CHAPTER - III

ELECTRICAL PROPERTIES

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ELECTRICAL PROPERTIES

SECTION : A : D.C. CONDUCTIVITY :

3.1 INTRODUCTION :

The electric and magnetic properties of a ferrites are highly dependent on physicochemical history and chemical composition, which have some sort of relation on the mechanism of charge transport. The mechanism of charge transport can fairly be understood from measurements of electrical conductivity, thermoelectric power, Hall coefficient and magneto-resistance.

Ferrites have wide spectrum of room temperature resistivity varying over range 10^{-3} ohm-cm to 10^{11} ohm-cm. They are semiconductors[1] in nature. The magnetic behaviour of ferrites is largely affected by the magnitude of conductivity. This has created a considerable interest in the study of electric cnductivity of ferrites[2,3,4].

Low resistivity in magnetite is attributed to simultaneous presence of Fe^{2+} ions and Fe^{3+} ions situated on crystallographically equivalent sites.[5] Oxides having sufficient concentration of metal ions in different valence state on crystallogrphically equivalent site require less activation energy and gives information on their low resistivity. The room temperature resistivity of iron rich ferrites[6] and Lanthanum magnetite[7] is as low as 10^{-2} ohm-cm. In such cases the transition from semiconducting to pseudometallic state can occur near the magnetic transformation temperature.

The comparison of conductivity versus temperature studies below the Curie temperature, with high paramagnetic region gives the relationship between spin alignment and electric conduction. The transport properties of many magnetic oxides are unaffected by spontaneous magnetisation. Certain oxides exhibit marked change in log ρ versus 1/T relationship, while Fe_3O_4 undergoes semiconductor to metal transition.[8] The breaks and discontinuities in log ρ versus 1/T plots for many ferrites have been observed by Komer et al[9] and Verwey et al[5]. Van Uitert et al[10] have reported effect of surface grinding on resistivity of Ni-Zn ferrites. They attributed the observed reduction in resistivity to volatisation of zinc during heat treatment, encouraging the formation of Fe^{2+} ions on the surface. Resistivity in ferrites is markedly influenced by cation distribution, crystal structure, grain size, chemical and oxidation state and varied scattering mechanisms.

Recently, Klinger[11] has reviewed the conduction mechanism by pointing out that the hopping of polarons is the main process of conduction in ferrites and suggested two phase mechanism for hopping of polarons. The conduction in ferrites is due to exchange of electrons from Fe^{2+} to Fe^{3+} ions on octahedral sites by hopping mechanism.

3.2 CONDUCTION MECHANISM :

Ferrites are semiconducting oxide magnetic materials. The resistivity of ferrites decreases with increase in temperature in accordance with relation,

$$\rho = \rho_0 \exp (\Delta E/kT)$$

Where ρ - Resistivity at temperature $T^{O}K$

ρ_c - Resistivity at 0^0C or ($T=273^{O}K$) which is temperature independent and depend on nature of material.

ΔE- Activation energy, the energy required to causes an electron jump from one iron to the other.

k - Boltzmann's constant

T - The absolute temperature.

Presence of foreign atom in solid solutions in matrix metal causes drastic changes in resistivity. The resistivity of ferrite can be altered by addition of small amount of foreign oxide to the system provided added ion has differents valency than iron. conduction mechanism has been explained either applying the carrier hopping model as sugggeted by Verwey, Hielman[12] or on the basis of band picture. In general the oxide crystal structure may conviniently be represented in terms of oxygen ions with relatively small number of metal ions occupying interstitial positions. though the bonding in transition metal oxides is mainly ionic, the electrical conductivity is determined solely by the electrons with d like wave function and impurity states. The conduction in ferrite is related to d electrons The exciton exchange between Fe^{+2} ions and Me^{+2} ions is neglected due to small tunneling amplitude of d electrons.

In a stoichometric compound the ferrous ion is created by thermal activation according to relation

$$Me_B^{+2} + Fe_B^{+3} \rightleftharpoons Me_B^{+3} + Fe_B^{+2} + E_g$$

Where B - octahedral sites

Me - divalent metal ions such as Ni,Cu,Mn,Mg etc.

E_g - Activation energy required to transfer electrons from Me_B^{+2} to Fe_B^{+3}

e.g. In stoichometric Nickel ferrite, (there is some tendency for valency changes) with Ni on octahedral sits of spinel structure,

$$Ni^{+2} + Fe^{+3} \rightleftharpoons Ni^{+3} + Fe^{+2}$$

3.3 CONDUCTION IN OXIDES :

For an oxide of composition of MeO, the activation of conduction electron can be represented by,

$$O^{2-}\ Me^{2+}\ O^{2-} Me^{2+} O^{2-} \rightarrow O^{2-} Me^{1+} O^{2-} Me^{3+} O^{2-}$$

where Me is divalent transition metal ion.

The energy needed for the relation of ion pairs Me^{3+} and Me^{1+} corresponds to a gap in the density of states. The terms contributing activation energy are :

1) The difference between ionisation energy and the electron affinity of free Me^{2+} ion.
2. The difference in maedelung energy of the two configuration ($Me^{3+}Me^{2+}$) and ($Me^{3+}Me^{1+}$).
3. The difference in crystal field stabilisation energy of the above configuration.
4. Energies of polarisation of surrounding crystal lattice.

3.4 CONDUCTION IN FERRITES :

The above mechanism of electron transport is not applicable to those simple ferrites in which Fe ions are trivalent. The electron transport in these ferrites may be represented by,

$$Me^{2+}\ O^{2-}Fe^{3+} \rightleftharpoons Me^{3+}\ O^{2-}Fe^{2+} + Eg$$

where Eg is activation energy and is the difference between third ionisation potential of Fe^{3+} and Me^{3+} ions in solid. Jonker[13] studied the ferrite $Co_xFe_{3-x}O_4$ and quantitatively predicted above stated mechanism.

The effect of impurities on electrical properties of ferrite (ionic crystal) can be understood to some extent from ionic state of ionic cations. The ionisation potential of O^{2-} ions is a dominant term. The substitution of 1% or so of the cations of another element of the same valency have little effect upon conductivity. If the dopant has higher valency, it will contribute donor centers. If the dopant has lower valency, it will provide acceptor centers.

Analogous consideration may apply to cations of mixed valency in ferrite, which result from the ideal metal to oxygen ratio. An oxygen ion valency will contribute two extra electrons to 3-d band. If these extra charges are detatched from these vacacies by thermal agitation, n-type conductivity is induced in oxygen deficient and p-type conductivity in oxygen excess materials. Some oxides are very difficult to prepare homogeneously with stoichiometric anions to cation ratio. Extrinsic semiconductor may then prevail throughout the temperature region amenable to electrical measuremet. Van Uietert[10] demonstrated that, activation energy of intrinsic conduction samples from which extrinsic effects have been suppressed, by introducing an impurity i.e. replacing 1 to 2 % Fe by Mn or Co. Eectrons donated by oxygen vacancies will fill impurity level in preferrence to iron conduction levels. Mixed valence state will be confined to impurity element, if its local concentration exceed twice that of oxygen vacancies. This technique is based on assumption that impurity band conduction is absent and allowed impurity concentration indicate that cation wave function do not extend significantly beyond nearest neighbouring distances in B lattice. The electrons and holes are known to move by thermally activated hopping mechanism except for pseudometallic composition region close to magnetite. By applying Van Uietert's consideration, Elwel et al[14] have calculated intrinsic activation energy for materials prepared under different oxidation conditions.

3.5 ELECTRON HOPPING AND POLARON :

An electron in crystal lattice interacts through its electric charge with surrounding ions or atoms of crystal lattice. This electrostatic interaction between an electron and ion create a local deformation of lattice. The deformation follows the electron, as electron moves through the lattice. The combination of an electron with its strain field is known as polaron.

The electrostatic interaction between electron and its neighbouring ion, result in polarisation of surrounding region, such that carrier is situated at the centre of a polarisation potential well. If this well is deep enough, a carrier may be trapped at a lattice site and translation to a neighbouring site may be determined by thermal activation. This has been explained by hopping mechanism. The electron takes part in diffusion process by jump from one lattice site to the other.Heikes and Johnston[15] have derived expression for mobility of charge carrier during the hopping mechanism as,

$$\mu = \frac{e^2 a^2 \nu_o}{kT} \exp (- q/kT)$$

where a - distance between nearest neighbouring cations.

ν_o - freqency of vibration of crystal lattice

q - activation energy.

If a potential well exeeds over many lattice units in a crystal, the excess charge may be considered to interact with a dielectric continum. This model was employed by Frolich[16] for formulation of interaction Hamiltonian for large polarons. A small polaron is being considered to behave as a particle moving in a very narrow band at low temperature. At high temperature, small polaron motion may result from the obsorption of one or more phonons leading to the hopping mechanism.

There is a strong experimental evidence for existence of small polarons and for hopping process[17,18]

3.6 CONDUCTIVITY :

Because of semiconducting behaviour of ferrite, conduction mechanism can be understood in terms of electrons and holes. Electrons are common charge carriers in almost all semiconductors. The electron deficiency is called as a hole and behaves as a positive charge. The conductivity in ferrites can be written as,

$$\sigma = e\,(n_e \mu_e + n_h \mu_h)$$

where e - charge of an electron

n_e - concentration of mobile electrons

n_h - concentration of mobile holes

μ_e - mobility of electrons

μ_h - mobility of holes

The temperature dependence of conductivity is expressed as,

$$\sigma = \sigma_o \exp\,(-E_g/kT)$$

where σ_0 - temperature independent constant.
E_g - Activation energy
T - Absolute temperature
k - Boltzman constant.

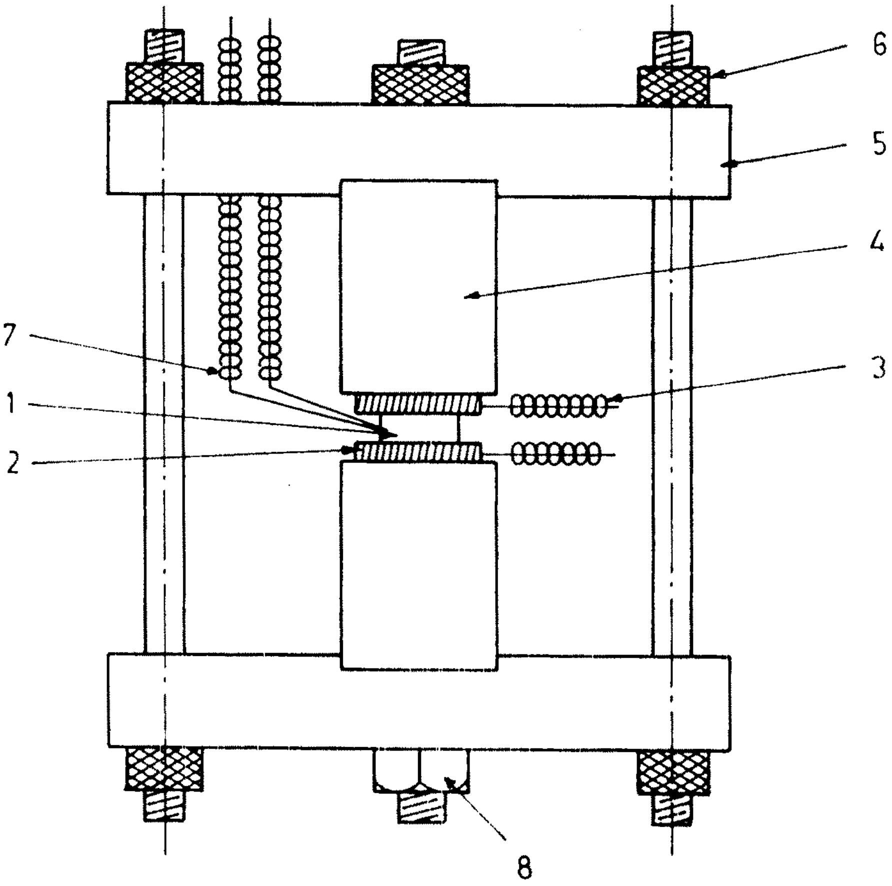
3.7 EXPERIMENTAL

The D.C. conductivity measurements were made by using a conductivity cell (Fig. 3.1) specially designed and fabricated by departmental workshop.

The conductivity cell consist of two cylindrical brass electrodes fitted in porcelain discs. The (pellet) was sandwitched between the electrodes with the help of connecting rods, provided with nuts. For good electrical contact two silver discs of about 1.5 cm diameter and 0.5 mm thickness were placed on either sides i.e. top and bottom side of the pellet. The porcelain discs were tightly held by three screws symmetrically situated along their periphery to ensure uiform pressure and good electrical contact between silver foil and pellet. The electrically insulated copper wires were used for external connections.

The entire assembly was then kept in temperature regulated furnace. The furnace temperature was then slowly increased. The caliberated Chromel-Alumel thermocouple was used to sense the temperature. Digital multimeters were used for precise measurements of currents and voltages. The electrical conductivity measurements were carried out in the range from $25\,^{\circ}$C to 600°C for the

Fig. 3·1a – THE CONDUCTIVITY CELL



1– Ferrite specimen (pellet), 2 – Silver discs, 3 – Silver wires with porcelin beads, 4 – Brass cylinders, 5 – Porcelin discs, 6 – Holding screws, 7 – Chromel Alumel thermocouple, 8 – Screws holding the brass blocks to porcelin discs.

