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A Comparative Analysis of the Properties of Zinc Oxide (ZnO) Nanoparticles Synthesized by Hydrothermal and Sol-Gel Methods

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Abstract

Objective: To study the structural, optical and conductivity properties of ZnO nanoparticles synthesized by two different methods such as hydrothermal and sol-gel methods. **Methods/Analysis:** ZnO is synthesized at various temperatures 100°C, 150°C and 200°C using hydrothermal method with oxalic acid and zinc acetate and using sol-gel method with sodium hydroxide, zinc chloride and zinc nitrate. **Findings:** For both methods, the average crystal size determined by X-ray Diffraction **(**XRD) is noted to be in the range 20–30 nm. The pattern confirmed the composition, crystallinity and the synthesized products are ZnO with high purity and the hexagonal phase. The absorption peak of ZnO nanoparticles has a blue-shift compared with that of the bulk. In hydrothermal method, the band gap is large (i.e) from 4.4–4.9 eV and in the sol-gel method 3.5–3.9 eV. ZnO nanoparticles synthesized by both methods exhibit similar luminescence. Scanning Electron Microscopy (SEM) pictures reveal the morphology as near-spherical prismatic nano particles for hydrothermal method and as nanoflakes for sol-gel method. The Energy Dispersive X-ray Spectroscopy (EDAX) analysis confirms the presence of ZnO only and no other element. The conductivity decreases with the growth temperature as well as the concentration of the ZnO samples by sol-gel method. In contrast, the conductivity of the sample prepared by hydrothermal method, increases with the growth temperature but decreases with the concentration. **Novelty:** In addition, conductivity of the synthesized ZnO nanoparticles is measured for various concentrations of ZnO. The results of both the methods are compared with each other and with those reported in the literature.

Keywords: Conductivity, EDAX, PL, SEM, XRD, ZnO

1. Introduction

Zinc Oxide (ZnO) is a material with multifunctional and salient properties such as high photostability, low dielectric constant, high chemical stability, high electrochemical coupling co-efficient and broad range of radiation absorption. In typical wurtzite hexagonal structure, ZnO crystallizes with the arrangement of Oxygen atoms in hexagonally closed structure, while the distorted tetrahedron structure is occupied by Zinc atoms. It has a wide band gap of 3.37 eV and large exciton binding energy of 60 meV even at room temperature. It provides the greatest assortments of very rich variety of structures among all known materials. ZnO is one of the extensively studied semiconductor materials because of its interest as a fundamental study and also its applied aspects such as, luminescence, electronics, optoelectronics, photocatalysis, varistors, solar energy conversion, laser technology, medicine, transparent UV protection films and chemical sensors.

Optical and surface morphological properties of ZnO nanomaterials synthesized by hydrothermal method have been investigated[1]. The use of the sol-gel synthesis for the production of ZnO nanopowders has been proposed and the structure and morphology have been investigated with respect to the type of precursor, temperature of synthesis and dripping time[2]. The effects of reaction temperatures,

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the precursors concentration and growth time on the properties of ZnO nanopowders synthesized by hydrothermal method have been invesigated[3]. The morphology, crystallite size and optical properties of ZnO nanopowders synthesized by simple precipitation method were investigated. They also correlated the optical properties with morphology and crystallite size[4]. ZnO nanoparticles were synthesized by wet chemical method, based on cyclohexylamine, in aqueous and ethanolic media and tested for the photogradation of cyanide ions[5].

A quick process for preparation of ZnO nanoparticles with the use of microwave irradiation and the advantages in yield and reaction time were reported[6]. ZnO nanoparticles were synthesized using wet chemical method at room temperature and characterized[7]. The growth mechanism and modeling of ZnO nanopowders have been presented[8]. The characterization of ZnO nanoparticles synthesized by sol-gel method using zinc acetate as a precursor, acetic acid as the complexing agent and triton X-100 as a surfactant has been studied[9]. One pot synthesis of ZnO nanoparticles via Chemical and Green method using aqueous leaf extract of Corriandrum Sativum have been reported[10]. The influence of the reaction conditions and sintering on the properties of ZnO nanoparticles synthesized by sol-gel process assisted by Polyvinyl Alcohol (PVA) have been investigated[11]. Reviews of the growth, properties and applications of ZnO nanoparticles have been presented[12,13]. The structural and optical properties of nanocrystalline ZnO powders controlled by the effect of PVP concentration in sol-gel method has been studied[14]. The influence of cobalt doping on optical properties of ZnO nanoparticles synthesized by simple solution method has been analysed[15]. The effect of Al doping on the properties of ZnO nanoparticles fabricated by Sol-gel method has been studied[16].

