CHAPTER IV

CHAPTER IV

DIELECTRIC PROPERTIES

4.1 INTRODUCTION

The d.c resistance of polycrystalline material must be corroborated by the a.c. resistance and dielectric constant so that it represents completely the conduction in the bulk material. Dielectric losses occur in the electric polarization within the lattice at high frequencies The dielectric losses may be indistinguishable from other losses such as losses in conduction. Dielectric constant is frequency dependent in case of polycrystalline materials. Both resistivity and dielectric constant of sintered pyrochlores exhibit dispersion with respect to frequency. Koops has explained this dispersion by considering the oxides compact as multilayer capacitor in which their grains and grainboandaries have different properties. A strong correlation between the conduction mechanism and dielectric behavior has reported by Iwanchi(1) variours other workers (2,3) have reported their work on various mixed oxides showing an important observation of decreasing dielectric constant with increase of frequency. At very high frequencies, dielectric losses occur due to the relaxation processes in the electronic polarization within the crystal lattice. For a particular frequency, losses may arise from the imaginary component of the dielectric constant and cannot be distinguished from those which results from the conductivity (4).

In oxides three principle of polarization can be distinguished within a frequency range from zero to u.v. frequency region. At optical frequencies the polarization mechanism is electronic. At frequencies below infrared the mechanism is atomic or ionic polarization and arises from the movement of cations, anions within the crystal latice. The part of permittivity at microwave frequency region is due to this mechanism. Below the microware frequency the polarization arises from the microstructure of pollycrystalline material and from the migration of free change carriers.

J.D. Siegwarth et. al (5) reported the measurments of the frequency dependence of the small signal dielectric constant, the dc polarization, the zero field specific heat etc.

4.2 POLARISATION AND DIELECTRIC CONSTANT

The externally applied alternating electric field across the ceramic sample induces the polarization in the material. There are following types of induced polarization namely electronic polarization (Pe), ionic polarization (pi), orientational polarization (Po) and space charge or interfecial polarization (Ps). The total polarization of antiphase material is the sum of

$$P = Pe + Pi + Po + Ps.$$

However, an interfecial polarization plays a significant role in the dielectric behavior of the oxides. The dielectric displacement found in dielectric material when subjected to alternating electric field E is given by

$$D = \varepsilon E \qquad \text{-----------------(4.1)}$$

where ε is dielectric constant. A dielectric response to uc field shows a complex dielectric constant involving a real as well as imaginary component, which are related by

$$\tan\delta = \varepsilon'' / \varepsilon' \qquad \text{----------(4.2)}$$

As ε depends on frequency and time, the real and imaginary parts of dielectric constant depend on frequency and time given by

$$\varepsilon = \left[E_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 T^2} \right] + i \left[\frac{Es - \varepsilon_\infty}{1 + \omega^2 T^2} \right] wT \qquad \text{----------(4.3)}$$

Where ε_s and ε_∞ represent low and high frequency dielectric constant respectively, W is the angular frequency and T is the relaxation time. From equation (4.2), via Debye equation the expression for loss tangent can be obtained as

$$\tan\delta = \varepsilon''/\varepsilon' = \frac{(\varepsilon_5 - \varepsilon_\infty)wT}{(\varepsilon_5 + \varepsilon_\infty)W^2 T^2} \qquad \text{------------(4.4)}$$

The plots of ε' and $\tan\delta$ as a function of frequency explore the dielectric properties of the material.

Koops has given a general model for inhomogeneous dielectric constant and which comprises of well conducting grains that are seperated by low conducting layers, leading to an equivalent parallel resistor and capacitor circuit shown in fig. 4.1. He studied the dispersion of resistivity and dielectric constant of some semiconductors at audio frequencies.

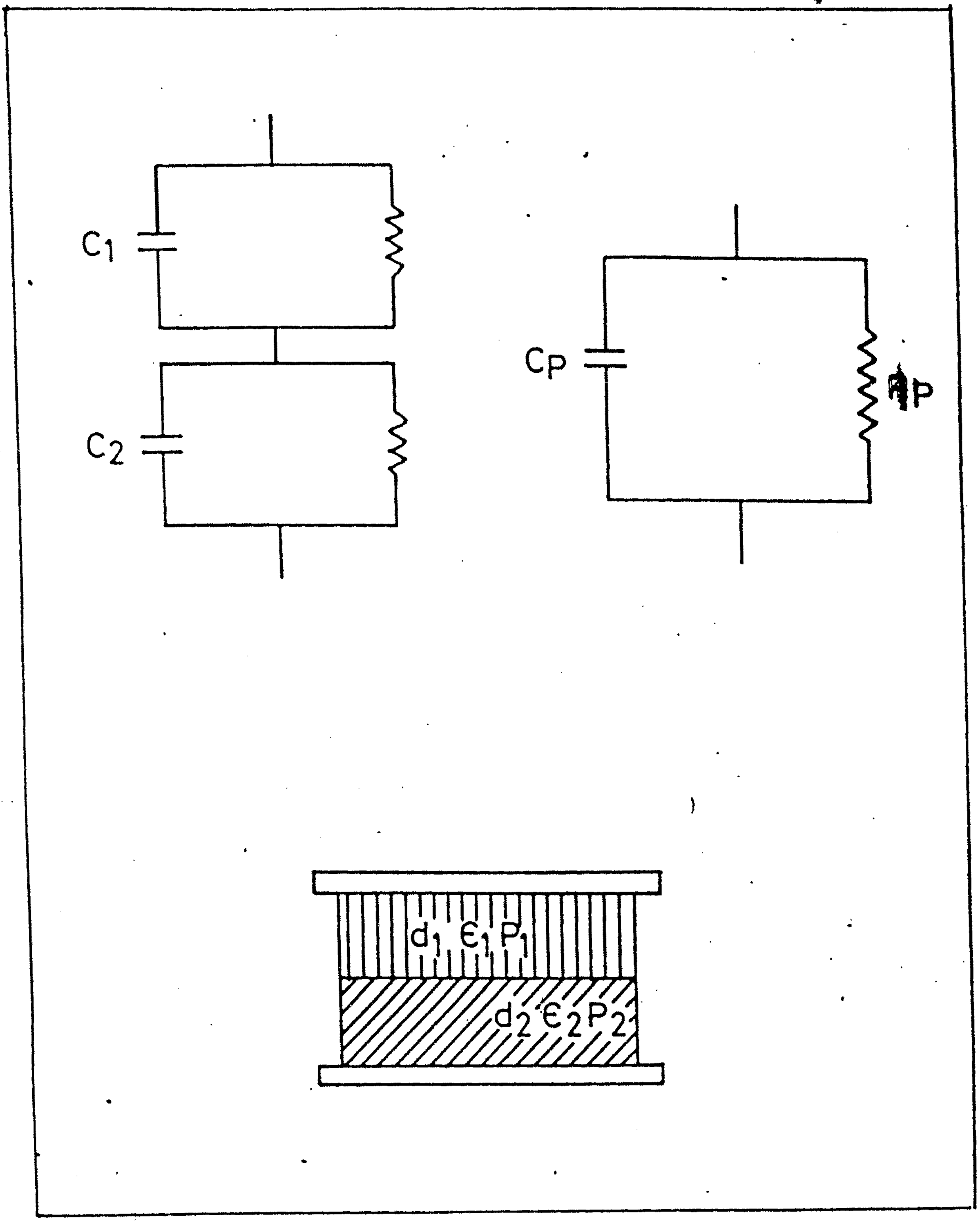

FIG. 4·1 — DOUBLE LAYER CAPACITOR.

4.3 EXPERIMENTAL

The dielectric measurements were carried out by using two probe method at University of Poona, Pune, with pellets in the frequency range 100 Hz to 1 MHz at room temperature. Hewlett packard precision LCR (4284 A), meter of range 20 Hz to 1 MHz was used for this purpose. The pellets used was coated with silver paste to ensure good electrical contacts. The pellet was then sandwiched between the silver foils in sample holder for measurements.

Before taking the readings for capacitance C and dispersion D, the HP impedence analyser was made on for an hour and then was used for measurements for various frequencies. The dielectric constant ε' was calculated from the measured capacitance (C_p) using the relation

$$\varepsilon' = \frac{11.3\,t}{A} \cdot C_p \qquad \text{-----------(4.5)}$$

where t = Thickness of pellet

C_p= Capacitance in PF

A = Cross-sectional area of flat surface of pellet.

The dielectric measurements were carried out by using two probe method on LCR meter bridge MIC 4070 D. at 1KHz fixed frequency. The values of capacitance are noted at various temperatures and then, by using the above retation 4.5 , dielectric constant is calculated.

4.4 RESULTS AND DISCUSSION

DILECTRIC CONSTANT WITH FREQUENCY

The variation of dielectric constant (ε') with frequency for different samples are shown in figures 4.2 to 4.7. In the same figures the variation of imaginary part of dilectric constant (ε'') and loss tangent ($\tan\delta$) with frequency is also plotted.

All the samples reveal the dispersion. The dielectric constant ε' decreases rapidly with increase in frequency and reaches a constant value. A comparative study of dispersion curves of these samples shows that the changes in the values of ε' at lower frequencies of the applied field is larger than that for higher frequencies. The high value of dielectric constant show large dispersion in comparison with the smaller values of ε' . The dielectric constant ε' is almost independent after a certain frequency to a value.

The intrinsic dielectric values of pyrochlores are found to lie between 10-20 usually. The very high ε' often observed at low frequencies have been ascribed to the effect of heterogeneity of the sample like pores, surfaces and layers on grains. Sometimes some electronic polarisation effect is supposed to be connected with the conduction hopping mechanism itself and it could be contribute to the low frequency dispersion of ε'.

