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High-frequency dielectric behaviour of polycrystalline zinc substituted cobalt ferrites

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The dielectric constant (ε') and complex dielectric constant (ε'') of zinc substituted cobalt ferrites have been measured at room temperature in the high frequency range 100 kHz to 1 MHz. The values of dielectric loss tangent (tan δ) have been computed from ε' and ε''. Plots of dielectric constant (ε') versus frequency show a normal dielectric behaviour of the spinel ferrites. The frequency dependence of dielectric loss tangent (tan δ) is found to be abnormal, giving a peak at certain frequency for all the ferrites under investigation. A qualitative explanation is given for the composition and frequency dependence of the dielectric constant and dielectric loss tangent. The dielectric constant for these mixed ferrites is approximately inversely proportional to the square root of the resistivity. A plot of dielectric constant versus temperature shows a transition near the Curie temperature. An attempt is made to explain the possible mechanism for this observation.

1. Introduction

The polycrystalline ferrites are very good dielectric materials. This is possible because, in the process of preparation of ferrites in polycrystalline form, when the ferrite powder is sintered under slightly reducing conditions, the divalent iron ions formed in the body lead to high-conductivity grains. When such a material is cooled in an oxygen atmosphere, it is possible to form layers of very low conductivity over the constituent grains such that they become separated by low conductivity layers and behave as inhomogeneous dielectric materials. Therefore, the ferrites possess dielectric constants as high as 10^5 and are useful in designing good microwave devices such as isolators, circulators, etc.

The abnormal dielectric behaviour of the spinel $NiAl_xFe_{2-x}O_4$ (where $x = 0.0$, 0.2, 0.4, 0.6. 0.8 and 1.0) as a function of frequency, composition and temperature was reported by Ahmed *et al.* [1]. The dielectric behaviour of the zinc substituted Ni-Mg ferrites as a function of temperature and frequency was reported by Elhiti [2]. The dependence of dielectric properties of Li-Ti ferrites as a function of frequency, composition and temperature has been studied by Mazen *et al.* [3]. The dielectric properties of Ni-Zn ferrites as a function of sintering temperature, sintering time and frequency have been investigated by Rao and Rao [4]. A strong correlation between conduction mechanism and the dielectric behaviour of ferrites has been reported by Iwauchi [5]. The dielectric properties of Cu-Cd ferrites were investigated by Kolekar *et al.* [6]. The dielectric constant of Ni-Zn ferrites were studied by Koops [21] as a function of temperature, sintering time, sintering atmosphere and cooling time. With a view to the understanding of dielectric phenomena in mixed Co-Zn ferrites, a systematic study of dielectric properties as a function of frequency, composition and temperature was undertaken, the results of the study are presented in this paper.

2. Experimental details

2.1. Sample preparation

The mixed Co-Zn ferrites having the chemical formula $Co_xZn_{1-x}Fe_2O_4$ (where $x = 0.2$, 0.4, 0.5, 0.6, 0.8 and 1.0) were synthesized by using a standard double sintering ceramic technique using cobalt oxide, zinc oxide and ferric oxide (purity 99%). The samples were presintered for 6 h in air at 900 °C. Final sintering of the specimens was carried for 6 h at 1200 °C, the sintering atmosphere being air. After the sintering process the furnace is cooled at the rate of 50 °C/h down to 800 °C and thereafter at a rate of 100 °C/h till the room temperature is reached.

2.2. Measurements

X-ray diffractometer studies of the Co-Zn ferrites using CuK_α radiation confirmed the spinel formation. The bulk density of the specimens has been determined accurately by the hydrostatic method [7]. The dielectric properties of the Co-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 formula

$$\varepsilon'' = \frac{1}{\varepsilon_0}\left[\frac{V_0(90^\circ) \times C_0}{V_{\text{in}} - V_0(90^\circ)}\right] \quad (1)$$

and

$$\varepsilon' = \frac{1}{\varepsilon_0}\left[\frac{V_0(0^\circ) \times C_0}{V_{\text{in}} - V_0(0^\circ)}\right] \quad (2)$$

where ε_0 is the permittivity of free space, 8.854×10^{-14} $\text{F} \cdot \text{cm}^{-1}$. The dielectric loss tangent ($\tan\delta$) can be obtained from the relation

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

3. Results and discussion

3.1. Lattice parameter vs. composition

X-ray diffraction patterns for all the Co-Zn ferrites have been obtained using CuK_α radiation. The lattice parameter as a function of zinc content is presented in Fig. 1. It may be observed from the figure that the lattice parameter varies almost linearly with the zinc content. A similar linear dependence has also been observed Song and Koh [8] and Ravinder [9] in the case of mixed cobalt substituted lithium ferrites and Li-Cd ferrites.

