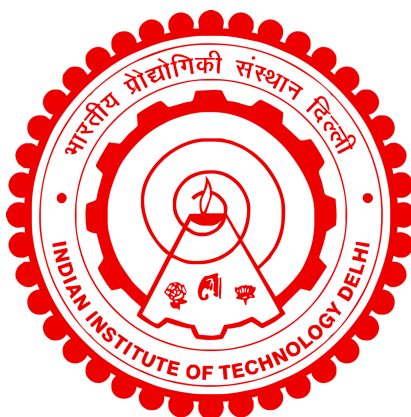


**LANTHANIDE ION DOPED
SODIUM - POTASSIUM BISMUTH FLUORIDE
NANOSTRUCTURES FOR PHOTONICS AND
BIOMEDICAL APPLICATIONS**

MANISHA BUNGLA



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

July 2024

**LANTHANIDE ION DOPED
SODIUM - POTASSIUM BISMUTH FLUORIDE
NANOSTRUCTURES FOR PHOTONICS AND
BIOMEDICAL APPLICATIONS**

by

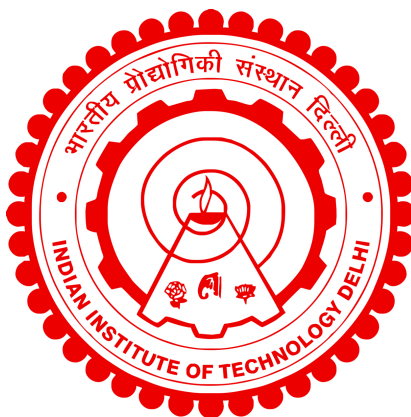
MANISHA BUNGLA

Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

JULY 2024

Dedicated to my parents

for their endless support and encouragement.

Certificate

This is to certify that the thesis entitled “**Lanthanide doped bismuth fluoride nanomaterials: Synthesis, characterization and applications in advanced photonics**”, submitted by **Ms. Manisha Bungla** (2019CYZ8127) to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of the original, bona fide research work carried out by him under our supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations related to the award of the degree.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma to the best of our knowledge.

Date:

Prof. Ashok K. Ganguli
Department of Chemistry,
Indian Institute of Technology Delhi
New Delhi-110016
INDIA


Prof. Paras N. Prasad
Department of Chemistry,
University at Buffalo
Buffalo, New York 14260-3000
USA

Prof. Pramit K. Chowdhury
Department of Chemistry,
Indian Institute of Technology Delhi
New Delhi-110016
INDIA

Acknowledgements

First and foremost, I would like to express my heartfelt gratitude to my supervisor, Prof. Ashok K. Ganguli, for his continuous support, guidance, motivation and good wishes throughout the course of this study. Beyond his role as a supervisor, I have found him to be a compassionate individual, always ready to provide support and guidance, during moments of uncertainty and doubt. I am truly fortunate to have had the opportunity to work under his guidance, and I am indebted to him for his guidance, encouragement, and belief in my abilities.

I am profoundly grateful to my co-supervisor, Prof. Paras N. Prasad, for his guidance and valuable feedback on my research. Thank you for introducing me to “scintillators” and giving me an opportunity to work at University at Buffalo, USA in my last year of Ph.D. You helped me to achieve a very multidisciplinary education and provided me with the chance to work with some amazing people.

I want to sincerely thank my co-supervisor Prof. Pramit K. Chowdhury for his immense patience unconditional time that he has dedicated to our lab through all these years. Your advice, comments, suggestions during the progress meetings have helped me grow in every aspect. Thank you always for allowing us access to your lab.

I whole-heartedly acknowledge and sincerely thank Dr. Mohit Tyagi (Technical Physics Division, BARC, Mumbai) for sharing his knowledge and carrying out the experiments related to scintillators. His continuous mentoring has been valuable in my learning journey in the field of scintillators, and I am immensely grateful for his guidance and support.

I would like to express my gratitude to my research committee members for their valuable comments and suggestions, which have greatly enriched my thesis. I would also like to express my thanks to all the past and present Head of the Department of Chemistry at IIT Delhi for their support in providing the necessary facilities required for the completion of my thesis. Additionally, I am grateful to all the faculty and staff members of the Department of Chemistry, for their assistance and support throughout my academic journey.

