

Influence of Gd Doping in Structural, Morphological and Optical Properties of ZnO Nanostructures Synthesised Via Sol-Gel Processes

Nudrat Jahan^{1*}, Monika Goyal²

Abstract

In this study, nanocrystalline Zn_{1-x}Gd_x (x=0.0 and 0.03) samples were synthesised via the Sol-gel combustion process. An array of analytical techniques was employed to examine the prepared samples to determine their different physical features. For both pristine and Gd-doped samples, the crystal symmetry is hexagonal with the P6₃mc space group which is verified via the Rietveld refinement analysis of X-ray diffraction (XRD) data. The atoms' bond length Zn-O and bond angle Zn-O-Zn/Gd are measured. The pure and Gd-doped materials surface morphology is studied by SEM (scanning electron microscopy) images at 5,000x magnification. EDS (energy dispersive x-ray spectroscopy) verifies the elemental compositions with the proper elemental stoichiometry. The crystallite size value varies from 18 to 25 nm for pristine and Gd-doped samples. FTIR (Fourier transform infrared) Spectra give details regarding the various modes of vibration related to the functional groups that exist in the samples. To examine their optical characteristics, the diffuse reflectance spectrum of UV visible is applied. Using Tauc's relation to compute the bandgap, it is discovered that Gd doping causes it to drop from 3.18 eV to 2.89 eV.

Keywords: Gadolinium, ZnO, doping, nanostructure, Sol-gel

INTRODUCTION

Zinc oxide (ZnO) is an inorganic compound possessing a high exciton binding energy of 60 meV and a straight band gap energy of 3.37 eV [1]. ZnO has n-type behaviour having high electron mobility which makes it particularly suitable for applications in electronics where electron transport is important, such as in the development of transparent conductive films and sensors. However, ZnO can also exhibit p-type behaviour under certain conditions, making it a versatile material for a range of electronic and optoelectronic devices particularly those involving light emission (LEDs, lasers) and light absorption (solar cells). The combination of these properties contributes to the efficiency and performance of devices in these application fields. [2,3]. Intrinsic or undoped ZnO may have certain limitations regarding its optical, electrical, or catalytic properties, and doping is a strategy to overcome these

*Author for Correspondence

Nudrat Jahan

¹Research Scholar, Department of Physics, GLA University, Mathura, Uttar Pradesh, India

²Associate professor, Department of Physics, GLA University, Mathura, Uttar Pradesh, India

Received Date: March 11, 2024

Accepted Date: April 18, 2024

Published Date: July 17, 2024

Citation: Nudrat Jahan, Monika Goyal. Influence of Gd doping in structural, morphological and optical properties of ZnO nanostructures synthesised via Sol-gel processes. Journal of Polymer & Composites. 2024; 12(Special Issue 4): S219–S225.

limitations and tailor the material for specific applications. It has been widely recognized that Group III elements, i.e., Ga, Al, and In, are utilized as n-type dopants in ZnO to improve the electrical as well as optical characteristics of the materials [4]. On the other hand, the rare earth group, i.e. Gd, Yb, Tb, Ce, Tm, Er, La, Eu and Dy as the p-type dopants to ZnO, are also gaining considerable interest among the various groups because of their unique optical properties, which boost the photocatalytic performance and give strong emission peaks in the visible and near-infrared range [5]. When ZnO is doped with Cu, then Cu has

a valence state of + 2. As the concentration of Cu doping increased the photoluminescence intensity under light excitation decreased [6], film crystallite size increased [7], the optical band gap decreased [8] and the absorption spectrum of Cu doped ZnO was redshifted when the crystallite size of the nanoparticles is 32–38 nm [9]. From the lanthanum group, Gadolinium (Gd) metal was chosen as a doping agent in the investigation discussed herein. Gadolinium has high chemical stability, efficient photon-to-electron conversion and UV absorptivity which make them well-known as n-type semiconductors for photocatalysis. The interesting optical and magnetic features of Gadolinium oxide nanoparticles (Gd_2O_3 -NPs) result in several energy absorption levels in the ultraviolet and visible range. These characteristics have found use in a variety of industrial applications, such as materials that are magnetocaloric, luminous, catalytic and as contrast agents for magnetic resonance imaging. Gd doping on ZnO makes it extremely beneficial for magnetic purposes, electronic conductivity can also be modified, optoelectronic, and other optical components can also be constructed, and mechanical strength can be affected by doping [10,11,12,13]. The characteristics of zinc oxide with Gd-doping differ from the ones found in pure ZnO [14]. In this work, ZnO nanoparticles are synthesized using the Sol-Gel technique, by varying the amount of Gd doping to investigate the vibrational band structure, surface morphology, and crystalline structure.

