

## A study of nanosized zinc oxide and its nanofluid

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**Abstract.** The synthesis and characterization of nanosized zinc oxide and its nanofluid in a polyvinyl alcohol (PVA) matrix have been done in the present investigation. Crystalline zinc oxide nanoparticles are synthesized using single-step chemical method while the nanofluids are prepared by the dispersion of nanoparticles in PVA solution using an ultrasonicator. The prepared nanoparticles are characterized using X-ray diffraction, SEM–EDX and UV–visible spectrum. The particle size distribution measurement is carried out by acoustic particle sizer. The ultrasonic velocities are measured in the synthesized nanofluid under different physical conditions using an ultrasonic interferometer. It is found that the degree of crystallinity of nanoparticles depends on the evaporation rate during its synthesis and ultrasonic velocity has non-linear relation with temperature for the present nanofluid.

**Keywords.** ZnO nanoparticles; ZnO–PVA nanofluid; structural, optical and ultrasonic properties.

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### 1. Introduction

Zinc oxide is a wide band-gap semiconductor. Several studies have been done for its characterization and application [1–4]. Metal oxide nanostructures can be used in solar cells, electroluminescent devices, electrochromic windows and chemical sensors [5]. The ZnO nanostructures can be found in several forms like rod/wire [6,7], thin film [8] and particles [9–11]. The nanostructured ZnO possess high surface area as well as good electrical, electrochemical and structural properties. The synthesis of ZnO nanoparticles and their structural/optical characterization can be seen in literature [9–11]. The ZnO powders at nanoparticle size can be used as antibacterial agents [12].

The sound propagation through random media (colloidal suspensions, porous materials and nanofluids) has also been a subject of great interest recently. Nanofluid is a

colloidal suspension of nanoparticles in a polymer matrix. Nanofluids have been of great interest due to their broad applications in different fields [13]. The preparation and characterization of ZnO nanoparticles, ZnO–ethylene glycol and ZnO–water nanofluids are reported in [13–15]. The anomalous behaviour of ultrasonic velocity in sintered ZnO provides information about the pore size, pore shape and their distribution [16]. Very few nanofluids and magnetic fluids are found to be characterized using ultrasonic technique [17–19] and no work has been reported for determining the ultrasonic properties in ZnO nanofluid to the best of the author's knowledge. In the present investigation, we have chosen ZnO–PVA nanofluid for the characterization. Initially, ZnO nanoparticles are synthesized through chemical route and characterized by XRD, SEM and UV–visible absorption spectrum. Later on, ZnO nanofluid is synthesized using polymer solution of PVA with the help of ultrasonicator. We have measured the particle size distribution in the prepared nanofluid for the justification of particle size. The ultrasonic velocity measurements are performed for ultrasonic characterization of the prepared fluid. The obtained results are analysed for the characterization.

## **2. Sample preparation and measurements**

Zinc oxide nanoparticles were prepared successfully by the one-step solvothermal reaction of zinc acetate in alcohols. Zinc acetate dihydrate (13.4 mmol) was dissolved in methanol and a solution of potassium hydroxide was prepared by dissolving potassium hydroxide (28.96 mmol) in methanol. The potassium hydroxide solution was added dropwise to the zinc acetate solution at 52°C under vigorous stirring. Nanoparticles started to precipitate and the solution became turbid. The heater and stirrer were removed after 2 h and the solution was allowed to sit for another 2 h. The ZnO nanoparticles were settled at the bottom and the excess mother liquor was removed. The precipitate was washed twice with methanol (50 ml) and collected by centrifugation process and allowed to dry at room temperature for one day. The obtained solid was crushed to get a white powder and the obtained powder was dispersed in PVA with ultrasonicator. The dispersed solution was translucent and stable for up to 2 weeks. Aggregation was found to occur at this stage. The size and shape of the particles were controlled by evaporation rate. Two samples of ZnO nanoparticles were prepared by controlling the evaporation rate.

The X-ray diffraction patterns of the powdered samples of the ZnO nanoparticles were analysed using an X'Pert-Pro, PANalytical (with  $\lambda=1.5405 \text{ \AA}$  Cu-K $\alpha$  radiation) operating at room temperature. A scanning electron microscope of Oxford model Leo 1550 was used for the morphological and average particle size study. The UV–visible absorption spectrum was recorded using Lambda 35, Perkin–Elmer double beam UV–visible absorption spectrometer for optical characterization.