At higher frequency the measured values may be regarded as intensive to both of these contributions and they are usually taken as actual

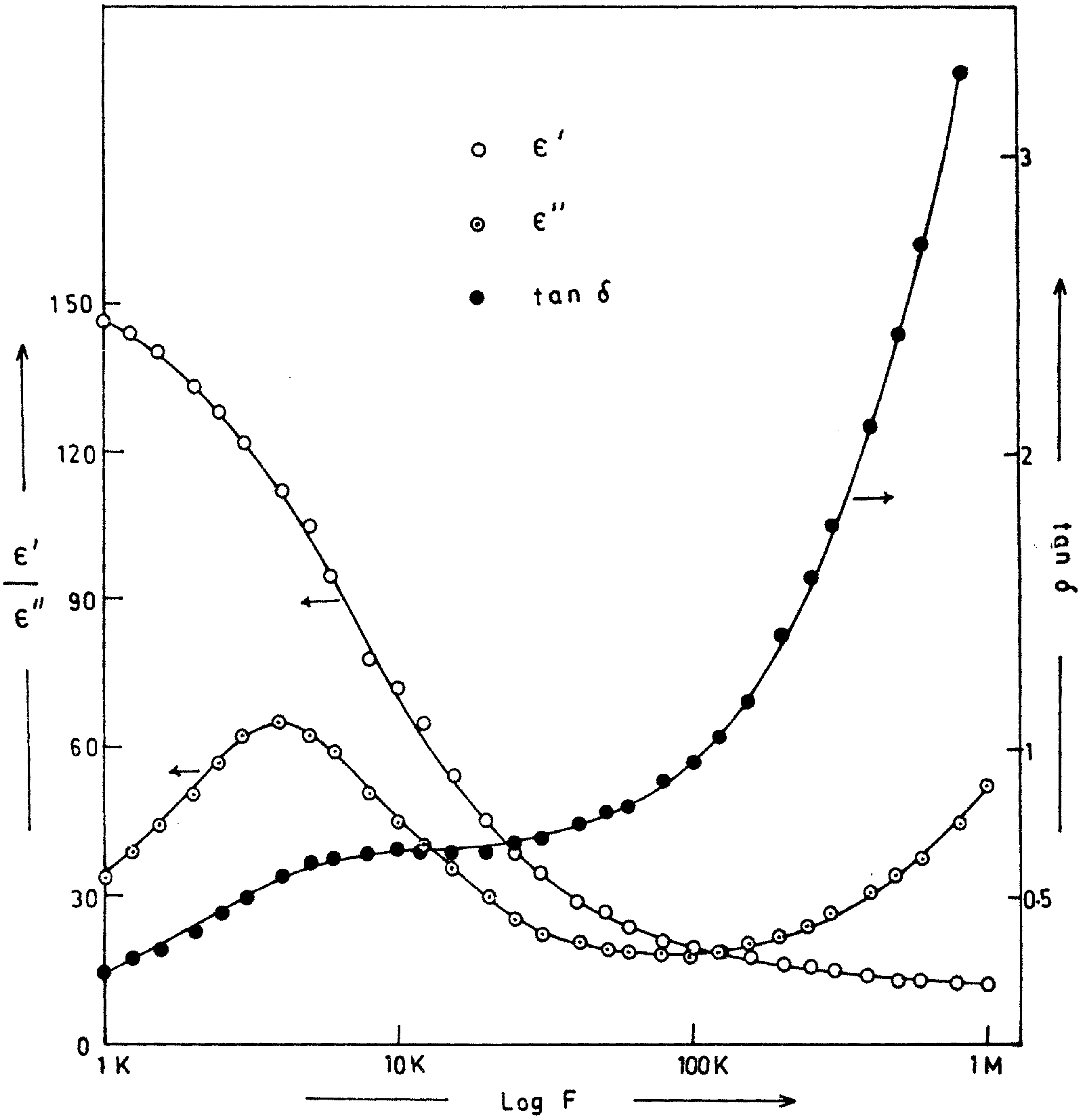

Fig. 4·2 – Variation of ϵ', ϵ'' and tan δ with Log F for $Y_2Ti_2O_7$.

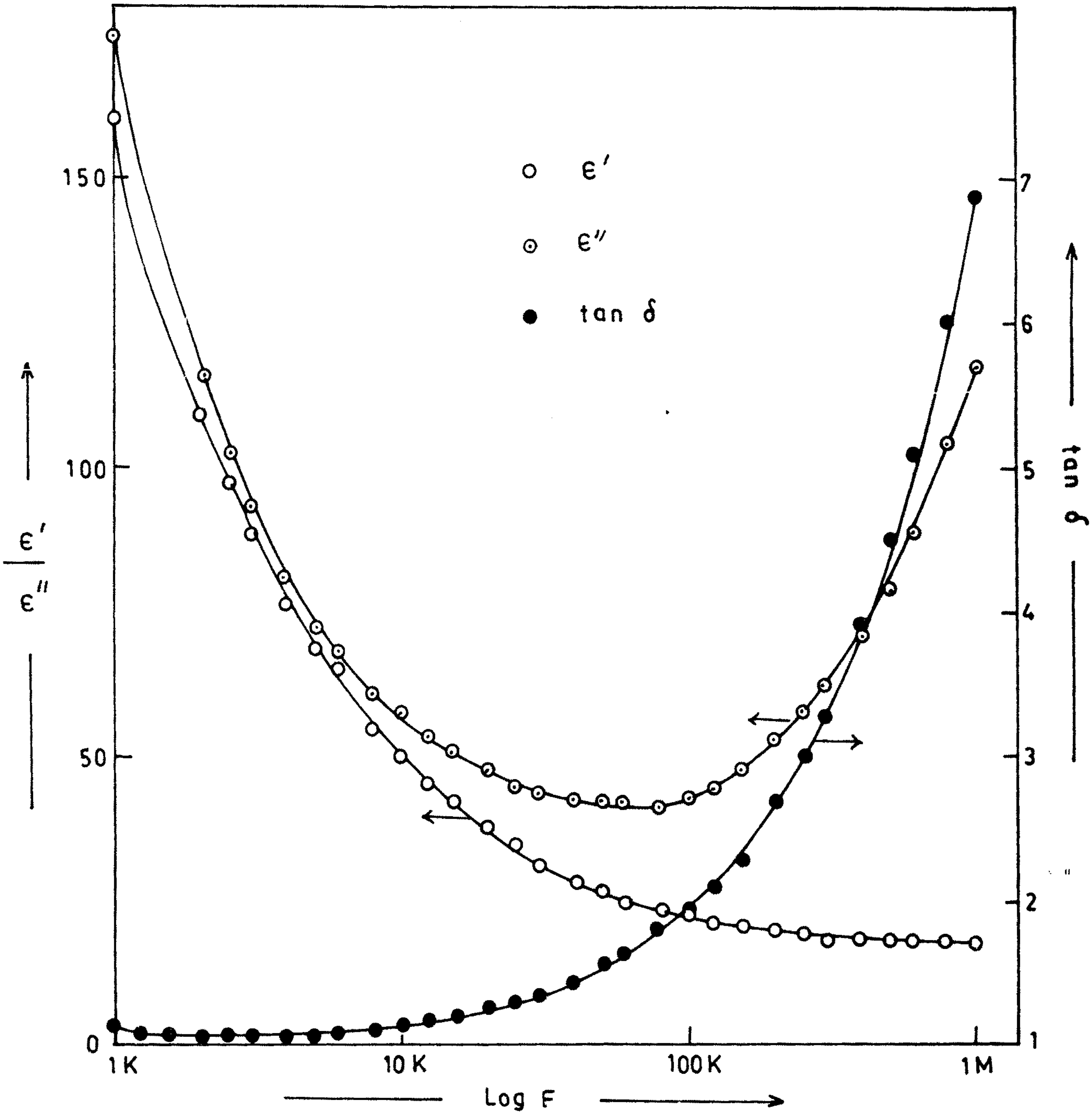

Fig. 4·3 – Variation of ε′, ε″ and tan δ with Log F for $Ce_2Ti_2O_7$.

