INVESTIGATION OF ULTRASONIC PARAMETERS OF ZnO - ETHYLENE GLYCOL NANOFLUIDS

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In the present work, Zinc oxide nano particles were synthesized by a simple polymer decomposition method using Zinc nitrate as a precursor material and Poly vinyl alcohol as an encapsulating agent. The prepared ZnO nanoparticles were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and UV-Vis absorption spectrum. Further as prepared ZnO nanoparticles were suspended in ethylene glycol, in order to obtain ZnO-Ethylene glycol nanofluid. The nanofluids were synthesized by the dispersion of ZnO nanoparticles in Ethylene glycol solution using an ultrasonicator. ZnO-Ethylene glycol nanofluid additionally characterized with ultrasonic interferometer to obtain ultrasonic parameters like adiabatic compressibility (β), acoustic impedance(Z) and thermal conductivity(k).

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1. Introduction

Nanofluid is the name presented by Argonne National Laboratory to illustrate the suspension of nanoparticles in a base fluid. Base fluids such as water, ethylene glycol and engine oil have very low thermal conductivities. The thermal conductivity of nanometer sized particles is typically in the order of magnitude higher than those of the base fluids. The addition of nanoparticles to the base fluid even at low volume concentrations, results in significant increases in thermal performance.[1-6] Recently, an increase in the thermal conductivity coefficient of nanofluids which contain a little amount of metallic particles like Cu or nonmetallic particles like ZnO, Al_2O_3, CuO, and SiC had also been reported. The natural potential of nanomaterials which are dispersed in base fluids for heat transfer also has an important effect on the rate of increase in thermal conductivity coefficient of nanofluids. For example, carbon nanotubes, due to their high thermal conductivity coefficient, are known as an ideal material for making nanofluids.[7-8]

ZnO is a unique material with a high exciton binding energy (60 meV), lending itself to applications in a variety of optical, acoustic, and electronic devices. Due to its attractive properties, ZnO structures ranging from the microscale (varistors, transparent conducting oxides) [9-10] to the nano scale (UV lasers) [11] have attracted increasing concentration in recent years. The large band gap (E_g = 3.3 eV). ZnO is useful for the fabrication of light emitting diodes [12], transparent solar cells, Electroluminescent memory devices [13,14] and related applications. Furthermore, its piezoelectric nature is suitable for constructing electromechanical coupled sensors and transducers. ZnO nanostructures have interesting properties due to the confinement of charge carriers and phonons, which allows not only the continuous tuning of its optoelectronic properties but also improvement in device performance. ZnO nanoparticles can be synthesized by various approaches including sol–gel processing [15], homogeneous precipitation [16], mechanical milling [17],

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organometallic synthesis [18], microwave method [19], spray pyrolysis [20], surfactant assisted combustion synthesis [21] and polymer assisted combustion synthesis [22].

In this paper a simple synthesis method, different from the one mentioned above, is proposed to produce ZnO nanoparticles. ZnO is an fascinating material from several points of view. It is one of the few oxides that shows quantum confinement effects. Here in we report the polymer decomposition method using zinc nitrate as a precursor. The nano particles were characterized by X-ray diffraction (XRD) analysis, UV- visible spectroscopy; Transmission electron microscopy (TEM) and Ultrasonic interferometer.

2. Experimental

2.1 Preparation of ZnO nanoparticles

Polymer decomposition method has been recognized as the cost effective and easy method. Zinc oxide nanoparticles were successfully prepared by polymer decomposition method. Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, MERCK, India) salt with appropriate amount of poly vinyl alcohol is dissolved in distilled water .The solution further mixed by magnetic stirring is put on the hot plate. As the temperature reached 100^0C, water started to boil and evaporate from the solution, which increased solution viscosity significantly, during which the mixture trapped with carbonaceous fumes and gases evolved with light brownish precipitate remained as a deposit. Then the powder is calcined for two hours at 400^0C. Calcined sample removed carbon impurities due to polymer decomposition showing a color change from brown to white colored powder of ZnO nanoparticles.

2.2. Characterization

The crystal structures of the calcined samples were characterized by powder X-ray diffraction (XRD) using an (Bruker D8 , Advance, Germany) X-ray diffractometer . XRD was performed within the range of $20^0 \leq 2\theta \leq 80^0$ by using CuKα as radiation (1.5406 Å) in configuration. The optical properties of the samples were characterized by UV-Vis Spectroscopy (Systronics, India) with a wavelength range of 200-800 nm. The particle size and morphology of the calcined powders were characterized by transmission electron microscopy (HR-TEM model no: JEOLJEM 200CX).

