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# Synthesis and characterization of Pr and Nb doped ZnO by spray pyrolysis technique

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### Abstract

Zinc oxide (ZnO) is a n-type semiconductor material which has a wide direct band gap of energy ~3 eV. Dopant in ZnO nanostructures is an effective way to improve ZnO's structural properties in various applications. In the present study Pr and Nb doped ZnO were synthesized on glass substrate by using chemical spray pyrolysis at 450°C temperature. The concentration of impurities is varied from (0% to 4 mol %) for (Pr-ZnO) and (1% to 4 mol%) for (Nb-ZnO). The synthesized thin films are characterized by X-Ray diffraction, which shows hexagonal structure with 57nm crystalline size for optimized concentration of Pr and it is indexed using JCPDS card number (01-079-0206) and for Nb doped ZnO JCPDS card number (01-079- 0208). Due to their excellent optical and electrical properties prepared films are used as a transparent window layer and electrodes in solar cell.

**Keyword:** ZnO, Pr, Nb, Structural and Optical properties, Chemical Spray Pyrolysis.

## Introduction

There has been great interest in the oxide semiconductor and its ternary alloys in recent years for its various application [1]. In present paper we deposit ZnO material doped with Pr and Nb at various concentration by using spray pyrolysis technique [2-7]. Spray pyrolysis is a well-established and widely used technique for the film processing. Basically, pyrolysis is a chemical reaction. The spray deposition based on the mechanical transformation of the solution to droplets steam by using compressed gas or ultrasonic waves. Among the various chemical methods solution spraying technique is the most popular today because its applicability to produce variety of conducting and semiconducting materials [8-10].

ZnO is known to be one kind of the important photocatalysts because of its unique advantage, such as its low price, high photocatalytic activity and nontoxicity, that has attracted a great deal of attention. Zinc oxide is a n- type semiconductor which has a wide and direct band gap energy of ~3.3ev at room temperature [11]. ZnO can be used for some application such as electronics, optoelectronics [12], sensors [13], photonic devices and photocatalyst [14]. ZnO nanostructures were deposited by using various technique such as Vapour phase deposition [15], Pulsed laser deposition [16], Thermal evaporation [17], sol-gel [18], Hydrothermal method [19], Chemical bath deposition [20] and Spray pyrolysis technique [21]. Doping of ZnO nanostructures is one effective way to improve the structural properties of ZnO for various applications. In particular, doping ZnO with rare earth materials is of interest in tailoring its optical properties.
In this work, we synthesized and characterized the undoped ZnO and Pr also Nb doped ZnO on glass substrate by using spray pyrolysis technique and then investigated optical and morphological properties. The spray pyrolysis technique has many advantages such as low cost, deposition equipment that is simple and easy fabrication of large area films. Precursor solution is sprayed through by nozzle above the surface of substrate which has been heated.

# Methodology

Nanocrystalline ZnO thin films were deposited on glass substrate by Spray Pyrolysis method. The substrate was very carefully cleaned using chromic acid, Substrate were boiled at $60^0$C temperature. When temperature reaches towards room temperature removed the glass slides from chromic acid and then washed with distilled water, after that before deposition substrate were cleaned ultrasonically. After cleaning with acetone, substrate was allowed to heat at high temperature ($450^0$C). (0.1M) of zinc acetate ($ZnCH_3COOH$) were diluted with (35ml) of distilled water, (60ml) methanol and (5ml) acetic acid. Deposition rate required up to (1-2 min.). Then dopant material of Pr (Praseodymium Oxide) of (0.1M) diluted in 25ml of solution (5 ml Nitric acid ($HNO_3$) + 20 ml distilled water). The distance maintained between spraying nozzle and hot plate is about 39cm. The dopant material was deposited at various concentration.

[In similar manner, Niobium was also doped in ZnO at various concentration. Synthesized pure ZnO and Niobium-doped ZnO (Nb-ZnO) nanoparticles containing (1% to 4 mol%) Nb. ZnO and Nb doped ZnO were synthesized on glass substrate by using chemical spray pyrolysis at $450^o$C temperature.

