INTERNATIONAL JOURNAL OF ADVANCE RESEARCH, IDEAS AND INNOVATIONS IN TECHNOLOGY

ISSN: 2454-132X
Impact Factor: 6.078
(Volume 11, Issue 2 - V11I2-1159)
Available online at: https://www.ijariit.com

Synthesis, Structural and Optical Characterization of Pure and Cobalt Doped Zinc Oxide Nanoparticles by Sol-Gel Method

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ABSTRACT

This study uses the sol-gel method to synthesize and characterize pure zinc oxide (ZnO) and cobalt-doped zinc oxide (Co-ZnO) nanoparticles. ZnO, a wide-bandgap semiconductor, is known for its optical transparency, high exciton binding energy, and antimicrobial properties, making it valuable for various applications in optoelectronics, sensors, and biomedical fields. Incorporating cobalt as a dopant modifies ZnO's structural and optical characteristics, enhancing its functionality in photocatalysis, spintronics, and magnetic storage devices. X-ray diffraction (XRD) analysis confirmed the hexagonal wurtzite structure for ZnO and Co-ZnO. However, Co doping led to decreased crystallite size, increased strain, and higher dislocation density, indicating lattice distortions. UV-Vis spectroscopy showed a shift in the absorption edge for Co-ZnO, suggesting bandgap narrowing, improving its visible-light absorption capabilities. This modification enhances the photocatalytic efficiency of Co-ZnO, making it highly suitable for environmental remediation and solar energy applications. The findings demonstrate that while pure ZnO is preferable for UV-blocking, optoelectronic applications, and sensors, Co-ZnO exhibits superior performance in photocatalysis and magnetic-based technologies. The study concludes that cobalt doping enhances ZnO's properties, expanding its potential applications in energy, environmental, and electronic industries.

Keywords: *ZNO, Co-ZNO, Crystallite Size, Dislocation Density, Strain, X-Ray Diffraction, Uv-VIS Spectroscopy*

INTODUCTION

Nanomaterial is composed of particles having nano-scale dimension called nanoparticles (NPs). They are very small sized particles (particle sizes in the range 1-100 nm) [15] exhibiting enhanced catalytic reactivity, thermal conductivity, non-linear optical performance and chemical steadiness owing to its large surface area to volume ratio. NPs have found wide applications in nano-engineering and nanotechnology, and is a developing area of research in science and technology. This is because NPs have unique properties, which are not present in bulk materials and can be exploited in numerous areas of science, industry and medicine. NPs have started being considered as nano-antibiotics because of their antimicrobial activities [5][14][16]. NPs have been integrated into various industrial, health, food, feed, space, chemical, and cosmetics industry of consumers which calls for a green and environment-friendly approach to their synthesis. This is because NPs have unique properties, which are not present in bulk materials and can be exploited in numerous areas of science, industry and medicine. NPs have started being considered as nano-antibiotics because of their antimicrobial activities. NPs have been integrated into various industrial, health, food, feed, space, chemical, and cosmetics industry of consumers which calls for a green and environment-friendly approach to their synthesis. A number of inorganic metal oxides, such as CeO, L2O3, TiO2, CuO, and ZnO were synthesized using different techniques including sol-gel, hydrothermal, solvo-thermal, microwave, etc. Of all these metal oxides, ZnO NPs is of highest interest because they are inexpensive to produce, safe and can be prepared easily. Moreover, they possess several novel properties, such as large band gap (3.37eV) [12][13] and high exciton binding energy (60meV), high refractive index, binding energy, large thermal conductivity, high catalytic activity, antibacterial, UV filtering properties, anti-inflammatory, wound healing. ZnO has also high biocompatibility and fast electric transfer

kinetics, such phenomena encourage the use of this material as a biomimic membrane to immobilize and modify the biomolecules. In many literatures, it is found that nano ZnO offers better performance compared to that of bulk size ZnO. Zinc is a necessary element to our health and ZnO nano particles also have good biocompatibility to human cells. Recently ZnO is listed as generally documented as safe material by FDA (food and drug administration, (US A). A numerous techniques have been used to prepare ZnO nanoparticles including sol-gel method, hydrothermal, microwave, solvothermal, thermal decomposition, chemical vapor decomposition (CVD) and alloy evaporation-deposition, laser deposition [16]. A simple, fast wet chemical route based on cyclohexyl amine for synthesizing zinc oxide nanoparticles in aqueous and ethanolic media was established by Abdul-AzizBari, and observed that when NH4OH is used as the solvent for zinc acetate to synthesis nano ZnO particles, the particles were spherical, while the particles were wire like when sodium hydroxide was used as solvent. Also, the results of Zaborski revealed the morphology of ZnO which was prepared in the presence of the ionic liquids was spherical while it changed to plate-like without ionic liquids. It is demonstrated that ZnO with different morphologies such as flowers and rods can be controllable obtained by simply varying the basicity in the solution.

