

Defect related microstructure, optical and photoluminescence behaviour of Ni, Cu co-doped ZnO nanoparticles by co-precipitation method



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ABSTRACT

In the present study Ni-doped ZnO and Ni, Cu-doped ZnO nanoparticles were successfully synthesized by co-precipitation method. Structural studies confirmed the dominant presence of hexagonal wurtzite ZnO phase at lower Cu concentration and CuO phase was observed at higher Cu (Cu = 5%) concentration. The existence of Cu²⁺ ions were dominant at Cu ≤ 3% (responsible for lattice shrinkage) and the presence of Cu⁺ ions were dominant at Cu > 3% (responsible for lattice expansion). The change in UV–visible absorption and energy gap were discussed by secondary phase generation and charge carrier density. The low absorption loss and high transmittance at Cu = 3% doped samples is used as potential candidate for optoelectronic devices. The increase of green band intensity and decrease of UV band at higher Cu concentration confirmed the existence of more defect related states.

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1. Introduction

Oxide-diluted magnetic semiconductors (O-DMSs) based on ZnO, TiO₂ and SnO₂ have attracted great attention in recent years due to the possibility of inducing room temperature ferromagnetism. ZnO (zinc oxide), which is a member of transparent conductor oxides (TCOs), is an attractive candidate for science and technological applications [1]. It is widely used in flat panel displays, touch panels [2], solar cells, lasers, light emitting diodes (LED) [3], piezoelectric devices [4], owing to its promising and unique properties such as simultaneously occurrence of high transmittance in the visible region of electromagnetic spectrum, low resistivity, abundance in nature, easy fabrication, non-toxicity, high energy band gap (~3.3 eV) [5,6], and high chemical stability under reducing atmosphere [7].

Sato and Katayama-Yoshida [8] have predicted theoretically that ZnO can behave like a ferromagnet at room temperature when a dilute amount of transition element is doped in it. Recently, many researchers have tried to dope other ions into ZnO to obtain two metal ions co-doped ZnO in order to change their structural, optical and magnetic properties by introducing additional carriers [9,10]. Liu et al. [11] noticed that the preparation details of Ni-doped ZnO has great influence on their magnetic properties, so that

annealing at 800 °C in Ar gas atmosphere significantly increases the magnetization of Zn_{1-x}Ni_xO material. Ni doped ZnO showed hexagonal wurtzite structure up to Ni = 2%, but for Zn_{0.97}Ni_{0.03}O, secondary phase of NiO emerged [12]. Since the substitution of Ni induces Ni related secondary phases at higher doping concentrations, the doping percentage of Ni is limited to 4%.

Substitution of Cu into ZnO lattice is used to tune its properties such as photocatalytic activity, gas sensitivity, and room temperature ferromagnetism [13]. The Cu related clusters are formed in the host lattice at higher doping concentration (≥4%) which decreases the charge density [14,15]. The doping percentage of Cu is limited to 4% to avoid the formation of metallic cluster. Han et al. reported in experiments that the Curie temperature of the bulk Zn_{0.94}Fe_{0.05}Cu_{0.01}O samples was above room temperature and the maximum saturation magnetization (*M_s*) of the sample doped with 1% Cu became 30 times larger than that of the sample without Cu at room temperature [16]. The exchange interaction between free delocalized carriers (holes from valence band) and the localized d spins of Ni and Cu ions was considered as the cause of the room-temperature ferromagnetism (RTFM) in Ni, Cu co-doped ZnO systems [17].

Most of the literature focused Ni-doped ZnO [11,12] or Cu-doped ZnO [13–15]. In the case of Ni, Cu co-doped ZnO nanocrystals, relatively fewer studies have been reported [17] since its synthesis is challenging due to the large driving force for phase segregation into NiO/CuO or other Ni/Cu related phases and ZnO. Therefore, detailed study of the influence of Cu doping concentration on Zn_{0.96}Ni_{0.04}O is necessary and effective for understanding its structure, optical and magnetic properties. In this connection,

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the present paper describes the effect of Cu on the structure, optical and magnetic properties of ZnNiO in detail.

2. Experimental procedure

2.1. Preparation of $Zn_{0.96-x}Ni_{0.04}Cu_xO$ nanocrystals

For the synthesis of $Zn_{0.96-x}Ni_{0.04}Cu_xO$ ($x = 0, 0.01, 0.03, 0.05$) nanocrystals, the analytical grade (AR), high purity chemicals (Merc, >99% purity) such as Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), Copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and sodium hydroxide (NaOH) were used as precursors. Initially, appropriate amount of Zinc nitrate hexahydrate, Nickel (II) nitrate hexahydrate and Copper (II) nitrate trihydrate were dissolved in double distilled water and kept stirring until get a clear solution. NaOH solution had been prepared separately by dissolving appropriate amount of NaOH in 50 ml double distilled water. The prepared NaOH solution was added drop wise into the initial precursor solution under constant stirring at room temperature. The mixed solution was kept stirring for two hours. The gelatinous precipitates were filtered and washed several times to remove the impurities. The final precipitates were dried using an oven at 80 °C for 2 h. The dried precipitates were collected and grounded using an agate mortar. Finally, the synthesized nanocrystals were annealed at 500 °C in air atmosphere for 2 h followed by furnace cooling. The same procedure was repeated to the remaining Ni concentrations.

