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Advances in Applied Science Research, 2013, 4(5):343-349

ISSN: 0976-8610
CODEN (USA): AASRFC

A study of magnetic properties in confined Sol-Gel synthesized NiS nano-clusters

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ABSTRACT

Nanoclusters of Nickel Sulfide are chemically synthesized following natural self assembling in Sol-Gel process. A biopolymer is chosen as a base matrix due to a rigid perfect capping of nano-clusters. The resulting specimen was examined by atomic force microscopy (AFM), optical absorption using UV-VIS spectroscopy and X-ray diffraction experiment (XRD). The study also includes DC I-V characteristics and conductivity analysis of solid specimen at room temperature (RT). Magnetism in the developed specimens was investigated at low temperature. A super paramagnetic nature of the specimen is observed at low temperature. In all the cases the developed specimens are amorphous in nature and particle size was found to vary between 40-90 nm and exist with stable quantum confinement. The developed Nickel Sulfide is found behave as magnetic semiconductor with indirect band gap.

Keywords: Nano-clusters, Electrical conduction, Superparamagnetism, Magnetic semi-conductor
PACS: 81.07.Bc; 73.61.-r; 81.16.-c; 75.50.Pp

INTRODUCTION

In the past organic-inorganic nano-composite becomes most interesting field of research [1, 2] in 'Solid State Physics' for their superior physical properties. The drastic change in the electrical, electronic and magnetic properties of the quantum sized nano system over its bulk counterpart due to interfacial interaction between nanostructure and external environment has considerable interest in modern science and technology [3-5]. The role of ion-conducting capping medium in synthesis of nano-materials and the properties of the material are studied. But it is rare to emphasize so far on period of retaining of the properties of the nano-materials, which is very important in the nano-electronics, nano-photonic device and biomedical technology. High attention has been paid on the 'oxide' nano-particles due to their applicability in many practical applications leaving a little attention on sulfide nano clusters. The objective of this work is to develop Nickel Sulfide nano-clusters, its nano-composite with Gum Arabica and to investigate their material characteristics.

The Nickel Sulfide is known as magnetic semiconductor although its nature of magnetism in the form of nano-composite is complicated. Nickel Sulfide is a photo-sensitive [6] material and may be used in photo-energy generation. A series of recent activity [6] demonstrating controllable fabrication of magnetic semiconductors and their incorporation into hetero-structures has led to several additional device suggestions. They include a spin filter, spin-resonant-tunneling diode, unipolar spin transistor, magnetic Zener tunnel diode and magnetic p-n diode. At the same time, progress on the problem of spin injection into nonmagnetic semiconductors has been reported, both from magnetic semiconductors and from magnetic metals. Electrical resistivity measurements [7] on the NiS system show that it has a high metallic conductivity (2×10^4 Ohms−1-cm−1) at room temperature. In this work Gum Arabica, a biopolymer has been used to develop nano-composite of Nickel Sulfide for AFM study. Gum Arabica [8,9] has been found from different species of Acacia namely Acacia Arabica, Acacia babul etc. The details of the experiments, results and analysis are given in the following sections.

MATERIALS AND METHODS

Sample preparation

In this work a natural self assembly of NiS nano-cluster was undertaken. The chemical sol gel route was chosen with Ni salt, Nickel carbonate compound, $NiCO_3$, $2Ni(OH)_2,4H_2O$, from E-mark India, boiled in ammonia solution at temperature about 100^0C. Filtering the sample, mixed with liquid ammonia (NH_3) solution and gum acacia powder heated in magnetic stirrer and slowly passing H_2S gas through it .The formation of NiS nano-cluster by natural self assembly in polymeric background of Gum Arabica biopolymers. The Ni_2S_3 specimen was developed using Ni (III) acetate in acetic acid medium following the mentioned chemical process. The composite of nano cluster was caste to develop the experimental sample. They were caste in smooth extended surface so as to ensure large surface to volume ratio. Finally the specimens were allowed to dry properly. The thickness of the specimen produced was approximately 0.7mm. Specimens were also developed, without polymeric background, for XRD, FTIR and Optical experiments.

