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RESEARCH ARTICLE

INVESTIGATION ON THE EFFECT OF MnON STRUCTURAL AND OPTICAL PROPERTIES OF ZnO NANOPARTICLES

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ABSTRACT

Zinc oxide and manganese added zinc oxide nanoparticles were synthesized by wet chemical technique. Highly stable pure and 0.5 weight percentage manganese doped Zinc Oxide nanoparticles have been prepared at room temperature. Characterization was carried out by FTIR, XRD, SEM, EDX and UV visible studies. The chemical composition of the products was characterized by FTIR spectroscopy. The detailed structural properties were examined using X-ray diffraction pattern which revealed that the synthesized nanoparticles are well crystalline and possessing wurtzite hexagonal phase. The SEM images of the samples clearly revealed the decrease in grain and porosity size with increasing concentration of Mn. The EDX results shown the presence of Zn, O and Mn.

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INTRODUCTION

Nanomaterials are fascinating due to their smaller particle size and large surface area. Among these nanomaterials, ZnO nanostructures are promising candidates for wide range of applications from optoelectronics to variety of sensors. Zinc oxide is a II-VI compound semiconductor. The properties such as wide bandgap, large excitation binding energy and low threshold power for optical pumping are considered to be the eminent features of ZnO. So ZnO is said to be efficient phosphor (Yang *et al*., 1997; Bagnall *et al*., 1997; Kawasaki *et al*., 1998; Ohtomo *et al*., 1999). II – VI compounds as a collective group of materials have been and still are the subject of much intensive investigation. The growth of semiconductor technology in the early 1950's highlightened the limitations of silicon and germanium of which perhaps the character and the magnitude of the forbidden energy gap were the most disadvantageous. At first the extension in the range of energy gaps was sought in the III –V compounds, where considerable success has been achieved with InSb and GaAs in the low and high energy gap areas respectively. GaAs is today probably the most developed and well understood compound in existence.

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Concurrently with the later developments in the III-V compounds, systematic studies were made for several of the II-VI compounds. The results of these studies have revealed much about the general nature of the II-VI compounds and the feature of chemical stability of the higher energy gap materials at room temperature offers an immediate advantage over the unstable III - V phosphides. II – VI compounds in their broadest sense includes compounds formed from elements of group II and group VI of the periodic table.

Zinc oxide has a wide band gap (Eg=3.37eV), large excitation energy of 60 meV, high chemical stability, good piezo- electric properties, nontoxicity and biocompatibility. To synthesize ZnO nanoparticles with transition metals by different routes such as wet chemical methods like sol-gel (Brus *et al*., 1996), co- precipitation (Abrishami *et al*., 2010), combustion (Yadav *et al*., 2009) etc. It has been used in a wide range of applications such as sensors, varistors, piezoelectric, transducers, surface acoustic wave devices, phosphors, transparent conducting oxides, optoelectronic devices, ferromagnetic devices, and heterogeneous photo catalysts (Riahi-Noori *et al*., 2008; He *et al*., 2007; Lee *et al*., 2006; Garcia *et al*., 2007; Fonoberov and Balandin, 2006; Kwon *et al*., 2008).

Experimental

Materials used

Analytical Reagent (AR) grade Zinc acetate dehydrate, Sodium Dodecyl sulphate, Sodium hydroxide and manganese chloride were used for synthesis of pure and manganese doped zinc oxide nanoparticles. They were purchased from Merc India and used used as received without any further purification.

Synthesis of Zinc oxide nanoparticles

For the synthesis of pure zinc oxide nanoparticles 10.966 g of Zinc acetate dehydrate was added to 250 ml water under vigorous stirring till the solution becomes homogeneous. 10.974 g of NaOH was added to the solution under stirring and to the solution 14.4 g of Sodium Dodecyl Sulphate was added under continuous stirring till pH value reached 12. This solution was kept for drying in a hot air oven and heated at 160 °C for overnight. Then the material was taken and grinded using a mortar and pestle and thus the obtained powder was washed several times using ethanol and deionized water. And the product was dried at 60 °C for overnight and the obtained product was kept for calcinations at 500 °C for four hours.

