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Influence of DL-Alanine Fuel Concentration on Structural and Magnetic Properties of Nickel Ferrite Nanoparticles

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ABSTRACT:Nano sized $NiFe_2O_4$ has been prepared through Sol-gel auto combustion route by using DL-Alanine as fuel. The phase formation of $NiFe_2O_4$ is investigated by XRD and Raman techniques.In the case of higher fuel content two molar (2M) in the mixture, it is noted that the as-prepared powders were highly crystalline, and exhibited the typical XRD peaks corresponding to the formation of the $NiFe_2O_4$.According to the XRD spectra, the sample prepared with 2M of fuel has better crystallinity than those prepared with one molar (1M) of fuel. Therefore, 2M of fuel is preferable to prepare single phase $NiFe_2O_4$ nanoparticles with better crystallinity. Nickel ferrite powders (NFO) were further investigated using Raman spectroscopy in order to differentiate the NFO from other phases like Fe_3O_4 and gamma Fe_2O_3, which have the similar structures and therefore similar XRD patterns. The Raman spectra for all the samples resemble to the inverse spinel structure of $NiFe_2O_4$. It is observed that sample $NiFe_2O_4$ powders that were prepared with different molar concentration (1M and 2M) of the fuel DL-Alanine added to the solution mixture have different magnetization. Sample added with 2M DL-Alanine fuel shows higher magnetization as compared to the sample added with 1M DL-Alanine fuel due to better crystallinity. The room temperature VSM studies show that the nano $NiFe_2O_4$ particles exhibit soft ferromagnetic nature with high saturation magnetization of 34.993 emu/g for 2 M fuel amount.

KEYWORDS:Nanoparticles, Sol-gel auto combustion, Fuel (DL-Alanine), Crystallinity, Raman, inverse spinel.

I. INTRODUCTION

The synthesis of spinel ferrite nanoparticles have drawn major attention due to their functional importance in high density magnetic storage, magneto-optical devices, magnetic fluids, microwave devices, telecommunication equipment, magnetic refrigeration, magnetically guided drug delivery and ferrofluid technology. The sphere-like Zinc ferrites shows enhanced photo Catalytic performance [1-4]The inverse spinel ferrite especially Nickel ferrites which is a soft magnetic material have attracted remarkably high attention due to its high saturation magnetization and high magneto crystalline anisotropy. [5-7]

The crystal structure is face centred cubic with the unit cell containing 32 O^{2-}, 8 Ni^{2+} and 16 Fe^{3+} ions. Nickel ferrite unit cell has 32 oxygen atoms in a cubic close packing with eight tetrahedral and sixteen octahedral sites. Half of the octahedral sites are occupied by the eight Ni^{2+} and eight Fe^{3+} cations. The eight tetrahedral sites are occupied by the other eight Fe^{3+} ions [8]. The stability, biocompatibility and relaxometric properties of super paramagnetic ferrite nanoparticles are influenced by the composition and microstructure which are sensitive to the preparation methodology used. Various physical and chemical techniques have been developed to synthesize nickel ferrite nanoparticles, including mechanical milling, inert gas condensation, hydrothermal reaction, ceramic method, sol–gel auto combustion

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route and co-precipitation [9] techniques. Among the available chemical methods, sol–gel auto combustion route has the advantage of good stoichiometric control, cheap precursors, easy route and the production of 100 % pure ultrafine particles. [3, 10,11]

In the present work, the influence of concentration of complexant/ fuel agents is seen on defect concentration and saturation magnetization of NFO powder. It is very important to select appropriate amount of DL-Alanine concentration. The properties of the resultant product varies with varying amounts of fuel as it effects reducing ability and amount of gases evolved.[8,12] The combustion flame temperature affects the particle size, crystallinity and phase purity[13]. Parameters like particle growth, agglomeration and segregation are controlled by the amount gases evolved. Large amount of heat was generated when fuel concentration was maintained as two molar. [4, 14]

