

Full Length Research Paper

# Synthesis, structural and dielectric properties of zinc sulfide nanoparticles

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Zinc sulfide (ZnS) nanoparticles were synthesized by the wet chemical method. The crystal structure and grain size of the particles were determined, using X-ray diffraction (XRD). The optical properties were studied by the Ultraviolet-Visible (UV-Vis) absorption spectrum. The dielectric properties of ZnS nanoparticles were examined using a HIOKI 3532-50 LCR HITESTER over the frequency range of 50 Hz – 5 MHz at different temperatures. The variation of the dielectric constant and dielectric loss were studied. The dielectric constants of the ZnS nanoparticles are high at low frequencies, and decrease rapidly when the frequency is increased. Further, electronic properties like valence electron plasma energy, Penn gap, Fermi energy and electronic polarizability of the ZnS nanoparticles, were estimated.

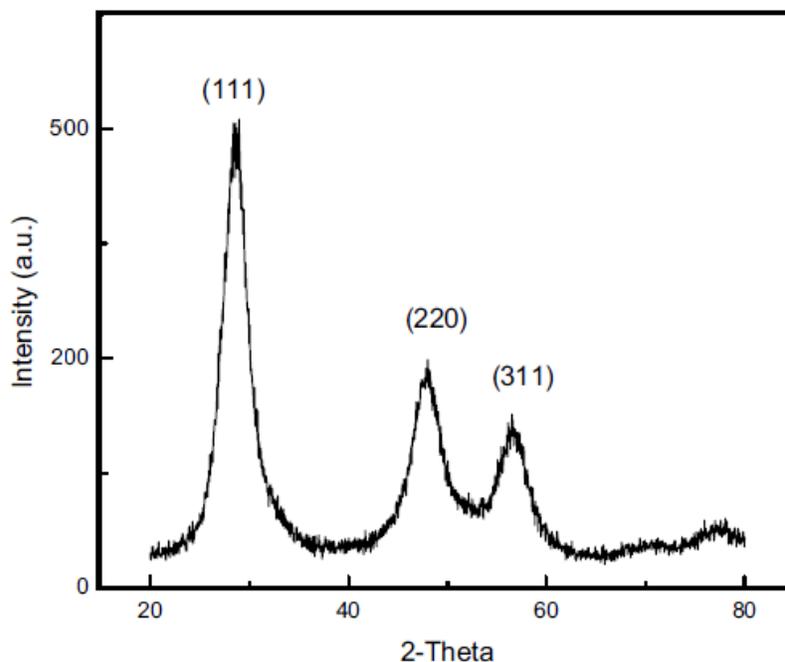
**Key words:** Nanoparticles, zinc sulfide (ZnS), x-ray diffraction (XRD), ultraviolet (UV) analysis, dielectric constant and dielectric loss.

## INTRODUCTION

In recent years, many efforts have been devoted to the 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. The II - VI nanostructures with their distinct properties have become potential candidates for applications in electronics and optoelectronics. Nanosized particles of semi conducting compounds in particular display grain size dependent optoelectronic properties, due to the size quantization effects (Bangal et al., 2005). The photo emission wavelengths, the band gap and lattice parameter are strongly dependent on the grain size rendering the tailorability of these properties as functions of grain size possible. Such unique tunability cannot be

achieved in bulk semiconductors. 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 (Pathak et al., 2012, 2013). Nanocrystalline semiconductors have electronic properties intermediate between those of molecular entities and macro crystalline solids, and are at present the subject of intense research (Weller, 1993; Henglein 1989; Dounghong et al., 1982). ZnS nanostructures have gained a lot of attention that can be attributed to the properties arising from their size in the nanometer range (Gupta et al., 1997). Nanobelts (Jiang et al., 2003; Meng et al., 2003), nanowires (Zhu et al., 2003; Verna et al., 1995), nanocables, nanorods, nanocable- aligned tetrapods, nanoparticles (Sugimoto et al., 1998) and



**Figure 1.** The XRD pattern of the ZnS nanoparticles

nanotubes were synthesized. These modify electronic, mechanical, luminescent and optical properties, and are used in nanoelectronics, photonics and as tools in biomedical applications. This paper deals with the preparation of ZnS nanoparticles using the wet chemical method. The prepared nanoparticles were characterized structurally and optically, using the powder XRD and the UV-Vis absorption spectrum. The dielectric studies have been carried out in the frequency range of 50 Hz to 5 MHz at different temperatures. Some of the electronic properties like plasma energy, Penn gap, Fermi energy and electronic polarizability of the ZnS nanoparticles were also determined.