Synthesis of manganese added Zinc oxide nanoparticles

For the synthesis of 0.5weight percentage manganese doped ZnO, 0.076 g manganese chloride was added to 250 ml of water under vigorous stirring and 10.966 g of Zinc acetate was added to it. Then 10.974 g of Sodium hydroxide was added to the solution under stirring and along with that 14.4g of Sodium Dodecyl Sulphate added under continuous stirring till the pH value reached 12 and the solution was kept for drying in a hot air oven and it was heated at 160 °C for overnight. Then the material was taken and grinded using a mortar and pestle and thus the obtained powder was washed several times using ethanol and deionized water. And the product was dried at 60 °C for two days and the obtained product was kept for calcination at 500 °C for four hours. FTIR studies were performed in order to determine the presence of functional groups and chemical bonding, as well as to study the surface changes on the particles. It can determine the quality or consistency of sample. FTIR transmission spectra were obtained using Bruker, Alpha T; Germany spectrometer in range 500-4000 cm^{-1}using resolution 2 cm^{-1}.

Characterization studies

The pure and manganese doped Zinc Oxide nanoparticles thus obtained were characterized by UV, FTIR, XRD, SEM and EDAX. The synthesized seven samples were characterized using UV-visible spectroscopy by taking 0.1 g of each sample diluted in 100 ml double distilled water. The absorption data was recorded as a function of wavelength using UV-Visible spectrophotometer model-2202, India. XRD (X-ray Powder Diffraction) is rapid analytical technique primarily used for phase identification of crystalline material. The average crystallite size was determined from XRD peaks using Scherer's formula (Fonoberov and Balandin, 2006). Field emission Scanning Electron Microscopy (SEM) is one of the most versatile and well known analytical technique it offers advantages like high magnification, large depth of focus, great resolution. Electrons generated from an electron gun enter a surface of sample and generate many low energy secondary electrons. The intensity of these secondary electrons is governed by the surface topography of the same. An image of the sample surface is therefore constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. EDX analysis is a useful tool widely used for chemical analysis. The intensity of backscattered electrons generated by electron bombardment can be correlated to the atomic number of the element within the sampling volume. Hence, qualitative elemental information can be revealed. The characteristic X-rays emitted from the sample serve as fingerprints and give elemental information of samples including semi-quantitative analysis, quantitative analysis, line profiling and spatial distribution of elements.

RESULTS AND DISCUSSION

UV-Visible studies

Fig. 1 shows the UV-Visible spectra for Zinc oxide ,0.5wt% Mn-ZnO. Which shows the absorption peaks at 381.62 nm and 377 nm respectively. The strong absorption band in UV region for Zinc oxide and manganese doped zinc oxide can be attributed to the band edge absorption of wurtzite hexagonal ZnO, blue shift relative to its bulk 380 nm. The zinc oxide sample that is doped with also shows the absorption band similar to zinc oxide. When Mn doped in ZnO nanoparticles, the position of the absorption spectra shifted towards the lower wavelength side or known as blue-shifted which correlated to the change in the optical band gap value. Generally, blueshifted in the bandgap was due to Mn doping in the ZnO nanoparticles with the replacement of Zn ions in the ZnO lattice by Mn ions. This indicates the band gap of ZnO nanoparticles increases when doped with Mn. Furthermore the blueshifted in the band gap energy with increasing the amount of Mn doping concentration can be defined as the separation in the energy between the top of the valence bond and the unoccupied energy states in the conduction band (Visvanatha *et al*., 2004).

FTIR analysis

Various peaks corresponding to the main absorption bands can be seen from the FTIR spectrum on fig. 2. The broad absorption peak around3577 cm-1 and 3578 cm-1 represents the O-H stretching of the hydroxyl group. The peak around 3100 represent the O-H stretching (Hao *et al.*, 2012). The absorption peaks observed between 1456 and 1330 cm -1 s, corresponding to the asymmetric and symmetric stretching of the carboxyl group C=O. The small peaks at 879.97 and 628.104 clearly indicate Zn-O stretching. From the studies, the stretching mode of undoped ZnO is at 628 .104 cm-1. When doped with Mn the values of absorption were found to be blueshifted at 618.8 and 595 are due to Mn-O stretching and bending. Undoubtedly, this can prove that the Zn-O-Zn network was perturbed by the presence of Mn in its environment with the change in the peak position of the ZnO absorption bands (Wu *et al.,* 2010).

