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Enhanced room temperature ferromagnetism and photoluminescence behavior of Cu-doped ZnO co-doped with Mn

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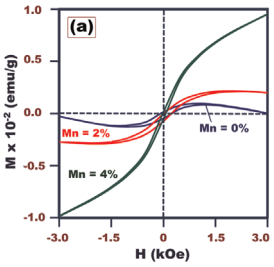
HIGHLIGHTS

- Mn, Cu co-doped ZnO nanoparticles were synthesized via the sol–gel method.
- Induced charge carriers and defects by Mn doping are responsible for enhanced magnetization.
- Suppression of UV and strong visible bands at higher Mn was due to the defect states.
- Better electrical and magnetic property of Mn=2% is to be used in opto-magnetic devices.

GRAPHICAL ABSTRACT

Mn, Cu co-doped ZnO nanoparticles were synthesized via the sol–gel method. Enhanced magnetization, suppression of UV and strong visible bands at higher Mn was due to the defect states.



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ABSTRACT

Cu, Mn co-doped ZnO nanoparticles were successfully synthesized by the sol–gel technique. XRD pattern described that Mn-doping did not affect the hexagonal wurtzite structure of the samples and no secondary phases were found. The reduced crystallite size at Mn=2% is due to the suppression of grain surface growth by foreign impurity. The enhancement of crystal size after Mn=2% is due to the expansion of lattice volume produced by the distortion around the dopant ion. The better dielectric constant and conductivity noticed at Mn=2% are explained by charge carrier density and crystallite size. The suppression of broad UV band by Mn-doping is discussed based on the generation of non-radiative recombination centers. Hysteresis loop showed the clear room temperature ferromagnetism in all the samples and the magnetization increased with Mn-doping. Better electrical and magnetic behavior of $Zn_{0.94}Cu_{0.04}Mn_{0.02}O$ sample is suggested for effective opto-magnetic devices.

1. Introduction

In recent years, a unique combination of both charges and spin degrees of freedom of dilute magnetic semiconductors (DMSs) have gained a subject of intense study. The development of materials with Curie temperature (T_C) above the room temperature is the key challenge in the establishment of spintronics as a practical technology. Theoretical predictions on transition metal (TM) doped ZnO showed the ferromagnetic ground state above room temperature [1,2]. ZnO based materials are gaining more interest due to its fascinating properties such as wide band gap (3.37 eV), large excitons binding energy (60 meV), abundant, cost effective, non-toxic, etc.

There has been a big controversy about the origin of ferromagnetism in TM doped ZnO. The presence of TM ion in the host semiconductors led to an exchange interaction between sp band electrons or holes and the d-electron spins localized at the TM ions, resulting in a versatile magnetic field [3]. The point defects

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such as interstitial, oxygen vacancies created by TM doping played a crucial role in mediating the room temperature ferromagnetism (RTFM) [4]. The ZnO based material showed ferromagnetic ordering only when the n-type conductivity of ZnO could be converted into p-type [5–7]. In addition, it was found that Cu is able to convert the conductivity of ZnO from n-type to p-type. Since higher Cu doping concentration led to grow antiferromagnetic CuO phase in ZnO phase, the Cu doping concentration is limited to 4% in our present study.

Quan et al. reported that the coupling of impurity–impurity spin states dominated in magnetization of Cu and Co co-doped ZnO system [8]. Since, Mn ions possess highest magnetic moment among 3d series due to its half-filled 3d shell structure, the Mn ion is doped with Cu to alter the room temperature ferromagnetic (RTFM) behavior of ZnO based DMS. It was reported that the ferromagnetism of TM doped metal oxide system strongly depended on host matrix, particle size, surface defects, type concentration of the dopants [9–11]. Therefore, the effect of Mn concentrations on structural, ac electrical conductivity, optical and magnetic properties of $Zn_{0.96}Cu_{0.04}O$ nanoparticles have been studied and the detailed discussions are given in our present paper.

2. Experimental procedure

The $Zn_{0.96-x}Cu_{0.04}Mn_xO$ (0, 0.02 and 0.04) nanoparticles were prepared by the sol–gel method. The sol was prepared by dissolving appropriate amounts of zinc acetate dihydrate, cupric acetate monohydrate and maganese (II) acetate tetrahydrate in N, N-Dimethyl formamide (C_3H_7NO) one by one with 20 min interval. The temperature of the sol was gradually raised to 80 °C and kept for 6 h to obtain gel. The gel was transferred into a hot air furnace which was kept at 150 °C for 12 h. The final products were collected and ground using an agate mortar. Finally, the synthesized nanoparticles were annealed at 500 °C in air atmosphere for 2 h followed by furnace cooling.

The crystal structure of $Zn_{0.96-x}Cu_{0.04}Mn_xO$ nanoparticles was determined by the powder X-ray diffraction (XRD) technique. XRD patterns were recorded by a RigaKuC/max-2500 diffractometer using Cu Kα radiation ($\lambda=1.5406$ Å) at 40 kV and 30 mA from $2\theta=30$–70°. Dielectric and ac conductivity measurements were carried out in the frequency range from 50 Hz to 200 KHz using LCR meter (Make: Vasavi electronics, Model: VE2816A) at room temperature. The samples used for this measurement was in the pellet form and the pellets were coated with silver paste to form parallel plate capacitor geometry.

