CHAPTER 3

ELECTRICAL PROPERTIES OF DOPED ZINC OXIDE NANOPARTICLES

SECTION-A: DC ELECTRICAL CONDUCTIVITY

3. A.1 Introduction

ZnO based varistor exhibits strong n-type conductivity with the electrons to move in the conduction band as charge carriers. Typical ZnO based varistor is a very complex chemical system containing several different dopants [1–6]. The electrical properties of ZnO are dependent on the composition and on structural characteristics, such as grain size, density, morphology and the distribution of second phases. The effect of dopants on the electrical properties of ZnO varistor has been investigated by several researchers [7–13]. It has been observed that the region of nonlinearity of Al doped ZnO can be extended to higher applied fields and consequently the conductivity of ZnO grains is improved [12]. While the conductivity of ZnO has decreased by the doping of both Co, Mn and Cu dopants, and the samples still showed a semiconductor behavior [12,13].

The control of defects and associated charge carriers is of paramount importance in applications that exploit the wide range of properties of doped ZnO. However, despite the many papers on ZnO, the relationship between defect chemistry, processing, and properties has not received much attention. Despite its simple chemical formula, ZnO has a very rich defect chemistry [14]. Defect studies have been considered for more than 40 years, but now there is a
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need to revisiting in the context of novel applications using nanostructured materials. In the past, defect chemistry was studied in relation to ZnO properties and applications in ZnO varistors: defects significantly alter grain boundary properties and also I-V characteristics [15, 16]. Solid surfaces contain segregated impurities, adsorbed gases that act as sources and sinks of electrons, and associated space charge regions. In nanostructured ZnO (as well as in other materials), the small length scales and large surface-to-volume ratio mean that surface defects play a stronger role in controlling properties. It is also critically important to understand defects in ZnO doped with aliovalent ions, either purposefully for achieving certain functionality or through accidental doping during the growth process. It is important to understand the relative dominance of carriers introduced by the doping over native defects.

Before considering the defect structure of ZnO in more detail, it is important to realize that ZnO has a relatively open structure, with a hexagonal close packed lattice where Zn atoms occupy half of the tetrahedral sites. All the octahedral sites are empty. Hence, there are plenty of sites for ZnO to accommodate intrinsic (namely Zn interstitials) defects and extrinsic dopants. The electronic energy levels of native imperfections in ZnO are illustrated in Fig. 3.A.1. There are a number of intrinsic defects with different ionization energies. The Kröger Vink notation uses: i = interstitial site, Zn = zinc, O = oxygen, and V = vacancy. The terms indicate the atomic sites, and superscripted terms indicate charges, where a dot indicates positive charge, a prime indicates negative charge, and a cross indicates zero charge, with the charges in proportion to the number of symbols. Fig. 3.1 shows that there are a number of defect states within the band gap of ZnO. The donor defects are: Zni" , Zni' , Zni X, V0" , V0' , Vo and the acceptor defects are: Vzn" , Vzn'. The
defect ionization energies vary from ~ 0.05-2.8 eV [17]. Zn interstitials and oxygen vacancies are known to be the predominant ionic defect types. However, which defect dominates in native, undoped ZnO is still a matter of great controversy [18].

Because of the different ionization energies, the relative concentrations of the various defects depend strongly on temperature. As shown below, both defects donate two electrons and so it is difficult to distinguish one from the other using electrical measurements.

**Defect chemistry in ZnO:**

Zn interstitials come from the Frenkel reaction:

\[ \text{Zn}_{Zn} \leftrightarrow \text{Zn}_i^x + V_{Zn}^x \]

Further ionization reactions [17] are:

\[ \text{Zn}_i^x \leftrightarrow \text{Zn}_i^* + e' \]
\[ \text{Zn}_i^* \leftrightarrow \text{Zn}_i^{**} + e' \]

The oxygen vacancies arise from the Schottky reaction:

\[ O \leftrightarrow V_{Zn}^x + V_{O}^x \]
Further ionization reactions are:

\[ V_0^x \leftrightarrow V_0^* + e^+ \]
\[ V_0^* \leftrightarrow V_0^{**} + e^+ \]
\[ V_{zn}^x \leftrightarrow V_{zn}^* + h^+ \]
\[ V_{zn}^* \leftrightarrow V_{zn}^{**} + h^+ \]

