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Rate of heating and sintering temperature effect on the electrical properties of Nd ferrite

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The real part of the dielectric constant (ε') and the dielectric loss angle ($\tan\delta$) as well as the ac conductivity of ferrite $Mg_{1+x}Ti_xNd_yFe_{2-2x-y}O_4$ $0.1 \leq x \leq 0.9$ at fixed Nd concentration of 0.025 were measured at different temperatures as a function of frequencies. The variation of activation energy as a function of the applied frequency was reported. The obtained data were discussed on the basis of the valence exchange between (Fe^{3+}, Fe^{2+}), (Fe^{2+}, Nd^{3+}) and (Fe^{2+}, Ti^{4+}). Also the effect of sintering temperature and heating rate of preparation were discussed.

1. Introduction

Ferrites have many applications in the frequency range from microwave to radio. The low electrical conductivity, high Curie temperature, and chemical stability resulting in low losses makes them attractive materials for microwave applications. The dielectric properties of these materials are very interesting and very sensitive to preparation conditions such as sintering temperature, sintering hours, sintering atmosphere, the amount and the type of substituents. Dispersion in the real part of the dielectric constant (ε') and loss tangent ($\tan\delta$) with frequency in polycrystalline ferrite is strongly dependent on the polarization process and related to the Verwey theory [1]. By introducing a relatively small amount of large ions such as rare earth, an important modification of both structure and magnetic properties can be obtained. This is because the rare earth ions play an important role in determining the magneto crystalline anisotropy in the 4f-3d intermetallic compounds. In fact, many studies reported the influence of various dopants and substituents on the magnitude of room temperature resistivity of magnesium ferrite. When the ferrite powder is sintered under slightly reducing conditions, the divalent iron ions are produced in the bulk of the material. These divalent ions form high conductivity grains sandwiched between two low conductivity layers and the result of this process is that, the ferrite behaves as an inhomogeneous dielectric material.

Several investigators have studied the frequency dependence of the dielectric properties of ferrites [2–5]. It was observed that the values of the dielectric constant, the dielectric loss and the ac conductivity increases with temperature and decreases with increasing the dilution with non magnetic ions. A remarkable peak was observed near T_c at which the variation from ferromagnetic phase to paramagnetic one takes place.

Another interesting point in ferrite materials is the change in the conduction mechanism with the variation of cation valences. As an example, Zn and Cd are the most important cations which are known to improve the magnetization and decrease the Curie temperature in ferrites [6, 7]. Bradiburn and Rigby [8] studied the temperature dependence of the electrical conductivity of Mg-ferrite. The effect of small concentration of cations such as manganese on the resistivity of manganese ferrite was studied by Van Uitert [3].

Since the ionic radius of the rare earth ion is larger than any other ion in the ferrite, therefore, this ion occupies the large dodecahedral sites. In this case, we have 16 octahedral, 24 tetrahedral and 16 dodecahedral sites per unit cell containing 8 formula units [9]. In some rare earth ferrites, the moments of the Fe^{3+}ions in the octahedral sites are antiferromagnetically coupled to the moments of Fe^{2+}ions on the tetrahedral sites. The moments of other trivalent ions on the dodecahedral sites are also coupled to those on the tetrahedral sites and may contribute to the magnetization of this sub-lattice. In the absence of the rare earth ions, the moments are mainly due to the Fe^{3+} ions. C.B. Kolekar *et al.* [10] studied the effect of Gd^{3+} substitution on the dielectric behavior of copper cadmium ferrites. They found that the real part of the dielectric constant (ε') for the substituted and non substituted rare earth ferrites have the same trend but differ in values with the peak shifts that takes place with varying frequency. The substitution of Gd^{3+} ions affects the conduction mechanism by localizing Fe^{2+} ions, producing hindrance to the polarization process, decreases the dielectric intensity and increases both dc and ac resistivity.

In the present work, we attempt to understand the effect of rare earth (Nd) substitution on the dielectric properties and ac conductivity of Mg-Ti ferrite. We have also investigated the effect of valence exchange between similar and different ions on the same or on different sites on such properties. The effect of heating rate and the sintering temperature on the behavior of polarization and conduction processes should be discussed.

