CHAPTER 6
ELECTRICAL CHARGE TRANSPORT AND DIELECTRIC RESPONSE IN ZnO NANORODS AND NANOTUBES

6.1 Introduction

ZnO is an n type semiconductor; its electrical properties originate from point native defects such as oxygen vacancies (V_o) and zinc interstitials (Zn_i^+) [1]. The high surface to volume ratio of grains, small size, enhanced contribution from grains and grain boundaries, quantum confinement of charge carriers, band structure modification and defects in grains are some of the factors which contribute to the electrical properties of nanostructured materials [2]. A useful technique to analyze the electrical properties of low conductivity materials and electroceramics is based on the study of complex impedance spectroscopy. Indeed, this technique offers several advantages such as the determination of relaxation frequency and separation of grain, grain boundary and grain-electrode effects. Generally, the high permittivity dielectric materials with good thermal stability have particularly attracted ever-increasing attention for their practical applications in microelectronics such as capacitors and memory devices. Materials with high dielectric constants and low dielectric losses have also received special attention due to the rapid developments in microwave telecommunications, satellite broadcasting, discrete and multilayer capacitors, dynamic random access memories and low-loss substrates for microwave integrated circuits [3-6]. Recently, ZnO nanostructures have been studied as conductive fillers in polymers with high electrical permittivity, and they have received increasing attention for their potential application in high charge-storage
capacitors [7]. ZnO seems to be a microwave-absorbing material and is used as a material in microwave components such as resonators, band pass filters and duplexers [3-8].

The grain boundary of ZnO nanorods and nanotubes contains a large number of defect structures such as dangling bonds, vacancies and micropores that can play an important role in their transport properties. The role played by the grains and grain boundaries in the transport properties can be easily determined using impedance spectroscopy. Almost all reports of ZnO nanorods and nanotubes focused on morphology, synthesis methods and growth mechanisms [9-12]. However, a few investigations on the transport properties and dielectric behaviour of ZnO nanostructures have been reported [4]. The high surface-to-volume ratio of ZnO nanorods and nanotubes will significantly modify their electrical properties compared to those of the bulk phase, which would be reflected in their impedance spectra and dielectric behaviour. Thus, the study of electrical transport and overall dielectric performance of this material is important. This chapter deals with the charge transport properties of ZnO nanorods and nanotubes through their grain and grain boundary regions using impedance and modulus spectroscopy. The dielectric absorption and dispersion behaviour of consolidated ZnO nanorods and nanotubes was studied as a function of temperature and frequency. Studies on the effect of temperature and frequency on the dielectric behaviour and impedance spectra of ZnO nanorods and nanotubes offer various informations about different polarization mechanisms, grain and grain boundary effect in nanostructured materials. The impedance and dielectric spectroscopy data of the consolidated nanotubes were recorded using a Hioki 3532-50 Hi-Tester in the frequency range of 100 Hz-2 MHz and at various temperatures between 303K and 543K.
6.2 Impedance Spectroscopy

6.2.1 General theory of Impedance Spectroscopy

Impedance spectroscopy is a highly powerful technique used to investigate electrical/dielectric properties in polycrystalline materials, nanostructured materials and electroceramic materials, such as ferroelectric materials, ionic conductors, positive-temperature coefficient resistors, and voltage-dependent resistors [13-15]. Frequency-dependent impedance provides valuable information on the physical origins of electrical/dielectric properties, e.g., separation of bulk-based responses from electrode-related contributions, along with the simultaneous measurement of materials constants such as resistivity and dielectric constants [14]. The technique ensures separation among the bulk, grain, grain boundaries and electrode electrolyte interface properties. It has great ability to analyze the relaxation phenomenon occurring in the material, whose time constants range over several orders of magnitude. Impedance spectroscopy can also be used to study the intergranular electrical barriers, origin of resistance or capacitance and their dispersion with small signal frequencies and the role of defects within the regime of the electric field [14]. The estimation of arc depression is attributed to the spatial distribution of the microstructural components governing the corresponding electrical responses.

