Structural and electrical properties of $CuLa_yFe_{2-y}O_4$ ferrites

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Abstract

Ferrite with the general formula $CuLa_yFe_{2-y}O_4$ (where y=0.02, 0.04, 0.06, 0.08 and 0.1), were prepared by standard ceramic technique. The main cubic spinel structure phase for all samples was confirmed by x-ray diffraction patterns with the appearance of small amount of secondary phases. The lattice parameter results were 8.285-8.348 Å. X-ray density increased with La addition and showed values between 5.5826 – 5.7461gm/cm^3. The Atomic Force Microscopy (AFM) showed that the average grain size was decreasing with the increase in La concentration. The Hall coefficient was found to be positive. It demonstrates that the majority of charge carriers of p-type, suggesting that the mechanism of conduction is predominantly caused by hopping of holes. The resistivity was noticed to increase with the increase in La substitution. The activation energy E_{av} decreased with the frequency increase. The AC conductivity was found to increase with the frequency and La addition. Dielectric constant was noticed to decrease with frequency and La addition. The dielectric loss factor decreased with La content because rare earths are known as low dielectric loss materials.

Key words
Ferrite, electrical properties, magnetic materials.

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دراسة الخواص التركيبية والكهربائية لفيرايت $CuLa_yFe_{2-y}O_4$

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الخلاصة

تم تحضير أحد انواع الفيرايت ذو الصيغة التركيبية العامة $CuLa_yFe_{2-y}O_4$ حيث أن (y=0.02, 0.04, 0.06, 0.08 and 0.1)، استخدمت بالتحضير الطريقة القياسية في معالجة المساحيق. طور التركيب الرئيسي لكل العينات spinel cubic الذي أكد بأنماط انحراف الاشعة السينية مع ظهور كمية صغيرة من الاطوار الثانوية. ثابت الشبيكة يتراوح قيمته بين (8.285-8.348Å). الكثافة المقاسة بالاشعة السينية تزداد مع زيادة تراكيز La حيث تتراوح قيمتها بين (5.5826-7461.5gm/cm^3). ان استعمال مجهر القوة الذري AFM بين بأن معدل الحجم الحبيبي يقل كلما زاد تركيز La. معامل هول بين بأن حاملات الشحنة الاغلبية تكون من نوع p، تم الاقتراح بأن امكانية التوصيل بالدرجة الاولى سببها قفز الفجوات. أما المقاومة النوعية لوحظت بأنها تزداد مع زيادة تركيزLa. طاقة التنشيط تنخفض كلما زاد التردد أما التوصيلية الكهربائية تزداد بزيادة تراكيز La وبزيادة التردد. ثوابت العزل الكهربائية $\varepsilon_1,\varepsilon_2$ تنخفض مع أضافة La والتردد.

Introduction

Electrical and magnetic properties of spinel ferrites depend upon the method of preparation, nature of dopants, dopant concentration, etc. Copper ferrite ($CuFe_2O_4$) is one of the important spinel ferrites because it exhibits phase transitions, changes semiconducting properties, shows electrical switching and tetragonality variation when treated under different conditions in addition to interesting magnetic and electrical properties with chemical and thermal stabilities [1]. It is used in the wide range of applications in gas sensing [2], catalytic applications [3-5], Li ion batteries [6] high density magneto-optic recording devices, color imaging, bio processing, magnetic refrigeration and ferrofluids [1-7]. Moreover, $CuFe_2O_4$ assumes great significance because of its high electric conductivity, high thermal stability and high catalytic activity for O_2 evolution from alumina-cryolite system used for aluminum production [8]. Vermenko, et al. (1973), studied the effect of small amount of ions of a rare-earth elements (REE) on the properties of ferrites with a spinel structure, where it was shown that such ferrites possess a slight solubility for ions of the REE and that it is the composition within the solubility range that exhibit interesting properties [9]. The purpose of this work is to study the structural, electrical and dielectric properties of copper ferrites as a function of composition and frequency.

