

Stabilization of structure in Mg doped ZnO – Its synthesis and characterization with PL studies

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Abstract: Mg doped ZnO is synthesized by nitriding at the 400°C. The synthesized material is characterized. XRD analysis shows the crystallite size of the synthesized material as 23.35 nm and also the secondary phase of MgO. SEM shows the morphology of the material, which is seen as flakes. EDAX confirms the purity of the material as well as the percentage of doping which is 2% Mg. FTIR vibrations confirm the presence of Zn, O and Mg. MgO has a cubic structure and when Mg is doped with ZnO, which has a tetragonal structure usually disrupts the structure. But, UV-DRS and PL studies show a small peak, at 381 nm, which is the characteristic peak for ZnO and red luminescence with two spectral emissions at 640 nm and 648 nm. The match 3 software, for XRD analysis was used which shows that the dopant Mg atoms also take tetragonal structure as that of ZnO structure. In this case, the dopant has increased the stability of the material, by changing its structure from cubic to tetragonal structure, which is confirmed by the red emissions from PL studies.

Key words: Nitriding, match 3, secondary phase, red luminescence, tetragonal

Introduction

ZnO is a broad band gap II-VI semiconductor having provocative properties. The interest in ZnO is fuelled and fanned by number of prospects in optoelectronic device applications owing to its wide band gap (3.3eV at 300 K), large bond strength and large exciton binding energy (60meV). Due to its vast areas of application, various synthesis methods have been employed to grow a variety of ZnO nanostructures, including nanoparticles, nanowires, nanorods, nanotubes, nanobelts, and other complex morphologies[1]. ZnO were found to be inhibiting strong bacterial growth properties [2]. Many methods have been used to prepare ZnO nano particles like sol-gel method [3], thermal decomposition, and chemical vapor deposition and alloy evaporation deposition method. Instead of single material, n-type and p-type materials has been used to improve the applications[4]. Among traditional n-type (IZO, ITO, doped ZnO, SnO and In₂O₃) and p-type (CuAlO₂ and SrCu₂O₂) materials, Indium tin oxide (ITO) has been

widely used for transparent conducting oxide (TCO) material due to electrical conductivity and optical transparency, but it has some disadvantages (high cost, low stability and toxicity). Therefore, recently doped ZnO have attracted extensive interest. The physical and chemical properties and applications of the ZnO are affected by the doping elements and concentration, and band gap modulation[5]. This strongly depends on the preparation method and condition. As a result, the ZnO was doped with elements (Al, Ga, In, Cu, Mg and so on) to increase electrical conductivity and transmittance in the visible range and stability against heat. ZnO generally present in the wurtzite hexagonal structure and MgO in a cubic phase[6]. When magnesium oxide is chosen as the dopant, it acts as a modifier oxide and enter into ZnO lattices. Thus, the oxygens of the modifier oxide disrupt the local symmetry of ZnO structure while the divalent magnesium ions (Mg^{2+} ions) take the interstitial positions in the vicinity of Zn^{2+} ions in the precipitation. But, when the Mg content increases it is difficult to obtain unique crystal structure. Such structural modifications yield the change in the optical band gap of zinc oxide nanoparticles. As magnesium is an alkaline earth metal, it is devoid of localized d levels, the complications with optical properties arising from the electronic structures much straighten out, and the alloy consequently provides a better scope so as to enhance the band gap of wurtzite ZnO. It is noteworthy that the ZnO doped with a transition metal oxide have recently received much attention by materials scientists owing to significant applications in the band gap engineering. Thus, the study on structural and optical characterization of the synthesized Mg doped ZnO nanoparticles is quite important for their practical applications.

Up to now, there are many techniques to synthesis Mg doped ZnO nanoparticles by complicated techniques and calcinated at various temperatures. In this present work the synthesis carried by nitriding and calcinated at the temperature 400° C. The structural and optical properties are studied.

2. Experimental Methods

Materials:

Zinc nitrate, magnesium nitrate, citric acid, urea, and poly ethanol glycol (Nice Company AR Grade) were purchased and used without further purification.

