Solid State Root Preparation, Characterization and Electrical Properties of NiCuZnFe$_2$O$_4$ / Paraformaldehyde Nanocomposites

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Abstract. In this investigation, the structural and electrical properties of nanocomposites of NiCuZn ferrite (NCZ) and paraformaldehyde (PFD) synthesized by solid state mixing route are reported. Synthesized nanomaterials have been characterized by FT-IR and TGA techniques. FT-IR results confirm the presence of NCZ and PFD in the samples. The DC conductivity measurements have been investigated. The dielectric constant $\varepsilon'$ and dielectric loss $\varepsilon''$ were found to increase as the PFD content increased to 50% and to decrease as the PFD content further increased. A dielectric cole-cole diagram can be obtained by plotting the dielectric loss $\varepsilon''$ against the dielectric constant $\varepsilon'$. The cole cole diagram is generally used for studying the dielectric polarization characteristics by following the variation of dielectric loss $\varepsilon''$ with dielectric constant $\varepsilon'$. From this work, it is possible to deduce interfacial polarization and dipolar polarization from dielectric cole-cole plots.

1. Introduction
The knowledge of the electric and magnetic properties of nanocomposite materials over a broadband frequency range is an essential requirement for accurate modelling and design in several engineering applications. Such applications span printed circuit board design, electromagnetic shielding, biomedical research and determination of EM radiation hazards [1–3]. The electric and magnetic properties of materials usually depend on several factors: frequency, temperature, linearity, isotropy, homogeneity, and so on. The interaction of incident electromagnetic fields with a material can be successfully investigated only when accurate information on the complex permittivity and magnetic permeability is attained. For example, from the knowledge of the frequency dependence of the complex relative permittivity and magnetic permeability of a material, the shielding effectiveness of a structure made of that material can be predicted.

Since polymers have the merits of lightness and good processability, and overcome the limit of the use of sintered ferrites as the electromagnetic wave absorber, many studies on the conducting polymer composite have been explored. One of those results, the polymer–ferrite composite, has been widely used as the electromagnetic wave absorber in the microwave band. The electromagnetic wave absorbing characteristics of the absorber due to magnetic loss can be determined from composition, complex permittivity, and permeability of composite. Since the electromagnetic wave-absorbing properties are directly related to the electromagnetic properties, it is of importance to analyze the electromagnetic properties of the absorber.
In the present study, various Paraformaldehyde (PFD) loaded Ni$_{0.48}$Cu$_{0.12}$Zn$_{0.4}$Fe$_2$O$_4$ (NCZ) matrix nanocomposites had been prepared using a mechanical milling approach. The samples were characterized using FTIR and TGA, the electrical and dielectric properties were measured and analyzed.

2. Experimental procedure
The starting materials are nanocrystalline Ni$_{0.48}$Cu$_{0.12}$Zn$_{0.4}$Fe$_2$O$_4$ prepared by Microwave hydrothermal method and commercial Paraformaldehyde powder. Nanoparticles of NiCuZn ferrite and PFD powders were first dried in an oven at $\sim 100^\circ$C, cooled to room temperature, followed by mechanical mixing process in a ball mill. The nanocomposites were prepared with x wt% of NiCuZn ferrite and (100-x) wt% of PFD. Appropriate amounts of the two materials were placed in a stainless steel vial containing four stainless steel balls, such that the ratio of the weight of the balls to that of the powder was 10:1. The material was milled for about 20 h and beyond the steady state to ensure maximum dispersion. To avoid excess heating, milling was interrupted after every 40 min for about 15 min for the material to cool down. The vial was opened only after the completion of milling. The 20-hrs milled powders were subjected to anneal at 110°C/30 min in an air atmosphere.

The prepared (x wt%) NCZ + (100-x wt%) PFD nanocomposites (x=100, 90, 70, 50, 30, 10, 0) were renamed as NCZ, NF1, NF2, NF3, NF4, NF5 and PFD respectively. The samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric analysis (TGA). The DC conductivity measurements have been investigated. The complex permittivity properties of NCZ-PANI nanocomposite samples have been measured. A dielectric coe-coe diagram can be obtained by plotting the dielectric loss $\varepsilon''$ against the dielectric constant $\varepsilon'$. The obtained experimental results were analyzed by using various theoretical models.

