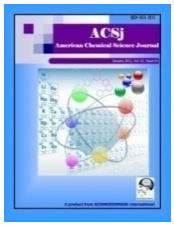

American Chemical Science Journal
5(2): 148-155, 2015, Article no.ACSj.2015.014
ISSN: 2249-0205

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Characterization and Elastic study on Zinc Sulphide Nanofluid Doped with Neodymium

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/ACSj/2015/13534
Editor(s):
(1) Santanu K. Maiti, Physics and Applied Mathematics Unit, Indian Statistical Institute, 203 Barrackpore Trunk Road, Kolkata, India.
(2) Francisco Marquez-Linares, Faculty of Chemistry, Nanomaterials Research Group School of Science and Technology, University of Turabo, USA.
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Reviewers:
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(3) Anonymous, Allahabad University, India.
(4) Anonymous, Indiana University, USA.
Complete Peer review History: http://www.sciencedomain.org/review-history.php?iid=698&id=16&aid=6653

Original Research Article

Received 21st August 2014
Accepted 5th October 2014
Published 23rd October 2014

ABSTRACT

Among the Semiconductor nanoparticle ZnS as an important II-VI semiconductor has been researched extensively because of the broad spectrum of potential application such as catalysis, cathode ray tube (CRT), field emission display (FED) phosphors for a long time. It can be used for electroluminescent devices and photodiodes. Zinc sulphide doped with Neodymium (ZnS: Nd) quantum dots have various applications in electronics, nonlinear optical devices and optical computers. ZnS: Nd nanomaterials with an average particle size of 21-25 nm are synthesized by the reaction of zinc acetate and hydrogen sulphide by chemical route technique. XRD, SEM, FTIR and EDS characterize the samples. The percentage of doping material in the crystal is confirmed from the EDS spectra. The average crystal size of the prepared ZnS nanopowder is determined by XRD. Ultrasonic velocity through doped and undoped sample is measured and compressibility is computed. The compressibility is found to be increased. Also variation of compressibility of ZnS: Nd nanofluid with various grain size have been carried out and found that compressibility increases with decrease of particle size.

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Keywords: Semiconductor; nanomaterial; ultrasonic velocity; elastic properties.

1. INTRODUCTION

Wide band gap II-VI semiconductor is expected to be the noval material which exhibits optical and transport properties [1]. Zinc sulphide is an extensively studied group II-VI semiconductor with wide application in field of Photoluminescence (PL), Electro luminescence (EL) and Cathodoluminescence (CL) due to better stability compared to other chalcogenides such as ZnSe [2]. It finds application as Light Emitting Diode, reflector, dielectric filter material and indicator, analysis of water pollution, environmental studies, and pathological investigations. The blue shift in the optical absorption spectrum, enhance oscillator strength, non linear optical effects, geometrical structure, chemical bonds, Ionization potential, mechanical strength and melting point [3,4]. The change in the properties of nanoparticle is driven mainly by two factors, namely, the increase in surface to volume ratio and change in the electronic structure of the material [5]. Since the elastic properties are decisive for designing devices like nanobelts, nanocantilevers etc, there is a mounting interest in the elasticity of ID nanostructures. Nanobelts and nanowires have shown great promise as functional and structural nanobuilding blocks on nanoelectronics, nano-optoelectronics, and nanolasers. In the design and development of such nanodevices, structural integrity is of paramount importance. For instance, mechanical contacts that occur at the building block interface may cause fatal damage of the devices [6]. Neodymium is one of the rare earth chemicals, with has high elastic stiffness constant that can be found in household equipment such as color televisions, fluorescent lamps, energy-saving lamps and glasses. The variation of compressibility of ZnS: Nd with various grain sizes are not yet reported in the literature. The aim of present work is to study the variation of compressibility of ZnS: Nd with particle size.