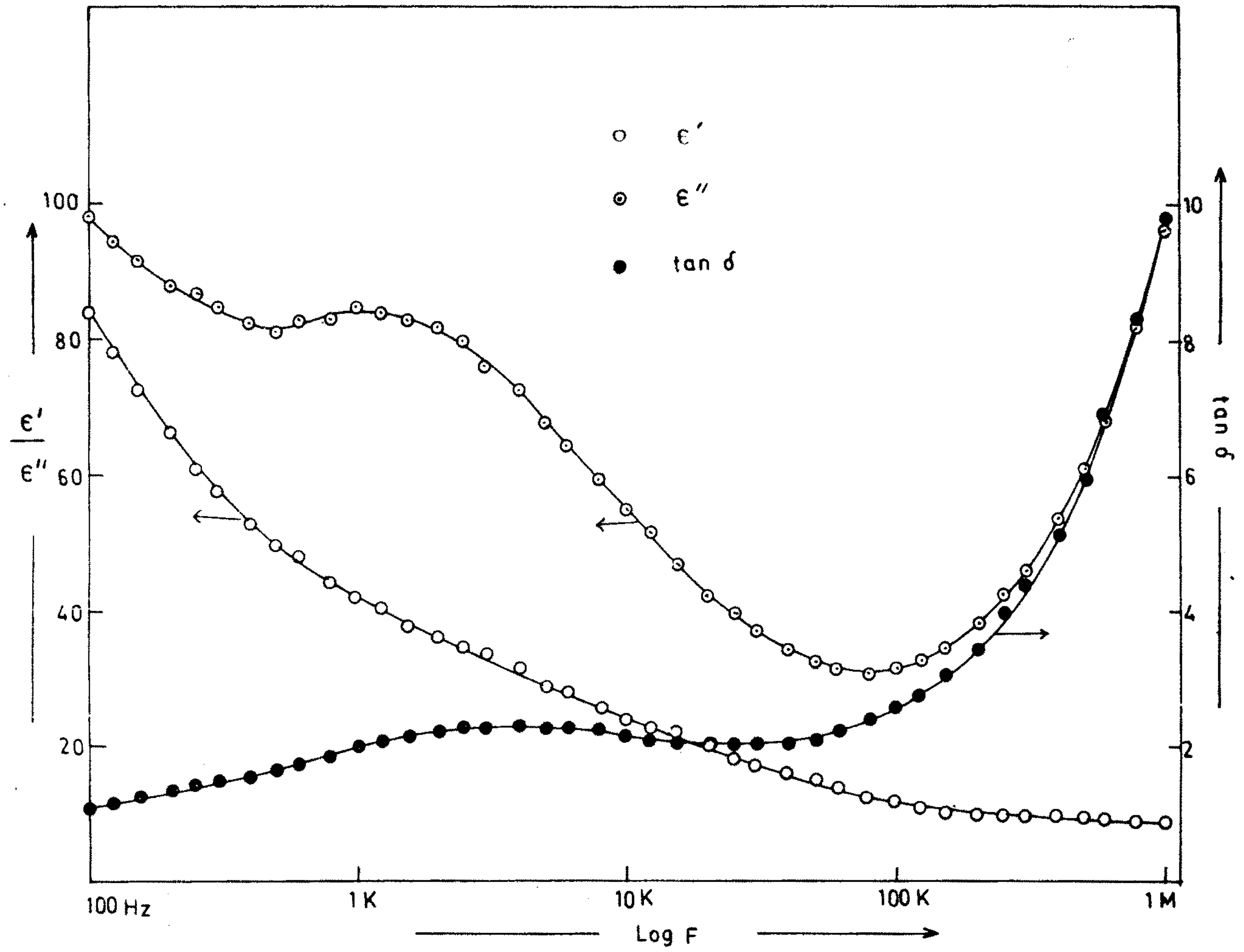

Fig. 4·4 — Variation of ϵ', ϵ'' and tan δ with Log F for $Sm_2Ti_2O_7$ ·

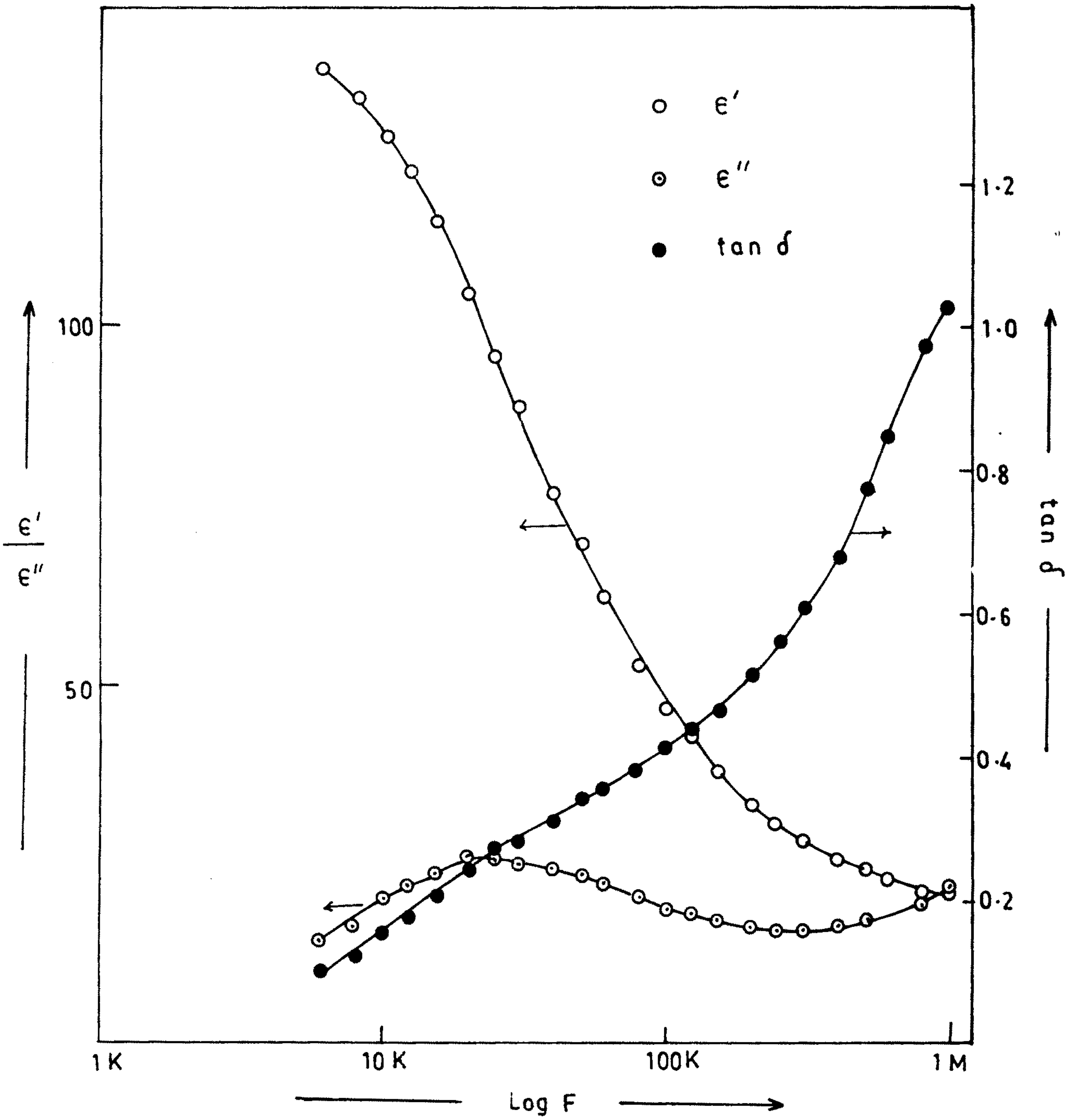

Fig. 4·5 – Variation of ϵ', ϵ'' and tan δ with Log F for $Y_2Sn_2O_7$.

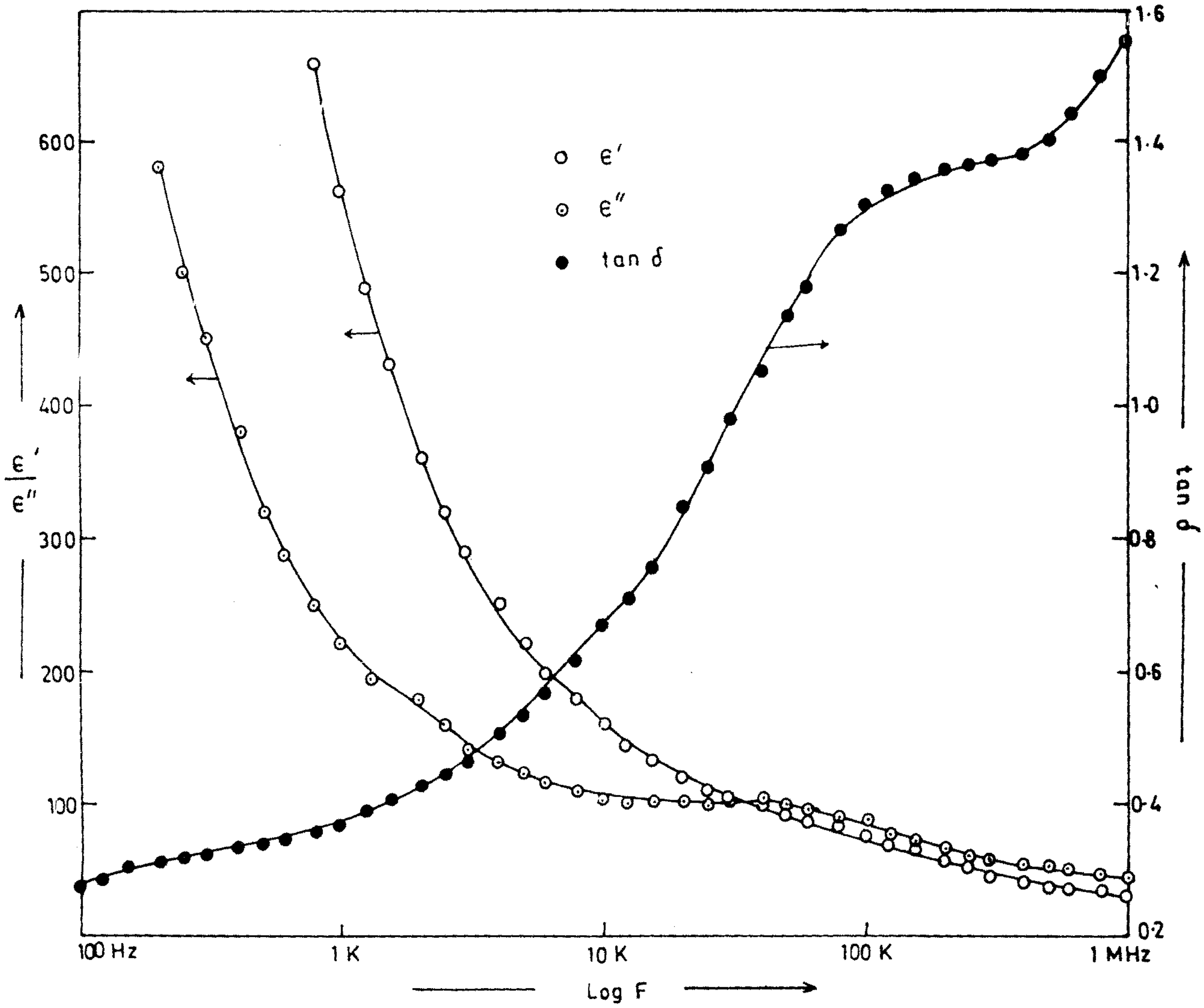

Fig. 4·6 — Variation of ε', ε'' and tan δ with Log F for $Ce_2Sn_2O_7$.

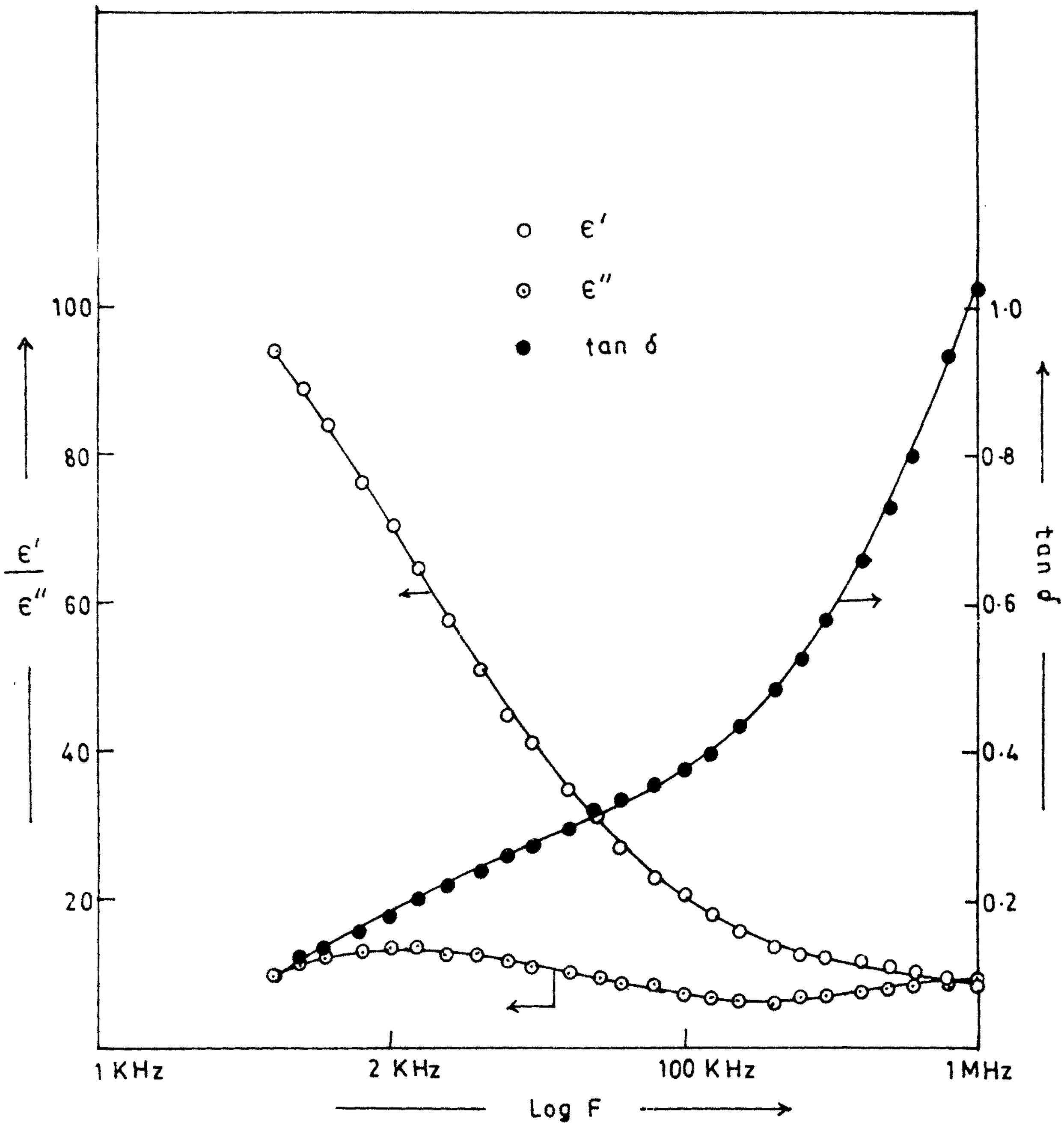

Fig. 4·7 — Variation of ε′, ε″ and tan δ with Log F for $Sm_2Sn_2O_7$ ·

intrinsic dielectric constant ε' corresponding to normal, ionic and electronic polarization.

