lifetimes (τ_R), radiative transition probability (A_R), total radiative transition probability (A_T) and branching ratio (β_R) to understand the quantum efficiency (η). Furthermore, the colorimetric parameters such as correlated color temperature (CCT), CIE coordinates and yellow to blue (Y/B) ratio were estimated from the PL emission data. The multipole-multipole interaction was confirmed by Dexter approximation to explain concentration quenching. This work primarily explains the essential features of borate glasses with Dy^{3+} ions doping to explain their potential use in tricolor w-LEDs and lasers.

1. Introduction

In the field of SSL, there have been various scientific innovations with an enormous implementation mainly in magneto-optical devices, liquid crystal displays (LCD), traffic signals, w-LEDs, lasers and many more [1–5]. In the last few years, the research area of oxide glasses has

attracted significant interest from scientists and researchers because of their remarkable properties. Due to incredible developments in controllable solid-state lasers, many scholars and physicists have drawn their attention towards crystalline and amorphous materials with Rare Earth (RE) ions doping. SSL-based products have created an opportunity for the significant growth of w-LEDs, because of their long-life duration,

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Down-conversion and up-conversion photoluminescence studies of Er^{3+} doped calcium zinc borosilicate glass for optical fiber amplifiers

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Down-conversion photoluminescence (DCPL)

Up-conversion photoluminescence (UCPL)

Emission

Gain cross-sections

ABSTRACT

A series of Er^{3+} ion doped calcium zinc borosilicate (CZBS) glass with composition $15\text{ZnO}-(10-x)\text{CaO}-10\text{SiO}_2-65\text{B}_2\text{O}_3-x\text{Er}_2\text{O}_3$ ($x = 0.1, 0.5, 1.0, 1.5, 2.0$ mol%) has been synthesized using conventional melt quenching technique. The non-crystalline nature of the as-synthesized glass is established through X-Ray diffraction (XRD). Fourier Transform Infrared (FT-IR) spectral studies present a full picture of the functional groups present in the glass system. The absorption, up-conversion (UC) and down-conversion (DC) photoluminescence (PL) and corresponding PL decay dynamics, and laser power dependent PL are investigated to better understand the optical properties and energy transfer mechanism in the glass matrices. The radiative properties such as transition probability (A_R), branching ratios (β_R), radiative lifetimes (τ_R) and near infrared (NIR) emission quantum efficiency (η) are estimated. The absorption, emission cross-sections and optical gain coefficients reveal the potential applications as laser amplifiers. The results favorably suggest the potential utility of these Er^{3+} doped CZBS glasses in solid-state lighting and optical communication devices.

1. Introduction

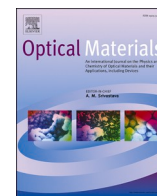
In recent years many studies have been conducted to explore and find new optical rare earth (RE) doped materials, both crystalline and amorphous, that find applicability in the field of photonics, such as effective optical laser medium, optical fiber amplifiers, atmospheric transmission, temperature sensors, and potential alternatives for conventional incandescent and fluorescent lamps [1]. Presently, glasses are among the most significant materials because of their wide range of applications in science and technology and frequent use in day-to-day life. The glass host matrix is a necessary component for constructing actuated photonic appliances. In general, relatively less phonon energy glasses can improve radiative emission, thus enhancing performance which is essential for the formation of the photonic devices [2,3]. High chemical durability enables the large-scale use of oxide glasses [4]. Among all the traditional forms of glasses, borates (B_2O_3) are best suited owing to their elastic assets such as over-bonding B-O bonds, small cation size, low fusion temperature, +3 valence of boron, low melting point, and suitable auxiliary with alkali and alkaline earth metals. For these reasons, borate (B_2O_3) is regarded as a favorable retainer of Er^{3+} ions doping compared to other glass matrices [5].