EXPERIMENTAL DETAILS

Compared to other approaches, the sol-gel technology has several advantages. In particular, it uses inexpensive raw materials, permits the achievement of an appropriate particle size at a reduced processing temperature, and permits the creation of new compositions by regulating stoichiometry. The Sol-Gel method was used in the current work to synthesize both pristine and Gd-doped ZnO. The sol-gel technique is a bottom-up process that produces nanoparticles by hydrolysis, condensation, and aggregation reactions. To get the desired structure precursor concentration, pH and temperature need to be adjusted with great care. Zinc Nitrate [$\text{Zn}(\text{NO}_3)_2$], Gadolinium, ethanol and citric acid are used. To produce a clear solution, 10.43 grams of Zinc Nitrate were mixed in 50 ml of the distilled water in one beaker and 4.202 grams of citric acid was added in 20 ml of distilled water in the other. The beakers were then placed on a magnetic stirrer, and ammonia solution and ethylene glycol were added to keep the pH of the solution steady. The mixture was heated to 100 °C for approximately six to seven hours, stirring it often. Similarly, 50 ml of distilled water was used to dissolve the zinc nitrate (0.97) and Gadolinium (0.03). Citric acid was subsequently added dropwise to 20 ml of distilled water, in addition to the ethylene glycol and ammonia solution, to maintain a pH of approximately 8.5 to 11. The prepared samples of pure and doped ZnO were further placed in a furnace for 4 hrs. at 200 °C and the samples were ground. After again the sample is placed in the furnace at 450 °C for 2 hrs. Lastly, the sample is ground for 30 min and the sample is collected for characterization. In our case, the X-ray source is a Shimadzu X-ray diffractometer with $\text{Cu-K}\alpha$ radiation, with a wavelength (λ) of 1.5418 Å (Angstroms). The FTIR spectra are prepared using Bruker Tenser 37 spectrometer which results in the wavenumber range of 400–4000 cm^{-1} . For characterizing the surface morphology and elemental composition of materials SEM-EDS technique (JEOL, Japan) is used. A spectrophotometer Lambda 850, PerkinElmer is used for investigating the UV-Vis (DRS) spectra having wavelength in the order of 200–800 nm.

RESULTS AND DISCUSSION

Structural and Morphological Properties

The process of analysing the structural features involves recognizing distinct crystallographic planes within the X-ray Diffraction (XRD) spectra shown in Figure 1. In both samples, the strongest peak (101) is visible. It is found that each peak in the graph is in perfect accord with the JCPDS-36-1451 standard data. [15]. The well-defined peaks in XRD pattern suggest a highly crystalline structure and analysis of the ZnO sample indicates that it possesses a hexagonal wurtzite crystal structure. The XRD spectrum for doped samples reveal pure or Gd cluster peaks, suggesting that the measured amount of dopants is below the limit of solubility [16].

The crystalline size D is determined by using the Debye-Scherrer equation $D = 0.9\lambda/\beta\cos\theta$, where θ is the diffracting angle, β is the full width at half maximum (FWHM), and λ is the wavelength of X-ray light. In Table 1 the value of crystalline size is shown.

