Anomalous Dielectric Behaviour of Nd-Doped Li-Ti Ferrite

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ABSTRACT

Investigations have been performed on Nd-doped Li-Ti ferrites with compositional formula $Li_{0.4}Ti_{0.1}Fe_{2.5-x}Nd_xO_4$ (where x = 0.0, 0.025, 0.05, 0.075 and 0.10) to understand the role of microstructure on the dielectric properties. A range of frequency and a wide range of temperature passing through the Curie point were chosen for the measurement. The prepared nano-ferrite samples exhibited an anomalous dielectric behaviour. A careful analysis of the dielectric properties, particularly ac conductivity revealed that the relaxation in these samples were of Maxwell-Wagner type. Using the obtained activation energy values conduction mechanisms were proposed. Curie temperature decreases with increase in Nd^{3+} concentration indicating super exchange interaction.

Keywords: Nd-doped Li-Ti ferrite, dielectric behaviour, activation energy, Curie temperature.

I. INTRODUCTION

In the early days Mg-Zn, Ni-Zn and Mn-Zn ferrites were used for microwave devices, which were later replaced by garnets having high resistivity and low dielectric losses. But because of low Curie temperature, high stress sensitivity and high cost of garnets the focus was directed towards Li-ferrite. Lithium based ferrites have become important materials for microwave applications such as circulators, isolators, phase shifters and many more due to their higher resistivity, low dielectric loss, high Curie temperature, squareness of hysteresis loop and low costs [1-6].

The structural and electromagnetic behaviour of Li-ferrites are tailored by the synthesis methods [6-10]. The intrinsic properties of Li-ferrites like dielectric constant, loss factor and conductivity were controlled by chemical composition and type of doped metal ions in spinel structure [11, 12]. It was reported that the substitution of Ti in Li-ferrite reduces the electrical conductivity [13]. Relatively larger ionic radii of rare earth cations play a significant role in optimizing the electrical properties of ferrites [14]. The rare earth doped Li-ferrites due to their valuable microwave device applications were also suitable for use as a cathode material in Li-batteries. The incorporation of large ionic radii metal ions into the spinel structure produces the structural distortion [15, 16] as well as the modification in the electrical transport properties [17, 18]. In our earlier communication [19] Nd-doped Li-Ti nano-ferrite was synthesized by combustion method. In the present paper we report the dielectric behaviour of these nanocrystalline ferrites in order to make them useful for microwave devices.

II. EXPERIMENTAL TECHNIQUES

The nano- sized Nd - doped Li - Ti ferrites with compositional formula Li $_{0.4}Ti_{0.1}$ Fe$_{2.5- x}$ Nd$_x$ O$_4$ (where X=0.0, 0.025, 0.050, 0.075 & 0.10) were prepared at 450 °C by combustion synthesis discussed earlier [19]. For dielectric measurement the prepared nano- ferrites were pressed into pellets by applying a hydrostatic pressure of nearly

300MPa. The dielectric response was measured using a Hewlett Packard 4194A Impedance analyzer, which can cover a frequency range from 100 Hz to 1MHz. For high temperature measurements, the samples were placed in custom built tube furnace, which can be operated between 30 ^{O}C and 800 ^{O}C. The temperature was measured using a Eurotherm Controller 800 via a K–type thermocouple mounted directly on the insulation (alumina) of the ground electrode of the sample fixture.

The dielectric constant ($\epsilon^{'}$) of the samples was calculated using the relation

$$\epsilon^{'} = \frac{C \times d}{\epsilon_o \times A} \qquad (1)$$

where 'C ' is the measured value of capacitance of the sample, 'd ' in the thickness, 'A' is the surface area, and 'ϵ_0' is the permittivity of air. From the loss factor and dielectric constant, ac conductivity of ferrite samples can be evaluated using the relation

$$\sigma_{ac} = 2\pi \epsilon_o \epsilon^{'} f \tan\delta \qquad (2)$$

where, 'f ' is the frequency of the applied field, 'ϵ_0' is the permittivity of air, '$\epsilon^{'}$' is the dielectric constant of the samples, 'tanδ' is the loss factor and 'σ_{ac}' is temperature and frequency dependent.

III. RESULTS AND DISCUSSION

3.1. Frequency Dependence

Figure 1 shows the variation of dielectric constant (ε') with frequency for LNF1 to LNF5. Dielectric constant decreases as frequency increases. The decrease is rapid at lower frequencies and slower at higher frequencies. Similar results were observed for other systems of ferrites [20-22]. The decrease in dielectric constant with frequency can be explained on the basis of Koops theory [23], which considers the dielectric structure as an inhomogeneous medium of two layers of the Maxwell-Wegner type [24].

In this model, the dielectric structure is assumed to be consisting of Well-conducting grains which are separated by poorly conducting grain boundaries. It was found that for ferrites, the dielectric constant is directly proportional to the square root of conductivity [21]. Therefore the grains have higher values of dielectric constant, while the grain boundaries have lower values. At lower frequencies the grain boundaries are more effective than grains in electrical conduction. Therefore dielectric constant is high at lower frequencies and decreases as frequency increases. The decrease in dielectric constant takes place when the jumping frequency of electric charge carries cannot follow the alternation of the applied ac electric field beyond a certain critical frequency.

In general, for granular oxide ceramic materials, the AC conductivity follows power law behaviour with frequency given by [25, 26];

$$\sigma_{AC} = A\omega^{s} \qquad (3)$$

where A is a constant having the unit of conductivity, the exponent 's' is a dimensionless parameter and ω is the angular frequency at which the conductivity was measured. In the present case,'s' was calculated for all compositions at room temperature over the studied range of frequency by plotting ln σ_{ac} versus ln ω, according (3) shown in Fig. 1. The exponent's' is a measure of degree of correction; viz. 's' should be zero for random hopping and tends to one as the correlation increases. Table 1 shows the value of 's' for LNF1 to LNF5 samples and it is lie between 0.5 to 0.8, which are in good agreement with reported values [27-29].

3.2. Temperature Depedence

Fig. 2 shows the variation of dielectric constant (ε') with temperature for LNF1 to LNF5 at seven selected Frequency. It is observed that the dielectric constant increases slowly with temperature in the low temperature range upto 400 ^{o}C and above this temperature, the dielectric constant increases rapidly for all samples. In agreement with Li ferrites [30]

Fig. 3 represents the variation of loss factor (tanδ) with temperature at different frequencies for LNF1 to LNF5. Clearly from these figures three abnormalities were seen in the temperature range 150-250 ^{o}C, 350°C – 450 ^{o}C & around 650 ^{o}C respectively. As a general trend by increasing frequency tanδ decreases the peak shifts to lower temperature. A closer look to the tanδ curves and at each separate frequency, tanδ increases with increasing temperature, due to the high thermal energy which is quite sufficient to disturb the aligned dipoles, increasing friction between them and though increases tanδ value, commonly observed in ferrites [30-32].

Fig. 4 are typical curve, correlates the ac conductivity (ln σ_{ac}) and the reciprocal of absolute temperature at different frequencies for LNF1to LNF5 and obeys the well known Arrhenius relation

$$\sigma = \sigma_0 \exp\left(\frac{-E}{kT}\right) \tag{4}$$

where 'σ_0' is constant, 'k' is Boltzmann's constant, 'E' is activation energy and 'T' is absolute temperature. The data gives more than one straight line with varying slopes indicating the existence of more than one conduction mechanism. By increasing frequency, the conductivity increases because the pumping force of the frequency helps in transferring the charge carries between the different localized states. This mechanism continues up to a certain frequency after which the conductivity may decreases due to the disturbance effect of frequency. The values of the activation energy as calculated from the experimental data are reported in table 1. The activation energy for LNF1 to LNF5 in the temperature region 150 - 250 ^{o}C (region 1) are in agreement with literature [31-37]. This small value of activation energy in region 1 confirm the electronic character of conduction process which consists of electron hopping between the different ions (Fe^{3+},Fe^{2+}) and (Fe^{2+}, Nd^{3+}) on octahedral sites. Similar results were observed in Nd- doped Mg-Ti ferrites [36].

