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FC and ZFC Magnetic Properties of Ferro-spinels (MFe_2O_4) Prepared by Solution-Combustion Method

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Abstract. Magnetic ferro-spinels MFe_2O_4 (M= Co and Ni) prepared by citrate-gel solution combustion method using metal nitrates with low sintering temperature (500^{o}C). From the XRD and TEM studies confirm that a nano crystalline nature of the prepared samples. Field Cooled (FC) and Zero Field Cooled (ZFC) magnetic studies of the prepared ferro-spinels are measured by using vibrating sample magnetometer (VSM). The resultant magnetization of the prepared samples as a function of an applied magnetic field 10 T was measured at two different temperatures 5 K and 310 K. Field Cooled (FC) and Zero Field Cooled (ZFC) magnetization measurements under an applied field of 100 Oe and 1000 Oe in the temperature range of 5–375 K were carried out, which shows the blocking temperature of these two samples at around 350 K.

Key words Spinel ferrites,citrate gel method, XRD, TEM, FC &ZFC

1. Introduction:

The expansion of the novel nano crystalline magnetic materials and their tunable electromagnetic properties has turn into one of the most important research goal of the 21st century. Ferri magnetic materials (ferrites) composed of iron oxides and metal oxides are more and tremendous magnetic materials broadly used in high frequency microwave applications like isolators, circulators, gyrators, phase shifters and cathode material in lithium ion batteries [1]. They exhibit both high electrical resistivity and useful magnetic properties which are not found in any other magnetic materials. In addition to their combined properties, they have very high degree of compositional variability. The crystal structure of ferrites is such that it can accommodate different cations at available sites with dissimilar valence states. Ferrites are distinct class of magnetic materials having spinel structure. They consist of abrupt magnetized domains and show the phenomenon of magnetic hysteresis and saturation magnetization. These ferrites have gained lot of interest because of their high electrical resistivity, low loss behavior and remarkably high electromagnetic flux induction.

The research on spinel ferrites is very mature, because of their potential applications and fascinating physics involved in it, even after so many decades, researchers are still interested in the design of various types of spinel ferrite materials, doped with different metallic ions with various valence states, synthesized by novel methods. It was observed that the air sintered spinel ferrites are characterized by microstructure consisting of relatively highly conductive grains separated by highly non conducting grain boundaries [2-3].

Nano crystalline $CoFe_2O_4$ is a well-known medium hard magnetic material, which has been analyzed due to its moderate coercivity, high chemical stability, fine electrical insulation, significant mechanical hardness and moderate saturation magnetization at room temperature. Due to their strong ferromagnetism and high curie temperature cobalt ferrite is used in electronic appliances as it causes the materials to stay magnetized even when the applied magnetic field is turned off, leading to a useful way of storing information. It finds innumerable applications in stress sensors as precursors for making ferro fluids and also as magnetic refrigerants [4-5]**.** Nano crystalline $NiFe_2O_4$ is a soft ferri magnetic material due to its nano crystalline nature and useful properties, the material shows a good potential for novel applications in humidity, gas sensing [6] and drug delivery [7-8]**.** There are number of other applications in heterogeneous catalysis [9-11], adsorption, sensors and magnetic technologies. Normally, ferrites become super-paramagnetic at room temperature for nano particles of less crystallite size [12-13]. Super-paramagnetic nature of ferrites finds applications in Biomedical field, Magnetic Resonance Imaging (MRI) [14], Targeted drug delivery [15], Hyperthermia for cancer treatment [16]**.**

Solution -combustion method is characterized by the high temperature, fast heating rates and short reaction times. These characteristics make the solution-combustion method an attractive route for the manufacture of nano crystalline materials at lower costs compared with the conventional ceramic methods. Relatively simple equipment,

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stabilization of metastable phases, formation of virtually any size and shape particles etc are the other advantages of the solution- combustion method.

All the facts revealed from the literature survey motivated us to prepare cobalt ferrite and nickel ferrites. In the present investigation we prepare the magnetic spinel ferrites MFe_2O_4 (M= Co and Ni) by citrate-gel auto combustion method using nitrates of respective elements and by keeping 1:1 ratio of metal nitrates to citric acid with low sintering temperature (500°C). The single phase of the prepared samples can be confirmed by the x-ray diffraction analysis and nano crystalline nature is observed from the transmission electron microscopy. Field Cooled (FC) and Zero Field Cooled (ZFC) magnetic studies of the samples can be measured by using vibrating sample magnetometer (VSM) which shows the super-paramagnetic nature of the prepared samples.