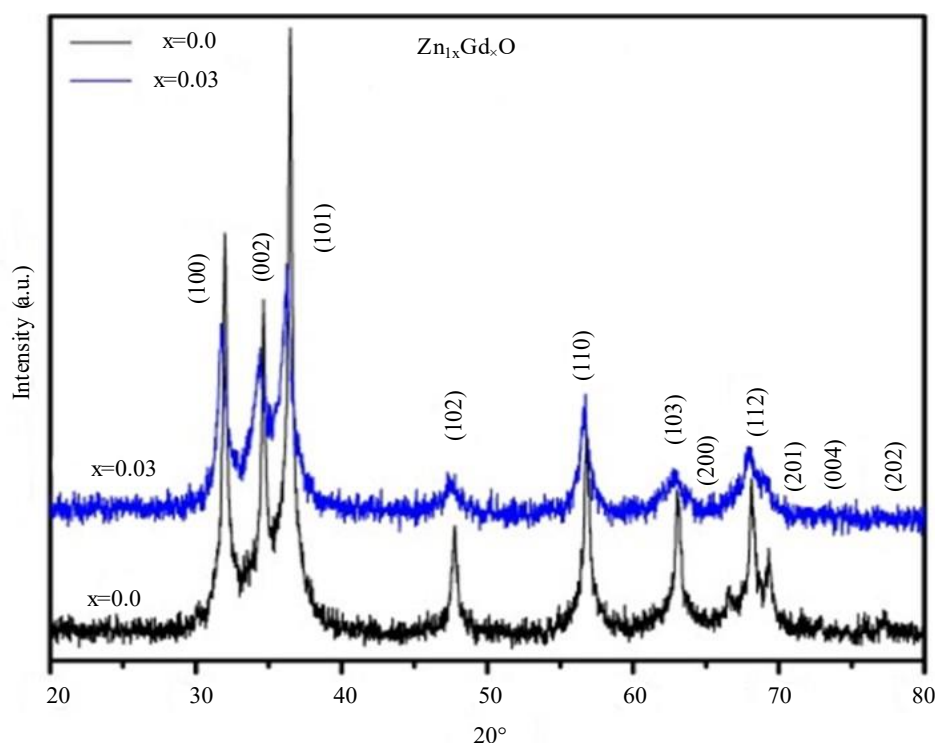


Figure 1. XRD of Pure and Gd-doped ZnO.

Table 1. Crystalline size of ZnO.

DOPING of Gd in ZnO	2θ	CRYSTALLINE SIZE D (nm)
X=0.00	36.48	24.97
X=0.03	36.22	18.25

The average crystalline size of pure ZnO is 24.97 nm and it increases to 18.25 in Gd -doped ZnO. Adding Gd ions compresses the ZnO lattice, generating greater strain. Other groups have presented similar findings regarding how Gd doping influences the structural alteration of ZnO [17].

FTIR spectra reveal information about the different functional groups that are present in a material as well as the bending and stretching modes of the metal-oxide pair. Figure 2 shows the FTIR spectra of samples that are Gd-doped and pure ZnO. FTIR spectra are plotted in the region 4000 cm^{-1} - 400 cm^{-1} . The band around 3449 cm^{-1} shows a hydroxyl (O-H) bond linked with ZnO.

The symmetric and asymmetric stretching vibrations of CH_2 are responsible for the peaks positioned approximately at 2929 cm^{-1} and 2850 cm^{-1} [18]. Different stretching modes like symmetrical and asymmetrical for the acetate carboxylic groups bound to ZnO have been viewed as doublet at 1500 cm^{-1} and 1400 cm^{-1} [14]. The area comprising metal-oxygen bonding (Zn-O and Gd-O) lies below 700 cm^{-1} [18]. The presence of the band at around 438 cm^{-1} is for Zn-O bonds in the FTIR spectrum which is shown in both the samples. At 464 cm^{-1} , new bands matching to Gd-O modes have been discovered for the doped sample.

The surface morphology of zinc oxide (ZnO) nanoparticles synthesized by the Sol-gel technique is represented in Figure 3a, 3b, 3c. The micrographs indicate the existence of an enormous amount of smaller nanoparticles, spherical in shape for ZnO when prepared by sol-gel method.

Optical Properties

The optical absorption characteristics of pure and doped ZnO nanoparticles were investigated by Ultra-Violet Visible Diffuse Reflectance spectra UV-VIS (DRS) for both the samples and it is

represented in Figure 4(a, b). The absorption edge of ZnO nanoparticles is approximately 345 nm in their pristine state but shifts to 330 nm in their 0.03 Gd-doped ZnO spectra. This fact is attributed to the reduction in crystalline size. The widely recognized Tauc's relation [19], is used to calculate the energy band gap (E_g) for both samples. The value of the energy band gap (E_g) can be obtained by extending the linear region of a graph of $(\alpha h\nu)^2$ vs photon energy ($h\nu$), which can be seen in inset Figure 4(b). The energy band gap (E_g)=2.86 eV for pristine and 2.94 for 0.03 Gd-doped ZnO.

