Synthesis, structural and optical characterisation of cobalt and indium co-doped ZnO nanoparticles

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Abstract. The undoped, 5% Co, In single doped and 5% In-Co double-doped ZnO nanoparticles were successfully prepared using sol-gel method. The structural and optical properties of the samples were investigated using XRD, UV-vis, TEM, EDS and Raman spectroscopy. There were no peaks associated with In or Co detected in the XRD patterns indicating that In^{3+} and Co^{2+} substituted for Zn^{2+} ions in the ZnO wurtzite structure this was also confirmed by the EDS and Raman results. TEM results showed that the prepared ZnO nanoparticles were spherically shaped. Single doping reduced the grain size and the energy band gap of the ZnO nanoparticles while combinational doping reduced them even further.

1. Introduction

Nano-materials of transition metal oxides have been found to be very interesting and currently they are investigated for their different properties compared to those of bulk materials [1]. For example, ZnO is an n-type semiconductor material having a wurtzite hexagonal crystal structure. It has a wide energy band gap of 3.36 eV and a large excitation binding energy of 60 meV [2]. It has a wide range of resistivity, high transparency at room temperature [3], high electron hall mobility, good chemical and thermal stability under operation conditions [3]. It's widely being used in a variety of applications such as opto-electronic devices [4], [5], light emitting diodes (LEDs) [6], flat panel displays [7], surface acoustic wave devices [8], chemical sensors, gas sensors [9] and solar cells [10]. Previous studies have shown that the physical properties of ZnO nanostructured materials depend on their size, shape and structural aspects and those factors are mostly influenced by the method of preparation [11][12] [13]. It has been reported that single doping ZnO nanoparticles with a controlled amount of impurities such as Cu, Al, In, Sb, Ga, Fe, Co, Ni, etc. can improve its structural, electrical and optical properties [14] while combinational doping is found to enhance its properties even further [15] [16]. Different methods such as chemical vapour deposition (CVD) [17], physical vapour deposition (PVD) [18], hydro thermal and sol-gel method [19] have been used to synthesize the undoped and doped ZnO nanoparticles. In this work we will be reporting on the structural and optical properties of 5% Co, In single doped and 5% In-Co co-doped ZnO nanoparticles prepared using sol-gel method.

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2. Experimental

2.1. Sample preparation and characterization

The undoped, single doped and double-doped ZnO nanoparticle samples were synthesised using chemicals zinc acetate dihydrate ($C_4H_6O_4Zn{\cdot}2H_2O$), ethanol (C_2H_6O), ethanolamine (C_2H_7NO), cobalt (II) nitrate hexahydrate ($CoN_2O_6{\cdot}6H_2O$) and indium (III) nitrate hydrate ($InN_3O_9{\cdot}xH_2O$). The water soluble salts; cobalt (II) nitrate hexahydrate and indium (III) nitrate hydrate were used as sources of Co and In metal dopants. All of these chemicals were purchased from Sigma-Aldrich. Single doped ZnO nanoparticles with Co and In were prepared at 5 wt. % while the double-doped ZnO nanoparticles sample were prepared at 2.5 wt. % of each dopant in order to obtain 5 wt. %.

When preparing the undoped ZnO nanoparticles 0.2 M of zinc acetate dihydrate solution was mixed with 0.2 M of ethanol in order to obtain homogeneity, this was done with continuous stirring. For the single doped ZnO nanoparticles, cobalt (II) nitrate hexahydrate or indium (III) nitrate hydrate were added into 0.2 M of zinc acetate dihydrate solution and for the co-doped ZnO nanoparticles the cobalt (II) nitrate hexahydrate and indium (III) nitrate hydrate were added simultaneously into 0.2 M of zinc acetate dihydrate solution then mixed with 0.2 M of ethanol in order to obtain homogeneity. This was also done while continuously stirring. Proportionate amounts of 0.2 M ethanolamine were added in all the solutions as a stabilizer. Thereafter the solutions were stirred for 2 hours at 70℃. The precipitates formed were collected using filter paper and annealed at 400 ℃ for 1 hour. After annealing all the samples were characterised using X-ray diffraction (XRD), Transmission Electron Microscope (TEM) and Ultraviolet-visible spectroscopy (UV-vis), Energy Dispersive Spectroscopy (EDS) and Raman spectroscopy.

