A COMPARATIVE STUDY BETWEEN ELECTRICAL PROPERTIES OF BULK AND SYNTHESIZED NANO MATERIAL OF ZINC SULPHIDE

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Abstract

Zinc sulphide nanoparticles were produced synthetically by wet chemical route by using cheap precursors. The size of the particles were determined by X-ray Diffraction(XRD) and scanning electron microscopy(SEM) and was compared to that of bulk ZnS. The SEM images revealed that bulk sized ZnS and ZnS nanoparticles were of different origin, structure and size Further studies were carried out to determine the difference in electrical properties (dielectric constant, dissipation factor, A.C. conductivity, resistivity) of these materials due to their size difference.

Keywords: Zinc Sulphide ,XRD,SEM, nanoparticles,electrical properties.

Introduction

Interests on nanoparticles have been generated in recent years due to their simple structure, characteristic physical, chemical and biological properties that are usually distinctly different from those of the bulk materials. In the last few decades, many efforts have been devoted to the technique of synthesis and study of the physicochemical characterization of nanometer-scale semiconductors. Nanoparticle synthesis has opened up alternative paths in the design of materials with new properties. The interest in semiconductor nanoparticles is justified by the fact that their fundamental physical and chemical properties can be very different from those of the bulk materials [1]. The nanostructures with their distinct properties have become potential candidates for applications in electronics and optoelectronics. Nanosized particles of semiconducting compounds in particular display grainsize dependent optoelectronic properties, due to the size quantization effects [2].The biggest hurdle in nanotechnology seems to be production of uniform sized nanoparticles and the control of grain size in a few nanometer ranges with considerable reproducibility. There has been considerable interest recently in semiconductors of nanometer dimensions due to the quantum size effect they exhibit [3]. Nanocrystalline semiconductors have electronic properties intermediate between those of molecular entities and macro crystalline solids, and are at present the subject of intense research [4,5,6]. ZnS nanostructures have gained a lot of attention that can be attributed to the properties arising from their size in the nanometer range [7,8,9]. Nanobelts [10,11] nanowires [12,13], nanocables, nanorods, nanocable- aligned tetra pods, nanoparticles [14,15] and nanotubes were synthesized and their modified electronic, mechanical, luminescent and optical properties were used in nanoelectronics, photonics and as tools in biomedical applications[16]. This paper deals with the preparation of ZnS nanoparticles using the aquous chemical method. The prepared

nanoparticles were characterized structurally using the powder XRD and the SEM. The dielectric studies have been carried out in the frequency range of 20Hz to 2MHz at different temperatures.

Materials and methods

Chemical compounds

Analar $ZnCl_2$ and Na_2S were purchased from Merck,Germany, these were allowed to react to produce ZnS nanoparticles.

Analar ZnS were purchased from Merck, Germany, for bulk material studies.

Method of preparation of Zinc Sulphide nanoparticles

Synthesis of ZnS nanoparticles was carried out by aqueous chemical method using $ZnCl_2$ and Na_2S as source materials. All the reagents were of analytical grade and used without further purification. The entire process was carried out in distilled water for its inherent advantages of being simple and environment friendly. All steps of the synthesis were performed at low temperature and ambient conditions. In a typical preparation solution of 1M Na_2S was added drop by drop to 1M $ZnCl_2$ solution which was kept on stirring using a magnetic stirrer at 70 ^{o}C for 2 hours, this resulted in formation of ZnS nanocolloid. The nanoparticles were collected by centrifugation at 2000 rpm for 15 minutes and further purification was made in ultrasonic bath. The resultant product was finally dried at 120 ºC for 2 h.

Characterization of ZnS nanoparticles

The prepared sample was subjected to characterization by X-ray diffraction (XRD) (Model D8, Bruker AXS) to determine the phase purity and average particle size of the sample, using CuKα radiation at 1.5409Å ($2\Theta = 10^0$-70^0, scan speed = 0.2 s/step, increment = 0.02, operating voltage

= 40 kV and operating current = 40 mA). The nanophase was identified by comparing peak positions and intensities (finger print method).

