Synthesis and Characterization of Magnesium Doped ZnO Using Chemical Route

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Abstract

Mg-doped zinc oxide (Zn$_{1-x}$Mg$_x$O) (0<x<0.8) nanostructure material is synthesized via a co-precipitation method using chemical route for application in sensing devices. The X-ray diffraction performed for analysis, confirms the growth of pure ZnO phase. Ultraviolet–visible spectroscopy and Fourier-transform infrared spectroscopy (FTIR) suggest the pure phase formation of ZnO. FTIR spectra also shows the presence of bands associated with CO$_2$ gas molecules and moisture present in the atmosphere. The formation of ZnO with no traces of Mg effect visible shift in XRD peak suggests the sample preparation process does not allow enough time to form a nanocomposite of Zn$_{1-x}$Mg$_x$O.

Keywords: ZnO, Spectroscopy, X-Ray Diffraction, FTIR, Doping

1. Introduction

There are various ceramic oxide materials that have been utilized as sensing materials for chemical and gas sensors such as SnO$_2$, ZnO, TiO$_2$ etc.[1, 2, 3, 4]. Among them since the discovery by Seiyama et al.[5] in 1962 that the electrical conductivity of ZnO changes drastically in presence of chemicals and reactive gases in the atmosphere, there have been
a great deal of efforts in utilizing this semiconducting metal oxide material as chemical or gas sensors due to its low dimensions, high compatibility with device processing. ZnO’s exciting morphologies such as nano-crystalline structures, nano-rods, nano-wires, and nano-spheres offers a great deal of adaptability for various device applications [6, 7, 8]. Tuning of high specific surface areas or high surface-to-volume ratios by stabilizing various surface morphology that allow easy adsorption of gases and chemicals makes ZnO a promising material for being utilized in nano-sensing devices.

Recently, multifunctional electronic devices are proposed based on the work on interfaces of materials with symmetry groups, such as, P63mc space group (e.g., ZnO), with a space group Fm-3m (e.g. MgO) or Pm3m (e.g., SrTiO3) space group. However, due to change of growth direction and solid state mixing limits of the two oxides many distinct properties may arise [9]. It have established that the substrate temperature and growth pressure affects strongly the polar (001) or non-polar (100) growth direction of wurtzite ZnO thin films [10,11]. Recent work suggest that alignment of coupling plane with substrates or doping of compatible elements such as Mg, Cr, Co, Cu may develop superior device properties as the central symmetry in ZnO is removed. Mg is chosen in this study as Mg$^{2+}$ (0.66 Å) ion is smaller than that of Zn$^{2+}$ (0.74 Å) which will substitute Zn$^{2+}$ in the ZnO matrix and hence will modify the morphology and properties of ZnO.

In this work we study the effect of Mg doping on the structural and optical properties of ZnO. In order to study the effect of Mg ion doing we chose the doping towards high end side as to investigate the solubility limit of two oxides and study the alloy of Zn$_{1-x}$Mg$_x$O on the structural and optical properties of the alloy or nanocomposite.
2. Experimental Techniques

2.1 Sample Preparation

Single phase and Mg doped ZnO nanocomposite are synthesized using chemical route. The steps involved in the preparation of samples is shown in Figure 1. The selected fabrication route effect significantly the morphology of nanostructured material. The observed modification in mechanical, thermal and optical property arises due to increase in surface to volume ratio of various morphologies.

Figure 1 Synthesis steps involved in the process of $\text{Zn}_1-x\text{Mg}_x\text{O}$ nanocomposite.
Zinc nitrate hexahydrate [Zn(NO$_3$)$_2$.6H$_2$O, AR grade) (Merck), Magnesium nitrate hexahydrate [Mg(NO$_3$)$_2$.6H$_2$O, AR grade) (Merck), hexamethylenetetramine (HMTA) [C$_6$H$_{12}$N$_4$, AR grade] (Merck) were used as received. The method of sol-gel produces the solid materials in nano form. It is suitable for fabricating metal oxides and the stabilization of various morphology solely depends on the processing parameter such as time and temperature as well as the precursors used. The precursors used in this work are zinc nitrate, magnesium nitrate, Hexamethylene tetramine (HMTA) and di-water.

3. Result and Discussion

3.1 Structural Properties

Figure 2 X-ray diffraction of pure and Mg doped ZnO nanomaterial calcined at 400 °C in the 2θ range from 20° – 80°.
The XRD measurement is done on the Bruker D8 discover powder X-ray diffraction with Cu-Kα (λ = 1.5406 Å) for 2θ range 20° – 80°. The grain size is estimated by Scherrer’s formula: 
\[ D = \frac{0.94λ}{βCosθ} \]
where D is average grain size, β is full width at half maxima (FWHM) of hkl peak and λ is the X-ray wavelength. Figure 2 shows the XRD pattern for the pure and Mg doped ZnO samples. The XRD reveals no change in the peak position with the increasing % of Mg doping from 20 % to 60 % except slight modification in the intensity and broadening in the peak which is associated with the variation in the grain size. It could be because of not given enough time to complete the reaction for forming the nanocomposite or due to the solubility limit of the two precursor due to high Mg doping concentration. All the samples show the formation of ZnO hexagonal structure as the peaks matches well with the ZnO ICDD card number (79-0205). The characteristic peaks located at 31.76°, 34.4°, 36.24°, corresponds to (100), (002), (101) plans of ZnO respectively [12].

