Investigations on Transition Metal Doped Pure Ferrite Nanoparticles

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***Abstract*— $FeCr_{0.2}Fe_{1.8}O_4$ nano-particles were synthesized by chemical co precipitation method. The developed particles were characterized by powder X-ray diffraction technique for crystalline properties. The diffraction peaks shows the single crystalline phase of the developed spinel ferrite particles. Effect of Cr^{3+} ion doping on dielectric properties was studied as a function of frequency in the range 100Hz-5MHz, using impedance analyzer. Electrical conductivity was found to increase with doping of Cr^{3+} ions. Activation energy found to decrease with Cr^{3+} ion doping. An exponential increase in ac conductivity was observed with increase in frequency. Increase in conductivity was explained on the basis of Maxwell-Wagner two layer model. Conductivity was found to increase with temperature. The developed particles were further utilized for ferrofluid preparation.**

***Index Terms*—Structural parameters; Electrical resistivity; activation energy; Dielectric parameters.**

I. INTRODUCTION

Much increasing interest of nanoparticle ferrites is the discovery of their unusual properties such as structural, electronic, optical and magnetic when their microstructure is reduced to nano region [1]. Polycrystalline ferrites are supposed to be very good dielectric material with high resistivity and vide range of technical applications in wide frequency range. As nanoparticle size, shape, crystallnity, particle size distribution play important role on physical, chemical, electrical properties of particles [2]. The properties and size of nanoparticle are very sensitive to preparation technique [3]. The spinel nanoparticle ferrites have been synthesized by various techniques [4-6]. The distribution of cations over tetrahedral and octahedral sites in ferrites has remarkable effect on electrical and magnetic properties [7]. In present report to investigate the effect of transition metal(Cr^{3+}) doping on structural and electrical properties in nano dimension we have synthesized nanoparticle $FeCr_{0.2}Fe_{1.8}O_4$ via chemical co-precipitation method using oleic acid as surfactant. Reduction in agglomeration of particles was observed when nanoparticles were caped with oleic acid [8].Results of investigation were analyzed in terms of crystalline size, X-ray density(ρ_x), measured density, effect of temperature and frequency on dielectric parameters of ferrite sample.Experimental

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Transition metal (Cr^{3+}) doped ferrite nano particle $FeCr_{0.2}Fe_{1.8}O_4$ were prepared by Chemical Co-precipitation method, Analytical grade chemical reagents used in this work were Ferrous chloride $FeCl_2$ and Ferric nitrate $Fe(NO_3)_3.9H_2O$ and $Cr(NO_3)_3.9H_2O$.0.25M aqueous solution of all the reagents in specific amount were mixed using stirring. The reaction temperature was kept 70°C for approximately 40 min. The precipitated reagent ammonia (NH_3) was mixed to homogeneous aqueous solution with constant stirring A specific amount of oleic acid in 1:2 ratio as a surfactant was added to prevent agglormation of precipitated particles and to protect from atmospheric oxygen. The PH of reaction temperature was constantly monitored and was achieved at 7.5.The precipitated particles were repeatedly washed with distilled water until the solution was free from Nitrate and Chloride ions. The product was dried in air at 100°C to remove water contents. The dried powder mixed homogeneously in cleaned mortar and pestle. The prepared material was analyzed for crystalline phase, various structural and physical properties using XRD. XRD pattern was taken at room temperature using Cuk_α (λ=1.54060A°) radiation in 2Θ range 20°-70°.Crystalline size (D) of synthesized particle was calculated using Scherrer formula [9].

$D=K\lambda/\beta Cos\Theta$ 1)

Here K is Scherrer constant, λ is X-ray wavelength, β is full width at half maximum and Θ is diffraction angle. Lattice constant (a), X-ray density (ρ_x), measured density (ρ_m), porosity (P), specific surface area(S) [16-17] were estimated using following relations

$a=d/sqrt\ (h^2+k^2+l^2)$ in Å 2)

Where d is interlplaner spacing

$\rho_x=8M/Na^3$ in gm/cm^2 3)

Where M is molecular weight of sample, N is Avogadro's number

$\rho_m=m/\Pi r^2h$ in gm/cm^2 4)

Where m is mass, r is radius, h is height of sample.

