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Preparation, structural, photoluminescence and magnetic studies of Cu doped ZnO nanoparticles co-doped with Ni by sol–gel method

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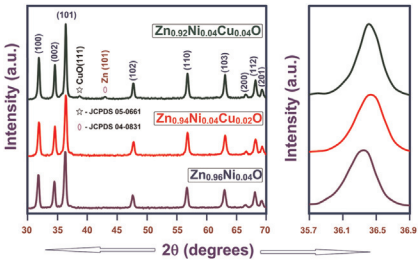
HIGHLIGHTS

- Ni, Cu co-doped ZnO nanoparticles were successfully synthesized by sol–gel method.
- Secondary phases, CuO (111) and Zn (101) were noticed at higher Cu content.
- Energy gap was tuned by Cu content.
- UV and visible emission band were discussed based on defect formation.

GRAPHICAL ABSTRACT

Secondary phases, CuO and Zn were noticed at higher Cu content. Tuning of energy gap and PL emission band were discussed based on defect formation.



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ABSTRACT

$Zn_{0.96-x}Ni_{0.04}Cu_xO$ nanoparticles have been synthesized by varying different Cu concentrations between 0% and 4% using simple sol–gel method. X-ray diffraction studies confirmed the hexagonal structure of the prepared samples. The formation of secondary phases, CuO (111) and Zn (101) at higher Cu content is due un-reacted Cu^{2+} and Zn^{2+} ions present in the solution which reduces the interaction between precursor ions and surfaces of ZnO. Well agglomerated and rod-like structure noticed at Cu=4% greatly de-generate and enhanced the particle size. The nominal elemental composition of Zn, Cu, Ni and O was confirmed by energy dispersive X-ray analysis. Even though energy gap was increased (blue-shift) from Cu=0–2% by quantum size effect, the s–d and p–d exchange interactions between the band electrons of ZnO and localized d electrons of Cu and Ni led to decrease (red-shift) the energy gap at Cu=4%. Presence of Zn–Ni–Cu–O bond was confirmed by Fourier transform infrared analysis. Ultraviolet emission by band to band electronic transition and defect related blue emission were discussed by photoluminescence spectra. The observed optical properties concluded that the doping of Cu in the present system is useful to tune the emission wavelength and hence acting as the important candidates for the optoelectronic device applications. Ferromagnetic ordering of Cu=2% sample was enhanced by charge carrier concentration where as the antiferromagnetic interaction between neighboring Cu–Cu ions suppressed the ferromagnetism at higher doping concentrations of Cu.

1. Introduction

In recent years, nanotechnology and nanomaterials have attracted several researchers from different fields due to their unique properties and potential applications in different areas such

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as spintronics devices, transparent electronics, piezoelectricity, optoelectronics, etc. [1–4]. ZnO is known as ionic semiconductor with a wide band gap of about 3.36 eV at room temperature and a high excitation binding energy of 60 meV, which give rise to its outstanding properties and potential applications in diverse fields [5–8].

Doping is a widely used method to improve electrical, optical and magnetic properties of semiconductor compounds, facilitating the construction of many electronic and optoelectronic devices. Transition metal (TM) ion alters the electronic and magnetic properties of ZnO due to the exchange interaction between s and p electron of host ZnO and d electron of TM ions [9]. Nickel (Ni) ion is an important with rich optical properties in different transparent materials and also has the advantage of Ni^{2+} ion is its sensitivity towards their legend field environment. Some researches on Ni doped ZnO have been reported and results showed that the luminescence properties of ZnO were changed after doping with Ni [10,11]. Liu et al. [12] 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 magnetizable of $Zn_{1-x}Ni_xO$ material. To avoid the secondary formation Ni concentration is limited to 4%.

Among the different TM elements, Cu gets much interest due to its similar electronic shell structure, physical and chemical properties to those of Zn [13]. Sharma et al. [14] have studied the doping dependent room temperature ferromagnetism (RTFM) and structural properties of ZnO:Cu^{2+} nano-rods. Cu-doped ZnO nanoparticles with 40 nm size have been synthesized by solution combustion method which showed a red-shift and narrowing of band gap [15]. The enhanced ferromagnetic order was observed in Ni and Cu doped ZnO powder where Cu acted as an acceptor [16]. The fabrication and magnetic characteristics of Ni and Cu co-doped ZnO nanorods are reported by Tang et al. [17]. They explained the room temperature ferromagnetism by the exchange interaction between free delocalized carriers (holes from valence band) and the localized d spins of Ni and Cu ions.

Different physical or chemical synthetic methods have been used to prepare the ZnO nanoparticles such as thermal decomposition [18], chemical vapor deposition, sol–gel [19], co-precipitation [20] and hydrothermal [21]. Among the different physical and chemical methods [18–21], sol–gel is one of the most important methods to prepare the nanopowders. Sol–gel method is a simple and easily reproducible method [22].