II. MATERIALS AND METHODS

Nano crystalline NiFe2O4 samples were synthesized by Sol-gel auto-combustion reaction. There are different methods including sol–gel and citrate methods, co-precipitation, solid-state reactions, sonochemistry, aerosol vapour methods, high temperature decomposition of organic precursors and many others to prepare ferrites with a spinel structure. [22]
The sol-gel auto-combustion reaction involves exothermic and self-propagating thermally-induced redox reaction of xerogel. Xerogel product formation resulted from aqueous solution containing desired oxidizer and reductant. Proportions between complexant and salts are depends on the valencies of the reacting elements in order to satisfy the ratio of oxidizer/reductant equal to one [23]. The thermal methods to synthesize ferrites are hydrothermal [24], solvothermal [25, 26], spray pyrolysis, mechano-thermal and seed-hydrothermal. In each of these methods, precursor salt of iron or nickel (M=Fe, Ni) is nitrate (M-$(NO_3)_2$), sulphide (M-SO_4), or chloride (M-Cl_2). Salts are dissolved in the solvent and desired pH value is maintained. Then, reactant mixture is kept in autoclave for a prescribed time and at a certain temperature [27].Then, product is cooled at room temperature.

III. EXPERIMENTAL

All the chemicals used in this reaction were of analytical grade and were used as purchased. Nickel nitrate Ni $(NO_3)_2.6H_2O$ (Thomas Baker, Analytical agent) and iron nitrate Fe $(NO_3)_2$ $.9H_2O$ (Thomas Baker, Analytical agent) were used as the reactants. Distilled water was used as a solvent whereas DL-Alanine ($C_3H_7NO_2$) (Thomas Baker, Laboratory agent) was used as fuel for combustion.

The aqueous solutions of Nickel nitrate and Ferric nitratewere prepared separately in stoichiometric ratio 1:2. 5mol/L of nitric acid was added to the aqueous nickel nitrate solution and it was stirred manually. The mixture formed was added to the iron nitrate solution while stirring. The aqueous DL-Alanine was added to the solution mixture slowly after one hour of vigorous stirring. The final solution was stirred for 120 minutes and heated at 75°C to initiate self-sustaining thermally-induced anionic redox and exothermic reaction. While heating, large volume of gases are evolved accompanied by a great mass loss and a dark brown gel like viscous solution was formed. Initially, small sparks and then a big spark appeared inside thebeaker which lead to the formation of dark brown fluffy product (as shown in Figure 1).

Fig.1 Synthesized Nickel ferrite powder in beaker

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The synthesized substance was grounded into a fine powder. Annealing for 2h at 500°C and 800°C respectively in air in a conventional furnace resulted in crystalline powders. Combustion was carried with two different concentrations of (2M and 1M:molar quantities of DL-Alanine) fuel and we observed that the amount of fuel controls the combustion rate and temperature, thereby affecting the properties of the final product. In this investigation the ratio of DL-Alanine: nickel nitrate: ferric nitrate was kept as (1M-2M):1:2.

IV. CHARACTERIZATION

The crystalline phases and crystallite size of as prepared and annealed NFO samples were determined by X-ray diffraction (XRD) technique using Cu Kα radiation for 2θ value ranges from 20° to 100° in high resolution X-ray diffractometer (Model Discover D8, Bruker).Magnetic characterization was carried out using vibrating sample magnetometer (VSM, Model 1640 MRS, CPX 900 Power amplifier) at room temperature upto a maximum field of 16 kOe. Raman spectra was carried out using Renishaw inVia Raman Microscope having an Ar+ excitation sourceof 488nm wavelength coupled with a ×50 objective, appropriate edge filter and peltier cooled charge coupled device detector.

V. RESULTS AND DISCUSSION

XRD analysis:

Figure2 compares the XRD patterns of as obtained $NiFe_2O_4$ powders that were prepared with different molar concentration (1M and 2M) of the fuel DL-Alanine added to the solution mixture in the experiment. In the case of higher fuel content (2M) in the mixture, it is noted that the as-prepared powders were highly crystalline, and exhibited the typical XRD peaks corresponding to the formation of the $NiFe_2O_4$. [15-16].It was interesting to observe that the as-prepared powder itself that was obtained at 75 °C, with 2M molar content of the fuel DL-Alanine was highly crystalline, exhibiting the single phase formation of $NiFe_2O_4$.