2. Experimental Techniques:

The nano crystalline spinel ferrites MFe_2O_4 (M= Co and Ni) were prepared by citrate-nitrate auto combustion method and flow chat for preparation as shown in fig(1). The AR grade citric acid, cobalt nitrate, nickel nitrate, ferric nitrate and ammonia solution were used as raw materials. The products of the system were produced by keeping the metal nitrates to citric acid ratio 1:1. Reaction process was carried by air atmosphere without protection of inert gases.

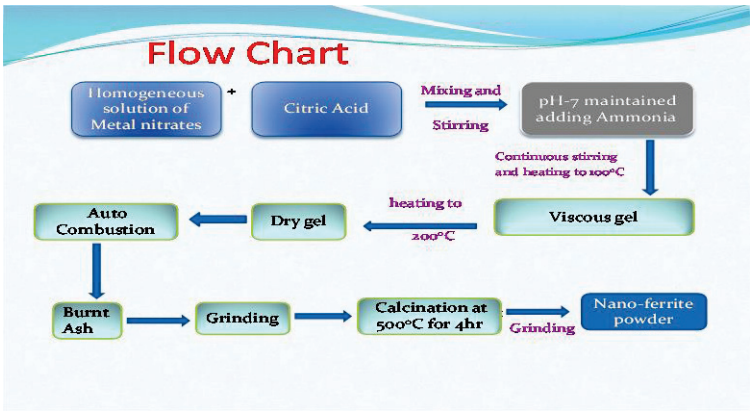


Fig (1) Flow chart for preparation

Required chemicals were weighed and dissolved separately in minimum quantity of distilled water. All the individual solutions were mixed together and then the ammonia solution was slowly added to adjust the pH value at 7. The proliferation of nitrate ions at low pH value is likely to decrease the enthalpy of exothermic reaction by decreasing the fuel to oxidizing ratio. Thus, the rate of combustion reaction decreases and particles agglomerates [17] so the pH value of the solution was maintained at 7, to avoid the agglomeration and preserve the stoichiometry of the mixed solution. The resultant solution was kept on a hot plate magnetic stirrer at 100°C till gels were formed, after that, increasing the temperature up to 200°C, the gels self-ignited in an auto combustion manner till whole citrate complex was consumed to yield nano ferrite powders. These synthesized ferrite powders were annealed at 500°C for 4 hours in a muffle furnace [18]. The heat treated powders were used for further characterization. The overall reaction for formation of nickel ferrite is given below.

$$Ni\,(NO_3)_2.6H_2O + 2Fe\,(NO_3)_3.9H_2O + 3C_6H_8O_7 \longrightarrow NiFe_2O_4 + 4N_2 + 18CO_2 + 7H_2 + 29\,H_2O.$$

From the above equations it is observed that the auto combustion synthesis process produces CO_2, H_2O, and N_2 without t he necessity of getting oxygen from outside

The phase confirmation of the synthesized samples was carried out by Philips X-ray diffractometer (Model 3710) using Cu K_α radiation of wavelength 1.5405A° at room temperature by continuous scanning in the range of Bragg's angles 10° to 80° in steps of 2°/min to investigate the phase and crystalline size. The average crystalline size of the ferrites was determined from the measured width of their diffraction pattern using the Debye scherrer's formula

$$D=0.91\lambda/\beta\cos\theta \qquad (1)$$

Where λ is the wavelength of the X-ray used for diffraction, β is the full width half maximum (FWHM) in radians.

Transmission electron microscopy (TEM) measurements were recorded on Philips apparatus (CM 200 model). Field Cooled (FC) and Zero Field Cooled (ZFC) magnetic studies of the samples can be measured by using vibrating sample magnetometer (VSM Lakeshore, model 7307).

