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# Spectroscopic Study of the Impedance of Biosynthesized Zinc Oxide Nanoparticles

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## ABSTRACT

Zinc Oxide nanorods (ZnO NRs) were bio-synthesized by co-precipitation and bacterial inoculation. Fourier Transform Infra-Red (FTIR) spectroscopy analysis was carried out to identify the elemental constituents of the ZnONRs, the composition of which were analyzed using Energy Dispersive Spectroscopy (EDX). Its structural and morphological properties were studied using X-ray Powder Diffractometer (XRD) pattern and Scanning Electron Microscopy (SEM) images respectively. Impedance Spectroscopy studies were carried out on the ZnONRs for frequency domain responses (10 Hz – 13MHz), impedance related functions, admittance, Immittance and modulus functions. From the results obtained, the dielectric constant, ε/ of the biosynthesized ZnONRs is very high (750), it decreases with increasing frequency and then reaches a constant value. The dielectric loss Ɛ// also decreases with increasing frequency. The dielectric loss angle, σ for the sample decreases continuously with increase in frequency. Finally, it was observed that the resistance and capacitance values depend on temperature and frequency.

**Keywords**: *Nanorods, FTIR, XRD, EDX, Dielectric constant, Dielectric loss, Dielectric loss angle*

## INTRODUCTION

Impedance Spectroscopy (IS) is becoming a popular analytical tool in materials research and development because it involves a relatively simple electrical measurement that can readily be automated and whose results may often be correlated with many complex materials variables: from mass transport, rates of chemical reactions, corrosion, and dielectric properties, to defects, microstructure, and compositional influences on the conductance of solids. IS can predict electrons behavior of the performance of chemical sensors and fuel cells, and it has been used extensively to investigate membrane behavior in living cells. It is useful as an empirical quality control procedure, yet it can contribute to the interpretation of fundamental electrochemical and electronic processes. (Evgenij and Macdonald, 2005)

A lot of factors contribute to the experimental value of dielectric constant of a sample. These include method of synthesis, macroscopic quantities – bulk resistance, capacitance, dielectric effect and a few microscopic quantities such as ion/charge effect - homogeneous reactions associated with dissociation and recombination of charges present, electronic effects usually at high frequency range while different polarization, interfacial, atomic, ionic etc usually occur at low frequency range. ZnO is one of the most promising materials for electrical devices, including transparent conductive films, light emitting diodes and photocatalyst, flat panel displays, photodetectors, gas sensors and solar cells. (Latif, 2012, Amrut, et al. 2013)

Although extensive work has been done on doped or hybrid ZnO NRs, much work has not been done on dielectric performance of bio-synthesized ZnO NRs. Moreover, synthesis method could have significant effect on dielectric performances of ZnO NRs. Hence, this work presents impedance spectroscopic (IS) studies on biosynthesized ZnO NRs considering its responses in frequency domain, impedance related functions, admittance, immittances and modulus functions.

## EXPERIMENTAL

Zinc acetate dihydrate, sodium hydroxide, were purchased from HiMedia Laboratories Private Limited, 23 Vadhani Industrial Estate, LBS Rd, Mumbai, India. All other reagents are of analytical purity grade and have been received from commercial sources. ZnO nanostructures were prepared by co-precipitation method. 0.02 M aqueous solution of zinc acetate dihydrate was put into 50 ml of distilled water under vigorous stirring. After 10 min stirring, 1.0 ml of Bacterial Inoculum (prepared from Bacto Yeast Nitrogen Base and glucose in demineralized water by a method of broth culture until turbid) was added into the above solution. After addition of Inoculum, 2.0 M NaOH aqueous solution was introduced into the above aqueous solution, resulting in a white aqueous solution at pH 12, which were then placed on magnetic stirrer for stirring for 2 hr. The precipitate was then taken out and washed repeatedly with distilled water followed by ethanol to remove the impurities for the final products. Then a white powder (of ZnONRs) was obtained after drying at a constant 60 0C overnight in a Mophorn Vacuum Drying Oven 0.9 Cu Ft.