Test and Measurements

The different experimental tools those used for test and measurements were, XRD and AFM analysis - which are important experiment for study morphological nature of the specimen. The experiments were carried out to characterize the material are DC I-V characteristics and conductivity measurement, Optical Absorption Spectroscopy using UV-VIS spectrophotometer and FTIR spectrophotometer to investigate energy band gap in developed nano-clusters, and magnetic moment measurement for investigation of the magnetic nature of the developed nano composite of NiS nano-clusters.

RESULTS AND DISCUSSION

XRD Analysis

XRD analysis of the developed specimen is carried out to examine its microstructure, morphology and is completed with Phillips PW1710 automatic diffractometer. XRD intensity distribution curve of the examined sample are shown in the Fig.1. The overall radial distribution function peak of the diffraction pattern corresponds to $2\theta = 38.83^o$.

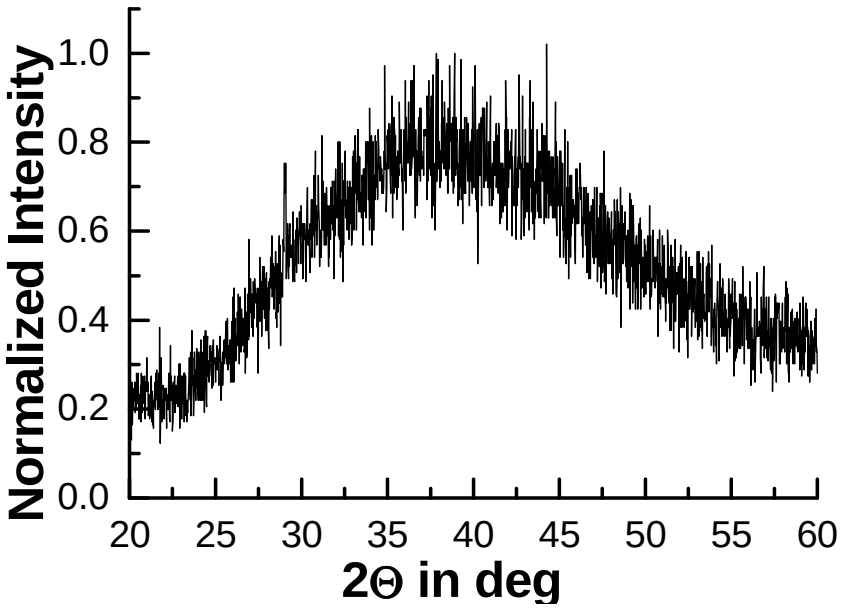

Figure 1. XRD spectrum of the NiS nano-composite between 2θ ranges 20-60 deg

From this intensity distribution by using Scherrer equation we obtain the particle size as $L = (0.9\ \lambda)/\{Cos\theta_b\ (\Delta 2\theta_b)\}$ Å, where λ is the wavelength of the X-ray radiation and for Cu K_α is equal to 1.5418 Å, θ_b is the glancing angle and $\Delta 2\theta_b$ is the difference in the angle at the two end of full width half maxima. The results do not show any Sharpe peak of the intensity distribution but an overall peak corresponding to $2\theta = 38.83^o$. In the neighborhood of $2\theta = 38.83^o$, there are discrete peaks which are relatively low intensities. These peaks are exploited to calculate the particle size using Scherrer Equation [10], and it has been found that the size vary between 40 – 90 nm. The overall impression of the XRD analysis of the developed specimen is a nano-composite of NiS cluster. The overall nature is

amorphous due to background bio-polymeric material and NiS clusters. It can be asses that small grain size caused the surface roughening to increase. It is also responsible for destroying the crystalline nature. Due to the smaller grain size and their large number density, the grain boundary effect becomes predominant in the composite. This forms surface defect that affects the structural and morphological property.

AFM Analysis

AFM study of NiS nano-clusters in bio-polymeric background was carried out using AFM model NANOSCOPE F (USA). The AFM photograph is shown in Fig.2.