3. Results and Discussion:

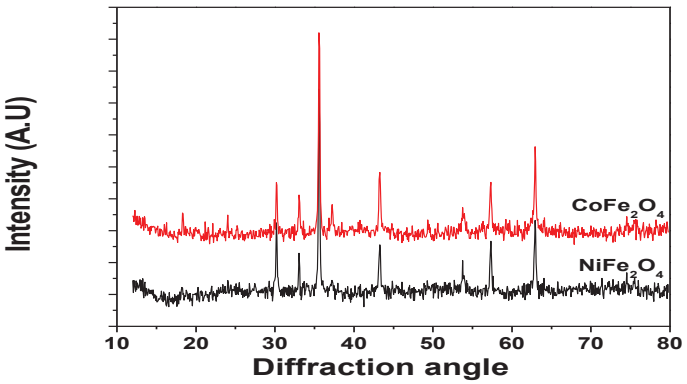
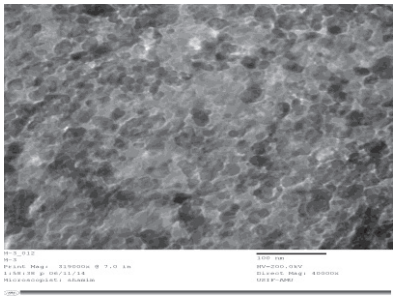
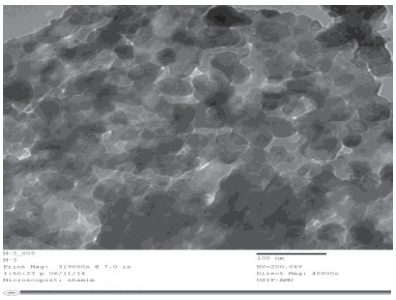


Figure (2) XRD Pattern of prepared nano ferrites

XRD pattern of the prepared samples were shown in below fig (1) and confirmed the single phase spinel structure which indicates the solubility of cations into their relevant lattice sites. The positions of the reflection peaks for investigated samples are almost identical to the corresponding peaks for the bulk material, this implies that the basic structure of the nano crystalline materials is basically same like the bulk counterparts. The peak broadening in the XRD pattern of the investigated samples confirmed the formation of nano-size crystallites. All main diffraction planes are indexed as (220), (311), (400), (422), (511) and (440) with maximum diffraction intensity from (311) plane co-inside with the standard pattern reported by the Joint Committee on Powder Diffraction Standards (JCPDS) for single phase cubic spinel with file no: 00-013-0207 with space group Fd3m. No characteristic peaks of impurities are detected in the XRD pattern. The crystallite size of the samples was calculated by measuring the FWHM of the most intensive peak (311). The average crystallite size of the nickel ferrite is 43 nm and cobalt ferrite is 36 nm which is already published in our earlier paper [19-20].



(3a) TEM image of $CoFe_2O_4$



(3b) TEM image of $NiFe_2O_4$

Fig (3a & 3b) shows TEM micrographs of the prepared nano crystalline cobalt ferrites and nickel ferrites respectively. Uniform spherical agglomerated particles in both morphology and size were obtained. The particle agglomeration is due to the magnetic interaction between the particles and permanent magnetic moment experienced by the nano particles which is proportional to their volume [21-23]. The TEM estimated particle size of the samples are larger than the average crystallite size calculated from the X-ray diffraction analysis, which is explained by following two reasons: (1) In X-ray diffraction analysis, X-rays can notice only the grains and they cannot considered the disordered grain boundaries which occupy considerable volume; (2) there is a chance of the accumulation of more than one crystallite forming an agglomeration of particles [24-25].

