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Effect of Gd^{3+} substitution on dielectric behaviour of copper–cadmium ferrites

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The dielectric constant, ε', loss tangent ($\tan\delta$) and a.c. resistivity ($\rho_{a.c.}$) are measured in the frequency range of 100 Hz to 5 MHz for the series of samples $Cd_x Cu_{1-x}Fe_{2-y}Gd_yO_4$ prepared by the ceramic technique. The dispersion in ε' for all the values of x and $y=0$ and 0.1 shows a normal behaviour except for $y=0.1$ and $x=0.4$. The lowering of dielectric intensity in substituted ferrites ($y=0.1$) and fast dispersion of ($\rho_{a.c.}$) with frequency, are explained as due to the reduced number of Fe^{3+} participating in the polarization process and the hindrances caused by Gd^{3+} to the polarization process by localizing Fe^{2+} ions thereby increasing the resistivity and activation energy. The dispersion in $\tan\delta$ for unsubstituted samples ($y=0.0$) shows a normal trend while substituted samples ($y=0.1$) show relaxation behaviour, which is explained by existing theories.

1. Introduction

Abnormal dielectric behaviour of copper containing ferrites has been reported in the literature and also by this laboratory [1, 2]. Dispersion in dielectric constant (ε') and loss tangent ($\tan\delta$) with frequency in polycrystalline ferrites is strongly dependent on the polarization process [3, 4], and is also related to the Verway conduction mechanism [5, 6]. The conduction mechanism in ferrites has been found to alter on substitution of various valency cations. Zinc and cadmium are the most versatile amongst these cations which are known to improve magnetization. However, this leads to a decrease in the Curie temperature [7, 8]. It is well known that zinc substitution lowers d.c.-resistivity, while cadmium improves it favourably in the ferrites [7]. The substitution of cations such as Li^{1+}, Ti^{4+} [3], Zr^{4+}, Si^{4+}, Nb, Sb, Sn, Ti [9], La^{3+} [10] and Al^{3+}, Cr^{3+} [11] etc., have been studied by different workers from the point of view of structural, electrical and magnetic behaviour [9–11]. The substitution of rare earth elements in garnets and hard magnetic materials have been studied extensively, but are given less attention in the study of soft ferrites. Therefore, it was thought to be of interest to study the Gd^{3+} substitution in Cu–Cd soft ferrites.

As a continuation of our previous work [2], the present communication attempts to understand the effect of Gd^{3+} substitution on the dielectric constant, ε', $\tan\delta$ and log of a.c. resistivity with frequency in the $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ ferrite system.

2. Experimental details

$Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ ferrite samples (with $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ and for $y = 0.0$ and 0.1) were prepared by the standard ceramic technique by using AR grade $CdCO_3$, Gd_2O_3 and CuO. The sintering was carried out at 975 °C for 48 h in two cycles. The crystal structure characterization was performed on a Philips X-Ray diffractometer using CuK_α radiation. The measurement of dielectric constant (ε'), loss tangent ($\tan\delta$) and a.c. resistivity ($\rho_{a.c.}$) in the frequency range of 100 Hz to 5 MHz was carried out using a L.F. impedance gain phase analyser, Hewlett Packard model 4191 A, at E.R.T.L., Bombay. The chemical analysis was performed using an atomic absorption spectrophotometric technique.

3. Results and discussions

The X-ray diffractograms of our polycrystalline powder samples show tetragonal structure for $x = 0.0$ and $y = 0.0$, 0.1, while all the others exhibit cubic symmetry without any ambiguity, thereby confirming the formation of ferrites. The samples with $x = 0.0$ to 1.0 for $y = 0.1$ show an additional peak of very low intensity near (3 1 1) on the lower angle side, which is possibly due to the high reactivity of iron with Gd^{3+} to form a $GdFeO_3$ phase of orthorhombic character [12]. The orthorhombic distortions in copper-containing ferrites after substitution of Al^{3+}, Cr^{3+} and La^{3+} have been reported in the literature [10, 11]. For calculation of average a, this reflection is not taken into consideration. The variation of lattice constant with Cd content in both cases ($y = 0.0$ and 0.1) obeys Vegard's law. However, the c/a ratio in Gd^{3+} substituted samples (for $x = 0.0$, $y = 0.1$) is less than that for unsubstituted ferrites ($x = y = 0$). The decrease of the c/a ratio on substitution of Gd^{3+} may be due to decreasing numbers of Cu^{2+} ions at B sites [13]. However, there is no appreciable effect on lattice constant with Gd^{3+} substitution which is possibly because of the comparable ionic radii of Cd (0.099 nm) and Gd^{3+} (0.11 nm), and further from our d.c.