In this method, a monochromatic signal \( V(t) = V_m \sin(\omega t) \) where \( \omega = 2\pi f \), \( f \) being the signal frequency is applied to the sample and the resulting steady current is \( I(t) = I_m \sin(\omega t + \theta) \) where \( \theta \) is the phase difference between voltage and current. The total complex impedance \( Z \) is given by \( Z = Z' - jZ'' \) where \( Z' = |Z|\cos \theta \) is the real part of the complex impedance and \( Z'' = |Z|\sin \theta \) is the imaginary part of the complex
impedance. The real part $Z'$ is plotted along X-axis and the corresponding imaginary part $Z''$ along Y-axis at different frequencies, which will give a semi circle or a set of semi circles corresponding to each relaxation processes in the complex impedance plane. The total ac response or dielectric response is represented by this diagram, which incorporates all mechanisms in the material under a given set of experimental conditions.

The complex impedance data are interpreted using an equivalent circuit model. This is a network of capacitors and resistors, which give a representation of what is happening within the system. A pure resistor, with resistance $R$, will display a phase angle of $0^0$ and have $Z=R$. This is represented by a single distinct point on the X-axis at $Z=R$. A sample with pure capacitance will display $Z=1/\omega C$, with a phase angle of $90^0$. This is displayed by a series of points on the Y-axis. Taking the case of resistor and capacitor in parallel, $Z'=R_p, R_p$ is the parallel resistance and $Z''=1/\omega C_p, C_p$ is parallel capacitance. This leads to $Z = \left[ \left( \frac{1}{R_p} \right) + j \omega C_p \right]^{-1}$. The contribution of each of the components, grain, grain boundary and sample electrode interface can be represented by a suitable combination of resistance and capacitance in parallel. The sample can thus be represented by an equivalent circuit containing three parallel R-C elements connected in series. The appearance of three overlapping semi-circular arcs indicate the presence of three polarization processes in the system with different response times, the grain response being at the high frequency side and electrode response at the low frequency side. One parallel R-C circuit has one time constant and hence can be conveniently used as a model to represent one polarization process. This R-C element in equivalent circuit is characterized by a relaxation time, $\tau$ which is a product of R and C. It is also possible to
express \( RC \) in terms of \( \omega_{\text{max}} \). This expression is \( \omega_{\text{max}} RC = 1 \), where \( \omega_{\text{max}} \) is the frequency at maximum loss. This allows the calculation for values of the \( R \) and \( C \) components.

### 6.2.2 Dielectric relaxation

The complex permittivity of a dielectric in an ac field is written as

\[
\varepsilon^* = \varepsilon' - j\varepsilon''
\]

where \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary part of \( \varepsilon^* \). The displacement due to polarization may persist even when the field is stopped. This gives rise to a decay time to attain the equilibrium and the phenomenon is called the Debye relaxation. The decay time is called relaxation time. The dielectric constant can be expressed as

\[
\varepsilon^*(\omega) = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) / 1 - j\omega\tau
\]

(1)

Now equating real and imaginary part leads to

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \frac{\omega^2\tau^2}{\omega^2\tau^2}}
\]

(2)

\[
\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + \frac{\omega^2\tau^2}{\omega^2\tau^2}}
\]

(3)

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{\varepsilon_0 + \varepsilon_\infty\omega^2\tau^2}
\]

(4)

Equation 2, 3 and 4 are known as Debye’s equations. The real part \( \varepsilon' \) is plotted along X-axis and the corresponding imaginary part \( \varepsilon'' \) along Y-axis at different frequencies as same in the case of impedance data. This diagram may be called the complex locus diagram or Argand diagram and was applied to dielectric by Cole and Cole \[16\]. It is often called as Cole-Cole plot. The Cole-Cole plots have been used to determine the molecular relaxation time \( \tau \). In a dielectric with single relaxation time Cole-Cole plot is a semi circle. The temperature dependence of \( \tau \) is influenced by a thermally activated
process. If the dielectric relaxation is related to the thermally activated process the relaxation time should have the form

$$\tau = \tau_0 \exp \left( \frac{E_a(\tau)}{K_BT} \right)$$

(5)

where $E_a$ and $K_B$ are the activation energy and the Boltzmann constant, respectively, and $\tau_0$ is the relaxation time at an infinite temperature.

6.2.3 Impedance Spectroscopy of ZnO nanorods and nanotube

For a detailed investigation of the transport properties of ZnO nanorods and nanotubes, the impedance measurements were made in the frequency range of 100 Hz–2 MHz at different temperatures. This analysis determines the correlation between the electrical and structural properties of the material. The impedance spectrum of ZnO nanorods and nanotubes are shown in figure 6.1 and 6.2.

