Lanthanide-doped optical materials for temperature sensing and latent fingerprint detection

Thesis submitted in partial fulfilment For the Award of Degree

DOCTOR OF PHILOSOPHY

In

Physics

By

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Dedicated

to

My parents,
brothers, sisters,
wife, son,
teachers and
well wishers

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It is certified that the work contained in the thesis titled " **Lanthanide-doped optical material for temperature sensing and latent fingerprint detection** " by "**Mr. Sachin Singh**" (Roll No. **19171026**) in partial fulfilment of the requirement for award of the degree of **Doctor of Philosophy** at **Indian Institute of Technology (BHU), Varanasi** is a record of his own work carried out under my supervision and guidance and this work has not been submitted elsewhere for a degree.

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I, "**Sachin Singh**" (Roll No. 19171026), certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of "**Dr. Sunil Kumar Singh**" from **July 2019 to December 2024**, at the **Department of Physics, Indian Institute of Technology (Banaras Hindu University), Varanasi.** The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any others work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, thesis, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

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It is certified that the above statement made by the student is correct to the best of my knowledge.

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INDEX

CONTENT **PAGES**

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

Å	Angstrom
CBM	Conduction Band Minimum
CCT	Color Correlated Temperature
CIE	Commission International de I′Eclairag
cm	Centimeter
CP	Color Purity
CM	$CaMoO_4$
CTB	Charge Transfer Band
DC	Down conversion
DI	Deionized
DMF	Dimethylformamide
DSC	Differential Scanning Calorimetric
EDX	Energy Dispersive X-Ray Analysis
E_g	Band Gap
EOH	Ethanol
Er	Erbium
ESA	Excited State Absorption
Eu	Europium
eV	Electron volt
FIR	Fluorescence Intensity Ratio
FT-IR	Fourier transform Infrared

FWHM	Full width at half maximum
g	Gram
GSA	Ground State Absorption
h	Hour
Ho	Holmium
HR-TEM	High Resolution Transmission Electron Microscope
hv	Photon Energy
ICDD	International Center for Diffraction Data
JCPDS	Joint Committee on Powder Diffraction Standards
K	Kelvin
LED	Light Emitting Diode
LER	Luminous Efficacy of Radiation
lm/W	Lumens per watt
Ln	Lanthanide
meV	Mili Electron Volt
mg	milligram
min	Minute
ml	Mililitter
MOF	Metal Organic framework
N	Avogadro's number
NCs	Nanocrystals
NIR	Near infrared

nm	Nanometer
NPs	Nanoparticles
ns	Nanosecond
OA	Oleic acid
OAm	Oleylamine
ODE	Octadecene
PL	Photoluminescence
PLE	Photoluminescence Excitation
PLQYs	Photoluminescence Quantum Yields
PMT	Photomultiplier tube
QDs	Quantum dots
*R*exp	Expected profile residual
*R*p	Profile residual
rpm	Round per minute
*R*wp	Weighted profile residual
s	Second
SEM	Scanning Electron microscope
SSR	Solid State Reaction
T	Temperature
Tm	Thulium
UC	Upconversion
UV-Vis	Ultraviolet-Visible

VBM	Valence Band Maximum
W/m^2	Watt per meter square
WLED	White Light Emitting Diode
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
Yb	Ytterbium
S_a	Absolute sensitivity
S_r	Relative sensitivity
k_b	Boltzmann Constant
λ_d	Dominant wavelength
λ_{em}	Emission wavelength
λ_{ex}	Excitation wavelength
τ_{av}	Average decay time
ΔE	Energy separation
°C	Degree Celsius
µm	Micro-meter

PREFACE

Luminescent materials, commonly referred to as phosphors, have garnered significant attention in scientific research due to their extensive applicability in diverse fields such as lighting, sensors, solar cells, and biomedical imaging. Phosphors are typically composed of a crystalline or amorphous host lattice embedded with specific dopants. These dopants introduce additional energy levels into the host lattice, enabling tailored emission properties for targeted applications. Among various dopants, lanthanide (Ln^{3+}) ions stand out for their unique optical properties, including upconversion and downconversion luminescence. Their well-shielded 4f transitions, combined with long luminescence lifetimes, high photostability, and sensitivity to environmental factors, make lanthanides invaluable in advanced optical materials.

Phosphors have been developed using various host lattices, such as phosphates, borates, vanadates, tungstates, molybdates, and garnets. Each host exhibits distinct structural, thermal, and chemical properties that influence luminescence performance. Among these, molybdate-based hosts like $CaMoO_4$ (calcium molybdate) have emerged as exceptional candidates, particularly for optical temperature sensing and latent fingerprint detection. The tetragonal scheelite structure of $CaMoO_4$, with its low phonon energy and broad energy bandgap, offers high thermal and chemical stability, making it suitable for lanthanide doping.