Although, there are few reports on the doping elements in the ZnO varistor, the effects of some dopants such as Fe on the electrical conductivity of ZnO varistor still remain unclear. This is because the doping effects have been studied in quite different systems under different experimental conditions. Therefore, it is necessary to investigate independently in a systematic way to understand the role of Fe doping in the electrical conductivity of ZnO varistor. Recently, Sedky et al [19] have presented in detail the effects of Fe doping on structural and I–V characteristics of ZnO samples. It is found that the addition of Fe improved the nonlinear properties of ZnO varistor and the electrical barriers could be formed. So, in the present work we have studied electrical conductivity of Fe doped ZnO and also of Co;Fe co-doped ZnO samples.

3. A.2 Experimental

The experimental set up of the DC electrical conductivity measurements is shown in Fig.3.A.2. The powder samples were pressed uniaxially into a pellet of thickness 1-2 mm and of diameter 10 mm by applying pressure of 120 Mpa for 3 min. The pellets were sintered at 300 °C for 3 hrs to get the thermal stability. Fine quality silver paint was applied on both sides of the pellets for good electrical contacts. The DC electrical conductivity measurements were carried by two probe method using KEITHLEY source meter (Model-2400) in the temperature range 300K-650K.
The sample was sandwiched tightly between two steel rods in a sample holder with the help of screws and kept in a cell. A suitable constant and low voltage (5 Volts) was applied across the pellet and the corresponding current through the sample was measured. The circuit diagram for DC electrical conductivity measurement is as shown in fig. 3.A.3
The measurements were recorded during heating cycle. The electrical conductivity \( \sigma \) is calculated by the formula,

\[
\sigma = \frac{I}{V} t / A \quad \text{(3.1)}
\]

where \( V \) is the applied voltage, \( I \) is the measured current, \( A \) is the area of the pellet and \( t \) is thickness of the pellet.

The Arrhenius equation which relates the electrical conductivity and the temperature is given by,

\[
\sigma = \sigma_0 \exp \left\{ -\frac{E_a}{K_B T} \right\} \quad \text{(3.2)}
\]

where \( E_a \) is the activation energy, \( K_B \) is Boltzmann constant, and \( T \) is the temperature. The activation energy is calculated from Arrhenius plot.

3. A.3 Results and discussion

3. A.3.1 DC Electrical Conductivity of Fe doped ZnO

The DC electrical conductivity of \( \text{Zn}_{1-x}\text{Fe}_x\text{O} \) samples at room temperature is as shown in Fig. 3.A.3.1a and the values are recorded in Table 3.1.
It is observed that the conductivity decreases with increase of Fe concentration and it is high for undoped ZnO. It is well known that the electrical conductivity of ZnO samples at room temperature is due to intrinsic defects created by oxygen vacancies. These defects introduce donor states in the forbidden band slightly below the conduction band and hence resulting in the conducting behavior of ZnO. This electrical conductivity is controlled by the intrinsic defects generated during synthesis and by the presence of dopants. It is known that during combustion process at high temperature (more than 1000 °C) oxygen vacancies will be produced which are responsible for electrical conductivity. From the observed result of decrease in conductivity of ZnO on Fe doping, it seems that the Fe doping affects the defect chemistry of the ZnO [20]. Therefore, we may believe that Fe in ZnO acts as a deep donor and decreases the concentration of intrinsic donors. This reduction in intrinsic donor concentration increases with increase of Fe content, which intern decreases the electrical conductivity.

**Table 3.1. Experimental values of electrical conductivity, activation energy for different concentration of Fe.**

<table>
<thead>
<tr>
<th>x (%)</th>
<th>Room temperature electrical conductivity (X \times 10^{-7} \text{(ohm-cm)}^{-1})</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(E_{aL})</td>
</tr>
<tr>
<td>0</td>
<td>5.42</td>
<td>0.47</td>
</tr>
<tr>
<td>0.5</td>
<td>4.37</td>
<td>0.52</td>
</tr>
<tr>
<td>1</td>
<td>2.37</td>
<td>0.53</td>
</tr>
<tr>
<td>2</td>
<td>1.73</td>
<td>0.56</td>
</tr>
<tr>
<td>3</td>
<td>0.759</td>
<td>0.59</td>
</tr>
<tr>
<td>4</td>
<td>0.254</td>
<td>0.61</td>
</tr>
</tbody>
</table>
The variation of electrical conductance as a function of temperature for 
Zn_{1-x}Fe_xO is shown in Fig. 3.A.3.1b.

