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RESEARCH ARTICLE

STRUCTURAL AND FREQUENCY DEPENDENT DIELECTRIC PROPERTIES OF ZnO NANOPARTICLES AND PANI / ZnO NANOCOMPOSITE BY MICROWAVE-ASSISTED SOLUTION METHOD.

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Abstract

Zinc Oxide nanoparticles were synthesized by microwave assisted hydrothermal method using Zinc Nitrate Hexahydrate ($\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$) as a starting material. Polyaniline / Zinc Oxide (PANI/ZnO) nanocomposite material was prepared by an in-situ polymerization of aniline in the presence of as-synthesized ZnO nanoparticles. The structure, morphology and functional group of the synthesized Zinc Oxide nanoparticles and PANI / ZnO nanocomposites were characterized by X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The sharp peaks in the X-ray diffraction pattern indicate that the obtained powder was ZnO and was crystalline in nature. The crystallite size of the sample were calculated from the full width at half maximum of X-Ray diffraction peaks by using Debye-Scherrer formula and were found to be 45nm. The absorption peaks in FTIR spectra of PANI / ZnO nanocomposites were slightly shifted to higher wave number than that of pure ZnO, which confirms that there was a strong interaction between polyaniline and Zinc Oxide nanoparticles. The TEM images revealed the uniform distribution of the ZnO nanoparticles in the PANI matrix. Dielectric studies of ZnO nanoparticles show the frequency dependent dielectric behaviour of ZnO nanoparticles. Results reveals that the dielectric constant decrease with the increasing frequency whereas the a.c conductivity of the sample increases with the increase in frequency.

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Introduction:-

ZnO is a semiconducting oxide material having wide band gap of 3.37eV at room temperature, which exhibits excellent optical and electrical properties. Due to its physical & chemical properties, zinc oxide is used in various applications such as photo catalysis, UV protection, solar cell and gas sensor applications. It has been widely used for its catalytic, electrical, optoelectronic and photochemical properties [1-4]. So many techniques are available for the synthesis of ZnO nanoparticles, namely, hydrothermal synthesis [5], physical vapour deposition [6], electrochemical deposition [7], chemical vapour deposition [8], pulsed laser deposition [9], microwave assisted

synthesis [10] and thermal evaporation [11]. Since, microwave assisted synthesis is a rapid technique and also cost effective compared to other methods, this method is chosen for producing ZnO nanoparticles. Zinc oxide (ZnO) is a common material that is readily used in semiconductor fabrication especially in solar cells and gas sensors due to its special properties. Zinc oxide, a versatile semiconductor material has been attracting attention because of the commercial demand for optoelectronic devices operating at blue and ultraviolet regions [12].

Experimental:-

Materials and Characterization Techniques:-

All the chemicals involved in this microwave assisted method were used as received from the chemical suppliers without any further purification and processing. Aniline (99.5%), Zinc Nitrate Hexahydrate ($\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$), Sodium Hydroxide (NaOH) and Ethylene Glycol were procured from E. Merck and Ammonium persulfate (98%) was purchased from Hi-media and used as received. All the chemicals were of analytical grade and solutions were prepared with double distilled water. Aniline monomer was distilled using cubic condenser for purification.

The prepared ZnO nanoparticles were characterized by X-Ray Diffraction technique (XRD) and Scanning Electron Microscope (SEM) to find the structure and morphology. Crystallographic studies were carried out using a X-Ray diffractometer (Bruker D8 with Nickel filtered Cu - $\text{K}\alpha$ radiation), in the scanning range of 2θ from 10° - 80° using Cu - $\text{K}\alpha$ radiations of wavelength 1.5406\AA . SEM images of the sample were recorded using the model HITACHI SEM, to study the morphology of the samples and their elemental analysis. HRTEM micrographs of the prepared samples were taken using the Model JEOL - J2000. FT-IR spectra of the sample were recorded in the range of $400 - 4000\text{cm}^{-1}$ using Shimadzu 8400S FT-IR Spectrometer.