#### EXPERIMENTAL PROCEDURE

ZnS nanoparticles were synthesized by the wet chemical method, using zinc chloride and sodium sulfide as the starting materials and were kept stirred using magnetic stirrer. The white precipitate of the ZnS nanoparticles is formed slowly in the solution. The nanoparticles were collected by centrifugation for 30 min. The obtained precipitate was then filtered and dried at 110°C for 2 h. The prepared ZnS was washed and dried. After drying, nanoparticles were grinded to obtain a fine powder for characterization. The XRD patterns of the synthesized samples were obtained using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5481 \text{ nm}$ ), the  $2\theta$  range used was from 10 to 70° at a scanning rate of 0.02 deg/sec. The optical absorption spectrum of the ZnS nanoparticles has been taken by using the VARIAN CARY MODEL 5000 spectrophotometer in the wavelength range of 300 to 700 nm. The dielectric constant and the dielectric loss of the pellets of ZnS nanoparticles in disk form were studied using a HIOKI 3532-50 LCR HITESTER in the frequency range of 50 Hz to 5 MHz.

## RESULTS AND DISCUSSION

### XRD studies

The structural properties of the prepared nanoparticles were studied using X-ray diffraction. Figure 1 shows the XRD pattern of the ZnS nanoparticles. The XRD pattern exhibits prominent broad peaks at  $2\theta$  values of 28.90°, 48° and 56.50°. This shows that the ZnS nanoparticles have a zinc blended structure, and the peaks correspond to diffraction at (111), (220) and (311) planes, respectively (Mahamuni et al., 1993). The broad peak indicates the nanocrystalline behavior of the particles. The synthesized nanoparticles have good crystallinity, and the average particle size obtained using the diffraction pattern was 2.6 nm. These values are in good agreement with the reported value of the particle size 2.8 nm.

### Optical absorption studies

Figure 2 shows the variation of the optical absorbance with the wavelength of the as-prepared ZnS nanoparticles. The optical absorption coefficient has been calculated in the wavelength range of 300 to 700 nm. The absorption edge has been obtained at a shorter wavelength. The optical absorption edge of the ZnS nanoparticles at 320 nm (3.80 eV), is slightly blue shifted from that of the bulk ZnS (340 nm,  $E_g = 3.65 \text{ eV}$ ). This nearness of the absorption peak to the bulk ZnS crystals is attributed to the near-band-edge free exactions (Mingwen et al., 2000). The broadening of the absorption

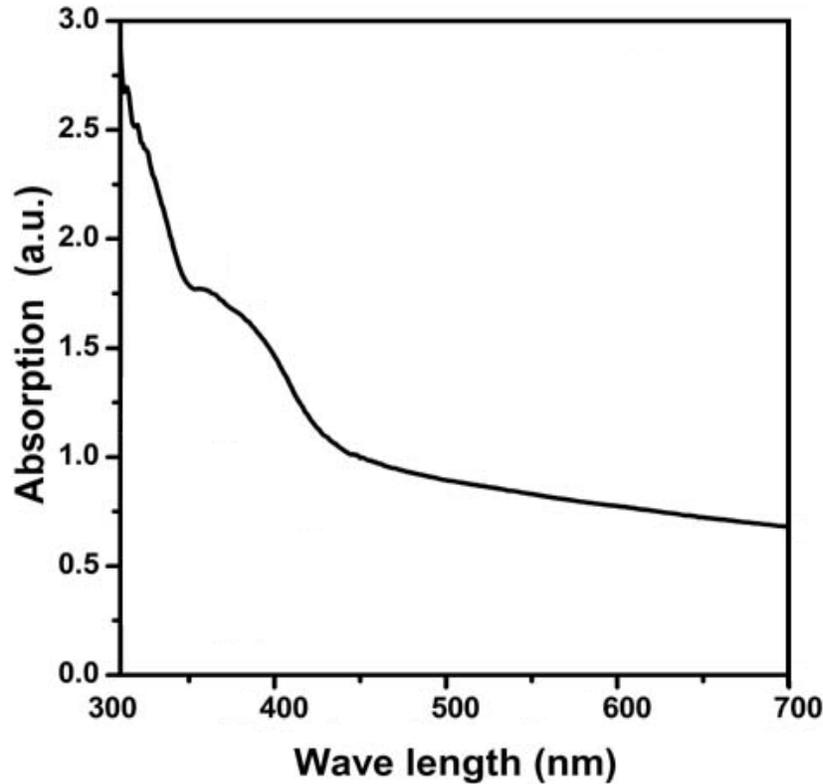


Figure 2. Optical absorption spectrum of ZnS nanoparticles.