I want to acknowledge the Central Research Facility (CRF) and the Nano Research Facility (NRF) at IIT Delhi for providing access to facilities necessary for the completion of my research. Additionally, I would like to thank CSIR and University at Buffalo, USA for the financial support, enabling me to pursue my academic aspirations and contribute to the advancement of knowledge in my field.

I am immensely grateful to our collaborators, Prof. G. Vijaya Prakash, Mr. Mohd. Shanu and Ms. Ib Singh Deo (Department of Physics, IIT Delhi) for conducting upconversion photoluminescence measurements. I am grateful for the valuable discussions, thought-provoking questions, and helpful suggestions provided by Prof. G. Vijaya Prakash. I extend my sincere thanks to Prof. Vivekanandan Perumal and Ms. Shruti Chowdhuri (Kusuma School of Biological Sciences, IIT Delhi, New Delhi) for conducting in-vitro imaging experiments, I would like to acknowledge Dr. Asifkhan Shanavas and Ms. Priyanka Sharma (INST Mohali) for carrying out photodynamic therapy measurements

I gratefully acknowledge the Solid State & Nanomaterial Research Lab, particularly Lab 235, where I conducted all of my Ph.D. research. The countless hours spent there were valuable to my academic and personal growth, and I miss the vibrant atmosphere of Lab 235.

I would like to thank all the members, past and present, of our research group. Specifically, I want to thank Dr. Nitin Yadav, Dr. Sandeep Kumar, Dr. Vaishali, Dr. Preeti Dagar, Dr. Shalini Tiwari, Dr. Moumita Naskar, Dr. Anirban Das, Dr. Antara, Dr. Soumen Ash, Dr. Priyanka Yadav, Dr. Kirandeep, Prabuddha, Akshita, Manoj, Nitika, Ipshita, Aarti, Haribrahma and Archita. Their contribution has been valuable in creating a supportive and enthusiastic learning environment. I extend special thanks to Dr. Preeti Dagar for always being there for me, not just as a senior, but as a true friend.

I want to extend special thanks to my current and junior colleagues, Prabuddha, Akshita, Nitika, Ipshita, Aarti, Haribrahma and Archita working alongside you has been an enriching experience filled with growth and laughter. I loved popping over to your sitting areas to talk about science or life and deeply miss seeing you all every day. Our lengthy conversations, simply sharing stories over coffee, and the way time

flies when we're together are moments I'll cherish forever. I wish that you all have bright futures ahead, and look forward to see your continued success.

I am equally grateful to my lab mates at University at Buffalo, USA (Sonali, Dr. Sonal, Moumita, Mehargan, Dr. JoJo Joseph, Dr. Avisek and Evgenii) collaborators at ILPB (Dr. Andrey Kuzmin) and the CTRC (Dr. Supriya Mahajan) for their guidance, support, and the enriching experiences we shared.

Special thanks to Amit for being my support system and patiently listening to my research woes. Thank you for always motivating me to explore the world and inspiring me to aim high. Your support has been the guiding force that has kept me going.

I want to take this moment to express my heartfelt appreciation to my close friend, Aprajita, for always being there to support me emotionally and financially throughout the journey. I would also like to extend my gratitude to my cousin, Mansee Bisht, for always being there for me. Her support and delicious home-cooked meals have been a source of comfort, especially after long days in the lab. I am truly grateful for her presence and kindness, which have made difficult times easier to bear. Thank you, Mansee, for your love and care.

Special thanks to my father (Mr. Narayan Singh) for his support and sacrifices throughout my academic journey. I want to express my heartfelt gratitude for your ongoing interest and support in my Ph.D. journey. Your questions and queries about my project, research papers serve as a source of motivation for me. Your encouragement keeps me focused and motivated to overcome challenges and succeed in my life. Thank you, for believing in me and giving me the chance to pursue my dreams. Your love and support have been the cornerstone of my success, and I am forever indebted to you. Also, I would like to thank my mother (Mrs. Nandi) for giving me complete freedom to delve into my passions and chase my dreams. Without her support, guidance, and affection, I would have not come this far. I want to extend my heartfelt gratitude to my uncle, Mr. Rajendra Singh Bisht, who has been a fatherly figure and a guiding light in my life. He had played a crucial role in shaping me into the person I am today. His dedication to science outreach programs and other initiatives aimed at the betterment of society serves

as a reminder of the importance of giving back and making a difference. Special thanks to my brother for his love and support throughout this journey.