3. Results and discussions

3.1. *X-ray diffraction*

From fig.1. the XRD patterns show that all the prepared samples have a hexagonal wurtzite structure with ZnO peaks observed at $2\Theta = 31.77°$, 34.43°, 36.27°, 47.56° and 56.63° which belongs to the (100), (002), (101), (102) and (110) planes respectively (JCPDS No.36-1451). No peaks associated with Co or In were detected in the XRD pattern indicating that Co^{2+} and In^{3+} ions have substitutionally replaced the Zn^{2+} ions. Additional peaks (indicated with *) were detected in the sample belonging to Al from the XRD sample holder. The lattice parameters a = b and c for the undoped and doped ZnO nanoparticles were determined using the (100) and (002) planes and were found to be similar to the reported values of the bulk ZnO (JCPDS No.36-1451); the results are tabulated in table 1.

The average grain sizes of the undoped and doped ZnO nanoparticles were estimated using Debye-Scherrer's equation and are also presented in table 1. The values indicate that the grain sizes of the doped ZnO nanoparticles are smaller compared to the grain size of the undoped ZnO nanoparticles and co-doping ZnO nanoparticles significantly reduces the grain size of ZnO nanoparticles. The strains of all the undoped and doped ZnO nanoparticles were determined and found to be inversely proportional to the grain size. The values of the strain can also be viewed in table 1.

Table 1. Lattice parameters, average grain size and strain.

Sample	Lattice parameters		D(nm)	ε ($\times \mathbf{10^{-3}}$)
	a (Å)	c (Å)		
Undoped-ZnO	3.2490	5.2049	42.476	2.3982
5% Co-ZnO	3.2582	5.2171	19.242	5.3116
5% In-ZnO	3.2429	5.1893	22.179	4.5884
5% In-Co-ZnO	3.2394	5.1836	11.858	8.6131

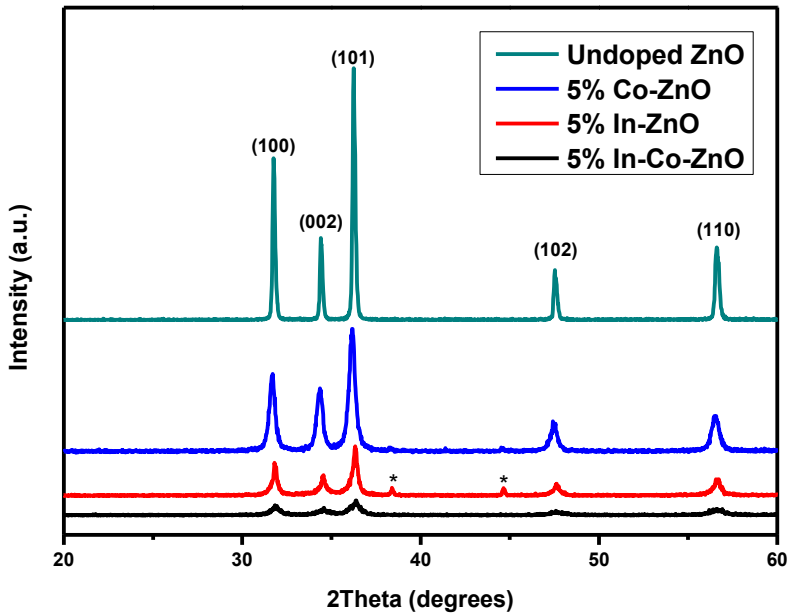

Figure 1. XRD patterns of undoped ZnO, 5% Co-doped ZnO, 5% In-doped ZnO and 5% In-Co co-doped ZnO nanoparticles.