# Result and Discussion

**1. XRD STUDIES:**

Fig. 1 represents the x-ray diffractogram of the ZnO films. From XRD data, it is seen that the films exhibit hexagonal (wurtzite) crystal structure with preferential growth along the (002) plane [24]. For both optimized sample the intensity of the (002) diffraction is highest at the substrate temperature of $450^0$C, indicating an improvement of the crystallinity at this temperature. All the peaks in the diffraction pattern were indexed on the basis of a JCPDS data card No. (01-079-0206) and JCPDS card number (01-079- 0208). The crystalline size if the ZnO thin films prepared at different concentration was evaluated from full width at half maxima (FWHM) of (002) peak using Scherrer's formula [25]. The grain size obtain for the optimized concentration (2%Pr) is 57 nm and for (4% Nb) is 15nm. It was observed that the grain size values increase with increasing concentration and decreases with decreasing concentration.

$$D = \frac{0.94\lambda}{\beta \cos\theta} \qquad \text{--------------- (1)}$$

Where λ : X- ray wavelength
θ : Bragg diffraction angle
β : FWHM

**2. Optical absorption studies**

For the direct transition, the optical band gap energy of undoped ZnO and doped ZnO was determined by using the equation [22],

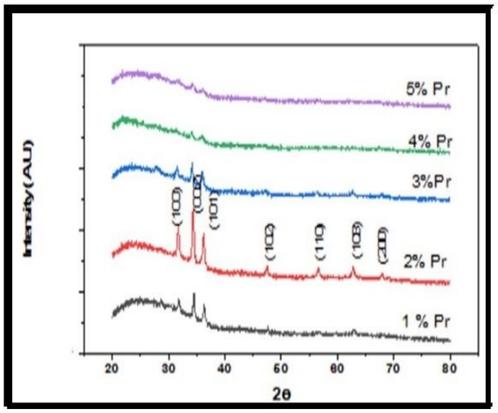


**Fig (a) Pr doped ZnO**

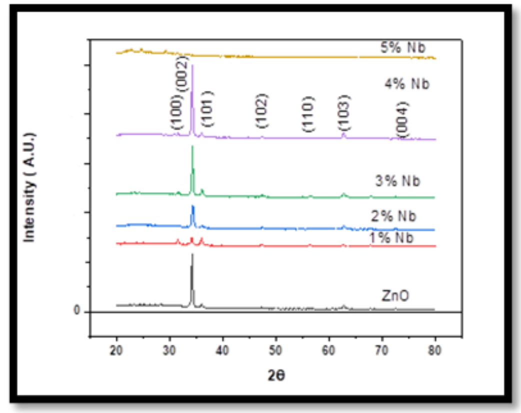


**Fig (b) Nb doped ZnO**

| Thin film | Un-doped ZnO | ZnO: Pr1% | ZnO: Pr2% | ZnO: Pr3% | ZnO: Pr4% | ZnO: Pr5% | ZnO: Pr6% |
|---|---|---|---|---|---|---|---|
| **Band gap(ev)** | 3.2538 | 3.2163 | 3.2087 | 3.7727 | 3.7816 | 3.7912 | 3.8024 |
| **Thin film** | **Un-doped ZnO** | **ZnO:Nb1%** | **ZnO:Nb2%** | **ZnO:Nb3%** | **ZnO:Nb4%** | **ZnO: Nb5%** | **ZnO:Nb6%** |
| **Band gap (ev)** | 3.2538 | 3.2454 | 3.2407 | 3.2404 | 3.2385 | 3.3224 | 3.3263 |