3.2 FTIR Analysis

![FTIR spectra](image)

Figure 3a-3b FTIR spectra of ZnO and Mg doped ZnO in the wavenumber range of 350-1000 cm⁻¹ and 1000 – 4000 cm⁻¹ range.
Fourier-transform infrared spectroscopy (FTIR) is performed in attenuated total reflection (ATR) mode using Perkin-Elmer Spectrum BX2 FTIR spectrometer for the samples. Figure 3a-3b shows FTIR spectra for pure and Mg doped ZnO samples in the range of 350 cm\(^{-1}\)-1000 cm\(^{-1}\) and 1000 cm\(^{-1}\)-4000 cm\(^{-1}\) respectively. In Figure 3a, peaks in the range from 400-560 cm\(^{-1}\) are designated to stretching vibration modes of Zn-O-Zn confirms formation of ZnO NPs calcined at temperature 400 °C [13]. All the modes present in pure and Mg doped ZnO samples are tabulated in Table 1.

| Different Modes Present in FTIR | Wave-number | ZnO | Zn\(_{0.8}\)M\(_{0.2}\)O | Zn\(_{0.6}\)M\(_{0.4}\)O | Zn\(_{0.4}\)M\(_{0.6}\)O |
|--------------------------------|-------------|-----|----------------|----------------|----------------|
| Zn-O-Zn mode                   | 400-560 cm\(^{-1}\) | ✓   | ✓              | ✓              | ✓              |
| CO\(_3^{2-}\) absorption bands | 1420 cm\(^{-1}\) |     | ✓              | ✓              | ✓              |
| CO\(_3^{2-}\) absorption bands | 1470 cm\(^{-1}\) |     | ✓              |               | ✓              |
| Intrinsic diamond peaks        | 1970 cm\(^{-1}\) |     |                 |               | ✓              |
| Intrinsic diamond peaks        | 2030 cm\(^{-1}\) |     |                 | ✓              | ✓              |
| Intrinsic diamond peaks        | 2160 cm\(^{-1}\) |     |                 | ✓              |               |
| Symmetric and asymmetric C=O   | 2330 cm\(^{-1}\) | ✓   | ✓              | ✓              |               |
| Symmetric and asymmetric C=O   | 2360 cm\(^{-1}\) | ✓   | ✓              | ✓              |               |
| Stretching vibration of O-H bond | 3380 cm\(^{-1}\) | ✓   | ✓              | ✓              |               |

Table 1. Different Infrared modes present in the pure and Mg doped ZnO nanocomposite.

Absorption bands at 1420 cm\(^{-1}\), 1470 cm\(^{-1}\) assigned to CO\(_3^{2-}\) absorption bands [13,14] while Modes at 2330 cm\(^{-1}\)-2360 cm\(^{-1}\) is assigned to symmetric and asymmetric C=O modes
respectively [13,14,16,17] which is associated with gas phase CO₂. Two bands of CO₂, 2330 and 2360 cm⁻¹ in Figure 3b is related to atmospheric CO₂.

The splitting of mode is not see on solid or adsorbed CO₂. The increasing in intensity is possibly due to either an increase of CO₂ in the cell or poor purge stability of instrument. Spectra also shows intrinsic diamond peaks at 1970 cm⁻¹, 2030 cm⁻¹ and 2160 cm⁻¹ coming from the instrument [19]. H-O-H asymmetric and symmetric stretch near 3400 cm⁻¹ is related to nonstructural water. Band at 3214 cm⁻¹ represents H-O-H bending overtone mode [20]. Asymmetric and symmetric stretching modes of water at 3756 cm⁻¹ and 3657 cm⁻¹ are associated with gas phase. Generally when water condenses, a broad band centered near 3400 cm⁻¹ [21] arises due to band collapse that corresponds to stretching vibration of O-H bond (3380 cm⁻¹) of hydroxyl group [22].

4. Conclusion

Pure and Mg doped ZnO nanocomposite samples are successfully prepared using zinc nitrate, magnesium nitrate and HMTA solution and successive calcination of the powder at 400 °C. The XRD reveals the pure phase formation of ZnO phase with no measurable peak shit in the XRD due to Mg doping in the ZnO which indicate further to optimize the sample preparation condition or the limit of the two solids. The pure phase formation of ZnO is further confirmed by FTIR with the presence of Zn-O-Zn mode. The other peaks present in the FTIR are successfully identified as the bands corresponding to CO₂ gas molecule and moisture present in the atmosphere. Hence these result confirm the pure phase formation of ZnO nanocomposite with very little or no effect due to Mg doping which needs to be further studied via fine tune of preparation conditions and can be utilized to fabricate novel functional devices.
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