3.2. Bulk density

A plot of bulk density versus zinc content is shown in Fig. 2. It can be seen from the figure that the bulk density increases with increase of zinc content. This confirms the observation that the addition of zinc to cobalt ferrites results in the densification of the material [10]. A similar variation was also observed by Ravinder and Raju [11] in the case of Li-Zn ferrites.

3.3. Dependence of dielectric properties on composition

The compositional formula of the mixed Co-Zn ferrites together with the corresponding cation distribution formulae are given in Table I. The room temperature values of dielectric constant (ε'), the dielectric loss tangent ($\tan\delta$) and complex dielectric constant (ε'') for mixed Co-Zn ferrites at 100 kHz are given in Table II. The values of electrical conductivity (σ) were measured at room temperature by the two probe method are also included in the table to facilitate the discussion. Table II demonstrates that the value of ε', ε'' and $\tan\delta$ decrease continuously with increasing zinc content.

Rezlescu and Rezlescu [12] have studied the composition, frequency and temperature dependence of copper-containing mixed ferrites such as $Cu_xMn_{1-x}Fe_2O_4$ and $Cu_xZn_{1-x}Fe_2O_4$. Murthy and Sobhanadri [13] investigated the dielectric properties of some

TABLE I Cation distribution in mixed Co-Zn ferrites

Sample No.	Molecular formula	Cation distribution formula
1	$CoFe_2O_4$	$\left(Fe^{3+}_{0.81}\ Co^{2+}_{0.19}\right)\left[Co^{2+}_{0.81}\ Fe^{3+}_{0.19}\right]O^{2-}_4$
2	$Co_{0.8}Zn_{0.2}Fe_2O_4$	$\left(Zn^{2+}_{0.2}\ Fe^{3+}_{0.7}\ Co^{2+}_{0.1}\right)\left[Co^{2+}_{0.7}\ Fe^{3+}_{1.3}\right]O^{2-}_4$
3	$Co_{0.6}Zn_{0.4}Fe_2O_4$	$\left(Zn^{2+}_{0.4}\ Fe^{3+}_{0.6}\right)\left[Co^{2+}_{0.6}\ Fe^{3+}_{1.4}\right]O^{2-}_4$
4	$Co_{0.5}Zn_{0.5}Fe_2O_4$	$\left(Zn^{2+}_{0.5}\ Fe^{3+}_{0.5}\right)\left[Co^{2+}_{0.5}\ Fe^{3+}_{1.5}\right]O^{2-}_4$
5	$Co_{0.4}Zn_{0.6}Fe_2O_4$	$\left(Zn^{2+}_{0.6}\ Fe^{3+}_{0.4}\right)\left[Co^{2+}_{0.4}\ Fe^{3+}_{1.6}\right]O^{2-}_4$
6	$Co_{0.2}Zn_{0.8}Fe_2O_4$	$\left(Zn^{2+}_{0.8}\ Fe^{3+}_{0.2}\right)\left[Co^{2+}_{0.2}\ Fe^{3+}_{1.8}\right]O^{2-}_4$

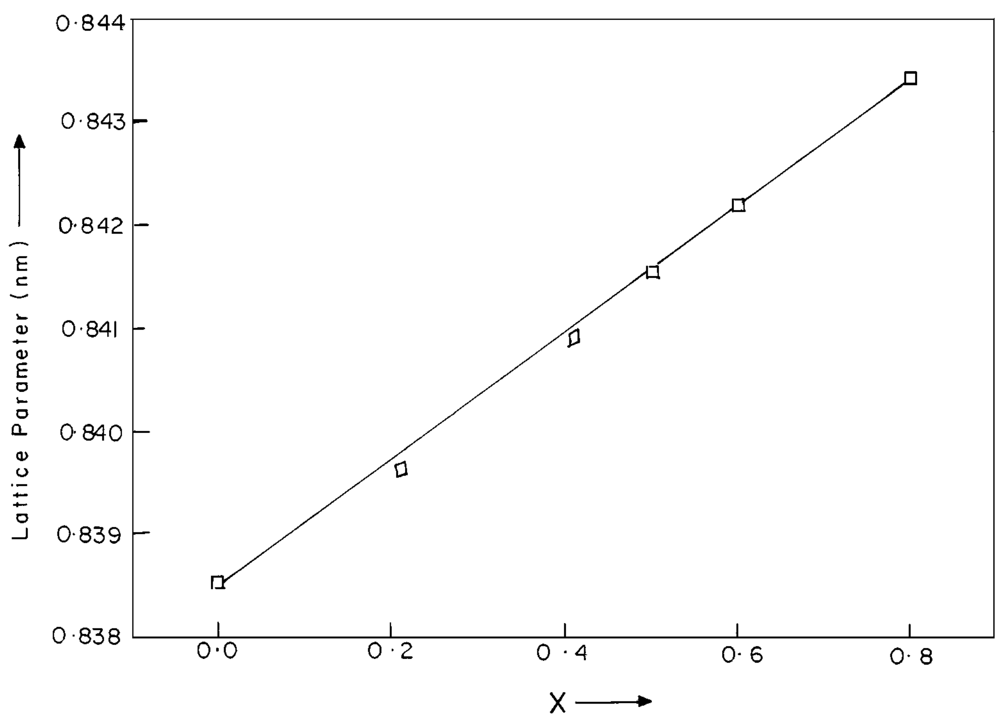

Figure 1 Variation of lattice parameter with zinc content for mixed Co-Zn ferrites.

