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TUNABLE OF OPTICAL AND ELECTRICAL PROPERTIES FOR PURE AND MN DOPED ZNO NANOPARTICLES

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Abstract

We have successfully synthesized pristine and manganese (Mn) doped ZnO nanoparticles by simple chemical precipitation method. Powder X- ray diffraction (XRD) results suggest that both pure and Mn doped ZnO nanoparticles show that hexagonal wurtzite type structures. Scanning electron micrograph (SEM) pictures depict that spherical shaped morphology with an average diameter of around 15-20 nm, which is well matched with crystalline size calculated from XRD results. A considerable red shift in the absorbance edge was found in Mn doped samples. The functional groups were analyzed by Fourier transform infra red spectra. The electrical property of ZnO has significantly improved by Mn doping. The samples were further characterized by Photoluminescence and Energy dispersive spectra analysis.

Keywords: Zno, Mn Doping, Scanning Electron Microscope, Photoluminescence, Electrical Properties.

1. Introduction

Transparent conducting oxides (TCO) have a wide range of applications, including transparent electrodes in flat-panel displays and solar cells, transparent and heat reflecting material for windows in buildings, solar collectors and lamps [1]. Transition – metal oxide nanomaterials, such as SnO_2, ZnO, TiO_2 and WO_3 have paying attention broad research interests owing to their unique physical and chemical properties and diverse potential applications in optical and electronic fields [2]. Among the various types of metal oxides, ZnO nanostructures are presently being widely investigated because of their immense potential for electronic, photonic and spintronics applications and also for use in gas sensors, biosensors and solar cell applications. ZnO is direct band gap energy of 3.37eV at room temperature and also a large exciton binding energy i.e., 60 MeV at room temperature, good transparency, non-toxic, inexpensive, fine particle size [3]. Many methods have been adapted for synthesis of ZnO nanostructures such as; hydrothermal [4] sol-gel [5], chemical precipitation [6] and microwave irradiation [7] methods. Compared to above mentioned methods chemical precipitation method is possible to achieve a high degree of homogenization together with a small particle size and faster reaction rates. Moreover the method is simple and cost effective compared to other methods. Pure ZnO is low sensing properties of gas and bio sensors, in-order to improve the sensing properties of ZnO to add a small amount of impurities such as metals (Sn, Mn, Mg & Cu) into ZnO host material. So in the present investigation we have choosing manganese (Mn) as a dopant to increasing the surface area as well as improve the optical and electrical properties of ZnO.

In this study, we report synthesis of pristine Mn doped ZnO nanoparticles by using chemical precipitation technique. The influence of Mn doping on structural, optical and electrical properties of ZnO have been investigated by using XRD, SEM-EDAX, UV, PL, FTIR and temperature dependent electrical resistance method.

2. Experimental Procedure

2.1 Synthesis of Mn doped ZnO nanoparticles

The Mn doped ZnO nanoparticles were prepared by chemical precipitation method. The starting materials used in this experiment were manganese chloride ($MnCl_2.2H_2O$) having 99% purity, Zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) which also possess 99% purity. Nanoparticles of Mn doped ZnO are prepared by reacting aqueous solution of 0.23 g of Manganese chloride with 5g of Zinc acetate dihydrate. Then the solution was kept under vigorous stirring. To the above solution, NaOH is added drop wise to get a homogeneous solution by fixing the pH 8. After the complete reaction, the precipitate is washed several times with distilled water and ethanol to remove organic impurities. The final product was dried in a vacuum oven at 100 ^oC for 1h and then annealed at 600 ^oC for 2 h to obtain the Mn doped ZnO nanoparticles. The similar procedure was carried out for the preparation of undoped ZnO except the addition of manganese chloride.

2.2 Characterization Techniques

The phase purity and structure of the sample was analyzed by powder X-ray diffraction patterns were recorded in Bruckers diffract meters with CuKα radiation source (λ-1.54 Å) operated at 40KV and 30 mA in the 2θ range 10 - 80^o. The particle size, morphology and elemental composition were analyzed using SEM-EDX was recorded on TeScan analyzer. The optical nature of the samples was analyzed by using UV-Vis spectra were recorded on a Perkin Elemer spectrometer in the range of 190 – 1100 nm. Photoluminescence spectra of the samples were collected at room temperature by using Cary Eclipse

(el02045776) Fluorescence spectrophotometer in the wavelength range of 300–600 nm with a Xe laser as an exciting source, and excitation wavelength of 325. The Fourier transformed infrared spectra (FT-IR) of the samples were collected using a 5DX FTIR spectrometer.

