

Abstract: The semiconductor nanoparticles have recently attracted a lot of attention due to the possibility of their application in various devices. In the present paper, nanoparticles of Zinc oxide are prepared by precipitation method using two different (EDTA and DNA) capping agents to control the agglomeration. XRD and SEM technique was used for structural characterization. For the study of dielectric properties, complex permittivity ($\varepsilon'$ and $\varepsilon''$) and loss tangent (tan $\delta$) with frequency is analyzed with frequency and temperature. The Dispersion parameters are calculated using Cole-Cole analysis and the results are compared.

Keywords: Cole-Cole analysis, Dielectrics, Dispersion parameters, Relaxation time, Surfactants.

1. Introduction

Research in semiconducting nanoparticles is one of the most investigated subjects, due to their wide field of applications. The novel properties of nanomaterials depend on their size, structure and shape. As a result of the high surface-to-volume ratio of the nanoparticles, the surface dependent properties change drastically from the bulk counterparts. In semiconductors, the quantum confinement modulates the band structure of the nanoparticles, and hence, many properties can be tuned by changing the nanoparticles size. Zinc oxide is a direct band gap II-VI versatile semiconductor material with wurtzite structure possessing several unique properties like high-specific surface area, nontoxicity, chemical stability, and high electron communication features especially in nanoforms. The exotic properties exhibited can be attributed to existence of intrinsic defects like O vacancies and Zn interstitials [1]. In this paper zinc oxide nanoparticles were synthesized using two capping agents and their dielectric properties were studied by varying frequency and temperature.

Synthesis: All Chemicals and DNA powder were obtained from commercial sources (SRI, Merck). We used aqueous solutions of DNA powder and EDTA as capping agent to control the particle size. The sample $Z$ is prepared using EDTA as capping agent and sample $ZD$ using DNA solution to prevent agglomeration. For both samples 0.1 M solution of Zinc Acetate, 0.1 M solution of Sodium Hydroxide are added drop wise into 0.01 wt% capping agent solution, kept at room temperature, at the rate of 10ml per hour under constant stirring using a magnetic stirrer. The rate of addition, speed of stirring and the temperature at which reaction takes place are the important factors in this synthesis process. In the first process Zinc oxide (Z) is obtained after annealing carbonate powder at 300$^\circ$C, whereas the second sample (ZD) was dried in a hot air oven at 60$^\circ$C Details of synthesis are given in [2], [3]. The XRD and SEM micrographs obtained reveal formation of nanoparticles and the sample ZD shows more homogeneous structures.

Fig. 1. Sem micrographs of Z and ZD

Changes in Dielectric Properties and Dispersion Parameters of ZnO with Surfactant and Temperature

P. P. Sharmila*

Associate Professor, Department of Physics, M. P. M. M. S. N. Trusts College, Shoranur, India

*Corresponding author: sharmilavishram@gmail.com
electric field is applied across the sample the resulting polarization in the material is lagged by a fixed phase angle due to the dielectric loss. This gives rise to two components of polarization inside the material, one is in phase and the other is 90° out of phase. These two components can be considered the real and imaginary components of the polarization when represented in a complex plane. Accordingly, there are two components for the dielectric permittivity of the material when a sinusoidal electric field is applied [4].

The dielectric studies of both samples were carried out by varying frequency from 20 Hz to 10 MHz. The value of capacitance of Z varied from 4 pF to 13 pF in the range studied. At low frequencies dielectric constant is found to be too high and it decreases exponentially with increase in frequency. This variation in the high range of frequency is plotted with log f and is given in Figure 3(a). The variation of dielectric constant with temperature is also studied in the temperature range 303 K to 423 K (Fig 3(b)). At all frequencies the dielectric constant is found to be high at room temperature and is found to decrease when temperature increased and at high temperature the value of dielectric constant was found to be almost a constant.

The dielectric property of Zinc Oxide nanoparticles is further investigated by analysing the annealed samples annealed at...
700°C and 900°C. Figure 4a, and 4b depicts the variation in dielectric constant of these samples with frequency. On close examination we can see that the increase in dielectric constant with temperature is becoming more and more obvious with increase in annealing temperature.

In the figure 4(a) the dielectric constant value is more or less same at high temperature and frequency were as in figure 4(b) the dielectric constant increase with an increase in temperature. When an electric field is applied on dielectric materials the dipoles gets oriented and energy is lost in the lattice for the rearrangement and relaxation process. This loss in energy is obtained as loss tangent. The variations in this loss factor with frequency at various temperatures are given in figure 5(a).

The variation of dielectric constant with temperature sample ZD is studied at various frequencies. The nature of variation of dielectric constant with temperature is same for all frequencies even though the range of values is different. The dielectric constant increases first, reaches a maximum, and then decreases. At high temperatures the value of dielectric constant remains constant. The dielectric constant is found to decrease with increase in frequency but the values increased and shifted upwards with increase in temperature, Figure 6(b).

