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Abnormal dielectric behaviour in the $Cd_xCu_{1-x}Fe_2O_4$ system

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The a.c. electrical parameters such as the dielectric constant (ε_r) and the loss tangent (tan δ) for samples slow-cooled and air-quenched at 400, 600 and 800° C of the $Cd_xCu_{1-x}Fe_2O_4$ system have been studied as a function of frequency in the range 50 kHz to 50 MHz. The frequency dependence of the above a.c. parameters is found to be rather abnormal, giving a peak at a certain frequency for all the samples, irrespective of the thermal history of the ferrites. This has been attributed to the reduction $Cu^{2+} \rightleftharpoons Cu^+$ in the process of sintering of the materials, and therefore to the existence of p-type charge carriers.

1. Introduction

The dielectric constant (ε_r) is frequency-dependent in the case of polycrystalline materials [1, 2]. Both a.c. resistivities and dielectric constants, for polycrystalline ferrites, exhibit a dispersion with frequency. The dielectric properties of copper-containing ferrites were investigated by Rezlescu and Rezlescu [3]. They studied dielectric parameters as a function of composition, frequency and temperature for Cu–Zn, Cu–Ni and Cu–Mn ferrites. The dielectric behaviour of Co–Zn and Mg–Zn ferrite systems as a function of temperature and frequency was reported by Josyulu and Sobhanadri [4]. They attributed the dielectric behaviour in the above systems to Maxwell–Wagner polarization. The dielectric properties of Ni–Zn ferrites in the frequency range 10^2 to 10^5 Hz has been investigated by Murthy and Sobhanadri [5]. A strong correlation between the conduction mechanism and the dielectric behaviour of the ferrites has been reported by Iwauchi [6]. The dependence of the dielectric properties of mixed ferrites of Co–Zn, on the composition and temperature, has been studied out by Ramana Murthy [7]. The temperature dependence of the dielectric parameters for Ca–Ni ferrites has been investigated by Vasiliu *et al.* [8].

In this communication an attempt is made to present the behaviour of the a.c. electrical parameters such as dielectric constant (ε_r) and loss tangent (tanδ) of the system $Cd_xCu_{1-x}Fe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0), for slow-cooled and quenched samples, as a function of frequency.

2. Experimental details

For measurements of dielectric constant (ε_r) and loss tangent (tanδ) at radio frequency, the LCR bridge Type TF 1245 (circuit magnification meter) made by Marconi Instruments Ltd, England, was used.

$Cd_xCu_{1-x}Fe_2O_4$ polycrystalline ferrite samples (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) were prepared by the standard ceramic method using AR grade CuO, $CdCO_3$ and Fe_2O_3. The details of the preparation have been explained elsewhere [9].

3. Results and discussion

The crystal structure data for slow-cooled $Cd_xCu_{1-x}Fe_2O_4$ system have been reported previously [9]. Similar data for the air-quenched system are not available in literature and therefore these data are presented in Table I. It can be seen that the lattice parameter (a) increases with increase of cadmium content and this is rather an expected result as the ionic radius of Cd^{2+} (0.099 nm) is larger than that of Cu^{2+} (0.070 nm). At the same time the quenching of ferrites makes the unit cell dimensions increase, and therefore the lattice parameter increases. This can also be expected, as the crystal structure at elevated temperature gets arrested in the process of quenching. All the compositions, either slow-cooled or air-quenched, exhibit a cubic structure except $CuFe_2O_4$ which is tetragonal in nature.

The frequency dependence of dielectric constant (ε_r) is presented in Figs 1 to 4, for slow-cooled and air-quenched samples. From Fig. 1 it can be seen that for the slow-cooled samples, ε_r increases with increasing frequency, reaches a maximum and then is found to decrease and further, beyond a particular frequency it remains constant for all the samples. It can also be seen from the same figure that the value of ε_r is a maximum for $CdFe_2O_4$.