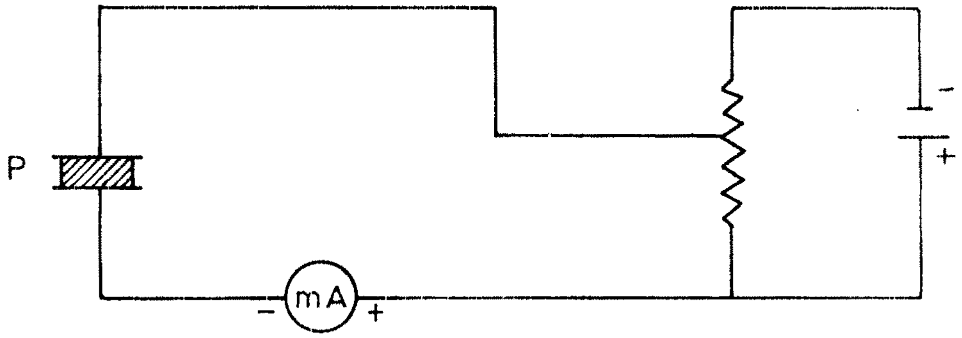


Fig3·1b–Sample holder and circuit diagram for electrical resistivity.

Fig. 3·1

following systems (i) Co_xZn_{1-x} Fe_2O_4(undoped) (ii) $Co_xZn_{1-x}Fe_2O_4$ doped with 0.05 At wt % of Al doped with 0.05 mol wt. % of $Gd_2\ O_3$ where X = 0,1.0 , 0.3, 0.5, 0.7,

The resistivity was calculated by using the formula

$$\rho = \frac{RA}{t}$$

R = V/I and

$A = \pi r^2$ where r is radius of pellet

t = thickness of pellet.

$$\rho = (\ V/I)[(\pi r^2)/(t)]$$

The graphs of log ρ → $10^3/T$ were plotted. From these plots, Curie temperature and activcation energy in paramagnetic and ferrimagnetic regions were determined.

The graphs of log ρ versus $10^3/T$ are plotted in Fig.3.2, 3.3 and Fig. 3.4 for the samples in undoped series and the samples in the series doped with (Al and Gd_2O_3) Aluminium & Gadolinium oxides

3.8 RESULTS AND DISCUSSION :

These graphs exhibit a linear relationship throughout the temperature range suggesting that resistivity obeys the relation,

$$\rho = \rho_o \exp\ (\Delta\ E/kT)$$

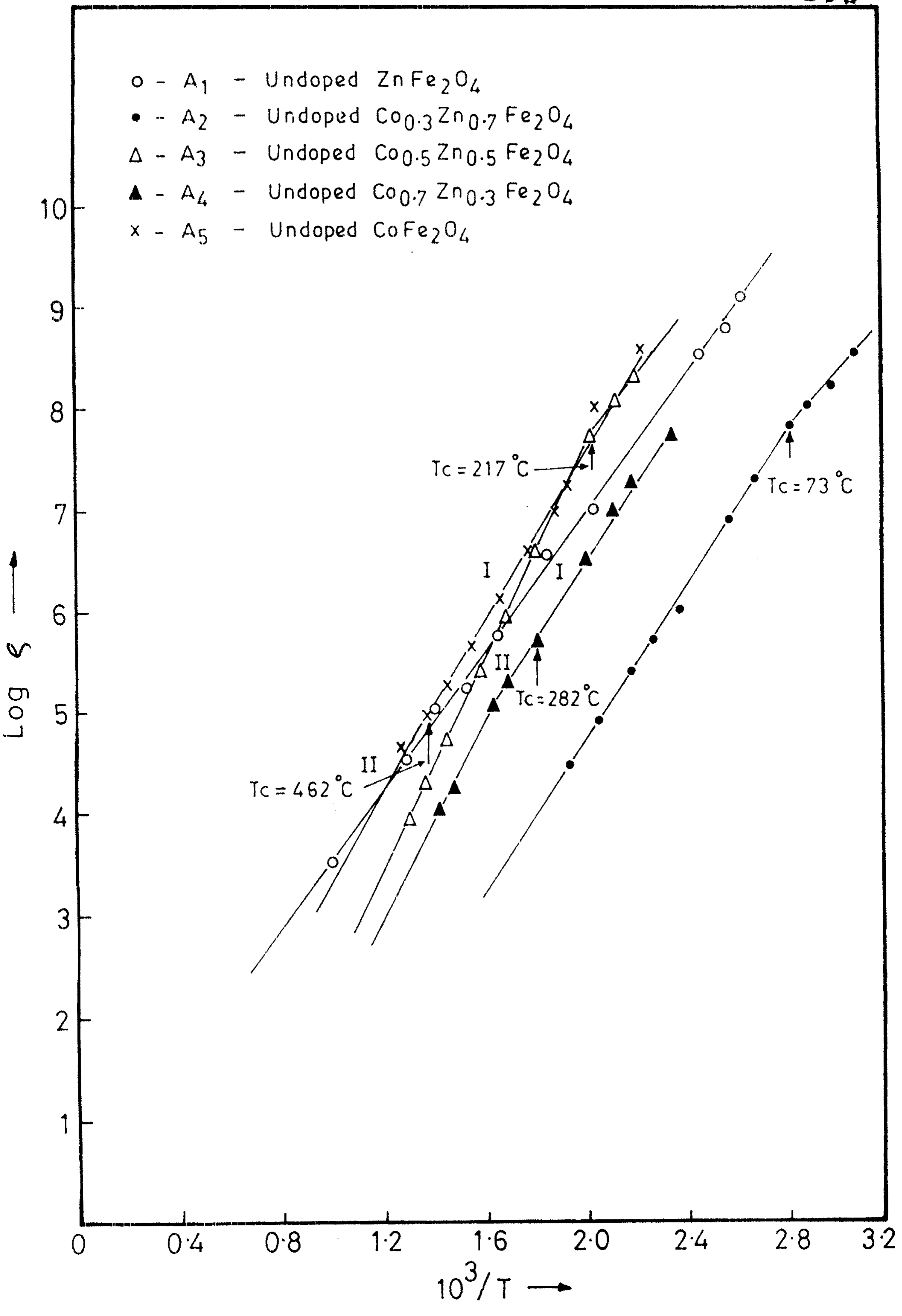

○ - A_1 - Undoped $ZnFe_2O_4$
● - A_2 - Undoped $Co_{0.3}Zn_{0.7}Fe_2O_4$
△ - A_3 - Undoped $Co_{0.5}Zn_{0.5}Fe_2O_4$
▲ - A_4 - Undoped $Co_{0.7}Zn_{0.3}Fe_2O_4$
x - A_5 - Undoped $CoFe_2O_4$
Tc = 217 °C
Tc = 73 °C
Tc = 282 °C
Tc = 462 °C
I
I
II
II
Log ϱ
$10^3/T$
0
0·4
0·8
1·2
1·6
2·0
2·4
2·8
3·2
1
2
3
4
5
6
7
8
9
10

Fig. 3·2

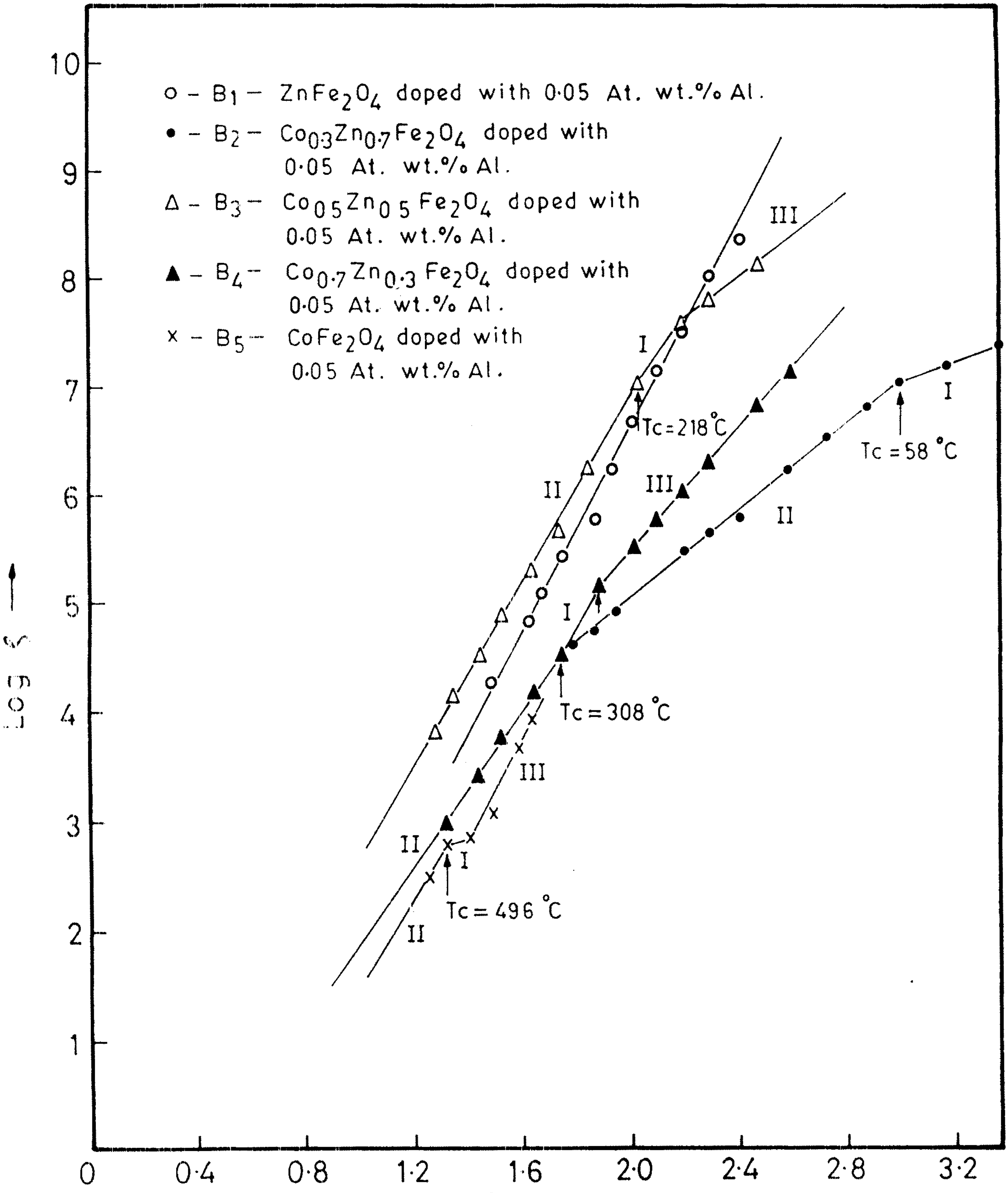

○ – B1 – $ZnFe_2O_4$ doped with 0·05 At. wt.% Al.
● – B2 – $Co_{0.3}Zn_{0.7}Fe_2O_4$ doped with 0·05 At. wt.% Al.
△ – B3 – $Co_{0.5}Zn_{0.5}Fe_2O_4$ doped with 0·05 At. wt.% Al.
▲ – B4 – $Co_{0.7}Zn_{0.3}Fe_2O_4$ doped with 0·05 At. wt.% Al.
× – B5 – $CoFe_2O_4$ doped with 0·05 At. wt.% Al.
Tc=218°C
Tc = 58 °C
Tc = 308 °C
Tc = 496 °C
I
II
III
Log ρ
$10^3/T$
0
0·4
0·8
1·2
1·6
2·0
2·4
2·8
3·2
1
2
3
4
5
6
7
8
9
10

