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Electrical and Dielectric Properties of Zn$_{0.8}$Co$_{0.2}$Fe$_2$O$_4$

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Abstract. — DC, AC electrical resistivity ($\rho_{dc}$ and $\rho_{ac}$ ($\omega$) and dielectric properties ($\varepsilon'$ and tan $\delta$) were studied for Zn$_{0.8}$Co$_{0.2}$Fe$_2$O$_4$ ferrite samples prepared at sintering temperatures ($T_s$) in the range 1273 to 1473 K by the usual ceramic technique. The experimental results indicated that the DC and AC electrical resistivity, Curie temperature ($T_c$) and activation energies for electrical conduction ($E_p$ and $E_f$) decrease as the sintering temperature increases. The DC electrical conductivity increases as the temperature increases. It was found that $\varepsilon'$, tan $\delta$ and $\rho_{ac}$ ($\omega$) decrease as frequency increases.

1. Introduction

Polycrystalline ferrites are good dielectric materials with low conductivity and have a wide field of technological applications in the range from microwave to radiowave frequencies. The electrical, dielectric, magnetic, thermal and structural properties of the magnetic semiconductor ferrites are very sensitive to the chemical composition, type and amount of additives, sintering temperature and time. The effect of sintering temperature on the electrical properties was reported for Ni-Zn ferrite [1-3], Cu-Co ferrite [4], Cu-ferrite [5], Ni-ferrite [6], Mn, Mg and Co-ferrite [7], Co and Zn-ferrite [8] and for many other ferrites [9]. The dielectric behavior was studied for Co-Zn ferrite [10-12], Ti-Li ferrite [13] and Mn-Zn ferrite [14]. When the electrical and dielectric properties was studied for Co-Zn ferrite, it was reported that the composition Zn$_{0.8}$Co$_{0.2}$Fe$_2$O$_4$ had a high value of dielectric constant and AC conductivity [10,15]. Therefore, the authors aimed to study the effect of sintering temperature ($T_s$) on the DC, AC electrical resistivity, dielectric constant ($\varepsilon'$), dielectric loss (tan $\delta$), Curie temperature ($T_c$) and activation energies for electrical conduction ($E_p$ and $E_f$) for this critical composition of Zn$_{0.8}$Co$_{0.2}$Fe$_2$O$_4$ prepared by the usual ceramic technique. The effect of frequency of the applied electric field on the real AC electrical conductivity, dielectric constant and dielectric loss was studied too.

2. Experimental

High purity CoO, ZnO and Fe$_2$O$_3$ oxides were mixed in molar ratios to give the composition Zn$_{0.8}$Co$_{0.2}$Fe$_2$O$_4$. The powders were vibromixed for two hours to obtain good homogeneity.
The mixed powders were pressed in the form of discs and sintered at temperatures of 1273 K, 1323 K, 1373 K, 1423 K and 1473 K for two hours at atmospheric pressure. After sintering, the furnace was switched off and the samples were left inside to cool slowly with a cooling rate of about 2 K/mn. The surfaces of the discs were smoothly polished then, coated with a thin layer of silver paste as contact electrodes for electrical measurements. The samples were placed between two electrodes in an evacuated cell of silica tube supported with a furnace. The temperature of the samples was measured and controlled using Chromel-Alumel thermocouples attached to the samples. The DC electrical conductivity was measured at different temperatures \( T \) in the range from 296 K to 526 K using Ohm's law. The real AC electrical conductivity \( (\sigma'_{ac}) \), dielectric constant \( (\varepsilon') \) and dielectric loss \( (\tan \delta) \) were measured using a complex impedance technique (lock-in amplifier, Stanford type SR 510, USA). The samples preparation and experimental measurements were carried out at Department of Physics, Faculty of Science, Tanta University.

