

## OPTICAL PROPERTIES OF EUROPIUM DOPED BUNCHES OF ZnO NANOWIRES SYNTHESIZED BY CO-PRECIIPITATION METHOD

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Europium doped bunches of ZnO nanowires have been synthesized by co-precipitation method. The synthesized nanowires are of diameter 60-100 nm and length upto several microns. The absorption spectra and photoluminescence spectrum of europium doped bunches of ZnO nanowires are studied. The effect of annealing temperature on photoluminescence properties is also studied. We report the generation of green emission is associated with recombination of delocalized electrons at singly occupied oxygen vacancies with deep trapped holes in ZnO and red emission is due to europium ion transitions by single wavelength light excitation at 325 nm in europium doped bunches of ZnO nanowires.

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### 1. Introduction

ZnO is a wide band gap (  $E_g = 3.37$  eV ) semiconductor material, with a large exciton binding energy ( 60 meV ) at room temperature [1]. Its excellent luminescent properties in ultraviolet (UV) and visible regions have been extensively studied. Due to superior chemical stability of ZnO, it is often chosen as a host material for optoelectronic applications. Rare-earth (RE) ions are believed to be the better luminescent centers because their 4f intrashell transitions can generate narrow and intense emission lines. It is reported that the spontaneous emission probability of optical transitions from rare-earth ions doped in nanoparticles can be significantly modified by changing the particle size, shape and surrounding medium [2-5].

A very little attention has been paid on the issue whether the photoluminescence properties of the doped nanoparticles change with varying the shape of particle. Recently, Suparna Sadhu and coworkers demonstrated simple solution based methods for making different shaped ZnO nanostructures and they try to understand the role of shape on the photoluminescence properties of doped ZnO nanostructures. They suggest that radiative transition of rare-earth ions can be modified by changing the shape of particles [6]. Several reports are available on the synthesis and studies of the luminescent properties of europium-doped semiconductors in various morphologies. Kanemitsu et al [7] reported the synthesis of Eu-doped ZnO nanorods by a micro-emulsion method. Paritosh Mohanty and coworkers reported synthesis of single crystalline europium-doped ZnO nanowires by a vapor transport method [8]. To the best of our knowledge no report is available on the synthesis of europium doped bunches of ZnO nanowire. In this paper, we report

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the synthesis and optical properties of europium doped bunches of ZnO nanowires by co-precipitation method.

## **2. Experimental Section**

### **2.1. Chemicals**

The zinc acetate dehydrate ( $\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ ), lithium hydroxide (LiOH), europium oxide ( $\text{Eu}_2\text{O}_3$ ) and nitric acid ( $\text{HNO}_3$ ) were from E.Merck Limited, Mumbai-400018, India. These chemicals were directly used without special treatment.

### **2.2. Sample preparation**

Europium-doped bunches of ZnO nanowires were synthesized by co-precipitation method. An aqueous solution of 0.1 M  $\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$  and 0.1M LiOH were prepared by dissolving each salt in double distilled water. 0.01M  $\text{Eu}_2\text{O}_3$  aqueous solution was prepared by dissolving the salt in double distilled water with addition of some drop of nitric acid. The aqueous solution of  $\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ , LiOH and  $\text{Eu}_2\text{O}_3$  was mixed and placed on magnetic stirrer for stirring at 60°C for 4h. The resulting white solid products were centrifuged, washed with double distilled water and ethanol. After washing, the product was dried in an oven at 200 °C. Finally, to study the effect of annealing on luminescence, the obtained product was annealed at 600 and 800 °C.

### **2.3. Instrumentation**

The crystal structure of europium doped ZnO nanowires were characterized by X-ray diffraction (XRD, Rigaku D/MAX- 2200H/PC, Cu  $K\alpha$  radiation ). The scanning electron microscopy (SEM) images were taken on a LEO Electron Microscopy Ltd, England. The optical absorption of the ZnO nanoparticles was examined with a Perkin Elmer Lambda 35 UV/VIS Spectrometer. The photoluminescence study was carried out on Perkin Elmer LS 55 Spectrometer.

