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Dielectric properties of polycrystalline mixed nickel–zinc ferrites

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Abstract

Dielectric properties such as dielectric constant (ε'), dielectric loss tangent ($\tan\delta$) and complex dielectric constant (ε'') has been investigated in the frequency range 100 kHz–1 MHz. The variation of these parameters with composition, frequency and temperature is explained qualitatively. The dielectric constant for these ferrites is approximately inversely proportional to the square root of the resistivity. An attempt is made to explain the possible mechanism. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The polycrystalline ferrites, which have many applications at microwave frequencies are very good dielectric materials. The dielectric properties of ferrites are dependent on several factors including the method of preparation, sintering temperature, sintering time and chemical composition. Ferrites have a very low conductivity, which is also one of the considerations for microwave application. With a view to the understanding of dielectric phenomena in mixed nickel–zinc ferrites, a systematic study of dielectric properties as a function of composition, frequency and temperature was undertaken; the results of the study are presented in this paper.

2. Experimental details

The ferrite samples used in the present investigation having the compositional formula $Ni_xZn_{1-x}Fe_2O_4$, where x ranges from 0.2 to 1.0 and were synthesized by using a standard double sintering ceramic technique. The final sintering was done at 1200°C for 6 h, with subsequent slow cooling to room temperature. The details of method of the preparation have been given in an earlier publication [1]. The dielectric properties of mixed Ni–Zn ferrites were measured in the frequency range 100 kHz to 1 MHz using the instrumental setup with a HP 4440B standard capacitor, range 40 pF–1.2 μF.

The values of dielectric constant (ε') and complex dielectric constant (ε'') are calculated using the formulae,

$$\varepsilon'' = \frac{1}{\varepsilon_o}\left[\frac{V_o(90°) \times C_o}{V_{in} - V_o(90°)}\right] \quad (1)$$

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and

$$\varepsilon' = \frac{1}{\varepsilon_o}\left[\frac{V_o(0°) \times C_o}{V_{in} - V_o(0°)}\right], \quad (2)$$

where ε_o is the permittivity of free space, 8.854×10^{-14} F cm^{-1}. The dielectric loss can be obtained from the relation,

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (3)$$

3. Results and discussion

3.1. Dependence of dielectric properties on composition

The room temperature values of dielectric constant (ε'), the dielectric loss tangent $(\tan\delta)$ and the complex dielectric constant (ε') for mixed Ni–Zn ferrites at 100 kHz are given in Table 1. The values of electrical conductivity (σ) are measured at room temperature by two probe method and Fe^{2+} concentration has been estimated by titration method are also included in the table to facilitate the discussion. An examination of Table 1 reveals that the values of ε', $\tan\delta$ and ε'' are found to decrease with increasing of zinc content is equal to 0.4 mole. Beyond $x = 0.4$ these parameters show a progressive increase with increase of zinc. Thus, it can be seen that among mixed Ni–Zn ferrites, the one with the composition $Ni_{0.6}Zn_{0.4}Fe_2O_4$ exhibits the lowest dielectric constant, the lowest dielectric loss tangent, the lowest complex dielectric constant, the lowest divalent iron concentration and the lowest electrical conductivity. Rezlescu and Rezlescu [2] have studied the composition, frequency and temperature dependence of copper containing mixed ferrites such as $Cu_xMn_{1-x}Fe_2O_4$ and $Cu_xZn_{1-x}Fe_2O_4$. El Titi et al. [3] have investigated the composition, frequency and temperature dependence of Cu–Cr ferrites. The dielectric properties of Cu–Cd ferrites were studied by Kolekar et al. [4]. Iwauchi [5] reported a strong correlation between the conduction mechanism and the dielectric behaviour of the ferrites starting with the supposition that the mechanism of the polarization process in ferrites is similar to that the conduction process [6]. They observed that the electronic exchange between $Fe^{2+} \leftrightarrows Fe^{3+}$ results in local displacements determining the polarization of the ferrites. They observed that the electron exchange between the $Fe^{2+} \leftrightarrows Fe^{3+}$ results in local displacements determining the polarization of the ferrites. A similar model is proposed for the composition dependence of the dielectric constants of mixed Ni–Zn ferrites. In this model the electron exchange between Fe^{2+} and Fe^{3+} in an n-type and the hole exchange between Ni^{3+} and Ni^{2+} in P-type ferrites results in local displacements of electrons or holes in the direction of the electric field which then cause polarization [2,6]. It can also be seen from the table that the composition $Ni_{0.2}Zn_{0.8}Fe_2O_4$ has the maximum divalent iron concentration among all the ferrites under investigation. Correspondingly the dielectric constant