On the other hand, from Fig. 2 it can be seen that with increasing frequency ε_r goes on decreasing for all the samples except for x = 0.0 and 1.0 compositions, for which it is found to increase initially and then pass through a maximum to remain constant at high frequencies. Further, in this frequency dependence for all the compositions quenched at 400° C, maxima are observed almost at the same frequency. It is seen from Fig. 3 that with increasing frequency, ε_r goes on increasing for all the compositions quenched at 600° C except for x = 0.0 composition, i.e. $CuFe_2O_4$, for which ε_r is found to decrease before it passes through a maximum. With further increase in frequency the trend of variation of ε_r is found to be similar to those for samples quenched at 400° C. From Fig. 4 it is seen that with increasing frequency ε_r is found to increase

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TABLE I Values of lattice parameter (a) for slow-cooled and air-quenched $Cd_xCu_{1-x}Fe_2O_4$ system

Composition x	Lattice parameter (nm)			
	Slow-cooled	Quenched at 400° C	Quenched at 600° C	Quenched at 800° C
0.0	$a = 0.825$ $c = 0.870$	$a = 0.826$ $c = 0.865$	$a = 0.8278$ $c = 0.8587$	$a = 0.830$ $c = 0.8537$
0.2	0.84479	0.84474	0.84510	0.84487
0.4	0.85104	0.84968	0.85054	0.85087
0.6	0.85538	0.85588	0.85655	0.85658
0.8	0.86145	0.86424	0.86228	0.86394
1.0	0.86863	0.86938	0.86882	0.86894

for all the compositions quenched at 800° C, except for $x = 0.0$ and 0.8 samples, for which it is found to decrease and then exhibit maxima.

Though the frequency dependence is different in slow-cooled and thermally treated samples, a peculiar result, showing maxima at certain frequencies, irrespective of the thermal treatment, is exhibited by all the samples of the system. It may further be noted that at higher frequencies ε_r practically remains constant for all the compositions of the system, irrespective of the thermal treatment they have undergone.

In Figs 5 to 8 the behaviour of the loss tangent ($\tan\delta$) as a function of frequency is presented for the slow-cooled and air-quenched samples of the system. It is seen that the nature of the variation of $\tan\delta$ with frequency is almost the same in all the samples; $\tan\delta$ goes on increasing with increase in frequency initially, reaches a maximum, and then decreases. In this case, the behaviour of the slow-cooled and air-quenched samples is very similar except for the slow-cooled $CuFe_2O_4$ sample. In general, the maximum peaks appeared somewhere in the frequency range 180 kHz to about 40 MHz. It can be seen from Fig. 7 that the maxima in the $\tan\delta$ peculiarly appeared at a frequency of 10 MHz when the samples were quenched at 600° C.

Looking as a whole, there is no definite behaviour so far as the frequency dependence of ε_r and $\tan\delta$ is considered, and which gives rise to some abnormality which needs to be discussed for all the samples irrespective of the heat treatment they have undergone. The only difference is that the peaks are found to shift in a certain frequency range. Rezlescu and Rezlescu [3] studied the behaviour of ε_r and $\tan\delta$ as a function of frequency, composition and temperature for copper-containing ferrites. They also observed abnormal behaviour of the above-mentioned parameters, and