In brief, the solvents, temperature and media of experiment affect the particle size and particle morphology of synthesized ZnO nanoparticles. The aim of this research is to find a simple route to prepare nano ZnO particles via Sol-Gel technique and characterize the final product using several characterization techniques including X-ray diffraction (XRD) [4], and ultraviolet-visible (UV-Vis) spectroscopy.

MATERIALS AND METHODS

In this study, the sample were prepared by sol-gel method:

a. Sample 1: Pure Zinc oxide (Zn1)
b. Sample 2: Cobalt doped Zinc oxide (Zn2)

Experimental Procedure

Synthesis of Pure Zinc Oxide (Zn1)

To prepare 1M of NaOH solution, measure 0.4g of sodium hydroxide pellet and dissolved in 10ml of distilled water and stirred until the solution dissolved. To prepare precursor solution, 16g of zinc acetate is dissolved 50ml of ethanol and stirred it for 10mins. After 10 minutes 10ml of distilled water added to precursor solution. After 10 mins 1.5ml of NaOH was added for gelation process and stirred it for 30 minutes and filtered the solution with filter paper. To remove impurities the solution was washed with distilled water for 2-3 times and added the gel to crucible and calcine it for 2 hours under 80ºC after drying keep for cooling under room temperature and grinded it and stored it in sample container.

Synthesis of Cobalt Doped Zinc Oxide (Zn2)

To prepare 1M of NaOH solution, measure 0.4g of sodium hydroxide pellet and dissolved it in 10ml of distilled water and stirred until the solution dissolved. To prepare dopant solution, 0.24g of cobalt nitrate is dissolved in 20 ml of ethanol. To prepare precursor solution, 100ml of ethanol and 32g of zinc acetate is stirred for 15mins. After this the dopant solution was added to the precursor solution and dissolved it until it mixed completely. Next step 20 ml of distilled water was added and stirred it for 10 mins. After this 3ml of NaOH solution was added dropwise for the gel formation and stirred it for 30 minutes. Next filtered the solution using filter paper and to remove impurities washed the solution with distilled water for 2-3 times and added the gel to crucible and calcine it for 2 hours under 80ºC after drying keep for cooling under room temperature and grinded it and stored it in sample container.

CHARACTERIZATION TECHNIQUE

X-Ray Diffraction (XRD)

Pure ZnO (Zn1)

The XRD graph is plotted using the software ORIGIN 8.0 and analysis of the graph is done using the same. The obtained data is verified data is verified using JCPDS card no. 36-1451. Shifts of the diffraction peaks are very small and quite consistent with that JCPDS data, which confirms the formation of ZnO. XRD pattern of ZnO by sol-gel method shows Hexagonal structure [4] with calculated (h,k,l) indices (100), (002), (101), (102), and so forth,[1][3][5][17] corresponding to the peak position 31.7968, 34.4550,36.2840, 47.55775 as shown in table1.

