Synthesis of praseodymium doped ZnO nanoparticles using solvent free, eco friendly method: effect of doping on the structural and optical properties of ZnO nanoparticles

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Abstract— **Praseodymium doped Zinc oxide nano particles was synthesized using a simple solvent free, economic and ecofriendly combustion method. The structural characterization of synthesized nano particles was carried out using XRD and SEM. The optical characterization was carried out using UV and Photoluminescence spectro fluorimeter. The X ray studies confirm the substitution of Pr in the ZnO nano particles. The absorption spectrum shows a greater blue shift due to the presence of Pr. The new emission peak with very high intensity was observed in the region of 322 nm along with the peak at 436 nm. The purity of the sample was confirmed using XRD and EDAX.**

Keywords **– solvent free synthesis, optical properties, blue shift, luminescence**.

I. INTRODUCTION

The wide band gap semiconductor nano materials are area of current interest due to their potential application in opto electronic and microelectronic devices [1]. ZnO, with a wide energy band gap of about 3.37 eV and large exciton binding energy of 60meV finds wide range of application in light-emitting diodes [2], solar cells [3], transparent conductors [4], field emission displays [5], sensors [6], etc

Generally, the electrical and optical properties of the semi conducting material systems are improved through doping of some foreign trace elements [7]. Recent studies on doping of rare earth materials have received considerable interests due to their possible applications in visible light-emitting phosphors (for displays) and other optoelectronics devices [8,9]. It is also well understood that the structural, optical and electrical properties of the rare earth cations depend on the host structure and dopant composition [10]

Considering the unique optical properties, along with the tunable emission wavelengths ranging from blue to infrared region, Pr^{3+} ion, a well known activator dopant has been chosen for the current study [11].We believe the sharp and narrow intense emissions (in the visible range) of this rare earth metal in its trivalent form is a good support for the fore mentioned application aspect [12]

There are various methods used to synthesize Zinc oxide nano particles of controlled size and shape. Some are soft chemical [13], microwave thermal evaporation [14], hydrothermal [15], vapor phase transport [16], electrochemical deposition [17]pulsed laser deposition [18], thermal oxidation [19] and also by solid state method[20] . Jayavel *et al* has reported recently the effect of Pr on ZnO by synthesizing through solution method [21]. We already reported in our earlier studies the synthesis of pure zinc oxide using solvent free ecofriendly method [22] and in our current study we are reporting the synthesis of Pr doped nano Zinc oxide particles in a simple way.

II. MATERIALS AND METHODS

A. Materials used

The following analytical grade materials were used without further purification: Zinc nitrate hexa hydrate $Zn(NO_3)_2.6H_2O$. A.C.S. reagent (Sigma-Aldrich, 99% purity by wt) $Pr(NO_3)_3.6H_2O$ A.C.S. reagent (Sigma-Aldrich, 99% purity by wt) and Glycerol (anhydrous) were obtained from Merck (99%). Methanol used for the following studies is HPLC grade.

B. Synthesis of Pr doped Zinc oxide

About 6.5 g of the Zinc nitrate hexa hydrate and 0.6 g of Praseodymium nitrate hexahydrate were weighed and made in to a paste with 2 drops of glycerol in a silica crucible. The amount of glycerol used was optimized after several trials in order to eliminate excess glycerol which leads to charring of substances. The initial temperature was set to 50 °C and the temperature was slowly raised to 600 °C in the muffle furnace. The substance is calcinated at 800 °C for 4 h. The yellow crystalline Pr doped Zinc oxide powder obtained was characterized.

C. Characterization

The morphology of the compound was examined by scanning electron microscope (SEM) using Hitachi Su-6600. The elemental analysis was carried out using the energy dispersive X- ray analysis (EDAX) technique. The x-ray diffraction patterns were studied using scifert – X –ray diffractomer with a CuKα radiation. The diffracted intensities were recorded from 10 to 70 angle.

The absorption and emission spectra were recorded using Cary 100 Bio UV-Visible spectrophotometer and Fluoromax-4P spectrofluorometer respectively. For spectral analysis, the Pr-doped ZnO nano particles are dispersed in HPLC methanol with the help of a sonicator. The nano particles are sonicated in methanol for 10 minutes and the spectrum was recorded at room temperature.