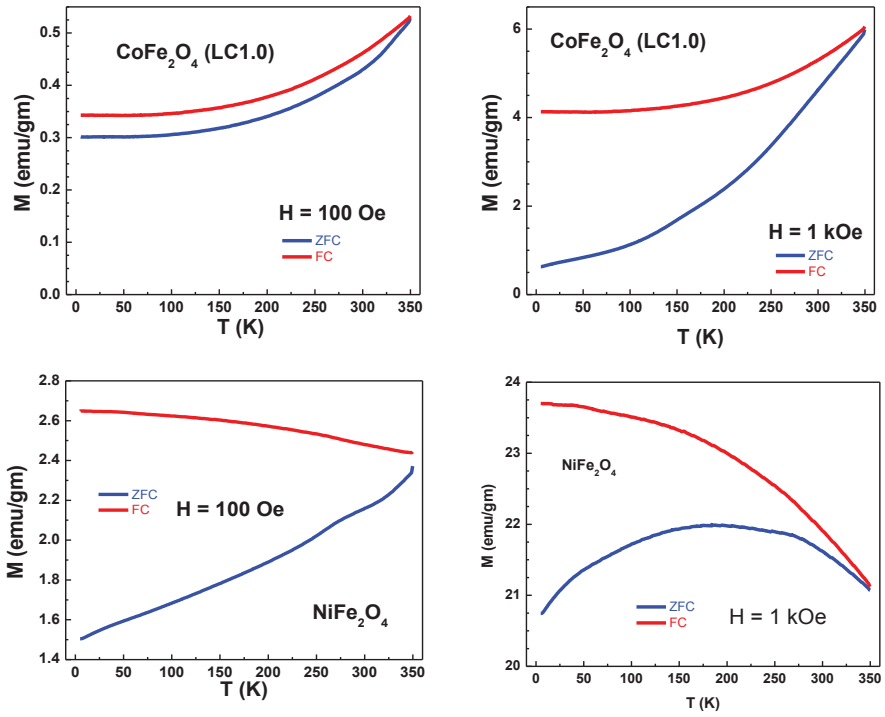


Fig (4) Magnetization-Temperature curves recorded in FC and ZFC modes for the sample $CoFe_2O_4$ and $NiFe_2O_4$ in an external magnetic field of 100 Oe and 1k Oe.

The magnetic behavior of investigated samples was analyzed from the temperature dependence of the magnetization measured in zero field cooled and field cooled modes which was shown in fig (4). In ZFC procedure, the sample is cooled (usually down to the liquid helium temperature) in the absence of a magnetic field and then a moderate measuring field is applied (here 100 Oe and 1000 Oe).Then the magnetization (M) values being recorded by gradually raising the temperature. The FC procedure differs from ZFC, only by the fact that the sample is cooled in a non-zero magnetic field. The discrepancy between the FC and ZFC magnetization is found in both the samples at different applied fields in the whole range of measured temperatures (5K to 375K) which indicates super-paramagnetic behavior [26].

The temperature at which this bifurcation in the two modes (FC & ZFC) is observed is defined as bifurcation temperature or blocking temperature (T_b). It is observed that the blocking temperature did not change with the increase in applied field but shows a strong bifurcation in the FC and ZFC curves under higher applied field i.e. at 1 k Oe, showing irreversibility of FC and ZFC magnetization curves. For both the samples the bifurcation or blocking temperature is observed at around 350 K, below blocking temperature the material shows some hysteresis and hence behaves as ferromagnetic material and above blocking temperature, hysteresis disappears and the material behaves as super-paramagnetic.

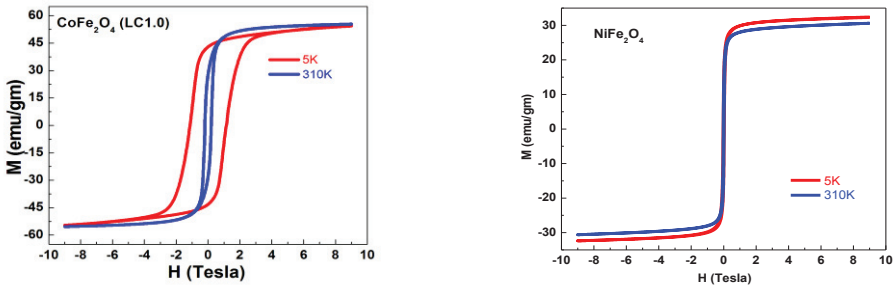


Fig (5) Hysteresis Curves for $CoFe_2O_4$ and $NiFe_2O_4$ at 5K and 310K

Table1. Coercivity (Hc) and Remanence (Mr) values of cobalt ferrite and nickel ferrites

Magnetic parameters	$NiFe_2O_4$		$CoFe_2O_4$	
	5K	310K	5K	310K
Coercivity(H_c) Tesla	0.04	0.02	1.09	0.19
Remanence (M_r) (emu/gm)	16.65	14.59	43.30	30.99

Fig 5. shows Magnetization Hysteresis curves for $NiFe_2O_4$ and $CoFe_2O_4$ samples at 5 K and 310 K. It is observed that the coercivity is more at lower temperature and it decreases with increase in temperature. The values of Coercivity (H_c) and remanence (M_r) were measured from the hysteresis curves and were recorded in table 1.

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