In normal dielectric behavior ε' dcreases with increasing frequency and reaches a constant value depending on the fact that beyond a certain frequency of electric field, the electron exchange doesnot follow the alternating field. This is why ε' remains constant beyond a certain frequency in the case of present system. Nevertheless, if dielectric values of pyrochlores can be decreased to low levels they may serve as technologically useful dielectrics in some applications.

There materials also exhibit unusual high values of dielectric constant. This has been ascribed to the formation of barrier at grainboundaries interfaces. These materials are expected to lose traces of oxygen during sintering at high temperature according to reaction.

$$0_o \longrightarrow 1/2\ 0_2 + V''_o + 2e' \qquad \text{------------}(4.6)$$

Where all the species are written a according to Kroger-Vink notation of defects. Electrons released in equation (4.6) make the material superconducting. During cooling of these samples after sintering re-oxidation takes place. Due to decreasing temperature and insufficient time available for diffusion of oxygen to the bulk of material, reoxidation is limited to the surface and grainboundaries. This makes grainboundaries insulating as compared to the grains which still remain superconducting. The difference in the conductivity of grains and grainboundaries gives rise to barrier at their interfaces imparting very high values of dielectric constant to resulting oxides.

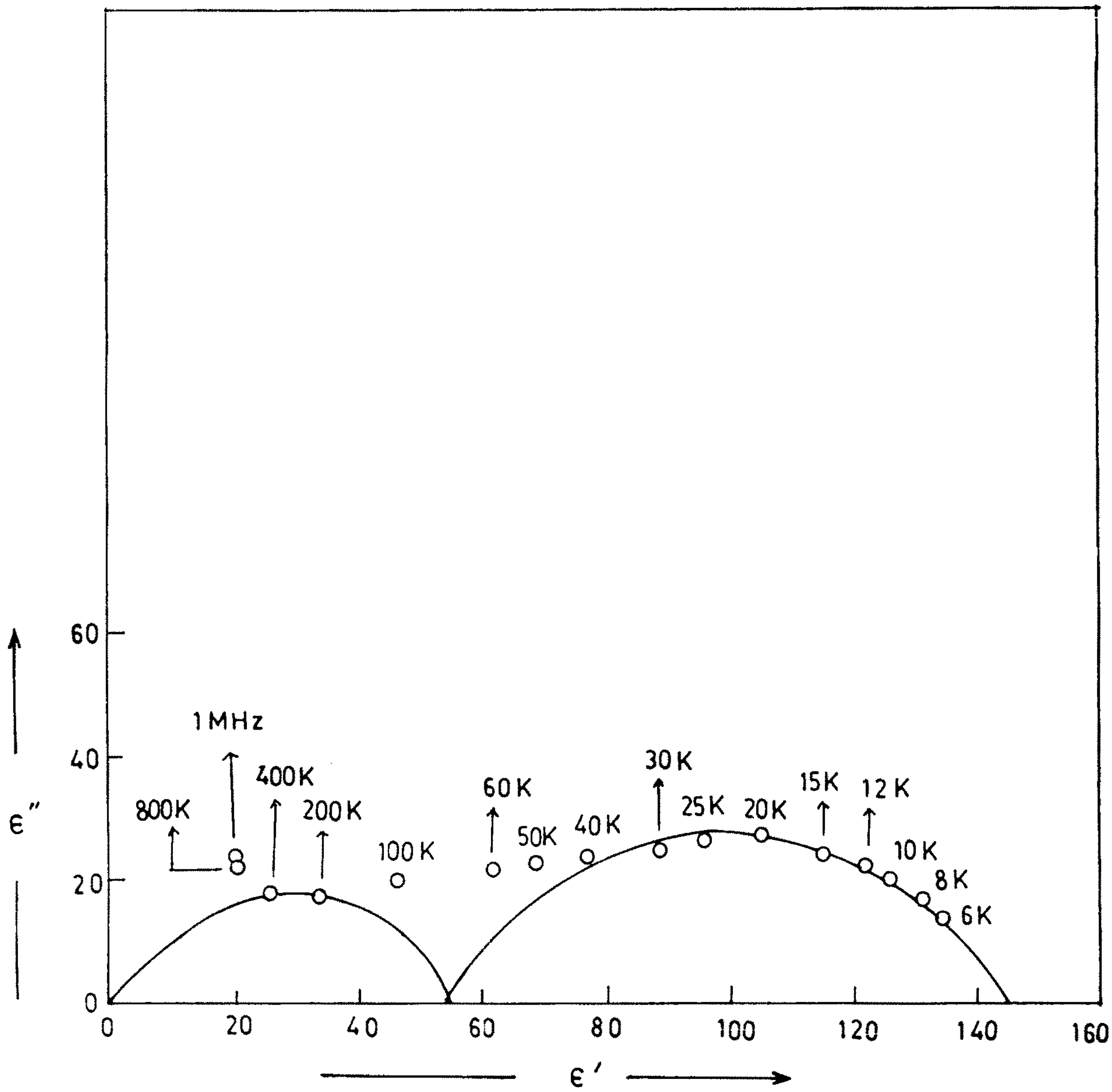

Fig. 4·8 — Variation of ϵ'' Vs ϵ' for $Y_2Sn_2O_7$.

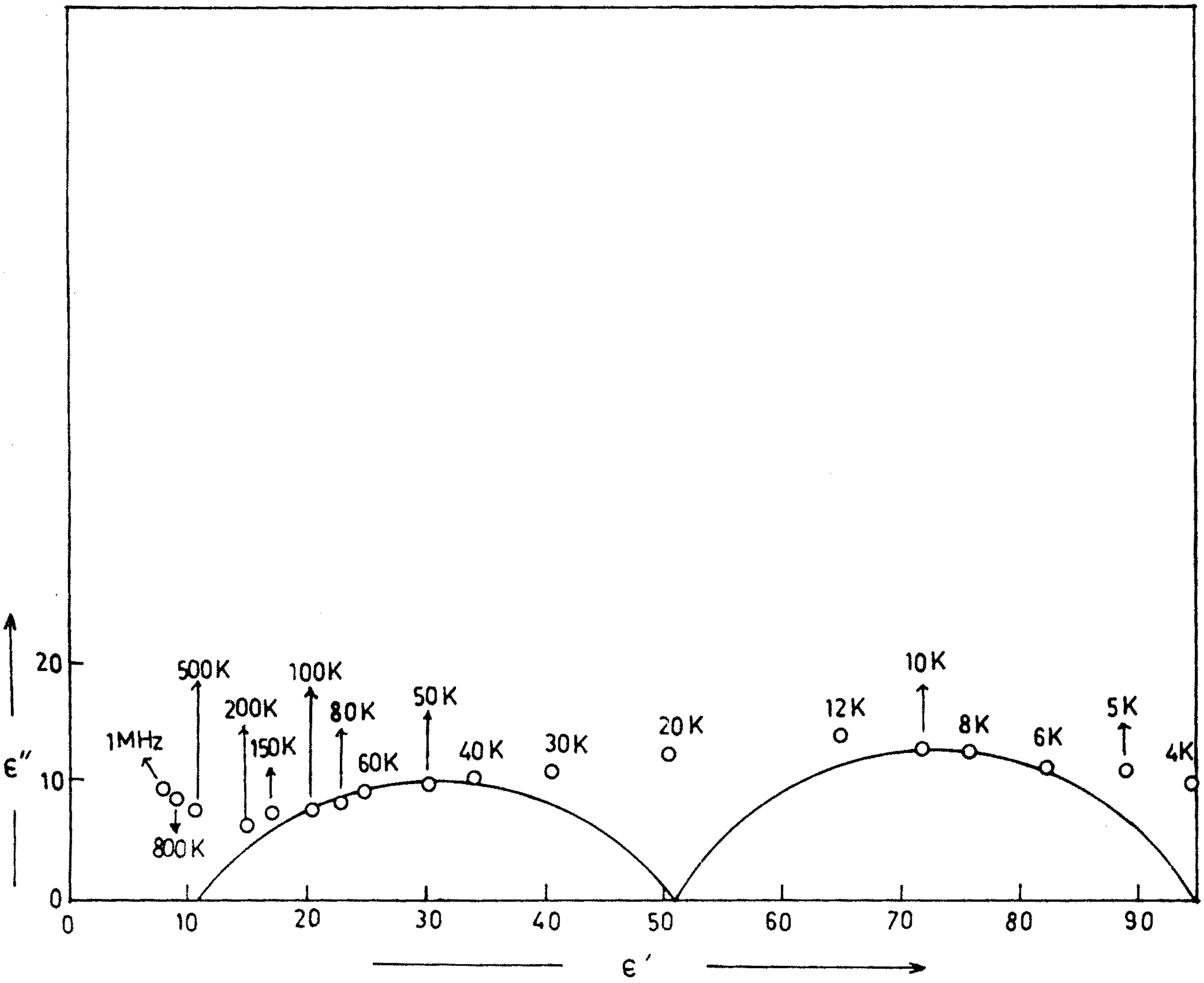

Fig. 4.9 — Variation of ε'' Vs ε' for $Sm_2Sn_2O_7$.

