



Preparation and Characterization of Nickel ferrite Nanoparticles via Co-precipitation Method

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Nickel ferrite (NiFe₂O₄) nanoparticles were synthesized using co-precipitation method. The X-ray diffraction (XRD) pattern was used to determine the structure of NiFe₂O₄ nanoparticles. The presence of NiFe₂O₄ nanoparticles was confirmed by the FT-IR spectrum. The details of the surface morphology of NiFe₂O₄ nanoparticles were obtained by Scanning Electron Microscopic analysis. The particle size of the NiFe₂O₄ nanoparticles could be determined by means of Transmission Electron Microscopy. This work aimed at the investigation of the dielectric properties such as the dielectric loss and the dielectric constant of NiFe₂O₄ nanoparticles at varied frequencies and temperatures. In addition, the magnetic properties of the NiFe₂O₄ nanoparticles were studied.

Keywords: Nickel ferrite (NiFe₂O₄), XRD, FT-IR, SEM, TEM and Magnetic properties.

1. Introduction

The last few decades saw substantial development in the field of nano technology, particularly in physical sciences. The synthesis of nano crystalline spinel ferrites plays an important role in determining their physical properties at nano and sub nano levels. Ferrites have established their potential in several applications due to their remarkable electrical and magnetic properties, and also in magnetic resonance imaging (MRI) enhancement, magnetic high-density information storage etc. Nickel ferrite is one of the multifaceted and technologically important soft ferrite materials because of its typical ferrimagnetic properties, lower eddy current losses, low conductivity and high electrochemical stability^{1,2}. Nickel ferrite (NiFe₂O₄) has a counter spinel structure. The location of the divalent cations (Ni²⁺) in the crystal structure is almost homologous to the magnetic properties of the nickel ferrite. However, nickel ferrite shows super-paramagnetic nature and it has diverse applications such as gas-sensor, magnetic fluids, catalysts, magnetic storage systems, photomagnetic materials, site-specific drug delivery, magnetic resonance imaging and microwave devices³⁻⁷. Various methods such as hydrothermal method⁸, co-precipitation method⁹, gel-assistant hydrothermal route¹⁰, thermolysis¹¹, wet chemical co-precipitation technique¹², self-propagating¹³, have been developed to prepare nanocrystallite nickel ferrite. This paper focuses on the synthesis of NiFe₂O₄ nanoparticles using the co-precipitation method, their characterization by means of powder X-ray diffraction, Scanning Electron Microscopy (SEM), FTIR, Transmission Electron Microscope (TEM),

and the determination of the dielectric properties and the magnetic behaviour of NiFe₂O₄ nanoparticles.

2. Experimental procedure

Nickel ferrite (NiFe₂O₄) nanoparticles were synthesized via co-precipitation method. Typical synthetic procedures required analytical grade 3M solution of sodium hydroxide (NaOH) which was slowly added to salt solutions of 0.4M ferric chloride (FeCl₃) and 0.2 M nickel chloride (NiCl₂). The pH of the solution was constantly observed as the NaOH solution was added drop wise. The reactants were consistently stirred using a magnetic stirrer until a pH level of >12 was achieved. A specified amount of oleic acid was added to the solution as the surfactant. The liquid precipitate was then brought to a reaction temperature of 80°C and stirred for 30 min. The product was cooled to room temperature and then washed twice with distilled water and ethanol to eliminate unwanted impurities and the residual surfactant from the prepared sample. Finally, the sample was centrifuged and then dried overnight at about 80°C. The acquired substance was then ground into a fine powder.

3. Results and Discussion

3.1 XRD analysis

The XRD pattern of the NiFe₂O₄ nanoparticles was recorded by using a powder X-ray diffractometer {Schimadzu model: XRD 6000 using CuKα (λ=0.154 nm) radiation}, with a diffraction angle between 30° and 60°. Figure 1 shows the XRD patterns of the as-prepared NiFe₂O₄ nanoparticles.

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The patterns show the formation of single phase cubic spinel crystal structure. The NiFe₂O₄ nanoparticles contained no impurity peaks within the limit of X-ray detection. The broad peaks of X-ray diffraction patterns stipulate that the particles of the synthesized samples are in nanometer range. The average crystallite size of the samples could be calculated using Scherrer's formula

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the X-ray wavelength (CuK_α radiation and equals to 0.154 nm), θ is the Bragg diffraction angle, and β is the FWHM of the XRD peak appearing at the diffraction angle θ . The average crystallite size was calculated from the X-ray line broadening using Scherrer equation and it was found to be about 18 nm which is almost similar to the reported value 16 nm¹⁴.

