Synthesis and characterization of ZnO nanoparticles by microwave assisted method

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Abstract - Nanoparticles of ZnO was prepared by microwave assisted method and characterized by XRD, FTIR, FESEM with EDS, UV-Vis and Photoluminescence spectroscopy. XRD confirms the hexagonal structure of nanoparticles with good crystallinity and average crystallite size is 35 nm. FESEM image shows the particle like structure. From FTIR spectrum, the stretching vibration of Zn-O is observed at 453 cm^{-1}. The optical properties of the prepared ZnO nanoparticles are investigated by measuring UV-Vis and luminescence spectroscopy at room temperature. The second harmonic generation (SHG) efficiency is found to be 1.4 times of KDP.

Keywords: ZnO nanoparticles; XRD; FTIR; photoluminescence and SHG efficiency.

I. Introduction

Nanomaterials have fascinated the scientific community in recent years because they exhibit unusual physical and chemical properties significantly different from their bulk counterparts [1]. ZnO is an II-VI semiconductor having wide bandgap of 3.37 eV at room temperature and it has hexagonal wurtzite structure. It has large excitation binding energy 60 meV and it has high transparency. ZnO are widely used in various applications such as solar cells, light emitting diodes, gas sensors, chemical sensors, photocatalyst, spintronics and biomedical applications due to their excellent properties [2-4].

The hydrothermal method is an efficient approach for controlled synthesis of nanostructures. Furthermore, it has some advantages such as large surface area, controllable particle size, production of particles with a narrow particle size distribution and low-cost compared to the physical methods like as arc-discharge, ball milling etc.,[5] In the present work, ZnO nanoparticles have been prepared by microwave assisted method using autoclave and its structural and morphological characterization, optical (linear, nonlinear) properties are investigated.

II. Experimental

Preparation of ZnO nanoparticles by microwave assisted method

0.5 M of $Zn(CH_3COO)_2.4H_2O$ was dissolved in 20 ml of deionized water. 1 M of NaOH was dissolved in 20 ml of double distilled water and added to the above solution under stirring for 15 min at room temperature. The stirred solution was transferred to a stainless steel autoclave bottle and kept at 473 K for 10 h in a hot air oven. The resulting precipitate was irradiated in a domestic microwave oven (2.45 GHz, 800 W) for 20 min. The product was annealed at 673 K for 4 h to get ZnO in powder form.

The structure was investigated using X-ray diffraction on a Riakgu Mini Flexell Desktop Diffractometer (CuK_α λ = 1.5406 Å). The morphology was studied by SEM on VEGA 3 TESCAN SEM with EDS attachment. The molecular structure was affirmed by JASCO 460 plus FT-IR spectrometer by KBr pellet method in the range 400-4000 cm^{-1}. The linear optical absorption was recorded using a Perkin Elmer Lambda 25 spectrophotometer. The luminescence was analysed by Fluoromax 4 spectrophotometer.

III. Results and Discussion

Structural analysis

The diffraction peaks and the lattice constants a=3.263 Å, c=5.225 Å are in good agreement with the standard diffraction data (JCPDS No: 89-1397). The presence of prominent peaks shows that the sample has polycrystalline nature (Fig. 1). Absence of impurity peaks shows the presence of high purity ZnO (which is also evident from EDAX spectrum).

In addition, the peak broadening implies the formation of nanoparticles. According to the Debye-Scherrer formula [6]

$$D = \frac{K\lambda}{\beta Cos\theta} \quad (1)$$

Where K is the Scherrer's constant, say 0.94 (approximating the particle morphology as a sphere), λ the wavelength of X-ray (1.5404 Å), β the full width at half maximum (FWHM), and θ is the Bragg diffraction angle. From eqn. 1 average crystallite size D is calculated as 34.9 nm.