The elemental composition of the ZnO NRs was analyzed using Energy Dispersive Spectroscopy (EDX) - BRUKER-X Flash 6130, and Fourier Transform Infra-Red (FTIR) spectroscopy - by SHIMADZU - IR TRACER 100 using KBr pellet method at room temperature through the wave range 400 - 4000 cm-1. The structural properties were characterized using X-Ray Diffraction (XRD) machine - D8 advance ECO XRD systems with SSD160 1D Detector, with Cu-Kα1 and Kα2 radiation of wavelength 1.5406 and 1.54438Å. The Scanning electron microscope (SEM) - ZEISS-EVO 18 Research was used to investigate the surface morphology of the samples while the optical properties of the samples were studied using VISIONlite 061408 UV – VIS (1600 series) spectrophotometer. For dielectric studies, ZnO NRs powdered sample was compressed into pellets of 13.01 mm diameter and 0.082 mm thickness by using a very high pressure (5 Ton). The pelletized ZnO NRs was characterized by an alternating current (AC) Impedance Spectroscopy (HIOKI 3532 – 50 LRCHiTESTER model) measurements were obtained in the 40 Hz to 10 MHz frequency range, a constant voltage (1.0V) and different temperatures 100 - 155 °C.

## RESULTS AND DISCUSSION

### Energy Dispersive X-ray Spectroscopy

Energy dispersive X-ray spectroscopy (EDX) was used for the elemental analysis of the sample. The EDX spectrum in fig.1revealed that only zinc (Zn), and oxygen (O) signals were detected and no other signal of secondary phase or impurity was detected. This implies the high purity chemical composition of the ZnO NRs

