Abnormal Dielectric Behavior in Ti-Ni Spinel Ferrite

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Abstract: *The dielectric constant ε' and dielectric loss tangent $\tan\delta$ were investigated as a function of frequency and temperature for the ferrite system $Ti_xNi_{1+x}Fe_{2-2x}O_4$ (where $0 \leq x \leq 0.625$). It was found that both ε' and $\tan\delta$ decrease with increasing frequency of applied electric field. The behavior of the dielectric constant with frequency was explained on the basis of hopping mechanism and Koops theory. It is noticed that dielectric constant decreases with increasing temperature up to certain temperature T_{MS} after that increase. Then the metal/semiconductor transition temperature, T_{MS}, was determined from $\varepsilon'(F, T)$ plots. The loss tangent $\tan\delta$ showed an abnormal behavior (loss peaks) with temperature and frequency for the pure and low substitution for the studied system. The loss peaks shifts to higher values of frequencies as temperature increases. The activation energy for dielectric relaxation showed an increase with increasing Ti and Ni contents. An attempt is made to explain the metallic like behavior and abnormal relaxation loss for the samples.*

Keywords: Dielectric properties, MS transition, Semiconductor, Ferrite

1. Introduction

Spinel ferrites have useful electrical, dielectric and magnetic properties and used in many applications such as magnetic cores, information storage systems, microwave devices, etc. [1, 2]. Among spinel ferrites, nickel ferrites, $NiFe_2O_4$, is one of the versatile and technologically important soft ferrite materials because of its typical ferromagnetic properties, low conductivity and high electrochemical stability. The influence of substitution for divalent (Ni^{2+}) and tetravalent (Ti^{4+}) ions instead of trivalent (Fe^{3+}) ions in $NiFe_2O_4$ were reported earlier [3]. Our previous studies [3] on the substituted nickel ferrite system ($Ti_xNi_{1+x}Fe_{2-2x}O_4$) shows the existence of excellent electrical properties for this type of ferrite in particular at higher substitutions. The electrical and dielectric properties of ferrites have a remarkable dependence on the nature of the ions and their distribution among tetrahedral (A) and octahedral (B) sites. Nickel ferrite is an inverse spinel ferrite, in which eight units of $NiFe_2O_4$ go into a unit cell of the spinel structure. Ni^{2+} ions were found to occupy only the octahedral (B-sites) and half of the iron ions exist in the tetrahedral sites (A-sites), whereas, the other half occupies the octahedral sites [4]. Kale et al. studied the cation distribution for the $Ti_xNi_{1+x}Fe_{2-2x}O_4$ system and reported that Ni^{2+} occupies the octahedral (B-sites), whereas both Fe^{3+} and Ti^{4+} ions are distributed over tetrahedral (A) and octahedral (B) sites [5]. Moreover, during the process of preparation of ferrites in polycrystalline form, when the ferrite powder is sintered under slightly reducing conditions, the impurity ions such as Fe^{2+} were formed in the ferrite lead to high-conductivity grains. The grain boundaries are formed during the sintering process due to superficial reduction or oxidation of crystallites as a result of direct contact with the firing atmosphere [6]. Thus, the ferrite can be considered as high conductive grains separated by thin low conductive layers (grain boundaries) and behave as inhomogeneous dielectric materials. The AC electric field on the specimen is concentrated in the grain boundary regions. Therefore, the electric and dielectric properties are affected by grain boundary phase and the defect distribution in ferrites. The

dielectric behavior of $Ti_xNi_{1+x}Fe_{2-2x}O_4$ spinel ferrite were not treated before in the literature. Therefore, our main goal of the present work is to study the effect of Ni and Ti substitution, temperature and frequency on dielectric constant and loss factor for the ferrite system $Ti_xNi_{1+x}Fe_{2-2x}O_4$ prepared by ceramic method.

