Influence temperature and dopant ratio on Zn(x)Mg(1-x)O nanoparticles by solvothermal method

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Abstract

In recent years, ZnMgO semiconductor alloys with a direct band gap tunable between 3.37 eV and 7.8 eV become one of the suitable materials for fabrication of ultra violet detectors. In this paper various high quality mixed oxides ZnMgO heterostructure nanoparticles have prepared by using solvothermal method and characterized with XRD, TEM, FT-IR, UV-Vis and Photoluminescence . In the XRD spectra we observed that the two prominent peaks of (002) plane at 34.20° and (220) plane at 62.40° which belongs to wurtzite of ZnO and Rock salt structure of MgO respectively. Approximately at the angle of 62.40° (103) plane of ZnO overlaps for unannealed samples. For the annealed samples no significant peaks has observed and the (002) peak of ZnO overlaps with the (220) peaks of cubic MgO. The TEM image indicates with exist of ZnMgO with the size 40-90 nm which form bead type of oriental aggregation throughout the region. Functional group has analysed using FT-IR spectra, a deep sharp bend was found around 470 cm^{-1}. In the PL we observed a systematic red shift in their PL peak position due to quantum confinement of carriers in nanoparticle quantum structures. For ZnMgO coaxial nanoparticle heterostructure, PL intensity was significantly decreased presumably due to surface passivation and carrier confinement.

Keywords: ZnxMg1-xO nanoparticles, Influence of temperature and ratio, TEM, XRD.

1. Introduction:

One-dimensional (1D) nanorod heterostructures which show composition modulation along the axial or radial direction have fashioned into versatile building blocks for many electronic and photonic nanodevice applications [1]. ZnO nanostructures have studied extensively for possible practical applications to nanometer-scale electronics and photonics including transistors, gas sensors, field emission devices, ultra-violet (UV) sensors, piezoelectric applications, biosensors and light emitting diodes (LEDs) [2]. Homogeneous carbon nanotubes and nanowires have already been

employed in various nanoscale devices. However, the ability to synthesize nanoscale heterostructures with well-defined crystalline interfaces opens up many new device applications [3]. ZnO materials have many fascinating properties such as a large bandgap energy corresponding to the UV region, and a possibility to magnetic semiconductors [4]. Recently, researchers have paid much attention to ZnO nanoparticles for their quantum confinement effects [2]. One of the interesting features of ZnO is the possibility to tune its band gap by substituting (alloying) bivalent metals like Cd and Mg in place of Zn to its band gap. While Cd is known to reduce the band gap, Mg substitution leads to enhancement of band gap [5]. As an important wide-band-gap semiconductor, ZnO shows attractive potential in UV laser diodes and light emitting diodes, because its large exciton binding energy (~60 meV) allows even a room-temperature excitonic emission [6]. ZnO based devices such as ZnO/ZnMgO or ZnO/ZnBeO optimize the device performance [7]. ZnO is nontoxic and has high transparency and high crystallinity [8]. Due to its wide direct band gap, the ZnMgO material system is an excellent choice for optoelectronic devices with part of the spectrum. ZnMgO also possesses unique figure of merit such as availability of lattice matched single crystal [9]. The wurtzite type ZnMgO alloy possesses attractive properties for possible applications in optoelectronic and display devices. The ionic radius of Mg^{2+} (0.57A°) is similar to that of Zn^{2+} (0.60A°), so replacement of Zn by Mg should not cause a significant change in lattice constants. By droping suitable Mg into ZnO it may possible to obtain a ternary ZnMgO with a wider band gap. However the large crystal structure dissimilarity between wurtzite hexagonal ZnO and rocksalt-cubic MgO can cause unstable phase mixing [10]. The Mg atoms has incorporated into ZnO atoms tends to decrease both the amount of interstitial oxygen vacancies and the electron density [8]. The oxygen vacancy is a deep donor. In p-type ZnMgO, V_O is stable in +2 and +1 charge state, and in n-type ZnMgO in the neutral charge state [11]. Zn, Mg and O is at low-cost and a large amount of deposit on the earth is favorable [12]. When the Mg and Zn atoms bond to O atom, the Mg atom is easier to lose electrons than Zn atom due to the different Pauling electronegativities [13]. The doping of ZnO with a metal could change its properties; doping with the II elements, (Cd,Mg) may modulate the value of the band gap and increase the UV luminescence intensity doping with the III elements, (Al, Ga, In) doping could influence electrical properties, such as electrical resistivity or carrier concentration [14]. The near band edge (NBE) emission intensity increased further and had greatly suppressed the deep level emission [15]. Semiconductors derive their great importance from the fact that their electrical conductivity can greatly altered via external stimulus (voltage, photon, flux, etc.,) making semiconductors critical parts of different kinds of electrical circuits and optical applications. Optical properties of the quantum dots can easily tuned with the change in size of the nanomaterial. So the different coloured emission can observed from the same material. The room temperature PL and absorption spectra of ZnMgO have tuned by adjusting the Mg concentration while the annealing temperature increases the diffused concentration of Mg increases [16]. The increasing Mg concentration also affects the deep level emission DLE region of the spectra [17]. There are two basic recombination mechanisms in semiconductors, namely radiative recombination and non-radiative recombination. In a radiative recombination event, one photon with energy equal to or near the band gap energy of the semiconductor has emitted [18]. The weak PL spectrum due to thermal annihilation suggests that non radiative recombination, rather than radiative recombination,is dominant at room temperature[19]. In the PL spectrum ZnO typically consists of a UV

