



Research Article

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Structural, optical and thermal studies of cobalt doped hexagonal ZnO by simple chemical precipitation method

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ABSTRACT

Cobalt doped zinc oxide nanoparticles were prepared through simple chemical precipitation method. X-ray diffraction studies confirm the prepared particles are in Wurtzite structure. Scanning Electron Microscopy and TEM studies show the shape and morphology of the particles. To identify the presence of cobalt in ZnO, XRD and FTIR studies were done. A thermal property of undoped and doped ZnO were studied by TGA & DTA analysis. Optical absorption measurements confirm the presence of exciton peak at 341 nm. Photoluminescence studies were done with the excitation wavelength of 395 nm.

Key words: Cobalt, nanoparticles, wurtzite, photoluminescence, TEM.

INTRODUCTION

Nanoscience and technology needs new materials which will be useful to make new class of nanodevices (1). Semiconductor, metallic nanoclusters and carbon based nanostructures are the materials gained more interests. Among these, Semiconductor nanoparticles obtained more importance because of its exciting optical properties like size dependent absorption and emission properties (2, 3). These novel physical and chemical properties which are essential for nano electronics (4), biological (5), and catalytic applications. These applications drive scientific community to probe its electronic structure through exciton dynamics. Zinc oxide (ZnO) is a II –VI group semiconductor with Wurtzite crystal structure a direct and wide band gap of 3.37eV, a large exciton binding energy (60meV) and high optical gain at room temperature (6-8). Wurtzite ZnO has been widely used to demonstrate numerous applications including field effect transistor (9) optical device (10), dye-sensitized solar cell (11) and solid state gas sensor (12, 13).

Currently, modification of ZnO properties by impurities/ dopant incorporation has become a hot topic. Doping ions in ZnO will make scientists to tailor its optical, electrical and magnetic properties through altering its electronic structure (14).

There are some reports on the effect of doping of various transition metals on the structural and electrical conductivity of ZnO prepared by several methods (15-19). Owing to the importance of metal doped ZnO nanoparticles, we prepared Co doped ZnO through simple chemical precipitation method where we altered the doping concentration of Co and studied the optical photoluminescence properties of these nanostructures.

EXPERIMENTAL SECTION

2.1. Chemicals

Zinc acetate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, cobalt acetate, and polyvinylpyrrolidone (PVP MWt 4000) used in this study were received from Aldrich, USA and all other chemicals and solvents used were obtained from commercial sources with high purity analytical grade reagent. Double distilled (DI) water was used for the preparation of all reagents.

2.2 Synthesis of $\text{ZnO}:\text{Co}^{2+}$ nanoparticles

ZnO nanoparticles doped with Co^{2+} (0.5-2.5 %) ions were prepared by simple chemical precipitation method. The reactants were zinc acetate, cobalt acetate, and polyvinyl pyrrolidone (PVP mw4000) which are all of analytical purity. Ultra pure deionized water and ethanol (equal volume) were used as the reaction medium. In a typical procedure, ethanol –water mixture solution of 100 ml of 0.2M Zinc acetate and different concentration of cobalt acetate in 25 ml water were added by constant stirring using magnetic stirrer. A selected concentration of PVP (1g) was added to the precursor solution, followed by an addition of 0.2M NaOH drop by drop to form the precipitate. The precipitate was washed with water and ethanol for several times and dried in oven for 2hrs at 120°C .

2.3 Apparatus

The XRD patterns of the powdered samples were recorded using X PERT-PRO diffractometer with a Cu K α radiation ($\lambda=1.5406 \text{ \AA}$). The crystallite size was estimated using the Debye-Scherrer equation of the major XRD peak. The size and morphology of the nanoparticles were studied using SEM (HITACHI model S-3000H), and TEM (PHILIPS-CM 200; 20-200 kv) microscopes. All samples were prepared by Drop Cost Method using carbon coated copper grid. The UV spectra of all the samples in deionized water were recorded using UV-1650PC SHIMADZU spectrometer. Fluorescence measurement was performed on a RF-5301PC spectrophotometer. Emission (350-600 nm) spectra were recorded under the different excitation wavelength at room temperature. The FT-IR spectra were obtained on an AVATOR 360 spectrometer using KBr pellet technique. Thermo gravimetric and differential thermal analysis (TG-DTA) was carried out with SDT Q 60020 thermometer in air atmosphere.

RESULTS AND DISCUSSION

3.1 XRD

The powder samples were characterized by XRD and the diffraction patterns are shown in fig (1). These patterns were compared with standard JCPDS (JCPDS 89-1397) [20] value.

The average grain size of the pure $\text{ZnO}:\text{Co}$ samples were calculated from the full width half maximum (FWHM) of the diffraction peaks using the Debye–Scherrer equation [21];

$$D = k\lambda / (\beta \cos\theta)$$

Where D= Crystalline diameter.