TABLE II Composition dependence of room temperature dielectric data for zinc substituted cobalt ferrites at 100 kHz

Sample No.	Ferrite composition	100 kHz ε'	$\tan\delta$	ε''	σ ($\Omega^{-1}\cdot cm^{-1}$)
1	$CoFe_2O_4$	74×10^5	0.44	33×10^5	1.48×10^{-4}
2	$Co_{0.8}Zn_{0.2}Fe_2O_4$	70×10^5	0.30	21×10^5	9.65×10^{-5}
3	$Co_{0.6}Zn_{0.4}Fe_2O_4$	66×10^5	0.28	18×10^5	9.35×10^{-6}
4	$Co_{0.5}Zn_{0.5}Fe_2O_4$	55×10^5	0.24	13×10^5	1.29×10^{-6}
5	$Co_{0.4}Zn_{0.6}Fe_2O_4$	50×10^5	0.10	5×10^5	2.52×10^{-7}
6	$Co_{0.2}Zn_{0.8}Fe_2O_4$	47×10^5	0.03	1×10^5	5.48×10^{-8}

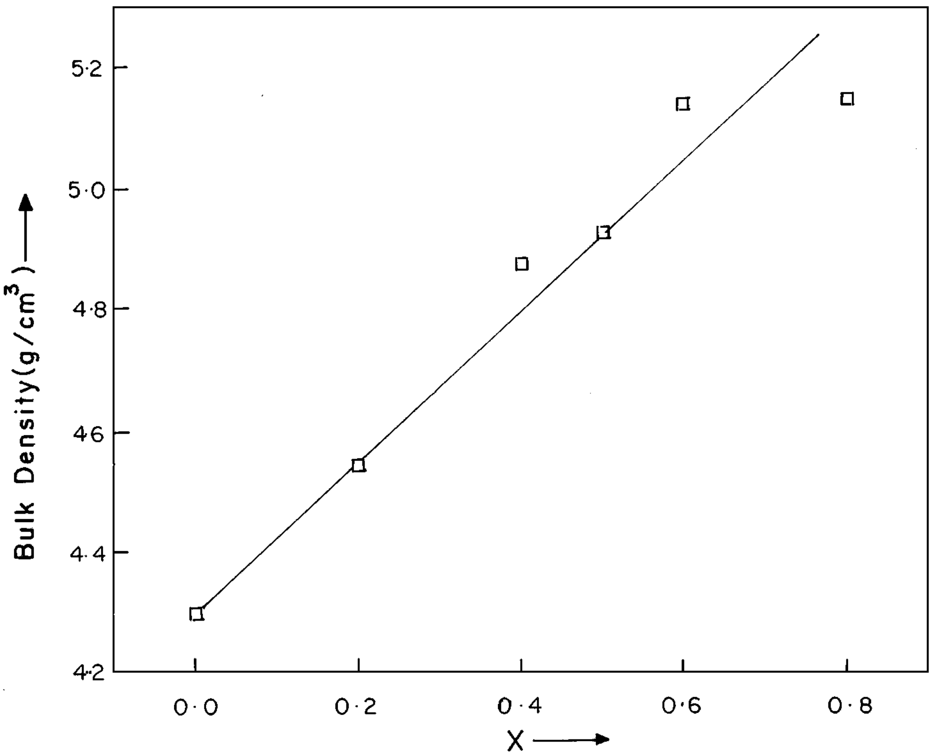

Figure 2 Plot of bulk density versus zinc content for mixed Co-Zn ferrites.