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**Fig. 4.** Variation in dielectric constant of Zinc Oxide(Z) nanoparticles annealed at a) 700°C b) 900°C

**Fig. 5.** The variation in dielectric loss of (a) Z and (b) ZD nanoparticles with frequency

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The loss factor gives a measure of energy lost in the lattice due to the polarization effects taking place on the application of electric field. The figure 7 depicts the variation in the loss factor with increase in the frequency at different temperatures. The graph indicates that there are multiple relaxation mechanisms present in the material and the variation in the polarization at different temperatures.

3. AC Conductivity Studies

The variation of capacitance (pF) of Z pellets with frequency of the applied field for temperature from 373 K to 403 K is given in figure 8. The capacitance of the pellet is found to decrease exponentially with an increase in frequency. At high frequency the capacitance is found to be more or less constant. This type of variation in frequency is common in metal oxides. The loss factor also decreased considerably with frequency at low temperature but at higher temperature this variation was very slight.
The ac electrical conductivity was calculated using the dielectric parameters and the value of conductivity were obtained in the range 10⁻⁶ Sm⁻¹. The conductivity of the material (Fig. 9(b)) increased very slowly in the low frequency regime, but showed a sudden increase at high frequency and then decreased.

The variation in AC conductivity of sample Z with temperature is given in figure 9(a). At all frequencies the conductivity showed a peak at temperature 313 K, but remained more or less same at high temperatures. The conductivity showed a clear increase with increase in frequency.

The conductivity of Zinc Oxide nanoparticles is found to increase with an increase in annealing temperature. The ac conductivity of Zinc Oxide nanoparticles were obtained as 9x10⁻⁸ Sm⁻¹, 7.63x10⁻⁵ Sm⁻¹ and 3.61x10⁻⁴ Sm⁻¹ for synthesized, annealed at 700°C and 900°C respectively at frequency 1kHz and temperature 373 K. The effect of sintering seems to reduce the grain boundary resistance [5].

The graph 10 depicts the variation of AC conductivity with temperature at different frequency of sample ZD. It shows that the conductivity first increase, reaches a maximum, then decreases. At high temperatures the value remains more or less same and then shows an increase beyond 403 K. The nature of variation of conductivity with temperature is similar at all frequencies.

4. Cole–Cole Analysis

To have a good insight about dielectric relaxations. Kenneth S. Cole and Robert H. Cole used [6], [7], [9] the Argand diagram or complex locus diagram in which the imaginary part of the complex dielectric constant is plotted against the real part at the same frequency and such plots are known as Cole-Cole plots.

The Cole-Cole analysis of the samples were done for temperatures 353 K to 373 K and semi circles are obtained with centers lying below the real axis and this indicates that multiple relaxation mechanism is present in the dipoles of the material [8]. Hence the relaxation time gets spread around the average
relaxation time and the value of spreading which is below 1 is given in the tables for both samples.

![Cole-Cole plot](image)

**Table 1**

Dispersion parameters of Zinc Oxide Synthesized with EDTA(Z)

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>α</th>
<th>ε''max</th>
<th>τ(10^8 s)</th>
<th>τ(10^7 s)</th>
<th>ε∞</th>
<th>ε'∞</th>
</tr>
</thead>
<tbody>
<tr>
<td>353</td>
<td>0.432</td>
<td>4.073</td>
<td>5.13</td>
<td>4.24</td>
<td>15.66</td>
<td>32.71</td>
</tr>
<tr>
<td>363</td>
<td>0.420</td>
<td>8.772</td>
<td>4.73</td>
<td>3.65</td>
<td>15.73</td>
<td>52.57</td>
</tr>
<tr>
<td>373</td>
<td>0.173</td>
<td>5.618</td>
<td>1.45</td>
<td>1.22</td>
<td>16.04</td>
<td>30.43</td>
</tr>
</tbody>
</table>

The optical dielectric constant decreased with temperature initially even though the decrease was little and then increased suddenly. The static dielectric constant also showed a similar variation.

![Cole-Cole plot](image)

**Table 2**

Dispersion parameters of Zinc Oxide nanoparticles prepared using DNA

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>α</th>
<th>ε''max</th>
<th>τ(10^8 s)</th>
<th>τ(10^7 s)</th>
<th>ε∞</th>
<th>ε'∞</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.66</td>
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<td>5.11</td>
<td>7.59</td>
<td>19.43</td>
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<tr>
<td>363</td>
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<td>0.34</td>
<td>2.74</td>
<td>2.30</td>
<td>8.87</td>
<td>17.22</td>
</tr>
<tr>
<td>373</td>
<td>0.20</td>
<td>13.96</td>
<td>1.67</td>
<td>1.25</td>
<td>12.65</td>
<td>51.19</td>
</tr>
</tbody>
</table>

5. Conclusion

Nanoparticles of Zinc oxide were successfully synthesized using EDTA and DNA. The SEM image shows that obtained nanoparticles were homogeneous in shape and size. The structural and dielectric properties of nanoparticles synthesized using DNA are done and compared with that of nanoparticles prepared using EDTA. To have a more knowledge about various conducting mechanism and relaxation methods prevailing in the sample Cole-Cole analysis was done and the results are compared.

### References