λ = wave length of X- ray radiation.

β = FWHM and θ is the Bragg angle.

By changing the concentration of the dopant varying the temp of the reaction medium, the size of the ZnO nanoparticles vary from 18 to 34 nm. The increases in size of ZnO is due to Co ions get substituted in more number on the surface of ZnO .

All the XRD peaks were indexed which confirms the prepared nanoparticles are hexagonal Wurtzite structure of ZnO . This is very much in agreement with existing literature (22). The crystallinity in the Wurtzite structure of ZnO is restored by the addition of Co as a dopant which is confirmed by increase in the intensity of main peak (101) as the concentration of Co increased from 0.5 to 2.5. No extra peaks were found in the pattern show the formation of single phase $\text{Zn}_{1-x}\text{Co}_x\text{O}$. This indicates that the doped Co atoms substitute Zn atoms without changing ZnO Wurtzite structure.

3.2 SEM and TEM study

3.2.1 SEM analysis

Morphology and structure of powders were further investigated by SEM analysis. The SEM micrographs of the ZnO nanoparticles are shown in the Fig. (2). It shows that the synthesized ZnO nanoparticles are well dispersed.

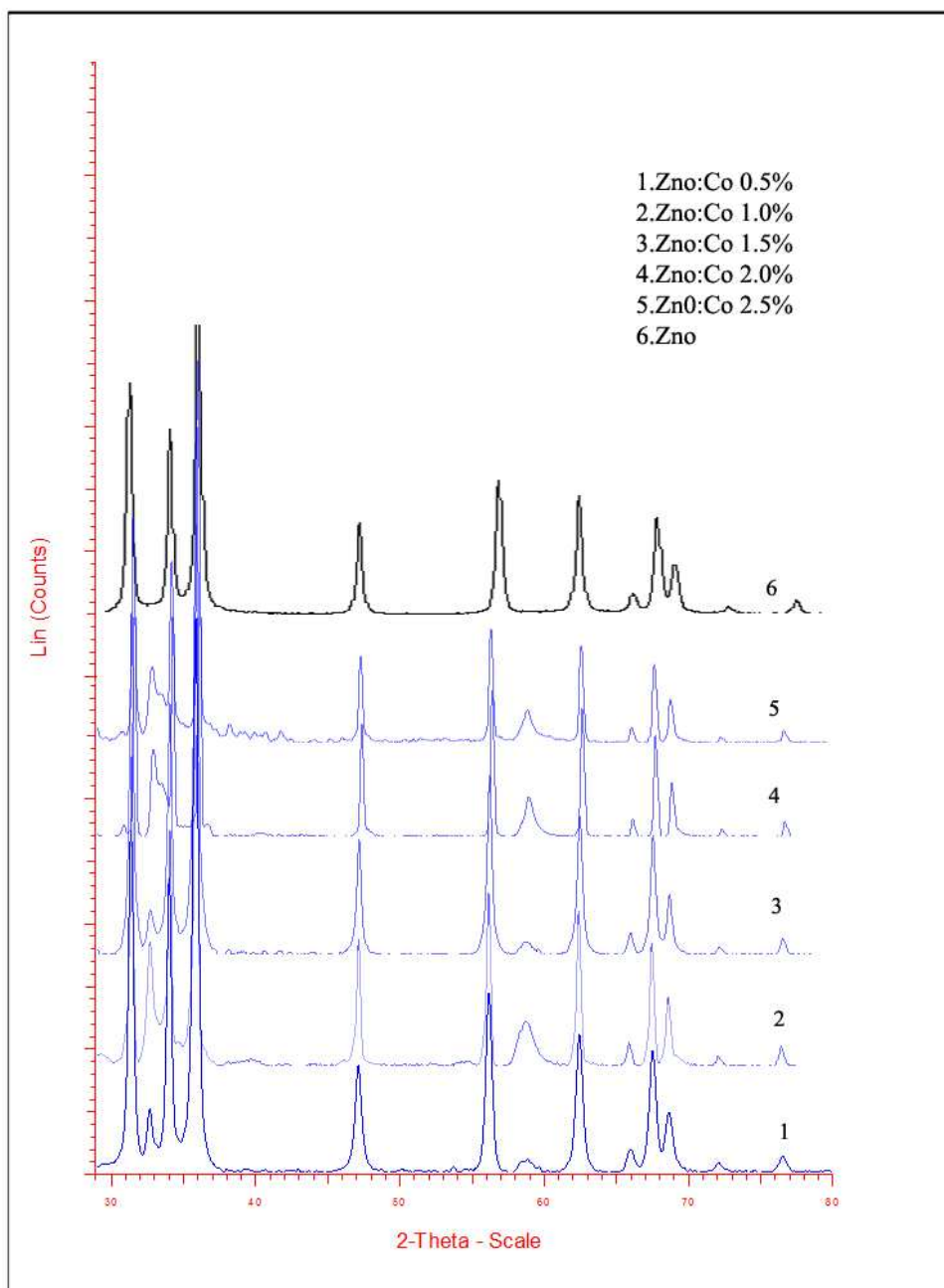
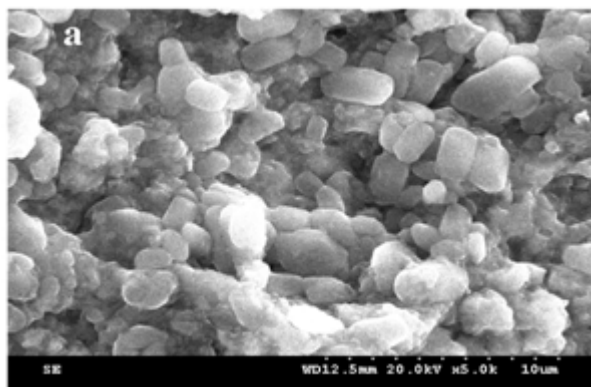


