# Effect of grain size on Neél temperature, magnetic and electrical properties of NiFe<sub>2</sub>O<sub>4</sub> nanoparticle synthesized by chemical co-precipitation technique

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### ABSTRACT

Nanocrystalline nickel ferrite has been prepared by chemical co-precipitation technique. X-ray diffraction patterns of as-dried and samples calcined at various temperatures have been studied. It has been observed that the sample in the as-dried condition is fully single phase and no extra peak could be observed in XRD patterns. The grain size has been obtained from Scherrer's formula and found as 7 nm in the as-dried condition. When the samples were calcined at higher temperatures subsequent grain growth has taken place. Samples calcined at 600°C led to the grain size as 16 nm. Further calcinations at 1200°C led to the grain size above 50 nm. Frequency dependence of real and imaginary part of initial permeability has been presented for the samples calcined at different temperatures. At lower firing temperatures i.e. when the grain sizes are smaller, the Neél temperature is lower. The coercivity of the samples in the as-prepared condition is almost zero, which is suggestive of superparamgnetic behavior at room temperature. Temperature and frequency dependence of resistivity and dielectric constant have been measured for the samples sintered at 1000-1350°C. Dispersion in the dielectric constants was exhibited by all the samples in the studied frequency range.

*Keywords:* Nickel Ferrite, superparamagnetism, coercivity, permeability, Neél temperature

## **1 INTRODUCTION**

Ultrafine particles of nanometer dimensions located in the transition region between molecules and microscopic structures have revolutionized the recent advances in biology, physics, and chemistry. For biomedical applications the use of particles, which does not have any remanance with the withdrawal of applied field and possess superparamagnetic behavior at room temperature is being increasingly introduced [1,2]. NiFe<sub>2</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles is well known for their better biocompatibility and successful self-heating temperature rising characteristics. Furthermore, applications in biology and medical diagnosis and therapy require the magnetic particles to be stable in water at neutral pH and physiological salinity. The colloidal stability of this fluid will depend first, on the dimensions of the particles, which should be sufficiently small so that precipitation due to gravitation forces can be avoided. The main reason for considering NiFe<sub>2</sub>O<sub>4</sub> nanoparticles as a hyperthermia agent is that these are expected to have urgently required magnetic properties for hyperthermia such as soft magnetism and small magnetic degradation at high frequency.

The exchange interaction in spinel ferrites where the antiparallel alignment of magnetic moments of A-site with B-site is mediated by oxygen ions is called superexchange interaction. The strength of the antiparallel coupling between the metal ions depends on the A-O-B bond angle with the strength being the maximum for an angle of 180°. The superexchange interaction is quite significant in ferrites due to the presence of metal ions in the A- and B- sites. Interesting magnetic properties such as magnetization, Curie temperature etc. of various ferrites have been observed to depend on the superexchange interaction strength, which is determined by the site occupancies of metal ions in the A- and B- sites. The size-dependent magnetic properties of ferrites have been investigated by many researchers for particles sizes less than 25 nm where the saturation magnetization decreases with particle size reduction due to surface spin effects. The much reduced M<sub>s</sub> in the nano-particle sample implies that outside a core of ordered moments, those on the surface layers are in a state of frozen disorder [3].

At lower firing temperatures i.e. when the grain sizes are smaller, the Neél temperature is lower. The decrease in Neél temperature with grain size can be explained on the basis of the finite size scaling theory. The finite size effect is predominant when the grain sizes are very small which results in a decrease in Neél temperature with grain size reduction. The small particles have a significant fraction of atoms on the surface and their exchange interaction should be weaker because of the lower coordination. They will have a reduced average Neél temperature compared to that of the interior atoms, which accounts for the decrease in Neél temperature at lower sintering temperature [3]. Real part of initial permeability, increases with the increase of grain growth. When the grain size is smaller the permeability is lower. The presence of small grain size interferes with wall motion, which decreases permeability and increases the stability region of real part of initial permeability. At higher frequencies, loss component of permeability are found to be lower if domain wall motion is inhibited and the magnetization is forced to change by rotation.

The purpose of the present study is to synthesize  $NiFe_2O_4$ nanoparticle by chemical co-precipitation technique and then sintered at various temperature to avail a wide spectrum of particle size for different application starting from particle size, which will be below 10 nm and thus opens a possibility to work with hyperthermia and targeted drug delivery up to the samples sintered at high temperature for conventional ferromagnetic applications.