Synthesis of ZnO Nanoparticles – Microwave Assisted synthesis:-

Zinc Nitrate Hexahydrate ($\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$) and Sodium hydroxide (NaOH) were taken in 1:4 molar ratio and dissolved completely in de-ionized water separately. Then the dissolved $\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$ was added with Ethylene Glycol. Further, NaOH solution was added drop wise into the above mixture under vigorous stirring. Then the prepared mixture solution was kept in the microwave oven (900 W, 2450 MHz) for about 30 minutes. Finally, the as-prepared sample was centrifuged several times in double distilled water, ethanol and dried at 150°C for 24 hours, resulting in the formation of ZnO nanoparticles.

Synthesis of PANI / ZnO Nanocomposites:-

To prepare Polyaniline / ZnO nanocomposite, Aniline was injected into 2M HCL containing different wt% of ZnO nanoparticles under ultrasonic action to reduce the aggregation of ZnO nanoparticles. After 12hrs, Ammonium Peroxydisulphate as an oxidant (APS), was dropped into the solution with constant stirring for 10 min. The polymerization was allowed to proceed for 3hrs at 30°C . Reaction mixture was filtered and washed with 2M HCL and de-ionized water and then dried at 90°C for 12hrs in vacuum. PANI / ZnO nanocomposite with fine tint green colour was obtained.

Results and Discussion:-

X-ray Diffraction technique (XRD):-

The XRD pattern of pure ZnO nanoparticles is shown in Figure 1a. The XRD result shows that the sharp and the well-defined diffraction peaks formed at 33° and 58.7° confirms the formation of ZnO nanoparticles and also indicate the good crystallinity of synthesized material. The characteristics peaks of ZnO formed at 33° , 45.6° , 58.7° , 69° and 73° corresponds to the miller indices (0 0 2), (1 0 2), (1 1 0), (2 0 1) and (0 0 4) respectively, which can be indexed with hexagonal phase (JCPDS Card No. 80-0075) [13]. The crystalline size of ZnO nanoparticles was calculated using the value of FWHM from the most intense XRD peaks as around 45nm by using Scherrer formula (1) [14].

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (\text{nm}) \quad \dots\dots\dots (1)$$

where D is the crystallite size, K is the shape factor (0.94), λ is the wavelength of X-rays ($\lambda = 1.54059\text{\AA}$), β is the full width at half maximum (FWHM) of the diffraction peaks and θ is the angle of diffraction. The XRD pattern of PANI / ZnO nanocomposite (Figure 2a) has a peak at $2\theta = 25^\circ$ belongs to PANI, representing the amorphous structure with low crystallinity. The XRD patterns of PANI/ZnO nanocomposite include the characteristic peaks of

both PANI and ZnO with the crystalline structure of hexagonal wurtzite, which confirms the formation of nanocomposite with lower crystallinity [15, 16a, b, c].

