Synthesis Structural and Optical Properties Of (Co, Al) co-doped ZnO Nano Particles

P Swapna1 and S Venkatramana Reddy2

Department of Physics, Sri Venkateswara University, Tirupati-517 502, Andhra Pradesh, India.

E-mail: swapna.pyl@gmail.com1 and drsvreddy123@gmail.com2

Abstract. We prepared (Co, Al) co-doped ZnO nanostructures using the method chemical co-precipitation successfully, at room temperature using PEG (Poly ethylene glycol) as stabilizing agent. Samples are prepared with different concentrations by keeping aluminium at 5 mol percent constant and varying the concentration of cobalt from 1 to 5 mol percent. After the preparation all the samples are carefully subjected to characterizations such as XRD, SEM with EDS, TEM, PL and UV-VIS-NIR. XRD pattern shows that all the samples possess hexagonal wurtzite crystal structure having no secondary phases pertaining to Al or cobalt, which shows successful dissolution of the dopents. TEM results shows the accurate size of particles and is confirmed the XRD data. SEM images of all the samples shows that particles are in nearly spherical shape, EDS spectrum reveals that incorporation of cobalt and aluminum in host lattice. PL spectrum shows that all the samples containing two prominent peaks centered at 420 nm and 446 nm. UV-VIS-NIR spectra has shown three absorptions peaks in the range of wavelength 550 nm to 700 nm, which are ascribed as typical d-d transitions of cobalt ions.

Key words: UV-VIS-NIR, Zinc vacancies, Oxygen vacancies, Local transitions and Poly ethylene glycol.

1. Introduction

In recent times a lot of research has been done on the transition metal oxides such as ZnO, SnO2, and TiO2 etc. The structural, optical and magnetic properties of transition metal doped wide band gap oxides are of significant interest due to their practical applications. Transition metal oxides are preferred due to their unique high Tc comparing with traditional materials like GaN, GaAs, GaP and InP. ZnO(Zinc Oxide) is a semiconductor with wide band gap 3.37 eV, having large binding energy (60 meV) with wurtzite crystal structure consisting of high optical gain at room temperature with peculiar unique photonic and spintronic properties [1-4]. Though ZnO excite at different Ultra Violet wavelengths, it show visible luminescence because of the formation of different types of defects such as Zinc vacancies, Oxygen vacancies etc.[4]. Wurtzite zinc oxide has been widely demonstrated due to their large applications including field effect transistor(FET) [5], Optical device [6], Dye-sensitized solar cell [7], Solid state gas sensors etc.[8,9]. Transition metals doped of ZnO, increases the optical absorption properties causing to changes in the forbidden band gap, it will make the semiconductor much effective and significant [4]. Several methods are available for the synthesis of ZnO nano particles such as a physical or chemical method, solution combustion [10], sputtering method [11], DC thermal plasma method [12], Chemical vapor deposition
(CVD), Sol-gel method [13], Chemical co-precipitation [14-16]. Among all these methods, chemical co-precipitation method is adopted widely for the synthesis of ZnO due to its low cost, high uniformity and considerable yield of nanoparticles. In the present work, Zinc Oxide nanostructures are successfully synthesized using chemical co-precipitation method at room temperature using Poly ethylene glycol (PEG) as stabilizing agent.

2. Experimental section

2.1. Synthesis

For the synthesis of pristine and co-doped ZnO nanopowders, Zinc acetate de hydrate (Zn(CH₃COO)₂ 2H₂O), Potassium hydroxide (KOH), Cobalt acetate tetra hydrate (Co(CH₃COO)₂ 4H₂O), and Aluminium chloride AlCl₃ (anhydrous) chemicals have been used. All the chemicals are analytical grade and used without further purification. To prepare pristine and co-doped ZnO nanopowders of 0.2M solution, Zinc acetate de hydrate is dissolved in de-ionized water, KOH solution is then added drop wise under constant stirring of 10 hrs to form white precipitate. Aluminium chloride and Cobalt acetate tetra hydrate solutions are mixed with the above one, drop wise to synthesize co-doped ZnO nano structures. The precipitate formed is filtered and washed several times with de-ionized water to remove unnecessary chemical species formed during the process of synthesis. After that all the samples are dried at 70°C for 9 hrs and grind the powders finely with the help of agate mortar. Eventually all the samples are annealed in the furnace at 500°C for 1hour.

