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Short Communication

**Structural, optical and dielectric studies in ZnO nanorods
by microwave assisted method**

ABSTRACT

P. Rejani*
Asha Radhakrishnan
B. Beena

*Nano Science Research Lab,
Department of Chemistry,
D.B.College,Sasthamcotta,
Kollam,Kerala, India.*

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ZnO nanorod was prepared by microwave assisted method. The crystal structure of the nano powders were confirmed by X-Ray diffraction analysis and the mean particle size was estimated by the Scherrer's formula .The surface morphology of the nano particles were analyzed by using SEM . The absorption spectrum of the material in the UV-Vis range was recorded .The energy band gap of the material was obtained from the absorption wavelength of the UV-Vis spectrum. The short emission wavelength of the material was confirmed by using Photoluminescence studies. The effects of frequency on the dielectric behaviour and ac electrical conductivity have been studied.

Keywords: *Nanoparticles; Optical band gap; Photoluminescence; Ac conductivity; Dielectric constant.*

INTRODUCTION

Semiconductor nanocrystals and nanoparticles have been studied extensively as their properties are dependent on size, morphology and surface composition (1). The n type semiconductor zinc oxide has numerous applications in various fields such as field emission displays (2), high efficient optoelectronic devices (3), UV laser technology at room-temperature(4) ,phosphors(5), photocatalysis(6),electromechanical coupled sensors and transducers, spintronics, super-hydrophobicity and super-hydrophilicity surfaces(7),cosmetics etc.. ZnO is a direct band-gap semiconductor with wide band-gap energy (~3.37eV) at room temperature and a very large excitation binding energy of about 59meV, which allows for more efficient excitonic emission at higher temperatures (8-9) better than other very important semiconductors .Dielectric and magnetic properties of oxides depend considerably on the size and shape of the particles (10). Nanodielectrics, is the subject of study related to dielectric phenomena of nanoscopic materials having morphology of particles, sheets, wires and tubes etc.

* Corresponding author:
P. Rejani
Nano Science Research Lab,
Department of Chemistry,
D.B.College, Sasthamcotta,
Kollam, Kerala, India 690 521.
Tel +96 476 2830323
Fax +96 476 2833323
Email rejanihari82@gmail.com

The area of nanodielectrics is relatively unexplored, but there is enormous scope to use nanomaterials in power electronic industry and as gate electrodes in thin film transistors (11).

In this paper, we report the synthesis characterization and optical properties of nanocrystalline ZnO rod prepared through microwave assisted methods.

EXPERIMENTAL

Preparation of nano ZnO rod

ZnO nanorods were prepared from Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). 0.5gm zinc nitrate hexahydrate salt was dissolved in 65ml of demineralized water. Appropriate quantity of a moderate alkali namely hexamethylenetetramine $\{(\text{CH}_2)_6\text{N}_4\}$, HMT} was mixed, to reach the p^{H} level 7. The prepared solution was then stirred well for 30min to obtain a homogeneously turbid liquid. Then the solution was microwave-heated by a 300W domestic microwave oven for 20 min to obtain a curdy white precipitate, which was cooled to room temperature, filtered, washed with water followed by drying in hot air oven.

Characterization

X-ray diffractogram ($2\theta=10-90^\circ$) was obtained on XPERT-PRO powder diffractometer with $\text{Cu-K}\alpha$ radiation. The FTIR spectrum was recorded using KBr wafer on the Thermo Nicolet FTIR model AVATAR 370 DTGS. In the present study, SEM of the sample was recorded using a JED-2300 system and HRTEM was taken using 300kv HRTEM (FEI-Model). The absorption spectra were recorded at room temperature using SHIMADZU UV-2550 UV Visible spectrophotometer. The photoluminescence measurement was carried out using Varian Cary Eclipse fluorescence spectrophotometer using xenon arc flash lamp as the excitation source. The dielectric permittivity measurement on the pellet of ZnO nanorods were carried out using HIOKI 3532-50 LCR Hi Tester in the frequency range 100Hz to 13MHz. The dependence of dielectric properties such as dielectric loss tangent, dielectric constant and dielectric loss factor on frequency has been studied at room temperature. From the permittivity studies, ac conductivity was evaluated.