Fig. 3·3

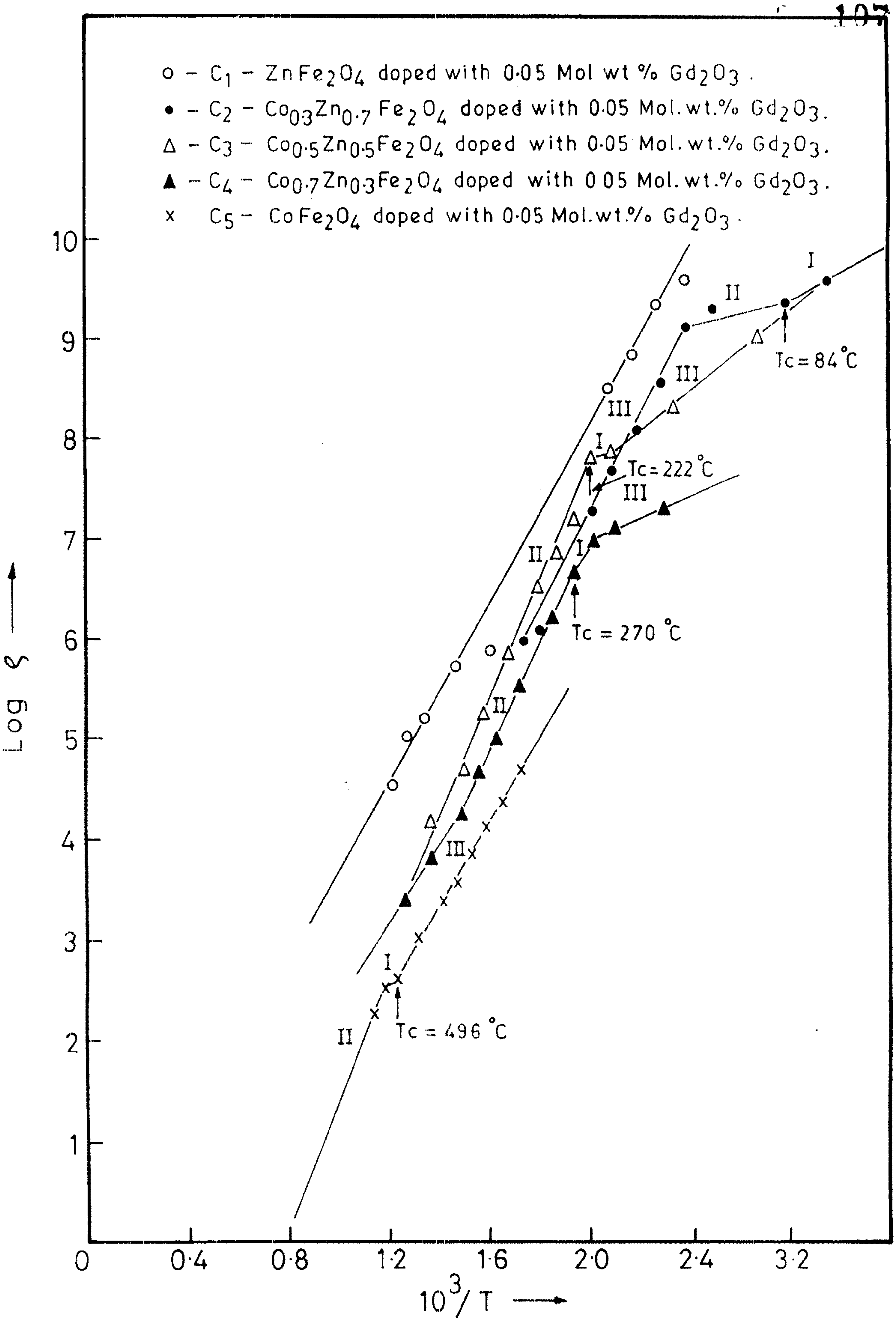

○ – C_1 – $ZnFe_2O_4$ doped with 0·05 Mol wt % Gd_2O_3 .
● – C_2 – $Co_{0.3}Zn_{0.7}Fe_2O_4$ doped with 0·05 Mol.wt.% Gd_2O_3.
△ – C_3 – $Co_{0.5}Zn_{0.5}Fe_2O_4$ doped with 0·05 Mol.wt.% Gd_2O_3.
▲ – C_4 – $Co_{0.7}Zn_{0.3}Fe_2O_4$ doped with 0·05 Mol.wt.% Gd_2O_3.
× C_5 – $CoFe_2O_4$ doped with 0·05 Mol.wt.% Gd_2O_3 .
Log ρ
10
9
8
7
6
5
4
3
2
1
0
0·4
0·8
1·2
1·6
2·0
2·4
3·2
$10^3/T$
I
II
III
Tc = 84 °C
Tc = 222 °C
Tc = 270 °C
Tc = 496 °C

Fig. 3·4

The activation energies are calculated for various regions of the graph and are reported in Table 3.1. From Fig.3.2 it can be clearly seen that the resistivity plots have two distinct region with a single break. The temperature at the break also known as transition temperatue nearly coincide with Curie temperature T_c of the respctive sample. The transition temperature is seen to be increasing with increase in cobalt content in the sample The values oobtained for T_c and the trend of T_c to increase with cobalt content are in good agreement with the earlier reported observations.[40]

Komar and Klivshin[19] have observed the changes in slopes of conductivity plots near Curie temperature. They have attributed this change to magnetic transition i.e. from paramagnetism to ferrimagnettism. Verwey[5] et al have also observed such breaks in Mn-Zn ferrites Irkhin and Turov[20] have praposed a theoretical explanation for existence of kinks at the Curie temperature. They havve concluded that the activation energy and effective mass of current carrying excitons in the intrinsic semiconductor depend on the spontaneous magnetisation.This leads to an additional temperature dependence of electrical resistance which is sharp near the Curie temperature. The kink is most marked for those case in which there is strong exchange interaction between the outer and inner electrons. The activation energy in paramagnetic region is higher than that in ferrimagnetic region. This is also in good agreement with the theory developed by Irkhin and Turov[2o] It is interesting to note that transition temperature increases continuously as the Cobalt content is increased. This is to be expected, since A-B interactions increase with icrease in Cobalt content, when higher percentage of Cobalt will be transferred to B site. Hence there is rise in the Curie temperature. Thus it can be seen that our observation and results and on d.c. conductivity measurements are in good agreement with those of earlier worker mentioned above.

The conductivity in ferrites has been associated with the presence of ions of given element in more than one valence state and these ions get distributed over the crystallographically equivalent sites. e.g. high conductivity of Fe_3O_4 is associated with transition of electron $Fe^{3+} \rightarrow Fe^{2+}$. The values of ΔE to cause normal electron hopping are of the order of 0.2 eV and less.[21] The high values of ΔE for our samples suggest that hopping process is favoured due to polarons.

In ferrites the conduction mechanism is explained on the basis of hopping of polarons due to thermal activation.[11]

Petitt and Forester[22] investigated the Mossabaur effect in Co-Zn ferrites and derived the following cation distribution formula

$$(Zn_x\ Fe_{1-x-y}Co_y)\ [\ Co_{1-x-y}Fe_{1+x+y}]O_4$$

where the brackets denote tetrahedral (A sites) and square brackets denote octahedral sites (B sites). It should be noted that cobalt occupies octahedral sites.[23] Therefore the conduction can take place in these ferrites as[24]

$$Co^{2+} + Fe^{3+} \rightleftharpoons Co^{3+} + Fe^{2+} + Eg$$

It has been shown that the lower temperature conductivity variation is attributed to $Fe^{3+} \rightarrow Fe^{2+}$, while the higher temperature conductivity to $Co^{2+} \rightarrow Co^{3+}$. For lowest concentrations of Cobalt $Fe^{3+} \rightarrow Fe^{2+}$ transition is responsible, whereas for higher concentration of cobalt $Co^{2+} \rightarrow Co^{3+}$ becomes equally dominant and hence overall value of activation energy is obtained. Thus the conductivity is arising due to hopping of electrons between Co^{2+} and Fe^{3+}.

The resistivity plots for Aluminium (Al) and Gadolinium oxide (Gd_2O_3) doped samples show three distinct regions and two breaks The transition temperature T_1 (1st break) nearly coincides with the Curie temperature for the samples.[25] Ghani et al[26] have observed three regions in temperature variation of resistivity in Cu-Ni ferrites. They have attributed the conduction mechanism in first region to the presence of impurity in the second region to the phase transition and in the third region the to magnetic disorder. From Table 3.1 it is clearly observed that the ΔE values are smaller in region I than in region II and region III. The first region is due to impurities or impurity phases which may play a role in conduction process in these materials. Similar results have been observed for Mn doped Ni-Zn[27], Cu-Co[28] mixed ferrites Li-Cu[29] mixed ferrite.

TABLE 3.1

VALUS OF ACTIVATION ENERGY (eV)

Series	Composition	Activation Energy eV			T_c
		I Region	II Region	III Region	conductivity
A	$Co_{0.3}Zn_{0.7}Fe_2O_4$	0.5461	0.745	-	79
	$Co_{0.5}Zn_{0.5}Fe_2O_4$	0.587	0.993	-	217
	$Co_{0.7}Zn_{0.3}Fe_2O_4$	0.640	0.820	-	282
	$Co_{1.0}Zn_{0.0}Fe_2O_4$	0.794	0.819	-	462
B	$Co_{0.3}Zn_{0.7}Fe_2O_4$	0.175	0.386	-	58
	$Co_{0.5}Zn_{0.5}Fe_2O_4$	0.331	0.662	0.807	218
	$Co_{0.7}Zn_{0.3}Fe_2O_4$	0.546	0.894	0.993	308
	$Co_{1.0}Zn_{0.0}Fe_2O_4$	0.621	0.621	0.795	496
C	$Co_{0.3}Zn_{0.7}Fe_2O_4$	0.221	0.999	0.894	84
	$Co_{0.5}Zn_{0.5}Fe_2O_4$	0.099	0.993	0.382	222
	$Co_{.7}Zn_{0.3}Fe_2O_4$	0.083	0.851	0.248	270
	$Co_{1.0}Zn_{0.0}Fe_2O_4$	0.497	0.994	0.791	486

NOTE : Series A undoped $Co_xZn_{1-x}Fe_2O_4$ ferrite system

Series B doped series $Co_xZn_{1-x}Fe_2O_4$ doped with 0.05 At.Wt.% Al.

Series C doped series $Co_xZn_{1-x}Fe_2O_4$ doped with 0.05 mol.Wt.% Gd_2O_3

However, the resistivity also depend on following factors :

1. Sintered polycrystalline sample contain pores. The pores are probably air filled and have resistivity different from ferrite itself
2. The grain size of individual crystallite in a polycrystalline sample can affect grain to grain contacts, thus influence conduction path as well as resistivity.
3. The chemical and/ or heat treatment may result in chemical inhomogenity.

SECTION : B : A.C. CONDUCTIVITY :

3.9 INTRODUCTION :

The d.c. resistance of a polycrystalline specimen is not necessarily indicative of conduction mechanism in bulk of material unless it is accompanied by a.c. measurements. This conclusion is derived from the work of Koops[30].

Ferrites show abnormally high dielectric constant and dispersion of dielectric constant and resistivity[31]. In case of polycrystalline materials, the dielectric constant is frequency dependent.[32,33] Blechstein[34] observed very high dielectric constant in case of Mn ferrites. Brodaman, Dowling, Steneck[35] also found high dielecric constants of the order of 10^5 in case of Mn-Zn ferrites. Koops[30] obtained the dielectric constant and resistivity characteristics of ferrite itself by extrapolating measurements to high frequencies. Koops explained the dispersion by considering the ferrite compact as a multilayer condenser in which ferrite grains and grain boundaries with different properties.

Dielectric properties of copper containing ferrites were investigated Rezlescu et al[36]. Josyulu and Sobhanadri[37] have studied dielectric behaviour of Co-Zn, Mg-Zn ferrite system as a function of temperature and frequency. They attributed the dielectric behaviour in such systems to the Maxwell[38]– Wagner[39] polarisation. Murthy and Sobhnadri[40] has investigated dielectric proprties of Ni-Zn ferrites in frequency range 10^2Hz to 10^5Hz. Ramanamurthy[41] studied dielectric properties of mixed ferrites of Co-Zn and established dependence of dielectric properties on composition and temperature. K. Iwauchi[42] obtained strong correlation between conduction phenomenon and dielectric dispersion in ferrite. In this chapter an attempt is made to present a.c. electrical properties of the mixed Co-Zn ferrite system undoped and doped with Aluminium and (Gd_2O_3)Gadolinium oxide. The parameters such as dielectric constant (ε') loss tangent ($\tan\delta$), and conductivity have been determined at various frequencies in the range of 10^2Hz to 10^7 Hz.

3.10 ALTERNATING ELECTRIC FIELD AND COMPLEXITY OF DIELECTRICS :

When an alternating electric field of the form $E = E_0 e^{i\omega t}$ is applied to a material, the response is not completely instantaneous due to which dielectric constant become complex in nature. The dielectric displacement is given by,

$$D = \varepsilon^* E$$

where $\varepsilon^* = \varepsilon' - i\,\varepsilon''$

ε' is a real part of dielecric constant.

ε'' is an imaginary part of dielectric constant.

For small valus of phase angle,

$$\tan\delta = \varepsilon''/\varepsilon'$$

ε' and ε'' are dependendent on frequency and time, in accordance with following relation.

$$\varepsilon^* = [\,\varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 T^2}\,] + i\,[\,\frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 T^2}\,]\omega T$$

with

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 T^2}$$

$$\varepsilon'' = \left(\frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 T^2} \right) \omega T$$

where ε_s - low frequency dielectric constant

ε_∞ - high frequency dielectric constant

ω - Angular frequency

T - relaxation time.

The loss tangent is therefore, given by,

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon_s - \varepsilon_\infty)\, \omega T}{(\varepsilon_s + \varepsilon_\infty \omega^2 T^2)}$$

The above equations for ε' and ε'' represent Debye's equations. The plots of ε', ε'' and $\tan \delta$ as a function of frequency explore the dielectric properties of material.

3.11 POLARISATION IN DIELECTRICS :

The transformation of an electrically neutral system of charges into system having a dipole moment, is called polarisation. When A.C. electric field is applied across a ferrite material, polarisation is induced in it. The total polarisation P of a multiphase material having permanent dipoles is given by,

$$P = P_e + P_i + P_o + P_s$$

where P_e - Electronic polarisation.

P_i - Ionic polarisation.

P_o - Oriental polarisation.

P_s - space charge or interfacial polarisation.

The interfacial polarisation plays significant role in ferrites as is explained by Maxwell[9] and Wagner.[10]

3.12 MAXWELL-WAGNER DIELECTRIC ABSORPPTION :

The dissipation of energy can occur by scattering of radiation on interfacial boundaries in a nonhomogeneous material. The nonhomogeneous dielectric may contain regions of different permittivity because of cracks and defects in solids. This gives misleading values of permittivity. If some part of medium is conducting, apparent dielectric relaxation may be expected. This is well recognised in visible region of transparent medium, when the distribution of small particles of second materal can make it opaque. Similar feature arises in a dielectric medium, when the particles of second phase are dispersed within principle one. The general effect of this absorption were evaluated by Wagner[10] and the dielecctric effect is referred to as Maxwell-Wagner absorption.