![Graph showing variation of electrical conductivity with temperature](image)

**Fig. 3.A.3.1b. Variation of electrical conductivity with temperature.**

It is found that conductivity increases with increase of temperature and
hence showing the semiconducting behavior of pure and Fe doped ZnO
samples. The graph of \( \ln \sigma \) verses \( 1000/T \) can be fit into Arrhenius plot. The
graph has two straight lines with different slopes representing two different
conduction mechanisms. In case of pure ZnO, conductivity raises slowly with
increase of temperature up to 400K, later drastic increase in conductivity has
been observed. But in case of Fe doped ZnO the conductivity variation is slow
up to 550K later it increases drastically.

The observed two-stage temperature dependence of conductance \( \sigma \) may
be represented as:

\[
\sigma = \sigma_L \exp \left\{ -\frac{E_{aL}}{K_B T} \right\} + \sigma_H \exp \left\{ -\frac{E_{aH}}{K_B T} \right\} \quad (3.3)
\]

In Equation (3.3), \( \sigma_L \) and \( \sigma_H \) are pre-exponential factors, \( E_{aL} \) and \( E_{aH} \) are the
activation energy for low and high temperature conductance stages.
respectively. Figures 3.A.3.1c and 3.A.3.1d show the Arrhenius plot of pure ZnO and Fe doped ZnO respectively and calculated activation energies are given in Table 3.1.

![Arrhenius plot of ZnO sample.](image1)

![Arrhenius plots Fe doped ZnO samples.](image2)
For pure ZnO the calculated values of $E_{al}$ and $E_{ah}$ are 0.47 eV and 0.97 eV respectively where as for Fe doped ZnO these values are 0.52 - 0.61 eV and 1.17 - 1.29 eV respectively and these values increase with increase of Fe concentration. The low temperature activation energy of ZnO samples is possibly associated with one of the following two donor ionization processes:

\[ V_0 \rightarrow V_0^+ + e^- \quad (3.4) \]

proposed by Simpson and Cordaro [21] for oxygen vacancy ($V_o$) or,

\[ Zn_i^+ \rightarrow Zn_i^{++} + e^- \quad (3.5) \]

proposed by Sukker and Tuller [22] for zinc interstitial ($Zn_i$) which forms a donor level 0.47 eV below the conduction band. In case of doped ZnO, one of these two forms a donor level 0.52 - 0.61 eV below the conduction band.

The high temperature activation energy can be associated with desorption of $O^{2-}$ species [23] according to the equation,

\[ O_2^- \rightarrow O_2 + e^- \quad (3.6) \]

The increase in activation energy of Fe doped ZnO can be explained as follows: When ZnO is substituted with Fe, which are in 3+ ion valence state, replaces the $Zn^{2+}$ ions and occupies zinc interstitial sites. The substituted Fe atoms cannot be easily ionized like Zn atoms because of their higher ionization potential (2 eV). Hence, the donor concentration is lowered by addition of Fe which results in the decrease of electrical conductivity. Thus, higher value of activation energy ($E_a$) is found for Fe doped ZnO samples and it increases with increase of Fe concentration ($x$).
3. A.3.2 DC Electrical Conductivity of Co:Fe co-doped ZnO

The DC electrical conductivity of Zn\(_{1-x-y}\)Fe\(_{x}\)Co\(_{y}\)O samples at room temperature is as shown in Fig. 3.A.3.2a. It is observed that the conductivity decreases with increase of Co concentration. The reason is same as in the previous discussion. Therefore, we may believe that Fe and Co in ZnO acts as deep donors and decreases the concentration of intrinsic donors at combustion temperature resulting in the decrease of electrical conductivity. This reduction in the intrinsic donor concentration increases with increase of Co content and hence results in the decrease of conductivity. The observed high conductivity in y=0 samples may also be attributed with secondary phase of Fe substituted ZnO.

