

Synthesis, Structural and Ultrasonic Studies on ZnS Nanofluid Synthesized by Wet Chemical Method

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Abstract: Initially ZnS nanoparticles were synthesized by wet chemical method at room temperature. The structural properties of ZnS nanoparticles were determined by X-ray diffraction technique which showed that ZnS nanoparticles have cubic zinc blende structure. Average particle size is in nanometer range while lattice constant is 5.380 Å. The prepared ZnS nanopowders were immersed in base fluid ethylene glycol (EG) to get ZnS nanofluids. The ultrasonic investigation of the base fluid ethylene glycol and ZnS nanofluids was carried out using ultrasonic interferometer technique operated at 2 MHz frequency. The ultrasonic velocity of base fluid EG and nanofluids of zinc sulphide were measured. The experimental data on ultrasonic investigation of the base fluid ethylene glycol and ZnS nanofluid is compared and reported in the result.

Keywords: X-Ray diffraction, ZnS, Cubic zinc blende, Ultrasonic measurements

1. Introduction

Nanofluids are two phase mixtures consisting of solid nanoparticles with nanometer sized particles which is well dispersed in base liquids/fluids such as water, ethylene glycol, lubricants and light oils [1]. The term nanofluid was introduced by Choi [2] as a fluid containing dispersed nanometer-sized solid particles. Nanofluids are used in several industrial sectors due to their high stability, and potential benefits in fields such as energy generation, medical, chemical processes, microelectronics, mechanical, automobiles and civil aspects [3]. Stability of nanofluid is play vital and is quite essential to apply them for applications [4]. From the literature it is found that there are only few reports available on the ultrasonic properties of nanofluids [5], [6]. The study of intra and intermolecular interactions in the fluid system is very much important and gives insight about the interacting properties of the molecules. Due to its wide variety of applications, ultrasonic velocity is significant for the study of various physical and chemical properties of the system and it is often used for the characteristics of materials which could be applied in industrial sector [7].

Zinc sulfide is an important II-IV semiconductor material with a wide band gap (3.72 eV for the cubic zinc blende phase and 3.77 eV for the hexagonal Wurtzite phase at 300 K) and a large excitation binding energy (40 meV) [8]. It has a wide range of applications such as in optical sensor, solid state solar window layers, photoconductors, phosphors and catalysts. Zinc sulfide nanoparticles exhibit remarkable physical properties which make it as a strong candidate in stable nanofluids and other applications [9], [10]. Even though water is the better coolant, Ethylene Glycol (EG) is frequently used due to its lower freezing point and can be applied in industrial fields as solvents, carriers, lubricants, binders, bases and coupling agents and also for extraction, separation, and purification of materials [11]. Ultrasonic

investigations of binary and ternary fluid mixtures of various types have been carried out by several investigators [12]. Studies on ultrasonic investigation and molecular interaction of ZnS nanofluid is very less focused area.

The aim of the present work is to study synthesis and characterization of ZnS nanoparticles and further to investigate ultrasonic properties such as ultrasonic velocity, density, adiabatic compressibility and bulk modulus of base fluid ethylene glycol (EG) and ZnS nanofluids.

2. Experimental Techniques

2.1 Synthesis of ZnS Nanoparticles

For the synthesis of ZnS nanoparticles in this study, zinc acetate dihydrate $Zn(CH_3COO)_2 \cdot 2H_2O$, sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$) were used, which were purchased from Sigma-Aldrich double distilled water was used as a solvent. All of the chemicals used were of AR grade without further purification. In the present work, ZnS nanoparticles have been prepared by wet chemical method at room temperature. For synthesis, zinc acetate (1.0 M) and sodium sulphide (1.0 M) were dissolved in minimum amount of distilled water separately and stirred continuously separate for 30 min. While stirring zinc acetate, freshly prepared sodium sulphide (1.0 M) solution was mixed drop by drop in (1.0 M) solution of zinc acetate. The resulting solution was stirred once again continuously for 30 min. In the final step, white precipitate of the ZnS nanoparticles is formed slowly in the solution. The obtained precipitate was then filtered using centrifuged machine 3000 r.p.m. for 15 min and then washed with ethanol to remove impurity present in it. The obtained precipitate was dried at room temperature and crushed to fine powder with the help of mortar and pestle and used for structural characterization. The prepared ZnS nanopowders were immersed in base liquid ethylene glycol

to get ZnS nanofluids with ultrasonicator at room temperature. Sonication is carried out for 20 min using an ultrasonicator to ensure better and stable suspensions of ZnS nanofluids

2.2 Characterization of ZnS nanoparticles

The crystallinity and the phase purity of the ZnS nanoparticles were examined by X-Ray powder diffraction (XRD) at room temperature on a Rigaku (Miniflex-II) X-ray diffractometer using monochromatic Cu-K α_1 radiation with $\lambda = 1.5405 \text{ \AA}$ operated at 30 kV and 15 mA with 2θ ranging from 10 to 80 degree at the speed of 5 deg / min. with sampling width 0.020 degree. Ultrasonic velocity at room temperature was measured for base fluid ethylene glycol and ZnS nanofluids using Ultrasonic Interferometer (F-81 Model) at a standard frequency of 2 MHz an accuracy of 1 m/s supplied by Mittal Enterprises, New Delhi, India.

3. Results and Discussion

3.1 Structural Properties (XRD)

The XRD pattern of ZnS nanoparticles is shown in **Fig. 1**. The peak broadening in the XRD patterns clearly indicate the formation of ZnS nanocrystals with a very small size. The XRD pattern exhibits five diffraction peaks at 2θ values corresponding to reflections from (1 1 1), (2 2 0) and (3 1 1), (4 0 0), (3 3 1) planes of the cubic (zinc blend) phase (JCPDS, no. 05-0566).