### 2 EXPERIMENTALS

We have used a standard co-precipitation technique to produce fine particles of NiFe<sub>2</sub>O<sub>4</sub>. The analytical grade of Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O were mixed in required molar ratio and added to 6M NaOH solution with constant stirring at room temperature. The mixture was heated to 80°C with constant stirring. When the reaction was completed the precipitate was filtered and washed 10 times with distilled water. Finally, the precipitate was collected and heated at 90°C for 36 hours. X-ray diffraction patterns of as-dried powder yielded single phase ferrite. The powder was given the shape of pellets and sintered at various temperatures in the range of 200-1350°C. Curie temperature has been measured by using impedance analyzer and laboratory built furnace. Microstructure has been studied using Scanning Electron microscope. Magnetization measurements have been accomplished by VSM.

### **3** RESULTS AND DISCUSSION

In Fig. 1, X-ray diffraction patterns of as-dried and samples calcined at different temperatures in the range of 200-1350°C have been presented. In the as-dried condition single phase NiFe<sub>2</sub>O<sub>4</sub> has formed with no extra peak. With the increase of sintering temperature peak width decreases which reflects the coarsening of particles. The size of the particles has been determined using Scherrer's formula from the FWHM of 311 peak and presented in Fig. 2. In the as-prepared condition, the grain size has been obtained as 7 nm. The grain size increases nonlinearly with the increase of sintering temperature. Lattice parameter presented in Fig. 3, is slightly higher than the conventional value which increases with sintering temperature. The increase in lattice parameter could be due to the deviation in cation distribution from the inverse spinel structure of NiFe<sub>2</sub>O<sub>4</sub>[1].



Figure 1. X-ray diffraction patterns of the as-dried and samples annealed at different temperatures.

In Fig. 4, microstructure of the as-dried and samples sintered at 1200, 1250 and 1350° C has been presented with magnification of  $\times 15000$ . It can be observed from the figure that the microstructure of the sample sintered at 1200° C is heterogeneous. Grain size of different ranges exist in the microstructure. With the increase of sintering



Figure 2. Variation of g.s. with sintering temperature

Figure 3. Variation of a with sintering temperature

temperature, microstructure becomes more homogeneous. It has been noticed with lower magnification (figure not shown) that there are more intergranular porosity for the sample sintered at 1200°C whereas more intrgranular porosity can be observed for the sample sintered at 1250 and 1300°C because of grain growth pores cannot migrate to the grain boundaries and therefore trapped within the grains. Intragranular porosity is more deleterious for magnetic properties since it acts as pinning centre for domain wall movement. Therefore, when there is exaggerated grain growth, there is deterioration of magnetic properties.



Figure 4. SEM micrographs of the sample in the as-dried and samples sintered  $(\times 15 \text{ k})$  at different temperatures.

In Fig. 5 temperature dependence of real part initial permeability has been presented in the temperature range of 600-1350°C. With the increase of sintering temperature, magnetic coupling increases. Magnetic coupling is the weakest for the sample sintered at 600°C. With the increase of sintering temperature improvement of magnetic coupling occurs. This has been reflected in the increase of Curie Temperature. Curie temperature estimated from the figures can be explained by finite scaling theory when the grain sizes are smaller. At lower firing temperatures i.e. when the grain sizes are smaller, the Neél temperature is lower.



As shown in Fig. 6, the finite size effect is predominant when the grain sizes are very small which results in a decrease in Neél temperature with grain size reduction. The small particles have a significant fraction of atoms on the surface and their exchange interaction should be weaker because of the lower coordination. They will have a reduced average Neél temperature compared to that of the interior atoms, which accounts for the decrease in Neél temperature at lower sintering temperature.



Figure 7. Frequency spectrum of real (a) and imaginary part (b) of permeability for the sample sintered at different temperature

In Fig. 7(a) and (b) frequency dependence of real and imaginary part of complex initial permeability has been presented. Real part permeability, increases with the increase of grain growth as expected i.e. when the grain size is smaller the permeability is lower. The presence of small grain size interferes with wall motion, which decreases permeability and increases the stability region of real part of initial permeability. The loss component represented by imaginary part of initial permeability decreases with frequency up to the measured frequency of this study of 13 MHz. At higher frequencies, losses are found to be lower if domain wall motion is inhibited and the magnetization is forced to change by rotation.

In Fig. 8, Field dependence of magnetization has been recorded for the samples in the as-prepared condition and sintered at  $1350^{\circ}$ C. The coercivity of the samples in the as-prepared condition is almost zero, which is suggestive of superparamgnetic behavior at room temperature [4]. Sample sintered at  $1350^{\circ}$ C shows shape of normal hysteresis loop of NiFe<sub>2</sub>O<sub>4</sub> sample in which hysteresis loop is open. Similar effect was found by Chander et. al. [5] for

Fe2.9Zn0.1O4. But the saturation magnetization is somewhat lower than bulk NiFe<sub>2</sub>O<sub>4</sub> which we obtained in our previous study as 50.3 emu/g [6].



