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Studies on the Structural, Optical and Magnetic Properties of Al doped ZnO Nanoparticles

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Abstract : Zinc oxide (ZnO) and Al doped zinc oxide (AZO) nanoparticles were synthesized by reflux method at 100 °C. X-ray diffraction results showed that Al doping decreases the average crystallite size of ZnO nanoparticles. Fourier transform infrared spectra were recorded to analyze the effect of Al doping on the vibrational frequencies of ZnO nanoparticles. Scanning electron microscopic investigation revealed that the surface morphology of ZnO nanoparticles is significantly modified by Al doping. Energy dispersive spectroscopy confirmed the presence of Al in AZO nanoparticles. The optical absorption measurement indicates that the absorption band edge is slightly shifted to higher wavelength region after Al doping. The calculated band gap value decreases from 3.37 to 3.36 eV. Photoluminescence spectra revealed that the emission peak intensity decreased by Al doping. Magnetic measurement demonstrates that the saturation magnetization of AZO nanoparticles decreased when compared with that of ZnO nanoparticles.
Keywords: Nanoparticles; Chemical synthesis; Powder diffraction; Photoluminescence spectroscopy; Dielectric properties

Introduction

Over the past few years many researchers have investigated on the preparation and characterization of II-VI semiconductor nanomaterials because of their excellent electrical and optical properties[1,2]. Especially, semiconductor nanoparticles have attracted much attention in many areas of potential applications such as light emitting diode (LED), solar cells, gas sensors, optical waveguides, piezoelectric transducers, catalysts and luminescent oxides[3,4]. Zinc oxide (ZnO) is one of the promising semiconductors used in the fabrication of optoelectronic devices operating in blue and ultraviolet region due to its wide direct band gap (~3.37 eV), large exciton binding energy (60 meV) and high electron mobility (100 cm^2 V^{-1} s^{-1})[1,5]. Several synthetic techniques such as reflux[3], auto-combustion[5], sol-gel[6], polymer pyrolysis[7], hydrothermal[8] and spray pyrolysis[9] have been employed for the preparation of ZnO nanostructures. Among them, process of reflux is particularly attractive because this method differs from traditional sol-gel method in two aspects: a) no expensive alkoxide reactants are necessary and b) no need of higher temperature calcinations to produce final product.

However, it is important to understand how the dopants influence the physical properties of ZnO nanomaterials because the addition of small amount of impurity effectively modifies the properties of a

material. Among the various dopants Al, Ga and In have been demonstrated to be the most suitable dopants[10] for ZnO nanomaterials. Al doped ZnO (AZO) nanoparticles have been used as transparent conductive paste because they are both conductive and transparent in the visible region[11]. Moreover, doping into ZnO lattice can be achieved by replacing Zn^{2+} ions by other ions with higher valency such as In^{3+}, Ga^{3+} and Al^{3+} to enhance the optical and electrical properties of ZnO[12]. The doping level depends on its electro-negativity and ionic radius but it is also strongly influenced by the method of synthesis[13]. So far, lot of works have been reported for the preparation of AZO nanoparticles by various methods[6,8,9,10,11,13,14]. The synthesis of fine particles of ZnO at 100 °C using reflux method is reported[3]. But, no systematic studies are available for the preparation of AZO nanoparticles by reflux method. Thus, the aim of the present work is to synthesize ZnO and AZO nanoparticles by reflux method and to study the effect of Al doping on the structural, morphological, optical and magnetic properties of ZnO nanoparticles.

Experimental

Materials preparation

ZnO and AZO nanoparticles were prepared by reflux method from high purity nitrates of Zn and Al. Zn $(NO_3)_2.6H_2O$ (4 g) was dissolved in 60 ml of double distilled water. A small amount of NH_4OH was slowly added drop-wise into the aqua solution of Zn $(NO_3)_2.6H_2O$ until the formation of gel. Then the gel was thoroughly washed with double distilled water and transferred to a flask fitted with a water condenser. The gel temperature was maintained at ~100 ˚C and continuously stirred for 6 h. After the reaction, white precipitate deposited at the bottom of the flask was filtered and dried at 50 ˚C for 24 hours. For the preparation of AZO nanoparticles the same procedure was followed by adding the Al $(NO_3)_3.9H_2O$ (0.4 g) into the Zn $(NO_3)_2.6H_2O$ (3.6 g) solution.