$P=1-(\rho_{m/}\rho_x)$ 5)

The fine powder was palletized in form of a pellet of 13mm in dia. and thickness (t) =2.628mm under a pressure of 37.5N/m^2 for 5min.using hydraulic press .Then pallet was used for the measurement of various dielectric parameters using impedance analyzer in frequency range from 100Hz to 5MHz.The real (ε′) and imaginary part (ε″) of dielectric constant, dielectric loss tangent (tanδ) and ac conductivity (σ_{ac}) were calculated using following standard relations.

$\varepsilon'=Ct/\varepsilon_0A$ 7)

$\varepsilon'' = \varepsilon' \tan\delta$ 8)

$\sigma_{ac} = \varepsilon' \varepsilon_0 2\Pi f \tan\delta$ 9)

Where C is capacitance in farad (F)
A is X-sectional area of pallet in m^2
ε_0 is constant of permittivity in free space, 8.85×10^{-14} Fcm^{-1}
f is frequency of applied field in Hz

II. RESULTS AND DISCUSSION

A. *XRD Analysis*

Fig.1 shows the X-ray diffraction pattern of the prepared ferrite sample .Analysis of XRD diffraction pattern shows strong diffraction from the (220), (311), (400), (422), (511) and (440) planes confirm the formation of cubic spinel structure of ferrite sample. The average crystalline size (D) of ferrite is calculated using Scherrer formula using most intense peak, i.e., (311) .The average crystalline size comes out to be 16.54nm.

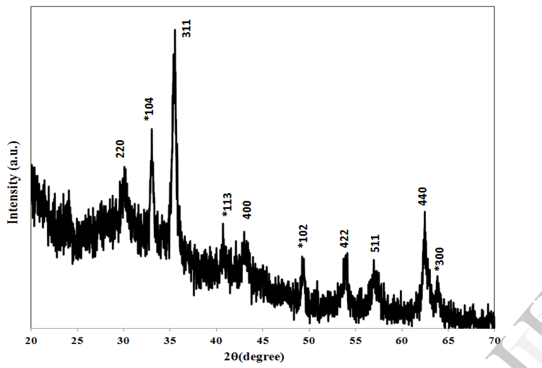

Fig.1 XRD pattern of $FeCr_{0.2}Fe_{1.8}O_4$ sample at room temperature.

B. *Dielectric Analysis*

Fig.2 shows frequency dependence of real part of dielectric constant (ε′) at different temperatures. Analysis shows that there is decrease in dielectric constant (ε′) with increase in frequency and there is increase in dielectric constant (ε′) with increase in temperature. It is being observed that, this increase is quite significant at lower frequencies and as frequency increases this increase in dielectric constant(ε′) becomes quite insignificant. At higher frequency electron exchange between Fe^{2+}/Fe^{3+} ions cannt follow with applied alternating electric field, which causes a decrease in contribution of space charge polarization in dielectric constant and we observe a decrease in dielectric constant .The sharp decrease in ε′with increase in frequency can also be explained on the basis of Maxwell-Wagner two layer model , according to which ferrite are consisted of well conducting grains followed by thin layer of poorly conducting grain boundaries [10]. The decrease in dielectric constant with increase in frequency is normal dielectric behavior was observed by several investigators [11-13] and was explained by Rezlescu and Rezlescu [14].This increase in dielectric constant with temperature could be because of increase in drift mobility of charge carriers as electron hoping between ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions present at octahedral site is thermally enhanced by increasing temperature which causes local displacement of charge carriers in the direction of applied electric field which in turn enhance their contribution to the space charge polarization .This ,in turn, lead to increase in the value of dielectric constant(ε′) [15]. It is known that dielectric constant of ferrite materials is due to interfacial, dipolar(alignment of permanent dipoles molecules), electronic(due to displacement of centre of negatively charged electron cloud relative to positive nucleus of atom by electric field) and ionic polarization(due to displacement of cations and anions in opposite direction when electric field is applied) [16] .Dipolar and interfacial polarization play dominant role at lower frequencies and both are temperature dependent . At higher frequencies electronic and ionic polarization are main contributors and both these does not depend upon significantly upon temperature[17].So significant increase in dielectric constant with temperature at lower frequencies arises from the combined effect of dipolar and interfacial polarization. At high frequencies dielectric constant (ε′) is almost constant due the dominant effect of ionic and electronic polarization.