Fig 6.1 Variation of real and imaginary parts of impedance of ZnO nanorods with temperature
Fig. 6.2 Variation of real and imaginary parts of impedance of ZnO nanotubes with temperature

This spectrum shows only one semicircle at low temperatures, but it gradually transforms into two semicircles at higher temperatures. The low-frequency semicircle can be attributed to the grain boundary effect, and the higher-frequency semicircle can be attributed to the grain interior. The arcs are not well resolved at low temperatures; the conduction process through the grain interior and grain boundaries may have an identical time constant $\tau$ at low temperatures [17].

The observation of two semicircles in the impedance spectrum suggests that the Maxwell-Wagner model can be employed for further analysis [18]. This model consists of two parallel RC elements connected in series: one RC element for the grain interior and the other for the grain boundary response. The proposed equivalent circuit is shown in figure 6.3.
Fig. 6.3 Equivalent circuit used to represent the electrical properties of grain and grain boundary effects.

$R_s$ in the equivalent circuit corresponds to the contact resistance of the sample and the electrode. $R_s$ denotes the shift of the impedance plot from the origin along the real $Z'$ axis. $R_g$, $C_g$ and $R_{gb}$, $C_{gb}$ are the resistance and capacitance values due to the grain interior and grain boundary region of ZnO nanorods and nanotubes, respectively. A depressed semicircle whose centre lies below the positive real axis suggests the departure from the ideal Debye behaviour. The grain and grain boundary contributions to the conduction process can be easily separated out using the Cole-Cole modification of the Debye equation [16-18].

The complex impedance $Z^*(\omega) = Z'(\omega) - jZ''(\omega)$ ................................. (6) consists of two overlapping semicircles and can be written as

$$Z^*(\omega) = R_s + \frac{(R_2 - R_1)}{(1 + j\omega\tau_g)^{1-\alpha_g}} + \frac{R_3 - R_2}{(1 + j\omega\tau_{gb})^{1-\alpha_{gb}}} ........................................ (7)$$
where \( \alpha_g = \alpha_{gb} = 0 \), provides the Debye equation of impedance distribution; \( R_3 \) and \( R_1 \) are the intercepts of the impedance semicircle on the \( Z' \) axis; and \( R_2 \) is the resistance that corresponds to the projection of the point of intersection between the two semicircles onto the \( Z' \) axis [18]. The mean relaxation times for the grain and grain boundary process are \( \tau_g = C_g R_g \) and \( \tau_{gb} = C_{gb} R_{gb} \) respectively. The physical parameters of ZnO nanorods and nanotubes extracted from the equivalent circuit are tabulated in table 6.1 and 6.2.

**Table 6.1. Magnitudes of parameters obtained by computer simulation of experimental data at various temperatures for ZnO nanorods**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_g ) (( \Omega ))</td>
<td>303</td>
</tr>
<tr>
<td></td>
<td>1.69x10^7</td>
</tr>
<tr>
<td>( R_{gb} ) (( \Omega ))</td>
<td>7.85x10^6</td>
</tr>
<tr>
<td>( C_g ) (pF)</td>
<td>2.35</td>
</tr>
<tr>
<td>( C_{gb} ) (pF)</td>
<td>5.86</td>
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<td>( \tau_g ) (( \mu s ))</td>
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</tr>
<tr>
<td>( \tau_{gb} ) (( \mu s ))</td>
<td>40.13</td>
</tr>
<tr>
<td>( \alpha_g )</td>
<td>0.33</td>
</tr>
<tr>
<td>( \alpha_{gb} )</td>
<td>0.31</td>
</tr>
<tr>
<td>( \sigma_g ) (( \Omega^{-1}m^{-1} ))</td>
<td>7.5x10^{-7}</td>
</tr>
<tr>
<td>( \sigma_{gb} ) (( \Omega^{-1}m^{-1} ))</td>
<td>1.62x10^{-6}</td>
</tr>
</tbody>
</table>
Table 6.2. Magnitudes of parameters obtained by computer simulation of experimental data at various temperatures for ZnO nanotubes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303</td>
</tr>
<tr>
<td>$R_g$ (Ω)</td>
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</tr>
<tr>
<td>$R_{gb}$ (Ω)</td>
<td>1.60×10^6</td>
</tr>
<tr>
<td>$C_g$ (pF)</td>
<td>51</td>
</tr>
<tr>
<td>$C_{gb}$ (pF)</td>
<td>0.31</td>
</tr>
<tr>
<td>$\tau_g$ (µs)</td>
<td>4.85×10^-4</td>
</tr>
<tr>
<td>$\tau_{gb}$ (µs)</td>
<td>4.9×10^-4</td>
</tr>
<tr>
<td>$\alpha_g$</td>
<td>0.35</td>
</tr>
<tr>
<td>$\alpha_{gb}$</td>
<td>0.34</td>
</tr>
<tr>
<td>$\sigma_g$ (Ω^{-1}m^{-1})</td>
<td>1.33×10^-6</td>
</tr>
<tr>
<td>$\sigma_{gb}$ (Ω^{-1}m^{-1})</td>
<td>8.5×10^-6</td>
</tr>
</tbody>
</table>