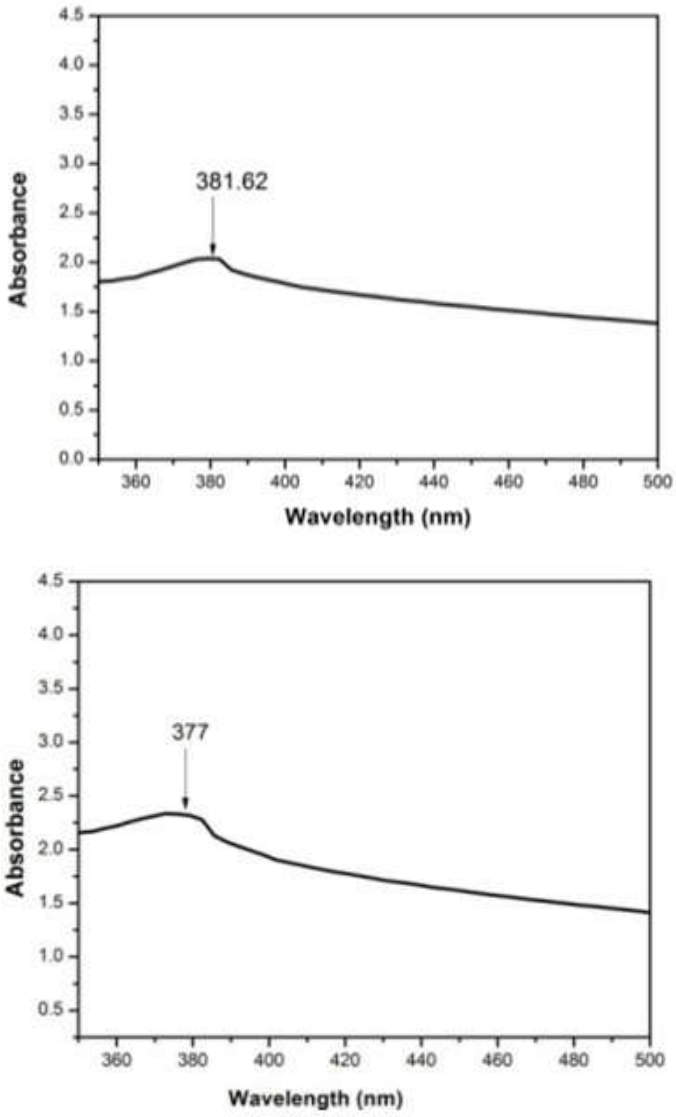

Fig. 1. UV spectra of (a) pure and (b) Mn doped ZnO

XRD Analysis

Fig 3: illustrates ZnO and manganese doped ZnO. (a) shows the XRD spectrum of ZnO. The eight major peakswere seen at 31.7, 34.6, 36.2, 47.6, 56.5, 62.9, 68.0 and 69.8 which can be assigned to diffraction from (100), (002), (101), (102), (110), (103), (112), (201) planes respectively. The sharp intense peaks of ZnO confirm the good crystalline nature of ZnO and diffraction peak can be indended to a hexagonal wurtize structured zinc oxide. The average crystallite size is estimated using the Debye-Scherrer formula (Cullity, 1978).

$$2d = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

Where, β is the full width at half maximum intensity (FWHM) corresponding to the diffraction angle 2θ in radian, and λ is the wavelength of Cu-kα radiation. The average crystallite size for the prepared nano composite is found to be 40.587 for pure sample and 48.510 for doped sample.