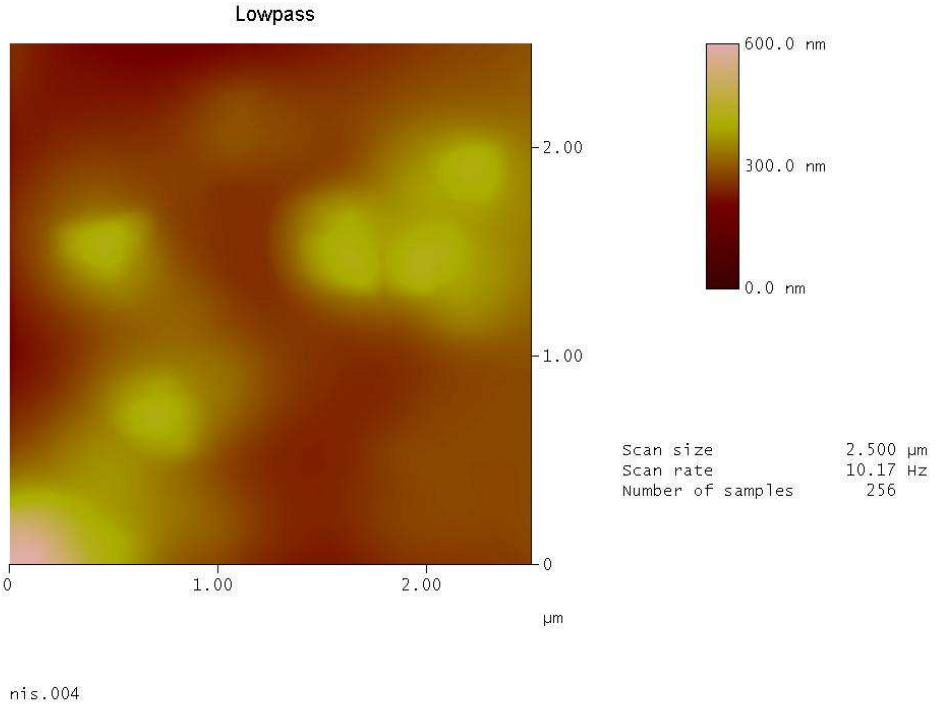

Figure 2. AFM Picture of NiS nano-clusters in bio-polymeric background

Fig. 2 shows the AFM results of NiS nano-clusters of size ranging between 30-50 nm. The estimated of NC's in bio-polymeric background are larger compared to those developed without bio-polymeric background.

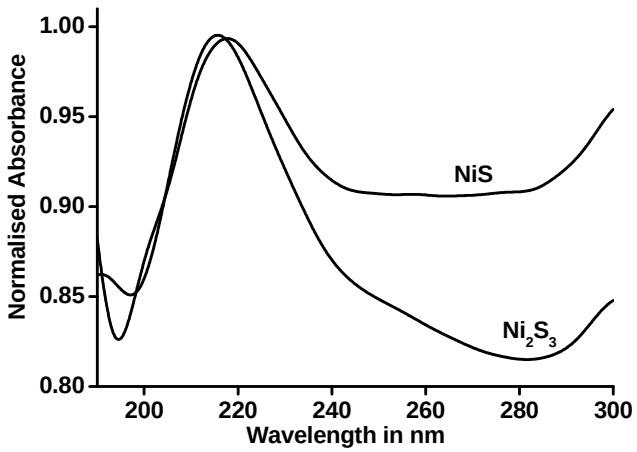

Figure 3. UV-VIS absorbance of NiS and Ni_2S_3

Optical Absorption Spectroscopy

UV-VIS absorption spectra of the specimens NiS and Ni_2S_3 pellet specimens were studied with UV-2450 UV-VIS spectrophotometer, Shimadzu, Japan in the range between 190nm to 900nm at adequate accuracy using integrating

sphere attachment and compensating $BaSO_4$ background. The results of the study between 190-300 nm are shown in Fig.3.

