Study of Structural, Dielectric and Magnetic Properties of MFe₂O₄ (M=Ni, Co) Spinel Ferrites

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Abstract: Spinel ferrites NiFe₂O₄ (NFO) and CoFe₂O₄ (CFO) were synthesized by conventional solid-state reaction method. Structural analysis of these ferrites was studied by recording XRD at room temperature. Rietveld refinement of XRD patterns confirms the presence of single-phase cubic symmetry (Fd3m) of both the samples without the presence of any secondary phase. The dielectric constant (\mathcal{E}') and dielectric loss (tan δ) were studied in the frequency range (100Hz to 7MHz) at different temperatures. The complex impedance spectroscopy was studied to find the impact of grains and grain boundaries in ferrites. The magnetic characterization was determined by M-H hysteresis loop which reveals the ferromagnetic behavior of spinel ferrites.

Keywords: Spinel ferrites, XRD, Rietveld refinement, Impedance spectroscopy, Magnetic properties.

1. Introduction

Ferrites, also known as soft magnets, are considered as a one of the most important magnetic materials due to their remarkable applications particularly for electromagnetic devices in the radio frequency region, since they have physical flexibility, high electrical resistivity, mechanical hardness and frequency-dependent permeability¹⁻³. These ferrites also possess numerous potential applications such as memory core, in microwave devices, etc. because of their high saturation magnetization, interesting hysteresis loop properties and high Curie temperature.^{4–8}

The ideal spinel ferrite exhibits $M^{2+}Fe^{3+}{}_{2}O_{4}$ (where M is a divalent cation) kind of structure. Distribution of cations on available tetrahedral site and octahedral site decides the physical properties (magnetic properties, as transport properties) of spinel ferrites. In normal spinel structure, M^{2+} ion occupies tetrahedral site whereas Fe^{3+} ion occupies octahedral site i.e M^{2+} [Fe^{3+}]O₄ (most of these ferrites are paramagnetic). Secondly, in the inverse spinel structure, tetrahedral sites are occupied by Fe^{3+} ion and octahedral sites by both M^{2+} and Fe^{3+} ions i.e. $Fe^{3+}[M^{2+}Fe^{3+}]O_{4}$. Spinel ferrites NiFe₂O₄ (NFO), CoFe₂O₄ (CFO) are normally found to be inverse spinels, with inversion parameter $\lambda \approx 1$ for NFO but λ lies between 0.76 to 0.93 for CFO. Inversion factor strongly depends upon the condition of sample preparation ^{9, 10}. NFO and CFO are promising materials for multifunctional devices due to their high magnetostrictive coefficient, moderate saturation magnetization and high coercivity^{11, 12}.

In the present work, spinel ferrites $NiFe_2O_4$ (NFO) and $CoFe_2O_4$ (CFO) have been studied. The structural, dielectric and magnetic properties were investigated systematically.

2. Experimental Details

NiFe₂O₄(NFO) and CoFe₂O₄(CFO) were synthesized by conventional solid state reaction method. The stoichiometric proportion of Sigma Aldrich grade NiO, Fe_2O_3 and Co_3O_4 , Fe_2O_3 (purity > 99%) were used to prepare NFO, CFO respectively. A mixture of raw materials was grinded for 2 hours in the agate mortar. The obtained homogenous mixture was first calcined at 673K for 3hrs and reground for 30 minutes to obtain a more uniform mixture. The final heat treatment (sintering) of calcined samples was carried out at 1093K for 3hrs at the heating rate 5K/min. The crystal structure investigation was done by using x-ray diffraction (XRD) data. XRD patterns were recorded by using RigakuMiniflex-II diffractometer with Cu K α radiation at room temperature within 2θ range (10°-80°) at the scanning rate of 2°/min. XRD data was further analyzed by Rietveld refinement using Full dielectric evaluation was recorded Prof program. The bv using impedance/gain phase analyzer (Newton's 4th Ltd) in frequency range Magnetic characterization was investigated at room 100Hz-7MHz. temperature using vibrating sample magnetometer (VSM) Lakeshore,7304. For Dielectric analysis, pellets of 10mm diameter and 1-2mm thickness were prepared by using hydraulic pellet press.