RESULTS AND DISCUSSION

The structure identity and purity of the prepared nano particles were verified by XRD. Figure 1 shows the XRD pattern for ZnO nanorod at different temperatures. The observed peaks of the nano crystallite match well with standard JCPDS files, and no other crystalline phases were detected. The average crystallite size of the powders were determined by using Scherrer's formula,

$$D = 0.9\lambda/\beta\text{Cos}\theta$$

Where D is the average crystallite size in nm, λ the wavelength of X-ray radiation, θ the Bragg's angle and β the full width at half maximum of the peak observed for the sample (12).

A hexagonal wurtzite crystalline structure with lattice parameters of $a=3.2498$ and $c=5.2066$ were observed. All peaks correspond to hexagonal ZnO without evidence of any other crystal phase or another material. ZnO of wurtzite crystal structure; has no center of inversion and an inherent asymmetry along the c-axis is present, which allows the anisotropic growth of the crystal along the [0001] direction (13-14). Here the major intensity of the peaks centered at $2\theta=31.5$ and 36.1 show a preferred growth in (1010) and (1011) directions, in agreement with the microrods observed in SEM micrograph. The grain size of ZnO nanorods has been found to be 26 nm.

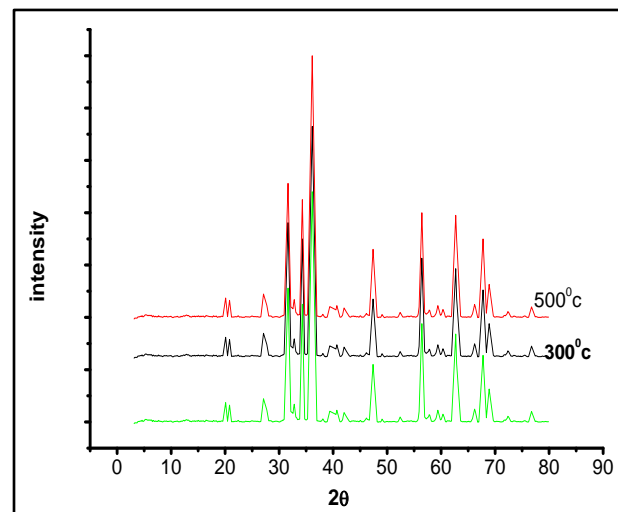


Fig. 1. XRD spectrum of ZnO rod at different annealing temperatures

A FT-IR spectrum of ZnO is shown in Figure 2. The room temperature spectrum shows bands in the region $\sim 3485\text{cm}^{-1}$ and $\sim 2355\text{cm}^{-1}$ due to the presence of adsorbed water molecules or surface hydroxyl groups and C=O residues, probably due to atmospheric moisture and CO_2 respectively. The spectrum also shows Zn-O absorption band near 480cm^{-1} .

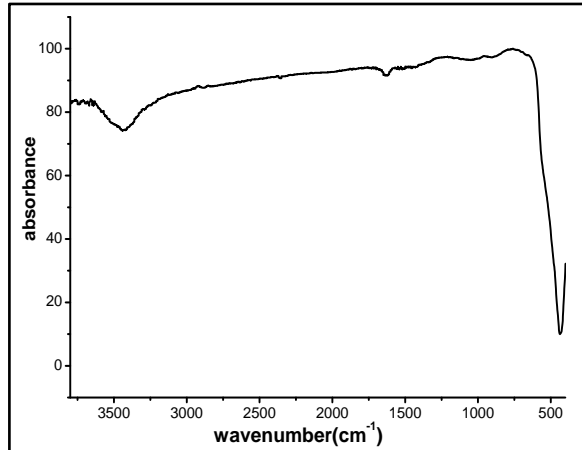


Fig. 2. FT-IR spectrum of ZnO nanorod

Figure 3 clearly shows ZnO crystals with rod like structure with average length of 1-2 μm . Chemical composition by EDS indicate stoichiometry (Figure 4). The resulting atomic-percent contents for ZnO nanorods were O; 30.42%, Zn; 69.58%. The high content of Zn indicates a high value of oxygen vacancies in their crystalline structures. The TEM micrograph, Figure 5, of the sample revealed that the ZnO nanorods synthesized in this study have an average diameter of about 96 nm and an average length 400nm.