Table 1
Composition dependence of dielectric data for mixed Ni–Zn ferrites at room temperature

Sample	Ferrite composition	100 kHz			Fe^{2+} concentration (%)	σ (Ω^{-1} cm^{-1})	ρ (Ω cm)	$\sqrt{\rho}$ ($\Omega^{1/2}$ cm$^{1/2}$)	$\varepsilon'\sqrt{\rho}$ ($\Omega^{1/2}$ cm$^{1/2}$)	T_c (K)	T_d (K)
		ε'	$\tan\delta$	ε''							
Group I											
I	$NiFe_2O_4$	31.79	0.47	14.94	0.664	2.06×10^{-4}	4.85×10^3	69.67	2.22×10^3	868	870
V	$Ni_{0.4}Zn_{0.6}Fe_2O_4$	45.73	0.51	23.32	0.812	2.92×10^{-4}	3.43×10^3	58.52	2.68×10^3	617	620
VI	$Ni_{0.2}Zn_{0.8}Fe_2O_4$	53.59	0.71	38.05	0.938	3.12×10^{-4}	3.21×10^3	56.61	3.03×20^3	605	600
Group II											
II	$Ni_{0.8}Zn_{0.2}Fe_2O_4$	28.23	0.46	12.99	0.426	4.90×10^{-5}	2.04×10^4	142.86	4.03×10^3	785	787
III	$Ni_{0.6}Zn_{0.4}Fe_2O_4$	22.28	0.45	10.03	0.362	2.12×10^{-5}	4.72×10^4	217.19	4.84×10^3	768	765
VI	$Ni_{0.5}Zn_{0.5}Fe_2O_4$	44.22	0.49	21.67	0.764	2.64×10^{-4}	3.79×10^3	61.55	2.72×10^3	648	652

for this composition has a value of 53.59. This high value can be explained on the basis of the fact that it has maximum number of ferrous ions whose exchange $Fe^{2+} \leftrightarrows Fe^{3+}$ gives rise to maximum dielectric polarization. Table 1 reveals that the variation of dielectric constant runs parallel to the variation of available ferrous ions on octahedral sites. It is also pertinent to mention that the variation of electrical conductivity runs parallel to the variation of ferrous ion concentration. Thus, it is the number of ferrous ions on octahedral sites that play a dominant role in the processes of conduction as well as dielectric polarization.

3.2. Variation of dielectric constant (ε') with frequency

The variation of the dielectric constant as a function of frequency for all the ferrite samples at room temperature is shown in Fig. 1. It can be seen from the figure that the dielectric constant decreases with increasing frequency. The decrease of dielectric constant with increase of frequency as observed in the case of mixed nickel–zinc ferrites is a normal dielectric behaviour of spinel ferrites. The normal dielectric behaviour was also observed by several investigators in the case of Li–Ti [7], Ni–Cu–Cn [8], Mg–Ti–Zn [9] and Co–Zn [10] ferrites.