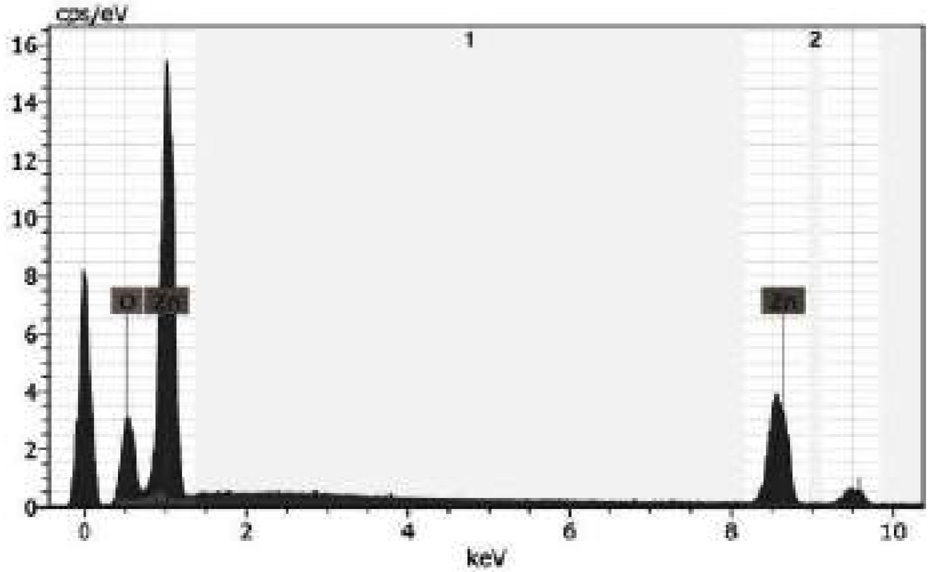

**Fig. 1** EDX spectrum of Bio-synthesized ZnO nanoparticles

### Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR measurement was carried out using KBr pellet method at room temperature through the wave range 400 - 4000 cm-1 as shown in Fig. 2. This was done to identify the possible biomolecules responsible for capping and stabilization of the bio-synthesized zinc oxide nanoparticles. It is also to indicate the reduction of metal (zinc) ions by the used bacteria. The spectral peaks observed are 871.82 cm$^{-1}$, 987.55 cm$^{-1}$, 1097.50 cm$^{-1}$, 1529.55 cm-**1**, 1550.77 cm$^{-1}$, 2358.94 cm$^{-1}$, 2881.66 cm$^{-1}$, 3664.75 cm-$^{1}$, 3701.40 cm$^{-1}$ and 3726.47 cm$^{-1}$. The stretch for ZnO nanoparticles was at 871 cm$^{-1}$ which was found to be around 860 - 900 cm$^{-1}$ aromatic ring -1,3- distribution of metal. (Coates, 2000, David, 2011). The peak around 925 – 1005cm$^{-1}$ gives C-C vibration from methyne, The peaks around 1050 – 1260cm$^{-1}$leads to C-O stretching alcohols, carboxylic acids, esters, ethers. Here the C-O stretching alcohols, carboxylic acids, esters, ethers show the peak at 1097.5 cm$^{-1}$. The peaks between 1485-1555cm$^{-1}$leads to -C=N- stretch and –NH bend of aromatics nitro compounds. Here, the -C=N- stretch and –NH bend primary amines show peaks at 1529.55 and 1550.77 cm$^{-1}$. The peak at 2358.94 cm$^{-1}$ indicates aromatic combination bands of methyl group $-CH_3$ and aliphatic nitrile of =C=O. (David, 2011). The peak 2881.66 indicates Sp$^3$ C-H stretching vibration from aldehydes.

The peaks observed around 3000 - 3700 are at 3664.75, 3701.40 and 3726.47 cm$^{-1}$ leading -OH and -NH stretching for primary, secondary amines, amides. Hence, the FTIR analysis of the bio-synthesized ZnO nanorods confirmed the participation of biological molecules in bio-reduction reactions, formation, capping and stabilization of ZnO nanoparticles.