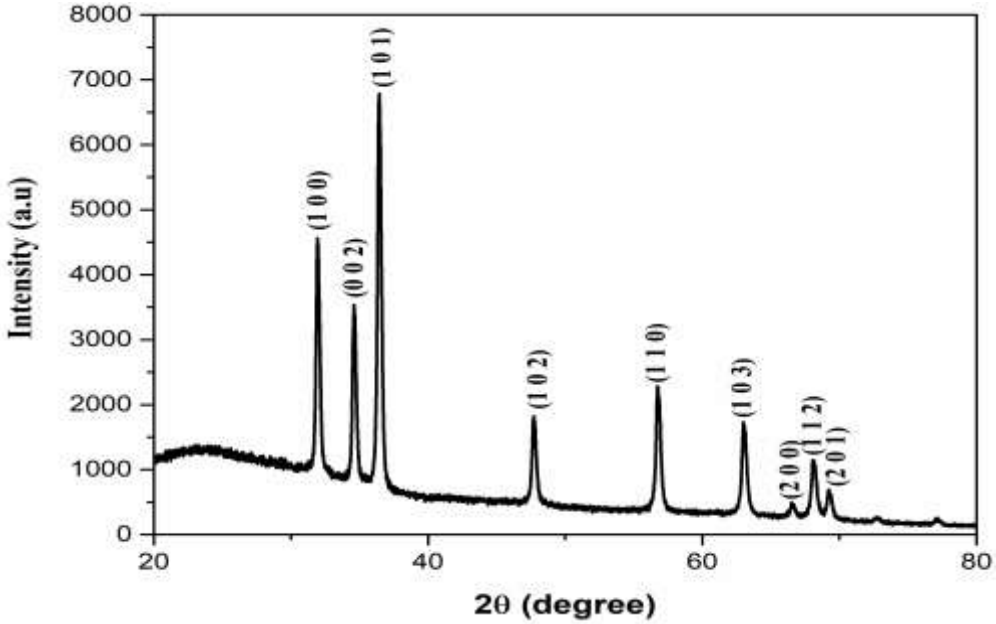

Fig. 1 XRD pattern of microwave assisted ZnO nanoparticles

Williamson-Hall method (W-H) suggests a way to calculate the microstrain of the prepared ZnO nanoparticles. Modified Scherrer equation is expressed as

$$\beta \cos\theta = (k\lambda / D) + (4\varepsilon \sin\theta) \quad (2)$$

The W-H plot is expected to be horizontal line, parallel to the sinθ axis, whereas in the presence of strain, it has a non-zero slope (Fig. 1b). The dislocation density strongly influences many of the properties of materials [7-8]. Dislocation density (δ) is calculated using the equation,

$$\delta = 1/D^2 \quad (3)$$

The calculated strain and the dislocation density value of microwave assisted ZnO nanoparticles are 0.00594 and $8.210X10^{14}$ lines/m^2 respectively.

Surface Morphology & Elemental Analysis

Field emission Scanning electron microscope was employed to study the topography of the nanoparticles. Cluster of nanoparticles was observed from the FESEM images (Fig.2a). Particles are in the range of 48-60 nm. Also, the samples should be dried properly to remove water molecules present (can be seen from FTIR spectrum (O-H vibrations observed) in the sample and grinding time should be increased. The preparation technique should be improved further to obtain particle homogeneity (i.e. to avoid cluster formations). Choice of different surfactants like polyvinyl alcohol may leads to the particle homogeneity.

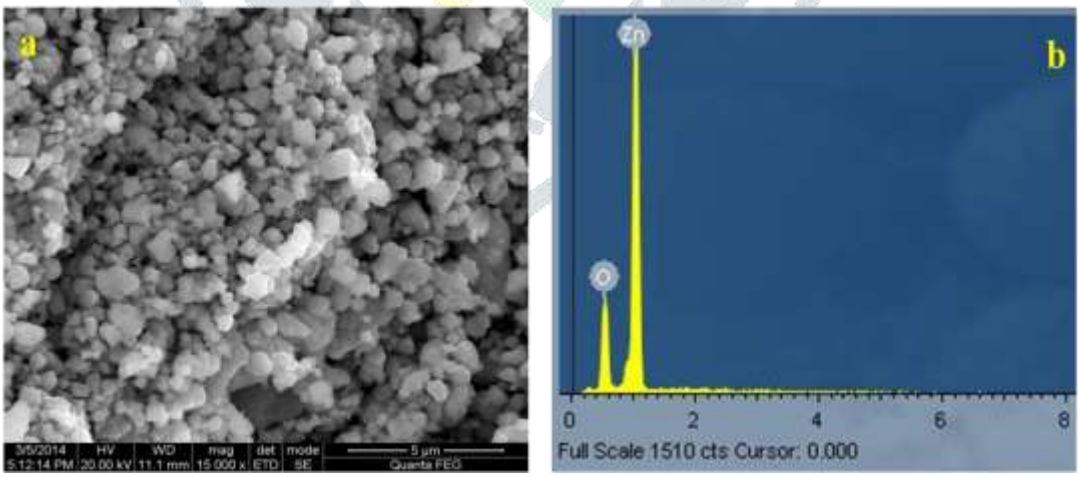

Fig. 2 (a) FESEM images and (b) EDS of microwave assisted ZnO nanoparticles

The elemental composition of the sample was investigated by Energy Dispersive X-ray Analysis (EDAX) (Fig.2b) and it reveals that there is no other impurity present in the prepared nanoparticles.

