Temperature, Frequency and Composition Dependence of Dielectric Properties of Nb Substituted Li-ferrites

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Samples having the chemical formula $Li_{0.5+x}Nb_x Fe_{2.5-2x} O_4$ ($0 \leq x \leq 0.20$) were prepared by the standard ceramic method. The real part of the dielectric constant έ and the ac conductivity σ_{ac} are measured at different frequencies from 50-10^5 Hz and in the temperature range (300-700 K) and then the dielectric loss tangent tan δ was calculated. The sample with x=0.2 showed the lowest values of σ_{ac} and έ, at any given temperature, as compared with the other samples. Moreover, έ and σ_{ac} showed an increase with temperature for all samples while tan δ (T) showed a maximum around 600 K. έ and σ_{ac} are decreased with frequency without relaxation. The effect of Nb concentration on the dielectric parameters is discussed according to the two layer model.

1. Introduction:

Amongest ferrites, Li and Li–substituted ferrites have great importance in many applications because of their square hysteresis loop in memory applications and microwave components such as phase shifters, isolators, and circulators [1-3]. To improve the electrical and magnetic properties of Li ferrites, divalent, trivalent and tetravalent ion substitution were studied [2,4-6] . The effect of pentavalent Nb ion on the electrical resistivity and magnetic properties of Mn-Zn ferrite was reported [7]. Moreover, the magnetic properties of Nb substituted Mn-Zn were investigated, using Mössbaur, [8]. Furthermore, the magnetic properties of Nb substituted Li ferrites were also studied [9]. The aim of the present work was to study the electrical properties (ac conductivity σ_{ac}, dielectric constant έ and dielectric loss tan δ) of Nb substituted Li-ferrites to know the optimum concentration of Nb which improves the dielectric properties and to correlate between these properties.

2. Experimental techniques:

Samples with the chemical formula $Li_{0.5+x}Nb_xFe_{2.5-2x}O_4$ ($0 \leq x \leq 0.20$) were prepared using the standard ceramic method [9]. The samples were presintered at 850^0C for 6 hrs and finally sintered at 1050˚ C for 6 hrs. The heating and cooling rates were 300 K and 60 K per hour respectively. X-ray diffraction patterns showed that the samples with x=0.0 and 0.1 have single spinel phase while $\gamma - Fe_2O_3$ and Nb_2O_5 phases with intensities less than 10% were detected for $x > 0.1$ [9]. The surfaces of the samples were coated with silver paste as a contact material for the electrical measurements. The real part of the dielectric constant έ is determined from the relation $\acute{\varepsilon} = \frac{C}{C_\circ}$ where $Co = \varepsilon o (\frac{A}{d})$; A being the cross sectional area, d is the thickness of the sample and ε_o is the permittivity of free space. The capacitance C is measured using PM6304 LCR meter. The ac electrical conductivity σ_{ac} is measured using the two electrode method and hence the dielectric loss tangent tan δ was calculated from the relation $\tan\delta = \frac{4\pi\sigma_{ac}}{\omega\varepsilon'}$, ω is the angular frequency.

The quantities έ, σ_{ac} and tan δ are determined at different temperatures (300-700K) as a function of frequency (for frequency ranged from 50 Hz to 100 kHz).

3. Results and discussion

Temperature dependence of σ_{ac}, έ and tan δ:

Figure.(1-a) shows the temperature dependence of σ_{ac} for different Nb concentrations at f = 10 kHz. The Figure shows that σ_{ac} increases gradually with temperature up to 550 K after which a rapid increase is obtained. The activation energy E_σ, which is calculated from the slope of the relation $\sigma = \sigma_o e^{-E\sigma/KT}$, where σ_o is the conductivity at infinite temperature and k is the Boltzmann's constant. These changes seem to be independent of the Nb concentration. The Curie temperature of the investigated samples was reported to be higher than 850 K [9]. Thus the change in E_σ at $T \approx 550$ K could not be described as a magnetic transition but it may be attributed to a change in the conduction mechanism, from extrinsic to intrinsic semiconductors [10].