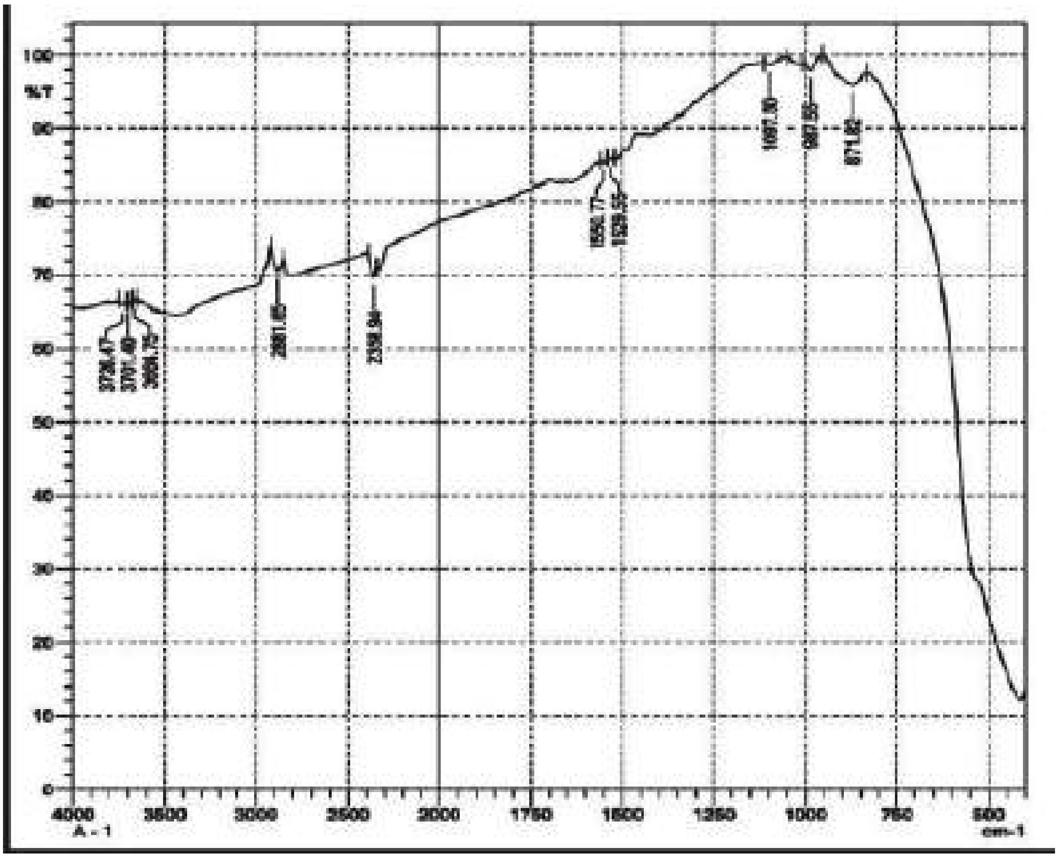

**Fig 2.** FTIR spectra of ZnO nanoparticles synthesized by biological method

**X-Ray Diffraction Analysis**

Fig.3 shows the X-ray Diffraction (XRD) pattern of the bio-synthesized ZnO nanorods. The ZnO NRs diffraction peaks shows highly oriented and crystalline structure of zinc oxide nanorods. The sharp and narrow diffraction peak positions with 2θ values of 31.84, 34.50, 36.34, 47.65, 56.73, 63.02, 66.54, 68.12, 69.26, 72.76, 77.16, 81.61, 89.87 were indexed as (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202), (104) and (203) hkl crystal planes. The peak intensity profiles were in good agreement with those of powder ZnO obtained from the International Center of Diffraction Data card (JCPDS) card No. 75-0576 (from ICDD 12 Campus Boulevard Newtown Square, PA. 19073-3273). This confirmed the formation of a crystalline hexagonal wurtzite structure of the ZnO NRs. It is also observed that there is no extra diffraction peaks of other phases, which implies its phase purity. The average grain size of the synthesized ZnO NRs was calculated to be 6.67 nm by using Debye-Scherrer's Eq. (1).

$$D = \frac{K\lambda}{\beta Cos\theta} Å \text{ ---------------------- } (1)$$

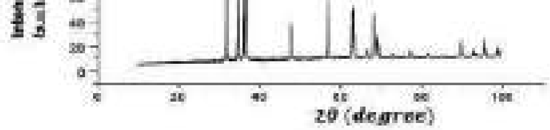

Fig. 3: The XRD Spectral of Bio ZnO NRs

Fig. 4: The SEM Micrograph Image of Bio ZnO NRs

**Frequency Domain Responses**

**The applied ac voltage signal is given by**

$$V(t) = V_0 e^{i\omega t} \qquad (1)$$

for a single frequency $f = {}^{\omega}/_{2\pi}$ . The resulting steady state current in the electrical network is given by

$$I(t) = I_0 e^{(i\omega t + \emptyset)} \qquad (2)$$

Where $\omega = 2\pi f$ and $\emptyset$ is the phase angle – phase difference between the applied voltage and the current. The implication of this is that for a purely resistive substance, $\emptyset = 0$ that is $Z(\omega) = Z'(\omega)$. In such case, the impedance is completely independent of frequency. In this IS study, our ZnO NPs proved not completely resistive over a range of frequency as shown by its Cole-Cole plot in Fig.5.

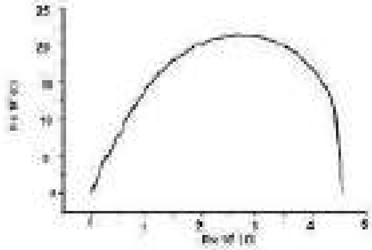

Fig.5. The Cole-Cole plot of bio-synthesized ZnO NPs

This is in support of Kronig-Kramer's relation which connects the real and imaginary parts, ensuring that $Z''$ and θ cannot be zero over all frequencies (Barsoukov and Macdonald, 2005). The frequency dependent spectroscopic plots of our biosynthesized ZnO NPs are shown in **Fig.6**