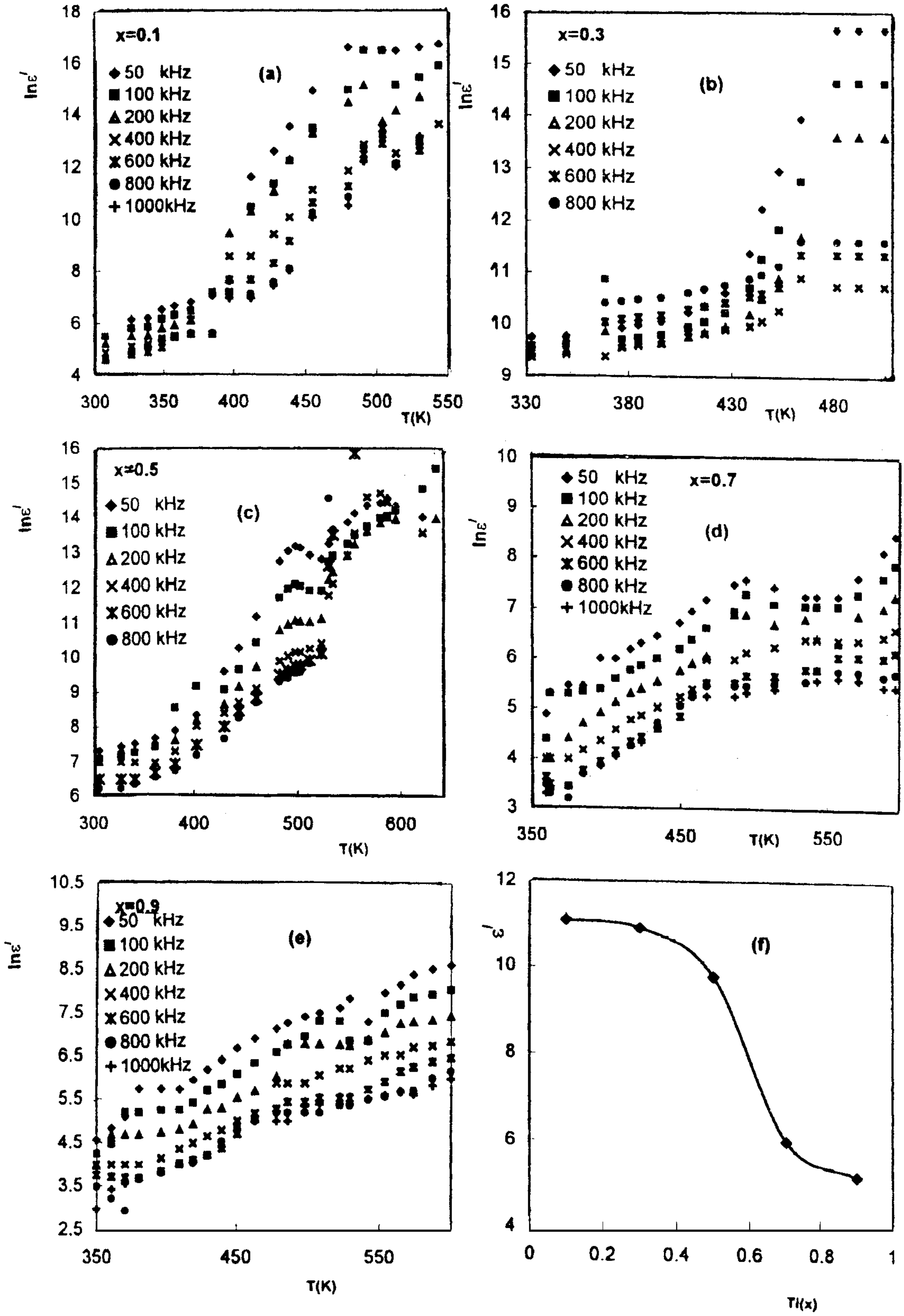


Figure 1 Relation between ε' and absolute temperature as a function of frequency for the ferrite $Mg_{1+x}Ti_xNd_yFe_{2-2x-y}$; $y = 0.025$ and $0.1 \le x \le 0.9$. (a) $x = 0.1$, (b) $x = 0.3$, (c) $x = 0.5$, (d) $x = 0.7$, (e) $x = 0.9$, and (f) Relation between ε' and Ti concentration (x) at $f = 400$ kHz and $T = 460$ K.

2. Experimental

Magnesium titanium ferrite doped Nd was prepared using the standard ceramic technique [11]. Analar grade form oxides (BDH) were mixed in stoichiometric ratios using agate mortar for 4 hours. The mixture was transferred to an electric sheaker and ball mill for another 4 hours. The samples were pressed to pellet form using hydraulic press with pressure of 5×10^8 N/m^2.

Presintering was carried out at 900°C for 15 hours using Lenton furnace type UAF 16/5 (England) with different heating rates (2, 4, 6°C/min). The samples were cooled to room temperature with the same rate as that of heating. The final sintering (firing) was performed at 1100°C, 1200°C and 1300°C for 100 hours, where the different rates were taken at 1100°C. The pellets were good polished to remove the layer from which the magnesium was evaporated. The two surfaces of each pellet were coated with silver paste (BDH) and checked for good conduction.

The real part of the dielectric constant (ε'), dielectric loss tangent ($\tan\delta$) and ac conductivity was measured using HIOKI bridge model 3530 (Japan) at different frequencies (50–1000 kHz) as a function of temperature. The temperature of the sample was measured using K-type thermocouple connected to temperature controller, where the junction of the thermocouple was just in contact with the sample to prevent any temperature gradient. The accuracy of measuring temperature was better than ±1°C.

3. Results and discussion

Fig. 1(a–f) correlates the real part of dielectric constant ($\ln\varepsilon'$) and absolute temperature for the ferrite $Mg_{1+x}Ti_xNd_yFe_{2-2x-y}O_4$, $0.1 \leq x \leq 0.9$ at fixed Nd concentration of $y = 0.025$ with sintering temperature of 1100°C for 100 hours and rate of heating 2°C/min. The measurements were carried out at different frequencies ranging from 50 kHz up to 1 MHz. From the figure, it is clear that the general trend at all Ti concentrations is the same except an additional hump appeared at $x = 0.7$. At all frequencies, ε' increases gradually with temperature up to about 450 K after which ε' increases suddenly and reaches nearly stable value at about 600 K. With increasing frequency ε' decreases, because the electric dipoles cannot follow up the field variation. Also at high frequency, the alternation of the dipoles increases the friction between them leading to an increase in the quantity of heat generated. The energy dissipation is increased and the aligned dipoles will be disturbed with the result of decreasing ε'. In the first region of temperature up to about 450 K, the