3. Result and discussions
The FTIR spectra of the NCZ-PFD nanocomposites are shown in Figure 1. It can be seen from the figure that the peaks observed at 3430 cm$^{-1}$and 2960 cm$^{-1}$ are ascribed to the hydroxyl stretching and C–H stretching vibrations, respectively. The peaks observed at 1250 cm$^{-1}$ and 1110 cm$^{-1}$ are associated with the C–O–C symmetrical stretching vibration, and the peaks at 949cm$^{-1}$ and 841cm$^{-1}$ correspond to the C–H bending wagging vibration and the deformation vibration of O– C–O of PFD [4,5] In addition, the absorption peaks at 609 cm$^{-1}$ and 409 cm$^{-1}$ observed are due to the intrinsic vibration of the tetrahedral and octahedral sites in the NCZ ferrite particles. It can be seen from the vibration spectra of spinel ferrite a high frequency band $\nu_1$ (600– 580 cm$^{-1}$) and the low-frequency band $\nu_2$ (440–400 cm$^{-1}$) has been observed. These bands are attributed to the intrinsic vibration of the tetrahedral sites and the octahedral sites, respectively. These results indicate that the NCZ nanoparticles are well dispersed in the PFD matrix.

Figure 1: FTIR spectra for NCZ-PFD nanocomposites samples
Thermal stability is an important material property of microwave absorption materials. Figure 2 shows the TG analysis of NiCuZn ferrite, and the NCZ–PFD nanocomposites in nitrogen atmosphere at a heating rate of 10ºC min\(^{-1}\). The ferrite nanoparticles (x=1) were thermally stable, only displaying a weight loss less than 8%. Nanocomposites with varying ratio of PFD to the ferrite showed three steps of thermal degradation. We attribute the weight loss up to 100°C to the evaporation of free water molecules from the nanocomposite. The maximum weight loss below 150°C is attributed to the evaporation of paraformaldehyde since its melting point is at 120°C. It is observed that there is a slight increase in maximum weight loss temperature in nanocomposites it may be due the interaction between the ferrite particles and polymer chains.

![TGA graphs for NCZ-PFD nanocomposites](image)

**Figure 2:** TGA graphs for NCZ-PFD nanocomposites

Figure 3 shows the conductivity of the NCZ, PFD and NCZ-PFD nanocomposites at room temperature. The incorporation of PFD polymer significantly affects the conductivity of resulting nanocomposites. The decrease in the conductivity of nanocomposites upon increasing the ferrite concentration can be attributed to the insulating behavior of the iron oxide in the core of the nanoparticles, which hinders the charge transfer thereby lowering the conductivity [6,7]. Conductivity increase with an increase in PANI content is also may be due to when the polymer makes chains, the electrical resistivity of the composites is reduced significantly due to the low resistivity of the polymer phase.

![DC conductivity of NCZ-PFD nanocomposites at room temperature](image)

**Figure 3:** DC conductivity of NCZ-PFD nanocomposites at room temperature

The frequency variation of real part of permittivity (\(\varepsilon'\)) for NF1 and NCZ, NF2, NF3, NF4, NF5 nanocomposites under investigation was measured in the frequency range of 100 kHz–1.8 GHz and obtained results are plotted in Figure 4 a & b, respectively. It can be seen from the figure (Fig.4a) that the value of \(\varepsilon'\) for sample NF1 is 25 at 100 kHz and remained constant with an increase of frequency up to
600 MHz. With further increase of frequency, a resonance and anti-resonance behavior have observed around 1.2 GHz. A similar behavior has been observed for all other nanocomposites (Fig.4b) under investigation. The frequency variation of \( \varepsilon' \) for nanocomposite samples can be understood based on electron hopping conduction mechanism.

Figure 5 a & b show the frequency dependence of imaginary part of permittivity (\( \varepsilon'' \)) for NCZ and NCZ-PFD nanocomposites in the frequency range of 100 kHz to 1.8 GHz. It can be seen from the figure (Figure 5a) that the value of \( \varepsilon'' \) for the NF1 sample is of 2.24 at 100 kHz and almost remained constant up to a frequency of 600 MHz. With further increase of frequency, a resonance peak has been observed around 1.2 GHz. A similar behavior has been observed for all other nanocomposites under investigation (Figure 5b).

As polymer content increases the value of \( \varepsilon' \) increases from 22 to 27.39 at 1 MHz (Table 1). The increase of real part of permittivity (\( \varepsilon' \)) is attributed to the content of PFD which raises the number of dipoles in the composite materials. The increase of dipoles tends to increase the local displacements (dielectric polarization) in the direction of external applied electric field for electrons, and the increased polarization causes a significant enhancement of the dielectric constant.