Characterization

X-ray diffraction (XRD) pattern with CuKα radiation was recorded using Rigaku diffractometer to confirm the formation of ZnO and AZO. Fourier transform infrared and scanning electron microscopic studies were carried out to analyze the effect of Al doping in molecular structure and surface morphology of ZnO nanoparticles, respectively. Energy dispersive spectroscopy (EDS) measurement was carried out to analyze the elemental composition of the synthesized materials. Optical absorption spectra of ZnO and AZO nanoparticles were recorded using UV-1800 Shimadzu spectrophotometer. Photoluminescence (PL) spectra were recorded using Cary Eclipse fluorescence spectrometer with a Xe lamp (15 W) as an excitation source. Magnetic measurements were carried out using vibrating sample magnetometer (VSM) (Lakeshore-7404) at room temperature with the maximum applied magnetic field of ±15 kOe.

Results and discussion

X-ray diffraction analysis

X-ray diffraction patterns recorded for the synthesized ZnO and AZO nanoparticles are presented in Fig. 1. The diffraction pattern of both the samples was compared with JCPDS data (card no: 891397)[16] and indexed, which confirms the hexagonal wurtzite structure of ZnO (space group $P6_3mc$). In the present work, no additional phases are observed which indicate the hexagonal wurtzite structure of ZnO is not disturbed by Al substitution.

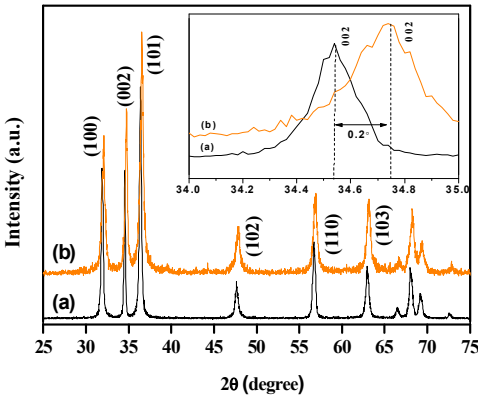

Figure 1: XRD patterns of (a) ZnO and (b) AZO nanoparticles

The strong and sharp peaks indicate that the synthesized nanoparticles are well crystallized. From the fullwidth at halfmaximum (FWHM) value of XRD peaks the average crystallite size of ZnO and AZO nanoparticles was calculated using Debye-Scherrer relation[10] $D = k\lambda/(\beta\cos\theta)$, where λ is the wavelength of X-rays used (1.5405Å), k is Scherrer constant (0.9, assuming that the particles are spherical), β is the fullwidth at halfmaximum in radians and θ is the angle of diffraction. The calculated average crystallite size lies in the range of 21-42 nm for ZnO and 17-29 nm for AZO nanoparticles, respectively. The diffraction peaks of AZO are much wider than the corresponding peaks of ZnO and the intensity of XRD peaks of AZO decreases when compared to that of ZnO, which indicate the decrease of crystalline quality when Al is doped into ZnO lattice[10]. Further, center of all diffracted peaks of AZO has a slight shift towards higher value of 2θ compared to that of ZnO. The (002) peak of AZO slightly shifts about 0.4° from the corresponding value of ZnO is reported[11]. 0.18° shift of (002) peak in Ni doped ZnO from that of the ZnO is reported[17]. In the present work, (002) peak of AZO shows 0.2° shift towards the higher value from the corresponding value of ZnO as shown in the inset of Fig. 1. This is due to the effect of lattice shrinkage by the replacement of Zn^{2+} (ionic radius 0.74Å) by Al^{3+} (ionic radius 0.53Å).

Fourier transform infrared spectral analysis

Fig. 2 shows the FTIR spectrum of ZnO and AZO nanoparticles recorded in the range of 400-4000 cm^{-1} using KBr pellet method. From the Fig. 2a, a strong absorption peak observed at 473 cm^{-1} corresponds to Zn-O stretching vibration[18]. Also, we have observed the strong absorption peaks at 893 cm^{-1} and 1378 cm^{-1} are assigned to the presence of carbonate moieties[19] which generally observed when FTIR measurement are carried out in air atmosphere. Furthermore, the vibrational frequencies observed at 1629 cm^{-1} and 3393 cm^{-1} are assigned to the formation of O-H bending and stretching vibrations, respectively. In the case of AZO nanoparticles, three strong absorption peaks were observed at 450 cm^{-1}, 1383 cm^{-1} and 3452 cm^{-1}. The peak appeared at 450 cm^{-1} indicates the presence of Zn-O stretching vibration[19].