3. Results and Discussion

3.1. EFFECT OF TEMPERATURE. — The effect of temperature \( (T) \) on the DC electrical resistivity \( (\rho_{dc}) \) is presented in Figure 1 for all the studied samples. Figure 1 clearly indicated that the DC electrical resistivity decreases as temperature \( (T) \) of the sample increases. This decrease in the resistivity is due to the semiconductive behavior of the studied composition \( \text{Zn}_{0.8}\text{Co}_{0.2}\text{Fe}_2\text{O}_4 \) which is controlled by the following form

\[
\rho_{dc} = \rho_0 \exp\left[\frac{E}{kT}\right]
\]

where \( \rho_0 \) is the pre-exponential constant, \( k \) is Boltzmann's constant and \( E \) is the activation energy in eV for electrical conductions. As shown in Figure 1, the logarithmic representation

Fig. 1. — Effect of temperature on the DC electrical resistivity for \( \text{Zn}_{0.8}\text{Co}_{0.2}\text{Fe}_2\text{O}_4 \) samples prepared at different sintering temperatures.
of equation (1) gives a straight line for each sample, the line being broken at the Curie temperature \((T_c)\). At the Curie (magnetic transition) temperature, the sample changes from the ferrimagnetic to the paramagnetic state. The activation energies for the paramagnetic \((E_p)\) and ferrimagnetic \((E_f)\) regions were determined from the slopes of the lines on both sides of \(T_c\) for each sample.

3.2. EFFECT OF FREQUENCY. — The frequency dependence of the real AC electrical conductivity \(\sigma'_{ac}(\omega)\) measured at room temperature is illustrated in Figure 2. It is clear that the real AC electrical conductivity increases as the frequency of the applied electric field increases. The relationship between the real AC electrical conductivity and the frequency can be written in the form of a power law [16] as follows:

\[
\sigma'_{ac}(\omega) = B\omega^n \tag{2}
\]

where \(B\) and \(n\) are constants which depend on both the temperature and composition and \(\omega = 2\pi f\) is the angular frequency. The logarithmic representation of equation (2) as shown in Figure 2 gives a straight line, the slope of which equals the exponent \(n\) for the studied samples.

![Fig. 2. — Frequency dependence of the real AC electrical conductivity.](image)

The effect of frequency on the real dielectric constant \((\varepsilon')\) and dielectric loss \((\tan \delta)\) measured at room temperature is presented in Figure 3a,b respectively. It is clear that both \(\varepsilon'\) and \(\tan \delta\) decrease as the frequency increases. Dielectric dispersion can be observed in Figure 3. This decrease in \(\varepsilon'\) and \(\tan \delta\) was observed earlier for Co-Zn ferrite [10,11], Ni-Zn ferrite [17] and Li-Ti ferrite [13]. The decrease in the values of both \(\varepsilon'\) and \(\tan \delta\) as the frequency increases can be related to the electron exchange interaction between the Fe\(^{2+}\) and Fe\(^{3+}\) ions which can not follow the alternation of the applied electric field beyond a certain critical frequency [17].
3.3. Effect of Sintering Temperature. — The Curie temperature ($T_c$) as a function of sintering temperature ($T_s$) was calculated from Figure 1 to be listed in the second column of Table I. It is clear that the Curie temperature decreases as the sintering temperature ($T_s$) increases. In this study $T_c = 314$ K for the sample sintered at 1473 K, while $T_c = 443$ K for Zn$_{0.8}$Co$_{0.2}$Fe$_2$O$_4$ sample prepared at a sintering temperature $T_s = 1523$ K [10], in another study $T_c$ does not appear for the sample prepared at $T_s = 1573$ K [18]. These deviations can be related to the variation of preparation conditions. The effect of sintering temperature on the exponent $n$ was calculated from Figure 2 to be listed in the third column of Table I. It is clear that the exponent $n$ increases as the sintering temperature increases. $n$ has values between 0.24 and 0.37 for the studied samples. It was reported earlier [19] that the exponent $n$ has values between 0 and 1. For $n = 0$, the electrical conduction is frequency independent or DC conduction while it is frequency dependent for $n > 0$.

The effect of sintering temperature on the activation energies for electrical conduction ($E_p$ and $E_f$) is shown in Figure 4. It is clear that the activation energy for the paramagnetic region ($E_p$) is higher than that for the ferrimagnetic region ($E_f$). This can be related to the fact that the ferrimagnetic state is an ordered state while, the paramagnetic state is a disordered state in which a charge carrier needs more activation energy to jump between adjacent sites. The activation energies decrease as the sintering temperature increases.

The activation energies for our sample sintered at 1473 K, were found to be $E_p = 0.38$ eV and $E_f = 0.13$ eV while the published results were $E_p = 0.64$ eV and $E_f = 0.43$ eV for sample prepared at 1523 K [10], $E_f = 0.22$ eV for sample prepared at 1473 K [20].