Figure 8. Field dependence of magnetization of as-prepared sample and sintered at 1350°C

The saturation magnetization in Fig 8 has been obtained as 13 emu/g for the as-prepared condition and 46 emu/g for the sample sintered at 1350°C. The much reduced  $M_s$  in the nano-particle sample implies that outside a core of ordered moments, those on the surface layer are in a state of frozen disorder. With the reduction of particle size more atoms remain on the surface, which are not exchange-coupled. As a result, the value of magnetization decreases. The effect is more prominent when the particle sizes are very small, however with the increase of particle size the saturation magnetization increases since core of the ordered moments become predominant.

In Fig. 9, temperature dependence of resistivity has been presented. Both the resistivity and the activation energy decreases with increasing sintering temperatures. When polycrystalline ferrites are considered, the bulk resistivity arises from a combination of crystallite resistivity and the resistivity of crystallite boundaries. The boundary resistivity is much greater than that of the crystallite resistivity. Thus the boundary have the greatest influence on the d.c. resistivity [7]. The decrease of resistivity are also related to the decrease of porosity at higher sintering temperature since pores are non-conductive, which increases resistivity of the material [7]. The resistivity increases with the increase of porosity at lower sintering temperature because charge carrier on their way face the pores. Decrease of activation energy with the increase of sintering temperatures may be attributed to the fact that at a high sintering temperature, partial reduction of  $Fe^{3+}$  to  $Fe^{2+}$  takes place and these places act as donor centre. The conduction mechanism is due to hopping of electron of the types  $Fe^{2+} \Leftrightarrow Fe^{3+}$ . The value of resistivity has increased by an order of magnitude for the sample annealed at 1200 and 1350°C than the sample prepared by conventional ceramic technique. However, the value of resistivity is quite high at 1000°C due to under firing.

In Fig. 10, The real part  $\varepsilon'$  of the dielectric constant for samples sintered at higher temperature are about two orders of magnitude smaller than those of the NiFe<sub>2</sub>O<sub>4</sub> prepared from chemicals of analytical grade [7]. The variation of dielectric constant, has been presented as a function of frequency up to f = 13 MHz. From Fig. 9 and 10, it can be

seen that the higher value of dielectric constants are associated with lower resistivity. Dispersion in the dielectric constants was exhibited by all the samples in the studied frequency range. To explain dielectric dispersion in ferrites, grain and grain boundaries were assumed to be two different layers each having a different conductivity but same dielectric constant. As the frequency rises from a low value the bulk resistivity and dielectric constant fall and become asymptotic to lower values at high frequencies. This variation has the characteristic of relaxation and is attributed to the granular structure of ferrites, in which crystallites are separated by boundaries having much higher resistivities than the crystallites. Thus the structure behaves as a compound dielectric. At low frequencies the impedance of the crystallites is negligible compared to that of the boundary [7]. The dielectric constant approaches to the value, which is analogous to calculating dielectric properties from measurements on a specimen between the plates of capacitor, using a dielectric length 1 / n times the actual value. At very high frequencies the boundary capacitance becomes short circuited with the boundary resistance and the bulk dielectric properties approach those of crystallites.



In Fig. 11, temperature dependence of dielectric properties have been presented for the frequencies of 10 and 100 kHz. Polycrystalline and poly-phase aggregates exhibit an interfacial or space charge polarization arising from differences between the conductivity of various phases present. This polarization resulting from heterogeneity is particularly important for compositions such as ferrites and semiconductors in which the electrical conductivity is appreciable; also for polycrystalline and polyphase materials at higher temperatures. The time constant for this interfacial polarization, and consequently the frequency at which it becomes important, is proportional to the product of resistivities of different phases. For most dielectrics this product is so large that the interfacial polarization is negligible even at low frequencies. For semiconductors and semiconducting ferrites this resistivity product is not so large, and the effect is important at room temperature. For other dielectrics this factor increase as the temperature is raised. At the same time, the conduction losses and ion jump losses also increase. These can in one sense be



Fig. 11. Temperature dependence of real part dielectric constant for the sample sintered at different temperatures.

considered local space charge polarization resulting from mobility barriers. As the conductivity increases at higher temperatures, the apparent dielectric constant also increases, the dielectric losses increase even more rapidly, and the effectiveness of insulation decreased. To minimize this increase, compositions having the lowest possible conductivity should be used. In our results, the variation of dielectric constant with temperature for the samples sintered at different temperatures follow this general behavior.

#### CONCLUSIONS

Grain size of the NiFe<sub>2</sub>O<sub>4</sub> nanoparticle prepared by chemical co-precipitation technique has been found as 6 nm in the as-dried condition with subsequent growth at higher sintering temperatures. Variation of Neél temperature with grain size can be explained by finite size scaling theory at low temperature which fits well with the experiment. Coercivity of the samples in nano level is almost zero, which is suggestive of superparamgnetic behavior at room temperature.

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