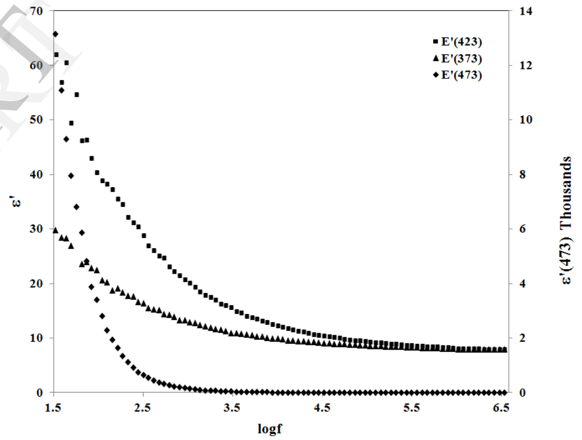

Fig. 2 Frequency dependence of Dielectric constant(ε′) at different temperatures i.e 373K,423K,473K.

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Fig.3 shows variation of dielectric loss tangent (tanδ) with frequency at different temperature. The dielectric loss arises when polarization lags behind applied ac electric field .Fig shows that the dielectric loss decreases rapidly in low frequency region because at lower frequencies due to high resistivity of grain boundaries, more energy is required for electron exchange between the Ferrous and ferric ions at octahedral site as a result of which loss is high [18].While it becomes almost frequency independent at higher frequencies because at higher frequencies jumping frequency of ions can not follow applied electric field. Also there is increase in dielectric loss with increase in temperature due to the increased conduction of thermally activated electrons.

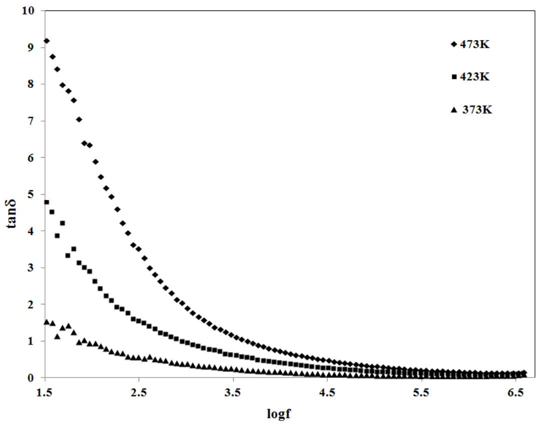

Fig.3 Frequency dependence of dielectric loss tangent(tanδ) at different temperature i.e 373K,423K,473K.

C. *Conduction mechanism*

The total conductivity can be approximated as

$$\sigma(\omega, T)=\sigma_{dc}(T) + \sigma_{ac}(\omega, T) = \sigma_{dc}(T) + A(T)\omega^{s(T)} \qquad 10)$$

Here σ_{dc} is temperature dependent dc conductivity and σ_{ac} is temperature and frequency dependent ac conductivity.A(T) is temperature dependent term and s(T) is universal power law exponent value lying in the range from 0 to 1. Fig.4 shows variation of log(σ) with frequency at different temperature. Conductivity increases with temperature which is due to increased hopping of thermally activated charge carriers. Variation shows that total conductivity almost remains constant in lower frequency region and shows dispersion for higher frequency which is in accordance with eq.(10).

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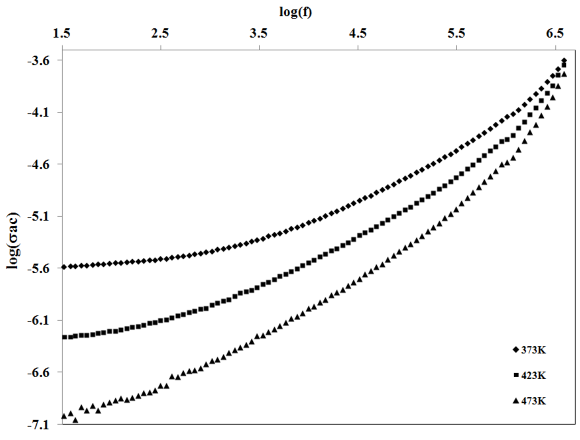

Fig.4 Frequency dependence of ac conductivity(σ_{ac}) at different temperature i.e 373K,423K,473K.