The effect of sintering temperature ($T_s$) on the DC and real AC electrical resistivity ($\rho_{dc}$ and $\rho_{ac}(\omega)$) is represented in Figure 5a, b for the dielectric loss ($\tan \delta$) and real dielectric constant ($\varepsilon'$). The results in Figure 5 were measured at room temperature, besides this $\rho_{ac}(\omega)$, $\varepsilon'$ and $\tan \delta$ were measured at a frequency of 1 kHz. The DC ($\rho_{dc}$) and real AC ($\rho_{ac}(\omega)$) electrical resistivity in Figure 5a decreased while the real dielectric constant ($\varepsilon'$) and dielectric loss ($\tan \delta$) in Figure 5b increase as the sintering temperature increases. During samples preparation,
Fig. 4. — Variation of activation energies for electrical conduction with the sintering temperature.

Fig. 5. — Effect of sintering temperature on the: a) DC and AC electrical resistivity, b) $\varepsilon'$ and tan $\delta$. 
Table I. — *Effect of sintering temperature* ($T_s$) *on both the Curie temperature* ($T_c$) *and the exponent* $n$.

<table>
<thead>
<tr>
<th>$T_s$ (K)</th>
<th>$T_c$ (K)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1273</td>
<td>349</td>
<td>0.237</td>
</tr>
<tr>
<td>1323</td>
<td>340</td>
<td>0.252</td>
</tr>
<tr>
<td>1373</td>
<td>332</td>
<td>0.276</td>
</tr>
<tr>
<td>1423</td>
<td>323</td>
<td>0.276</td>
</tr>
<tr>
<td>1473</td>
<td>314</td>
<td>0.309</td>
</tr>
</tbody>
</table>

the chemical reaction completely takes place and no oxides of high resistivity remain without interaction at higher sintering temperature. On the other hand, the grains grow up in size decreasing the grain boundary density between them. The samples became more dense and homogeneous as the sintering temperature. Mossbauer investigation of Co-Zn ferrites proved the cation distribution formula [21] as follows:

$$ (Zn_xFe_{1-x-y}Co_y)[Co_{1-x-y}Fe_{1+x+y}]O_4 $$

where the first and second square brackets denote the tetrahedral (A-sites) and octahedral (B-sites) sites respectively. Zinc ions occupy the tetrahedral sites while cobalt and iron ions have two valences therefore partially occupy both the tetrahedral and octahedral sites. The presence of cobalt ion on the octahedral sites for the spinels predominates the following ion exchange interaction [22]:

$$ Co^{2+} + Fe^{3+} = Co^{3+} + Fe^{2+} $$

In Co-Zn ferrites, the n-type semiconductor is due to the hopping of electron from $Fe^{2+}$ to $Fe^{3+}$ ion, while the p-type is related to the jumping of hole from $Co^{2+}$ to $Co^{2+}$ ions [23]. For sample sintered at higher temperature, $Co^{3+}$ may also present along with $Co^{2+}$ and hopping of holes is probable according to previous ion exchange interaction, the conduction mechanism is enhanced and the resistivity of the sample ($\rho_{dc}$ and $\rho_{ac}^{'}$) is reduced as indicated in Figure 5a. The higher is the activation energy and Curie temperature, the higher is the electrical resistivity [24]. This explains the decrease in both the DC and AC electrical resistivity in Figure 5, Curie temperature in Table I and activation energies for electric conduction in Figure 4 as the sintering temperature increases.

4. Conclusion

The results of this work could be summarized as follows:
The DC and AC electrical resistivity ($\rho_{dc}$ and $\rho_{ac}^{'}(\omega)$), activation energies for electrical conduction ($E_F$ and $E_p$) and Curie temperature ($T_c$) decrease while the real dielectric constant ($\varepsilon'$) and dielectric loss (tan $\delta$) increase as the sintering temperature ($T_s$) increases. The DC electrical resistivity decreases as the temperature increases. The real AC electrical conductivity $\sigma_{ac}^{'}(\omega)$ increase while the dielectric constant ($\varepsilon'$) and dielectric loss (tan $\delta$) decrease as frequency of the applied electric field increases.
References