To all those who have supported, believed, and contributed to this journey, whether through words of encouragement, gestures of kindness, or shared moments of celebration, I extend my deepest gratitude.

Manisha Bungla

Abstract

In recent years, there has been significant interest in lanthanide (Ln^{3+}) ion-doped luminescent materials due to their exceptional properties, including superior photostability, long lifetimes, sharp-band emissions, tunable emission and low toxicity. These features have encouraged investigations into various host materials, particularly those of the NaREF_4 type, encompassing a wide range of rare earth elements such as Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. However, the utilization of NaREF_4 matrices often necessitates substantial quantities of costly rare earth salts, imposing constraints on their development and application. Hence, there is a fundamental need to explore alternative non-rare earth host materials.

This thesis contributes to the understanding of bismuth fluoride based luminescent materials, providing insights into their synthesis, characterization and applications, in the field of bioimaging, photodynamic therapy and X-ray imaging thus paving the way for their widespread utilization in various domains. In this thesis, we present a simple strategy requiring only 1 minute at room temperature to synthesize the novel bismuth-based compounds NaBiF_4 and $\text{K}_{0.3}\text{Bi}_{0.7}\text{F}_{2.4}$ in high yield. Compared to traditional methods, our approach is straightforward and user-friendly, offering the potential for significant cost reduction by replacing expensive rare earth elements with bismuth. Further the $\text{NaBiF}_4:\text{Yb}^{3+}$, Tm^{3+} UCNP are used as luminescent probes for in vitro imaging of cells. Further a newly selected combination of $\text{K}_{0.3}\text{Bi}_{0.7}\text{F}_{2.4}$ and methylene blue has been explored for NIR-laser-activated PDT application. The methylene blue loaded UCNP show promising PDT mediated cytotoxicity against glioblastoma cells. This work paves a new way for the $\text{K}_{0.3}\text{Bi}_{0.7}\text{F}_{2.4}:\text{Yb}^{3+}$, Er^{3+} UCNP to be employed in a range of biological applications in the future. Further, the fabrication, scintillation properties of organic-inorganic nanocomposite self-standing films of $\text{NaBiF}_4:\text{Gd}^{3+},\text{Tb}^{3+}$ and $\text{K}_{0.3}\text{Bi}_{0.7}\text{F}_{2.4}:\text{Ce}^{3+}/\text{Gd}^{3+}/\text{Tb}^{3+}$ NSs are discussed in detail. The application in radiography is demonstrated by recording

X-ray images using a commercially available charge-coupled device camera. We attained a resolution comparable to the non- flexible commercial CsI (TI) scintillator and significantly superior to the commercial $\text{Gd}_2\text{O}_2\text{S: Tb}$ (GOS: Tb) scintillators commonly used for screens.

In the final chapter, we summarize all the major results that have been discussed in the preceding chapters and future perspectives and directions regarding this rapidly growing field for future research activities.