Additionally, due to strong mechanical strength and thermal endurance, silica is now acknowledged to have the most relevance among all glass matrices when added to borate glasses (borosilicate glass) [6]. In both laboratories and households, borosilicate glasses are the most frequently used. It has increased glass formation capabilities, improved heat and corrosion resistance, good optical transparency, and is eco-friendly [7]. Functional bonds have been found to increase B-O/Si-O/B-O-Si functionality and decrease B- and S- interactions, hence strengthening the glass [8].

The exceptional spectral characteristics and suitability for optoelectronic applications has garnered interest in glass doped with Erbium (Er^{3+}) ion. This ion has been utilized in various vitreous host materials, including oxide, zirconate, borate, fluorozirconate, and germanate glass-ceramics [9], as well as in construction of broadband erbium-doped fiber amplifiers (EDFA) [10]. The local coordination environment of the rare earth ions and their spectroscopic properties are affected by the local structure of glasses, which are amorphous materials with short-range order. The impact of glass composition and erbium concentration on the UC process has been assessed among glass host materials. Due to the remarkable applications in optical amplifiers, triple displays, solid-state lasers, undersea communications, fluorescent lights, etc., Er^{3+} actuated

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Research Article

Physical, structural and optical characterization of Dy³⁺ doped ZnF₂-WO₂-B₂O₃-TeO₂ glasses for opto-communication applications

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ARTICLE INFO

Keywords:

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Urbach analysis
Hydrogenic excitonic model
Mott & davis relation

ABSTRACT

A series of ZnF₂-WO₂-B₂O₃-TeO₂ (ZWFBT) glasses doped with different concentration of Dy³⁺ ions were prepared by using the melt quench method. The non-crystalline behavior of as-quenched ZWFBTdy glasses was approved by XRD spectra. The presence of different functional groups were identified by monitoring FT-IR spectra of ZWFBTdy glasses. The Differential Scanning Calorimetry (DSC) was used to estimate glass transition temperature (T_g) and thermal stability (ΔT) of an un-doped glass along with doped glasses. Physical parameters were estimated for Dy³⁺ doped ZWFBT glasses by using the formula available in the literature. The energy band gaps of as-quenched ZWFBTdy glasses were estimated by using three different theoretical models such as Mott and Davis relation, Hydrogenic Excitonic Model (HEM), and Urbach analysis. The optical absorption spectra were used to estimate the bonding parameters (δ) for elucidating the kind of bonding amide Dy³⁺ ions and its nearby ligands in the as-quenched glasses. The obtained experimental data from optical absorption spectra were compared with theoretical data calculated in the ambit of the Judd-Ofelt (J-O) theory. The J-O intensity parameters were estimated and a similar trend was observed ($\Omega_2 > \Omega_6 > \Omega_4$) for the as-prepared ZWFBTdy glasses. The results obtained using J-O intensity parameters are found consistent with the bonding parameters. The radiative parameters such as branching ratio, radiative transition, radiative lifetime, total radiative transition, absorption, and emission cross-sections were evaluated and discussed. The gain coefficient was evaluated for the NIR transitions of as-quenched ZWFBTdy glasses. The obtained results suggested that the as-prepared ZWFBTdy glasses were auspicious candidates for laser emission and optical communication applications.

1. Introduction

During the past three decades, optical properties of lanthanide (La³⁺) activated materials are widely premeditated for their potential usage in various areas such as lasers, fiber communication, luminescent display devices, 3D memory devices, optical detectors, w-LEDs, and waveguides [1–5]. The wide absorption as well as luminescent spectra, easier manufacture procedure, less fabrication cost, makes the glass hosts more suitable than the crystalline hosts and has drawn the attention of researchers from the spectroscopic & technological perspective [6,7]. The design and development of an opto-communication device for the aforementioned uses necessitate the detailed examination of the

physical, structural and optical properties of La³⁺ doped glasses. Such studies possess the evidence concerning radiative transition probability, lifetime and gain coefficient, etc. of La³⁺ doped glasses. The ligand fields formed by the glass host can create a significant impact on the physical, structural as well as optical properties of La³⁺ doped glasses. Moreover, a glass host having fewer phonon energies can enhance radiative properties and in turn possess a high gain coefficient for attaining effective lasers and optical fiber amplifiers [8,9].

