International Journal of Advance and Applied Research
www.ijaar.co.in
ISSN – 2347-7075 Impact Factor – 8.141
Peer Reviewed Bi-Monthly
Vol. 11 No. 6 July-Aug 2024

Effects of Ag and Co Doping on the Structural and Optical Characteristics of ZnO Nanoparticles

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DOI- 10.5281/zenodo.13335634

Abstract:
Pure and Ag, Co-doped ZnO nanoparticles were synthesized using a chemical co-precipitation method without capping agents. X-ray diffraction (XRD) analysis revealed that all synthesized ZnO powders retained a pure hexagonal wurtzite structure, with no significant structural alterations due to Ag and Co doping. Energy-dispersive spectroscopy (EDS) confirmed the presence of Ag and Co dopants within the ZnO matrix. Photoluminescence (PL) spectra exhibited a light blue emission, indicative of the optical properties of the doped ZnO nanoparticles. The study demonstrates that while Ag and Co doping does not alter the fundamental crystal structure of ZnO, it does influence its optical characteristics, with potential implications for various applications in optoelectronics and sensing technologies.

Keywords: ZnO, X-ray diffraction, optoelectronics.

Introduction:

Nanotechnology has gained significant prominence across various research fields due to its potential for miniaturization and the unique properties associated with nanoscale materials. Zinc oxide (ZnO) is particularly noteworthy for its applications in electronic and optical devices, attributed to its wide band gap of 3.37 eV and substantial excitation energy of 60 meV. ZnO-based quantum dots have recently become a focal point in research, exploring diverse aspects such as nanocrystal shapes (e.g., wire, rod, cone, and spherical), lattice structures, doping, and surface modifications. These investigations extend to optoelectronic properties, including luminescence, binding energy, and band gap adjustments [1].

Various methods have been employed to synthesize ZnO powders, including chemical vapor deposition (CVD), thermal evaporation, and conventional sputter deposition. However, these techniques often involve complex procedures and sophisticated equipment, limiting their large-scale industrial application. In contrast, the chemical co-precipitation method is a more cost-effective and straightforward approach, which has recently gained traction among researchers. This method simplifies the synthesis process, making it more accessible for large-scale production [2].

In this study, we utilized the chemical co-precipitation method to prepare pure ZnO and Zn0.90Co0.05Ag0.05O nanoparticles. The doping of ZnO with cobalt (Co) and silver (Ag) ions is of particular interest because it can significantly alter the luminescent properties of the material. Previous research has shown that doping can lead to shifts in the near band edge (NBE) emission, either towards blue or red wavelengths, and can induce dramatic changes in visible emission. Notably, Ag has been reported as a prominent luminescent activator in compound semiconductors, as highlighted by Park et al [3].

In this work, we focused on incorporating two dopants, Co2+ and Ag2+, into the ZnO host material. Our study aims to synthesize ZnO and Zn0.90Co0.05Ag0.05O nanoparticles using the chemical co-precipitation method without capping agents, and to investigate the effects of varying cobalt concentrations while keeping the silver concentration constant. This approach allows us to analyze the structural and optical properties of the doped nanoparticles, contributing valuable insights into the influence of dopants on the luminescent behavior of ZnO-based materials.

Materials and Methods:

In this study, zinc acetate dihydrate and KOH powders of analytical grade were used as precursors, with AgNO3 and cobalt acetate serving as dopants. A 0.2 M solution was prepared using zinc acetate and KOH. AgNO3 and cobalt acetate solutions were added dropwise to the zinc acetate solution under continuous stirring for 10 hours at room temperature, resulting in the formation of a fine precipitate. After 48 hours, the precipitate was filtered, washed with deionized water to remove impurities, and dried in an oven at 700°C for 7 hours. The dried product was then ground and annealed at 300°C for 1 hour in a furnace.

The chemical composition was analyzed using Energy Dispersive Spectroscopy (EDS, model CARL-ZEISS EVOMA 15). The size and structural properties of the nanoparticles were characterized by X-ray Diffraction (XRD). Photoluminescence (PL) studies were performed using an OBIN YOUNFLUROLOG-3 spectrometer with a 450W xenon arc lamp as the excitation source. This comprehensive characterization enabled the analysis of the structural and optical properties of the synthesized ZnO nanoparticles.