Fig. 3.A.3.2a. Room temperature electrical conductivity variation of Zn\(_{1-x-y}\)Fe\(_{x}\)Co\(_{y}\)O

The variation of electrical conductivity with temperature is as shown in Fig. 3.A.3.2b. The increase of electrical conductivity with temperature shows the semiconducting behavior of Zn\(_{1-x-y}\)Fe\(_{x}\)Co\(_{y}\)O samples. This variation in conductivity can be fit in to Arrhenius plot (ln\(\sigma\) versus 1000/T). It has two
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slopes representing two different conduction mechanisms. The conductivity rises slowly with increase of temperature up to 500 K, later drastic increase in conductivity has been observed. The observed two-stage temperature dependence of conductance $\sigma$ may by equation 3.3.

**Table 3.2. Experimental values of electrical conductivity, activation energy for different concentration of Co ($y$).**

<table>
<thead>
<tr>
<th>$y$ (%)</th>
<th>Room temperature electrical conductivity $(X 10^{-8}$ (ohm-cm)$^{-1}$)</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E_{aL}$</td>
</tr>
<tr>
<td>0</td>
<td>1.81</td>
<td>0.61</td>
</tr>
<tr>
<td>0.005</td>
<td>1.60</td>
<td>0.62</td>
</tr>
<tr>
<td>0.010</td>
<td>0.99</td>
<td>0.64</td>
</tr>
<tr>
<td>0.020</td>
<td>0.5</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Fig. 3.A.3.2b. Variation of electrical conductivity variation with temperature in $\text{Zn}_{1-x-y}\text{Fe}_x\text{Co}_y\text{O}$
The Fig. 3.A.3.2c shows the Arrhenius plot and calculated activation energies are given in Table 3.2. $E_{aL}$ and $E_{aH}$ vary in between 0.61-0.67 eV and 1.29-1.36 eV respectively.

![Arrhenius plot](image)

**Fig. 3.A.3.2c. Arrhenius plot of Zn$_{1-x}$Fe$_x$Co$_y$O**

The low temperature activation energy of ZnO samples is possibly associated with one of the following two donor ionization processes proposed by Simpson and Cordaro [21] for oxygen vacancy (Vo) or proposed by Sukker and Tuller [22] for zinc interstitial (Zn$_i$) which forms a donor level 0.47 eV below the conduction band. In case of co-doped ZnO, one of these two forms a donor level 0.61-0.67 eV below the conduction band. The high temperature activation energy can be associated with desorption of O$_2^-$ species [23].

When ZnO is substituted with Fe$^{3+}$ and Co$^{2+}$, they replace the Zn$^{2+}$ atoms and occupy zinc interstitial sites and acts as deep donors. The substituted Fe and Co atoms cannot be easily ionized like Zn atoms because of their higher ionization potential. Hence, the donor concentration is lowered by addition of Fe and Co which results in the decrease of electrical conductivity. Thus, higher value of activation energy ($E_a$) is found for co-doped ZnO samples.
3. B.1 Introduction

Every material has a unique set of electrical characteristics that are dependent on its dielectric properties. Accurate measurements of these properties can provide scientists and engineers with valuable information to properly incorporate the material into its intended application for more solid designs or to monitor a manufacturing process for improved quality control. A dielectric materials measurement can provide critical design parameter information for many electronics applications. For example, the loss of a cable insulator, the impedance of a substrate, or the frequency of a dielectric resonator can be related to its dielectric properties. More recent applications in the area of industrial microwave processing of food, rubber, plastic and ceramics have also been found to benefit from knowledge of dielectric properties.

An understanding of the mechanism involved in the changes caused by the addition of substitutions is very important and this provides information for the preparation of metal oxides suitable for specific applications. Also metal oxides having very high dielectric constants are useful in designing good microwave devices such as isolators, circulators etc. The study of the effect of composition and frequency on the dielectric behavior and AC electrical conductivity offers much valuable information on the behavior of the localized electric charge carriers which can lead to a good explanation and understanding of the mechanism of electric conduction and dielectric polarization in these materials. During the recent years, various properties of ZnO have been...
investigated by researchers [24–25]. Oshio et al [24] have studied the role of 
Mn doping in ZnO to decide the increase/decrease of leakage current in its 
film. They have also studied the dielectric properties of the ZnO:Mn film and 
showed that the large resistivity is the bulk properties of the material. Hong et 
al [25] has studied the ZnO nanoparticles in a non-aqueous suspension to 
reduce the aggregation among nanoparticles and improve the compatibility 
between nanoparticles and the organic matter by grafting the poly (styrene). 
Han et al [26] have studied the low frequency dielectric properties and the 
transverse optical phonon mode in the single crystal of ZnO. Qi long et al [27] 
have observed by X-ray study that the sintering temperature of ZnO–Nb₂O₅– 
TiO₂–SnO₂ ceramics is lowered after addition of CuO–V₂O₅ due to the liquid 
phase effect of Cu₂V₂O₇ and Cu₃(VO₄)₂.

