Study on the effect of Er dopant on the structural properties of ZnO nanorods synthesized via hydrothermal method

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Abstract. Rare earth Er-doped ZnO nanorods were prepared by a simple hydrothermal method in order to search for a new functional for potential application in optoelectronic. Nanorods were deposited onto glass substrates with zinc nitrate, hexamethylenetetramine and Erbium chloride as starting materials. The results obtained by XRD spectrum indicated the presence of hexagonal (wurtzite) structure for both pure and Er doped ZnO NRs with additional cubic phase of Er2O3 that appeared in the doped sample. The size and lattice strain of particles have increased after doping with Erbium. The increase of their sizes can be explained by the incorporation of Er atoms into ZnO lattice.

1. Introduction

Nanostructured ZnO materials have been widely studied due to their potential applications in electronic, optical and photonic devices [1]. ZnO is an II–VI group semiconductor material with a direct energy band gap of 3.37 eV, and a large exciton binding energy (60 meV) at room temperature [2]. ZnO is very flexible functional material exhibiting wide structural morphologies, such as nanorods, nanobelts and nanowires [3-5] etc. There are a number of techniques for preparing nano-sized ZnO materials. Hydrothermal is considered as an easy and simple method due to its suitability to any type of doping and easy control of dopant concentration, good potential for environmentally safe large scale production, tolerable growth condition and low reaction temperature for obtaining nanostructures in a specific shape and size [6-7]. Moreover, the particle shape can be controlled easily by modifying the precursor solution or using a novel method for preparation or by doping process. The doping of ZnO nanorods by rare earth elements is an interesting topic in the last few years because it has pronounced effect on structural, optical and electrical properties of ZnO owing to their good properties. Rare earths are better luminescent materials because of the sharp and intense emission due to their 4f intra shell transitions [8]. To date, a number of research workers have reported the study of the effect of rare earths on the
structural and optoelectronic properties of ZnO nanostructures. Senol et al [7] have investigate the effect of Er and Yb doping influence on structural, optical and electrical properties of ZnO nanopowders. Cerrato et al [9] have reported the effect of rare earths (La, Ce, Pr, Er and Yb) on the structural, optical and electrical properties of ZnO prepared via hydrothermal properties in order to develop new photocatalysts. Habubi et al [10] have carried out the synthesis and characterization of undoped and Er$^{3+}$ doped ZnO. In the previous work [11] we have used a green synthesis method for the preparation of Yb doped ZnO and the study of their structural and optical properties. In this study, Er doped ZnO nanorods have been prepared by hydrothermal method, samples were characterized using X-Ray Diffraction, the analysis of X-ray peak profile was used to estimate the crystallite size and lattice strain. The aim of this study is to investigate the effect of Er dopant on the structural properties of ZnO.

2. Experimental details
Different process steps followed for the synthesis of ZnO nanorods are shown in Figure 1. ZnO nanorods in this study were grown using the hydrothermal process. The chemicals used in the experiment were purchased from Sigma-Aldrich. Firstly, an equi-molar aqueous solution of 0.1 M zinc nitrate ($\text{Zn(NO}_3\text{)}_2$) and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, HMT) was prepared using deionized water under constant stirring during 30 min. Then, a 2.5% mole of Erbium chloride was dissolved in distilled water separately. The obtained solution of Erbium was added to the mixture and kept under magnetic stirring for 30 min. These mixtures were heated at a constant temperature of 90°C in an oven for 24 h and then; ZnO and Er-doped ZnO powder were separated from the solution by using a centrifuge and washed with acetone and distilled water. The obtained materials were deposited on glass substrates, and dried at 90°C for 2 hours.

![Figure 1](image)

Figure 1. Schematic diagram of the steps followed for the synthesis of hydrothermal growth pure and Er doped ZnO nanorods.

