Structural and optical properties of undoped and Er³⁺-doped ZnO nanoparticles synthesized by laser ablation in Ethanol

Nadir F. Habubi^{1*}, Raid A. Ismail², Esraa H. Hadi³

^{1,3}Physics Department, Education Faculty, University of Mustansiriyah Baghdad -Iraq

²Departement of Applied Sciences, The University of Technology. Baghdad –Iraq

E-mail address:

nadirfadhil@uomustansiriyah.edu.iq

*Corresponding author E-mail nadirfadhil@uomustansiriyah.edu.iq

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ABSTRACT. In this paper, we report on the fabrication and properties of undoped and 8.4% Er³⁺-doped ZnO nanoparticles synthesized by laser ablation in ethanol at laser fluence values 2.92 J/cm². The synthesized nanoparticles are characterized by structural properties using X-ray diffractometer, scanning electron microscope and the optical properties are carried out through UV–Visible spectrophotometer. The X-ray diffractometer pattern indicates that these nanoparticle were polycrystalline in nature with a hexagonal (wurtzite) phase. SEM reveals that The synthesized ZnO and Er-ZnO NPs have a spherical shape. Moreover, the optical band gaps calculated through UV spectroscopy are found to be decreased with doping from 3.3 to 3.2 eV .

1. INTRODUCTION

ZnO semiconductors, with a direct wide band gap of 3.37 eV have been intensively studied due to their multifunctional characteristics for adverse range of applications in optical, electronic, optoelectronic, piezoelectric, photocatalytic, and power devices [1-5]. In the past decade, ZnO has been explored for new device applications when extra functionalities are intentionally introduced through proper doping or alloying with impurity ions despite the considerable challenges. It is worth noting that much effort has also been made through doping rare earth (RE) ions (e.g., Er³⁺ and Eu³⁺) into the ZnO host, which undergoes upconversion (UC) luminescence and/or energy transfer, in realizing new optoelectronic and photonic device applications such as solid-state full-colour displays, infrared detectors, solar cells, biological fluorescent labels, and all-solid compact lasers [6]. The Er³⁺-doped semiconductors are the potential optoelectronic materials [7] due to the Er intra-4f shell transition with a photoemission at a wavelength of 1.54 μm, which lies in the minimum loss region of silica-based optical fibers [8]. Up to now, physical doping methods such as ion implantation [9], laser ablation [10], magnetron sputtering [11], and high temperature calcinations [12] have mainly been used to introduce Er into ZnO substrate. Here, a laser ablation in ethanol has been used to prepare undoped and Er³⁺-doped ZnO. The structural and optical properties of the undoped and Er³⁺-doped ZnO was investigated.

2. EXPERIMENTAL

ZnO and Er-ZnO nanoparticles were produced by laser ablation of a ZnO and Er-ZnO plates in ethanol at room temperature. The zinc target (purity of 99.99% provided from Ludeco) and doping with Er₂O₃ taken from SPEX INDUSTRIES, INC. METHUCHEN, NJ08840 U.S.A) with high purity (99.999%) was fixed at bottom of quartz vessel containing of 5 ml of ethanol. Ablation is carried out in each sample for 5 min using an Nd:YAG _yttrium aluminum garnet_ laser (type HUAFEI) operating at 1064nm wavelength with a repetition rate of 10 Hz and a pulse width of 10 ns at fluences 2.92 J /cm². The laser beam was focused on the Zn and Er-ZnO target surface with a beam size of 2.37 mm in diameter using a lens with a focal length of 11cm. Figure (1) shows the experimental setup of PLAL system. . The structural properties were studied by means of X-ray

diffraction (XRD) (XRD-6000, Shimadzu X-ray diffractometer) using $\text{CuK}\alpha$ X-ray source. The shape and size of ZnO and Er-ZnO nanoparticles were examined by field emission scanning electron microscopy (FE-SEM Image Library). The optical absorption of nanoparticles was studied with the aid of UV-Vis spectrophotometer.

Fig. 1 Experimental setup for pulsed laser ablation in liquid system.

3. RESULTS AND DISCUSSION

Fig.(2) shows the XRD pattern of the prepared samples. Evidently, all the diffraction peaks in XRD pattern are well assigned to hexagonal wurtzite ZnO as reported in JCPDS card no.36-1451, and no impurity phase related to Er^{3+} could be found. The diffraction peaks shift to lower angle slightly with the Er-ZnO, indicating that the lattice expanded after doping and dopants occupy the interstitial positions or form substitutional defects in the lattice.