FTIR Analysis

The infra red (IR) absorption of NiS and Ni_2S_3 powder specimen provides information [11] about energy difference due to electronic transition or vibration states originating from bond bending, bond stretching of molecular constituents of the specimens. The analysis was carried out using FTIR model, IR affinity 1, Shimadzu, Japan, at high resolution (resolution was 1 cm^{-1}) using KBr window. IR absorption for a molecule provides information about energy difference between vibrational states, originating from bond bending and bond stretching. Fig. 3 shows the FTIR vibrational spectrum of the developed complex and also compared to that of the pure Gum Arabica. The functional group region appears from 4000 cm^{-1} to about 1550 cm^{-1}. The results obtained from Fig. 3 shows evidence of direct band gap of the specimens in IR region .The estimated direct Band Gap NiS at 0.28eV and Ni_2S_3 at 0.12eV respectively. Anuar et al [12] studied the optical absorption of their developed NiS by sol-gel process and the estimated band gap measured to be 1.3 eV. Sartale and Lokhande [13] reported that Nickel sulfide has a band gap of approximately 0.5 eV

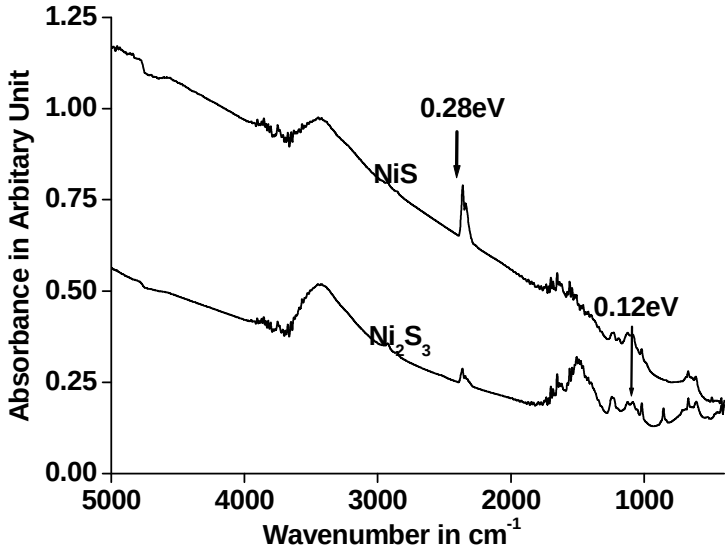

Figure 4. FTIR absorbance of NiS and Ni_2S_3

DC I-V Characteristics

For the experiment of DC I-V characteristics the sample was sandwiched between two high polished flat copper plates act as electrodes for electrical measurement. The applied field direction was perpendicular to the 2-D plane of the specimen. The DC I-V characterization of the specimens at room temperature was carried out using by Keithley 2400 Source meter (USA) and plotted using characterization software. The overall nature of I-V characteristic is an apparent indicator of formation of localized energy level of the NC's in host background matrix. The conductance (G) of the specimen was estimated and plotted as a function of applied voltage (V) as shown in Fig.5. The formation of localized energy level in the recorded I-V characteristic may be attributed due to 3-D confinement [14,15] of quantum dot like ionic nano-cluster within the dielectric host.

The following noise in the mesoscopic systems [16] the observed nature of the conductance plot shown in Fig.5 appeared to be like that of a telegraph noise. In fact it arises due to transition between two locally stable states at room temperature (RT). The nature of the conductivity fluctuation is due to presence of quantum dots in the system. The observed conductance fluctuation is thus a direct evidence of nano-clusters in the system. In this experimental result, the observed noise appeared as an admixture of Nyquist –Johnson, shot noise and 1/f types of noise originating mostly from the quantum confinement of 3D nano-clusters in the specimen. Apparent nature of conductance fluctuation is the indicator of formation of localized energy levels in host background.