Fig: 1. XRD patterns of ZnO with different concentration of cobalt ion.



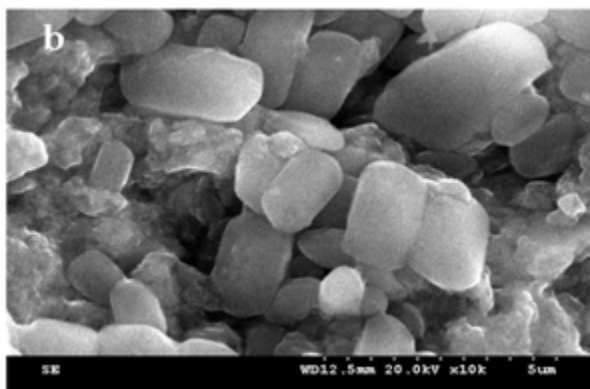


Fig: 2(a, b) SEM Micrograph of ZnO Nanoparticles

3.2.2 TEM ANALYSIS

TEM images are used to study the microstructures of the prepared samples and to measure several particles. The variations in XRD results were well supported by TEM measurements. Fig (2) shows the representative TEM images of the prepared samples. The morphology of the sample was found to be nearly spherical in nature having diameters ranging from 10 to 16nm for different samples.

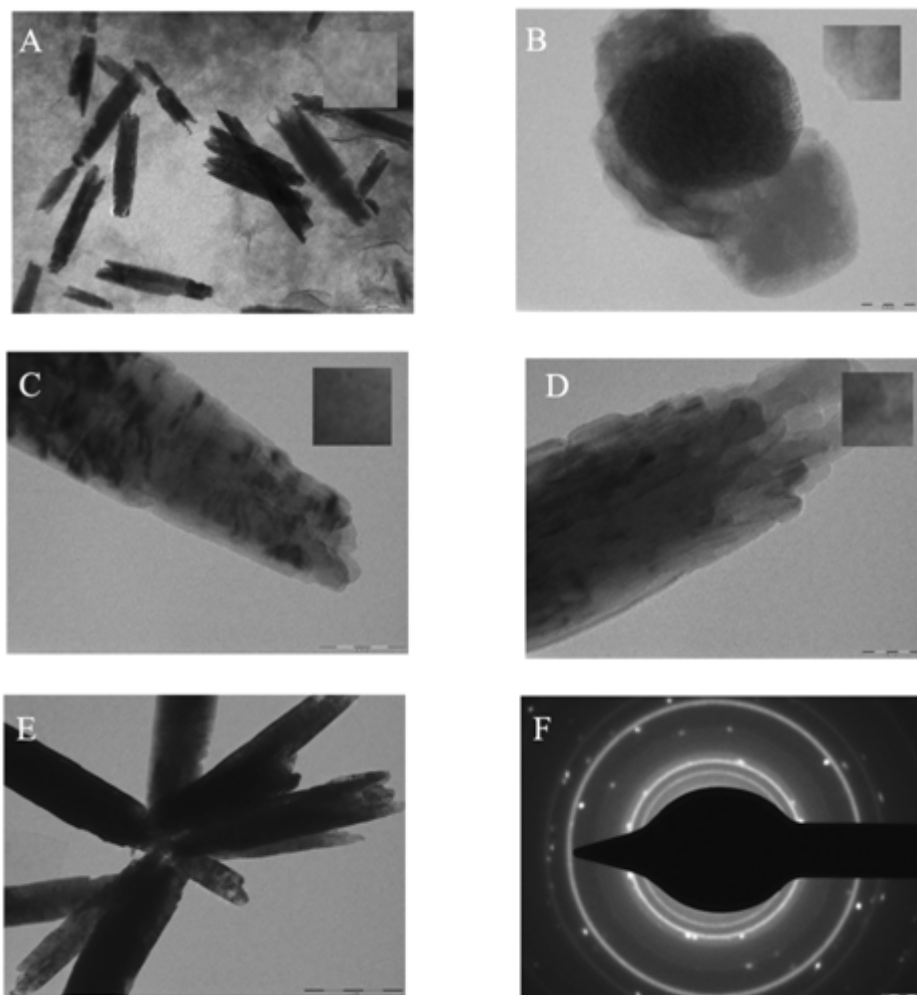


Fig: 3. (A B C D E and F) shows TEM images of ZnO; Co

Fig (3) clearly shows that the diameters of these spherical nano particles were in agreement with those obtained using XRD results. The nano ball like structure in Fig (3A) indicates the formation of nanorods.