The measured grain and grain boundary values of the conductivity, the capacitance and the dielectric constant of ZnO nanorods and nanotubes increase with increasing temperature. This is caused by the enhanced thermal movements of defects and charge carriers present in the grain interior and the interfacial region of the nanorods and nanotubes. In ZnO nanotubes, the conductivity due to the grain boundary contribution is found to be higher than that of the grain interior at all temperatures. But in ZnO nanorods, the conductivity due to grain interior is found to be a little higher than that of the grain.
boundary region at higher temperatures (503-543K). Below these temperatures, the overall impedance of the ZnO nanorods is contributed by grain interior and conductivity is contributed by grain boundary region as same in the case of ZnO nanotubes. In ZnO nanorods and nanotubes, large numbers of charge carriers are accumulated at the grain boundary region due to its high surface-to-volume ratio, causing an enhanced conductivity in the grain boundary region. But at higher temperature, there is a possibility of disappears the grain boundaries. As a result, some grain boundary regions of ZnO nanorods may vanish at higher temperatures. ZnO nanotubes have high surface to volume ratio and large grain boundary region compared to that of nanorods due to its large surface area, therefore the disappearing of grain boundary region is not notable in ZnO nanotubes. This is the reason for why at higher temperature, the overall conductivity of ZnO nanorods is contributed by grain interior and impedance contributed by grain boundary region.

The conductivity reported by J. Jose et.al. [19] for nanophase ZnO having particle size of 10nm is in the range \(1.87 \times 10^{-7}\) to \(1.4 \times 10^{-6}\ \Omega^{-1}\text{cm}^{-1}\) for grain interior and \(3.75 \times 10^{-7}\) to \(4.25 \times 10^{-6}\ \Omega^{-1}\text{cm}^{-1}\) for grain boundaries at 313-393 K and the contribution to conductivity by grain boundaries were found to be higher than that due to the grains. According to Lee et.al. [20] the impedance spectrum for nanophase ZnO having a grain dimension of 60 nm is reported to single semicircle and conductivity is in the range of \(0.2 \times 10^{-5}\) - \(0.2\times10^{-3}\ \Omega^{-1}\text{cm}^{-1}\) at 723-873K.

To elucidate the dielectric relaxation response in ZnO nanorods and nanotubes, it is important to estimate the activation energy of relaxation. For a thermally activated process, the relaxation time will obey the equation (5). According to equation (5) we can
calculate the activation energies of relaxation for grain and grain boundary region. The variation of the grain and the grain boundary resistance and the corresponding relaxation time of ZnO nanorods and nanotubes evaluated from the impedance spectrum were expressed as a function of temperature and are shown in figure 6.4 and 6.5.

Figure 6.4 and 6.5 clearly shows that there is a substantial drop in the grain and grain boundary resistance with an increase in temperature. The decrease in the relaxation time, which is constant with increasing temperature, is suggestive of an increased dipole density and a faster polarisation process. The logarithmic plot of $1/R_g$, $1/R_{gb}$ and $\tau_g$, $\tau_{gb}$ varies linearly with an inverse of temperature and demonstrates the Arrhenius behaviour. Figure 6.4 and 6.5 also shows that the plots are not linear; there is a sudden change observed in the slope in a higher temperature region.