The chemical composition of glasses plays an important role in imparting the unique luminescence characteristics. Oxide based glasses such as phosphate, borate and telluride glasses are known to have high luminescence. Amongst these, telluride glasses are most suitable

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Judd-Ofelt Parameterization and Luminescence Characterization of Dy³⁺ Doped Oxyfluoride Lithium Zinc Borosilicate Glasses for Lasers and w-LEDs

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ABSTRACT

In this work, Oxyfluoride Lithium Zinc Borosilicate glasses of varying Dy³⁺ ions concentration were prepared by using a melt quench technique. The optical and luminescence characteristics of Dy³⁺ ions were analyzed by XRD, absorption and emission spectroscopy. The Judd-Ofelt (J-O) parameters estimated by correlating absorption spectral measurements. The emission profiles displayed three principle bands in blue, yellow, red regions and quenching was detected at 1 mol% of Dy³⁺ ions. The radiative properties were evaluated for the protuberant luminous levels of Dy³⁺ ions within the ambit of J-O theory. The color coordinates at 351 nm pumping wavelength provide the worthy white emission. The decay profiles of ⁴F_{9/2}→⁶H_{13/2} showed exponential nature up to 1 mol% and non-exponential elsewhere. It has been observed that 1.0 mol % Dy³⁺ ions doped OFLZBS glasses are aptly fit for white light generation. This observation showed that as-quenched glasses may have great potentials for lasers and w-LEDs applications.

1. Introduction

Over the past several years, lanthanide ions activated materials have been captivating the attention of researchers owing to their numerous luminescent possessions [1, 2]. Further, Rare Earth (RE) ions can be easily recognized from other unique features because they can emit as well as absorb over slender wavelength regions. The luminescence efficiency can be evaluated for RE doped glasses which are mainly pronounced by their electronic transitions such as 4f–4f and 4f–5d [3–8]. Furthermore, the sheltering properties on the 4f electrons due to 5s / 5p orbitals are responsible for the prominent absorption and emission of RE ions [1–8]. Quite recently, RE doped materials are used to fabricate the opto-electrical devices such as solid state lasers, optical data storage, display, sensors, light emitting diode (LEDs), fibre amplifiers, etc. [9, 10, 11]. Moreover, the RE ion activated amorphous materials are much worthier than crystalline materials owing to some precise properties such as low coefficient of thermal expansion, high optical clarity, high refractive index, more resistant to thermal shock, low glass transition temperature. In this digital world, w-LEDs are being used globally because of the most developing lighting system. Presently, the w-LEDs are developed by combining blue/near-ultraviolet LED chip covered over single or multiple phosphors [12]. It has been observed that in

phosphor-based w-LEDs, the radiation becomes pretentious via the phosphor coupled with epoxy resin as well as the concentration. Likewise, for pc-based w-LEDs the luminescent efficiency directly connected with the sealant and depreciates at high energy and high temperature excitation sources [13–15]. These major drawbacks cannot be seen in glasses as no epoxy resin present in glasses.

The glass host matrix is a significant factor for fabricating RE activated photonic devices. The radiant possessions of RE doped glasses are powerfully influenced via phonon energies of the host along with ligand fields' environment. Generally, low phonon energy glasses can enhance radiative emission which, in turn, escalates luminous efficiency essential for designing photonic devices [15, 16]. Nowadays, researchers are focusing on fluoride glasses owing to its lower phonon energies than oxide glasses [17, 18]. However, oxide glasses are more appropriate for hands-on uses by virtue of their outstanding characteristics like great thermal stability as well as chemical durability [19]. Amid all the glass formers, borate glass is an extraordinary glass former on account of its specific properties i.e., trivial melting point, high transparency, cheap fabrication cost, relatively easy preparation, high index, low coefficient of thermal expansion, etc. [20]. Further, the addition of silica into borate glasses (borosilicate glass) is believed currently utmost significant glass matrix as a result of their extreme mechanical as well as