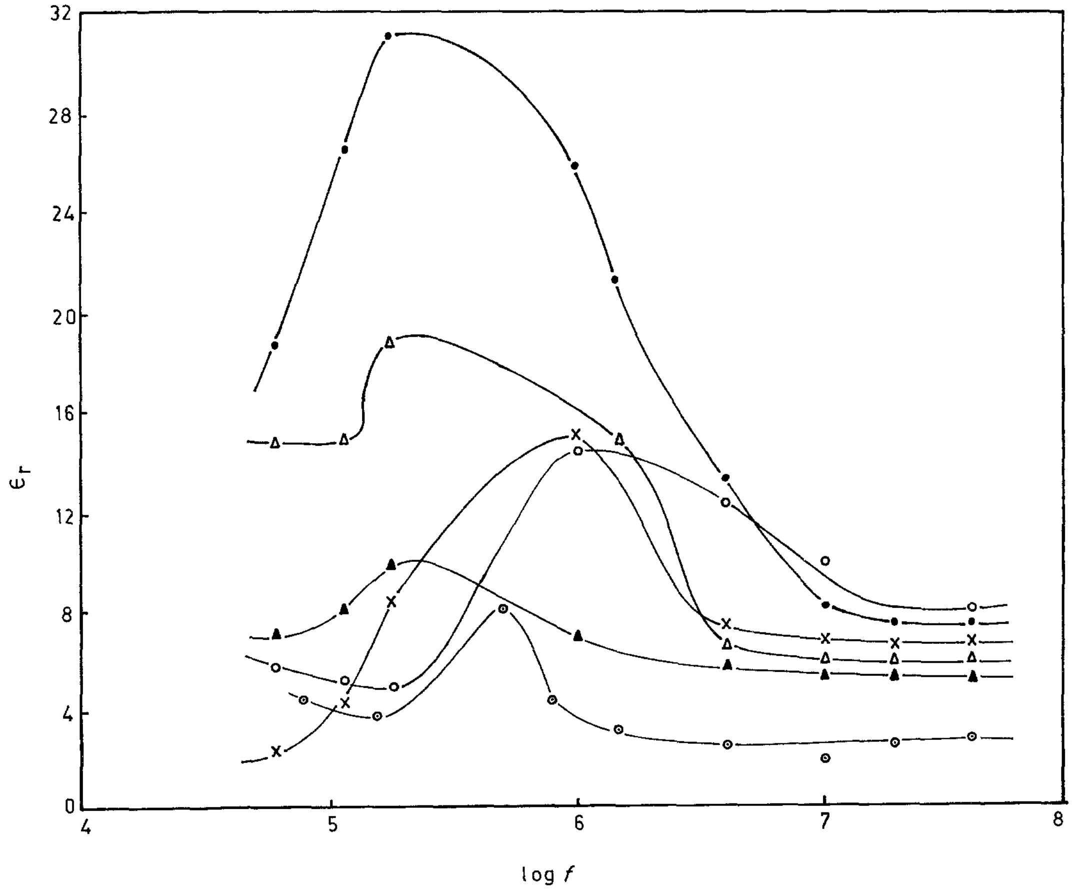

Figure 1 ε_r against $\log f$ for slow-cooled $Cd_xCu_{1-x}Fe_2O_4$ system. x = (⊙) 0.0, (▲) 0.2, (x) 0.4, (△) 0.6, (○) 0.8, (●) 1.0.

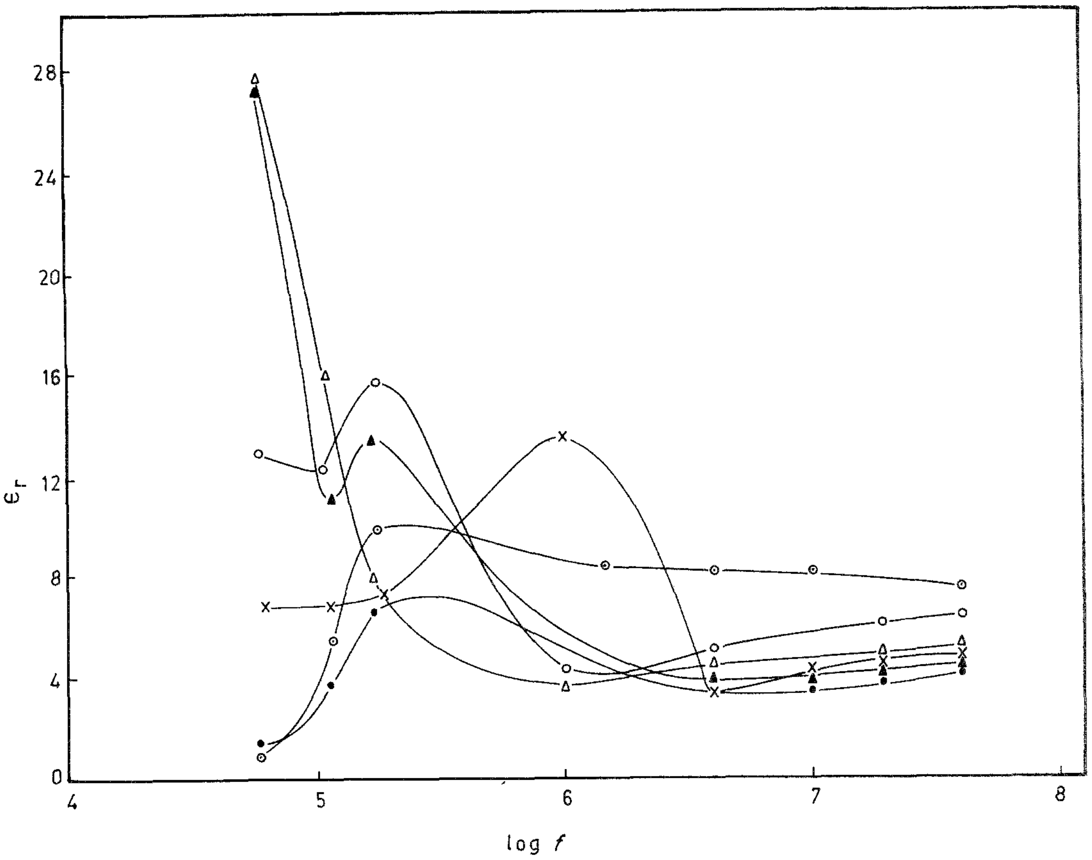

Figure 2 ε_r against log$f$ for $Cd_xCu_{1-x}Fe_2O_4$ system quenched at 400° C. x = (⊙), 0.0, (▲) 0.2, (x) 0.4, (△) 0.6, (○) 0.8, (●) 1.0.