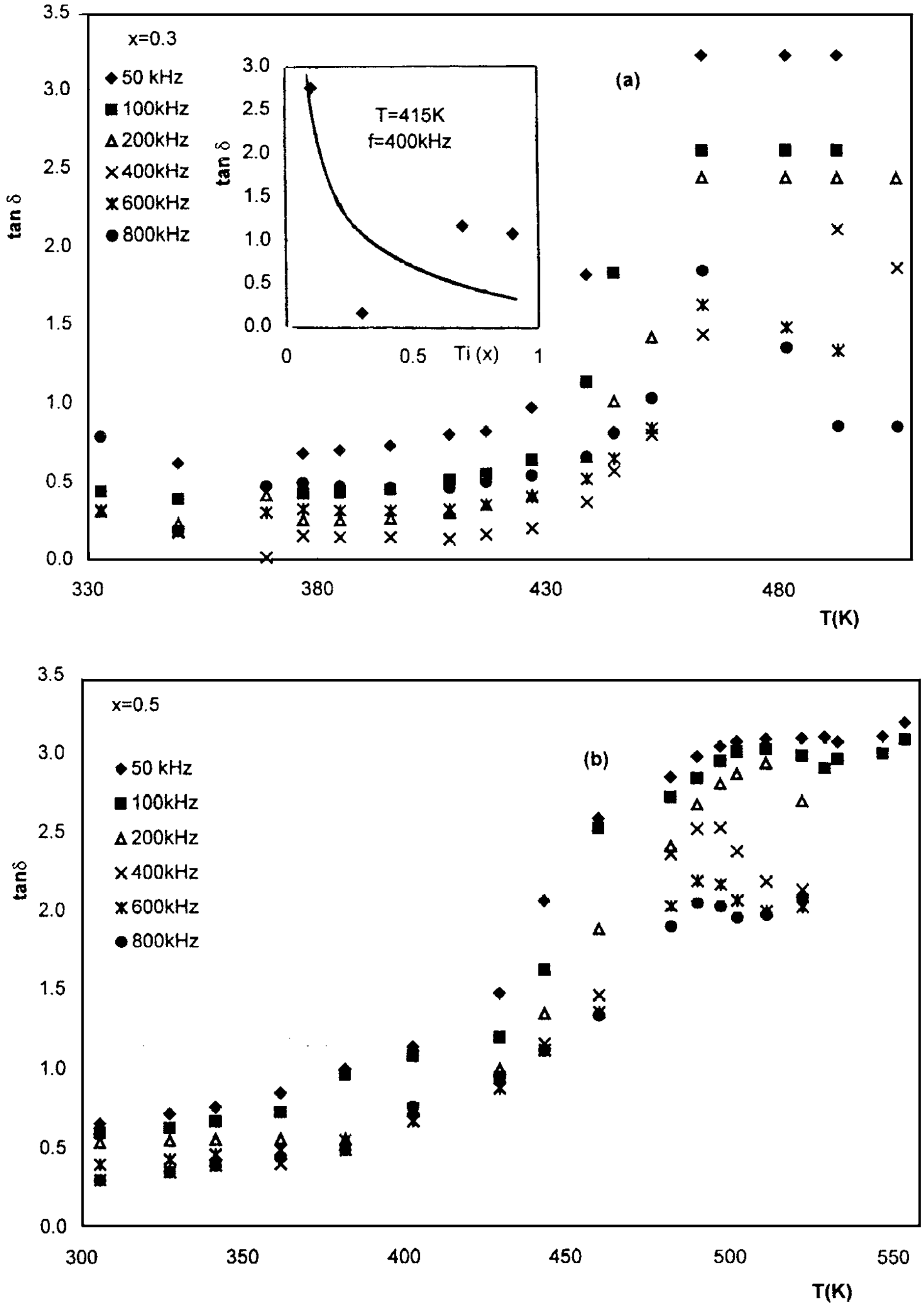


Figure 2 Relation between $\tan\delta$ and absolute temperature as a function of frequency: (a) $x = 0.3$ and (b) $x = 0.5$.

small thermal energy given to the sample due to heating will free more frozen dipoles and the applied electric field will orient them in its direction. Above 450 K, no more dipoles liberation so the polarizability as well as ε' became nearly constant. In the investigated samples, the main source of polarization is the valence exchange between iron ions, which is maximum in case of minimum Ti concentration. Therefore, comparatively high ε' was obtained at $x = 0.1$ as shown in Fig. 1f.

Fig. 2a and b is a typical curve correlates the tangent of the dielectric loss angle ($\tan\delta$) and the absolute temperature at different frequencies where the titanium concentration was $x = 0.3$ and 0.5 respectively. From the figure, it is clear that the data can be divided into 3 regions. The first one from room temperature up to about 430 K at $x = 0.3$ and up to 400 K at $x = 0.5$. In this region, a slight variation of $\tan\delta$ with temperature was observed. In the second region above 430 K and 400 K for $x = 0.3$, $x = 0.5$ respectively up to the Curie temperature, a drastic increase in $\tan\delta$ was obtained against temperature. The third region above the Curie temperature at which $\tan\delta$ was slightly decreased or kept constant. Similar to the data of $\ln\varepsilon'$, $\tan\delta$ gives nearly the same behavior where the relaxation process takes place around the same temperature. As a general trend, by increasing frequency $\tan\delta$ decreases and the peak shifts to lower temperature. A closer look to the figure and at each separate frequency, $\tan\delta$ increases with increasing temperature, due to the high thermal energy which is quite sufficient to disturb the aligned dipoles, increasing the friction between them and though increases the energy dissipation as well as $\tan\delta$. From the inset of Fig. 2a and b, one can find that increasing Ti^{4+} ions concentration in the system decreases $\tan\delta$. This means that the titanium concentration plays a significant role especially in rotational and vibrational motion of the dipoles. Generally, it was found by Prakash and Bajal [12] that when the ferrite samples were cooled to room temperature in an oxidizing atmosphere, a considerable amount of oxygen was absorbed and some of Fe^{2+} ions formed in the sample were changed into Fe^{3+} ions [$Fe^{2+} \Leftrightarrow Fe^{3+} + e^-$], where the formed ($Fe^{3+}$) ions prefer the octahedral sites. In the general formula $Mg_{1+x}Ti_xNd_yFe_{2-2x-y}O_4$ and by increasing Ti^{4+} ion concentration in the presence of Nd^{3+} ions, the Fe^{3+} decreases from 2 to $2 - 2x - y$ where the Ti^{4+} ions occupying the octahedral site, share the Fe^{3+} ions in the polarization process. This may be due to the interaction between the tetrahedral site with both octahedral and dodecahedral sites. It was expected that the valence exchange between the different ions (Fe^{3+}, Fe^{2+}), (Fe^{2+}, Nd^{3+}) and (Fe^{2+}, Ti^{4+}) takes place. The possibility of the first two is predominant and affect directly on the dielectric properties of the investigated samples. The effective number of ferrous ions that was formed under slightly reducing conditions on octahedral sites decreases with increasing Ti concentration which may explain the decrease in $\tan\delta$.