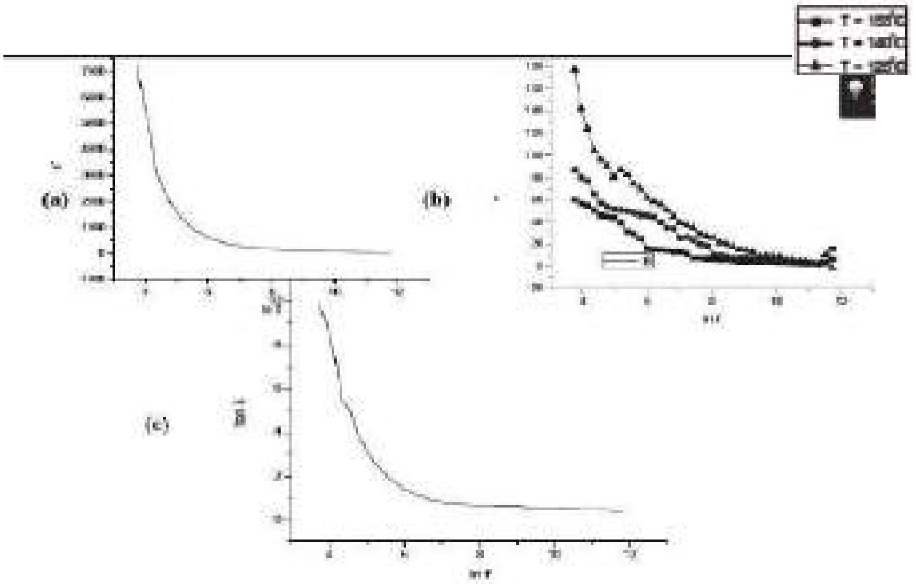

Fig. 6 (a) A plot of $Z'$ against ln f (b) A plot of $Z''$ at different temperatures against ln f and (c) A plot of tan δ against ln f

From fig. 6 (a), it is observed that dielectric constant ($Z^{\prime}$) decreases with increase in frequency (f). The decrease in the value of dielectric constant on increasing frequency may be attributed to a combined contribution due to electronic, ionic, and interfacial polarization. The large value of the dielectric constant $\varepsilon^{\prime}$ obtained at lower frequencies is caused by the oxygen vacancies, and grain boundary defects. The observed dielectric dispersion at low frequencies can be explained on the basis of the Maxwell-Wagner theory of interfacial polarization (Muhammad et al, 2010, Geethalakshmi et al, 2014).When frequency increases, polarization decreases until it disappears except ionic and electronic polarization, which makes dielectric constant decrease rapidly. (Baljinder, et al. 2016)

The dielectric loss ($Z^{\prime\prime}$) decreases as frequency increases. When frequency increases, the increase in hopping electrons results in local displacement in the direction of the extent electric field. This leads to an increase in electric polarization and therefore aids dielectric loss. (Hassouna et al. 2012, Aparna, et al. 2016)

The behaviour of tangent of dielectric loss angle (Tan $\delta$) as a function of frequency for ZnO NRs is shown in fig. 6(c). For this sample, Tan $\delta$ is also observed to be decreasing with increasing frequency. This occurred when the jumping rate of charge carriers lags behind the alternating electric field beyond a certain critical frequency. At low frequencies, more energy is required for electron transfer or ion exchange, while small energy is required at high frequency for ion exchange. Low dielectric losses are desirable being the energy dissipation in the dielectric system. (Muhammad, et al. 2009)

## A.C. Conductivity and Time Domain Responses

In the time domain, the relationship between the properties of the material sample and response to alternating voltage $v(t)$ or current $i(t)$ is complex. Evgenij and Macdonald (2005) established that response of capacitive element is

$i(t) = \left(\frac{dv(t)}{dt}\right)C$ (where C is the capacitance of the material sample) (3)

That of inductive element is

$v(t) = \left(\frac{di(t)}{dt}\right)L$ (where L is the inductance of the material sample) (4)

The equations transform into

$$I(j\omega) = C.\omega.j.v(j\omega)$$

$$I(j\omega) = -\frac{v(j\omega)}{L.\omega.j} \quad (\text{j} = \mathit{square\ root}\ (\text{-}))$$

$$\text{Thus,}\ \ v(j\omega) = V_m\pi$$

$$I(j\omega) = I_m\pi.\exp(\theta j)$$

This is a form of Ohm's law

$$I(j\omega) = -\frac{V(j\omega)}{Z\,(j\omega)}$$

For capacitance,

$$Z(j\omega) = -\frac{1}{(c.\omega.j)} \qquad (5)$$

For inductance,

$$Z(j\omega) = L.\omega.j \qquad (6)$$

The complex quantity $Z(j\omega)$ is the impedance function. From Fourier Transform,

$$Z(j\omega) = -\frac{F[V(t)]}{F[i(t)]}$$

Thus the complex number, $Z = a + jb$

$j \equiv \sqrt{-} \equiv \exp\left[\frac{j\pi}{2}\right]$

The impedance vector is $Z(\omega) = Z' + Z''$

The relaxation time also called time constant, τ, of a 'parallel *RC* element' is given by