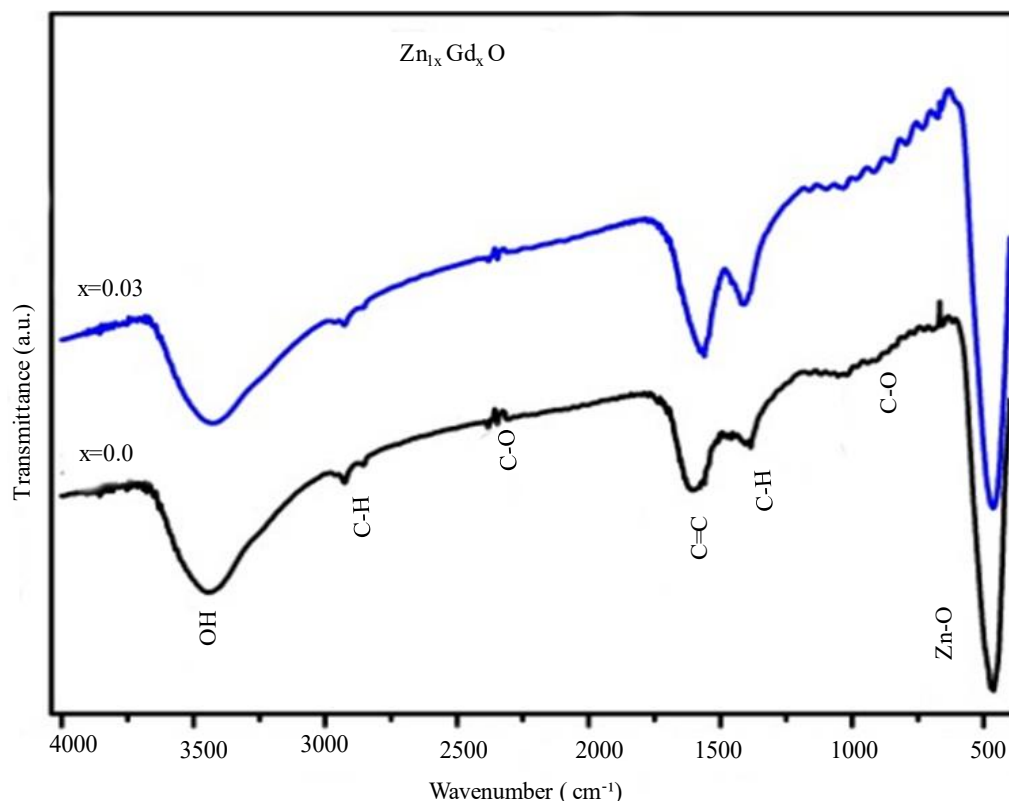
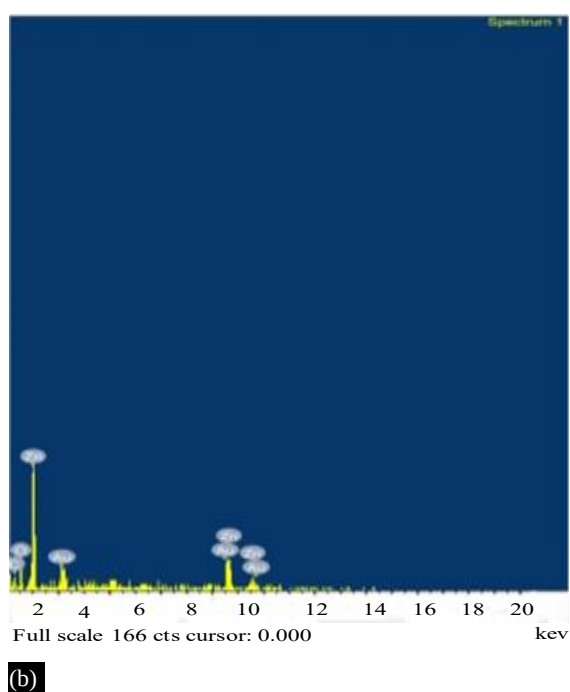
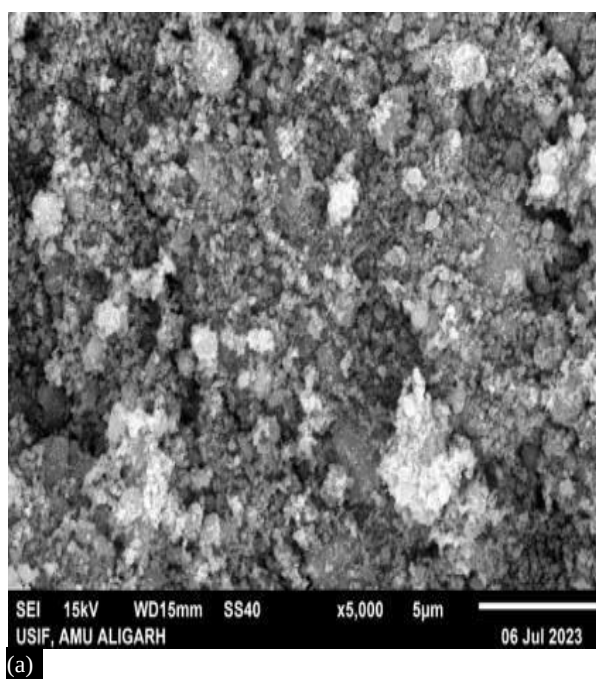