2.2. Characterizations

The prepared nanopowders are carefully subjected to the following characterizations. Powder X-RAY Diffraction pattern is recorded on Bruker diffractometer within 2θ range of 20° to 80° using CuKα as x-ray source (λ=1.53906 Å). The surface morphology and chemical analysis of pristine and doped Zinc Oxide nano structures are studied by SEM with EDS (model CARL-ZEISS EVOMA 15). The properties obtained from XRD are confirmed by (TEM) and high resolution TEM (Model: JEOL JSM 2100). Photoluminescence studies were carried out by PL spectrometer (Model: HORIBA Jobin-Yvon FluoroLog 3) with a 450 w Xenon arc lamp used as an excitation source.

3. Results and Discussions

3.1. Structural Properties

3.1.1. XRD Analysis. Figure 1 represents the XRD (x-ray Diffraction) pattern of pristine and all the concentrations of co-doped ZnO nanopowders. The diffraction peaks of all the concentrations correspond to hexagonal wurtzite phase of ZnO and the diffraacted peak positions are consistent with the standard pattern (JCPDS CARD NO: 36-1451). Absence of secondary phases represents no impurity phases pertaining to aluminium or cobalt within the detection limit of the instrument. The peaks corresponding to co-doped ZnO have high intensity comparing with the pure ZnO. The intensity of diffraction peaks increases with the increase of cobalt concentration.
The nanoparticle size is calculated by the Debye-scherrer formula \( d = \frac{0.91\lambda}{\beta \cos \theta} \), where \( d \) is the crystallite size, \( \lambda \) is the wavelength of the X-rays and \( \theta \) is the Bragg’s angle of diffracted rays. The estimated particle size of pristine and doped ZnO are 20 nm, 19 nm respectively. From the diffraction calculations, we observe that nano particle size decreases with the increased cobalt concentration. It is noted that from XRD pattern co-doped ZnO have high crystallinity comparing with pristine ZnO.

3.2. Morphological and Compositional Analysis

3.2.1. SEM and EDAX Analysis. Figure 2 indicates the SEM pictures of pristine and co-doped Zinc Oxide nanostructures. SEM pictures show that particles are in Non-uniform size and almost spherical shape. The agglomeration is large in pure ZnO comparing with co-doped ZnO. Agglomeration gradually decreases with the increased cobalt concentration. On the other hand it might be due to the adding of stabilizing agent PEG. Figure 3 indicates the EDS spectra of Pristine and co-doped Zinc Oxide nano structures. EDAX Spectrum shows the presence of aluminium and cobalt in the host lattice also indicates absence of impurities it is good agreement with the X-ray diffraction analysis. EDAX Spectrum reveals that all the elements are in near chemical stoichiometry.
Figure 2: SEM images of (a) Undoped ZnO (b) 1 mol% (c) 3 mol% (d) 5 mol% of Co doped ZnO nanostructures (Here Al = 5.0 mol% is kept as constant)
Figure 3: EDS spectrum of (a) Undoped ZnO (b) 1 mol% (c) 3 mol% (d) 5 mol% of Co doped ZnO nanoparticles (Here Al = 5.0 mol% is kept as constant).

3.2.2. TEM, HRTEM AND SAED Analysis. TEM is used to find the particle size accurately by direct measurement. Figure 4 shows the typical TEM pictures of pristine and co-doped Zinc Oxide nano structures. TEM pictures shows that all the particles are spherical in shape and the size of nano particles are coincide with XRD calculations. From the TEM images it is evident that agglomeration decreases with uniform distribution of particles by adding of PEG stabilizer to host ZnO lattice. HRTEM pictures clearly shows that nano structures are about 5nm with clear lattice fringes. Nano particles are single and poly crystalline in nature showing high crystallinity, it is good agreement with the XRD analysis. The crystalline rings in SAED pattern could be indexed to the hexagonal wurtzite phase of Zinc Oxide. The halo ring patterns in SAED confirmed that both pristine and co-doped Zinc Oxide nano structures are in crystalline nature. Figure 5 shows the typical HRTEM images and SAED pattern of pristine and co-doped ZnO nanostructures.
Figure 4: TEM images of (a) Undoped ZnO (b) 1 mol% (c) 2 mol% (d) 3 mol% (e) 4 mol% (f) 5 mol% of Co doped ZnO nanostructures (By keeping Al = 5.0 mol% as constant).

