Dielectric and electrical studies of Li-Ti mixed nanoferrites

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ABSTRACT

The polycrystalline samples of the Li-Ti mixed nanoferrites, $Li_{0.5+0.5x}Ti_xFe_{2.5-1.5x}O_4$, (0.02 = x = 0.1) were prepared by combustion method. The IR spectra in the range $400 – 800 \ cm^{-1}$ were recorded at room temperature. Thermoelectric power measurement shows n-type conductivity. Dielectric constant and loss values increase with increase in temperature and decreases with increase in frequency. Two relaxations were observed in the temperature dependence of tanδ. The activation energy required for the relaxation was calculated from the conductivity data. These relaxations were attributed to the electron hopping between Fe^{2+} and Fe^{3+} ions on octahedral sites and the creation of oxygen defects.   © 2012 Trade Science Inc. - INDIA

INTRODUCTION

Lithium ferrites have become very attractive in microwave application and also as replacement for garnets and other spinel ferrites because of their good remnance and squareness ratio along with the highest T_c among spinel ferrites[1]. Jefferson and West[2, 3] have reported that Ti^{4+} substitution as a replacement for iron in lithium ferrite enhances its physical properties by reducing saturation magnetization values. The incorporation of titanium into lithium ferrite necessitates the adjustment of both monovalent lithium and trivalent iron ions. Many recent researchers[4-6] have studied IR absorption spectra of some mixed ferrites. The results from IR study can be used to interpret the electrical and magnetic properties[7]. Polycrystalline Li-Ti mixed ferrites are supposed to be good dielectric materials. More-over, the dielectric properties of ferrites are dependent on several factors including the method of preparation[8], the sintering temperature[9] and the sintering atmosphere[10]. Several studies have been reported on dielectric[11, 12] and thermoelectric[13, 14] properties of Li-Ti mixed ferrites. However, nanoscale ferrites have shown anomalous dielectric behavior[15]. In the present investigation, the electrical properties such as thermoelectric, electrical and dielectric measurements carried out for Li-Ti mixed nanoferrites at different temperatures are reported.

EXPERIMENTAL

Polycrystalline samples of Li-Ti mixed nanoferrites $Li_{0.5+0.5x}Ti_xFe_{2.5-1.5x}O_4$ (0.02 = x = 0.1) were prepared by combustion method. The details of the method of

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preparation were given in the earlier publication[16]. The notations LT1 to LT5 represent, respectively x = 0.02, 0.04, 0.06, 0.08, 0.10 Ti concentration in the samples. The IR spectra in the range 400-800 cm^{-1} were recorded at room temperature. The thermo-emf developed across the sample due to the temperature gradient has been measured over a temperature range 30 – 300 °C. Hewlett Packard HP-4192A Impedance Analyzer was used to study the anomalies in the dielectric properties. ε' and tanδ were measured at six selected frequencies (5K, 10K, 100K, 200K, 500K and 1MHz) during controlled heating from room temperature to 400 °C.