Ni-Zn ferrites as a function composition, frequency and temperature. Elhiti *et al.* [14] have investigated the dielectric behaviour of Cu-Cr ferrites as a function of composition and frequency. These workers explained the dielectric behaviour of the ferrites starting with the supposition that the mechanism of the polarization process in ferrites is similar to that of the conduction process [15]. They observed that the electronic exchange between $Fe^{2+} \leftrightarrows Fe^{3+}$ results in local displacements of electrons in the direction of the applied electric field and that these displacements determine the polarization of the ferrites. A similar explanation is proposed for the composition dependence of the dielectric constants of mixed Co-Zn ferrites. It can be seen from Table I that the number of ferrous ions on the octahedral sites which take part in the electron exchange interaction $Fe^{2+} \leftrightarrows Fe^{3+}$, and hence are responsible for the polarization is maximum in the case of cobalt ferrite, therefore a high value of the dielectric constant is expected and is observed (7,400,000). As the zinc content in the mixed Co-Zn ferrites is continuously increased the number of ferrous ions on the octahedral sites which are available for polarization decreases, resulting in a continuous decrease in the dielectric constant. Moreover, it can be seen from Table II that the values of electrical conductivity decrease with increasing zinc content. This decrease in the electrical conductivity is because of the decrease in the number of ferrous ions on the octahedral sites which play a dominant role in the mechanisms of conduction and dielectric polarization. This result is in agreement with the assumption made by Rabinkin and Novika [15].

3.4. Frequency dependence of dielectric constant (ε')

The variations of dielectric constant as a function of frequency for mixed Co-Zn ferrites with different compositions are shown in Figs 3 and 4. An examination of figures show that the magnitude of the dispersion of the dielectric constant is maximum for $CoFe_2O_4$ and decreases as the zinc content is increased.

The decrease of dielectric constant with increase of frequency as observed in the case of mixed Co-Zn ferrites is a normal dielectric behaviour. This normal dielectric behaviour was also observed by several investigators [16–20]. The normal dielectric behaviour of spinel ferrites was explained by Rezlescu and

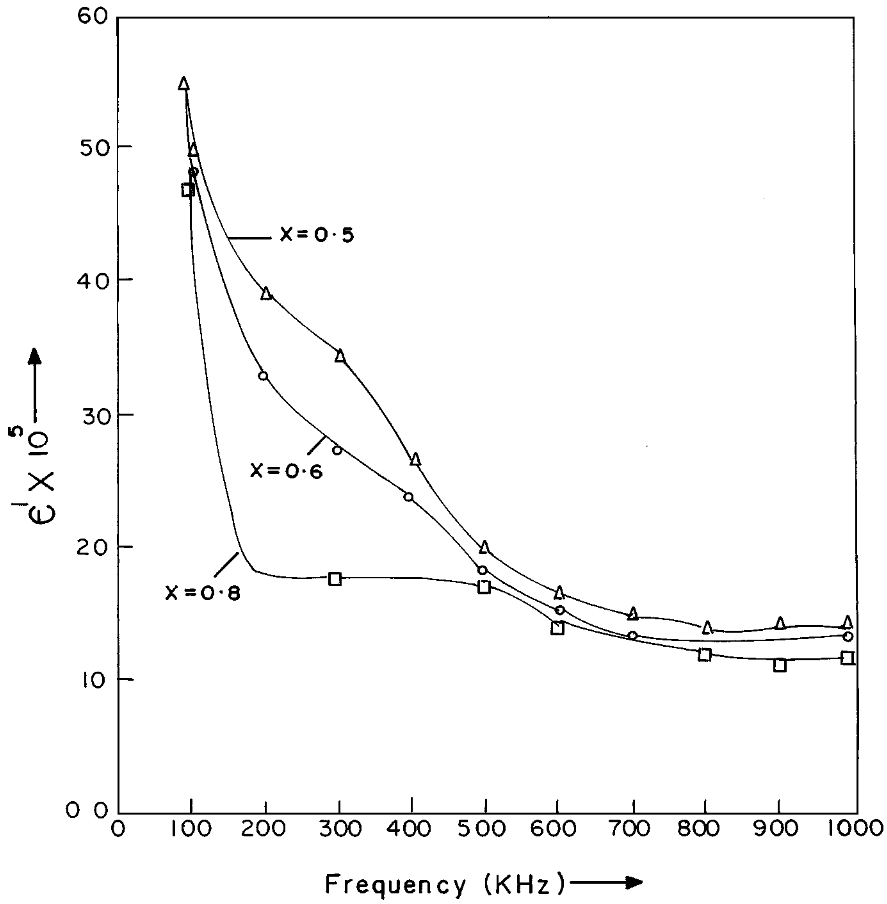

Figure 3 Plot of dielectric constant (ε') vs. frequency for $Co_xZn_{1-x}Fe_2O_4$ ($x = 0$, 0.2 and 0.4).