X-Ray Diffraction (XRD) analysis

From the XRD results, it is clear that the pure ZnS nanoparticles have been obtained in powder form. The broadened peaks in the XRD pattern indicate the formation of ZnS nanocrystals with small crystallites. The three diffraction peaks at 2θ values of 28.978^0, 47.62^0, 56.65^0 correspond to the (111), (220) and (311) diffraction planes, respectively of the spherical nanocrystalline structure of ZnS were observed. These values were very close to those reported by Jia Xiang Yang et.al.[17].

The average crystallite size (D) was calculated from the full-width at half-maximum (FWHM) of the most intense peak of the (111) plane of ZnS nanoparticles using the Debye-Scherrer formula for spherical particles [Eq. (1)].

$$D = 0.89\lambda / (\beta \cos \theta) \qquad\qquad\qquad (1)$$

Where λ is the wavelength (Cu Kα), β is the full width at the half-maximum of the ZnS nanoparticles and θ is the diffraction angle.

From this equation the average particle size was estimated to be 29 nm which was also supported from FESEM.

FESEM analysis and EDAX study

Figures A and B show the FESEM results of bulk ZnS and prepared ZnS nanoparticles. It is seen that the ZnS nanoparticles are homogenously dispersed and almost spherically shaped with an average diameter ranging from 20-60 nm. Difference in size and structure between bulk and nano ZnS is evident from these figures.
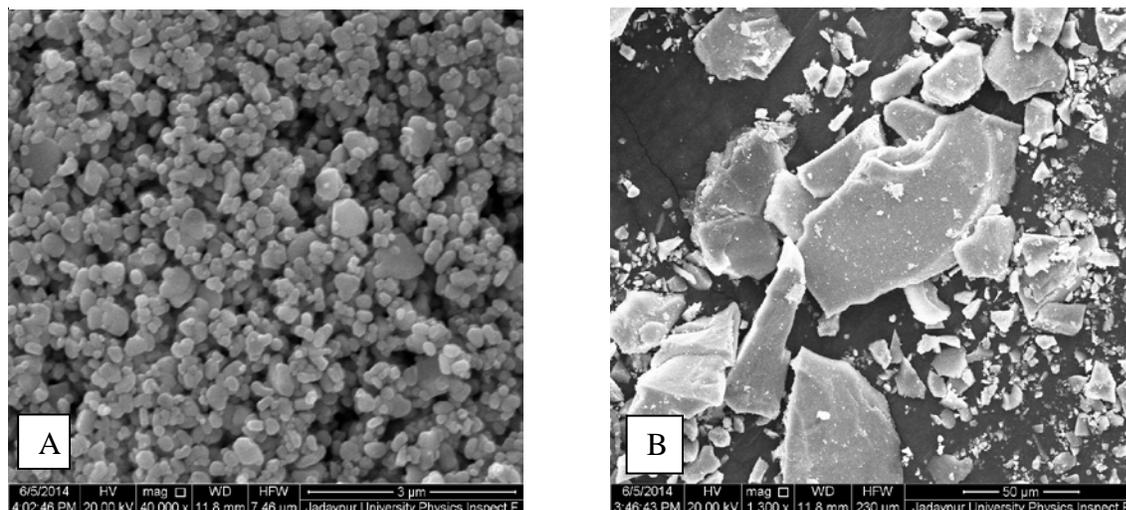
Fig A: SEM image of synthesized nanoparticles of ZnS ranging from 20-60 nanometers.
Fig B: SEM image of bulk ZnS showing large chunks of ZnS ranging from 6-60 micrometers.

Electrical Analysis of ZnS Nanoparticles

Electrical studies have been carried out in the frequency range of 20 Hz to 2MHz at room temperature for a particular material, synthesized by two different routes. Electrical properties such as dielectric constant (ε_r), dissipation factor (tan δ), A.C conductivity ($\sigma_{a.c.}$) and resistivity (ρ) of the samples were measured by using LCR meter (HP Model 4274 A, Hewlett-Packard, USA). For the measurement of electrical properties sample pellets of uniform thickness were prepared, and silver paste was coated on two extreme surfaces of the pallet to make those surfaces conducting.

