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Preparation and Characterization of ZnO and Mg-ZnO nanoparticle

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ABSTRACT

ZnO is one of the most promising materials since it has a high mechanical and thermal stability, and wide band gap (3.37 eV). Meanwhile, doping with selective elements offers an effective method to enhance and control the electrical and optical properties of ZnO nanostructures, which is crucial for its practical applications. Mg-doped ZnO have considerable interests owing to their unique optical, electric and piezoelectric properties. In this paper, we report the Synthesis of Mg-doped ZnO nanoparticles successfully with diameters ranging from 50 to 100 nm via precipitation method. The surface morphology of synthesized material was investigated by using scanning electron microscope (SEM) and the elemental analysis by energy-dispersive X-ray spectroscopy **(***EDAX). The presence of Mg was confirmed by infrared spectroscopic (IR) studies. The structure and phases of Mg-ZnO were analyzed by powder X-ray diffraction (XRD) method and the Optical properties were measured by using UV–Vis spectrophotometer.*

Keywords: EDAX; Mg doped ZnO; Nanoparticle; Precipitation; Powder XRD.

INTRODUCTION

The important properties of nanostructured materials have started motivation among scientists to explore the possibilities of using them in technological applications. In particular, the electronic and optical properties of nanostructured materials have been of interest because of their potential applications in the fabrication of micro electronic and optoelectronic devices [1,2]. Among the nanostructured metal oxides, ZnO is considered to be one of the best metal oxides that can be used at a nanoscale level. ZnO itself has normally a hexagonal or wurtzite structure and it is well-known as an n-type II–VI semiconductor with a wide direct band-gap of about 3.37 eV and a large exciton binding energy of 60 meV [3]. From this point of view, nanostructured ZnO powders display a great power in many applications such as gas sensors [4], solar cells [5], varistors [6] and photocatalyst with high chemical activity [7]. Recently, extensive progress has been made on the research front of ZnO-based nanomaterials motivated by both basic sciences and potential advanced technologies [8, 9].

Meanwhile, doping with selective elements offers an effective method to enhance and control the electrical and optical properties of ZnO nanostructures, which is crucial for its practical application. And, ZnO doped with proper elements, such as Li, Al, Mn and Cr has been studied [10–12]. By doping with MgO, which has a wider band-gap (7.3 eV) [13], the band-gap of ZnO can be modulated for the realization of light-emitting devices operating in a wider wavelength region. The ZnO nanostructures are also being used in several industrial applications such as medicine, gas sensors, varistors, etc. The availability of a rich genre of nanostructures makes ZnO as an important material [14-16]. The doping of ZnO with a metal could change its properties, doping with the Group II elements (Cd, Mg) may modulate the value of the band gap and increase the UV luminescence intensity [17]. While Cd is known to reduce the band gap [18], Mg substitution leads to the enhancement in band gap [19].

A number of chemical methods of synthesis have been applied to synthesize nanostructured ZnO powders, for example by using hydrothermal [20], precipitation [21], sol–gel [22] and thermal decomposition [23] methods. Among these chemical routes, precipitation and thermal decomposition are a common method that can be used for large scale production. Moreover, the particle shape can be controlled easily by modifying the precursor solution with an appropriate surfactant such as diethylene glycol (DEG), cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS). To date, a number of research workers have reported the fabrication of nanostructured ZnO powders with spherical [24], rod-like [25], flower-like and sheet-like [26] structures. Only a few reports [27, 28] have involved the synthesis of porous ZnO through an oxalate intermediate by a chemical route. Therefore, a synthesis of porous Mg doped ZnO nanopowders via the precipitation method in the presence of CTAB could be worthwhile investigating.

In this paper, we report synthesis and characterization of ZnO and Mg doped ZnO nanopaerticles by precipitation method and its characterization by using XRD, SEM, EDAX and UV-Vis and IR spectroscopic methods.