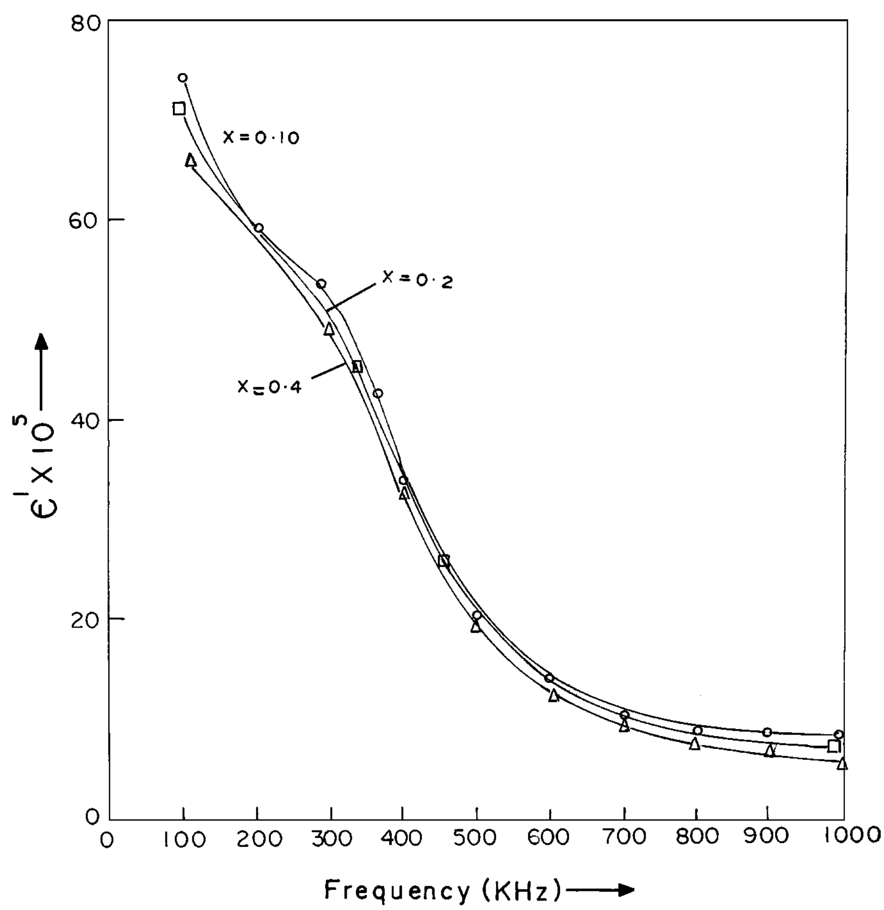

Figure 4 Plot of dielectric constant (ε') vs. frequency for $Co_xZn_{1-x}Fe_2O_4$ ($x = 0.5$, 0.6 and 0.8).

Rezlescu [12]. Following their work, the dependence of the dielectric constant on composition can be dispersion explained. The observation that $CoFe_2O_4$ shows a maximum dielectric dispersion among the mixed Co-Zn ferrites may be explained on the basis of the available ferrous ions on octahedral sites. In the case of $CoFe_2O_4$ the ferrous ion content is higher than in other mixed Co-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 electric field increases gradually, and though the same number of ferrous ions is present in the ferrite material, the dielectric constant (ε') decreases from 7,400,000 at 100 kHz to 900,000 at 1 MHz. This reduction occurs because beyond a certain frequency of the externally applied electric field. The variation of the dispersion of ε' with composition can also be explained on the same lines as above.

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

Figs 3–5 show the variation of tan δ with frequency for mixed Co-Zn ferrites. It can be seen from the figures that in the case of $CoFe_2O_4$, $Co_{0.8}Zn_{0.2}Fe_2O_4$, $Co_{0.6}Zn_{0.4}Fe_2O_4$, $Co_{0.5}Zn_{0.5}Fe_2O_4$ and $Co_{0.4}Zn_{0.6}Fe_2O_4$ tan δ shows a maximum at 700 kHz and for $Co_{0.2}Zn_{0.8}Fe_2O_4$ tan δ shows a maximum at 900 kHz. A qualitative explanation can be given for the occurrence of the maximum in the tan δ versus frequency curves in the case of mixed Co-Zn ferrites. As pointed 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+}. In contrast, the conduction in the p-type specimen is due to hopping of holes between Co^{3+} and Co^{2+} ions. As such, when the hopping is nearly equal to that of the externally applied electric field, a maximum of loss tangent may be observed. As such it is possible, in the case of $CoFe_2O_4$, $Co_{0.8}Zn_{0.2}Fe_2O_4$, $Co_{0.6}Zn_{0.4}Fe_2O_4$, $Co_{0.5}Zn_{0.5}Fe_2O_4$ and $Co_{0.4}Zn_{0.6}Fe_2O_4$ where the hopping frequencies are of the appropriate magnitude, to observe a loss maximum at 700 and 900 kHz, respectively.

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

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

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

$$\tau = p/2$$

or

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

Equation 5 shows that f_{max} is proportional to the jumping or hopping probability. Now an increase of f_{max} with increasing zinc content indicates that the hopping or jumping probability per unit time increases.

