

The Influence of Incorporation of Al^{3+} Ions on the AC Electrical and Dielectric Properties of Ni Spinel Ferrites

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Abstract

The mixed spinel ferrites $NiAl_xFe_{2-x}O_4$ with different concentrations of Al content *i.e.* $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 , were prepared by using the standard double sintering technique by mixing high purity metal oxides Al_2O_3 , NiO and Fe_2O_3 . Two probe electrode method was used at room temperature to determine the *ac* electrical conductivity (σ_{ac}), real dielectric constant (ϵ') and imaginary dielectric constant (ϵ''), and the dielectric loss tangent ($\tan \delta$) over a variable applied frequency in range of ($10KHz - 1MHz$). σ_{ac} shows a continuous increasing with the increasing of the applied frequency. The obtained results from the dielectric parameter for all the samples decreases with increasing of frequency, which indicated to normal spinel ferrite behavior. The variation of *ac* and dielectric parameters were explained on the basis of electronic exchange between the ferric ions (Fe^{3+}) and ferrous ions (Fe^{2+}) or trivalent nickel ions (Ni^{3+}) and divalent nickel ions (Ni^{2+}). The experimental results reveal that the *ac* electrical and dielectric properties, which can be influenced changed by substitution of the Al content in Ni spinel ferrites. These results of the mixed $Al-Ni$ spinel ferrite suggest uses as a soft ferrite material, which can be used for different an interesting technological and scientific applications.

Keywords

$Al-Ni$ Spinel Ferrite, Dielectric Properties, *ac* Electrical Conductivity

1. Introduction

The properties of spinel ferrites, that have the chemical formula $D_1^{2+}T_2^{3+}O_4^{2-}$ has a cubic structure packed of oxygen (O^{2-}) ions [1-6], have two sublattices tetrahedral (T_d) and octahedral (O_h). These sublattices are occupied by metal cations depending on their radii and the valancey to form the cation distribution for the given chemical formula of spinel ferrite. Cation distribution among T_d and O_h sublattices play an important role in controlling the electromagnetic and dielectric properties of spinel ferrite. Among of them, $Al-Ni$ spinel ferrite system exhibit excellent properties and can be used for a variety of applications. The investigation of the electromagnetic and dielectric properties of ferrite materials offers valuable information about the behavior of localized electric charge carriers and can interpret the mechanism of electrical conduction and dielectric polarization. The

remarkable electromagnetic and dielectric properties of ferrites enable them to have a wide range of technological applications, aiming at a better material with excellent chemical stability, low eddy current, high permeability, high electrical resistivity, microwave components, biomedical potential applications in magnetic resonance imaging. In spite of, poor detailed studied has been reported in the literature on *ac* electrical and dielectric properties of $Al-Ni$ spinel ferrite. Therefore, it was interesting in the present work to investigate the dielectric and *ac* conductivity properties of Ni ferrite when added Al content.

2. Experimental

2.1. Preparation of the Samples

The standard double sintering techniques was used to synthesize 25 grams of the mixed $NiAl_xFe_{2-x}O_4$ spinel ferrites, where x is the concentration of Al^{3+} ions which is

given by values of 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5. High pure metal oxides Al_2O_3 , NiO and Fe_2O_3 were weighted using a sensitive electric balance (ADAM model PW124) with an accuracy $1 \times 10^{-4} gm$. The weighted metal oxides were mixed and then grounded into a very fine powder for 5 hr's. The mixed powders of metal oxides was pre-sintered at $750^\circ C$ for 3 hr's soaking time using a laboratory Furnace (BIFATHERM model AC62). Then, the prefired powders was well ground for 3 hr's and pressed with a hydraulic press under constant pressure of $3 \times 10^8 pa$, by using a small quantity of butyl alcohol as a binding material. Finally, the powders were pressed to get samples have a disc shape with a radius of 0.55 cm and thickness of (0.4- 0.5) cm. Then, all samples were sintered at $1200^\circ C$ for soaking time of 5 hr's. After sintering process, the samples were cooled down gradually to room temperature. After that, the samples were polished to obtain uniform parallel surfaces to study the *ac* electrical and the dielectric properties.

2.2. Measurements

Two probe electrode method was used at room temperature to determine the *ac* electrical conductivity (σ_{ac}), real dielectric constant (ϵ'), the imaginary dielectric constant (ϵ'') and the dielectric loss tangent ($\tan \delta$) over a variable applied frequency in range of (10KHz – 1MHz) by using a signal generator model (GW INSTRON GFG – 8250A) and digital storage oscilloscope model (GFG – 8250A).