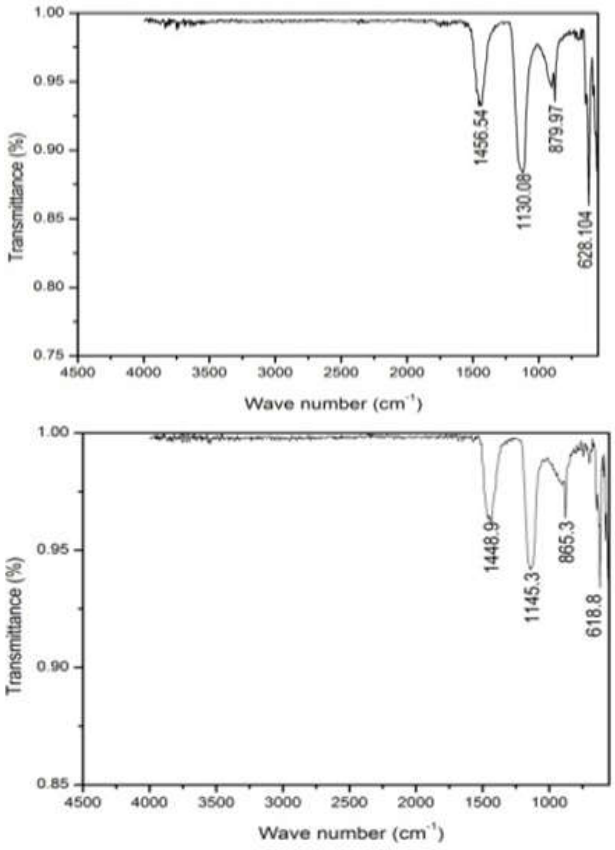

Fig. 2. FTIR Spectra (a) pure and (b) Mn doped ZnO

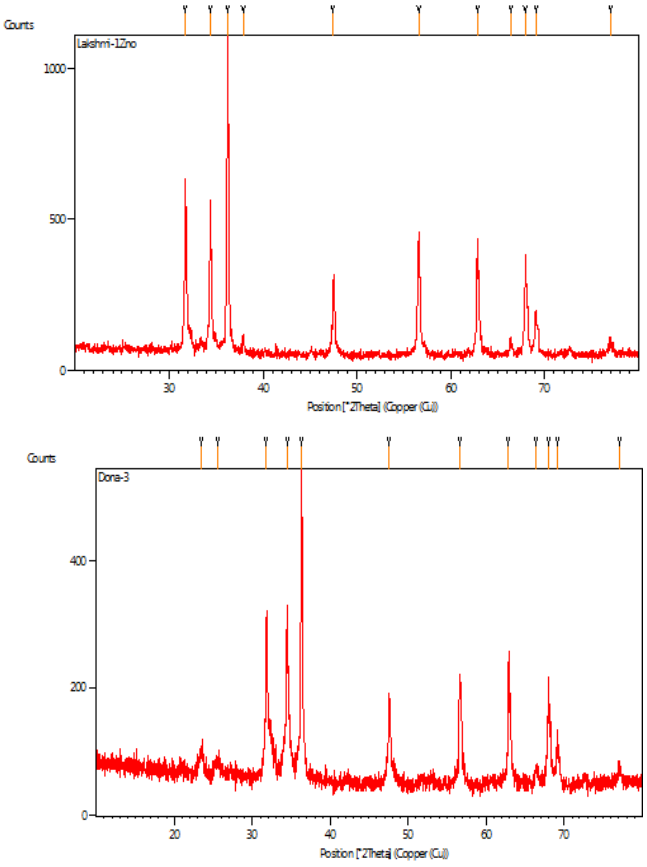

Fig. 3. XRD Pattern of (a) pure and (b) Mn doped ZnO

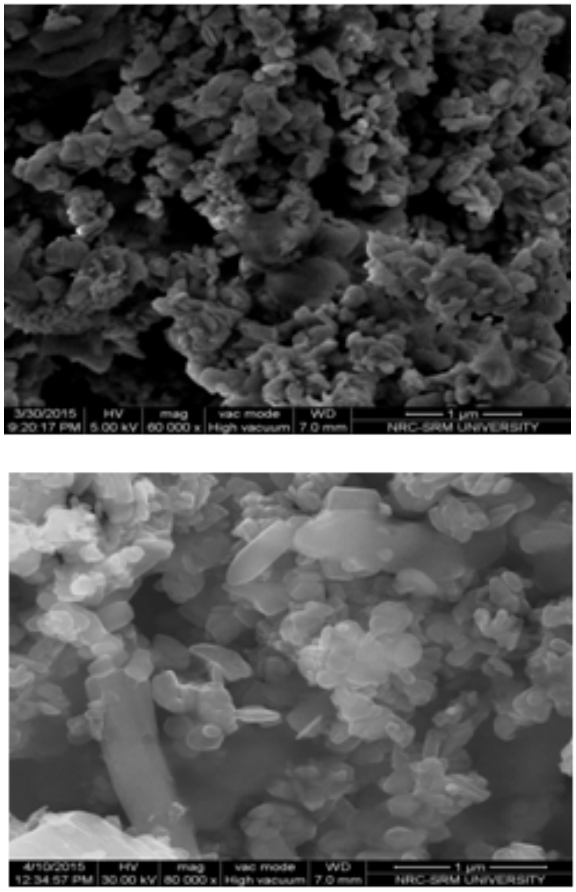

Fig. 4. SEM images of (a) pure and (b) Mn doped of ZnO nanoparticles

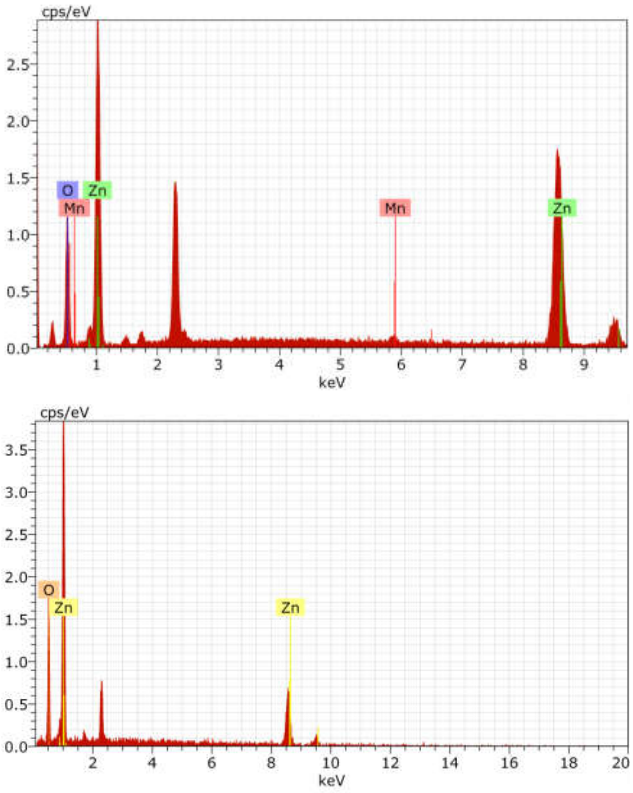

Fig. 5. EDX Spectra of (a) pure and (b) MndopedZnO

Fig 4(a) shows the SEM image of undoped ZnO nanoparticles and the corresponding EDX is given in 5(a) The SEM image reveals that the particle are spherical in shape and mono dispersed with the size less than 50 nm. SEM and EDX images of Mn doped ZnO is in 4(b) and 5(b) respectively. It clearly indicates the transformation of spherical rod shape with the particle size confinement with the result of Mn doping. In elemental analysis of zinc oxide the peaks at 1.6 keV, 8.6 keV, 9.6keV confirms the presence of zinc and the peak at 0.53 keV shows the presence of oxygen. The EDX spectra for manganese doped also confirm the presence of zinc, oxygen and manganese. The peks at 0.6 keV, 5.9 keV, 6.5keV shows the presence of manganese. The peak value at 1.6 keV, 8.6 keV, 9.6keV confirms the presence of zinc and the peak at 0.53 keV shows the presence of oxygen in the EDS spectra of manganese doped ZnO.

Conclusion

In summary, Zinc oxide (ZnO) and the transition metal manganese doped at various percentage zinc oxide was synthesized by using zinc acetate dihydrate as a precursor. The characterization of the samples was done using FTIR, UV-Visible spectrophotometer, XRD, SEM and EDX. The presence of functional groups and chemical bonding was determined by FTIR. The absorption peak of all the synthesized samples was determined by UV-Visible spectrophotometer. The average crystallite size of all the samples was determined using XRD. The XRD peaks correspond to the hexagonal wurtize structure. The SEM image was taken to determine the of the sample morphology it has been found the formation of nanoparticle within size range of 40 nm- 49 nm. The EDX spectra were taken to reveal the qualitative elemental information the formation of zinc, oxygen and manganese were determined.

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