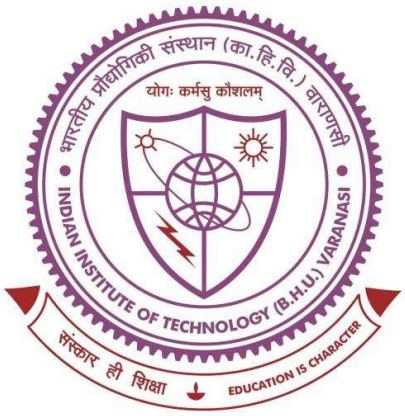
Study of Some Low Dimensional Metal Oxides for Optoelectronic Device Applications



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**

Chapter 7

Summary and future scope

This chapter provides a summary of the overall findings of the study conducted for this thesis. The significance of our findings for lighting and display devices and UV detector applications is also highlighted. The future scope and future work to be carried out are also discussed in this chapter.

7.1 Summary

The present thesis discusses interesting studies on rare-earth doped reddish-orange phosphors for the applications in white LEDs, tunable light emitting sources, display devices, and also focuses on the development of cost effective Ag-ZnO based nanocomposites for efficient UV detectors. The samples were synthesized by facile urea-assisted auto-combustion and co-precipitation methods. The Bi_2O_3 phosphor has been employed as a host lattice for the synthesis of reddish-orange emitting phosphors owing to their multitudinous features such as outstanding thermal and chemical stability, low cost and environment-friendly synthesis, and good solubility for rare-earth elements. The nanocomposites of transition metal (Ag) with ZnO nanomaterials have been used to develop novel UV detectors with enhanced photoresponse. The crystal structure and phase formation were validated by the XRD patterns. The estimation of the crystallite size and microstrain is also done by employing the Williamson-Hall method. The HR-SEM analysis is used to examine the morphology and estimation of the average grain size of the prepared samples. The photoluminescence properties of the phosphors are studied by the PL excitation, emission, decay, and temperature-dependent PL measurements. The I-V characteristics and responsivity measurements were carried out to investigate the enhancement in photocurrent and device performance. The samples studied for the present thesis are Li^+/Sm^{3+} co-doped Bi_2O_3, Na^+/Sm^{3+} co-doped Bi_2O_3, Sm^{3+}/Eu^{3+} co-doped Bi_2O_3, and Ag-ZnO nanocomposites. Chapter wise summary of studied composition can be explained as follows:

Chapter 1 This chapter provides introduction and a detailed explanation of the low-dimensional materials, metal oxides, various optoelectronic devices, rare earth ions, luminescence phenomena etc. 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. At the end of this chapter motivation behind the thesis is discussed.

Chapter 2 In this chapter, we have included different synthesis processes such as co-precipitation and urea-assisted auto combustion methods involved in the synthesis of phosphors and nanocomposites. Moreover, various characterization techniques and instrumentations like XRD, FTIR, XPS, PL, UV-Vis, I-V *etc.*, employed in the sample characterization have been explained thoroughly.

Chapter 3: In this chapter, we have investigated the consequences of Li^{+} ion incorporation with different co-doping concentrations on structural and optical properties of Sm^{3+} doped Bi_2O_3 phosphors. A series of undoped, Sm^{3+} doped, and Sm^{3+}/Li^{+} co-doped Bi_2O_3 nano-sheets were successfully synthesized by a facile and cost-effective co-precipitation method. The XRD and FTIR results were used as probes for phase quantification and chemical bonding authentication of the samples and validate the monoclinic crystal structure of the synthesized samples. The XPS analysis validates the oxidation state and ensures the existence of all constituents in the sample. Moreover, it corroborates the presence of oxygen vacancies in the samples. The optical band gap and Urbach energy of the samples were examined using UV-Vis absorption spectroscopy. For the investigation of surface morphology, elemental confirmation, and to validate their estimated contents in the samples, HR-SEM and EDX analysis were performed. PL studies of the samples clearly indicate a nearly two-fold augmentation in the emission intensity in the co-doped samples and the CIE and CCT analysis confirm their applicability as red phosphors for warm white light emitting diodes, and display devices.

Chapter 4: The present chapter has been conducted to investigate the role of Na^{+} ions co-doping on the structural and optical properties of Sm^{3+} doped Bi_2O_3 nanophosphors. This chapter focuses on the facile and room temperature synthesis of Sm^{3+} doped and alkali metal (Na^{+}) ion co-doped Bi_2O_3 nanophosphors using co-precipitation method, including the study of their structural and optical properties. The XRD results reveal the monoclinic crystal structure of the synthesized nanophosphors. An improved crystallinity is observed in co-doped samples, which also helps in improving the PL emission intensity. The HR-SEM analysis suggests that the prepared nanophosphors have nano-sheet-like morphology. The corresponding EDX spectra confirm the presence of all elements in the phosphors. The TEM images substantiate the nano-sheet-like morphology, obtained from the HR-SEM micrographs and confirm the polycrystalline nature of the phosphors. The XPS analysis confirms the presence of all the elements, validates their oxidation states, and verifies the EDX data. The UV-Vis absorption spectroscopy reveals the decrease in the bandgap of the phosphors with the increase in doping and co-doping concentrations, which may arise due to the formation of intermediate trap levels within the bandgap region and increased oxygen vacancies. These results were further validated by the corresponding Urbach energy values. The PL spectra was recorded at 481 nm excitation and the maximum emission corresponding to $4_{G_{5/2}} \rightarrow 6_{H_{7/2}}$ transition was observed at 598 nm. The fluorescence intensities were found to increase nearly ten-fold in 5% Sm^{3+} doped and 1% Na^{+} co-doped Bi_2O_3 nanophosphor, as compared to the 5% Sm^{3+} doped Bi_2O_3 nanophosphor. The obtained CCT values for 5% Sm^{3+} doped and 5% Sm^{3+} doped and 1% Na^{+} co-doped Bi_2O_3 nanophosphors were found to be 2808 K and 1969 K, respectively. This implies that co-doping leads to a significant decrease in the CCT. Thus, we can corroborate that the co-doping of Na^{+} ion leads to a substantial enhancement in the luminescence intensity of the rare-earth-doped