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Structural, thermal, and luminescence kinetics of $\text{Sr}_4\text{Nb}_2\text{O}_9$ phosphor doped with Dy^{3+} ions for cool w-LED applications

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ABSTRACT

In this study, a series of white-light-emitting strontium niobium oxide ($\text{Sr}_4\text{Nb}_2\text{O}_9$: $x\text{Dy}^{3+}$ ($x = 0.01, 0.03, 0.05, 0.07$, and 0.10 mol)) phosphors were synthesized via solid-state reaction approach and analyzed by using XRD, SEM, diffuse reflectance, photoluminescence (PL), and temperature-dependent PL (TDPL) spectroscopy. The cubic structure of $\text{Sr}_4\text{Nb}_2\text{O}_9$ microparticles was identified by inspecting the diffraction pattern of the freshly generated phosphor. The formation of heterogeneous microstructures, including some aggregation, was seen in the SEM image of $\text{Sr}_4\text{Nb}_2\text{O}_9$ phosphor. Diffuse reflectance and PL were examined for varying dopant ions concentration to explore the optical luminescence characteristics of $\text{Sr}_4\text{Nb}_2\text{O}_9$ phosphor materials. Further, absorption spectra were obtained by using the diffuse reflectance spectra. The PL spectra of as-prepared phosphor exhibit two peaks at 483 nm and 580 nm, corresponding to the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transitions, respectively. By correlating absorption and PL spectra, Judd oflet parameters were evaluated. The intensity of PL spectra of as-prepared phosphors increases up to 7 mol% and beyond that, it decreases. It is also affirmed that the PL intensity is maximum for the 7 mol% Dy^{3+} ions-doped $\text{Sr}_4\text{Nb}_2\text{O}_9$ sample. The PL lifetime of the level $^4\text{F}_{9/2}$ was evaluated by exciting the Dy^{3+} ions at 350 nm. By applying the Inokuti-Hirayama model to decay curves, the energy transfer process was explored. The CIE chromaticity coordinates of all the as-prepared phosphors lie in the white zone of the chromaticity diagram. The PL intensity remains 71% at 200 °C that of at room temperature, indicating the phosphor's exceptional

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Energy transfer mechanisms and color-tunable luminescence of $\text{Tm}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped $\text{Sr}_4\text{Nb}_2\text{O}_9$ phosphors for high-quality white light-emitting diodes

Ravina,^a Kanishk Poria,^b Mukesh K. Sahu,^c A. Kumar,^a Anu,^d Sajjan Dahiya,^e Nisha Deopa^{*a} and A. S. Rao^d

This paper investigates the synthesis and luminescence characteristics of $\text{Tm}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped $\text{Sr}_4\text{Nb}_2\text{O}_9$ (SNB) phosphors as potential candidates for white light-emitting diodes (WLEDs). The study explores the energy transfer mechanisms and color-tunable characteristics of these phosphors. The SNB phosphors were prepared using a solid-state reaction method, and their structural and morphological properties were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and Fourier-transform infrared (FT-IR) spectroscopy. The diffuse reflectance, photoluminescence (PL) and time resolved photoluminescence (TRPL) properties were investigated, revealing efficient energy transfer processes from Tm^{3+} to Tb^{3+} and Eu^{3+} ions. The energy transfer mechanisms were determined through critical distance calculations and analysis of multipolar interactions. The co-doped phosphors exhibited tunable emission colors ranging from blue to white light, with controllable correlated color temperatures (CCTs) and high color rendering indices (CRIs). The CIE chromaticity coordinates were optimized to approach neutral white light. The PL intensity is maintained at 81.19% at 150 °C of that of room temperature which showcases the remarkable thermal stability of the as-prepared phosphors. The results highlight the potential of $\text{Tm}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped SNB phosphors for generating high-quality, color-tunable white light for advanced lighting applications.