In the present work, hydrothermal and sol–gel methods are used to prepare ZnO nanoparticles. The optical properties, particle size, conductivity and crystallinity of the synthesized ZnO nanopowders are investigated. The results of the two methods are compared with each other and with those reported in the literature.

2. Experimental Procedure: Synthesis of ZnO Nanoparticles

2.1 Hydrothermal Method

Aqueous solution of Oxalic acid and Zinc acetate dihydrate, under hydrothermal condition, are used. Oxalic acid with 0.1M molarity is taken in a beaker. Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) solution with 0.1M molarity is mixed with the oxalic acid and this mixture is left for stirring for 6 hours. A white precipitate is formed. Impurities are removed by filtering and washing with acetone and de-ionized water. It is then dried with various temperatures such as 100°C, 150°C and 200°C for 2 hours.

2.2 Sol-gel Method

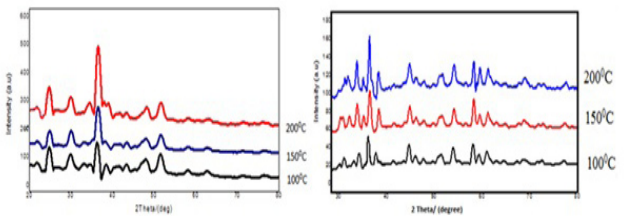
Zinc nitrate ($Zn(NO_3)_2$), Zinc chloride ($ZnCl_2$) and Sodium hydroxide (NaOH) are used as precursors. 1.0M molarity of NaOH is prepared with distilled water and continuously stirred at a desired reaction temperature, 50°C. After obtaining the desired temperature, a solution of $ZnCl_2$ 0.5M and another of $Zn(NO_3)_2$ are slowly added (dripping for 26 min) under constant stirring for 2 hours. A colourless precipitate of ZnO is formed and then the colour of the precipitate changes to white. The solution was agitated for a period of two hours, maintaining the desired temperature. The gel formed was filtered, washed with de-ionized water several times and dried for various temperatures such as 100°C, 150°C and 200°C.

All the chemicals used in all the methods of synthesis are of analytical reagent grade.

3. Results and Discussion: Characterization Studies

3.1 Structural Studies – X-ray Diffraction (XRD) Analysis

XRD patterns of the grown ZnO samples are recorded with the intensity data over a 2θ range of 20°-80°. Figure 1 shows the XRD patterns of ZnO nanoparticles prepared by 1. hydrothermal method and 2. sol-gel method at different annealing temperatures.



(a) (b)

Figure 1. XRD patterns of ZnO nanoparticles prepared by **(a)** hydrothermal method and **(b)** sol-gel method at different annealing temperatures.

It is observed that,

- The nature of ZnO is good crystalline which is confirmed by the sharp and intense diffraction peaks and they agree with the reported Joint Committee on Powder Diffraction Standards (JCPDS) data.
- The particles have a hexagonal phase with Wurtzite structure with hexagonally closed pack lattice of oxygen atoms and half the tetrahedral sites of zinc atoms[11].
- No characteristic peaks other than ZnO are observed which confirms that the synthesized products are of high purity.
- The intensity of the diffraction peaks increases and becomes sharper with increase in temperature, implying that the crystalline structure tends to have more integrity.
- A definite line broadening of the diffraction peaks is an indication that the synthesized ZnO materials are in nanometer range.

  The size (D) of the particles is calculated from the XRD line broadening measurement by Debye Scherrer's formula,

$$D = \frac{0.89\lambda}{\beta \cos\theta} \quad (1)$$

- where λ is the wavelength of (Cu K_a) X-rays, θ is the half diffraction angle and β is the Full Width at Half Maximum (FWHM).