Yanhong et al [28] have studied the surface photo-voltage of ZnO 
(nanoparticles/nanorods). As a result of quantum confinement effect the photo-
voltage of ZnO nanoparticles are different for their different sizes and under the 
positive and negative electric field they have observed an asymmetry in photo-
voltage response for the ZnO nano rods. Hsu and Huang [29] have studied the 
dielectric constant of ZnO doped (Zr₀.₈Sn₀.₂) TiO₄ films, which decreases with 
increasing frequency. Youn et al [30] have also supported the results of Hsu et 
al. Jose and Khadar [31] have studied the conductivity mechanism of ZnO–Ag 
nano-composites. Though, various researchers have studied the electrical 
properties of ZnO, but a complete systematic study of various dielectric 
parameters in a wide frequency is still lacking. So in this work we have studied 
systematically the dielectric properties of doped ZnO synthesized by solution 
combustion method in the frequency range from 1 KHz to 5 MHz by 
impedance spectroscopy. It is to be mentioned that the impedance spectroscopy
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is one of the powerful tools for the characterization of electrical properties of ZnO. Studying dielectric data in the different functions allows different features of the materials to be recognized.

3. B. 1.1 Polarization in dielectrics

Jonscher has interpreted the mechanism of polarization in ceramic materials. Polarization is the process of alignment of permanent or induced atomic or molecular dipoles under the influence of an external electric field. Depending upon the type of dielectric material and the direction of application of electric field, the polarization mechanisms have been classified as,

(i) Electronic polarization ($P_e$): An electronic polarization occurs due to displacement of the center of gravity of electron cloud relative to the center of gravity of positively charged nucleus, under the influence of an external electric field. This phenomenon exists in all dielectric materials with an external applied field.

(ii) Ionic polarization ($P_i$): In an ionic polarization, the cations and anions get displaced from their mean positions in opposite directions within the crystal under the influence of an external electric field. This polarization is sensitive below infrared frequencies.

(iii) Orientational polarization ($P_o$): Orientational polarization is the characteristic of polar dielectrics, which arises due to alignment of permanent dipole moment along the applied field direction. This polarization is limited only up to microwave frequency range.

(v) Space charge polarization ($P_s$): Space charge polarization exists in heterogeneous material containing semi-conducting impurities where the charges migrate within the impurity regions and store at interphases are trapped at grain boundaries. There appears field distribution due to built up space
charges and this shows an increase in permittivity known as interfacial polarization. The process during which the migrational polarization sets in occurs in or decays can last for few seconds, minutes and even hours. This explains why this polarization occurs at very low frequencies.

![Diagram of polarization types](image)

**Fig.3.B.1. Total polarizability**

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The total polarization of the dielectric can be represented as

\[ P = P_e + P_i + P_0 + P_s \]

Where, the symbols have their usual meaning.

3. B. 2 Experimental

AC conductivity measurements as well as dielectric characterization of the prepared samples at room temperature were performed using a PSM 1735 (NumetriQ) Impedance Analyzer Interface (IAI, shown in fig. 3.B.2) with a Kelvin fixture over the frequency range 1 KHz to 5 MHz.

![NumetriQ Phase Impedance analyzer (Model PSM-1735)](image)

The parallel plate method, employed to determine the permittivity of the material, as shown in Fig. 3.B.3, involves sandwiching the samples (device under test or DUT), which are in the form of pellets (silver coated), configured in the Kelvin fixture to form a capacitor. The real \( (\varepsilon', called \text{ Dielectric constant}) \) and imaginary \( (\varepsilon'', called \text{ Dielectric loss}) \)
parts of the permittivity can be calculated from the capacitance ($C$) and \( \tan \delta \) (called dielectric loss factor), respectively.

![Diagram of parallel plate test fixture measurement method and equivalent circuit model of the parallel plate capacitor.]