3.13 KOOPS THEORY :

Non conducting oxides, have dielectric constant in the range between ten and twenty. In case of ferrites, high dielectric constants are reported by several workers. To explain the abnormal behaviour regarding dispersion in dielectric constant and resistivity, observed in case of Ni-Zn ferrite, Koops gave a phenomeno-graphical theory. According to Koops' theory measured capacitance C_p and parallel resistancce R_p of specimen result from an equivalent circuit diagram The R_1, R_2, C_1, C_2 are constants, whereas R_p and C_p obey dispersion formula (Fig. 3.5). It can be proved that two capacitors and two resistors are needed to build two poles having a finite value of d.c. resistance showing typical tan $\delta \rightarrow \omega$ curve which has been found with material.

Sintered ferrite is not a homogneous material. It may be reasonably supposed that grains of ferrite are moderately good conductors and that the outer layers, the inter grain contact pores are high resistivity regions (Fig.3.6a). Then the in homogeneous dielectric structure is not unlike that discussed by Maxwell[9] and Wagner[10]. This is represented as double layer dielectric, where subscript 1 refers to the boundary layer and 2 refers to the ferrite grains (Fig.3.6b). The resistance R_2 and possible R_1 may contain contribution from dielectric losses in addition to a purely ohmic term.

Consider the specimen as a parallel plate capacitor of plate area A. Then,

$$C_1 = \frac{\varepsilon_0 \varepsilon_1 A}{d_1} \qquad C_2 = \frac{\varepsilon_0 \varepsilon_2 A}{d_2}$$

$$R_1 = \frac{\rho_1 d_1}{A} \qquad R_2 = \frac{\rho_2 d_2}{A}$$

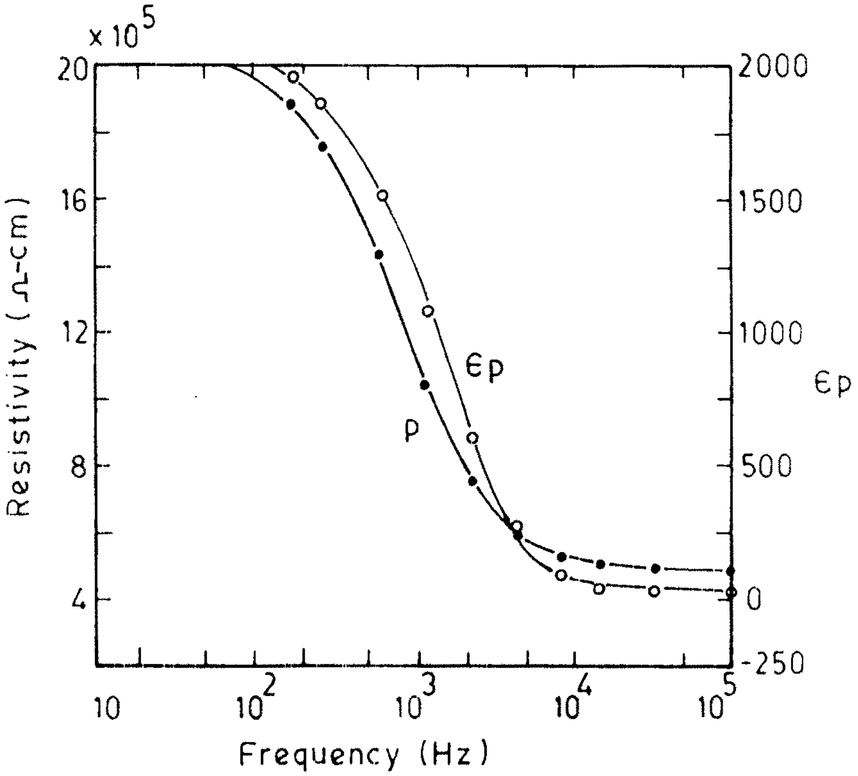


Fig. 3·5 a — Dispersion in resistivity and dielectric constant for a nickel-zinc ferrite.

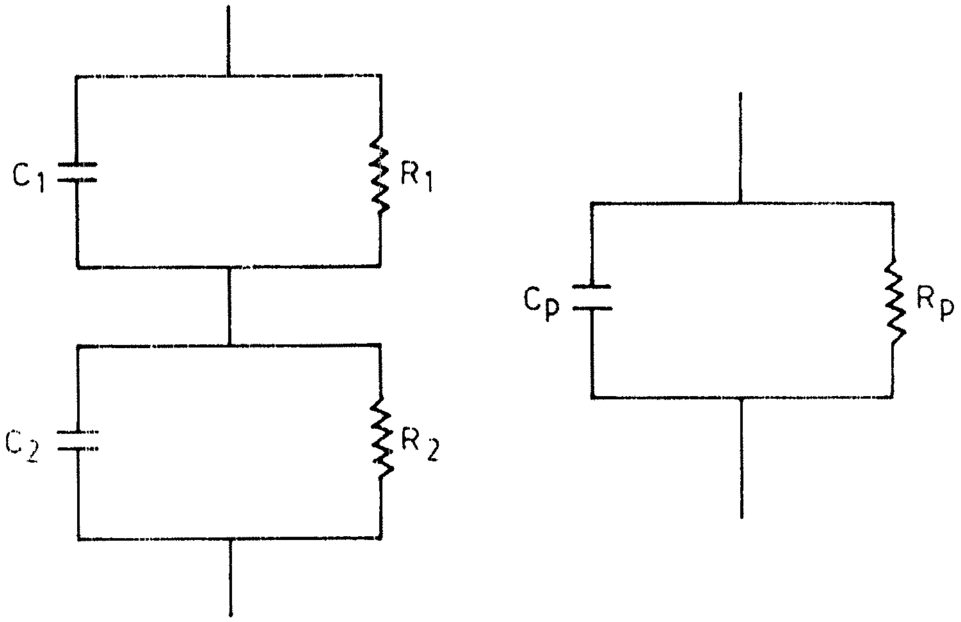


Fig. 3·5 b — If the two circuits are equivalent and C_1, C_2, R_1 and R_2 are constants then Cp and Rp are not constants with respect to frequency but obey dispersion formula.

Fig. 3·5

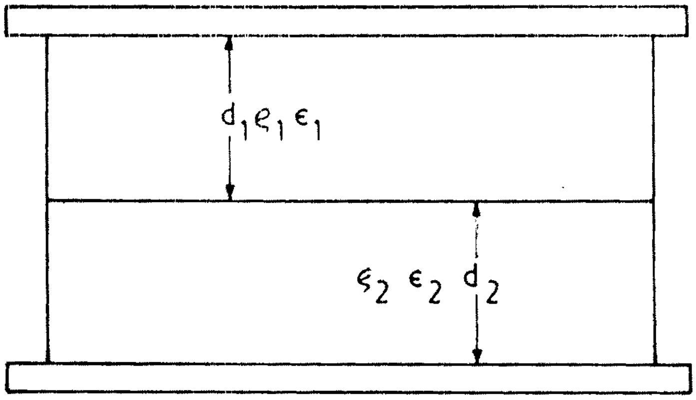


Fig. 3·6 a – Capacitor with double layer dielectric

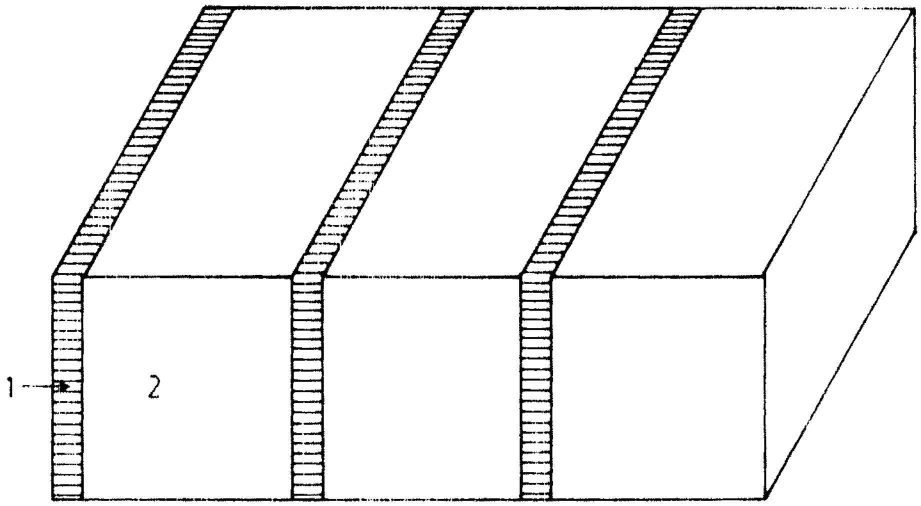


Fig.3·6b-Model of a grain structured conductor Layers of poorly conducting material saparate the grains.

Fig. 3·6

where $\varepsilon_0 \varepsilon$ is the permittivity and ρ the resistivity. It then follows by equating the impedences in two representaions of Fig.3.5b

$$\rho_p = \rho_p^{\infty} + [(\rho_0 - \rho_\infty)/ (1 + \omega^2 \tau_\rho^2)]$$

and

$$\varepsilon_p = \varepsilon_p^{\infty} + [(\varepsilon_0 - \varepsilon_\infty)/ (1 + \omega^2 \tau_\varepsilon^2)]$$

where ρ_p = parallel resistivity

ρ_p^{∞} = high frequency value of ρ_p

ρ_p^0 = low frequency value of ρ_p

τ_ρ = Relaxation constant of ρ_p

ω = frequency in radian persecond

ε_p = Apparent parallel dielectric permittivity

ε_p^0 = low frequency value of ε_p

ε_p^{∞} = high frequency value of ε_p

τ_ε = relaxation of constant of ε_p

The τ's are relaxation constant and $\omega = 2\pi\nu$ where ν is the measuring frequency. Koops made following assumptions :

i) $x = d_1/d_2 << 1$ i.e. ratio of thickness of layer to the thickness of grain is much smaller than unity.

ii) $\rho_1 >> \rho_2$ i.e. resistivity of layer (ρ_1) is greater than that of grains (ρ_2).

iii) Although x is small $x\rho_1 > \rho_2$ by resonable factor

iv) $\varepsilon_1 = \varepsilon_2$ i.e. Dielectric permittivity of layers = Dielectric permittivity of grains.

After omitting sideway admittances between the grains, with the help of common a.c. calculus he found that,

$$\rho_p \approx \rho_2 + [\, x\,\rho_1 / (1 + b\,\rho_1 \rho_2 \omega^2 / x)]$$

and,

$$\varepsilon_p \approx \varepsilon_2 + [\, (\varepsilon_2 / x) / (\, 1 + b\,\rho_2^2 \omega^2 / x^2) \,]$$

where b is a constant.

Thus at very high frequencies

$$\rho_p^{\infty} = \rho_2 \quad \text{and} \quad \varepsilon_p^{\infty} = \varepsilon_2$$

and at very low frequencies,

$$\rho_p = \rho_2 + x\,\rho_1 , \; \varepsilon_p = \varepsilon_2 + (\varepsilon_2 / x)$$

Hence in order to obtain value of ε and ρ which are characteristics of ferrite, the measurement should be extended and extrapolated to high frequencies. Koops found that the value of x of the order of 0.01 but in those cases where very low frequency dielectric constant of he order of 10^4 or 10^5 are found the above theory would suggest effective boundary layer to be of few Angstrom unit thick.

If the losses in capacitor are represented by a complex dielectric constant,

$\varepsilon = \varepsilon_p - i\,\varepsilon''$ instead of a parallel resistance then it follows that,

$$\varepsilon'' = 1.16 \times 10^{11} / \omega\rho_p$$

where ρ_p is in Ω - m.

The theoretically calculated frequency variation of ε and ρ are in some cases very similar to those experimentally measured.

3.14 EXPERIMENTAL :

The measurements of dielecric constant, loss tangent, resistivity and quality factor with variation in frequency are carried out by using Precision L.C.R. meter 4284 A. for frequency spectrum from 20 Hz to 1 MHz and precision L.C.R. meter 4275 A for frequency spectrum 10 KHz to 10 MHz . Both precision LCR meters are Hewlett Packard make.

All the measurements were done at room temperature. The samples used were in pellet form. For good ohmic contact, silver paste is applied to top and bottom surface of pellet. Pellet was pressed firmly in the sample holder which was supplied by manufacturer. The instrument was set for lower frequency to obtain constant value of R,C,Q and tan δ. Then each sample was scanned from 100 Hz to 10 MHz.