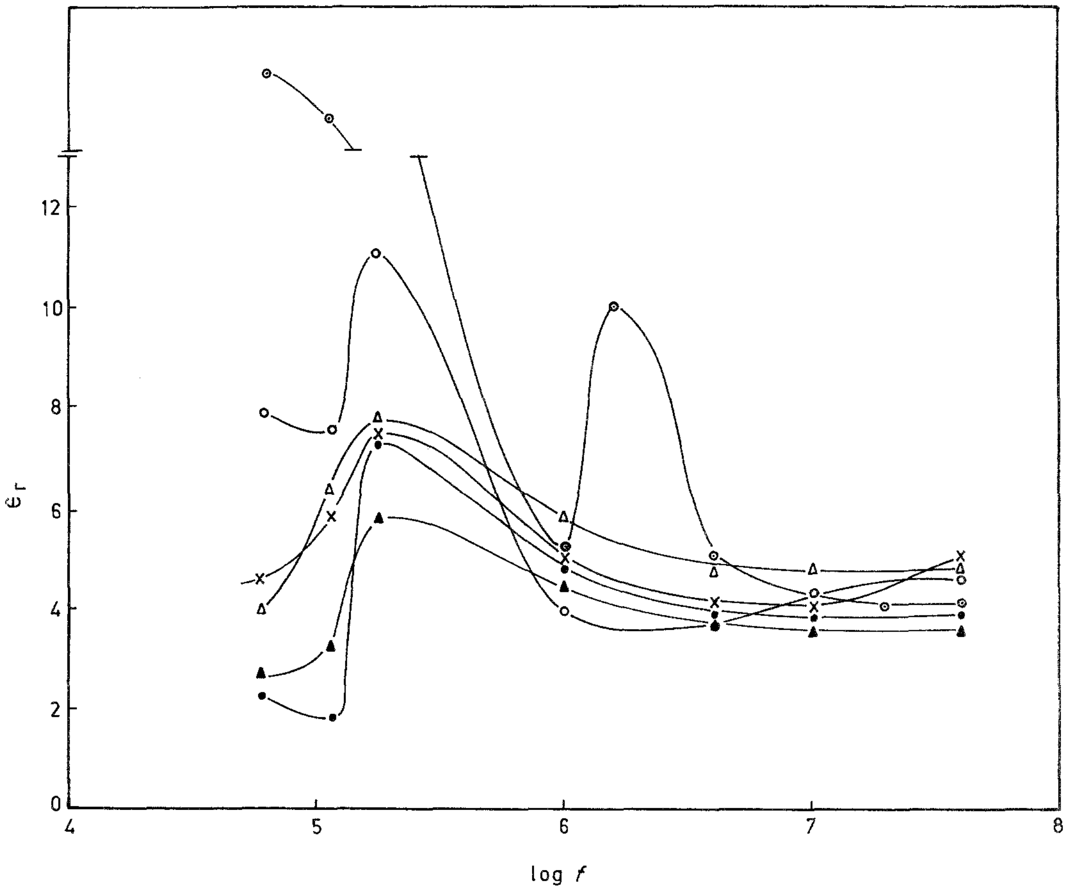

Figure 3 ε_r against log$f$ for $Cd_xCu_{1-x}Fe_2O_4$ system quenched at 600° C. x = (⊙), 0.0, (▲) 0.2, (x) 0.4, (△) 0.6, (○) 0.8, (●) 1.(

