

# (Ni, Al) co-doping influence on structural and optical properties of ZnO nanoparticles synthesized via co precipitation method

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## Abstract

Pure and (Ni, Al) co-doped ZnO nanostructures are prepared lucratively by chemical co-precipitation process at room temperature by means of poly ethylene glycol (PEG) as stabilizing agent. Zinc acetate dehydrate and potassium hydroxide are used as preliminary materials. The synthesized samples are characterized by XRD, Scanning Electron Microscopy (SEM) with EDS, Photoluminescence (PL), and Transmission Electron Microscopy (TEM). X-RAY Diffraction pattern reveals that both pristine and co-doped samples acquire hexagonal wurtzite crystal structure with no secondary phase and nonappearance of secondary phase indicates the nonexistence of impurities. SEM descriptions illustrate that all the particles are almost spherical shape and EDAX analysis reveals that doing well incorporation of dopants and lack of impurities. PL spectrum shows that all the samples containing peaks in the visible region, which will be defect related peaks. Doped samples show high intensity peaks compared with the undoped sample. TEM images reveals the nature of the particles as spherical and size of nanoparticles are confirmed the XRD data. HRTEM images plainly be evidence for nanoparticles are about 5nm with unambiguous lattice fringes. Copyright © 2018 VBRI Press.

**Keywords:** Structural studies, SEM, TEM, photoluminescence.

## Introduction

In modern years Zinc Oxide (ZnO) is a momentous material in the research community owing to its ample band gap (3.37eV), great exciton binding energy (60meV), large piezo electric constants, large nonlinear optical co-efficients and high thermal conductivity. Comparing with all materials, it has richest family of nanoparticles. ZnO is a progressive material for the applications such as photo catalysis [1], opto electronics [2], self-cleaning materials [3], sensors, solar energy, biomedical sciences, and spintronics [4-6]. In a present study tuning of the band gap of ZnO through the merger of dopant elements and altering the properties of ZnO is the stride in progression in the preparation of electronic and optoelectronic devices. Defects and impurities are leading role in optoelectronic properties for the preparation of electronic and optoelectronic devices [7]. Among these ZnO materials, Aluminum doped ZnO is a key material in optoelectronics, energy and sensors because of its progress in the conductivity with no loss of optical transmission [8, 9]. In the present work we prefer aluminum and nickel as dopant materials into ZnO due to their important optical and magnetic properties for numerous applications notably such as spintronics and dilute magnetic semiconductors (DMSs). Despite the fact that there are diverse methods for the synthesis of ZnO nanoparticles such as solution combustion, sputtering method, DC thermal plasma method, Chemical vapor deposition (CVD), Sol-gel

method and Chemical co-precipitation [10-16], we have selected Chemical co-precipitation for the synthesis as of the cost valuable and high yield rate.

## Synthesis of samples

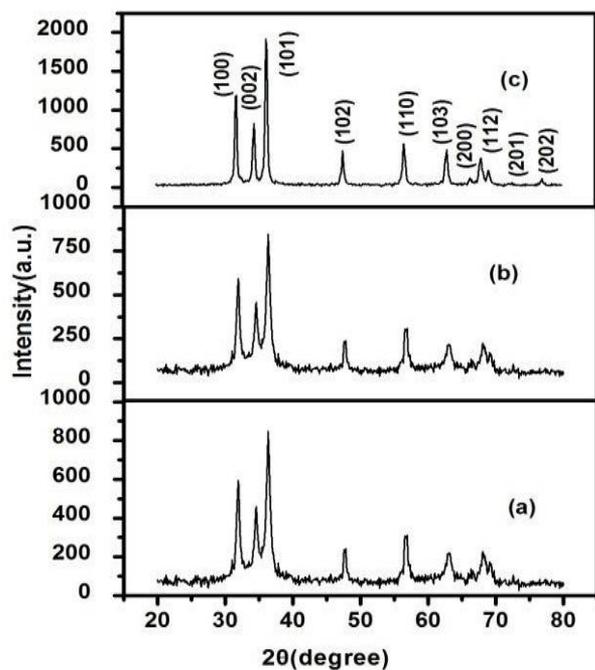
Pristine and co-doped (Ni, Al) ZnO nanoparticles have synthesized effectively at room temperature by chemical co-precipitation method via poly ethylene glycol as stabilizing agent. Primary materials are Zinc acetate dehydrate ( $Zn(CH_3COO)_2 \cdot 2H_2O$ ), Potassium hydroxide (KOH). Doping essentials are Aluminum nitrate nano hydrate, nickel chloride. All the chemicals are analytical grade and used with no further purification. Pristine ZnO nanoparticles are synthesized by 0.2M Zinc acetate solution is equipped by potassium hydroxide as solvent by means of maintaining pH at 12 and put in 2ml of PEG to the solution to stabilize the particle size. Following that continuous stirring of 10hrs, white precipitate is produced after that filtered the precipitate and washed quite a few times with de-ionized water to take away the un reacted species followed by dry the samples at 70°C for 10 hrs and grind the samples with the aid of agate mortar. Doped nanoparticles are synthesized by adding aluminum nitrate nano hydrate and nickel chloride solutions drop wise, to the Zinc acetate solution by observance of aluminum at 3 mol percent stable and varying the concentration of nickel from 0.1 to 1 mol percent. At the end all the samples are annealed at 500°C for one hour prior to obtainable the characterization of samples.