TABLE I Lattice parameters, a and c, and ΔE for $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ ferrite system

x	Lattice parameter (nm)		Activation energy ΔE (ev)	
	$y = 0.0$	$y = 0.1$	$y = 0.0$	$y = 0.1$
0.0	$a = 0.825$	$a = 0.826$ $c = 0.870$	0.66 $c = 0.857$	0.80
0.2	$a = 0.847$	0.846	0.73	0.67
0.4	0.853	0.851	0.79	0.68
0.6	0.857	0.856	0.40	0.74
0.8	0.864	0.863	0.43	0.52
1.0	0.869	0.869	0.30	0.49

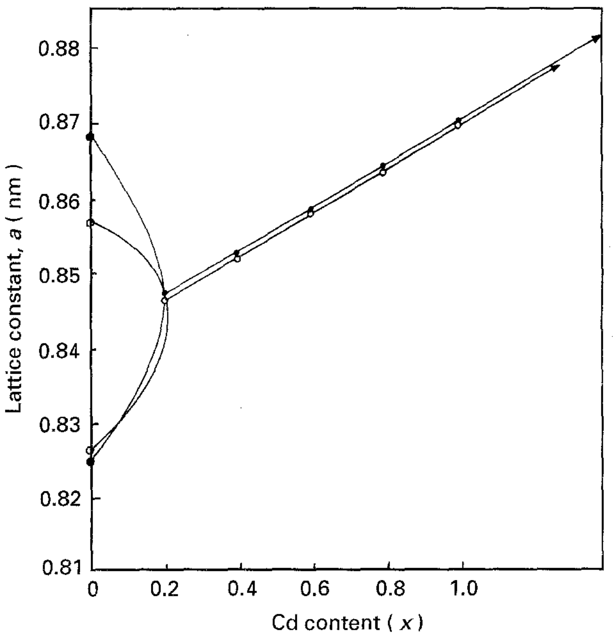

Figure 1 Plot of lattice constants a and c with Cd content. —○— $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$, $y = 0.1$ and —●— $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$, $y = 0.0$.

resistivity study it is found that Gd^{3+} preferentially occupies octahedral B sites which do not contribute much to the value of the lattice constant [14]. The data of lattice constants a and c and activation energy ΔE obtained from d.c. electrical studies are presented in Table I. The graphs of lattice constants a and c with Cd content are given in Fig. 1. The frequency dependence of ε' is presented in Figs 2 and 3 and tanδ in Figs 4 and 5. The plots of log a.c. resistivity with frequency is given in Figs 6 and 7.

From Figs 2 and 3 it is observed that the dispersion in ε' is analogous to Koops phenomenological theory [15]. The dispersion of ε' is higher for frequencies below 1 MHz and beyond this value, it levels off for the series of samples for all values of x and $y = 0.0$, while for $y = 0.1$ the dispersion is high below 100 kHz and beyond this frequency it levels off. This behaviour may be due to the fact that in substituted samples, the polarization process reaches its saturation limits at low frequency when compared with unsubstituted ones. The values of dielectric intensity at different frequencies for substituted samples are also found to be lower than those for $y = 0.0$. The dielectric intensity and dispersion with frequency in substituted ferrites can be explained on the basis of space charge polarization due to the inhomogeneous structure as per interfacial polarization [16, 17]. In the present case the decrease of dielectric intensity is due to the increase of d.c. resistivity ($\rho_{d.c.}$) and the activation energy (ΔE) after substitution [16, 18]. The substitution of Gd^{3+} for Fe^{3+} thus produces hindrance to the polarization process and localizes the Fe^{2+} in the lattice, thereby affecting the Verway conduction mechanism and polarization as well as increasing the resistivity and activation energy (ΔE) and totally thus affecting the dielectric intensity. The dispersion of a.c. log resistivity (Figs 6 and 7) shows a rather normal trend. However, the rate of dispersion is high in substituted samples, which is also indicative of increasing a.c. resistivity but may also come from increasing porosity in the substituted samples.

