

Dielectric properties of nano-particles of zinc sulphide

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Abstract. The dielectric properties of nano-particles of ZnS have been studied over a temperature range from 300 to 525 K. The dielectric constant, dielectric loss and ac conductivity of the samples are larger than those of bulk ZnS crystals. Dielectric properties of composites consisting of nano-particles of Ag of different concentrations dispersed in nano-particles of ZnS have also been studied.

Keywords. Nano-particles; quantum size effect; semiconductors.

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1. Introduction

The synthesis and characterization of small particles of materials is currently an area of intense theoretical and experimental research. The revelation that physical properties of such systems are bound to be appreciably different from those of the bulk crystals excited much interest in the study of micro-materials termed nano-particles, small particles, clusters, microclusters or microcrystals [1–3]. Quantum size effect of confinement of electron in small particles has been theoretically predicted. It is expected that quantum size effect on electronic properties will be pronounced in mesoscopically small crystals and that electrical conductivity of small particles may be affected by a three dimensional quantum size effect [4–6]. Experimental studies on the electrical properties of nano-particles are limited [7]. The present paper reports the dielectric properties of nano-particles of ZnS and those of composites of nano-particles of Ag of different concentration dispersed in the former, over a temperature range of 300 to 525 K.

2. Experimental

Nano-particles of ZnS were prepared by chemical method taking into advantage its very small solubility in water. All the chemicals used were of analytical grade and were used without further purification. Freshly prepared aqueous solutions of chemicals were used for synthesis. Nano-particles of ZnS were prepared at room temperature by dropping simultaneously 10 ml of 1 M solution of zinc sulphate and 10 ml of 1 M solution of sodium sulphide into 80 ml of distilled water containing 10 ml 0.1 M solution of ethylene diamine tetraacetic acid (EDTA) which was kept stirred vigorously using a magnetic stirrer. The high insolubility of ZnS formed out of the chemical reaction caused the formation of a number of new nuclei while preventing the growth of

Table 1. Composition of pellets mixed with nano-particles of Ag.

Sample	Wt% of Ag	Sample code
ZnS	0	ZnS-0
	5	ZnS-1
	15	ZnS-2
	20	ZnS-3

already existing ones, thus limiting the particle size. The role of EDTA was to stabilize the particles against aggregation which may lead to an increase in the particle size. Nano-particles of silver were prepared according to Lee and Meisel's [8] method.

Composite samples were prepared by dispersing in distilled water by ultrasonication different weight percentages (wt%) of nano-particles of Ag and ZnS. The suspensions were concentrated by evaporating off the liquid phase. The particles were washed repeatedly using distilled water with the help of an ultrasonic disintegrator to remove any adsorbed ions. The particles were finally dried at about 100°C. Pellets of nano-particles of ZnS, and composite pellets with nano-particles of Ag dispersed in ZnS, of diameter 13 mm and thickness 1–2 mm were made by applying a pressure of 4 tonnes/cm² in a hand operated hydraulic press. Both the faces of pellets were then coated with silver electrodes for electrical measurements. For the purpose of reference, sample codes were assigned to the pellets as in table 1.

The crystal structure of particles was determined by X-ray powder diffraction using a Shimadzu XD 610 powder diffractometer. The average size of the particles was determined from the broadening of the diffraction lines and making use of Scherrer equation [9]. The diffraction pattern of ZnS nano-particles displayed three intense lines, corresponding to the wurtzite (8H) structure, confirming the crystallinity of the particles [10]. The X-ray diffraction pattern of the silver particles revealed three strong characteristic peaks of Ag. The average sizes of the particles determined from X-ray line broadening were 8 and 12 nm respectively for ZnS and Ag nano-particles. The diffraction peaks of the nano-particles were found to be shifted to slightly larger angles than expected for the corresponding bulk crystals, suggesting a possible lattice contraction [11].

