Frequency, Temperature and Composition Dependence of Dielectric Properties of Nd^{3+} Substituted Cu-Zn Ferrites

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Abstract: The frequency, temperature and composition dependence of ac resistivity ρ_{ac}, dielectric constant ε' and dielectric loss ε" of $Cu_{0.5}Zn_{0.5}Nd_xFe_{2-x}O_4$ ferrites (where x= 0.0, 0.02, 0.04, 0.06, 0.08 and 0.1) have been studied at low frequency range. For all samples, ρ_{ac}, ε' and ε" are found to decrease with increasing the frequency. The composition dependence of ρ_{ac}, ε' and ε" shows that, generally, ρ_{ac} increases while both ε' and ε" decrease with increasing x. The obtained results are satisfactorily explained using the non uniform model of Koops.

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1. Introduction

Ferrites are well known dielectric materials which are useful in microwave applications. It is known that the intrinsic properties of ferrites depend on their chemical composition, heat treatment and type of additive or substituted ions [1]. The dielectric properties depend on the doping level as well as the valence of substituted ions. The effect of substitution and addition of different ions on the magnetic and electrical properties of Cu-Zn ferrite have been studied by several authors [2, 3]. Moreover, the influence of Nd oxide substitution on the magnetic properties of Cu-Zn ferrite was studied by members of our lab [4]. As an extension of these studies, this paper aimed to study the effect of Nd^{3+} ion substitution with different concentrations on the dielectric properties of Cu-Zn ferrite. As we aware, such a work was not previously studied.

2. Experimental techniques

Ferrite samples with the chemical formula $Cu_{0.5}Zn_{0.5}Nd_xFe_{2-x}O_4$ (x= 0.0, 0.02, 0.04, 0.06, 0.08 and 0.1) were prepared by the usual standard ceramic method. X-ray diffraction identification, the density and porosity were performed. More details about the samples preparation and characterization are given elsewhere [4]. For measuring the electrical resistivity, the sample's surfaces were rubbed with silver paste as a contact material. Parallel capacitance (C_p) was measured using PM 6304 LCR meter. The real part of the dielectric constant (ε') was calculated using the formula [5] $\varepsilon' = \frac{C_p d}{\varepsilon_o A}$, where d is the thickness, A is the cross-sectional area of the sample and ε_o is the permittivity of free space (ε_o = 8.85x10^{-12} F/m). The ac resistivity (ρ_{ac}) was measured using the two probe method and hence the dielectric loss tangent (tanδ) and the imaginary part of the dielectric constant ε" were obtained from the relations $\rho_{ac} = \frac{1}{\varepsilon' \varepsilon_o \omega \tan\delta}$ and $\varepsilon'' = \varepsilon' \tan\delta$, where ω is the angular frequency = 2πf. The parameters ρ_{ac}, ε' and ε" were measured in the frequency range (100 Hz to 100 kHz) from room temperature up to 500 K.

3. Results and Discussion

X-ray diffraction patterns showed that all investigated samples have cubic spinel phase [4]. Although we replace Fe^{3+} ion (radius=0.64 Å) by the larger ion Nd^{3+} (radius=1.08 Å), the lattice parameter remained nearly constant. This was attributed to the change of the oxygen parameter by the Nd^{3+} substitution, such that the ionic radius of the octahedral B-site seems to increase at the expense of the tetrahedral A-site [4].

3.1 Frequency dependence of the dielectric properties

3.1.1. ac resistivity

The variation of the ac resistivity (ρ_{ac}) with frequency (f) is illustrated in Figure (1) for $Cu_{0.5}Zn_{0.5}Nd_xFe_{2-x}O_4$ samples. It is obvious that ρ_{ac} decreases with increasing f. Similar trend has been reported for different ferrites [5, 6]. This behavior could be explained in view of Koops's model [9]. According to this model, the polycrystalline ferrite is considered to be composed of two layers; grains and grain boundaries. The grains are large and of low resistive material, ρ_1. The grain boundaries are thin and of high resistive material, ρ_2. Following Koops's model, the total impedance ρ could be written as

$$\rho = \rho^{\infty} + \left[\frac{\rho^{o} - \rho^{\infty}}{1 + \omega^2 \tau^2}\right]$$

where the superscripts 0 and ∞ refer to low and high frequency values respectively and τ is a relaxation time.

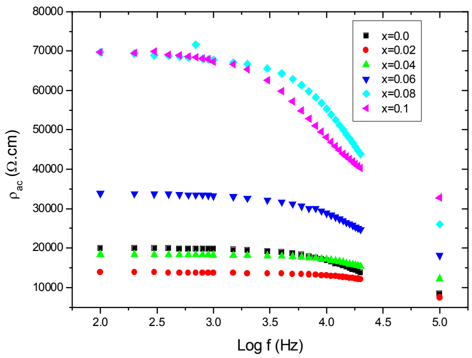

Fig. (1) Variation of the ac resistivity (ρ_{ac}) with frequency (f).