spectrum could be due to the quantum confinement of the nanoparticles. From the absorption peak the optical energy bandgap of the ZnS nanoparticles has been calculated using the formula:

$$E_{gn} = h\nu = hc / \lambda \quad (1)$$

Where  $E_g$  is the bandgap,  $h$ , is Planck's constant,  $c$ , is the velocity of light, and  $\lambda$  is the maximum absorption of the ZnS nanoparticles. The value of the bandgap is found to be 3.80 eV. The absorption band edge was shifted to 480 nm and the corresponding bandgap is 3.80 eV, which is higher compared to the bulk ZnS bandgap (3.65 eV). The measured transmittance ( $T$ ) was used to calculate the absorption coefficient ( $\alpha$ ) using the relation,

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t} \quad (2)$$

where  $T$  is the transmittance and  $t$  is the thickness of the crystal. Optical band gap ( $E_g$ ) was evaluated from the absorption spectrum and optical absorption coefficient ( $\alpha$ ) near the absorption edge is given by,

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (3)$$

where  $E_g$  is the optical band gap of the crystal and  $A$  is a constant. The Tauc's plot of  $(\alpha h\nu)^2$  against the photon energy ( $h\nu$ ) at room temperature (Figure 3) shows a linear behaviour, ( $\alpha$ -absorption coefficient and  $h$ -Planck's constant) which can be considered as an evidence of the indirect transition. Hence, assuming indirect transition between valence band and conduction band, the bandgap ( $E_g$ ) is estimated by extrapolation of the linear portion of the curve to the point  $(\alpha h\nu)^2 = 0$ . Using this method, the band gap of the ZnS nanoparticles was found to be 3.80 eV.

### Dielectric properties of ZnS nanoparticles

Dielectric studies shows the effects of temperature and frequency on the conduction phenomenon in nano-structured materials. Dielectric behavior can effectively be used to study the electrical properties of the grain boundaries. 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

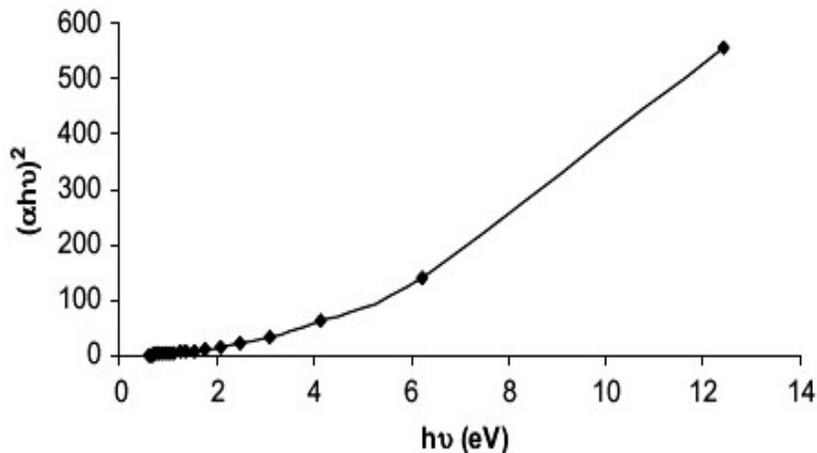


Figure 3. Plot of  $\alpha$  vs. photon energy for ZnS nanoparticles.