emission band and a broad emission band. At room temperature, The UV emission band which has related to a near band-edge transition of ZnO, namely, the free excitons recombination. The broad emission band literally between 420 nm and 700 nm observed nearly in all samples regardless of growth conditions had called deep level emission band (DLE)[18]. Large numbers of methods for the synthesis of ZnO have reported in the literature, such as precipitation, microemulsion, non-microemulsion, ultrasonic radiation precipitation, microwave irradiation, mechanical milling, and solution combustion and sol–gel methods. Different physical methods such as pulse laser deposition, vapor phase transparent process, chemical vapor deposition, and vapor transparent deposition have developed for the nano-ZnO preparation. To date, a number of research workers have reported the synthesizing of nanostructured ZnO powders with spherical, rod-like, flower-like and sheet-like structures [20]. In the present work, we have attempted to prepare, for the first time, $Zn_{1-x}Mg_xO$ nanoparticles (quantum dots) by using some simple microwave assisted solvothermal methods and characterize the prepared samples. The results have reported here and discussed.

2. Experimental

2.1 Preparation of ZnxMg1-xO nanoparticles by solvothermal method

The mixed oxides were prepared as solutions and polycrystalline nanoparticle powders with various compositions (x = 0.4, 0.5, 0.6 & 0.02) using solvothermal method. The precursors used for this preparation are magnesium acetate, urea and zinc acetate and the solvent ethylene glycol. After weighing the proper amount of the constituents, they were all put together in the round bottom bowl. The proper constituents of $Zn_{1-x}Mg_x$ and urea have taken as 1:3 molar ratio. And the 50 ml of Ethylene Glycol has placed in a round bottom bowl. The mixture was stirred at room temperature for 30 minutes a homogeneous solution had obtained. A domestic (electroflux 800 W) microwave oven operates at 2.45 GHz and a six stage variable power. Solution was refluxed for the necessary time (20 min) in such way to evacuate all the solvents in the bowl. The contents allowed to transfer to the beakers and they had washed at least 5 or 6 times with double distilled water. Some fine deposits had settled down at the bottom of bowl, which could be clearly seen. Then the settled down powder was filtered using Whatmann filter paper and the collected powder has allowed to dry. After this process, the yields have washed with acetone. The result was to bring out of fine particles of $Zn_{1-x}Mg_xO$.Fig.1 shows flow chart diagram of ZnxMg1-xO preparation.

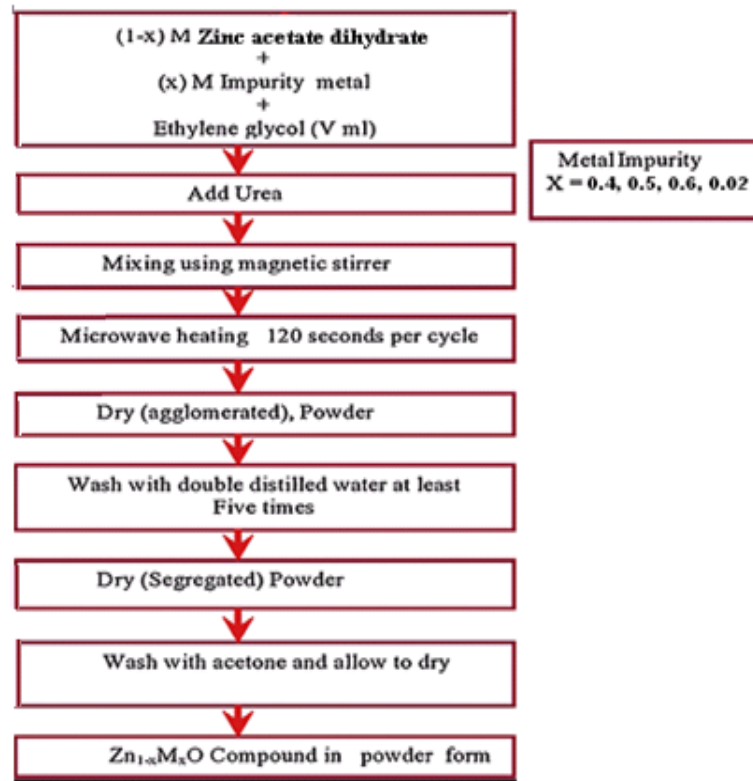Fig. 1.Flow chart diagram of ZnxMg1-xO preparation