Fig (3B) shows that the previously formed nano ball is grown to form nano rods. It looks like ginger in shape. Figs (3C) and (3d) present a rod like structure which indicates the formation of nano rods by combination of nano particles. Fig (3d) shows a well crystallized nanorods formation and looks similar to ice bars. Further the areas of various dark shades gives information about the presence of nano particles in close to each other.

Fig (3D and 3F) show that the representative Selected Area Electron Diffraction (SAED) pattern for the sample with 1.5 % Co doped ZnO. This SAED pattern shows that the prepared ZnO nanoparticles were crystalline in nature.

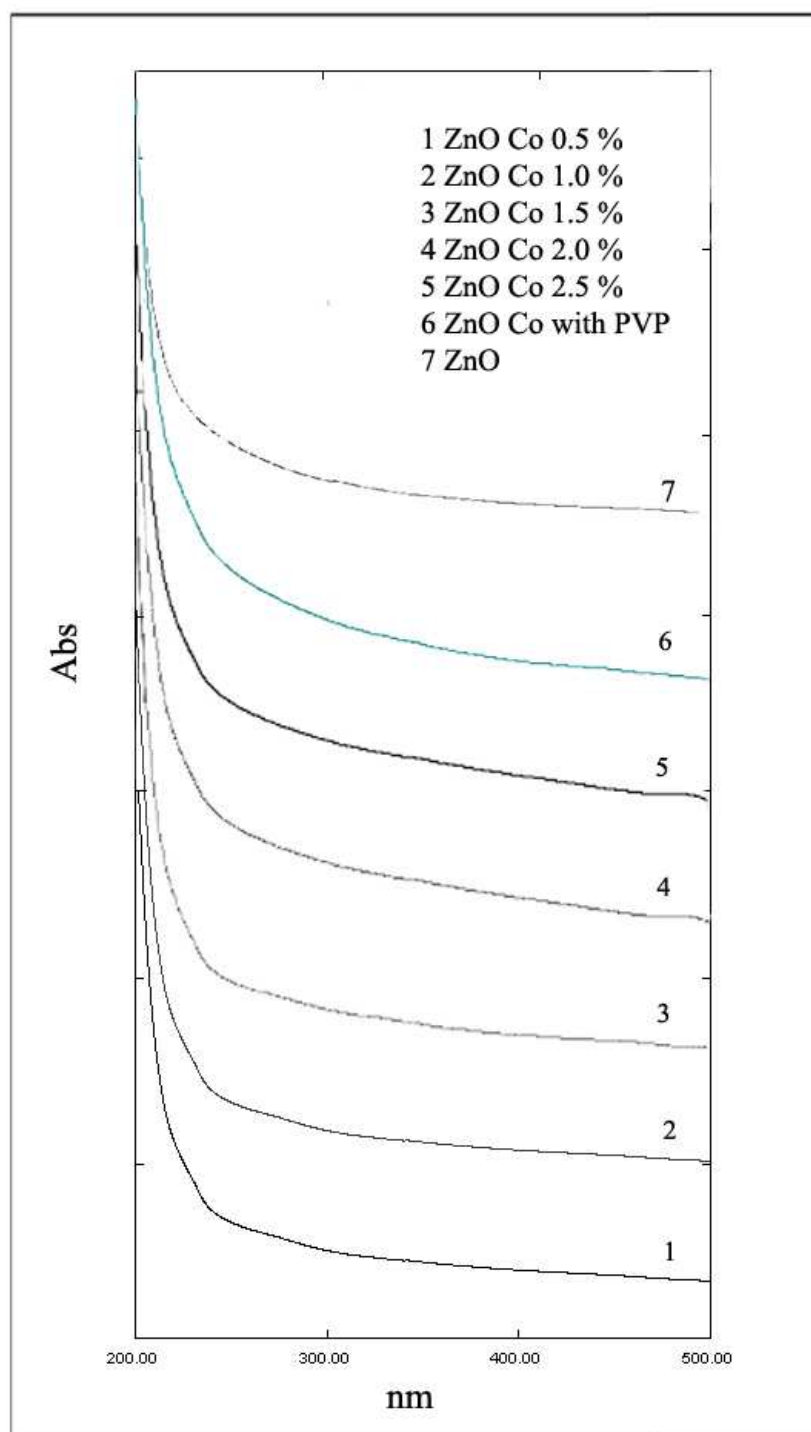


Fig: 4. UV-Visible Spectroscopy of undoped and doped ZnO Nanoparticles.