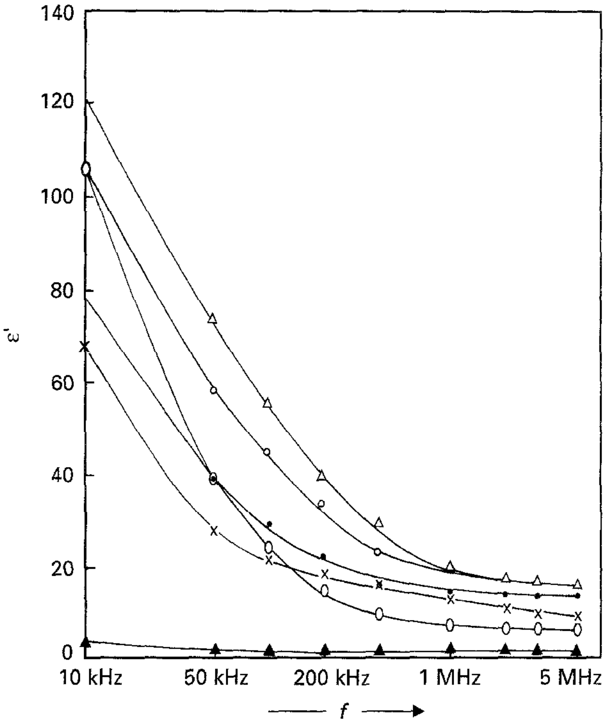

Figure 2 Plot of dielectric constant ε' with frequency for $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ ($y = 0.0$). —●— $x = 0.0$; —○— $x = 0.2$; —△— $x = 0.4$; —×— $x = 0.6$; —▲— $x = 0.8$; —0— $x = 1.0$.

From Figs 4 and 5, it can be observed that all the undoped samples ($y = 0.0$) show dispersion in tan δ with frequency which is a trend expected for ferrites except for $x = 0.4$ and 0.8, which show peaking behaviour. The maximum in tan δ for $x = 0.4$ occurs at about 10 kHz, while for $x = 0.8$ at 150 kHz. Fig. 5 shows peaking behaviour in the dispersion relation of tan δ with frequency except for $x = 0.0$. The peak frequencies for $x = 0.2$, 0.4 is 100 kHz and for $x = 0.6$ (10 kHz) $x = 0.8$ (1 kHz). The peak frequency is found to decrease with increasing Cd content.

The peaking behaviour in tan δ with frequency is attributed by different workers to a jump frequency [4, 5] equal to the frequency of the applied field, and the larger dispersion in ε' with respect to ε'', is attributed to the complex dielectric constant. The