## Results and discussion

### Structural properties

#### XRD analysis

XRD patterns of pure and (Al, Ni) co-doped ZnO nanoparticles are shown in **Fig. 1**. From the XRD pattern, pure and (Ni, Al) co-doped samples (Al-3 mol%, Ni-0.3 mol%, & Al-3 mol%, Ni-0.5 mol%) acquire hexagonal wurtzite crystal structure and are consistent with the JCPDS card number 36-1451. The secondary phase is not come across relating to Aluminium or Nickel within the detection limit of the instrument. The particle sizes of pure and co-doped ZnO nanoparticles are in the range of 20-22 nm. The crystallite size of nanoparticles can be deliberate using the Debye Scherer formula  $D = 0.91\lambda / \beta \cos\theta$ , where D is the crystallite size,  $\lambda$  is the wavelength of x-rays and  $\theta$  is the Bragg's angle of diffraction. The particle sizes estimated from the formula are declining by the enhance of nickel doping concentration.

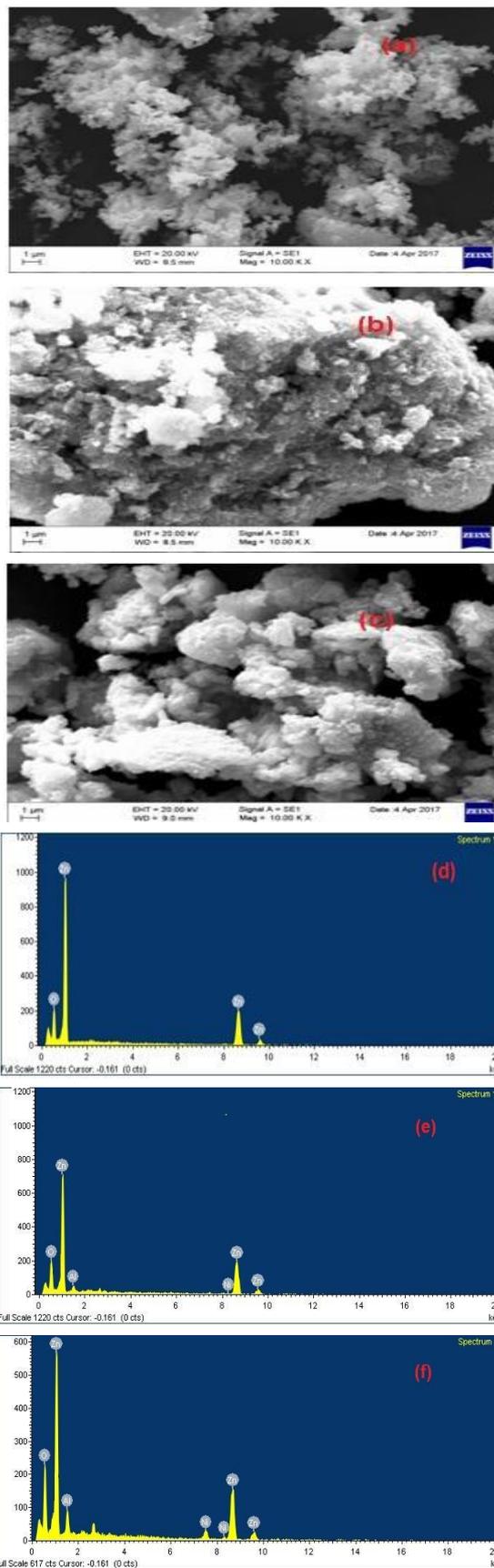


**Fig. 1.** XRD patterns of (a) Pure ZnO, (b) Al-3 mol%, Ni-0.3 mol%, (c) Al-3 mol%, Ni-0.5 mol% co-doped ZnO nanoparticles.

