

[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 $(Fe^{3+})_A[Ni^{2+}Fe^{3+}]_B O_4$ (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 $\tan\delta$ as a function of frequency F (at selected temperatures) showed abnormal behavior (relaxation peaks) for the samples with $x \leq 0.25$ 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 $\tan\delta$ with increasing frequency can be explained according to Koops theory and Maxwell Wagner theory as discussed in the case of $\epsilon'(F)$. 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 $\tan\delta$ shows a maximum at a frequency of 32KHz, 914Hz and 600Hz respectively. The resonance condition for observing maximum $\tan\delta$ 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 $x \leq 0.25$.

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
ϵ'	---	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 $\tan\delta$ can be explained by a Rezlscu model [29]. According to this model the peaks of $\tan\delta(f)$ 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 $x \leq 0.25$. The dielectric loss can be 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 $x \geq 0.25$ 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 $x \geq 0.25$ 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 $x \leq 0.25$.

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

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

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 $x \leq 0.25$ 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 ($\approx 10^{13} \text{ s}^{-1}$). 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 vice versa.

4. Conclusions

1. The real dielectric constant ϵ' and dielectric loss factor $\tan\delta$ 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 $\epsilon'(T)$ 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. $\tan\delta(F, T)$ 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 $x \geq 0.25$ because the grain boundary defects and correlated states are effective at low frequency region.

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