2. EXPERIMENTAL METHODS

2.1 Synthesis of ZnS:Nd Nanoparticles

In our study, ZnS: Nd nanoparticles are prepared by passing hydrogen sulphide gas to an aqueous solution of zinc acetate. The reaction can be represented as

$$(CH_3COO)_2 Zn + H_2S \longrightarrow 2CH_3COOH + ZnS \quad (1)$$

In this method, firstly a one molar solution of zinc acetate is prepared. For this, 21.95 gm of zinc acetate is taken and dissolved it in 100ml of distilled water taken in a conical flask. The solution is mixed with 3.36gm (1M percentage) of rare earth Neodymium oxide solution and stirred well. Four-five drops of Tri Ethyl Amine (TEA) was added to the solution to prevent the agglomeration of nanoparticle. This capping agent is added to solution to maintain the particles in the nanosize. After this, put a magnet inside the solution and then place the conical flask on a magnetic stirrer. Then hydrogen sulphide gas is passed into this solution. Hydrogen Sulphide gas is passed for 4 minutes, and white precipitate of ZnS is formed. The excess acetic acid formed is washed out from the sample using double distilled water. After washing the sample many times with distilled water, filtered, placed in a furnace and heated up to 150℃ so that the water content in the sample should be removed. After annealing, sample is taken and made into fine powder form.

2.2 Characterization Methods

X-ray diffraction patterns were carried out using Philips X-ray diffractometer using monochromatic Cu K α beam. The surface topography and microstructure were studied using Field Emission Scanning Electron Microscopy (FESEM). Infrared spectra were recorded using a Nicolet (Impact 410) FTIR spectrometer, using transparent pellets of the compounds in KBr matrices. KBr was used as the background file. All spectra were measured from approximately 4000 to 400 $cm^{-1.}$ Energy Dispersive X-ray Spectrum Analysis (EDAX) was used to determine percentage composition of Nd in ZnS.

3. RESULTS AND DISCUSSION

3.1 Determination of Particle Size from XRD Pattern

The XRD pattern, Figs. 1 (a-c), consists of sharp intense peaks of ZnS: Nd which confirms the good crystalline nature of ZnS: Nd and peaks originated from (111), (220), (311), (422), (200), (331), (400), (222), and (420) reflections of hexagonal ZnS [4]. The XRD patterns of nanometer sized particles are quite striking because of the size dependent and structure specific features observed [1]. Therefore XRD

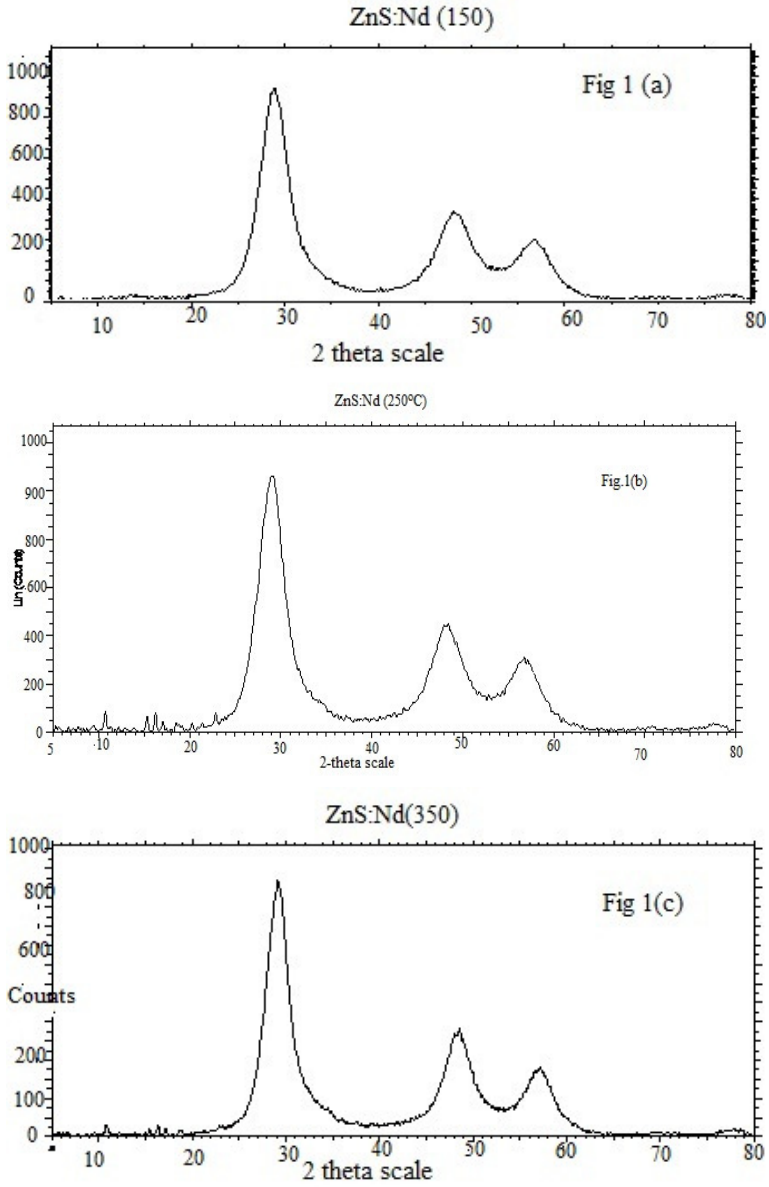
techniques are widely used for the particle size determination and structure determination of nanoparticles. The patterns are compared with JCPDS card No: 77-2100. Particle Size, can be calculated by the formula [4,7], Debye-Scherrer's formula