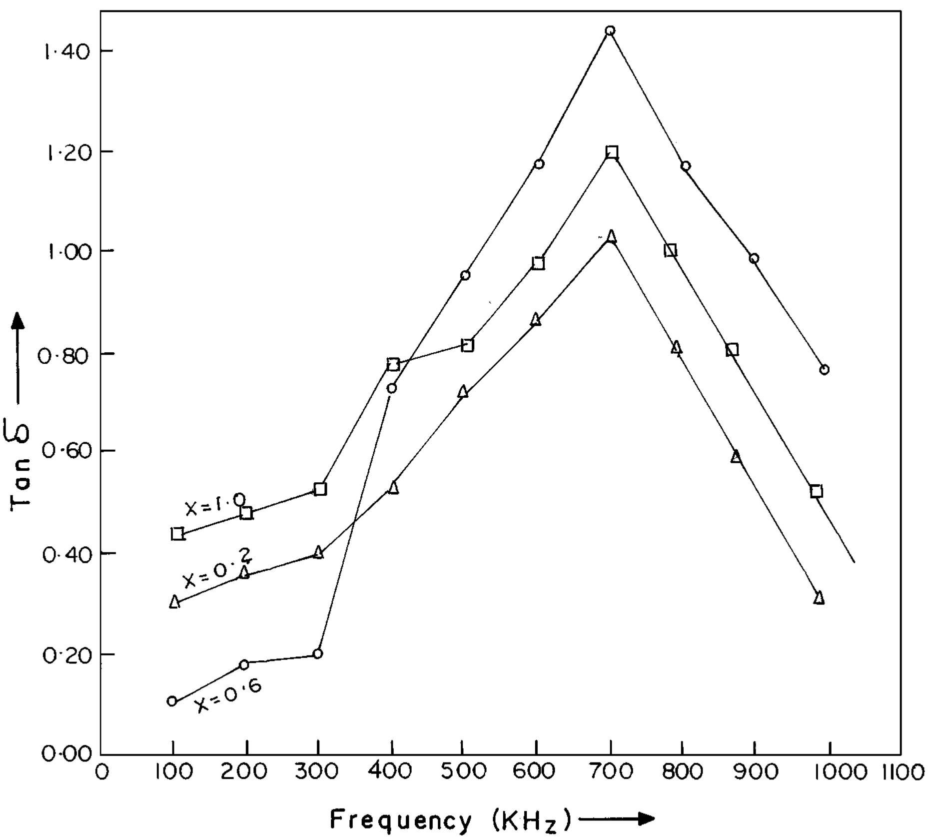

Figure 5 Plot of dielectric loss tangent (tan δ) vs. frequency for $Co_xZn_{1-x}Fe_2O_4$ ($x = 0.2$, 0.6 and 1.0).

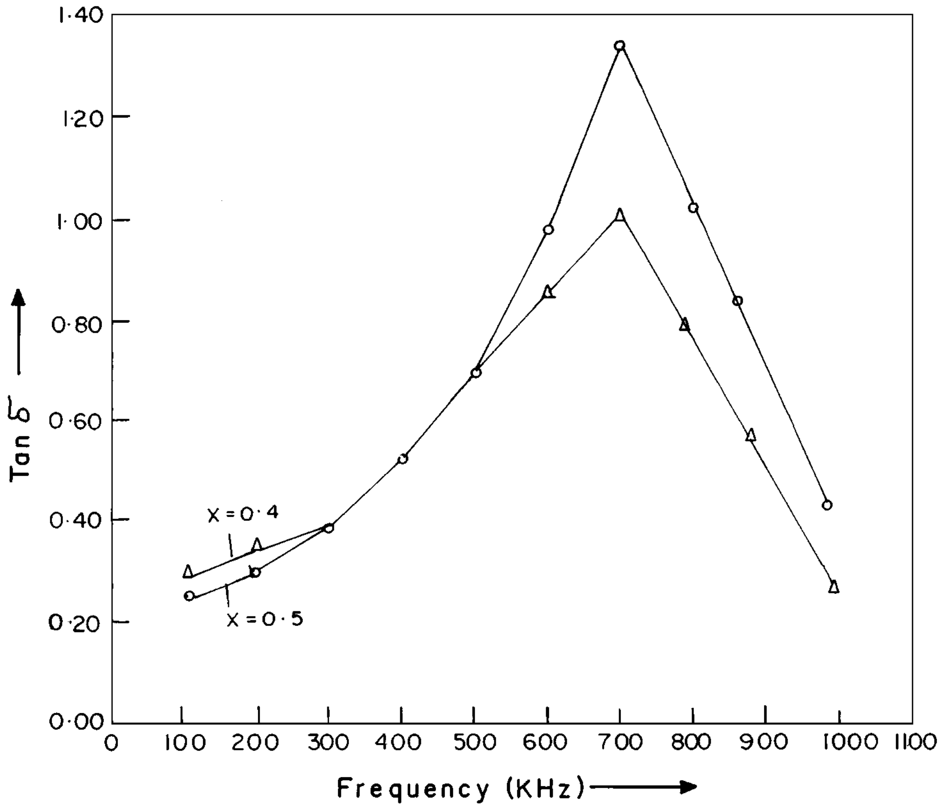

Figure 6 Plot of dielectric loss tangent (tan δ) vs. frequency for $Co_xZn_{1-x}Fe_2O_4$ ($x = 0.4$ and 0.5).

