Synthesis and Characterization of Copper Doped Lithium Ferrite Nanocomposite

P. Hajasharif, K.Ramesh, S.Sivakumar, P. Sivagurunathan

Abstract: In this paper copper doped lithium ferrite nanoparticles effectively synthesized using sol-gel technique. The synthesized product was analyzed by using TG/DTA, XRD, FT-IR, FE-SEM, HR-TEM, VSM and CV studies. TG/DTA study indicates that the thermal stable of the prepared copper doped lithium ferrite nanoparticles. XRD result confirms that copper doped lithium ferrite nanoparticles have development of cubic phase with Fd3m group and also average crystallite size calculated for different ratios using Scherrer's formula around 40 nm.

FT-IR spectra confirm the presence of absorption band of lower frequency (v_2) at octahedral site and higher frequency (v_1) at tetrahedral site of prepared nanocomposites. The FE-SEM image of $Cu_xLi_{1-x}Fe_2O_4$ (x=0.2) nanocomposites clearly specifies that the spherical morphology with agglomerated particles and the same is confirmed by HR-TEM study. The EDAX analysis showed that the existence of Cu, Fe and O elements. VSM study reveals that copper doped lithium ferrite nanoparticles are paramagnetic in nature. Copper doped lithium ferrite nano composites exhibits the higher specific capacitance value at 587 Fg^{-1} for 10 mVs^{-1} studied from CV.

Keywords: Copper doped lithium ferrite, XRD, FE-SEM, HR-TEM, VSM and CV.

I. INTRODUCTION

Nanotechnology was incorporating to considerate and organize of matter with the dimensions of 1–100 nm, which where unique physical occurrences that support innovative applications. The physical and chemical properties of nanomaterial such as are governed largely by their size and shape. Therefore, nanomaterial is concentrating on emerging easy and effective technique for engineering nanomaterial with controlled size [1]. The field of spinel ferrite is very primitive but significant one, owing their different possible applications and fascinating physics elaborate on in it. More than half-a-century, science researchers and engineers are still interested in several forms of ferrite nanomaterial synthesized by various methods and its several possessions as a purpose of frequency, compositions and temperature etc. The investigation of electrical and magnetic behavior carrying same importance for ferrite based nano composite [2].

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Spinel ferrites had a general formula $(M^{2+})[Fe_2^{3+}]O_4^{2-}$ where Fe^{3+} and M^{2+} are the bivalence and trivalence cations playing on tetrahedral A- site and octahedral B-site interstitial locations of face centered cubic lattice designed by O^{2-} ions. Spinel structures having normal spinel behavior and inverse spinel behavior [3]. Lithium ferrite is broadly used as magnetic material, and its nanoparticle was low-cost replacement to the garnet created materials for the microwave applications in the industries and is a hopeful applicant for cathode materials in support of rechargeable lithium ions batteries [4]. Copper ferrite ($CuFe_2O_4$) were interested material because of their applications in highly developed technologies [5] and mainly used in technical applications like currency counting machine and memory core, etc., owing their numerous properties. The copper doped in lithium ferrite nanomaterials is desired to elude volatilization of lithium at high temperatures. There are various methods for preparing the copper doped lithium ferrite materials such as, sol-gel [6], co-precipitation [7] hydrothermal [8], and solid state reaction methods [9]. At present investigation, the sol-gel method used to synthesize copper doped lithium ferrite. The synthesized samples were analyzed by using TG/DT analysis, XRD, FT-IR, FE-SEM with EDAX, HR-TEM, VSM and CV.
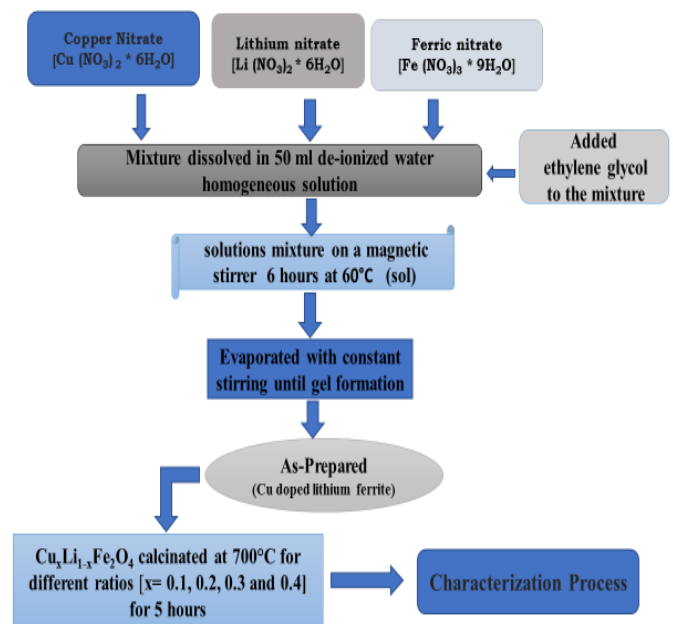
II. EXPERIMENTAL DETAILS

