



# Lithium ferrite nanoparticles for ferrofluid applications

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## Abstract

Nanoparticles of Lithium ferrite in the particle size range of 10 nm have been prepared by a citrate precursor method at a relatively low temperature of 200°C. The particles show characteristic infra red (IR) spectrum of lithium ferrite and broadened X-ray diffraction (XRD) patterns typical of the nanoparticle nature. The sample decomposed at 200°C has the  $\beta$ -LiFe<sub>5</sub>O<sub>8</sub> type (a disordered type of spinel) structure which on annealing at 350°C transforms to the  $\alpha$ -LiFe<sub>5</sub>O<sub>8</sub> type (an ordered type spinel) structure as shown by both IR spectra and XRD studies. Magnetization curves indicate a particle size distribution consisting of both ferromagnetic particles and a superparamagnetic fraction. With  $4\pi M_s$  values of 2000 G these particles could be useful for applications in certain low magnetization ferrofluids.

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## 1. Introduction

Ferrofluids are stable colloidal solutions of ferro or ferrimagnetic nanoparticles of ~10-nm size dispersed in a liquid carrier. While magnetite (Fe<sub>3</sub>O<sub>4</sub>) is the most commonly used material, other ferrites and metallic particles have also been used in ferrofluid synthesis [1,2]. These fluids have diverse engineering application in seals, dampers, speakers, lubricants, etc. The devices based upon them are increasing at a spectacular rate.

The most important parameters which control the magnetic properties of dispersed fine magnetic particles—controlling the properties of fluid—are magnetization of particles, size and size distribution. The typical size of the magnetic particles (diameter) in a magnetic fluid is 100 Å. It is desirable to develop the ability to prepare particles with controlled size and size distribution. Therefore the first and foremost step in the preparation of ferrofluids is the synthesis of nanoparticles of the adequate size range and their characterization. In this paper we report the synthesis of nanoparticles of lithium ferrite (LiFe<sub>5</sub>O<sub>8</sub>) by a citrate

precursor method and the thorough characterization by X-ray diffraction (XRD), infra red (IR) spectroscopy, and magnetization measurements. Although lithium ferrite possesses a magnetization comparable to other ferrites, to our knowledge, it has not yet been tried for ferrofluid application.

Ferrofluids consists of nanoparticles in the 1–15 nm size range and the major difficulty associated with the study of such nanoparticles is their synthesis. Preparation of nanoparticles requires low temperature processing to control particle growth. The conventional ceramic methods employed in the preparation of materials invariably yield large particles in the micrometer size range owing to the high temperature, usually more than 1000°C, required for the diffusion controlled solid state reaction. In recent years the advent of low-temperature methods of synthesis, e.g., chemical methods, has made the preparation of nanoparticles a reality. Nevertheless, for the preparation of particles in the lowest size ranges (<25 nm) very few methods exist. The citrate precursor method has proved to be a versatile method for the synthesis of nanoparticles in the case of garnets and ferrites [3,4]. In the present study our aims have been (i) to prepare a citrate precursor for synthesis of lithium ferrite (ii) to decompose it at a relatively low temperature to produce nanoparticles of lithium ferrite,

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(iii) to characterize the samples by infrared spectroscopy, XRD and magnetization measurements.

## 2. Experimental

The citrate precursor used in the preparation of lithium ferrite samples was prepared as follows. Lithium and iron nitrates in the 1:5 stoichiometric ratio of cations were dissolved in deionized water and mixed with an aqueous solution of citric acid in a 1:1 M ratio of cations to citric acid. Ammonia solution was added drop by drop with constant stirring until the solution just started smelling of ammonia, to get a clear solution. The solution was warmed to 90°C and left at that temperature for 5–6 h to complete the reaction. The solution thus obtained is evaporated very slowly to obtain the lithium iron citrate precursor. The dried precursor was decomposed and annealed in two stages, at 200°C and 350°C, for 3 and 6 h respectively.

The XRD patterns were recorded on a Rigaku X-ray diffractometer model D Max 2B using Cu K $\alpha$  radiation. The FT IR spectra were recorded on a Perkin-Elmer model Spectrum 2000 Optica in the wave number range 4000–400 cm $^{-1}$ . The magnetization measurements were carried out on a DMS model 880 vibrating sample magnetometer up to an applied field of 10 kOe.

## 3. Results

The precursor obtained on gradual evaporation of the solution is in the form of red brown flakes and is hygroscopic in nature. During the decomposition there is a substantial weight loss due to removal of nitrates and citrates. The powder obtained after decomposition is brown in color.

The XRD pattern of the dried precursor shows amorphous nature. Fig. 1(a) and (b) depicts the XRD patterns of the samples decomposed and annealed at 200°C and 350°C respectively. It may be noted that the width of the lines is large. The particles size obtained using Scherrer formula from the linewidth of (3 1 1) line is  $\sim 10$ -nm [5]. The 350°C annealed sample shows more number of lines and sharper lines as is evident in Fig. 1(b). The  $d$ -values in this case interestingly are closer to the  $\alpha$ -lithium ferrite.

The IR spectra of the 200°C and 350°C samples are shown in Fig. 2. The characteristic IR spectrum of lithium ferrite phase is clearly evident in both the samples [6]. It is evident that the 200°C annealed sample show fewer absorptions than the 350°C annealed sample. The spectra for the 350°C annealed sample shows all the absorptions expected for the 1:3 ordering in lithium ferrite.