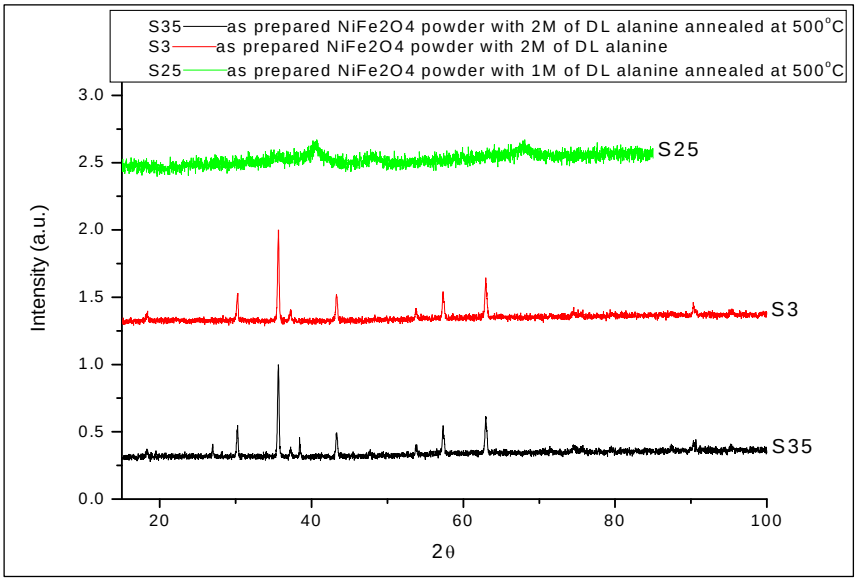

Fig. 2. Comparison of X-ray diffraction patterns of chemically prepared $NiFe_2O_4$ powders prepared with different concentration of the fuel DL - Alanine (1M and 2M).It is noted that the observed peaks are weak for the 1M concentration in comparison to the 2M concentration

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Raman Spectra studies:

Nickel ferrite powders (NFO) were further investigated using Raman spectroscopy (as shown in Fig 3)in order to differentiate the Nickel ferrite from other phases like Fe_3O_4 and gamma Fe_2O_3, which have the similar structures and therefore similar XRD patterns[17]. The Raman spectra are of good quality and matches with earlier reports for $NiFe_2O_4$[18].This powder crystallizes in a spinel structure with 5 active Raman bands , namely $\mathbf{A_{1g}+E_g+3T_{2g}}$. The low frequency (<700 cm^{-1}) spectra also match with that of Fe_3O_4 exhibiting similar structure. According to the space group symmetry and factor group analysis, five Raman active modes such as A_{1g}, T_{2g} and $2E_g$ modes are predicted. The modes from tetrahedral and octahedral sites can be distinguished by Raman Spectroscopy. Raman peaks over the region 680 cm^{-1} represents the tetrahedral modes in ferrites, whereas the peak at 460-400cm^{-1} corresponds to modes of the octahedral sites. The peaks at 336 & 666 cm^{-1} shows Eg vibrational modes.