1, 2 and 5 wt% of the ZnO nanoparticles (prepared at low evaporation rate) were dispersed in a solution of 3 wt% PVA using ultrasonicator to form the nanofluid. The particle size distribution measurements were done by an acoustic particle sizer model APS-100 (Matec Applied Sciences, Massachusetts, USA). Ultrasonic velocity was measured at 2 MHz using ultrasonic interferometer in the temperature range of 25–65°C. Water was circulated around the sample using a specific thermostat. The measured value

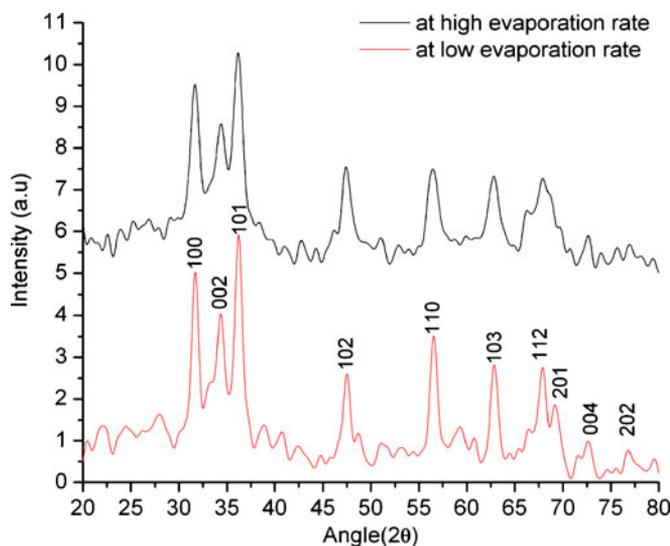
of ultrasonic velocity was accurate to  $\pm 0.1\%$  with an error of measurement of  $\pm 0.5^\circ\text{C}$  in temperature.

### 3. Results and discussion

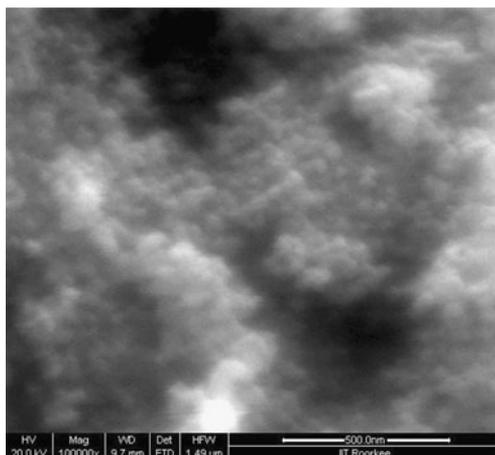
#### 3.1 Structural and optical characterization

The structural analyses of the ZnO nanoparticle samples, synthesized at low and high evaporation rates were carried out by XRD and UV–visible absorption spectrum measurements. The XRD patterns of both the samples are shown in figure 1.

X-ray diffraction pattern (figure 1) shows that narrower and higher intense peaks are obtained in the diffraction pattern for samples formed at low evaporation rate than for samples formed at high evaporation rate. Thus the degree of crystallinity and particle size of the samples increase with decrease in evaporation rate. The crystallite/particle size has been calculated using the Debye–Scherrer equation for all diffraction peaks. The particle size of the sample is found ranging between 35 and 50 nm. The intensity peaks of XRD pattern are coordinated with JCPDS file number 790206 and it is confirmed that the crystalline sample is of ZnO which is hexagonal in structure with lattice parameters  $a = 3.249 \text{ \AA}$  and  $c = 5.206 \text{ \AA}$ . The size and morphology of the ZnO nanoparticles have been determined using scanning electron microscopy. Figure 2 shows the typical scanning electron micrograph (SEM) images of ZnO nanoparticles. The SEM image shows random distribution of the ZnO nanoparticles having non-spherical shape and diameter in the range of 30–60 nm. The EDX spectrum (figure 3) of the ZnO nanoparticles reveals that our sample contains zinc, oxygen, gold, and potassium as constituent components. The trace of gold is due to the sample coating during SEM imaging and potassium can broadly