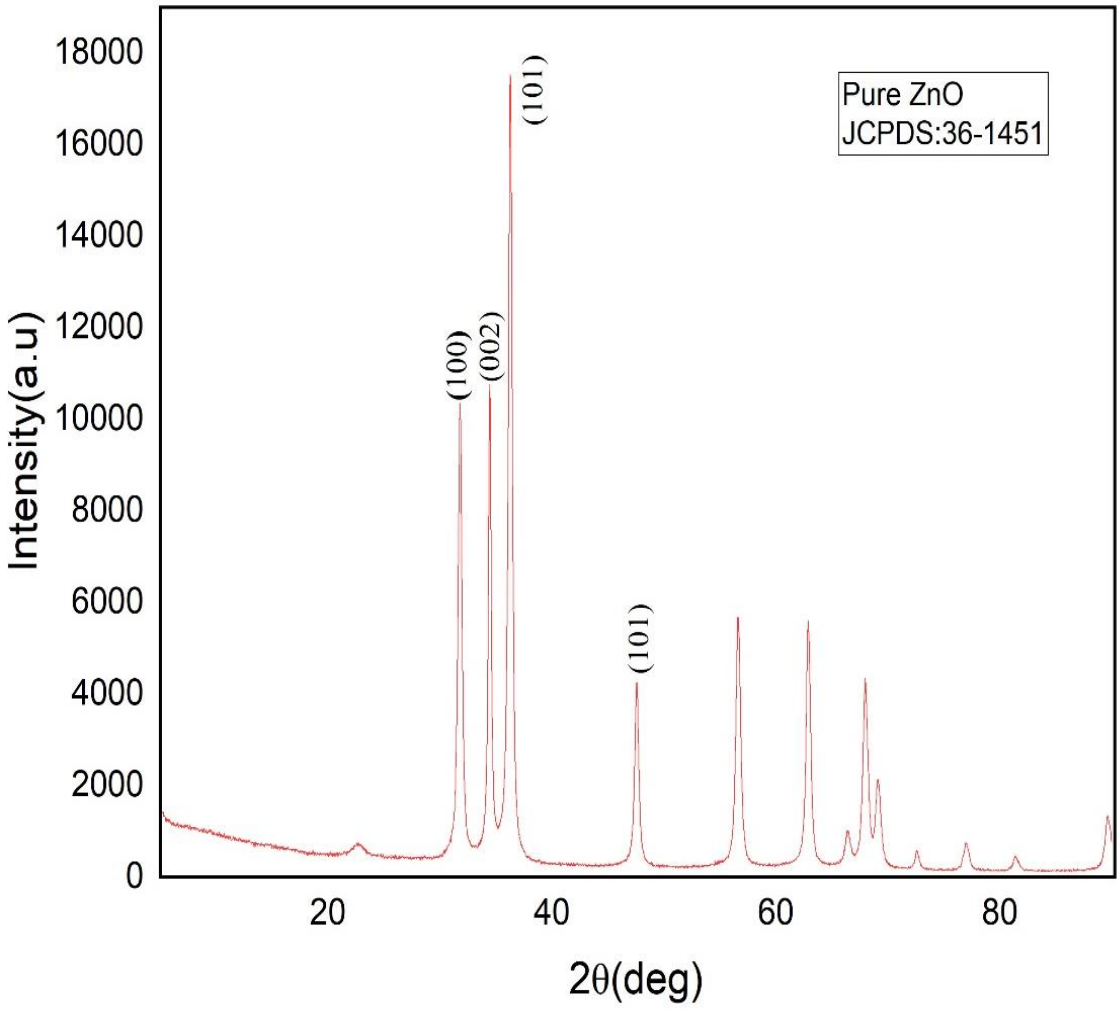

Fig 1 XRD graph of Zn1

Notably, the peak at 101 is the most prominent, suggesting a preferred orientation of the crystal lattice. This prominent peak indicates a high degree of crystallinity and ordering in the zinc oxide nanoparticles [17]. The sol gel method appears to have facilitated the growth of crystalline zinc oxide nanoparticles with a preferred orientation. The presence of multiple peaks confirms the polycrystalline nature of the nanoparticles [8]. Overall, the XRD graph provides valuable insights into the structural properties of the zinc oxide nanoparticles, highlighting their crystalline nature and preferred orientation.

Table 1 Tabulation of XRD calculation for Zn1

S.no	2θ	FWHM (nm)	[HKL]	d-spacing (Å)	Strain (no unit)	Dislocation density (m^{-2})	Crystalline size (nm)
1	31.79687	0.4634	[100]	3.2	0.11141	0.1107	26.3
2	34.45504	0.3514	[002]	2.6	0.33568	0.0537	30.4
3	36.28403	0.4617	[101]	2.72	0.10968	0.0917	24.31
4	47.57751	0.4240	[102]	2.00	0.09690	0.0717	25.5

Cobalt Doped Zinc Oxide (Zn2)

The XRD graph is plotted using the software ORIGIN 8.0 and analysis of the graph is done using the same. The obtained data is verified data is verified using JCPDS card no. 01-079-2205. Shifts of the diffraction peaks are very small and quite consistent with that JCPDS data, which confirms the formation of Co doped ZnO. XRD pattern of Co doped ZnO by sol-gel method shows Hexagonal structure with calculated (h,k,l) indices (100), (002), (101), (102), and so forth, corresponding to the peak position 31.7968, 34.4550,36.2840, 47.55775 as shown in table[2] [3][7]. Notably, the peak at 101 is the most prominent, suggesting a preferred orientation of the crystal lattice. This prominent peak indicates a high degree of crystallinity and ordering in the cobalt doped zinc oxide nanoparticles. The sol gel method appears to have facilitated the growth of crystalline cobalt doped zinc oxide nanoparticles with a preferred orientation. The presence of multiple peaks confirms the polycrystalline nature of the nanoparticles. Overall, the XRD graph provides valuable insights into the structural properties of the cobalt doped zinc oxide nanoparticles, highlighting their crystalline nature and preferred orientation.