Fig. 6.4 Variation of grain and grain boundary resistance and relaxation time of ZnO nanorods with temperature
Fig. 6.5 Variation of grain and grain boundary resistance and relaxation time of ZnO nanotubes with temperature

The activation energy experienced by the grain and the grain boundary of ZnO nanorods for conduction in the temperature range of 303-463K are 0.073 eV and 0.076 eV, respectively, and the same energy at the temperature range of 503-543K are 1.8 eV and 1.5 eV, respectively. The activation energy experienced by the grain and the grain boundary of ZnO nanotubes for conduction in the temperature range of 303-463K are 0.079 eV and 0.069 eV, respectively, and the same energy at the temperature range of 503-543K are 1.12 eV and 1.01 eV, respectively. The activation energy of relaxation for the grain and the grain boundary region of ZnO nanorods in the temperature range of 303-463K are 0.048 eV and 0.049 eV, respectively and the same energy in the temperature range of 503-543K are 1.21 eV and 0.88 eV, respectively. The activation
energy of relaxation for the grain and the grain boundary region of ZnO nanotubes in the temperature range of 303-463K are 0.059 eV and 0.058 eV, respectively and the same energy in the temperature range of 503-543K are 1.03 eV and 0.9 eV, respectively. These analogous activation energy indicate that the charge carries responsible for both the conduction mechanism and the relaxation phenomena are the same in both ZnO nanorods and nanotubes. The reported activation energy for ZnO ceramics is 0.066 eV [17]. Large values of activation energy at higher temperatures indicate that the electrical conductivity of ZnO nanorods and nanotubes is thermally activated from the deep donor level to the conduction band [1]. High activation values are usually associated with a hopping type of electronic transport mechanism.

6.3 Electric Modulus Spectroscopy

The electric modulus spectroscopy is widely used to study the electrical relaxation in ionically and electronically conducting materials, as it has the advantage of suppressing electrode polarizing effects [5, 21]. It provides more information relating to charge transport processes, such as the mechanism of electrical transport, conductivity relaxation and ion dynamics as a function of frequency and temperature. The combined usage of impedance and modulus spectroscopic plots can be used to rationalise the dielectric properties [22]. This technique also presents an alternative approach based on polarization analysis.

Complex electric modulus plots give more importance to elements with the smallest capacitance occurring in the dielectric system [23]. The electric modulus is defined as the electric analog of the dynamical mechanical modulus and is related to the complex permittivity $\varepsilon^*(\omega)$ by
\[
M^*(\omega) = \frac{1}{\varepsilon^s(\omega)} = \{\varepsilon'(\omega) - i\varepsilon''(\omega)\} = M' + iM'' \quad \text{.......................... (8)}
\]

where \(M'\) and \(M''\) are the real and imaginary parts of the electrical modulus, respectively, \(M_\infty = 1/\varepsilon_\infty\) is the inverse of the high-frequency dielectric permittivity. The electric modulus \(M^*(\omega)\) as expressed in the complex modulus formalisms are

\[
M^*(\omega) = j(\omega C_0)Z^* = M' + jM''
M' = \omega C_0 Z'' \quad \text{.......................................................... (9)}
M'' = \omega C_0 Z'
\]

Where \((M', Z')\) and \((M'', Z'')\) are real and imaginary part of modulus and impedance respectively, \(j = (-1)^{1/2}\), \(\omega\) is angular frequency and \(C_0\) is the geometrical capacitance,

\[
C_0 = (\varepsilon_0 A)/t, \quad \text{where} \quad \varepsilon_0 \text{ is the permittivity for free space, } A \text{ is the area of the electrode surface and } t \text{ is the thickness.}
\]

The real and imaginary part of the complex electrical modulus is calculated from the values of \(\varepsilon'\) and \(\varepsilon''\) using the following relation

\[
M' = \frac{\varepsilon'}{(\varepsilon'^2 + \varepsilon''^2)} \quad \text{and} \quad M'' = \frac{\varepsilon''}{(\varepsilon'^2 + \varepsilon''^2)} \quad \text{.......................... (10)}
\]

### 6.3.1 Electric Modulus Spectroscopy of ZnO nanorods and nanotubes

Figure 6.6 and 6.7 shows the imaginary part of the electric modulus \((M'')\) and the impedance \((Z'')\) of ZnO nanorods and nanotubes with increasing frequency at high temperatures. As temperature increases the peak positions are shifted towards the higher frequency side. The low-frequency side of the peak signifies the range of frequencies in which charge carriers can perform successful hopping from one defect site to another. The higher-frequency side of the \(M''\) peak represents the range of frequencies in which the charge carriers are spatially confined to their potential wells, and the electrons/holes can make only short-range motions within the well.
Fig. 6.6 Variation of the imaginary part of the modulus and impedance of ZnO nanorods with frequency at different temperatures