3. Results and Discussion

3.1. X-ray Diffraction Analysis

X-ray diffraction analysis is a useful technique to determine the crystalline nature and average grain sizes of the samples. Fig. 1 shows the powder XRD pattern of pristine and Mn doped ZnO nanoparticles. From the pattern, it was clearly seen that both the pure and doped samples show that hexagonal wurtzite type structure and the results are good in agreement with the standard JCPDS (card no. 89-1397) data. In Mn doped samples, the peak intensity was decreases and shift towards the lower angle side, this result clearly indicate the substitution of Mn^{2+} into ZnO host lattice site. The calculated lattice parameters of pure ZnO as a = 3.2535 (Å), c = 5.2134 (Å) and volume V = 47.78 (Å). After these parameters decrease for Mn (5 wt.%) doped ZnO samples (table 1), the observed variation in lattice parameters is consistent with the smaller radius of the Mn^{2+} ion (0.71 Å) with respect to the Zn^{2+} ion radius (0.74 Å) and with the small amount of Mn concentration used for doping.

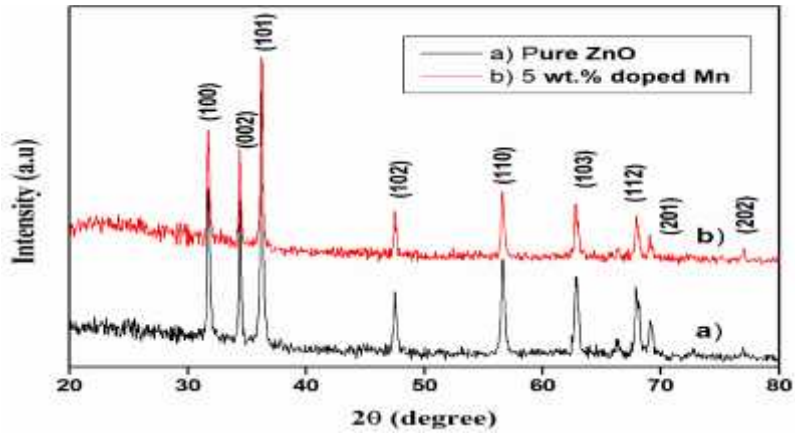


Fig.1. XRD pattern of pure and Mn doped ZnO nanoparticles

Table.1 shows the lattice parameters and average crystalline size of pure and Mn doped ZnO nanoparticles

Samples	Crystallite size (nm)	Lattice Parameters a (Å)	c (Å)	Cell Volume ($Å^3$)
ZnO	28	3.2535	5.2134	47.78
Mn doped ZnO	21	3.2512	5.1123	46.79

The average crystalline sizes of the pure and Mn doped ZnO nanoparticles were calculated by using Scherrer's equation [8].

$$d = \frac{K^{a}}{\cos -}$$

Where d is the mean crystallite size, K is the shape factor taken as 0.89, λ is the wavelength of the incident beam, β is the full width at half maximum and θ is the Bragg angle. The average crystalline size of pristine ZnO was found to be 28 nm and it was further decreased to 21 nm for 5 wt % Mn doped ZnO. This result suggests that the grain growth of ZnO is reduced by Mn doping.