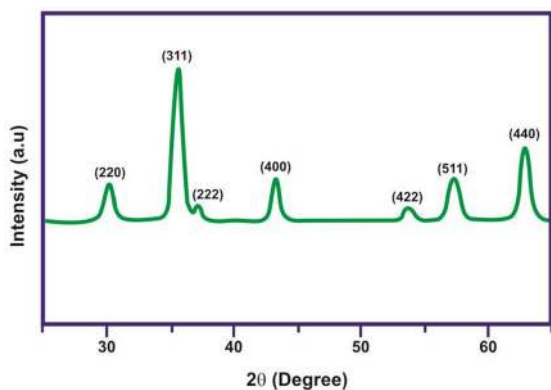


Figure 1. XRD pattern of NiFe₂O₄ nanoparticles.

3.2 FTIR analysis

The FTIR spectrum of the NiFe₂O₄ nanoparticles was taken using an FTIR model Bruker IFS 66W Spectrometer. In order to determine the chemical structure of the sample, the FTIR spectrum was observed above the frequency range of 4000-500 cm⁻¹ as shown in Figure 2. The decomposition of hydroxide to oxide phase for the formation of spinel ferrites was well reflected in the FTIR spectrum. It has been reported that the IR bands of solids are usually attributed to the vibration of ions in the crystal lattice. The bands at 552 cm⁻¹ and 464 cm⁻¹ represented tetrahedral and octahedral modes of NiFe₂O₄, respectively¹⁵. The band located at 3389 cm⁻¹ could be attributed to the symmetric vibration of -OH groups. The bands with peaks observed at 1038 cm⁻¹ could be assigned to O-H bending vibration¹⁶. The peak at 2333 cm⁻¹ was ascribed to H-O-H bending vibration of the free or absorbed water¹⁷.

3.3 SEM analysis

SEM studies were carried out using JEOL, JSM- 67001. The samples needed a coating of gold for SEM analysis for the avoidance of charging effect. The morphology and the size distribution of the NiFe₂O₄ nanoparticles were determined using SEM. Typical SEM images of NiFe₂O₄ synthesized

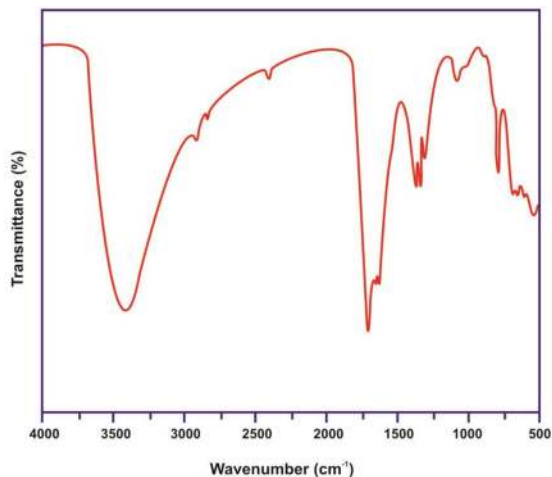


Figure 2. FTIR spectrum of NiFe₂O₄ nanoparticles.

particles are shown in Figure 3. SEM micrograph depicts that the samples contain micrometrical aggregation of tiny particles. The existence of high dense agglomeration indicates that pore free crystallites are present on the surface. The SEM images show the agglomerated form of NiFe₂O₄ nanoparticles. As the nanoparticles possess high surface energies, they tend to agglomerate and grow into larger assemblies.

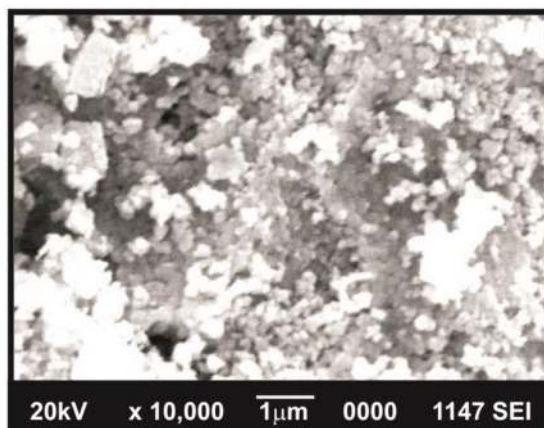


Figure 3. SEM image of NiFe₂O₄ nanoparticles.