2. Experimental

Polycrystalline samples of $Ti_xNi_{(1+x)}Fe_{(2-2x)}O_4$ (where x = 0.0, 0.125, 0.25, 0.375, 0.50 and 0.625) are prepared by a double sintering ceramic method [3]. The structural analysis of the samples was done by X-ray diffraction using SHIMADZU XRD600 diffractometer with Cu kα radiation ($\lambda = 1.54060$ Å) at a speed of $8^°$/min and step of $0.02^°$. The XRD patterns confirmed the presence of a single phase spinel cubic structure for the prepared samples. The details of XRD analysis and the method of preparation for NiTi ferrite were reported earlier [3]. Dielectric constant ε' and loss factor tanδ measurements were carried out by two-probe method using an LCR bridge meter (Model HIOKI 3532-50 LCR Hi tester).

Dielectric parameters ε' and tanδ were measured in the frequency range from 100Hz to1MHz at selected temperatures. This work was carried out in materials science laboratory, Phys. Dept., Fac. of Science at Kafrelsheikh University, Egypt.

3. Results and Discussion

3.1 Dielectric behavior

The dielectric constant characterizes the most important electrical property of the dielectrics. The dielectric constant (or relative permittivity), ε^* of a dielectric material placed in the AC electric field is a complex quantity because the orientation polarization lags behind the polarizing electric field as the frequency of the applied field is increased. The complex dielectric constant, ε^*, can be expressed as: $\varepsilon^* = \varepsilon' + j\varepsilon''$. In this expression ε' is the real dielectric constant which characterizes the energy stored in the dielectric material, the
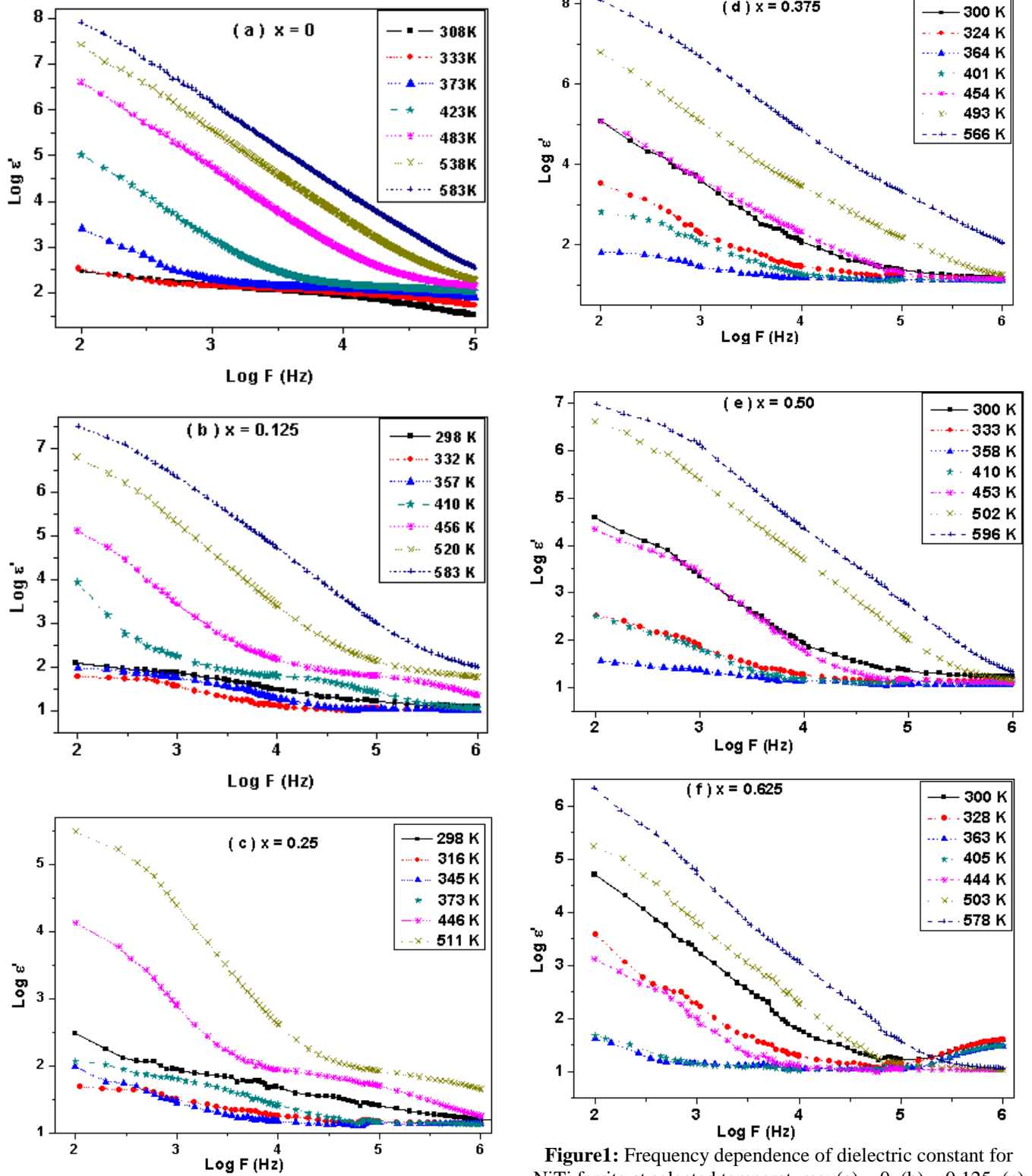
Figure1: Frequency dependence of dielectric constant for NiTi ferrite at selected temperatures; (a)x=0, (b)x=0.125, (c) x=0.25, (d) x=0.375, (e) x=0.5 and (f) x=0.615