3.2. SEM analysis

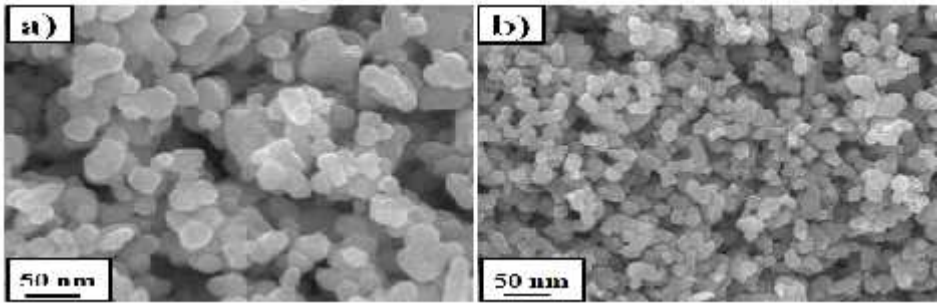
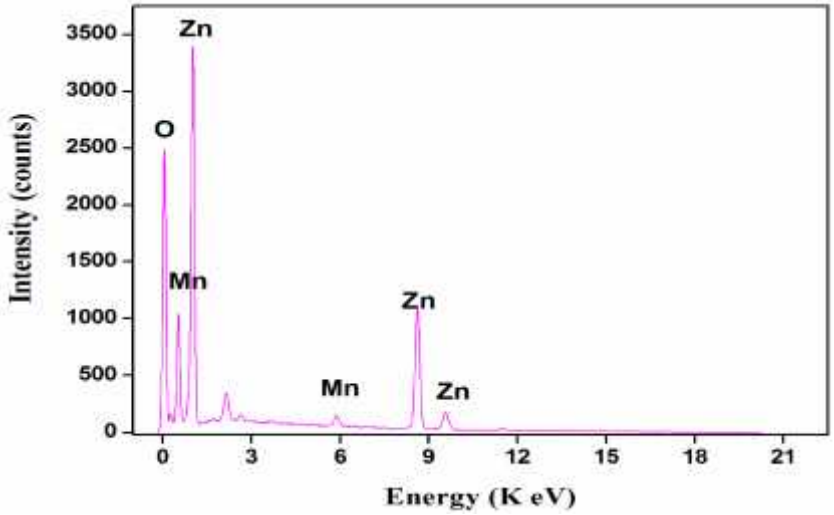


Fig. 2. SEM images of a) pure ZnO b) Mn doped ZnO

The surface morphology and average particle size of the samples were analyzed by using SEM. Fig. 2 shows the SEM pictures of both pure and Mn doped ZnO samples. From the micrograph, clearly seen that both the samples in spherical shaped morphology with uniform particles distribution. The average particles size of pristine ZnO was found to be 25-30 nm, and further it was decrease to 22-26 nm for Mn (5 wt.%) doped ZnO samples. These values are well matched with the average crystalline size calculated from the XRD results.

3.3. EDS Analysis

The composition analysis of the samples was investigated by EDS spectra. Figure 3 shows the EDS spectra of Mn doped ZnO nanoparticles. The samples mainly compose elements of Zn, O & Mn. The calculated stoichiometry ratio from the EDS measurements was well matched with initial precursor which had been taken for synthesis process. The atomic ratio of Zn/O/Mn is 1.78:3.08:0.8.



3.4. UV Analysis

The optical property of the sample was recorded on UV-Vis transmission spectra analysis. Figure 4 shows the UV-Visible transmission spectra of pure and Mn doped ZnO nanoparticles as a function of wavelength. Both the samples have a strong absorption maximum below 300 nm. The absorption edge was shift towards the higher angle side and also decreases the intensity of peak for Mn doped ZnO samples. The red shift can be attributed to the agglomerations in the samples and decreases the band gap energy of pure ZnO [9]. While the optical band gap of ZnO nanoparticles is calculated using the Tauc relation [10]. The band gap energy was calculated as 3.73 eV and 3.53 eV for pure and Mn doped ZnO nanoparticles. The observed decrease in band gap energy confirms that Mn^{2+} ion is substituted in the ZnO host lattice.