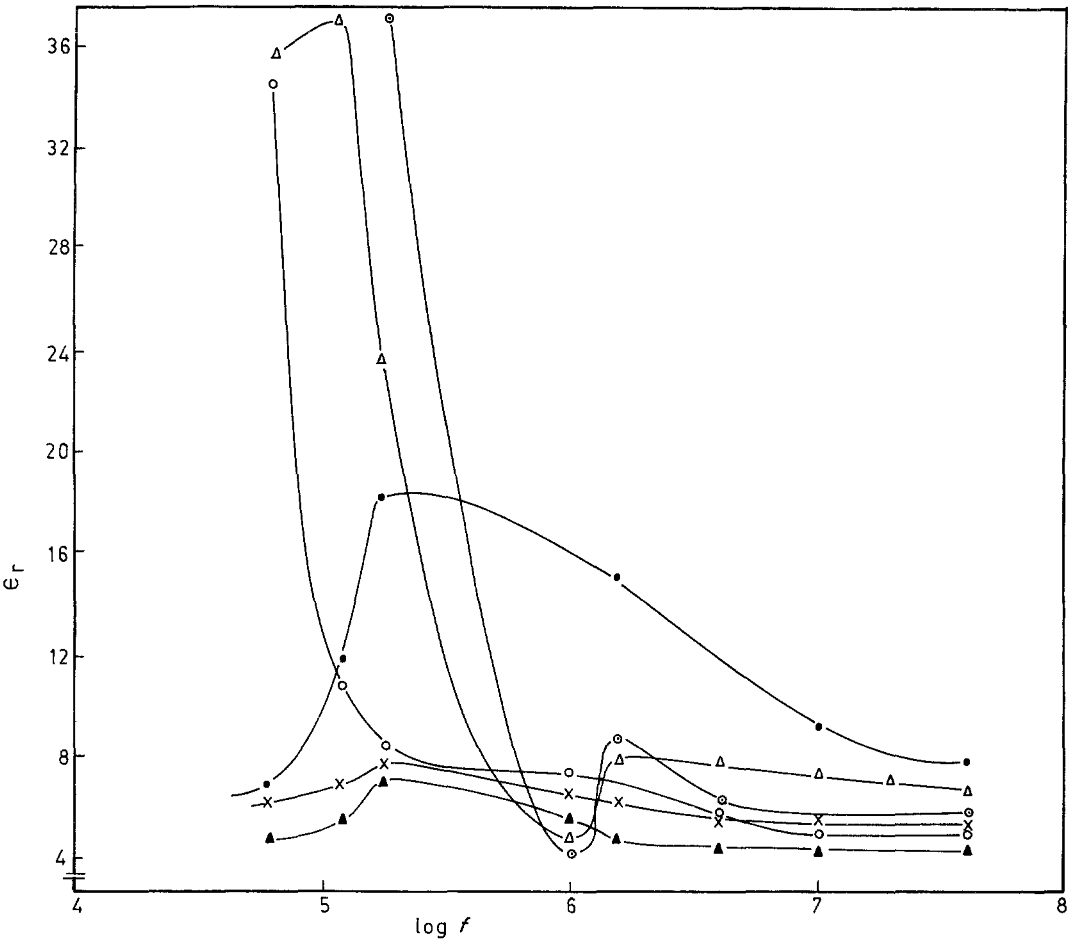

Figure 4 ε_r against log$f$ for $Cd_xCu_{1-x}Fe_2O_4$ system quenched at 800° C. x = (⊙), 0.0, (▲) 0.2, (x) 0.4, (△) 0.6, (○) 0.8, (●) 1.0.