Fig. 6.7 Variation of the imaginary part of the modulus and impedance of ZnO nanotubes with frequency at different temperatures
The region where the peak occurs is indicative of the transition from long-range to short-range mobility with an increase in frequency. This behaviour of the modulus spectrum is suggestive of a temperature-dependent hopping type mechanism for electrical conduction (charge transport) in the system [24]. An interesting point is that the observed modulus peaks are broader than those predicted by Debye’s theory of dielectric relaxation and are significantly asymmetric. The broadening of these peaks points to the spread of relaxation with different mean-time constant which is a trait of non-Debye type of relaxation [25]. The asymmetric broadening of impedance peaks with an increase in temperature confirms the existence of temperature-dependent electrical relaxation phenomena in the material. Additionally the shifting of the peak frequencies in a forward direction with temperature implies that the relaxation time decreases with increasing temperature. The peak frequency gives an estimate of the conduction relaxation time in accordance with the relation $\omega_m \tau_m = 1$. A logarithmic plot of the conduction relaxation time $\tau$ versus the inverse absolute temperature is shown in figure 6.8 and 6.9, demonstrating the Arrhenius behaviour.

The activation energies for relaxation evaluated from the slope of both modulus and impedance peaks of ZnO nanorods are 0.864 eV and 0.860 eV, respectively and that for ZnO nanotubes are 0.90 eV and 1.03 eV, respectively. A nearly similar activation energy for relaxation, obtained from impedance ($Z''$) and modulus ($M''$) plots, indicates the localised conduction (dielectric relaxation) of the charge species in ZnO nanotubes at higher frequencies [26].
Fig. 6.8 Variation of relaxation time with temperature in ZnO nanorods (for modulus and impedance data)

Fig. 6.9 Variation of relaxation time with temperature in ZnO nanotubes (for modulus and impedance data)
Figure 6.10 and 6.11 shows the variation of normalised parameters $M''/M''_{\text{max}}$, $Z''/Z''_{\text{max}}$ of ZnO nanorods and nanotubes as a function of frequency, measured at 303K and 523K, respectively. The overlapping of these two peaks provides evidence of delocalised or long-range relaxation. There is an appreciable mismatch between $M''/M''_{\text{max}}$ and $Z''/Z''_{\text{max}}$ peaks in both the ZnO nanorods and nanotubes at room temperature.

**Fig. 6.10** Normalised imaginary part of the impedance and modulus of ZnO nanorods as a function of the frequency at 303K and 523K. This provides us with the idea that the hopping of charge carriers between different defect sites constitutes the conduction mechanism in ZnO nanorods and nanotubes at low temperatures (localised conduction). However, as the temperature increases, the $M''/M''_{\text{max}}$ and the $Z''/Z''_{\text{max}}$ peaks almost overlap, suggesting the development of both localised and delocalised conduction [24]. According to the ideal Debye theory of relaxation, the impedance and modulus maxima are supposed to peak at the same
frequency at a measured temperature, which is not observed in the present case. According to Jonscher, the poly-dispersive relaxation is the outcome of many body interactions in the dielectric relaxation phenomenon and is purely dependent on the universal dielectric power law [27].

Fig. 6.11 Normalised imaginary part of the impedance and modulus as a function of the frequency at 303K and 523K

6.4 Dielectric Absorption in ZnO nanorods and nanotubes.

Dielectric absorption in a material is characterised by dielectric loss (ε'') and loss tangent (tanδ) values. The variation of ε'' and tanδ of ZnO nanorods and nanotubes with frequency at different temperatures are represented in figure 6.12, 6.13, 6.14 and 6.15. These figures show that the values of ε'' and tanδ of both ZnO nanorods and nanotubes increase with increasing temperature and decrease with increasing frequency.
Fig. 6.12 Variation of the imaginary part of the dielectric constant of ZnO nanorods with frequency at different temperatures

Fig. 6.13 Variation of the imaginary part of the dielectric constant of ZnO nanotubes with frequency at different temperatures
Fig. 6.14 Variation of the loss tangent of ZnO nanorods with frequency at different temperatures