Fig. 3 is a typical curve, correlates the ac conductivity ($\ln\sigma$) and the reciprocal of absolute temperature at different frequencies for the sample $x = 0.3$ sintered at 1100°C with aheating rate of 4°C/min. From the figure, it is clear that the data obeys the well known Arrhenius relation $\sigma = \sigma_o \exp(-E/kT)$, where σ_o is constant, k, E and T are the Boltzman's constant, activation energy and absolute temperature respectively. 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 carriers between the different localized states. This mechanism continues up to a certain frequency after which the conductivity may

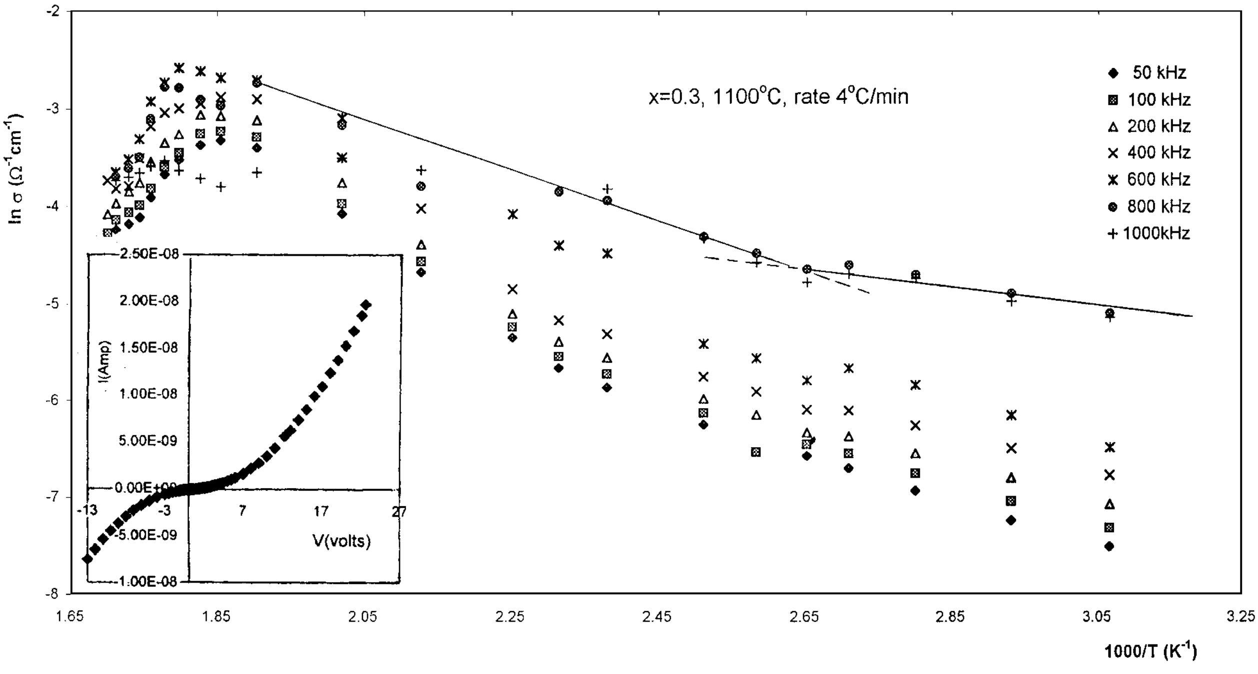


Figure 3 The dependence of the ac conductivity ($\ln\sigma$) on the reciprocal of absolute temperature ($1000/T$) at different frequencies for the sample $x = 0.3$, 1100°C, rate of heating 4°C/min.

TABLE I Activation energies of low (E_I) and high (E_{II}) temperatures regions in eV, at different Ti concentration (x) and sintering temperature of 1100°C and rate 2°C/min)

	Ti(x)									
	$x = 0.1$		$x = 0.3$		$x = 0.5$		$x = 0.7$		$x = 0.9$	
f(kHz)	E_I (eV)	E_{II} (eV)	E_I (eV)	E_{II} (eV)	E_I (eV)	E_{II} (eV)	E_I (eV)	E_{II} (eV)	E_I (eV)	E_{II} (eV)
50	0.310	0.230	0.053	1.090	0.139	0.018	0.338	0.380	0.383	0.418
100	0.310	0.230	0.057	0.556	0.087	0.482	0.290	0.380	0.319	0.402
200	0.300	0.270	0.072	1.134	0.066	0.566	0.250	0.350	0.318	0.425
400	0.300	0.270	0.168	1.134	0.140	0.614	0.250	0.350	0.233	0.446
600	0.590	0.330	0.050	0.620	0.070	–	0.446	–	0.616	0.531
800	0.460	0.330	0.042	0.620	0.048	0.755	0.425	0.425	0.552	0.531
1000	0.380	0.330	0.042	0.620	–	–	0.312	0.488	0.360	0.595