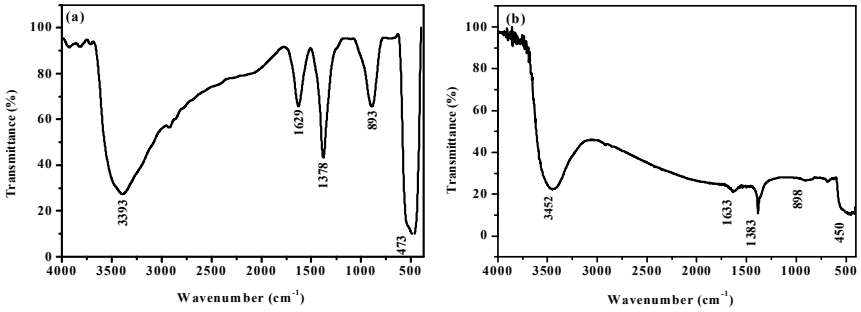

Figure 2: FTIR spectra of (a) ZnO and (b) Al doped ZnO nanoparticles

The broad and weak absorption peaks centered at 3452 cm^{-1} and 1633 cm^{-1} are attributed to O-H stretching and O-H bending vibrations, respectively[19]. The characteristic absorption band of Al-O stretching mode is observed between 580 and 620 cm^{-1} [8]. But, in the present work, we didn't observe the peaks related to Al-O mode of vibration. On the other hand, for ZnO nanoparticles the absorption peaks at 1629 cm^{-1} and 893 cm^{-1} show a strong absorption but AZO nanoparticles exhibit weak absorption peaks due to incorporation of Al into ZnO. Thus, the change in peak intensity of FTIR spectrum is due to the effect of Al doping into the ZnO nanoparticles.

SEM with EDS analysis

Scanning electron microscopic (SEM) images of ZnO and AZO nanoparticles are shown in Figs. 3a and 3b, respectively. Fig. 3a indicates that the prepared ZnO sample consists of nearly spherical shaped nanoparticles with the existence of soft agglomeration. SEM results show that the size of agglomerated average ZnO nanoparticles is approximately 150 nm. Fig. 3b reveals the distribution of AZO nanoparticles with their size and shape on its surface which differ from that of ZnO nanoparticles. This may be attributed to the effect of Al doping in ZnO. Inset of figures 3a and 3b show the typical energy dispersive spectrum (EDS) of ZnO and AZO nanoparticles, respectively. EDS results show the sharp peaks of Zn, Al and O thus confirming the presence of Al in the AZO nanoparticles.

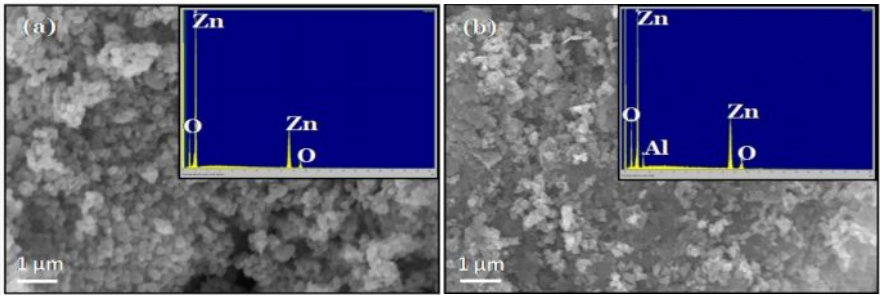

Figure 3: SEM images of (a) ZnO and (b) AZO nanoparticles. (inset) EDS spectra of (a) ZnO and (b) AZO nanoparticles

UV-vis. spectral analysis

Fig. 4 shows the UV-vis. absorption spectra of ZnO and AZO nanoparticles. From the figure, it is clearly seen that the strong UV emission observed at 367 and 369 nm for ZnO and AZO nanoparticles, respectively, which indicates that the absorption band edge is slightly shifted from lower wavelength to higher wavelength region which may be due to the doping of Al can influence the UV peak position of ZnO nanoparticles. Further, the band gap calculated from the absorption spectra was found to be 3.37 eV (367 nm) and 3.36 eV (369 nm) for ZnO and AZO nanoparticles, respectively. The band gap (3.37 eV; 367 nm) calculated from ZnO nanoparticles from the present study has slightly blue shifted when compared with that of the band gap (3.32 eV ; 373 nm) of bulk ZnO nanomaterials which may be attributed to the reduction of particles size[14].

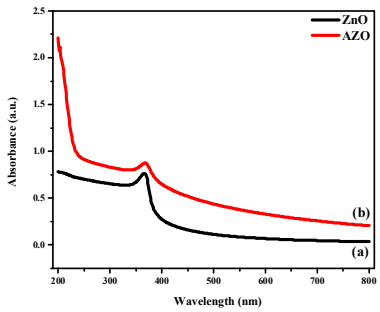

Figure 4: Optical absorption spectra of (a) ZnO and (b) AZO nanoparticles

Photoluminescence studies

The room temperature photoluminescence spectra recorded for ZnO and AZO nanoparticles are given in Fig. 5. The PL spectrum of ZnO nanoparticles exhibits the four emission peaks appeared at 360 nm, 391 nm, 411 nm and a sharp emission peak at 494 nm. The weak and strong emission peak observed at 360 and 391 nm, respectively which is assigned to the UV emission.