Nano fluids were subjected to ultrasonic studies at room temperature. The velocity values of ultrasonic wave propagation through nano fluid samples were measured using single frequency continuous wave ultrasonic interferometer (Model VCT-70A, Mittal Enterprises, India) with an accuracy of ± 0.05 % at frequency of 2 MHz. Nanofluids are suspensions of nano particles in fluids that show significant enhancement of their properties at modest nanoparticle concentrations. Nano fluids are considered to offer important advantages over conventional heat transfer fluids. Nano fluids contain suspended metallic and metal oxide nanoparticles, which increases the thermal conductivity of the base fluid by a substantial amount [7].

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the as-prepared sample and calcined ZnO nanoparticles in the range of $2\theta = 20^0–80^0$ are as shown in Fig. 1. The marked peaks could be indexed as the ZnO hexagonal wurtzite structure (JCPDS data card no: 36- 1451). The crystallite size of the ZnO nanoparticles was determined by the X-ray line broadening method using the Scherer equation:

$$D = \frac{k\lambda}{\beta_D cos\theta} \quad (1)$$

where D is the crystallite size in nanometers, λ is the wavelength of the radiation (1.54056 A ° for CuK_α radiation), k is a constant equal to 0.94, β_D is the peak width at half-maximum intensity, and θ is the peak position.

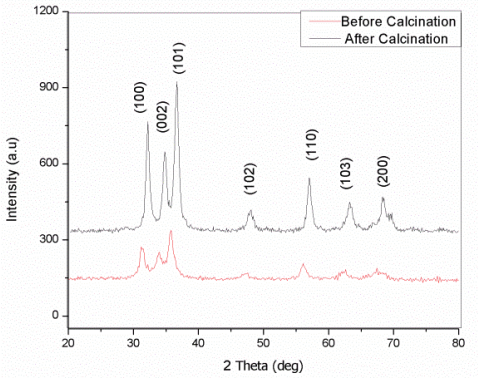

Fig. 1. XRD pattern of the as prepared and calcined ZnO nanoparticles

Applying the Scherer formula [23] and the full width at half maximum (FWHM) to the all planes , average values of crystallite sizes have been calculated for the as-prepared ZnO as 6.98 nm and calcined ZnO nanoparticles as 9.43 nm respectively.

3.2. UV- Vis Spectroscopy

Fig. 2. shows the absorption spectra (a) and corresponding calculated band gap (b) of samples, in which the band gap is estimated from the optical absorption spectra. For a direct band gap semiconductor, the relationship of the absorption coefficient and the band gap energy can be described by the following equation [24,25]:

$$(\alpha h\nu)^{\frac{1}{2}} = A(h\nu - E_g) \quad (2)$$

where A is a constant, and *a*, *hv* and E_g are denoted as the absorption coefficient, photon energy and optical band gap, respectively. The optical band gap (Eg) is obtained by plotting $(\alpha\ h\nu)^2$ versus (*hv*) and extrapolating the tangent of the curve to $(\alpha h\nu)^2$. It can be clearly seen that the absorption edge exhibits a red shift and the band gap decreases with calcination. The band gap obtained for as-prepared and calcined samples are 3.42 eV and 3.32 eV with absorption emission peaks at 365 nm and 369 nm respectively.