सार

हाल के वर्षों में, लैंथेनाइड (Ln^{3+}) आयन-अपमिश्रित (Ln^{3+}) में महत्वपूर्ण रुचि रही है ल्यूमिनसेंट सामग्री उनके असाधारण गुणों के कारण, जिसमें बेहतर फोटो शामिल है -स्थिरता, लंबे जीवनकाल, तेज-बैंड उत्सर्जन, ट्यून करने योग्य उत्सर्जन, कमजोर ऑटोफ्लोरेस-सेंस, कम विषाक्तता, और उच्च प्रवेश गहराई। इन सुविधाओं ने किया है प्रोत्साहित विभिन्न मेजबान सामग्रियों की जांच, विशेष रूप से NaREF_4 प्रकार की, Sc, Y, La, Ce, Pr, Nd, जैसे दुर्लभ पृथ्वी तत्वों की एक विस्तृत श्रृंखला को शामिल करते हुए, एसएम, ईयू, जीडी, टीबी, डीई, हो, एर, टीएम, वाईबी, और लू। हालाँकि, NaREF_4 का उपयोग मैट्रिसेस को अक्सर महंगे दुर्लभ पृथ्वी लवण की पर्याप्त मात्रा की आवश्यकता होती है, जो कि लागू होती है उनके विकास और आवेदन पर बाधाएं। इसलिए, एक मौलिक है वैकल्पिक गैर-दुर्लभ पृथ्वी मेजबान सामग्री का पता लगाने की आवश्यकता है।

यह थीसिस बिस्मथ फ्लोराइड आधारित ल्यूमिनसेंट की समझ में योगदान देती है सामग्री, उनके संश्लेषण, लक्षण वर्णन और अनुप्रयोगों में अंतर्दृष्टि प्रदान करना, बायोइमेजिंग, फोटोडायनामिक थेरेपी और एक्स-रे इमेजिंग के क्षेत्र में इस प्रकार फ़र्श विभिन्न डोमेन में उनके व्यापक उपयोग के लिए रास्ता। इस थीसिस में, हम एक प्रस्तुत करते हैं उपन्यास को संश्लेषित करने के लिए कमरे के तापमान पर केवल 1 मिनट की आवश्यकता होती है बिस्मथ-आधारित यौगिक NaBiF_4 और $\text{K}_{0.3}\text{Bi}_{0.7}\text{F}_{2.4}$ उच्च उपज में। पारंपरिक तरीकों की तुलना में, हमारा दृष्टिकोण सीधा और उपयोगकर्ता के अनुकूल है, जो महंगे दुर्लभ पृथ्वी तत्वों को बदलकर महत्वपूर्ण लागत में कमी की संभावना प्रदान करता है बिस्मथ। इसके अलावा NaBiF_4 : Yb^{3+} , Tm^{3+} UCNPs का उपयोग ल्यूमिनसेंट जांच के रूप में किया जाता है कोशिकाओं के इन विट्रो इमेजिंग के लिए। इसके अलावा $\text{K}_{0.3}\text{Bi}_{0.7}\text{F}_{2.4}$ का एक नया चयनित संयोजन और एनआईआर-लेजर-सक्रिय पीडीटी अनुप्रयोग के लिए मेथिलीन ब्लू का पता लगाया गया है। वहीं मेथिलीन ब्लू लोडेड यूसीएनपी के खिलाफ पीडीटी मध्यस्थता साइटोटॉक्सिसिटी का वादा करते हुए दिखाते हैं

ग्लियोब्लास्टोमा कोशिकाएं। यह काम $K_{0.3}Bi_{0.7}F_{2.4}:Yb^{3+}, Er^{3+}$ के लिए एक नया मार्ग प्रशस्त करता है यूसीएनपी को भविष्य में जैविक अनुप्रयोगों की एक श्रृंखला में नियोजित किया जाना है। इसके अलावा $K_{0.3}Bi_{0.7}F_{2.4}$ का एक नया चयनित संयोजन और एनआईआर-लेजर-सक्रिय पीडीटी अनुप्रयोग के लिए मेथिलीन ब्लू का पता लगाया गया है। वही मेथिलीन ब्लू लोडेड यूसीएनपी के खिलाफ पीडीटी मध्यस्थता साइटोटॉक्सिसिटी का वादा करते हुए दिखाते हैं ग्लियोब्लास्टोमा कोशिकाएं। यह काम $K_{0.3}Bi_{0.7}F_{2.4}:Yb^{3+}, Er^{3+}$ के लिए एक नया मार्ग प्रशस्त करता है यूसीएनपी को भविष्य में जैविक अनुप्रयोगों की एक श्रृंखला में नियोजित किया जाना है। रेडियोग्राफी में आवेदन रिकॉर्डिंग द्वारा प्रदर्शित किया जाता है व्यावसायिक रूप से उपलब्ध चार्ज-युग्मित डिवाइस कैमरा का उपयोग करके एक्स-रे छवियां। हम पर-गैर-लचीले वाणिज्यिक सीएसआई (टीआई) सिंटिलेटर के बराबर एक संकल्प रखा गया और वाणिज्यिक $Gd_2O_2S:Tb$ से काफी बेहतर (GOS: Tb) सिंटिलेटर आमतौर पर स्क्रीन के लिए उपयोग किया जाता है।