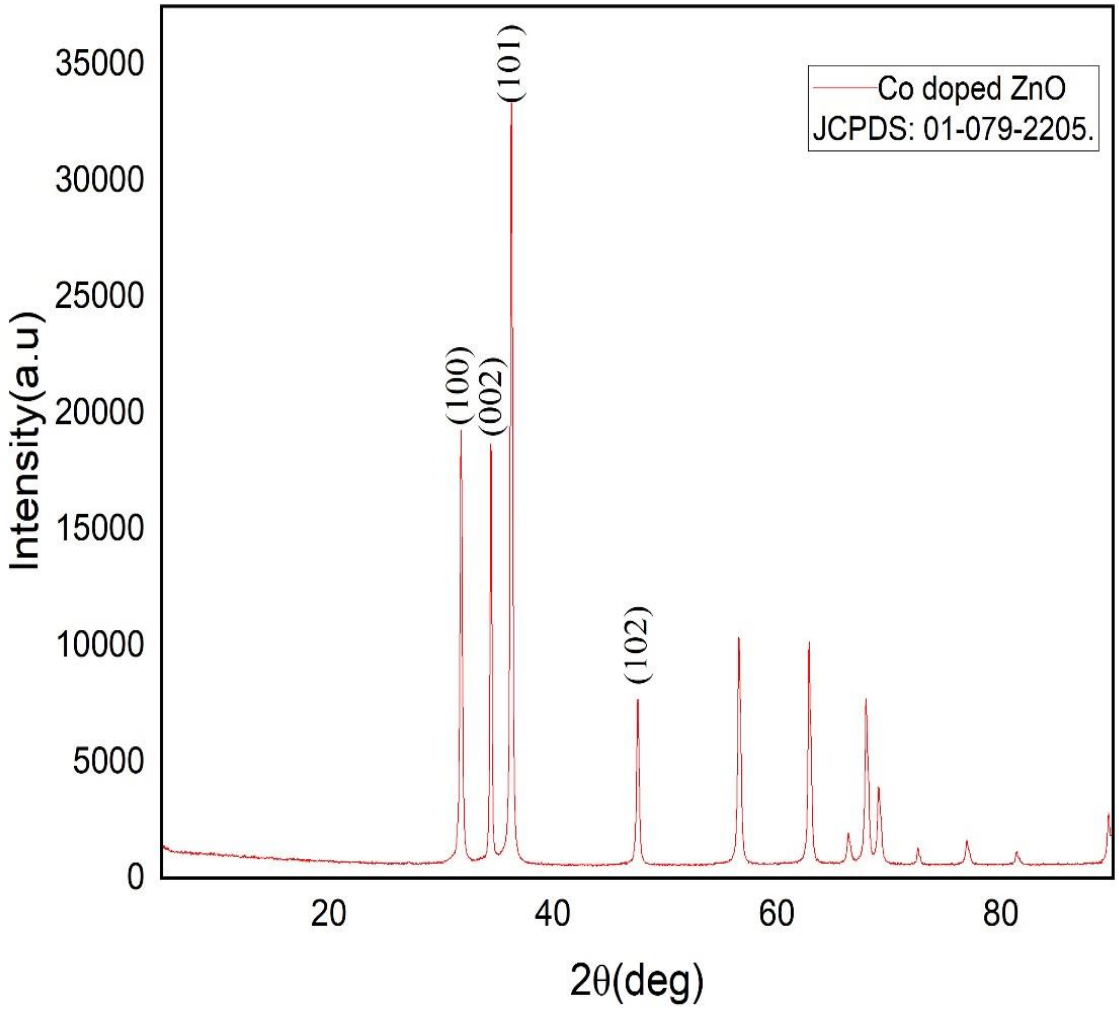

Fig 2 XRD graph of Zn2

Table 2 Tabulation of XRD calculation for Zn2

S.no	2θ	FWHM (nm)	[HKL]	d-spacing (Å)	Strain (no unit)	Dislocation density (m^{-2})	Crystalline size (nm)
1	31.7947	0.25891	(100)	3.2	0.06225	0.0319	5.59
2	34.4586	0.20201	(002)	2.6	0.04823	0.0194	7.16
3	36.2847	0.26317	(101)	2.72	0.06252	0.0284	5.93
4	47.5814	0.27531	(102)	2.00	0.06297	0.0361	5.26

Result and Discussion

It is clear from XRD pattern that all the characteristics diffraction peaks can be indexed to the diffractions of (100), (002), (101), & (102) planes with the clear hexagonal structure [3]. These diffraction peaks are close agreement with the standard value of JCPDS data. From the XRD graph and calculation it is clear that the Co-doped sample shows lowering of intensity peaks as compared to pure ZnO NPs. This lowering of intensity of diffraction peaks of Co-doped sample signifies that the crystalline character of the ZnO NPs had reduced considerably due to Co-doping. Further, we observe that the characteristic peak of (101) plane related to doped sample shifts toward the higher angle as compared to the pure ZnO NPs. The decrease in the crystallite size is chiefly due to the distortion in a host ZnO lattice by the introduction of impurities. Compared to pure ZnO the crystalline size, grain size, strain and dislocation density as lower in Co-doped ZnO [6] so the decrease in these shows that the cobalt doped zinc oxide is better than the pure zinc oxide which is used in most of the application, whereas pure zinc oxide is used for particular application which is larger in size.