Until now, some articles have been published about Ni-doped ZnO nanoparticles and Cu-doped ZnO nanoparticles. Even though some of the literature focussed on Ni and Cu-doped ZnO nanoparticles, the detailed study about Ni, Cu co-doped ZnO nanoparticles is nearly scanty. The main goal of the present work is to prepare Ni, Cu co-doped ZnO nanoparticles by sol–gel method and the characterization studies such as structure, crystallite size, surface morphology, band gap and photoluminescence behavior of the nanoparticles.

2. Experimental

2.1. Preparation of $Zn_{0.96-x}Ni_{0.04}Cu_xO$ ($x=0.00$, 0.02 and 0.04) nanoparticles

During the preparation of $Zn_{0.96-x}Ni_{0.04}Cu_xO$ ($x=0.00$, 0.02 and 0.04) nanoparticles, the high purity chemicals (> 99% purity) such as Zinc acetate dihydrate ($Zn(CH_3CO_2)_2 \cdot 2H_2O$), Nickel acetate tetrahydrate ($Ni(CH_3CO_2)_2 \cdot 4H_2O$), Copper acetate monohyrate ($(CH_3COO)Cu \cdot H_2O$), N,N dimethyl-formamide (DMF) were used without further purification. The appropriate amount of Zinc and Nickel acetates were dissolved in N,N dimethyl-formamide (DMF) one by one under constant stirring for 1 h using magnetic stirrer. Followed by Zinc and Nickel acetates, the appropriate amount of Copper acetate was added into the solution under constant stirring for another 1 h.

The prepared homogeneous solution was kept at 60 °C for 1 h under constant stirring to ensure the complete reaction. Then, the resulting sols were evaporated using muffle furnace. The collected precipitates were dried by using micro-oven for two hours. The dried precursors were collected and ground in an agate mortar. Finally, the collected nanopowders were annealed at 500 °C under air atmosphere for 2 h followed by furnace cooling. The same procedure is repeated to the remaining samples synthesized with nominal compositions of $Zn_{0.96-x}Ni_{0.04}Cu_xO$ ($x=0.00$, 0.02 and 0.04).

2.2. Characterization techniques

The crystal structure of $Zn_{0.96-x}Ni_{0.04}Cu_xO$ ($x=0.00$, 0.02 and 0.04) nanoparticles was determined by powder X-ray diffraction technique (XRD). XRD patterns were recorded by RigaKu C/max-2500 diffractometer using Cu Kα radiation ($\lambda=1.5406$ Å) at 40 kV and 30 mA from $2\theta=30$–70°. The topological features and composition of Zn, O, Ni and Cu were determined by energy dispersive X-ray (EDX) spectrometer using K and L lines. The surface morphology of $Zn_{0.96-x}Ni_{0.04}Cu_xO$ nanoparticles were studied using a scanning electron microscope (SEM, JEOLJSM 6390). SEM technique is used to study the particle size, surface morphology and distribution of the particles of the sample.

The UV–visible optical absorption and transmittance studies were carried out to explore their optical properties. The optical absorption and transmittance were determined using UV–visible spectrometer (Model: lambda 35, Make: PerkinElmer) in the wavelength ranging from 300 nm to 700 nm at room temperature using cm^{-1} quartz cuvettes. Halogen and deuterium lamp are used as sources for visible and UV radiations, respectively at room temperature.

The chemical bonding existing in $Zn_{0.96-x}Ni_{0.04}Cu_xO$ nanoparticles was studied by Fourier transform infra red (FTIR) spectrometer (Model: PerkinElmer, Make: Spectrum RX I) from 400 to 4000 cm^{-1}. The sample used for FTIR studies is in the form of pellets prepared by mixing the nanoparticles with KBr at 1 wt%. The photoluminescence (PL) spectra of $Zn_{0.96-x}Ni_{0.04}Cu_xO$ nanoparticles have been carried out between the wavelength ranging from 320 nm to 520 nm under the excitation of Xenon lamp laser with 310 nm line using a fluorescence spectrophotometer (F-2500, Hitachi) at room temperature. The magnetization (M) and magnetic hysteresis (M–H) loops were measured at room temperature using vibrating sample magnetometer (VSM, Make: Lake shore, Model: 7404).

3. Results and discussion

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

The typical XRD patterns of Cu-doped and Ni, Cu co-doped ZnO nanoparticles synthesized by sol–gel method are shown in Fig. 1a. All the diffraction peaks can be indexed as pure ZnO phase with a hexagonal symmetry. Fig. 1b illustrates the magnified and high resolution XRD spectra along (101) plane which shows the variation of peak position and peak intensity as a function of Cu between 0% and 4%. The XRD spectra of $Zn_{0.96}Ni_{0.04}O$ nanoparticles prepared using N,N-dimethyl formamide (DMF) as a solvent clearly shows the nanocrystalline nature corresponding to the diffraction angles 31.59° (100), 34.25° (002), 36.09° (101), 47.39° (102), 56.46° (110), 62.77° (103), 66.24° (200), 67.79° (112) and