imaginary part ε'' represents the energy losses by dielectric material and the ratio ($\varepsilon''/\varepsilon'$) represent the loss tangent factor tanδ. The typical plots of the measured ε' (as log ε') as a function of frequency (log F) at selected temperatures for Ti Ni ferrite are shown in Fig. 1(a)- (e). It is noticed that the decrease in ε' is rapidly at lower temperatures and low frequencies and becomes slow at higher frequencies i. e. the samples exhibit pronounced dispersion extending up to 10^5 Hz. The decrease in $\varepsilon'(F)$ is a normal dielectric behavior in ferrites, which indicates the formation of heterogeneous

structures with the samples under investigation [7]. The decrease in ε' with increasing in frequency takes place when the hopping frequency of the charge carriers (electrons and holes) cannot follow the alternating frequency of applied AC electric field beyond a certain critical frequency [8]. All the samples have high values of ε' ranged from $10^2 \sim 10^7$ (at frequency 10^2 Hz and temperature range 300- 595K). Such high values of ε' were observed for Ni-Zn [7, 9, 10], Mn-Mg [9, 11], Mg-Zn [6], Cu-Ge [12], and Li- Ni [13] ferrites. However, the high values of ε' at low frequencies (and the decreasing in ε'(F)) could be explained on the basis of Koop's theory [7] for the inhomogeneous double-layer dielectric structure. The dielectric structure was supposed to be composed of two successive layers of the Maxwell-Wagner type [14,15]. The first layer is the fairly good conducting ferrite grains, which are separated by the second thin layer of poorly conducting grain boundaries [16]. The grain boundaries were found to be more effective at lower frequencies, while the ferrite grains were more effective at
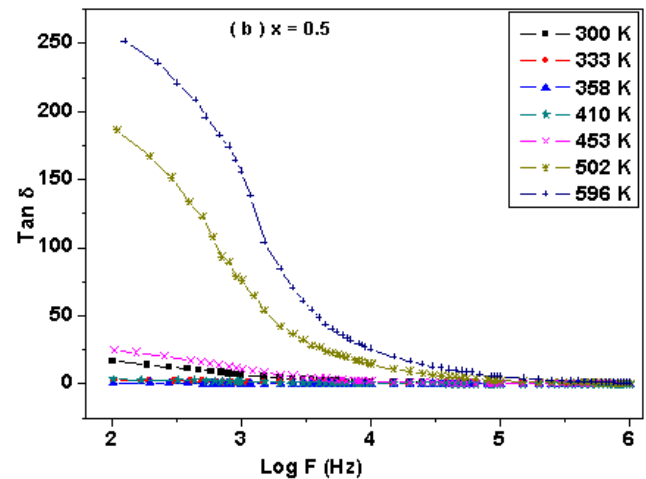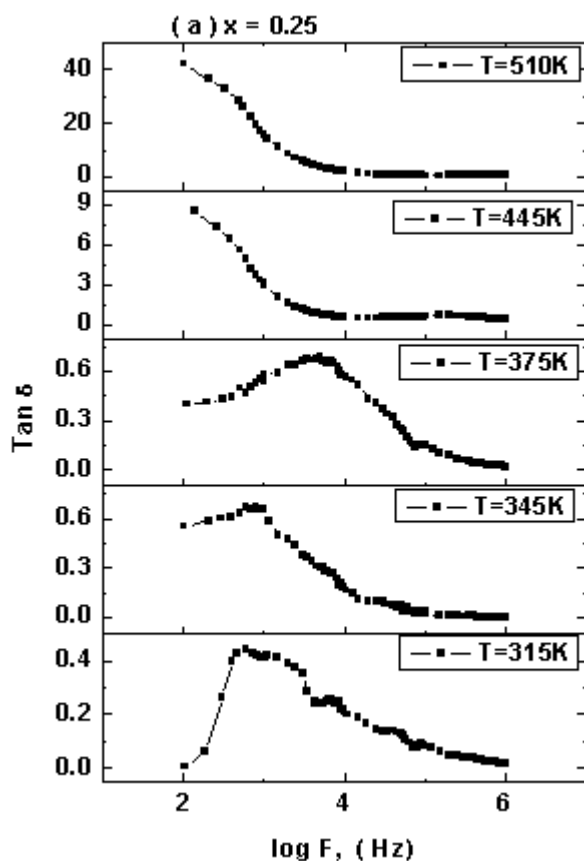