3.2. *TEM*

Fig.2. shows the TEM images of (a) Undoped ZnO nanoparticles and (b) 5% In-Co-ZnO nanoparticles. Both the undoped and 5% In-Co co-doped ZnO nanoparticles are found to be spherical. In Fig.2 (a) big rods can be seen alongside the spherical nanoparticles and these rods are basically created when spherical nanoparticles come together. Consequently smaller particles can be seen within the rods; similar results were reported by L. Xu et al. [20]. Fig.3. shows the EDS images of 5% In-Co co-doped ZnO nanoparticles. The elements Zn, O, In and Co were observed in the image which confirms that Co and In were successfully incorporated into the ZnO nanoparticle structure. While C, Cu, Si elements may be from the TEM sample grid.

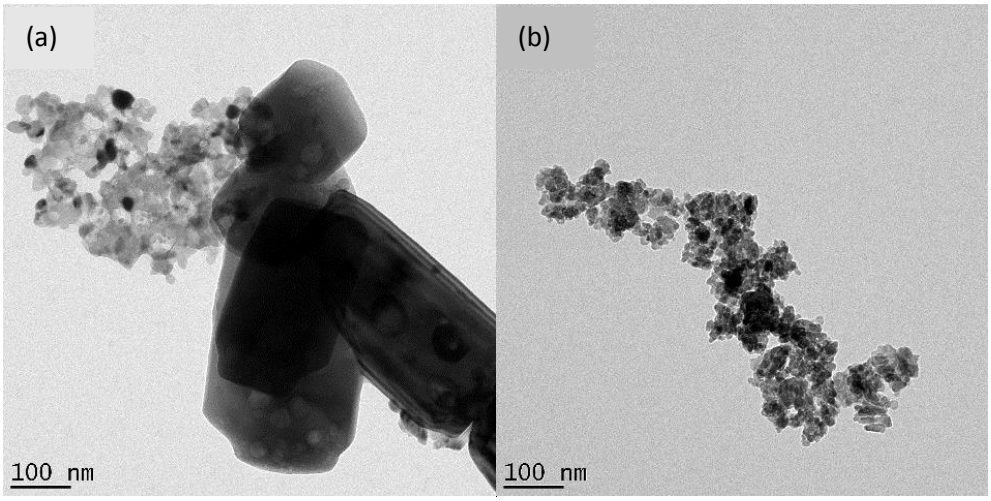

Figure 2. TEM images of (a) undoped ZnO (b) 5% In-Co-ZnO

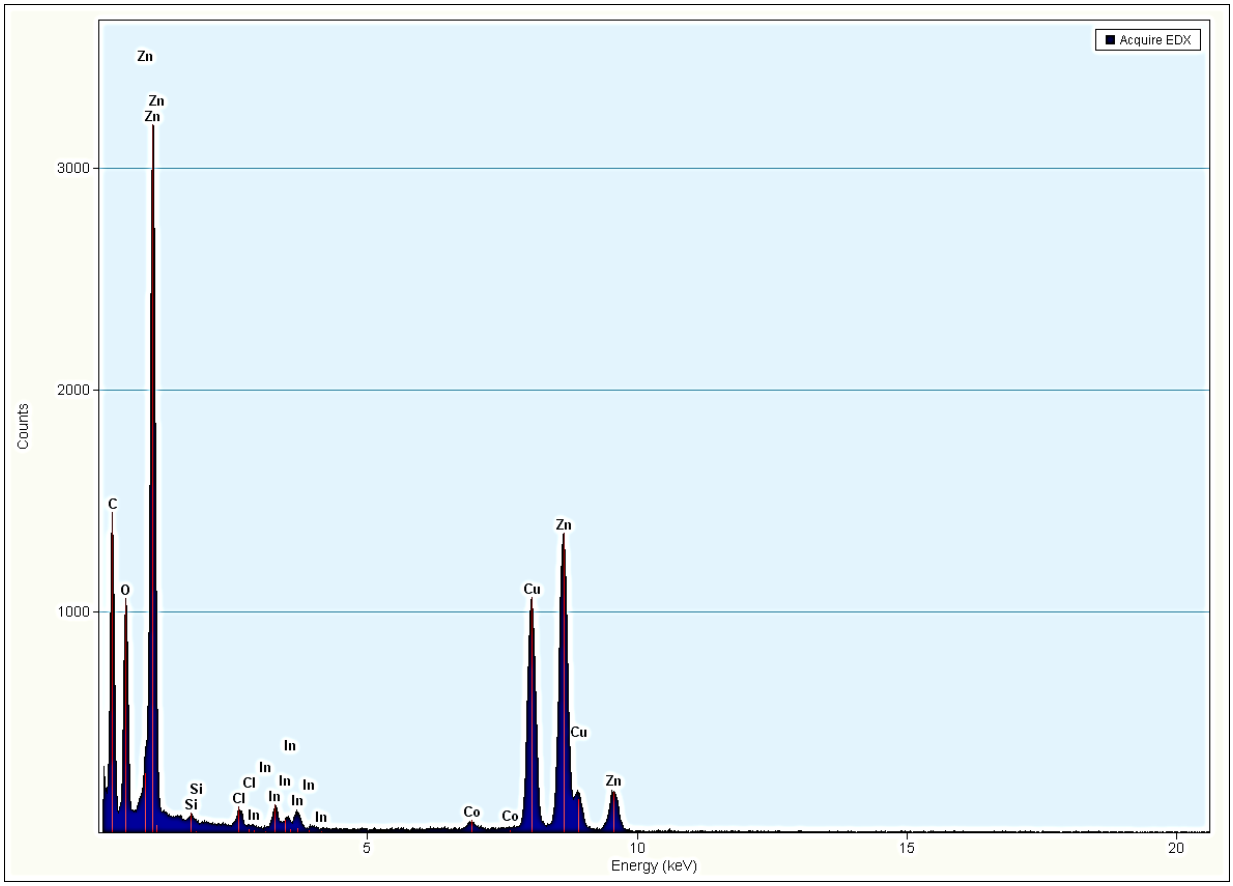

Figure 3. EDS image of 5%In-Co-ZnO nanoparticles.

3.3. UV-vis spectroscopy

The optical absorption spectra of the undoped and doped ZnO nanoparticles were recorded as shown in Fig. 4 in order to report the optical properties of these nanoparticles. For the nanoparticles doped with Co three additional