Figure 2. FTIR spectra of ZnO samples prepared by sol-gel technique.



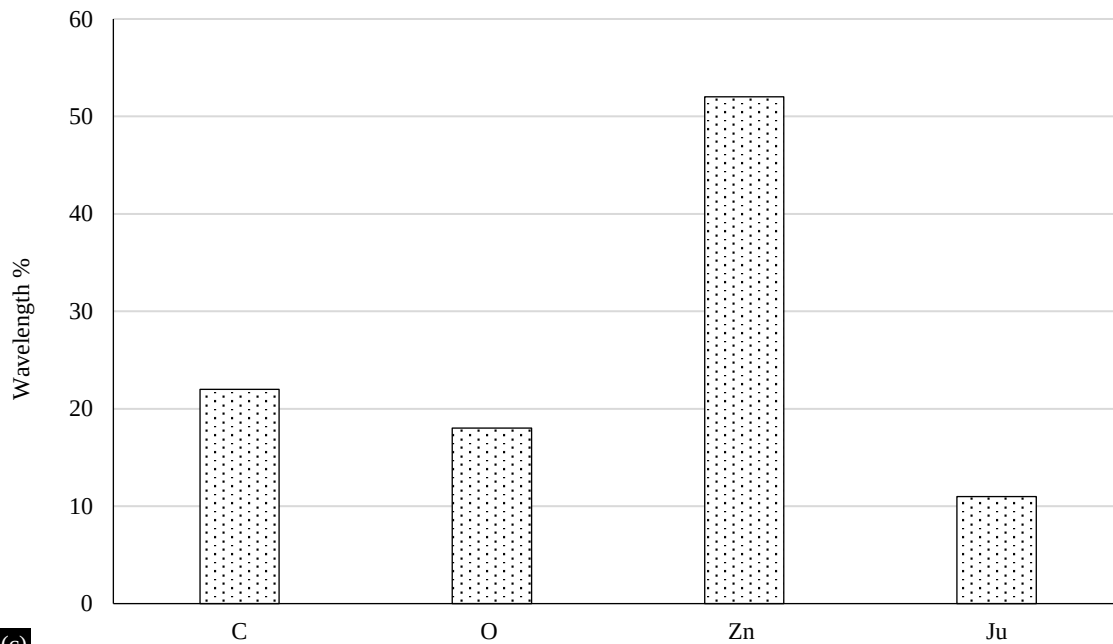


Figure 3. SEM micrograph with EDS pattern.