The present thesis focuses on exploring lanthanide-doped $CaMoO_4$ optical materials for dual applications: contactless temperature sensing and latent fingerprint detection. Optical temperature sensing utilizing thermally coupled and non-thermally coupled levels in lanthanide-doped phosphors is a promising alternative to traditional methods, offering

advantages such as non-invasive measurement, high sensitivity, and operation over a broad temperature range. Lanthanide ions, such as Er^{3+}, Ho^{3+}, Tm^{3+}, and Yb^{3+}, embedded in the $CaMoO_4$ host, enable precise temperature sensing through their unique luminescent responses to temperature variations. Additionally, this thesis explores the use of upconversion luminescence properties of lanthanide-doped $CaMoO_4$ for latent fingerprint detection, a critical aspect of forensic science. These materials convert near-infrared excitation into visible light, producing vibrant, high-contrast images of latent fingerprints on various substrates. This technique addresses challenges associated with traditional fingerprint detection methods, such as low visibility and poor contrast on complex backgrounds, by leveraging the color-tunable and dual-mode emission properties of the doped $CaMoO_4$ phosphors.

The findings of this thesis contribute to the broader understanding of $CaMoO_4$ as a versatile optical material, advancing its potential for practical applications in both temperature sensing and forensic imaging. Through a combination of material synthesis, advanced characterization techniques, and application-specific investigations, this work lays the groundwork for the development of next-generation luminescent materials. Detailed synthesis procedures and characterization techniques are discussed in Chapter 2. The thesis is divided into six Chapters. The brief explanation of each Chapter is given below:

Chapter 1 introduces the foundational concepts, providing a historical overview of luminescent materials and the evolution of phosphors. The role of lanthanides in optical applications is discussed, with a focus on their unique spectroscopic properties and emission mechanisms. The chapter also examines the structural and optical characteristics of the $CaMoO_4$ host, highlighting its suitability for lanthanide doping. Applications in optical

thermometry and latent fingerprint detection are introduced, establishing the motivation and scope of the research.

Chapter 2 details the synthesis and characterization techniques used in this thesis. A comprehensive description of the hydrothermal, solid-state, and sol-gel combustion methods employed to prepare lanthanide-doped $CaMoO_4$ phosphors is provided. Characterization techniques of phosphor materials such as X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Raman spectroscopy, and photoluminescence analysis are discussed in detail by including their working phenomenon. Additionally, the software used for the data analysis named FullProf, ImageJ, color calculator CIE 1931, and OriginPro 9.0, etc., are briefed.

Chapter 3 investigates and compare the temperature sensing capabilities of Er^{3+}/Yb^{3+} doped $CaMoO_4$ phosphors in both bulk and nanoparticle forms. This chapter also discussed the detailed structural and optical characterization of pristine $CaMoO_4$ and Er^{3+}/Yb^{3+} doped $CaMoO_4$ phosphors. The results reveal enhanced temperature sensitivity in the nanoparticle-based samples, attributed to their reduced particle size and improved energy transfer efficiency. The chapter demonstrates the potential of nanoscale $CaMoO_4$ materials in developing high-sensitivity optical thermometers.

Chapter 4 explores the impact of Bi^{3+} co-doping on the temperature sensing performance of Er^{3+}/Yb^{3+} doped $CaMoO_4$ phosphors. The reitveld refinement of optimised Er^{3+}/Yb^{3+} doped $CaMoO_4$ and $Bi^{3+}/Er^{3+}/Yb^{3+}$ doped $CaMoO_4$ has been done for the detailed structural analysis. The addition of Bi^{3+} ions introduces structural asymmetry, enhancing upconversion emission and temperature sensitivity. The findings highlight the role of co-

doping in optimizing the luminescent properties of $CaMoO_4$ phosphors for advanced sensing applications.

Chapter 5 focuses on the multifunctionality of $CaMoO_4$: $Ho^{3+}/Tm^{3+}/Yb^{3+}$ phosphors, demonstrating their applicability in non-thermally coupled level (NTCL)-based temperature sensing and latent fingerprint visualization. The chapter highlights the high sensitivity and color-tunable emissions of these materials, which enable precise temperature sensing and high-contrast fingerprint imaging under near-infrared excitation.

Chapter 6 consolidates the findings of the thesis, emphasizing the adaptability of $CaMoO_4$ as a robust host matrix for functional lanthanide doping. The chapter discusses the broader implications of the research and proposes future directions, including the optimization of material properties and exploration of additional applications in emerging optical technologies.

This thesis advances the understanding of lanthanide-doped $CaMoO_4$ materials and underscores their potential in addressing challenges in temperature sensing and forensic science. I hope this thesis inspires further research in the field of optical materials and their interdisciplinary applications.