SITE-SELECTIVE DUAL-MODE EXCITATION NON-LINEAR SPECTROSCOPY AND SPATIAL PHOTOLUMINESCENCE MAPPING/IMAGING OF NANOPHOSPHORS FOR BIOPHOTONIC APPLICATIONS

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by

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Submitted

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to the

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To My Parents and Teachers

For being the ground underneath

CERTIFICATE

This is to certify that the thesis entitled, **"Site-selective dual-mode excitation non-linear spectroscopy and spatial photoluminescence mapping/imaging of nanophosphors for biophotonic applications"** *being submitted by* **Ms. Ib Singh Deo***, to Indian Institute of Technology Delhi, New Delhi, for the award of the degree of* **Doctor of Philosophy** *in physics is a record of bonafide research work carried out by her under my supervision and guidance. She has fulfilled the requirements for the submission of thesis, which to the best of my knowledge has reached the requisite standard.*

The material contained in the thesis has not been submitted in part or full to any other university or institute for the award of any degree or diploma.

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(Ib Singh Deo)

Abstract

The thesis is driven by the significant advancements in optical spectroscopy and the high demand for improved images for a diverse array of biophotonics and nanophotonics applications. The ability to selectively excite selected sites or dopants through dual-wavelength laser excitation in specially synthesized rare earth doped nanophosphors remains an underexplored area, representing a novel facet of spectroscopy and imaging. The single-wavelength excitation (Vis or NIR) and emission of rare earth doped nanophosphors have been the subject of extensive research. However, there is a need for research on the site-selective dual-excitation of nanophosphors. The objective of the thesis is to conduct a comprehensive analysis of the spectral characteristics of rare earth doped nanophosphors under dual-wavelength laser excitation and image and map the optically active emitting sites.

This thesis focuses on advancing experimental techniques for controlling light and studying the spectral characteristics and optical responses of various rare earth doped nanophosphors using innovative site-selective spectroscopy and spatial photoluminescence mapping/imaging methods. The novelty of the thesis lies in the judicious design and purposeful choice of excitation wavelengths and nanophosphors to investigate the dual-excitation site-selective spectroscopy. The thesis begins with a study of both theoretical and experimental optical studies concerning the rare earth doped fluoride nanophosphors. This is succeeded by an extensive investigation of dual-excitation photoluminescence spectroscopy and spatial photoluminescence mapping/imaging in different nanophosphors. The thesis additionally includes a preliminary study into the use of these nanophosphors as biological markers for biophotonic applications.

The research also investigated the synthesis, comprehensive characterizations, and applications of various rare earth doped nanophosphors, emphasizing their unique optical properties and potential applications in diverse fields. The thesis presented an innovative method of site-selective spectroscopy, highlighting the advantages of dual-wavelength excitation in terms of sensitivity, enhanced spectral resolution, and the ability to probe multi-energy level systems. A significant finding of the study is the observation of upconversion emission from europium. The thesis further illustrates the design and development of several innovative optical measurement techniques, encompassing dual-excitation photoluminescence measurements and an advanced modified optical microscope for spatial photoluminescence mapping and imaging.

The extensive research conducted has significantly enhanced the understanding of site-selective spectroscopy and dual-mode excitation photoluminescence in rare earth doped nanophosphors. This knowledge not only deepens theoretical insights but also paves the way for practical applications, potentially expediting the transition from laboratory findings to real-world utilization.

सामान्य सारांश

यह शोध प्रबंध प्रकाशिक स्पेक्ट्रोस्कोपी में हुई महत्वपूर्ण प्रगति और बायोफोटोनिक्स तथा नैनोफोटोनिक्स अनुप्रयोगों की विविध श्रृंखला हेतु बेहतर छवियों की उच्च माँग से प्रेरित है। विशेष रूप से संश्लेषित दुर्लभ मृदा अपमिश्रित नैनोफॉस्फोर में द्वि-तरंगदैर्ध्य लेज़र उत्तेजन के माध्यम से चयनित स्थलों या अपमिश्रकों को चुनिंदा रूप से उत्तेजित करने की क्षमता अभी भी एक अनन्वेषित क्षेत्र है, जो स्पेक्ट्रोस्कोपी और इमेजिंग के एक नए पहलू का प्रतिनिधित्व करता है। दुर्लभ मृदा अपमिश्रित नैनोफॉस्फोर का एकल तरंगदैर्ध्य उत्तेजन (Vis या NIR) और उत्सर्जन व्यापक शोध का विषय रहा है। हालाँकि, नैनोफॉस्फोर के स्थल-चयनात्मक द्वि-उत्तेजना पर शोध की आवश्यकता है। इस शोध प्रबंध का उद्देश्य द्वि-तरंगदैर्ध्य लेज़र उत्तेजन के अंतर्गत दुर्लभ मृदा अपमिश्रित नैनोफॉस्फोर की वर्णक्रमीय विशेषताओं का व्यापक विश्लेषण करना और प्रकाशिक रूप से सक्रिय उत्सर्जक स्थलों का चित्रण एवं मानचित्रण करना है।