Experimental Section:

60 g of zinc nitrate was dissolved in a 75 mL of double distilled water which was mixed with 60 g of citric acid (dissolved in 10 mL of water) and 60 g of urea (dissolved in 10 mL of water) and kept in a magnetic stirrer for 10 min. After 10 minutes, 3.5% molecular weight of magnesium nitrate was taken and dissolved in 10 mL of water which was mixed with a zinc nitrate solution. This event was kept in a magnetic stirrer for one hour at a temperature of 80 °C. Then, 10 mL PEG (poly ethylene glycol) was added and again kept in the hot plate for 10 hours at a constant temperature. Later it was kept in muffle furnace for 400 °C of temperature up to 3 hours.

Instrumental Used:

The synthesized material were characterized using the instruments XRD of Scanning Mode 2 Theta/Theta of scanning type continuous scanning X-Ray 40 kV/30 mA and the data was recorded using $CuK\beta$ radiation. JEOL JSM 6510-LV scanning electron microscope with MOXTEK 550i thin film coated IXRF energy dispersive

spectrometer (EDAX) was used for morphological and for determining the percentage of elements present in the sample. The photo luminescence studies were done using LS 45 fluorescence spectrometer by PerkinElmer model. Reflection and transmission studies were done using JASCO UV-Vis DRS photometric mode V - 650 series model. The band gap of the material was studied using UV Spectrum-JASCO V-650 series of Kubelka-Munk model.

3.Results and Discussions

3.1 STRUCTURAL ANALYSIS

The XRD analysis is used to investigate the crystal structure of the sample. It is performed with $\text{CuK}\alpha$ irradiation of wavelength $\lambda=1.54 \times 10^{-10} \text{A}^\circ$ in the angular range 20-80°. The grain size can be calculated using Debey-Scherer's formula

$$D = K\lambda / \beta \cos\theta \text{ nm}$$

where θ is the diffracting angle, β is Full Width Half Maximum (FWHM) of the peak, K is the Dimensionless shape factor. The calculated parameters are shown in the table 1. The XRD pattern of the Mg doped ZnO is shown in the Fig 1. The diffracting peaks observed is corresponding to the standard XRD pattern of ZnO nanoparticles which are associated with the JCPDS card no 36-1451. The maximum intensity reaches at the [101] and the crystallite size at this angle is 23.35 nm. Secondary phases at [222][7] and [110][8] are attributed to the doping of Mg in ZnO. Both Mg and Zn have approximately the same ionic radii (0.57 Å for Mg and 0.60 Å for Zn)[9], MgO has a cubic structure and ZnO has a tetragonal structure. At 400°C, and in the present synthesis method, it is seen from Match 3 software that Mg ions which usually disrupts the structure of Zn which is tetragonal. It is also seen from the (Match 3 table) that the percentage of Mg is 64% and that of Zn is only 36%. But, the percentage of doping of Mg is only (3.5% molecular weight of Magnesium Nitrate) in ZnO, but, the calculated density which is 1.674 g/cm³ for Mg and for ZnO it is 5.725 g/cm³, which correlates well with the doping percentage. In general the crystal structure dissimilarity between wurtzite-hexagonal ZnO and rock salt cubic MgO can cause unstable phase mixing[10]. But the Match 3 software shows that the Mg⁺ ion changed its structure to the Zn⁺ion which is hexagonal in nature.

| S.NO | XRD Parameters | 400°C |
|------|-----------------------------|----------------------------------------|
| 1 | Crystallite size(D) | 23.35 nm |
| 2 | Micro Strain (ϵ) | 0.00506 |
| 3 | Dislocation density (S) | $18.3 \times 10^{14} (\text{nm})^{-2}$ |
| 4 | d-spacing | $2.39 \times 10^{-10} \text{m}$ |
| 5 | FWHM (β) | 0.374 |