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1 Introduction

With technological advancements, especially the widespread utilization of rare earth ion-doped phosphors, white light-emitting diodes (WLEDs) have progressively emerged as the optimal choice for next-generation lighting solutions. This preference arises from their inherent advantages, including cost-effectiveness, high efficiency, and environmental friendliness.^{1–3} Currently, white light can be achieved through two approaches. The first involves integrating a blue InGaN chip with $\text{YAG}:\text{Ce}^{3+}$ yellow phosphors. However, this approach lacks the red segment of the spectrum, leading to a diminished color rendering index (CRI) and an elevated correlated color

temperature (CCT). This deviation from the natural white light region poses a challenge to achieving high-quality white light illumination. Another approach involves using a near-ultraviolet chip combined with three-color phosphors. This method is capable of meeting the requirements for a high color rendering index (CRI) and achieving a suitable correlated color temperature (CCT).⁴ By employing this approach, it becomes possible to produce white light that closely resembles natural lighting conditions. Therefore, the development of color-tunable phosphors on a single-phase substrate is a highly significant research direction within the field of white light-emitting diodes (WLEDs). This approach aims to create phosphors that can be adjusted to produce a wide range of colors, enabling versatile and customizable lighting solutions.

Rare-earth ions exhibit a remarkably diverse electronic structure, rendering them capable of emitting photoluminescence across a wide range of wavelengths, including visible and infrared light. Particularly in the visible light region, their emission ability and vivid colors stand out, making rare-earth ions highly desirable for various applications, such as lighting and display technologies.⁵ The fusion of three primary colors—red, green, and blue—is well-known to yield white light.

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Luminescence Studies on Dy³⁺ Doped Calcium Aluminum Borosilicate (CABS) Glasses for White Light Emission and Applications in w-LEDs

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Abstract

Dy³⁺ doped calcium aluminum borosilicate (CABS) glasses have been synthesized via quick melt quench technique. CABS: xDy³⁺ glasses (x = 0.1, 0.5, 1, 1.5 and 2 mol%) were subjected to various morphological and photoluminescence studies. X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy were conducted to study the structural and bonding nature of the undoped glass. The excitation spectra of Dy³⁺ doped CABS glasses under 574 nm emission show many sharp peaks amongst which the transition from ⁶H_{15/2} → ⁶P_{7/2} (351 nm) had the highest intensity. Under 351 nm excitation, glasses exhibit sharp peaks in the blue, yellow and red regions corresponding to the transitions ⁴F_{9/2} → ⁶H_{15/2}, ⁶H_{13/2}, ⁶H_{11/2} and ⁶H_{9/2} respectively. The dipole–dipole nature of the interaction between the Dy³⁺ ions is confirmed via Dexter theory and Inokuti-Hirayama (I-H) model. CIE coordinates estimated from the emission profiles of these glasses under 351 nm excitation fall in the white region. Considering that these glasses exhibit sharp visible emission under UV excitation, have stable yellow to blue (Y/B) ratios and fast decays with intense energy transfers, we propose to utilise these glasses for white light generation and other white light LED (w-LED) and solid-state lighting (SSL) applications.

Keywords Glasses · Dexter theory · I-H Model · Photoluminescence · w-LEDs · SSL

Introduction

Climate change implications have made one thought clear in today's world that we need to develop more energy efficient resources so that our carbon footprint is systematically reduced leading to a better world for the future generations to live in [1, 2]. This has accelerated research in the development of white light emitting diodes (w-LEDs) that are considered to be fourth generation solid state devices having many favourable properties over the conventional incandescent luminescence sources like high luminous efficiency,

low power consumption, longer lifetimes, non-toxicity, eco-friendly and lower production cost [3–8].