Experiment:

X-ray diffraction:

X-ray diffraction (XRD) analysis was employed to examine the structural and phase composition of ZnO and Zn0.90Co0.05Ag0.05O nanoparticles. The XRD patterns, depicted in Fig. 1, reveal the three prominent crystallographic planes: (100), (002), and (101), which confirm the hexagonal wurtzite structure of ZnO. These findings align with previously reported results [4-5]. Notably, no additional peaks corresponding to Co or Ag clusters were detected, indicating that the dopants did not form separate phases and affirming the sample purity.

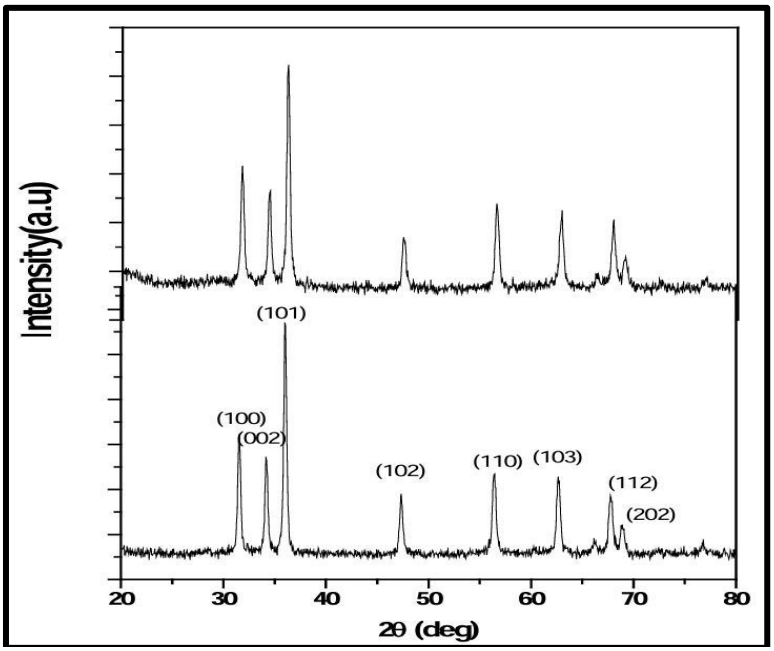

Figure 1. Pure ZnO and Co and Ag doped in ZnO.

The average nanocrystalline size was calculated using the Debye-Scherrer formula:

$$D = \frac{K\lambda}{\beta cos\theta}$$

Where β is the full width at half maximum (FWHM) of the XRD peaks, θ is the Bragg angle, λ is the wavelength of Cu Kα radiation, and k is a shape factor (0.89).

Energy Dispersive Spectroscopy:

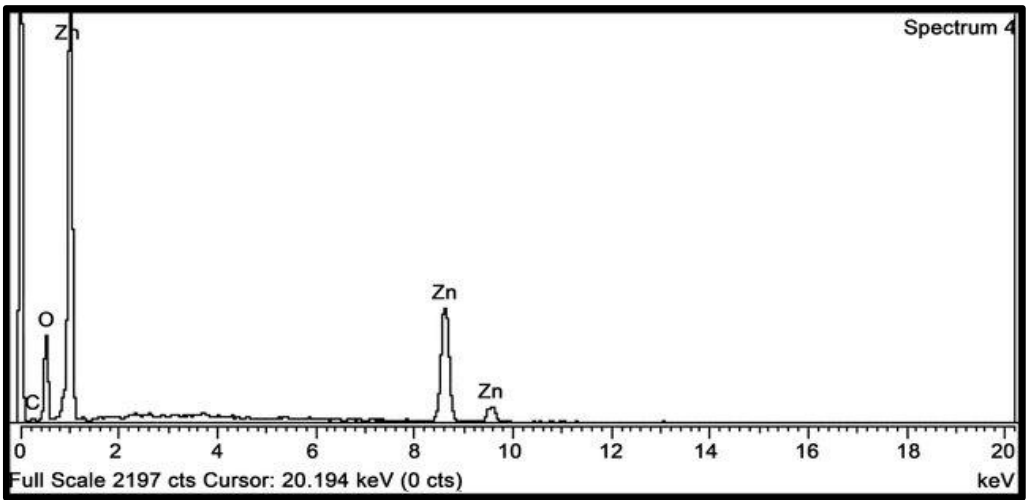

Figure 2. Energy dissipative spectroscopic analysis of Pure ZnO and Co and Ag doped in ZnO.