3. Results and discussion

3.1 Structural analysis

Fig. 1(a) depicts the XRD pattern of both the samples. XRD analysis reveals the presence of only Fd-3m cubic space group without any presence of secondary phase and impurity. For detailed crystal structure studies, XRD data was further refined by Rietveld refinement using Full Prof software. The refinement of XRD parameters requires that the shapes and intensities of diffraction peaks must be replicated. Rietveld refinement of both the samples was carried by using Fd-3m space group. In order to model a crystal structure with the Rietveld refinement, we have to fit a large number of experimental data with crystallographic parameters. The initial step of refinement was fitting of zero point shift, the unit cell, and background parameters. The background was modeled by using a cosine fourier series and the shape of peaks was defined by pseudo-Voigt functions. The fairly good fitted data is found after performing series of steps of refinement shown in Fig.1 (b). The observed and calculated XRD patterns obtained from the Rietveld refinement shows good agreement by minimizing the difference between them. The magnified patterns of XRD around diffraction angle $2\theta \sim 35^{\circ}$ are represented in the Fig. 1(c). The pattern clearly shows that the main peak of CFO shifts towards the lower diffraction angle signifies the dimension of a unit cell is different from NFO. This is attributed to the larger ionic radii of $Co^{2+}(0.74\text{\AA})$ as compared to $Ni^{2+}(0.69\text{\AA})$. Average crystallite size (D) of both samples are listed in Table 1 and calculated by using Debye-Scherer formula defined as¹³:

$$(3.1.1) D = \frac{k\lambda}{\beta\cos\theta}$$

where, constant k=0.89, β is the broadening of the X-ray diffraction peak measured at half maximum (in radian), λ (1.54 Å) is the X-ray wavelength, D is the diameter of the particle, and θ is the diffraction angle at full width half maxima (FWHM). Refined structural parameters 'a' and the volume of a unit cell, together with the values of a goodness of fit χ^2 , the weighted residual factor R_{wp} and the residual factor R_p are listed in Table1. Rietveld analysis revealed that lattice parameters 'a' and volume of the unit cell of ferrite phase are almost similar to that of cubic Fd-3m phase which attributes that no appreciable phase change takes place in samples. Bond length and bond angle for prepared samples is displayed in Table 2, which revealed very small distortion occurs in the structure of both ferrites. The crystal structures of NFO established by VESTA program with the help of structural parameters generated from the Rietveld refinement are shown in Fig 1 (d). The similar structure is obtained for the other sample.



FIGURE 1: (a) Represents XRD patterns (b) Rietveld refined patterns (c) magnified pattern of XRD around diffraction angle 20~35° (d) 3-dimensional representation of cubic (Fd-3m) structure, obtained for NFO at room temperature.

Samples	Lattice Parameter	Average Size (nm)	R-Factor
		$\mathbf{R_p}\mathbf{R_{wp}} \chi^2$	
	a =8.3363 Å	38	1.82 2.53
NFO	$V = 579.3214 \text{ Å}^3$		3.48
	a =8.3909 Å	35	
CFO	V=590.7808Å ³		1.43 1.88
			2.22

TABLE 1: Refined parameters for prepared samplesNFO and CFO

Samples	Bond distance (Å)	Bond angle (degree)
NFO	Ni1/Fe1 $-$ O = 2.11511	O - Fe1 - O = 88.355,91.645,180
	Ni2/Fe2 - O = 1.75187	O - Fe2 - O = 109.471
CFO	Co1/Fe1 - O = 2.12897 Co2/Fe2 - O = 1.76335	O - Fe1 - O = 88.355,91.645,180 O - Fe2 - O = 109.471
	C02/162 = 0 = 1.70333	0 - 1.62 - 0 - 109.471