3. Results and Discussions

3.1 XRD pattern of ZnxMg1-xO nanoparticles

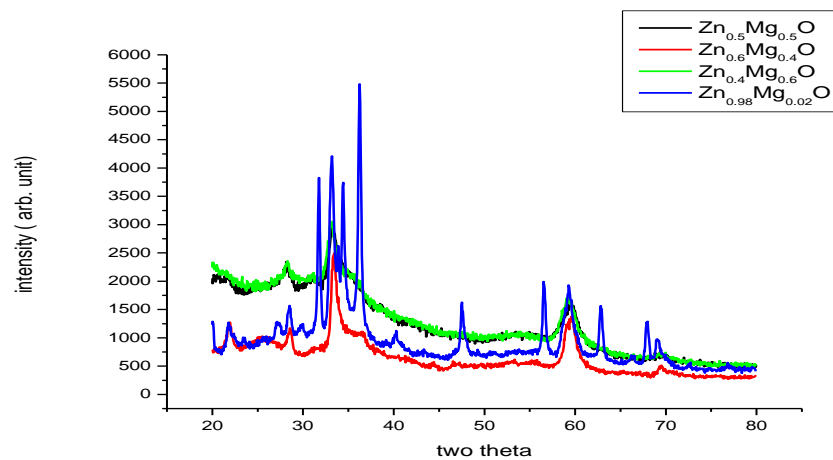XRD pattern of unannealed and annealed samples are given in Fig.2 and Fig.3 respectively.
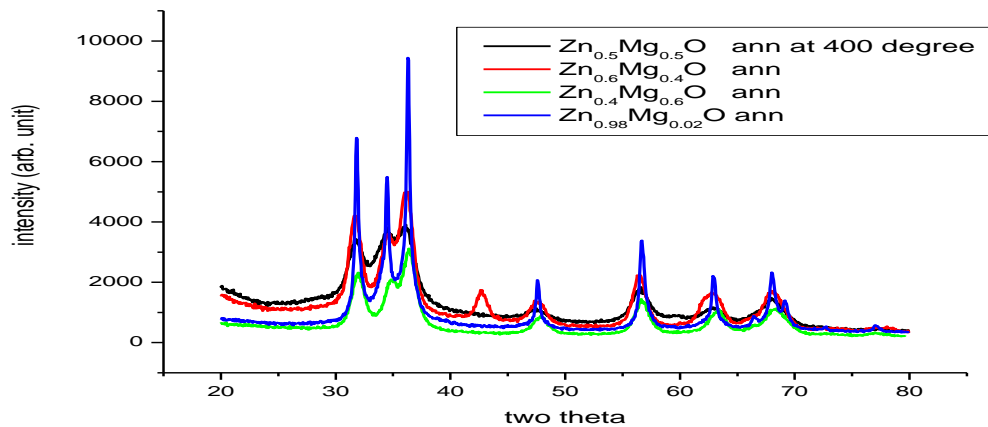

Fig.2 XRD pattern of unannealed ZnMgO samples.

Fig. 3 XRD pattern of four annealed ZnMgO samples at 400°C.