The high value of activation energy observed for LNF1 to LNF5 in the temperature region 350°C to 450°C (region 2) in agreement with the reported value [38, 39]. Higher values of activation energies in general may have two causes, viz. ionic conduction and small polaron conduction. Klinger and Samakhvalov [40] in a review article on conduction of ferrites have totally ruled out the possibility of ionic conduction in ferrites up to 1000°C. This assertion is reasonable as ionic conductivity involves exchange of ions between two sublattices and therefore requires a very high temperature. As such, the ionic conduction in Nd-doped Li-Ti ferrites is ruled out. This large value of activation energy in region 2 can be regarded as due to small polarons [28, 40]. The small values of activation energy in region 1 indicate the metallic behaviour of the ferrite under investigation. The drastic increase in the activation energy in region 2 indicates the semiconducting trend which is almost the general behaviour of the ferrites. So, one may assign this type of transition as metal to semiconductor transition [39].

The third peak around the temperature 650°C is attributed to Curie temperature (T_C) at which the samples transform from ferrimagnetic to paramagnetic state. The observed Curie temperature for LNF1 to LNF5 is in perfect agreement with Li-Ti mixed ferrites [31, 41-43]. It is important to note that the T_C value decreases with increase in

Nd^{3+} concentration. This decrease in T_C is caused by the weaker Fe-R super exchange interactions compared to the Fe-Fe interactions when Fe^{3+} is substituted by Nd^{3+} ions at octahedral site [42].
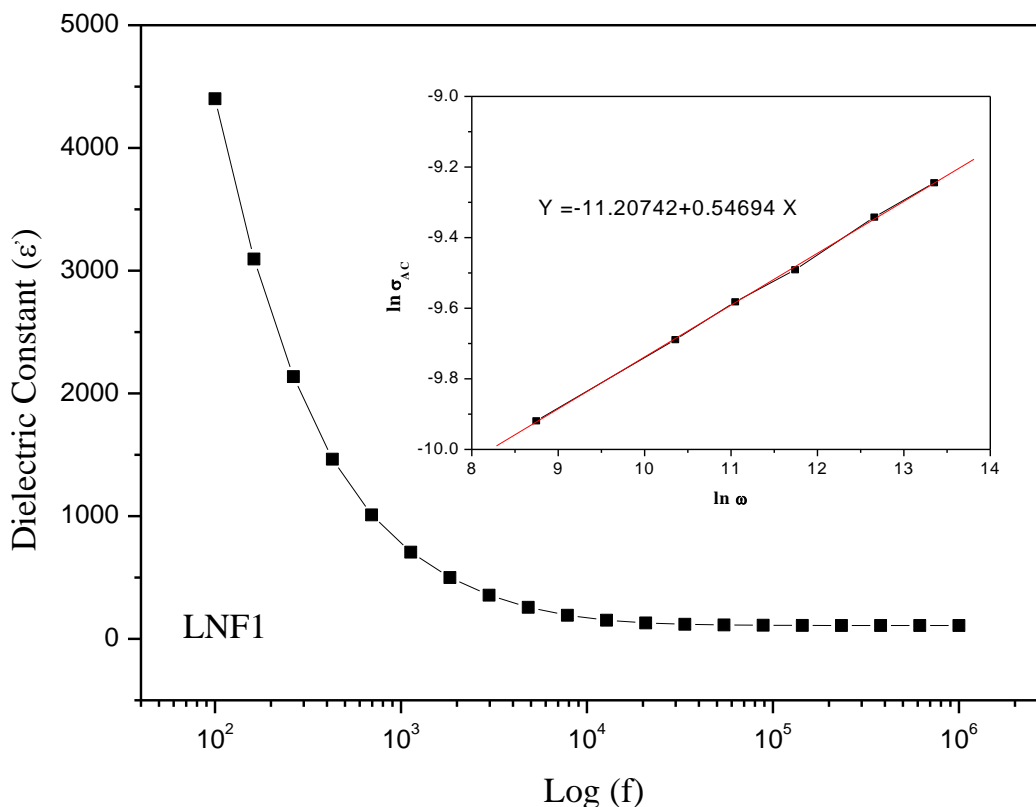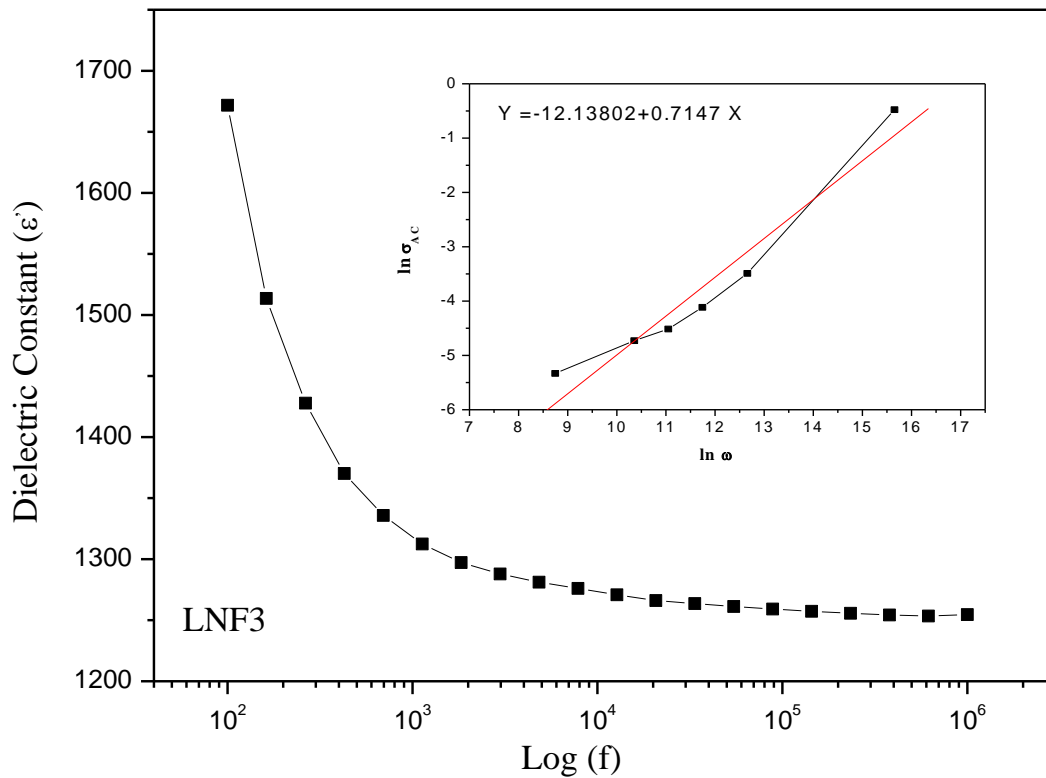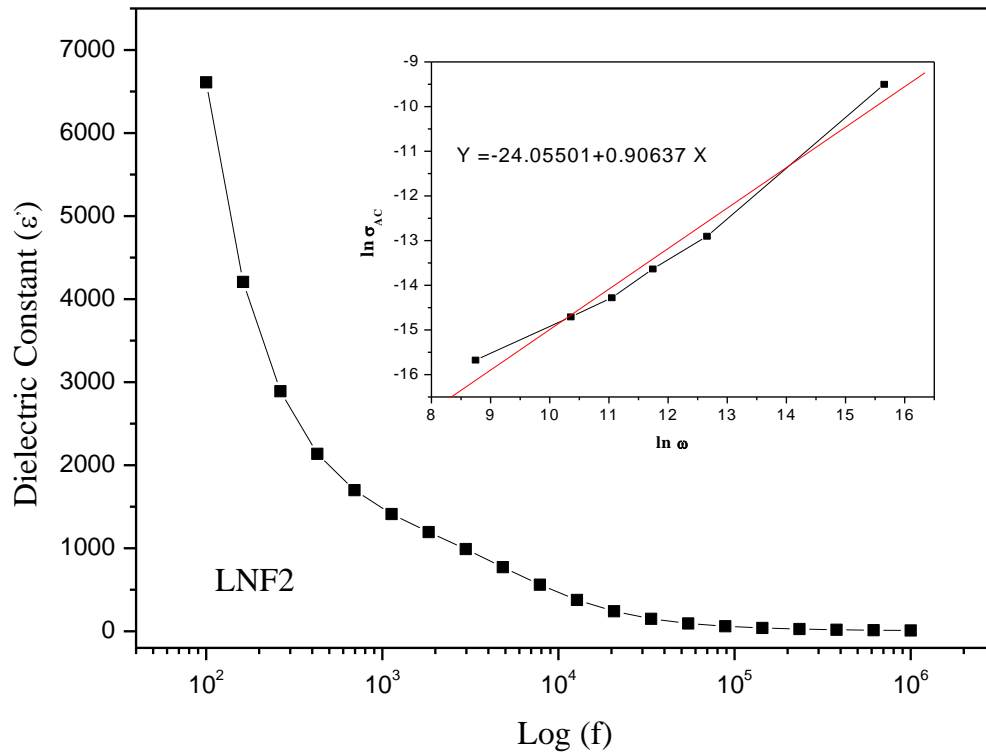
IV. CONCLUSIONS