$$D = K\lambda / \beta Cos\theta \quad (2)$$

K=0.89, λ the X-ray wavelength = 0.154095 Nm, β the full width at half maximum and θ the half diffraction angle.

3.2 XRD Patterns of ZnS:Nd at Various Temperatures

Particles annealed at temperatures, 150℃, 250℃ and 350℃, have grain sizes 21.7nm, 22 nm and 25 nm respectively. From the Table 1, it is observed that there is a continuous increase in the particle size with temperature.



Figs.1(a-c). XRD Patterns of ZnS:Nd at 150, 250 and 350℃

Table 1. Particle size of nanomaterial ZnS:Nd at various temperatures

Temperature ℃	FWHM	$\beta \times 10^3$	2θ	θ	Particle size(D) Nm
150	0.364	6.34	12.875	6.4375	21.7
250	0.343	5.98	13.051	6.5255	22
350	0.312	5.44	13.352	6.676	25

XRD results showed that the crystallite sizes of ZnS: Nd nanopowder were 21.7 nm at 150℃, 22nm at 250℃ which increased to 25 nm at 350℃. From the figures it is clear that the intensity of crystalline peaks increases with increase in temperature. Simultaneously the peaks become narrower as the temperature was increased showing the increase in crystallite size. The continuous increase in the particle size with temperature can be attributed to the atomic diffusion. From the atomic perspective, diffusion is a stepwise migration of atom from lattice site to lattice site. In Fact, the atom in solid material are in constant motion, rapidly changing position. For an atom to make such a move the atom must have sufficient energies to break bonds with its neighbor atoms and then cause some lattice distortion during the displacement. As the temperature increases the atom gain sufficient energy for diffusion motion and thereby increasing crystallite size [7] The increase in the particle size on annealing is due to the merging of the smaller particles into larger ones [8]. The potential energy difference between small and larger particles can occur through solid state diffusion [9]. Also arrived at the conclusion that the optimum temperature for nanoparticle preparation of ZnS:Nd is 150℃.

3.3 Fourier Transform Infra Red Analysis

The Fourier Transform Infrared spectrum, *see* Fig. 2, of synthesized ZnS:Nd has been compared with reported value for different stretching and bending modes. For ZnS:Nd annealed at 350ºC the absorption peaks were observed at 3396.15 cm^{-1}, 1625.88 cm^{-1}, 1545.39 cm^{-1}, 1384.10cm^{-1},1019.87cm^{-1}, 829.06cm^{-1}, 675.89cm^{-1} and 608.40 cm^{-1}. The broad absorption peaks centered at 3389.47cm^{-1} and 2922.47cm^{-1} corresponds to valence vibrations of occluded water. The bands centered at 2926.4cm^{-1} may be due to C-H stretching vibrations, bands observed at 1019.8 and 1384.1 cm^{-1} may be due to C-N Stretching vibrations and those at 1625.8 may be ascribed to N-H stretching vibrations. The band present at 1019.8cm-1 was due to C-C stretching vibration. The bands due to C-H bending vibrations was observed at 829.06cm^{-1}. The FTIR measurements are carried out in order to confirm the formation of crystalline ZnS:Nd nanoparticles and identify adsorbed species on to the crystal surface. The characteristic band of Zn-S stretching vibrations was observed around 675.8 cm-1 which is in good agreement with reported value [10]. The changes in the observed value are due to formation of nanophase. Bands around 483.72cm^{-1}. and 418.56cm^{-1} can be assigned to the Nd-O band.