Molecular Structure Confirmation: FT-IR Spectrum

The synthesized sample have been admixed with KBr, thoroughly mixed and pelletized by pressing under a pressure of 7 tons for few minutes.

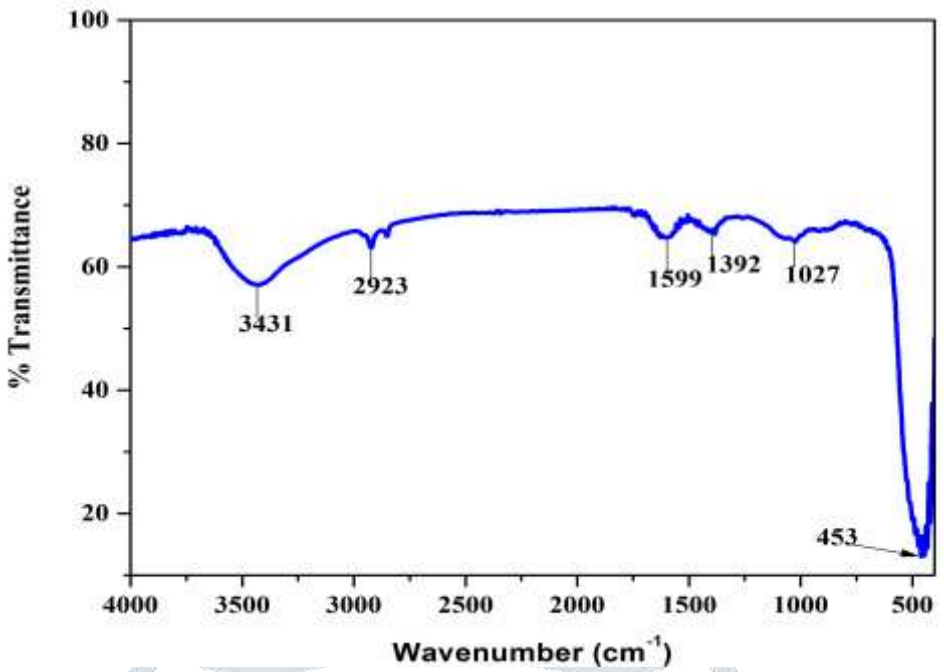

Fig. 3 FTIR spectrum of microwave assisted ZnO nanoparticles

The presence of O-H was observed from the peaks 3431cm^{-1}, 1599 cm^{-1}, 1392 cm^{-1}, 1027 cm^{-1}. These bands may be due to atmospheric water molecules. O-H elimination from the compound can be done by drying the pellet to about 110 ºC. The band 2923 cm^{-1} associated with the symmetrical stretching of C-H. The presence of C-H may be due to citric acid usage. The characteristic Zn-O frequency was observed from the strong absorption peak at 453 cm^{-1}[9-10].

Linear optical properties: UV-Vis study

The strong absorption occurs at 374 nm, which is in the UV region and the weak absorption area covers almost the whole of the visible region ranging between 400 and 800 nm. The transmittance can be improved by varying the concentration of the solution.

The optical band gap energy E_g and the absorption coefficient α are related by the equation