![TEM images of ZnO nanostructures](image)

Figure 5: HRTEM pictures of (a) Pure ZnO (b) co-doped ZnO (Al-5 mol% , Co-5 mol%), SAED Pattern of (c) Undoped ZnO (d) co-doped ZnO (Al-5 mol% , Co-5 mol%)

3.3. Optical Properties
3.3.1. Photoluminescence (PL) Studies. Photoluminescence (PL) spectroscopy is significantly used to analyse the emission nature of pristine, (Co, Al) co-doped Zinc Oxide nanostructures.
structures. There are three absorption peaks which might be substitutional. These peaks might be ascribed to defect states such as Zinc vacancies (V_{zn}), Oxygen vacancies (V_{o}), and interstitials (Z_{ni}) respectively.

With the increase of concentration of cobalt the position of defect peaks remain same and the peak intensities have been increased and this might be ascribed to Oxygen vacancies. We observed that initially from 1 to 2 mol percent the intensity of defect peaks increases with the increased cobalt concentration and it is ascribed to Oxygen vacancies and Zinc interstitials (Z_{ni}). At 3 mol percent concentration the intensity of defect peak decreases, this represents that the impact of Cobalt ions on the defect states of ZnO is considerably low and the impact of aluminium ions is high. With the further increase of Cobalt concentration, the intensity of defect peaks increases which might be due to the substitutional incorporation of Cobalt in to host lattice, hence each substitutional Cobalt atom might creates one Interstitial Zn atom (Z_{ni}). It increases the intensity of defect peak 446 nm comparing with 420 nm peak, this increased intensity correlates not only with the cobalt concentration but also ascribed to the Oxygen vacancies. As reported in the previous literature, that varying concentration of cobalt in Zinc Oxide lattice is an excellent method for the exploration of intrinsic point defects in host lattice such as zinc interstitials, interstitial oxygen, Zinc vacancies and oxygen vacancies. Particle size is also determined based on the density of defect states and is inversely proportional to size of nanostructures, and is confirmed by XRD. Hence from this data we emphasized that the existence of cobalt in host lattice could be substitutional.

### 3.3.2. UV-VIS-NIR Analysis

#### 3.3.2.1. Absorption Spectra

Absorption spectroscopy is a significant, powerful technique used to investigate the optical properties of nanoparticles. UV-VIS-NIR Spectroscopic measurements are carried out at room temperature to investigate cobalt doping effect on band gap in the range of 200 nm to 800 nm. Figure 7 show the UV-VIS absorption spectra of pure and co-doped ZnO nanostructures. There are three absorption peaks in 550 nm to 700 nm range. These might be ascribed as typical d-d transitions of cobalt ions appeared at 566 nm, 620 nm, and 656 nm. From PL data we emphasized that the existence of cobalt in host lattice could be substitutional. These cobalt dopants form narrow bands in the forbidden band and split in to t_{2g} and e_{g} state because of the crystal field which is consistent with the d-d transition. The configuration of occupied states becomes d^{7} with spin-up t_{2g}^{3} d_{x2} and spin-down e_{g} states near the fermi level, for the existence of oxygen vacancies in the ZnO lattice near Co^{2+}. We observed interactions between the band electrons and the localized’d’ electrons of the cobalt ions substituting Zinc ions using the concept of sp-d exchange. The optical absorption co-efficient ‘α’ of a semiconductor close to the band edge can be expressed by the following equation.

\[
\alpha = K(h\theta - E_g) n / h\theta
\]
Figure 7: Absorption spectra of (a) Pure ZnO (b) 1 mol% (c) 2 mol% (d) 3 mol% (e) 4 mol% (f) 5 mol% of Co doped ZnO nanostructures (Here Al = 5.0 mol% is kept as constant).

4. Conclusions

Pristine and co-doped Zinc Oxide nanostructures are synthesized successfully using chemical co-precipitation method using PEG as stabilizing agent at room temperature. The prepared samples are characterized with XRD, SEM with EDS, TEM, HRTEM, SAED pattern, PL and UV-VIS-NIR and analyzed different type of properties such as structural, morphological, compositional and optical. TEM and EDS analysis is consistent with XRD data. PL Spectrum reveals two prominent peaks which ascribed to defect states like oxygen vacancies (V\textsubscript{O}) and Zinc vacancies (V\textsubscript{zn}). UV-VIS-NIR shows three absorption peaks in the range of wavelength 550 nm to 700 nm which are attributed to typical d-d transitions of cobalt ions.

5. References

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