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

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July 2024

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by

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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.

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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 $K_{0.3}Bi_{0.7}F_{2.4}$ 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 $NaBiF_4$:Yb^{3+}, Tm^{3+} UCNPs are used as luminescent probes for in vitro imaging of cells. Further a newly selected combination of $K_{0.3}Bi_{0.7}F_{2.4}$ and methylene blue has been explored for NIR-laser-activated PDT application. The methylene blue loaded UCNPs show promising PDT mediated cytotoxicity against glioblastoma cells. This work paves a new way for the $K_{0.3}Bi_{0.7}F_{2.4}$:Yb^{3+}, Er^{3+} UCNPs 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 $NaBiF_4$: Gd^{3+},Tb^{3+} and $K_{0.3}Bi_{0.7}F_{2.4}$: Ce^{3+}/Gd^{3+}/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 Gd_2O_2S: 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 $K_{0.3}Bi_{0.7}F_{2.4}$ 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 $K_{0.3}Bi_{0.7}F_{2.4}$ 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। 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।

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Abbreviations

NIR	**N**ear infrared
nm	**N**anometer
UCNP	**U**pconversion **N**anoparticles
DMEM	**D**ulbecco's **e**agle **m**edium
MTT	**3**-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium Bromide
PL	**P**hotoluminescence
ESA	**E**xcited state absorption
ETU	**E**nergy transfer upconversion
MB	**M**ethylene blue
TEOS	**T**etraethylorthosilicate
NSs	**N**anoscintillators
XEOL	**X**-ray excited optical luminescence
RL	**R**adioluminescence

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 $2\pi\hbar$