Table 1 XRD parameters of synthesized Mg doped ZnO at temp 400°C

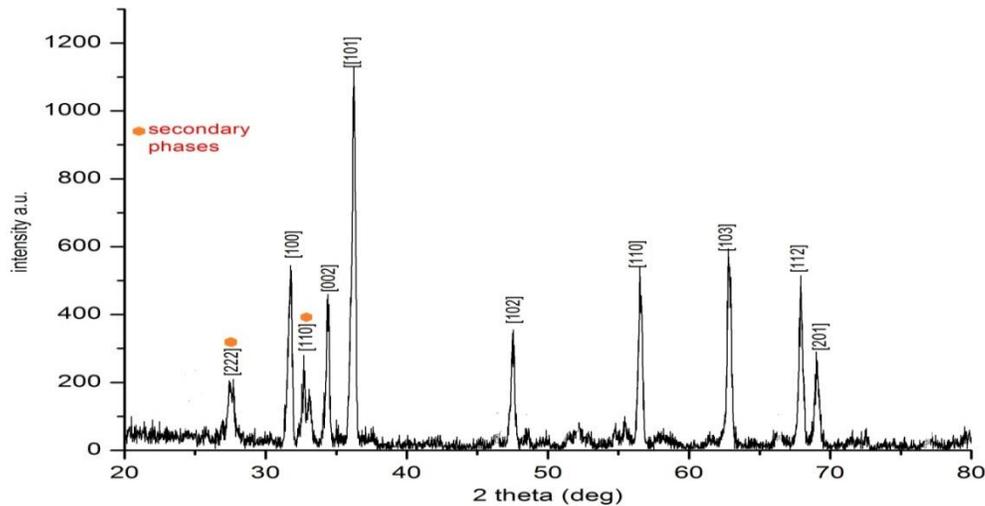


Fig 1 XRD pattern of synthesized Mg doped ZnO at temp 400°C

| <i>Magnesium (64.0 %)</i> | | <i>Zn O (36.0 %)</i> | |
|---------------------------|----------------------------|----------------------|---------------------------|
| Formulasum | Mg | Formulasum | ZnO |
| Entrynumber | 96-901-3062 | Entrynumber | 96-210-7060 |
| Figure-of-Merit | 0.810618 | Figure-of-Merit | 0.808555 |
| Total numberofpeaks | 32 | Total numberofpeaks | 36 |
| Peaksin range | 32 | Peaksinrange | 36 |
| Peaksmatched | 18 | Peaksmatched | 14 |
| Intensityscale factor | 0.38 | Intensityscalefactor | 0.35 |
| Spacegroup | P 63/m mc | Spacegroup | P 63/m mc |
| Crystalsystem | hexagonal | Crystalsystem | hexagonal |
| Unitcell | a= 3.2485 Å, c= 5.2772Å | Unitcell | a= 3.2417 Å c= 5.1876Å |
| Calc.density | 1.674 g/cm ³ | Calc.density | 5.725 g/cm ³ |

Match 3 Table for synthesized Mg doped ZnO at temperature 400°C

3.2 SEM(SCANNING ELECTRON MICROSCOPY): The morphology of ZnO particles is studied using SEM. Fig 2 represent the SEM pictures of ZnO particles. The high resolution SEM image shows the presence of crystalline particles. The shape of ZnO particle obtained is granular and well dispersed. Sometimes the surface properties of ZnO are influenced from the incorporation of dopant. Especially the amount and kind of dopant can play an important role on the surface properties. The Mg doped ZnO particles are flake like structures and inhomogeneous in nature.