nanophosphors, and therefore, they can have potential applications in solid-state lighting and display devices. The decay curves analysis further supports the enhancement in emission intensity for 1% Na^{+} co-doped phosphor. The temperature-dependent PL analysis reveals that PL emission decays by ~ 44.7% at 423 K (150 ^{o}C) and the thermal activation energy for 1% Na^{+} co-doped phosphor was calculated to be 0.23 eV.

Chapter 5: This chapter demonstrate the study of a series of Sm^{3+}, Eu^{3+} co-doped Bi_2O_3 phosphors synthesized by a facile auto-combustion route. The study of structural, optical, and thermal stability of the phosphors have been carried out in detail. The XRD analysis corroborates that all the prepared phosphors have tetragonal crystal structure. An augmentation in the crystallinity of the phosphors has been observed with increase in doping concentration. The XPS study reveals that all the elements are present in the samples in their respective oxidation states. The information regarding vibrational states and functional groups in the samples was provided by FTIR analysis. The UV-Vis-NIR absorption study suggests that the band gap of the phosphors decreases after doping and co-doping, which may arise due to the formation of additional trap states within the conduction and valance band region. The PL excitation and emission studies were carried out at 481 ($6_{H_{5/2}} \rightarrow 4_{I_{9/2}}$) nm excitation wavelength and 598 nm ($4_{G_{5/2}} \rightarrow 6_{H_{7/2}}$) emission wavelengths, respectively. The phenomena of energy transfer from Sm^{3+} to Eu^{3+} ions have been discussed thoroughly. The thermal stability of the phosphors was examined using temperature dependent PL analysis over the range of 303- 543 K. A significant shift in the CIE coordinates from orange to reddish-orange region was observed after Eu^{3+} co-doping in Sm^{3+} doped phosphors. Thus our study corroborates that, Sm^{3+} and Eu^{3+} co-doped Bi_2O_3 phosphors in proper composition can prompt effective energy transfer phenomena and are potential candidates to realize efficient and thermally stable lighting and display devices.

Chapter 6: This chapter provides a study of the structural, optical and electrical properties of various compositions of ZnO and Ag-ZnO nanocomposites by a facile precipitation method. The work is mainly focussed on the detailed structural and electrical analyses of ZnO and its various nanocomposites comprised of silver metal nanoparticles. The correlation of enhanced photocurrent with structural and optical properties of the nanocomposites have been investigated thoroughly. The structural analysis ascertains the formation of ZnO nanoparticles and Ag-ZnO nanocomposites with good crystallinity and without any impurity and also decrease in strain and stress for Ag (13.7wt%)-ZnO nanocomposite is observed by increasing higher concentration of Ag nanoparticles. UV-Vis spectrum clearly shows a broad peak attributed to the SPR enhanced absorption due to Ag- nanoparticle. FE-SEM and EDX analysis have been carried out for the morphological and elemental analysis. Moreover, the current-voltage (I-V) characteristics of all samples have been measured under dark and incident UV illumination. Upon UV illumination, a clear enhancement in the photocurrent in the Ag (13.7wt%)-ZnO sample is observed which is ascribed to the reduced microstrain and the LSPR phenomena. Our study corroborates that this composition is a suitable candidate for UV- photodetectors.

7.2 Future scope of the study

We have successfully synthesized and studied the effect of alkali metal ion co-doping on the structural and optical properties of rare earth ion doped Bi_2O_3 phosphors synthesized via co-precipitation method. We have also studied the thermal stability and energy transfer phenomenon in the rare earth co-doped Bi_2O_3 phosphors, synthesized via urea-assisted auto combustion process. Further study has to be carried out to fabricate the cost-effective LED device by coating prepared phosphors on the commercially available blue chip and studying the quantum efficiency of the device. Improvement in the luminescence thermal quenching of the phosphors is still a challenge for the research community.

Therefore, there is scope in improving the thermal stability of rare earth ion doped Bi_2O_3 phosphors. The Bi_2O_3 phosphor has proven to be an excellent host phosphor for rare-earth elements, therefore, other applications such as luminescence thermometry, anti-counterfeiting and latent fingerprint detection can also be explored.

Moreover, the structural, optical and electrical studies of the Ag-ZnO nanocomposites have been carried out via facile precipitation method for UV detector applications. Thin film of ZnO with other dopants and preparation methods has to be studied with different compositions to enhance the responsivity of UV detector. In addition, transport and photocatalytic properties of doped ZnO should be explored via different preparation techniques.