$$\alpha = (k / h\nu)\,(h\nu - E_g)^{\beta} \qquad (4)$$

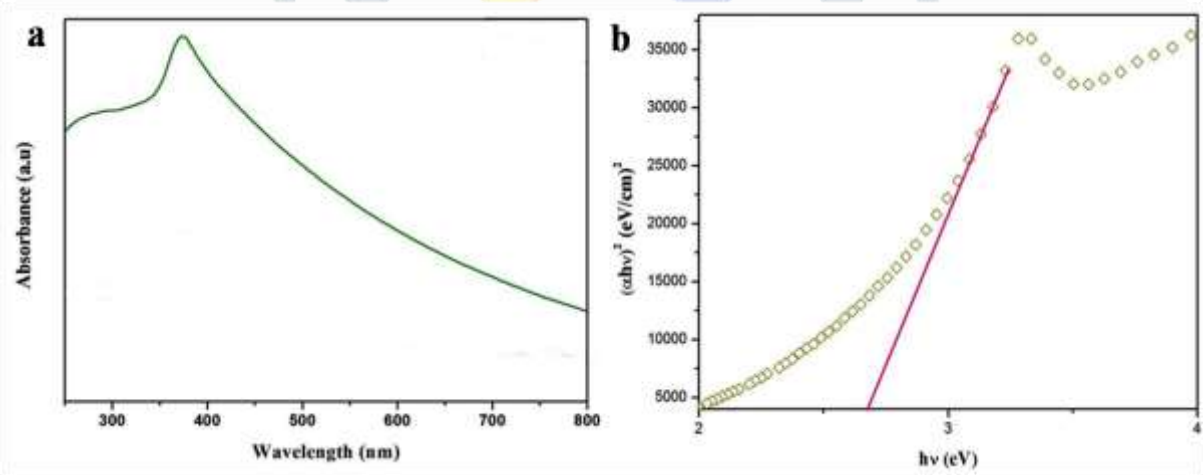

Fig. 4 (a) Absorbance and (b) optical bandgap of microwave assisted ZnO nanoparticles

Where, k is constant, h is Planck's constant, hυ is the incident photon energy and β is a number which characterizes the nature of electronic transition between valance band conduction band. For direct allowed transitions β=1/2 and it is known that ZnO is direct band gap semiconductor. Therefore the formula used is

$$\alpha = (k/h\upsilon)\,(h\upsilon - E_g)^{1/2} \qquad (5)$$

$$(\alpha h\upsilon)^2 = C\,(h\upsilon - E_g) \qquad (6)$$

Where, C is a constant. By plotting the graph for $(\alpha h\upsilon)^2$ vs hυ, the energy gap E_g of the sample is estimated. The optical energy band gap of synthesized ZnO is found to be ~ 2.6 eV[11].

Luminescence studies

In contrast to the UV spectra, fluorescence spectra of ZnO nanoparticles are sensitive to the preparation procedure and also to the environmental conditions. The sample was excited with the wavelength 340 nm. The ZnO nanoparticles exhibited a strong emission peak at 365 nm (3.39 eV). The microwave assisted ZnO nanoparticles exhibit a remarkable blue emission with peak at 440 nm. From the luminescence spectra, the observed emission peak at 465 nm may be attributed to the transition from Zinc intestinal Zn_i (Zinc intrinsic) to the valence band (VB). Green–yellow emission is observed at 533 nm in luminescence spectra, due to the recombination of photo generated holes with a singly ionized charge state of specific defect.