## **3. Result and discussion**

### **3.1. Structural Study**

Fig. 1 shows the XRD pattern of europium doped bunches of ZnO nanowires synthesized by co-precipitation method. All of the peaks matched well with the bulk ZnO, which could be indexed as the hexagonal wurtzite structure of ZnO ( $P6_3mc$ ,  $a=3.2498 \text{ \AA}$ ,  $c = 5.2066 \text{ \AA}$ , JCPDS no. 36-1451). The broadening in the X-ray diffraction pattern indicate the nanocrystalline nature of material. Furthermore, it can be seen that the diffraction peaks are higher and narrower also, implying that the ZnO crystallizes well. No characteristic peak of impurities such as  $\text{Zn}(\text{OH})_2$  was observed.

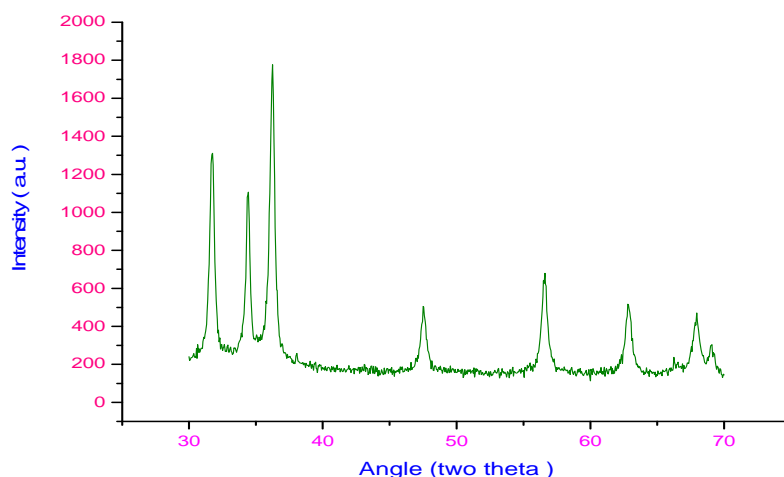


Fig. 1. XRD pattern of bunches of Eu-doped ZnO nanowires synthesized by co-precipitation method.

### 3.2. Morphology study

Fig. 2 shows SEM image of europium doped ZnO nanowires synthesized by co-precipitation method. The SEM image show that europium doped ZnO nanomaterial have nanowire-like morphology. It seems that Eu-doped ZnO nanowires form bunches due to agglomeration as product was formed by heating at 200° C. Eu-doped ZnO nanowires have diameter 60-100 nm and lengths in micro-meter range.

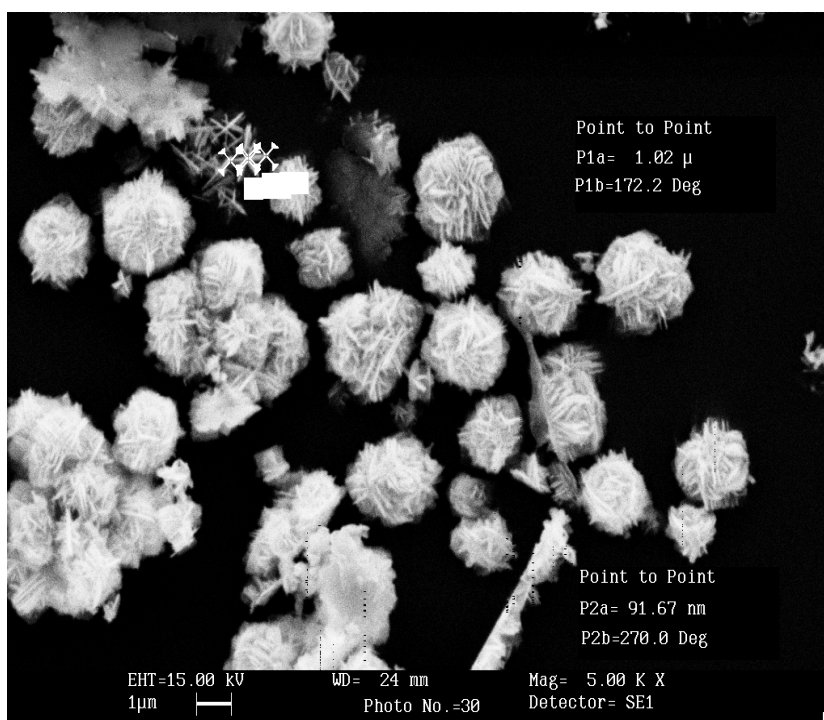


Fig. 2. SEM image of bunches of ZnO nanowires synthesized by co-precipitation method

