Study of Some Low Dimensional Metal Oxides for Optoelectronic Device Applications

Thesis submitted in partial fulfilment for the

Award of Degree

Doctor of Philosophy

in

Physics

by

Prashant Kumar Pandey

DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI – 221005

Roll Number: 17171005 **2023**

भारतीय प्रौद्योगिकी संस्थान
काशी हिन्दू विश्वविद्यालय

INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY

Certificate

It is certified that the work contained in the thesis titled ***"Study of Some Low Dimensional Metal Oxides for Optoelectronic Device Applications"*** by Prashant Kumar Pandey has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of the comprehensive examination, candidacy, and SOTA for the award of Ph.D. Degree.

Signature:

12/1/2023

Supervisor

Dr. Praveen Chandra Pandey
(Associate Professor)
Department of Physics
Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005 (U.P), India

Associate Professor
Department of Physics
Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005

भारतीय प्रौद्योगिकी संस्थान
काशी हिन्दू विश्वविद्यालय

INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY

Declaration by the candidate

I, ***"Prashant Kumar Pandey"***, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of ***"Dr. Praveen Chandra Pandey"*** from ***"July 2017"*** to ***"January* 2023"**, at the ***"DEPARTMENT OF PHYSICS"***, Indian Institute of Technology (BHU), 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 other's work, paragraphs, text, data, results, *etc*., reported in journals, books, magazines, reports dissertations, thesis, *etc*., or available on websites and have not included them in this thesis and have not cited as my work.

Date: 12/01/2023
Place: IIT (BHU), Varanasi

Signature of the Student
(*Prashant Kumar Pandey*)

CERTIFICATE BY THE SUPERVISOR

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

12/1/2023
Supervisor

Dr. Praveen Chandra Pandey
(Associate Professor)
Associate Professor
Department of Physics
Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005

12/01/23
Signature of Head of Department

Prof. Sandip Chatterjee
अध्यक्ष / Head
भौतिकी विभाग/Deptt. of Physics
भारतीय प्रौद्योगिकी संस्थान/
Indian Institute of Technology
(का०हि०वि०) / (BHU)
वाराणसी/Varanasi-221005

भारतीय प्रौद्योगिकी संस्थान
काशी हिन्दू विश्वविद्यालय

INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY

Copyright transfer certificate

Title of the Thesis: Study of Some Low Dimensional Metal Oxides for Optoelectronic Device Applications

Name of the Student: Prashant Kumar Pandey

Copyright Transfer

The undersigned hereby assigns to the Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the *"DOCTOR OF PHILOSOPHY"*.

Prashant
Signature of the Student
(*Prashant Kumar Pandey*)

Date: 12/01/2023
Place: IIT (BHU), Varanasi

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for the author's personal use provided that the source and the Institute's copyright notice are indicated.

Acknowledgments

First of all, I would like to express my sincere gratitude to my research supervisor Dr. Praveen Chandra Pandey for his valuable guidance, motivation, and continuous encouragement during my entire research work. The completion of this research work is indeed an outcome of his support, valuable ideas, and suggestions.

I express my gratitude to the Head of the Department for providing me required facilities. I am extremely thankful to my RPEC members Dr. Saurabh Tripathi and Dr. A. K. Singh for the invaluable inspiration, kind support, and numerous insightful suggestions during the entire course of this research. I am also grateful to Dr. V. Kumar (Jammu University) for his valuable support in carrying out the measurements and sample characterizations.

I use this opportunity to express my gratefulness to all the faculty members of the Department of Physics for their kind encouragement and motivation during my research period. I am also thankful to the entire non-teaching staff of the Department of Physics, and CIFC IIT (BHU) Varanasi for their assistance and for providing measurement facilities.

I would like to extend my thanks to my lab companions and friends Raj Kumar, Prashant Dixit, Vaibhav, Hemant, Umang, Satyam, and Sanket for providing me with a conducive environment to carry out my research work. I would also like to express my sincere appreciation to my colleagues and dearest friends Rohit, Digvijay, Vivek, Deepak, Abhishek, Balveer, Alam, Uma and *all research scholars of the department for their lively friendship and continuous support at all stages of my research.*

I feel short of words to express my appreciation, gratitude, and indebtedness to my family members, my father Shri Satya Narayan Pandey and mother Smt. Suman Pandey, and my whole family for their unbounded love, blessings, encouragement, and support during my entire academics. Many others that have been involved also deserve recognition. It is, however, not possible to list them all here. Their support in this effort is, however, greatly appreciated.

Finally, I am grateful to the Almighty God for giving me the patience to make this endeavour a success.

Sincerely

(Prashant Kumar Pandey)

Dedicated

To

My Beloved

Family

Table of contents

List of figures

List of tables

Preface

Metal oxide based nanomaterials and nanocomposites have drawn significant interest of the research community worldwide and played crucial role in developing excellent optoelectronic devices for several technological applications. The key motivation of this thesis work is to synthesize and study the luminescence properties of the rare-earth doped Bi_2O_3 phosphors and structural, optical, and electrical properties of Ag-ZnO nanocomposites for diverse applications such as light emitting diode, color-tunable devices, and UV- detectors. The Bi_2O_3 has been used as a host matrix for the preparation of red emitting phosphors whereas, ZnO has been used as a host for UV- detection owing to their multitudinous properties such as excellent thermal and chemical stability, low cost, environment-friendly synthesis, near-UV absorption, and good solubility for rare-earth elements.