3.4 TEM analysis

Transmission Electron Microscopic (TEM) image was taken using an H-800 Transmission Electron Microscopy (Hitachi, Japan) with an accelerating voltage of 100kV. The colloidal nanoparticles solution had to be dried on the copper grid before analysis. Figure 4 shows the TEM image of the NiFe₂O₄ nanoparticles. In the TEM image most of the particles appear to be spherical; however, some elongated particles are also present in the image. Some moderately agglomerated particles as well as segregated particles are also present in the sample. The estimated average size of the nanoparticles by TEM was about 28 nm which was almost similar to that of the reported values¹⁸.

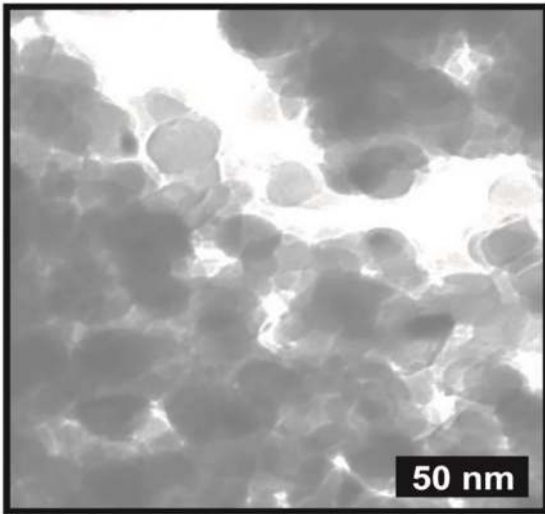


Figure 4. TEM image of NiFe₂O₄ nanoparticles.

3.5 Magnetic measurements

The magnetic behavior of NiFe₂O₄ nanoparticles was investigated using VSM (Lakeshore VSM 7410). The high coercivity values account for the slower rate of growth of crystallite size that takes place during the heating process. It is not only the temperature but also the morphology that seems to significantly influence the magnetic properties. The increased value of the coercivity could be attributed to the magnetic spin orientation along the axis that eases magnetization¹⁹. On account of the grain boundaries and free surface, the magnetic properties improved²⁰. Figure 5 shows the magnetic hysteresis loops of the NiFe₂O₄ nanoparticles at room temperature. The magnetic parameters, namely retentivity, coercivity, and saturation magnetization of the sample were measured to be 3875 G, 0.142emu/g, and 0.343emu/g respectively.

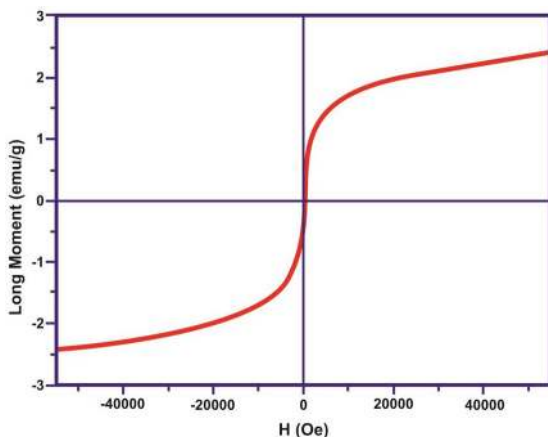


Figure 5. Magnetic properties of NiFe₂O₄ nanoparticles.

3.6 Dielectric Properties

The dielectric properties of the NiFe₂O₄ nanoparticles were analyzed using an HIOKI 3532-50 LCR HITESTER

over the frequency range 50Hz-5MHz. The NiFe₂O₄ nanoparticles pellets in disk form were studied at different temperatures. For measurements, the samples were obtained with the diameter of ~10 mm and thickness ~1 mm and a sample was placed between the electrodes having a conventional four terminal sample holder for investigations involving temperature variations along with a conventional two terminal sample holder for ambient conditions alone. The sample was mounted between copper platforms and electrodes. To ensure good electrical contact, the faces were coated with silver paint. The capacitance and the dissipation factor of the parallel plate capacitor which was formed by the copper plate and the electrode having the sample as a dielectric medium were measured. Analysis on the dielectric behaviour of NiFe₂O₄ nanoparticles provided much useful information about the electric field distribution within the as grown NiFe₂O₄ nanoparticles. At various temperatures and at a frequency ranging from 50Hz to 5MHz the measurements were performed. The dielectric constant and dielectric loss were determined from the equations 2 and 3 respectively.