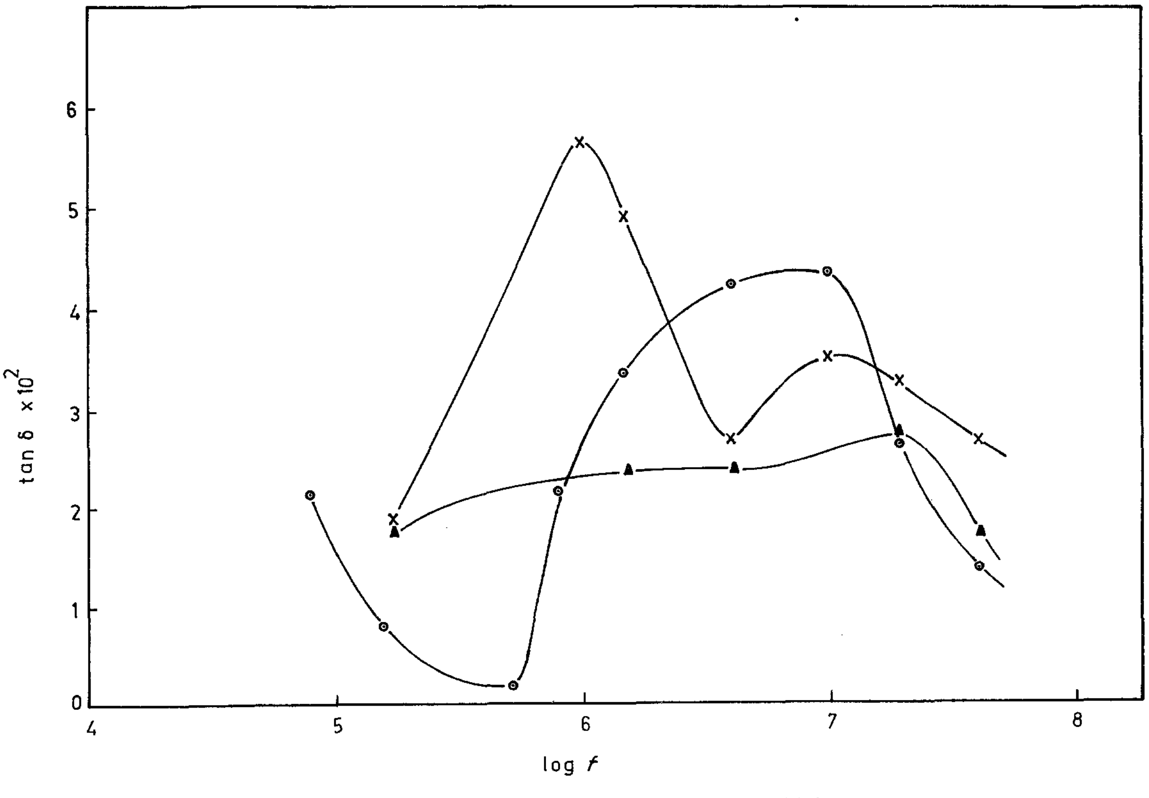

Figure 5 tanδ against log$f$ for slow-cooled $Cd_xCu_{1-x}Fe_2O_4$ system. x = (⊙) 0.0, (▲) 0.2, (x) 0.4.