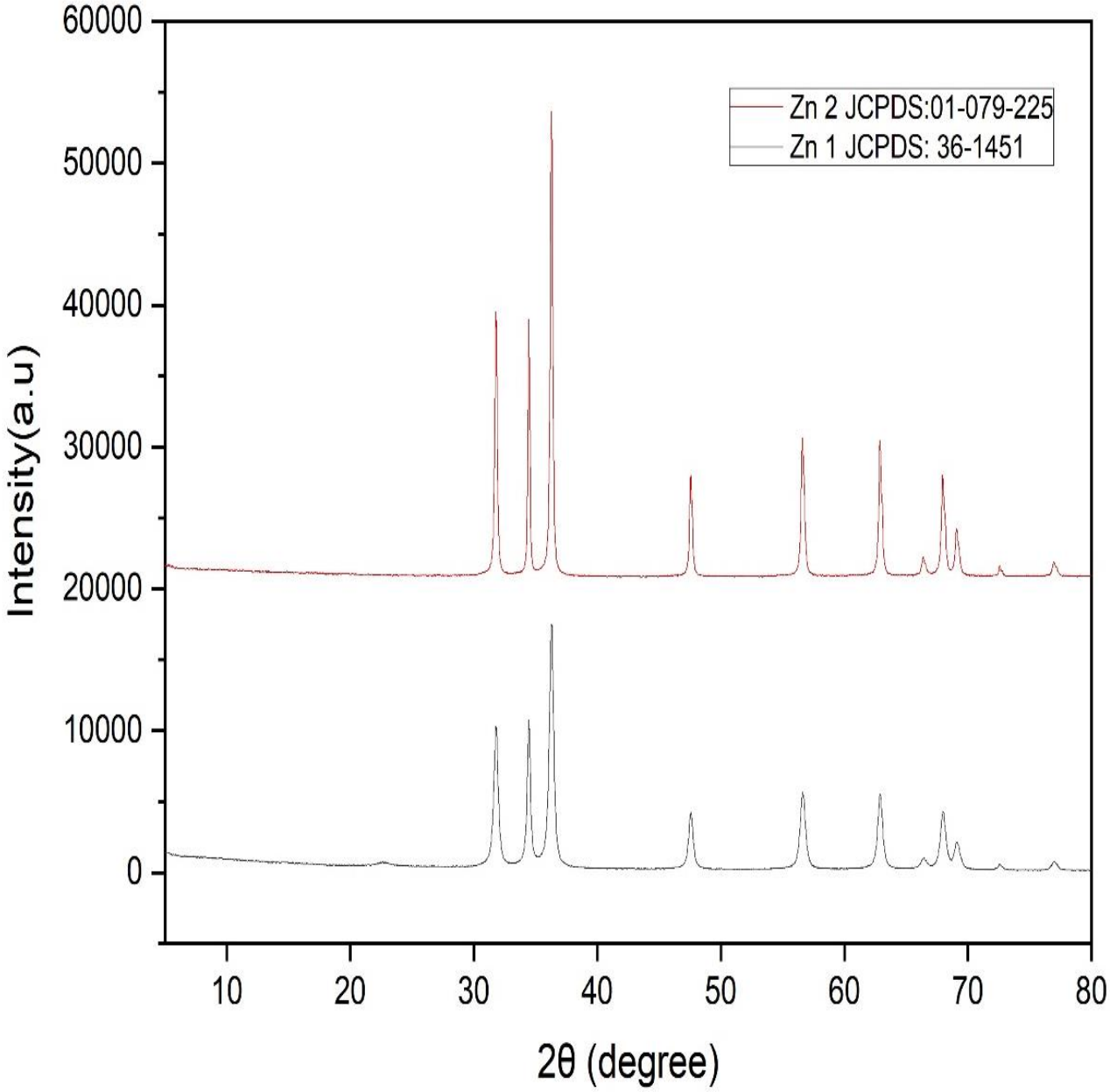

Fig 3 Stack representation of XRD graph of Pure and Co-doped ZnO

UV- VIS SPECTROPHOTOMETRY ANALYSIS

UV-Visible Spectrophotometry Graph

Pure Zinc Oxide (Zn1)

The UV-Vis absorbance analysis of pure ZnO reveals a strong absorption peak at 361 nm, indicating its bandgap-related optical transition. The estimated bandwidth of 1.23 eV suggests moderate spectral broadening, likely due to the influence of quantum confinement effects. The measured particle size of 147.1 nm confirms a nanostructured morphology, which can significantly impact the material's optical and electronic properties. This absorption band is attributed to the electronic transitions of the iron oxide nanoparticles, specifically the transfer of electrons from the oxygen 2p orbitals to the iron 3d orbitals [9]. This tailored optical behaviour makes Co-doped ZnO a promising candidate for UV-blocking coatings, photocatalysis, and optoelectronic applications such as sensors and solar cells [9].