$$C = \epsilon_r \epsilon_0 A/d \quad (2)$$

$$\tan \delta = 1/2 \times 3.14 \times f \times R_p C_p \quad (3)$$

where A is the area of the sample and d is the thickness of the sample. The relative permittivity (ϵ_r) is usually known as dielectric constant. A study of the dielectric nature of NiFe₂O₄ nanoparticles could furnish useful information about the electric field allocation within the NiFe₂O₄ nanoparticles. The frequency dependence of the dielectric constant and the dielectric loss at various temperatures is shown in Figures 6 and 7 respectively. It could be learned that both the dielectric constant and the dielectric loss exhibited homologous nature. The dielectric constant of materials is influenced by the totality of electronic, ionic, bipolar and space charge polarizations of the frequencies²¹. All the four polarization mechanisms seem to be active at low frequencies. Lower frequencies and high temperatures normally aid the progress of space charge polarization. The low value of the dielectric constant with increasing frequency could be ascribed to the loose or weak bond of ions at the lower frequency range²². Still greater values of the dielectric constant at lower frequency values are possible due to the charge accumulation at the grain boundaries. Another possibility to gain higher values is due to heterogeneous dielectric structure which possesses the interfacial/space charge polarization. Due to the fact that beyond a certain frequency of the external field, the polarization decreased with the increase in frequency and then reached a constant value, the hopping between various metal ions could not follow the alternating field. It was noticed that the value of the dielectric constant decreased with increase in the frequency²³. The dielectric loss is a broad indication of the energy dissipation in the dielectric system.

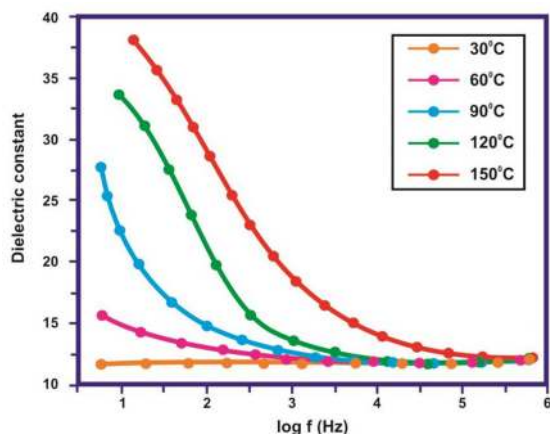


Figure 6. Dielectric constant plot for NiFe₂O₄ nanoparticles

Figure 7 shows the curve explaining how the dielectric loss factor varies with the frequency at various temperatures. It becomes clear from the graph that the dielectric loss decreases with the increase in frequency and attains a low value in the high frequency region. The study clearly showed that the dielectric loss suddenly dropped at lower frequencies and attained constancy at higher frequencies. Further, it could be observed that owing to the space charge polarization the dielectric loss decreased with the increase in the frequency for all temperatures^{24,25}.

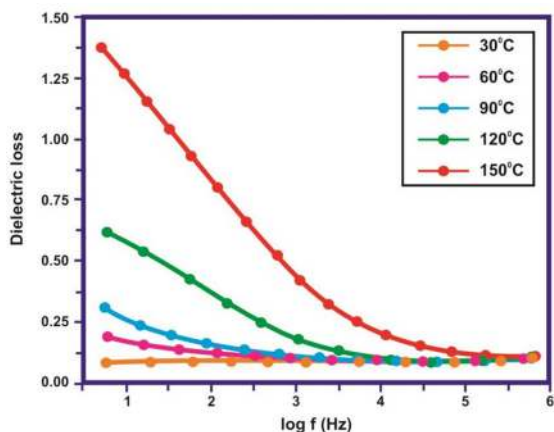


Figure 7. Dielectric loss plot for NiFe₂O₄ nanoparticles

4. Conclusion

The paper thoroughly discussed the synthesis of NiFe₂O₄ nanoparticles by the employment of co-precipitation method. The fact that the NiFe₂O₄ nanoparticles belonged to the cubic spinel structure was established by XRD. FTIR spectrum also supported the formation of NiFe₂O₄ nanoparticles. That the nanoparticles agglomerated to form spherical-shaped particles was also confirmed and made clear by the SEM analysis. The average particle size of NiFe₂O₄ nanoparticles was found to be 28 nm. The impact of the frequency and the

temperature on the dielectric loss and the dielectric constant for NiFe₂O₄ nanoparticles was studied. From the dielectric studies it became evident that the frequency negatively impacted both the dielectric constant and the dielectric loss as decreased with increase in the frequency. A study of the magnetic properties was also carried out using VSM measurements.

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