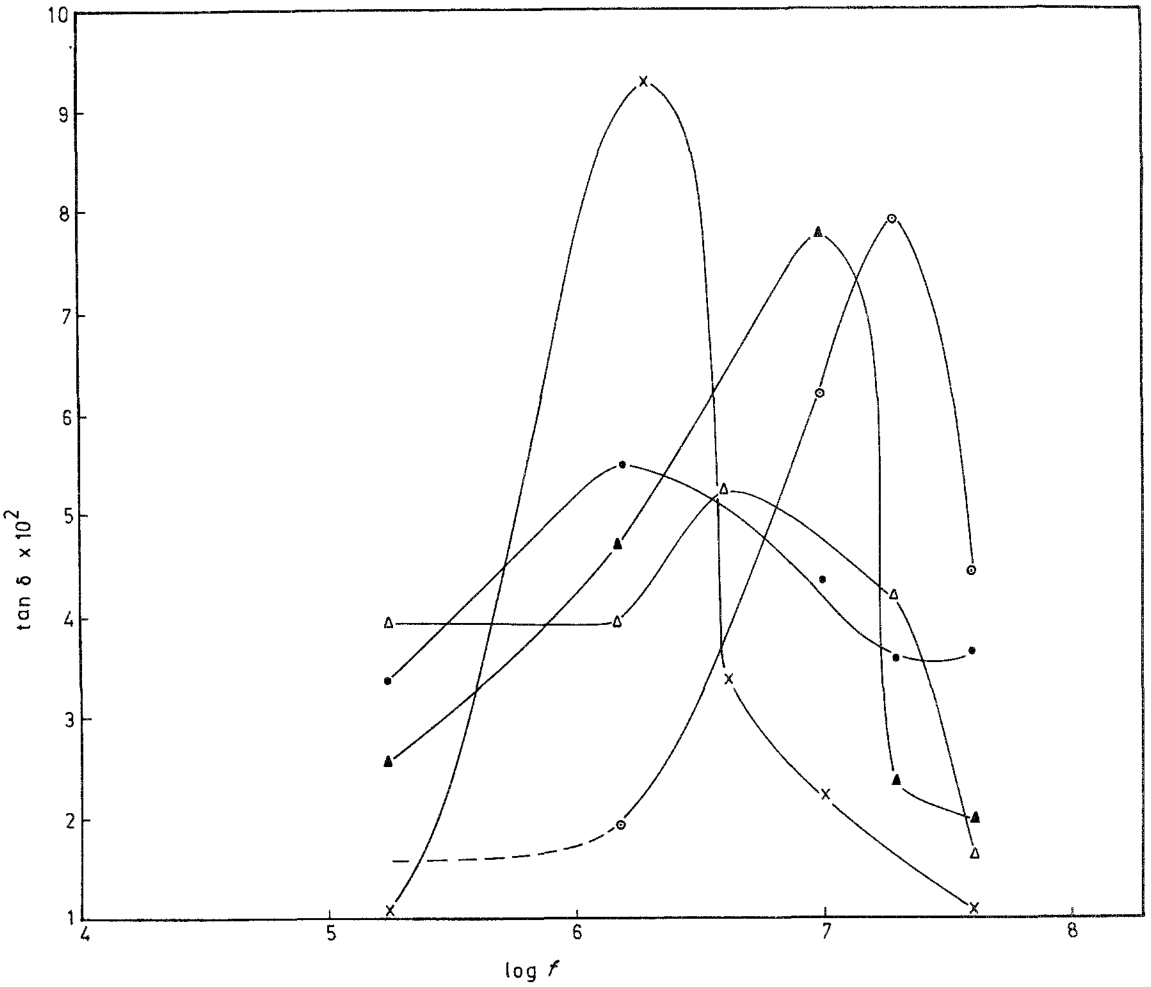

Figure 6 tanδ against log*f* for $Cd_xCu_{1-x}Fe_2O_4$ system quenched at 400° C. x = (⊙) 0.0, (▲) 0.2, (x) 0.4, (△) 0.6, (●) 1.0.

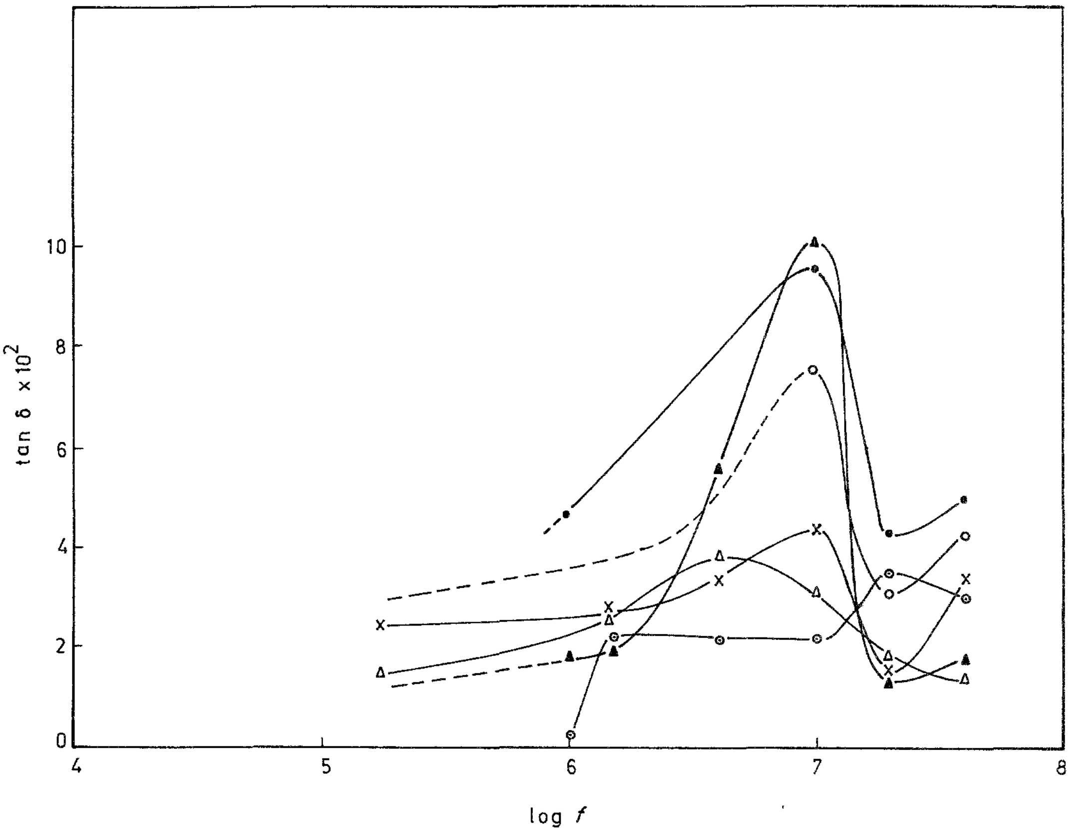

Figure 7 tanδ against log*f* for $Cd_xCu_{1-x}Fe_2O_4$ system quenched at 600°C. x = (⊙) 0.0, (▲) 0.2, (x) 0.4, (△) 0.6, (○) 0.8, (●) 1.0.