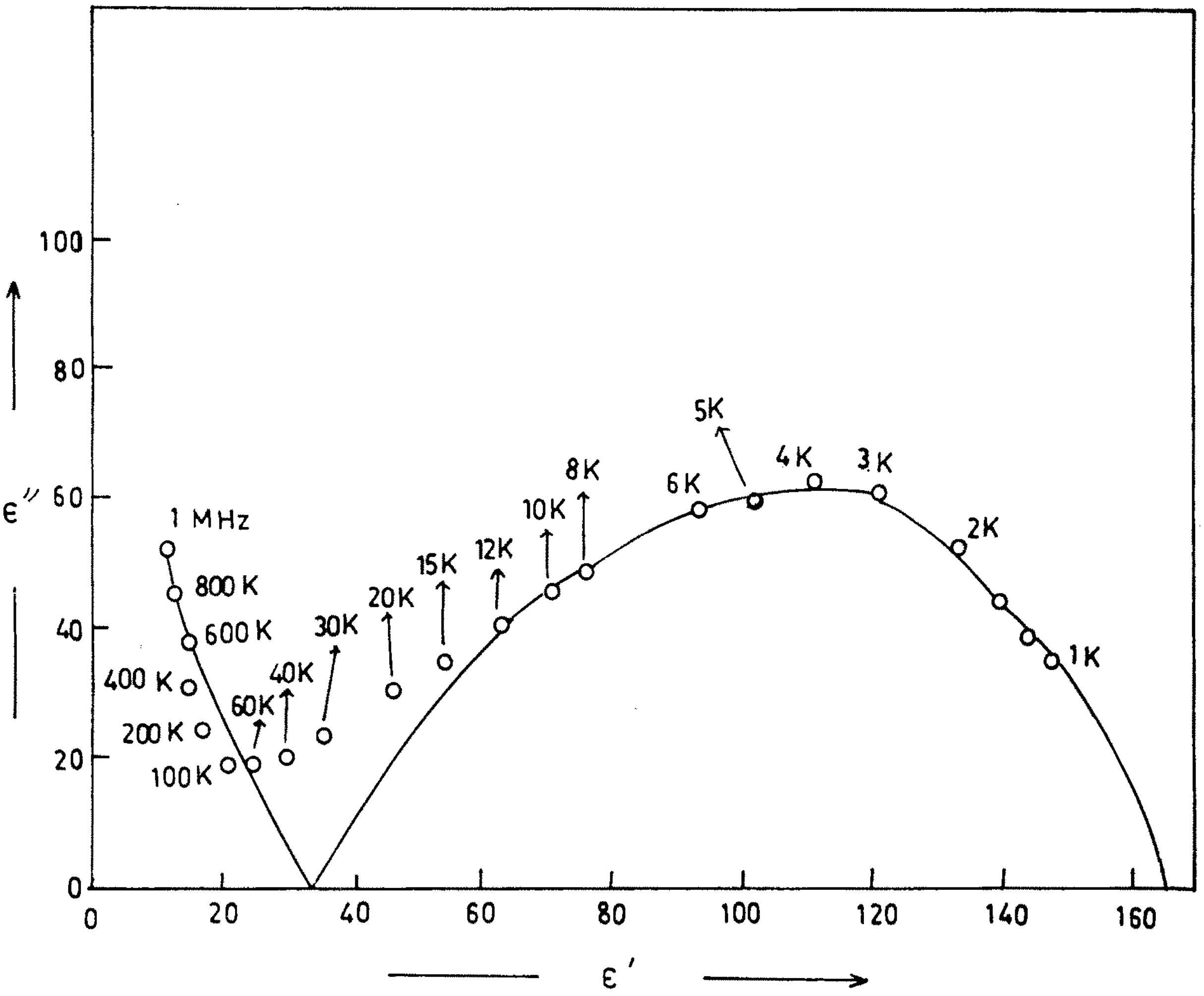

Fig. 4·10 – Variation of ε″ Vs ε′ for $Y_2Ti_2O_7$.

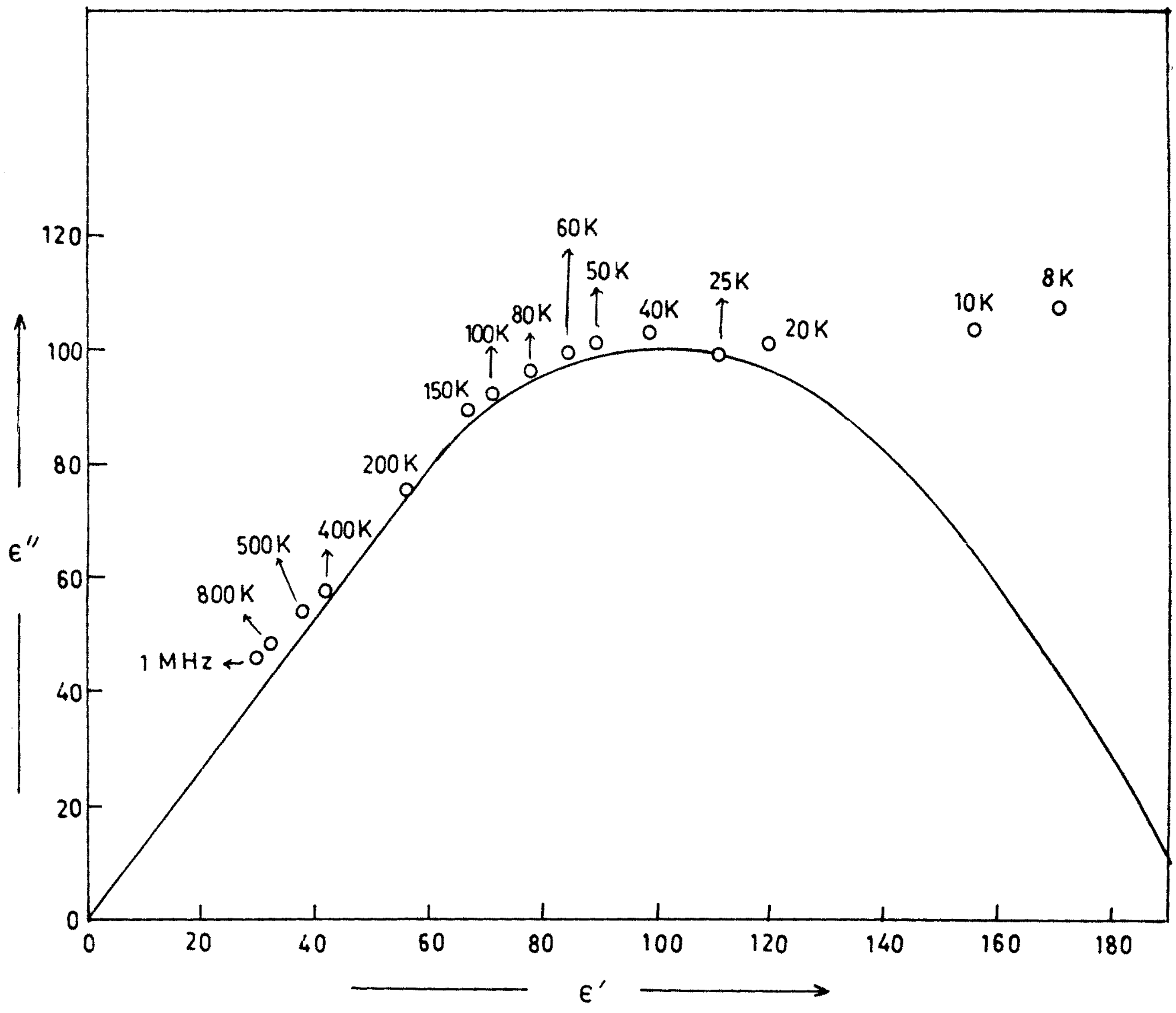

Fig. 4·11 — Variation of ϵ'' Vs ϵ' for $Ce_2Sn_2O_7$.

