Morphological, Electrical And Dielectric Characterization Of Aluminum Substituted Nickel Spinel Nanoferrite.

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ABSTRACT:

An attempt has been made to synthesize aluminium substituted nickel nanoferrite by microwave assisted sol-gel auto combustion method with generic chemical formula $Ni_{1-x}Al_xFe_{2-y}O_4$ (x=0, y=0 & x=0, y=0.5). The synthesized samples were characterized by XRD . The X-ray diffraction analysis confirms the single phase formation with cubic structure. The XRD studies revealed that the lattice parameter (a), the particle size (D), X-ray density (ρx) decreases with Al substitution. Electrical characterisation as conductivity is measured by four probe precision impedance analyser (6500 B). Electrical conduction in ferrite can be explained by Verway hoping mechanism of electron. The dielectric properties of the ferrite samples have been measured with different temperature at constant frequency of 100 Hz. The result confined the variation of dielectric constant increases with increase in temperature along with calculation explained with Maxwell interface polarization in accordance with Koop's phenomenological model.

Keywords: sol-gel method, XRD, electrical conductivity, dielectric constant, etc.

1. Introduction

Nanocrystalline ferrites, specially spinel ferrites have been under intense research due to their novel properties and technological applications [1]. Amongest spinel ferrites, nickel ferrite is found to be most versatile material because of their unique electric, dielectric, magnetic and optical properties which makes them suitable for many applications like microwave devices, transformers, electric generators, storage devices [2]. Substituted nickel ferrite have wide applications as a magnetic material due to their high electrical resistivity, low eddy current and dielectric losses [3,4].The electrical conductivity and dielectric behaviour in ferrites depend upon several factors viz. methods of preparation, type and stiochometric concentration of substitution and sintering and calcinations temperature [5].

The electric and dielectric properties of $NiFe_2O_4$ and substituted NiFe2O4 have been studied by several investigators. Among them G. Arvind et al (2014) [6] have studied variation of electrical conductivity and dielectric constant with temperature of Li- Ni nanoferrite. Gillard and Bertrand (1950) [7] have studied the resistivity of nickel ferrite as a function of temperature. Uitert(1956) [8] has studied the effect of minor additions of manganese or cobalt on high resistivity of nickel ferrous ferrite

above 300 K. S.C. Choudhari et al(2013) [9]. have reported the electrical resistivity, dielectric behaviour and thermoelectric power as a function of temperature of Cr substituted $NiFe_2O_4$ on the basis of polarisation mechanism . The influence of sintering temperature on the dielectric constant of $NiFe_2O_4$ synthesised from nano size powder of NiO and Fe_2O_3 has been reported by Shamina Choudhary et al(2012) [10]. The electrical conductivity and dielectric measurement have been performed for nano crystalline $NiFe_2O_4$ spinel for four different average grain size ranging from 8nm to 97 nm by N. Panpandian et al(2002) [11]. It was pointed out that the conduction mechanism is found to be due to hoping of both electrons and holes. The dielectric properties and ac conductivity of Al doped Ni-Cd nano ferrite have been investigated and explained by Khalid Mujasam Batoo et al(2009) [12] on the basis of space charge polarisation according to Maxwell-Wagner model and Koop's phenomenological theory.

The present work deals with the synthesis of Al substituted Nickel ferrite via Sol-Gel Auto combustion method and investigation of their X-ray diffraction electrical and dielectric properties.

2. Experimental

2.1 Synthesis Technique: Nanoparticles of $Ni_{1-x}Al_yFe_{2-y}O_4$ (x=0, y=0 & x=0, y=0.5) have been synthesised by sol- gel auto combustion method. The Stoichiometric amount of AR grade nickel nitrate $Ni(NO_3)_2.6H_2O$ iron nitrate $Fe(NO_3)_2.9H_2O$ aluminium nitrate $Al(NO_3)_2.9\ H_2O$ were used while urea was used as fuel. The mixture of metal nitrate was dissolved in distilled water. The solutions as prepared were mixed together to form a homogeneous transparent aqueous solution. The aqueous solution was then heated and continued stirred on the magnetic strirrer at 60^0C, till aqueous solution get converted into wet gel by evaporating the water. Further, the wet gel fired in a specially designed microwave oven, to get the resultant ash powder. The ashes of raw substances obtained were grinded in a pestle mortar for 4 hrs. Finally these samples were annealed at 800^0C for several hours at a heating rate of 100^0 C/hr to get desired nano powder.