$$\tau = RC$$

At maximum frequency,

$$\omega_{max}RC = 1$$

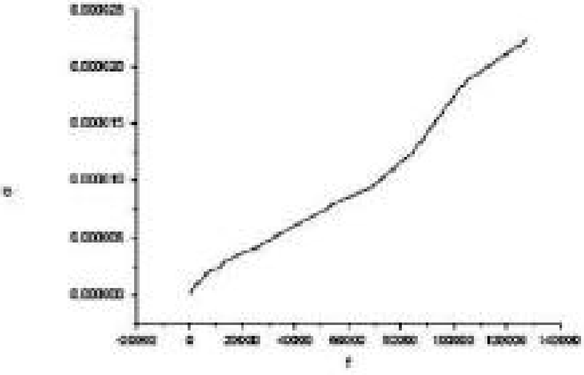

Fig 7 A plot of electrical conductivity against frequency

The Cole–Cole plot shown in fig.5 confirms the distribution of relaxation time. Also, the periodic conductivity σ in our ZnONRs is observed to increase with increasing frequency. The relaxation is equally observed in the whole frequency range as a gradual increase in conductivity with increasing frequency as shown in fig. 7. This is supported by the report of Tripathi, et al. 2009 and Ziaul, et al. 2011.

## Impedance Domain

Impedance is defined as a complex quantity which is only real at $\theta = 0$ and therefore, $Z(\omega) = Z'(\omega)$ for a purely resistive behavior.

$$Z(\omega) = |Z|\exp(-i\emptyset)$$

$$Z(\omega) = |Z|cos\emptyset - i|Z|sin\emptyset$$

$$Z(\omega) = z^{/}(\omega) - iZ^{//}(\omega)$$

$Z'$ is the real while $Z''$ is the imaginary part of the complex impedance. It is only when $Z(\omega) = z^{/}(\omega)$ that $Z' = R$ which is an ordinary linear resistance, that $Z(\omega)$ is purely real. Here, the relaxation time is given by $\tau = RC$ Where at maximum frequency of loss, $\omega_{max}\,RC = 1$

These impedance responses help to give information on the nature of the conducting species, within the sample itself and whether conduction is by ions or electrons. (John, *et al.* 2009).The spectroscopic plots of some impedance responses of the ZnO NRs are shown in **Fig.4**