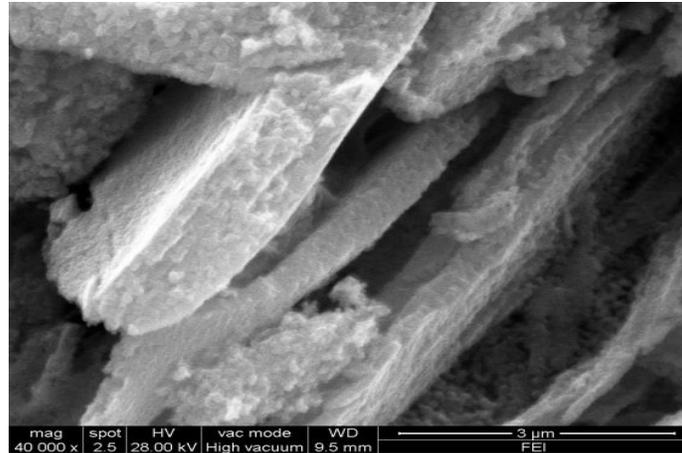


Fig 2 SEM pattern of Mg doped ZnO Nanopowders at temp 400°C

3.3 EDAX (ENERGY DISPERSIVE X-RAY): The EDAX graph Fig 3 shows that Mg disrupts and occupies the Zn site [11]. The elemental content in the synthesized sample has been determined with the help of energy dispersive X-ray analysis. The EDAX analysis exhibited clear peaks of only Zn, Mg and O elements, whereas no additional peaks were detected, which means there are no impurities. The percentage of Zn, Mg and O elements present is given in the table 2.

| Element | 400°C |
|---------|-------|
| Zn | 39.58 |
| O | 58.09 |
| Mg | 2.32 |

Table 2 The atomic percentage calculated for synthesized Mg doped ZnO at temperature 400°C

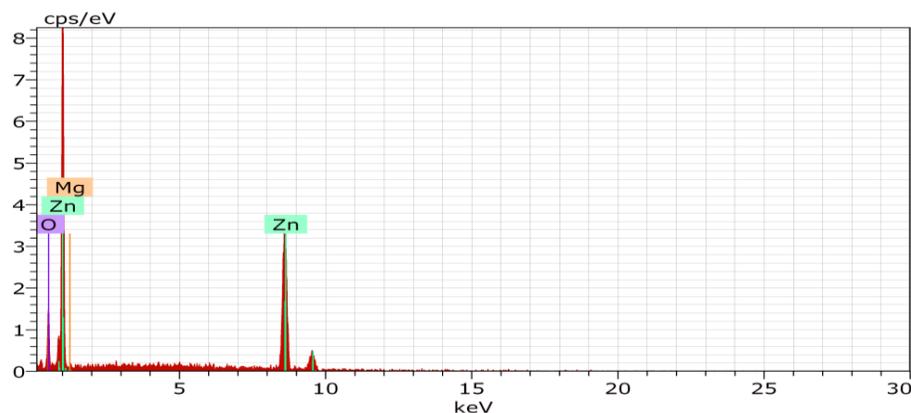


Fig 3 EDAX pattern for synthesized Mg doped ZnO at temperature 400°C

3.4 FTIR (FOURIER TRANSFORM INFRARED) SPECTROSCOPY: FTIR spectroscopy is performed in order to quickly establish the presence or absence of the various vibrational modes present in synthesized particles. The Fig. 4 shows the FTIR spectrum of the synthesized ZnO acquired in the range of 500-4000 cm^{-1} and the table 3 shows the interpretation values. The stretching of the spectrum is maximum at temperature 400°C, it might be due to the incorporation of Mg in ZnO lattice. Various modes of vibration are observed at different regions of FTIR

spectrum. The broad peak at 3418 cm^{-1} [12] indicated the -OH stretching vibrations. The band at 1492.44 cm^{-1} [13] is attributed to the Mg-O stretching vibration. The absorption at 861 cm^{-1} [14] is due to the formation of tetrahedral coordination of Zn. The presence of peaks at $523, 440\text{ cm}^{-1}$ [15] is the characteristic peaks of Zn-O stretching vibration. It is in the lower frequency side is due to some structural changes by doping with Mg[16].