### 3.3. Optical study

#### 3.3.1. Absorption spectrum

Fig. 3 shows the absorption spectra of bunches of ZnO nanowires (a) as prepared (b) heated at 600° C and (c) heated at 800° C. The UV absorption peaks are at 344 nm, 351 nm and 371 nm, for as prepared bunches of ZnO nanowires, heated at 600° C and heated at 800° C, respectively. The blue-shifted absorption onset at 344nm, 351nm and 371nm as compared at ~ 382 nm for bulk ZnO, is observed for as prepared bunches of ZnO nanowires, heated at 600° C and heated at 800° C, respectively.

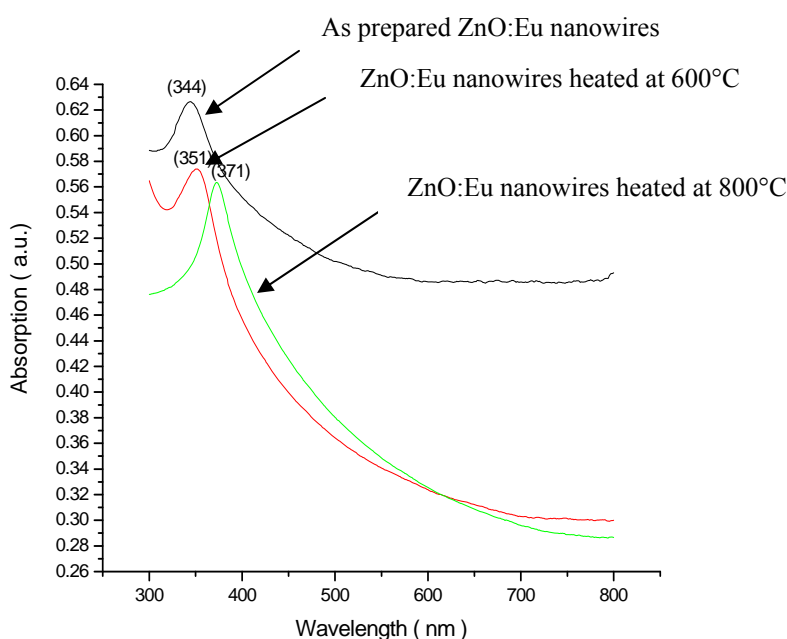


Fig. 3. Absorption spectrum of bunches of Eu-doped ZnO nanowires synthesized by co-precipitation method

R. N. Bhargava et al. [9] reported first time the optical transitions associated with localized levels of a rare-earth impurity can be modulated by quantum confinement. The effect of the quantum confinement on impurity critically depends on the size of the host crystal. As the size of the host decreases, the degree of confinement and its effect increases. The confinement of the atomic impurity achieved in a nanocrystalline size host allows transferring the energy efficiently to the atom. The caged atom derives the oscillator strength from the host in a very different manner. The 'Quantum Confined Atom' model is developed on the basis of the changes observed in the optical properties of a localized impurity as a function of the size of the nanocrystalline host. They observed that upon heating the rare-earth doped nanocrystal, the particle size increases and the efficiency decreases. Similar results are also obtained on heating europium doped bunches of ZnO nanowires.

#### 3.3.2. Photoluminescence spectrum

S.A.M. Lima et al. [10] reported the combined emission spectra of ZnO and Eu (III) ion when Eu (III) ion-containing zinc oxide was excited by 393 nm. Similar features are also found in our case. Fig. 4 shows the PL spectra of europium doped bunches of ZnO nanowires excited using a wavelength of 325 nm. A very broad emission peak has been observed. It seems that the wide

band is a result of sum of emission peaks at 520 nm, 550 nm, 580 nm, 620 nm and 650 nm. The peak at 520 nm is due to green emission from europium doped bunches of ZnO nanowires. This green emission from nanowires is associated with recombination of delocalized electrons at singly occupied oxygen vacancies with deep trapped holes [11-12]. The peak at 550 nm, 580 nm, 620 nm and 650 nm is due to europium ion transitions  $^5D_0-^7F_0$ ,  $^5D_0-^7F_1$ ,  $^5D_0-^7F_2$  and  $^5D_0-^7F_3$  respectively.