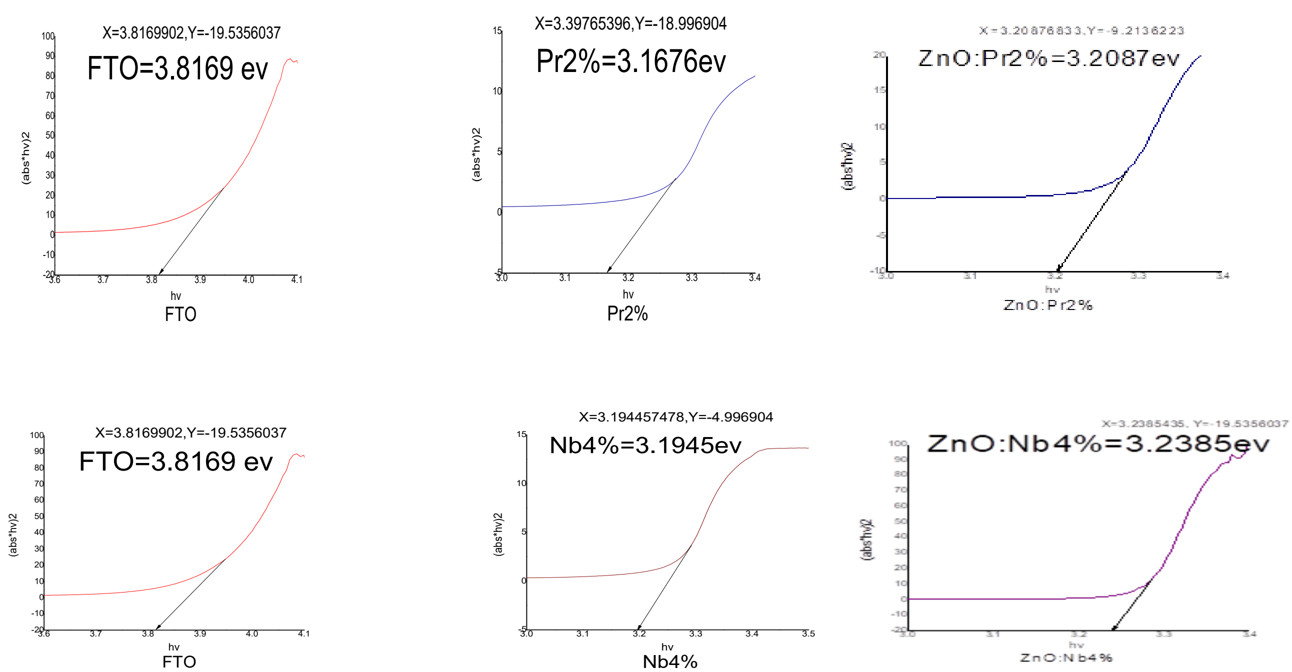


**Fig. 3 UV-Vis Spectra for optimised 2 % Pr doped ZnO & 4 % Nb doped ZnO**

$$\alpha = \text{Const.} \frac{(h\upsilon - E_g)^{1/2}}{h\upsilon} \qquad \text{-----------(2)}$$

Where $h\upsilon$ is the photon energy and $E_g$ is the optical band gap which could be calculated from $(\alpha h\upsilon)^2$ verses $h\upsilon$ plot , which are shown in figure. By extrapolating the linear part of plot to α = 0, optical band gap was estimated. From Fig., it is observed that as concentration rate increases, band gap increases, it becomes maximum (3.9712ev) at temperature 450$^0$C.

Optical spectra of undoped ZnO and doped ZnO are shown in following figure. The value of $E_g$ so obtained which vary from (3.1to 3.9eV) which indicate the variation of band gap with increasing molar concentration of Pr [23].

Optimized condition of Pr doped ZnO is at 2% and bandgap of this sample is 3.2087 eV. Similarly, optimized condition of Nb doped ZnO is at 4% and bandgap of this sample is 3.2385 eV.

**3. FTIR SPECTRA:**

FTIR spectra of pure ZnO, Nb-doped ZnO and Pr-doped ZnO photocatalyst are measured to identify the functional group. The absorption peak of ZnO is found at 510 cm$^{-1}$. The weak stretching C-O bond is found at 1100 cm$^{-1}$ [26]. As doping concentration goes on increasing there is observed that curve becomes flatter, which shows that doping of Pr and Nb elements in ZnO is successfully done. No any other impurities are found in sample, so there is no other functional group is present in sample.