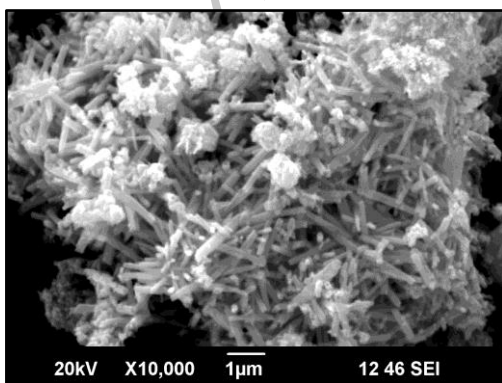


Fig. 3. SEM image of ZnO nanorods

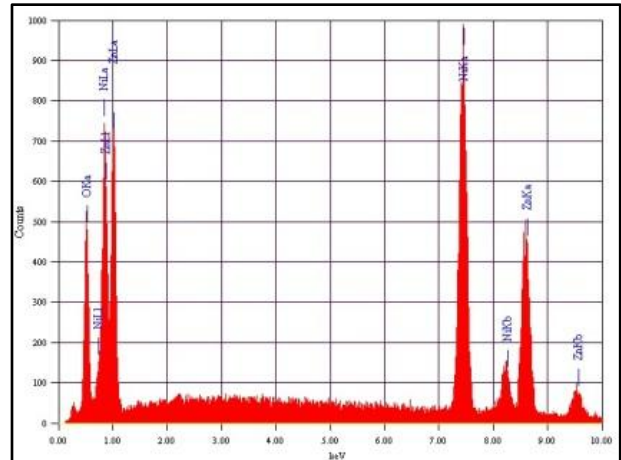


Fig. 4. EDS of ZnO nanorod

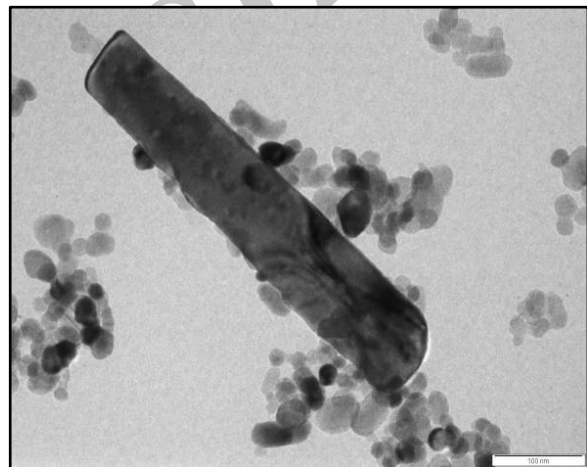
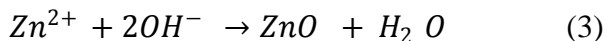
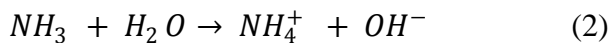


Fig. 5. TEM micrograph of ZnO nanorod

The surface morphology of the as synthesized ZnO is revealed by scanning electron micrograph. Microwave irradiation might have played an important role in the fast synthesis of ZnO nanorods. As a polar material, ZnO may be affected significantly by microwave irradiation. The applied microwave field induces a rotation of polarized dipole of polar materials, which can generate heat due to molecular inner friction. The presence of an internal electric field also leads to orientation effects of dipolar molecules and hence reduce the action energy. The reduction in surface energy of the polar crystal may be the primary driving force for the faster nucleation, growth of the material and morphology evolution. The formation of the ZnO nanorods may be

explained as follows. In the first stage OH^- ions are formed as a result of the reaction of H_2O with HMT and subsequently ZnO nuclei are formed. In the second stage the formed ZnO nuclei grow preferentially along the [0001] direction, resulting in the formation of single-crystalline ZnO nanorods [13].

In this study, hydroxide anions are provided by hydration of hexamethylenetetramine (HMT). When HMT is used as the hydroxide anion-generating agent, the reactions involved in the formation of ZnO crystals are believed to be as follows:



UV visible absorption spectrums of the samples were recorded in the range 200-800 nm is shown in Figure 6.