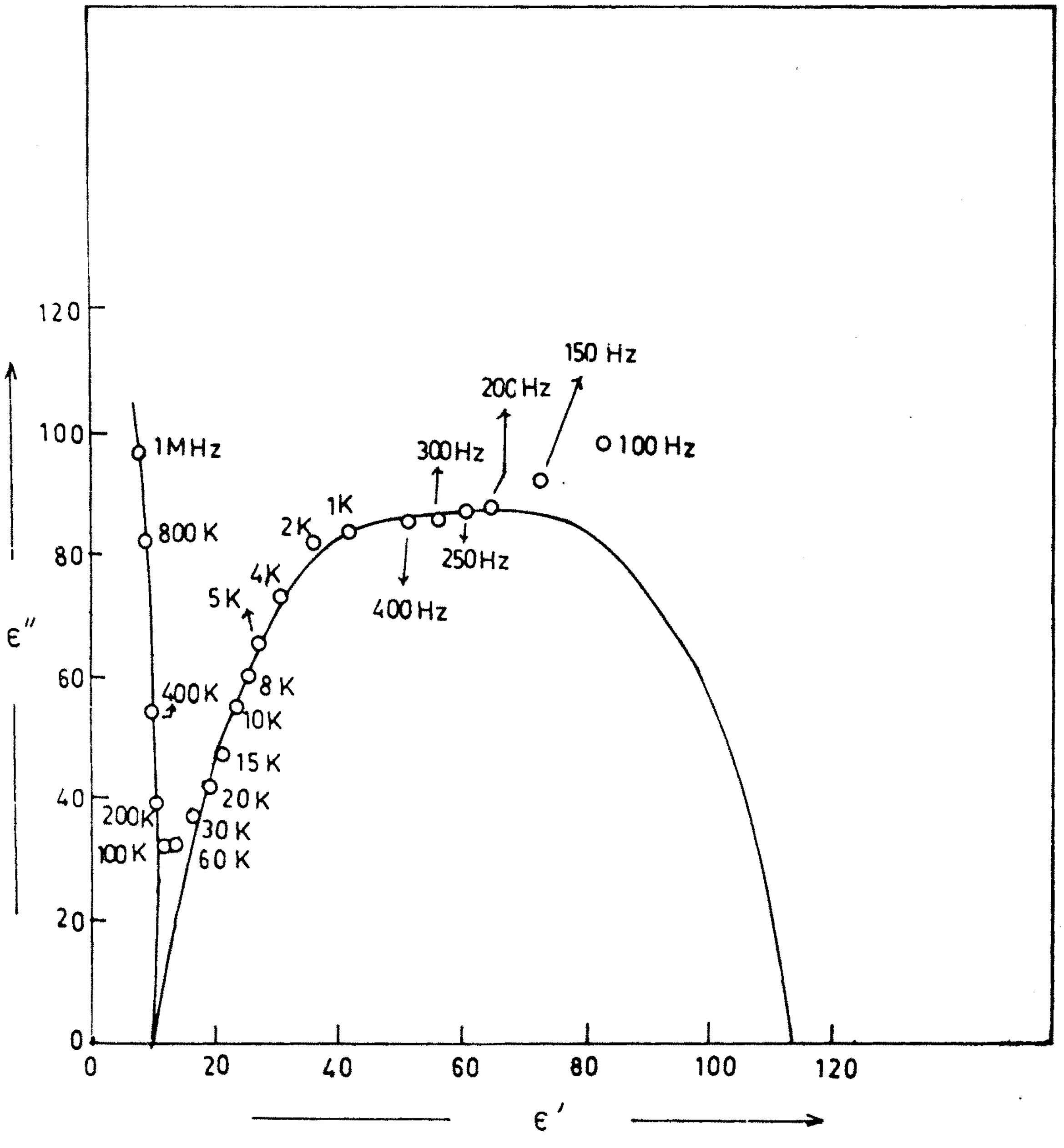

Fig. 4·12 — Variation of ϵ'' Vs ϵ' for $Sm_2Ti_2O_7$ -

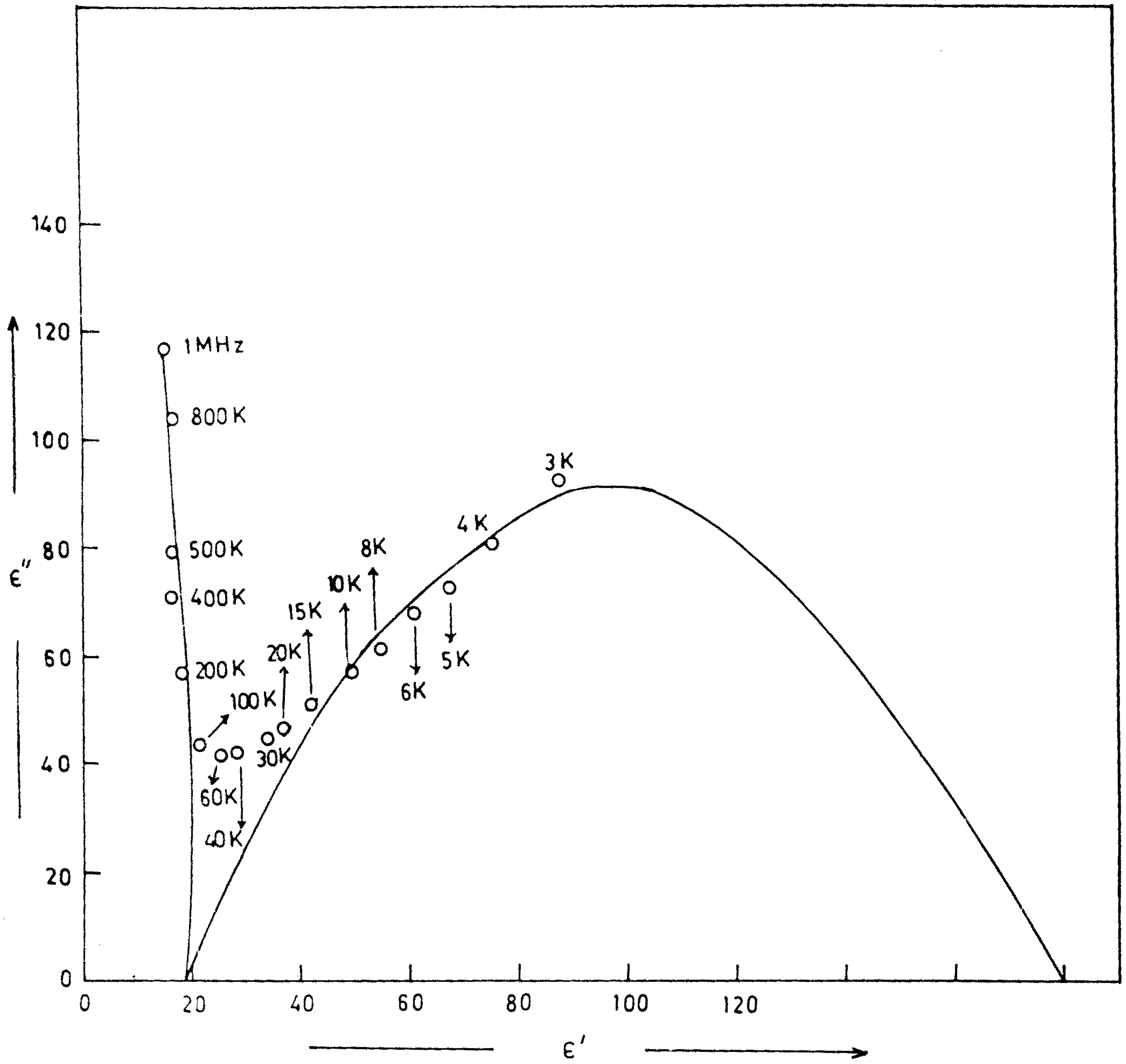

Fig. 4.13 — Variation of ε'' Vs ε' for $Ce_2Ti_2O_7$.

DIELECTRIC CONSTANT WITH TEMPERATURE:

The dielectric constant with temperature are measured with LCR meter bridge (MIC - 4070D) at 1 KHz. The dielectric Constant ε' Versus temperature plots are shown in figures 4.14 to 4.19. The dielectric constant slowly decreases and shows minima at certain temperature, again it increases with temperature. The temperature at which minima in dielectric Constant is observed is correlated with n to - p transition from thermoemf data, and maximum resistivity from conductivity data. These temperatures are noted in table 4.1. It is observed that these three temperatures are nearly same. This behavior can be explained on the basis of oxygen vacancy concentrations and the reactions proposed by the equations 3.21 and 3.22 . As the anion vacancy concentration is increased, it is supposed that the resistivitiy increases due to interaction of vacancies with each other and with cations (8) which effectively reduce the concentration of mobile vacancies. At higher temperatures the dielectric constant increased not because of any ferroelectric behavior but rather due to exponential decrease of the electrical resistivity as demonstrated in Figures 3.3 to 3.8 for the present samples. Also these samples exhibited p-type senconduction at and above these temperature. Similar results have been observed in Titanate pyrochlores (9).

Thus, the overall dielectric behaviour of these materials has been proposed to have two contributions. i) one of the ferroelectric nature in local microregions and ii) other of interfacial polarization due to difference in the conductivity of grains and grain-boundaries as well as chemical microhetrogenetics. The formation of barrier layers is confirmed by plotting the imaginary part of dielectric constant ε'' against it's real part ε'. Cole-cole plots of these samples are shown in figures 4.8 to 4.13. The overall electrical properties of polycrystalline ceramics has contribution from grains, grainboundaries and solid electrode interfaces (6). Each of these contributions can be represented by a suitable combination of resistance and capacitance in parallel. The samples can thus be represented by and equivalent circuits containing R and C elements in series. Two depressed circular arcs observed for $Y_2Sn_2O_7$ and $Sm_2Sn_2O_7$ samples. The lower frequency arc is associated to grainboundries while the higher frequency to the grains. If the time constant for these RC elements is defferent (ratio greater than 10) each paralel element gives rise to a single semicircle with a center on ε' axis, if there is only single value of relaxation time(7). If any of the above processes have the distribution of relaxation time, then one obtains a depressed circular arc in the impedance plot having it's center below the ε' axis. The samples $Y_2Ti_2O_7$, $Ce_2Ti_2O_7$, $Sm_2Ti_2O_7$ and $Ce_2Sn_2O_7$ show a single semiarc . From these plots, there is also contribution from electrode speciman interface. The detailed analysis of impedance plots and the complex plain modulus plots give complementary information to the information given by Cole-Cole plots.

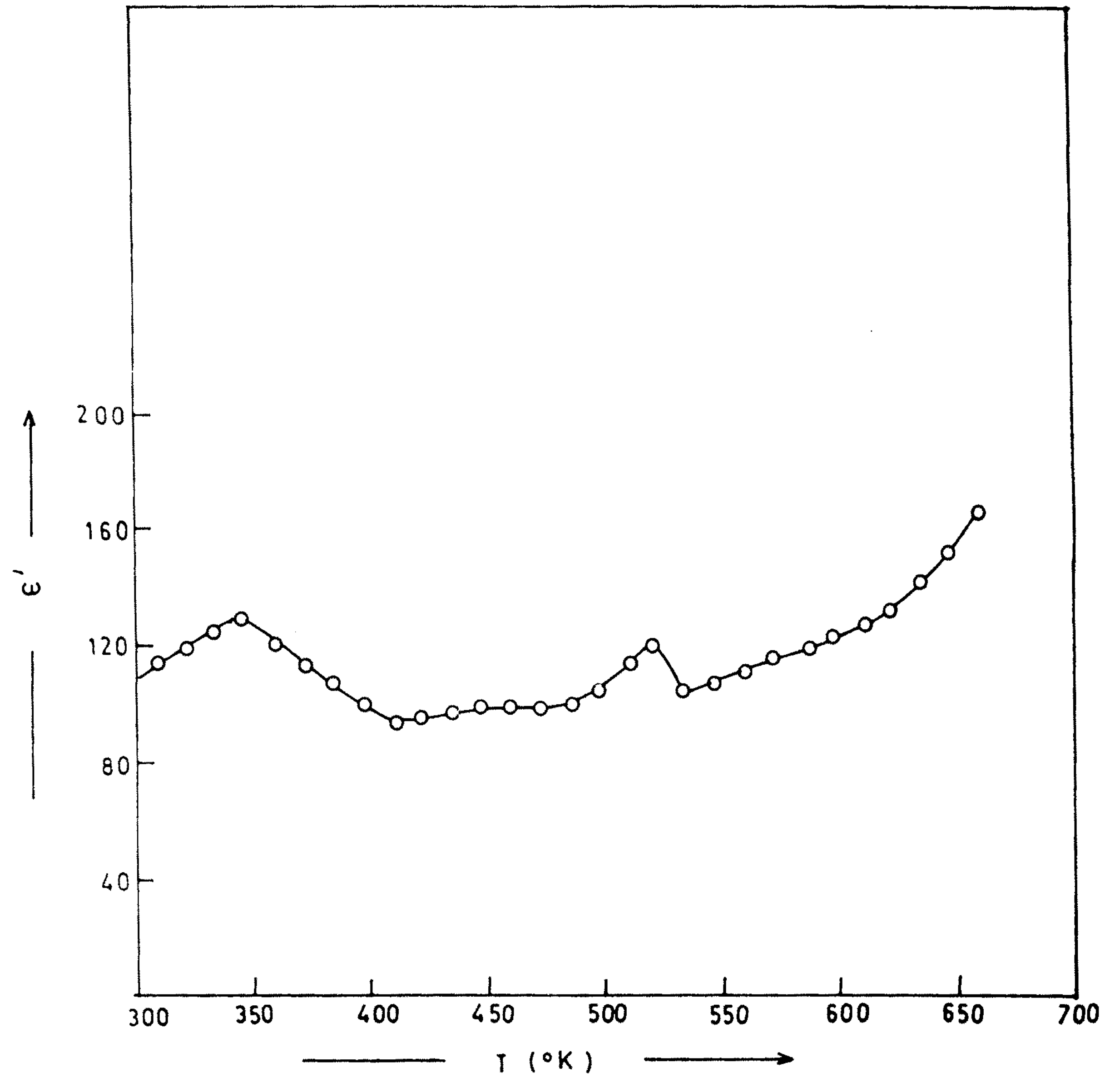

Fig. 4.14 – Temperature variation of dielectric constant for $Y_2Ti_2O_7$.