Experimental

Ferrites with the general formula $CuLa_yFe_{2-y}O_4$ (where y=0.02, 0.04, 0.06, 0.08 and 0.1), were prepared by standard ceramic technique. High purity powders of CuO, Fe_2O_3 and La_2O_3 were weighted and mixed according to the general composition formula by moles ratio. The powders were mixed and blended homogenously through dry mixing using a ball mill. After mixing of the powders, they were pressed at room temperature under a pressure (17MPa) to produce sample in shape of a pellet, The samples were finally sintered at 900˚C for (2h) and then left to cool down to room temperature. The spinel structure was characterized by x-ray diffraction carried out using Shimadzu XRD-6000 diffractometer with Cu kα radiation (λ=1.5405 Å) at scanning speed 5 deg/min. The atomic force Microscope AFM studies were performed on Angestrom Advanced Inc., 2008, USA. The AC measurements were performed using Agilent impendence analyzer 4294 A. The Hall Effect measurements were performed using four-point probe on Ecopia HMS-3000.

Results and Discussion

1. X-ray Diffraction

X-ray diffraction patterns of the samples with y=0.02, 0.04, 0.06, 0.08 and 0.1 are shown in Fig.1 . The characteristic peaks belong to the (Fd3m) cubic spinel space group. The main phase was cubic spinel structure for all samples were confirmed by x-ray diffraction patterns with the appearance of small amount of secondary phases. The lattice parameter results were (8.285-8.348)Å. X-ray density generally increased with La addition and showed values between (5.5826 – 5.7461)gm/cm^{3}as shown in Table 1.

The X-ray patterns were used to calculate the lattice parameter (a) from the d-spacing using equation (1), for cubic structure

$$a= d_{hkl} (h^2+k^2+l^2)^{1/2} \quad (1)$$

Where (*h*, *k* and *l*) are the Miller's indices.

The X-ray density (d_x) determined as follows

$$d_x=(ZM/Na^3) \quad (2)$$

where (Z) is the number of molecules per unit cell (Z=8), M is the molecular weight , the value of M various with y concentrations and (N= 6.022 *10^{23} /mol^{-1}) is Avagadro's number [10].