3.6. Relationship between the dielectric constant (ε') and the resistivity (ρ)

The computed values of resistivity (ρ), $\sqrt{\rho}$ and $\varepsilon'\sqrt{\rho}$ are given in Table III along with the value of ε' and tan δ. It can be seen from the table that the ε' is approximately inversely proportional to the square root of resistivity. As such the product $\varepsilon'\sqrt{\rho}$ remains nearly constant as shown in Table III. A similar relationship between ε' and $\rho^{1/2}$ was found by Koops [21] and Reddy and Rao [22] in the case of Ni-Zn and Mn-Mg ferrites Hudson [23] 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 III shows that this result holds good in the case of mixed Co-Zn ferrites too.

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

Fig. 8 shows the variation of dielectric constant at 100 kHz with temperature for mixed Co-Zn ferrites. The dielectric constant increases gradually with increasing temperature upto a certain 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 [23–25]. The value of T_d for each composition are given in Table IV. The Curie temperature values $(T_c)_1$ determined by the gravity method are also included in the table for the purpose of comparison where it can be

TABLE IV Curie temperatures (T_c) and dielectric transition temperature (T_d) for mixed Co-Zn ferrites

Sample No.	Ferrite composition	T_c (K)	T_d (K)
1	$CoFe_2O_4$	828	825
2	$Co_{0.8}Zn_{0.2}Fe_2O_4$	713	715
3	$Co_{0.6}Zn_{0.4}Fe_2O_4$	628	632
4	$Co_{0.5}Zn_{0.5}Fe_2O_4$	493	495
5	$Co_{0.4}Zn_{0.6}Fe_2O_4$	407	410
6	$Co_{0.2}Zn_{0.8}Fe_2O_4$	378	380

TABLE III Variation of dielectric constant (ε'), tan δ, resistivity and f_{max} in the case of mixed Co-Zn ferrites

Sample No.	Ferrite composition	ε'	tan δ	f_{max} (kHz)	ρ ($\Omega \cdot$ cm)	$\sqrt{\rho}$ ($\Omega^{1/2}\cdot$ cm$^{1/2}$)	$\varepsilon'\sqrt{\rho}$ ($\Omega^{1/2}\cdot$ cm$^{1/2}$)
1	$CoFe_2O_4$	74×10^5	0.44	700	6.76×10^3	83	0.61×10^9
2	$Co_{0.8}Zn_{0.2}Fe_2O_4$	70×10^5	0.30	700	10.36×10^3	102	0.71×10^9
3	$Co_{0.6}Zn_{0.4}Fe_2O_4$	66×10^5	0.28	700	10.70×10^4	327	2.12×10^9
4	$Co_{0.5}Zn_{0.5}Fe_2O_4$	55×10^5	0.24	700	77.52×10^4	880	4.84×10^9
5	$Co_{0.4}Zn_{0.6}Fe_2O_4$	50×10^5	0.10	700	3.97×10^6	1992	9.96×10^9
6	$Co_{0.2}Zn_{0.8}Fe_2O_4$	47×10^5	0.03	900	18.25×10^6	4272	20.0×10^9