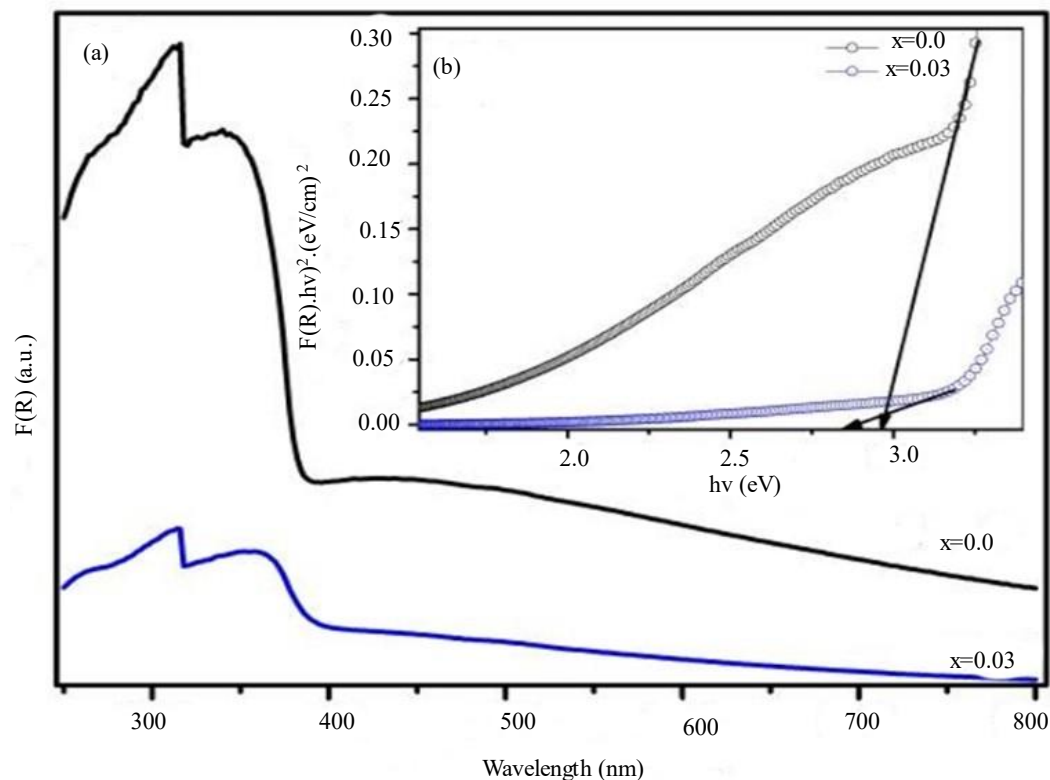


Figure 4. UV-vis (DRS) and inset graph shows Tauc's plots.

CONCLUSION

We have successfully synthesized, nanocrystalline $Zn_{1-x}Gdx$ ($x=0.0$ and 0.03) specimens using Sol-gel combustion techniques. The standard data from JCPDS-36-1451, which displays a hexagonal crystal structure showing space group $P6_3mc$, closely fits the data acquired from the investigation of the surface pattern of ZnO nanoparticles produced via Sol-gel combustion. Using Scherrer's equation, the

average crystalline size of both pure and Gd-doped ZnO has been calculated to be approximately 24.97 and 18.25 nm, respectively. The Scanning Electron Microscopy SEM (Model No. JSM 6510 LV, make – JEOL, Japan) images show the ZnO nanoparticles as large spherical-shaped particles. The Zn-O vibrational mode present in our samples is confirmed by FTIR spectra. The optical energy band gap of ZnO and doped specimens are determined using Tauc's plot and found at 2.86 eV and 2.94 eV respectively.

Acknowledgments

Nudrat Jahan expressed gratitude to her supervisor Prof Monika Goyal. Prof. M. W Khan and Dr. M. Abushad, Department of Physics, A.M.U for helping and providing lab facilities for the preparation of samples. I am thankful to the Department of Physics, A.M.U. Aligarh for performing XRD, Ms Uzma Meraj, Department of Chemistry,

A.M.U Aligarh for using the lab for UV-VIS (DRS). The authors are thankful to University Sophisticated Instrument Facility (USIF), for microscopy facilities at A.M.U., Aligarh.