MATERIALS AND METHODS

Zinc sulphate, Magnesium sulphates were procured from Loba chemicals (Mumbai, India). Sodium hydroxide and cetyltrimethylammonium bromide were procured from S.D. Fine-CHEM Ltd. (Mumbai, India). All the chemicals were of analytical grade and used as received for the experiments. Double distilled water was used throughout the experiments.

Synthesis of ZnO and Mg-ZnO nanoparticle: To prepare ZnO nanoparticles, 100 mL of 0.2 M NaOH was added drop wise into a solution containing 100 mL of 0.1 M Zinc sulphate solution under constant stirring. About 10 mg of CTAB was added as capping agent which inhibits anomalous growth of magnesium hydroxide crystals during the course of precipitation. Then the resulting solution was kept at room temperature for three hours under constant stirring. The so obtained white precipitate was centrifuged, washed several times with distilled water and then with alcohol and dried at 80°C in an oven for 5 hours. To prepare Mg doped ZnO, NaOH was

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added to a mixture of 0.1 M Zinc sulphate and 0.01 M of Magnesium sulphate solution and same procedure was repeated. The obtained samples were calcined in air at 400^o C for 2 hours to get Mg-ZnO nanoparticles.

The diffraction patterns for the prepared Mg-ZnO nanoparticles were recorded on X-ray diffractometer (PHILIPS-1710) equipped with Cu Kα radiation (λ= 0.154 nM) with a scan rate of 0.02^o S^{-1}. The average particle size of nanoparticles was determined by using Scherer equation which is given by,

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where K is shape factor (0.89), λ is the x-ray wavelength (1.54 A^o), β is the peak broadening at half maximum and θ is the Bragg angle.

The surface morphology and the elemental analysis of the prepared nanoparticles was analyzed by scanning electron microscope (SEM) fitted with an energy dispersive X-ray spectroscopy (EDAX) (JEOL JSM-840A). The sample was coated with gold using low voltage sputtering and then analyzed under SEM operating at a voltage of 20 kV. A UV-VIS-NIR spectrophotometer (USB 4000, Ocean Optics– USA) was employed to measure the optical parameters. FTIR spectra were recorded using Thermo Nicolet Avatar 370 DTS in the range of 400 to 4000cm^{-1}.

RESULTS AND DISCUSSION

3.1 XRD analysis

Fig. IA illustrates a typical XRD spectrum of ZnO nanoparticles prepared by the precipitation method. Six major diffraction peaks were seen at 31.7, 34.6, 36.2, 47.6, 56.5, 62.9 and 68.0, which can be assigned to diffraction from (100), (002), (101), (102), (110), (103) and (112) planes respectively, according to the data base in JCPDS card (No-780-0075). This revealed that the resultant nanoparticles were pure ZnO with a hexagonal structure. No impurities could be detected in this pattern, which implies hexagonal phase ZnO nanoparticles could be obtained under the current synthetic route. Fig 1B depicts the XRD pattern of Mg doped ZnO nanoparticle. Three diffraction peaks were seen at 16.2, 32.6 and at 58.9, which can be assigned to diffraction from (111), (310) and (221) planes respectively. The average crystalline size of MgO and Mg-ZnO was calculated using Scherer equation and was found to be 86 nm and 59 nm respectively.

3.2 SEM/EDAX Analysis

Fig 2 shows the SEM pattern of ZnO (A) and Mg-ZnO (B) nanoaprticle. The shape of the ZnO nanoparticle obtained is granular and well dispersed. The Mg-ZnO nanoparticle are flake like structures. Fig 3 shows the EDAX spectrum of Mg-ZnO nanoparticle. The stoichiometry of sample was examined by EDAX spectrum and Zinc, Oxygen and Magnesium signals have been detected, suggesting that the nanoparticle is only made up of Zn, O and Mg. We did not see the presence of any foreign element in the compound and these results indicated that Mg-ZnO nanoparticle contains 100% Mg-ZnO.