Dielectric constant ϵ , dielectric loss ($\tan \delta$), and ac conductivity σ_{ac} , of the samples were determined using a Hewlett Packard Model 4192A LF impedance analyzer. Dielectric constant, dielectric loss and ac conductivity measurements at different frequencies from 10 kHz to 13 MHz were carried out over a temperature range of 300 to 525 K.

3. Results

The variations of dielectric constant ϵ , dielectric loss ($\tan \delta$) and ac conductivity σ_{ac} of the samples as a function of frequency and temperature are shown in figures 1 to 3. The numerical values of dielectric constant of the samples at different temperatures and frequencies are given in table 2. It is seen that ϵ of ZnS-0 is almost independent of frequency at low temperatures (figure 1a), showing a very slow decrease with frequency

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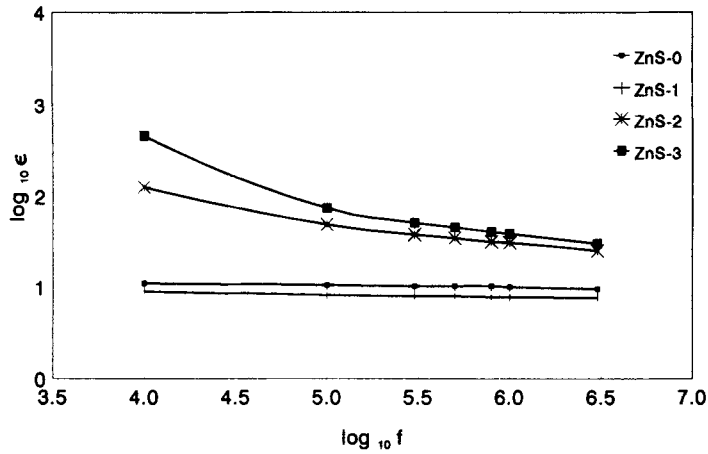


Figure 1a. Variation of dielectric constant at 343 K with frequency of nano-particles of ZnS and composites with different wt% of nano-particles of Ag.

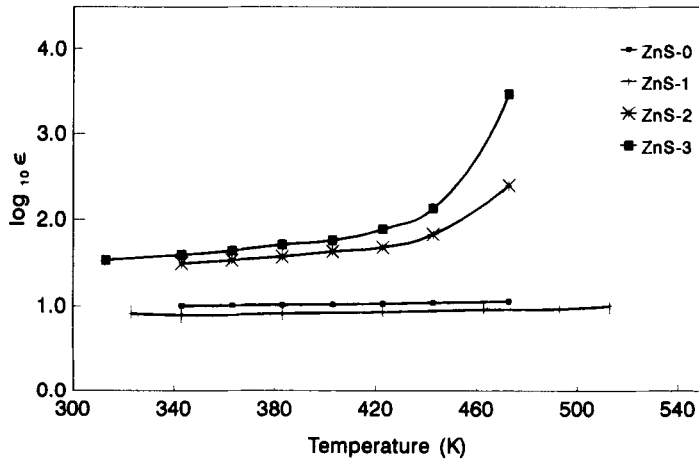


Figure 1b. Variation of dielectric constant at 1 MHz with temperature of nano-particles of ZnS and composites with different wt% of nano-particles of Ag.

from 10.9 at 10 kHz to 9.54 at 3 MHz. The general trend in the $\log \epsilon$ vs frequency graph at higher temperature is similar but the rate of decrease in the value of ϵ with frequency is larger at high temperatures. ϵ of ZnS-1 is slightly lesser than that of ZnS-0, but increases with increase in the wt% of Ag. At a frequency of 10 kHz, ϵ of ZnS-2 was as high as about 127 and 7220 respectively at 343 and 473 K, the values for ZnS-3 being 459 and 12400 respectively. ϵ of all the samples, at low as well as high frequencies, increased with temperature, the rate of increase being strongly temperature dependent for ZnS-2 and ZnS-3 samples (figure 1b). The numerical value of ϵ of ZnS-0 at 1 MHz increased at a low rate from 10.1 at 343 to 11.4 at 473 K. The large values of ϵ for ZnS-2 and ZnS-3, although appear to be anomalous at first glance, may be considered to be