According to Koops's assumptions that $\rho_2 >> \rho_1$, h <<1 (where h is the ratio of the grain boundary thickness to the grain thickness) and $h\rho_2 > \rho_1$, one can write the total impedance as

$$\rho \cong \rho_1 + \frac{h\rho_2}{1+(b\rho_1\rho_2\omega^2/h)}$$

where b is a constant [8]. Thus, at very low frequency, the impedance ρ^0 is given by

$$\rho^o = \rho_1 + h\rho_2$$

According to the assumption that $h\rho_2 > \rho_1$, then the impedance at low frequency results mainly from the resistivity of the grain boundaries which have high resistivity. According to the above discussion, it is clear that Koops's model explains satisfactorily the frequency dependence of the resistivity of our investigated samples.

On the other hand, it was suggested that the conduction mechanism in ferrites is due to electron hopping between Fe^{2+} and Fe^{3+} [5]. The increase in frequency enhances the electron hopping frequency and hence increases the conductivity i.e. decreases the resistivity.

3.1.2 Real part of the dielectric constant

Figure (2) shows the frequency dependence of the real part of dielectric constant ε' for $Cu_{0.5}Zn_{0.5}Nd_xFe_{2-x}O_4$ samples. Increasing the frequency, it can be seen that ε' initially decreases by a small rate at low frequencies then it decreases by a rapid rate at high frequencies within our range. In fact, the decrease of ε' with increasing frequency was reported by several authors for different ferrites [9-11]. Moreover, the similarity between the frequency dependence of both the resistivity and the real part of the dielectric constant allows supposing that both parameters have the same origin [5, 12].This means that the dielectric properties are mainly governed by the conduction mechanism in ferrites [5], wherein the electron hopping takes place. The electron exchange between Fe^{3+} and Fe^{2+} gives local displacements of electron which induces polarization in ferrites. Therefore, at low frequency, where the electron hopping can match the frequency of the applied field, the dielectric constant has a maximum value. By increasing the frequency of the applied field, the electron exchange cannot follow the alternating field and so the dielectric constant decreases [13].

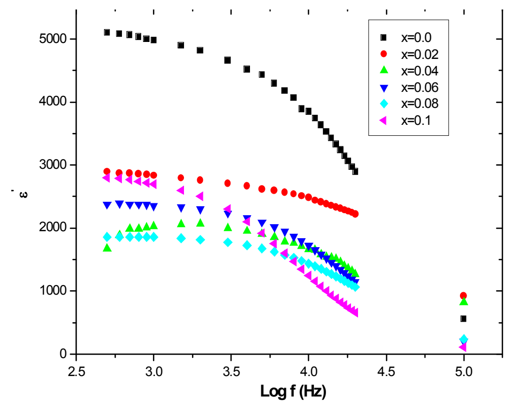

Fig. (2) Frequency dependence of the real part of the dielectric constant ε'.

3.1.3 Imaginary part of the dielectric constant

The variation of the imaginary part of the dielectric constant ε" (which represents the dielectric loss) with frequency f is shown in Figure (3). It can be seen that ε" decreases continuously with increasing the frequency. Such a decrease in ε" could be discussed as follows. The electric dipole loss which results from the dipole orientation (relaxation) decreases, especially at high frequencies, as the dipole orientation can not follow the applied field frequency.

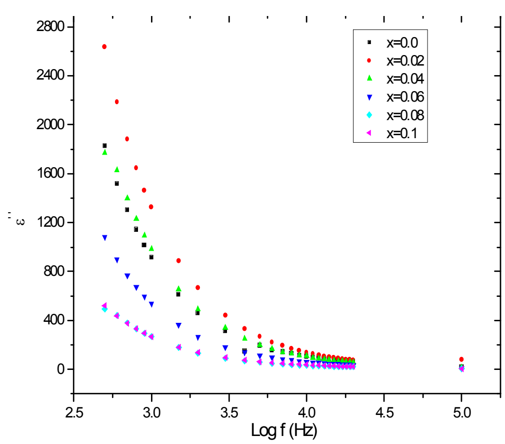

Fig. (3) Variation of the imaginary part of the dielectric constant ε" with frequency.