3.4 Scanning Electron Microscopy (SEM)

The scanning electron micrographs of ZnS nanomaterials synthesized under aqueous medium [5]. The SEM of ZnS:Nd Fig. 3 exhibit non-spherical morphology with self aligned prismatic nanoparticles. The image also confirms that the nanoclusters, consists of a high density of ZnS: Nd nanoparticle, with length 2µm with average particle size varied from 20 to 25 nm. In SEM measurement the grain size is measured and calculated by taking the noticeable grain boundaries. While in the case of XRD, measurements are taken from the crystalline area that diffracts the X-ray waves. Thus the XRD measurement size of capped ZnS:Nd particle was found to be smaller that the size found when using SEM measurement [11].

3.5 Energy Dispersive Spectrum Analysis (EDS)

EDS is a technique used for identifying the elemental composition of the specimen. The purity and composites of the product is studied and the dried powder samples were analyzed in EDS. In EDS spectrum, Fig. 4 each of the peaks reveals the presence of Zn and S confirming the presence of pure ZnS. Small percentages Nd is labeled in the spectrum. The higher a peak in a spectrum, the more concentrated the element is in the spectrum. Other peaks correspond to C and O_2, which is due to sputtered coating of glass substrate on EDX stage. EDS of ZnS: Nd nanoparticle is plotted using the recorder and the EDS data is measured as Zinc Sulphide ≈ 95.88% Neodymium ≈ 4.12%.