Nd–doped Li-Ti nano-ferrites have exhibited anomalous dielectric behaviour. The dielectric data revealed that the dielectric polarisation in these ferrites is of Maxwell-Wagner type relaxation. The three abnormalities were attributed to valance exchange between different ions in octahedral site, small polarons and phase transition of the samples from ferrimagnetic to paramagnetic respectively. The decrease in T_C with increase in Nd^{3+} concentration is attributed to super exchange interaction.

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Inset: $Y = -11.20742 + 0.54694\ X$

Inset equation: $Y = -24.05501 + 0.90637\,X$ (LNF2, plot of $\ln\sigma_{AC}$ vs $\ln\omega$)

Inset equation: $Y = -12.13802 + 0.7147\,X$ (LNF3, plot of $\ln\sigma_{AC}$ vs $\ln\omega$)
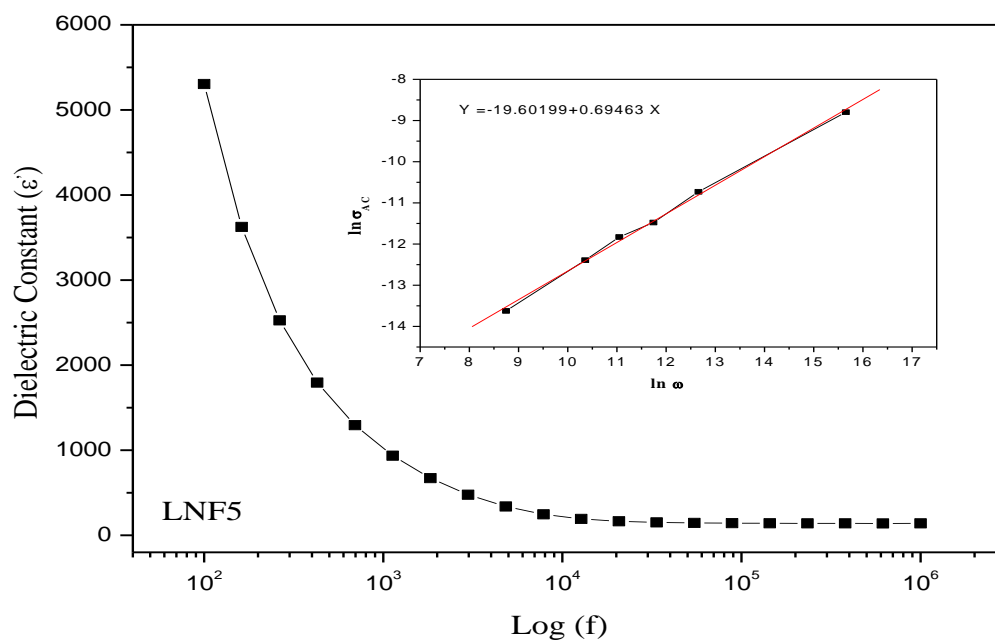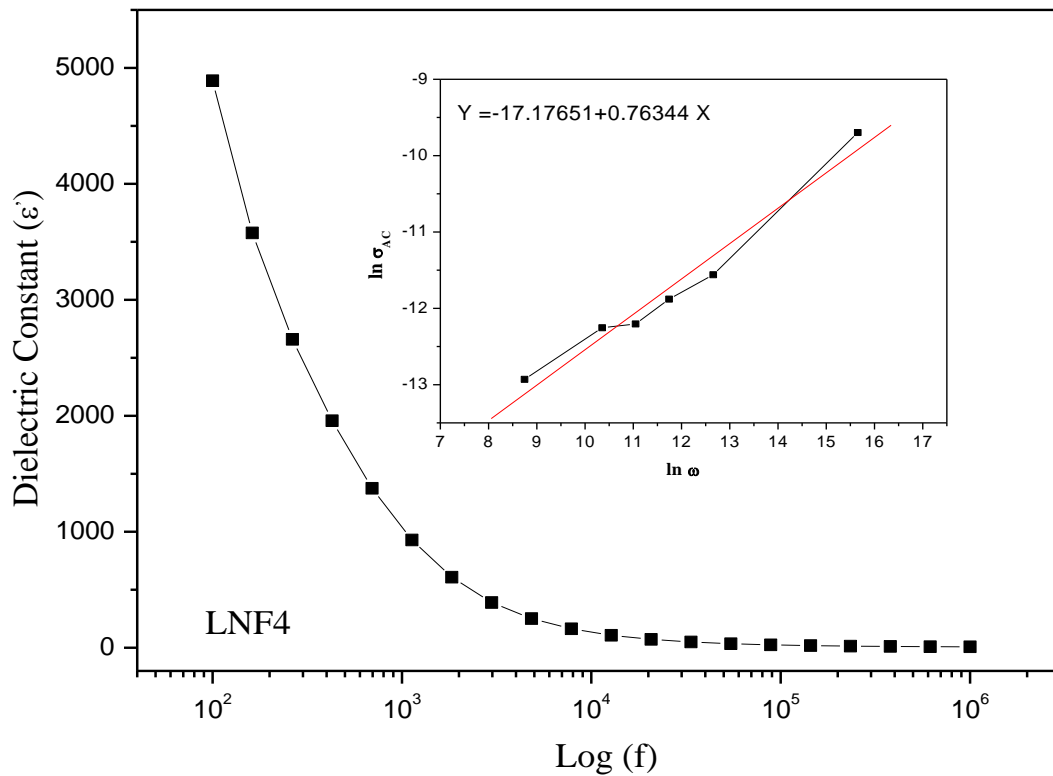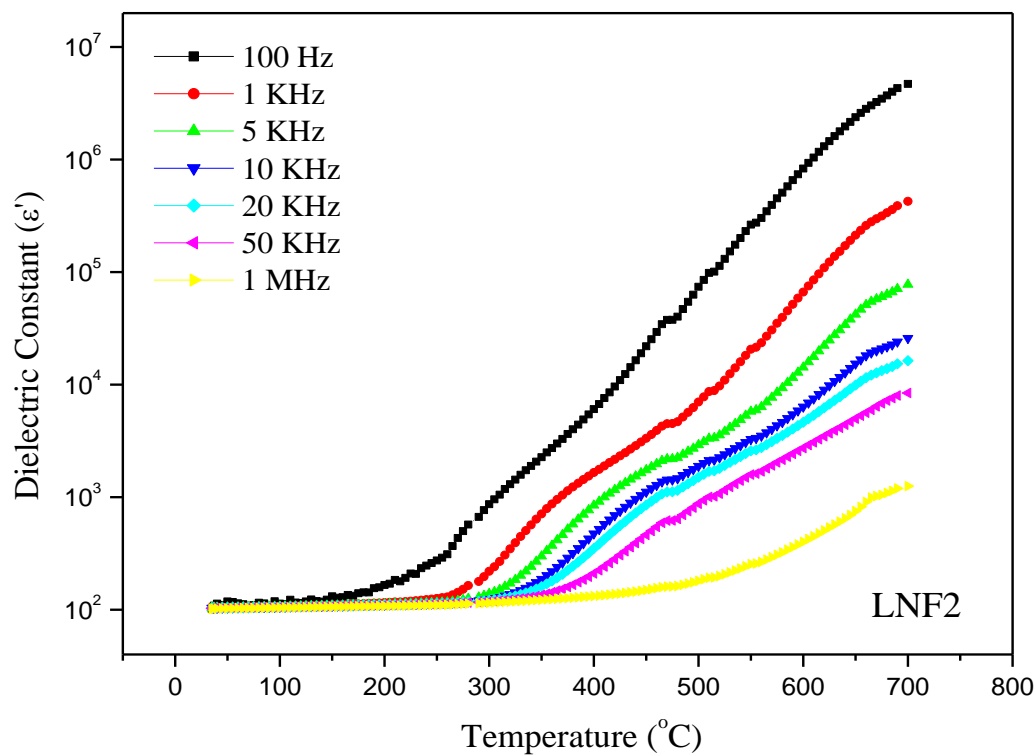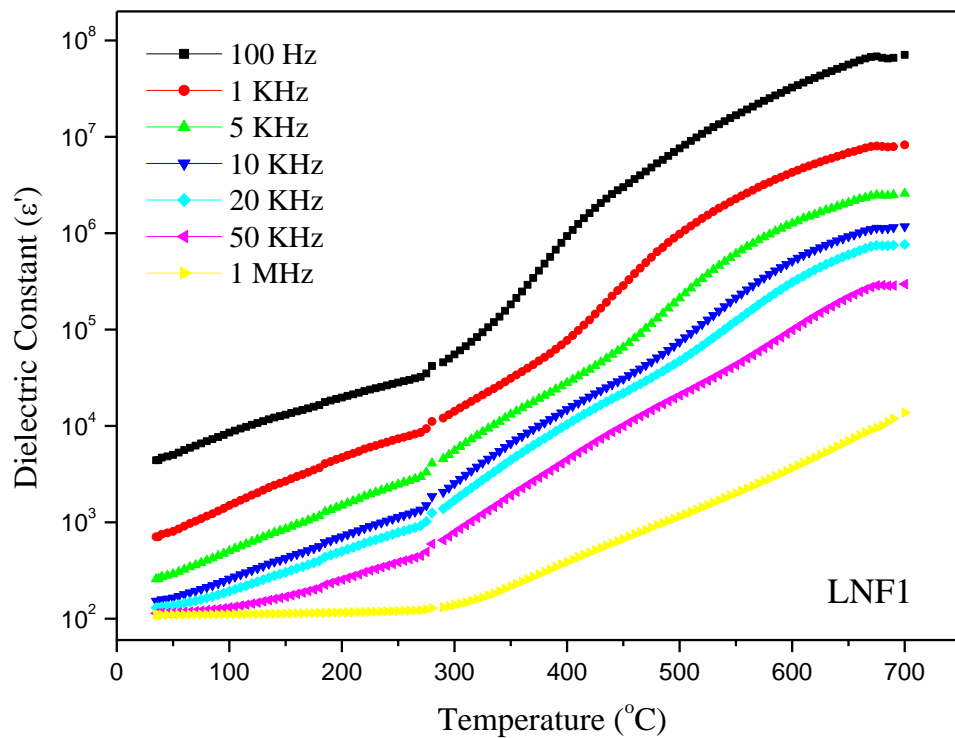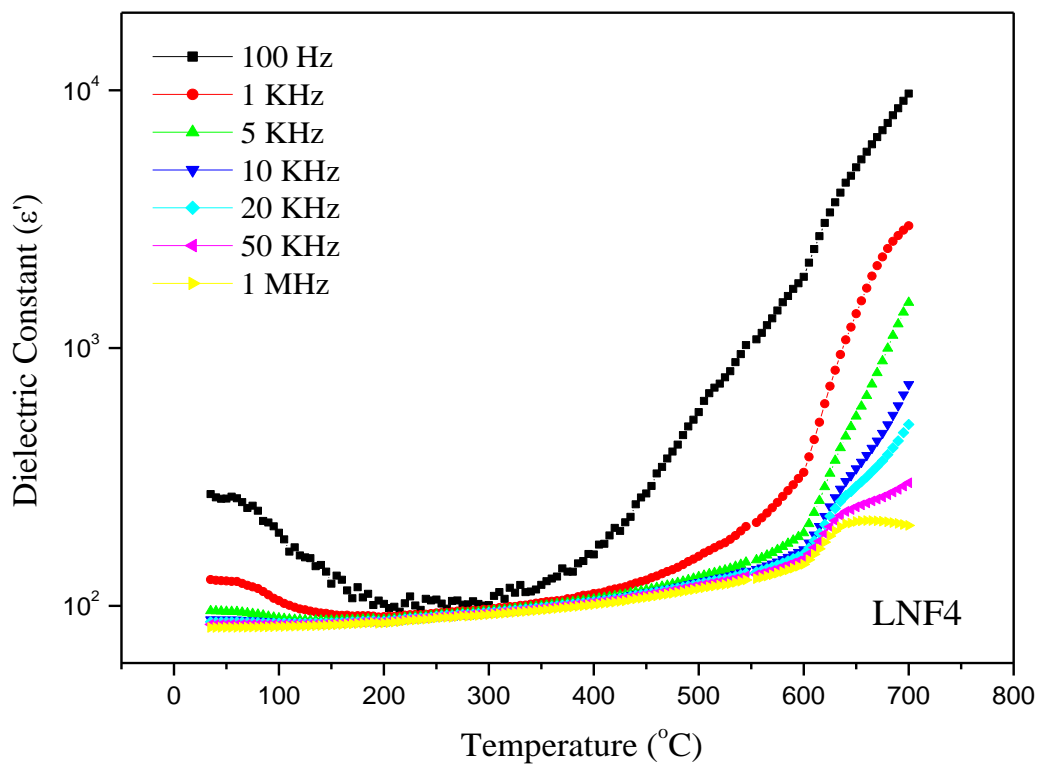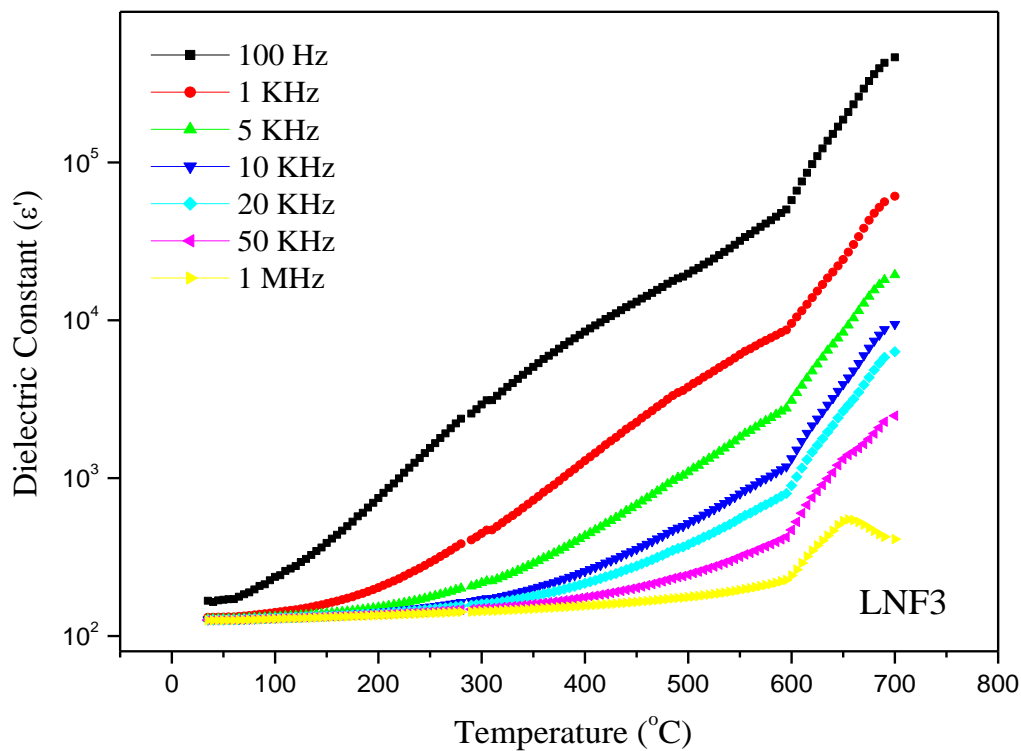