3.3 Optical studies.

3.3.1 UV-VISIBLE

Fig (4) shows the UV-Visible absorption spectra collected from different $\text{Zn}_{1-x}\text{Co}_x$ thin films. The absorption band between 338-341.4 originates from ZnO. The position of the absorption spectra is observed to shift towards the lower wavelength side with increasing Co doping concentration in ZnO. This indicates that the band gap of ZnO material increase with doping concentration of Co^{2+} ions. The increase in the band gap (or) blue shift can be explained by the Burstein-effect. This is the phenomenon that the Fermi level merges into the conduction band with the increase of the carrier concentration. Thus the low energy transitions are blocked (23, 24)

3.3.2 PL Spectroscopy

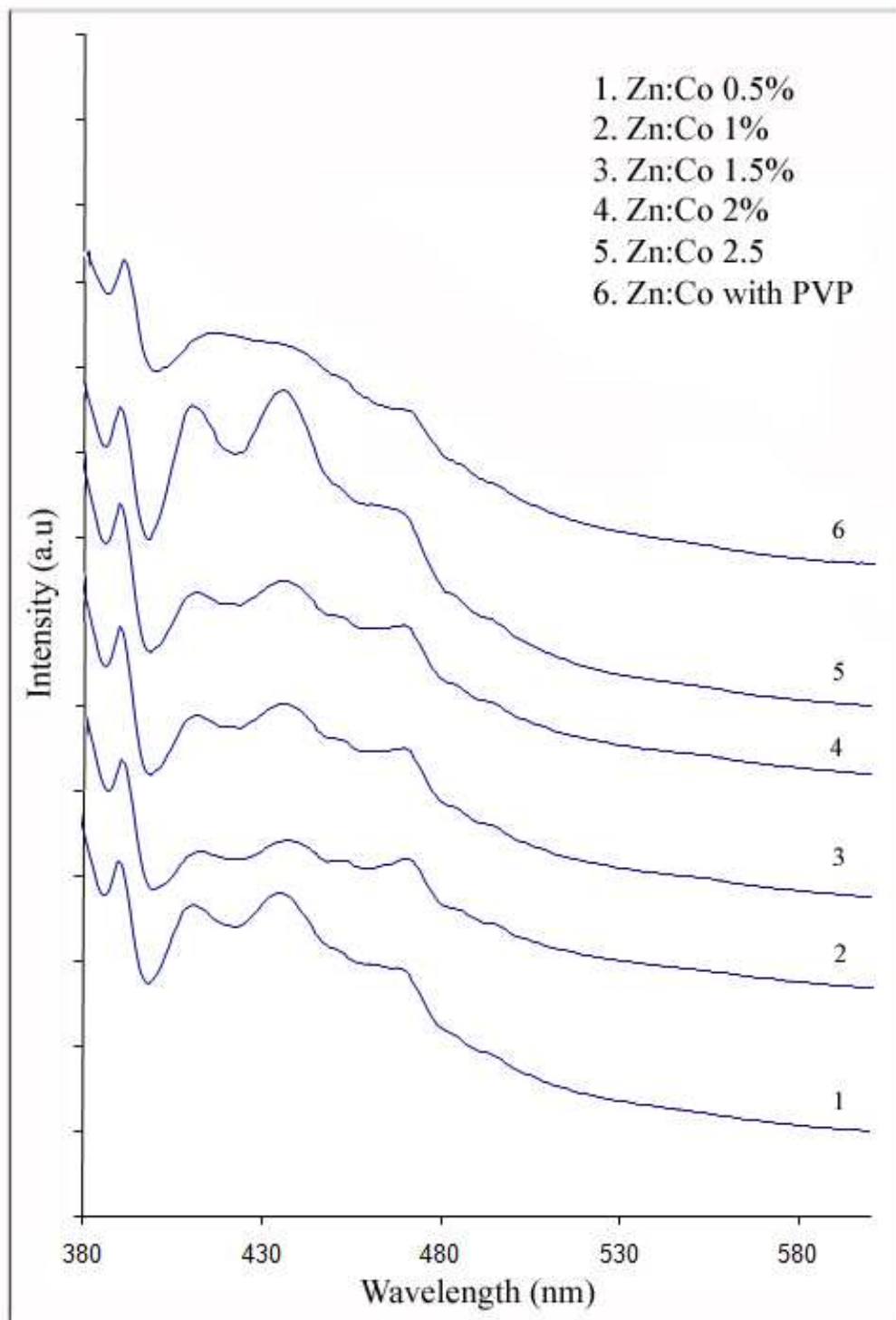


Fig: 5. PL Spectroscopy of undoped and doped ZnO Nanoparticles.