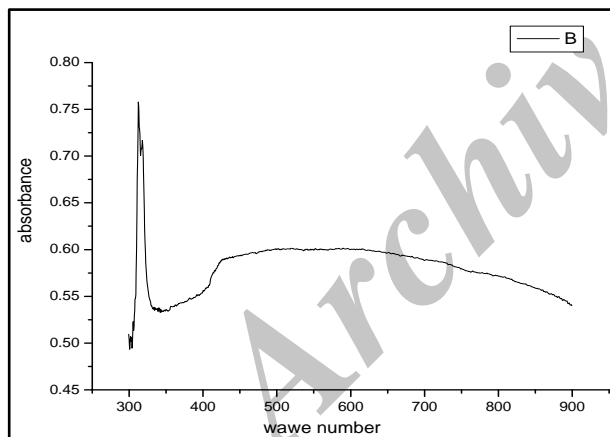


Fig. 6. UV visible absorption spectrum of ZnO nanorod

The spectrum shows a narrow absorption peak in the region 335nm. UV spectrum gives information about excitonic or interband transition of nanomaterials. The fundamental absorption which corresponds to electron excitation from the valence band to the conduction band is used to determine the nature and value of the optical band gap. The relation between absorption coefficient, α ,

and the incident photon energy, $h\nu$, is given by the relation,

$$\alpha h\nu = A(h\nu - E_g)^n$$

Where E_g is the band gap of the material, A is the absorption coefficient and n is $1/2$ for an indirect transition or 2 for direct transition. The value of the band gap energy of ZnO was calculated by assuming the direct transition .i.e., $n=2$, because optical absorption in ZnO is direct allowed transition (15). The value of band gap is determined by plotting $(\alpha h\nu)^{1/n}$ versus $h\nu$ and extrapolating the straight line portion to $h\nu$ axis (Figure 7). The optical band gap thus obtained for nano ZnO rod was found to be 3.34eV.

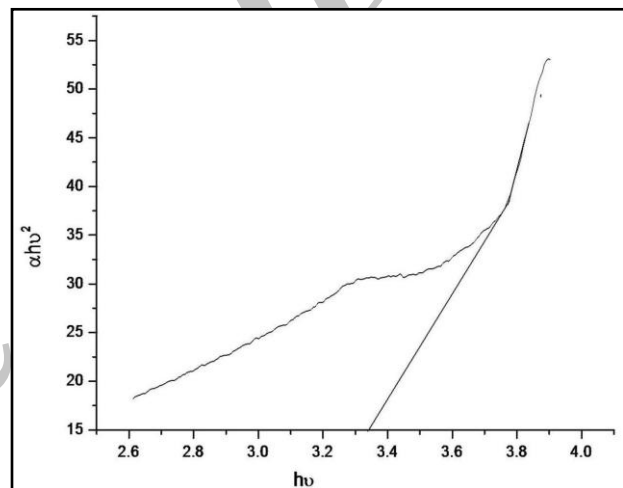


Fig. 7. Plot of $(\alpha h\nu)^2$ vs $h\nu$ for ZnO nanorod

Figure 8 shows the room temperature photoluminescence spectrum for ZnO nanorod. The emission spectra were obtained using light of 355nm as excitation source. The UV emission peak at ~390nm corresponds to the near band-edge emission. The smaller peaks at 427nm and 491 nm are completely independent of size of nano particles and most probably they originate from defect levels present in nano Zinc Oxide. An earlier study (16) on the photoluminescence property of zinc oxide has reported similar size independent features at 420 and 485nm. They have attributed the feature at 420nm to interstitial oxygen levels in zinc oxide and the feature at 485 nm to the transition between vacancy of oxygen and interstitial oxygen. Many previous reports (16,17) on photoluminescence emission spectra of

zinc oxide show a broad peak in the green region between 520 and 550nm in case of both bulk zinc oxide as well as quantum dots. This broad peak has been reported (18) to be due to the recombination of electrons occupying the single oxygen vacancy with photo excited holes.