3.15 RESULTS AND DISCUSSION :

In Fig. 3.7 the variation of dielectric constant ϵ' at fixed frequency against the dopant is shown. It is clearly seen that the

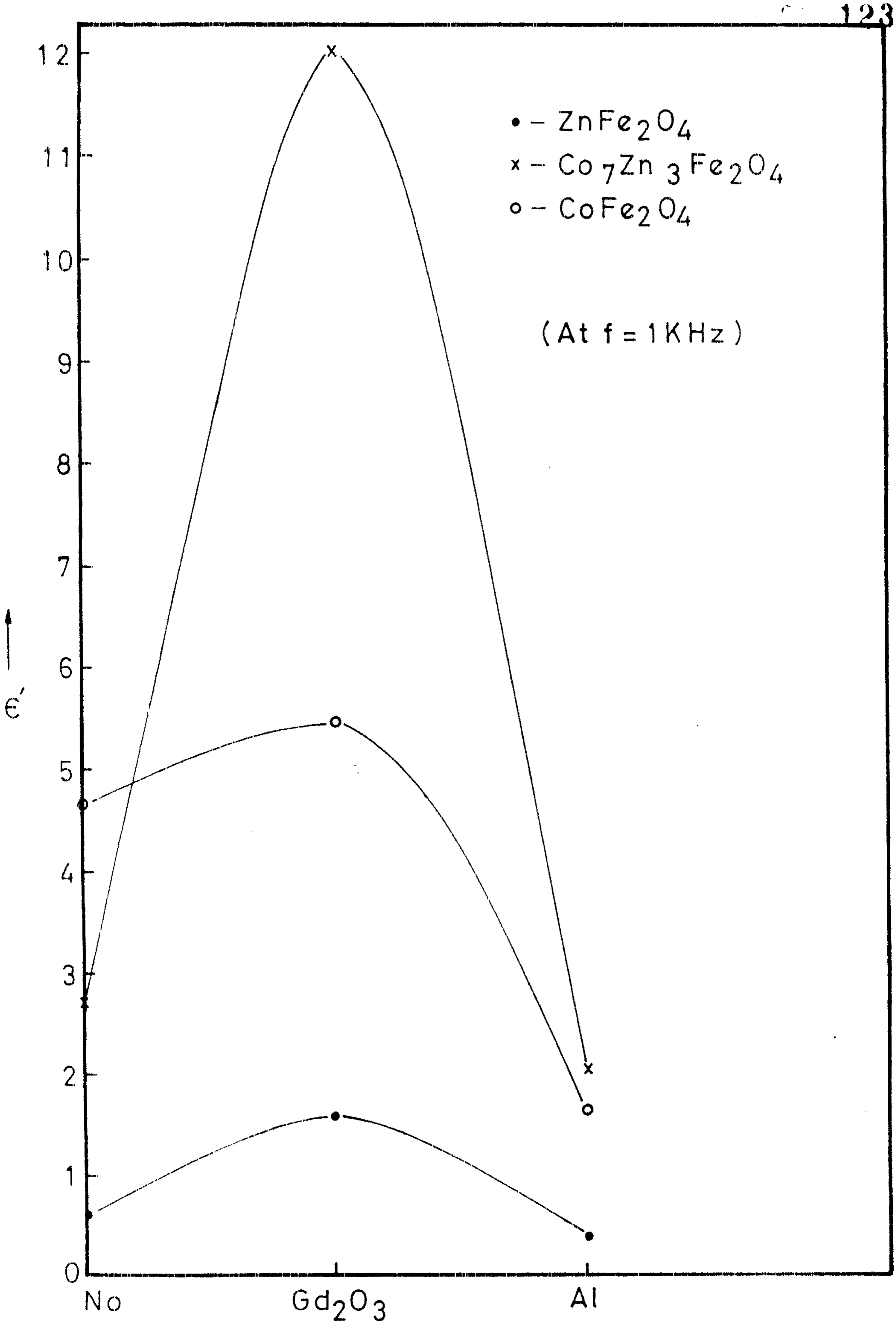

12
11
10
9
8
7
6
5
4
3
2
1
0
ε′
● – $ZnFe_2O_4$
x – $Co_7Zn_3Fe_2O_4$
o – $CoFe_2O_4$
(At f = 1KHz)
No
Gd_2O_3
Al

Fig. 3.7

trend exhibited by the three types of samples is similar. The dielectrc constant shows a large value where the dopant is Gd_2O_3.

In Fig. 3.8 the variation of ρ_{ac} with various dopants is shown. It is clearly seen that ρ_{ac} is minimum in all the three samples. viz. $CoFe_2O_4$, $Co_{0.7}Zn_{0.3}Fe_2O_4$ and $ZnFe_2O_4$ containing the dopant Gd_2O_3 . In Fig. 3.9 variation of dielectric constant ϵ' with zinc concentration is shown.

In Fig. 3.10, 3.11, 3.12 the variation of dielectric constant with frequency at different zinc concentration has been depicted It is seen that variation in ϵ' is as observed by many other workers and at high frequency it attains fixed value.The value of ϵ' shows the dispersion with frequency.

In Fig.3.13, 3.14, 3.15 the variation of a.c. resistivity ρ_{ac} with frequency is shown. It is seen that ρ_{ac} decreases with frequency. i.e. shows usual dispersion and attain constant value at higher frequencies.

In Fig. 3.16, 3.17, 3.18 the variation of loss tangent with frequency at various zinc concentration has been shown. The figures clearly indicate dispersion with frequency. Thus our observations on a.c. conductivity measurements are consistent with those of Koops.[6]

Electrical conductivity of Co-Zn ferrite has been studied by many workers[37,43]. They have attributed conduction mechanism

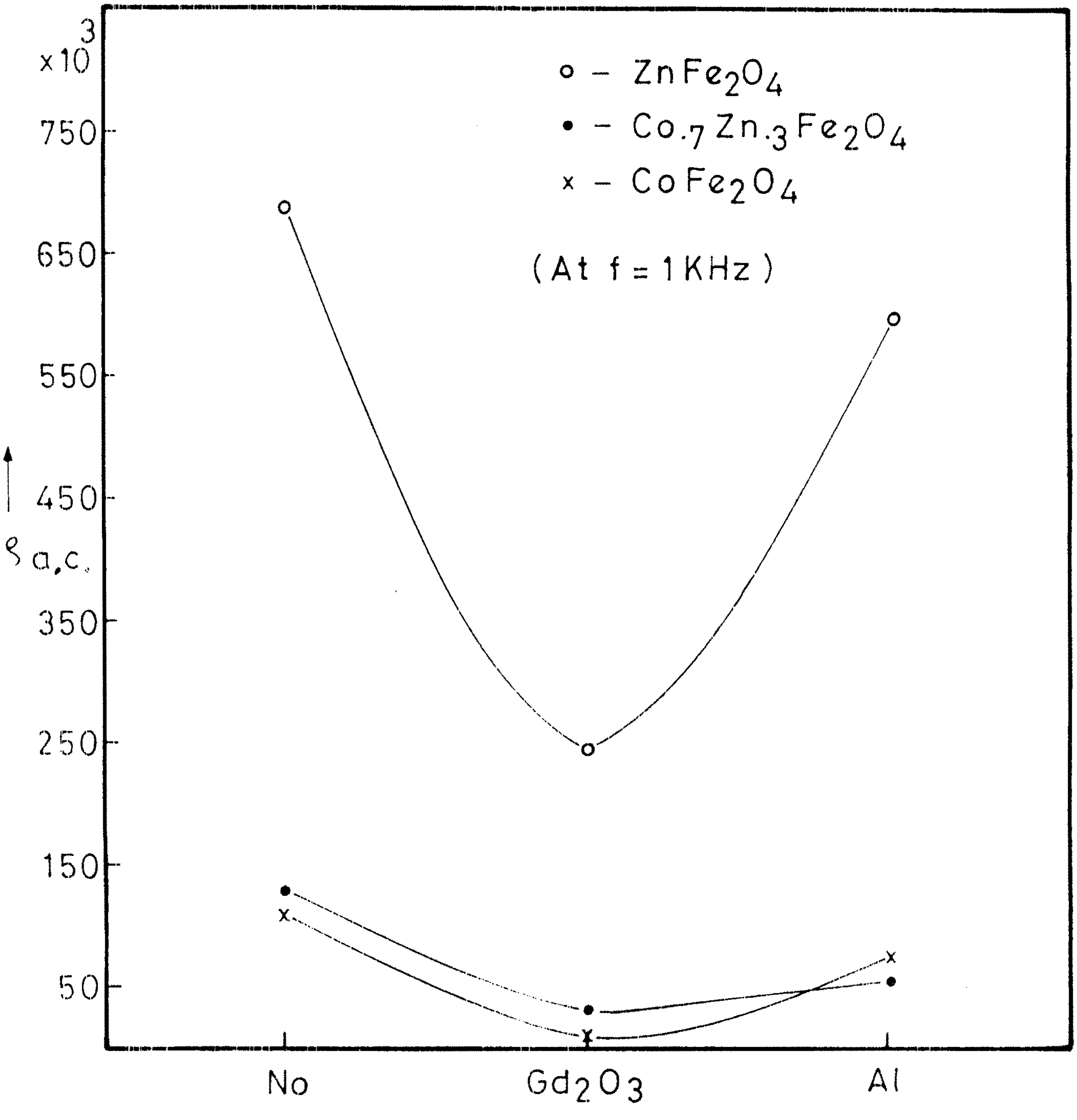

x10 3
750
650
550
450
350
250
150
50
ρ a.c.
o – ZnFe2O4
• – Co.7 Zn.3 Fe2O4
x – CoFe2O4
(At f = 1 KHz)
No
Gd2O3
Al

Fig. 3·8

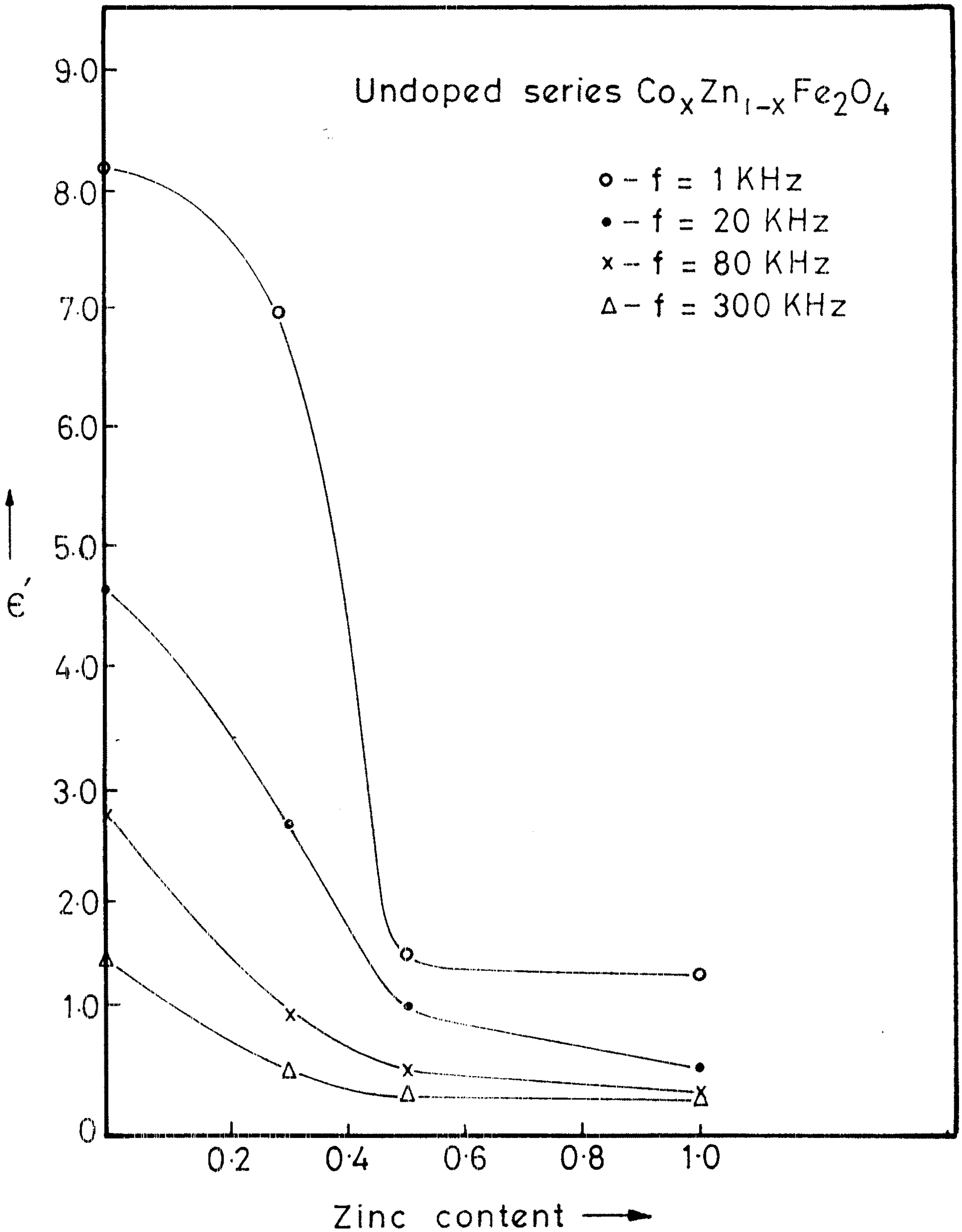

Undoped series $Co_xZn_{1-x}Fe_2O_4$
○ – f = 1 KHz
● – f = 20 KHz
x – f = 80 KHz
Δ – f = 300 KHz
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0
ε′
0·2
0·4
0·6
0·8
1·0
Zinc content

