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Synthesis, Structural & Dielectrical Properties of Citrate-Gel Prepared Lithium Nano Ferrites

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ABSTRACT
Nano particles of Lithium ferrites with the Chemical formula $Li_{0.5}$ $Fe_{2.5}$ O_4 were synthesized by citrate-gel auto combustion technique at a very low temperature(180^0C).The X-Ray diffraction analysis of as synthesized powder and sintered powder has confirmed the formation of single phase cubic spinel structure. The as prepared sample was composed of nearly spherical nano particles with an average particle size 42.83nm,further annealing at 673 K for 4 hours did not increase the particle size noticeably(44nm). The surface morphology of the sample was investigated by Scanning Electron Microscope(SEM). The dielectric parameters such as dielectric constant ,loss tangent ,AC conductivity of the sample were studied as a function of frequency in the range of 20Hz to 2MHz at room temperature using Agilent E4980 Precession LCR Meter. The dielectric constant , loss tangent ,AC conductivity of the sample shows a normal dielectric behavior with frequency. The DC Resistivity of the sample was measured by two probe method from the room temperature to well beyond the Curie temperature. The discontinuity in the resistivity vs temperature graph shows the Curie temperature of the sample.
Keywords: ferrites, Nano-particles, XRD, SEM, LCR meter

I. INTRODUCTION

Magnetic nano particles continue to be a fascinating subject of interest both from the fundamental and application point of view[1]. Their properties at the nano level are quite different from their bulk size and they exhibit different magnetic and electric properties[2-6]. Nano ferrites are very important group of magnetic materials due to their extensive use in a wide range of applications

Lithium ferrites ($Li_{0.5}$ $Fe_{2.5}$ O_4) are useful materials for microwave devices and memory core applications[7-10]. Though lithium ferrites have been a thoroughly investigated ferrite system[10-11], because of their excellent square loop characteristics, this system is being revisited to investigate the finite size effects as well as to devise new materials based on lithium ferrite for microwave and other applications. Bulk Lithium Ferrite has an inverse cation distribution of the form $(Fe^{3+})_A[Li_{0.5}$ $Fe_{1.5}]_B$. The interplay between the superexchange interactions of Fe^{+3} ions at A and B sublattices gives rise to ferri magnetic ordering of magnetic moments[12-13].
The wider use of lithium ferrites particularly in microwave devices is restricted due to the difficulties experienced in sintering the material at the high temperatures. The irreversible loss of lithium and oxygen during the sintering was the main cause that made lithium ferrites technologically difficult to prepare. The Citrate-Gel method provides an easy alternative for the preparation of nano $Li_{0.5}$ $Fe_{2.5}$ O_4 at low temperatures(180^oC)

The properties of ferrites are dependent on several factors, namely method of preparation, grain size, chemical composition, sintering temperature and atmosphere[14].

Several researchers synthesized spinel ferrites are prepared by conventional methods like double sintering method, solid state reaction method, hydro thermal method etc. which has the disadvantages such as high period heating, which may result in divalent volatilization and change the stoichiometry[15]. In this context we use citrate-gel auto combustion technique for synthesis. This method is mentioned in below flowchart. The citrate – gel process is simple, easy and doesn't require any elaborate and expensive experimental setup [16-17].

II. Experimental Details:

The lithium nano ferrite particles having the Chemical formula $Li_{0.5}$ $Fe_{2.5}$ O_4 were synthesized by citrate gel auto combustion technique using the below mentioned raw materials.