अंतिम अध्याय में, हम उन सभी प्रमुख परिणामों को संक्षेप में प्रस्तुत करते हैं जिनकी चर्चा पिछले अध्याय और भविष्य के दृष्टिकोण और इस बारे में दिशाएं तेजी से भविष्य की अनुसंधान गतिविधियों के लिए बढ़ते क्षेत्र।

Contents

Certificate

Acknowledgements

Bibliography

Abstract

Contents

List of Figures

List of Tables

Abbreviations

Symbols

1	Introduction	1
1.1	Lanthanides and their Luminescence	1
1.1.1	Energy levels of the Lanthanide ions	2
1.1.2	Selection rules	5
1.1.3	Luminescence quenching	6
1.2	Overview of upconversion mechanism	7
1.2.1	Role of the Host material	11
1.2.2	Activators	13
1.2.3	Sensitizers	13
1.3	Scintillators	14
1.3.1	History and comparison of inorganic scintillators	15

1.3.2	Mechanisms of XEOL processes in lanthanide doped fluoride NSs	17
1.4	Synthesis methods of host materials	18
1.4.1	Co-precipitation method	19
1.4.2	Reverse micelles	19
1.4.3	Thermal decomposition method	20
1.4.4	Hydrothermal method	21
1.5	Motivation of the thesis	22
2	Characterization techniques	27
2.1	Powder X-Ray Diffraction (XRD)	27
2.2	Field emission scanning electron microscopy (FESEM)	28
2.3	Energy dispersive X-ray spectroscopy (EDX)	30
2.4	Transmission Electron Microscopy (TEM)	31
2.5	Ultraviolet-visible (UV-VIS) spectroscopy	33
2.6	Photoluminescence spectroscopy	33
2.7	Radioluminescence	36
2.8	Cell sensitivity assay	36
2.9	Confocal microscopy	37
3	NaBiF₄: Yb³⁺, Tm³⁺ submicron particles as luminescent probes for in vitro imaging of cells	39
3.1	Introduction	39
3.2	Experimental section	42
3.2.1	Materials	42
3.2.2	Synthesis of NaBiF ₄ :Yb ³⁺ , Tm ³⁺	42
3.2.3	Cell culture and cytotoxicity assay	44
3.2.4	Confocal imaging	45
3.2.5	Characterization	45
3.3	Results and discussion	46
3.3.1	Structural and morphological investigations	46
3.3.2	Studies of upconversion photoluminescence and the energy transfer mechanism	48
3.3.3	Upconversion photoluminescence decay kinetics	53
3.3.4	Effect of NaBiF ₄ :Yb ³⁺ , Tm ³⁺ on viability of human cancer cell lines	54
3.3.5	Bioimaging and cellular uptake of NaBiF ₄ :Yb ³⁺ , Tm ³⁺ in human cancer cell lines	55
3.4	Conclusions	55
4	Methylene blue loaded K_{0.3}Bi_{0.7}F_{2.4}: Yb, Er upconversion nanoparticles for Near-Infrared activated photodynamic therapy	59