It is being observed from plot that with increase in temperature this dispersion in frequency shifts towards higher frequency. In the low frequency region, grain boundaries are more effective with high resistance due to which we obtain constant plateau region (σ_{dc}). At higher frequencies, the increase in conductivity is due to increased hoping of charge carriers (ferrous and ferric) at octahedral site and also due to grain effect [19]. s(T) universal power law exponent is being calculated from the variation of logσ_{ac} with logw at different temperatures which shows decreasing behavior with increasing temperature which is in accordance with CBH(correlated barrier hopping)model .

D.C electrical conductivity of transition metal doped ferrite system was recorded as a function of temperature is shown in fig.5. From graph it is being observed that σ_{dc}(D.C. electrical conductivity) increases with increase in temperature which revels the semiconducting nature of ferrite sample. The plot shows an Arrhenius-type temperature dependence i.e. $\sigma = \sigma_o \exp(-\Delta E/k_B T)$, where ΔE is activation energy, k_B is Boltzmann constant and T is absolute temperature. Activation energy (ΔE) was calculated from slope of 1000/T vs log σ_{dc} in two different temperature ranges. ΔE =0.42 in temperature range 333K- 503K and ΔE =2.34 in temperature range 568K-618K. In most ferrite samples, a straight line is found in these plots in a wide temperature range but in this ferrite sample a change in slope is being observed which points to two parallel conductivity mechanism with different activation energies.

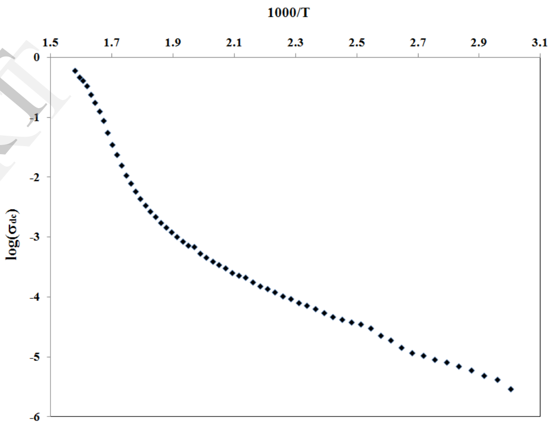

Fig.5 Arrhenius plot for dc conductivity.

III. CONCLUSION

Transition metal doped $FeCr_{0.2}Fe_{1.8}O_4$ nanoparticles were successfully synthesized using chemical co-precipitation technique. XRD pattern confirm the formation of spinel structure of prepared sample. Dielectric constant(ε′) increases with increase in temperature and decreases with increase in frequency of applied field which shows significant increase with temperature at low frequencies and becomes approximately temperature independent at higher frequencies. Dielectric loss tangent (tanδ) decreases with increase in frequency which shows fast decrease at low frequency and becomes approximately frequency independent at higher frequencies because at higher frequencies hoping of electron between Ferrous and ferric ions could not synchronize with applied electric field. AC conductivity increases with increase in frequency and temperature.

Table 1: Table showing crystalline properties viz. crystalline size (D(311)), lattice constant (a), lattice volume (V), X-ray density (ρ_x), measured density (ρ_m), porosity (P), and electrical properties viz. electrical resistivity (ρ_{dc}), activation energy (ΔE), and dielectric constant (ε'), universal power law exponent s(T), relaxation time ($\Gamma_{M''}$).

Crystalline properties		**Electrical properties**	
Quantity	**Value**	**Quantity**	**Value**
D_{311}	16.54nm	ΔE	0.42(eV)
A	8.36(Å)	ρ_{dc} at 373k	$8.4*10^4$(Ωm)
V	583.83 $(Å)^3$	s (373K)	0.68
ρ_x	5.249 (g/cm^2)	s (473K)	0.46
ρ_m	1.43 (g/cm^2)	$\Gamma_{M''}$ (373K)	$2.3*10^{-4}$ sec.
P	0.73 (fraction)	$\Gamma_{M''}$ (473K)	$1.0*10^{-5}$ sec.

Conductivity is approximately constant in lower frequency region and shows dispersion at higher frequency region. Calculated values of s(T) universal power law exponent shows decreasing behavior with increasing temperature which is in accordance with CBH(correlated barrier hopping)model. Relaxation time($\Gamma_{M''}$) decreases with increase in temperature which ensure the increase in conductivity with increase in temperature.

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