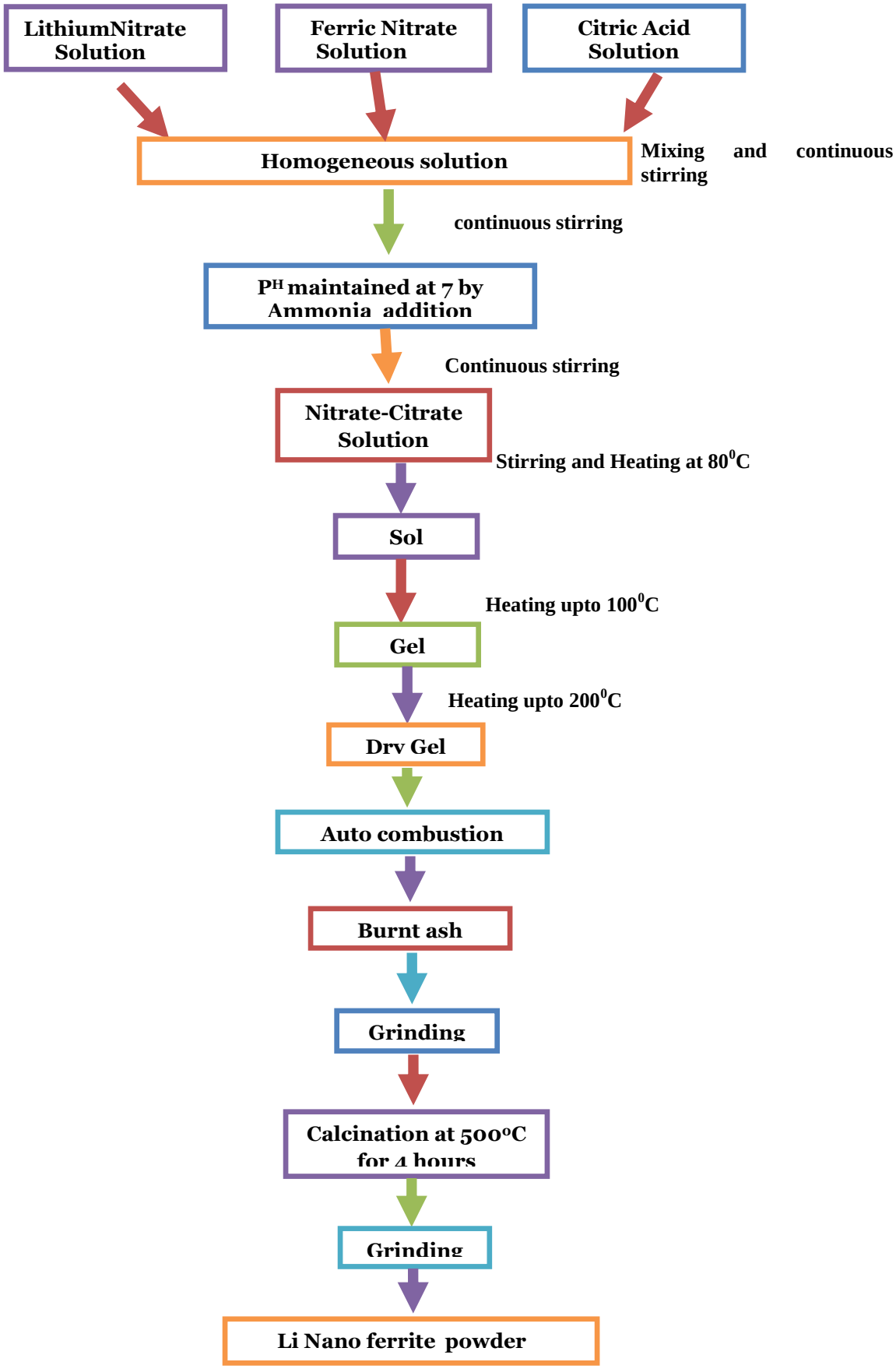
2.1 Raw Materials:

*Lithium Nitrate-99% Pure (AR Grade) ($LiNO_3$)
*Ferric Nitrate-99% pure(AR grade) ($Fe(NO_3)_29H_2O$)
*Citric acid - 99% pure (AR grade) ($C_6H_8O_7.H_2O$) .
*Ammonia - 99% pure (AR grade) (NH_3)

2.2 The flow chart for the synthesis of lithium nano ferrite:

In this method Nitrates and Citric acid (all are SDFCL-sd fine Chem.Limited 99% pure AR grade)having molar ratio 1:3 were dissolved in deionized water. Citric acid acts as chelating agent and helps in the homogenous distribution of metal ions. The burnt powder was grind in Agate Mortar and

Pestle to get a fine Ferrite powder. Finally the burnt powder was calcinated in air at 500^{o}C temperature for four hours and cooled to room temperature.



2.3 Structural Characterization by X-ray diffraction studies:

The structural Characterization was carried out using X-ray Diffractometer Bruker D8 advanced system with a diffracted monochromatic beam with Cu Kα radiation of wavelength 1.5405A^o. The diffraction pattern of lithium nano ferrite particles between the Bragg Angles 5^o to 80^o in steps of 0.04^o/Sec. were shown in fig.

The crystalline size was calculated for the sample using the high intensity 311 peak and using Scherrer formula [18] while taking into account the intensity broadening[19].