Dielectric constant (ϵ_r) analysis

Dielectric Studies shows effect of frequency on the conduction phenomenon in the nano structured materials. The dielectric properties of materials are mainly due to contributions from the electronic, ionic, dipolar and space charge polarizations. Among these, the most important contribution to the polycrystalline materials is electronic polarization [18]. The dielectric constant is evaluated using the relation: $\epsilon_r = (C*d)/A\epsilon_0$, where *d* is the thickness of the sample and *A*, is the area of the sample.

Figure 1 shows the variation of the dielectric constant with respect to the logarithm of frequency. The results suggest that the dielectric constant strongly depend on the frequency of the a.c. signal also on the different temperatures of the ZnS nanoparticles. The dielectric constant has higher values in the lower-frequency (20 Hz) due to the contribution of electronic, ionic, dipolar and space charge polarizations which has a strong dependence on frequencies [19] and then it decreases up to the high frequency (2 MHz). The electrode blocking layer is a dominated mechanism at lower frequency, thus the dielectric behavior is affected by electrodes polarization. At higher frequency the dipole cannot rotate rapidly, so that, their oscillations lag behind those of the field. As the frequency is increased further the dipole will be completely unable to follow the field, and the orientation polarization ceases, so decrease approaching a constant value at higher frequencies due to interfacial polarization only [20].

It can be seen that figure 1(a) has much higher value of ϵ_r compared to figure 1(b), due to the difference in size of synthesized ZnS material. ZnS nanoparticle is much conducting than ZnS bulk particle, so it helps to increase the value of dielectric constant as shown in figure 1(a).
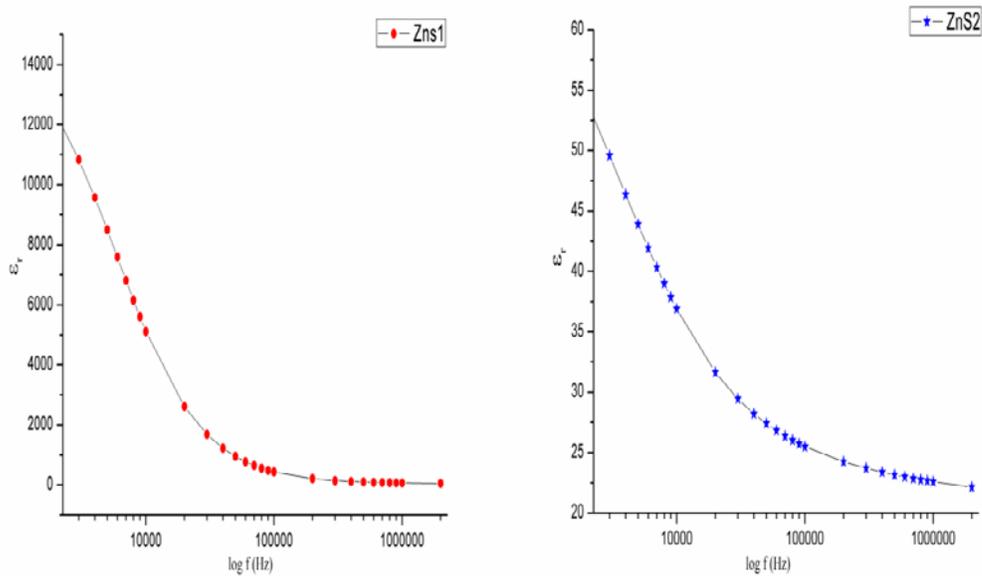
Fig. 1

Dissipation factor (tan δ) analysis

Figure 2(a, b) shows the variation of the dielectric loss with respect to the logarithm of frequency. Dielectric loss also shows a trend similar to the one shown by the dielectric constant. The decrease in the dielectric loss with the increase in frequency for all the temperatures suggests that the dielectric loss is strongly dependent on the frequency of the applied field. The high values of dielectric loss at low frequencies could be related to the charge lattice defect of the space charge polarization [19].