3. Results and discussion

3.1. Structural studies
The crystallinity and structure of the synthesised samples were analysed by X-ray diffraction data recorded. The typical XRD diffraction peaks of pure and Er doped ZnO nanorods are shown in the
Figure 2 and 3. For the pure ZnO, the characteristic peaks (100), (002), (101), (102), (110), (103), (200), (112), and (201) correspond to the hexagonal (wurtzite) structure of ZnO (JCPDS Card no 01-075-1526) with preferred orientation along (101) plane. For the doped material, the XRD pattern is found to be similar to that of pure wurtzite ZnO structure with additional peaks that appeared at \( \theta = 20.81^\circ, 2\theta = 28.85^\circ, 2\theta = 48.99^\circ \) and \( 2\theta = 58.13^\circ \) indexed respectively to (211), (222), (440) and (622) (JCPDS Card no 01-071-8212). The all additional peaks observed correspond to single-phase cubic structure of \( \text{Er}_2\text{O}_3 \) [12]. This indicating the formation of Erbium phase in ZnO lattice; by the hindered incorporation of Er in ZnO lattice due to the large difference between the radii of \( \text{Er}^{3+} (0.89\text{Å}) \) and \( \text{Zn}^{2+} (0.74\text{Å}) \) [13]. In addition, the position of (101) peak in the Er-doped ZnO nanorods slightly shifts to lower angle compared to the peak position in the pure ZnO which indicating that the lattice expanded after doping and dopants form substitutional defects in the lattice because of the difference between the ionic radius.

![X-ray diffraction spectrum of pure ZnO nanorods.](image)

**Figure 2.** X-ray diffraction spectrum of pure ZnO nanorods.
3.2. Crystallite size and strain

Furthermore, the average crystallite size $D$ is estimated according to the Debye Scherer formula [14]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where $k=0.9\ \lambda\ (\text{nm})$ represents the wavelength of CuKα radiation (1.5418 Å), $\theta$ is the Bragg angle of the X-ray diffraction peak and $\beta$ stands for full width at half maximum of the diffraction peak.

The lattice strain of all the particles has been calculated by using the tangent formula [15]:

$$\varepsilon = \frac{\beta}{4 \tan \theta} \quad (2)$$

The lattice constants of the a and c axis of the pure and Er-doped ZnO nanorods have been determined by using the following equations:

$$2d \sin \theta = n\lambda \quad (3)$$

$$\frac{1}{a^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \quad (4)$$

Where $d$, (hkl), $\theta$, $\lambda$, $a$ and $c$ are lattice spacing, miller index, bragg diffractive angle, X-ray wavelength, and lattice constants, respectively.

The FWHM, average crystallite size, lattice strain, and lattice constants $a$ and $c$ of the particles obtained according to the XRD spectra of the preferential crystallographic (101) peak orientation are listed in the Table 1. The calculated average crystallite size ($D$), lattice strain and lattice constants
were found to be increased after doping. This is due to the increase in the Er atoms in Zn sites. The increase in the number of dopant atoms may lead to increased numbers of point defects, which would give rise to higher grain boundary mobility and grain growth rates. The slight shift in the XRD spectrum and the change in the lattice constants with Er doping indicated that Er has really doped into ZnO lattice.

In addition, the plot in Figure 4 presents an estimation of these pure and Er doped ZnO particles size calculated using Hall method where the obtained size average was found to be 577 (41) and 668(95) respectively.

### Table 1. The information on crystallite size, lattice strain and lattice parameters of pure and Er doped ZnO NRs.

|                | 2θ  (degree) | FWHM (degree) | Crystallite size (Å) | Lattice strain | Lattice constant (a) (Å) | Lattice constant (c) (Å) |
|----------------|--------------|---------------|----------------------|----------------|--------------------------|--------------------------|
| Pure ZnO       | 36.55°       | 0.1514        | 577                  | 0.091          | 3.2337                   | 5.1804                   |
| Er doped ZnO NRs | 36.39°       | 0.1457        | 668                  | 0.10           | 3.2376                   | 5.1845                   |

### Figure 4. Size estimation in pure Zinc Oxide NRs (a) and (b) of Er doped ZnO NRs.

### Conclusion

To summarize, pure and Er doped ZnO nanorods were synthesized by hydrothermal method, the structural properties were characterized using X-Ray Diffraction. The average crystallite size was estimated using the Debye Scherer formula. The results of XRD revealed the presence of Hexagonal (wurtzite) structure for both pure and doped materials with additional cubic phase structure of Er₂O₃ that appeared in the doped material. Their particle size is found to be 577 and 668 Å for pure and Er doped ZnO respectively. The modification of structural properties after doping with Erbium indicating that Er has really doped into ZnO lattice.
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