Figure (1-b) indicates the change of έ with temperature for different Nb concentrations at f = 10 kHz. The data in the figure shows that έ has a small value and is nearly independent of temperature up to $T \approx 550$ K for the sample with x=0 and up to $T \approx 600$ K for substituted samples. The constancy of έ with

temperature can be attributed to the impurities in the samples which are localized at low temperature (up to T≈600 K). Such a behavior is a general trend in ionic solids [11]. For higher temperatures, the charge carries are free to move through the crystal causing a polarization and hence έ increases.

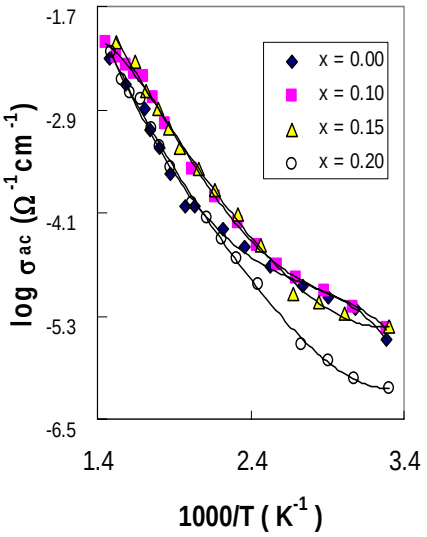

Fig.(1-a): Variations of log σ_{ac} with the inverse of absolute temperature at f=10 kHz.

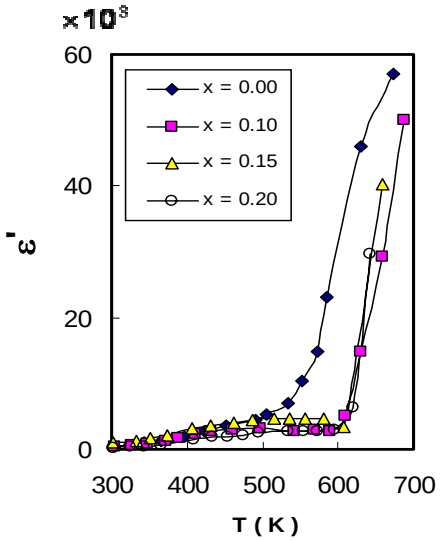

Fig.(1-b): Variations of έ with absolute temperature at f=10 kHz.

Figure (1-c) shows the changes of tan δ with temperature. It seems that tan δ has, in general, small values and indicates a peak around 600 K. The appearance of a maximum in tan δ could be explained according to Koops's model [12] in which the solid is assumed to be composed of grains and grain boundaries. Each one has different parameters where the grains have low resistivity and large thickness while the grain boundaries have high resistivity and small thickness. Moreover, it was assumed that [13] each of the grains and grain boundaries has its characteristic peak. Thus the observed peak in tan δ may be attributed to the contribution from the grain boundaries, where the impurities reside, which take part in the conduction at low temperatures. The role of the grains may appear at higher temperatures.

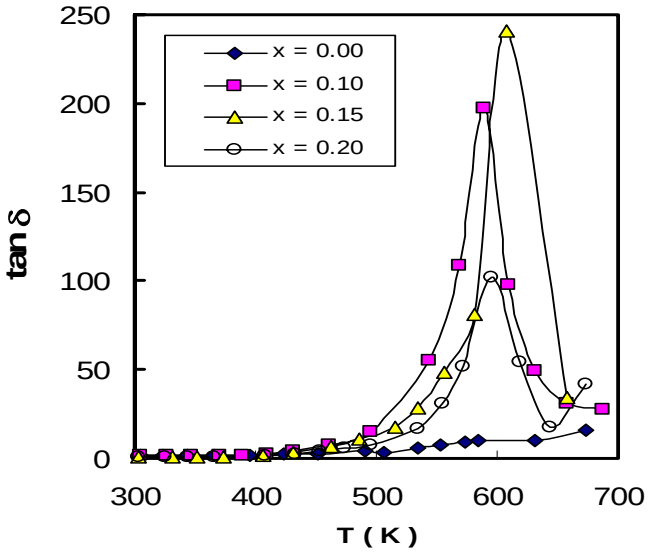

Fig.(1-c): Variations of tan δ with absolute temperature at f=10 kHz.