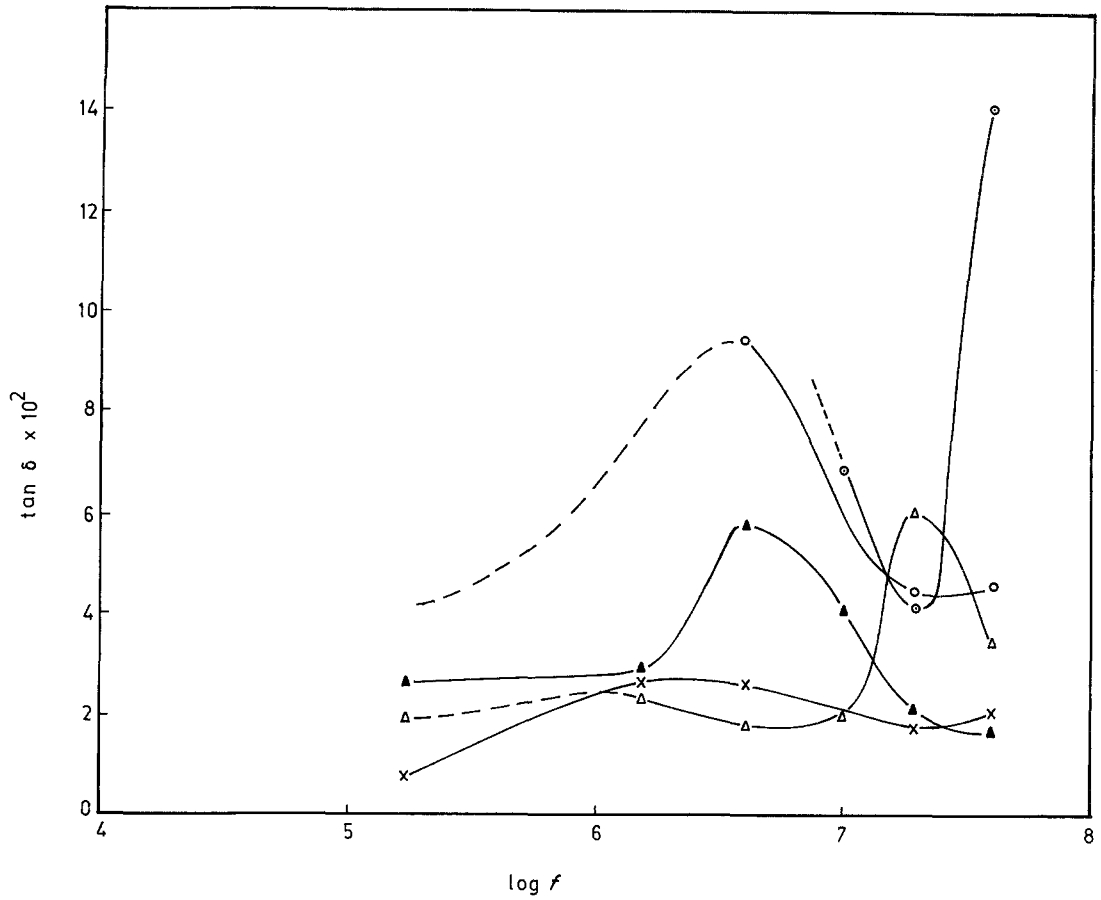

Figure 8 tanδ against log$f$ for $Cd_xCu_{1-x}Fe_2O_4$ system quenched at 800°C. x = (⊙) 0.0, (▲) 0.2, (x) 0.4, (△) 0.6, (○) 0.8.

attributed it to the existence of the Cu^+ ion, which happens to be common to all the systems they studied. The possibility of the reduction of Cu^{2+} to Cu^+ in the process of preparation of copper-containing ferrites could probably have influenced the behaviour of these compounds. The effect of the above-mentioned reduction and the presence of Cu^+ ions is to give p-type conductivity to these materials, and therefore the abnormal behaviour that is found in the system under investigation could be attributed to p-type conduction.

In fact, in spinel ferrites one can expect that with increasing frequency, ε_r should go on decreasing, which is rather a normal behaviour. However, to explain the abnormal dielectric behaviour of ferrites containing copper, one can say that the mechanism of the polarization process in ferrites is similar to that of the conduction process [10]. By the electronic exchange $Fe^{2+} \rightleftharpoons Fe^{3+}$, one obtains local displacements of electrons in the direction of the applied electric field, which in turn determines the polarization in the ferrites.

In general, all the compositions of the Cu–Cd system, either slow-cooled or thermally treated, exhibit an abnormal behaviour of the a.c. parameters ε_r and tanδ. This particular behaviour could be explained under the assumption that in the polarization process of the ferrites containing copper, two types of carrier (n and p) take part, and further the appearence of p-carriers is due to $Cu^{2+} \rightleftharpoons Cu^+$ exchange that takes place in these ferrites.

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