In low signal frequency range, when the electrical dipoles are an able to follow the variation of

the electric field, the dissipation factor decreases with the increases of signal frequency [21].

DF generally varies depending on the dielectric material and the frequency of the electrical

signals. In low dielectric constant (low-k), temperature compensating ceramics, *DF* is low,

whereas in high dielectric constant ceramics, the value of *DF* is higher. However, in our study

the same thing is observed. As, ZnS nanoparticle gives rises to high-k, its dissipation factor value

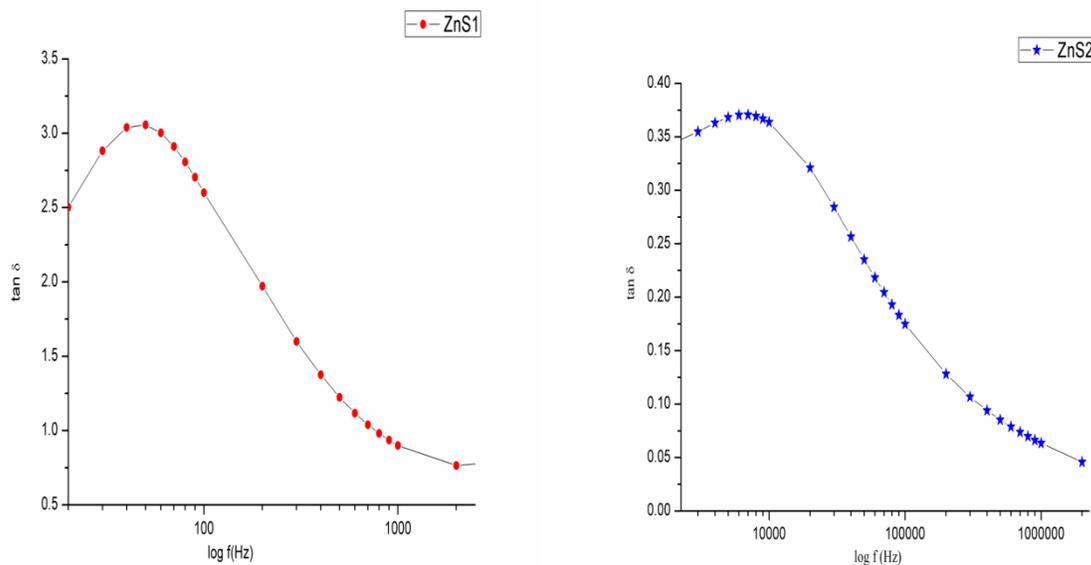is 7% higher than that of the bulk one.

Fig. 2

A.C conductivity ($\sigma_{a.c}$) analysis

Total electrical conductivity contains two parts: A.C conductivity & D.C conductivity. During

A.C conductivity electric field varies, whereas during D.C it remains constant. Also A.C

conductivity has weak temperature dependence and dominates at higher frequency and low temperature and D.C conductivity depends strong on temperature and dominates at lower frequency and high temperature. The relation for frequency dependent A.C conductivity is: $\sigma_{a.c}$ (ω) $=A\omega^s$, where A is a constant factor, s is a function of temperature that is not a constant term but decreases with the increase in temperature (0<s<1) [22].