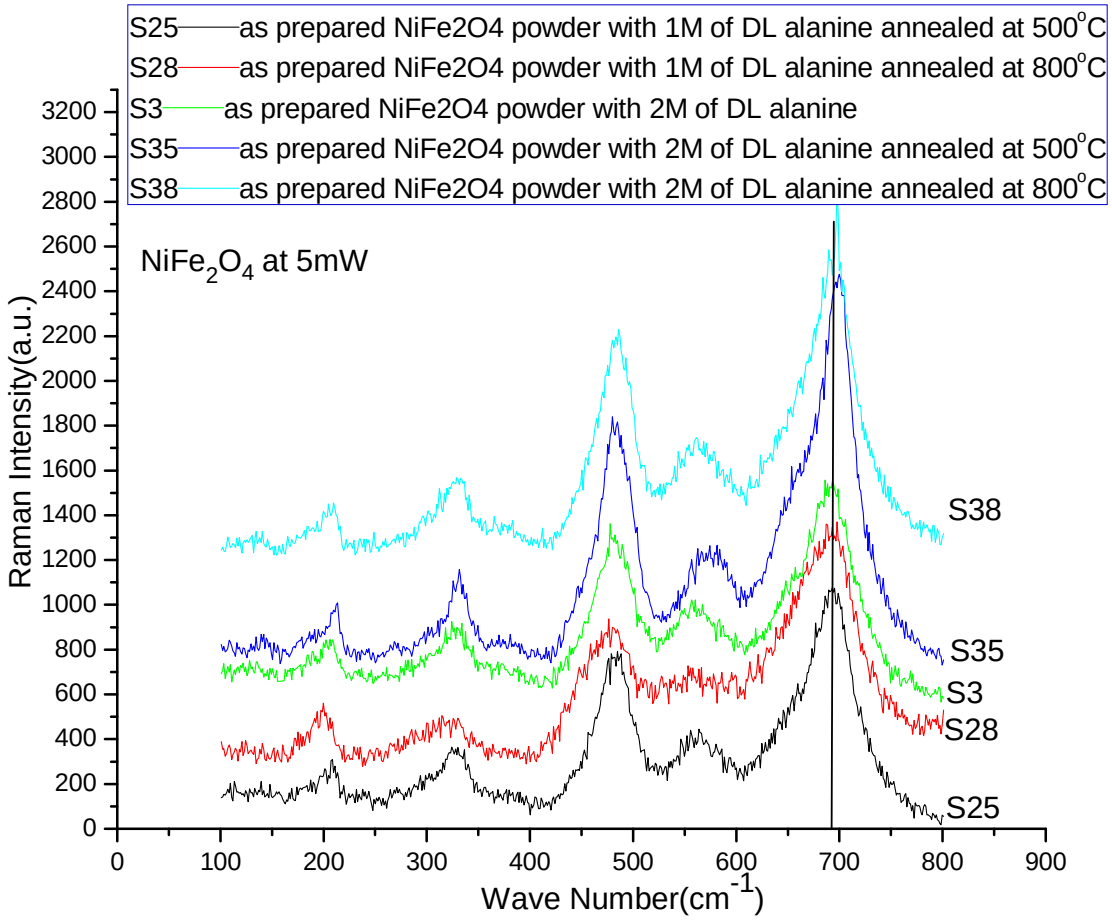

Fig. 3. Raman spectra of $NiFe_2O_4$ nanoparticles: S25, S28, S3,S35, S38 samples compared. The Raman spectra for all the samples resemble that of the inverse spinel structure of $NiFe_2O_4$.It is noted that as the particle size increases, the Raman band shifts to higher frequency and becomes narrow.

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Magnetic measurements:

The magnetic characterization of the samples was performed by VSM at room temperature with maximum applied field of 16 kOe. The magnetic hysteresis curves of the as-synthesized, 500°C and 800°C annealed powder samples of sample no. 3 are compared in Fig.4.

The maximum saturation magnetization [19] observed is 34.993 emu/grams. The low value of saturation magnetization Ms compared with that of bulk Ni-Ferrite (56 emu/grams) can be understood on the basis of core-shell model, which explains that the finite size effects nano particles lead to a canting of spins on their surface and thereby reduces its magnetization.