The σ_{ac} of the prepared samples was calculated by using following the relation [1]

$$\sigma_{ac} = l/AZ \quad (1)$$

where l , Z and A are the thickness, the impedance and the area of a flat surface of the disc samples, respectively.

The dielectric constants such as real dielectric constant (ϵ'), the imaginary dielectric constant (ϵ'') can be calculated as [7]

$$\epsilon' = \frac{C}{C_0} \quad (2)$$

where C and C_0 are the capacitance of the filled and the empty of the disc sample.

$$\epsilon'' = \frac{\sigma_{ac}}{2\pi f \epsilon_0} \quad (3)$$

where f is the applied frequency and ϵ_0 is the permittivity of free space.

Now, the dielectric loss tangent ($\tan \delta$) can be determined in terms of real and imaginary parts of dielectric constant as [1]

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (4)$$

3. Results and Discussion

3.1. AC Electrical Conductivity

The variation of the *ac* electrical conductivity (σ_{ac}) with

the applied frequency in the range of (10KHz – 1MHz) was studied at room temperature for the samples of $NiAl_xFe_{2-x}O_4$ spinel ferrite. As shown in Figure 1, σ_{ac} shows a continuous increasing with the increasing of the applied frequency. All samples exhibit a normal behavior of σ_{ac} with the variation of the applied frequency. This behavior was caused by the applied force driven by the frequency, which may be helped in transferring the charge carriers between the different conduction states. The behavior of the dispersion is associated with *Al* content in the prepared samples and is found to decrease as increasing of *Al* concentration (x). The same trend for spinel ferrites was confirmed from different researchers [8-10].

Furthermore, the total electrical conductivity (σ), can be expressed by [11]

$$\sigma = \sigma_{ph} + \sigma_{ac}(T, f) \quad (5)$$

where σ_{ph} is the contribution from the electron-phonon interaction, which is related to the drift of electric charge carriers and follows the Arrhenius relation as given by the following relation [1]:

$$\sigma_{ph} = \sigma_0 e^{-\Delta E/KT} \quad (6)$$

where σ_0 is the temperature-dependent conductivity, ΔE is the activation energy of the conduction mechanism, K is the Boltzmann constant and T is the temperature. As introduced in Eq. (6), the σ_{AC} is function the temperature and applied frequency, which is given by [11-13].

$$\sigma_{ac}(T, f) = A(T)f^{S(T)} \quad (7)$$

By taking the logarithms for two sides of an equation (7), it follows

$$\ln \sigma_{ac}(T, f) = \ln A(T) + S(T) \ln f \quad (8)$$

where $A(T)$ has electrical conductivity unit and $S(T)$ is the universal exponential factor taking the values of order ($0.0 < S(T) < 1.0$). The dependence on temperature of these parameters $A(T)$ and $S(T)$ is explained in terms of the conduction mechanism [13]. $S(T)$ was estimated for all samples at constant room temperature over the studied range of frequencies by fitting the σ_{AC} curves as shown in the inset of Figure 1. Also, $S(T)$ was calculated from the slope of the curves of $\ln \sigma_{ac}(T, f)$ versus $\ln f$ as shown in Figure 2. Herein, the estimated values of $S(T)$ were tabulated in Table 1. From this Table its noticed that the value of $S(T)$ is less than one. The obtained results are agreed well with the reported values of other workers [5, 13, 14], which are explained according to the hopping conduction model.

From the Eq. (7), it is clear that, σ_{ac} is directly proportional to the applied frequency, therefore, as shown in the Figure 1. As a results, σ_{ac} for the *Al-Ni* spinel ferrite increase as the applied frequency still increasing. This may be attributed to the electron hopping or the electron exchange, i.e. $Fe^{3+} + e^- \Leftrightarrow Fe^{2+}$ or $Ni^{2+} + h^+ \Leftrightarrow Ni^{3+}$ which occurs by the electron transform between the adjacent O_h sites in the spinel lattice [1].

However, the increasing of σ_{ac} for the ferrites is explained based on Verwey mechanism [1]. That is, the electron hopping may be occurred between the ions of the same element that present in more than one valence state and distributed randomly over crystallographically inequivalent lattice sites [10]. Depending upon the sintering conditions, the number of such ions may be produced during the preparation of the ferrite samples.