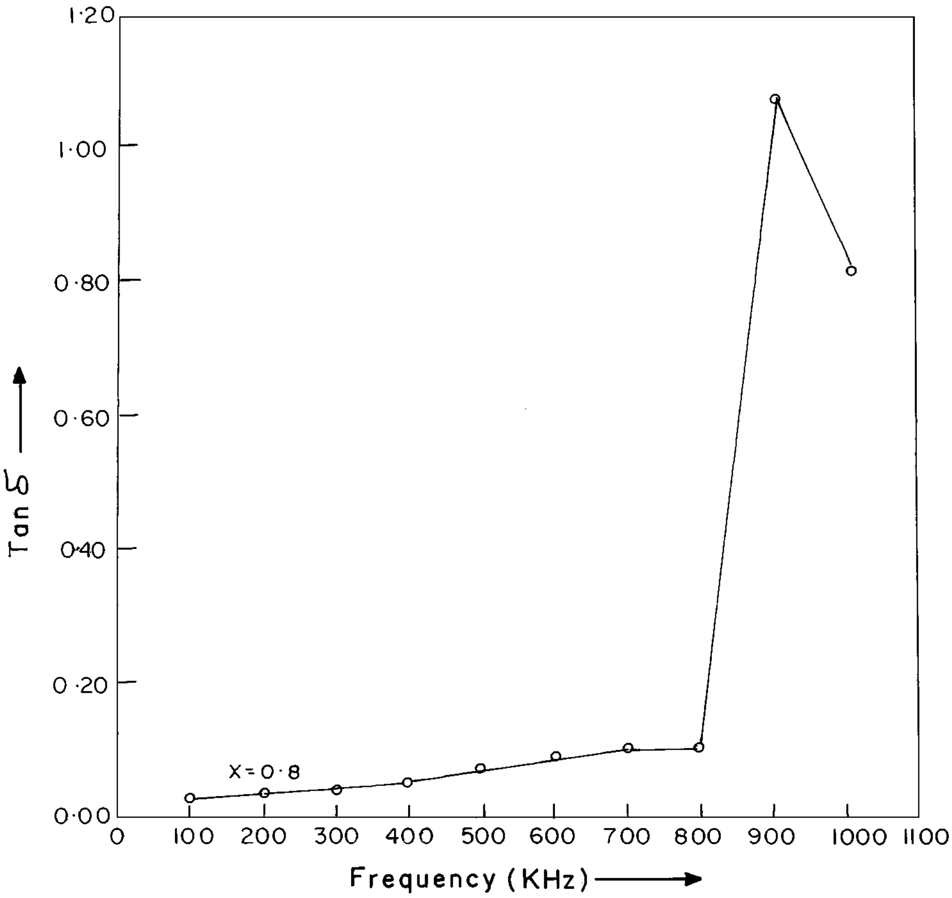

Figure 7 Plot of dielectric loss tangent (tan δ) vs. frequency for $Co_{0.2}Zn_{0.8}Fe_2O_4$.

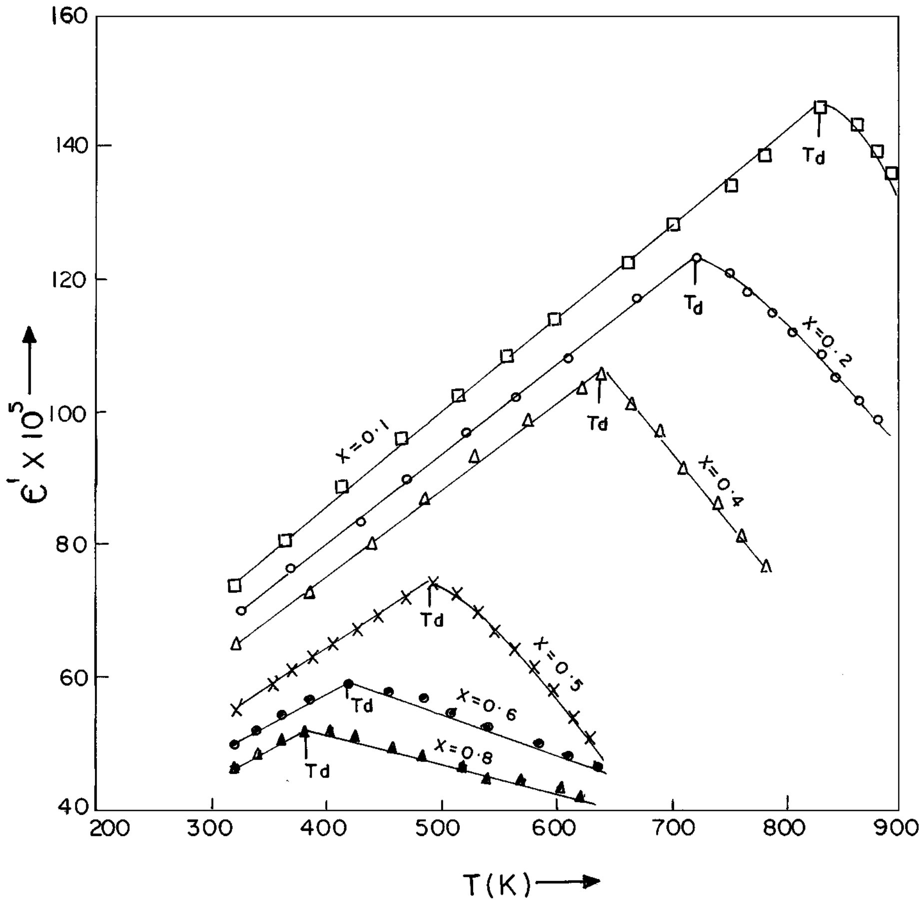

Figure 8 Variation of dielectric constant (ε') with temperature of 100 kHz for mixed Co-Zn ferrites.

seen 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 paramagnetic.

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