CHAPTER 8

DIELECTRIC BEHAVIOUR

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8.1   INTRODUCTION

Do solids have built-in electrical field within them? Any distribution? (handwritten margin note)

The study of dielectric properties of solids often gives good insight into the electrical field distribution within them. Studying the dielectric constant as a function of frequency and temperature, the various polarization mechanisms in solids can be understood. In addition to the dielectric constant, relative dielectric loss factor, dielectric loss tangent, conductivity and moreover, the temperature dependence of these properties would be a more useful piece of information. Considerable work in this direction has been carried out on a variety of solids by several workers (1-4). Brower and Fang (5-7) have studied the dielectric constant of some Czochralski grown Scheelite group tungstates and molybdates, viz. $CaWO_4$, $CaMoO_4$, $SrWO_4$, $SrMoO_4$, $PbWO_4$ and $PbMoO_4$ at $24.5^{o}C$ in air atmosphere at 1.59 KHz. Further, the variation of dielectric constant of flux-grown $BaMoO_4$ with frequency and temperature has been reported by Arora et al (8). A careful look at the properties of $CaMoO_4$ crystals (chapter 5) suggests that it may be useful to study the variation of dielectric constant

and loss factor of $CaMoO_4$ with respect to frequency and temperature which, to author's knowledge, has not so far been reported.

As an extension to the study of properties of the grown crystals described in the preceding chapters 5, 6 and 7, the present chapter embodies the studies made on the dielectric studies and attempts have been made to draw some qualitative conclusions, taking in view the existing theories of various sources of polarization.

8.2 EXPERIMENTAL DETAILS

Single crystals of calcium molybdate, grown in our laboratory by the flux cooling method, using unstirred supersaturated high-temperature solutions of lithium chloride melt at 750°C, have been used. The dielectric measurements were carried out on (i) the unoriented thin single crystalline platelets, and (ii) the polycrystalline samples in the form of pressed pellets. Some of the grown crystals were grounded to fine powder using a ball-mill and then pressed into the form of circular pellets of 10 mm diameter and 2 mm thickness, using a stainless-steel

die and a hand-operated hydraulic press at different pelletising pressures varying from 9.8×10^2 kg.cm^{-2} to 16.9×10^2 kg.cm^{-2}. On the other hand, the single crystalline platelets used for the measurements were about 1 mm thick and surface area of 0.12 cm^2. The geometrical dimensions of the samples were measured using a travelling microscope (least count 0.001 cm).

The dielectric measurements were carried out using the two electrode method. The crystal or the pellet, as the case may be, was annealed, cleaned and dried before the measurements. After applying the silver paste on both the experimental surfaces under the check of an optical microscope, the specimen was mounted inbetween two flat stainless-steel circular parallel electrodes of a specially designed porcelain conductivity cell, shown schematically in Fig. 8.1. Both the upper and the lower cylindrical tubes of the cell can be screwed in for proper contact of the sample with the electrodes. It may be mentioned that the measurements were repeated on samples obtained from the same growth run.

The capacitance and the dissipation factor were measured using GenRad 1620-A/-AP Capacitance

Measuring Assembly with built-in GR 1311-A Audio
Oscillator, GR-1232-A-AP Tuned Amplifier and Null
Detector, 1232-P2 Preamplifier and GR 1615 Capacitance
Bridge, shown in the experimental set-up for dielectric
measurement in Fig. 8.2.

The frequency response of dielectric
constant was studied first at room temperature (25°C)
for both the sets of samples. Further, to study the
effect of temperature on the dielectric constant, the
ceramic cell was enclosed in a specially built resistance
heating furance, capable of giving accurately a temper-
ature of about 500°C. The temperature was raised slowly
by regulating the power from 230 V, 50 Hz mains through
a dimmerstat. To monitor the accurate temperature of
specimen, a Pt-Pt 10 % Rhodium thermocouple was used.
The measurements were also made at different frequencies
at room temperature on the pellets of the same area and
thickness but prepared at different pelletising
pressures.