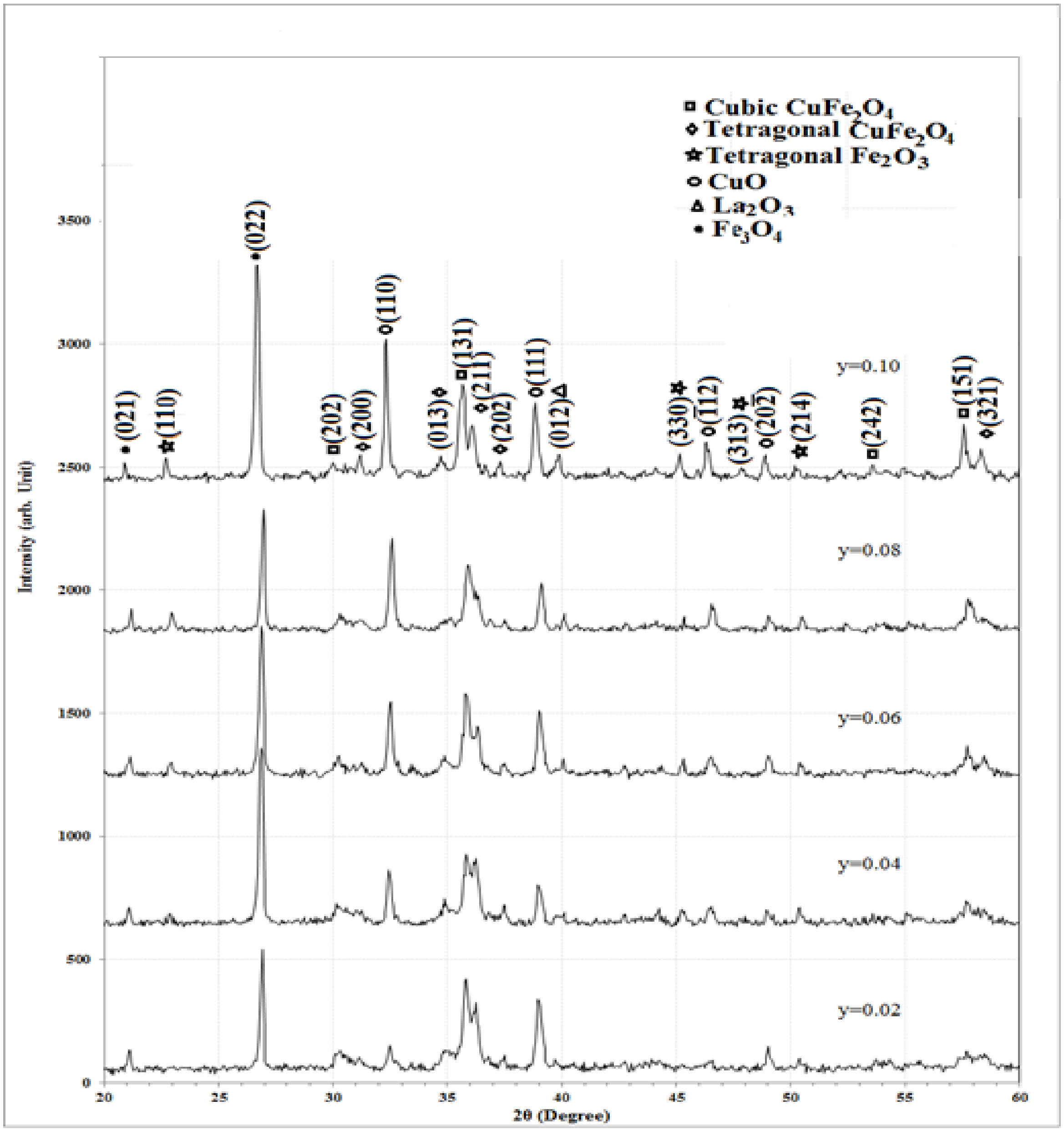

Fig.1: XRD patterns of $CuLa_yFe_{2-y}O_4$ ferrites.

Table1: Effect of La content on Lattice parameter (a), density of unit cell (d_x), Molecular weight (M) unit cell volume(v).

y	d_{hkl} (Å)	hkl	M (gm/mol)	a (Å)	V ($cm^{3)}$)	d_x (gm/cm^3)
0.02	2.505	(131)	240.911	8.308	$5.735*10^{-22}$	5.5826
0.04	2.504	(131)	242.572	8.305	$5.728*10^{-22}$	5.6278
0.06	2.505	(131)	244.233	8.308	$5.735*10^{-22}$	5.6596
0.08	2.498	(131)	245.894	8.285	$5.687*10^{-22}$	5.7461
0.1	2.517	(131)	247.555	8.348	$5.818*10^{-22}$	5.6549

2. AFM

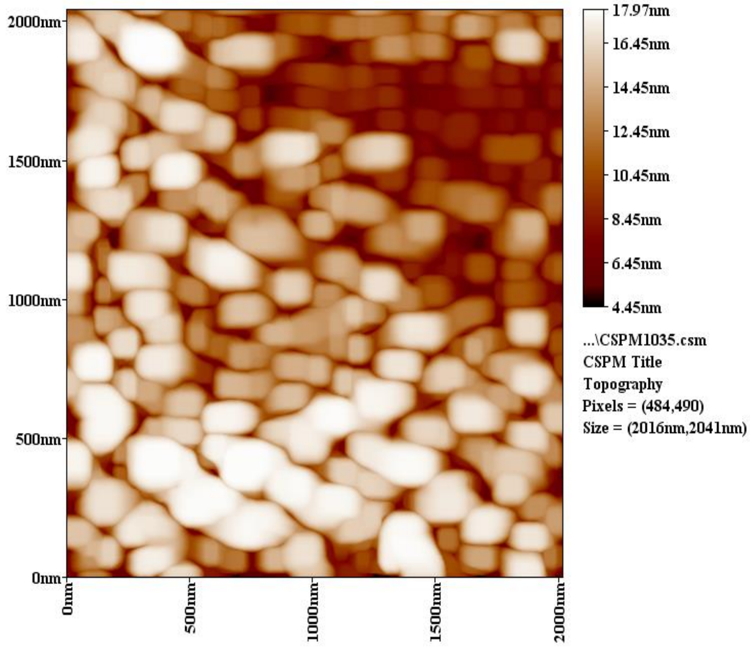

Fig.2: AFM micrographs for the composition ($CuLa_{0.04}Fe_{1.96}O_4$).