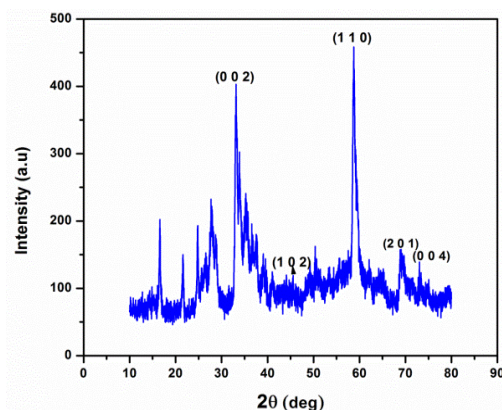


Figure 1a:- XRD pattern of ZnO NPs

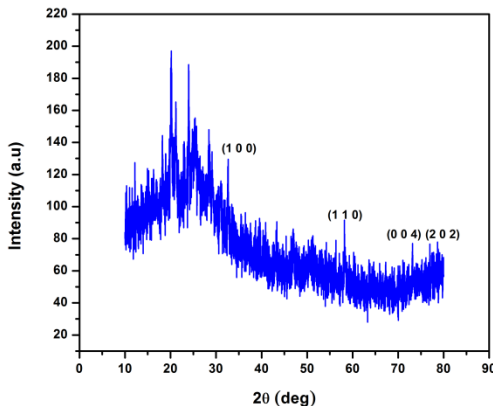


Figure 1b:- XRD pattern of PANI/ ZnO Nanocomposite:-

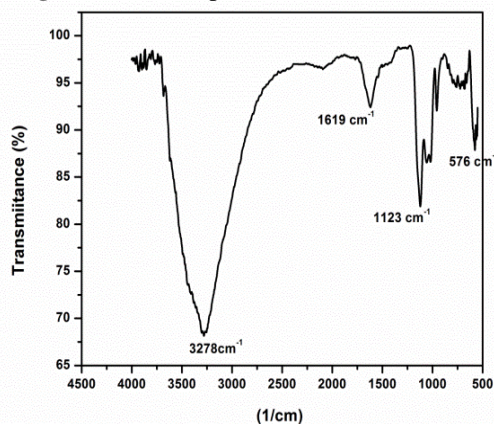


Figure 2a:- FT-IR spectra of ZnO NPs

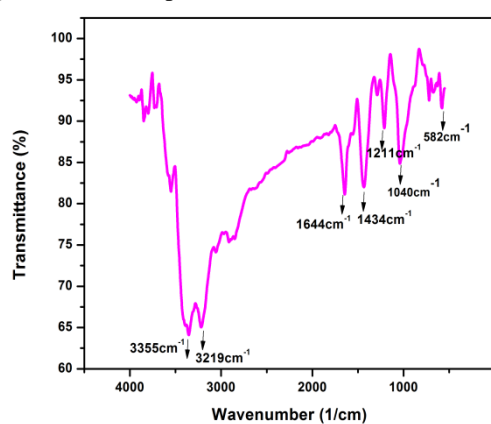


Figure 2b:- FT-IR spectra of PANI/ ZnO Nanocomposite

FT-IR Spectroscopy:-

The FT-IR spectra of ZnO nanoparticles and PANI / ZnO nanocomposite synthesized by microwave assisted hydrothermal method are shown in Figures 2a and 2b. The peak at low wave number region of 576 cm^{-1} is assigned to ZnO group [17, 18]. The sharp peak at 1123 cm^{-1} is due to C-H plane bending vibration[19]. The band appears at 1619 cm^{-1} may be attributed to C=C Stretching mode of quinoid ring[20]. The peak at 3278 cm^{-1} is due to the absorption of water during the preparation of IR pellet[21].

Table 1.2:- Functional group analysis for ZnO nanoparticles.

Wave number cm-1	Assignments
3278	Absorption of water
1619	C=C Stretching mode of quinoid ring
1123	C-H plane bending vibration
576	ZnO group

Table 1.3:- Functional group analysis for PANI / ZnO Nanocomposites.

Wave numbers (cm ⁻¹)	Assignments
3355	N-H band stretching vibration
3219	Hydrogen bonded NH bond
1644	Benzoid ring stretching
1434	C-C Stretching in quinoid, C-H bending in benzonoid ring
1040	SO ³⁺ vibration
582	C=C Stretching mode of quinoid rings

SEM Analysis:-

Figure 3a shows the SEM micrograph of the pure ZnO nanoparticles synthesized by microwave assisted hydrothermal method. It can be observed that nanosized ZnO particles are formed as nanoclusters. From the SEM image of composite PANI / ZnO Nanocomposite (Figure 3b), it is observed that ZnO nanoparticles are surrounded by polyaniline matrix and hence it appears as agglomerated macromolecules.