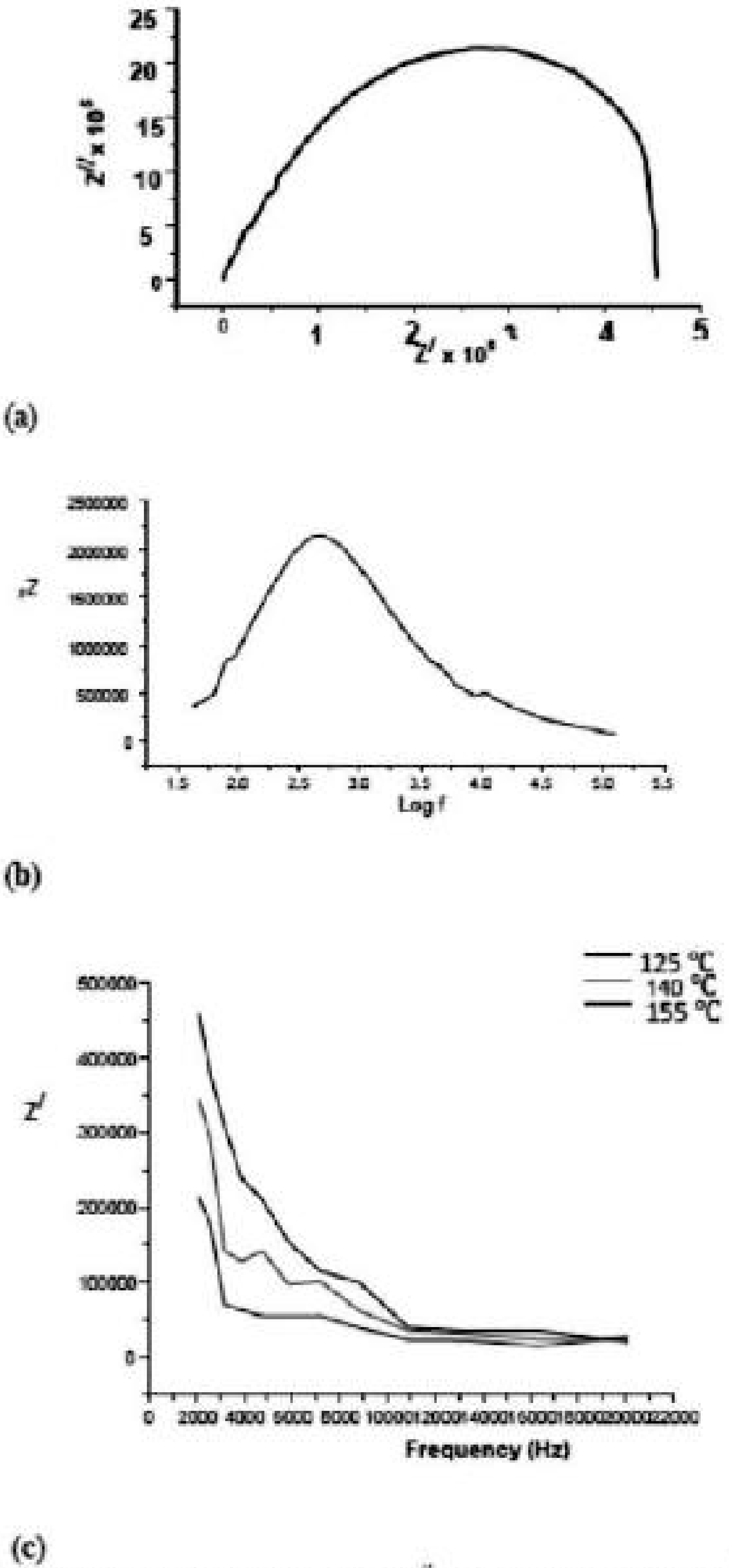

Fig.8 (a) Imaginary impedance $Z''$ versus real impedance $Z'$ (b) Imaginary impedance $Z''$ versus log f (c) Variation of real part of impedance of ZnONRs with frequency at different temperatures.

From fig. 8 (a) the imaginary Impedance, $Z^{//}$ plotted against real $Z^{/}$ shows a semicircle from which the resistance R and capacitance C values may be obtained. The intercepts on the $Z^{/}$ axis give the value of R, while the value of C can be calculated by applying equation $\omega_{max} RC = 1$ to the frequency at the peak of the semicircle. In this sample – ZnO NRs, the value of the resistance is 4.125 (MΩ) as shown in the characteristic graph Fig. 5. The capacitance value is calculated to be 7.79 x $10^{-11}$ or 0.78 $p^{F}$. This value is for the bulk capacitance of a sample. Hence, this may be interpreted in terms of the bulk response of the sample and a single parallel R*C* element. There is no 'electrode spike' in the curve at low frequency. Therefore, there was no impedance barrier to charge transfer between the metal electrode and the sample, so the conducting species were electrons. (John, et al. 1990; Ziaul, et al. 2011)

The variation of the real part of impedance Z with frequency at different temperatures is shown in **fig. 8 (c).** The curves show that $Z^{/}$ becomes independent' value of about 50,000 (add units). In particular, at 155o, $Z^{/}$ decreased most rapidly from 200,000 to 50,000 (add units) between corresponding frequencies of about 2000 Hz to 3000 Hz (Tripathi, et al. 2009, Baljinder, et al. 2016).

## CONCLUSION

In this study, zinc oxide nanoparticles have been successfully synthesized by co-precipitation and bacterial inoculation. The crystallite size of the ZnO NRs was calculated to be 6.7 nm by using Debye-Scherrer's formula. The SEM and XRD spectrum confirmed the formation of a crystalline hexagonal wurtzite structure of the ZnO NPs while the EDX spectrum revealed its purity. It is observed that dielectric constant ($Z^{/}$) decreases with increase in frequency (f), indicating its enhancement by polarization due to oxygen vacancy. Dielectric loss ($Z^{//}$) reduced drastically in this sample which makes it desirable for applications as inductive and capacitive materials as well as microwave absorbers. The alternating current (a.c.) conductivity (σ) increases with increase in frequency as well as increase in temperature. This shows that hopping electrons are responsible for electronic polarization in the biosynthesized ZnO NPs. The relaxation is observed as an increase in conductivity as frequency increases within the whole range of frequency.