**Fig 3.B.3** (a) Parallel plate test fixture measurement method; (b) Equivalent circuit model of the parallel plate capacitor.

Since the capacitor formed using the Kelvin fixture (Fig. 3.B.3(a) has a small capacitance due to its large impedance, the equivalent circuit of the capacitor is considered to comprise an equivalent parallel capacitance ($C$) and an equivalent parallel conductance ($G$), as shown in Fig. 3(b). The admittance ($Y$) and the complex admittance ($Y^*$) of the circuit in Fig. 3(b) can be expressed as:

\[
Y = j\omega C = j\omega |\varepsilon| C_0
\]

\[
Y^* = G + j\omega C = j\omega \left( \frac{C}{C_0} - j\frac{G}{\omega C_0} \right) C_0
\]

Where $C_0$ is the air capacitance (without DUT), and $\omega$ is the angular frequency.

Therefore, the complex relative permittivity can be defined as

\[
\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{3.7}
\]

and calculated by

\[
\varepsilon' = \frac{C}{C_0} = \frac{\varepsilon C}{\varepsilon_0 A} \tag{3.8}
\]
where $C$ is the capacitance, $t$ is the thickness and $A$ is the cross-sectional area of the DUT.

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\text{Energy stored per cycle}}{\text{Energy lost per cycle}}$$

The loss tangent or $\tan \delta$ is defined as the ratio of the imaginary part of the dielectric constant to the real part.

The AC electrical conductivity of samples was calculated using the relation

$$\sigma_{ac} = 2\pi f \varepsilon ' \varepsilon_0 \tan \delta$$

where $f$ is the frequency of the applied field.

Errors introduced by the Kelvin fixture include those due to edge capacitance on the edge of the electrodes (stray capacitance), residual parameters of the Kelvin fixture, such as electrical length, residual impedance, stray admittance, and air gaps caused when sandwiching the DUT between the electrodes. Errors due to the residual parameters of the test fixture were effectively minimized by performing “Open,” “Short,” and known “Load” calibrations on the DUT contact using various standard resistance test fixtures (SI No. 523 [32]) of 5Ω, 50Ω, 5KΩ, and 500KΩ [32]. Silver electrodes were used to minimize errors due to air gaps [33].

3. B.3 Results and discussion

3. B.3.1 Fe doped ZnO

(a) Frequency dependence of dielectric constant $\varepsilon'$

It is well known fact that the ZnO is a polar molecule, has permanent dipole moment and responds quickly to the applied electric AC field. Whereas, in case of Fe doped ZnO; hoping between $\text{Zn}^{2+}$ and $\text{Fe}^{3+}$ ions will give rise to
permanent electric dipoles. The frequency dependence of $\varepsilon'$ at room temperature is shown in the fig. 3.B.3.1a.

![Fig. 3.B.3.1a. Variation of dielectric constant ($\varepsilon'$) with frequency](image)

It is clear from the figure that $\varepsilon'$ value decreases with increase in frequency reaching a constant value at higher frequencies. The large values of dielectric constant at low frequencies are due to the predominance of the species of like oxygen vacancies, grain boundary defects etc. While the decrease in dielectric constant with frequency is natural because of the fact that any species contributing to polarisability is bound to show lagging behind the applied field at higher and higher frequencies. From the observed higher value of dielectric constant we can conclude that, the electron exchange between $\text{Zn}^{2+}$ and $\text{Fe}^{3+}$ ions is predominant at lower frequencies. At higher frequencies, the dielectric constant reaches a constant value due to the fact that beyond certain frequency the electron exchange between $\text{Zn}^{2+}$ and $\text{Fe}^{3+}$ cannot follow the applied alternating field.
(b) Frequency dependence of Dielectric loss and dielectric loss factor

The dielectric loss arises when the polarization lags behind the applied AC field and is caused by the impurities and imperfections in the crystal lattice. The frequency dependence of $\varepsilon''$ and $\tan\delta$ at room temperature is shown in the figures 3.B.3.1b to 3.B.3.1c.