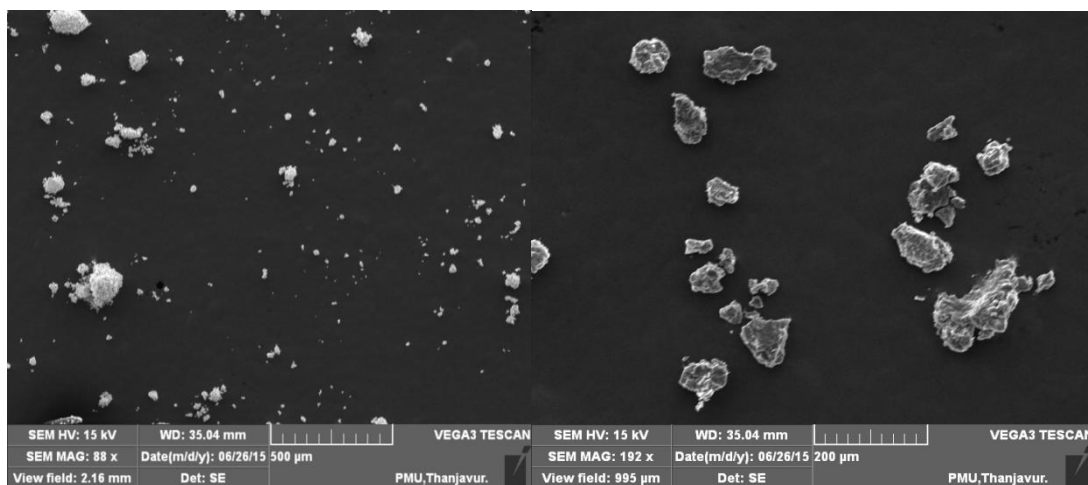


Figure 3a:- SEM image of ZnO NPs

Figure 3b:- SEM image of PANI / ZnO Nanocomposite

Microstructural properties by HRTEM and SAED pattern:-

The morphology and particle size of Zinc Oxide nanoparticles were observed using HRTEM micrograph (Figure. 4a). These particles with particle size of 50nm were observed. The particle size of ZnO nanoparticles was observed as 50nm and it is same for PANI / ZnO nanocomposites. The presence of rod-like shaped PANI / ZnO nanocomposites was observed from HRTEM micrograph. The particle size observed from HRTEM micrograph matches with the particles size calculated from the XRD investigation. These results confirm the formation of crystalline Zinc Oxide nanoparticles. The corresponding SAED pattern of ZnO nanoparticles is shown in Figure 4b. SAED pattern provides rings made up of bright spots, denotes the crystalline nature of the prepared ZnO nanoparticles.

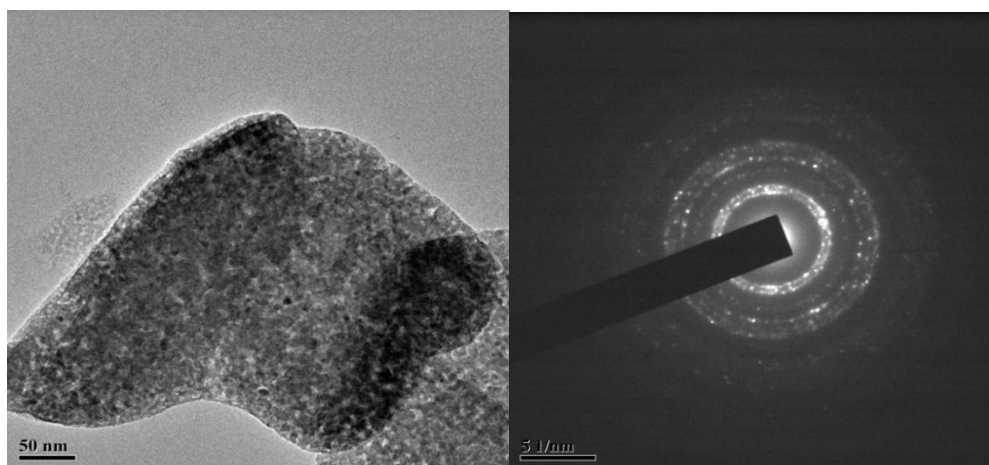


Figure 4a:- HRTEM image of Pure ZnO NPs

Figure 4b:- SAED pattern of ZnO NPs

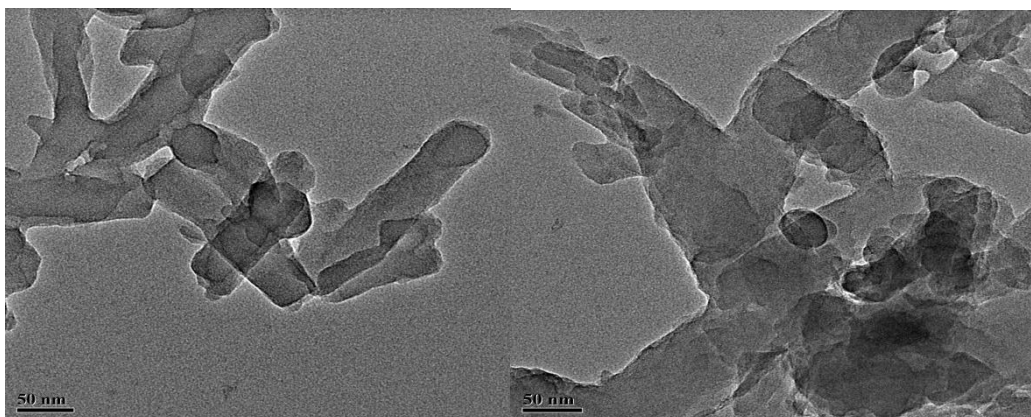


Figure 4a:- HRTEM micrograph of PANI / ZnO **Figure 4b:-** SAED pattern of PANI / ZnO