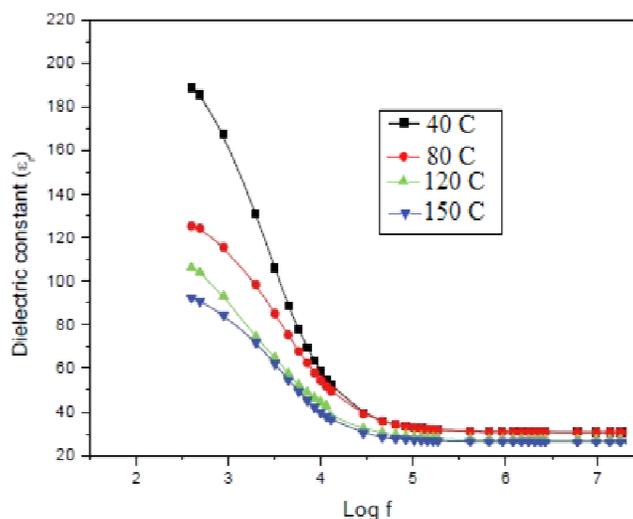


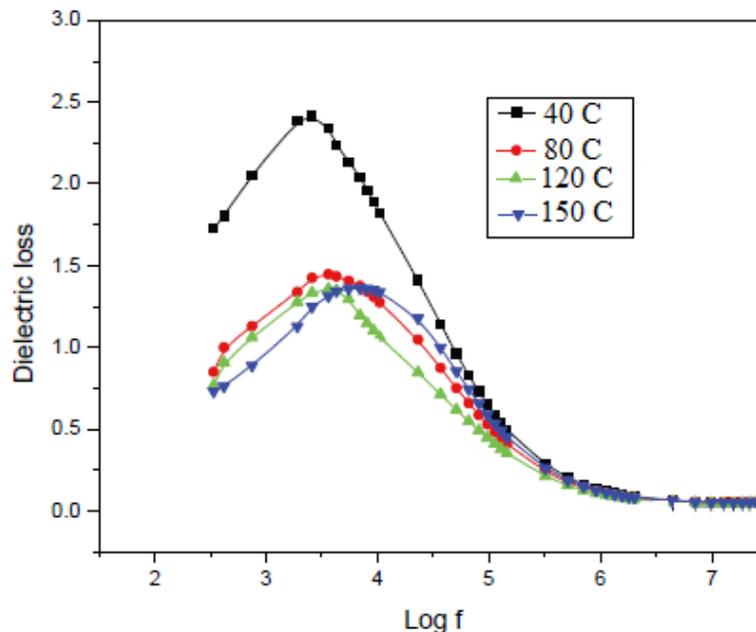
Figure 4. Dielectric constant of ZnS nanoparticles, as a function of frequency at different temperatures.

in bulk form is from the electronic polarization, present in the optical range of frequencies. The next contribution is from ionic polarization, which arises due to the relative displacement of the positive and negative ions. Dipolar or orientation polarization arises from molecules having a permanent electric dipole moment that can change its orientation when an electric field is applied. Space charge polarization arises from molecules having a permanent electric dipole moment that can change its orientation when an electric field is applied. The dielectric parameters, like the dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan\delta$ ) are the basic electrical properties of the ZnS nanoparticles. The measurement of the dielectric constant and loss as a function of frequency and different temperatures reveals the electrical processes that take place in ZnS nanoparticles and these parameters have

been measured. The variations of the dielectric constant and dielectric loss of the ZnS nanoparticles at frequencies of 50 Hz to 5 MHz and at different temperatures of 40 to 150°C are displayed in Figures 4 and 5. The dielectric constant is evaluated using the relation:

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \quad (4)$$

where  $d$  is the thickness of the sample and  $A$ , is the area of the sample. The results suggest that the dielectric constant and dielectric loss strongly depend on the frequency of the a.c. signal and the different temperatures of the ZnS nanoparticles. The dielectric



**Figure 5.** Dielectric loss of ZnS nanoparticles, as a function of frequency at different temperatures.

constant has higher values in the lower-frequency (50 Hz) and then it decreases up to the high frequency (5 MHz). The dielectric constant of ZnS nanoparticles is high at lower frequencies due to the contribution of the electronic, ionic, dipolar and space charge polarizations, which depend on the frequencies (Xue and Kitamura, 2002). Space charge polarization is generally active at lower frequencies and indicates the purity and perfection of the nanoparticles. Its influence is strong at higher temperature and is noticeable in the low frequency range (Smyth, 1956).

Most of the atoms in the nanocrystalline materials reside in the grain boundaries, which become electrically active as a result of charge trapping. The dipole moment can easily follow the changes in the electric field, especially at low frequencies. Hence, the contributions to the dielectric constant increase through space charge and rotation polarizations, which occur mainly in the interfaces. Therefore, the dielectric constant of nanostructures materials should be larger than that of the conventional materials (Meera et al., 2010). One of the reasons for the large dielectric constant of nanocrystalline materials at sufficiently high temperature is the increased space charge polarization due to the structure of their grain boundary interfaces. Also, at sufficiently high temperature the dielectric loss is dominated by the reason for the sharp increase of the dielectric constant at low frequencies and at lower temperatures. As the temperature increases, the space charge and ion jump polarization decrease, resulting in a decrease in the dielectric constant.