TABLE 2: Bond distances and Bond angles for both the samples

3.2. Dielectric analysis

Fig. 2 depicts the frequency dependent behavior of dielectric constant (ε') and dielectric loss (tan δ) for both the samples. It is observed that ε' and dielectric loss (tan δ) of both samples increases with the rise in temperature, which can be ascribed to the rise in thermally activated charge carriers. NFO and CFO both show dispersion at low frequencies which attributes to normal dielectric behavior of these samples. Dielectric constant value is higher at low frequency and decreases continuously with increase in frequency followed by a constant value at higher frequencies. This type of behavior is mainly attributed to the interfacial polarization can be explained by Maxwell-Wagner and Koop's phenomenological theory¹⁴⁻¹⁶. According to these models, the dielectric design of a ferrite is supposed to be comprised of two layers; the first one being a conductive layer (ferrite grains) and the other being the poor conductive layer (grain boundaries). The polarization in ferrite follows the same mechanism as of the conduction process which relies on the synthesis method, chemical composition, cation distribution and crystallite size. The local dislocation of the electrons (electron exchange between Fe^{+2} to Fe^{+3} , Ni^{+2} to Ni^{+3} and Co^{+2} to Co^{+3} ions) in the direction of the applied field is responsible for electrical polarization in ferrites. In addition, Koop's phenomenological theory¹⁶ depicts that at lower frequency grain boundaries are more dominating than grains. Hence acquires a high dielectric constant due to the high resistivity of grain boundary region. While at high frequency, the grains are more effective than grain boundary resulting in a low value of dielectric constant due to the low resistivity of grains. Also, it is found that NFO with large particle size has higher dielectric constant (ε) value. It can be attributed to decrease in grain boundary area with increase in average crystallite size, which behave as a hindrance for domain wall motion results in increase of mean free path of electron and hence increases dielectric constant.

Fig. 2 (insets) show the variation of dielectric losses $(\tan \delta)$ with frequency. Tan δ shows similar dispersion behavior as that of dielectric constant (ε '). The dielectric loss originates due to the polarization lags behind the applied alternating field and its reason is mainly imperfection and impurities in the crystal lattice. It is observed from the plots, dielectric loss (tan δ) of NFO shows anomalous behavior followed with a relaxation peak. This peak is observed in the dielectric loss when the hopping rate of electrons between Fe²⁺ and Fe³⁺ are approximately in resonance with the frequency of applied field. So, the maximum electric energy is transmitted to the electrons and therefore the losses enhance at resonance¹⁷.

Fig. 2(b) represents the temperature dependent behavior of dielectric constant at different frequencies. Dielectric analysis revealed that ε 'increase with the increase in temperature acquiring maxima, followed by a consequent decrease in dielectric values with further increase in temperature. One can see from the plots, that at low frequencies the increment in dielectric constant (ε) is more prominent than at the higher ones as temperature increases. In general, dielectric constant results of the contribution of dipolar, electronic, interfacial and ionic polarization. High value ε' at low frequency is attributed to significant contribution comes from the interfacial and dipolar polarization, while interfacial polarizability has no impact on dielectric response at high frequency^{18,19}. At lower frequencies, a hump is observed at the higher temperature which is attributed to an accumulation of the space charges at the interface provided by the ferrite phase on the application of electric field. The pile up of space charges contributes to polarization and consequently enhances the dielectric constant. As long as the dependence of dielectric constant on frequency is concerned, the ε' declines with rise in frequency, representing a normal and relax or behavior²⁰.



Figure 2: (a) Variation of dielectric constant (ε') and (inset) dielectric loss (tan δ) with frequency for both samples at different temperatures, (b) Variation of dielectric constant (ε') with temperature for both samples at various frequencies.