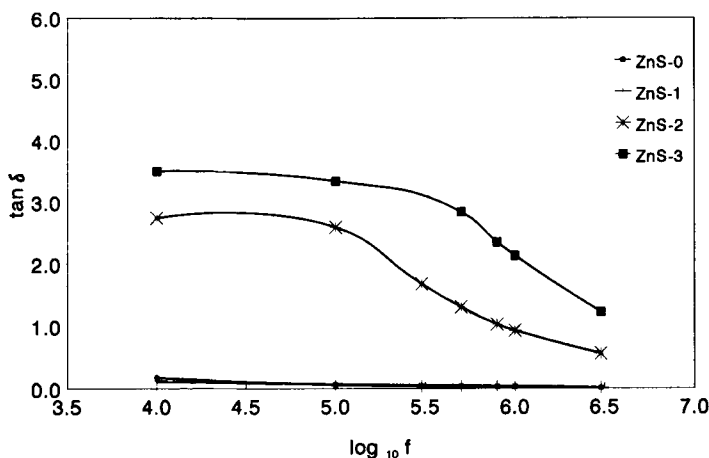


Figure 2a. Variation of dielectric loss factor at 423 K with frequency of nano-particles of ZnS and composites with different wt% of nano-particles of Ag.

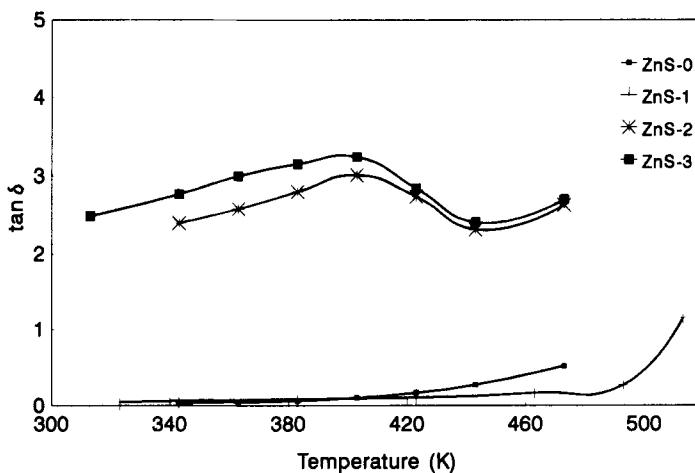


Figure 2b. Variation of dielectric loss factor at 10 kHz with temperature of nano-particles of ZnS and composites with different wt% of nano-particles of Ag.

representing the actual behaviour of the samples from the fact that they vary regularly with frequency and temperature.

The value of $\tan \delta$ decreased with frequency (figure 2a), the rate of decrease being larger at larger frequencies. $\tan \delta$ of ZnS-0 and ZnS-1 had low numerical values but increased with wt% of Ag in the samples, attaining a value of about 2 to 3 at lower frequencies. $\tan \delta$ increased only slightly with temperature for ZnS-0 and ZnS-1, but for ZnS-2 and ZnS-3 it was strongly frequency- and temperature-dependent. At lower frequencies, it increased with temperature slowly from a large value of about 2, attaining a maximum value of about 3, then decreased and again showed a tendency to increase (figure 2b).

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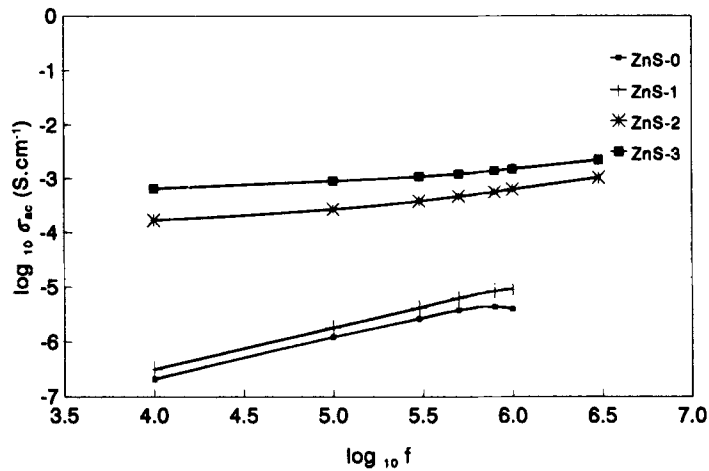