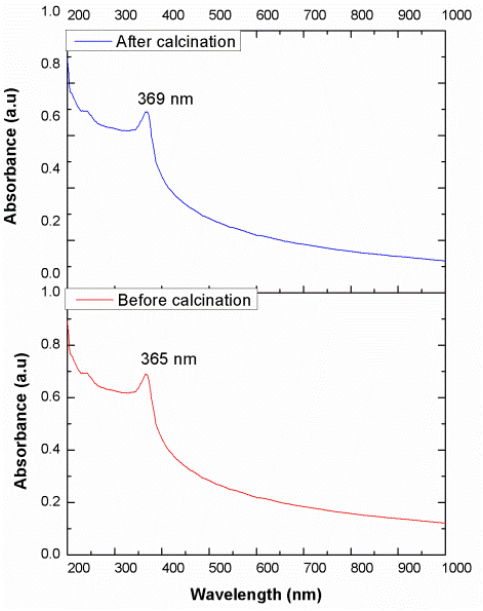

Fig. 2.a. Absorbance of the ZnO nanoparticles before and after calcinations

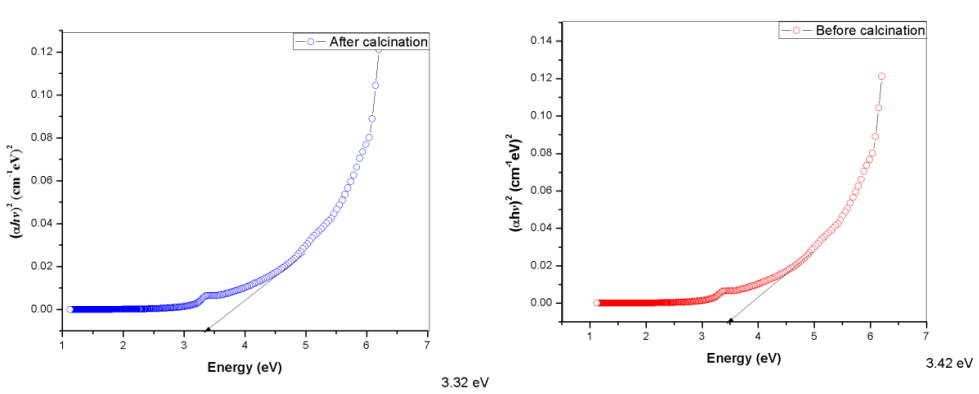

Fig. 2.b. Absorbance of the ZnO nanoparticles before and after calcinations

3.3. Transmission Electron Microscopy

A typical TEM micrograph of the ZnO nanoparticles obtained by polymer decomposition method is shown in Fig. 3. The powder consists of particles range from 10- 35 nm sizes. The morphology of pure ZnO nanoparticles clearly indicates the formation of presence of hexagonal wurzite structure. Inset Fig. 3 shows the Selected Area Electron Diffraction pattern of the pure ZnO nanopowder. Sharp diffraction rings appear in the diffraction pattern and strong diffraction spots exist in these rings. The diffraction pattern corresponds with zinc oxide. As shown in Fig. 3, no amorphous phase can be detected in the diffraction pattern.

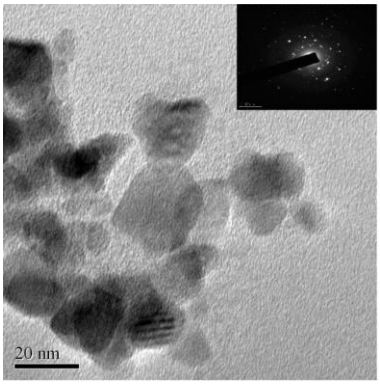

Fig.3. TEM analysis of pure ZnO nanoparticles

3. 4. Ultrasonic studies

The ultrasonic parameters like adiabatic compressibility(β), acoustic impedance(Z) and thermal conductivity(k), are calculated using ultrasonic velocity of ZnO-Ethylene glycol nanofluid for different concentrations obtained by ultrasonic interferometer.
The ultrasonic velocity is determined by following expression[26].

$$v = \lambda \mathrm{f} \tag{3}$$

where f = 1.9925 MHz, λ is wavelength determined from Nanofluid interferometer, v is Ultrasonic velocity.

The adiabatic compressibilty of the ZnO- ethylene glycol nanofluid is determined by the Newton-Laplace's relation [27].

$$\beta = \frac{1}{\rho v^2} \tag{4}$$

where ρ is density of nanofluid and v ultrasonic velocity.

The acoustic impedance of ZnO- ethylene glycol is calculated for all concentrations using the relation [28].

$$Z = \rho v \tag{5}$$

where ρ is density of nanofluid and v ultrasonic velocity.

The thermal conductivity for ZnO- ethylene glycol nanfluid is ddetermined by using modified version of Bridgman's equation [29].

$$k = 2.8 \left(\frac{N}{V}\right)^{2/3} Kv \tag{6}$$

where N is avagadro number , V is molar volume of the nanofluid , K is Boltzmann's constant and v ultrasonic velocity.