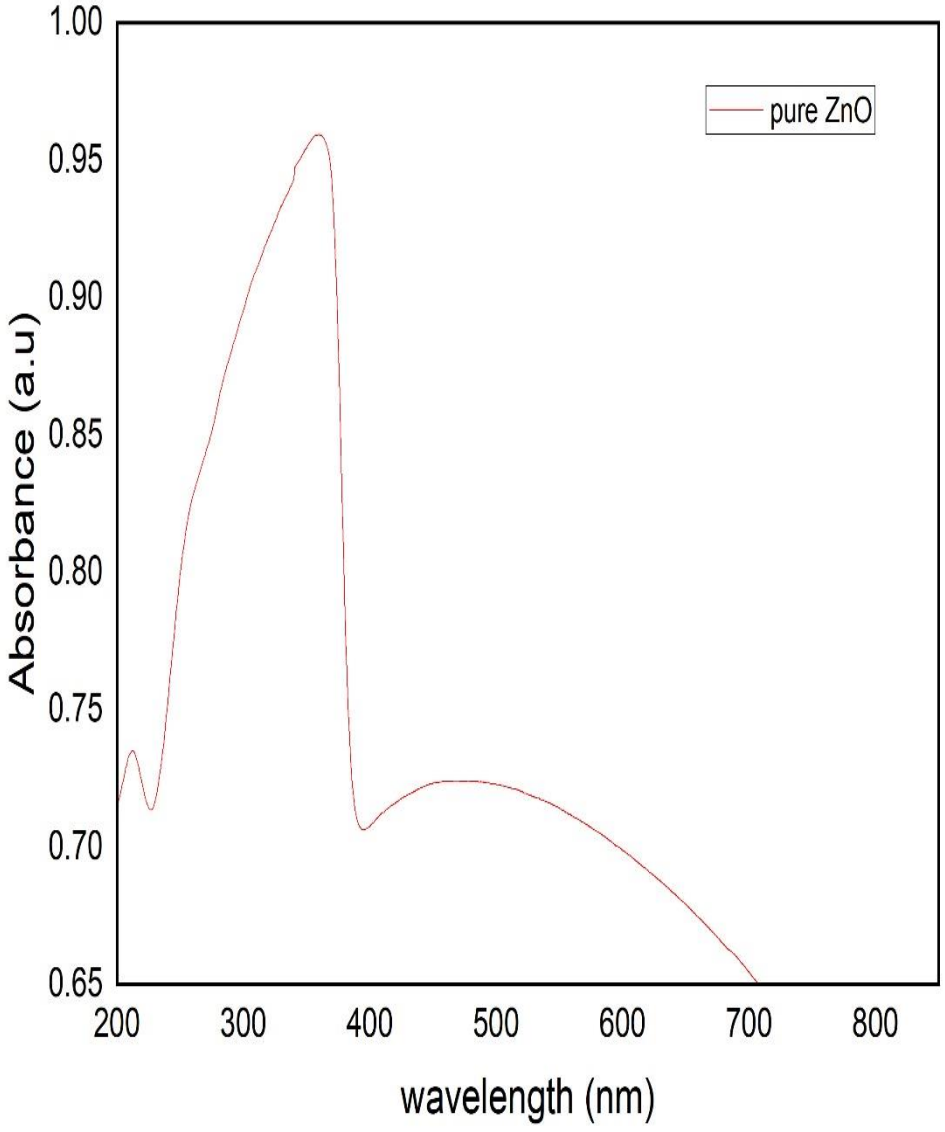

Fig 4 UV-vis graph of pure ZnO (Zn1)

Cobalt Doped Zinc Oxide (Zn 2)

The UV-Vis absorbance spectrum of Co-doped ZnO presented in the graph shows a peak at 355 nm, indicating strong absorption in the UV region. This peak corresponds to the optical bandgap transition of the material, with a calculated bandwidth of 1.18 eV [14]. The absorbance curve exhibits a steep rise around 300-400 nm, which is characteristic of ZnO and its modified electronic structure due to Cobalt doping. The estimated particle size of 145 nm suggests a nanostructured morphology, which influences the optical and electronic properties. This absorption band is attributed to the electronic transitions of the iron oxide nanoparticles, specifically the transfer of electrons from the oxygen 2p orbitals to the iron 3d orbitals. The shift in the absorption edge compared to pure ZnO indicates bandgap modification, which can enhance the material's performance in applications like UV shielding, photocatalysis, and optoelectronic devices[9][10].