For the unannealed samples it has found that except the $Zn_{0.98}Mg_{0.02}O$ all the other three samples show only two prominent peaks of (002) at 34.20° and (220) planes at 62.40°. Of these two peaks the (002) peak angle belongs to hexagonal wurtzite structure of ZnO and (220) belongs to cubic structure of MgO. Also about at the angle 62.4° (103) plane of ZnO overlaps. For the annealed samples at 400°C, the peaks are almost similar for all the four samples and no significant shifts of the peaks has observed. As seen for the unannealed samples the (002) peak of ZnO overlaps with the (220) peaks of cubic MgO in the three samples except the $Zn_{0.98}Mg_{0.02}O$. The particle size was calculated using Debye–Schererformula,

$$D = \frac{0.9\lambda}{\beta \cos\theta} - - - - - - - (1)$$

where λ is the wavelength for the K component of the employed copper radiation (1.54056A°), β is the corrected full width at half maximum (FWHM) and θ is the Bragg's angle. The grain sizes of the Magnesium doped ZnO unannealed nanoparticles have calculated in the ranges by using this formula are 233 nm,472 nm,294 nm & 52.33 nm for the samples x=0.5, 0.4, 0.6 & 0.02 respectively. The grain sizes of the Magnesium doped ZnO annealed nanoparticles have calculated in the ranges by using this formula are 559 nm,373 nm,200 nm & 22.60 nm for the samples x=0.5, 0.4, 0.6 & 0.02 respectively [8,14,20,22].

3.2 TEM image of ZnxMg1-xO nanoparticles

The sample for which made TEM measurements had dispersed in double distilled water and sonicated (50 W/cm²) for 5 min. The dispersed solution has dropped on a copper grid and allowed to dry overnight in ambience.

This was then analyzed with TEM. The grain sizes estimated using transmission electron microscope (using the 200 nm scale bar) was less than 20 nm, which is shown in Fig.4.
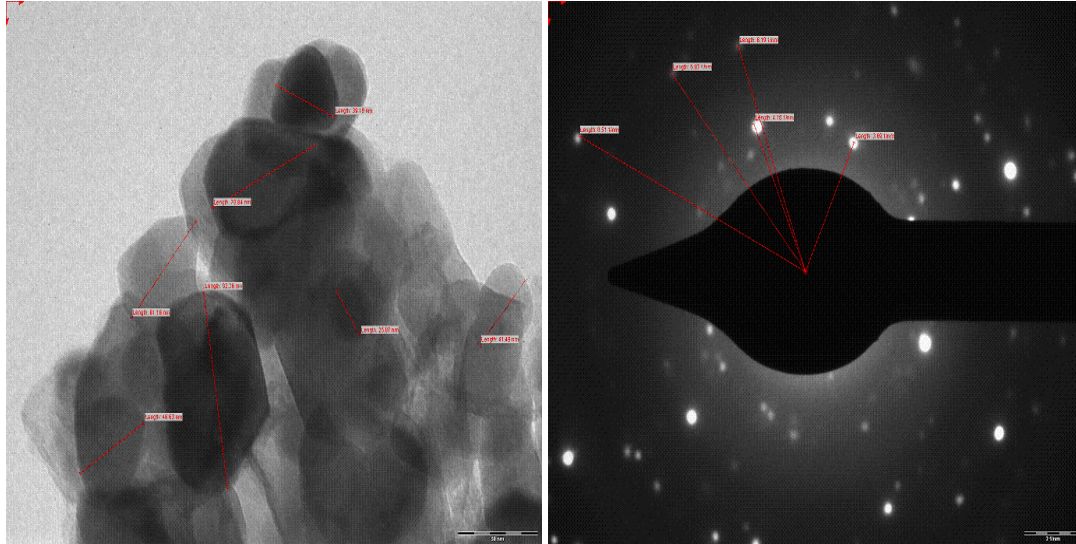

Fig. 4 TEM image and SAED pattern of ZnMgO samples at 400˚C.

The TEM image indicates with exist of ZnMgO with the size 40-90 nm which forms bead type of oriental aggregation throughout the region. The selected area electron diffraction (SAED) pattern Fig.4 shows the spot type pattern which is indicative with exist of single crystalline particles with the size 4-8 nm. No evidence has found more than one pattern, suggesting the single phase nature of the material [21].

3.3 FTIR spectra of ZnxMg1-xO nanoparticles

Functional group has analyzed using FT-IR spectra. It has shown in Fig .5. A deep sharp bend has found around 470 cm^{-1}. It might be due to the Zn-O co-ordination [13].
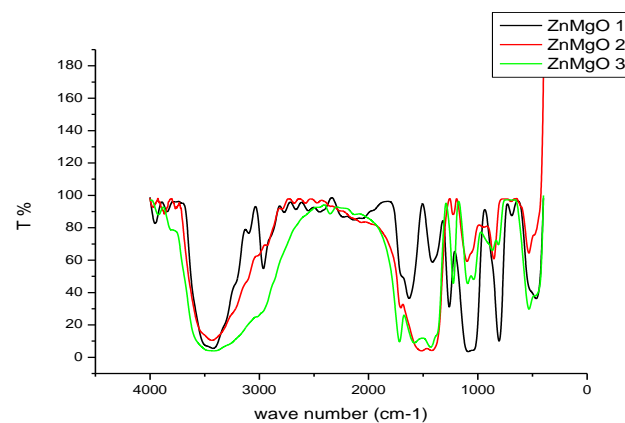

Fig. 5 FTIR pattern of ZnMgO samples at 400˚C.