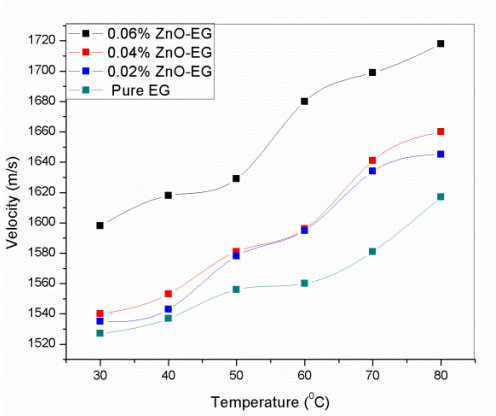

*Fig.4. Ultrasonic velocity of base fluid and ZnO-Ethylene glycol nanofluid at low concentrations(*0.02%,0.04% and 0.06%)

Fig.4. indicates ultrasonic velocity of base fluid and ZnO-Ethylene glycol nanofluid at different concentrations (0.02,0.04 and 0.06). From Fig.4, it is found that ultrasonic velocity increases with increase in concentrations of nanofluids. With the propagation of ultrasonic vibrations through the nanofluids, the Brownian motion in the fluid resulting in increase in velocity and the random movements of nanoparticles are increased with increase in concentration. Size, ultrasonic velocity is quite sensitive to the size, morphology and dispersion of the particles. Ultrasonic velocity increases with the concentration of nanofluid in respect with particle fraction but at very higher concentrations ultrasonic velocity increases with the concentration of nanofluid due to agglomeration of nanoparticles.

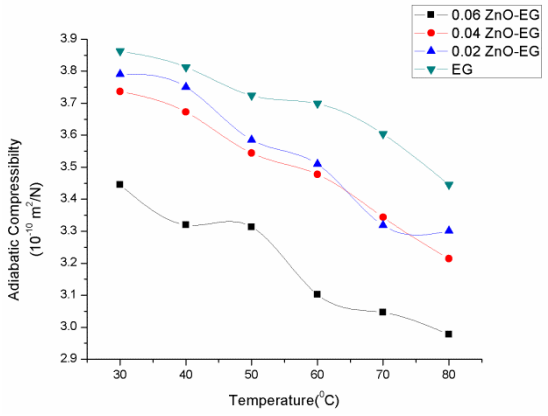

*Fig.5. Adiabatic compressibility of base fluid and ZnO-Ethylene glycol nanofluid at low concentrations(*0.02%,0.04% and 0.06%)

Fig.5. indicates adiabatic compressibility of base fluid and ZnO-Ethylene glycol nanofluid at different concentrations (0, 0.02,0.04 and 0.06). From Fig.5, it is observed that adiabatic compressibility decreases with increase in concentrations of nanofluids. The decrease in adiabatic compressibility shows the weaker force of interaction between particles and base fluid molecules. Compressibility decreases due to the fact that metal ions form a core compact structure with the solvent molecules through hydrogen bonding. Weak forces operating between molecules results in variation in the values of adiabatic compressibility.

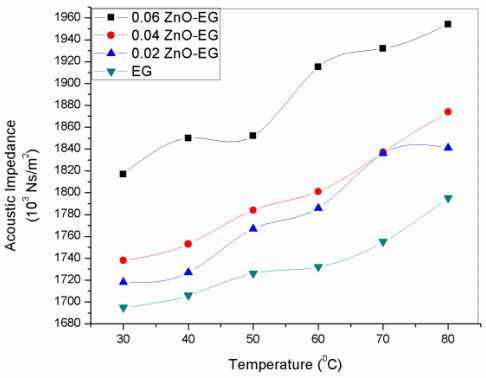

*Fig.6. Acoustic impedance of base fluid and ZnO-Ethylene glycol nanofluid at low concentrations(*0.02%,0.04% and 0.06%)

Fig.6. indicates acoustic impedance of base fluid and ZnO-Ethylene glycol nanofluid at different concentrations (0, 0.02,0.04 and 0.06). From Fig.6, it is observed that acoustic impedance increases with increase in concentrations of nanofluids.