Fig. 3·9

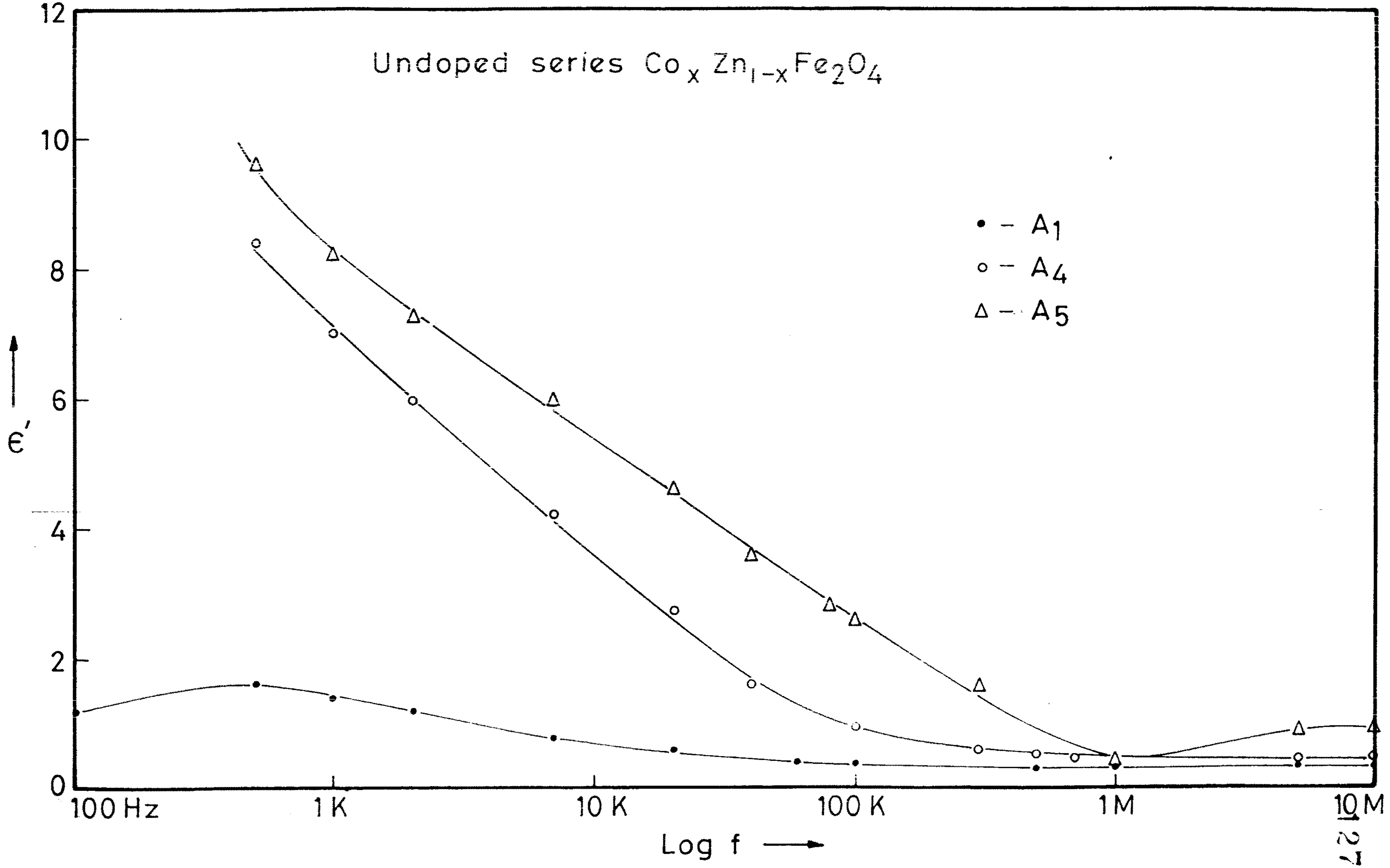

Undoped series $Co_x Zn_{1-x} Fe_2O_4$
• – A_1
○ – A_4
Δ – A_5
ε′
0
2
4
6
8
10
12
100 Hz
1 K
10 K
100 K
1 M
10 M
Log f

Fig. 3·10

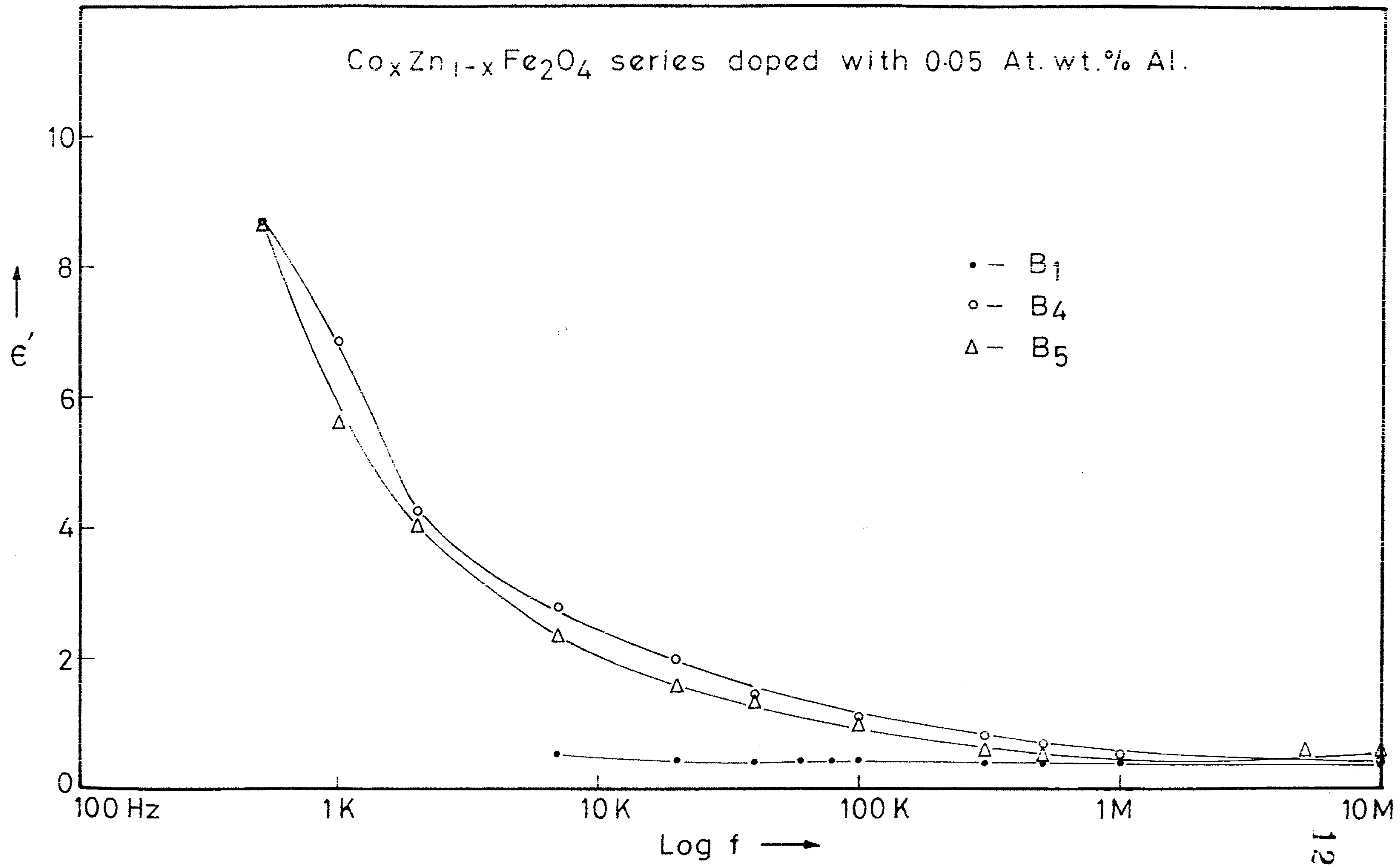

$Co_xZn_{1-x}Fe_2O_4$ series doped with 0·05 At. wt.% Al.
• – B_1
○ – B_4
△ – B_5
ϵ′
0
2
4
6
8
10
100 Hz
1K
10 K
100 K
1M
10 M
Log f

Fig. 3·11

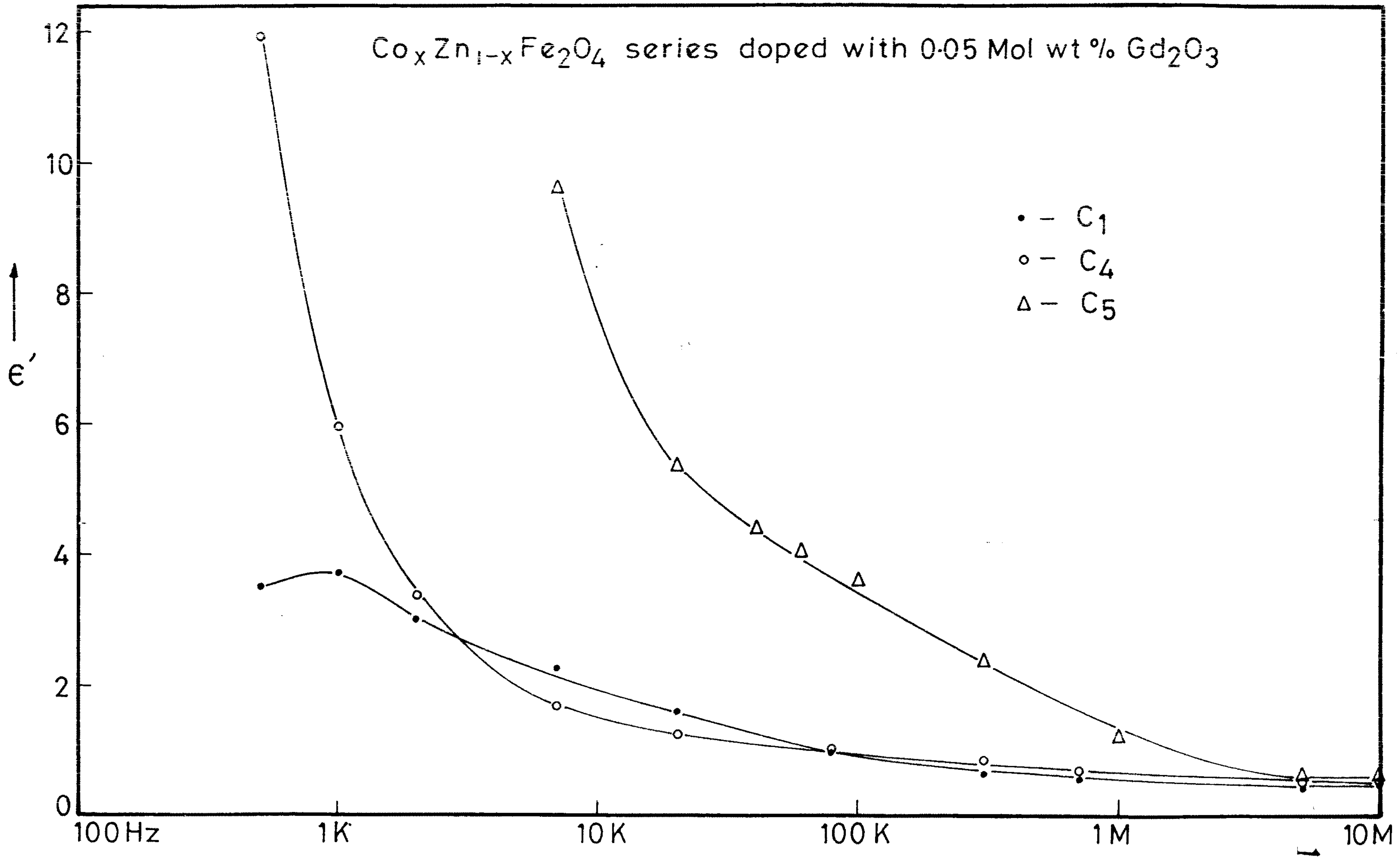

$Co_xZn_{1-x}Fe_2O_4$ series doped with 0·05 Mol wt % Gd_2O_3
• – C_1
○ – C_4
Δ – C_5
ϵ'
12
10
8
6
4
2
0
100 Hz
1K
10 K
100 K
1 M
10 M
Log f

Fig. 3·12

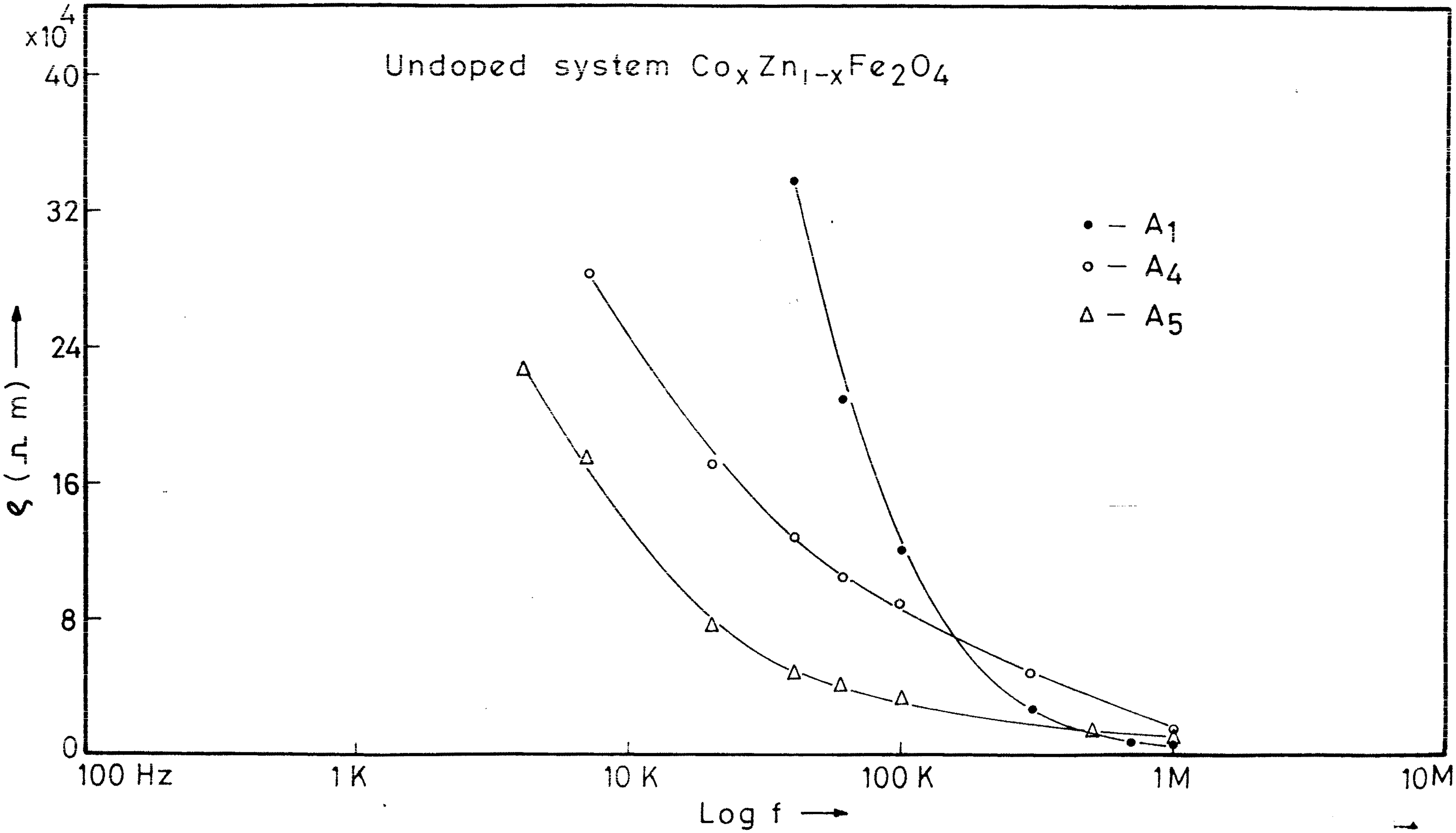

Undoped system $Co_xZn_{1-x}Fe_2O_4$
$\times 10^4$
40
32
24
16
8
0
ρ (Ω m) ⟶
100 Hz
1 K
10 K
100 K
1M
10M
Log f ⟶
● – A_1
○ – A_4
Δ – A_5