2.1 Materials and method

Fig. 1. Flow chart for synthesis of copper doped lithium ferrite nanoparticles

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Analytical grade chemicals are used for the present work. Copper nitrate hexahydrate [$Cu(NO_3)_2*6H_2O$], lithium nitrate hexahydrate [$Li(NO_3)_2*6H_2O$], ferric nitrate nanohydrate [$Fe(NO_3)_3*9H_2O$] and ethylene glycol chemicals are used without any purification. The whole synthesis of copper doped lithium ferrite procedure deionized water was used.

Typically, ferrite nanocomposite was synthesis via sol-gel method. 2m mol of [$Cu(NO_3)_2.6H_2O$], [$Li(NO_3)_2.6H_2O$] and 4m mol of [$Fe(NO_3)_3.9H_2O$] were individually dissolved into 50 ml deionized water. The powders completely dissolved in the deionized water. A certain quantity of ethylene glycol was added into above mixed solution with constant stirring at 60 °C for 6 hours after wards and kept under stirring until a viscous gel was formed. Further, the sample was calcined at various heat treatments using muffle furnace. The achieved fluffy xerogel element was further dried and manually milled well. Fig.1 shows the flow chart for synthesis of copper doped lithium ferrite nanoparticles.

2.2. Instrumentation details used for characterization

The synthesized sample of copper doped lithium ferrite nanocomposite and further, characterized. The thermal degradation of the prepared sample was analyzed through TG/DT analysis. TG/DT analysis can be performed using the instrument NETZSCH-STA 449 F3 Jupiter with a heat rate of 10°C min⁻¹ under air atmosphere. The phase identification of the copper doped lithium ferrite nanoparticles was analyzed by using PW3040/60 X'pert PRO powder X-ray diffractometer with CuKa radiation (λ =1.5418Å) at 40 kV and 30 mA. The step scans were performed for 2 hours values in the angular series of 10°C to 80°C with a scanning speed value 10 min⁻¹. The Functional group analysis (FT-IR) was recorded from 4000 cm⁻¹ to 400 cm⁻¹ on a Shimadzu FT-IR 8201PC infrared spectrometer. Field emission - scanning electron microscope (FE-SEM) analysis helps to use for size of the morphology were carried out by JEM 2100F. EDAX was recorded using a thermal emission scanning electron microscope, JSM6701F model. High resolution transmission electron microscope (HR-TEM) images recorded using JSM-2100F JEOL. Magnetic study was performed using a lakeshore 7410 vibrating sample magnetometer (VSM) with a highest magnetic field 20 kOe at normal room temperature. An electrochemical behavior was performed using cyclic voltammeter (CV) with the model number CHI 660.

