2aPAa4. Synthesis and frequency dependent ultrasonic characterization of NiO-EG nanofluids
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In the present paper, we have synthesized the NiO nanoparticles with chemical route. Further, the uniform suspensions of NiO nanoparticles in ethylene glycol of different concentrations have been prepared. Samples were characterized with Acoustical Particle Sizer (APS-100) for the frequency dependent ultrasonic attenuation in the respective samples; subsequently the particle size determination and their distribution have been determined with help of ultrasonic attenuation. The morphological parameters were also investigated with the microscopic techniques. There is good agreement between data produced by ultrasonic spectroscopy and the microscopic measurements.

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Introduction

Nanoparticles suspensions in fluids are attracting the interests of researchers because of many advanced properties leading to potential applications in microelectronics, instrumentation and biomedical industries. Uniform suspensions of nanoparticles in conventional heat transfer fluids like water, ethylene glycol etc. are termed as nanofluids. Nanofluids are considered as elegant heat transfer fluids [1]. Ultrasonic waves provide very elegant solution in dispersing the nanoparticles in fluids to form homogeneous and stable suspensions for sustainable and efficient performance for a large time span. In addition to that ultrasonics is being used in determination of particle size distribution in a suspension with the help of frequency dependent ultrasonic attenuation in the liquid suspensions if some other physical parameters are known for the samples.

Transition metal oxides are important class of semiconductors having applications in diverse fields as electronics, catalysis and energy transformation. Being a member of same family NiO is also an important insulating material having a phase transition at -196°C temperature from rock salt structure to rhombohedral crystal structure with slight distortion along <111> direction [2]. It has a wide band gap of 4.0eV in bulk form[3]. NiO demonstrate superparamagnetism in nanocrystalline form having diameter of ~20nm due to surface effects [4]. NiO nanostructures have shown excellent catalytic activity [5]. These excellent properties of NiO paves the way for the applications in battery cathode [6] gas sensors [7] and electrochromic devices [8]. At present, there are number of methods are available for like sol-gel technique, solid state reaction method electrochemical method, thermal decomposition of precursors and chemical methods etc. the synthesis of nickel oxide nanoparticles.

In present work, NiO NPs have been synthesized using the simple chemical route followed by annealing at temperature 400°C with the help of ultrasound. The NiO NPs are obtained by annealing at 400°C have been dispersed homogeneously in Ethylene Glycol using ultrasonicator (20 KHz, 200 Watt) to get nanofluids of required concentrations. Synthesized nanoparticles suspensions are then subjected to further characterizations. Transmission Electron Microscopy and ultrasonic attenuation spectroscopy (UAS) techniques are applied to measure the particle size distribution of synthesized nanoparticles, which are in good agreement with each other.

Experimental details

Synthesis

Nickel oxide nanoparticles were prepared through the chemical route with the help of ultrasonic irradiation. NaOH solution (0.1M, 100ml) was added in nickel chloride (0.1M, 50ml) aqueous solution.
Polyethylene glycol (0.5ml) is used as surfactant in the reaction with optimized conditions. The mixture was exposed to ultrasonic irradiation (20 KHz, 200 W) for three hours to form precipitate. The precipitate was washed with ethanol and water to separate the impurities and then we annealed it in 400°C for one hour. Resulting annealed powder sample was used for further morphological and structural characterizations. Subsequently, NiO nanoparticles were suspended in ethylene glycol with the help of ultrasonic irradiation again to form uniform suspensions (i.e. NiO-EG nanofluids) of different concentrations.

**Microscopic and Ultrasonic Spectroscopic Measurements**

The synthesized product was subjected to transmission electron microscopy and ultrasonic spectroscopy for determination of the particles size distribution. HR-TEM: FEI Tecnai G2 F30 STWIN at 300 keV was used for microstructural characterization at high magnifications and reciprocal space analysis of nanoparticles. Particle size distribution was also determined with the Acoustic Particle Sizer (APS-100) with the help of ultrasonic attenuation in the frequency range 20-99MHz in ethylene glycol liquid matrix.

**Results and Discussion**

SAED pattern (fig.1) of sample shows the good crystalline nature in nanoparticles. The indexing of ring pattern confirms the formation of NiO structures. TEM image confirms the formation of some spherical and ellipsoidal nanoparticles of 18-25 nm diameters as shown in fig.2. Histogram is also plotted for the particle size and frequency of particles of that size in the TEM image for better representation in fig.3.

Frequency dependent ultrasonic attenuation is plotted in fig.4 in the frequency range of 20-99MHz. Ultrasonic attenuation in the liquid suspension of different concentrations is increasing with the increase of concentration and frequency. Viscous drag loss ($\alpha_{VD}$), viscous dissipation ($\alpha_V$), scattering and thermal losses are the main parameters for the increase in ultrasonic attenuation in NiO-EG suspensions.