Fig. 3·13

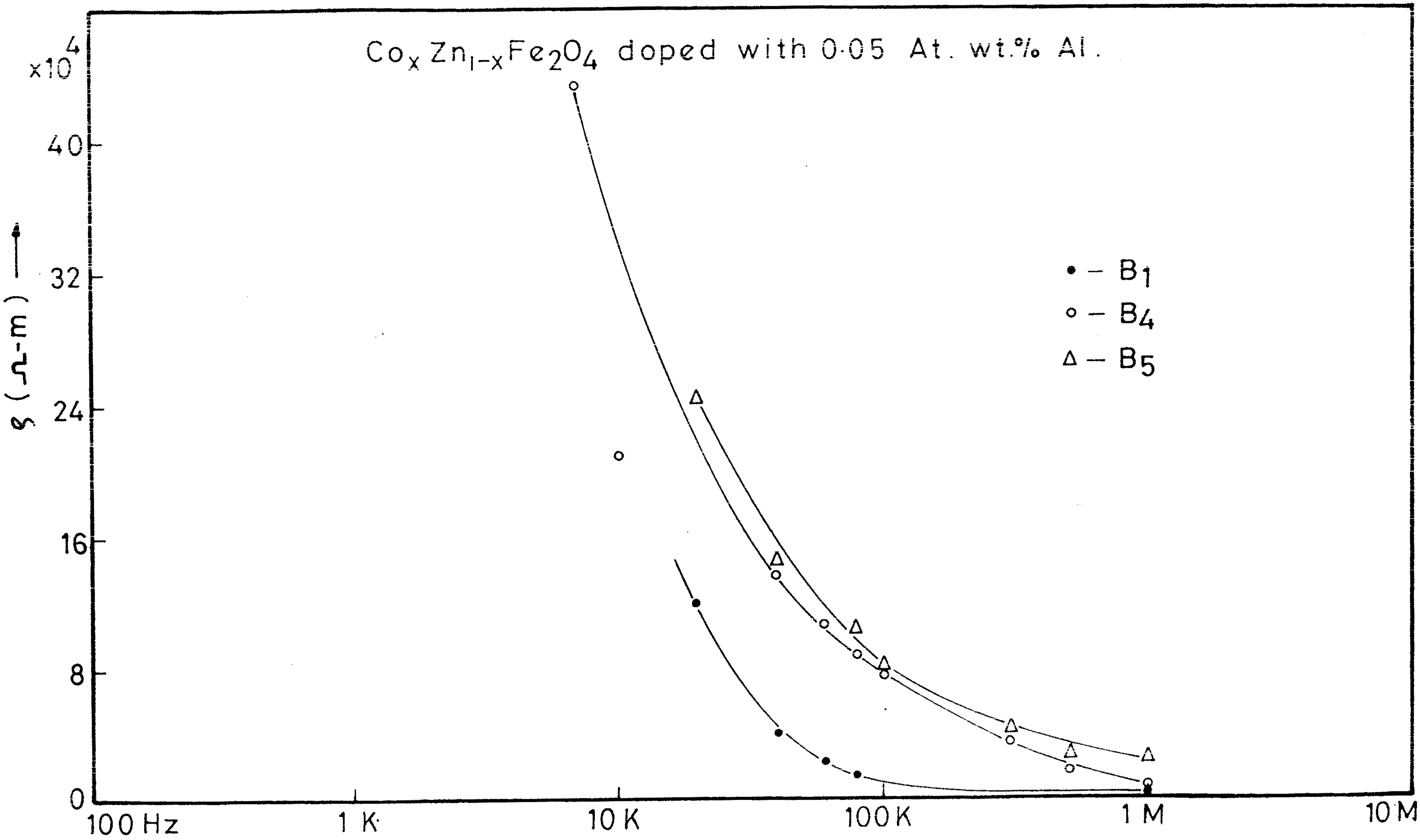

$Co_x Zn_{1-x} Fe_2O_4$ doped with 0·05 At. wt.% Al.
$\times 10^4$
ρ (Ω-m) ⟶
40
32
24
16
8
0
100 Hz
1 K
10 K
100 K
1 M
10 M
Log f ⟶
● — B_1
○ — B_4
Δ — B_5

Fig. 3-14

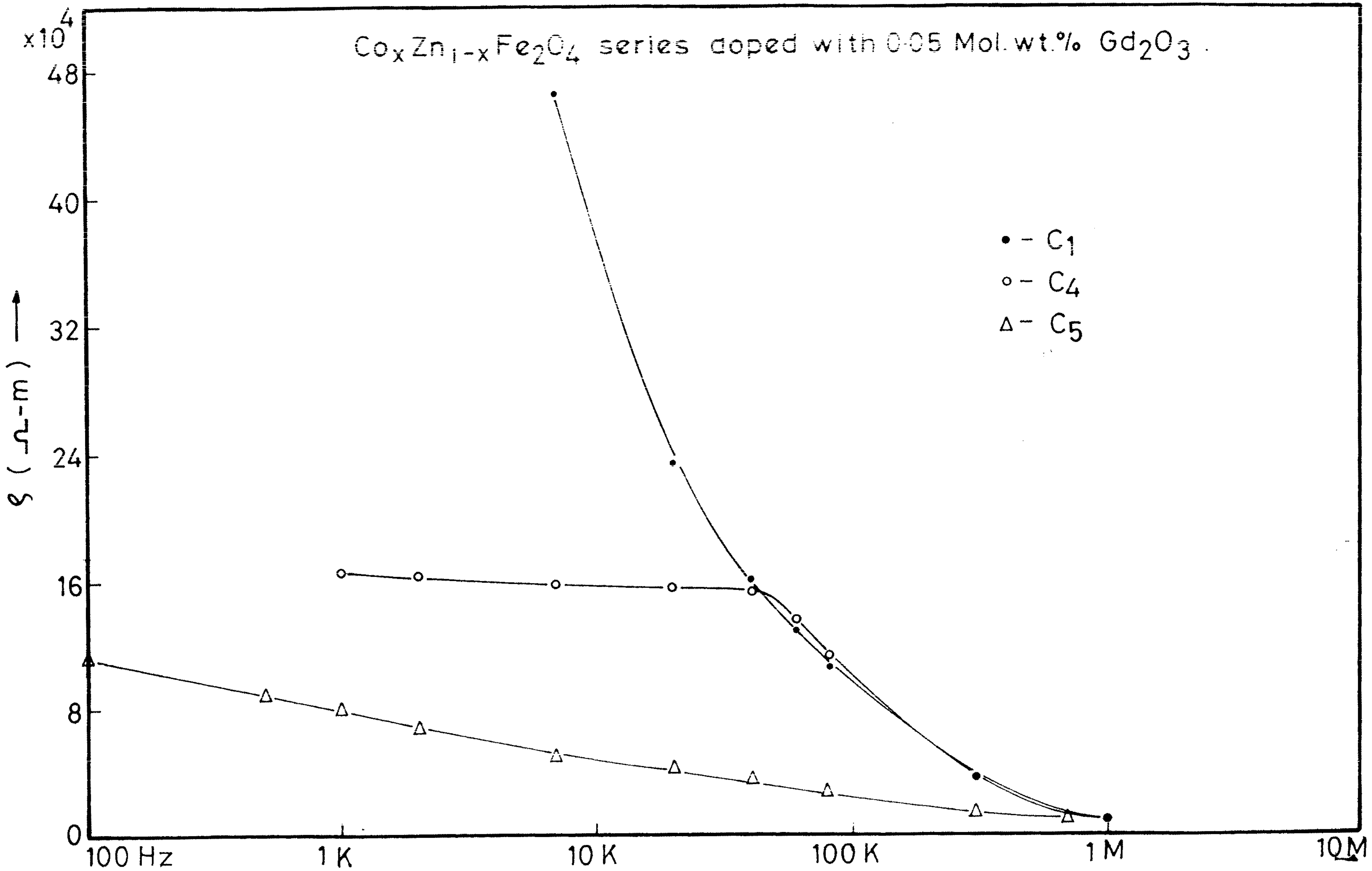

$Co_xZn_{1-x}Fe_2O_4$ series doped with 0·05 Mol. wt.% Gd_2O_3 .
$\times 10^4$
48
40
32
24
16
8
0
ρ (Ω-m) ⟶
• - C_1
○ - C_4
△ - C_5
100 Hz
1 K
10 K
100 K
1 M
10 M
Log f ⟶

Fig. 3·15

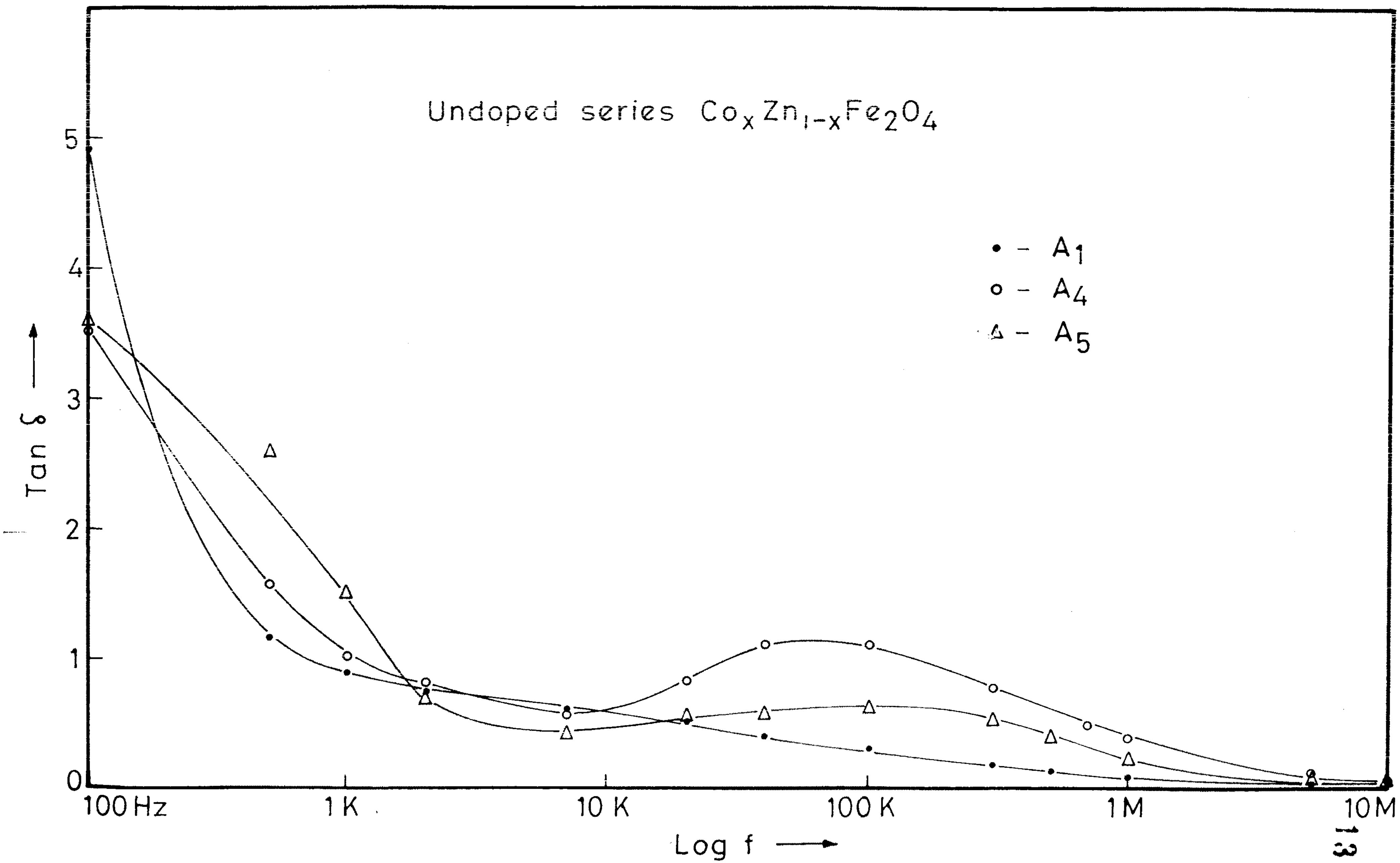

Undoped series $Co_xZn_{1-x}Fe_2O_4$
● – A_1
○ – A_4
△ – A_5
Tan δ
5
4
3
2
1
0
100 Hz
1 K
10 K
100 K
1 M
10 M
Log f