Scherrer Formula:

$$\text{Crystalline size of the sample } D = \frac{0.91\lambda}{\beta \cos\theta}$$

Where λ is the wavelength of X-ray used[20]

β is the Width of diffraction peak i,e. Full Width Half Maxima(FWHM)

θ is the peak position.

Lattice parameter(a) of the sample was calculated by the formula

$$a=d*(\sqrt{h^2+k^2+l^2}) \quad [21]$$

Where a= Lattice Constant

(hkl) are the Miller Indices

d is the inter planner spacing,

The X-ray density of the prepared sample was calculated using the relation

$$dX = \frac{8M}{a^3 N} \text{ [g/cm}^3\text{][22]}$$

Whwre M = molecular weight of the sample

a is the lattice parameter and N is the Avogadro number.

The Volume of the Unit Cell **V= a^3**

2.4 Dielectric Properties:

To measure the dielectric properties, the powders were added with a small amount (2%) Poly Vinyl Alcohol(PVA) as a binder to press the powders into circular pellets of diameter of 13mm and thickness of 1mm applying a pressure of 5 tons. The prepared pellets were sintered at 500^{o}C for 4 hours in air in muffle furnace for the densification of the sample. For dielectric measurements silver paint was applied on both sides of the pellets and air dried to have good ohmic contact.

The dielectrical properties of lithium nano ferrite particles were carried out using Agilent E4980 Precession LCR Meter. Pellet shaped samples were employed for the evaluation of the dielectrical properties. By using the LCR meter , Capacitance of the pellet, tanδ(loss tangent) and Capacitance of air with same thickness as pellet were measured.

The real part of the dielectric constant(ε') was determined from the following formula

$$\varepsilon' = \frac{C_p}{C_{air}}$$

where **ε'**= real part of dielectric constant

C_p = Capacitance of the pellet in faraday

C_{air}= Capacitance of the air in faraday

The imaginary part of the dielectric constant(ε") or dielectric loss was measured by using the following relation **ε" = ε' tan** □

The ac conductivity was calculated using the values of frequency(f) and loss tangent factor

□$_{AC}$ **= 2**□**f** ε_o **ε ε'tan** □ [23]

where $\varepsilon_{o=}$ constant permittivity of free space= 8.85X10^{-12} F/m

f is the frequency of the applied field

2.5 DC Resistivity Studies:

The dc electrical resistivity of the sample is obtained by a simple two probe method from the room temperature to well beyond the Curie temperature of the sample.

The dc electrical resistivity of the sample is measured by the formula

$$\rho = \frac{RA}{L}$$

Where R = resistance of the sample

A is the area of the pellet, L is the thickness of the pellet.

III. Results and Discuussions:

3.1 XRD Analysis:

Fig (1) and Fig(2) shows the X-Ray diffraction pattern of synthesized and sintered lithium nano ferrites.

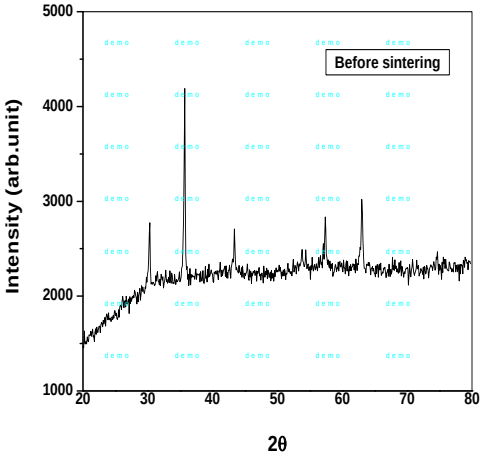


Fig (1) XRD Pattern of the Lithium Ferrite before sintering

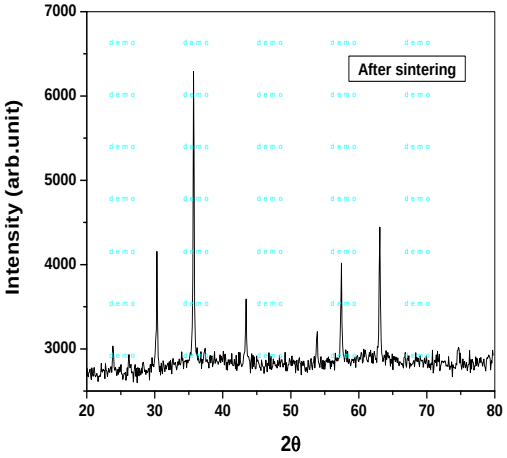


Fig (2) **XRD Pattern of the Lithium Ferrite After sintering**

From the XRD pattern of the as synthesized powder, it is clear that the as burnt powder is also in single phase with a spinel structure which indicates that the ferrite can be directly formed after the auto combustion of the gel with out sintering. The broad peaks in the XRD pattern indicates the fine particle nature of the particles. From the XRD pattern of the as synthesized powder and sintered powder it is clearly shows that the positions of the reflections peaks are almost identical to each other. This implies that the basic structure of the nano particles is essentially same as that of the bulk material.