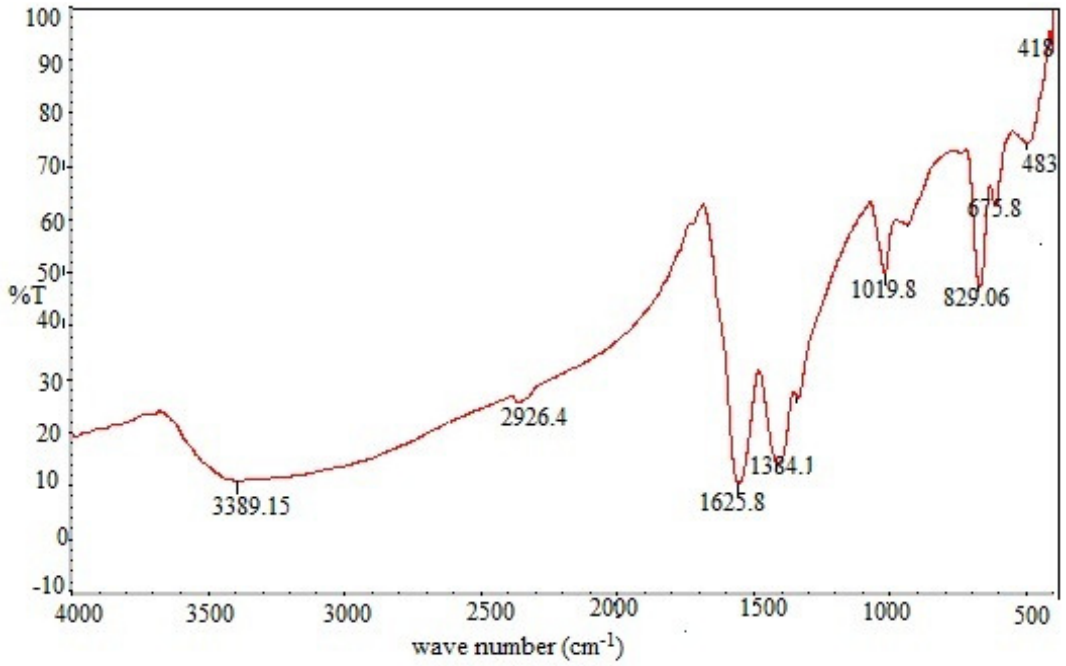


Fig. 2. FTIR spectrum of ZnS:Nd

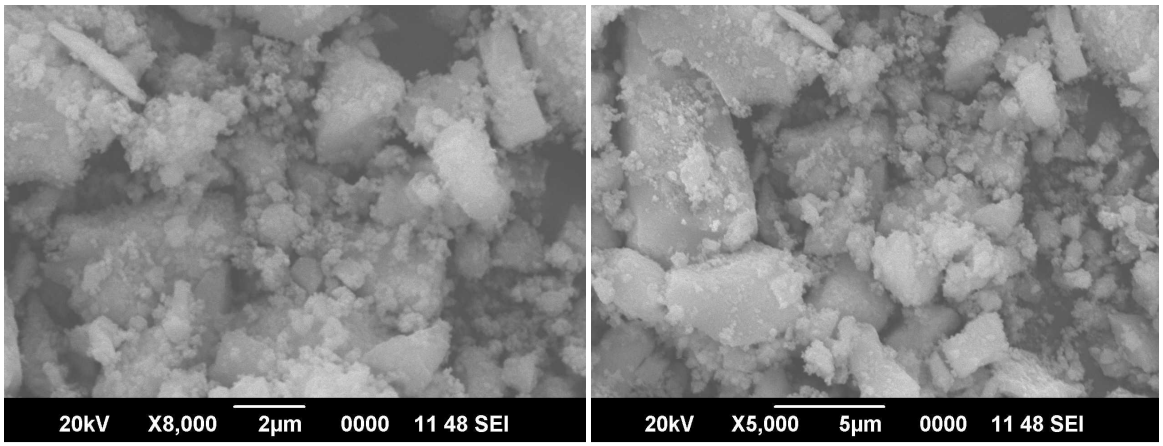


Fig. 3. Scanning electron micrograph of ZnS:Nd

3.6 Ultrasonic Velocity Measurements

The ultrasonic velocity is measured using ultrasonic interferometer (Mittel enterprises, F-80 model) at a standard frequency of 2 MHz with an accuracy of 1m/s [12]. The nanofluid of ZnS:Nd has been formed by dissolving in ethylene glycol and is used as the medium to propagate the ultrasonic wave. Ultrasonic waves of frequency 2MHz 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.

