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### Influence of rare-earth doping on the photoluminescence of Zinc Oxide nanophosphors Partha P. Pal\* and J. Manam

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#### Abstract

This paper reports the photoluminescence studies of Eu (RE)-doped ZnO nanophosphors synthesized by precipitation method using ethanolic solution as solvent. The prepared samples are characterized by a Philips Holland TW 1710 XRD measuring instrument with Co target. The ZnO structure is found to be wurtzite. The particle sizes are found to be in the range of 70 nm to 90 nm. The prominent peaks for EU doped ZnO for different concentrations of Eu are (100), (002), (101), (102), (110). The XRD results revealed that the presence of dopants has not altered the basic structure of the compound. The PL studies of Eu doped ZnO were carried out by FL 2500 Flourescence spectrophotometer in the wavelength range 350 nm to 700 nm. The emission spectra Eu:ZnO for the different doping concentrations. The broad emission spectrum around 550 nm observed in case of undoped (zero wt% Eu doped) ZnO is generally known to result from the superposition of green and red emission due to self-activated centers. However the emission spectra for Eu doped ZnO calcined at 200<sup>0</sup> C shows peaks at 620 nm suggesting a possible red emission which arises due to <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>2</sub> transition of Eu<sup>3+</sup> ion.

#### Keywords: Photoluminescence, Rare-earth, ZnO

#### **1.0 INTRODUCTION**

In recent years the semiconductor nanocrystals attracted considerable interest after the observation of enhanced luminescence efficiency and shortening of radiative lifetime by orders of magnitude from milliseconds to nanoseconds when compared with the bulk counterparts. Zinc oxide (ZnO) is a wide band gap (Eg= 3.37 ev) semiconductor material with a large exciton binding energy (60 Mev) at room temperature. A representative of II-VI compound semiconductor, ZnO has attracted considerable attention over the last few years due to its extensive application as a green emitting phosphor and properties like outstanding stability, high electrical conductivity, good piezoelectric

## ISSN 2277 – 6362 International Journal of Luminescence and Applications Vol.1 (II)

characteristics and biocompatibility. It shows excellent luminescent properties under electron beam and UV excitation for which it is used in the production of many photoelectronic devices as transparent conducting oxides (TCO), like solar cells. In order to improve the TCO properties of ZnO, it is usually doped with metallic ions. Recently, rare-earth (RE)-doped materials have been of great scientific interest in photonic devices and nextgeneration flat panel displays where ZnO can be used as a perfect host material due to its superior chemical stability. At present it is hard to find any paper which discussed the photoluminescence studies of the Eu doped ZnO synthesized by this method which is stated below. Our paper not only discuss the variation of photoluminescence intensity on different doping concentration but also effect of doping on the crystal structure.

#### 2.0 EXPERIMENTAL

#### 2.1 Synthesis

In the preparation of pure ZnO sample  $ZnCl_2$  and NaOH in requisite amount were separately dissolved in ethanol to prepare 0.05 M ethanolic  $ZnCl_2$  solution and 0.20 M ethanolic NaOH solution respectively. Both the solutions were prepared in equal volume and at room temperature. These two solutions were mixed and constantly stirred with a magnetic stirrer for 6 hrs at room temperature. The resulting powder was filtered with Whatman-42 filter paper. After filtration, the filterpaper was dried to collect the sample. It was then washed in ethanol.

Europium (Eu) doped ZnO sample was prepared by adding EuCl<sub>3</sub> salt in a stoichiometric ratio to the Zinc solution before mixing the two ethanolic solutions. Calculated amount of EuCl<sub>3</sub> was taken to prepare 0.25,0.5 and 1.0 wt% doped ZnO sample. Prepared samples were then annealed at 200 ° C for 2 hrs.

#### 2.2 Instrumentation

The crystal structure of undoped and europium doped ZnO powders were characterized by a Philips Holland TW 1710 XRD measuring instrument with Co target. The diffractogram of the samples were taken at room temperature in a wide range of Bragg angle  $2\theta$  ( $20^{\circ} \le 2\theta \le 110^{\circ}$ ) at a scanning rate of 2.00 degree per minute. The

photoluminescence (PL) studies of undoped and Eu doped ZnO were carried out by personal computer based Fluorescence spectrophotometer (Hitachi F-2500) in the wavelength range 350 nm to 700 nm. The optical reflectance studies of the undoped and Eu doped ZnO powder sample are carried out by a HR 4000 UV-Vis-NIR spectrophotometer with DH-2000-BAL lamp.