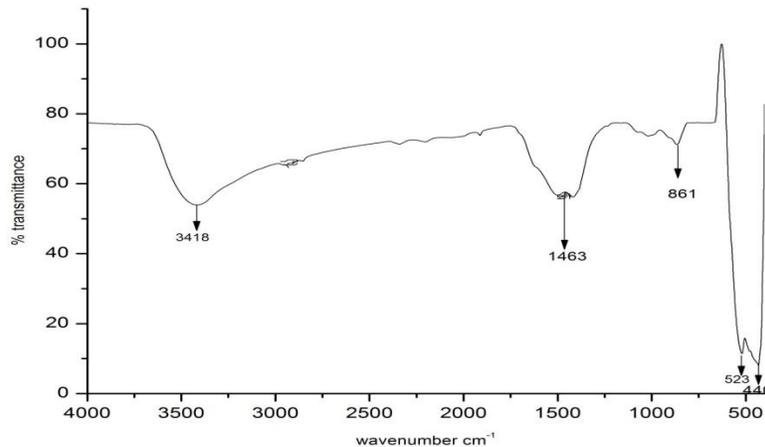


Fig 4 FTIR pattern for synthesized Mg doped ZnO at temperature 400°C

| 400°C | Assignment |
|-----------|----------------------|
| 3418(m-s) | O-H stretching |
| 1463 (m) | Mg-O stretching |
| 861 (w) | Weak Zn-O stretching |
| 523(w) | Zn-O stretching |
| 440(w) | Zn-O stretching |

Table 3 FTIR peak interpretation for synthesized Mg doped ZnO at temperature 400°C

3.5 UV-DIFFUSE REFLECTANCE SPECTRA: The UV diffuse reflectance spectra of synthesized ZnO is given in Figure 5. It is highly useful to determine the band gap energy of each sample. The reflectance edge is 317 nm for the temp 400°C. But slowly it shifted towards the red band emission and hence it indicates the incorporation of magnesium in the zinc oxide interstitial site. The sample shows that the reflectance is increasing from UV to visible range with more than 80% of reflectance. The bandgap energy calculation of ZnO material is performed based on the diffuse reflectance spectra by using Kubelka-Munk plot[17] shown in the Fig 6. The optical band gap has been calculated and found to increase from 3.18 eV for undoped ZnO[18] to 3.39 eV for Mg-doped ZnO, because MgO has a wider bandgap than ZnO[19]. This increase in the bandgap might be due to an increase in carrier concentration that blocks the lowest states in the conduction band, this effect is known as Burstein-Moss effect. Hence Mg^{2+} ions may be substituted for the Zn^{2+} ions without changing the ZnO structure.

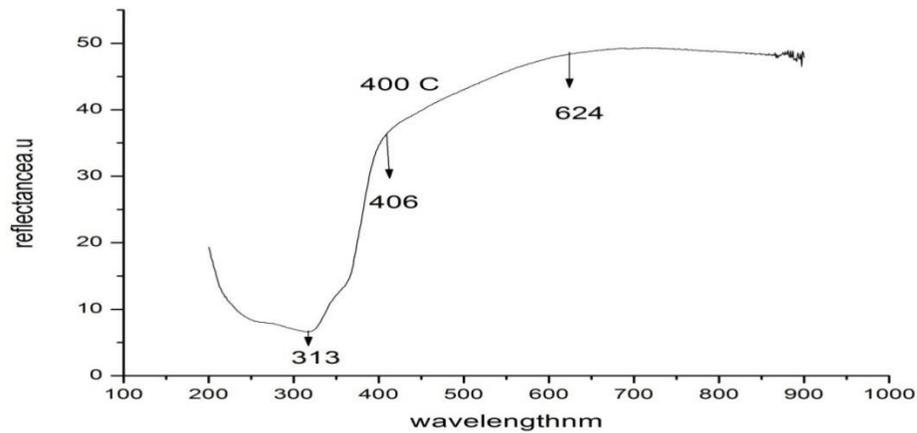


Fig 5 UV-Vis DRS Reflectance spectra for synthesized Mg doped ZnO at temperature 400°C