Fig. 6.15 Variation of the loss tangent of ZnO nanorods with frequency at different temperatures
As temperature increases, the position of loss peak shifts into the region of higher frequencies. This behaviour of dielectric loss is due to the existence of the broad spectrum of the relaxation time in the material. The Cole-Cole plots reflect the deviation from the ideal Debye behaviour and introduce a parameter \( \beta \) that reflects the distribution of the relaxation time. According to the Cole-Cole equation [16], the frequency dependence of the imaginary part of the dielectric constant \( (\epsilon'') \) concerned with a single relaxation can be written as follows:

\[
\epsilon'' = (\Delta \epsilon'/2) \frac{\sin(\beta \pi/2)}{\cosh(\beta z) + \cos(\beta \pi/2)} \tag{11}
\]

where \( z = \ln(\omega \tau) \), \( \Delta \epsilon' = \epsilon_\infty - \epsilon_s \), \( \epsilon_\infty \) is the dielectric permittivity at a high frequency and \( \epsilon_s \) is the static dielectric permittivity, \( \omega \) is the angular frequency, \( \tau \) is the mean relaxation time and \( \beta = (1 - \alpha) \), where \( \alpha \) shows either the deformation of the semi-circle arc in the Cole–Cole plot or a measure of the broadening of the relaxation time. The values of \( \beta \), \( \epsilon_\infty \) and \( \epsilon_s \) of ZnO nanorods and nanotubes at different temperatures are calculated using equation (11) and listed in table 6.2.

**Table 6.2 Dispersion parameters from Cole-Cole analysis**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>ZnO nanotubes</th>
<th>ZnO nanorods</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \epsilon_s )</td>
<td>( \epsilon_\alpha )</td>
</tr>
<tr>
<td>303</td>
<td>114</td>
<td>14</td>
</tr>
<tr>
<td>403</td>
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<td>463</td>
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<tr>
<td>503</td>
<td>270</td>
<td>17</td>
</tr>
<tr>
<td>543</td>
<td>797</td>
<td>22</td>
</tr>
</tbody>
</table>
The $\beta$ value is found to increase with increasing temperature. Thus, the spreading factor $\alpha$ decreases with increasing temperature. The increase in temperature causes a reduction in the mean time of the stay of electric dipoles in the system, resulting in a decrease of relaxation time with temperature. This will cause the reduction of spreading factor $\alpha$ with temperature, and the result agrees well with that obtained from the impedance spectrum.

The frequency dependence of real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the dielectric constant also follow the ‘universal relaxation law’ as given by

$$\varepsilon',\varepsilon'' = B(T) \omega^{(n-1)}$$

where $B(T)$ is weakly dependent on temperature and the exponent $n$ lies in the range between 0 and 1. The exponent $n$ is the measure of deviation from the ideal Debye behaviour. The value of $n$ calculated from the experimental data varies from 0.33 to 0.14 for ZnO nanorods and 0.35 to 0.16 for ZnO nanotubes in the temperature range 303K to 543K, respectively. It is found that the temperature exponent $n$ decreases linearly with increasing temperature; this is in agreement with the theoretical prediction.

6.5 **Dielectric Dispersion in ZnO nanorods and nanotubes.**

The variation of the real part of the dielectric constant ($\varepsilon'$) with a frequency at various temperatures for ZnO nanorods and nanotubes is given in figure 6.16 and 6.17. The trend of these graph indicate the existence of more than one type of polarisation mechanism in both ZnO nanorods and tubes. A high degree of dispersion observed at the low-frequency region is due to interfacial polarization and orientational polarisation is dominant at higher frequencies ($>10^4$ Hz). ZnO nanorods and nanotubes have a high dielectric constant value in low-frequency regions, which decreases with increasing frequency and attains a constant value at higher frequencies.
M.K.Gupta et.al. [28] reported a similar result in the case of flower-like ZnO nanocrystals. ZnO nanorods and nanotubes exhibit an interfacial polarisation or space charge polarisation due to its structural inhomogeneity created by a large surface-to-volume ratio. When an external electric field is applied, the space charges move under this field and are trapped by defects in the interfaces, forming many dipole moments. Therefore, at low frequencies, space charge polarisation is dominant. This type of polarisation may be explained on the basis of the Maxwell-Wagner theory of dielectric dispersion [18]. The effect of grain boundaries is found to be more pronounced at low frequencies. The hopping of electrons/holes between positive and negative surface defect centres in the grain boundary region may constitute the dielectric polarisation at low
frequencies. The value of the dielectric constant does not decrease continuously to zero at high frequencies as would be expected in the case of interfacial polarisation.