#### 3.0 RESULTS AND DISCUSSIONS

#### 3.1 XRD Results

The X-ray diffraction of undoped and Eu doped ZnO samples were taken at room tempearature which are shown in the fig.1. XRD pattern of undoped and doped ZnO shows typical peak patterns which can be indexed as ZnO wurtzite structure in the standard data (JCPDS, 36-1451). The prominent peaks for both undoped and Eu doped ZnO were found at (100), (002), (101), (102), (110). The rest of the peaks were found at same positions which suggested that small amount of rare earth material (Eu) doping was unable to make any significant changes in the lattice structure of the host lattice.

The crystallite sizes of the powders were estimated from X-ray line broadening using Debye –Scherrer's equation:

Where, K=shape factor which is dimensionless and has a typical value of about 0.9, but varies with the actual shape of the crystallite,

 $\lambda$  = x-ray wavelength,

 $\beta$ = line broadening at half the maximum intensity (FWHM) in radians,

 $\theta$  = Bragg angle

and, D = Diameter of the particles

The particle sizes were found to be in the range of 70 nm to 90 nm.

#### 3.2 Photoluminescence study

#### 3.2.1. Photoluminescence emission spectra:

3.2.1.1 Emission Spectra for Undoped ZnO :

The room-temperature photoluminescence emission spectra of the undoped ZnO powders shown in the fig.2. The spectra mainly consists of four emission bands: a strong UV

## ISSN 2277 – 6362 International Journal of Luminescence and Applications Vol.1 (II)



Fig. 1: XRD patterns of nanocrystalline undoped and Eu doped Zno

emission band at 380 nm, a weak blue band at 450 nm, a week blue-green band at 472nm, and a green band at 532nm. The UV emission is the most intense emission and corresponds to the exciton recombination related near-band edge emission of ZnO. The weak blue and weak blue-green emissions are possibly due to surface defect in the ZnO powders as in the case of ZnO nanowires reported by Wang and Gao. The green band emission corresponds to the singly ionized oxygen vacancy in ZnO. Oxygen vacancy acts as radiative center in the luminescence process.

#### 3.2.1.2 Emission Spectra for Eu doped ZnO :

The room-temperature photoluminescence spectra of the Eu doped ZnO powders of three different concentratations calcined at 200 ° C for 2 hrs. shown in the fig.3 The strong peak at 620 nm is suggesting a possible red emission which arises due to  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of Eu<sup>3+</sup> ion. The peaks at 594 nm arises due to  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition of Eu<sup>3+</sup> ion.

#### 3.2.1. Photoluminescence excitation spectra:

Fig. 5 shows the photoluminescence excitation spectra of the Eu doped ZnO (1.0 wt %) powder calcined at 200 ° C



Fig 2: Room temperature PL emission spectra for the excitation at 275 nm of the nanocrystalline ZnO

![](_page_2_Figure_10.jpeg)

Fig 3: Room temperature PL emission spectra for excitation wavelength 393 nm of the Eu doped ZnO of different concentrations

## ISSN 2277 – 6362 International Journal of Luminescence and Applications Vol.1 (II)

for 2 hrs. The main peaks of excitation spectra at 394 nm, 415nm,464 nm and 534 nm can be identified as excitations corresponding to the transitions  ${}^{7}F_{0} \longrightarrow {}^{5}L_{6}$ ,  ${}^{7}F_{0} \longrightarrow {}^{5}D_{3}$ ,  ${}^{7}F_{0} \longrightarrow {}^{5}D_{2}$  and  ${}^{7}F_{0} \longrightarrow {}^{5}D_{1}$  respectively of Eu<sup>3+</sup> ions.

#### 2.0 CONCLUSION

This paper presents the Photoluminescence study of both pure and Eu doped Zinc Oxide nanophosphors prepared by a simple precipitation method where rare earth material Eu was successfully doped with ZnO. XRD study revealed the wurtzite structure of ZnO and the particle size was found to be in the range 70-90 nm. Photoluminescence spectra of all the samples shows a great improvement on the luminescence properties after a little addition of rare earth material and which is in the agreement with the studies of other researchers. Eu doped sample gives an intense emission with red color suggested by the sharp peaks of Eu doped ZnO compared to the broad green emission of undoped ZnO. This broad green emission of pure ZnO and the strong emission from  $Eu^{3+}$  ions of Eu:ZnO have a great applications in many display devices. All these studies are important on the sense that the semiconductor nanocrystals show a variety of unique optical, electronic and chemical properties which originate mainly due to two reasons, i.e., quantum confinement effects and large surface to volume ratio.

![](_page_3_Figure_5.jpeg)

Fig 4: PL excitation spectra of the Eu doped ZnO of different concentrations for wavelength 519 nm

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