8.3   Measurements

The dielectric constant, ϵ' , of the
samples was computed using the formula

$$\epsilon' = \frac{\epsilon}{\epsilon_o} \tag{8.1}$$

where ϵ and ϵ_o are the permittivity of the dielectric material and free space ($\epsilon_o = 8.854 \times 10^{-12}$ farad. meter^{-1}), respectively.

Further, permittivity of the dielectric material, ϵ , was calculated by substituting the values of the capacitance read out from the Bridge in the following equation,

$$\epsilon = C_{read} (t/A) \text{ farad. meter}^{-1} \tag{8.2}$$

where t and A are the thickness and the area, respectively, of the dielectric.

8.4   RESULTS

8.4.1   Effect of frequency

The variation of dielectric constant (ϵ') and loss, i.e., tan δ, at different frequencies (range : 10^2 to 10^4 Hz) at room temperature (25^oC) are shown in Figs. 8.3 and 8.4 for both the pellet and the crystal. The values of dielectric constant for the

pelletised sample (Fig. 8.3) are greater than that of the single crystalline platelets (Fig. 8.4). The value decreases from 60.68 at 200 Hz to 32.79 at 10^4 Hz in the case of pellet, while in the case of crystalline platelet it decreases from 36.05 at 200 Hz down to 19.95 at 10^4 Hz. However, the broad nature of variation in both the specimens is the same; both exhibit a decreasing trend. The value of tan δ also decreases from 0.196 at 20C Hz to 0.122 at 10^4 Hz in the case of pellet while in the case of crystal it decreases from 0.072 at 200 Hz down to 0.0181 at 10^4 Hz.

8.4.2   Effect of pressure

The measured density of different pellets prepared at various pelletising pressures is found almost the same i.e. only 92 % of the reported (9) X-ray density. Interestingly, ε' is independent of pelletising pressures at any frequency. This effect has been well-illustrated in Fig. 8.5.

8.4.3   Effect of temperature

The variation of dielectric constant (ε') and loss (tan δ) of calcium molybdate at 10^4 Hz but at different temperatures is graphically shown in

Figs. 8.6 and 8.7. Seemingly, the nature of variation
is the same for pelletised samples and single crystalline
platelets in the studied temperature range (298-698 K).

8.5   DISCUSSION

The dielectric constant of a material at
lower frequencies depends on the excitation of bound
electrons, lattice vibrations,dipole orientation and
space-charge polarization (atomic or electronic). These
four polarization mechanisms are indicated schematically
in Fig. 8.8. At very low frequencies all the four contri-
butions may be active, and they can be correlated to
"oscillators" with specific eigen frequencies and
damping. The manner of variation of dielectric constant
with frequency and temperature as observed in the present
study would indicate which contributions are particularly
dominant.

The simplest correlation between the
dielectric constant and the frequency is given by
the first Debye equation (10).

$$K'(w) = K'_{\infty} + (K'_s - K'_{\infty}) / [1 + (w\tau)^2] \quad (8.3)$$

where K'_{∞} = dielectric constant far above the frequency
w , K'_s = static dielectric constant, w = $2\pi\nu$ and
τ is the relaxation time of strongly damped oscillators.
In this equation the frequency appears explicit, while
the temperature is implicit in K'_s , K'_{∞} and τ . Our
dielectric measurements are in the lower frequency
region; the contribution of bound electrons and atoms
results mainly in the high frequency part which can be
expressed as $K'_{\infty} = K'_e + K'_a$. However, according to
Szigeti ([1]) the electronic and atomic polarizations
are not independent. The influence of electronic
polarization on atomic polarization is two-fold: long-
-range and short-range interactions. Both parts increase
with K'_{∞} . Numerical evaluation is not possible because
the value of the involved parameters and their inter-
-relation are not well known.