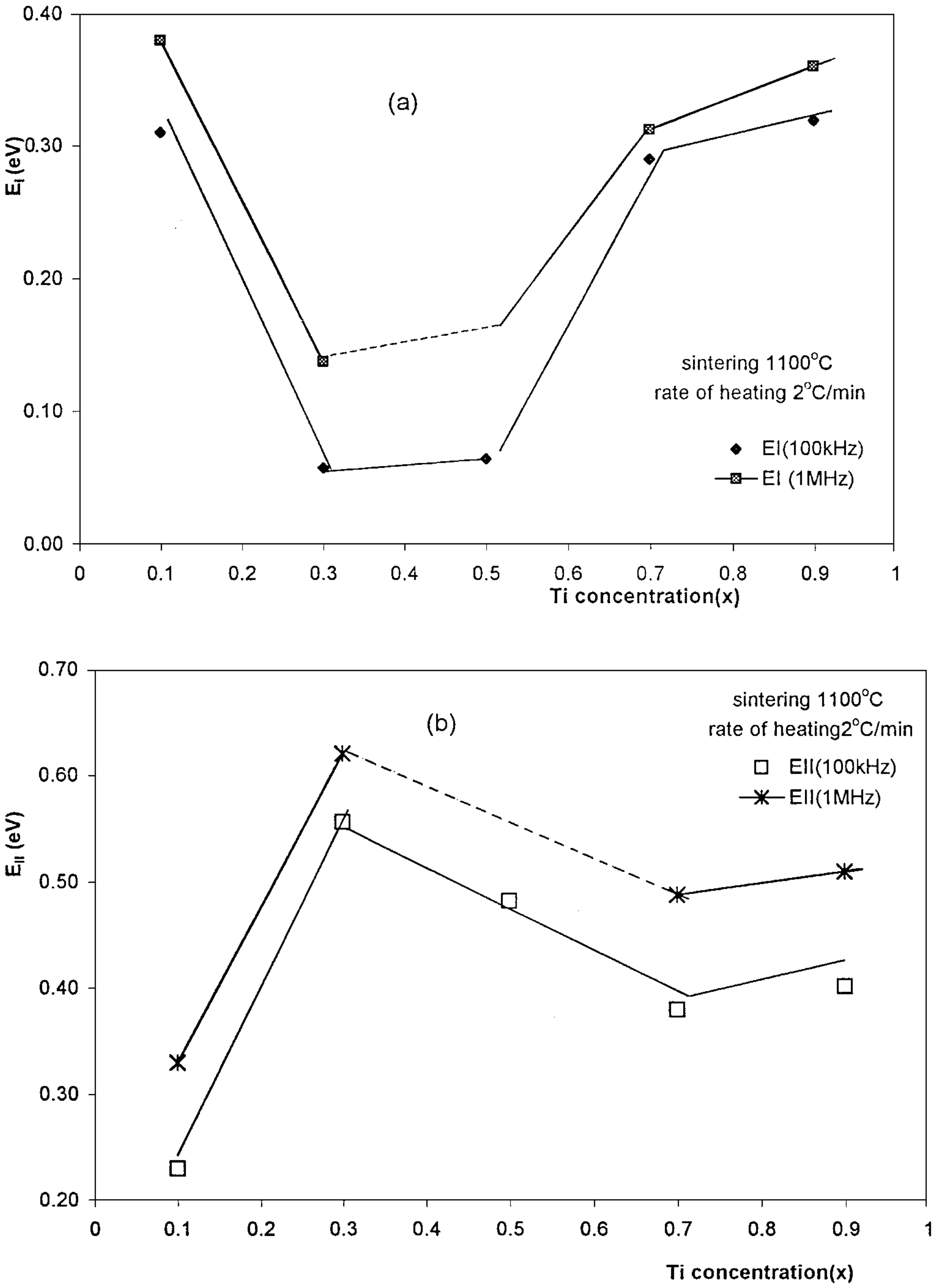


Figure 4 (a) Relation between E_I in low temperature region and Ti concentration at 100 kHz and 1 MHz. (b) Relation between E_{II} in low temperature region and Ti concentration at 100 KHz and 1 MHz.

decreases due to the disturbance effect of frequency. The change in the slope takes place around 400 K where the larger value of the activation energy in the high temperature region can be regarded as due to thermally activated mobility of the charge carriers and not to a thermally activated creation of these charge carriers. Consequently, this would provide a simple explanation of the large increase of the conductivity at this region. The small values of the activation energy in the low temperature region confirm the electronic character of the conduction process which consists of electron hopping between the ions of different valences. Also by increasing the temperature, the conductivity increases because the thermal energy helps in the conduction processes until reaching the peak value after which it decreases as the thermal energy becomes too large and so the polarization ceases. The figure indicates that after approximately 560 K a peculiar behavior in the conductivity was appeared as a drastic increase until the resistance reaches approximately 0.08 Ohm. This means that the samples under investigation at this high sintering time (100 hours) behave as a semiconductor at relatively high temperature. The I–V characteristics shown in the inset of the figure enhances this expectation. The values of the activation energy as calculated from the experimental data were reported in Table I. These data are calculated from two temperature regimes, the first one from room temperature up to about 400 K (E_{I}). The small values of the activation energy in this region indicate the metallic behavior of the ferrite under investigation as mentioned above. The drastic increase in the activation energy in the secong region (above 400 K), indicates the semiconducting trend which is almost the general behavior of ferrites. So, one may assign this type of transition as metal to semiconductor transition.

The activation energies (E_{I}, E_{II}) as a function of $\mathrm{T_i}$ concentration at 100 kHz and 1 MHz, is shown in Fig. 4a and b. The figure shows that the behavior of the activation energy in the low and high temperature regions is opposite to each other. In the high temperature region (E_{II}) increases up to the critical concentration approximately $x = 0.3$, then decreases with nearly stable value. This means that increasing Ti concentration decreases the conductivity of the samples which agrees well with the above results. In the low temperature region, (E_{I}) decreases with increasing Ti concentration, then increases again. This was attributed to the valence exchange between (Fe^{3+}, Fe^{2+}), (Fe^{2+}, Ti^{4+}) respectively.

Fig. 5 clarify the effect of heating rate on the real part of the dielectric constant (ε') at 100 kHz and 1 MHz for the sample of $x = 0.9$ at a fixed temperature of 535 K and at a sintering temperature of 1100°C. The two frequencies gave the same trend where ε' decreases with the heating rate untill reaching a minimum value at 4°C/min. This rate can be considered as a critical rate of heating.