The variation of complex permittivity with frequency reveals the dispersion due to Maxwell-Wagner type interfacial polarization (and the presence of space charge at grain boundaries) in agreement with Koops phenomenological theory. [8] Moreover, the polarization in ferrites (and also ferrite-based materials such as ferrite-polymer composites) is through a mechanism similar to the conduction process. By electron exchange between \( \text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} \), [9] one obtains a local displacement of electrons in the directions of the electric field and these electrons determine the polarization. The polarization decreases with increase in frequency and then reaches almost a constant or maximum value due to the fact that, beyond a certain frequency of external ac electric field, the electronic exchange \( \text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} \) [9] cannot follow the ac field. The relatively large values of \( \varepsilon' \) at low frequencies are due to the predominance of the species like \( \text{Fe}^{2+} \) ions, interfacial dislocations, oxygen vacancies, grain boundary defects, etc. The decrease in \( \varepsilon' \) with frequency is natural because of the fact that any species contributing to the polarization will be lagging behind the applied ac field at higher frequencies. From the dielectric properties studies, it can be concluded that the presently investigated nanocomposites possess low dielectric constant and loss over a wide range of frequency.

![Figure 4 a & b: Real part of the permittivity of NCZ-PFD nanocomposites.](image-url)
There are many empirical, semi-empirical and highly formalized expressions for predicting the dielectric constant of composite materials. These all models are derived by making an assumption that the materials contain spherical inclusions with dipole interactions. Spherical inclusions produce the smallest dipole moment, given the amount of particle polarizable material.

The effective dielectric constant has been estimated using Lichtenker’s, [10] Rayleigh’s, [11] Bruggmann’s [12] and Giordano’s [13] models and obtained results are plotted in the Figure 6. For the sake of comparison, we have also included present experimental results obtained on NCZ-PFD nanocomposites. In the present system, the deviation between experimental results and theory starts above 50wt% of PFD. It is also observed that the experimental values are nearer to theoretical values evaluated using the equations proposed by Giordano up to 50wt% of PFD. The deviation between experimental and theoretical values above 50wt% of PFD is because of nanocomposite composed of dielectrics may exhibit different behavior due to the infringement of the electric flux at the boundary region of two different phases [14].

Figure 6 Variation of dielectric constant with PFD content.

Figure 7 a & b gives the plots between ε’ and ε” at different frequencies of NCZ-PFD nanocomposites. Although some slight differences exist in their shapes of these curves, in general they show a semicircle behavior and a relaxation occurs in the NCZ-PFD nanocomposites at high frequency. The relaxation observed in the NCZ-PFD nanocomposites is of Maxwell–Wagner relaxation and electron polarization type. In these nanocomposites, the existence of interfaces gives rise to interfacial polarization or the Maxwell–Wagner effect.[15,16] This phenomenon appears in heterogeneous media due to the accumulation of charges at the interfaces and the formation of large dipoles on particles or clusters. Interfacial relaxation depends on the conductivity and permittivity of the constituents of the composite.
Figure 7 a & b Complex permittivity Cole-Cole plots of NCZ-PFD nanocomposites.

Table 1: Electrical and dielectric properties of NCZ-PFD nanocomposites

| Sample Code | Conductivity S/cm | $\varepsilon'$ at 1MHz | $\varepsilon''$ at 1 MHz |
|-------------|-------------------|-------------------------|-------------------------|
| NCZ         | 1.13x10^{-6}      | 22                      | 2.12                    |
| NF1         | 2.46x10^{-4}      | 22.89                   | 2.24                    |
| NF2         | 8.07x10^{-4}      | 24.74                   | 2.54                    |
| NF3         | 1.245x10^{-3}     | 27.39                   | 2.78                    |
| NF4         | 2.339x10^{-3}     | 26.82                   | 2.82                    |
| NF5         | 2.934x10^{-3}     | 25.35                   | 2.89                    |
| PFD         | 4.48x10^{-3}      | -                       | -                       |

4. Conclusions

The NCZ-PFD nanocomposites were efficiently prepared by the use of mechanical milling approach. The structural characteristics of nanocomposites were investigated through FTIR and TGA. Conductivity and dielectric studies of nanocomposites had been investigated. The measurements of cole-cole properties found out that with the addition of PFD each dielectric and magnetic losses had been increased, relaxation mechanism have been analyzed. Therefore, the NCZ-PFD nanocomposites might be an attractive candidate for microwave adsorption materials.

5. References

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