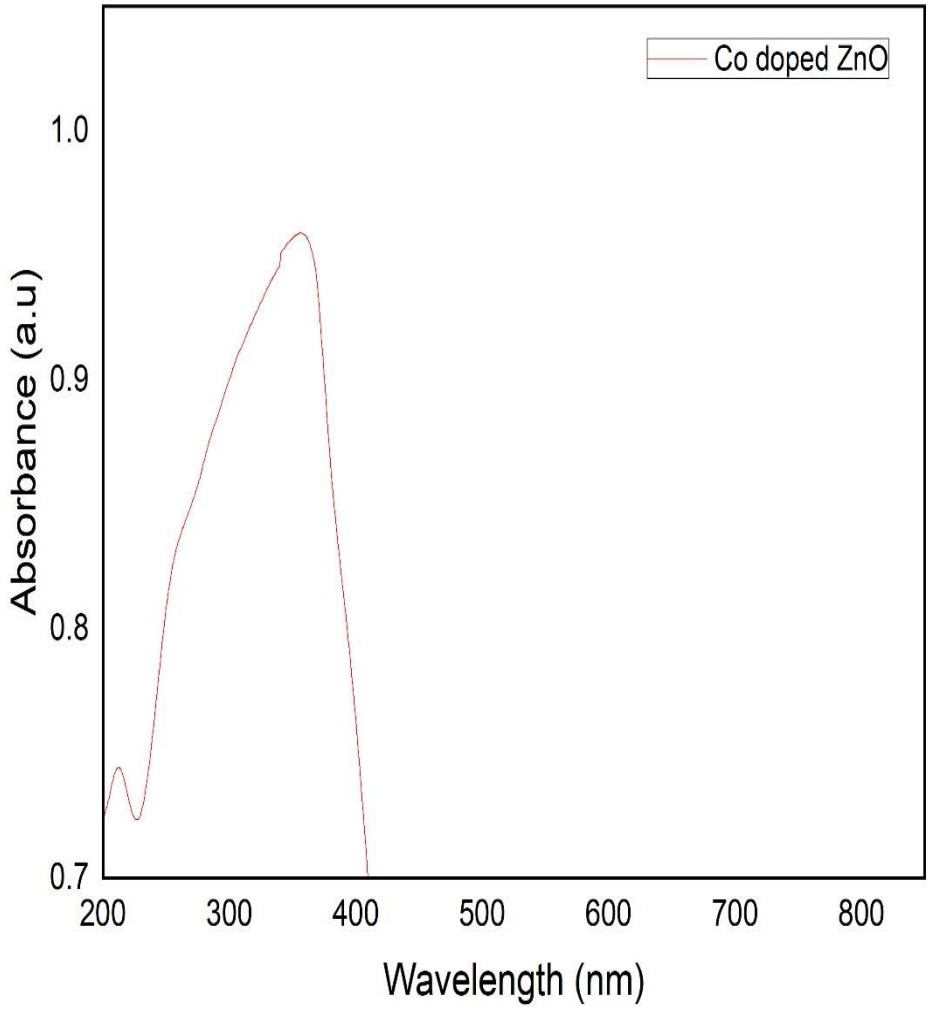

Fig 5 UV-vis graph of Cobalt doped ZnO (Zn2)

Table 3 Tabulation of UV-vis Spectrophotometry data

Properties	Zn 1	Zn 2
Peak value(nm)	361	355
Particle value(nm)	147.1	145
Bandwidth(nm)	1.23	1.18

Result and Discussion

The UV-Vis absorption spectra of pure ZnO and cobalt-doped ZnO nanoparticles were analysed using a double-beam spectroscopy. Pure ZnO exhibited a sharp absorption edge at approximately 365nm, characteristic of its wide band gap. Upon cobalt doping, a noticeable red shift in the absorption edge was observed, indicating a decrease in the bandwidth [11]. The UV-Vis spectrum of zinc oxide nanoparticles can be influenced by electronic transitions, such as charge transfer or d-d transitions. Compared to pure zinc oxide the particle size and bandwidth of the cobalt doped zinc oxide is smaller because cobalt doped zinc oxide is increased in surface area and bandwidth is narrower whereas pure zinc oxide is broader absorption. So cobalt doped zinc oxide is better than the pure zinc oxide. Zinc oxide nanoparticles can exhibit different optical properties, such as absorption, scattering, or fluorescence, depending on their size, shape and composition.