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## REFERENCES

Amrut S. Lanje, Satish J. Sharma, Raghumani S. Ningthoujam, Ramchandra B. Pode (2013): "Low temperature dielectric studies of zinc oxide (ZnO) nanoparticles prepared by precipitation method" Advanced Powder Technology 24(1):331–335

Aparna, P. U. Divya N. K., Pradyumnan P. P. (2016): "Structural and Dielectric Studies of Gd Doped ZnO Nanocrystals at Room Temperature". Journal of Materials Science and Chemical Engineering, 4, 79-88

Baljinder Kaur, Lakhbir Singh, V. Annapu Reddy , Dae-Yong Jeong, Navneet Dabra, Jasbir S. Hundal (2016): "AC Impedance Spectroscopy, Conductivity and Optical Studies of Sr doped Bismuth Ferrite Nanocomposites". Int. J. Electrochem. Sci., 11 4120 – 4135

Coates J. (2000): "Interpretation of Infrared Spectral, A practical approach in Encyclopedia of JABU Journal of Science and Technology (2019, Vol 4:4) Analytical Chemistry" – R.A. Meyers (Ed) O John Wiley and Sons Ltd., pp 10815-10837.

Cullity, B.D. (1978): "The Elements of X-Ray Diffraction". Addison-Wesley, p.102.

David Cameron (2011): "Baltic Sea Region programme" Advanced Surface technology Research Laboratory (ASTRaL) University of

Lappeenranta Finland

Evgenij Barsoukov, J. Ross Macdonald (2005): "Impedance Spectroscopy: Theory, Experiment, and Applications" 2nd Edition, John Wiley & Sons, Inc.:Hoboken, NJ. ISBN 0471-64749-7.

Geethalakshmi, K., Prabhakaran T. and Hemalatha J. (2012): "Dielectric Studies on Nano Zirconium Dioxide Synthesized through Co-Precipitation Process". Materials and Metallurgical Engineering Vol:6, No:4, 2012

Hassouna Dhaouadi, Ouassim Ghodbane, Faouzi Hosni, and Fathi Touati (2012): "Mn3O4 Nanoparticles: Synthesis, Characterization, and Dielectric Properties." HINDAWI.ISRN Spectroscopy Volume 2012, Article ID 706398, 8 pages

John T. Irvine S., Derek C. Sinclair, and Anthony R. (2009): "West Electroceramics: Characterization by Impedance Spectroscopy" P RAMANA © Indian Academy of Sciences journal physics. Vol. 72, No. 6 pp. 969–978

Lanje A. S. , Sharma S. J., Pode, R. B. and Ningthoujam R. S. (2010): "Dielectric study of Tin oxide nanoparticles at low temperature". Applied Science Research, 2010, 2 (2): 127-135

Latif I., Entisar E. AL-Abodi, Dhefaf H. Badri, Jawad Al Khafagi (2012): "Preparation, Characterization and Electrical Study of (Carboxymethylated Polyvinyl Alcohol/ZnO) Nanocomposites" American Journal of Polymer Science 2(6): 135-140

Muhammad Naeem Ashiqa, Muhammad Javed Iqbalb, Iftikhar Hussain Gulc (2010): "Structural, magnetic and dielectric properties of Zr–Cd substituted strontium hexaferrite (SrFe12O19) nanoparticles" Journal of Alloys and Compounds. Vol. 487, pp 341-345.

Tripathi R. A Kumar, and Sinha T P (2009): "Dielectric properties of CdS nanoparticles synthesized by soft chemical route". PRAMANA °c Indian Academy of Sciences Vol. 72, No. 6

Ziaul Raza Khan, M. Zulfequar, Mohd. Shahid Khan (2011): Chemical synthesis of CdS nanoparticles and their optical and dielectric studies. J Mater Sci 46:5412–5416