It can be seen from the figure that the dispersion in ε' is analogous to Maxwell–Wagner interfacial polarization [11,12], in agreement with Koops phenomenological theory [13]. The dispersion of the dielectric constant is maximum for the sample with $x = 0.8$. This maximum dielectric dispersion may be explained on the basis of available ferrous ions on octahedral sites. In the case of $x = 0.8$ the concentration of ferrous ions is higher than in other compositions of mixed Ni–Zn ferrites. As a consequence, 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 ferrous ions is present in the ferrite material, the dielectric constant deceases from 53.59 at 100 kHz to 31.21 at 1 MHz. The reduction occurs because beyond a certain frequency of the externally applied electric field, the electronic ex-

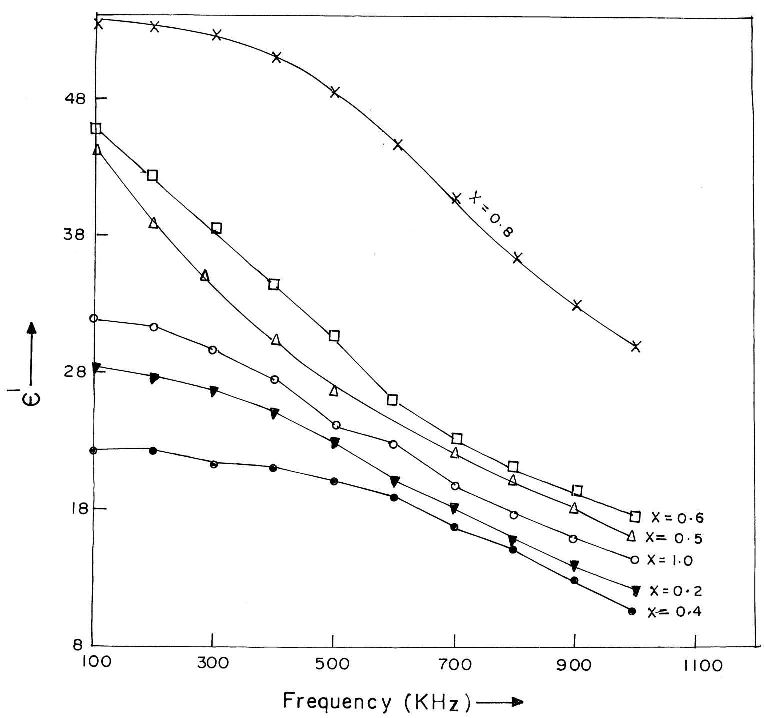

Fig. 1. Plot of dielectric constant (ε') vs. frequency for $Ni_xZn_{1-x}Fe_2O_4$ ($x = 0.2, 0.4, 0.5, 0.6, 0.8$ and 1.0).

change between ferrous and ferric ions, i.e., $Fe^{2+} \leftrightarrows Fe^{3+}$, can not follow the alternating field. The variation of the dispersion of ε' with composition for other mixed nickel–zinc ferrites explained by the fact that the electron exchange between Fe^{2+} and Fe^{3+} in an n-type semiconducting ferrite and hole exchange between Ni^{3+} and Ni^{2+} in a p-type semiconducting ferrite can not follow the frequency of the applied alternating field beyond a critical value of the frequency.