Fig(5) shows the photoluminescence (PL) spectrum of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ textured thin films at room temperature with different levels of Co contents which is an effective method for the investigation of intrinsic point defects in ZnO such as Zinc vacancies, interstitial oxygen, interstitial zinc and oxygen vacancies (25). As shown in fig (5) all samples exhibit a strong UV emission at 395nm, 420nm and 440nm and two relatively weak emission bands centre at 445 and 480nm. The UV luminescence band belongs to the exciton recombination corresponding to near-band-edge emission of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films (26). The position of each samples UV emission peak is marked in the spectra and it can be clearly observed that the UV emission peaks generate red-shift phenomenon. This could mainly due to the sp-d exchange interactions between the band electrons and the localized Co^{2+} electrons of the Co^{2+} ions substituting Zn ions (27-29).

The s-d and p-d exchange interactions cause a negative and positive correction to the conduction and valence band edges respectively, which therefore leads to band gap narrowing (30). Besides the intensity of UV emission decreases successively with the concentration of Co^{2+} increasing from 0.5% to 2.5%. This may be due to more defect states below the conduction band occurs via Co doping, so that some of the excited electrons in the conduction band relax to the defect states which leads to decreasing in UV emission intensity (31). The weak peak at 455nm and 480nm is blue emission is attributed to the transition from extended Zn; states.(ie), the electrons can first transit to the conduction band or Zn; state and finally transit to the valence band with blue emission.