Frequency dependence of σ_{ac}, έ and tan δ:

Figure (2 – a) shows the variations of the ac conductivity σ_{ac} with the frequency "f" at a constant temperature of 348 K. As a normal behavior, σ_{ac} increases with f and could be expressed, at a constant temperature, as $\sigma_{ac} = \sigma_{ac} + \sigma(\omega)$ where σ_{ac} is the dc conductivity. Moreover,the frequency dependence of the conductivity, $\sigma(\omega)$ follows the relation [14]

$$\sigma(\omega) = A\,\omega^{n}$$

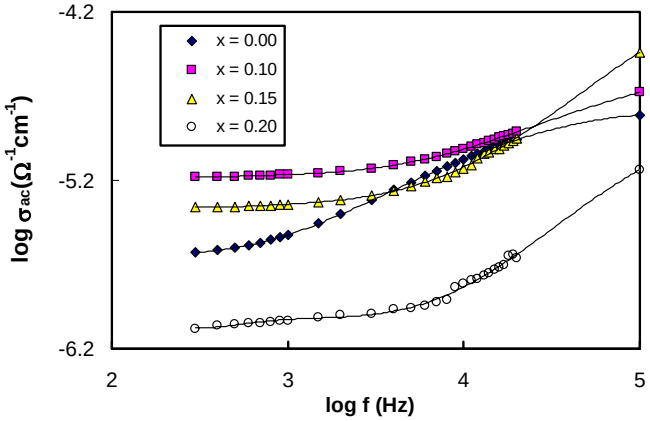

Fig.(2-a): Frequency dependence of σ_{ac} at T=348 K.

where $\omega = 2\pi$ f, n is a dimensionless exponent and A has the dimensions of $\Omega^{-1}cm^{-1}$. Moreover, the plot of log σ (ω) versus log ω at T = 348 K showed two regions depending on the frequency range. The following table summarizes the values of A_1 and n_1 for the low frequency range (up to 4kHz) and A_2 and n_2 for the high frequency range (4kHz – 100kHz) concerning the investigated samples. It is clear that A's and n's are compositional dependent as was previously reported[15].

X	-log A_1	-log A_2	n_1	n_2
0.00	10.870	7.198	1.240	0.414
0.10	8.145	8.829	0.520	0.702
0.15	8.670	10.210	0.625	0.990
0.20	7.930	10.730	0.356	0.960

The variations of έ with frequency is shown in Fig (2 – b). It is seen that έ decreases gradually with increasing f. Such a behavior was previously reported for different ferrites [15–18] and could be explained assuming that the dielectric constant έ and the conductivity have the same origin where the conduction occurs through the electron hopping between Fe^{2+} and Fe^{3+} ions on the octahedral sites. By increasing the frequency, the electron hopping cannot follow the electric field fluctuations causing the dielectric constant έ to decrease as we found experimentally. It is worthy to note that the sample with x = 0 i.e $Li_{0.5}\ Fe_{2.5}\ O_4$ has the highest value of έ. This is due to the fact that this sample has the highest concentration of Fe^{2+}. This leads to an increase of charge carriers and hence the polarization inside the sample. According to Koops's model [12] the dielectric constant at low frequency comes from the grain boundaries which have a high dielectric constant. At high frequency έ results from the grains which have a small dielectric constant.

Figure (2–c) shows the variations of tan δ with the frequency for different Nb concentrations at T =348 K. From this figure it is clear that tan δ decreases exponentially with increasing the frequency following the relation [19] tan δ = $\frac{4\pi\sigma_{ac}}{\omega\varepsilon'}$. The decrease of tan δ with f could be accounted for using Koops's model. In the low frequency region which corresponds to high resistivity (due to grain boundaries) more energy is required for electron exchange between Fe^{2+} and Fe^{3+} ions. Thus the energy loss is high. In the high frequency range which corresponds to low resistivity (due to the grains) a small energy is needed for electron transfer between Fe^{2+} and Fe^{3+} ions in the grains and hence the energy loss is small.