III. RESULTS AND DISCUSSION

A. XRD studies on Pr doped nano Zinc oxide

The structural characterization was carried out using powder XRD.

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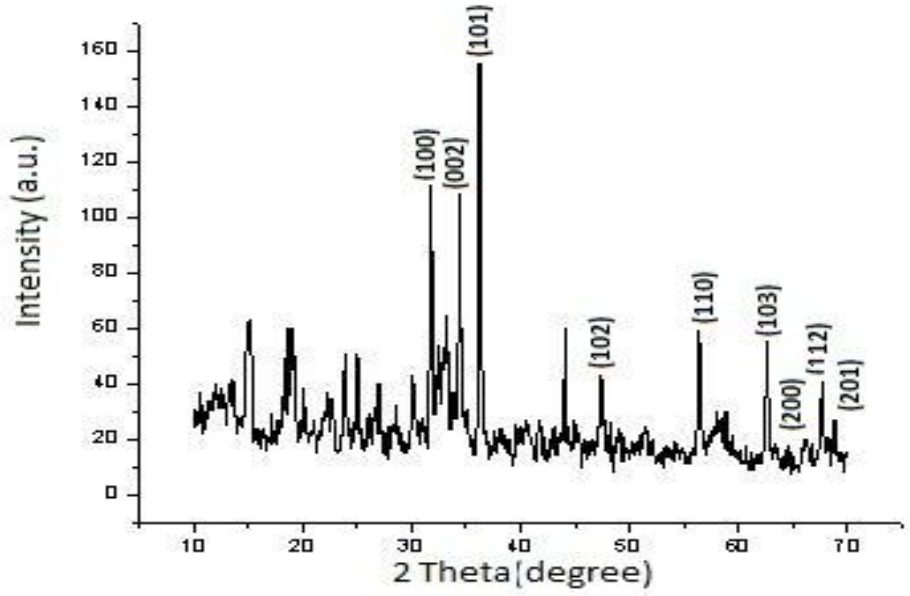

Fig. 1. XRD spectrum for the Pr roped Zinc oxide nano particle.

Fig. 1 shows typical XRD pattern of the as-obtained nano particles. All the diffraction peaks are matched with the peaks obtained for the hexagonal phase of ZnO reported in JCPDS card .No. (JCPDS-89-1397). The extra peaks between 10-30 confirms the presence of Pr. The analysis of powder XRD pattern at room temperature shows that the sample formed is single phase with the hexagonal symmetry. The sharp line indicates that the powder formed is crystalline. The addition of Pr dopant does not alter the crystalline nature of the compound

B.SEM and EDAX analysis

The surface morphology of the resulting powder was examined using scanning electron microscope. The SEM micrographs of the Pr doped ZnO powder is shown in Fig. 2

