

Preparation of lithium ferrite nanoparticles by high energy ball milling and characterizations

J. Touthang¹, Mamata Maisnam^{1*}, W. Surachanda Singh² and Sumitra Phanjoubam²

¹Department of Physics, National Institute of Technology Manipur, Langol-795004, India

²Department of Physics, Manipur University, Canchipur-795003, India

*Corresponding author

ABSTRACT

Ferrites are ferrimagnetic ceramic materials with inherent useful electromagnetic properties. Of them, spinel-structured ferrites are promising materials for microwave device applications; stress/torsion sensors and energy storage applications like anode materials in lithium batteries, fuel cells, solar cells etc. Nanostructured spinels further have high and wide scope of potential applications. In the present study, two different types of varied sized ferrimagnetic lithium ferrite spinel nanoparticles prepared using chemical sol-gel auto-combustion method were chosen. The prepared spinel particles were heated at 300 °C for 1h. After heating the powders were milled using a High Energy Ball Mill for 30 minutes to further grind the particles and then subjected to various characterizations. Structural characterization was done using X-Ray Diffraction Method (XRD). The study revealed the spinel structure of these samples. Structural parameter such as lattice constant was determined using XRD data and found that the lattice parameter agrees with the standard data. DLS study found the agglomerations of the nanoparticles. The synthesized nanospinel particles were also characterized by the UV-Vis Spectroscopy, the Fourier Transform Infrared Spectroscopy (FTIR). Finally the magnetic hysteresis properties were studied using a Vibrating Sample Magnetometer (VSM).

Keywords: Ferrite nanoparticles, Sol-gel auto-combustion method, XRD, FTIR, Magnetization

I. INTRODUCTION

Ferrimagnetic spinel ferrites have been given considerable interest among the researchers all over the world because of their unique and versatile properties [1]. They are good electromagnetic materials and they have been in use in many technological devices. They crystallized as the spinel AB_2O_4 , where A and B denotes the lattice sites tetrahedrally and octahedrally coordinated by the oxygen ions [6-7]. Lithium ferrites ($Li_{0.5}Fe_{2.5}O_4$) which crystallizes in an inverse spinel structure are widely investigated materials due to their importance in construction and engineering of many electrical components. They show interesting properties for the microwave applications such as in circulators, isolators, and phase shifters due to their high resistivity, low dielectric losses, high Curie temperature, square hysteresis loop and low cost [2-5]. By adopting different synthesis route and doping with magnetic or non-magnetic impurities a variety of lithium ferrites not found in nature may be tailored with correlated and interesting electromagnetic properties. Recently, ferrite nanoparticles achieved great attention from researchers worldwide for their diverse novel applications like hyperthermia, ferrofluids, drug delivery, MRI contrast agents etc.

Magnetic and electrical behaviours for the nanosized ferrites show different behaviour when compared with their bulk counterparts. In the present study, we report the synthesis of cobalt and yttrium substituted lithium ferrite nanoparticles by chemical sol-gel method and high energy ball milling and the studies of their structural, optical and magnetic properties.

II. EXPERIMENTAL

Substituted spinel lithium ferrite of varied sized nanoparticles having compositional formula $Li_{0.495}Co_{0.01}Fe_{2.495}O_4$ (Sample 1), and $Li_{0.495}Co_{0.01}Y_{0.10}Fe_{2.395}O_4$ (Sample 2) were synthesized by chemical sol-gel method. The raw materials used were highly pure lithium nitrate, iron nitrate, cobalt nitrate and yttrium nitrate. The starting materials were taken in stoichiometric proportion and dissolved in ethylene glycol in the ratio 3:1. The mixture was heated at 40 °C for about 30 min until a clear solution was formed. The temperature was increased to 80 °C and kept for 20 min and then to 100 °C. After a few minutes the gel dried and gets self-ignited itself producing a highly voluminous fluffy product. This final product obtained is the as-prepared nanosized substituted lithium ferrite spinels. This product was heated at

300°C for 1h. High Energy Ball Milling was used to further grind the samples in an attempt obtain the ferrite nanoparticles.