It is observed that magnetization increased with annealing temperature. Crystal size was determined from line width of reflection (3 1 1) in XRD patterns using the Scherrer's Formula. It was found that crystallite size of product was greatly accelerated with increasing of temperature. [20]

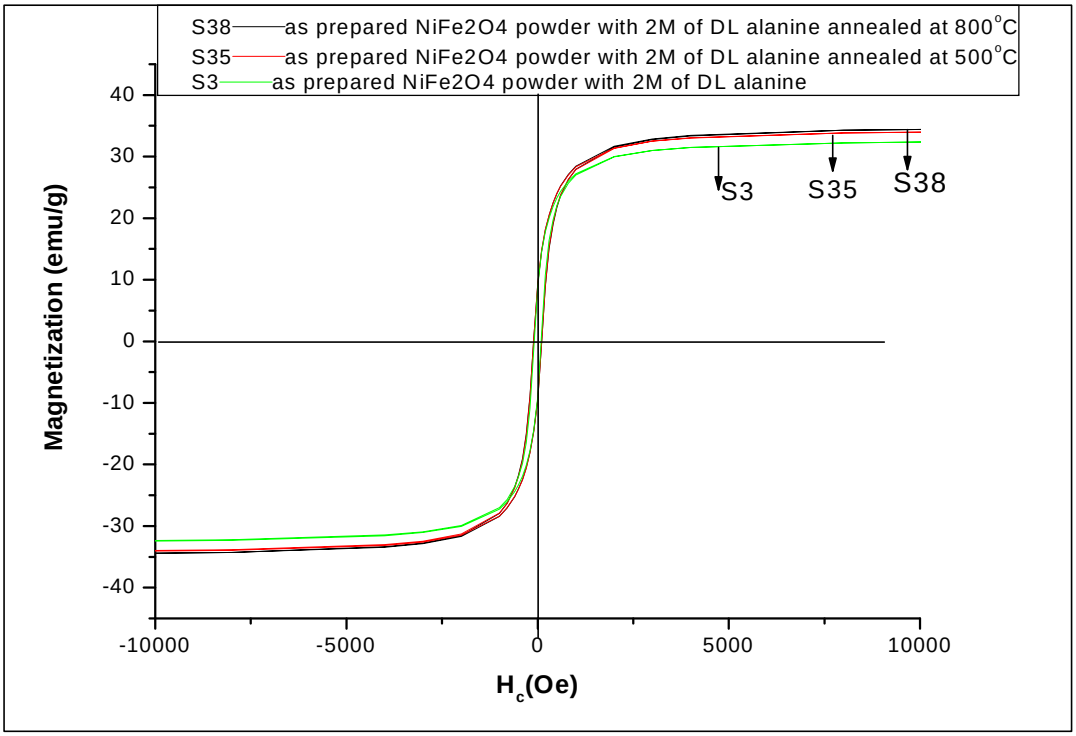

Fig. 4. Hysteresis loops of NiFe2O4 powder prepared with 2M DL - Alanine fuel at different annealing temperature. Annealed samples of Nickel ferrite powder possessed higher saturation magnetization moment due to their high degree of crystallization and uniform morphologies

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Table 1 XRD analysis and magnetic characterization results of $NiFe_2O_4$ (2M DL-Alanine) sample annealed at 500 °C and 800°C. Higher the saturation magnetisation value for samples annealed at higher temperature.

Sample	Annealed temperature (° C)	Crystallite size (nm)	Lattice constant(a=b=c) (Armstrong)	Saturation magnetization M_s (emu/g)	Coercivity H_c (Oe)	Remanence M_r (emu/g)
S3	-	32.338	8.372	32.547	89.551	9.344
S35	500° C	35.204	8.355	34.493	105.797	9.681
S38	800° C	36.214	8.342	34.993	106.095	9.841

It is observed that sample $NiFe_2O_4$ powders that were prepared with different molar concentration (1M and 2M) of the fuel DL-Alanine added to the solution mixture have different magnetization. Sample added with 2M DL-Alanine fuel shows higher magnetization as compared to the sample added with 1M DL-Alanine fuel due to better crystallinity as shown in Fig.5. The lattice constant values are in good agreement with earlier reported values of 0.833nm for nano $NiFe_2O_4$ [21].