Fig. 6a and b shows the effect of heating rate on the activation energy in both low and high temperature regions at 100 kHz and 1 MHz at $x = 0.1$. The data illustrates that the trend of E_{I} is opposite to that of E_{II}. The activation energy (E_{I}) decreases reaching its minimum value at the rate of 4°C/min. and then increases again. This means that the conductivity reaches its maximum value at this suggested critical rate (4°C/min). This behavior may attributed to the maximum hopping of electrons between the iron ions of different

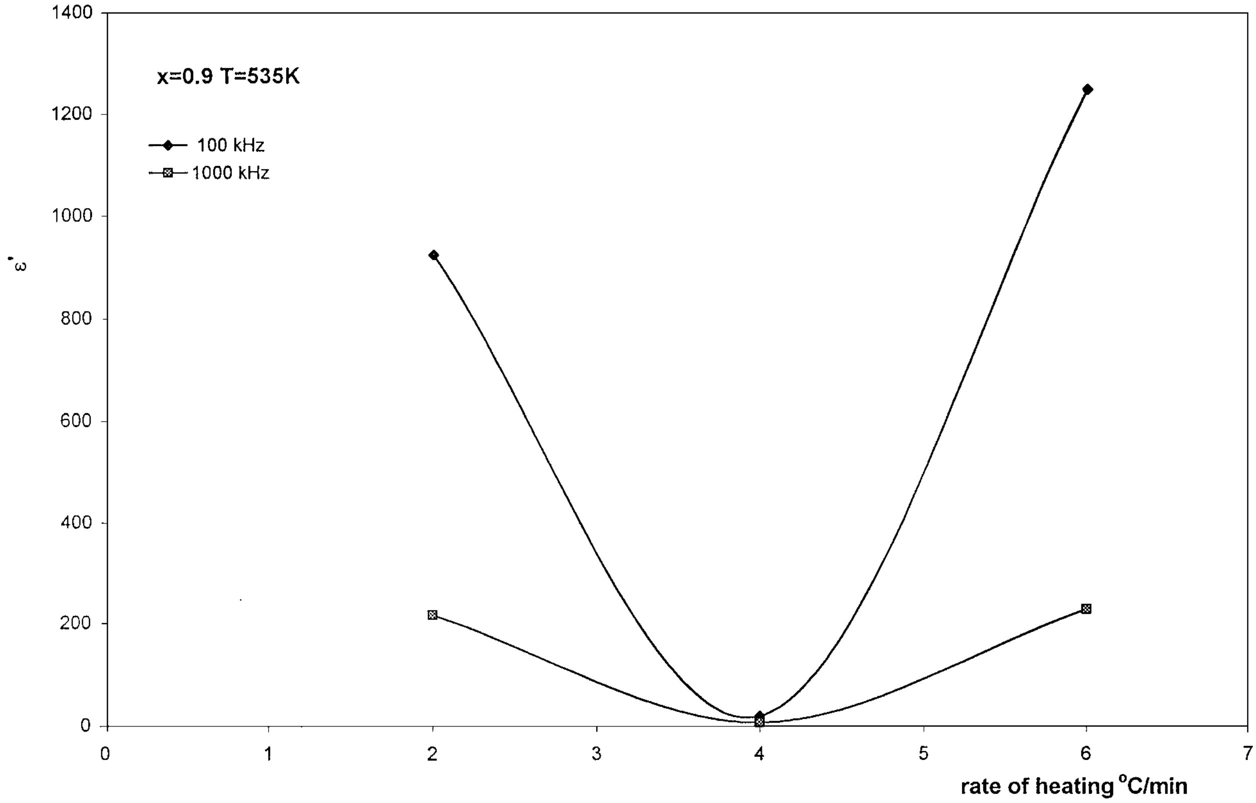
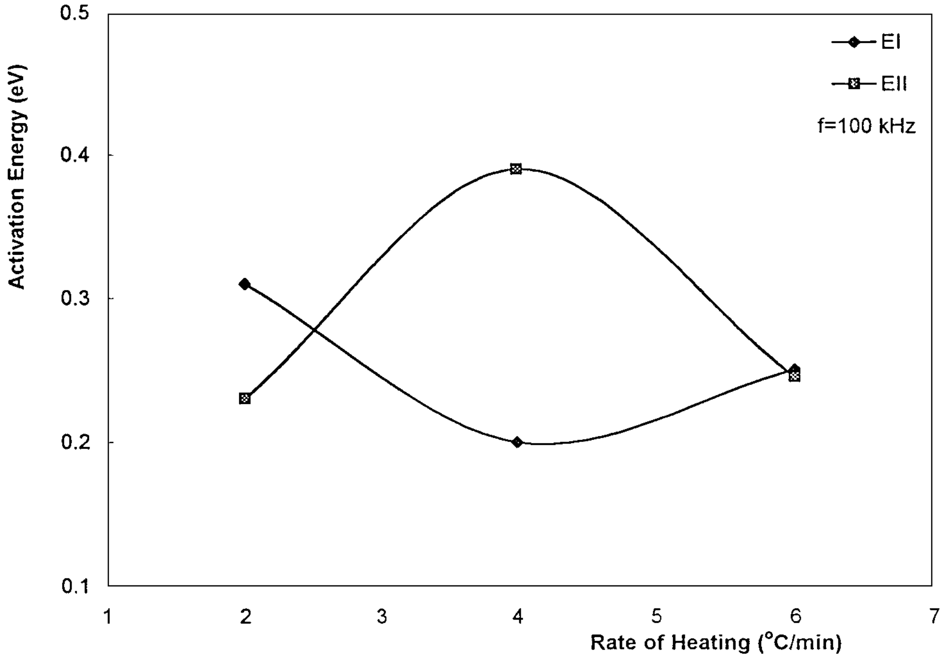
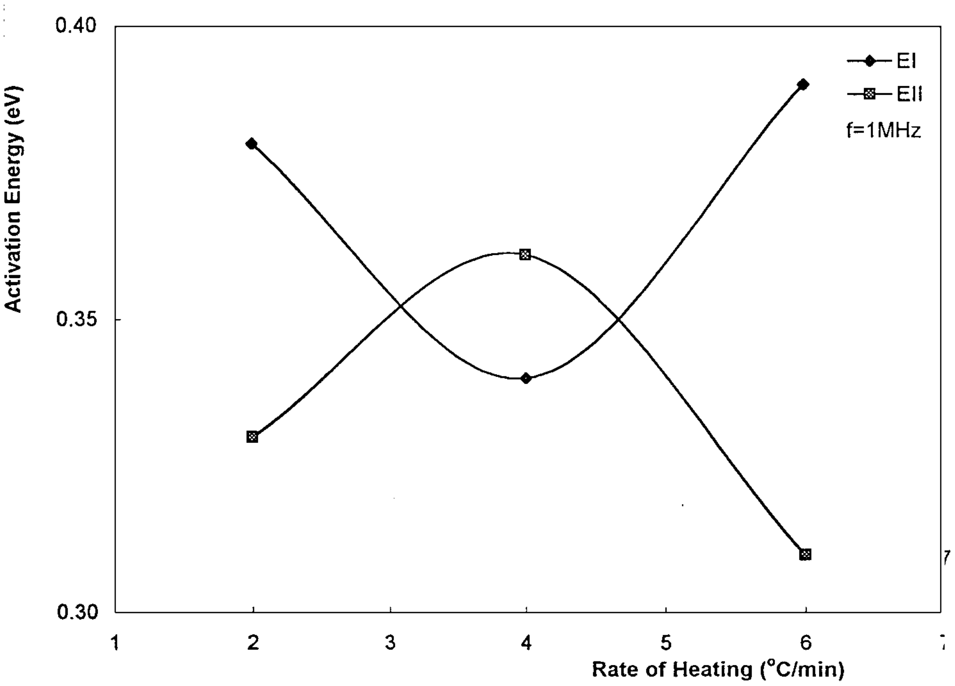