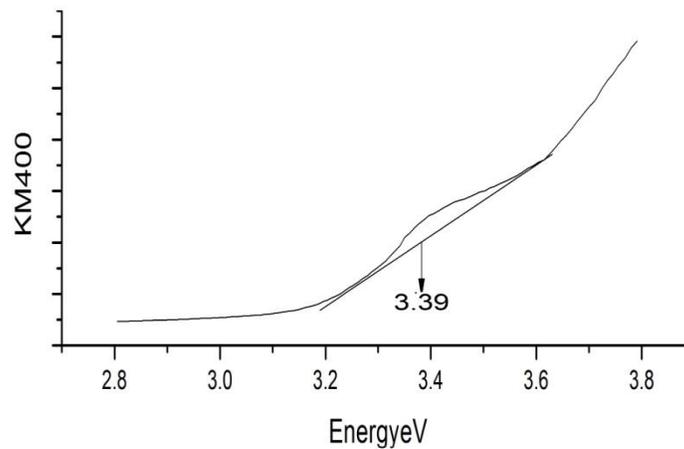


Fig 6 Band gap energy of the material

3.6 PHOTO LUMINESCENCE

The photoluminescence spectra of synthesized Zinc oxide recorded with the excited wavelength of 381 nm, 640 nm and 648 nm shown in the Fig 7. The fluorescence at 381 nm corresponds to the characteristic near band edge emission (NBE). It is due to the surface defects such as oxygen vacancies, oxygen ion vacancy occupied by two electrons (f centers). These energy levels will be present in the forbidden energy due to the secondary phase of MgO [20]. The red luminescence is a wide range of states from 640 nm (1.9375 eV) to 648 nm (1.9169 eV) and a small peak at 640 nm may be due to MgO secondary phase with slightly higher intensity, and this may be due to

segregation of MgO phase[21] which is also confirmed with the XRD studies. But the structural change of MgO has taken from cubic to tetragonal phase and thus 20.6 meV variation in the emission of red region is seen at 648nm. It may be due to the present case which has been assigned to electronic transitions due to oxygen interstitials. Hence the transition of carriers to oxygen interstitial located at 1.9169 eV[22] which is below the conduction band. Due to the increase in concentration of oxygen vacancies and surface recombination effects on the material[23] which influence the grain size and residual stress in the particle. In general ZnO is a hexagonal close packed structure where Zn atoms occupy half of the octahedral sites are empty which acts as defects. Mg doped ZnO structures have changed the optical properties significantly.

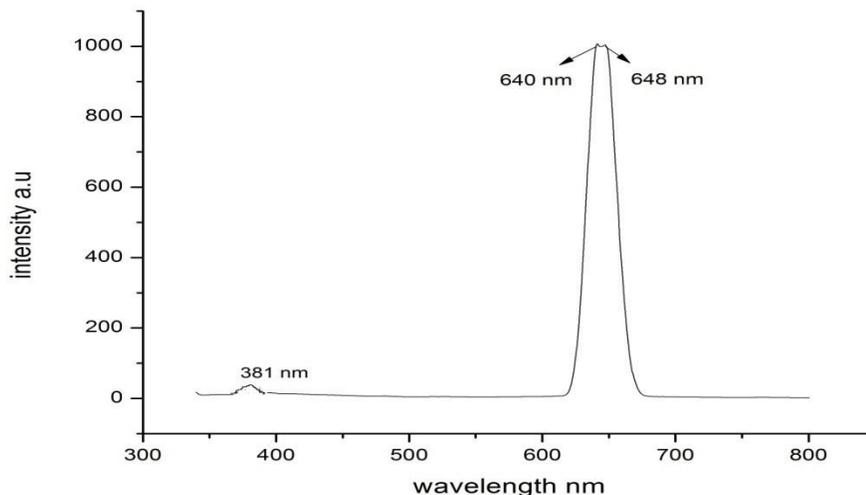


Figure 7 PhotoLuminescence for temp 400°C

Conclusions: Mg doped ZnO was synthesized by nitriding at the temperature 400°C. XRD, EDAX, FTIR, SEM analysis and PL studies were carried out. It is concluded that the synthesized material is pure and the secondary peaks which are due to doping Mg. MgO, which usually has a cubic structure changes itself to tetragonal structure, which is confirmed by Match 3 software. Further, stabilization of structure has occurred in this case rather than disruption of the structure due to doping of Mg. This is also confirmed by the PL studies which has two spectral emissions at 640 nm and 648 nm, in addition to the characteristic small peak of ZnO at at 381 nm.

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