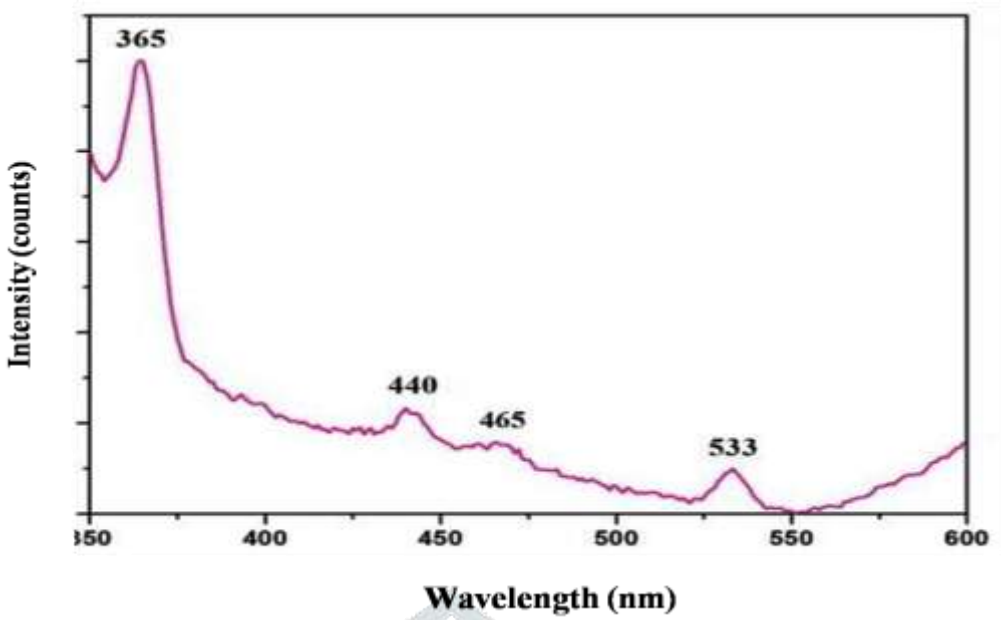

Fig. 5 Luminescence spectrum of microwave assisted ZnO nanoparticles

The mechanism of the luminescence suggests that visible luminescence is caused by the transition from deep donor level to valence band due to oxygen vacancies and by the transition from conduction band to deep acceptor level due to impurities and defect states. This luminescence mechanism can be used to control the optical properties of ZnO for optical device applications [12].

Nonlinear Optical Studies

The sample was packed in a circular copper ring and then sandwiched between two well cleaned glass plates. Then it was illuminated with Q-switched Nd:YAG Laser (1064nm@450mJ, 9ns, 10 Hz) and the generated output was scattered from the sample so that a convex lens was employed for collimation and then it was directed towards the iHR 320 Horiba Jobin Yuon grating monochromator. The grating with 1200 grooves/mm and blaze of 500 was selected to detect the signal from the sample. The photomultiplier tube (PMT) is act as a detector. The obtained signal was then recorded as spectrum by using a data acquisition system. Before testing the sample for its frequency conversion efficiency, UV-Vis transmittance was carried out to study its absorbance in visible region and from the fig. 4, it was observed that, there is very low absorbance in visible region. It was very clear that the sample has no absorption in the visible region (400 -700 nm).

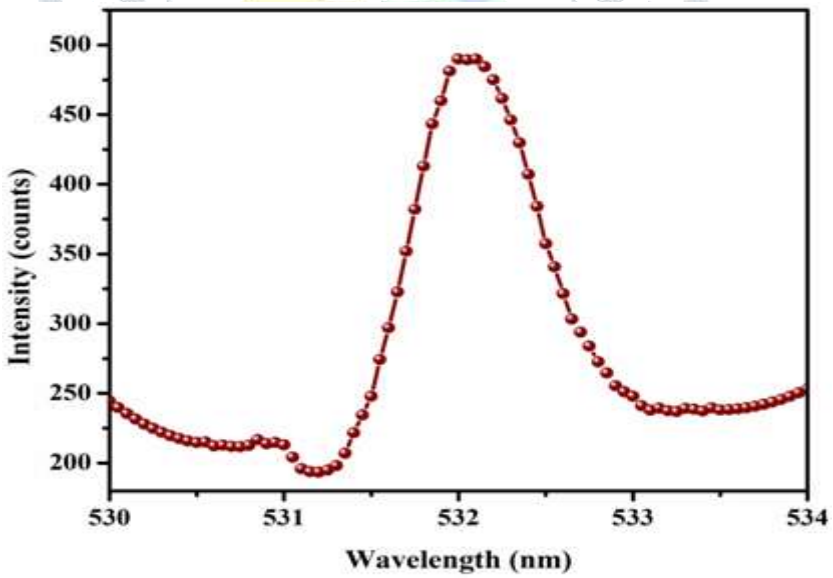

Fig. 6 SHG efficiency of microwave assisted ZnO nanoparticles

Now, the sample is probed with fundamental wavelength of Nd: YAG Laser and we observe that the material exhibit the second harmonic generation of 1064 nm i.e., 532 nm. The maximum conversion efficiency of SHG for the ZnO was found to be 1.5 times of KDP (Fig. 6) [13-14].

IV. Conclusion

ZnO nanoparticles was synthesized by the microwave assisted method. XRD pattern demonstrates a hexagonal structure of ZnO. FESEM image shows the particle like structure and the presence of Zn and O atoms is confirmed by EDS. The FT-IR spectrum represents the characteristic vibrational modes of Zn-O. From the optical band gap values showed quantum confinement of synthesized samples and this also confirmed by luminescence spectrum. The nonlinear optical studies were done by using a Q-switched Nd: YAG laser and the second harmonic generation efficiency was estimated was 1.5 times that of KDP. Overall results, ZnO nanoparticles will be useful in optoelectronic and photocatalytic applications.

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