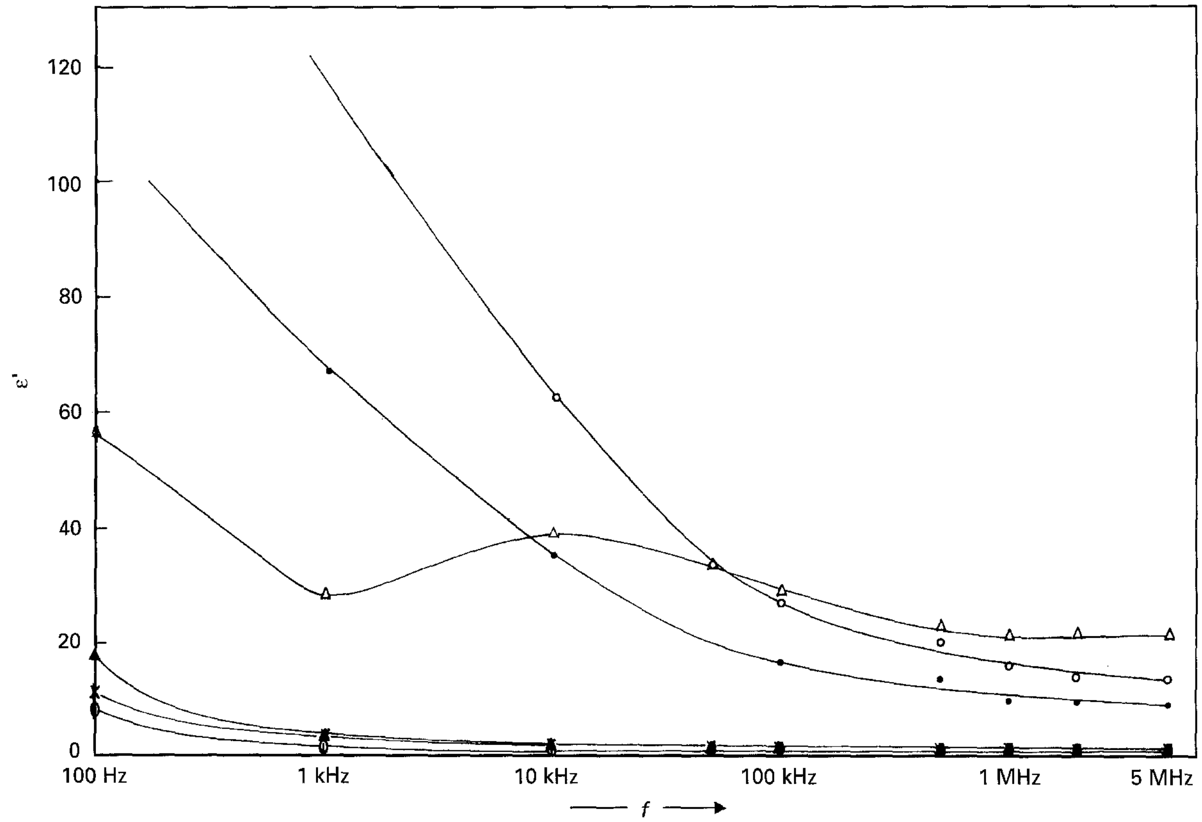

Figure 3 Plot of dielectric constant ε' with frequency for $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ ($y = 0.1$). —●— $x = 0.0$; —○— $x = 0.2$; —△— $x = 0.4$; —×— $x = 0.6$; —▲— $x = 0.8$; —0— $x = 1.0$.

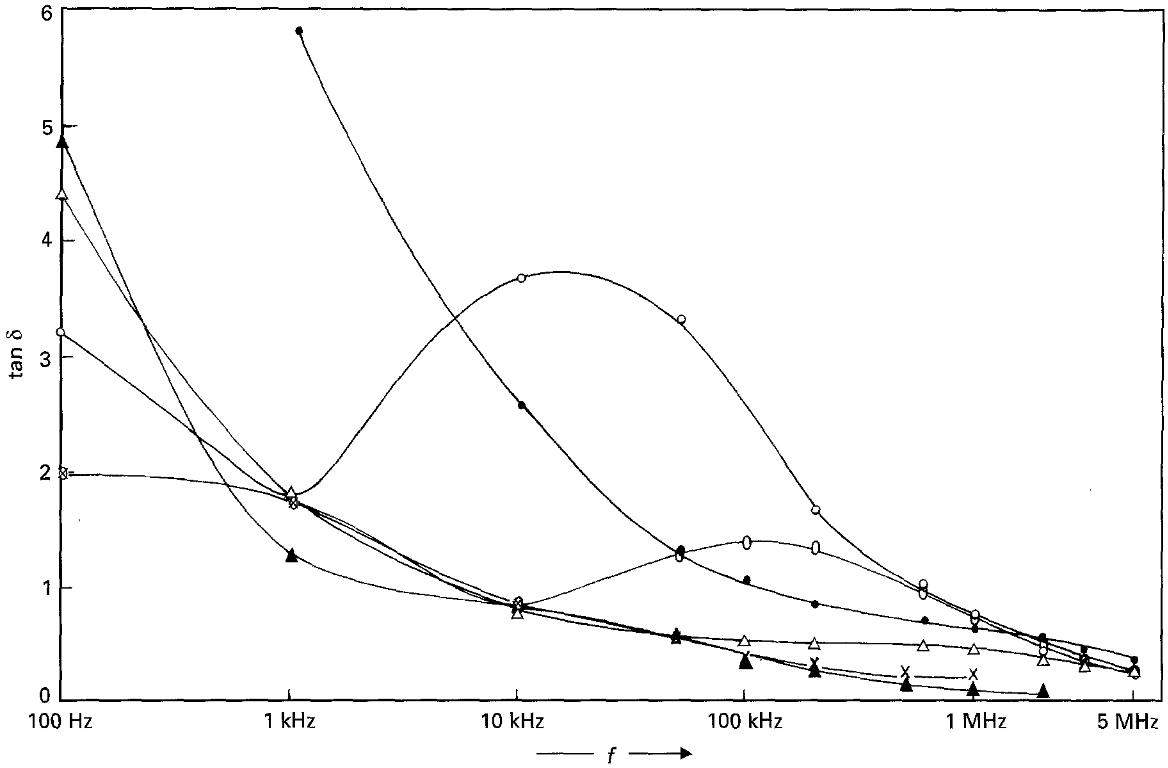

Figure 4 Plot of tan δ versus frequency for $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ ($y = 0.0$).—●— $x = 0.0$; —○— $x = 0.2$; —△— $x = 0.4$; —×— $x = 0.6$; —▲— $x = 0.8$; —0— $x = 1.0$.