The grain size of the sample was evaluated by measuring the FWHM.

All Bragg reflections have been indexed, which confirm the formation of cubic spinel structure in single phase without any impurity peak. The strongest reflection comes from the (311) plane, which denotes the spinel phase. The peaks indexed to (220),(311),(400),(422), (511) and (440)planes of a cubic unit cell, all planes are the allowed planes which indicates the formation of cubic spinel structure in single phase.[24]

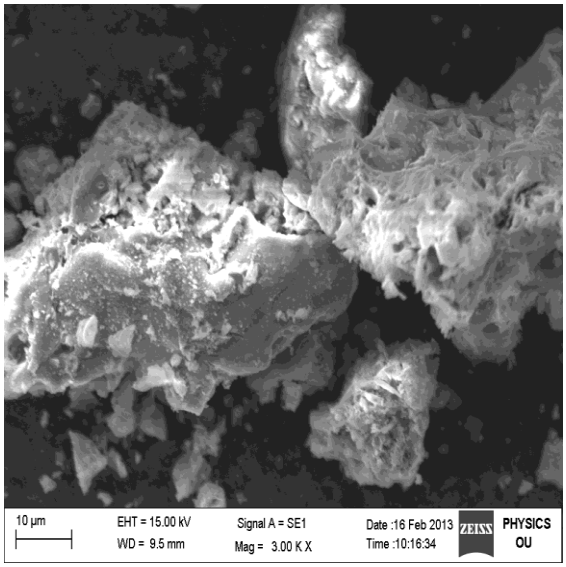
Calculated values of Particle size, Lattice Parameter, The X-ray density, Volumes of the synthesized and sintered nano particles were shown in table(1). From the table one can conclude that after calcinations at 400^{o}C for 4 hours, the reflection peaks of the sample become sharper and narrower, indicating the improvement of crystallinity. As the temperature increases particle size and X-ray density are increases and lattice parameter and volume of the unit cell decreases.

Table(1)

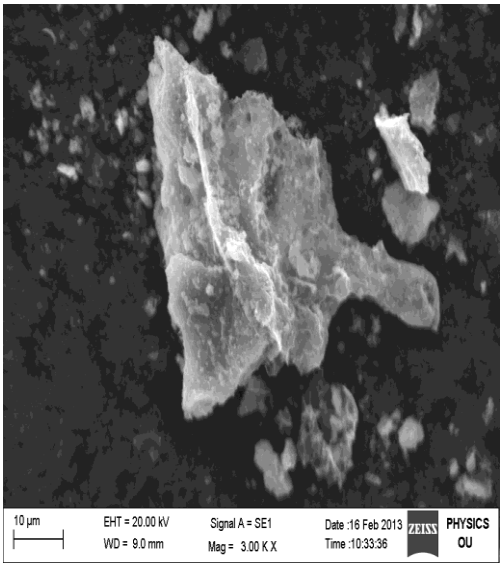
Sample	2θ(degrees)	FWHM	Particle size(nm)	Lattice Parameter in A^{o}	X-ray density g/cm^{3}	Volume of the unit cell
Before Sintering	35.681	0.197	42.83	8.3389	4.7436	579.864
After Sintering	35.710	0.190	44.41	8.3332	4.7533	578.675

3.2 SEM ANALYSIS:

The morphological analysis were performed using SEM(Scanning Electron Microscope). The secondary electron images were taken at different magnifications to study the morphology. It can seen from SEM micrographs that the morphology of the particles is very similar. They indicate that the particle size of the samples lies in the nanometer region having a spherical shape and a narrow size distribution. The particle sharpness is more or less spherical with some cluster/agglomeration between the particles. The SEM micrographs of the synthesized & sintered nano particles are shown in below fig(3) & fig(4)