The photoluminescence (PL) spectra of $Zn_{0.96-x}Cu_{0.04}Mn_xO$ nanoparticles have been carried out between the wavelength ranging from 350 to 580 nm using a fluorescence spectrophotometer (Model: F-2500, Make: Hitachi) at room temperature. A Xenon lamp with a wavelength of 320 nm and power of 150 W is used as the excitation source. The magnetization (M) versus magnetic field (M–H) loops was carried out at room temperature using vibrating sample magnetometer (VSM, Make: Lake shore, Model: 7404).

3. Results and discussion

Structural study of DMS is important for interpreting the ferromagnetic behavior associated with the materials. The crystal structure of the $Zn_{0.96-x}Cu_{0.04}Mn_xO$ samples was examined by XRD pattern. Fig. 1 shows the XRD patterns of $Zn_{0.96-x}Cu_{0.04}Mn_xO$ (0, 0.02 and 0.04) nanoparticles at room temperature. The inset of Fig. 1 shows the magnified and clear change of XRD peaks along (101) plane between 35.8° and 37°. All the diffraction peaks are

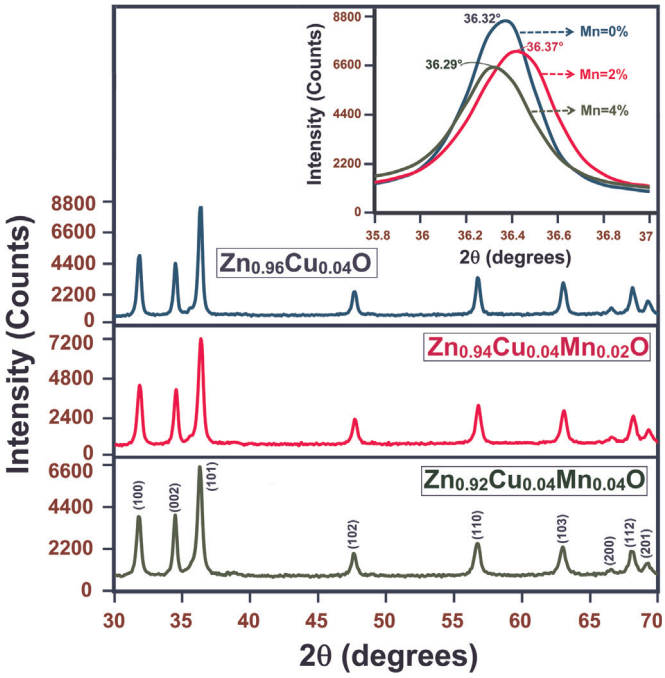

Fig. 1. X-ray diffraction pattern of $Zn_{0.96-x}Cu_{0.04}Mn_xO$ ($x=0$, 0.02 and 0.04) nanoparticles between 30 and 70°.

well fit with the standard data of pure ZnO ($a=3.2488$ Å, $c=5.2061$ Å, space group $P6_3mc$, 186, JCPDS data card no. 36-1451). It can be seen that the dominant crystal phase of the samples is the wurtzite hexagonal structure. The XRD pattern reveals that the Mn and Cu co-doping cannot disturb the wurtzite structure of host ZnO. There is no indication of any secondary phase or clusters, confirming that the samples are only one single. The highest intensity of the XRD peaks was obtained from undoped $Zn_{0.96}Cu_{0.04}O$ sample indicating a better crystal quality. In Mn co-doped samples, the peak intensity is less than the undoped $Zn_{0.96}Cu_{0.04}O$ sample. It is gradually decreased with the increase of Mn concentration which indicates that dopant incorporation deteriorates the crystallinity of the samples due to the ion size difference between Zn and Mn.

From the inset of Fig. 1 one can observe that the Bragg angle of the intense (101) diffraction plane slightly shifted towards higher values from 36.32° (without Mn dopant) to 36.37° for Mn=2%. This is evidence for creation of internal compressive micro stress. According to the Bragg's law of scattering, the scattering angle is inversely proportional to the inter-planner distance. Therefore, Shift of position towards higher angle meant that the inter-planner distance become short when Mn doped with Zn–Cu–O. This compression of inter-planner distance creates the stress inside the lattice. In addition a line broadening was also observed in the XRD spectra. The further increase of Mn concentration shift the peak position towards the lower angles from 36.37° (Mn=2%) to 36.39° (Mn=4%). It is commonly known that the peak position shift and the XRD line broadening may be the result of pure size or micro strain, or both size and microstrain. The average crystallite size of the samples is calculated using Debye Scherrer's formula [12] after accounting the appropriate background correction from X-ray line broadening,

$$\text{Average crystallite size } (D) = \frac{0.9\lambda}{\beta \cos\theta}. \quad (1)$$

where, λ is the wavelength of X-ray used (1.5406 Å), β is the angular peak width at half maximum in radian along (101) plane and θ is the Bragg's diffraction angle.