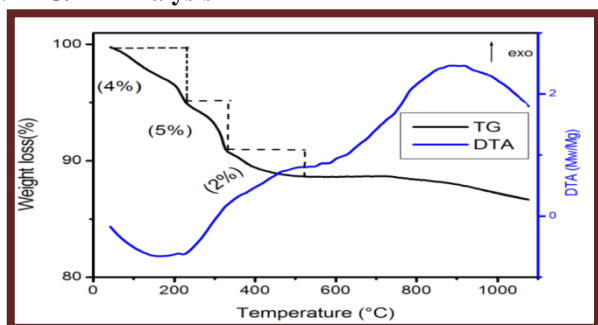### III. RESULTS AND DISCUSSIONS

3.1 TG/DT Analysis

Fig. 2. TG/DTA analysis for copper doped lithium ferrite nanoparticles

From Fig.2, the TG study, the first weight loss is reached at 47–227 °C (4%), which is attributed due to the loss of water molecules. The second loss of weight is reached at 228 - 331°C (5%) due to elimination of organic matter. The third weight loss is 332 to 523 °C (2%) accredited to the formation of crystallization turning point due to other impurities corresponding to the total weight loss is about 11 % of copper doped lithium ferrite nanoparticles were due to the leaving of nitrate. After 451 °C in which no weight loss have been observed. In this study thermally stable at 400°C to 800°C, in which heat treatment is necessary for crystalline of sample. From DTA curve showed the peak of exothermic was noted at 502°C and the endothermic peak at 225°C was accredited to crystallization of sample [10]. The results observed from TG/DTA, 700°C is suitably fixed for further characterizations of the prepared samples.
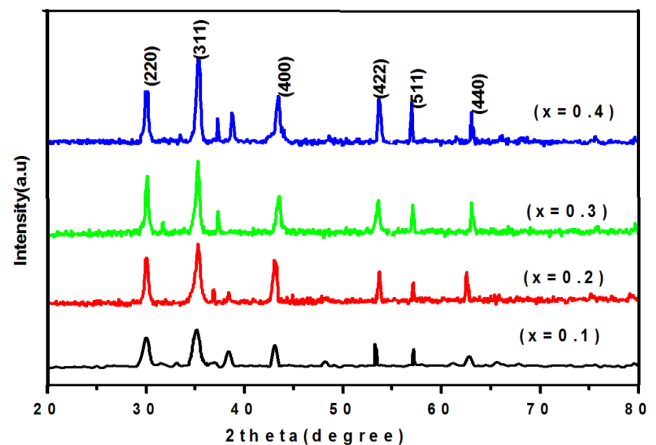
3.2 XRD analysis

Fig. 3. XRD analysis for copper doped lithium ferrite nanoparticles (x=0.1, 0.2, 0.3 and 0.4)

X-ray diffractometer analysis of copper doped lithium ferrite nanocomposites for different concentrations $Cu_x Li_{1-x} Fe_2O_4$ (concentrations of x=0.1, 0.2, 0.3 and 0.4) calcinated at 700°C as shown in Fig.3. From the results, showed that all ratio of copper doped lithium ferrite nanocomposites are well crystalline nature. The XRD peaks are well indexed to the planes (220), (311), (400), (422), (511) and (440) of pure spinel cubic phase belongs Fd-3m space group, which is completely matched with standard JCPDS of copper doped lithium ferrite nanocompsite [11] further size of the crystal was calculated by using Debye-Scherrer's formula, the calculated crystallite size and lattice parameter was tabulated.

From the Table.I, showed that the concentration of copper content (x) increases, crystallite size also increases. Lattice parameter 'a' was determined from the diffraction peak using following formula: $a_2 = d_2*(h_2 + k_2 + l_2)$ where d is the inter-reticular distance and h, k, l are the Miller indices of the plane. From the values, lattice parameter increase with

Table-I: Structural parameter of copper doped lithium ferrite nanoparticles

Concentration (x)	Crystallite size (nm)	Lattice Parameter (Å)
0.1	33	8.167
0.2	36	8.358
0.3	38	8.372
0.4	41	8.519

increase in copper content (x) this may be due to doping ion has larger ionic radii than the displaced ion. In the current work, Cu^{2+} ions of ionic radius 0.071 nm substitute Li^{1+} (0.078 nm) and Fe^{3+} (0.067 nm) respectively.
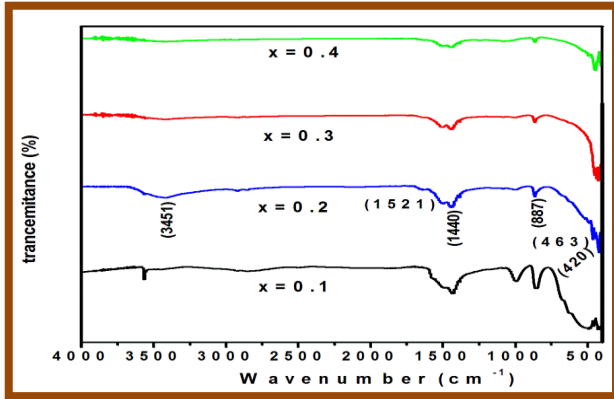
3.3 FTIR Study