XRD studies were done to confirm the structure of the samples. The optical properties of these nanoferrites were characterised using the UV spectrometer (Perkin Elmer, UV/VIS Lambda 35) and Fourier Transform Infrared Spectrometer (Perkin Elmer-FTIR). The magnetic properties of these ferrites were studied from M-H measurement using a Vibrating Sample Magnetometer (VSM). From the M-H measurements, the value of saturation magnetization (M_s), Coercivity (H_c) and Remanence (M_r) of these samples were obtained. The particle size distribution of the nanoparticles were studied using a Zetasizer ZS90 (Melvm). The results of the measurements were analysed.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns for the synthesized nanoparticles. The intense peaks in the patterns for both the samples are indexed with specific planes namely (220), (311), (400), (422), (511), (440). These intense peaks confirmed the formation of single phase with spinel structure in the samples. These peaks agree with the standard data. The lattice parameter obtained from the XRD data are tabulated in table 1. It is found that the lattice parameter for sample 1 and sample 2 has been found to be 8.313 Å and 8.321 Å respectively. The result may be due to the difference in the incorporation of ions of different ionic radius in the two samples.

The FTIR spectra measured in the wave number range 1200-300 cm^{-1} from the ferrites nanoparticles is shown in figure 2. Two broad metal-oxygen bands are seen in the figure and these bands are normally observed for all spinels ferrites. One band which is observed in the range 600-575 cm^{-1} is caused by the stretching vibrations of the tetrahedral metal-oxygen bond while the other band which is observed in the range 500-425 cm^{-1} is caused by the stretching metal-oxygen bond vibrations in the octahedral sites. And the graph showed that the mode of vibrations of the tetrahedral bonds is higher than that of octahedral bonds. The spectra further indicate presence of splitting in both the absorption bands.

Figure.4. shows the UV- visible absorption spectra of the samples. In the entire UV-VIS spectrum, a broad maximum absorption peak has been observed around 350-650nm for both the samples. This may be due to the Fe-ions which form the major components in the samples. The figure showed that the maximum absorption peak for sample 2 shift towards higher wavelength as compared to sample 1. This red shift for sample 2

may be due to the presence of larger sized particle compared to sample 1.