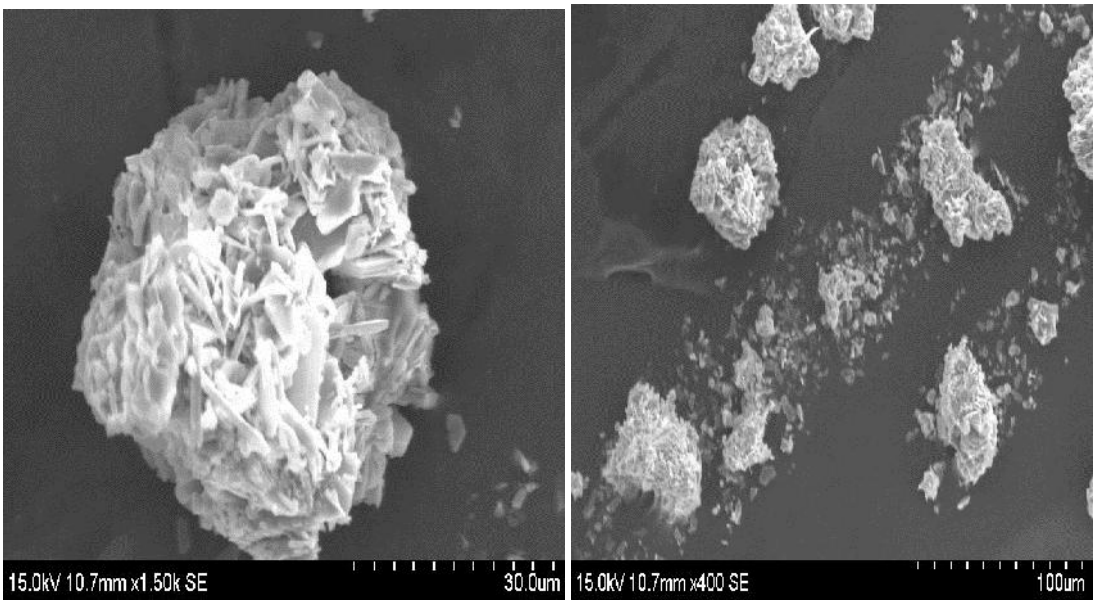

Fig. 2. A & B. SEM micrograph of the Pr-doped Zinc oxide nano particle.

From the images, it is clear that Pr-doped ZnO specimens are composed of a number of non-uniform nanorod like structures. These nano rods aggregated to form a flower like structure. Their average diameters were evaluated to be about 150–200 nm, with their length even up to 1–3µm. The Pr compositions in the nanorods were estimated using the energy dispersive X-ray analysis shown in Fig. 3. The EDAX results were collected from several parts of the doped nano rods,

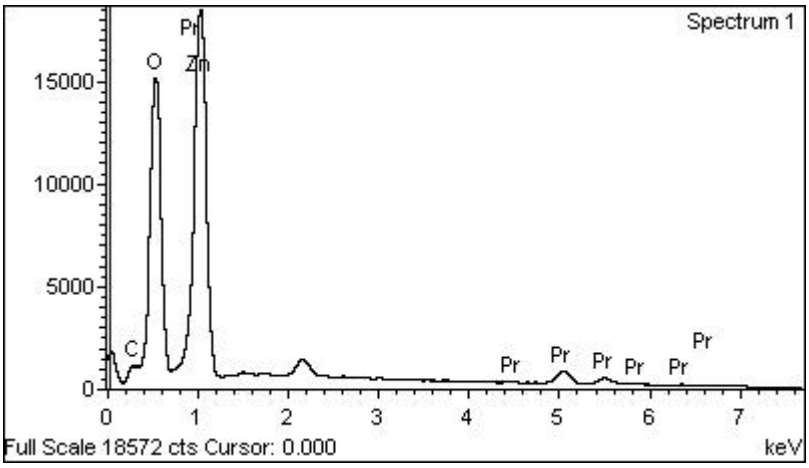

Fig. 3. The EDAX spectrum for the Pr doped Zinc oxide nanoparticle.

Fig. 3 clearly reveals the composition of Zinc, oxygen and Pr. The absence of any extra peak in the EDAX spectrum shows the absence of impurities.

C. Optical characterization

The yellow crystalline Pr doped Zinc oxide powder was not soluble in water and almost in all organic solvents. Hence UV–Visible spectra were recorded for the Pr doped Zinc oxide nano particles dispersed in methanol solution and are represented in Fig. 4.