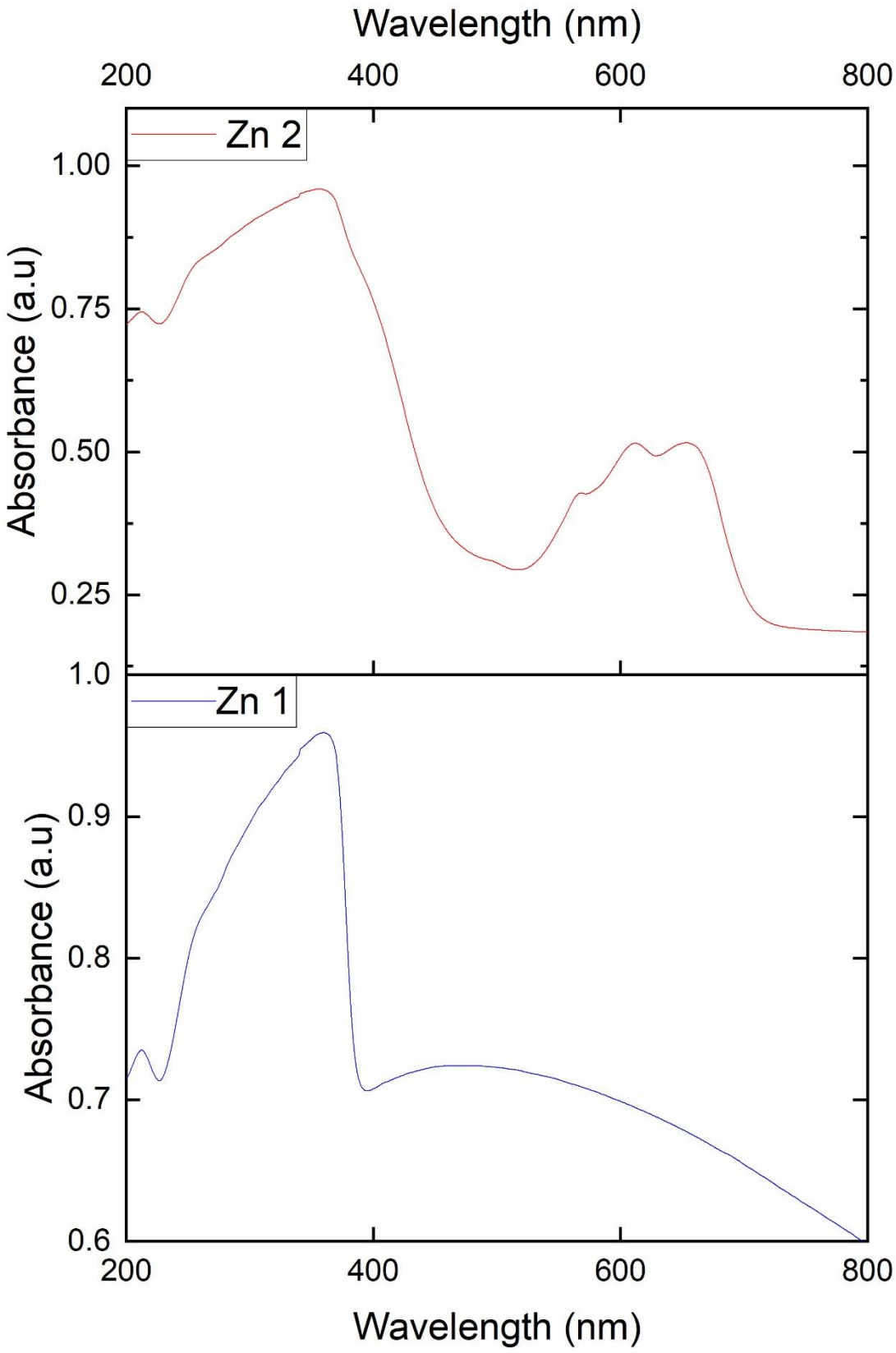

Fig 6 Stack representation of UV-vis spectrograph data of Pure and Co-doped ZnO

CONCLUSION

This study investigated the structural, and optical properties of cobalt-doped zinc oxide (Co-ZnO) and pure zinc oxide (ZnO) synthesized via the sol-gel method. The comparison focused on crystallite size, dislocation density, strain, d-spacing, UV analysis, and their respective applications. The structural analysis revealed that pure ZnO exhibits a larger crystallite size with lower dislocation density and strain [3].

This indicates higher crystallinity, structural stability, and fewer lattice defects, making it a suitable material for optoelectronic applications such as UV sensors, transparent conductive films, and gas sensors. In contrast, Co-ZnO demonstrated a reduction in crystallite size and an increase in dislocation density and strain due to cobalt incorporation, which caused lattice distortions. These structural modifications impact its overall performance, particularly in applications where controlled defect formation is essential, such as photocatalysis and spintronics. The d-spacing measurements showed a slight increase in Co-ZnO compared to pure ZnO, which may be attributed to the substitution of Zn^{2+} ions with larger Co^{2+} ions [6]. This slight expansion in the lattice can influence the electronic band structure, further affecting optical and electrical properties. On the other hand, Co-ZnO exhibited a broader absorption spectrum with a reduced bandgap due to cobalt doping, shifting its optical response towards the visible region. This enhanced visible-light absorption makes Co-ZnO an excellent candidate for photocatalytic applications, such as environmental remediation and solar energy conversion. In terms of particle size, pure ZnO displayed larger particle dimensions, contributing to better optical transparency and stability in optoelectronic applications. Meanwhile, the smaller particle size of Co-ZnO enhances its photocatalytic [2] efficiency by providing a higher surface-area-to-volume ratio, which facilitates improved charge carrier dynamics and reaction rates.

Moreover, the cobalt in ZnO induces room-temperature ferromagnetism, making Co-ZnO promising for applications in spintronics and magnetic storage devices. This magnetic behavior, absent in pure ZnO, expands the potential uses of Co-ZnO in emerging technologies requiring multifunctional materials. In pure ZnO and Co-ZnO depends on the specific application. Pure ZnO, with its higher crystallinity, lower defect density, and UV transparency, is better suited for optoelectronic devices, sensors, and transparent conductive coatings [3]. Conversely, Co-ZnO, with its reduced bandgap, enhanced visible-light absorption, and magnetic properties, is more advantageous for photocatalysis, spintronics, and magnetic storage applications [2]. The structural and optical modifications induced by cobalt doping offer significant advancements in multifunctional materials, paving the way for innovative applications in energy, electronics, and environmental technologies.

From this investigation we may conclude that cobalt doped zinc oxide is mostly used in wide application whereas pure zinc oxide is used for specific application.

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