Figure 1: Variation of dielectric constant with logarithmic frequency for LNF1 to LNF5 at room temperature and variation of ln σ_{ac} versus ln ω is shown in the inset.
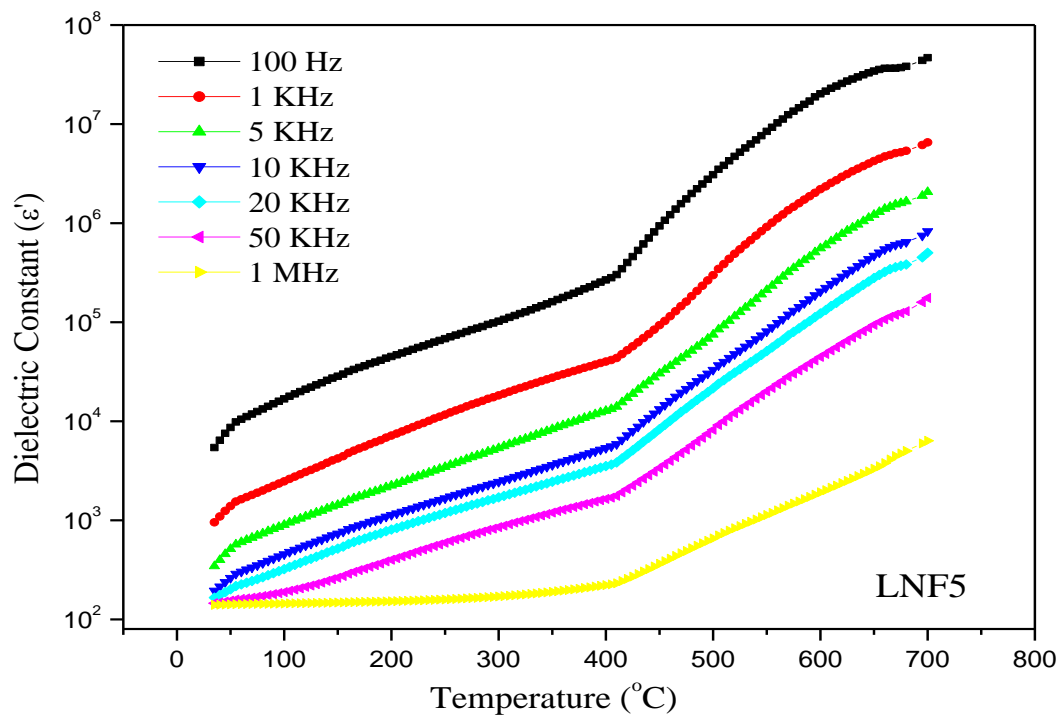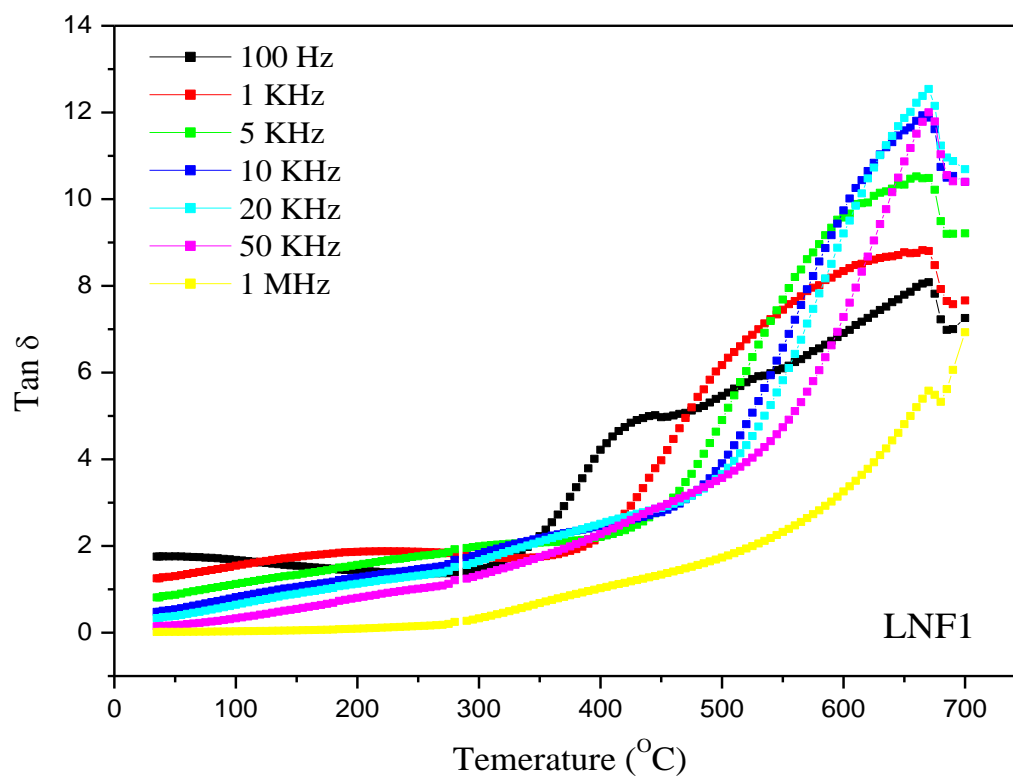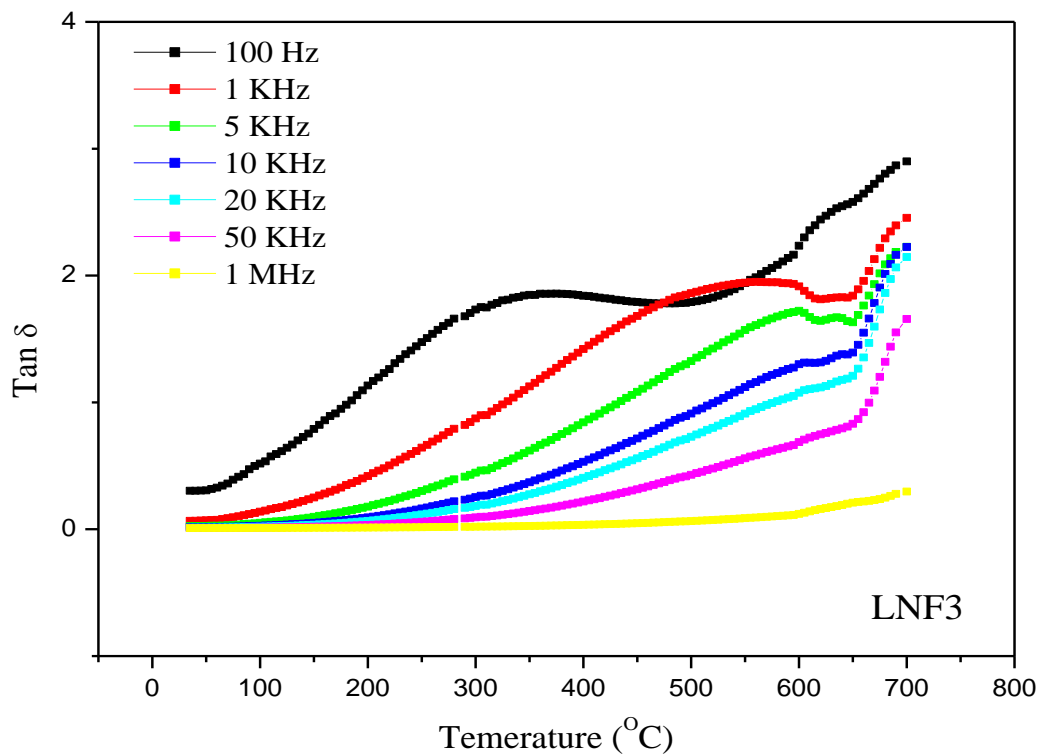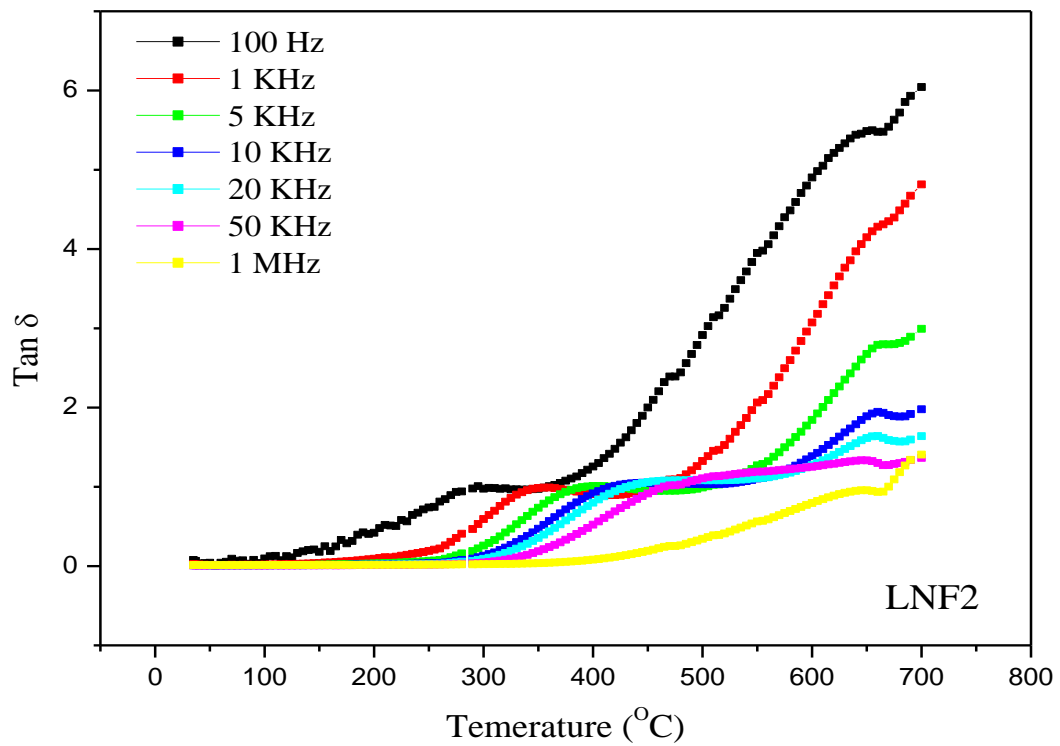
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Figure 2: Variation of dielectric constant (ε') with temperature for LNF1 to LNF5.