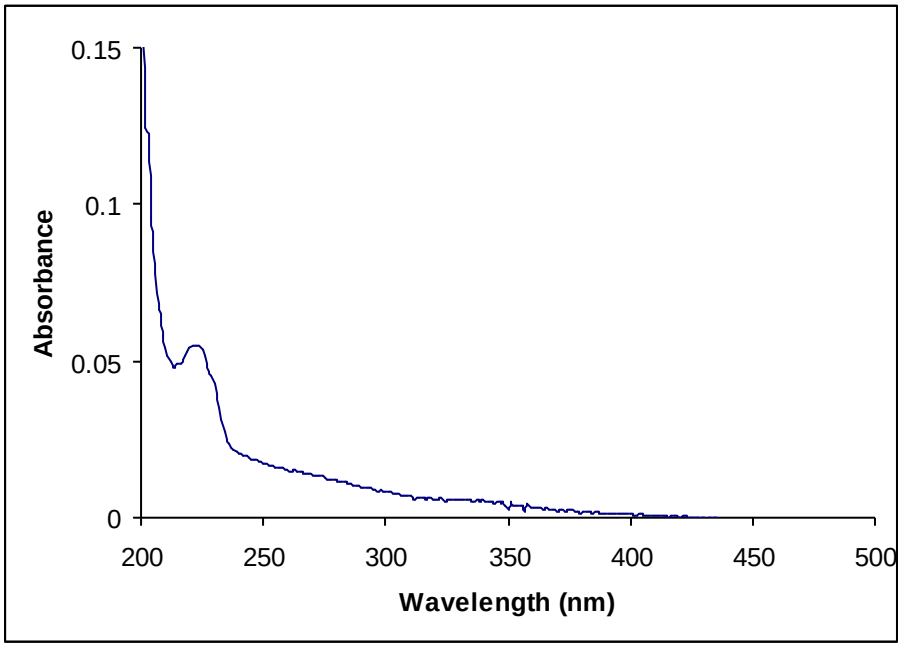

Fig. 4. UV–Visible spectrum of Zinc oxide nano particle by calcinations at 300 °C using methanol as solvent

The absorption band observed at 224 nm is the characteristic peak of Zinc oxide nano material. There is a huge blue shift in the absorption spectrum compared to the bulk Zinc oxide whose absorption maximum [23] occurs 373 nm. This blue shift is due to the decrease in the size effect of nano structures..
The emission spectrum was recorded at the excitation wavelength of 225 nm using Fluoromax-4P spectrofluorometer and is represented in Fig. 5.

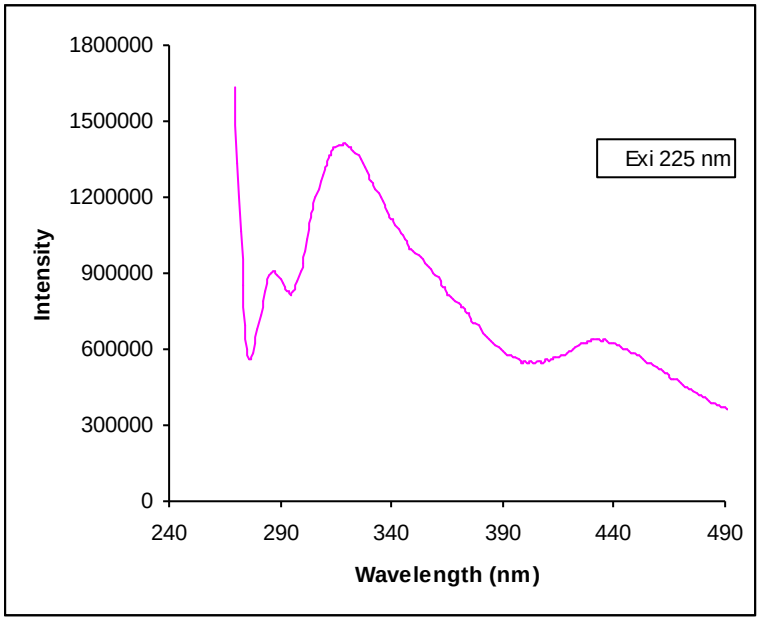

Fig. 5. The fluorescence spectrum of Zinc oxide nanoparticle using methanol as solvent

The emission spectrum shows two characteristic peaks one at 322 nm and the other around 436 nm. The strong violet emission around 436 nm is the result of recombination of electron between zinc interstitial and hole in the valence band [24]. The enhanced emission compared to Zinc oxide nano particle around 430 nm is due to the presence of Pr. The very strong emission in the infra red region around 324 nm is due to the incorporation of Pr in ZnO.. Since the emissions are very strong it is very difficult to measure any peak due to the defects around 500nm -600 nm.

IV. CONCLUSION

The present study illustrates a simple, very economic and ecofriendly method for the synthesis of Pr doped Zinc oxide nano particles through the direct combustion of Zinc nitrate, praseodymium nitrate in the presence of minimum amount of glycerol as organic dispersant.. The SEM analysis tells us about the morphology of the particle which are of nano rods. The presence of extra peak in the XRD analysis confirms the presence of Pr in the compound and the sharpness of the peak confirms the crystalline nature. The absence of extra peak in the EDAX analysis reveals the purity of the compound. The incorporation of dopant brings about huge blue shift in the absorption spectrum of the compound and a new peak in the emission spectrum with very high intensity.

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