Figure 5 Relation between ε' and rate of heating at 100 kHz and 1 MHz at fixed temperature of 535 K.



(a)



(b)

Figure 6 (a) Dependence of the activation energies E_{I}, E_{II}; in the low and high temperature regions respectively on the heating rate at 100 kHz for $x = 0.1$. (b) Dependence of the activation energies E_{I}, E_{II}; in the low and high temperature regions respectively on the heating rate at 1 MHz for $x = 0.1$.

valences [$\mathrm{Fe}^{2+} \Leftrightarrow \mathrm{Fe}^{3+} + \mathrm{e}^{-}$] on the octahedral sites as well as the Fe^{3+} ions exchange with the rare earth ions (Nd^{3+}) ions on the dodecahedral sites. In the high temperature region, the activation energy increases due to high thermal energy, increase the lattice vibration, generating more phonons, interact with the hopping electrons and decreases the conductivity of the sample. The maximum phonon generation was expected to occur at 4°C/min which was enhanced by the maximum value of (E_{II}).

When comparing Fig. 5 with Fig. 6a and b one can find that minimum polarization corresponds to minimum activation energy in the low temperature region (E_{I}) at 4°C/min. This may be due to increasing of the liberation of charges from the trapping centers at such rate.

Fig. 7a and b shows the relation between the activation energies (E_{I}), (E_{II}) and the sintering temperature at 100 kHz and 1 MHz respectively. The figure shows that E_{I} decreases with increasing sintering temperature, reaching a minimum value at 1200°C and then increases. This means that the resistivity decreases reaching its minimum value at 1200°C and then increases, where there is a complete diffusion of the rare earth