Rare earth (RE) ion doped glassy materials are being developed and researched for their immense utility in solid state lighting and w-LED applications [9–11]. RE doped glasses find usage in various applications like 3D display devices, optical fibres, temperature dependent sensors, solid state lasers, optical waveguides, Q-switched devices etc. [12–17]. Different shades of white light can be generated by tuning the red, green and blue (RGB) emissions from the luminescent materials. There are three methods to generate white light [3]: The first method involves usage of some electronic circuit that combines the light coming from RGB LEDs. Second method involves fabrication of a yellow phosphor on a blue emitting LED. Third method involves combining blue and yellow or RGB phosphors with a UV light emitting source. The major disadvantage associated with these methods is the thermal degradation of the epoxy resin used for encapsulation of phosphors leading to deterioration of luminous efficiency and colour properties [18, 19]. Therefore, it is imperative to develop better alternatives to luminescent phosphors in order to tackle these disadvantages. RE doped glassy materials

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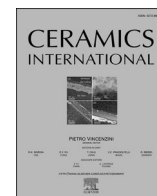
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Dysprosium ion concentration variations and their comprehensive influence on the physical, structural and optical properties of multi-component borate glasses for luminescence tailoring

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ABSTRACT

A set of Zinc Strontium Lithium Fluoroborate (ZSLFB) glasses with different concentrations of Dysprosium ions (Dy^{3+}) was created using the melt quench technique. The presence of non-crystallinity and various functional groups have been confirmed via X-Ray Diffraction (XRD) and Infrared Fourier Transform FT-IR measurements, respectively. The band gap values obtained from Tauc plot were utilised to analyse the optical characteristics. The photoluminescence (PL) emission spectra display three well-defined intensity peaks at wavelengths of 481, 574, and 664 nm. The intensity of peaks exhibits an ascending trend until a concentration of 0.5 mol% of Dy^{3+} ions is reached, after which it decreases. The PL intensity maintains up to 82 % at 200° C to room temperature, showing excellent thermal stability. The Judd Ofelt (J-O) parameter values pursue the $\Omega_2 > \Omega_6 > \Omega_4$ pattern, which shows its asymptotic nature. The CIE coordinates were assessed and determined to fall inside the white region. The interaction in the non-radiative energy transfer process was elucidated by utilizing the Dexter theory and Inokuti-Hirayama (I-H) model.

1. Introduction

Glasses are among the most frequent bulk host materials due to their ease of fabrication, increased transparency, superior rare-earth ion solubility, ability to alter geometry, and strong stability rapidly. Glasses have conventionally been used in a wide range of applications, including display devices, soldering, submarine communication, shielding, optical amplifiers, and scintillators [1–4]. The potential applications of rare-earth ion (REI) infused inorganic oxide glasses and glass ceramics in photonics devices, such as LEDs, displays, storage devices, fibre amplifiers, and waveguides, have garnered significant interest recently [5,6]. Research on how well the composition of the glasses can be adjusted to change the physical, optical, and photoluminescence characteristics is intriguing in these kinds of applications. However, choosing the appropriate glass matrix is crucial for designing a capable optical system [7].

The hunt for increased luminescence from borate glasses containing rare-earth (RE) ions has been sparked by these exciting qualities, which

include large-scale production, shape flexibility and affordability. However, the high phonon energy of borate glass leads to less attention, but it is not harmful in the case of Eu, Dy, Sm and Tb. Instead, it is possible that the elevated phonon energy could facilitate the relaxation process, which is favourable and critical for PL.

The introduction of ZnF_2 enhances radiative emission by diminishing the phonon energy by removing the OH ligand from the borate host [8]. Strontium carbonate enhances glass network stability, decreases expansion coefficient, and enhances bio-activity, making it useful in medical fields, particularly for bone generation. Lithium oxide decreases glass matrix hygroscopicity and stabilises it by generating non-bridging oxygen (NBO) [9].

Dy^{3+} ions, a promising ion for creating w-LEDs and enhancing healing properties, are frequently added to glasses as dopants to examine their spectroscopic characteristics. A higher amount of quantum efficiency is achieved through light emanating from the metastable state $^4\text{F}_{9/2}$. Pumping Dy^{3+} ions doped glasses is simple because blue LEDs and commercial UV LEDs can easily pump them. Dy^{3+} ions' visible

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