RESULTS AND DISCUSSION

IR study

The IR spectra of prepared samples show first primary band at 587cm^{-1} which is due to stretching vibrations of the tetrahedral group (υ_1)[17, 18]. It has a structure consisting of three subsidiary bands υ_1 (1), υ_1 (2), υ_1 (4) at 710, 670 and 547 cm^{-1} respectively. It has been shown by Patakova et al[5] that the presence of Fe^{2+} ions in ferrites can produce the splitting/shoulders on absorption bands. This is attributed to the John-Teller distribution produced by the Fe^{2+} ions, which causes local deformation in the lattice owing to the non cubic component of the crystal field potential and hence leads to the splitting of the band υ_1. The band at υ_2(1) and υ_2
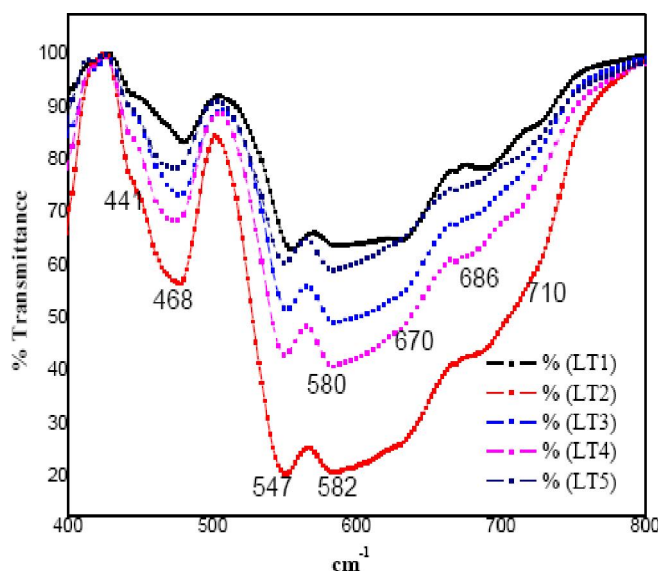

Figure 1 : IR transmission curves of LT1 to LT5 at room temperature

(2) at 468 and 441cm^{-1} respectively can be attributed to Li-O vibrations[12].

As there are four cations (Ti^{4+}, Fe^{3+}, Fe^{2+} and Li^+) on octahedral sites, it is difficult to attribute the occurrence of the primary band υ_2 to particular octahedral cation-oxygen complex. The frequency band that appears around 540-710 cm^{-1} and 441 - 470 cm^{-1} are separated markedly because the bond lengths of Fe^{3+}-O^{2-} are not equal for the tetrahedral and octahedral metal complexes.

Thermoelectric power

Using the values of thermo-emf, the Seebeck coefficient (S) for each composition has been evaluated, and given in TABLE 1 these values are in agreement with reported value[13]. From the Figure 2 it is observed that Seebeck coefficient is positive indicating that all the samples under investigation were n-type semicon-
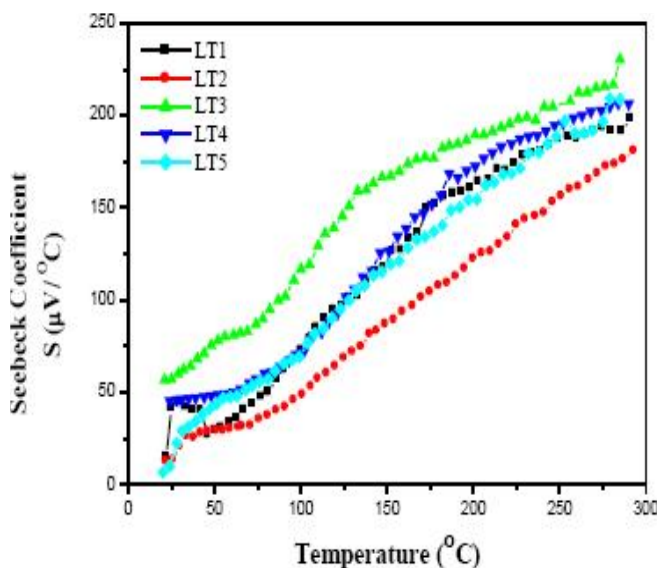