यह शोध प्रबंध प्रकाश नियंत्रण हेतु प्रायोगिक तकनीकों को उन्नत करने और नवीन स्थल-चयनात्मक स्पेक्ट्रोस्कोपी तथा स्थानिक प्रकाश-प्रकाश-प्रकाश मानचित्रण/प्रतिबिंबन विधियों का उपयोग करके विभिन्न दुर्लभ मृदा-मिश्रित नैनोफॉस्फोरों की वर्णक्रमीय विशेषताओं एवं प्रकाशिक प्रतिक्रियाओं का अध्ययन करने पर केंद्रित है। इस शोध प्रबंध की नवीनता द्वि-उत्तेजना स्थल-चयनात्मक स्पेक्ट्रोस्कोपी की जाँच हेतु उत्तेजना तरंगदैर्ध्यों और नैनोफॉस्फोरों के विवेकपूर्ण डिज़ाइन और उद्देश्यपूर्ण चयन में निहित है। यह शोध प्रबंध दुर्लभ मृदा-मिश्रित फ्लोराइड नैनोफॉस्फोरों से संबंधित सैद्धांतिक और प्रायोगिक, दोनों प्रकार के प्रकाशिक अध्ययनों से आरंभ होता है। इसके बाद विभिन्न नैनोफॉस्फोरों में द्वि-उत्तेजना प्रकाश स्पेक्ट्रोस्कोपी और स्थानिक मानचित्रण/प्रतिबिंबन की व्यापक जाँच की जाती है। इस शोध प्रबंध में जैव-प्रकाशिक अनुप्रयोगों के लिए जैविक चिह्नकों के रूप में इन नैनोफॉस्फोरों के उपयोग पर एक प्रारंभिक अध्ययन भी शामिल है।

इस शोध में विभिन्न दुर्लभ मृदा-मिश्रित नैनोफॉस्फोरों के संश्लेषण, व्यापक लक्षण-वर्णन और अनुप्रयोगों की भी जाँच की गई, जिसमें उनके अद्वितीय प्रकाशिक गुणों और विविध जैव-चिकित्सा एवं तकनीकी क्षेत्रों में उनके संभावित अनुप्रयोगों पर बल दिया गया। थीसिस ने साइट-चयनात्मक स्पेक्ट्रोस्कोपी की एक अभिनव विधि प्रस्तुत की, जिसमें संवेदनशीलता, उन्नत स्पेक्ट्रल रिज़ॉल्यूशन और बहु-ऊर्जा स्तर प्रणालियों की जांच करने की क्षमता के संदर्भ में दोहरे-तरंगदैर्ध्य उत्तेजना के लाभों पर प्रकाश डाला गया। अध्ययन का एक महत्वपूर्ण निष्कर्ष यूरोपियम से अपरूपांतरण उत्सर्जन का अवलोकन है। थीसिस कई अभिनव ऑप्टिकल माप तकनीकों के डिजाइन और विकास को आगे बढ़ाती है, जिसमें दोहरे-उत्तेजना फोटोल्यूमिनेसेंस माप और स्थानिक फोटोल्यूमिनेसेंस मैपिंग और इमेजिंग के लिए एक उन्नत संशोधित ऑप्टिकल माइक्रोस्कोप शामिल है।

किए गए व्यापक शोध ने दुर्लभ पृथ्वी डोप्ड नैनोफॉस्फोर में साइट-चयनात्मक स्पेक्ट्रोस्कोपी और दोहरे-मोड उत्तेजना फोटोल्यूमिनेसेंस की समझ को काफी बढ़ाया है।

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Abbreviations

PL	Photoluminescence
LASER	Light Amplification by Stimulated Emission of Radiation
UC	Upconversion
DC	Downconversion
UC-PL	Upconversion Photoluminescence
DC-PL	Downconversion Photoluminescence
nm	Nanometre
RE	Rare Earth
QD	Quantum Dot
ET	Energy Transfer
GSA	Ground State Absorption
ESA	Excited State Absorption
ETU	Energy Transfer Upconversion
CR	Cross-relaxation
PA	Photon Avalanche
NR	Non-radiative
MPR	Multi-Phonon Relaxation
UV	Ultraviolet
Vis	Visible
NIR	Near-infrared
NP	Nanoparticle
XRD	X-ray diffraction
PXRD	Powder X-ray diffraction
ICDD	International Centre for Diffraction Data
JCPDS	Joint Committee on Powder Diffraction Standards
SEM	Scanning Electron Microscopy
BSE	Backscattered Electrons
SE	Secondary Electrons
EDX	Energy Dispersive X-ray Spectroscopy
TEM	Transmission Electron Microscopy
CCD	Charge-Coupled Device
SEAD	Selected Area Electron Diffraction
HRTEM	High-resolution Transmission Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
SQUID	Superconducting Quantum Interference Device
EPR	Electron Paramagnetic Resonance
BF	Bright Field
DF	Dark Field
FWHM	Full Width at Half Maximum
J-O	Judd-Ofelt
I-H	Inokuti- Hirayama
Y-T	Yokota-Tanimoto

Symbols

I	Upconversion emission intensity
P	Laser Power
n	Number of pump photons absorbed for each emitted up-converted photon
H	Hamiltonian
H_{FI}	Free ion Hamiltonian
H_{CF}	Crystal field Hamiltonian
f_{exp}	Experimental oscillator strength
f_{cal}	Calculated oscillator strength
Ω_λ	Judd-Ofelt parameters
m	Mass of the electron
e	Charge of the electron
c	Speed of light in vacuum
λ	Wavelength
δ_{rms}	R.M.S deviation
λ_P	Emission peak wavelength
$\Delta\lambda_P$	Effective bandwidth
$\sigma(\lambda_P)$	Stimulated emission cross-section
ΔG	Gain bandwidth
τ_{exp}	Gain per unit length
R_{DA}	Distance between the donor and acceptor ions
C_{DA}	Donor-acceptor interaction parameter
C_{DD}	Donor-donor interaction parameter