The particle morphology of the ZnO nanoparticles is greatly influenced by the reaction temperature. In both synthesis methods, there is a decrease in crystallite size when temperature increases and the decrease in hydrothermal method is steeper than in sol-gel method. The crystallite size is same in both methods at 150^{0}C. FWHM increases with the reaction temperature but the size of the ZnO nanoparticles decreases with it, which may be due to the following reasons. 1. different crystallographic planes have different growth rates and 2. the quantum confinement effects, which is also confirmed by the Ultraviolet-Visible (UV-Vis) Absorption Studies. This behaviour is in contrast to that observed by Aneesh et al[3], where the FWHM decreases and the crystallite size increases.

3.2 Morphological Studies - Scanning Electron Microscopy (SEM)

Figure 2 shows the morphology of the samples observed in SEM. These images confirm the formation of ZnO nano powders. The morphology is analysed for various temperatures such as 100^{0}C, 150^{0}C and 200^{0}C. SEM pictures reveal the morphology as near-spherical prismatic nanoparticles for hydrothermal method and as nanoflakes for sol-gel method.

3.3 Dispersion Studies – Energy Dispersive X-ray Spectroscopy (EDAX)

EDAX spectra are shown in Figure 3 for the ZnO nanoparticles prepared by 1. hydrothermal method and 2. sol-gel method. Element with large concentration in the sample can be noted from the EDAX spectrum, as the one with highest peak. EDAX reveals the presence of required elemental composition of both Zinc (Zn) and Oxygen (O) in the samples.

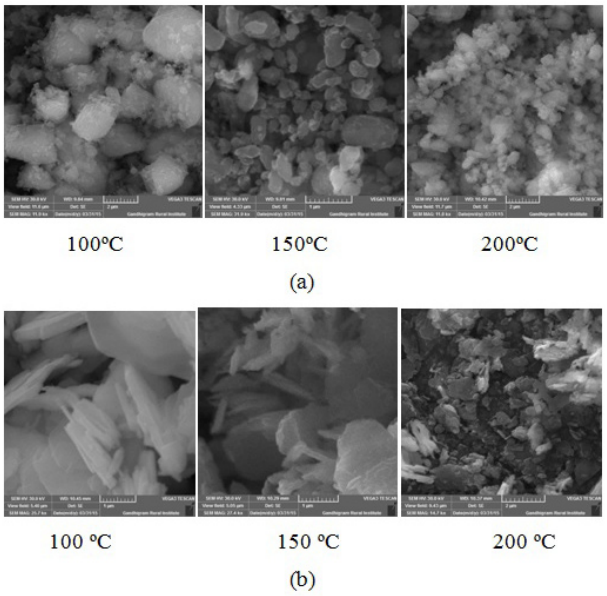


Figure 2. SEM images of ZnO nanoparticles prepared by **(a)** hydrothermal method and **(b)** sol-gel method.

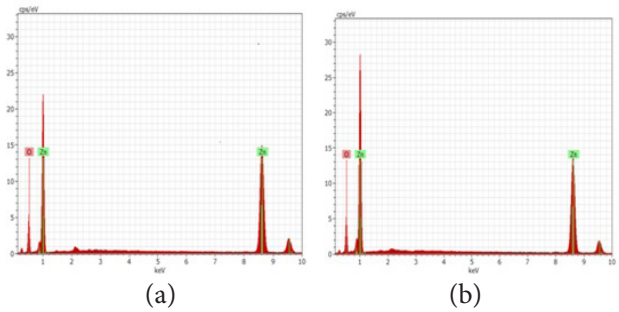


Figure 3. EDAX spectrum of ZnO nanoparticles prepared by **(a)** hydrothermal method and **(b)** sol-gel method.