Figure 2 : Variation of Seebeck coefficient (S) with temperature

TABLE 1 : The activation energy from region I and region II for LT1 to LT5

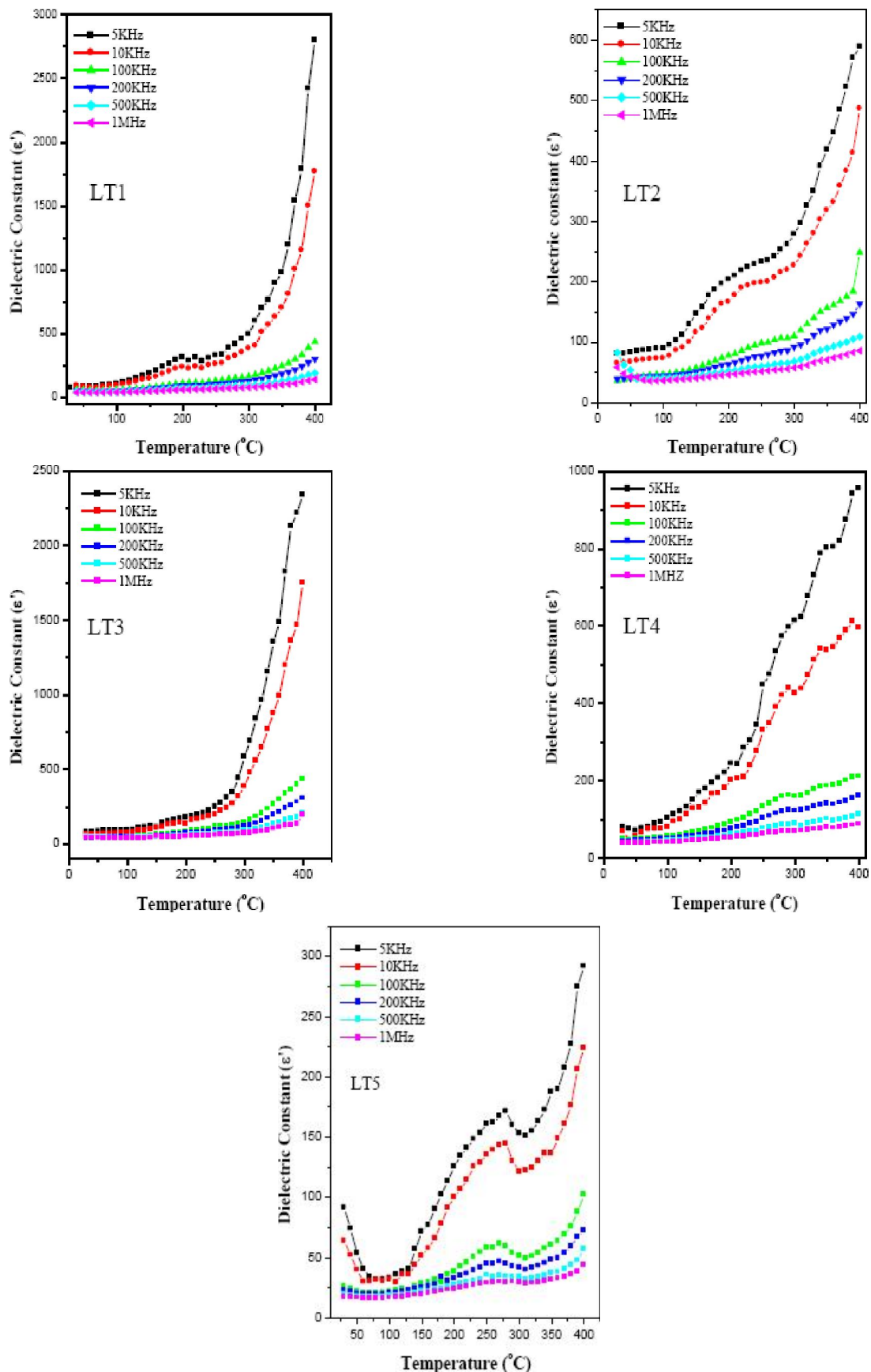| Sample	Notation	Region I (570-680)K E$_a$ (eV)	Region II (350-550)K E$_a$ (eV)	Seebeck Coefficient S (μV/°C) @ RT
$Li_{0.51}Ti_{0.02}Fe_{2.47}O_4$	LT1	0.36	0.50	44.30
$Li_{0.52}Ti_{0.04}Fe_{2.44}O_4$	LT2	0.24	0.55	30.00
$Li_{0.53}Ti_{0.06}Fe_{2.41}O_4$	LT3	0.28	0.68	60.27
$Li_{0.54}Ti_{0.08}Fe_{2.38}O_4$	LT4	0.45	--	45.96
$Li_{0.55}Ti_{0.1}Fe_{2.35}O_4$	LT5	0.47	--	22.59