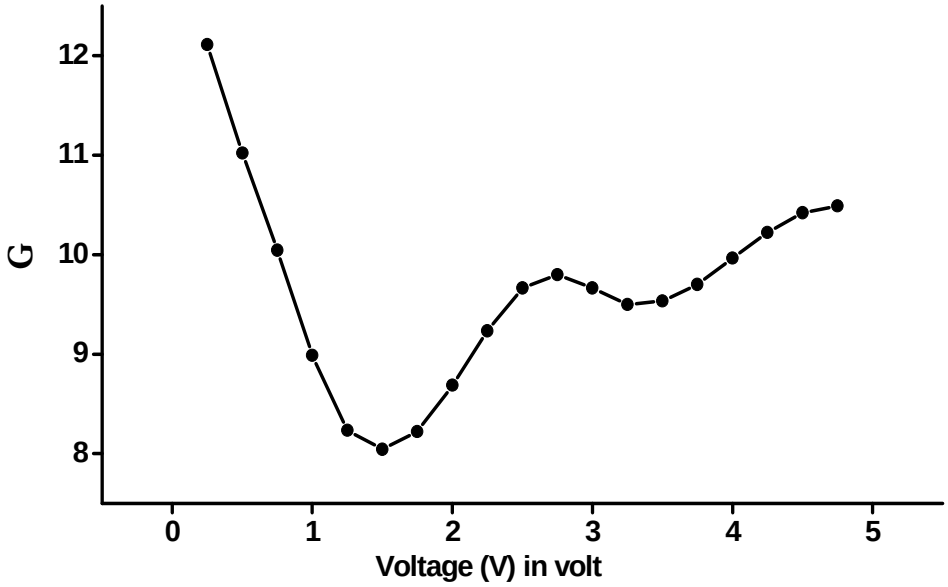

Figure 5. Conductance (G) in μmho vs Voltage (V) characteristics of NiS at RT

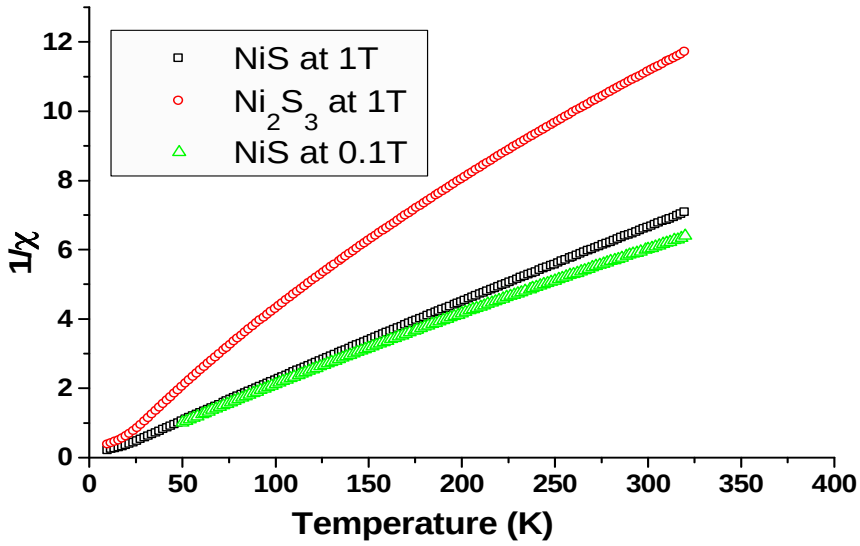

Figure 6. Variation (1/χ) with temperature for specimens at mentioned magnetic field

There are plateau regions in conductance curve shown by Fig.5. The plateaus occur when the conduction process is terminated i.e. here we try to explain the disorder in the sample. This disorder affect the Landau levels broaden into landau bands. As well as the disorder potential is weak i.e. we mean to say the quantum confinement and the Landau bands are merge to continuum . In strong disorder the localized states are predominates and passing of information through electron is prohibited. Since the localization length of a cluster is small, the overlapping of adjacent wave functions are not strong, so one may get plateaus that is conduction enhancement does not takes place. Due to the introduction of nano-cluster enhancement the ionic conductivity is increased over the pure polymer. At room temperature it behaves as a small band gap semiconductor and at room temperature exhibits electrical noise like appearance as marked characteristics of nano-composite. The NiS nanoclusters are distributed in the polymeric matrix of Gum Arabica, and there exists size distribution also. Since the density of states in nano regime are much smaller than that of bulk one, by altering the size of the particles means the extension of effective potential, which

may easily change the band gap. It is interesting to note that within a nano-composite there are three types of energy band gap probably due to presence of other form of Nickel sulfide.