3.4 Optical Studies -Ultraviolet-Visible (UV-Vis) Absorption Studies

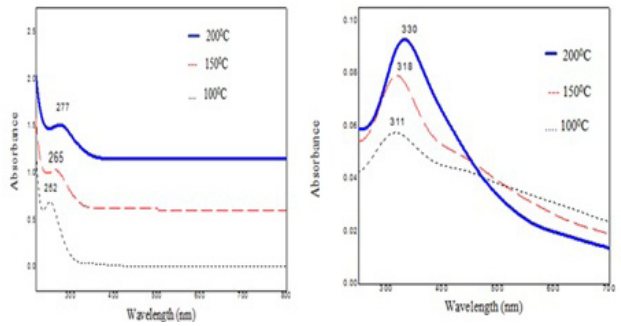
Figure 4 depicts the spectra of optical absorption in ZnO nanoparticles prepared by 1. hydrothermal method and 2. sol-gel method annealed at various temperatures, 100^{0}C, 150^{0}C and 200^{0}C. UV-Vis absorption of ZnO nanoparticles was recorded in the wavelength range of 200 – 800 nm.

ZnO has a band gap of 3.37 eV and hence a peak in the absorption spectra[7] is expected to occur at ≈ 358 nm. Exciton binding energy in ZnO ≈ 60 meV and hence shows unique features of exciton absorption.

It is observed that,

- The absorbance increases with temperature, and hence, there should be a decrease in band gap.
- Hydrothermal method shows a widened shoulder peaks at 252, 265 and 277 nm implying the absorption spectra with a strong blue shift. This indicates that the exciton in ZnO has a Bohr radius larger than the size of the ZnO nanopowders. These results are in good agreement with those of Oladiran and Olabisi[7].
- Strong excitonic absorption peaks at 311, 318 and 330 nm in sol-gel method confirm the lower particle size of ZnO[1] and the photosensitivity of the sample in the UV region[2].
- No emission peaks are observed indicating the absence of free exciton recombination via a collision process of exciton-exciton and oxygen interstice.

The band gap energies are calculated by extrapolating the straight line portion of the plot of modified Kubelka-Munk function (αhν)[2] against photon energy[4] (hν), as shown in Figure 5.



(a) (b)

Figure 4. UV-Vis absorption spectra of ZnO nanoparticles by **(a)** hydrothermal method and **(b)** sol-gel method at different annealing temperatures

The UV cut-off provides the value of band gap in the range 4.4 to 4.9 eV in hydrothermal method and 3.5 to 3.9 eV in sol-gel method higher than that of bulk ZnO of 3.37 eV. Hydrothermal method shows larger blue shift than sol-gel method. This blue shift, (the absorption maximum shifted to lower wavelengths), is due to quantum confinement effects[3] that led to the decrease in the particle size smaller than the exciton Bohr radius for ZnO and the radiative recombination of photo-generated holes with singularly ionized oxygen vacancies[17, 18].

3.5 Photoluminescence (PL) Emission Studies

Both physical and applied aspects of ZnO nanoparticles can be well understood from the luminescence studies of them. Figure 6 depicts the photoluminescence spectrum of ZnO nanoparticles synthesized by 1. hydrothermal and

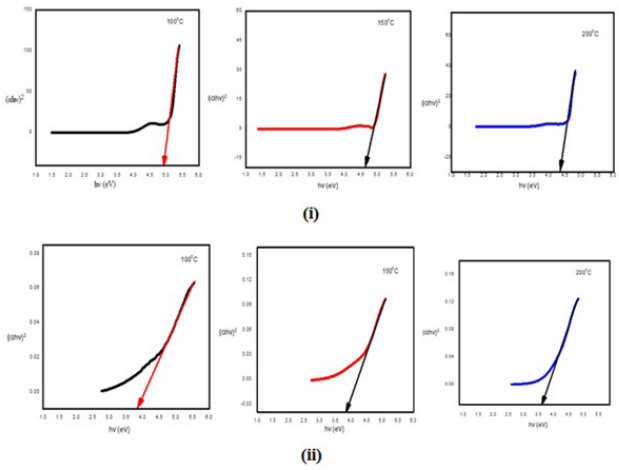
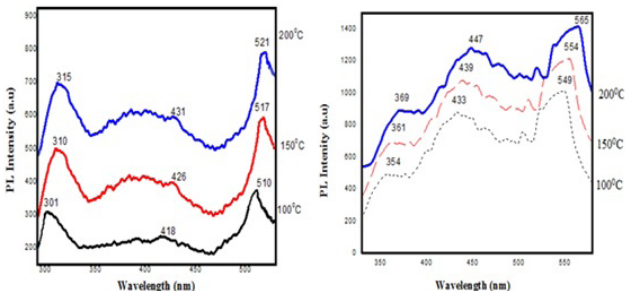


Figure 5. UV band gap measurement for **(i)** hydrothermal method and **(ii)** sol-gel method at different annealing temperatures.