absorption peaks are observed between 550-700 nm. These peaks are attributed to $^4A_2(F) \rightarrow {}^2A_1(G)$, $^4A_2(F) \rightarrow {}^4T_1(P)$ and $^4A_2(F) \rightarrow {}^2E(G)$ transitions which suggest that the tetrahedrally coordinated Co^{2+} ions substituted for Zn^{2+} ions in the hexagonal ZnO wurtzite structure [21] [22].

The energy band gap values have been determined and found to be 3.10, 2.48, 2.74, 2.37 eV for the undoped ZnO, 5% Co-ZnO, 5% In-ZnO and 5% In-Co-ZnO nanoparticles, respectively. It can be seen that the value of the undoped ZnO nanoparticles is smaller compared to the reported value of the bulk ZnO [23] and this could be due to the fact that nanostructured materials have different properties from the bulk materials. A red shift is observed between the undoped ZnO nanoparticles and the doped ZnO nanoparticles. It has been reported by K. Ando et al. [23] that this red shift could be attributed to the fact that Co^{2+} and In^{3+} ions substituted for the Zn^{3+} ions in the crystal lattice**.**

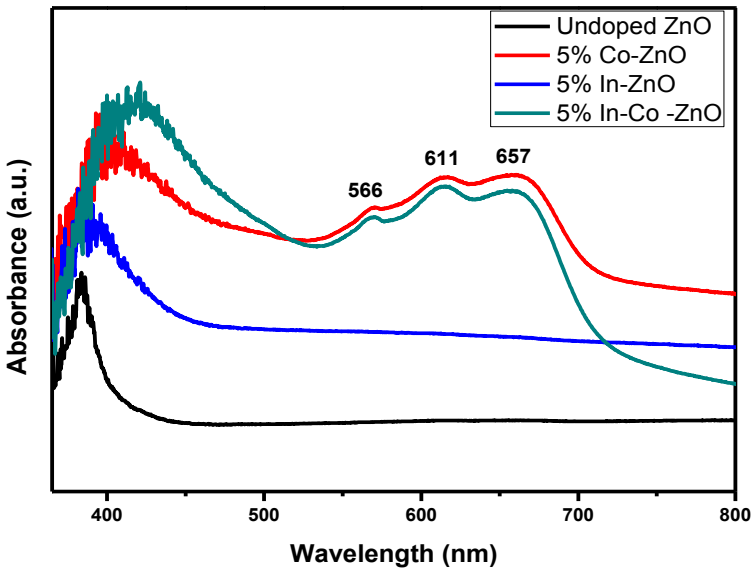

Figure 4. Optical Absorbance spectra of Undoped ZnO, 5% Co-ZnO, 5% In-ZnO and 5% In-Co-ZnO nanoparticles.

