

Structural, Morphological and Infrared Characterizations of Copper doped Zinc Oxide Nanoparticles

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Abstract: A systematic investigations on the structural, morphological and infrared characterizations of copper doped zinc oxide ($Zn_{0.94}Cu_{0.06}O$) nanoparticles have been carried out in the present work. A simple and inexpensive sol-gel auto combustion technique was employed for the synthesis of $Zn_{0.94}Cu_{0.06}O$ nanoparticles. The prepared nanoparticles were characterized by X-ray diffraction technique (XRD), Scanning electron microscopy (SEM) and Fourier transformer infra-red spectroscopy (FTIR). XRD pattern reveals the formation of single phase with hexagonal wurtzite structure. The crystalline size calculated using Scherrer's formula was found in 21 nm. SEM analysis shows the spherical morphology with agglomeration of Cu^{2+} doped ZnO nanoparticles. FTIR confirms the successful incorporation of Cu^{2+} in to ZnO nanoparticles without disturbing its crystal structure.

Index Terms - Cobalt ferrite nanoparticles, X-ray diffraction, M-H plot.

I. INTRODUCTION

Nanotechnology has able to generate many new materials and devices with a huge range of applications, such as in nanoelectronics, nanomedicine, biomaterials energy production, and consumer products. In the recent year ZnO is one of the most important functional material and it exhibit novel optical, electrical and magnetic properties. ZnO is one of the most important oxide material with a wide bandgap of 3.37 eV and has a large exciton binding energy (60 meV) useful for various applications such as optoelectronic devices, piezoelectronic transducers, high frequency electronic devices[1-3]. A number of synthesis techniques have been used for the fabrication of transition metal doped nanocrystalline ZnO, these techniques give different particle morphologies, size as well as it modifies the properties of the material. In literature sol gel auto combustion technique [4-6], ball milling technique[7, 8], spray pyrolysis for thin film deposition [9, 10], hydrothermal technique[11, 12], co-precipitation technique[13, 14], chemical electrodeposition[15, 16] etc. were successfully adopted for the synthesis of transition metal doped nanocrystalline ZnO. Among these techniques, sol gel auto combustion technique is of great importance for the production of tailored oxide nanoparticles. Since, it is simple, low cost, less time consuming and easy to control of particle size. Also by adopting sol gel auto combustion technique we get accurate composition and constituent phases mixed at molecular level, assure high purity and well crystallized powders.

Transition metal doped ZnO has great interest in research field that it was induced to enhance the optical, magnetic and electrical properties of oxide material. Due to the exchange interaction between s and p electron of host ZnO and d electron of transition metal, also it changes its electronic structure. Many authors have studied the changes predicted by doping of transition metal ions into ZnO lattice [17-19]. The transition metals such as Fe, Cu, Ni, Co etc. doped with ZnO lattice which have remarkable change in structural, optical, electrical properties and potential application in semiconductor devices [14, 20, 21]. Among all these transition metal elements, Cu^{2+} has much interest since it exhibit a drastic change in optical, electric and magnetic properties of ZnO, which will increase its practical applications [22-24]. Cu^{2+} ions are easily incorporated on Zn^{2+} site such as ionic radii of Cu^{2+} (0.73 Å) close to ionic radii of Zn^{2+} (0.74 Å) ions [14]. In the present work, the preparation of $Zn_{0.94}Cu_{0.06}O$ via sol gel auto combustion technique and effect of Cu^{2+} ions on the structural, morphological and infrared properties were investigated.