Fig. 3·16

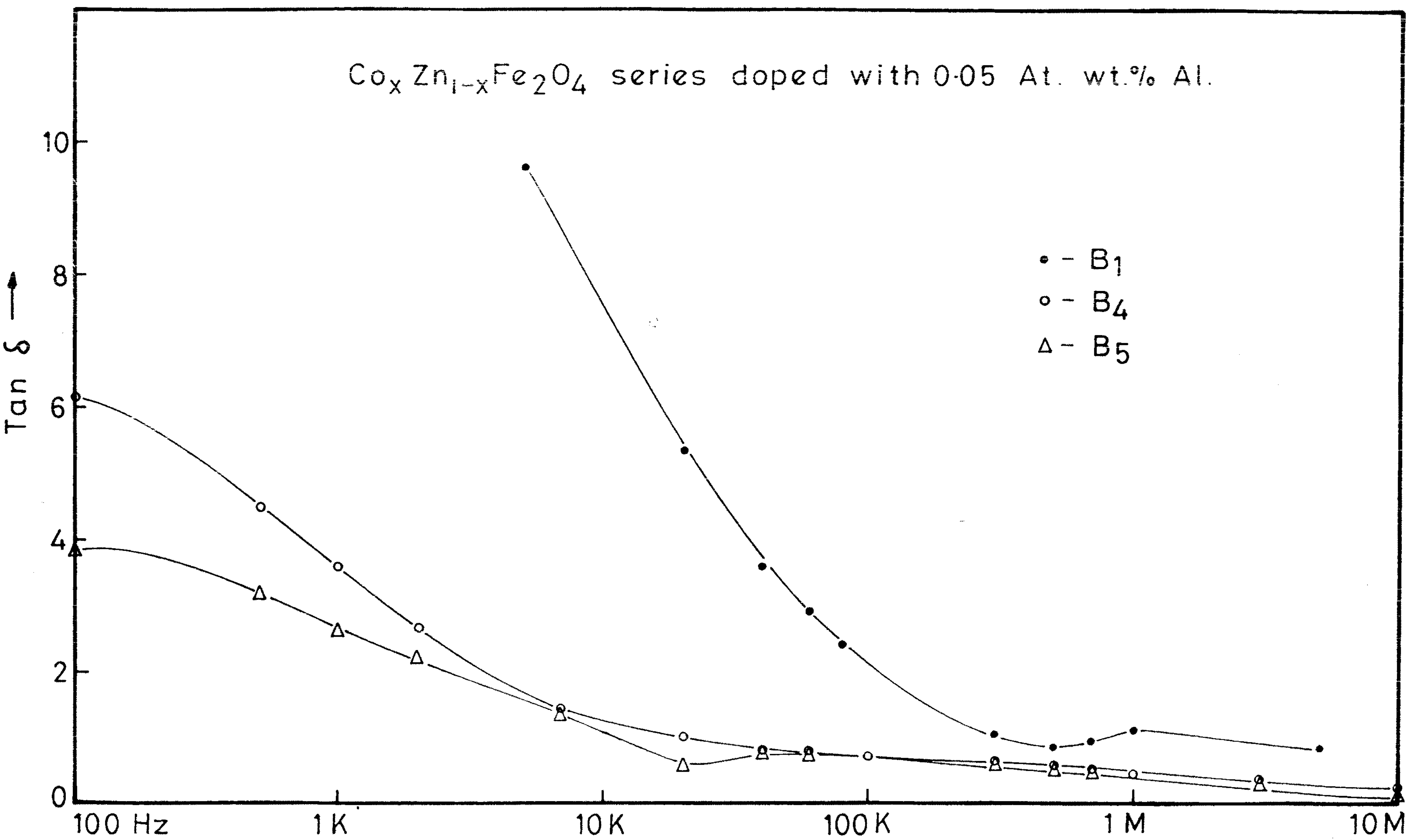

$Co_x Zn_{1-x} Fe_2 O_4$ series doped with 0·05 At. wt.% Al.
● – B_1
○ – B_4
△ – B_5
Tan δ ⟶
10
8
6
4
2
0
100 Hz
1 K
10 K
100 K
1 M
10 M
Log f ⟶

Fig. 3·17

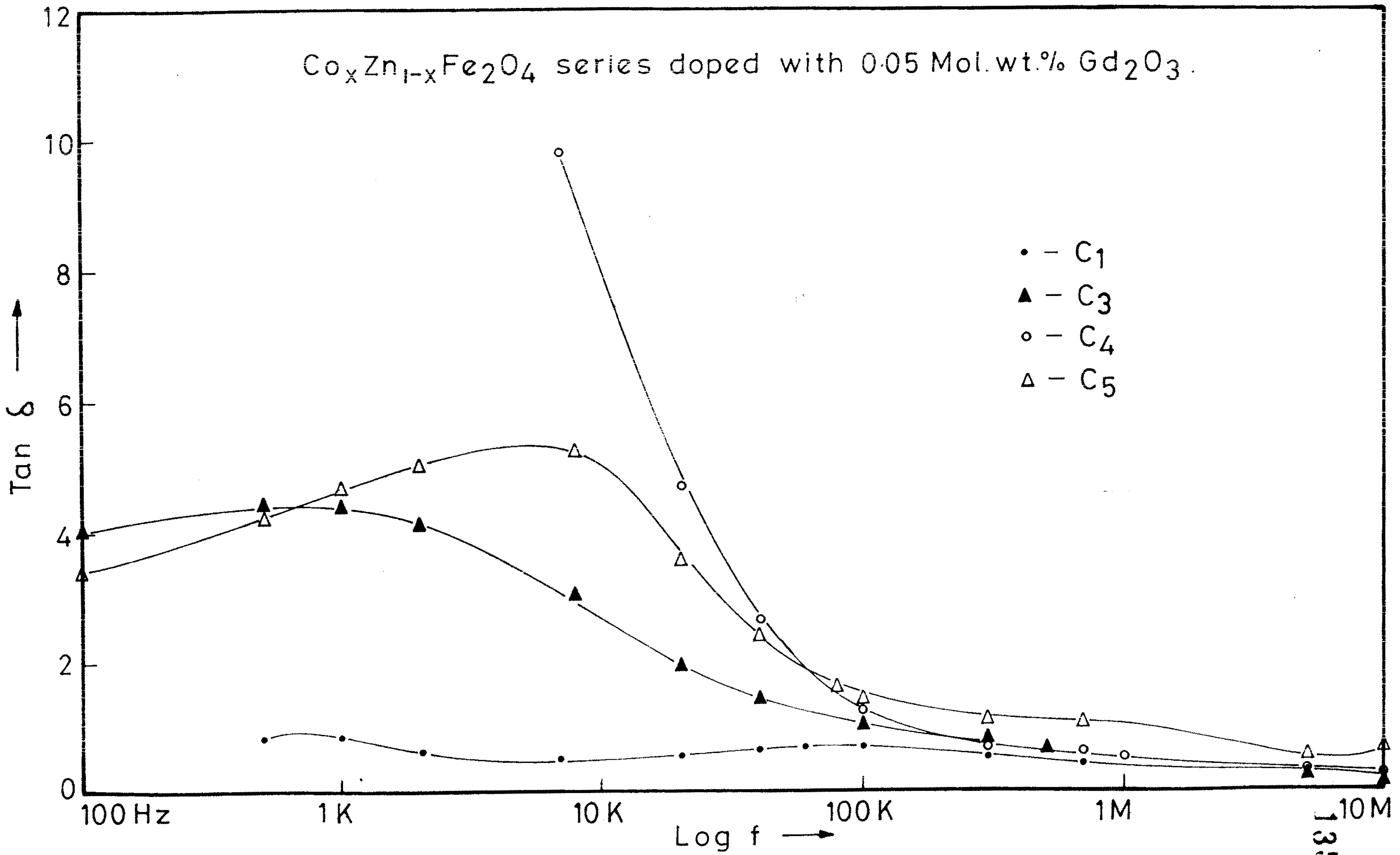

$Co_xZn_{1-x}Fe_2O_4$ series doped with 0·05 Mol.wt.% Gd_2O_3.
• – C_1
▲ – C_3
○ – C_4
△ – C_5
Tan δ →
12
10
8
6
4
2
0
100 Hz
1 K
10 K
100 K
1M
10M
Log f →

Fig. 3·18

to the hopping of electrons. The hopping at B site can take place between $Co^{2+} + Fe^{3+} \rightleftarrows Fe^{2+} + Co^{3+}$. In Cobalt-zinc ferrites as zinc concentration is reduced more number of divalent Cobalt ions will be present at B site. As the number of Cobalt ion is increased the mechanism $Co^{2+} \rightarrow Co^{3+}$ become more and more dominant and an increase in dielectric loss is arising due to the hopping between these ions. The variation in dielectric constant with frequency can be associated with the presence of Fe^{3+}, Fe^{2+} and Co^{3+}, Co^{2+} ions in the system A.

According to Rabin and Novikova[44] the polarisation process in ferrite takes place through mechanism similar to the conduction process by electronic exchange $Fe^{3+} \rightarrow Fe^{2+}$ .One obtains local displacement of electrons in the direction of field, these displacements determine polarisation. The decrease of polarisation with increasing frequency for spinel ferrite can be explained from the fact that beyond certain frequency of electric field, the electron exchange cannot follow the change in direction of field.

The resistivity of $ZnFe_2O_4$ is mainly governed by Fe^{3+} Fe^{2+} type of transition i.e. electron hopping. The activation energy needed for electron hopping is 0.2 eV. Whereas on addition of cobalt in the system containing zinc the predominent reaction is

$$Co^{2+} + Fe^{3+} \rightleftarrows Fe^{2+} + Co^{3+}$$

Devale and Kulkarni[45] investigated that d.c. resistivity of $FeCoCrO_4$ and concluded that the presence of Co^{2+} ions on B site lowers the resistivity. $Co^{3+} \rightarrow Co^{2+}$ type hopping contribute to p-type conduction. This type of conduction is normally observed at higher temperatures. Cobalt ferrite is a p-type conductor while zinc ferrite is n-type conductor. Hence the low resistivity of mixed ferrite.

Doping of Aluminium does not significantly change ρ_{ac}, however, there is a noticable drop in ρ_{ac} on doping Gd_2O_3 .This may be due to the fact that on doping of Gd_2O_3, Gd^{3+} ions take the octahedral site replacing Fe^{3+} (I.R.studies), there by liberating Fe^{3+} ions which according to conduction mechanism $Fe^{3+} \rightleftarrows Fe^{2+}$ causes an increase in conduction and hence lowerring of ρ_{ac}.

Such change in ρ_{ac} is not observed in case of Aluminium doped samples. This may be because of different electronic configuration of Al^{3+} and Gd^{3+} ions.

Koops[30] and Moltgen[46] were among earliest to investigate the low frequency dispersion in Ni-Zn ferrite. and Cu-Zn ferrite. They have interpreted their result by considering the dielectric as an inhomogeneous medium of Maxwell-Wagner type (two layer model). Following this theory Koop[30] and other described the dielectric relaxation in ferrite at room temperature. Based on this Smit and Wign[47] studied ε' loss of Ba, Ni and Zn ferrite and found the values to be in good agreement with the theoretical values. Comparing the present result on Co-Zn ferrite with those in literature for different ferrites, it can been seen that ε' decreases with increasing frequency, thereby obeying Koops theory.

The loss tangent almost decreases exponentially with frequency as can be expected from the relation.

$$\tan\delta = \frac{1}{\omega \varepsilon_p \rho_p}$$

where ω = frequency

ε_p = parallel dielectric constant

ρ_p = polarisation resistivity

This may be attributed mainly to the increase in conductivity with rise of frequency. These results can be observed from Fig.3.16, 3.17, and 3.18. Similar results for resistivity versus frequency are observed in Fig. 3,13, 3.14 and 3.15.

The dielectric loss peaks were not observed for any of the samples of undoped series $Co_xZn_{1-x}Fe_2O_4$ at room temperature Thus it is clear that the jump frequency is outside the frequency spectrum that had been studied and may be below room temperature. Aluminium doped samples show a similar behaviour as that of undoped saamples.

For the two samples $Co_{0.5}Zn_{0.5}Fe_2O_4$ (C_3) and $CoFe_2O_4$(C_5) doped with Gd_2O_3 (Fig. 3.18) , dielectric loss peaks are observed at frequencies of 2 KHz and 7 KHz respectively. Thus addition of cobalt shift resonant frequency to high frequency side. The appearence of peaks in tan δ versus frequency curve are attributed to a strong correlation between the hopping conduction mechanism and dielectric behaviour of ferrites. When the jump frequency coincide with that of the external field a maximum in tan δ is observed.

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