3.4. Raman spectroscopy

The vibrational properties of the Co and In single doped, Co and In co-doped ZnO nanoparticle and undoped ZnO nanoparticle samples were investigated with the excitation wavelength of 514 nm at room temperature. From Group theory it is predicted that the ZnO wurtzite hexagonal structure of a space group C_{6v}^4 will indicate the phonon modes near the centre of Brillouin zone given by the equation $\Gamma = A_1 + 2B_1 + E_1 + 2E_2$ [24]. Here A_1, E_1 and $2E_2$ are Raman active modes and $2B_1$ is the forbidden mode of ZnO. A_1 and E_1 are polar and are split into two, being transverse optical (TO) and longitudinal optical (LO) phonons were E_2 is nonpolar and is divided into E_2^{low} and E_2^{high} [24]. The Raman peaks at 329, 377, 407, 435, 536-558 and 581 cm^{-1} belong to the E_2^{high}- E_2^{low}, A_1 (TO), E_1 (TO), E_2^{high}, A_1 (LO), and E_1 (LO) modes, respectively. The Raman peaks at 435 cm^{-1} are thought to be confirming that the samples prepared are of the ZnO wurtzite hexagonal structure and similar results were obtained [25] [15], while the peaks around 581 cm^{-1} are thought to be from defects such as oxygen vacancies (VO), zinc interstitials (Zni) and/or free carriers [25] [26].

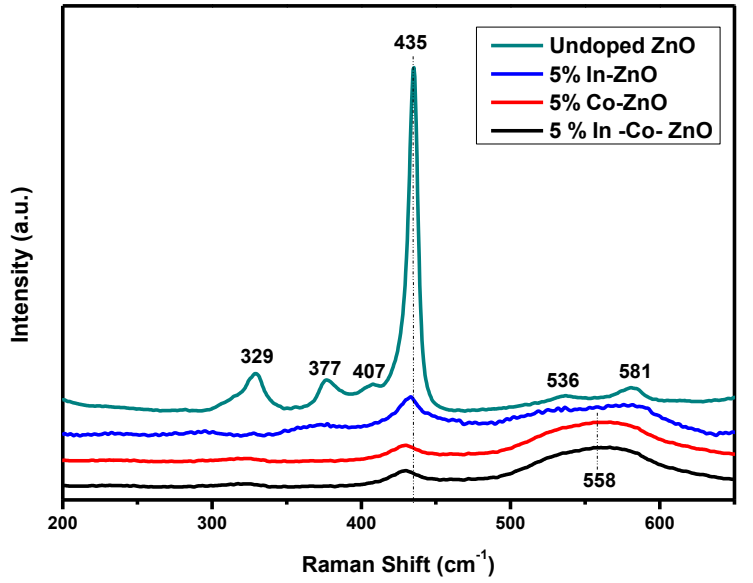

Figure 5. Raman spectroscopy of undoped doped ZnO, 5% of Co, 5% In and 5% of In/Co co-doped ZnO nanoparticles.

4. Conclusion

The In and Co single doped ZnO nanoparticle, In and Co co-doped ZnO nanoparticle and undoped ZnO nanoparticle samples were successfully synthesised using sol-gel method. The effect of doping In and Co on the structural and optical properties of ZnO were investigated. XRD results showed that all the prepared samples were of the ZnO wurtzite crystal structure and the results were corroborated by the Raman results. TEM images showed that the prepared samples were spherical in shaped. EDS confirmed that In and Co were indeed substitutionally replacing the Zn^{2+} ions in ZnO nanoparticles. The energy band gap of the prepared samples were determined and found to be smaller to the energy band gap of the bulk ZnO.

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