Fig. 4. FTIR Spectrum of copper doped lithium ferrite nanoparticles

The FT-IR spectrum of copper doped lithium ferrite nanoparticles with different concentrations $Cu_x Li_{1-x} Fe_2O_4$ (x=0.1, 0.2, 0.3 and 0.4) calcinated at 700°C are shown in Fig.4. FT-IR spectra of copper doped lithium ferrite nanoparticles measured in the region of 4000 cm^{-1} - 400 cm^{-1}. The wide band around 3451 cm^{-1} and absorption peaks at 1521 cm^{-1} matches to the respective hydroxyl group. A sharp peak around 1440 cm^{-1} in the spinel ferrite is accredited to the symmetric vibration of the nitrate group. Usually, the metal oxide vibrations happen below 1000cm^{-1}. Fe–O–H bending vibrations were observed at 887 cm^{-1}. In the present work, The higher absorption band at 463 cm^{-1} specified as Fe^{3+}–O^{2-} stretching of tetrahedral complexes and lower band at 420 cm^{-1} corresponded to metal stretching of octahedral Cu^{2+}–O^{2-} [12].
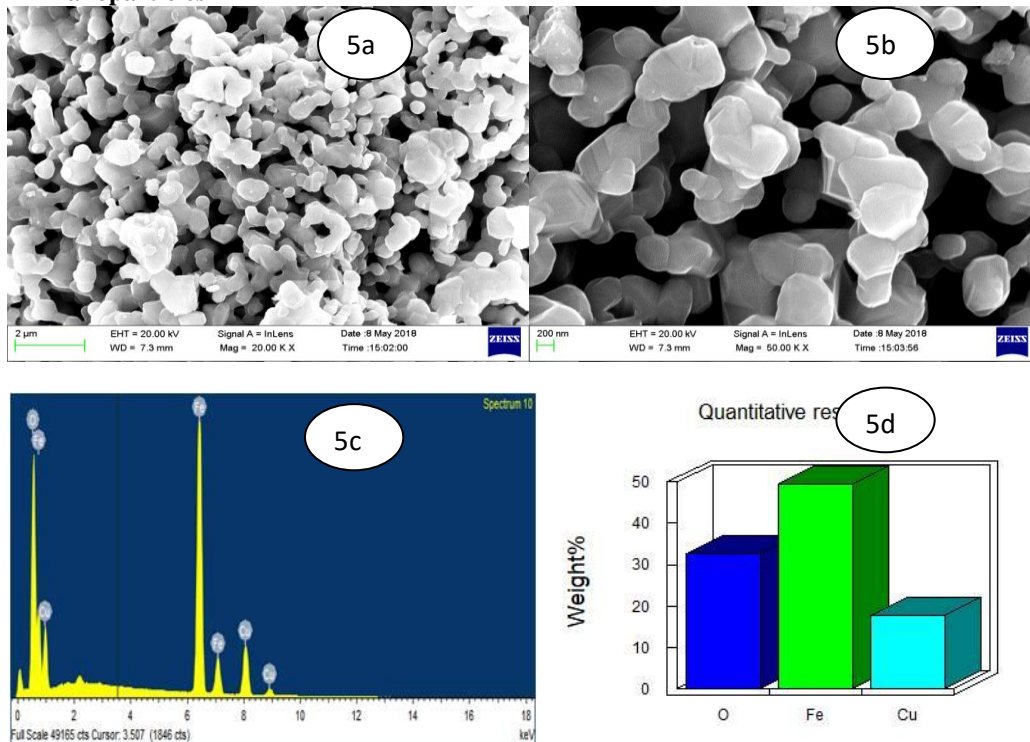
3.4 FESEM Study

Fig. 5 (a), 5(b). FE-SEM spectrum of copper doped lithium ferrite nanoparticles with different magnification, 5(c) EDAX Spectrum and 5(d) Atomic weight percentages of copper doped lithium ferrite nanoparticles