II. EXPERIMENTAL METHOD

Preparation

The synthesis of $Zn_{0.94}Cu_{0.06}O$ nanoparticles were carried out using, the high purity (A.R. grade, 99% pure) chemicals using zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) as starting material and copper nitrate hexahydrate ($Cu(NO_3)_2 \cdot 6H_2O$) as doping source. Zinc nitrate and copper nitrate acted as oxidant while citric acid as fuel during the reaction. The ratio of fuel and oxidant were taken as 1:1 by propellant chemistry. Zinc nitrate and copper nitrate were dissolved in 100 ml distilled water to get a homogeneous solution for 30 min by using magnetic stirrer. Citric acid had been dissolved separately in 100 ml distilled water for 30 min and add to the nitrate solution. Then the solution was stirring and continuously heating at 90°C until water gets evaporated, thus the sol is converted into gel. The gel subsequently in to bulge form and it get strong self combustion reaction to give the fine powder. The detail synthesis procedure was also reported in our earlier report [25, 26]. The as prepared sample was sintered at 600°C for 5hr in muffle furnace.

Characterizations

The structural analysis was carried out by X-ray diffraction technique (XRD) analysis (Bruker D8 advance) with $Cu K\alpha$ radiation in the 2θ range of 20°-80°. The surface morphology was taken on scanning electron microscopy (SEM) using JEOL JSM-6360 microscope. The functional group and structural changes during the combustion reaction of $Zn_{0.94}Cu_{0.06}O$ nanoparticles were studied using Fourier transformer infra-red spectroscopy (FTIR) recorded at the range of 400-4000 cm^{-1} (FTIR, Perkin Elmer, Spectrum).

III. RESULTS AND DISCUSSION

X-Ray diffraction studies

The X-ray diffraction pattern of the $Zn_{0.94}Cu_{0.06}O$ nanoparticles are shown in Fig.1. XRD analysis were used to determine the phases as well as crystal structure of the sample. Each XRD peaks identified the single phase with hexagonal wurtzite structure of ZnO lattice without any

impurities, there is no secondary phases were found. The XRD pattern show the formation of strong and narrow diffraction peaks with good crystallinity.

The lattice parameters 'a' and 'c' of the pure and Cu²⁺ doped ZnO nanoparticles were estimated using the eq.(1) [27].

$$\frac{1}{d^2} = \left[\frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right) \right] \quad (1)$$

where, θ is the diffraction angle, λ is incident wavelength ($\lambda = 0.15406$ nm) and h, k, and l are the Miller indices. The lattice parameter 'a' and 'c' of Cu²⁺ doped ZnO nanoparticles are as 3.254 Å and 5.215 Å respectively. The crystalline size is calculated from most intense peak of XRD patterns i.e 101 peak. The crystallite size (D) of Cu²⁺ doped ZnO nanoparticles were estimated using the Debye-Scherrer's eq.(2) [28].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

where, D is crystalline size, λ is the wavelength of X-ray radiation, β is full width at half maximum (FWHM) and θ is the Bragg angle. The crystallite size of Cu²⁺ doped ZnO nanoparticle is 22 nm.

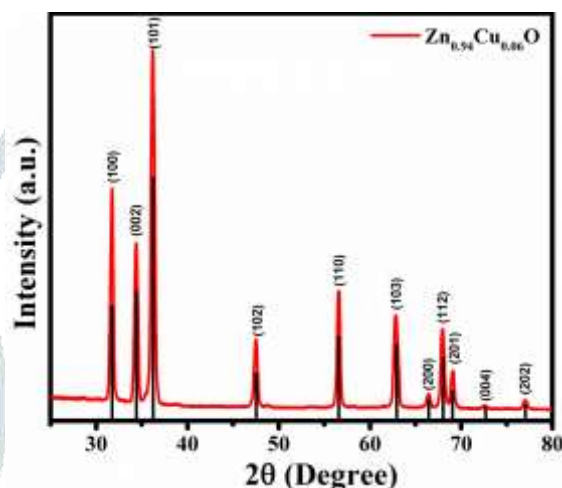


Fig. 1 X-ray diffraction pattern of Zn_{0.94}Cu_{0.06}O nanoparticles

Scanning Electron Microscopy

Scanning electron microscopy technique gives information regarding the morphology of Cu²⁺ doped ZnO nanoparticles. The SEM micrograph of Cu²⁺ doped ZnO nanoparticle is shown in Fig.2. respectively. SEM image show the particles are quasi spherical and agglomerated. SEM image clearly show the nanocrystalline nature of Cu²⁺ doped ZnO nanoparticles.