2.2 X-ray Diffraction Studies: The structural characterization of the synthesized sampleswas carried out by Philips X-ray diffractometer (Model 3710) using Cu K_α radiation of wavelength λ=1.54 ˚A at room temperature. The average crystalline size of the ferrites was determined from the most intense peak(311) pattern using Debye Scherer›s formula,

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

Where ,β is the full width half maximum (FWHM) in radians and θ is the Bragg's angle for the actual peak.

Being cubic spinel, the lattice parameter (a) for the samples were calculated using the formula: $d = \frac{a}{\sqrt{h^2+k^2+l^2}}$ (2)

Where, d_{hkl} is the inter-planner spacing, a is lattice parameters. h k l are the Miller indices of the crystal planes.

The cell volume (V) were calculated from following equation using XRD data

$V = a^3$ (3)

The X-ray density (ρx-ray),bulk density (ρm) and porosity (P) were also calculated using following formulae, $\rho_{x\text{-}ray} = \frac{ZM}{NV}$ (4)

$$\rho_m = \frac{m}{(\pi r^2)h} \quad (5)$$

$$P = 1 - \frac{\rho_m}{\rho_{x-ray}} \quad (6)$$

Where Z is the number of formula units in a unit cell which is 8 for spinel ferrite, M is the molecular mass of the sample, N is the Avogadro's number, m is the mass of the pellet, r is the radius of the pellet and h is the height of pallet.

2.3 Electric and Dielectric measurements : The electrical conductivity of samples is measured at various temperatures for studying their electrical behavior. The conductivity is measured by taking sample in the pellet form, and by applying d.c. voltage across the pellet in four probe Impedance Analyzer at the frequency of 100 Hz. The temperature dependence of the prepared ferrites conductivity is plotted in accordances with the following Arrhenius type equation:

$\log\sigma = \log\sigma_0 - \frac{E_a}{K_B T}$ (7)

where σ is the conductivity, σ_0 is the conductivity at absolute temperature, K_B is Boltzman's constant, and T is the temperature.

The dielectric constant (ε') of prepared sample was calculated using the following relation: $\varepsilon' = \frac{cd}{\varepsilon_0 A}$ (9)

where, c is the capacitance, d is the thickness of sample, A is the cross section area and ε_0 is the free space permittivity.

3. Results And Discussions

3.1. XRD Analysis: The X-ray diffraction patterns of the samples were shown in **Figure 1.** The XRD pattern analyzed using X- Powder software and the crystalline phases were identified by comparison with reference data from the JCPDS card No. 520278 for Nickel ferrites ($NiFe_2O_4$). The XRD patterns showed a single phased cubic spinel belonging to the space group Fd3m. All the Braggs reflections were indexed, which confirmed the formation of a well defined single phase cubic spinel structure without any impurity peaks. All the peaks are allowed peaks. The strongest reflection has come from (311) plane that indicates spinel phase. The diffraction peaks can be indexed to the planes of (111),(2 2 0), (311), (222), (400), (400), (242), (333), (533) ,(226) and (4 40). The observed broadening of diffraction peaks indicates the nano crystallinity of the samples. The particle size of the synthesized ferrite samples has been calculated from the most intense peak corresponding to (311) using the classical Scherrer formula [13]. The values of the particle size, lattice constant, X-ray density, measured density deduced from the X-ray data are given in **Table 1**

It was found that the lattice constant decreases with Al substitution. The decrease in the value of the lattice constant with Al ion substitution can be explained on the basis of ionic radii. As the larger Fe^{3+} ions (0.67 Å) are replaced by smaller Al^{3+} ion (0.51 Å) the lattice parameter decreases. X-ray density decreases with Al substitution and this is attributed due to decrease in lattice constant and particle size.Similar trend were reported by Ahmad et al.(2013) [14] and S. S. Suryawanshi et al.(1999) [15].