![Figure 3.B.3.1b. Variation of dielectric loss ($\varepsilon''$) with frequency](image1)

![Figure 3.B.3.1c. Variation of dielectric loss factor ($\tan\delta$) with frequency](image2)
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It is observed that for each sample dielectric loss decreases substantially with increasing frequency and reaches a constant value. When the frequency of the applied AC electric field is much smaller than hopping frequency of electrons between Zn$^{2+}$ and Fe$^{3+}$, the electrons follow the field. Thus maximum value of $\varepsilon''$, and hence $\tan\delta$ is observed at low frequency. As frequency increases hopping probability per unit time is decreasing continuously. This is probably due to the fact that the deep donor Fe$^{2+}$ cannot follow the applied high frequency which in turn reduces hoping between Zn$^{2+}$ and Fe$^{3+}$ and thus at higher frequencies of the field, the loss is minimum.

(c) Compositional dependence of $\varepsilon'$, $\varepsilon''$ and $\tan\delta$

Figures 3.B.3.1d to 3.B.3.1f represent variation of $\varepsilon'$, $\varepsilon''$ and $\tan\delta$ with Fe concentration in ZnO. It is observed that, the $\varepsilon'$, $\varepsilon''$ and $\tan\delta$ decrease with increase of Fe concentration for all frequencies. It is known that in these types of semiconductors the mechanism of electric conduction is similar to that for dielectric polarization. At lower concentration of Fe, the hopping mechanism between Fe$^{3+}$ and Zn$^{2+}$ is predominant which results in higher value of $\varepsilon'$, $\varepsilon''$ and $\tan\delta$ values. As the concentration of Fe is increased, Fe in ZnO acts as a deep donor and decreases the concentration of intrinsic donors. It impedes the conduction mechanism and does not contribute in the conduction process but provides the impedance to it and hence reduction in the dielectric constants values. The density of a material also plays an important role in the variation of dielectric constant. High porosity and low density results in low dielectric constant and dielectric losses [34]. It is also clear from the observed SEM figures that, Fe doped samples exhibits high porosity and hence $\varepsilon'$, $\varepsilon''$ and $\tan\delta$ have lower values.
Fig. 3.B.3.1d. Variation of dielectric constant ($\varepsilon'$) with Fe concentration

Fig. 3.B.3.1e. Variation of dielectric loss ($\varepsilon''$) with Fe concentration
Fig. 3.3.1f. Variation of dielectric loss factor (\(\tan \delta\)) with Fe concentration

(d) Frequency and compositional dependence of AC electrical conductivity

The variation of AC electrical conductivity (\(\sigma_{ac}\)) with frequency at room temperature is shown in Fig.3.3.1g.
It can be seen that the AC electrical conductivity increases with increase of frequency. As frequency increases hopping between charge carriers increases which results increase in AC conductivity value of all samples. At any frequency, conductivity is found to decrease with increase of Fe concentration. The increase of concentration decreases the concentration of intrinsic donors. Thus hopping between Zn$^{2+}$ and Fe$^{3+}$ is not so ease at higher concentration of Fe. In other words Fe doping ceases hopping mechanism and hence resulted decrease in AC electrical conductivity with increase of Fe concentration.

3. B.3.2 Co:Fe co-doped ZnO

(a) Frequency dependence of dielectric constant

In Fe doped ZnO; hoping between Zn$^{2+}$ and Fe$^{3+}$ ions will give rise to permanent electric dipoles whereas in Co:Fe co-doped ZnO it is due to hopping between Co$^{2+}$, Fe$^{3+}$ with Zn$^{2+}$ host. The frequency dependence of $\varepsilon'$ at room temperature is shown in the fig. 3.B.3.2a.

![Graph showing variation of dielectric constant ($\varepsilon'$) with frequency](image)

**Fig. 3.B.3.2a. Variation of dielectric constant ($\varepsilon'$) with frequency**
It is clear from the figure that $\varepsilon'$ value decreases with increase in frequency reaching a constant value at higher frequencies. The large values of dielectric constant at lower frequencies are due to the predominance of the species of like oxygen vacancies, grain boundary defects etc. While the decrease in dielectric constant with frequency is natural because of the fact that any species contributing to polarisability is bound to show lagging behind the applied field at higher and higher frequencies. From the observed higher value of dielectric constant we can conclude that hopping is predominant at lower frequencies. At higher frequencies, the dielectric constant reaches a constant value due to the fact that beyond certain frequency the electron exchange between $\text{Co}^{2+}, \text{Fe}^{3+}$ with $\text{Zn}^{2+}$ cannot follow the applied alternating field.