The vibration contributions can be less
or more than the electronic contribution, depending on
the spectral position of the eigen frequency of
electronic and atomic oscillators. The contribution of
space charge will depend on the purity and perfection of
crystal. Its influence will be noticeable mainly in the
low frequency region.

The variation of dielectric constant and loss with frequency at room temperature are shown in Figs. 8.3 and 8.4 for pellet and crystal respectively. The dielectric constant has a high value at low frequencies and it decreases with increasing frequency. The increase of dielectric constant with lowering frequencies can be understood by space-charge polarization caused by unidentified impurities or crystal defects (12, 13). The observed higher values of dielectric constant in the case of pelletised samples compared to the platy crystals may be due to the interstitial polarization occuring in the former case.

The Figs. 8.3 and 8.4 also indicate that the dielectric loss decreases with the increase in frequency. The loss factor is the sum of various dielectric loss processes which include the losses due to the series resistance and the capacitance of the electrode. The later contribution, perhaps, is responsible, as interpreted by Narayana et al (14) for the frequency dependent loss factor.

The temperature has a complicated influence (15) on the dielectric constant. The temperature coefficient of dielectric constant can be positive or

negative at low temperatures, but it is always positive
at high temperatures. Increasing the temperature of the
crystal decreases the number of oscillators per unit
volume, though their relaxation period diminishes. The
increase of atomic distance influences the electronic
and ionic polarization. In addition, there is a pure
temperature-dependent effect. The anharmonic forces of
lattice also contribute to the dielectric constant (16).
The influence of defects and impurities will also
depend on temperature.

In view of these complications we do
not have a reliable theory of temperature influence
on dielectric constant. The variation of dielectric
constant with temperature, as shown in Fig. 8.6, in the
case of a pellet is found to be temperature independent
in the temperature region of $25^{\circ}C$ to $165^{\circ}C$ (or 298-
438 K). In the temperature range $175^{\circ}C$ to $275^{\circ}C$ (or
448-548 K), the value of ϵ' increases slowly and
beyond that i.e. $285^{\circ}C$ to $425^{\circ}C$ (or 558-698 K) there is
a much faster variation. On the other hand, in the case
of platy crystals the value increases rather slowly
linearly from $25^{\circ}C$ to $265^{\circ}C$ (or 298-538 K) following
the relation

$$\epsilon' = 3.26 \times 10^{-2}t + 19 \qquad (8.4)$$

and, later in the temperature range $285^{\circ}C$ to $415^{\circ}C$ (or 558-688 K) it increases exponentially; this suggests that the dielectric oscillators get thermally activated and their relaxation time can be given as (17,18)

$$\Upsilon = \Upsilon_0 \exp. (H/kT) \qquad (8.5)$$

where Υ_0 is a pre-exponential constant and H is the activation energy of oscillators.

Summing the two behaviours, the dielectric loss decreases with frequency (Figs. 8.3 and 8.4) and increases with temperature (Fig. 8.7). The increase at lower frequencies is caused by crystal defects and that at high frequency by the infrared absorption. The nature of variation of dielectric loss with temperature (Fig. 8.7) is similar to the variation of dielectric constant with temperature (Fig. 8.6).

The initial variation of dielectric constant with temperature may be attributed to the

atomic polarizability and expansion of the lattice (19);
the subsequent exponential increase may be ascribed to
space-charge polarization of thermally generated charge
carriers (20), whose relaxation time $\mathcal{T}$ can be expressed
as mentioned in equation (8.5). From the graphs of ln ϵ'
versus 1/T, in the temperature range 285-698 K, shown
in Fig. 8.9, the activation energies have been obtained
as 0.275 eV and 0.351 eV for pellet and crystal
respectively.

8.6   CONCLUSIONS

1.   The dielectric constant and dielectric loss
      for single crystals as well as polycrystalline
      pellets of calcium molybdate have been
      determined.

2.   The dielectric constant and the dielectric
      loss decrease with the increase in frequency,
      while they increase with the increase in
      temperature.