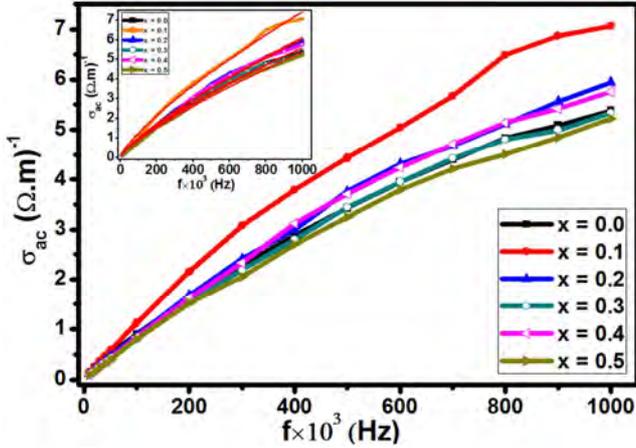


Figure 1. σ_{ac} against the applied frequency of all the samples, the inset is the fitted curves of σ_{ac} .

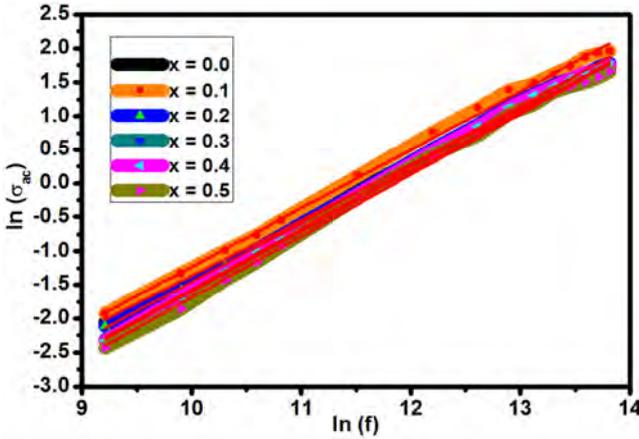


Figure 2. Fitted $\ln \sigma_{ac}$ against the logarithm of frequency $\ln f$ for all the samples.

Table 1. The values of $S(T)$ that estimated from Figures. 1 and 2.

x	$S(T)$	
	Figure 1	Figure 2
0.0	0.747	0.822
0.1	0.766	0.865
0.2	0.782	0.871
0.3	0.773	0.891
0.4	0.777	0.902
0.5	0.782	0.906

It is, well, known that, partial reduction of the electron hopping, $Fe^{3+} \rightleftharpoons Fe^{2+}$, can take place at an elevated firing temperature [1]. Thus; the hopping of electron, $Fe^{3+} \rightleftharpoons Fe^{2+}$, occurs only by electron transform between the adjacent O_h sites in the spinel lattice formed in the prepared spinel ferrite. This

causes the increasing in electrical conductance [10]. In general, the average percentage of the increasing of the conductivity for all samples of the given system is 98.0%. This indicates to the high concentration of the divalent iron (Fe^{2+}) ions existence in the spinel structure lattice. A further comparison, at the highest frequency for all samples, it was found that, the sample with $x = 0.1$ showed a rapidly increasing of σ_{AC} which was equal to $7.06 \Omega^{-1} \cdot m^{-1}$, while the lowest value of σ_{AC} was recorded to the sample of $x = 0.5$, which was equal to $5.22 \Omega^{-1} \cdot m^{-1}$, this may be due to a maximum and lower concentration of the Fe^{2+} ions among all the mixed $Al-Ni$ spinel ferrite, respectively. A similar behavior was observed in various ferrite systems by several investigators [5, 10].

Based on the Figure 1, it is clear that, the highest value of the σ_{ac} is obtained for the sample with $x = 0.1$ at different frequencies values as shown in Figure 3. When Al content is introduced the σ_{ac} , firstly increased and then decreased with an increasing of the Al content. This indicates that, the σ_{ac} depends, strongly, on the increasing of the Al^{3+} ions in the samples.