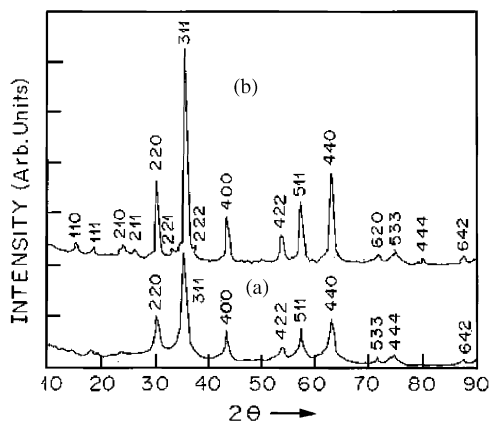


Fig. 1. XRD pattern of the sample annealed at (a) 200°C, and (b) 350°C.

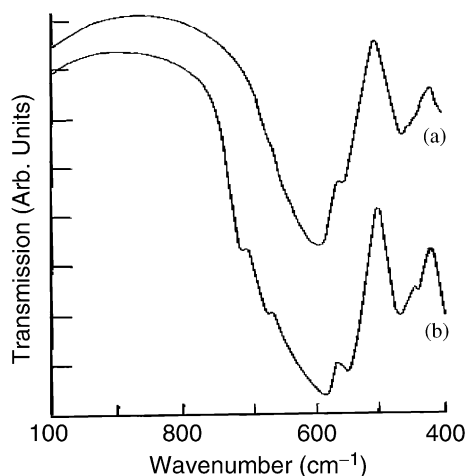


Fig. 2. IR spectra of sample annealed at (a) 200°C, and (b) 350°C.

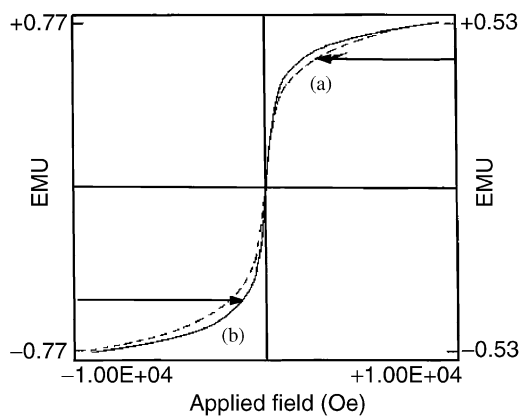


Fig. 3. Hysteresis loops of sample annealed at (a) 200°C, and (b) 350°C.

The hysteresis loops recorded in an applied field of 10 kOe for the samples decomposed and annealed at 200°C and 350°C are given in Fig. 3(a) and (b). The curves for both the samples do not show saturation even at 10 kOe applied field and they do not show any hysteresis. The saturation magnetization values obtained by extrapolation of  $M$  vs.  $1/H$  plots are 35 and 50 emu/g respectively for 200°C and 350°C samples.

#### 4. Discussion

The sample decomposed at 200°C, as seen in Fig. 1(a), surprisingly shows the lithium ferrite phase. The large linewidth is a clear indication of the nanoparticulate nature. The average particle size obtained from the line broadening is  $\sim 10$  nm, which is well within the limit of 1–15 nm required for ferrofluid application.

The 350°C annealed sample as seen in Fig. 1(b) shows a nearly complete set of XRD reflections of lithium ferrite phase indicating better crystallization. Interestingly the  $d$ -values in this case match with the ordered  $\alpha$ -lithium ferrite indicating a phase transformation. It is important that both these samples show lithium ferrite phase even at such low temperatures of their preparation.

IR Spectra of both the samples as shown in Fig. 2(a) and (b) show characteristic absorptions of disordered and ordered lithium ferrite respectively, substantiating the observations in the XRD studies. The less absorption in the 200°C sample clearly shows that it has the disordered form, which confirm the XRD observation for this sample. The 350°C annealed sample shows all the absorptions expected for the ordered Li-ferrite. Owing to the presence of Li and Fe ions on the B-sites lithium ferrite shows unique atomic ordering [6]. A regular arrangement of three Fe followed by a Li ion in rows along [1 1 0] direction gives ordered lithium ferrite. This 1:3 ordering results in an increase in the number of allowed modes of vibrations and IR active modes compared to ordinary spinel structure. Therefore well-defined sharp absorptions in the IR spectrum establish the presence of ordered lithium ferrite in this sample.

The  $M - H$  curves of the 200°C and 350°C annealed samples given in Fig. 3(a) and (b) indicate a particle size

distribution consisting of both ferrimagnetic and superparamagnetic fractions in the samples. The curves do not show saturation even up to applied fields of 10 kOe. Such magnetization behaviors suggest the presence of superparamagnetic nanoparticles in the samples. Therefore magnetization behavior confirms the nanoparticulate nature of the samples observed earlier in XRD studies. The saturation magnetization values calculated are sufficiently high for application in certain low magnetization ferrofluids. The magnetization values are lower than the bulk values owing to the presence of a small amount of undecomposed carbon present in the sample because of the low temperatures employed for decomposition and annealing.

#### 5. Conclusion

The results presented show that nanoparticles of lithium ferrite could be obtained by the citrate precursor method at relatively low temperature. The sample decomposed at 200°C and 350°C, respectively, show disordered and ordered forms of lithium ferrite in the XRD patterns. The characteristic IR spectra of lithium ferrite shown by these samples substantiate the above. Magnetization studies show that these particles are in the superparamagnetic regime and have adequate properties for application in low magnetization ferrofluids.

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