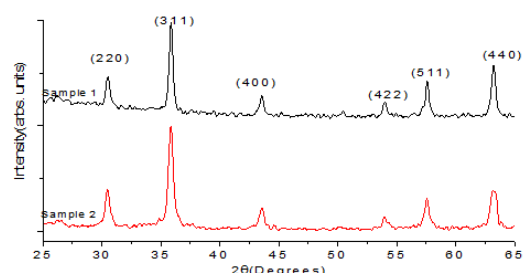


Figure .1. XRD patterns for the nanoparticle samples

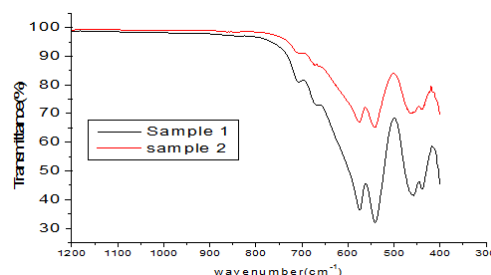


Figure. 2. FTIR spectra for the nanoparticle samples

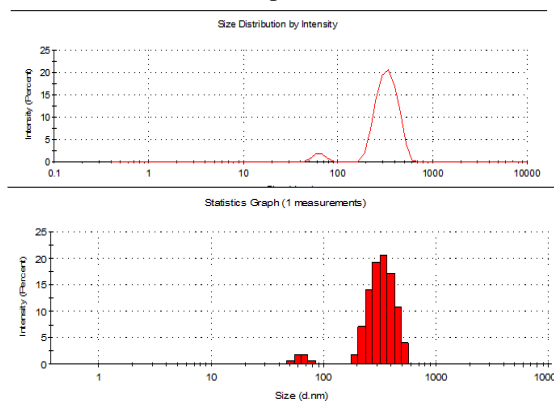


Figure. 3 (a). Particle size distribution study for sample 1

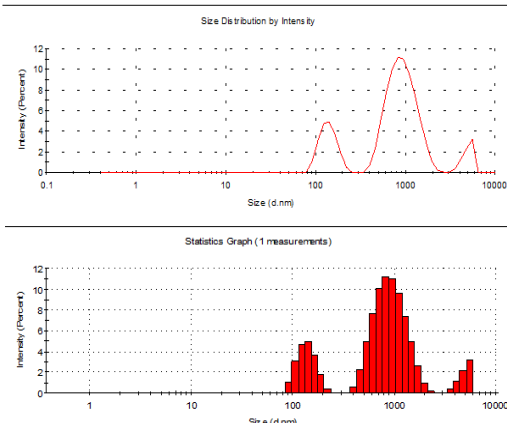


Figure. 3(b). Particle size distribution study for sample 2

The particle size distribution of the samples was studied using a Zetasizer and the distribution plots are shown in figure 3(a) and 3(b). It is found from the distribution plot that sample 1 contains nanoparticles of the range 40-80nm. Bigger sized particles ranging from 200-500 nm are also found in the distribution graph for this sample which may be the agglomerates of the smaller nanoparticles (figure.3 (a)). Similarly sample 2 shows nanoparticles of size ranging from 80-200nm as seen in figure.3(b) and the agglomerates size are found to range from 400-1000nm. Incorporation of bigger sized ions (yttrium) into the spinels results in the change of size of the ferrite particles as obtained in sample 2. These ferrimagnetic spinel particles have the strong tendency to attract among themselves and hence the formation of clusters is observed (Figure 3). The smaller sized particles are found to form smaller agglomerates compared to that of bigger sized particles.

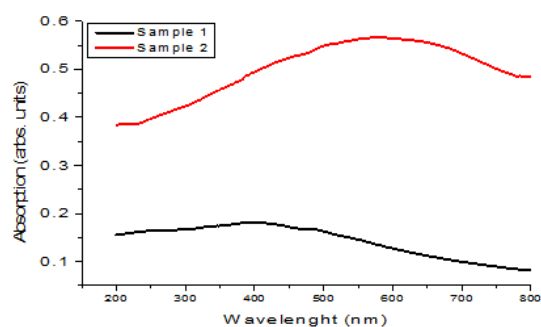


Figure.4. UV-Vis spectra for the nanoparticle samples

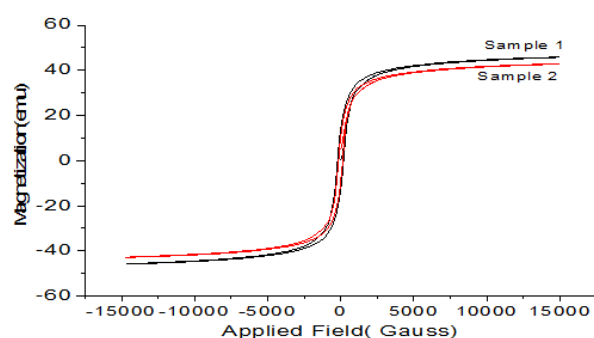


Figure.5. M-H loop for the nanoparticle samples

Table. 1. Structural and magnetic hysteresis parameters for the synthesized nanoparticles.

Samples	Lattice parameter, a (Å)	Saturation magnetization, M_s (emu/g)	Remanence, M_r (emu/g)	Coercivity, H_c
Sample 1	8.313	45.79	13.39	205.66
Sample 2	8.312	42.82	10.11	139.24

The M-H hysteresis loop traced for the different sized nanoparticle samples is shown in Figure. 5. Various magnetic hysteresis parameters viz, magnetization (M_s), remanence (M_r) and coercivity (H_c) were obtained from the loop and tabulated in Table 1. The magnetization (M_s), remanence (M_r) and coercivity (H_c) of the sample 1 has been found to be higher from that of sample 2. Particle size sensitively influences the magnetic hysteresis of spinel ferrites. Magnetic hysteresis is related to intergranular domain wall motion [9] and when the magnetization is not easily reversed, the coercivity, H_c is high. For such range of particles size, coercivity is known to be inversely proportional to the size of the particles. As the size decreases, they tend to contain lesser number of domain walls and the hindrances to intergranular domain wall movement increases. Sample 2 has been further diluted with non-magnetic yttrium ions compared to sample 1; hence a reduction in M_s and M_r is expected in sample 2.

IV. CONCLUSIONS

Different sized and types of lithium ferrite spinel nanoparticles were successfully synthesized by chemical sol-gel autocombustion method and high energy ball milling. XRD studies confirmed the formation of single phase spinel structure in the synthesized samples. The size of the nanoparticles measured using a Zetasizer range from 40- 200 nm though the size of the agglomerates was found to be much bigger. The UV-vis spectrometer spectra showed a red shift for the sample with bigger particle size. Fourier Transform Infrared Spectra showed broad metal-oxygen bands splitting in both the absorption bands. The M-H measurement showed value of saturation magnetization (M_s), Remanence (M_r) and Coercivity (H_c) dependant on the particle size of the samples.

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