3.3. Variation of the dielectric loss tangent (tan δ) with frequency

Figs. 2 and 3 show the variation of $\tan\delta$ with frequency for all mixed nickel–zinc ferrites under investigation. It can be seen from the figures that in the case of $NiFe_2O_4$, $Ni_{0.8}Zn_{0.2}Fe_2O_4$, $Ni_{0.6}Zn_{0.4}Fe_2O_4$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ $\tan\delta$ shows a maximum at frequency of 900 kHz, in the case of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ $\tan\delta$ shows a maximum at a frequency of 800 kHz, and in the case of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ $\tan\delta$ shows maximum at 600 kHz. A qualitative explanation can be given for the occurrence of the maximum in the $\tan\delta$ vs. frequency curves in the case of mixed Ni–Zn ferrites. As printed out by Iwauchi [5], there is a strong correlation between the conduction mechanism and the dielectric behaviour of ferrites. The conduction mechanism in n-type ferrites is considered as due to hopping of electrons between Fe^{2+} and Fe^{3+} and the hopping of holes between Ni^{3+} and Ni^{2+} in p-type ferrites. As such, when the hopping frequency is nearly equal to that of the externally applied electric field, a maximum of loss may be observed. As such it is possible that in the case of $NiFe_2O_4$, $Ni_{0.8}Zn_{0.2}Fe_2O_4$, $Ni_{0.6}Zn_{0.4}Fe_2O_4$, $Ni_{0.5}Zn_{0.5}Fe_2O_4$, $Ni_{0.2}Zn_{0.8}Fe_2O_4$ and $Ni_{0.4}Zn_{0.6}Fe_2O_4$ the hopping frequencies are of the appropriate magnitude to observe a loss maximum at 900 kHz, 800 kHz and 600 kHz, respectively.

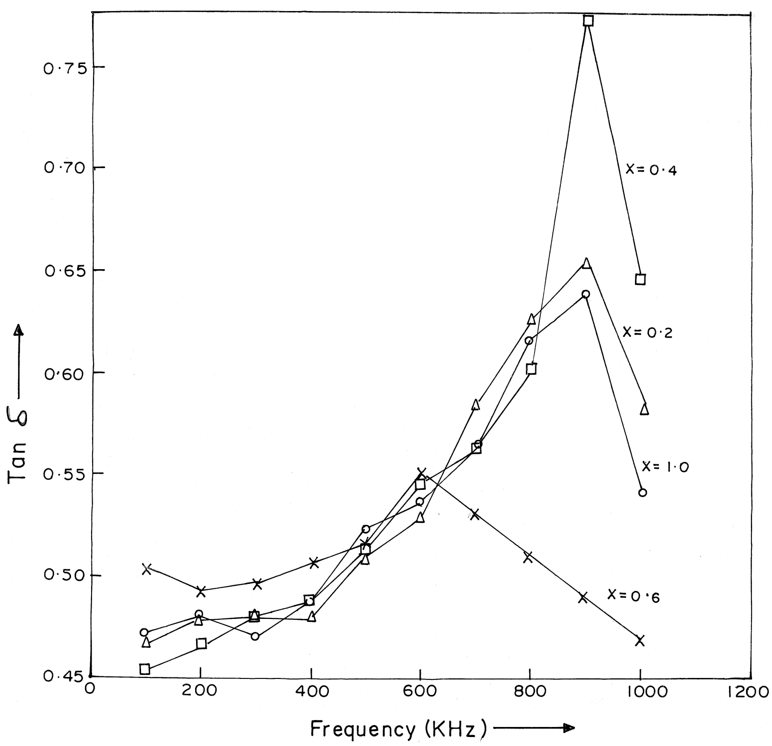

Fig. 2. Plot of dielectric loss tangent constant ($\tan\delta$) vs. frequency for $Ni_xZn_{1-x}Fe_2O_4$ ($x = 0.2, 0.4, 0.5, 0.6$ and 1.0).