2.2. Characterization techniques

The crystal structure of $Zn_{0.96-x}Ni_{0.04}Cu_xO$ ($x = 0, 0.01, 0.03, 0.05$) nanocrystals was determined by powder X-ray diffraction. XRD patterns were recorded by Rigaku C/max-2500 diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA from $2\theta = 30^\circ$ to 70° . The topological features and composition of Zn, O, Ni and Cu were determined by energy dispersive X-ray (EDX, HITACHI, and S-2400) spectrometer on K and L lines. The surface morphology of $Zn_{0.96-x}Ni_{0.04}Cu_xO$ nanocrystals was studied using a scanning electron microscope (SEM, JEOLJSM 6390). The UV–Visible optical absorption study was carried out to explore their optical properties. The spectral absorption was determined using UV–Visible spectrometer (Model: lambda 35, Make: Perkin Elmer) in the wavelength ranging from 300 to 600 nm at room temperature. The presence of chemical bonding in $Zn_{0.96-x}Ni_{0.04}Cu_xO$ samples was studied by FTIR spectrometer (Model: Perkin Elmer, Make: Spectrum RX I) from 400 to 4000 cm^{-1} . The sample used for this measurement is in the form of pellets prepared by mixing the nanocrystals with KBr at 1 weight%.

3. Results and discussion

3.1. X-ray diffraction (XRD) – structural studies

XRD is an important tool to investigate the structural properties, crystallite size and can determine the presence of any unwanted impurity phases. The XRD patterns of the prepared Ni, Cu co-doped ZnO nanoparticles are compared with that of Ni-doped ZnO nanoparticles as shown in Fig. 1. The peaks observed in the XRD pattern confirm the crystalline nature of the nanoparticles, which were identified to originate from (100), (002), (101), (102), (110), (103), (200), (112) and (201) reflections of pure ZnO phase with a hexagonal symmetry (JCPDS card No. 36-1451, space group P63mc). All the samples show single phase wurtzite structure up to Cu = 3%. When doping concentration is higher than 3%, a new phase, CuO (111) (JCPDS card No. 05-0661) phase is

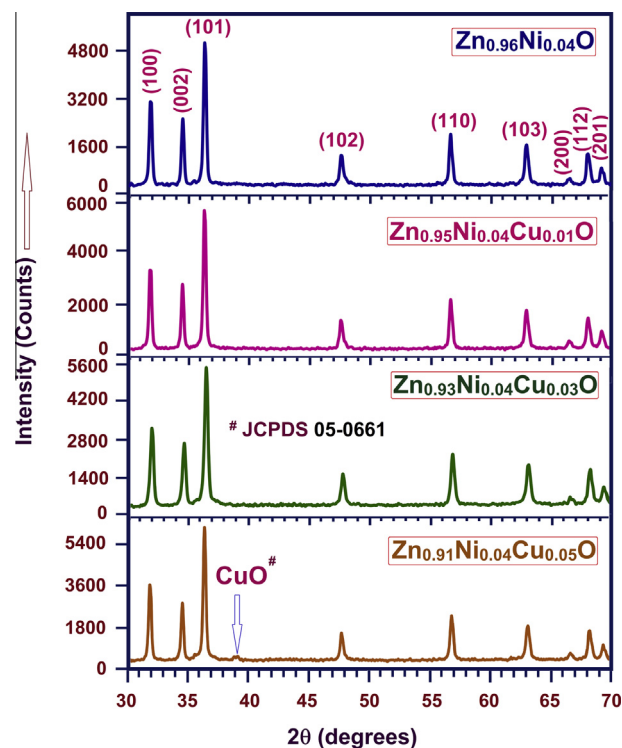


Fig. 1. Powder X-ray diffraction pattern of $Zn_{0.96-x}Ni_{0.04}Cu_xO$ nanoparticles for different Cu concentrations from 0% to 5% at room temperature.

observed corresponding to the peak position 38.9° . The segregation of a second phase at Cu = 5% indicates that the Cu-doping concentration limit in Zn–Ni–O is around 3% in our experiment settings.

Fig. 2a illustrates the variation of intensity and peak position from 35.6° to 37.1° and Fig. 2b shows the variation of peak intensity along (101) plane with different Cu concentrations from 0% to 5%. With the increase of Cu content ($Cu \leq 3\%$), the peak position of (101) plane shifts towards the higher angles compared with the undoped $Zn_{0.96}Ni_{0.04}O$. The further increase of Cu shifts the peak position towards the lower angles. Shift of peak position towards higher angle is a sign of lattice constant shrinkage, which is attributed to the inward relaxation of the lattice due to the substitution of the Zn^{2+} ions by the smaller Cu^{2+} ions [18]. Mean while, peak position shift towards lower angle is explained from a relative saturation of Cu atoms substituting Zn atoms and entering in Zn vacancy sites takes place and then the Cu atoms begin to lie interstitially in the ZnO lattice. The amount of mono-valent copper (Cu^+) in Zn sites is the another reason which leads to outward relaxation of the nearest O atoms [19]. The diffraction peaks shift towards higher and lower angles by Cu concentration was previously reported [20,21]. These shifts clearly suggest the incorporation of Cu into the ZnO lattice without altering the crystal structure.

The X-ray diffraction intensity increases with the Cu concentration up to 1% and a slight decrease in intensity is observed by the addition of Cu = 3% and the further increase of Cu increases the XRD intensity. The decrease in intensity at Cu = 3% can be attributed to the suppressed crystallization and the increase in intensity at Cu = 4% can be ascribed to the larger crystallite size. The co-existence of hexagonal phase and a minor second phase (CuO) and the shift of peak position towards the lower angle at Cu = 5% conclude that the optimum doping concentration of Cu in the present system is about 3%.

The average crystallite size of the sample is calculated after appropriate background correction from X-ray line broadening of the diffraction peaks of (101) plane using Debye Scherrer's formula [22],

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