Figure 3 : The variation with temperature of dielectric constant ε' for LT1 to LT5
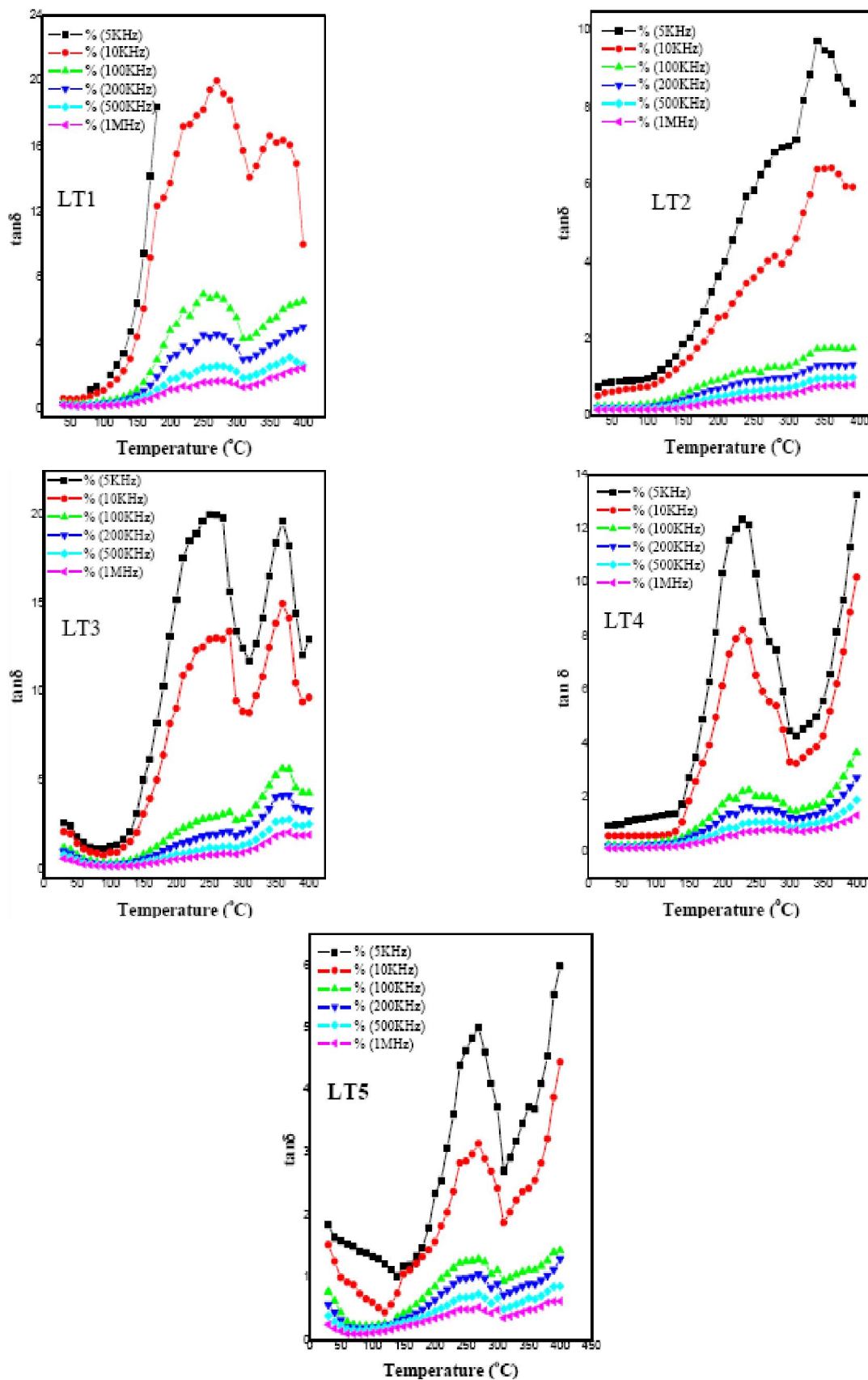