### Morphological analysis

#### SEM with EDS analysis

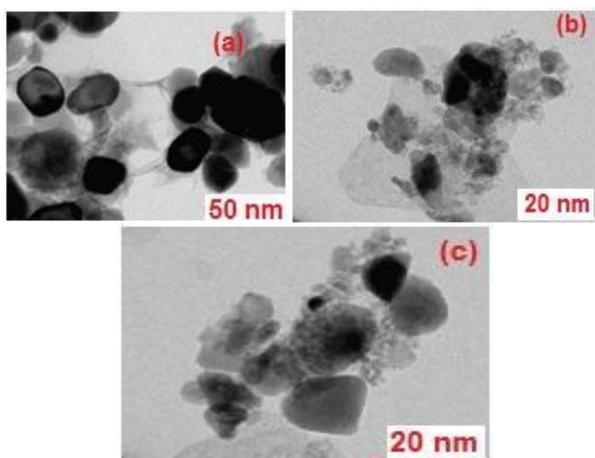
Scanning electron microscopy (SEM) is preferred to analyse the surface morphology of the pure and (Ni, Al) co-doped ZnO nanoparticles. **Fig. 2** shows the SEM with EDS spectra of the pure and (Ni, Al) co-doped ZnO nanoparticles. SEM images illustrate that the particles are in nonidentical spherical shape and principally agglomerated. The agglomeration is big in co-doped samples comparing with of pure ZnO nanoparticles. EDS spectrum reveals the incorporation of aluminium and nickel into the ZnO nanoparticles, which is also confirmed through the XRD data.



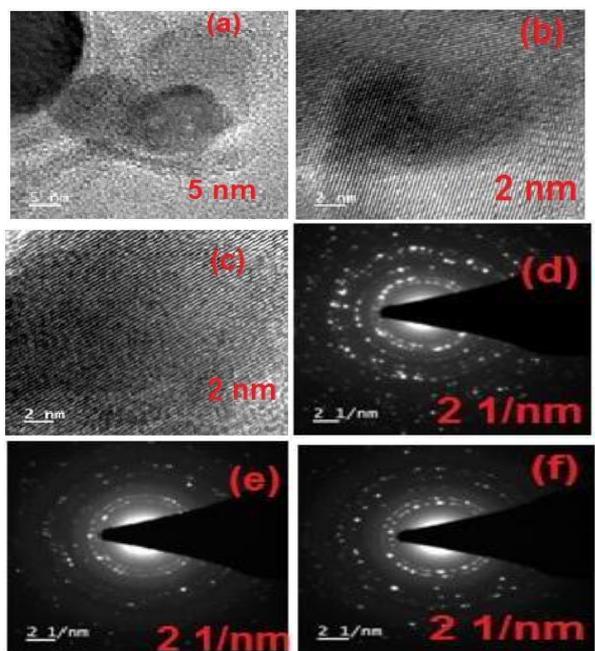
**Fig. 2.** SEM images of (a) Pure ZnO (b) Al-3 mol%, Ni-0.3 mol%, (c) Al-3 mol %, Ni-0.5 mol %, and EDS images of (d) Pure ZnO (e) Al-3 mol%, Ni-0.3 mol%, (f) Al-3 mol%, Ni-0.5 mol %, co-doped ZnO nanoparticles.

### TEM, HRTEM & SAED analysis

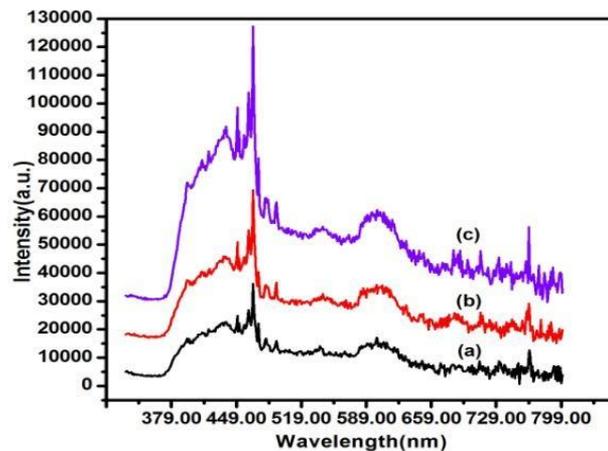
Transmission electron microscopy (TEM) is used for the determination of particle sizes of pure and (Ni, Al) co-doped ZnO nanoparticles. **Fig. 3** show the TEM graphical representation of the pure and co-doped samples. TEM pictures shows that the particles are in unidentical quasi globular shape and particle sizes are equivalent with the estimated particle sizes of XRD data. **Fig. 4** shows the HRTEM images and SAED pattern of the pure and (Ni, Al) co-doped ZnO nanoparticles. HRTEM pictures of the pure ZnO nanoparticles shows that the nanoparticles are 5nm clear lattice fringes and HRTEM images of the co-doped ZnO nanoparticles shows that nanoparticles are 2nm clear lattice fringes. SAED pattern of pure and (Ni, Al) co-doped ZnO nanoparticles are confirmed with the XRD data.