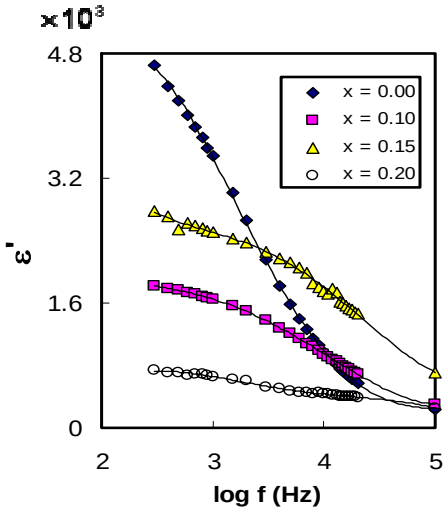

Fig.(2-b): Frequency dependence of έ at T=348 K.

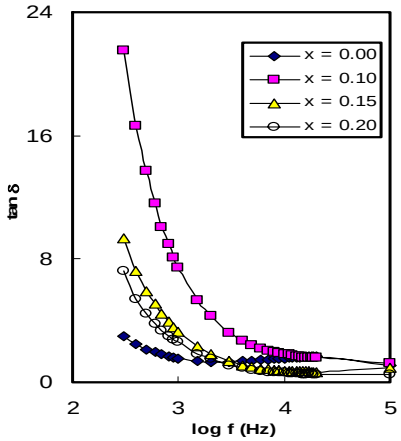

Fig.(2-c): Frequency dependence of tan δ at T=348 K.

Composition dependence of σ_{ac}, έ and tan δ:

Figure (3–a) shows the variations of σ_{ac} with the Nb concentration(x) at different frequencies. It is clear that σ_{ac} slightly increases with x up to x = 0.1. For higher Nb concentration, σ_{ac} decreases rapidly with x. Such a result can be interpreted according to the previous assumptions [9], that for $x \leq 0.1$ the Nb ions occupy the A-sites and for $x > 0.1$, Nb_2O_5 and α - Fe_2O_3 phases are formed at the grain boundaries. Our results suppose further assumption that the

enterance of Nb into the A-site causes a small portion of Fe^{3+} to migrate from A to B sites and converting to Fe^{2+} ions [20] for $x \leq 0.1$. Hence the Fe^{2+} concentration on B-sites increases and thus the conductivity slightly increases. For $x \leq 0.1$. the presence of α - Fe_2O_3 and Nb_2O_5 at the grain boundaries increases the grain boundary thickness and hence according to Koops's model increases the resistivity i.e the conductivity decreases .

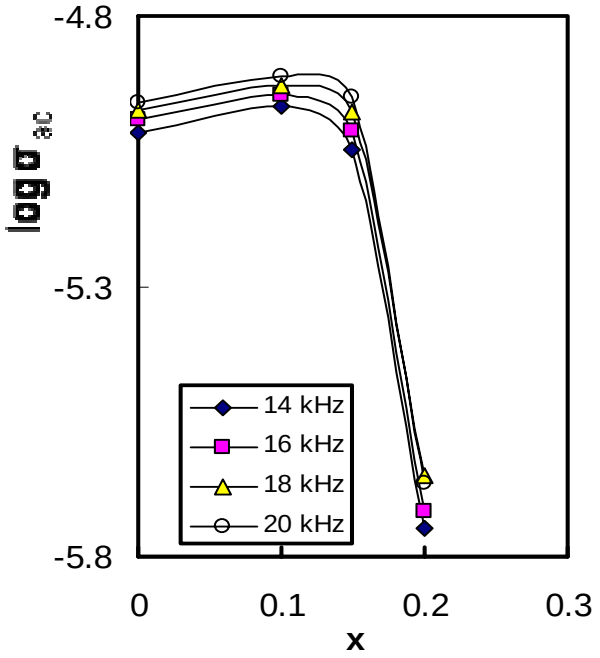

Fig.(3-a): Dependence of έ on the Nb concentration x at 348 K and different frequencies.

Figure (3–b) indicates the variations of έ with (x) at different frequencies. From the figure it is clear that έ slightly increases with x up to x = 0.1, as the behavior of σ_{ac} with x. A maximum value of έ is observed around x = 0.15 which could be explained as follows: for $x \leq 0.1$, the lattice parameter increases linearly with x and Nb ions occupy the A-sites. For $x > 0.1$, the lattice parameter is independent of x and α - Fe_2O_3 and Nb_2O_5 phases are formed. This means that, for $x > 0.1$, localized charges are suddenly appeared at the grain boundaries i.e the charge density is abruptly increased. This leads to the rapid increase in έ. For higher Nb concentration, the grain boundary thickness increases, due to further accumulation of α - Fe_2O_3 and Nb_2O_5 phases, which according to Koops's model causes a decrease in έ.