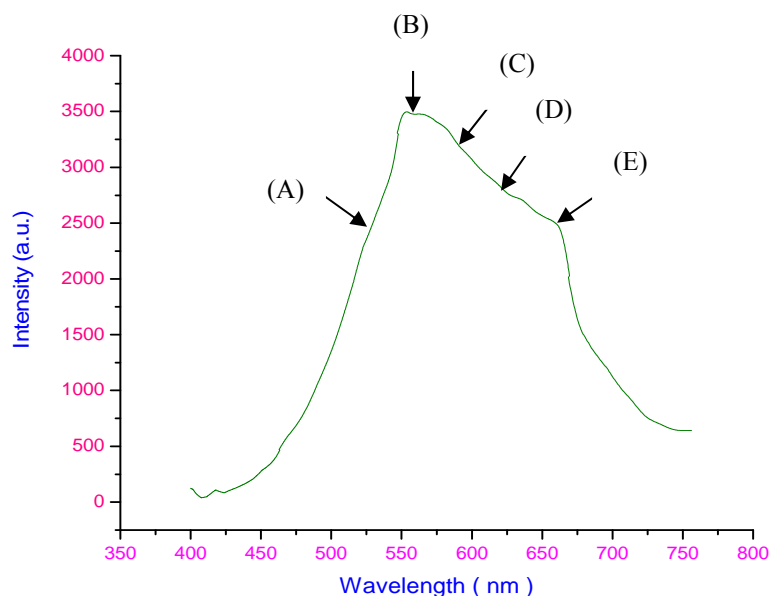


Fig. 4 Photoluminescence spectra of europium doped bunches of ZnO nanowires synthesized by co-precipitation method. Wide emission band is due to (A): green emission from ZnO, and europium ion transitions (B):  $^5D_0-^7F_0$ , (C):  $^5D_0-^7F_1$ , (D):  $^5D_0-^7F_2$ , (E):  $^5D_0-^7F_3$ .

Further, the effect of heating on the photoluminescence ( PL ) properties of bunches of ZnO nanowires was studied. The PL intensity decreases with increase of annealing temperature as shown in Fig. 5, it is due to increase of size of the particles with annealing temperature.

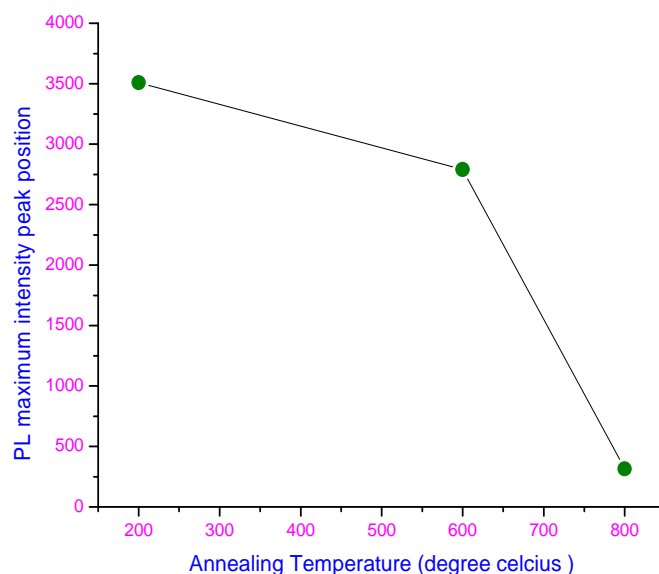


Fig. 5 PL maximum intensity peak position of europium doped bunches of ZnO nanowires (a) as prepared heated at 200 °C, (b) heated at 600 °C and ( c ) heated at 800 ° C.

#### 4. Summary

Bunches of europium doped ZnO nanowires have been successfully synthesized by co-precipitation method. Photoluminescence study revealed a wide band emission from europium doped bunches of ZnO nanowires. The wide band is a result of presence of emission peaks at 520 nm, 550 nm, 580 nm, 620 nm and 650 nm. The photoluminescence intensity decreases with increase of annealing temperature.

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