Energy Dispersive Spectroscopy (EDS) was used to verify the presence of Co and Ag ions within the ZnO matrix. Fig. 2 shows the EDS spectra for Zn0.90Co0.05Ag0.05O, indicating a high atomic percentage of Zn and O with minimal presence of Ag and Co, confirming the doping and the overall purity of the samples [6].

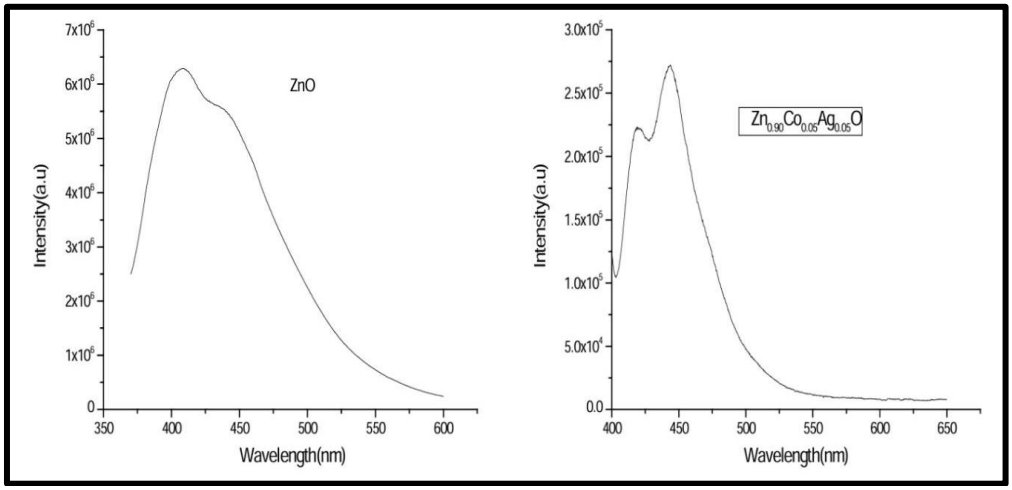

Figure3. photoluminescence (PL) spectra of pure ZnO and ZnO doped Co and Ag

Fig. 3 presents the photoluminescence (PL) spectra of ZnO and Zn0.90Co0.05Ag0.05O nanoparticles, showing a broad emission peak at 408 nm. This peak corresponds to blue luminescence, which is characteristic of self-activated, undopedZnO nanoparticles due to oxygen vacancies. The PL spectra also reveal a red shift and an additional blue emission peak at 443 nm for the doped Zn0.90Co0.05Ag0.05O nanoparticles. This shift indicates that the electrons are transitioning from surface states to different energy levels associated with the Ag and Co impurities [7].

The observed PL peak position shifts from 408 nm to 443 nm as the Co2+ concentration increases, while the Ag concentration is maintained at 5%. This shift suggests that the presence of Co2+ significantly influences the electronic environment of the ZnO host material, altering the energy levels and thus affecting the emission wavelength. The modification in PL characteristics demonstrates the interaction between Co2+ and Ag dopants, impacting the luminescence behavior of ZnO nanoparticles.

Conclusion:

In conclusion, the study successfully synthesized undopedZnO and ZnO nanoparticles doped with Co2+ and Ag2+ using a chemical co-precipitation method. X-ray diffraction (XRD) analysis confirmed that the nanoparticles maintained a hexagonal wurtzite structure with no additional peaks, indicating the purity of the samples. The average nanocrystalline size was calculated using the Debye-Scherrer formula, validating the consistency of the structural properties. Energy Dispersive Spectroscopy (EDS) further confirmed the incorporation of Co and Ag into the ZnO matrix, with a high atomic percentage of Zn and O and minimal presence of the dopants, ensuring sample purity. Photoluminescence (PL) studies revealed a broad emission peak at 408 nm for undopedZnO, signifying blue luminescence due to self-activation by oxygen vacancies. Upon doping with Co2+ and Ag2+, the PL peak exhibited a red shift to 443 nm, indicating changes in the emission properties due to the interaction of electrons with the dopant levels. Overall, the results highlight the influence of Co2+ and Ag2+ doping on the optical properties of ZnO nanoparticles, demonstrating their potential for applications in optoelectronic devices where controlled luminescence is essential.

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