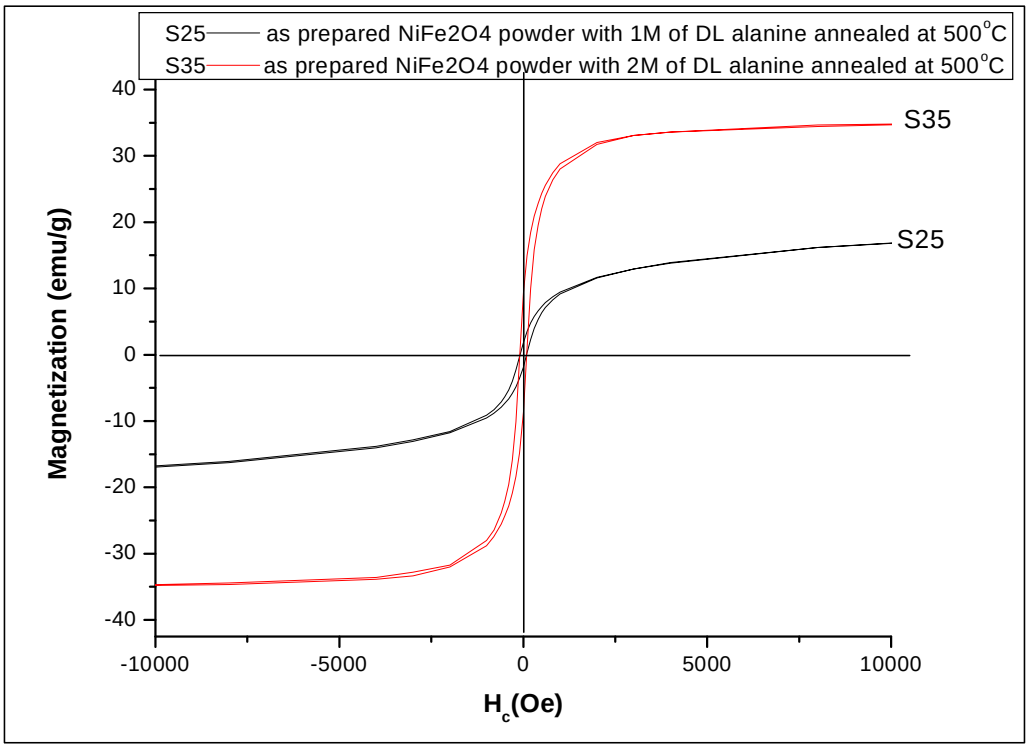

Fig. 5. Room temperature hysteresis loops of as prepared $NiFe_2O_4$ powder prepared by sol-gel auto combustion method with different molar concentration of DL-Alanine fuel (1M and 2M) annealed at 500°C. Saturation magnetisation value is higher for the fuel with 2M concentration.

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Table 2 Comparative magnetic characterization results for 1M (S25) and 2M (S35) DL-Alanine amount annealed at 500° C.Saturation magnetisation value is higher for the fuel with 2M concentration

Sample	Saturation magnetization M_s(emu/g)	Coercivity H_c(Oe)	Remanence M_r(emu/g)
S25 (1M DL-Alanine)	18.403	83.252	1.904
S35 (2M DL-Alanine)	34.493	91.915	9.716

VI. CONCLUSION

In summary, nano sized $NiFe_2O_4$ has been prepared through sol-gel auto-combustion route by using various amounts of DL-Alanine as fuel. The phase formation of $NiFe_2O_4$ is investigated by XRD and Raman techniques. According to the XRD spectra, the sample prepared with 2M of fuel has better crystallinity than those prepared with 1M of fuel. Therefore, 2M of fuel is preferable to prepare single phase $NiFe_2O_4$ nanoparticles with better crystallinity and saturation magnetisation. The particle size distribution estimated from XRD is less than 37 nm. The room temperature VSM studies show that the nano $NiFe_2O_4$ particles exhibit soft ferromagnetic nature with high saturation magnetization of 34.993 emu/g. So, it can have potential applications in soft magnets, ferrofluid and low loss materials at high frequencies, drug delivery and magnetic resonance imaging.

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