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

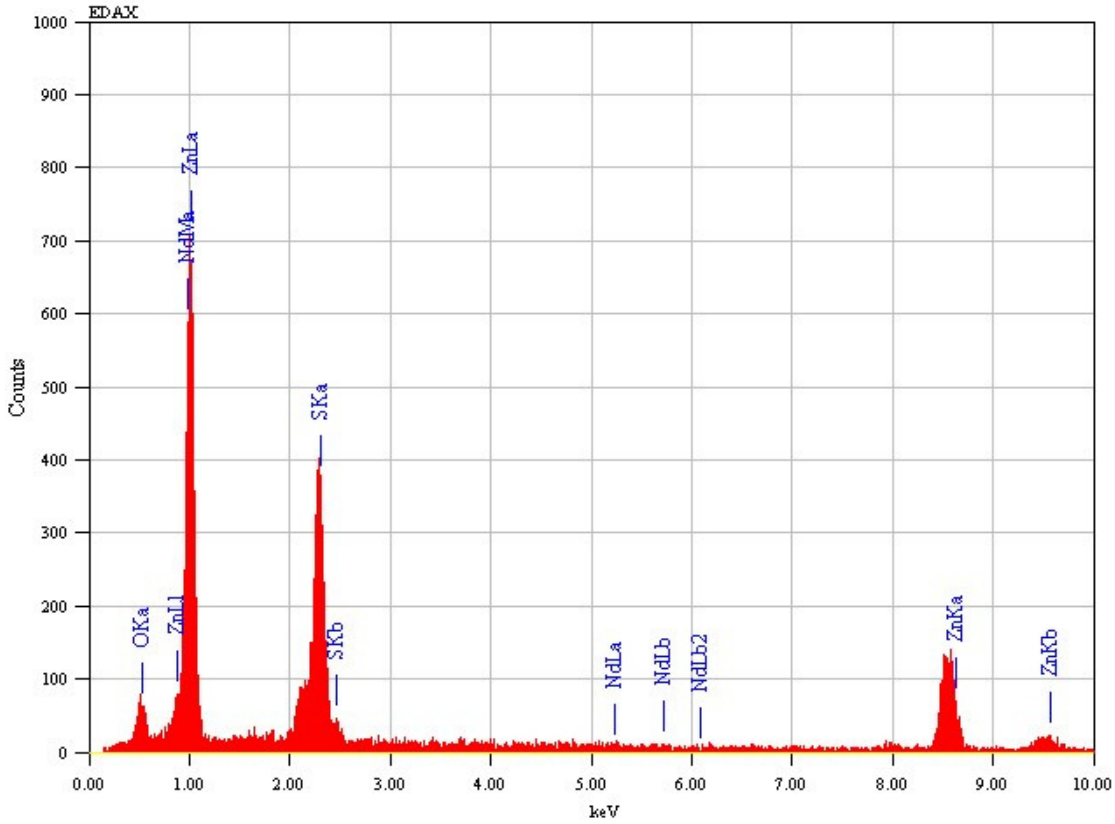


Fig. 4. Energy dispersive spectrum of ZnS:Nd

The compressibility can be calculated by the equation

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

Where ρ is the density of the fluid and K is the bulk modulus. It is found that Compressibility of ZnS increases on doping with Nd. The elasticity of ZnS:Nd increases with increase in mole percentage of Nd_2O_3. The large value of elastic constant in ZnS doped with Nd is owing to the chain entanglement mechanism in ZnS with the structural modification by alkaline rare earth ions doping [13].

3.7 Variation of Compressibility with Grain Size

2 gm of doped ZnS was dissolved in 5ml of ethylene glycol and taken in the cell. For doped ZnS nano fluid and for undoped ZnS nanofluid. The density ZnS:Nd nanofluid and ZnS nanofluid have been carried out as, ρ =1.1614×10^3 Kg/m^3 and ρ =1.1132×10^3 Kg/m^3. Also variation of compressibility of Zn S: Nd with various grain sizes have been carried out and found that compressibility increases with decrease of particle size. i.e., Bulk modulus decreases with decrease of particle size.

From Table 2 it is clear that compressibility of nanofluid increases on doping with Neodymium rare earth ions. An increase in bulk modulus, Table 3, or decrease in compressibility is attributed to the fact that strong cohesive interaction forces act among the molecules and atoms after the dispersion of ZnS:Nd nanoparticles in the ethylene glycol [14]. In order to explain the high value of compressibility in ZnS doped with Nd, the chain entanglement mechanism in ZnS with the structural modification by alkaline earth Nd ions was used [15].

Table 2. Compressibility variation of ZnS nanofluid on doping with Nd ions

Fluid	Readings	λ/2	Mean λ (Nm)	V = f λ (m/s)	β =1/ρv^2 (Å)
ZnS nanofluid	11.889	0.092			
	11.797	0.089	0.18260	365.2	67.35
	11.708	0.093			
	11.615				
ZnS:Nd nanofluid	14.968				
	14.887	0.081			
	14.8	0.087	0.1726	345.2	70
	14.409	0.091			

Table 3. Compressibility variation of ZnS:Nd nanofluid with particle size

Temperature (°C)	Particle size (Nm)	λ (mm)	V= f λ (m/s)	β =1/ρv^2 (Å)	K=1/ β (GPa)
150	21.7	0.1726	345.2	70	0.142
250	22	0.1777	355.4	68	0.147
350	25	0.191	382.0	59	0.169

4. CONCLUSION

The size and crystal structure of ZnS: Nd was studied using XRD. The XRD results indicated that the particle size of nano ZnS: Nd is much small as compared to that of pure ZnS and decreases with the Neodymium loading. From the XRD results, it is found that as temperature increases, particle size also increases. The change in particle size cause large variation in the physical properties. Absorption bands in the FTIR spectrum of ZnS:Nd was explained and compared it with reported value of ZnS. The change in the observed value is due to the formation of nanophase. The ultrasonic velocity through ZnS:Nd nanofluid has been measured and compressibility was computed. On doping with Neodymium the compressibility of the nanofluid was found to be increased. Also variation of compressibility of ZnS:Nd with various grain sizes have been studied and found that compressibility increases with decrease of particle size.

ACKNOWLEDGEMENTS

The authors are thankful to the Dr.J.Alexander foundation, and M.G University Kottayam, Kerala for financial and technical support.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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