Magnetic Measurement

NiS and Ni_2S_3 were prepared by chemical synthesis to develop black experimental specimens. The dried sample of Nickel Sulfides was crushed into fine powder. The magnetic moment of the specimens were measured between temperatures 10-300 K with external magnetic field as parameter. The said measurement was carried out in VSM model Quantum Design (USA). The magnetization/gm of the specimens (M) is recorded as a function of temperature between the temperature range10-300 K at two different fields 0.1 T and 1.0 T. The results thus obtained are shown in Fig. 6. The measured M shows variation with fields and temperature as well. It has been found that temperature between RT to 40 K magnetic behaviour is paramagnetic and that between 40K to 10K the specimen appeared as ferromagnetic however there exists no sharp phase transition. Thus overall magnetic nature of disordered nano sized NiS clusters appeared to be complicated in nature. The value of observed magnetic susceptibility (χ) of the Ni_2S_3 specimen shows a weak ferromagnetic in nature however ordered NiS bulk solid is known to be an anti-ferromagnetic material. The values of χ from this present study may be due to presence of other sulfide of Nickel in the form Ni_xS_y. The nature of magnetism in the later is not properly known. Thus overall magnetic nature of disordered nano sized NiS clusters appeared to be very complicated in nature. The value of observed susceptibility χ shows a paramagnetic in nature however ordered NiS bulk solid is known to be an anti-ferromagnetic material. Fig.7 shows an exclusive characteristic variation of magnetic susceptibility of Ni_2S_3 with temperature measured at 1.0T field. The region between arrow mark the behavior of the specimen appears to be ferromagnetic and temperature above 30 K the specimen is paramagnetic. The Ni_2S_3 specimen is however showed a super-paramagnetic in nature.

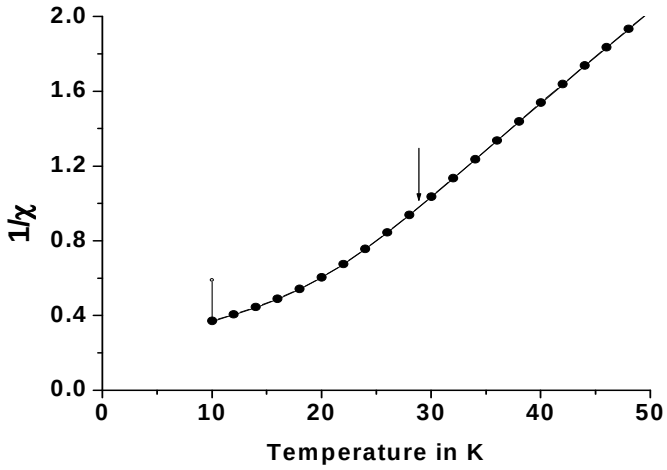

Figure 7. Variation (1/χ) with temperature at 1.0 T magnetic field for Ni_2S_3 specimen

The nature of magnetism in Nickel Sulfide is complicated and interesting. Following analysis of experimental data Coley et al [17] showed that nickel sulfide has temperature dependent magnetic susceptibility and has an itinerant-electron anti-ferromagnet with no local moment. Wei Wang et al [18] showed from a hysteresis scan of NiS Nano Tube that there exists a weak ferromagnetism at room temperature. In the work [18] the observed value of magnetic permeability-μ shows a weak ferromagnetic nature however ordered NiS bulk solid is known to be an anti-ferromagnetic material.

Nanomagnetism is a highly interesting subject of solid state magnetism and nanotechnology [19-21]. The novel phenomena super-paramagnetism and its effects appear only on the nanoscale. The present nano Ni_2S_3 specimen is however showed a super-paramagnetic in nature without any sharp transition.

CONCLUSION

Formation of ionic nano-clusters within polymeric substrate is distinct and clear from I-V characteristic curve. From the study of optical absorption spectroscopy we can assume that as if three type of sized dependent nano-composite formed and it is confirmed that NiS nano-cluster is a the small band gap semiconductor. The overall magnetic nature of the NiS nano composite is amazing. Apart conflicting claim the present study finds a weak ferromagnetism below 40 K and paramagnetic above it in the developed NiS specimen. The scope of further studies on the system may provide many interesting aspect of material science.

Acknowledgements
Authors are thankful to U.G.C., New Delhi for CPE grants. Authors are also thankful to UGC-DAE-CSR, Indore, India, for accessing their VSM facilities.

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