Figure 3a. Variation of ac conductivity at 343 K with frequency of nano-particles of ZnS and composites with different wt% of nano-particles of Ag.

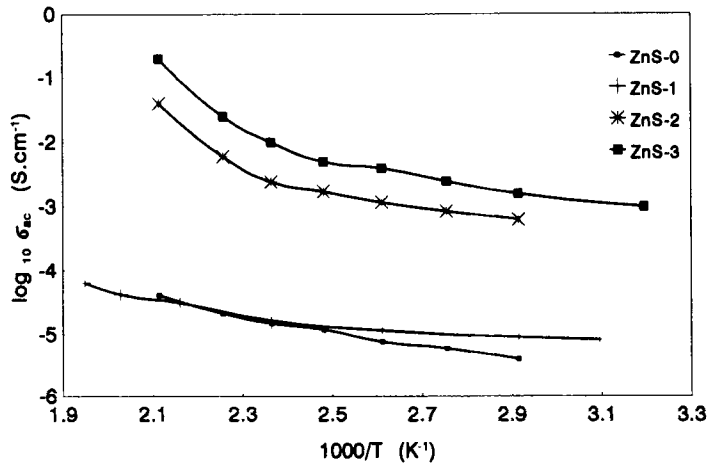


Figure 3b. Variation of ac conductivity at 1 MHz with temperature of nano-particles of ZnS and composites with different wt% of nano-particles of Ag.

The ac conductivity (σ_{ac}) increased with both frequency and temperature (figures 3a and 3b). σ_{ac} of ZnS-1 was slightly larger than that of ZnS-0, but its rate of increase with frequency was the same for both ZnS-0 and ZnS-1. σ_{ac} of ZnS-2 and ZnS-3 increased almost linearly with frequency. As regards variation with temperature, σ_{ac} of ZnS-0 increased at a low rate up to about 415 K and thereafter the increase was rapid. The numerical value of σ_{ac} at 1 MHz increased from about $4 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at 343 K to $4.2 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 473 K. At a constant frequency, σ_{ac} increased with temperature at a slow rate initially and beyond a particular temperature the increase was rapid (figure 3b). Numerically, σ_{ac} increased by about an order of magnitude on changing the

Table 2. Dielectric constant of nano-particles of ZnS and composites with different wt% of nano-particles of Ag.

Sample	T(K)	10 kHz	100 kHz	500 kHz	1 MHz	3 MHz
ZnS-0	343	10.9	10.4	10.2	10.1	9.5
	383	11.5	10.8	10.6	10.4	9.8
	423	12.8	11.3	10.9	10.7	10.0
	473	17.2	13.0	11.8	11.4	10.5
ZnS-1	343	8.9	8.2	7.9	7.8	7.5
	383	9.6	8.7	8.4	8.2	8.0
	423	10.5	9.2	8.7	8.5	8.2
	473	13.0	10.5	9.6	9.2	8.6
ZnS-2	343	350.0	48.9	34.6	30.7	25.2
	383	959.0	69.0	43.4	37.3	29.7
	423	2892.0	117.0	59.2	48.2	36.5
	473	6044.0	2030.0	500.0	251.0	114.0
ZnS-3	343	459.0	74.7	45.4	38.8	30.4
	383	1620.0	136.0	62.3	50.8	38.5
	423	4590.0	379.0	106.0	76.8	52.8
	473	12400.0	7760.0	4630.0	2930.0	1160.0

temperature from about 313 to 473 K at a frequency of 1 MHz. σ_{ac} increased greatly with increase in wt% of Ag. σ_{ac} of ZnS-2 and ZnS-3 is more than 4 orders of magnitude larger than that of ZnS-0 and ZnS-1.