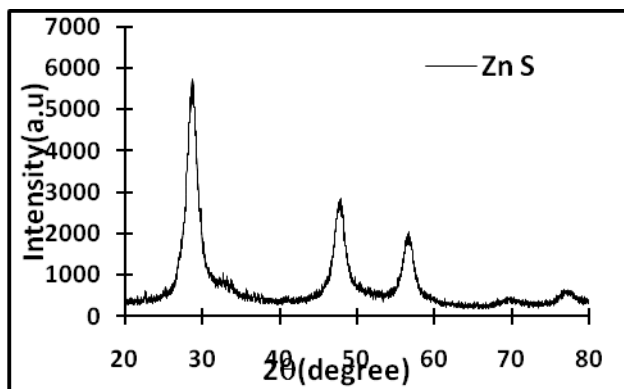


Figure 1: X-ray diffraction pattern of ZnS nanoparticles

The peak broadening at lower angle is more meaningful for the calculation of particle size. Therefore size of nanoparticles has been calculated using Debye-Scherrer's formula using (111) reflection from the XRD pattern. The synthesized nanoparticles have good crystallinity and the average particle size obtained using the diffraction pattern was found to be 4.940 nm.

$$t = 0.9 \lambda / \beta \cos\theta \quad (1)$$

Where, t is the average particle size, λ is the wavelength, β is the full-width at half-maximum (FWHM) of the peak, and θ is the angle of diffraction. The lattice constant (a) was calculated according to the relation

$$a = d (h^2 + k^2 + l^2)^{1/2} \quad (2)$$

The structural parameters such as lattice constant, crystallite size and volume of the unit cell of ZnS nanoparticles are given in **Table 1**.

Table 1: Lattice constant (a), crystallite size (t) and volume of unit cell of ZnS nanoparticles

Sample	Lattice Constant (\AA)	Crystallite Size(t) (nm)	Volume of unit cell (V) (\AA^3)
ZnS nanoparticles	5.380	4.940	155.7

The lattice constant of prepared ZnS nanoparticles is found to be 5.380 \AA which is close to that of reported values of cubic ZnS [13].

3.2 Ultrasonic measurements

The ultrasonic velocity is measured using ultrasonic interferometer (Mittal enterprises, F-81 model) at a standard frequency of 2 MHz with an accuracy of 1.0 m/s and density measurement were performed by pre-calibrated specific gravity bottle with an accuracy of $\pm 2 \times 10^{-2} \text{ kgm}^{-3}$. The nanofluids of ZnS has been formed by dissolving in ethylene glycol and is used as the medium to propagate the ultrasonic wave. Ultrasonic waves of frequency 2 MHz are formed by a quartz plate fixed at the bottom of the cell. The waves are altered by a movable metallic plate kept parallel to the quartz plate. If the separation between these plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. The acoustic resonance gives rise to maximum anode current. The distance between the plates is now increased or decreased. Maximum anode current is observed when the variation is half wavelength or multiple of it. From the knowledge of wavelength λ and frequency f the velocity of ultrasonic wave can be obtained by the relation.

$$V = f\lambda \quad (3)$$

The adiabatic compressibility can be calculated by the equation.

$$\beta = 1/(\rho v^2) \quad (4)$$

Where, ρ is the density of the fluids.

The Bulk modulus can be calculated by the equation.

$$K = 1/\beta \quad (5)$$

From the knowledge of wavelength the velocity of ultrasonic wave can be obtained by the relation. The behaviour of ultrasonic velocity can be understood with its related quantities. The ultrasonic velocity is well related to bulk modulus (B), adiabatic compressibility (k), and density (ρ) of the medium. From **Table 2** it is clear that ultrasonic velocity of base fluid ethylene glycol is measured and is found to be 1650 m/s and ultrasonic velocity for ZnS nanofluid is found to be 1584 m/s. The ultrasonic velocity of ZnS nanofluid is decreases as compared to that of base liquid ethylene glycol due to strong interaction of ZnS nanoparticles and ethylene glycol while density of base liquid ethylene glycol and ZnS nanofluids under investigation is found to be increased.

Similar result has been observed [14]. An increase in bulk modulus and decrease in adiabatic compressibility is attributed to the fact that strong cohesive interaction forces among molecules and atoms after the dispersion of ZnS nanoparticles in the base fluid ethylene glycol.

Table 2: Ultrasonic Velocity (V), Density (ρ), Adiabatic compressibility (β), and Bulk Modulus (K) at room temperature.

Fluids	Ultrasonic Velocity (V) (m/s)	Density (ρ) Kg/m ³	Adiabatic Compress (β) A ^o	Bulk Modulus K = 1/ β A ^o
Ethylene Glycol (base fluid)	1650	1113	3.300	0.3030
ZnS Nano-fluids	1584	3282	1.214	0.8223

4. Conclusions

ZnS Nanoparticles were successfully synthesized by wet chemical method. The crystal structure of the prepared nanoparticles is determined using X-ray diffraction data. X-ray diffraction studies revealed that the synthesized nanoparticles have cubic zinc blende structure. The particle size of ZnS nanoparticles is found to be 4.940 nm. A base fluid ethylene glycol and ZnS nanofluid has been examined using ultrasonic investigation. The ultrasonic velocity for ZnS nanofluids is found to be decrease than base fluid ethylene glycol may be due to strong molecular interaction between nanoparticles and ZnS nanofluid while density of base fluid ethylene glycol and ZnS nanofluids under investigation is found to be increase. The observed result indicate that ZnS based nanofluids and their ultrasonic properties leads to the understanding of the molecular interactions between the ZnS nanoparticles and base fluid ethylene glycol.

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