peaking behaviour in copper containing ferrites has been attributed by Kulkarni and Vaingankar [2] to the presence of p-type charge carriers in addition to the n type given by $Cu^{2+} \rightarrow Cu^{1+}$ exchange which occurs on octahedral sites of spinels. The peaking behaviour in this case, therefore, may be due to higher rates of dispersion of ε', in substituted samples with respect to ε'' and as well as due to the possibility of the presence of p-type charge carriers. $Cu^{2+} \rightarrow Cu^{1+}$ contributes to the polarization process. The value of

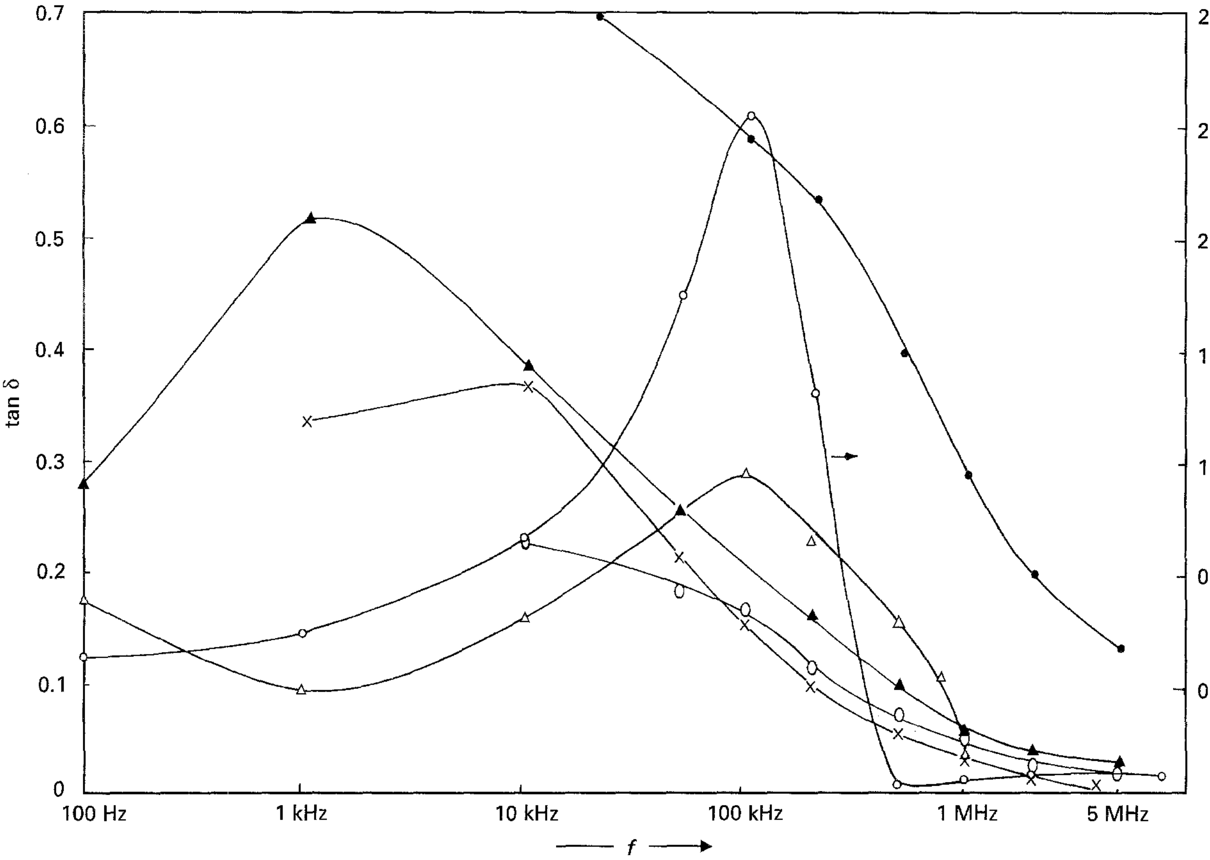

Figure 5 Plot of tan δ versus frequency for $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ ($y = 0.1$). —●— $x = 0.0$; —○— $x = 0.2$; —△— $x = 0.4$; —×— $x = 0.6$; —▲— $x = 0.8$; —0— $x = 1.0$.