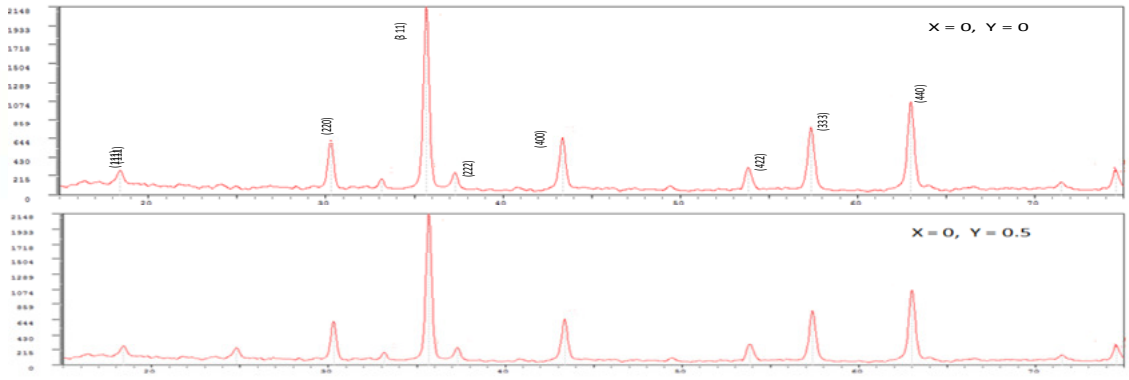

Figure 1: X-ray diffraction pattern of $Ni_{1-x}Al_xFe_{2-y}O_4$ (x=0, y=0 & x=0, y=0.5)

Table 2: XRD parameters of $Ni_{1-x}Al_xFe_{2-y}O_4$ (x=0, y=0 & x=0, y=0.5)

Sr. No.	Compound	Lattice Parameters a (Å)	Cell Volume (Å)^3	Bulk Density (D) gm/cm^3	X-Ray Density (Dx) gm/ cm^3	Porosity (%)	Particle Size (nm)
1.	$Ni\,Fe_2\,O_4$	8.3366 A^0	579.38	2.7349	5.3740	49.1	28.49
2.	$Ni\,Al_{0.5}\,Fe_{1.5}\,O_4$	8.2487 A^0	561.25	2.4995	5.206	51.99	11.85

3.2 Electrical properties: Figure 2 shows the variation of electrical conductivity (log σ) with inverse of temperature (1000/T)..The conductivity of the ferrite samples increases with increasing the temperature. That is, temperature increases and resistivity of the ferrites decreases, indicating the semiconducting behaviour. From the figure, it is clear that the plots yield a change in slope at a particular temperature. This change in slope occurs while crossing the Curie temperature (the temperature at which the ferromagnetic material changed to paramagnetic). The discontinuity at the Curie temperature was attributed to the magnetic transition from well-ordered ferromagnetic state to disordered paramagnetic state which involves different activation energies. The activation energies of the prepared samples at ferromagnetic region and paramagnetic region were given in **Table 2**. It is observed that the activation energy in the ferromagnetic region is smaller than the paramagnetic region; this is due to the effect of spin disordering. The electrical conductivity of ferrites can be explained on the basis of the Verwey hopping mechanism [16] which involves the exchange of charge carriers, that is, electrons between the ions of the same element that are present in more than one valence state (Fe^{+2}, Fe^{+3}), distributed randomly over the crystallographic lattice sites.