Electrical studies:-

Determination of AC conductivity of ZnO Nanoparticles:-

The dielectric properties of ZnO Nanoparticles can be explained as a function of frequency of the applied electric field and temperature. Figure 5a and 5b. shows the variation of ac conductivity with varying frequency for ZnO nanoparticles and PANI / ZnO at different temperatures. The ac conductivity of ZnO Nanoparticles was calculated using the formula,

$$\sigma_{ac} = \epsilon_0 \epsilon_r \omega \tan \delta$$

where ϵ_0 is the permittivity of free space (8.85×10^{-12} Farad/metre), ϵ_r is the dielectric constant, $\omega(2\pi f)$ is the angular frequency and $\tan \delta$ is the loss factor. It is observed from the figure that the ac conductivity remains almost constant upto 1 KHz. Above 1 KHz, it increases gradually upto 40 KHz and then increases rapidly from 40 – 620 KHz. As T increases, σ_{ac} decreases. The result revealed that ZnO nanoparticles shows frequency dependence behaviour and the temperature independence behaviour of conductivity.

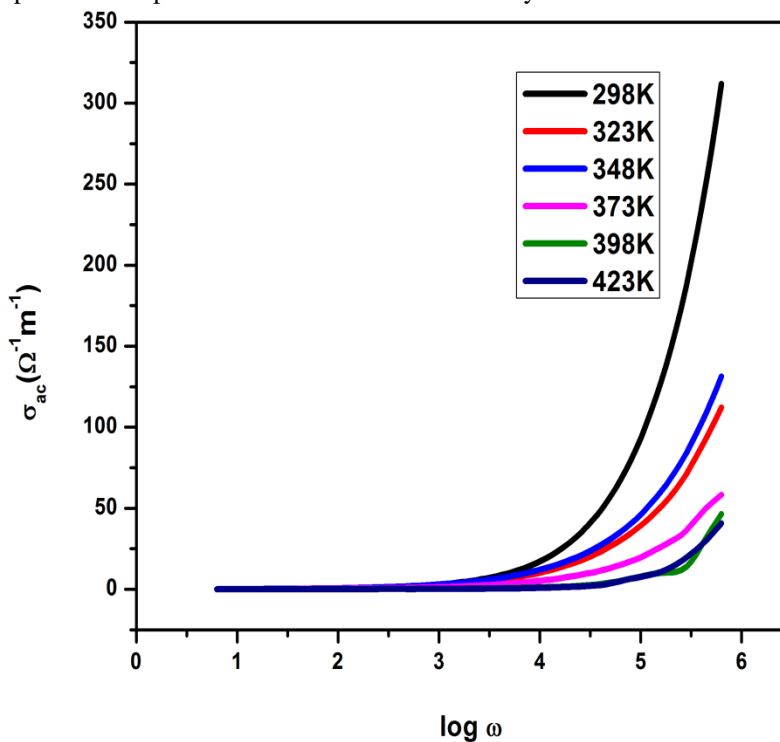


Figure 5a:- Variation of ac conductivity with the Frequency of ZnO NPs.