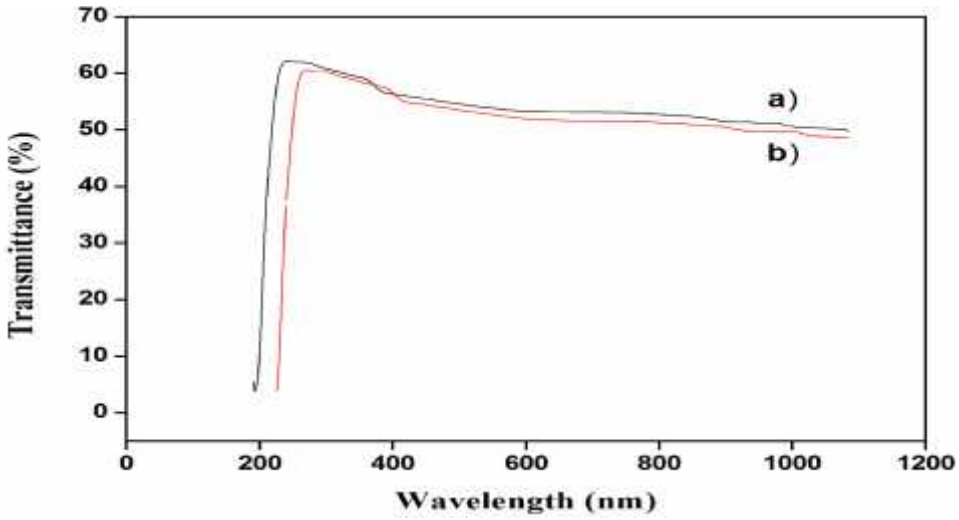


Fig. 4. UV-Vis transmission spectra of a) pure ZnO b) Mn doped ZnO nanoparticles

3.5. FTIR analysis

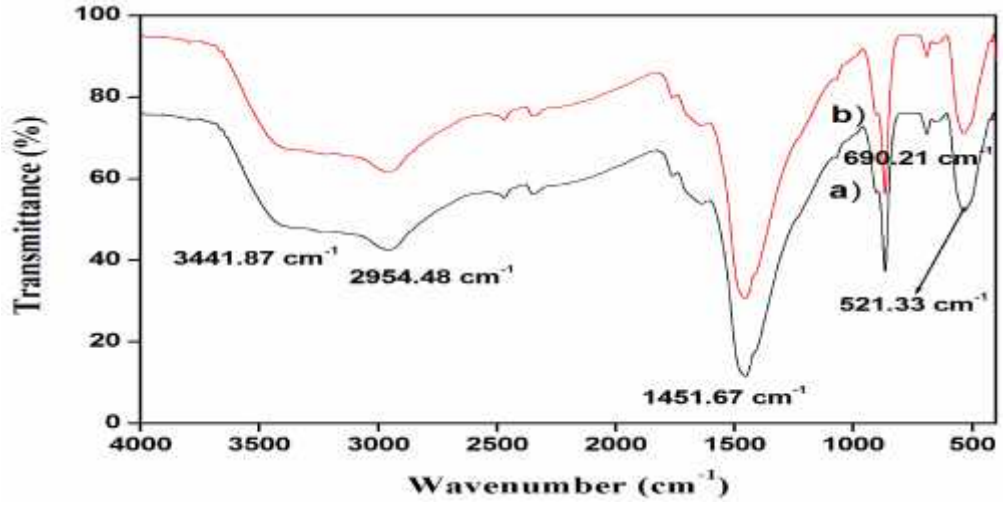


Fig. 5. FTIR spectra of a) pure b) Mn doped ZnO nanoparticles

The functional groups and bonding configuration was investigated by FTIR spectra. Fig. 5 shows the FTIR spectra of pure and Mn doped ZnO nanoparticles. The absorption peak at 3441.87 cm^{-1} represents the O-H stretching of the hydroxyl group. The absorption band appeared at 2954.48 cm^{-1} due to the C-H (acetate) stretching. The absorption peak appeared at 1451.67 cm^{-1} corresponding to the stretching vibration of C=O carboxyl group [11]. The peaks in the range of 400-700 cm^{-1} were attributed to ZnO stretching mode [12]. However Zn-O absorption peaks shifted lower position for Mn doped samples, which indicates the Mn replaced by Zn in-to ZnO lattice site.