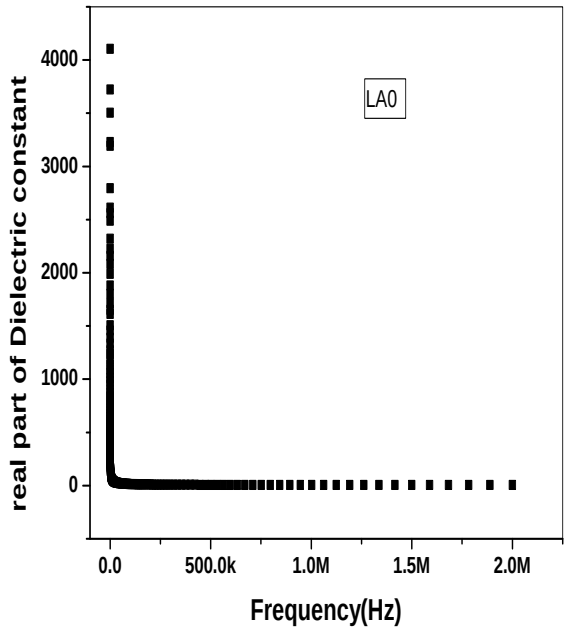
Fig(3)SEM diagram of Lithium nano ferrite before sintering



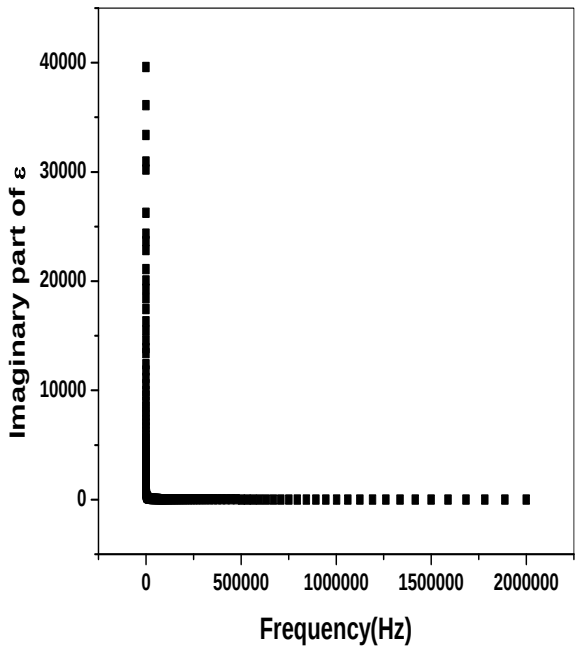
Fig(4)SEM diagram of lithium nano ferrite after sintering

3.3 Dielectrrical properties of Lithium Nano Ferrites:

The dielectrical properties of the sample as a function of frequency in the range of 20Hz to 2MHz at room temperature were studied. Fig(5), fig(6) and Fig(7) shows the variation of real part of dielectric constant ,imaginary part of dielectric constant and loss tangent as a function of frequency. From these plots it is observed that lithium ferrite have higher dielectric parameters at lower frequency and there is a decreasing trend in value with increasing frequency which is a normal behavior of ferromagnetic materials. The decrease in dielectrical properties with frequency can be explained on the basis of Koops Theory[25], which consider the dielectric structure as an inhomogeneous medium of the Maxwell-wagner type [26]. In this model, the dielectric structure is assumed to be consisting of well-conducting grains which are separated by poorly conducting grain bounderies. It was found that for ferrites, the permittivity is directly proportional to the square root of the conductivity[27]. Therefore the grains have higher values of conductivity and permittivity, while the grain boundaries have the lower values. At lower frequencies the grain boundaries are more effective than grains in electrical conduction. Therefoe permittivity is high at the lower frequencies and decreases as frequency increases.