3.4 FT-IR STUDY

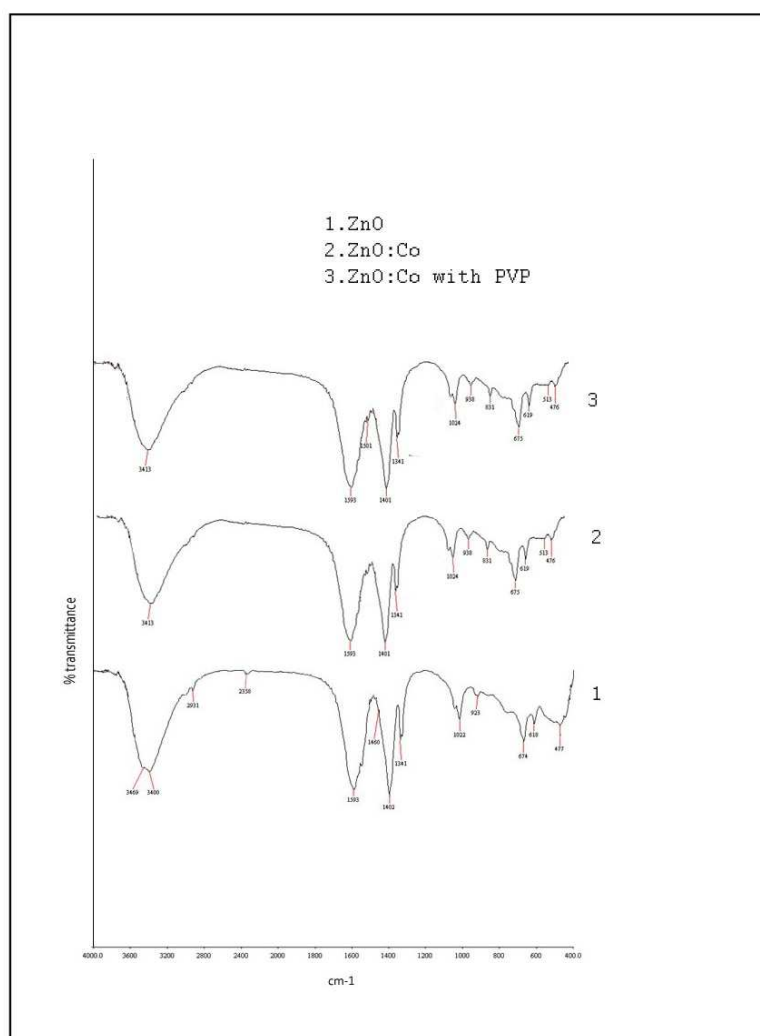


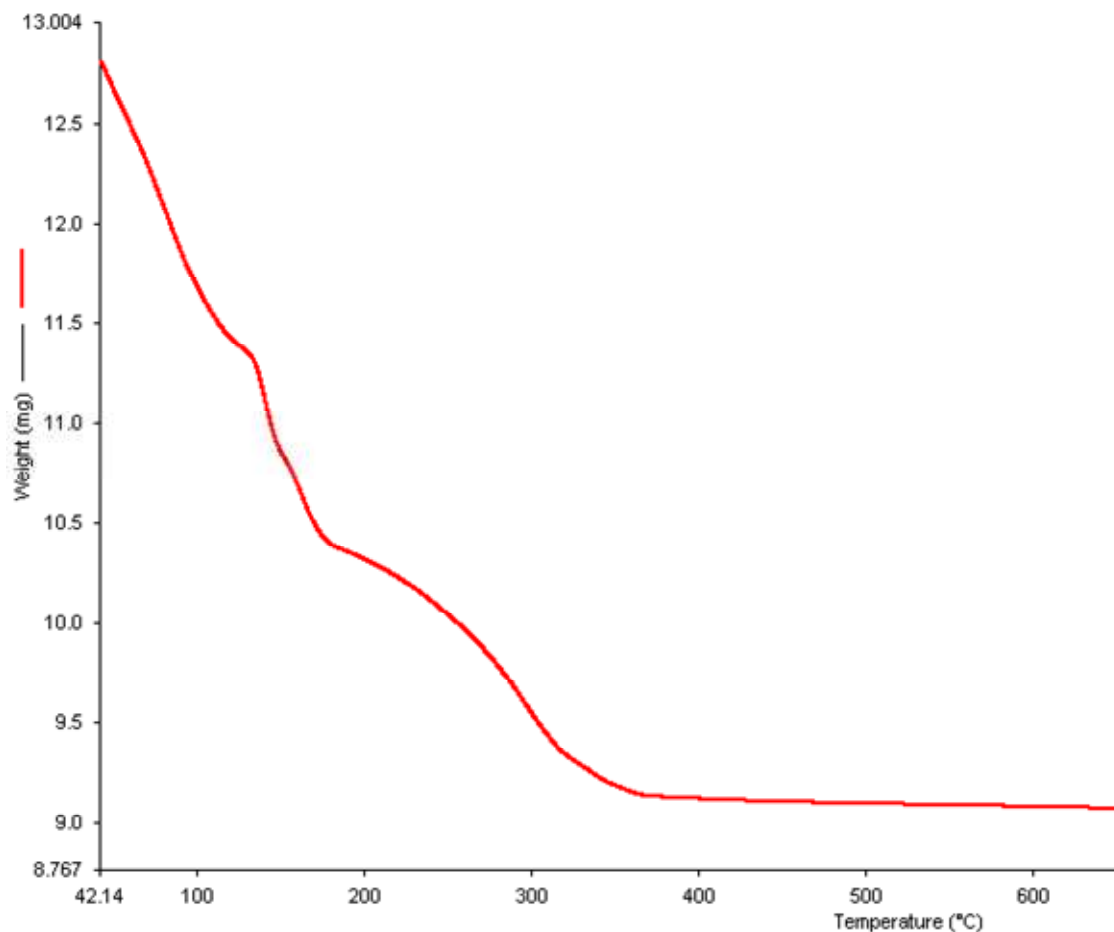
Fig: 6. FTIR spectroscopy of ZnO; cobalt ion.

The Wurtzite structure of ZnO in the prepared films was further supported by FT-IR analysis. For FT-IR analysis the KBr pellets are prepared and their spectra were shown in Fig. 6. Two principal absorption peaks are observed

between 1650 and 1400 cm^{-1} corresponding to the asymmetric and symmetric stretching of the carboxyl group (C=O) [32]. FTIR spectrum of the film annealed at room temperature shows decrease in absorption of carboxylate group (C=O) suggesting the removal of organic residuals. The spectra show absorption peak at 437 cm^{-1} corresponding to the stretching mode of Zn–O. These results confirm the formation of ZnO Wurtzite structure in the Co doped ZnO thin films annealed at room temperature.

3.5. TG DTA STUDY:

Thermal properties of doped ZnO precursor have been studied using TG/ DTA.