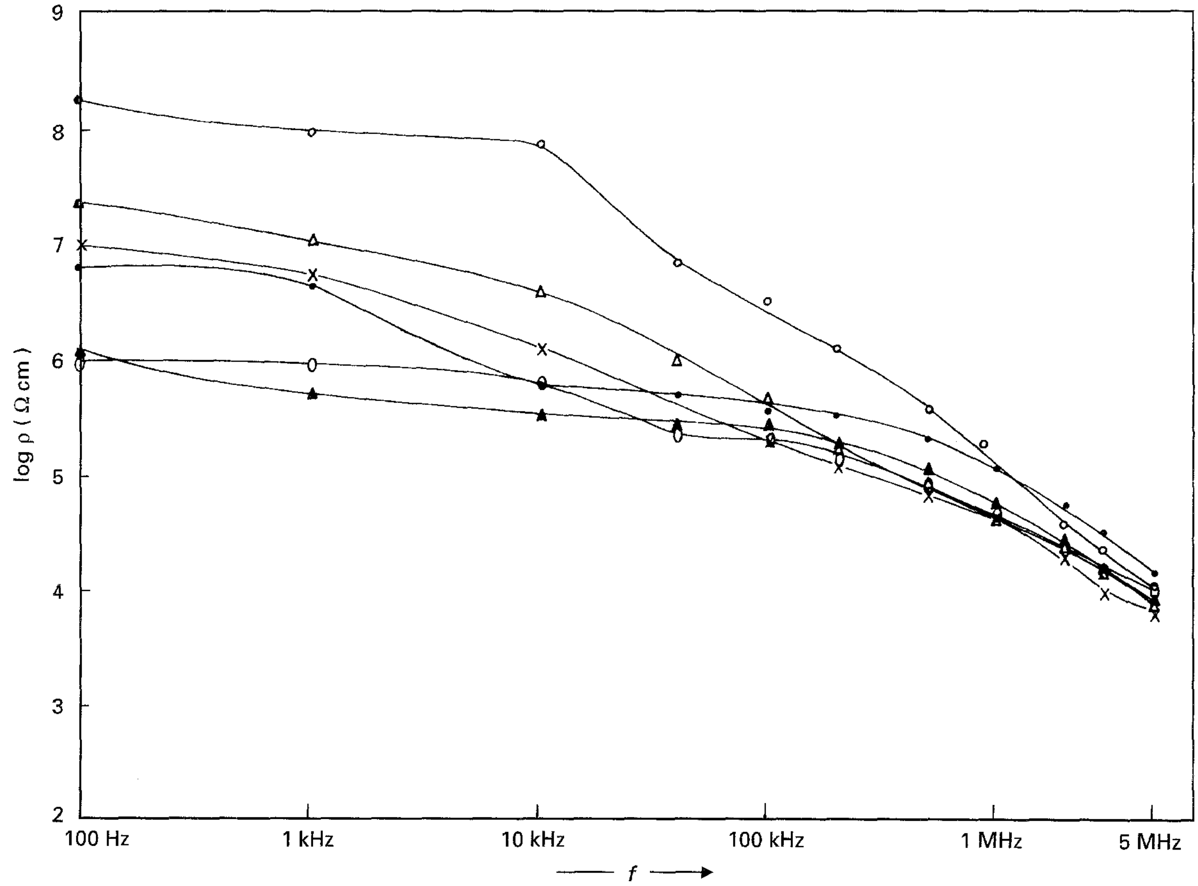

Figure 6 Plot of a.c. log resistivity with frequency for $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ ($y = 0.0$). —●— $x = 0.0$; —○— $x = 0.2$; —△— $x = 0.4$; —×— $x = 0.6$; —▲— $x = 0.8$; —0— $x = 1.0$.