Fig. 2 XRD pattern for ZnO and Er-ZnO nanoparticles films ablated in ethanol.

Table 1 Summary of X-ray characterization.

<i>Laser fluences (J/cm²)</i>	<i>Samples</i>	<i>2 θ (deg)</i>	<i>hkl Plane</i>	<i>d observe (Å)</i>	<i>FWHM (deg)</i>	<i>D (nm)</i>	<i>δ × 10¹⁴ lines.m⁻²</i>	<i>η × 10⁻⁴ lines⁻².m⁻⁴</i>
2.92	ZnO	36.2491	(101)	2.47618	0.1508	55.153	3.28742	6.2825
		31.7787	(001)	2.81357	0.1657	49.592	4.06607	6.9869
		34.4257	(200)	2.60305	0.1456	56.831	3.09617	6.0969
	Er-ZnO	36.501	(101)	2.4473	0.1479	56.275	3.1575	6.15716
		32.018	(001)	2.7789	0.1637	50.228	3.9637	6.89850
		34.672	(200)	2.572	0.1396	59.313	2.8424	5.84179

The average crystallite size *D* for a known X-ray wavelength λ at the diffraction angle θ of ZnO and Er-ZnO nanoparticles was calculated by using Scherrer formula [13,14] (the peak widths of the strong diffraction planes have been taken for calculation) and listed in Table (1).

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

where the β is the full width at the half maximum of the characteristic spectrum in units of radians and *K* is the Scherrer constant ($1 > K > 0.89$). The average crystallite size of ZnO and Er-ZnO particles was found to be around (49.592 and 59.313)nm from XRD analysis. This difference in crystallite size can be ascribed to the difference in the lattice constants obtain. The strain value δ and the dislocation density η can be evaluated by using the following relations [15,16], their values were tabulated in Table 1:

$$\delta = \frac{1}{D^2} \quad (2)$$

$$\eta = \frac{\beta \cdot \cos(\theta)}{4} \quad (3)$$

The results revealed that the strain and dislocation density are decreasing with the increase in crystallite size.

The SEM technique was employed to explore the size and distribution of particles in the materials. The images of undoped and 8.4% Er³⁺ doped ZnO are shown in Fig. (3). It can be found that the sample synthesized crystalline are closely packed and have smaller sizes. The crystallites are nearly spherical shaped and it seems that the particles were agglomerated and form a cluster. The estimated grain size range (30- 60)nm.

Fig. 3 SEM images of undoped and 8.4% erbium doped.

UV/Visible spectrum of ZnO and 8.4% Er^{3+} doped ZnO is shown in Fig. (4). The absorption spectrum of Er^{3+} doped ZnO shows pronounced shoulder at 388 nm, corresponding to the energy band gap of 3.2 eV.

A strong UV absorption band at 388 nm is assigned to the ZnO band-to-band transition.

Fig. 4 Absorption spectra of undoped and 8.4% erbium doped in ethanol prepared at 2.92 J/cm^2 .

The optical band gap of the nanoparticles was estimated from an extrapolation of a plot of $(\alpha h\nu)^2$ as a function of the photon energy in the absorption spectra. This is possible because the absorption coefficient (α) can be expressed as $\alpha h\nu \propto (h\nu - E_g)^{1/2}$ and the intercept provides a good approximation to the band gap (E_g) [17]. It has been found that energy band gap 3.3 eV for ZnO and 3.2 eV for Er-ZnO respectively. The decrease in band gap from 3.3 eV for ZnO to 3.2 eV with respect to the bulk band gap (3.37 eV) is due to the effect of the dopant, behaved as a substitutional impurity located in the lattice position of ZnO on the other hand due to formation of nano-sized ZnO and Er-ZnO particles (laser fragmentation effect).

Fig. 5 $(\alpha h\nu)^2$ as a function of incident photon energy for undoped and 8.4% erbium doped.

4. CONCLUSION

In summary, we successfully demonstrated the synthesis of high purity ZnO and Er-ZnO NPs colloid at room temperature by Nd:YAG laser ablation of ZnO and Er-ZnO target in ethanol. The produced nanoparticles were polycrystalline in nature with hexagonal (wurtzite) phase. The SEM images clearly show that the synthesized undoped and 8.4% erbium doped NPs have a spherical shape and particle sizes of ZnO increase with doping due to the lattice expanded after doping and it seems that the particles were agglomerated and form a cluster. The ZnO NPs exhibited high absorption in the UV region and lowered absorption in visible and IR regions. The energy gap decrease due to the effect of the dopant and laser fragmentation effect.

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