3.2 Composition dependence of the dielectric properties

Figure (4) represents the composition dependence of ρ_{ac} along with the porosity P%, ε' and ε'' (at a frequency=10 kHz) for $Cu_{0.5}Zn_{0.5}Nd_xFe_{2-x}O_4$ samples. This figure shows that ρ_{ac} generally increases with Nd concentration (x). The main factors that affect the resistivity in ferrites are the amount of Fe^{2+} ions and the porosity. It was found by many authors that the electrical resistivity is inversely proportional to the amount of Fe^{2+} ions as the decrease of Fe^{2+} ion concentration limits the hopping probability between Fe^{3+} and Fe^{2+} ions [14, 15]. Furthermore, the resistivity is directly proportional to the value of porosity because the increase of porosity hinders the motion of charge carriers [16]. For our samples, it can be seen that the increase of Nd content is on the expense of the iron concentration. So, as the Nd content increases, there is a continuous reduction of Fe^{2+} ion content, i.e. the decrease of the carrier concentration. This leads to increase the resistivity. Moreover, the increase of porosity causes the mobility of the carriers to decrease which enhances the resistivity.

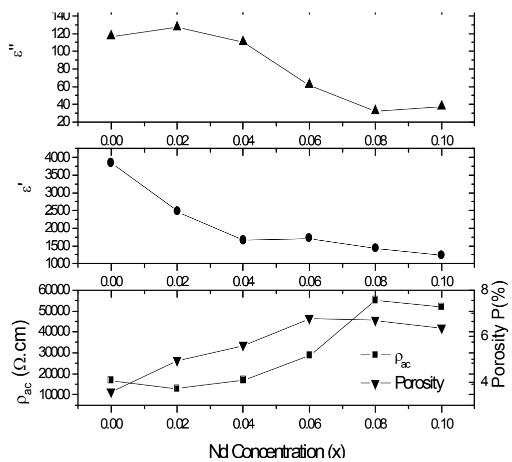

Fig. (4) Composition dependence of ρ_{ac}, ε' and ε'' (f=10 kHz).

On the other hand, ε' and ε'' have almost a reverse trend to ρ_{ac} which has been reported for Li-Mg [17], Li-Cd [18] and Li-Ti [19] ferrites. This reverse trend of ε' with ρ_{ac} for our investigated samples could be explained on the basis of the relation between the mobility μ of the electron hopping and resistivity $\rho = \frac{1}{ne\mu}$. Increasing the Nd content decreases the electron exchange between Fe^{2+} and Fe^{3+} ions, i.e. the mobility becomes small and then this leads the resistivity to increase. Meanwhile such a decrease in the electron hopping causes the polarization to decrease i.e. ε' decreases.

Furthermore, the reverse behavior of ε'' with ρ_{ac} is expected as the increase of resistivity decreases the loss ε'' and vice versa which is in a good agreement with the relation [5] $\rho_{ac} = \frac{1}{\varepsilon'' \varepsilon_o \omega}$

3.3 Temperature dependence of the dc resistivity

Figure (5) illustrates the variation of the dc resistivity ρ_{dc} with the temperature for all samples. It is obvious that the electrical resistivity decreases with increasing temperature, i.e. the resistivity exhibits a normal semiconducting behavior. This could be described by the well known relation [20].

$$\rho = \rho_o \exp\left(\frac{E_\rho}{KT}\right)$$

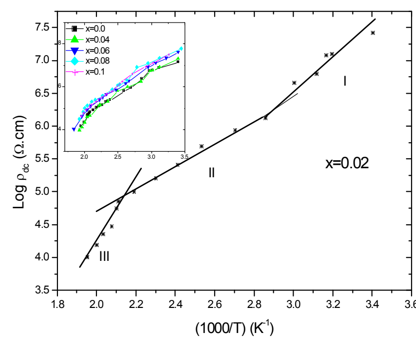

Fig. (5) Temperature dependence of the dc resistivity ρ_{dc} for the sample of x=0.02. (other samples are plotted inside the inset)

where ρ_o is a constant, E_ρ is the activation energy of the resistivity, K is Boltzmann's constant and T is the absolute temperature. Moreover, one can notice that each curve could be divided into three regions. Each region has different activation energy (E_ρ). The first region ranged from room temperature up to nearly 360 K. The conduction phenomenon in this region is attributed to the presence of impurities i.e. extrinsic conduction mechanism [21-23]. The formation of such impurities is due to the oxygen loss during the sintering process. The loss of oxygen leads to the formation of Fe^{2+} ions on the account of Fe^{3+} ions for charge compensation. These Fe^{2+} ions act as donor centers [24]. On the other hand, the transition temperatures, T_ρ, between the second and third regions have values that agree well to the determined values from the magnetic measurements T_c [4]. Therefore, the change in the activation energy at T_ρ could be attributed to a magnetic transition from the ferrimagnetic to the paramagnetic state. The effects of the magnetic transitions on the electrical properties of ferrites were reported by many authors [21-23].