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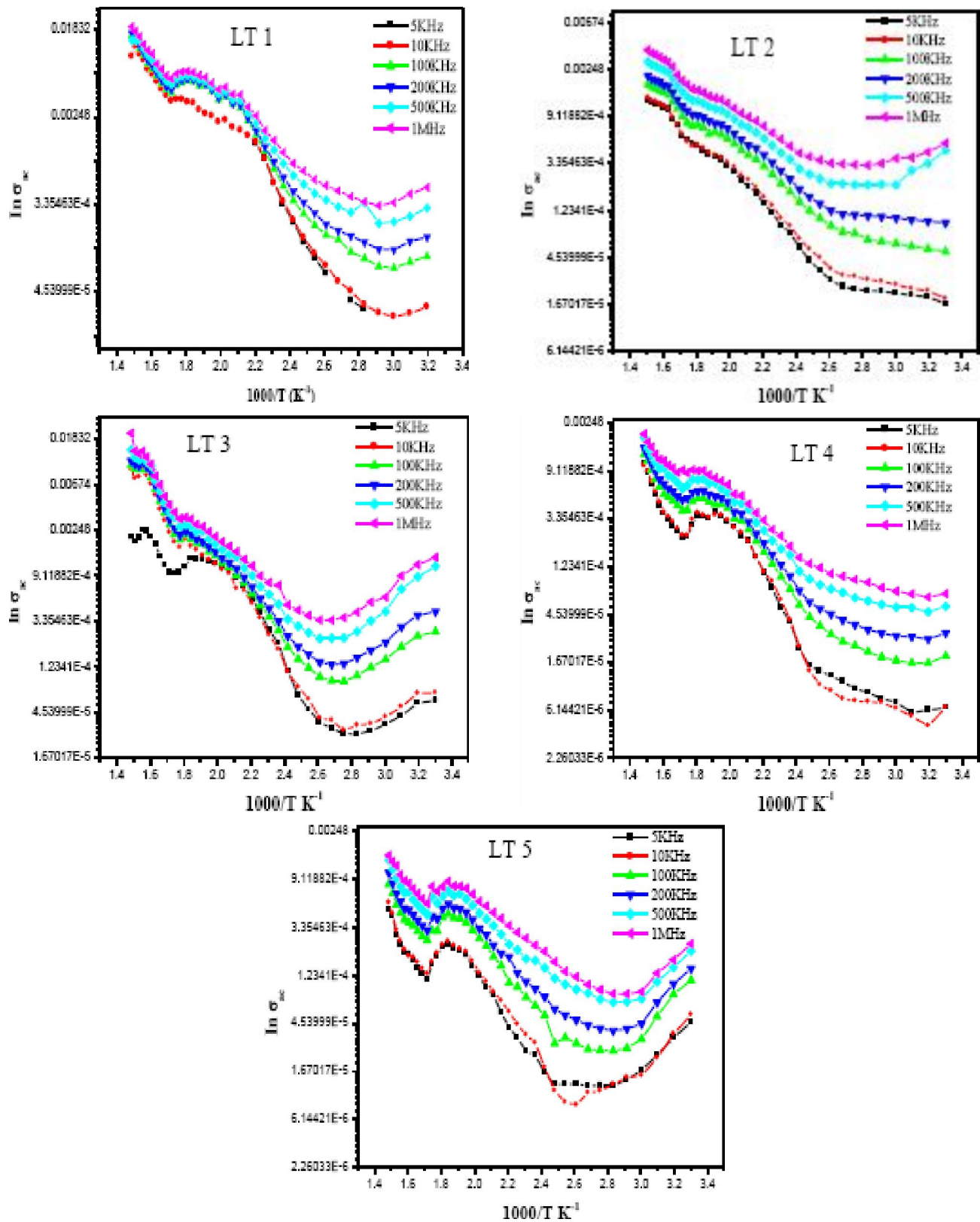**Figure 4 : Tanδ variation with temperature for LT1 to LT5**