3.6. Photoluminescence Spectra Analysis

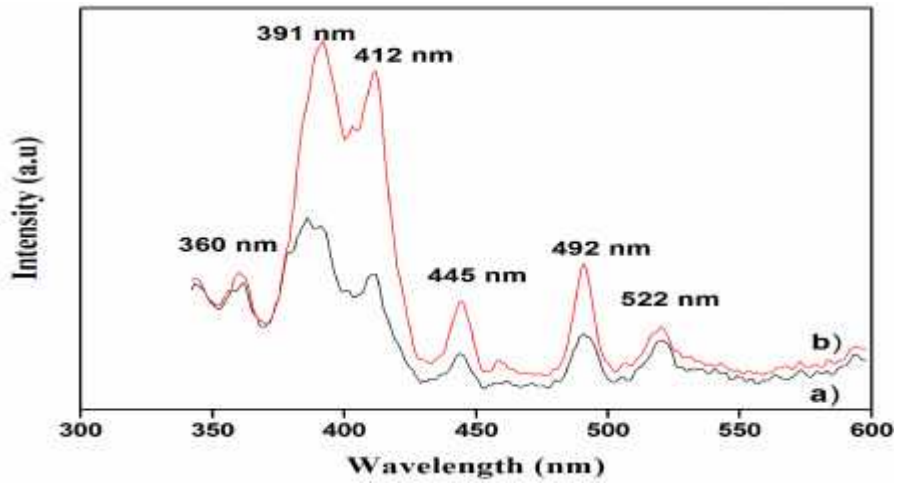


Fig. 6. Photoluminescence spectra of a) pure b) Mn doped ZnO nanoparticles

Photoluminescence (PL) spectroscopy is a useful technique for the study and characterization of materials and dynamical processes occurring in materials, specifically the optical properties of the materials. Fig. 6 shows the photoluminescence spectra of pristine and Mn doped ZnO samples measured from 300 to 600 nm using a 325 nm He–Cd laser. From the graph, both the samples exhibited serious of peaks at 360 nm & 391 nm (UV emission), violet, blue green emissions at 412 nm, 492 nm and green emission at 521 nm. The UV emission peak can be assigned as a near band edge emission (NBE) of ZnO, which is originating from the direct exciton recombination [13]. The emission peaks at 412 nm (2.93 eV), 492 nm (2.54 eV) and 521 nm (2.41 eV), related to a radiative transition from donors Zinc interstitial (Zn_i) and Oxygen vacancy [14]. All the emission peaks intensity is increases for Mn doped samples, this result indicate the optical property of the ZnO has significantly improved by the Mn doping.

3.7. Electrical measurements

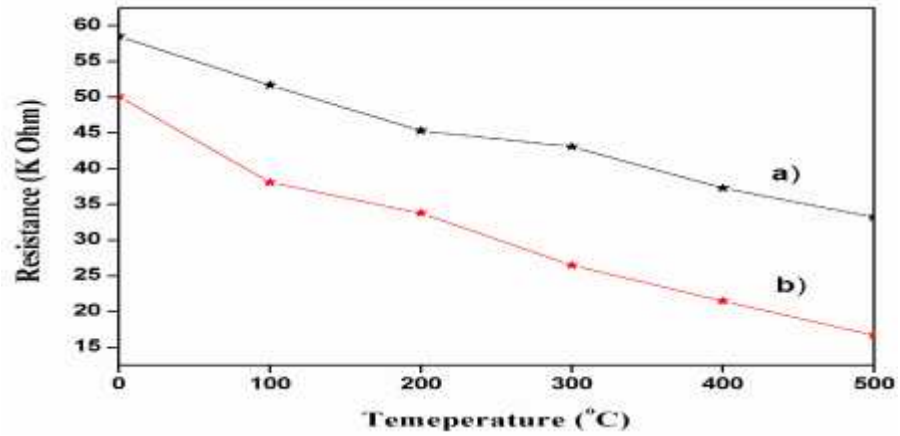


Fig.7. Electrical measurements of a) pure b) Mn doped ZnO nanoparticles

The electrical resistance of the samples was analyzed by using LCR four probe method. The synthesized nano powders were pressed in the form of pellet using pelletizer. The resistance of the sensor (SnO_2) was measured using two-electrode contact (99.9% pure silver paste) and the distance between two electrodes was maintained at 3.8 mm. Fig.7. Electrical measurements of pure Mn doped ZnO nanoparticles. It was noted that resistance value gradually decreases with the increase of temperature, this behavior resemble that semiconducting nature of the samples. The resistance value was found to be 33.2 KΩ and 16.7 KΩ for pristine and Mn doped ZnO nanoparticles respectively (at 500 ^{o}C). The significant improvement in the electrical properties is mainly related to the increase in mobility for Mn doped samples. Moreover decreasing the band gap energy and also particle size (i.e, increasing the surface area) is a key role for Mn doped ZnO samples to enhance the electrical properties of pristine ZnO. The preliminary studies examine in the electrical property confirm the Mn doped sample is more preferable for gas sensor applications.

4. Conclusions

In summary, pure and Mn doped ZnO nanoparticles were prepared by simple chemical precipitation method. Powder XRD results suggest that both pure and Mn doped ZnO nanparticles have hexagonal wurtzite type structure and the results are good in agreement with the standard JCPDS (card no. 89-1397) data. Spherical shaped morphology and average diameter of around 28-21 nm was observed by SEM micrograph. A considerable red shift in the absorbance edge and decreasing band gap energy from 3.73 eV to 3.53 eV conformed by UV-Vis transmission spectra. Moreover optical properties of ZnO have significantly improved by Mn doping, which is confirms the PL spectra analysis. The results obtain in the electrical measurements confirms the Mn doped samples increase the mobility of charge carriers, and also may find possible potential applications in high performance gas sensor devices.

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