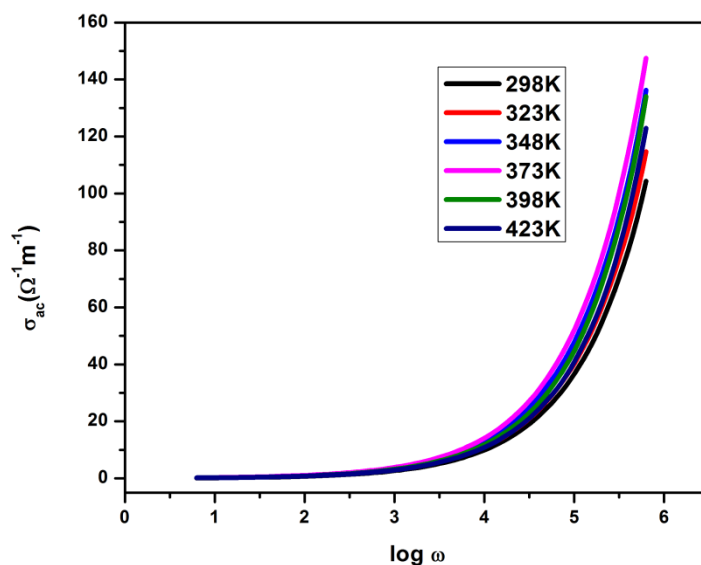


Figure 5b:- Variation of ac conductivity with the Frequency of PANI / ZnO nanocomposite

Dielectric constant of ZnO Nanoparticles:-

Figure 6a & b shows the variation of dielectric constant (ϵ_r) with varying frequency in the range of 10Hz - 620 KHz. The ϵ_r decreases faster at lower frequency and slowly at higher frequency. The frequency dependence of electrical properties shows that the dielectric constant ϵ_r decreases due to the increase of ac conductivity with increasing frequency. The rapid decrease of ϵ_r in the low frequency region was due to space-charge contribution.

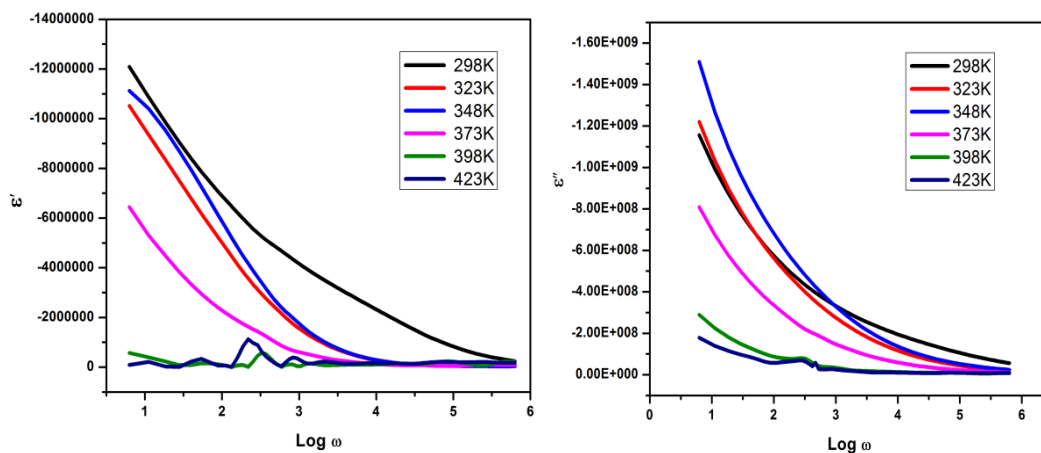


Figure 6:- Frequency dependence of dielectric constant(real & Imaginary) of ZnO NPs

Conclusion:-

ZnO Nanoparticles were prepared using a microwave assisted hydrothermal method. The XRD analysis confirmed that pure ZnO nanoparticles were formed in this method. Crystallite size for ZnO nanoparticles synthesized in this method was found to be 50nm. The results obtained from TEM studies exactly matches with that of XRD results, which confirmed the formation of ZnO nanoparticles. FT-IR analysis also confirmed the formation of Zinc Oxide nanoparticles. XRD and FTIR of PANI / ZnO nanocomposite revealed that PANI undergoes interaction with ZnO Nanoparticles which are embedded in polymer matrix. SEM and TEM micrograph shows the uniform distribution of ZnO Nanoparticles in PANI / ZnO nanocomposite. Dielectric studies of ZnO nanoparticles and PANI / ZnO nanocomposite shows the frequency dependence dielectric behavior of ZnO nanoparticles. Results reveals that the dielectric constant decrease with the increasing frequency whereas the a.c conductivity of the sample increases with the increase in frequency. The decrease of dielectric constant ϵ_r was due to the increase of ac conductivity with increasing frequency. The rapid decrease of the dielectric constant(ϵ_r) in the low frequency region was attributed to space-charge contribution.

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