From the results uptained from XRD and FT-IR the ratio 0.2 is suitably fixed for further characterizations, the morphological analysis of $Cu_x Li_{1-x} Fe_2O_4$ (x=0.2) nanocomposites calcinated at 700 °C as shown in Fig. 5a and 5b. From Fig 5a, shows the FE-SEM image is clearly indicate and illustrated in the synthesized product was

spherical in nature with the smooth surfaces and small agglomeration no other obvious defectsof the prepared samples. Fig 5c,

displays the quantitative chemical analysis of the materials confirmed by EDAX analysis of the product exhibits the Cu, Fe and O elements were presented. No any other impurities were appeared in the EDAX spectrum showed the good crystallinity of the copper doped lithium ferrite nanoparticles. In the EDAX analysis disappearing of Li element is due to EDAX detector cannot detect elements due to lesser atomic number. Li has very low energy of characteristic radiation, so not easy to detect. Fig. 5d shown that the atomic weight percentages of Cu, Fe and O.
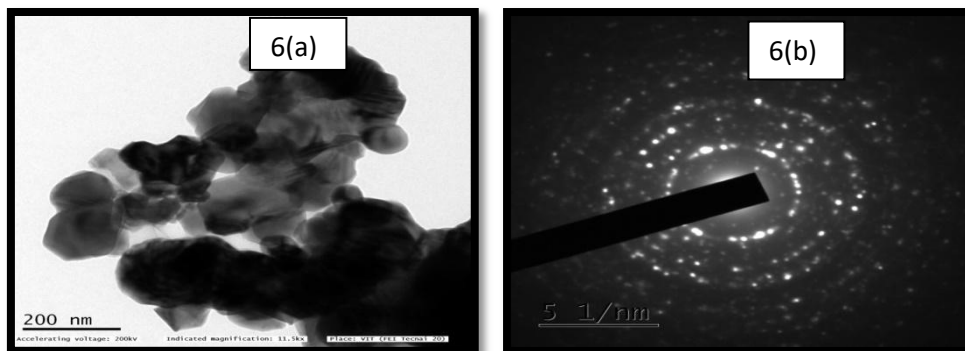
3.4 HR-TEM Study

Fig. 6(a). HR-TEM Spectrum of copper doped lithium ferrite nanoparticles at 200nm and 6(b) SAED pattern of copper doped lithium ferrite nanoparticles

High magnification of nanomaterials are mainly studied using HR-TEM. The high resolution makes it perfect for imaging the materials on the atomic scale and morphological analysis also performed by the HR-TEM images. Fig.6(a) shows the typical pictorial of HR-TEM pictures of the preparations copper doped lithium ferrite nanoparticles. From the figure, the synthesized nanocomposites was spherical in nature with the small agglomerations. Fig.6(b) illustrates the high-resolution SAED Pattern of copper doped lithium ferrite nanoparticles. It clearly visualize that the synthesized nanocomposites are well crystallinity dispersion sharp rings formed in the prepared sample along with the major (311) plane, its strengthen the results obtained in XRD [13].
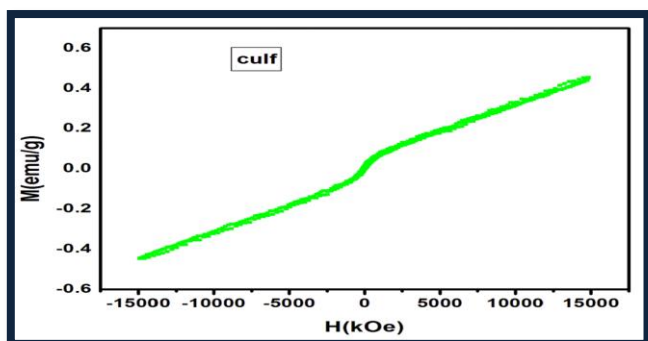
3.5 VSM study