4.1	Introduction	59
4.2	Experimental section	61
4.2.1	Characterization	62
4.2.2	Singlet oxygen generation analysis	63
4.2.3	In vitro cellular experiments	63
4.2.4	Intracellular ROS generation Assay	64
4.2.5	Fluorescent imaging of cells	64
4.2.6	Statistical Analysis	65
4.3	Results and discussion	65
4.3.1	Structural and Morphological Investigations	65
4.3.2	Studies of upconversion photoluminescence and energy transfer mechanism	66
4.3.3	Upconversion photoluminescence decay kinetics	70
4.3.4	Loading of methylene blue dye	71
4.3.5	Singlet Oxygen ($^1\text{O}_2$) Detection	72
4.3.6	In vitro studies	74
4.4	Conclusions	75
5	NaBiF₄: Gd/Tb nanoscintillator for high-Resolution X-ray imaging	77
5.1	Introduction	77
5.2	Experimental section	79
5.2.1	Synthesis of NaBiF ₄ :Tb ³⁺	79
5.2.2	Preparation of thin film	80
5.2.3	Characterization	80
5.3	Results and discussion	81
5.4	Conclusions	92
6	K_{0.3}Bi_{0.7}F_{2.4}: Ce/Gd/Tb nanoscintillator with reduced afterglow and light scattering for high-resolution X-ray imaging	95
6.1	Introduction	95
6.2	Experimental section	97
6.2.1	Synthesis of K _{0.3} Bi _{0.7} F _{2.4} :Tb	97
6.2.2	Preparation of thin film	98
6.2.3	Characterization	98
6.3	Results and discussion	98
6.4	Conclusions	107
7	Summary and future outlook	111
7.1	Conclusions	111
7.2	Future scope	112

List of Figures

1.1	Splitting of $4f^n$ electronic energy levels due to coulomb repulsions, spin-orbit coupling and crystal field effect	3
1.2	Dieke diagram: energy levels of the $^{2S+1}L_J$ multiplet manifolds of trivalent lanthanide ions.	4
1.3	Schemes of possible mechanisms for luminescence concentration quenching: (a) energy migration among donors (circles) in a chain followed by its migration to a killer site (red circle) which acts as non-radiative sink; (b) cross relaxation between pairs of centers.	8
1.4	Principal UC processes for lanthanide-doped UCNPs: (a) excited-state absorption (ESA), (b) energy transfer upconversion (ETU) . . .	9
1.5	History and development of common inorganic scintillators.	15
1.6	Schematic illustration of the scintillation process in lanthanide doped fluoride NSs.	17
2.1	Illustration of Bragg's law	28
2.2	Interaction of electrons with matter	29
2.3	Schematic representation of a photoluminescence instrument	34
2.4	Setup for measurement of emission spectra	35
3.1	Synthesis of $\text{NaBiF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ by non – aqueous quaternary reverse micellar route.	43
3.2	Powder XRD patterns of NaBiF_4 codoped with $\text{Yb}^{3+}, \text{Tm}^{3+}$	46
3.3	TEM micrographs of NaBiF_4	47
3.4	FE -SEM micrographs of (a) NaBiF_4 and $\text{NaBiF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ submicron particles with different concentrations of Tm^{3+} ions (b) 0.5 mol% Tm^{3+} , (c) 1 mol% Tm^{3+} , (d) 2 mol% Tm^{3+} , (e) 3% mol% Tm^{3+} , (f) 4 mol % Tm^{3+} , (g-j) FE-SEM elemental mapping of NaBiF_4 submicron particles showing the presence of elements.	48
3.5	Schematic energy level diagram of $\text{NaBiF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ showing the various energy transfer mechanisms in the UC PL process.	49
3.6	(a) NIR to visible UC luminescence spectra of $\text{NaBiF}_4: 20\% \text{Yb}^{3+}, (0.5 - 4\%) \text{Tm}^{3+}$ submicron particles for excitation at 360 mW power density and (b-d) Laser power dependence PL emission spectra under 980 nm CW diode laser excitation.	50