The expression for viscous dissipation ($\alpha_V$) and the viscous drag loss ($\alpha_{VD}$) [9-10] are given as following respectively:

\[
\alpha_V = \frac{\omega^2}{2\rho_m\nu^3} \left( \frac{4}{3} \eta_d + \eta_V \right) 
\]

\[
\alpha_{VD} = 18k\phi(1 - \delta)^2 \left[ \frac{y^2(1 + y)}{[2y^2(2 + \delta) + 9y\delta]^2 + 8\delta^2(1 + y)^2} \right] 
\]

where $\eta_d$ and $\eta_V$ are the dynamic and volume viscosities of the nanofluid, $\kappa$ is the wave number, $\delta = \rho_m / \rho_s$, $y = r\sqrt{\omega/2\eta_d}$. Ultrasonic attenuation with respect to concentration caused by scattering at
micro-scale in low frequency limit was calculated by Biwa and his co-workers. They calculated the dependence of ultrasonic attenuation on concentration as \[ \frac{d\alpha}{d\phi} = -\alpha + \frac{\gamma_{\text{ sca}}}{(8/3)\pi r^3} \]

where \( \gamma_{\text{sca}} \) is scattering cross-section and it depends on particle size, the frequency of wave, bulk modulus and density of carrier fluid and morphology of suspended particles.

Thermal loss is caused by temperature variation produced by propagation of sound waves in different components of suspension.

Viscous wavelength is the dominating parameter for the ultrasonic attenuation in suspensions below 48MHz and it is influenced by viscous dissipation. Viscous wavelength can be represented as;

\[ \lambda_v = \sqrt{2\eta l(\rho_m \omega)} \] \hspace{1cm} (4)

where \( \eta \) is viscosity of the matrix and it is comparable to particle size \( d \) of the NPs and \( \rho_m \) is density of liquid matrix. Above 48MHz, viscous drag loss, scattering loss and thermal losses are prominent due to thermal wavelength. Thermal wavelength depends on thermal conductivity, density and specific heat of particles and frequency if waves as:

\[ \lambda_T = \sqrt{\frac{2K_S l}{(\rho_S C_S \omega)}} \] \hspace{1cm} (5)

Where, \( K_S, \rho_S \) and \( C_S \) are thermal conductivity, density and specific heat of the dispersed particle and \( \omega \) is frequency of the wave. Thermal wavelength is of the order of particle size of the NPs in the base fluid in which it is dispersed. Viscous losses and thermal losses depend upon the particle size of nanoparticles and the frequency of ultrasonic waves in the medium. Thus, ultrasonic frequency and viscoelasticity are the governing parameters for the ultrasonic attenuation in the suspensions of NiO in ethylene glycol. In high frequency region, the larger interaction of ultrasound with the dispersed nanoparticles causes the larger scattering resulting larger increase in ultrasonic attenuation in frequency region above 48MHz. A polynomial fit study to the ultrasonic attenuation provides that attenuation in liquid suspensions of nanoparticles can be written as \( \alpha = \sum \alpha_n f^n \). For \( n=0 \), the coefficient of frequency is equivalent to attenuation in ethylene glycol matrix. While for \( n \neq 0 \), the coefficient of frequency is a function of particle size. Effective viscosity of a fluid decreases monotonically towards the zero with the increase in frequency. Thus it can be claimed that viscous drag losses are dominant here. The ultrasonic attenuation data with other required parameters such as thermal conductivity and crystal structural parameters etc. are used for determining particle size distribution (PSD) by Acoustical particle sizer (APS-100). The plot of PSD of NiO NPs in the ethylene glycol is shown in Fig. 5. The PSD based on ultrasonic attenuation spectroscopy confirms that the particle sizes of NiO NPs lie in the range 18-25nm. Thus the results for PSD are confirmed by the TEM method.
Conclusions

We have successfully synthesized the NiO nanoparticles with good crystallinity and the particle size in the range of 18-25nm. The ultrasonic spectroscopic method for the determination of size distribution of NiO nanoparticles in ethylene glycol is done and cross matched with the transmission electron microscopy images. For ultrasonic spectroscopic method no special sample preparation is required. In competition to Dynamic light scattering method of determining particle size distribution, opaque suspensions can also be used successfully. Viscoelastic behavior of the NiO-EG suspensions is confirmed. These uniform suspension samples have potential applications in any heat transfer management systems in industrial applications.

References

Figures –

**FIGURE 1.** SAED pattern for NiO nanoparticles.

**FIGURE 2.** TEM image for NiO nanoparticles.

**FIGURE 3.** Histogram for particle size of NiO in TEM image.
FIGURE 4. Frequency dependent ultrasonic attenuation for different concentration of NiO nanoparticles in ethylene glycol.

FIGURE 5. Particle size Distribution of NiO nanoparticles by APS-100