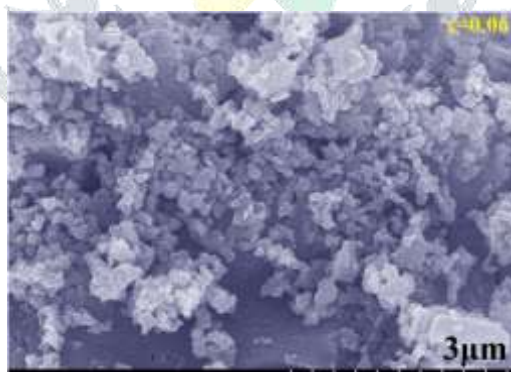


Fig.2. SEM images of Zn_{0.94}Cu_{0.06}O nanoparticles

Fourier transform infrared spectroscopy

Fourier transformation infra-red spectroscopy (FTIR) of Zn_{0.94}Cu_{0.06}O nanoparticle recorded at the range of 500-4000 cm⁻¹ shown in Fig.3. The FTIR is used for the information about the chemical bonding, elemental constituents, vibrational frequencies and stretching modes in the nanoparticles. From the FTIR spectra extensive observation peak around the 3460 cm⁻¹ to 3350 cm⁻¹ are recognized to O-H stretching vibration in ZnO lattice of H₂O [29]. Symmetric and asymmetric nature of C-H stretching mode found at 2800 to 2950 cm⁻¹ weak absorption peak. The absorption peak between 2280 and 2340 cm⁻¹ is of the CO₂ molecule exists in air. The sharp peak found at 1300 to 1600 cm⁻¹ is recognized to bonding of H-O-H that can be reveals to small amount of H₂O in ZnO nanoparticles. The vibrational bands found at 740 cm⁻¹ to 1150 cm⁻¹ are associated to the ZnO stretching frequencies bands. From these results it reveals that Cu²⁺ ions are successfully incorporated in to ZnO lattice.

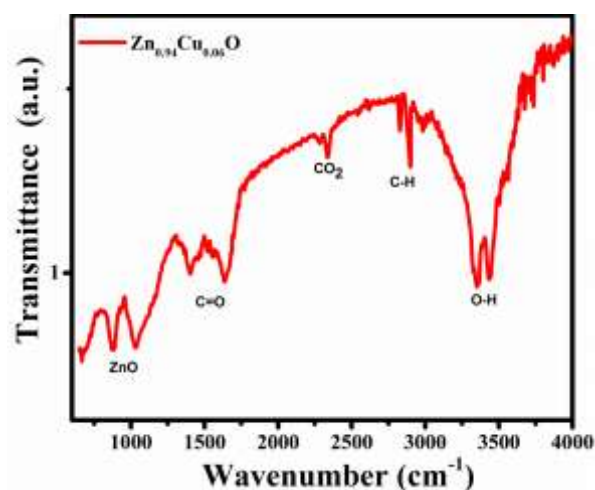


Fig.3. FTIR spectra of $Zn_{0.94}Cu_{0.06}O$ nanoparticles

IV. CONCLUSION

In the present study, sol gel auto combustion technique for synthesis of Cu^{2+} doped ZnO nanoparticle has been successfully achieved. The influence of Cu^{2+} ions on to structural, morphological and infrared properties of ZnO nanoparticles were investigated. From X-ray diffraction measurement shows the hexagonal wurtzite structure, there is no impurity phases observed. SEM analysis confirms the quasi spherical morphology of Cu^{2+} doped ZnO nanoparticles. The FT-IR results confirms the successful accompanying of Cu^{2+} ions in to ZnO lattice.

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