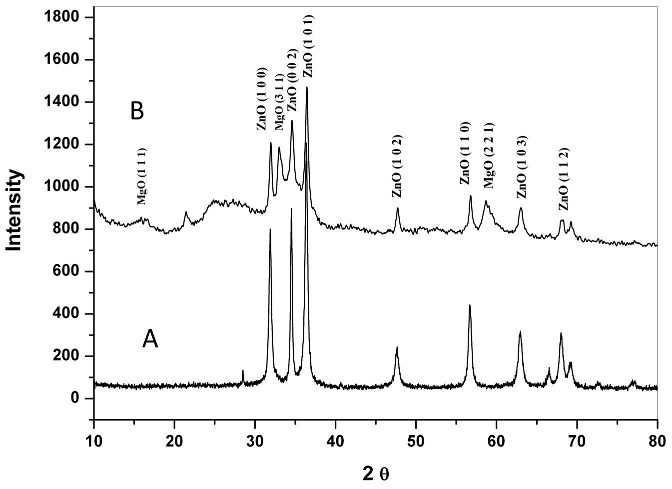

Fig. 1 XRD pattern of ZnO (A) and Mg-ZnO (B) nanoparticles calcined at 400^{0}C.

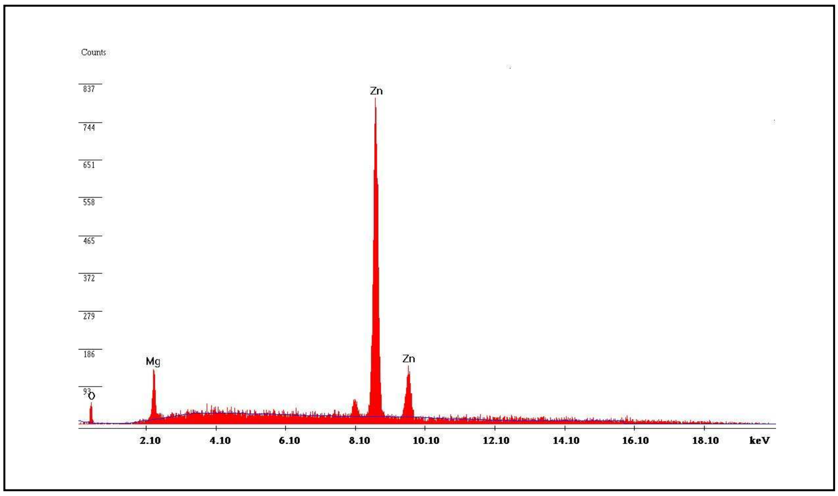

Fig. 2 FESEM pattern of MgO (A) and Mg-ZnO (B) nanoparticles.