3.3 Complex impedance analysis

Fig.3 depicts Nyquist plots (Z" vs. Z') obtained for both the samples. Impedance spectroscopy can be used to examine the impact of grains and grain boundaries in ferrites^[21]. In general, it is observed that Nyquist plot is composed of two semicircles. Semicircle at lower frequency represents the grain boundary effect and at higher frequency represents the grains. The two semicircle arc in the Nyquist plot of NFO confirmed the simultaneous contribution of grain boundaries and grains while single semicircle observed for CFO signifying the grain contribution is more prominent. The radius of the semicircle arc relies on the morphology and grain size of the spinel ferrite. The radius of the semicircle at a lower frequency was smaller than at higher ones, thus indicating the grainboundary contributionis more prominentfor NFO. The appearance of two semicircular peaks signifies two types of relaxation phenomena with different relaxation times. It is demonstrated from impedance analysis that the radius of the semicircles shows decreasing patterns with the increase in temperature. It reveals that the resistivity decreases with increase in temperature supporting the typical negative temperature coefficient of resistance behavior of both the samples.



Figure 3: Nyquist plots for both the samples at different temperatures.

3.4 Magnetic Analysis

Fig.4 depicts the behavior of magnetization (M) with varying magnetic field (H) upto 6kOe at room temperature. Hysteresis loop show saturation above 1kOe and 2kOe for NFO and CFO respectively, demonstrating room temperature ferromagnetism of ferrites. The values of saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_c) is observed from hysteresis curve are summarized in Table 3.

The value of saturation magnetization (M_s) for NFO and CFO is 37.48emu/g and 65.54emu/g. It is found that saturation magnetization is larger for CFO (with smaller crystallite size). However, the enhancement in the saturation magnetization can also be illuminated based on the A-B super exchange interaction between A-site (tetrahedral) and B-site (octahedral) sub-lattices. The difference in the magnetization of B and A-sites gives net magnetization of the spinel ferrites and it is also found that the B-site (octahedral) has larger magnetic moment than the A-site (tetrahedral). The magnetic moment per formula unit can be calculated by using relation²²:

(3.4.1)
$$\eta = \frac{M_s \times M_w}{N_A \times \mu_B}$$

where, M_s is saturation magnetization, M_w is molecular weight and value of a product ($N_A \times \mu_B$) is 5584.86. The calculated values for the magnetic moment are listed in Table 3, which specifies that the magnetic moment increased as the crystallite size decreased. This increment in magneton number is attributing to the strong A-B interaction occurs in CFO. The value of coercivity (H_c) increases with the decrease in crystallite size. It may ascribe that the surface anisotropy arises with decrease in crystallite size because of more surface spins disorder, which can enhance the coercivity²³. The lower value of coercivity (H_c) signifies the easy-magnetization characteristic of these samples. Similar results were also reported earlier by other researchers²⁴⁻²⁶.



Figure 4: M-H hysteresis loop for both the samples.

Table 3: Saturation magnetization (M_s), remanent magnetization (M_r), coercivity (H_c) andmagnetic moment per formula unit (η) for both the samples.

Samples	M _s (emu/g)	Mr(emu/g)	H _c (Oe)	$\eta(\mu_B)$
NFO	37.48	7.34	122.60	1.57
CFO	65.56	18.60	317.30	2.75

4. Conclusion

In summary, the spinel ferrite NFO and CFO have been prepared by conventional solid-state reaction method. XRD analysis follows with Rietveld refinement confirmed the existence of single-phase cubic spinel symmetry with space group Fd-3m for both the samples. Average crystallite size of these ferrites also determined from Debye-Scherer formula. The dielectric constant and dielectric loss exhibit normal dispersion behavior of samples which can be described by Maxwell–Wagner polarization and Koop's phenomenological theory. It is found that the dielectric constant and dielectric loss (tan δ) increase with the increase in temperature followed by relaxation peak which is due to hopping rate of electrons between Fe²⁺/Fe³⁺ are almost in resonance with the frequency of applied electric field. The complex impedance analysis revealed the existence of two and one semicircular arcs for NFO and CFO respectively, which represents influence of grain and grain boundary on resistivity. Magnetic analysis revealed that saturation magnetization (M_s) and coercivity (H_c)changes with change in the crystallite size, which indicates that magnetic properties can be controlled by adjusting crystallite size.

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