3.4 UV-Vis absorption spectroscopy of ZnxMg1-xO nanoparticles

The optical properties of the Mg doped ZnO nanostructures have studied by UV-Vis absorption spectroscopy. From the Fig.6 The hump like structures of the UV-Vis spectra, the excitation wavelengths of all the four samples have fixed and the photoluminescence measurements have taken using the same.
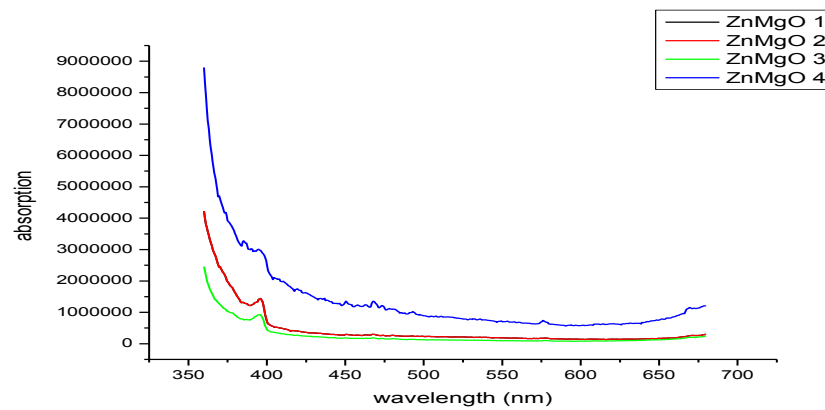

Fig. 6 UV-Vis absorption pattern of ZnMgO samples at 400˚C.

The direct optical band gap (Eg) of ZnMgO nanoparticles has determined by the relationship between the absorption coefficient (α) and the photon energy (hν). The E_g values were found to be 2.56, 2.59, 2.6 & 2.8 eV for the ZnMgO samples x=0.6, 0.5, 0.4 & 0.02 respectively.

3.5Photoluminescence of ZnxMg1-xO nanoparticles

Fig.7 shows the room temperature PL spectra of ZnMgO nanoparticles. PL spectra shows the UV emission band at 473-524 nm. Photoluminescence measurements confirmed the results of optical absorption UV-Vis spectrum studies. The UV emission was near-band-edge emission (NBE) caused by the exciton recombination [13]. The increase in band gap has attributed to the decrease of particle size of Mg-doped ZnO nanoparticles.
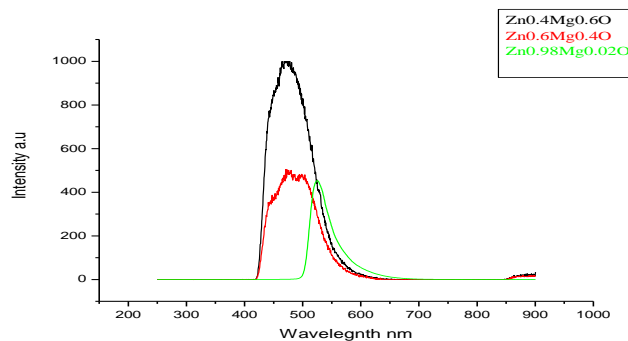

Fig. 7 PL Spectrum of ZnMgO samples at 400˚C.

7

Moreover, with the increase in Mg concentration, the band edge shifted towards the higher wavelength (lower energy side). The band edge emission showed a red shift with increasing levels of Mg ions [22].

4. Conclusion:

Zn1-xMgxO was prepared by solvothermal method. All the samples have tested for their structure using X-ray diffraction both for unannealed and annealed ones. The XRD patterns of the annealed samples shows prominent peaks without secondary phase of Mg for any ratio. Band gap energies have studied using the UV-vis spectra and they are in good agreement with the standard values. Having the excitation values for the different samples from UV-vis the photoluminescence studies were carried out. The TEM image indicates with exist of ZnMgO with the size 40-90 nm which forms bead type of oriental aggregation throughout the region. Functional group was analyzed using FT-IR spectra; a deep sharp bend was found around 470 cm^{-1}. In the PL we observed a systematic red shift in their PL peak position due to quantum confinement of carriers in nanoparticle quantum structures.

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