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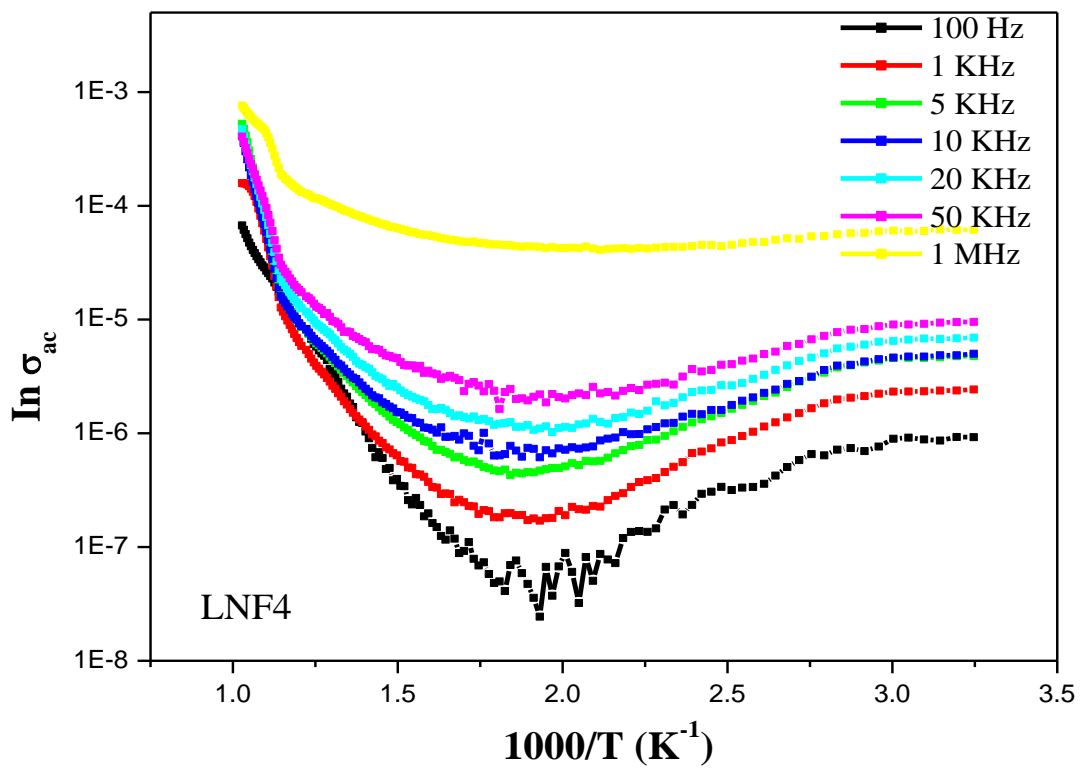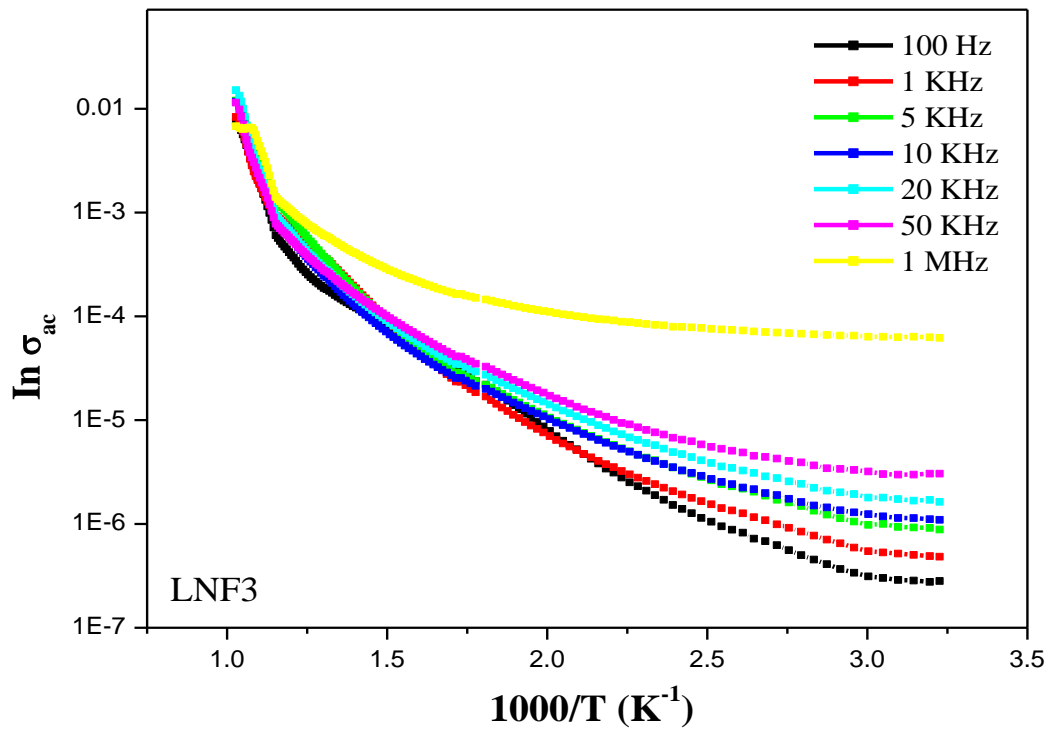ISSN (O) 2319 - 8354
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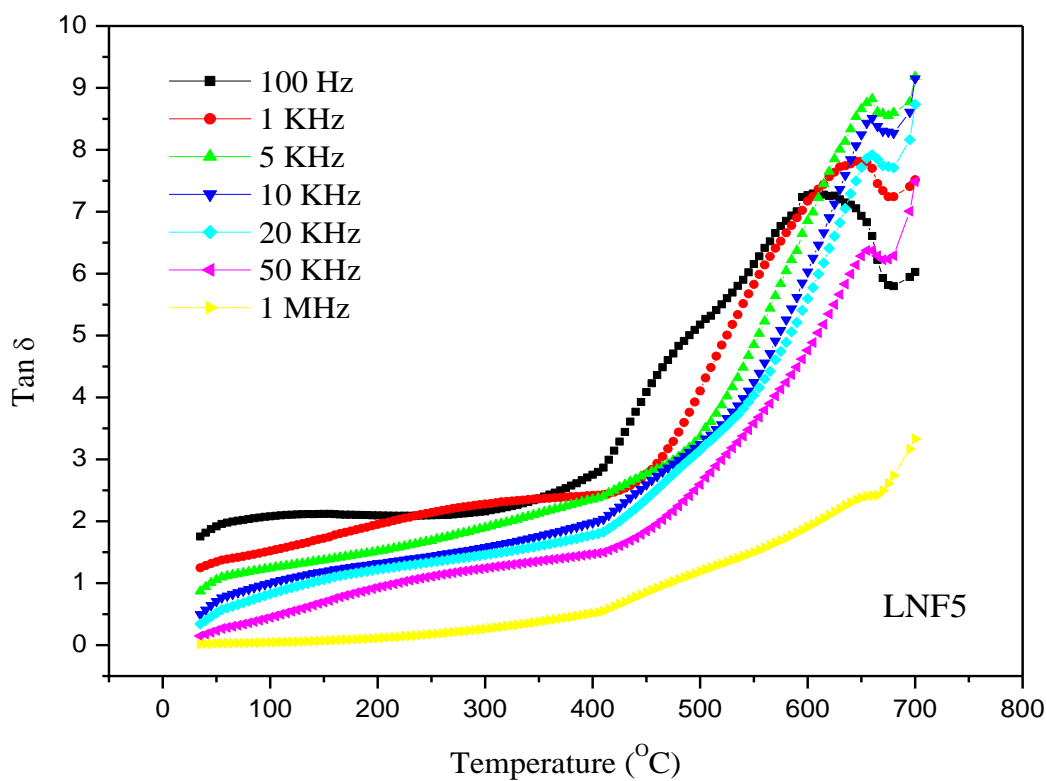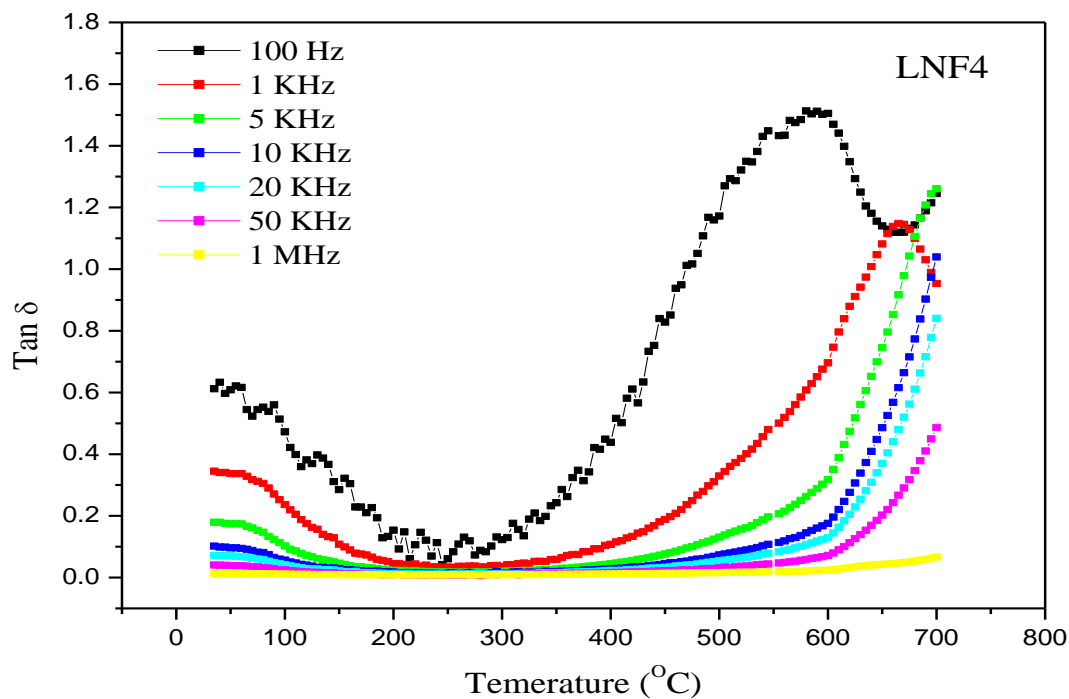