REFERENCES

1. Wang, Zhong Lin. "Ten years' venturing in ZnO nanostructures: from discovery to scientific understanding and to technology applications." *Chinese Science Bulletin* 54 (2009): 4021-4034.
2. Kumaresan, S., K. Vallalperuman, and S. Sathishkumar. "A Novel one-step synthesis of Ag-doped ZnO nanoparticles for high-performance photo-catalytic applications." *Journal of Materials Science: Materials in Electronics* 28 (2017): 5872-5879.
3. Hjiri, Mokhtar, Nassim Zahmouli, R. Dhahri, S. G. Leonardi, L. El Mir, and G. Neri. "Doped-ZnO nanoparticles for selective gas sensors." *Journal of Materials Science: Materials in Electronics* 28 (2017): 9667-9674.
4. Zhao, Lin, Guangjie Shao, Shitao Song, Xiujuan Qin, and Sihuzhi Han. "Development on transparent conductive ZnO thin films doped with various impurity elements." *Rare metals* 30 (2011): 175-182.
5. Zamiri, Reza, A. F. Lemos, Avito Reblo, Hossein Abbastabar Ahangar, and J. M. F. Ferreira. "Effects of rare-earth (Er, La and Yb) doping on morphology and structure properties of ZnO nanostructures prepared by wet chemical method." *Ceramics International* 40, no. 1 (2014): 523-529.
6. Fang M, Tang CM, Liu ZW. "Microwave-assisted hydrothermal synthesis of Cu doped ZnO single crystal nanoparticles with modified photoluminescence and confirmed ferromagnetism". *J Electron Mater* (2018); 47:1390–6.
7. Kayani ZN, Iram S, Rafi R. "Effect of Cu doping on the structural, magnetic and optical properties of ZnO thin films". *Appl Phys Mater Sci Process* (2018); 124:468–70.
8. Das BK, Das T, Parashar K. "Structural, bandgap tuning and electrical properties of Cu doped ZnO nanoparticles synthesized by mechanical alloying". *J Mater Sci: Mater Electron* (2017); 28:15127–34.
9. Ouidette S, Djamel D, Laid H. "Structural and optical properties of Cu doped ZnO aerogels synthesized in supercritical ethanol". *J Porous Mater* (2018); 25:595–601
10. Dash, Debasrita, and Dojalisa Sahu. "Growth and Gd doping of ZnO nanostructures with enhanced structural, optical properties and photocatalytic applications." In *IOP Conference Series: Materials Science and Engineering*, vol. 1219, no. 1, p. 012037. IOP Publishing, 2022.
11. Murmu, P. P., R. J. Mendelsberg, J. Kennedy, D. A. Carder, B. J. Ruck, A. Markwitz, R. J. Reeves, P. Malar, and T. Osipowicz. "Structural and photoluminescence properties of Gd implanted ZnO single crystals." *Journal of Applied Physics* 110, no. 3 (2011).
12. Ma, Xiying, and Zui Wang. "The optical properties of rare earth Gd doped ZnO nanocrystals." *Materials Science in Semiconductor Processing* 15, no. 3 (2012): 227-231.
13. Mithal, Deepika, and Tapanendu Kundu. "Effect of Gd³⁺ doping on structural and optical properties of ZnO nanocrystals." *Solid State Sciences* 68 (2017): 47-54.

14. Bae, Jong Seong, Jung Hyun Jeong, Soung-soo Yi, and Jung-Chul Park. "Improved photoluminescence of pulsed-laser-ablated $Y_2O_3:Eu^{3+}$ thin-film phosphors by Gd substitution." *Applied Physics Letters* 82, no. 21 (2003): 3629-3631.
15. Ashoka, S., G. Nagaraju, C. N. Tharamani, and G. T. Chandrappa. "Ethylene glycol assisted hydrothermal synthesis of flower like ZnO architectures." *Materials Letters* 63, no. 11 (2009): 873-876.
16. Bae, Jong Seong, Jung Hyun Jeong, Soung-soo Yi, and Jung-Chul Park. "Improved photoluminescence of pulsed-laser-ablated $Y_2O_3:Eu^{3+}$ thin-film phosphors by Gd substitution." *Applied physics letters* 82, no. 21 (2003): 3629-3631.
17. Dakhel, A. A., and M. El-Hilo. "Ferromagnetic nanocrystalline Gd-doped ZnO powder synthesized by coprecipitation." *Journal of Applied Physics* 107, no. 12 (2010). Obeid M M, Jappor H R, Al-Marzoki K, Al-Hydary I A, Edrees S J and Shukur M M 2019 RSC Adv. 9 33207-33221.
18. R. Elilarassi and G. Chandrasekaran, "Structural, optical and magnetic properties of nanoparticles of ZnO : Ni — DMS prepared by sol–gel method," *Mater. Chem. Phys.*, vol. 123, no. 2–3, pp. 450–455, 2010.
19. D. B. Bharti, "Synthesis of ZnO nanoparticles using a hydrothermal method and a study its optical activity," no. June 2016, pp. 317–320, 2017.