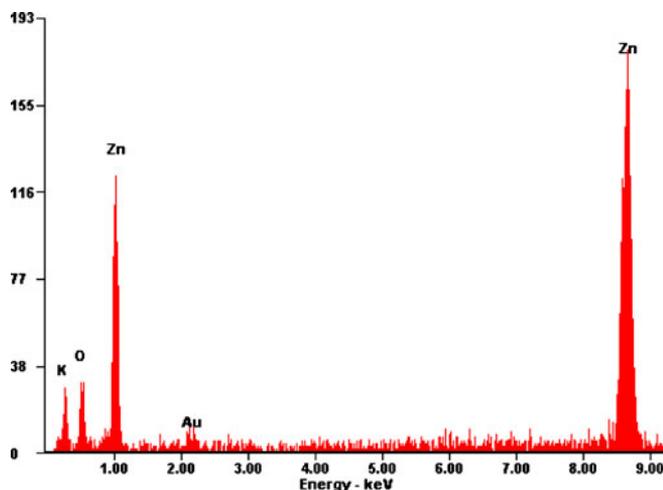
**Figure 1.** XRD patterns of the powder sample of ZnO nanoparticle at high and low evaporation rates.



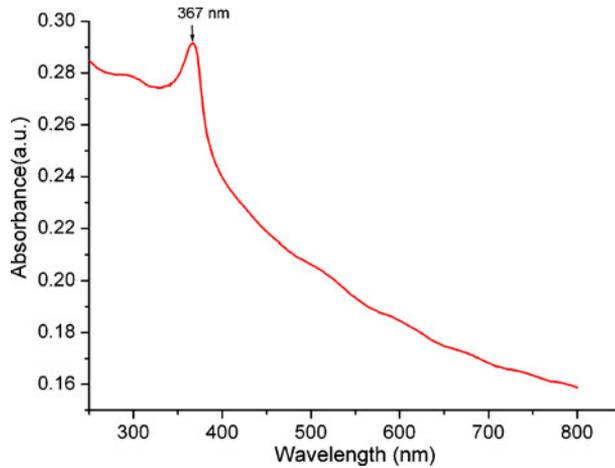
**Figure 2.** SEM image of the agglomerated ZnO nanoparticles.

be attributed to the fact that potassium hydroxide was used in the reaction process. The high-intensity peaks for zinc and oxygen justify that the sample contains mainly ZnO.

The room-temperature UV–visible absorption spectrum of the ZnO nanoparticles is recorded in the wavelength range of 250–800 nm. Figure 4 represents the UV–visible absorption spectrum of the ZnO nanoparticles. The spectrum has a peak at 367 nm (3.38 eV). The absorption peak for 40 nm ZnO nanoparticles has been reported at 361 nm (3.44 eV) elsewhere [20,21]. The absorption peak for 5–6 nm ZnO nanoparticles has been found to be between 360 and 365 nm [5,9]. The variation in absorption peak is due to variation in particle size. The band gap for normal-sized ZnO is 3.3 eV. Thus at nanoscale, the band gap increases for the ZnO.



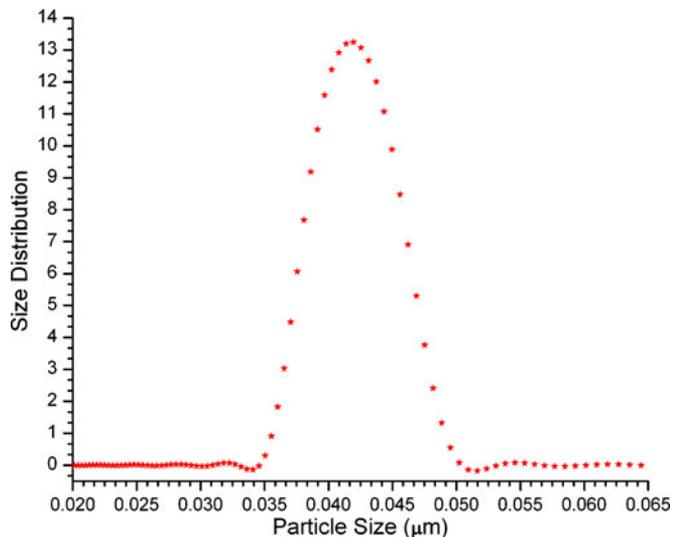
**Figure 3.** EDX spectrum of ZnO nanoparticles using zinc acetate as the precursor material.