3.7	Log-log dependence of UC PL intensity ($^1D_2 \rightarrow ^3F_4$, $^1G_4 \rightarrow ^3H_6$, $^3H_4 \rightarrow ^3H_6$) on pump power and excitation at 980 nm.	52
3.8	UC - PL lifetime measurements of NaBiF ₄ :Yb ³⁺ , Tm ³⁺ submicron particles excited at 980 nm.	53
3.9	Cell viability of (a,b) Huh-7 and (c,d) A549 cells determined using the MTT assay at varying concentrations of NaBiF ₄ : 20% Yb ³⁺ , 2% Tm ³⁺ and NaBiF ₄ : 20%Yb ³⁺ , 3%Tm ³⁺ . The bar graphs represent mean ($\pm$ SD)of three independent experiments.	54
3.10	Confocal laser scanning microscopy images of unfixed human cancer cell lines Huh7 and A549 incubated with NaBiF ₄ :Yb ³⁺ ,Tm ³⁺ variants after 24 hr using 473 nm laser excitation. Magnification: 100 $\times$. Scale bar = 20 μ m.	56
4.1	Powder XRD pattern of KBF: Yb, Er	65
4.2	(a) FE-SEM, (b) histogram of the particle size distribution with an average size of 40 nm (b) TEM (c) HRTEM images of the KBF nanoparticles.	67
4.3	FE-SEM micrographs of KBF:20Yb, Er NPs with different concentrations of Er ³⁺ ions (a) 1 mol% Er ³⁺ , (b) 2 mol% Er ³⁺ , (c) 3 mol% Er ³⁺ ,(d) 4 mol% Er ³⁺ (e)EDX spectra of KBF:Yb,Er NPs showing the presence of elements.	68
4.4	Schematic energy level diagram of KBF: Yb, Er showing the various energy transfer mechanisms in the UC PL process.	69
4.5	(a) NIR to visible UC photoluminescence spectra of K _{0.3} Bi _{0.7} F _{2.4} : Yb ³⁺ , (1 - 4%) Er ³⁺ nanoparticles for excitation at 980 nm and 50 mW power (b) and laser power dependence PL emission spectra under 980 nm CW diode laser excitation (c) Log-log dependence of UC PL intensity ($^4F_{9/2} \rightarrow ^4I_{15/2}$, $^2H_{11/2}/^4S_{3/2} \rightarrow ^4I_{15/2}$) on pump power and excitation at 980 nm (d) Overlap between MB absorption and KBF: Yb, Er emission spectra.	70
4.6	(a) PL lifetime measurements of KBF:Yb, Er UCNPs upon excitation at 980 nm.	71
4.7	UV-Vis spectra of KBF:Yb, Er nanoparticles and methylene blue loaded KBF:Yb, Er@SiO ₂ nanoparticles (b) Upconversion PL spectra of KBF:Yb, Er and MB loaded KBF:Yb, Er nanoparticles.	73
4.8	Singlet oxygen generation with NIR laser λ = 980 nm in (a) UCNPs and (b) methylene blue	73
4.9	Percentage cell viability of a) glioblastoma cell line (C6) and b) normal mouse fibroblast cell line (L929) when treated with UCNPs (75 μ g/mL or 100 μ g/mL) in presence & absence of laser irradiation, c) Quantitative & d) qualitative analysis of UCNP mediated generation of intracellular ROS, e) Confocal images of C6 cells stained for live (green) and dead (red) cells post photosensitization with UCNPs. . .	75