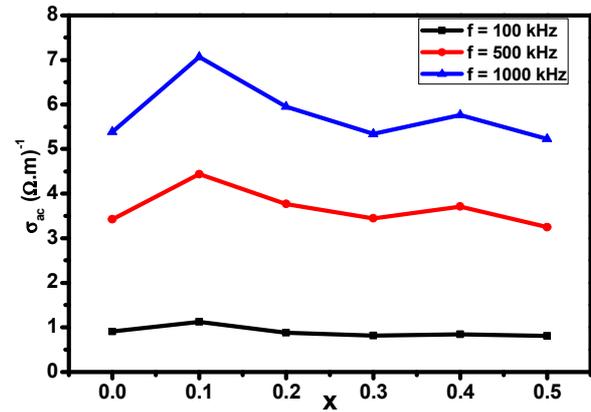


Figure 3. Variation of σ_{ac} with the concentration of Al content.

The relaxation time (τ_σ) of σ_{ac} can be described in terms of [1]

$$\sigma_{ac} = \sigma_{h\omega} + \frac{\sigma_{l\omega} - \sigma_{h\omega}}{1 + (\omega\tau_\sigma)^2} \quad (9)$$

where $\sigma_{l\omega}$ and $\sigma_{h\omega}$ are ac electrical conductivity at low and high applied frequency, respectively. The τ_σ is a characteristic time constant of ferrimagnetic materials and the applied frequency. The τ_σ was calculated at different values of σ_{ac} for all samples. It was found that, the average value of τ_σ is given, nearly, by $\tau_\sigma = 4.13 \times 10^{-7} s$. This agreed well with the obtained results for the mixed $Cu - Zn$ ferrite [10].

3.2. Dielectric Properties

Dielectric parameters such as real dielectric constant (ϵ'), the imaginary dielectric constant (ϵ'') and the dielectric loss tangent ($\tan \delta$) for mixed $Ni-Al$ ferrites were studied in the frequency range of (10KHz – 1MHz) at room temperature as in

the Figures 4 and 5. It can be noted from these Figures That, ϵ' and ϵ'' for all the samples decreases with increasing of the applied frequency. This decrease in dielectric parameters is more rapid in the low frequency region, but ultimately this decrease becomes shiftless at higher applied frequencies. This behavior is subjected to dielectric polarization under the application of *ac* field. The decrease of dielectric constants with an increase of frequency as observed in the case of mixed *Al-Ni* ferrites is a normal dielectric behavior of spinel ferrites. Several investigators [5, 14-19] reported the normal dielectric behavior of the spinel ferrite.

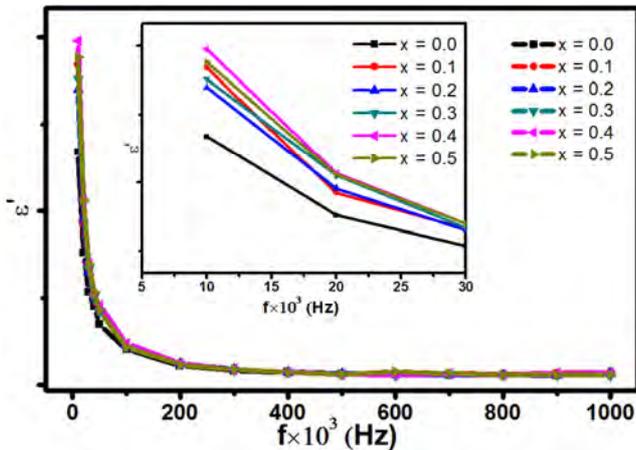


Figure 4. A Plot of ϵ' against the applied frequency for all the samples were recorded at room temperature.

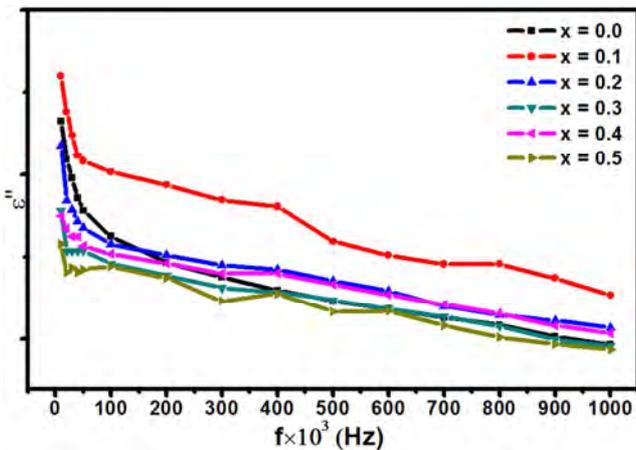


Figure 5. A Plot of ϵ'' against the applied frequency for all the samples were recorded at room temperature.