**Fig. 3.** TEM images of (a) Pure ZnO (b) Al-3 mol%, Ni-0.3 mol%, (c) Al-3 mol %, Ni-0.5 mol%, co-doped ZnO nanoparticles.



**Fig. 4.** HRTEM images of (a) Pure ZnO (b) Al-3 mol%, Ni-0.3 mol%, (c) Al-3 mol %, Ni-0.5 mol% and SAED pattern of (d) Pure ZnO (e) Al-3 mol%, Ni-0.3 mol%, (f) Al-3 mol %, Ni-0.5 mol%, co-doped ZnO nanoparticles.

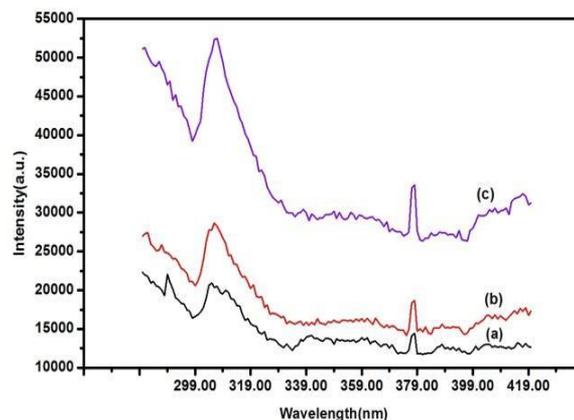


**Fig. 5** Emission spectra of (a) Pure ZnO (b) Al-3 mol %, Ni-0.3 mol%, (c) Al-3 mol%, Ni-0.5 mol%, co-doped ZnO nanoparticles.

### Optical properties

Photoluminescence spectroscopy (PL) is used for the investigation of emission character of pure and (Ni, Al) co-doped ZnO nanoparticles. PL Spectrum is recorded in the wavelength range of 400 nm to 800nm. **Fig. 5** shows the room temperature photoluminescence spectrum (RTPL) emission spectra of pure and co-doped ZnO nanoparticles. The emission peaks appeared at 421 nm, 425 nm, 445, and the broad emission band centered at 600 nm. The emission peak appeared at 425 nm is recognized to originating from the existence of Zinc associated defects [17]. The emission peaks at 421 nm and 445 nm are credited to defect states such as Zinc vacancies ( $V_{zn}$ ), Oxygen vacancies ( $V_o$ ), and Zinc interstitials ( $Z_{ni}$ ) respectively [18-20]. The broad band appeared from 570 nm to 620 nm centered at 600 nm shows the presence of a multiplicity of defects, and are large ascribed to Oxygen vacancies ( $V_o$ ) [21]. As a result, Zinc and Oxygen defects are expected to be responsible for the visible emission. **Fig. 6** shows the excitation spectra of pure and (Ni, Al) co-doped ZnO nanoparticles.

**Fig. 6** show the excitation nature of the pristine and co-doped samples and the excitation wavelength is 305 nm.



**Fig. 6.** Excitation spectra of (a) Pure ZnO (b) Al-3 mol%, Ni-0.3 mol%, (c) Al-3 mol %, Ni-0.5 mol%, co-doped ZnO nanoparticles.

## Conclusion

Pure and (Ni, Al) co-doped ZnO nanoparticles have been synthesized at room temperature by poly ethylene glycol as capping agent. XRD pattern reveals that all the samples acquire hexagonal wurtzite structure without any secondary phases connecting to Aluminium or Nickel, which indicates formation of no impurities. SEM pictures shows the agglomeration of the particles, comparing with pure ZnO nanoparticles descriptions showing high agglomeration. EDS spectra reveals the successful incorporation of dopant impurities into the ZnO nanoparticles. TEM images are in the region of confirming the XRD data. HRTEM images of pure and co-doped ZnO nanoparticles shows that nanoparticles are regarding 5 nm and 2 nm clear lattice fringes respectively. SAED pattern of pure and (Ni, Al) co-doped ZnO nanoparticles are coincided by means of the XRD data. PL studies shows that all the peaks are in the visible region characteristically corresponding to defects.

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