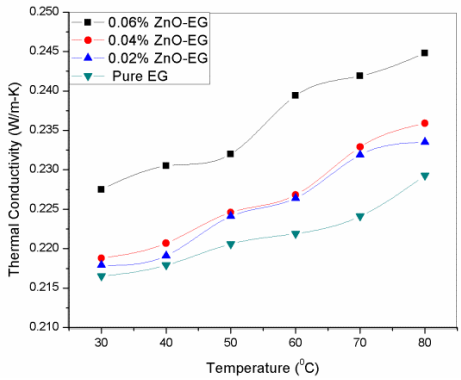

*Fig.7. Thermal conductivity of base fluid and ZnO-Ethylene glycol nanofluid at low concentrations(*0.02%,0.04% and 0.06%)

Fig.7. indicates thermal conductivity of base fluid and ZnO-Ethylene glycol nanofluid at different concentrations (0, 0.02,0.04 and 0.06). From Fig.7, it is observed that thermal conductivity increases with increase in concentrations of nanofluids. Comparing the thermal conductivities of base fluid and ZnO-Ethylene glycol nanofluid , ZnO-Ethylene glycol nanofluid has better thermal conductivity. Nanofluids have high thermal conductivities at very low nanoparticles concentrations, the exact mechanism of which is not known. Brownian motion of suspended nanoparticles is attributed as one of the key factors of the greatly enhanced thermal conductivity.

Table1,2 and 3 indicates the ultrasonic parameters like ultrasonic velocity, adiabatic compressibility, acoustic impedance and thermal conductivity values for the base fluid and ZnO-Ethylene Glycol nanofluid at different concentrations.

Table 1.Thermal Conductivity Studies of base fluid (Ethylene Glycol):

S.No	Temperature	Velocity (m/s)	Adiabatic Compressibility (10^{-10} m^2/N)	Acoustic Impedance (10^3 Ns/m^3)	Thermal Conductivity (W/m-K)
1	30	1527	3.8625	1695	0.2165
2	40	1537	3.8128	1706	0.2179
3	50	1556	3.7242	1726	0.2206
4	60	1560	3.6988	1732	0.2219
5	70	1581	3.6037	1755	0.2241
6	80	1617	3.4455	1795	0.2293

Table 2. Thermal Conductivity Studies of 0.02% ZnO-Ethylene Glycol nanofluid

S.No	Temperature	Velocity (m/s)	Adiabatic Compressibility (10^{-10} m^2/N)	Acoustic Impedance (10^3 Ns/m^3)	Thermal Conductivity (W/m-K)
1	30	1535	3.7906	1718	0.2179
2	40	1543	3.7505	1727	0.2191
3	50	1578	3.5855	1767	0.2241
4	60	1595	3.5097	1786	0.2264
5	70	1634	3.3181	1836	0.2319
6	80	1645	3.3008	1841	0.2335

Table 3. Thermal Conductivity Studies of 0.04% ZnO-Ethylene Glycol nanofluid

S.No	Temperature	Velocity (m/s)	Adiabatic Compressibility (10^{-10} m^2/N)	Acoustic Impedance (10^3 Ns/m^3)	Thermal Conductivity (W/m-K)
1	30	1540	3.7367	1738	0.2188
2	40	1553	3.6724	1753	0.2207
3	50	1581	3.5440	1784	0.2246
4	60	1596	3.4776	1801	0.2268
5	70	1641	3.3435	1837	0.2329
6	80	1660	3.2141	1874	0.2359

4. Conclusions

ZnO nanoparticles have been effectively synthesized by a polymer decomposition method. The XRD results indicated that the synthesized ZnO nanoparticles had the pure wurtzite structure without any impurities and secondary phases. The crystallite sizes increases with calcination and the crystallite size before and after calcinations are as 6.98 nm and 9.43 nm for ZnO nanoparticles respectively. From UV analysis the band gaps before and after calcinations are observed to be 3.42 eV and 3.32 eV respectively.

From TEM analysis it is observed that the obtained pure ZnO nanoparticles are of crystalline in nature. TEM image indicated that the grain size of ZnO is between nm. Ultrasonic

inteferometer is employed for achieving ultrasonic parameters like ultrasonic velocity (*v*), adiabatic compressibility (β), acoustic impedance(Z) and thermal conductivity(k). From acoustic parameters it is observed that ultrasonic velocity increases with increase in concentrations of nanofluids, adiabatic compressibility decreases with increase in concentrations of nanofluids, acoustic impedance increases with increase in concentrations of nanofluids and thermal conductivity increases with increase in concentrations of nanofluids. Enhancement in thermal conducivity of ZnO-Ethylene glycol nanofluid is observed.

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