Figure 2: Frequency dependence of dissipation factor tan δ at selected temperatures for the samples x = 0.25 and x=0.5.

Higher frequencies [7, 16, 17]. So, the very high values of dielectric constant at low frequency region are mainly related to the presence of the grain boundaries. During high sintering temperature the ferrite contains an amount of easily polarizable Fe^{2+} and/or Ni^{3+} ions. Owing to the disordered structure of the grain boundaries, the polarization is due to discontinuous hopping of charge carriers between localized states as a result of many-body interactions between its constituent parts [18].

Iwauchi reported that there is a strong correlation between the conduction mechanism and the dielectric behavior of ferrites [19]. Hudson has shown that the materials with low resistivity exhibiting high dielectric loss and dielectric constant and vice versa [20]. It is reported that for certain spinel ferrites the value of dielectric constant is approximately inversely proportional to the square root of the resistivity [21- 23]. The values of dielectric constant for pure Ni ferrite (x=0) increases as the temperature increase while for the samples with 0.125≤ x≤0.625, the value of ε' decrease gradually up to a certain temperature (T_{MS}) after that increases with increasing temperature (Fig. 1). From the foregoing, we can conclude that the pure Ni ferrite has a semiconductor behavior at all temperature ranges, whereas the substituted Ti -Ni ferrites have a metallic like behavior up to a certain temperature, $T_{M/S}$, after that the samples have a semiconductor character. The values of metal/semiconductor transition points, T_{MS} and dielectric constant (at T_{MS}&1KHz) were determined from ε'(F) curves and listed in Table 1. The values of transition temperatures $T_{M/S}$ in table 1 gives as qualitative agreement with the results of AC measurements on Ti-Ni ferrite in our previous [24]. The abnormal behavior of dielectric constant and consequently the resistivity may be related to different aspects such as the presence of some impurities, the presence of different types of charge carriers, cationic migration and/or spin canting. In our case there is no such possibility in the presence of any impurities as confirmed by X-ray analysis [3]. The cationic migration and presence of different types of charge carriers in such samples may give rise to metallic behavior in the samples. The spin canting is the final possibility for the appearance of such phenomenon. With the variation of both temperature and composition, the spin canting angles might change and this may be responsible for such metallic behavior of the samples