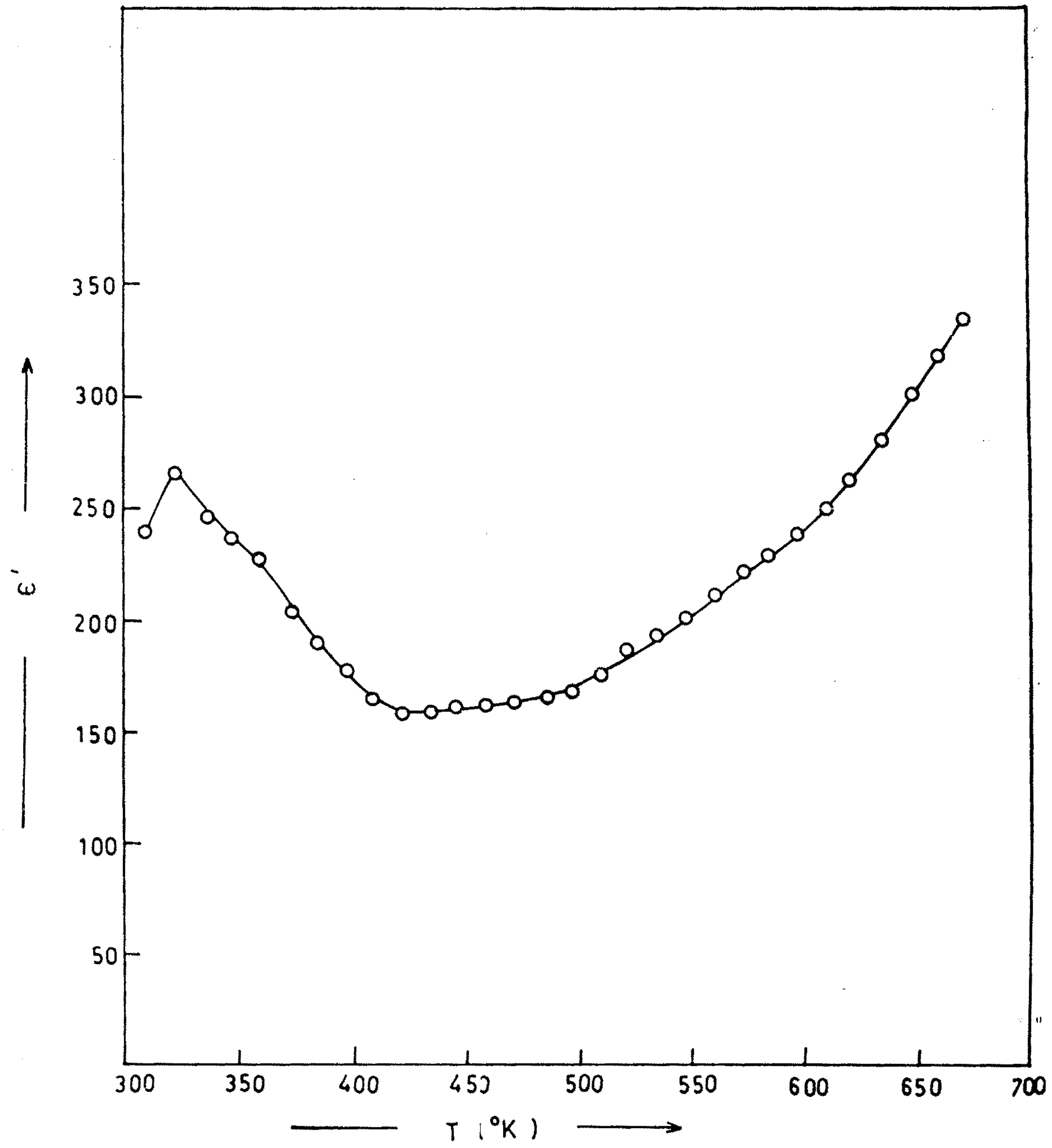

Fig. 4·15 – Temperature variation of dielectric constant for $Ce_2Ti_2O_7$.

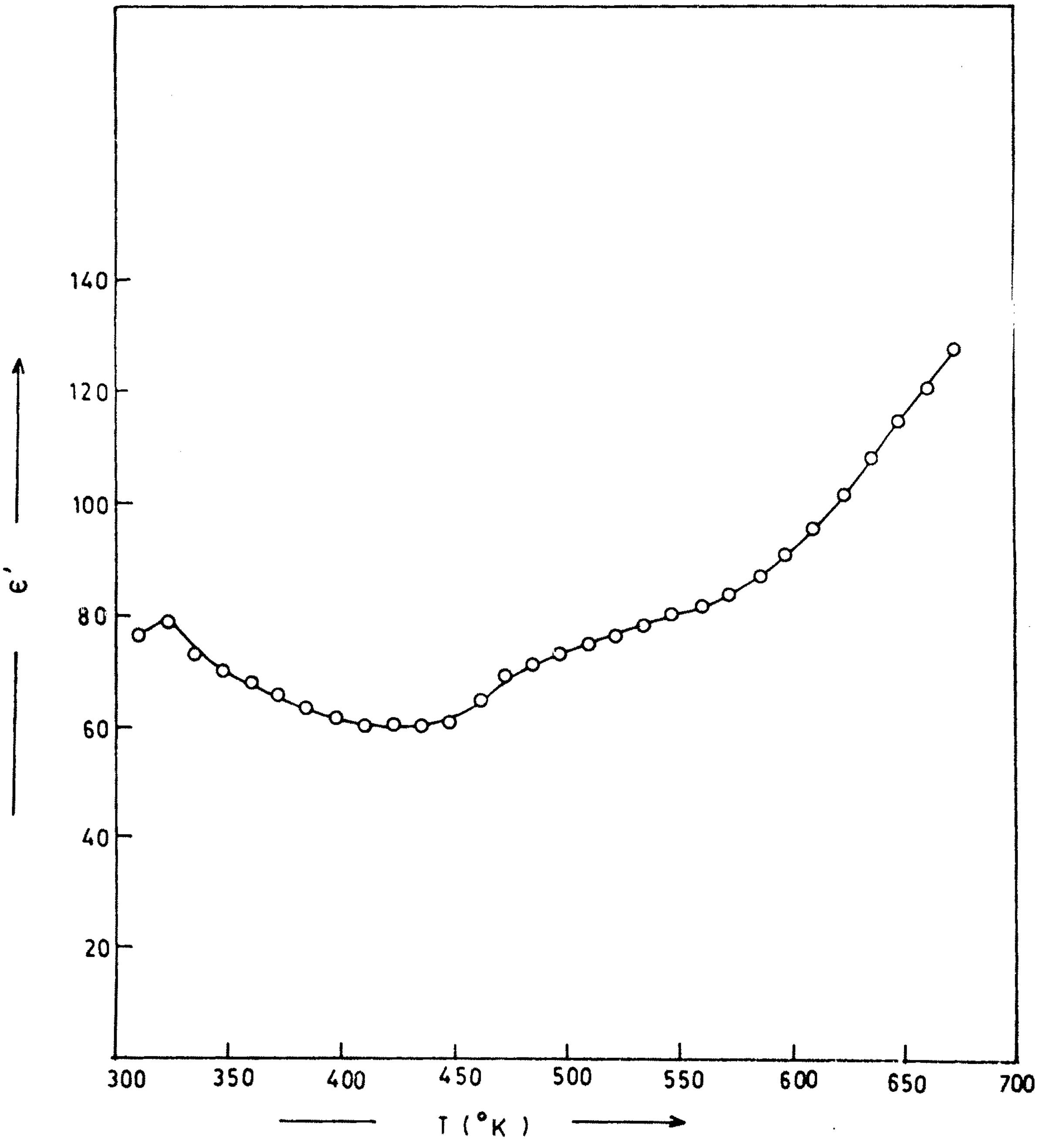

Fig 4·16 – Temperature variation of dielectric constant for $Sm_2Ti_2O_7$.

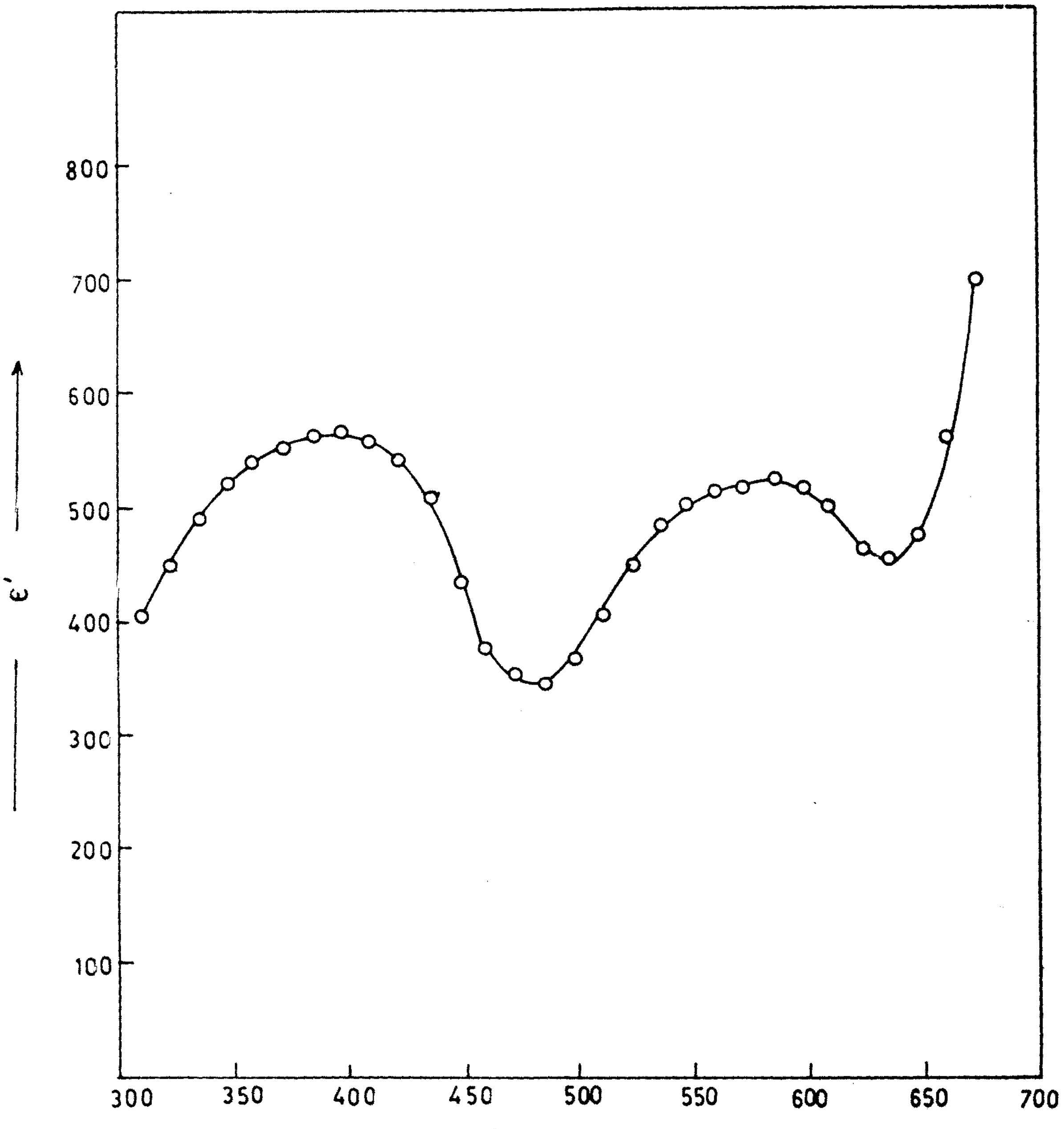

Fig. 4.17 – Temperature variation of dielectric constant for $Y_2Sn_2O_7$.