**Figure 4.** UV-visible absorption spectrum of the ZnO nanoparticles.

### 3.2 Particle size distribution and ultrasonic velocity

The particle size distribution measured using acoustic particle sizer (APS-100) is plotted in figure 5, which clearly explains that the size of the suspended particle in the PVA suspension (nanofluid) is in the range 35–50 nm. The maximum numbers of particles are in approximately 42 nm size. This confirms that the prepared solution is a nanofluid. It is observed that the present nanofluid is found to be stable for more than one week. The



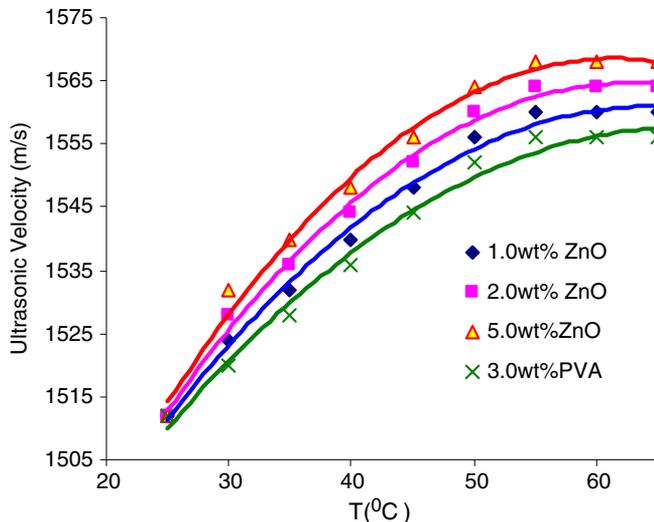
**Figure 5.** Particle size distribution curve.

stability of the nanofluid suspension can be accurately determined with Zeta potential measurement [22].

The ultrasonic velocities measured for pure PVA solution and the three nanofluids in the temperature range 25–65°C are shown in figure 6. The velocity curves indicate that the ultrasonic velocity in the samples increases with the temperature and it becomes approximately constant after 55°C. Ultrasonic velocity is found to be higher for the nanofluids than for pure PVA solution. It is also observed that the magnitude of velocity increases with the particle volume fraction.

The behaviour of ultrasonic velocity can be understood with its related quantities. The ultrasonic velocity is well related to bulk modulus ( $B$ ), compressibility ( $k$ ), and density ( $\rho$ ) of the medium ( $V = \sqrt{B/\rho} = 1/\sqrt{k\rho}$ ;  $k = B^{-1} = (\lambda + 2\mu)^{-1}$ ;  $\lambda$  and  $\mu$ : Lamé moduli). The density, compressibility and Lamé moduli of a fluid medium are altered by the dispersion of nanoparticles and are functions of particle volume fraction [23–25]. Hence, the enhancement in velocity by the dispersion of nanoparticles is due to change in density, compressibility, bulk modulus and Lamé moduli of the nanoparticle suspension with volume fraction. The velocities of the present nanofluids are found greater than the velocity in pure matrix state, which indicates that by the dispersion of solid particles – there is a change in density and bulk modulus. An increase in bulk modulus or decrease in compressibility is attributed to the fact that strong cohesive interaction forces act among the molecules and atoms after the dispersion of ZnO nanoparticles in the PVA matrix.

The velocity of the nanofluid is independent of particle size in low-frequency region [24–26]. Here all the nanofluids are prepared with ZnO nanoparticles primed at low evaporation rate and temperature-dependent velocity is measured at low frequency (2 MHz). Thus it may be concluded that temperature-dependent velocity at low frequency in ZnO



**Figure 6.** Velocity vs. temperature for pure PVA solution and nanofluids.

nanofluid depends only on the particle volume fraction. The ultrasonic velocity in the nanofluid is a quadratic function of temperature at low frequency [25].

$$V = V_0 + V_1T - V_2T^2, \quad (1)$$

where  $V_0$  is the ultrasonic velocity at initial temperature,  $V_1$  and  $V_2$  are the absolute temperature coefficients of velocity and  $T$  is the temperature difference between experimental and initial temperature. The first two terms in eq. (1) are found normally for simple liquid system, but the third non-linear term is caused by nonlinear change in bulk modulus/density of nanofluid system with temperature. It affirms that eq. (1) is also justified for the present nanofluid.

#### 4. Conclusions

The following conclusions can be drawn on the basis of the above discussion:

- The XRD pattern shows that the degree of crystallinity of the ZnO nanoparticle depends on the evaporation rate during its synthesis.
- The band gap of ZnO increases at nanoscale.
- The temperature variation of ultrasonic velocity in ZnO–PVA nanofluid mainly depends on the particle volume fraction of the dispersed particles in low-frequency region and is larger than the velocity for pure matrix. A non-linear relation between velocity and temperature is found for the present nanofluid samples.

The present results along with known physical properties of the nanocrystalline ZnO, offer a new dimension for further study and characterization of nanofluids.

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