(a) (b)

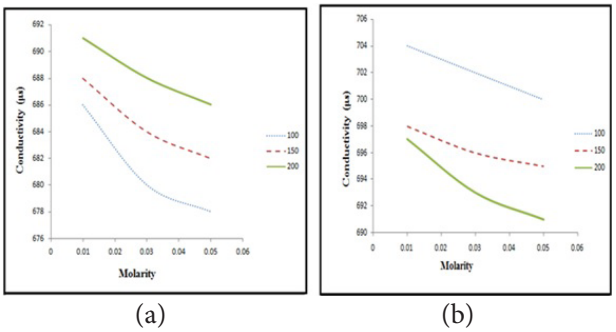
Figure 6. PL spectrum of the ZnO nanoparticles prepared by **(a)** hydrothermal method and **(b)** sol-gel method with different annealing temperatures.

2. sol-gel methods. It is observed that ZnO nanoparticles synthesized by both the methods exhibit similar luminescence.

- Strong emission peaks centred at 301, 306 and 312 nm for hydrothermal method and 354, 361 and 368 nm for sol-gel method are observed. The blue shift in the bandgap of ZnO nanoparticles is confirmed by these excitation peaks which correspond to the transition from band to band[3].
- Blue emission peaks observed at 418, 426 and 431 nm for hydrothermal method and 433, 439 and 447 nm for sol-gel method are the artifacts arising due to the improper alignment of the measurement set-up or the inappropriate choice of components in a PL system.
- Photo-generated holes recombine radiatively with electrons created by specific defect in the surface or subsurface which are of singly ionized charge state[1,6]. A transition occurs between oxygen vacancy of single charge and hole which is photo-excited or defects which are Zn interstitial related[3]. Green-yellow emission peaks observed at 510, 517 and 521 nm for hydrothermal method and 549, 554 and 565 nm for sol-gel method are due to either of these two effects.

3.6 Conductivity Studies

Figure 7 depicts the conductivity of ZnO synthesized by hydrothermal and sol-gel methods for various temperatures and concentrations. The conductivity decreases, when the growth temperature as well as the concentration of the prepared ZnO samples by sol gel method increases. In contrast, the conductivity of the sample prepared by hydrothermal method increases as the growth temperature increases, but decreases as the concentration increases.



(a) (b)

Figure 7. Conductivity of the ZnO samples prepared by **(a)** hydrothermal method and **(b)** sol-gel method.

4. Conclusion

ZnO nanopowders are synthesized by hydrothermal and sol-gel methods at different temperatures such as 100^{0}C, 150^{0}C and 200^{0}C for 2hrs. In both the methods, the mean crystal size, calculated from XRD pattern, is found to be in the range 20-30 nm. The pattern confirmed the composition, crystallinity and the synthesized products are ZnO with high purity and the hexagonal phase. Crystallite size decreases as temperature increases. The peak in absorption spectra of the prepared ZnO nanoparticles shows a blue-shift comparatively larger than the bulk. When the temperature increases, the absorbance also increases and the band gap decreases. In hydrothermal method, the band gap is large (i.e) from 4.4-4.9 eV and hence it has large applications in solar field. ZnO nanoparticles synthesized by both the methods exhibit similar luminescence. SEM pictures reveal the morphology as near-spherical prismatic nanoparticles for hydrothermal method and as nanoflakes for sol-gel method. The EDAX analysis confirms the presence of ZnO only and no other elements is present. The maximum peak is obtained for Zinc. In both hydrothermal as well as sol-gel methods, a pure ZnO occurrence is obtained. The conductivity decreases with the growth temperature as well as the concentration of the ZnO samples by sol gel method. In contrast the conductivity of the sample prepared by hydrothermal method increases as the growth temperature increases, but decreases as the concentration increases.

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