Fig. 7. M-H Curve of copper doped lithium ferrite nanoparticles

Fig.7 indicate that the magnetic hysteresis loop of $Cu_xLi_{1-x}Fe_2O_4$ (x=0.2) nanocomposites were performed in the magnetic field range of -15000 Oe to 15000 Oe at normal room temperature. For VSM study synthesized materials were calcinated at 700°C for 3 hours. Magnetic measurement of $Cu_xLi_{1-x}Fe_2O_4$ (x=0.2) ferrite nanocomposites can be defined on the source of cation distribution. From the observation, it is found that Li^{1+} ions occupy at B-sites (octahedral) while Cu^{2+} ions are occupying

mutually A and B sites. The magnetic moment of Cu^{2+} ions is extra than that of Li^{1+} and is not as much as that of Fe^{3+} ions. The lesser value of coercivity is due to the survival of paramagnetic nanocomposite, along with S shape curve that describes the behavior of soft magnetic material [14]. Values of saturation magnetization, coercivity and retentivity are presented in Table II.

Table-II: Magnetization values of copper doped lithium ferrite nanoparticles

Saturation magnetization(Ms)	Magnetic coercivity(Hc)	Magnetic retentivity(Mr)
0.45095 emu/g	83.546 Oe	7.1234 emu/g

From the Table II, the magnetization values are changed than that of undoped lithium ferrite nanocomposite [15]. From these the copper doped lithium ferrite was stable with good crystalinity and its suitable for magnetic recording devices.
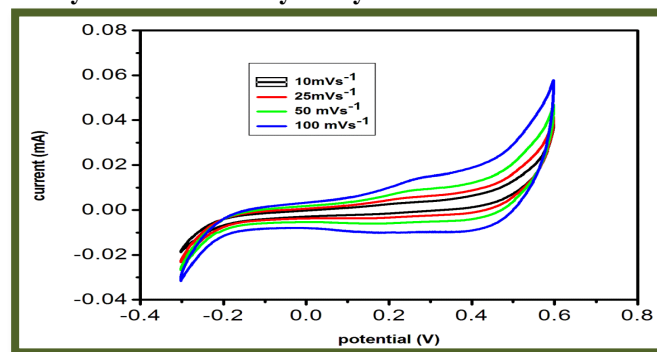
3.6 Cyclic Voltammetery Study

Fig. 8. Cyclic voltammetery of copper doped lithium ferrite nanoparticles

Cyclic Voltammetery was useful to study the supercapacitor behaviour of the $Cu_x Li_{1-x} Fe_2O_4$ (x=0.2) ferrite nanocompsite calcinated at 700°C. The CV experiments performed with predictable three-electrode system in 0.2 M tetra butyl ammonium for chlorate electrolyte in the potential window -0.3 V to 0.6 V for the different scan rate of 10 mVs^{-1}, 25 mVs^{-1}, 50 mVs^{-1} and 100 mVs^{-1}, these results are pictured in the Fig.8. The higher capacitance value noted at 587 Fg^{-1} for the lower scan rate of 10 mVs^{-1} and the lower capacitance value 216 Fg^{-1} for high scan rate of 100 mVs^{-1} using CV study.

Table-III: Specific capacitance values for different scan rates

Scan rates (mV/s)	10	25	50	100
Specific capacitances (F/g)	587	412	305	216

Table.III shows that, when the scan rate is increased, the capacitance values are decreased, for the reason that lower scan rates specify the ion diffusion both inner and outer most of the penetration and the high scan rate denote that the ion diffusion occur only for external surfaces of the electrodes [16].

IV.   CONCLUSION

In summary, copper doped lithium ferrite $Cu_x Li_{1-x} Fe_2O_4$ (x=0.2) ferrite nanocomposite were calcinated at 700 °C prepared by sol-gel method. TG/DTA analysis revealed thermal losses of the prepared nanocomposite. The structural, compositional and capacitive behaviour of the synthesized properties was well studied. The X-ray diffraction confirmed that the resulting product was very well crystalline, form and calculated the average crystallite size, lattice parameter. FT-IR spectra showed the presence of functional group and active sites. FE-SEM and HR-TEM pictures shows that the spherical nature of the prepared copper doped lithium ferrite nanocomposite. EDAX spectrum shows the Cu, Fe and O are presented. The magnetic measurement of copper doped lithium ferrite nanocompsite confirms that the low coercivity is due to the presence of paramagnetic in nature. The CV study confirms higher specific capacitance values were estimated, it's suitable for supercapacitor applications.

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