[25]. In $Ti_xNi_{1+x}Fe_{2-2x}O_4$ ferrite, Ni^{2+} ions occupy octahedral B-sites, whereas both Fe^{3+} and Ti^{4+} ions are distributed over tetrahedral (A) and octahedral (B) site [5]. The presence of Ti^{4+} ions at B-site will act as an electrostatic trap for electron exchange between Fe^{3+} and Fe^{2+} by forming electrostatic bonds with Fe^{2+} ions [26]. At the same time the replacements of iron ions by Ti^{4+} ions will reduce the concentration of Fe^{3+}/Fe^{2+} ions and the entry of nickel ions at the octahedral site will increase Ni^{2+}/Ni^{3+} concentration. The transition metal cation in octahedral sites is an intermediate of an anion sublattice. When strong cation-anion-cation interactions dominate over the weak cation-cation interactions, these materials will then have semiconductor behavior. In the case of strong cation-cation interactions between octahedral B-sites, materials with a metallic behavior will be formed [27].

In pure $NiFe_2O_4$ ferrite with cation distribution $(Fe^{3+})[Ni^{2+}Fe^{3+}]O_4^{2-}$ (here the parentheses and square brackets refer to the tetrahedral A- site and the octahedral B-site, respectively), the cation-cation interactions are less predominant whereas the cation–anion-cation interactions are stronger between $[Fe^{3+}-O^{2-}-Fe^{3+}]$ and $[Ni^{2+}-O^{2-}-Ni^{2+}]$ [27]. According to ligand field and crystal field theories, the $[Ni^{2+}-O^{2-}-Ni^{2+}]$ interactions are dominant, which makes this sample to be semiconductor (see Fig 1).

An increase in Ti^{4+} and Ni^{2+} ions in octahedral site reduce $[Fe^{3+}-O^{2-}-Fe^{3+}]$ and increase $[Ni^{2+}-O^{2-}-Ni^{2+}]$ interactions. Also, an increase in temperature causes an increase in hopping of the localized charge carriers between $[Fe^{3+}-O^{2-}-Fe^{3+}]$ and $[Ni^{2+}-O^{2-}-Ni^{2+}]$ linkages and in this way give rise to the semiconductor character with the gradual transfer from n-type to p-type [3]. It is presumed here that at metallic interval, diminishing localized states and alignments of the spins give rise to the efficient conductive channels in the form of $[Fe^{3+}-Fe^{2+}]$ and $[Ni^{2+}-Ni^{3+}]$ links. These channels may cause the delocalization of the charge carriers and as a result, cause metallic behavior for the samples.

3.2 Dielectric Loss Tangent

Figure 2 (a)- (b) for loss tangent tanδ as a function of frequency F (at selected temperatures) showed abnormal behavior (relaxation peaks) for the samples with x≤ 0.25 and normal behavior for higher substitution x>0.25 (the typical figure is showed for samples with x=0.25, 0.5). The decreasing in tanδ with increasing frequency can be explained according to Koops theory and Maxwell Wagner theory as discussed in the case of ε'(F). The loss tangent relaxation peaks can be observed in the samples when the hopping frequency of the charge carriers coincides with the frequency of external electric field [19]. At room temperature for $NiFe_2O_4$, $Ti_{0.125}Ni_{1.125}Fe_{1.75}O_4$ and $Ti_{0.25}Ni_{1.25}Fe_{1.5}O_4$ samples tanδ shows a maximum at a frequency of 32KHz, 914Hz and 600Hz respectively. The resonance condition for observing maximum tanδ is $\omega_r\tau=1$, where $\omega_r= 2\pi f_r$ is the angular frequency at maximum and τ is the relaxation time [19]. The relaxation time τ is related to the jump probability per unit time (p) by the relation $\tau=1/(2p)$ or $f_r \propto p$. Jump probability (p) has directly proportional to temperature and inversely proportional with jumping length (L). Eraky et al. [3] reported that for Ni-Ti ferrite the jump length increases

gradually with increasing compositional parameter x, so, at constant temperature (e.g. room temp.) f_r must be decreased with increasing x, as we observed in this work. On the other hand, as the temperature rises for certain sample the mobility of localized charge carriers can be activated by temperature and this increase hopping probability or briefly for a certain sample as temperature increase maximum relaxation frequency f_r, must move toward higher frequencies, which give a good agreement with our results for samples with x≤0.25.