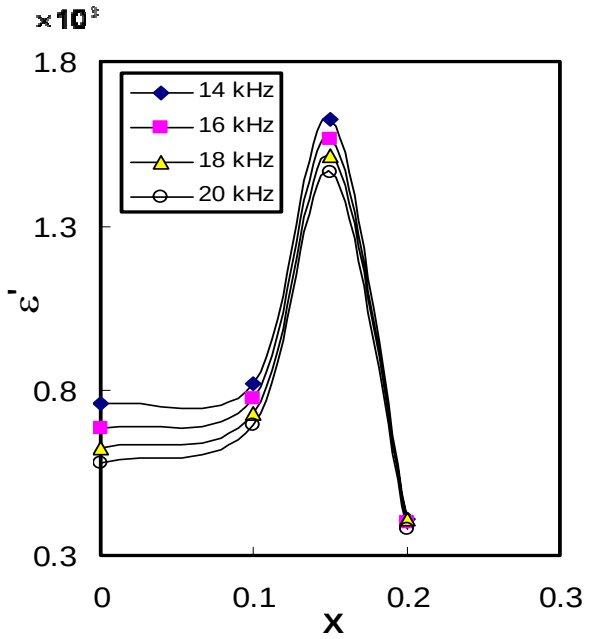

Fig.(3-b): Dependence of έ on the Nb concentration x at 348 K and different frequencies.

Figure (3–c) shows the variation of tan δ with x at different frequencies and at a constant temperature (348K). The data shows that tan δ is more or less independent of x up to x = 0.1. For $0.1 < x \leq 0.15$ a sudden drop in tan δ is observed. For x > 0.15, tan δ is nearly constant. The variations of tan δ with x could by explained through the relation [19]

$$\tan \delta = \frac{4\pi \sigma_{ac}}{\omega \varepsilon'} \qquad (1)$$

According to eq. (1), tan δ is a function of σ_{ac} and έ at a constant frequency. For $x \leq 0.1$, both σ_{ac} and έ are slightly increased with x leading to a constancy of tan δ. Similarly, for x > 0.15, both σ_{ac} and έ are rapidly decreased such that tan δ remained constant. For $0.1 < x \leq 0.15$, σ_{ac} is almost constant while έ revealed a sharp increase. Thus tan δ is expected to show a sharp decrease which we found experimentally. Moreover, the behavior of tan δ with x reflects the fact that high conductivity is accompanied by a large eddy current and hence an increase in the energy loss.

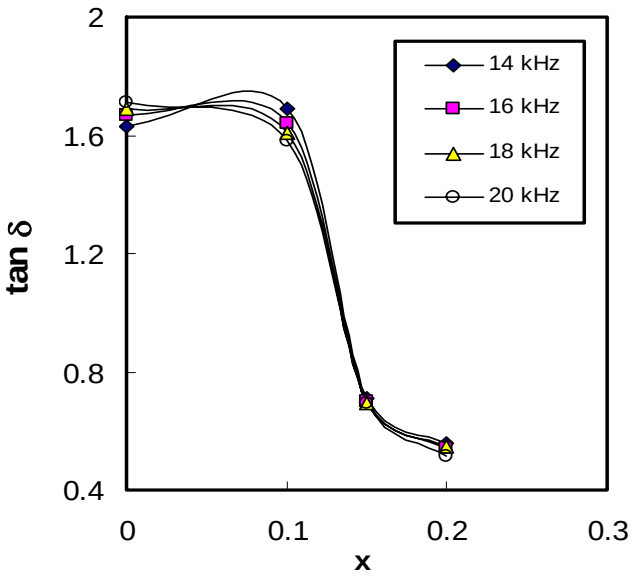

Fig.(3-c): Dependence of tan δ on the Nb concentration x at 348 K and different frequencies.

4. Conclusion:

1. The addition of Nb to Li-ferrite improved the dielectric properties, specially for Nb concentration higher than 0.1, where the energy loss is decreased.
2. Koops's model seems to explain satisfactory the dielectric properties of Nb substituted Li-ferrite

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