Figure 3: Variation of loss factor (tan δ) with temperature for LNF1 to LNF5.
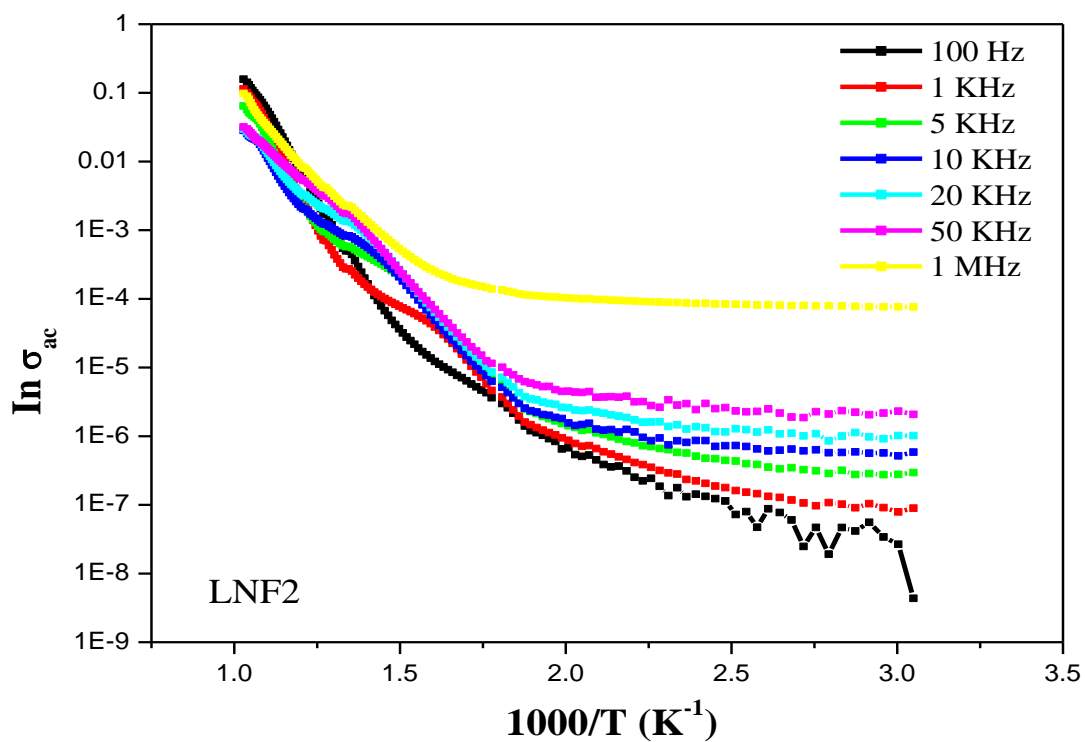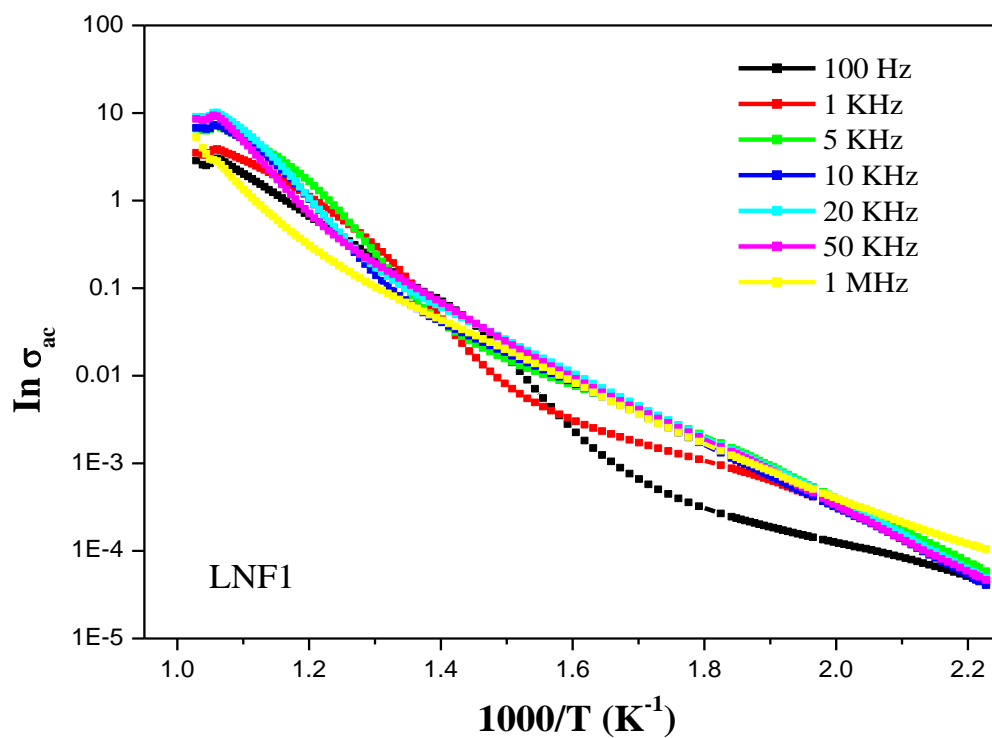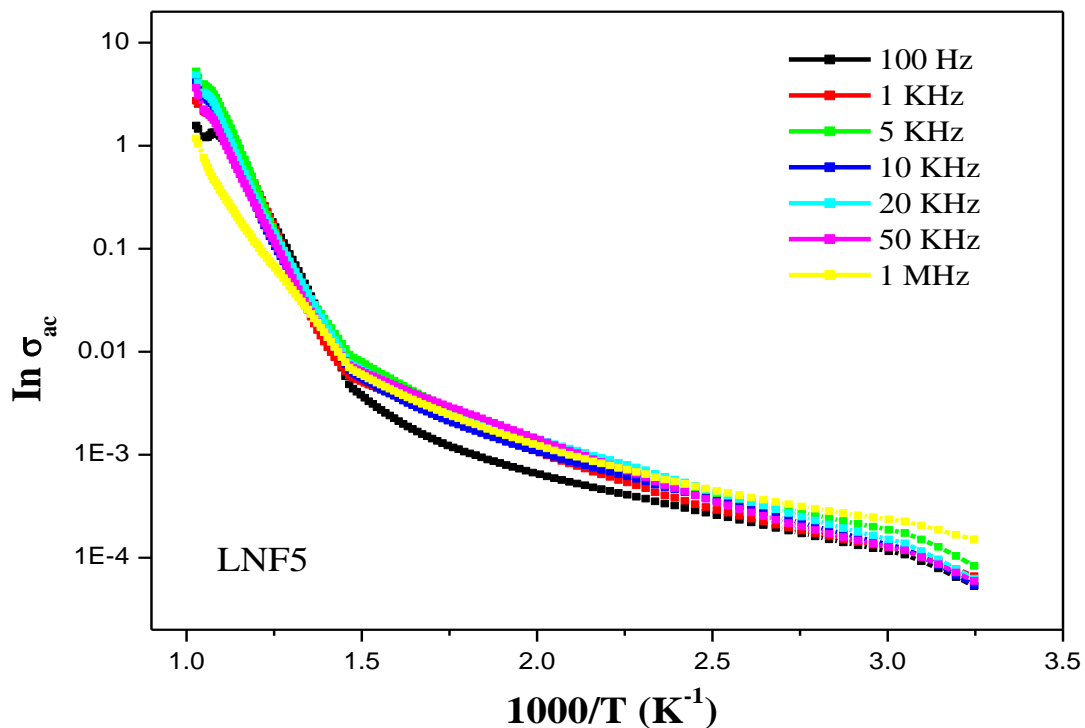
Figure 4: Variation of ln σ_{ac} with temperature for LNF1 to LNF5.

Table 1: Composition, Curie temperature, Activation energy and s-value for LNF1 to LNF5

Composition	Curie Temperature T_C (^{O}C)	Activation Energy (Ea) in eV		s-value
		I region	II region	
LNF1	675	0.67	0.86	0.55
LNF2	670	0.75	1.02	0.91
LNF3	660	0.87	1.14	0.71
LNF4	655	0.86	1.22	0.76
LNF5	665	0.71	0.98	0.69