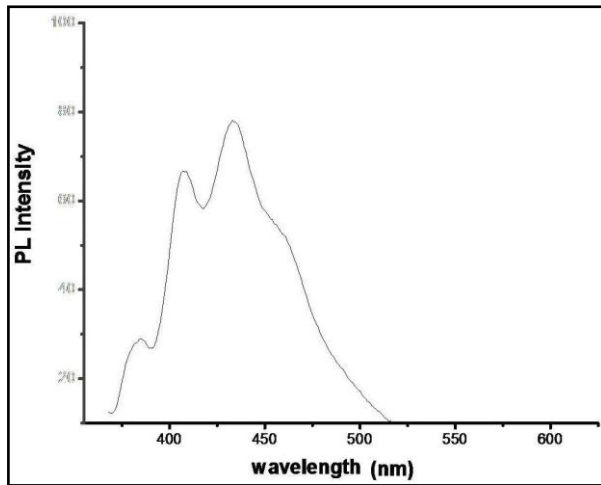


Fig. 8. PL spectrum of ZnO nanorod

In the case of zinc oxide nanorod synthesized in the present work, the intensity of this broad green peak is quenched, indicating the absence of recombination induced defects. The quenching of this visible emission has been reported earlier in case of Au/ZnO nanocomposites and tetraoctyl ammonium bromide coated zinc oxide particles.

The dielectric constant (ϵ') of a material determines the relative speed that an electromagnetic signal can travel in that material. The values of the real part of the dielectric constant (ϵ'') at different frequencies were derived from the measured capacitance (c) and knowing the geometrical dimensions of the pellets using the expression

$$\epsilon' = c \cdot d / \epsilon_0 A$$

Where c is the capacitance, d is the thickness of the pellet. Variation of dielectric constant with log frequency at room temperature for ZnO nanorods was shown in Figure 9. The dielectric constant is found to decrease rapidly with frequency.

Variation of ϵ' in the low frequency region is due to the interfacial polarization or space charge polarization and is exhibited by many dielectric solids. In a nano crystalline material, majority of atoms reside in the grain boundary or within a few atomic layers from the boundary (19). The oxide materials are reported to contain oxygen vacancies. An oxygen vacancy is equivalent to a positive charge and hence possesses a dipole moment. In nano structured materials density of defect is very high. Therefore the grain boundaries of nano structured ZnO should be rich in oxygen vacancies and thereby should contain high density of dipoles. Exposed to an external electric field, the dipoles will rotate leading to an increased polarization in ZnO nanorods. Thus the high value of dielectric constants in the low and medium frequency regions can be accounted for this type of polarization.

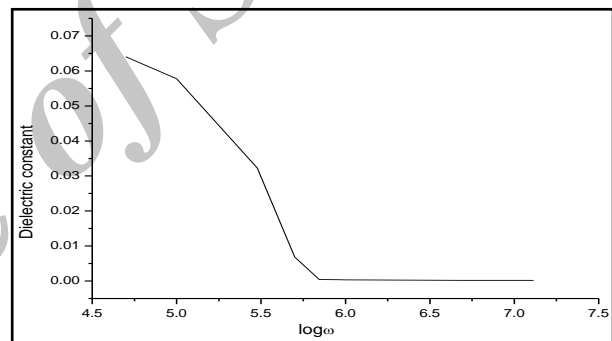


Fig. 9. Variation of dielectric constant with log frequency for ZnO nanorod

The frequency dependence of ac electrical conductivity (σac) of nano zinc oxide rod was studied. It was observed that σac increases with frequency. The ac electrical conductivity of the samples were calculated using the equation

$$\sigma ac = 2 \pi f \epsilon_0 \epsilon' \tan \delta$$

The ac conductivity has been attributed to losses due to bound charges. The behavior of frequency dependence of σac may be mainly due to the disordered nature of the grain boundaries and grain boundary interfaces.

CONCLUSIONS

Pure hexagonal-phase ZnO nanorod was synthesized through fast and simple microwave irradiation method from the solution comprising Zinc nitrate and hexamethylenetetramine. The grain size of ZnO nanorods have been found to be 26 nm. The nanorods structures were found to have an average diameter of about 96 nm and an average length 400 nm from HRTEM. The sample shows strong absorption in the UV range below 380 nm and is nearly transparent in the visible range. The absorption peaks are blue shifted compared to the bulk zinc oxide. Optical studies on synthesized rod has shown a band gap of 3.34 eV. The photoluminescence spectrum shows main peaks due to excitonic emission. The green defect induced peak at 520-550 nm reported in case of bulk zinc oxide and zinc oxide synthesized by other routes is strongly quenched in the present samples. The dielectric properties and ZnO nanorod and particles were investigated over a wide range of frequencies range from 100 Hz to 13 MHz. The dielectric constant of nano zinc oxide rod was found to be high compared to that of bulk. This simple and fast route for the synthesis of various shapes of ZnO materials will be attractive for the fabrication of future electronic device.

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