(b) Frequency dependence of Dielectric loss and dielectric loss factor

The frequency dependence of $\varepsilon''$ and $\tan\delta$ at room temperature is shown in the figures 3.B.3.2b and 3.B.3.2c.

![Graph showing dielectric loss vs frequency](image)

3. B.3.2b. Variation of dielectric loss ($\varepsilon''$) with frequency
In each sample, dielectric loss is found to decrease considerably with increase of frequency and reaches a constant value. When the frequency of the applied AC electric field is much smaller than hopping frequency of electrons between \( \text{Zn}^{2+}, \text{Co}^{2+} \) and \( \text{Fe}^{3+} \), the electrons follow the field. Thus maximum value of \( \varepsilon'' \), and hence \( \tan\delta \) is observed at low frequency. As frequency increases hopping probability per unit time is decreasing continuously. This is probably due to the fact that the deep donors \( \text{Co}^{2+} \) and \( \text{Fe}^{3+} \) cannot follow the applied high frequency which in turn reduces hopping with \( \text{Zn}^{2+} \). Thus at higher frequencies of the field, the loss is minimum.

![Graph showing variation of dielectric loss factor (tan δ) with frequency](image)

3. B.3.2c. Variation of dielectric loss factor (tan δ) with frequency

(c) Compositional dependence of \( \varepsilon' \), \( \varepsilon'' \) and \( \tan\delta \)

Figures 3.B.3.2d-f show variation of \( \varepsilon' \), \( \varepsilon'' \) and \( \tan\delta \) with Co concentration in Fe: ZnO. It is observed that at a particular frequency, \( \varepsilon' \), \( \varepsilon'' \) and \( \tan\delta \) values decrease with increase of Co concentration. The hopping mechanism between in \( \text{Fe}^{3+} \) and \( \text{Zn}^{2+} \) is predominant which results in higher value of \( \varepsilon' \) and hence \( \varepsilon'' \) and \( \tan\delta \) values.
Fig. 3.B.3.2d. Variation of dielectric constant ($\varepsilon'$) with Co concentration

3. B.3.2e Variation of dielectric loss ($\varepsilon''$) with Co concentration
3. B.3.2f. Variation of dielectric loss factor (tan δ) with Co concentration

As the concentration of Co is increased the values are found to decrease predominantly. This is because of the fact that the substituted Co in Fe: ZnO acts as a deep donor and decreases the concentration of intrinsic donors. It hinders the conduction mechanism and does not contribute in the conduction process but provides the impedance to it. This leads to decrease in dielectric constants values.

(d) Frequency and compositional dependence of AC electrical conductivity (σ_ac)

The variation of AC electrical conductivity with frequency at room temperature is shown in Figs.3.B.3.2g. It can be seen that the AC electrical conductivity increases with increase of frequency. As frequency increase, hopping between charge carriers increases, which resulted increase in σ_ac value of all samples. At any frequency, conductivity is found to decrease with increase of Co concentration. The increase of Co concentration decreases the concentration of intrinsic donors which resulted decrease in σ_ac.
3. B.3.1g. Variation of AC electrical conductivity with frequency

On comparison, the Co:Fe co-doped ZnO samples exhibit lower values of $\varepsilon'$, $\varepsilon''$, $\tan\delta$ and $\sigma_{ac}$ than that of Fe doped ZnO. Also in the case of Co:Fe co-doped samples, a drastic decrease in the values of $\varepsilon'$, $\varepsilon''$ and $\tan\delta$ is observed from the frequency 1 KHz to 10 KHz. Above 10 KHz these values do not vary with frequency. But in case of Fe:ZnO, the $\varepsilon'$, $\varepsilon''$ and $\tan\delta$ value varies drastically with frequency from 1K Hz to 1MHz and constancy occurs above the frequency of 1MHz. From these observations it seems that the substituted Co affects the dielectric behavior of Fe doped ZnO. The added Co cannot follow the applied higher frequency as like Fe and also it further reduces the hopping between $\text{Fe}^{3+}$ and $\text{Zn}^{2+}$. This reduction in hopping increases with increase of Co content. Thus, Co:Fe doped ZnO samples exhibit lower values of $\varepsilon'$, $\varepsilon''$, $\tan\delta$ and $\sigma_{ac}$. It is an interesting observation and it need further investigations to know the exact mechanism in Co:Fe co-doped ZnO samples.
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