3.4 Temperature dependence of the dielectric properties

3.4.1. ac resistivity

Figure (6) illustrates the variation of the ac resistivity ρ_{ac} with the temperature at different frequencies for the unsubstituted sample as an example. It is obvious that ρ_{ac} has similar behavior as ρ_{dc}. So, the temperature dependence of ρ_{ac} could be discussed on the same way as ρ_{dc}. In fact, our all investigated samples show the same trend. This can be noticed from the inset of Figure (6) that shows the temperature dependence of the ac resistivity for all investigated samples at f= 10 kHz. Moreover, generally, the dispersion of ac resistivity decreases with increasing the temperature for all samples. This behavior was detected for many other ferrites [25].

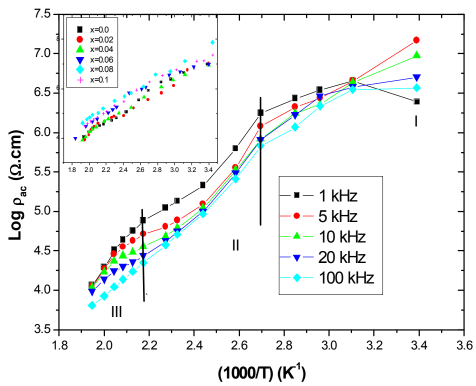

Fig. (6) Temperature dependence of the ac resistivity ρ_{ac} at different frequencies for the sample $Cu_{0.5}Zn_{0.5}Fe_2O_4$. (the inset shows the temperature dependence of the ac resistivity ρ_{ac}, at f= 10 kHz, for all samples.)

3.4.2. Real part of the dielectric constant

The temperature dependence of ε' is shown in Figure (7) for all samples (at f= 10 kHz). From the graph, it can be seen that ε' initially increases up to a certain transition temperature beyond which the value decreases. Such a temperature variation of ε' was reported earlier for many ferrites [26]. This behavior can be explained as follows: at relatively low temperature, the charge carriers on most cases can not orient themselves with respect to the direction of the applied field, therefore, they possess a week contribution to the polarization and ε'. As the temperature increases, the bound charge carriers get enough excitation thermal energy to be able to obey the change in the external field more easily. This in turn enhances their contribution to the polarization leading to an increase of ε' [25]. Moreover, the values of the transition temperature are in good agreement with those obtained for Curie temperatures from the dc resistivity measurements. This suggests that these changes are accompanied with the magnetic transition from the ferrimagnetic (ordered) state to the paramagnetic (disordered) state [27].

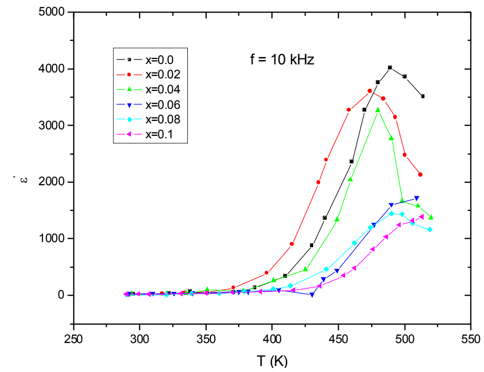

Fig. (7) Temperature dependence of ε' (at f= 10 kHz) for all samples.

3.4.3. Imaginary part of the dielectric constant

The variation of ε" with temperature for all samples (at f= 10 kHz) is illustrated in Figure (8). One can notice that ε" increases continuously with increasing temperature. This result is in a good agreement with the decreasing resistivity with temperature on the same way of the above discussion in section (3.2).

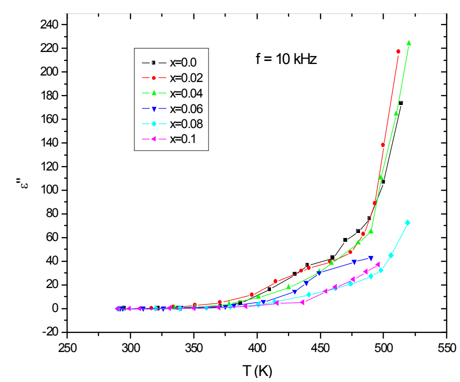

Fig. (8) Temperature dependence of ε" (at f= 10 kHz) for all samples.

Conclusion

1. ρ_{ac}, ε' and ε" decrease with increasing frequency for all samples.
2. ε' and ε" have almost a reverse trend of ρ_{ac} with increasing the Nd concentration.
3. The substitution with Nd ions generally improves the dielectric properties of Cu-Zn ferrite which are promising results for different applications.

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