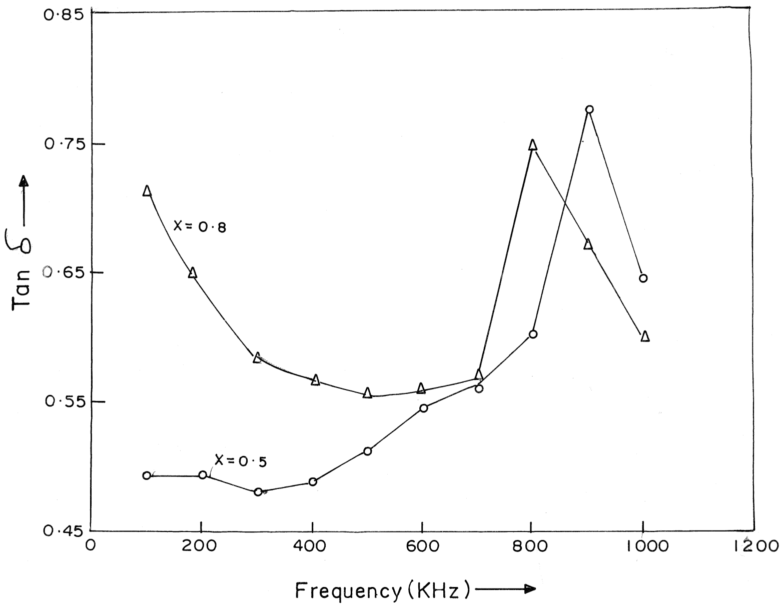

Fig. 3. Plot of dielectric constant (ε') vs. frequency for (△) $Ni_{0.2}Zn_{0.8}Fe_2O_4$ and (○) $Ni_{0.5}Zn_{0.5}Fe_2O_4$.

The condition for observing a maximum in the dielectric losses of a dielectric material is given by

$$\omega\tau = 1 \tag{4}$$

where $\omega = 2\pi f_{max}$ and τ is the relaxation time. Now the relaxation time τ is related to the jumping probability per unit time, p, by an equation $\tau = 1/2p$ or

$$f_{max} \propto p \tag{5}$$

Eq. (5) shows that f_{max} is proportional to the jumping or hopping probability. Now a decrease of f_{max}

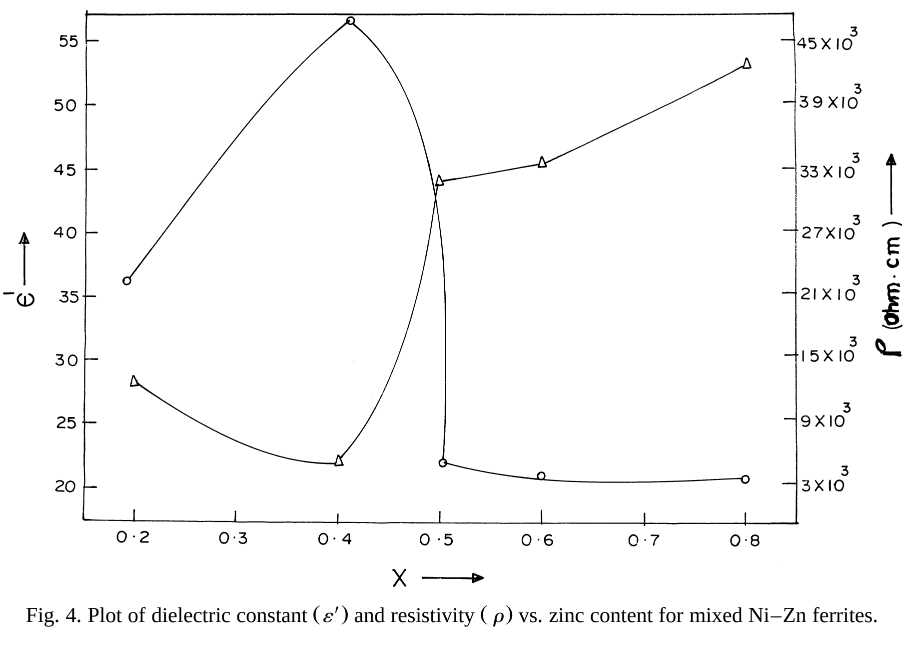

Fig. 4. Plot of dielectric constant (ε') and resistivity (ρ) vs. zinc content for mixed Ni–Zn ferrites.

with increasing zinc content indicates that the hopping or jumping probability per unit time is decrease continuously.