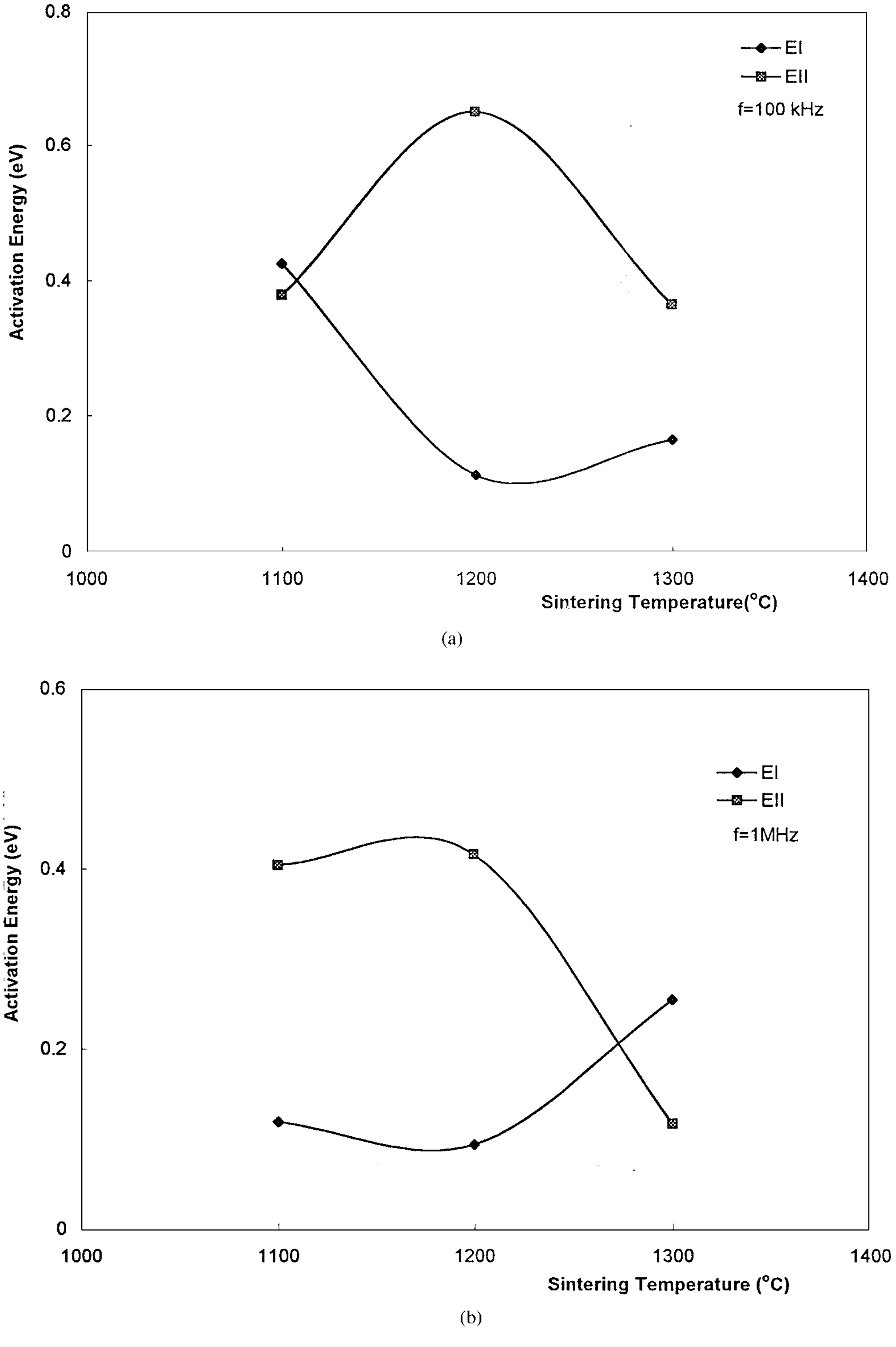


Figure 7 (a) Relation between E_{I}, E_{II}; in the low and high temperature regions respectively; and sintering temperature at 100 kHz. (b) Relation between E_{I}, E_{II}; in the low and high temperature regions respectively; and sintering temperature at 1 MHz.

ions in the spinel compound. The behavior of the activation energy at high temperature region (E_{II}) seems to be opposite to that of (E_{I}).

The dependence of the real part of the dielectric constant ($\ln \varepsilon'$) on the sintering temperature at heating rate of 4°C/min is shown in Fig. 8. The general trend of the samples is the decrease in (ε') with increasing sintering temperature up to the minimum value and then increases. This can be attributed to the polarizability, which decreases under the effect of the dipole orientation as well as the change in the grain size. The effect of sintering temperature on the grain size is carefully studied by carrying out scanning electron micrographs Fig. 9 (a, b). The obtained data are reported in Table II. It is clear that the grain size decreases with increasing sintering temperature. This may be due to the

TABLE II The average grain size of the samples with $x = 0.3$ sintered at different temperatures and with a heating rate 4°C/min

Sample, sintering conditions	Average grain size (μm)
$x = 0.3$, 1100°C, 4°C/min	3.180
$x = 0.3$, 1200°C, 4°C/min	1.490
$x = 0.3$, 1300°C, 4°C/min	1.305

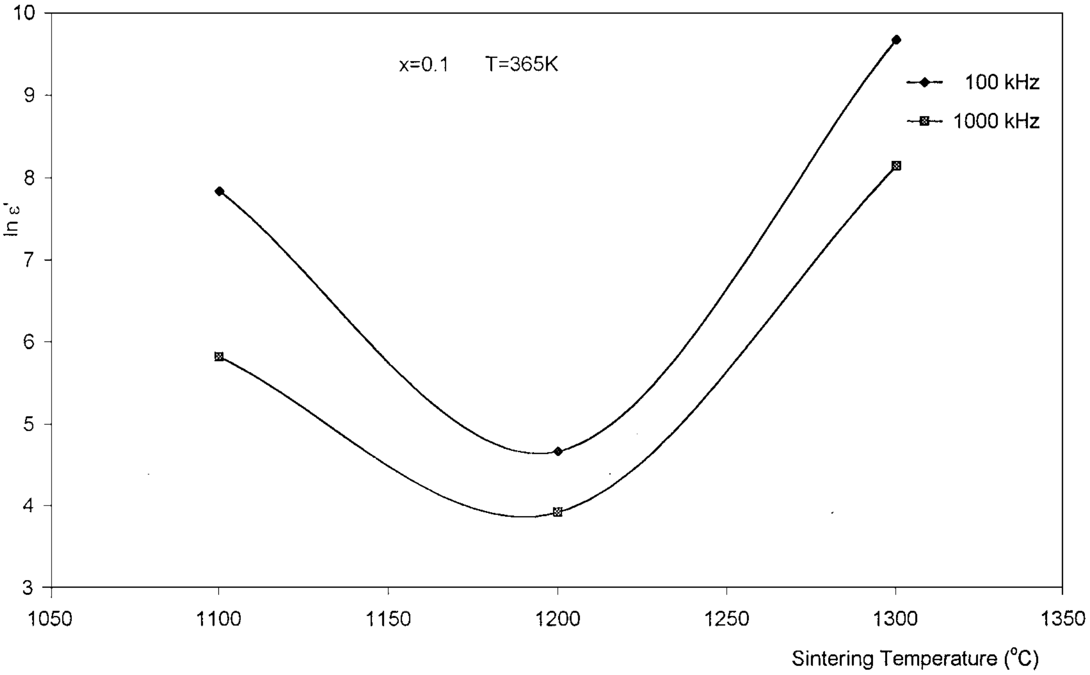


Figure 8 Dependence of (ln ε') on the sintering temperature at 100 kHz and 1 MHz at fixed temperature and at heating rate of 4°C/min for $x = 0.1$.

existence of R^{3+} ion with larger radius (Nd^{3+}) which generally retards the densification and impedes the grain growth. The critical sintering temperature is 1200°C which was enhanced by the results obtained from the electrical properties. It was an obvious result, because at sintering temperature $> 1200°C$ and for high sintering period (100 hours), the intragranular porosity increases leading to more defects in the samples as well as increasing microcrack formation [13]. We can conclude that the most suitable sintering conditions are 1200°C with a heating rate of 4°C/min. also, the increase of Ti^{4+} ion concentration decreases ε' as well as the ac conductivity.

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