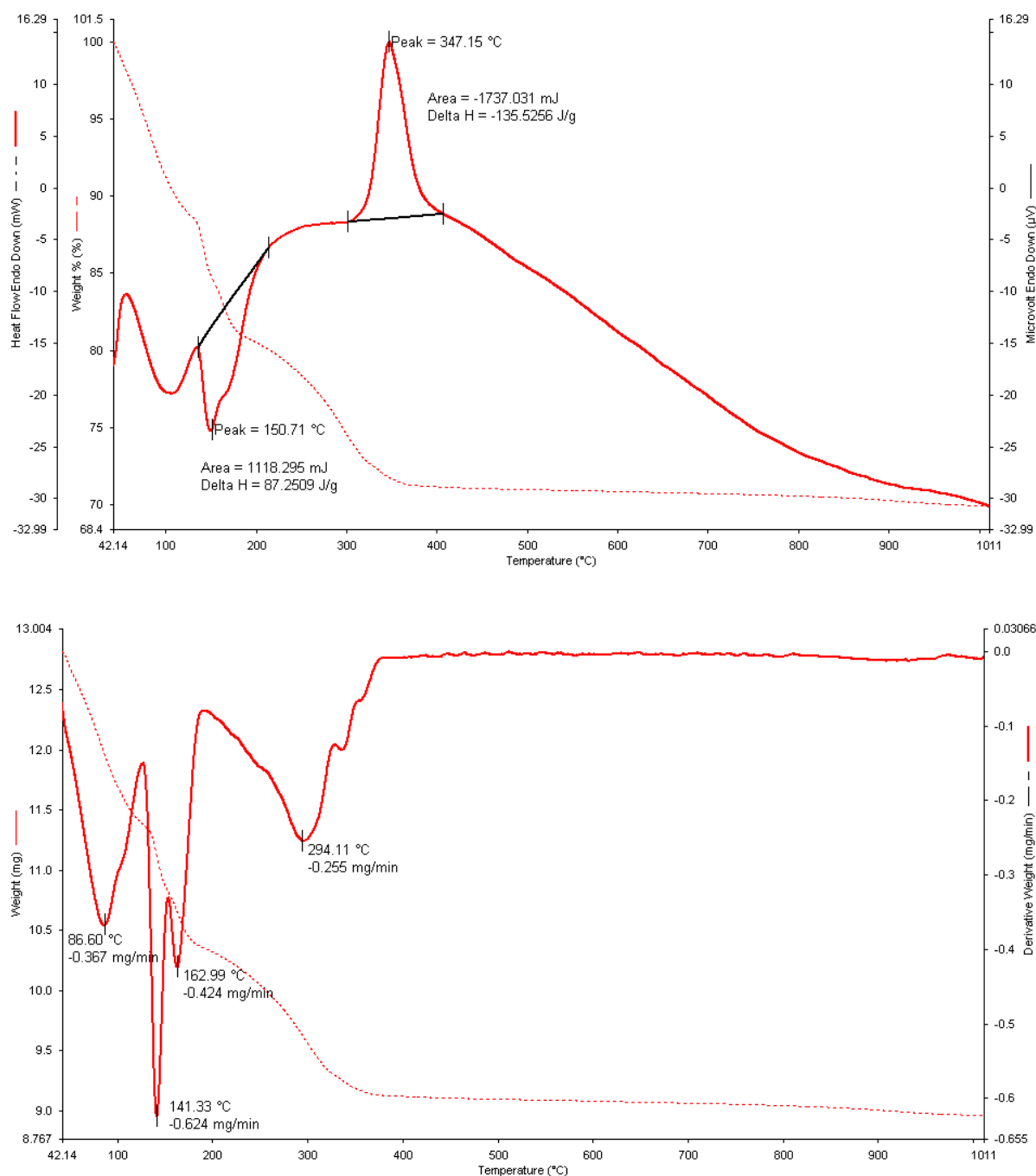


Fig: 7. TG-DTA curves of ZnO; cobalt with pvp.

Fig (7) shows that the typical DTA-TGA curves for the prepared Co doped ZnO nanoparticles (2wt %) precursor. The exothermic peak round 150⁰ C is associated with the decomposition of residual OH groups and the condensation of non bonded oxygen, which causes 20% of the weight loss. An exothermic peak at 350⁰ C was clearly observed, which is possibly related to the crystallization of ZnO. (33)

CONCLUSION

The pure and Co-doped ZnO nanorods were prepared by the chemical precipitation method at room temperature. The addition of Co as a dopant has a large impact on the morphology of ZnO films, with regard to both quality of crystallisation and orientation of the crystallites. Films of well-aligned ZnO hexagonal nanorods with good crystal structure are obtained by using controlled concentration of Co as a dopant. Synthesized nanorods are dense and uniformly grown on the substrate. The distribution of Co atoms in nanorod is uniform. The average diameter of doped nanorods is about 50 nm, which is smaller than that of pure ZnO nanorods (about 80 nm). At room

temperature, the emission peak position of doped nanoparticles show a shift in UV region and the luminescence performance enhances in the VL region, which are respectively attributed to the tune effect of Co-doping on the energy level of ZnO nanoparticle and increase in the amount of defects because of doping. In addition, the emission property of Co-doped ZnO nanorod arrays exhibit novel performance towards low temperature in the VL region, which is ascribed to the abundance of surface states due to Co-doping and decrease in the vibration of phonons in wurzite hexagonal nanoparticles. Thermal properties of ZnO nanoparticles shows can withstand up to 1011 ° C. These properties of Co doped ZnO nanoparticles can be used in opto-electronics and thermally stable devices.

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