3.4. Relation between the dielectric constant (ε') and the resistivity (ρ)

The values of resistivity (ρ), $\sqrt{\rho}$ and $\varepsilon\sqrt{\rho}$ are also included in Table 1. It can be seen from the table that the ε' is roughly inversely proportional to the square root of resistivity. As such the product $\varepsilon'\sqrt{\rho}$ remains nearly constant as shown in the Table 1. A similar relationship between ε' and $\rho^{1/2}$ was found [14] for data obtained by Koops [13] for $Ni_{0.4}$-$Zn_{0.6}Fe_2O_4$ samples fired in various atmospheres and Ravinder [15] in the case of mixed Li–Cd ferrites. Hudson [16] has shown that the dielectric losses in ferrites are generally reflected in the resistivity measurements, materials with low resistivity exhibiting high dielectric losses and vice versa. Table 1 shows that this result holds good in the case of mixed nickel–zinc ferrites, too.

Fig. 4 shows that the plot of dielectric constant (ε') vs. the zinc content (x) is an inverse image of that of resistivity vs. zinc content. This is a confirmation of the correlation between dielectric constant and resistivity [6].

3.5. Variation of dielectric constant (ε') with temperature

Fig. 5 shows the variation of dielectric constant at 1 MHz with increment of temperature for all the mixed Ni–Zn ferrites. The dielectric constant increases gradually with increasing temperature up to the particular temperature, which is designated as the dielectric transition temperature T_d. However, beyond this temperature the values of dielectric constant for all the samples were found to decrease continuously. A similar temperature variation of the dielectric constant has been reported earlier [16–18]. The value of T_d for each composition are given in Table 1. The Curie temperature T_c values determined by the gravity method are also included in the table for the purpose of comparison. It can be seen

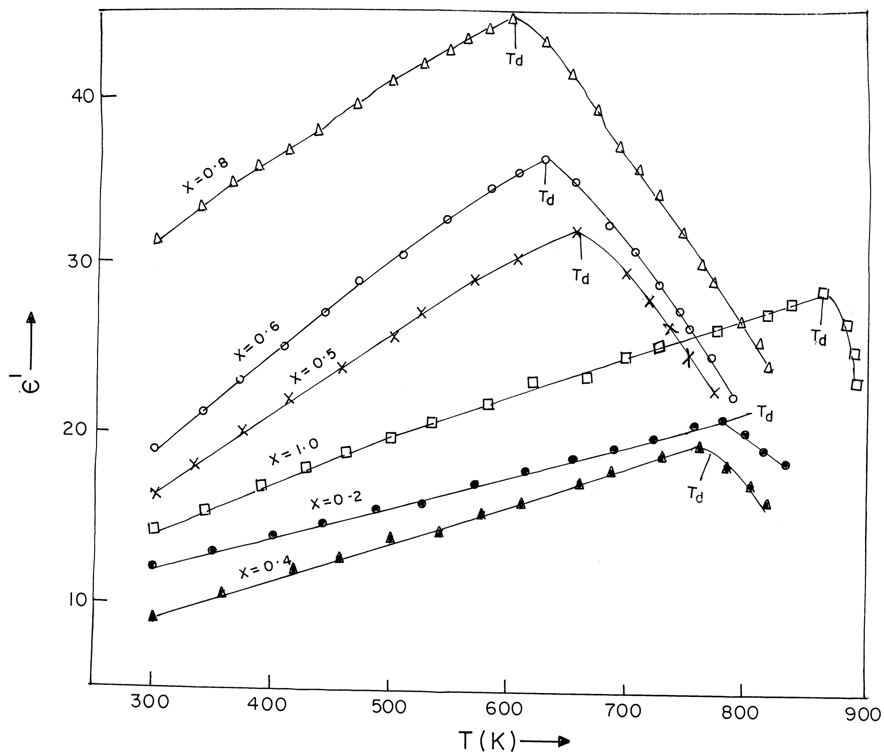

Fig. 5. Variation of dielectric constant with temperature at 1 MHz for mixed Ni–Zn ferrites.

from the table that the values of T_d and T_c are in good agreement, thereby indicating that the change in the behaviour of the dielectric constant with temperature may be due to a magnetic transition, where the material becomes a paramagnetic.

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