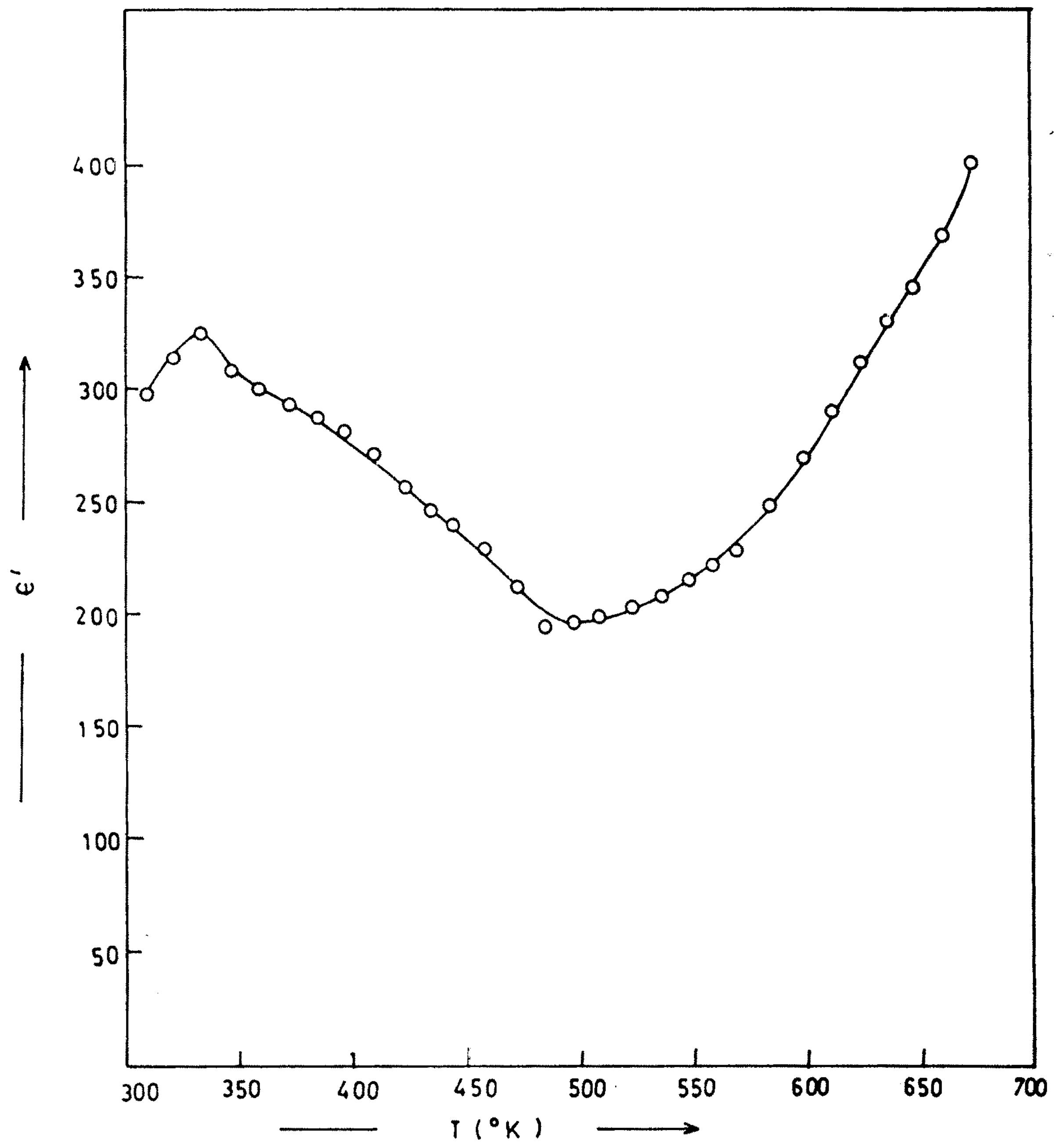

Fig. 4·18 – Temperature variation of dielectric constant for $Ce_2Sn_2O_7$ ·

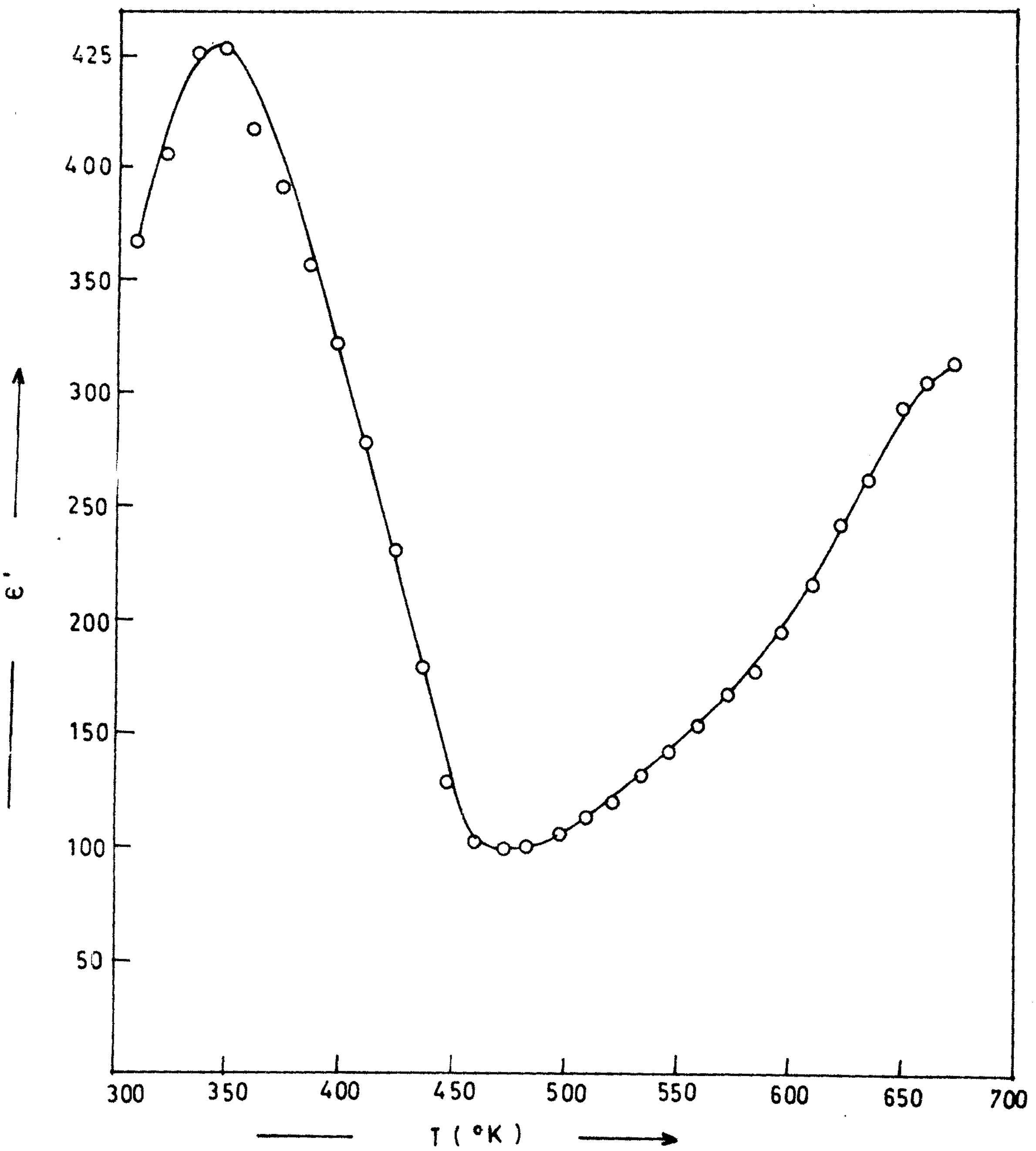

Fig. 4·19 – Temperature variation of dielectric constant for $Sm_2Sn_2O_7$.

Table 4.1 : Values of temperaturs for resistivity maxima,

thermoemf n to - p transition and dielectric constant minima.

Sample	Dielectic Constant minima for ε' Vs T °K	Resistivity maxima for log ρ Vs $\frac{1000}{T}$ °K	Thermo emf n to p- transition for ∝ Vs T °K
$Y_2Ti_2O_7$	410.5	410.5	506.0
$Ce_2Ti_2O_7$	423.0	423.0	387.0
$Sm_2Ti_2O_7$	450.0	510.5	450.0
$Y_2Sn_2O_7$	475.0	510.5	600.0
$Ce_2Sn_2O_7$	485.5	485.5	487.0
$Sm_2Sn_2O_7$	423.0	423.0	458.0

REFERENCES

1. Iwachi K.Jap ; J.Appl. phys. **10,** 1520 (1971)

2. Ramanmurthy S ; J. Mat. Sc.Lett. **3,** 1049 (1984)

3. Krotzseh M ; phy. Stat. sol. **6,** 479 (1964)

4. Reziescu. N. and Rezlescu E ; phys. Stat. Solidi **23 (a),** 575 (1974).

5. J.D.Siegwarth and W.N.Lawless ; J. of Appl. physics **47,** 19 (1976)

6. O.P.Thakur Devendrakumar, Om Prakash and Laxman Pandey ; Bull. of Mat. Sci **19,** ***2,*** 403 (1996)

7. Shail Upadhyay, Devendrakumar and Om Prakash Bull. of Mat. Sci. **19** ***3***, 519 (1996)

8. T. Vand Dijk, De Vries and A.J.Burggraaf ; phy. Stat. Sol. **58(a),** 116 (1980).

9. L.H.Brixner ; J.Inorg Chem. **3** **7**,1066 (1964).