Such kind of dielectric dispersion in ferrites is analogous to Maxwell-Wagner model and Koops phenomenological theory, which suggests that ferrite system consist of a combination of highly conducting grains separated by poorly conducting grain boundaries [11]. The dispersion of the dielectric constant is maximized at $x = 0.1$. This maximum dielectric dispersion may be explained based on available Fe^{2+} ions on O_h sites. In the case of $x = 0.1$, the concentration of Fe^{2+} ions is expected to be higher than in other compositions of mixed *Ni-Al* ferrites. Consequently, it is possible for these ions to be polarized to the maximum possible extent. Further, as the frequency of the externally

applied field increases gradually, though the number of Fe^{2+} ions is present in the ferrite material, the real dielectric constant ϵ' decreases from 259.92 at 10 kHz to 126.84 at 1 MHz. The reduction occurs because beyond a certain frequency of the externally applied electric field, the electronic exchange between Fe^{2+} and Fe^{3+} ions, cannot follow the alternating field. The variation of the dispersion of dielectric parameters with composition for other mixed *Ni-Al* ferrites explained by the fact that the electron exchange between Fe^{2+} and Fe^{3+} ions in an *n*-type semiconducting ferrite and hole exchange between Ni^{3+} and Ni^{2+} in a *p*-type semiconducting ferrite cannot follow the frequency of the applied *ac* field beyond a critical value of the frequency.

As dielectric polarization in ferrites magnitude depends upon the percentage of Fe^{2+} and Fe^{3+} ion pairs at T_d and O_h sites. Fe^{2+} ions concentration largely affects the conduction phenomenon and depends upon type of cation substituting, synthesis route, sintering time and sintering temperatures. In the present case relative ϵ' and ϵ'' both decreases. Which can be explained by low Fe^{2+} ion concentration at O_h site causing a low value of resistivity and hence a high value of dielectric parameter. As σ_{ac} and relative ϵ' and ϵ'' has similar behavior mechanism [5].

The dielectric loss factor ($\tan \delta$) arises when the polarization lags behind the applied alternation electric filed. The variation of $\tan \delta$ with frequency for the investigated samples at different Al content are shown in Figure 6. In this Figure $\tan \delta$ decreased sharply at frequency of range of 10 kHz to 50 kHz, whereas it decreased slowly in frequency of range of 50 kHz -200 kHz, after that, unchanged up to 1 MHz for all samples. The obtained results confirm the semiconductor behavior of given ferrite samples. It is known that, there is a strong correlation between the conduction mechanism and dielectric polarization in ferrites, which is attributed to the hooping mechanism.

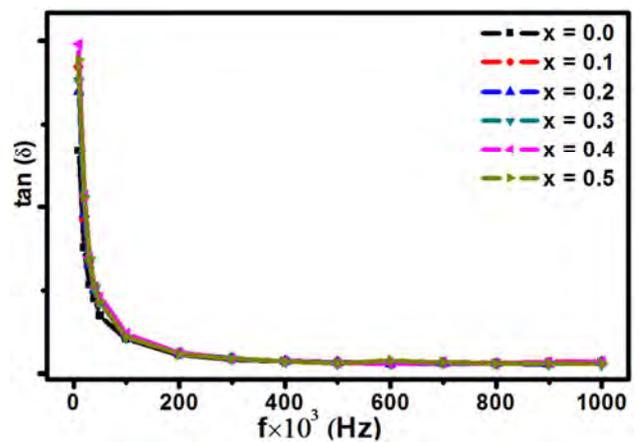


Figure 6. A Plot of $\tan \delta$ against the applied frequency for all the samples at room temperature.

4. Conclusion

Substitution of the non-magnetic Al^{3+} ions in *Ni* spinel ferrites were successfully prepared by double sintering

technique. *ac* electrical conductivity showed increasing with increasing of the applied frequency. The dielectric constant (real and imaginary) and dielectric loss tangent were found to decrease for all samples with increasing of the applied frequency. Furthermore, Al content has significant influence on *ac* conductivity and the electromagnetic properties, such as dielectric constant, dielectric loss tangent of *Ni-Al* ferrites, so, the mixed *Ni-Al* spinel ferrite is considered a soft ferrite material, which is proved an interesting material for technological and scientific applications.

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