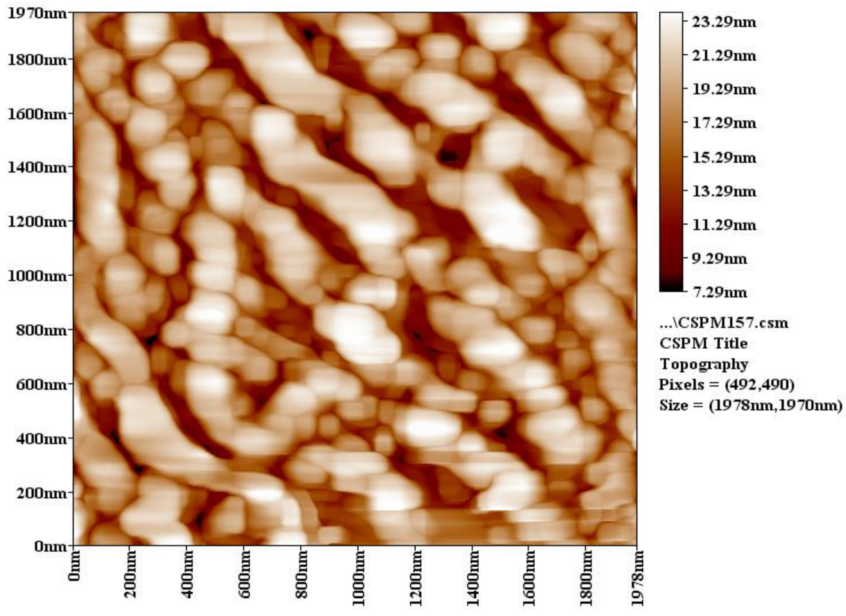

Fig.3: AFM micrographs for the composition ($CuLa_{0.1}Fe_{1.9}O_4$).

The atomic force microscopy (AFM) showed that the average diameter of the grains decreased from 125.75 nm to 88.25 nm with the increase in La substitution.

3. Hall-Effect

Table 2: Lanthanum ion content effect on Hall mobility, sheet concentration, Resistivity, conductivity and Hall coefficient.

Sample no.	Sheet concentration [/cm^3]	Mobility [cm^2/V.s]	Resistivity [Ω. cm]	Magneto-resistance[Ω]	Conductivity [1/Ω. cm]	Average hall coefficient [m^2/C]
1	4.087E+6	1.170E+3	3.916E+8	1.245E+9	2.554E-9	4.582E+11
2	1.691E+6	9.201E+2	1.204E+9	9.297E+8	8.308E-10	1.108E+12
3	7.312E+5	1.915E+3	1.337E+9	2.026E+9	7.478E-10	2.561E+12
4	7.125E+6	1.462E+2	1.798E+9	3.459E+9	5.563E-10	2.628E+11
5	1.443E+6	8.039E+2	1.614E+9	1.593E+9	6.195E-10	1.298E+12

The resistivity was found to increase with La content due to the decrease in charge mobility. This may suggest that the resistivity here is mainly governed by charge carrier mobility rather than carrier concentration. The results of holes coefficient listed in Table 2 showed a p-type semiconductor behavior. Then the conduction mechanism in this ferrite is hopping of electrons between $Fe^{3+}$and Fe^{2+}ions and hopping of halls between $Cu^{+2}$and Cu^{+3} which is the dominant one. The number of hopping of holes between $Cu^{+2}$and Cu^{+3} ions increases with La^{+3}doping. This is because of Fe^{3+} ions migration from the octahedral to the tetrahedral sites. The decrease in Hall mobility with La addition can be attributed to the restrictions in the lattice by the large La^{3+} doping ions.