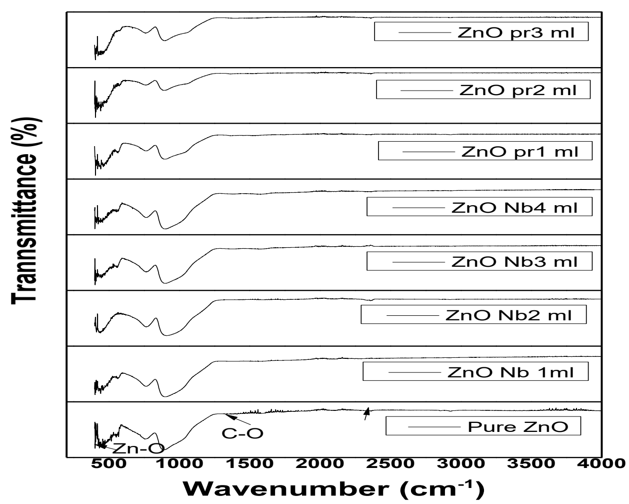


Fig. FTIR analysis

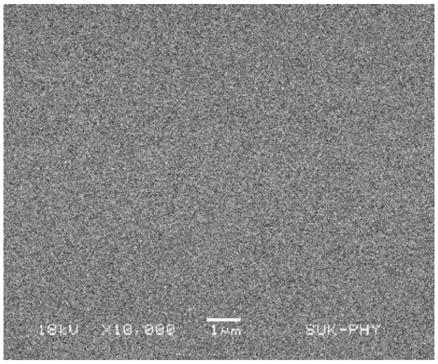

**Fig (a) Pure ZnO**

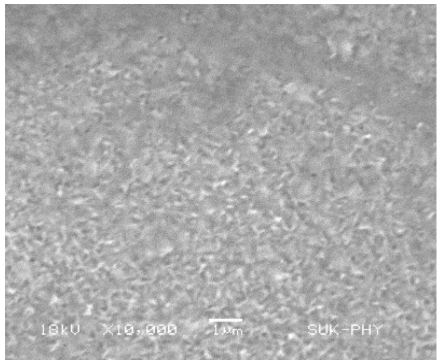

**Fig (b) Nb doped ZnO at 4%**

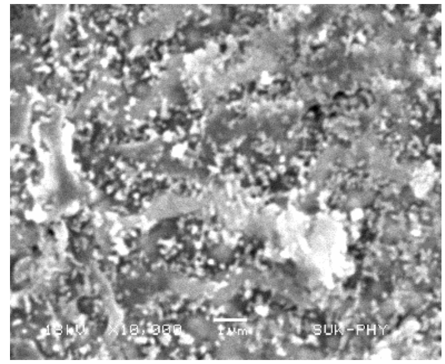

**Fig (c) Pr doped ZnO at 2%**

**4. Morphological Properties:**

To study the surface morphological properties of prepared films they were characterized by Scanning electron microscope at same magnification. It clearly shows the impact of doping concentration on deposited films. Images are shown in following figure. SEM images of pure ZnO showed rough surface topography with tiny grains distributed over the smooth background. For optimized concentration of Pr Doped ZnO and Nb doped ZnO SEM images are shown in following figure.

## Conclusions

The dopant thin film of Pr and Nb - ZnO were successfully deposited by a spray pyrolysis technique. The films were deposited onto glass substrate at 450$^0$C temperature. Substrate temperature during deposition was found to have Influenced the phase. The films have good optical quality properties. The optical energy gap is varied from (3.1 to 3.9 eV) for varied concentration. The synthesized thin films are characterized by X-Ray diffraction method which shows hexagonal structure for optimized concentration of (2% Pr) with 57nm crystalline size and it optimized by JCPDS card number (01-079-0206). Similarly, for Nb X-Ray diffraction method which shows hexagonal structure for optimized concentration of (4% Nb) with 15 nm crystalline size and it optimized by JCPDS card number (01-079- 0208).

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**Conflicts of interest:** The authors stated that no conflicts of interest.

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