In dielectric materials, dielectric losses usually occur

due to the absorption current. The orientation of the molecules along the direction of the applied electric field in polar dielectrics requires a part of the electric energy to overcome the forces of internal friction. Another part of the electric energy is utilized for rotations of the dipolar molecules and other kinds of molecular transfer from one position to another, which also involve energy losses. In nanophase materials, the grain boundaries have an amorphous or glassy structure. All the in homogeneities, defects, space charge formation etc. together produce an absorption current, which results in dielectric losses. Due to the presence of the dangling bonds on the surface layers, the nanoparticles will be highly reactive, and there is a chance of adsorption of gases like oxygen or nitrogen. These adsorbed gases can also cause an increase in the dielectric loss. In nanophase materials, in homogeneities like defects and space charge formation in the inter phase layers produce an absorption current resulting in a dielectric loss. Figure 5 shows the variation of the dielectric loss with respect to the logarithm of frequency at different temperatures of 40, 80, 120 and 150 °C. 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 (Xue and Kitamura, 2002).

In the proposed relation only one parameter, such as the high frequency dielectric constant is required as the input, to evaluate the electronic properties, like valence

**Table 1.** Electronic properties of the ZnS nanoparticles

Parameter	Value
Plasma energy ( $\hbar\omega_p$ )	16.69eV
Penn gap ( $E_p$ )	3.56 eV
Fermi energy ( $E_F$ )	12.46eV
Electronic polarizability (using Penn analysis)	$5.39 \times 10^{-24} \text{ cm}^3$
Electronic polarizability (using Clausius-Mossotti relation)	$5.40 \times 10^{-24} \text{ cm}^3$
Electronic polarizability (using bandgap)	$4.91 \times 10^{-24} \text{ cm}^3$

electron plasma energy, average energy gap or Penn gap, Fermi energy and electronic polarizability of the ZnS nanoparticles. The theoretical calculations show that the high frequency dielectric constant is explicitly dependent on the valence electron Plasmon energy, an average energy gap referred to as the Penn gap and Fermi energy. The Penn gap is determined by fitting the dielectric constant with the Plasmon energy (Ravindra et al., 1981). The valence electron plasma energy,  $\hbar\omega_p$ , is calculated using the relation (Kumar and Sastry, 2005),

$$\hbar\omega_p = 28.8 \left( \frac{Z\rho}{M} \right)^{1/2} \quad (5)$$

According to the Penn model (Penn, 1962), the average energy gap for the ZnS nanoparticles is given by:

$$E_p = \frac{\hbar\omega_p}{(\epsilon_\infty - 1)^{1/2}} \quad (6)$$

where  $\hbar\omega_p$  is the valence electron plasmon energy and the Fermi energy (Ravindra et al., 1981) given by:

$$E_F = 0.2948(\hbar\omega_p)^{4/3} \quad (7)$$

Then we obtained the electronic polarizability  $\alpha$ , using a relation (Ravindra and Srivastava, 1980; Penn, 1962),

$$\alpha = \left[ \frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_p^2} \right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \text{ cm}^3 \quad (8)$$

Where  $S_0$  is a constant given by

$$S_0 = 1 - \left[ \frac{E_p}{4E_F} \right] + \frac{1}{3} \left[ \frac{E_p}{4E_F} \right]^2 \quad (9)$$

The value of  $\alpha$  obtained from equation (6) closely matches with that obtained using the Clausius-Mossotti relation,

$$\alpha = \frac{3}{4} \frac{M}{\pi N_a \rho} \left[ \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right] \quad (10)$$

Considering that the polarizability is highly sensitive to the bandgap (Reddy et al., 1995), the following empirical relationship is also used to calculate  $\alpha$ ,

$$\alpha = \left[ 1 - \frac{\sqrt{E_g}}{4.06} \right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \text{ cm}^3 \quad (11)$$

Where  $E_g$  is the bandgap value determined through the UV absorption spectrum. The high frequency dielectric constant of a material is a very important parameter for calculating its physical or electronic properties. All the above parameters as estimated are shown in Table 1.

## Conclusion

Nanoparticles of ZnS are synthesized using the wet chemical method. The crystal structure and grain size of the particles are determined using XRD studies, and the particle size of the ZnS nanoparticle is found to be 2.6 nm. From the optical absorption spectrum, the blue shift of 320 nm with respect to its bulk counterpart is contributed by the quantum confinement effect. The value of the bandgap is found to be 3.80 eV. The dielectric constant and dielectric loss of the ZnS nanoparticles are measured in the frequency range of 50 Hz to 5 MHz at different temperatures. The dielectric studies reveal that both the dielectric constant and dielectric loss decrease with an increase in the frequency. The dielectric characterization shows the low value of the dielectric constant at higher frequencies. The dielectric constant of the ZnS nanoparticles is found to be much higher than that of the bulk ZnS. Some of the electronic properties like the plasma energy, Penn gap, Fermi energy and electronic polarizability of the ZnS nanoparticles have been calculated.

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