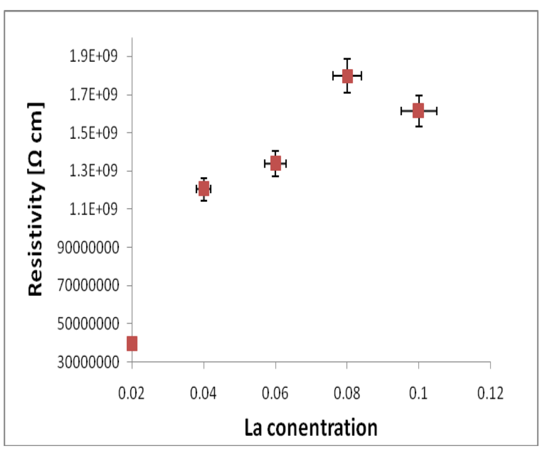

Fig.4. Effect of La concentration as a function of resistivity.

4. AC measurement

The activation energy E_σ decreased with the frequency increase as shown in Fig.6. The AC conductivity σ was found to increase with the frequency and La addition as shown in Fig.7. The temperature dependence of the electrical conductivity (σ) is given by the relationship

$$\sigma=\sigma_0 \exp [- E_\sigma / KT] \quad (3)$$

where K is the Boltzman's constant, E_σ is the activation energy for conduction and σ_0 is a constant.

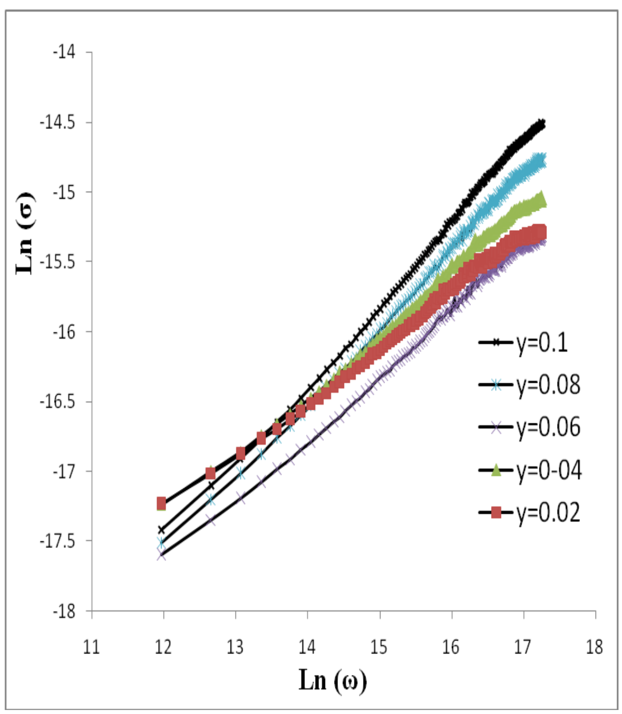

Fig.5: Effect of conductivity as a function of frequency.

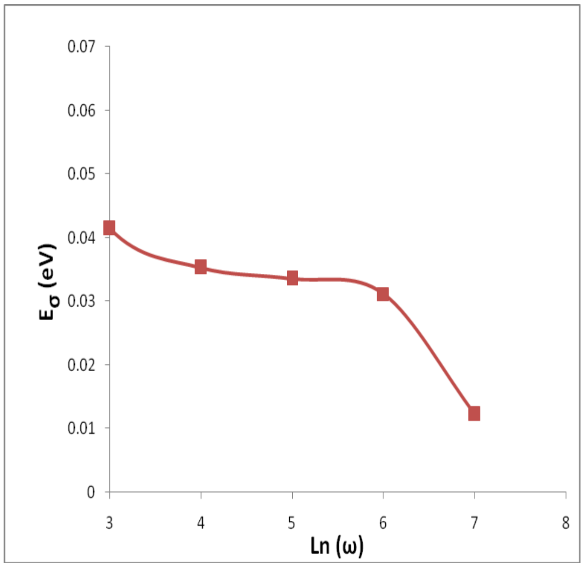

Fig.6: Effect of activation energy as a function of frequency.