Figure 3(a, b) shows the variation of the A.C conductivity with respect to the logarithm of frequency. Presence of nanoparticle increases its mobility, as we know decrease in size of a material increases its mobility and with increase in mobility A.C. conductivity increases.
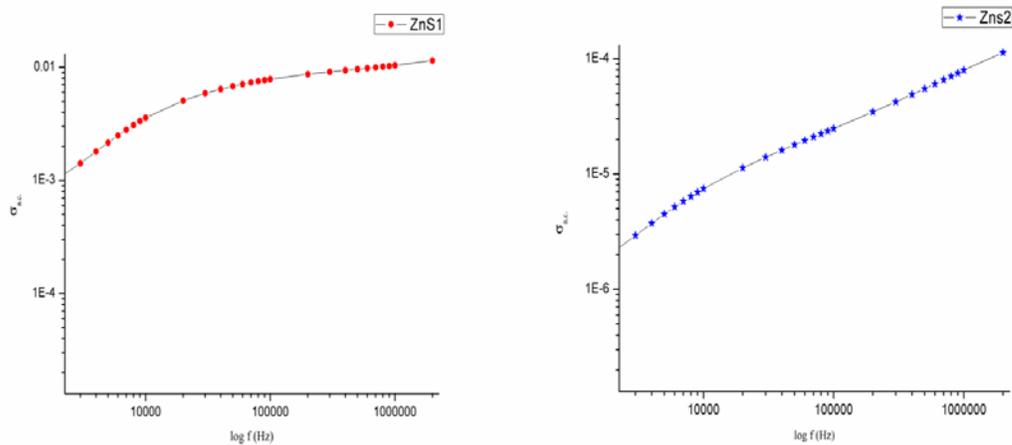

Fig. 3

Resistivity (ρ) Analysis

For application in various fields, thermal conductivity is the most important property, but, due to large experimental errors this property cannot be measured. Since through the Wiedmann–Franz equation resistivity (ρ) is easy to measure and can be translated into thermal conductivity when needed, it was selected in this study to compare the thermal properties of nanoparticles [23]. It

can be seen that resistivity value in figure 4(a) is much lower than the resistivity value in figure 4(b), and it decreases with an increase in frequency. As we know resistivity is inversely proportional to conductivity so, the decrease in resistivity increases its conductivity. Hence it is quite obvious that, as ZnS nanoparticle has better electrical properties, so its resistivity is pretty small with respect to the bulk one.
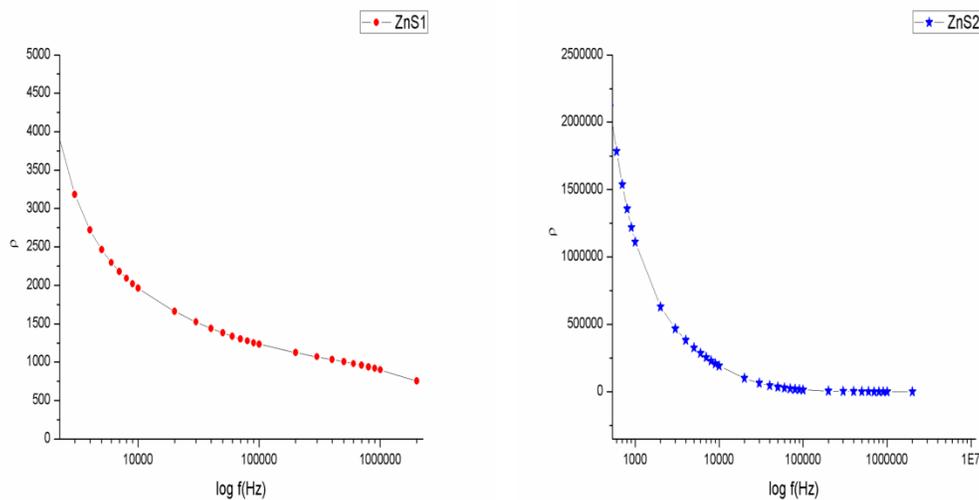

Fig. 4

Conclusion

From all the above mentioned analysis, it can be concluded that, synthesis by wet chemical method produced ZnS nanoparticles and the same material of two different sizes, one in nano form, another one in bulk form exhibited wide variation in their electrical properties ZnS nanoparticle shows considerable high dielectric constant, high A.C. conductivity and low resistivity with respect to the ZnS bulk particle, which indicates its good electrical conductivity.

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