At higher frequencies, the rotational displacement of dipoles results in orientational polarisation. The possible source of orientational polarisation is the existence of a number of oxygen vacancies and zinc interstitials in nanotubes. There is a tendency of the occupied cations to be associated with the positive ion vacancies so that the associated pairs have dipole moments. When an external field is applied, the Zn$^{2+}$ ions and the O$^{2-}$ vacancies in the neighbourhood exchange their positions by a single jump and try to align along the direction of the field. It is obvious that the orientation of a molecule involves the energy required to overcome the resistance of the surrounding

Fig. 6.17 Variation of real part of the dielectric constant of ZnO nanotubes with frequency at different temperatures
molecules, which makes the orientational polarisation strongly temperature dependent; this is known as ion-jump polarisation.

As the frequency increases, the electric dipoles in the material begin to lag behind the applied electric field and $\varepsilon'$ decreases exponentially. However, at higher frequencies, these dipoles fail to cope with rapid variations of the electric field, and thus they show practically no dispersion. Thus, the dielectric constant attains a constant value at higher frequencies. When the temperature is increased in steps, the value of the dielectric constant also increases. At lower frequencies, the rapid increase in the dielectric constant with temperature is primarily due to interfacial polarization, which is strongly dependent on temperature. As the temperature increases, large numbers of oxygen vacancies, in addition to some other defect structures such as zinc interstitials, are released. These defect structures accumulated at the grain boundary region are responsible for the enhanced polarisation mechanism at higher temperatures.

The orientational dipole moments refers to the permanent dipole moment formed by the bound charges within one potential well, while the hopping dipole moments or interfacial dipole moments are formed due to the transition of a separate charged particle from one potential well to another potential well. Therefore at low frequencies the interfacial polarization mechanisms constitute interwell hopping of charge carriers and at higher frequencies orientational polarization constitute intrawell hopping of charge carriers. The average hopping distance of interwell hopping is in the order of few nanometers while intrawell hopping is in the order of $\lambda^0$ (one lattice spacing)[29]. According to the equation,

$$P = \sum x_i q_i$$
corresponds to high value of polarization due to interwell hopping at low frequencies and polarization decreases with increasing signal frequency [29]. At higher frequencies, the space charges cannot follow the change of the field and hence do not produce space charge polarization. The dipoles are also unable to follow rapidly with varying electric field [30]. Damping of these dipoles accounts for the reduction of dielectric constant at higher frequencies.

6.6 Conclusions

A detailed investigation of transport properties and the modified dielectric behaviour of ZnO nanorods and nanotubes are analysed by impedance and modulus spectroscopy. The grain and grain boundary parameters are extracted from the equivalent circuit, modelled by Maxwell-Wagner. The distinguishable role of grain and grain boundary region in controlling the transport behaviour of ZnO nanorods and nanotubes at all temperatures is discussed. A significant conductivity is contributed by the grain boundary region of the ZnO nanotubes at all temperatures. Whereas, in ZnO nanorods the conductivity is mainly through the grain interior at higher temperatures, but at low temperatures, the conductivity constituted by the grain boundary region. The dielectric relaxation frequency and the grain boundary conductivity of ZnO nanorods and nanotubes follow the same Arrhenius behaviour with the nearest activation energy, which shows that the species responsible for both conductivity and relaxation phenomena are the same. The modulus analysis gives an evidence of localised conduction at low frequencies and a combined effect of localised and delocalised conduction at higher frequencies. The asymmetric broadening of the impedance and modulus peaks emphasis the poly-dispersive relaxation mechanism in both ZnO nanorods and nanotubes. The
experimental results show that the variation of the real part of the dielectric constant as a function of frequency at different temperatures exhibits a dispersive behaviour at lower frequencies. All regions in the frequency-dependent dielectric loss peak of ZnO nanorods and nanotubes exhibit a common feature with regard to the power-law relation between loss and frequency. The experimental results conclude that the behaviour of electrical charge transport and dielectric response with regards to different frequencies and temperatures are same in both nanorods and nanotubes, however, the ZnO nanorods are found to be little more dielectric than ZnO nanotubes.

6.7 References


22. K.Sambasiva Rao, D.Madhava Prasad, P.Murali Krishna, B.Tilak, and K.Ch.Varadarajulu, Impedance and modulus spectroscopy studies on Ba$_{0.1}$Sr$_{0.81}$La$_{0.06}$Bi$_2$Nb$_2$O$_9$, Mater.Sci.Eng.B 133 (2006) 141.