Dielectric properties

The dielectric constant ε_1 and dielectric loss factor ε_2 determined as follows:

$$\varepsilon_1 = c\,t/(\varepsilon_0 A) \quad (4)$$

$$\varepsilon_2 = 1.8 \times 10^{10} (\sigma/f) \quad (5)$$

where ε_0 is the permittivity of free space, ε_0 is constant value = 8.859×10^{-14} F/cm, t is the thickness of the sample, A is the cross-sectional area of the flat surface of the pellet, c is the capacitance, f is the frequency and σ is the ac conductivity.

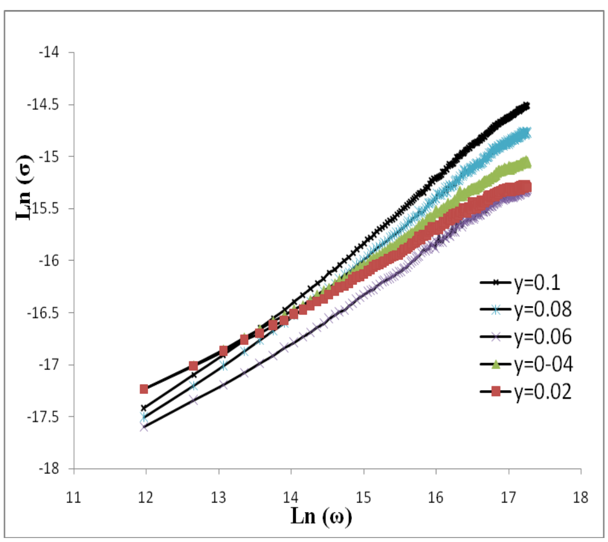

Fig.7: Effect of conductivity as a function of frequency.

Fig.8 shows the dependence of the real part of dielectric constant ε_1 on the frequency ω, for different La doping contents. The dielectric constant is found to decrease more rapidly at low frequencies than at higher frequencies, showing the usual dielectric dispersion. The dispersion of dielectric constant with frequency is due to Maxwell-Wagner type interfacial polarization and is in agreement with koop's phenomenological theory [11,12]. The polarization in ferrite is through a mechanism similar to the conduction process. The presence of Fe^{3+} and Fe^{2+} ions has rendered ferrite materials dipolar. Rotational displacement of dipoles results in orientational polarization. In ferrites, the rotation of $Fe^{2+} \leftrightarrow Fe^{3+}$ dipoles may be visualized as the exchange of electrons between the ions so that the dipoles align themselves in response to the alternating field. The existence of inertia to the charge movement would cause relaxation of the polarization. In general the dielectric constant increase with La content may be due to the various contributions to the polarization.

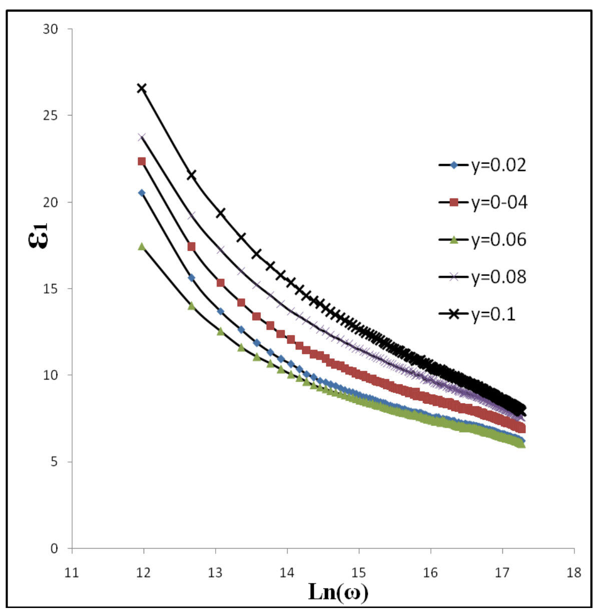

Fig.8: Effect of dielectric constant with frequency and with La addition.