5.1	Powder XRD patterns of (a) NBF: x%Tb and (b) NBF: 20%Gd, x%Tb.	81
5.2	(a-f)Elemental mapping results of NaBiF ₄ : 20Gd/20Tb NPs (g) EDX spectrum.	82
5.3	(a) FE-SEM, (b) TEM (c) HRTEM images of the NBF: Gd, Tb nanoparticles.	83
5.4	(a) PL spectra of NBF: x% Tb (x= 2-24%) under 376 nm excitation (b, c) NBF:20Gd, x% Tb under 273 nm excitation (d) PL emission spectra from Gd ³⁺ ions corresponding to emission at 310 nm.	84
5.5	(a) RL spectra of NBF: Tb (b) NBF: 20% Gd, Tb (x= 0.5-25%) nanoparticles.	85
5.6	(a) PL decay curves of NBF: xTb and (b) NBF: 20% Gd, x%Tb (x = 15, 20, 25) nanoparticles.	85
5.7	Proposed energy conversion and transport and luminescence mechanisms in the NBF: Gd/Tb nanoscintillator.	86
5.8	(a) Absorption spectra of PMMA-NBF film and NBF:20Gd, 20Tb(b) XEOL emission spectra of the NBF: 20Gd/20Tb NPs and the commercial CsI (Tl) single crystal, (c) Persistent luminescence decay curve of NBF: 20Gd/20Tb samples for 60 min after switching off X-ray (d) Radioluminescence stability of NBF: 20Gd/20Tb powder samples under continuous X-ray irradiation for 60 min.	87
5.9	Fabrication of PMMA- NBF: Gd/Tb composite films	88
5.10	(a) FESEM image of PMMA-NBF film (b) Cross-sectional FE-SEM image of a PMMA-NBF thin film (c) EDX spectrum of PMMA: NBF (Gd, Tb) composite films.	89
5.11	(a) Absorption spectra of PMMA-NBF film of thickness 3 and 6 μ m; (b) transmission spectra of PMMA-NBF film (c) excitation and PL spectra of PMMA-NBF film (d) XEOL spectra of PMMA-NBF with different loading percentages.	90
5.12	(a) Radioluminescence spectra of (a) NBF: Gd/Tb exposed to varied X-ray tube currents (b) NBF: Gd/Tb film under varied X-ray tube voltages (c) NBF: Gd/Tb integrated RL intensity as a function of varying tube current at constant tube voltage (d) NBF: Gd/Tb integrated RL intensity as a function of varying tube voltages at constant current.	91
5.13	(a) X-ray radiography setup consisting of X-ray source, object, CCD camera, and the composite screen (b) image formed by a duplex wire with a resolution of 100 microns.	92
5.14	Performances of different scintillators in X-ray imaging.	93
6.1	Powder XRD patterns of (a) KBF:x%Tb and (b) KBF:15%Ce/Gd/Tb.	99
6.2	(a) TEM, (b) FE-SEM, (c) HR-TEM and (d) EDX spectrum of the KBF: Ce/Gd/Tb nanoparticles.	99

6.3	Photoluminescence spectra of (a) KBF: Tb under 376 nm excitation (b) KBF: Gd/Tb film under 274 nm excitation (c) KBF: Ce/Gd/Tb (d) Lifetime measurements of KBF: Ce/Gd/Tb under 350 nm excitation	100
6.4	Proposed energy conversion and transport and luminescence mechanisms in the KBF: Ce/Gd/Tb nanoscintillator.	101
6.5	Radioluminescence spectra of (a) KBF: Tb (b) KBF: Gd/Tb (c) KBF: Ce/Gd/Tb (d) XEOL emission spectra of the KBF: 15Ce/15Gd/10Tb NPs and the commercial CsI(Tl) single crystal.	102
6.6	(a) FESEM image of PMMA-KBF film (b) Cross-sectional FE-SEM image of a PMMA-KBF thin films.	104
6.7	(a) Transmission spectra of KBF:PMMA film (b) XEOL spectra of KBF:PMMA with different loading percentages (c) RL stability test of KBF:PMMA film (d) Afterglow spectra of the KBF:PMMA film recorded after cessation of X-rays (radiation time, 5 min) immediately.	106
6.8	(a) X-ray radiography setup consisting of X-ray source, object, CCD camera, and the composite screen (b) image formed by a duplex wire with a resolution of 11.6 lp mm^{-1}	107
6.9	Performances of different scintillators in X-ray imaging.	108

List of Tables

1.1	Phonon energies of commonly used host matrices for lanthanide ions .	11
3.1	Parameters obtained by the exponential fitting of the UC PL lifetime data	53
4.1	Parameters obtained by the exponential fitting of the UC PL lifetime data	71

Abbreviations

NIR	Near infrared
nm	Nanometer
UCNP	Upconversion Nanoparticles
DMEM	Dulbecco's eagle medium
MTT	3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium Bromide
PL	Photoluminescence
ESA	Excited state absorption
ETU	Energy transfer upconversion
MB	Methylene blue
TEOS	Tetraethylorthosilicate
NSs	Nanoscintillators
XEOL	X-ray excited optical luminescence
RL	Radioluminescence

Symbols

c	speed of light in vacuum
ϵ	dielectric constant/permittivity
ω	rate of phonon emission
λ	wavelength
$\hbar$	reduced Planck's constant
l	orbital angular momentum in units of $2\pi\hbar$