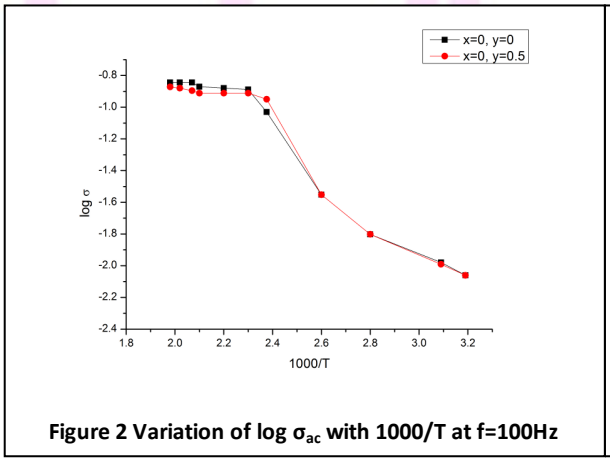

Figure 2 Variation of log σ_{ac} with 1000/T at f=100Hz

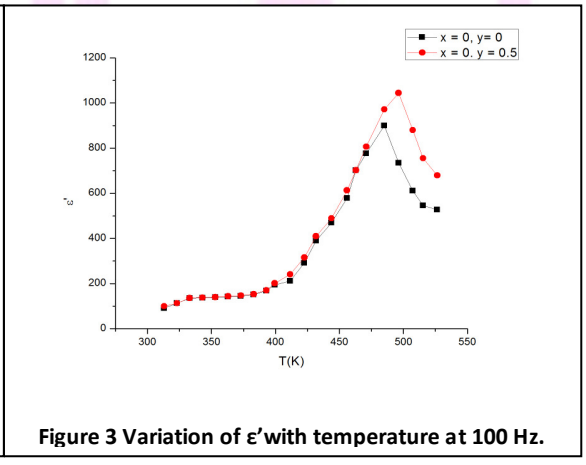

Figure 3 Variation of ε'with temperature at 100 Hz.

Table 5: Transition Temperature for synthesized compounds

Sr. No	Compound	X	Activation Energy ΔE (eV)		Transition Temperature [T_t] [K]
			Ferromagnetic	Paramagnetic	
1)	$NiFe_2O_4$	0	0.225	0.583	473
2)	$NiAl_{0.5}Fe_{1.5}O_4$	0.5	0.255	0.292	450

3.2 Dielectrical properties

The variation of dielectric constant (ε') at 100 MHz with temperature is shown in **figure 3**. It can be seen that, the dielectric constant increases gradually with increase in temperature. The variation of ε' with temperature reveals the dispersion due to Maxwell (1936) [17] and Wagner (1993) [18] type interfacial polarisation which in agreement with Koop's phenomenological theory (1951) [19]. According to Rabinkin and Novikova [20] the polarisation in ferrite is through mechanism similar to conduction process. By electron exchange between Fe^{+2} and Fe^{+3}, the local displacement of electrons in the direction of the applied field occurs and these electrons determine the polarisation. It is evident that by increasing the temperature, the dielectric constant increases up to a certain temperature designated as dielectric transition temperature (T_d). However beyond this temperature the values of dielectric constant were found to decrease continuously. The similar temperature variation has been reported by G.Arvind et al(1960)[6].The behaviour of dielectric constant with temperature can be explained as follows: as the temperature increases the charge carriers get thermal energy for hopping between Fe^{+2} and Fe^{+3} on the octahedral sites. This electron hopping causes local displacement in the direction of applied field increasing dielectric polarisation and dielectric constant. However beyond dielectric transition temperature the electrons and the ions are less oriented towards the external field and hence the dielectric constant decreases.

Conclusion

We have successfully synthesized the ferrite phase $Ni_{1-x}Al_yFe_{2-y}O_4$ (x=0, y=0 & x=0, y= 0.5) nano particles, through sol–gel auto-combustion technique. The XRD studies confirms that sample exhibit the spinel structure. It is observed that lattice parameter decreases with the Al doping, which is explained on the basis of smaller ionic radii of the Al^{3+} ion than the Fe^{3+} ion. The temperature variation of electrical conductivity of the synthesised samples exhibiting the semiconducting nature and shows the definite break, which corresponds to ferromagnetic –paramagnetic transition. The activation energy in ferromagnetic region is less than in

paramagnetic region. The dielectric constant increase with increase of temperature and afterword decreases. This is explained in the light of electron hopping mechanism and space charge polarization discussed by Maxwell–Wagner model and Koop's phenomenological theory.

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