Figure 5 : Variation of ac conductivity with temperature for LT1 to LT5 samples

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ductors up to 300 °C. In the case of n-type semiconducting materials, the hot surface becomes positively charged as it loses some of its electrons whereas the cold junction becomes negatively charged owing to diffusion of electrons.

Dielectric behavior

ε' and tanδ were measured at six selected frequencies (5K, 10K, 100K, 200K, 500K and 1M Hz) during controlled heating from room temperature to 400 °C for LT1 to LT5 samples and are shown in the Figure (3, 4). Dielectric constant and loss values increase with increase in temperature and decreases with increase in frequency. With the rise in temperature the number of carrier's increases, resulting in an enhanced build up of space charge polarization and hence an increase in the dielectric constant, which are in agreement with reported values[12].

The samples under investigation were in nanoscale[16] and two relaxations were observed for LT1 to LT3 samples. This observation was similar to those reported by Fang[15], while in samples LT4 and LT5 only one relaxation was observed, as it was shifted above 400°C (shown in Figure 4). Relaxation is often better understood from the changes in the dielectric loss tangent (tanδ), which is shown in Figure 4 for LT1 to LT5.

AC conductivity

The variations of conductivity with temperature of LT1 to LT5 are shown in Figure 5. Similar behavior was reported in the literature[14, 19]. Clearly two regions can be noticed in LT1 to LT3 whereas in LT4 and LT5 there is only one region and which can be confirmed from Figure 4. Since the Curie temperature of Li-Ti mixed ferrites, $Li_{0.5+0.5x}Ti_xFe_{2.5-1.5x}O_4$, $(0.02 = x = 0.1)$ was greater than 480 °C[19] and as the range of temperature measurement was up to 400 °C, it is expected that relaxations in LT4 and LT5 samples may be seen at temperatures above 400 °C. The activation energies calculated from the two different regions were attributed to electron hopping and ionic conduction. The activation energy, E_a was calculated for all compositions from the slopes of the curves in Figure 5, at different frequencies. The mean values of E_a for the samples are given TABLE 1. The E_a from region I (570 – 680 K)

was attributed to the electron hopping between Fe^{2+} and Fe^{3+} ions on octahedral sites and were less when compared to the literature values[19]. These activation energy values suggest the activation energy for electron charge transfer in LT1 to LT5. However, the E_a, from region II (350 – 550 K) indicates the energy required for ionic conduction and the formation of the ions can be explained as below. During pellet formation high pressure was applied, which will lead to the formation of defects at the interface as predicted by Fang[15] and hence those defects will trap space charges to form dipoles. Hence, there will be large number of dangling bonds in the interface and combine with space charges and polar molecules such as H_2O in the atmosphere, which causes relaxation with longer relaxation time or higher activation energy. Hence, the activation energy required for these defects are calculated and tabulated in TABLE 1 for LT1 to LT3, where as for LT4 and LT5 relaxation peak was shifted above 400 °C as shown in Figure 4. The higher activation energy in region II suggests the ionic conductivity as reported in the literature[14].

CONCLUSIONS

The IR studies confirm the formation of spinel structure and gives information about the distribution of ions between tetrahedral and octahedral sites. Thermoelectric study confirms that the prepared nano Li-Ti mixed nano ferrite was n-type semiconductor up to 300 °C. The dielectric study reveals two relaxations and the activation energy were calculated from the conductivity data. The first relaxation was attributed to electron hopping between Fe^{2+} and Fe^{3+} ions on octahedral sites. The high values of activation energy for second relaxation in region II was attributed to lithium-ion conduction process.

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