Table 1: Transition temperature (T_{MS}), dielectric constant (ε' at T_{MS} &1KHz), relaxation activation energy (E_r) and maximum frequency f_∞ for Ti-Ni ferrite

Sample	x=0	x=0.125	x=0.25	x=0.375	x=0.50	x=0.625
T_S, K	---	332	316	364	358	363
'	---	1.55	1.49	1.44	1.3	1.10
E_r, eV	0.21	0.57	0.61			
f_∞, s^{-1}	10^8	10^{13}	10^{13}			

In general the relaxation peaks for loss tangent tanδ can be explained by a Rezlscu model [29]. According to this model the peaks of tanδ (f)curves can be ascribed to the presence of collective contribution polarization. For the ferrite under investigation, the conduction process attributed to the presence of two types of charge carriers; n-type as electron transfer between Fe^{3+} and Fe^{2+}, and P-type as hole exchange between Ni^{2+} and Ni^{3+} at the octahedral sites [3]. Since the direction of displacement of electrons is opposite to that of holes under the application of external electric field, in the same time the mobility of holes is relatively very small with respect to that of electrons, the resulting polarization of both types of charge carriers will give rise to peaking behavior as in Fig.2 for samples with x≤0.25. The dielectric loss can caused by the impurities and imperfections in the crystal lattice. Structural defects give rise to trapping centers for the charge carriers, also known as correlated states [30]. We have indicated that relaxation peaks move toward low frequencies as compositional parameter, x, increase. For the samples with x≥0.25 the relaxation peaks not observed because the grain boundary defects are effective at low frequencies. The response time of the charge carrier in the trapping centers is higher than the time taken for hopping between the sites of the charged ions. It thus follows that we cannot detect the relaxation peaks for samples with x≥0.25 at low frequency (<300HZ) which results from correlated states, but experimentally the relaxations at higher frequencies corresponds to the hopping of charge carriers between charges ions were observed for x≤0.25.

The temperature dependence of dielectric relaxation frequency f_r can be expressed by [31, 32]:

$f_r = f_\infty \exp (-E_r/kT)$ (1)

Where E_r is the activation energy for the dielectric relaxation process, f_∞ is the maximum frequency and k is the Boltzmann constant. The activation energy E_r and f_∞ were estimated from a plot of ln f_r vs. reciprocal of the temperature for samples with x≤0. 25 and listed in Table 1. It is noticed from Table 1 that as Ti and Ni exist in the ferrite a marked increasing in relaxation activation energy occur and the maximum

frequency f_∞ jumps to be approached to the optical phonon frequency ($\approx 10^{13}$ s^{-1}). Since the mechanism of dielectric polarization in ferrites is similar to that for electric conduction [29], this leads to the result that the higher dielectric polarization is associated with a lower activation energy for dielectric relaxation and vise versa.

4. Conclusions

1. The real dielectric constant ε' and dielectric loss factor tanδ decreases as the frequency of electric field increases, this is the normal dielectric behavior of ferrite and were explained on the frame of Koops theory.
2. ε' decreases as temperature increase up to certain temperature ($T_{M/S}$) after that ε' increases. This abnormal behavior for ε'(T) lead to suggestion of metallic like behavior for the samples. The metal/semiconductor phenomena in the samples under investigations can be used in some technological applications such as sensors or switching applications.
3. tanδ (F, T) curves showed abnormal dielectric behavior (relaxation peaks) for pure and low substitutions. These peaks shifts towards higher values of frequency as temperature increases. The activation energy for dielectric relaxation increases as Ti^{4+} ions contents increases.
4. The relaxation peaks not detected for samples with x≥0.25 because the grain boundary defects and correlated states are effective at low frequency region.

Acknowledgments

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