4. Discussion

The dielectric constant of single crystals of cubic ZnS at 25°C was reported to be 8.3 by Berlincourt *et al* [12]. The low frequency dielectric constant of polycrystalline ZnS [13] over a temperature range of 300 to 500 K was reported to increase only by a small amount from a value of 8.21 to 8.58. Also, in the case of thin films of thickness 2500 Å, the dielectric constant undergoes a very small decrease from 8.3 to 8.2 with frequency in the range from 10^2 – 10^5 Hz [14]. Samara [15] has reported that ϵ for cubic ZnS is strongly frequency dependent in the temperature range of 75.7 to 300 K, dielectric response was linear, ϵ having a value 8.1 at 75.6 K and 8.3 at 300 K. He also observed that at room temperature and at 100 kHz, $\tan \delta$ is approximately 0.15.

In the present study, for pellets of ZnS nano-particles, ϵ at constant temperature (figure 1a) decreased at a slow rate with increase in frequency. Similarly, ϵ increased with temperature (figure 1b) both at low as well as high frequencies, the magnitude of increase in ϵ over a given temperature range being larger at low frequencies. ϵ of pellets of ZnS nano-particles is larger by about 25% than that of the bulk ZnS crystals [12, 13]. $\tan \delta$ for ZnS has a low numerical value which decreased with frequency (figure 2a). At constant frequency, $\tan \delta$ increased rapidly with temperature (figure 2b). $\tan \delta$ of pellets of nano-particles of ZnS is larger than that of the corresponding values of bulk crystals reported in the literature [15]. Also, σ_{ac} of pellets of nano-particles of ZnS is many orders of magnitude larger than that of the bulk crystals [16, 17].

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Unlike the ionic crystals where the effective field,

$$E_{\text{eff}} = E + 4/3 \pi P,$$

for semiconductors E_{eff} should be essentially equal to the macroscopic field E , i.e.,

$$E_{\text{eff}} = E$$

This leads to an expression for ϵ of the form

$$\epsilon - 1 = 4\pi(\alpha/V),$$

where V is the volume. The large value of ϵ of pellets of nano-particles of ZnS compared to the corresponding bulk value may be attributed to the small value of V in the above expression. The large values of ϵ , $\tan \delta$ and σ_{ac} of nano-particles of ZnS compared to the corresponding bulk values may be due to the small volume of the particles [15] and the disorder in their structure due to excess surface stress [18]. But the large increase in the values of ϵ , $\tan \delta$ and σ_{ac} when the nano-particles of ZnS are mixed with nano-particles of Ag must be expected to be caused by some other factor which causes a large increase in the electronic polarizability. The static dielectric constant ϵ of heteropolar semiconductors like CdS and ZnS can be written [15] as

$$\epsilon = \epsilon_{\alpha} + \epsilon_1,$$

where ϵ_{α} is the high frequency or electronic contribution to the dielectric constant (dielectric constant in the absence of lattice vibrations) and ϵ_1 is the lattice contribution to the dielectric constant. Samara [15] has shown that for compound semiconductors, ϵ is dominated by the electronic contribution ϵ_{α} and the lattice contribution ϵ_1 is considerably smaller. The large value of ϵ in the case of ZnS, on the addition of nano-particles of Ag must be attributed to the large increase in ϵ_{α} , and the enhanced magnitude of $\tan \delta$ must be due to the disorder in the structure of the particles [18].

5. Conclusion

The dielectric properties of nano-particles of ZnS and composites with nano-particles of Ag of different concentrations dispersed in ZnS have been studied over a temperature range of 300 to 525 K. The large values of dielectric constant, dielectric loss and ac conductivity of nano-particles of ZnS compared to the corresponding values of bulk single crystals may be due to the small volume of the particles and the disorder in their structure.

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