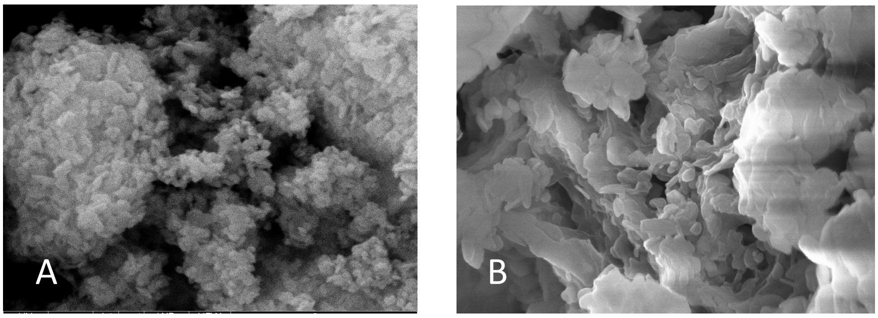

Fig. 3 EDAX spectra of Mg-ZnO nanoparticle

3.3 FT-IR spectroscopy

Fig 4A and B shows the FT-IR spectrum of ZnO and Mg-ZnO nanoaprticles recorded in the range of 500 to 4000 cm^{-1}. The KBr technique has been used to record the spectra. Fig 3A shows the FT-IR spectrum of ZnO nanoparticle. The band located near 600 cm^{-1} can be attributed to the Zn-O stretching mode. The band at 3200 to 3600 cm^{-1} corresponds to the stretching vibration of –OH bond and at 1680 cm^{-1} which appears at wavelength just half of 3200 to 3600 cm^{-1} has been assigned to the first overtone of fundamental stretching mode of –OH. These stretching vibrations correspond to the water molecule bound on the surface of sample. The band at 1435 cm^{-1} (B) is attributed to the Mg-O stretching vibration [29] and it is absent in case of ZnO.

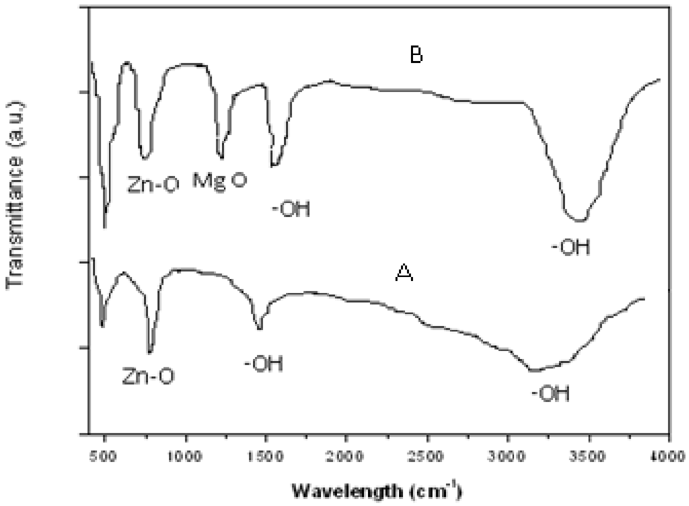

Fig. 4 FT-IR spectra of ZnO (A) and Mg-ZnO (B) nanoparticle.

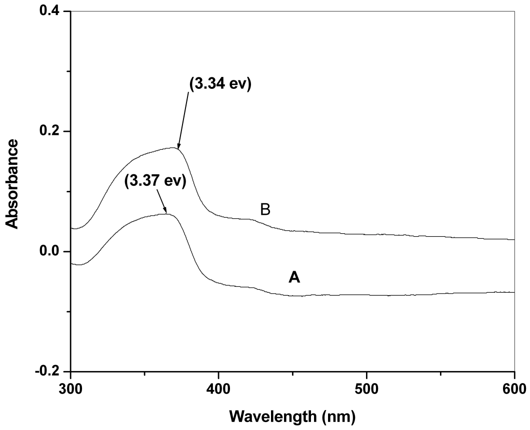

Fig. 5 UV-Vis spectra of ZnO (A) and Mg-ZnO (B) nanoparticle

3.4 Uv-Vis studies

Fig 5A and 5B shows the UV-Vis spectra of ZnO and Mg-ZnO nanoparticle obtained by precipitation method. ZnO and Mg-ZnO shows the absorption peaks at 364 and 372 nm respectively. The small shift in the absorption is attributed to the doping of Mg to ZnO. The band gaps (E_g) of ZnO and Mg-ZnO were calculated by using the formula $E=hc/\lambda$, where h is plank's constant, c is the velocity of light and λ is the wavelength. The band gap of ZnO and Mg-ZnO were found to be 3.38 eV and 3.34 eV nm respectively.

CONCLUSION

ZnO and Mg-ZnO have been synthesized using simple, inexpensive precipitation method by using CTAB as surfactant. The average crystalline size of ZnO and Mg-ZnO was found to be 86 and 59 nm respectively. The optical band gap of doped and undoped was studied. The band gap of doped ZnO was shifted slightly towards longer wavelength region.

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