The research work presented in this thesis has been divided into **seven** chapters.

Chapter 1 presents a brief introduction about the low-dimensional materials, metal oxides, optoelectronic devices, luminescence phenomena and their classification, phosphor materials, properties of the rare-earth elements, and UV- detectors. This chapter discusses the limitations and challenges of the phosphors and low-dimensional materials used for the application in the commercial wLEDs, tunable light sources, and UV-detection. The challenges and limitations of these applications which lead to the exploration of new doped phosphors and nanomaterials have also been discussed in this chapter. This chapter also includes a focussed study on the structural and luminescence properties of the Bi_2O_3 phosphors and ZnO based UV-detector used in the thesis work. Based on the study of various low- dimensional materials used in different optoelectronic applications, the motivation behind the thesis work has been outlined at the end of this chapter.

Chapter 2 deals with the methodology of sample preparation and different experimental tools and analysis techniques that have been used for sample synthesis and studying the various structural, luminescence and electrical properties of the prepared compositions. The synthesis techniques include urea assisted auto-combustion and co-precipitation methods. The specifications and working of the instruments used to characterize the samples are also discussed. The structural analysis is done using the XRD and FTIR data. To check the morphology and particle size of the prepared phosphors we have performed HR-SEM and TEM analyses. The elemental confirmation and oxidation states of the phosphors were validated using XPS analysis. The absorption characteristics and band gap energies were analyzed using the UV-Vis absorption spectroscopy. To shed light on the luminescence properties of the phosphors we have performed PL analysis. We have used temperature-dependent PL analysis to study the thermal stability of the phosphors prepared for solid state lighting applications and display devices. Moreover, the structural and optical properties of various compositions of Ag-ZnO nanocomposites were carried out and their correlations with electrical properties have been investigated thoroughly. The electrical analysis of the samples was probed to study the photoresponse and I-V characteristics of the fabricated Ag-ZnO based nanocomposites for UV detector applications.

Chapter 3 presents the study of pure Bi_2O_3, Sm^{3+} (1% – 5%) doped Bi_2O_3 and Li^+ (0.5% – 3%) co-doped in 5% Sm^{3+} doped Bi_2O_3 (Bi_2O_3:5Sm^{3+}) phosphor synthesized via co-precipitation method. The structural analysis has been carried out for phase identification, authentication of phase purity, and calculation of crystallite size and microstrain. Some results from the absorption spectra such as red-shift in the doped and co-doped samples have been discussed. The effects of Li^{+} co-doping on the reddish-orange emission of Sm^{3+} doped Bi_2O_3 has been discussed in this chapter. The reduced microstrain and increased crystallinity of the phosphors as a result of Li^{+} co-doping and their correlation with the luminescence of Sm^{3+} ions are discussed.

Chapter 4 describes the result of Na^{+} co-doping on the photoluminescence and structural properties of Sm^{3+} doped Bi_2O_3 phosphors. The structural and elemental properties were investigated by XRD, FTIR, and XPS analysis. The chapter also presents the morphological study of the phosphors and an augmentation in the grain size after Na^{+} co-doping has been discussed. Photoluminescence excitation and emission analysis evince the improvement in the intensity after 1% Na^{+} co-doping in the 5% Sm^{3+} doped Bi_2O_3 phosphor. Moreover, the temperature-dependent PL study is discussed which reveals good thermal stability of the phosphor. The reddish-orange emission of the prepared Na^{+} co-doped Bi_2O_3:5%Sm^{3+} phosphor shows that it can be a potential red phosphor for lighting and display devices.

Chapter 5 deals with the study of energy transfer dynamics, and emission color tuning in Sm^{3+}/Eu^{3+} co-doped Bi_2O_3 phosphors. The chapter demonstrates a viable scheme for tailoring the PL emission of phosphors through precisely controlling dopant concentrations. We have reported that the emission is tuned from reddish-orange towards the red region as depicted in chromaticity diagram. A detailed energy transfer process between the rare earth ions is discussed. Furthermore, the temperature-dependent PL study has been carried out to elucidate the thermal stability of the phosphors. Therefore, this chapter shows that our research opens up new possibilities for the development of color-tunable luminous materials for various optoelectronic and display device applications.

Chapter 6 presents the structural, optical, and electrical properties of Ag-ZnO nanocomposites, synthesized by precipitation method. The structural and elemental properties were investigated by XRD and FTIR analysis. Moreover, the correlation of structural and optical properties with enhanced photocurrent has been investigated thoroughly. The absorption and electrical properties infer that the samples have a broad absorption and an enhanced photoresponse in the UV region of the electromagnetic spectrum.

Conclusion of the overall studies has been summarized in the last **chapter 7**. This chapter also comprises further future research plans on this topic.