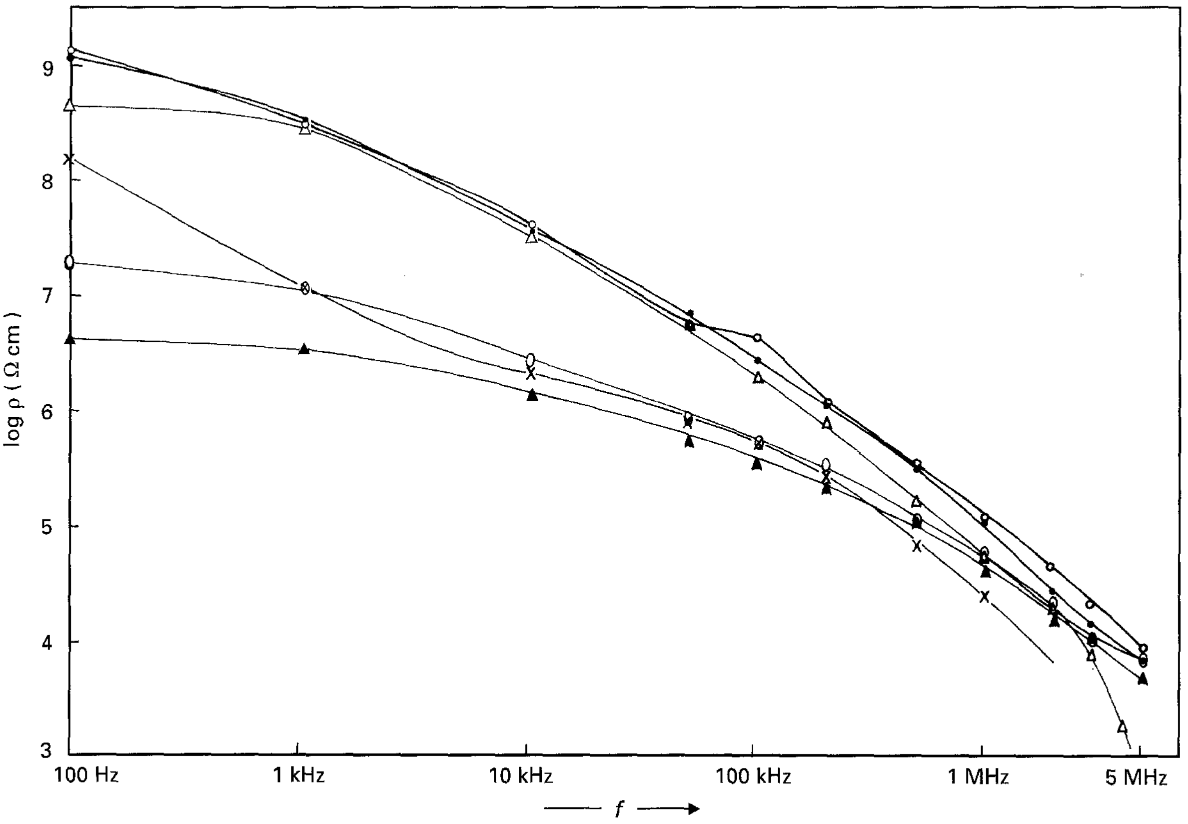

Figure 7 Plot of a.c. log resistivity with frequency for $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ ($y = 0.1$). —●— $x = 0.0$; —○— $x = 0.2$; —△— $x = 0.4$; —x— $x = 0.6$; —▲— $x = 0.8$; —0— $x = 1.0$.

tan δ was also found to decrease on substitution, with an increase in a.c. resistivity, which supports our results.

4. Conclusions

1. The dielectric constant ε′ for these substituted and non-substituted series of mixed ferrites exhibit a similar trend of variation of the electrical conductivity ($\rho_{a.c.}$).
2. The main process for the conduction mechanism in these ferrites depends upon the electronic exchange between $Fe^{2+} \rightleftharpoons Fe^{3+}$; on octahedral sites, which is responsible for the process of polarization.
3. Substitution of Gd^{3+} affects the Verway conduction mechanism, by localizing Fe^{2+} ions, thereby producing hindrances to the polarization process and decrease of dielectric intensity and increase of d.c. and a.c. resistivities and activation energy.
4. The peaking behaviour of tan δ in substituted samples, points to the presence of Cu^{1+} ions, and its contribution to conduction and the polarization process, is reflected by the increase in resistivities of doped samples.
5. Decrease of loss tangent values in substituted ferrites confirms the increase of resistivity supporting the Verway conduction mechanism.

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