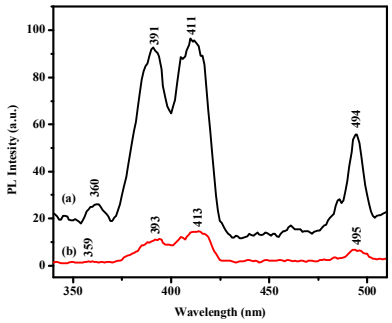

Figure 5: Room temperature PL spectra of (a) ZnO and (b) AZO nanoparticles

Generally, the UV emission should be attributed to near band-edge emission of the wide band gap of ZnO and originated due to the free exciton recombination between the photogenerated electrons in conduction band and holes in the valance band[14]. The near band edge emission at 386 nm was attributed to the free exciton recombination in ZnO is reported[10]. The strong emission peak at 411 nm arises due to violet emission. In

addition, a sharp blue emission peak observed at 494 nm corresponds to the single ionized oxygen vacancies in ZnO and resulted from the recombination of a photon-generated hole with the single ionized charge state of the defects[21]. As the Al is introduced into ZnO, the intensity of the emission peak is decreased when compared with that of ZnO which indicates that the number of oxygen vacancies decreased and UV emission peak position of AZO experiences a slight shift from 360 nm to 359 nm.

Magnetic properties

The hysteresis loop of ZnO and AZO nanoparticles are shown in Fig. 7. From the figure, it is observed that both the prepared nanoparticles show a ferromagnetic nature at room temperature. Generally, the room temperature ferromagnetism observed in ZnO and AZO nanoparticles mainly depend on the method of preparation and number of oxygen vacancies because the presence of oxygen vacancy plays an important role in altering the magnetic behaviour[22].

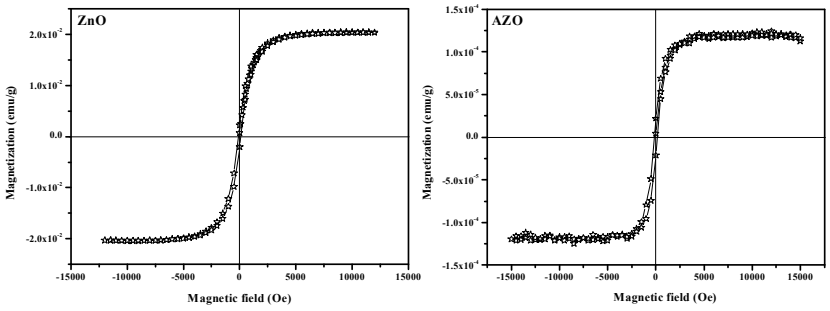

Figure 7: Room temperature hysteresis loop of (a) ZnO and (b) AZO nanoparticles

The ferromagnetic behaviour of AZO nanoparticles by sol-gel method for different Al doping concentrations is investigated[6]. They have reported that the ferromagnetism in ZnO nanoparticles induced by Al doping, a non-magnetic element. Also, they reported that the Al doping increased the number of oxygen vacancies and hence the ferromagnetic behaviour induced in ZnO nanoparticles. Hence, in the present work, room temperature ferromagnetic properties for pure ZnO as well as AZO nanoparticles are studied. Moreover the saturation magnetization (M_s), coercivity (H_c) and retentivity (M_r) of the prepared ZnO and AZO nanoparticles are estimated to be about $2.0x10^{-2}$, $2.1x10^{-4}$ and 114 Oe, and $2.1x10^{-3}$, $1.2x10^{-4}$ and 94 Oe, respectively. Also, it is observed from the results, the decrease in magnetic properties of AZO nanoparticles may be due to the number of oxygen vacancies decreased by Al doping[6].

Conclusion

ZnO and AZO nanoparticles were synthesized by reflux method. XRD results revealed that no additional peaks or secondary phase formation by Al doping in ZnO nanoparticles. FTIR results furnish the structural confirmation and the effect of Al doping on the vibrational frequencies of ZnO. SEM images show that the shape, size and distribution of particles on the surface of ZnO are influenced by Al doping. EDS confirms the presence of Al in the AZO nanoparticles. The optical absorption study reveals that the absorption band edge is slightly shifted to higher wavelength region after Al doping. The strong UV emission observed from the photoluminescence studies which indicate that the synthesized nanoparticles are good in optical quality. Room temperature ferromagnetic behaviour observed for ZnO and AZO nanoparticles reveals that the magnetic properties such as saturation magnetization and retentivity of the prepared AZO nanoparticles decreased when compared with that of pure ZnO nanoparticles.

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