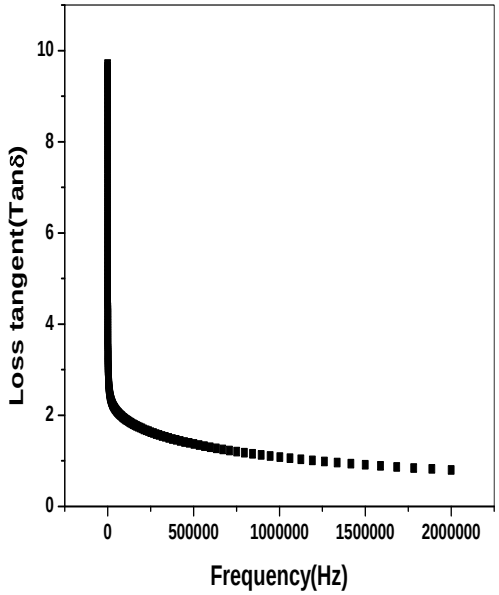


Fig(5) Variation of dielectric constant(□') with frequency

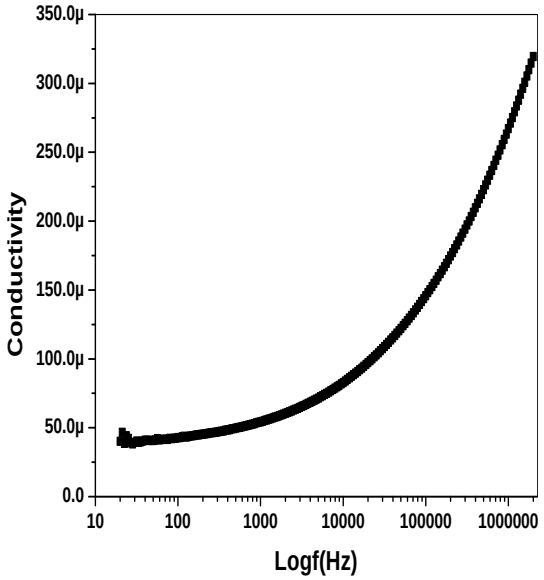


Fig(6) Variation of dielectric constant(□') with frequency

Fig(6)



Fig(7) Variation of Loss tangent with frequency

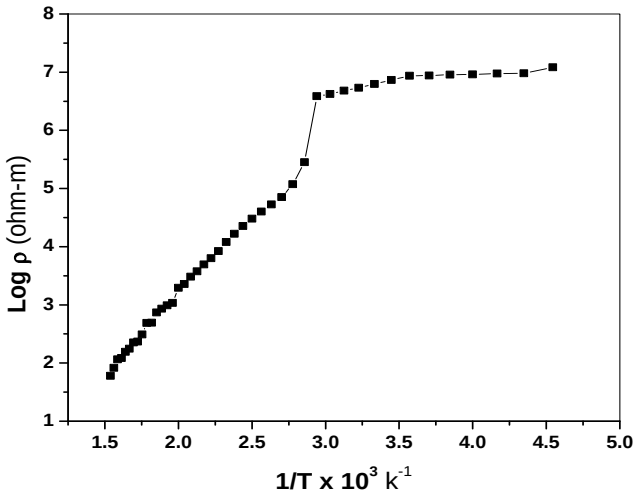


Fig(8)Variation of Conductivity with frequency

Figre (8) shows the variation of the AC Conductivity of lithium ferrite as a function of frequency in the range of 20Hz to 20MHz at room temperature. AC conductivity shows an increasing trend with the increase in frequency for the sample. AC conductivity variation is linear in frequency in the low frequency regime because at low frequencies the grain boundaries are more active and hence the hoping of Fe^{+2} and Fe^{+3} ions is less at lower frequencies. As the frequency of the applied field increases, the conductive grains become more active there by promoting between Fe^{+2} and Fe^{+3} ions, thereby increasing the hoping conduction. A gradual increase in conductivity was observed with frequency.

3.4 DC RESISTIVITY:

DC Resistivity of the sample was measured by the two probe method from the room temperature to well beyond the Curie temperature. A graph is plot between the log p vs 1000/T, this graph shown in below fig(9). From the graph, one can observe that as the temperature increases, resistivity values slowly decreases, at one point the resistivity value rapidly changes, this anomaly represents the Curie temperature of the sample and alsofound that it is nearly equals to ~340^{o}C. after the Curie Temperature resistivity follows the linear behavior i.e while further increasing the temperature corresponding resistivity values decreases linearly.



Fig(9)Variation of resistivity with temperature

IV. CONCLUSIONS

1. Citrate Gel auto combustion technique is a convenient way for obtaining a homogeneous nanosized Lithium ferrites.
2. X-ray diffraction pattern confirms the formation of cubic spinel structure in single phase without any impurity peak. It is in good agreement with the standard data from ICSD

3. SEM analysis reveal largely agglomerated, well defined nanoparticles of the sample powder with inhomogeneous broader grain size distribution
4. The dielectric constant, loss tangent, AC conductivity of the sample shows anormal dielectric behavior with frequency has been explained on the basis of space charge polarization mechanism as discussed in Maxwell-Wagner Model.
5. Low values of conductivity around room temperature indicate that the given sample may be good for the microwave applications that require negligible eddy currents.
6. The discontinuity in the curve (graph is plot between the log ρ vs 1000/T) shows the Curie point of the sample

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V. Acknowledgments

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