The dielectric loss factor ε_2 versus frequency ω is shown in Fig. 9. The decrease in (ε_2) with increasing frequency agrees well with Deby's type relaxation process [13]. The dielectric loss factor was noticed to decrease with La content because rare earths are known as low dielectric loss materials. The Conduction in ferrite is attributed to hopping of electrons from Fe^{3+} to Fe^{2+}ions. The number of such ion pairs depends upon the sintering conditions and amount of reduction of Fe^{3+} to Fe^{2+} at elevated temperatures. The resistivity of ferrite is controlled by the Fe^{2+} concentration on the B-site. The most probable mechanism for n-type conduction is electron hopping between Fe^{3+} and Fe^{2+}ions, such as

$$Fe^{2+} \leftrightarrow Fe^{3+} + e^- \quad (6)$$

The hole exchange between $Cu^{2+}$and Cu^{1+} ions was responsible for transportation of p-type charge carriers. The coupling mechanism for whole exchange can be represented as

$$Cu^{2+} \leftrightarrow Cu^{1+} + e^+ \text{ (hole)} \quad (7)$$

The La^{3+} ion occupies an octahedral site (B-site), which leads to the replacement of some Fe^{3+} ions from B-sites.

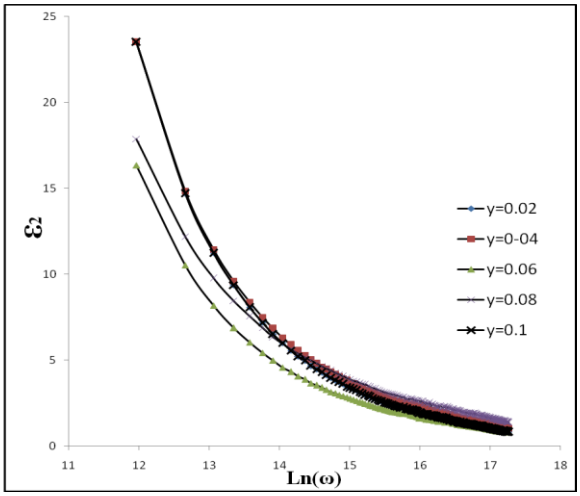

Fig.9: Effect of dielectric loss with frequency and with La addition.

Fig.10. shows that the temperature dependence of the electrical conductivity (σ) was given by the equation (3).

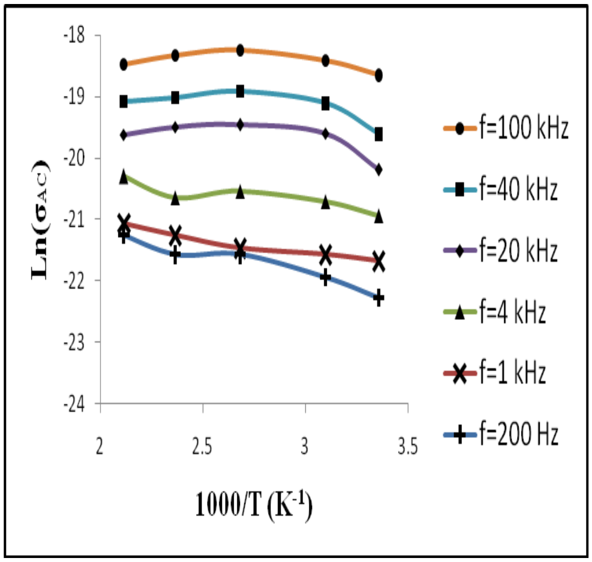

Fig.10: Temperature dependence of the AC conductivity (σ).

Conclusions

To summarize the main ideas obtained, the following conclusion can be drawn from this work:

1. X-ray density generally increased with La addition and showed values between 5.5826 – 5.7461 gm/cm^{3}.
2. The grain size plays a major role in determining the electrical properties. The average grain size was decreasing with the increase in La concentration.
3. The results of Hall coefficient showed a p-type semiconductor behavior. The conduction mechanism in this ferrite is hopping of halls between $Cu^{+2}$and Cu^{+1}.
4. The AC conductivity was found to increase with the frequency and La addition.
5. Dielectric constant was noticed to decrease with frequency and with La addition and dielectric loss was noticed to decease with the frequency and with La addition

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