3.   The dielectric constant is found independent
      of pellitizing pressures in the case of
      polycrystalline pellets.

4.   The different polarizations that contribute
     to the dielectric constant are identified
     from the nature of variation of the dielectric
     constant with frequency and temperature.

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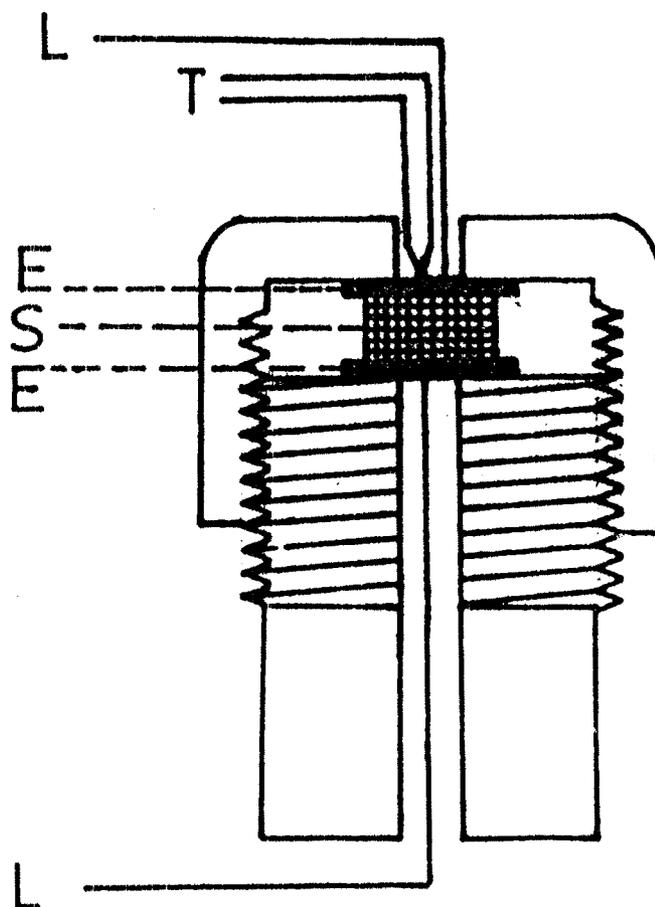
Fig. 8.1 Schematic diagram of the conductivity cell.

Fig. 8.2   GenRad 1620 A Capacitance Measuring
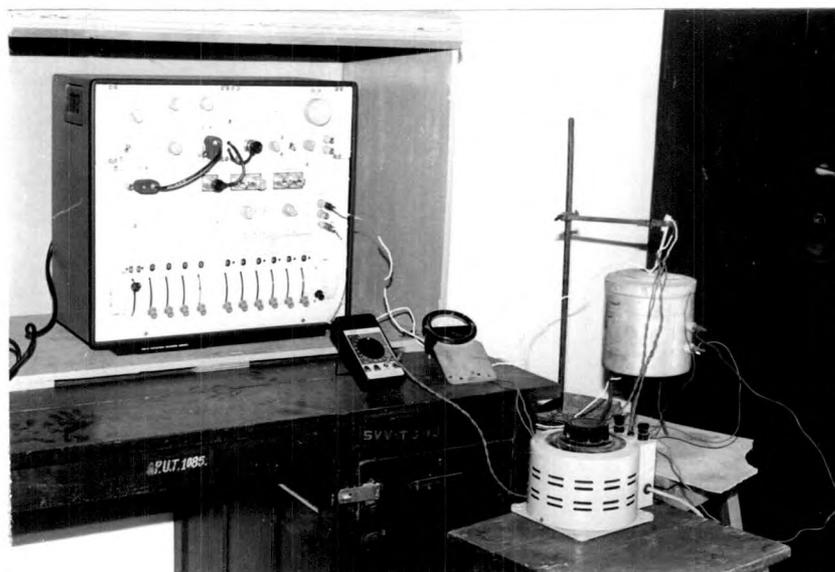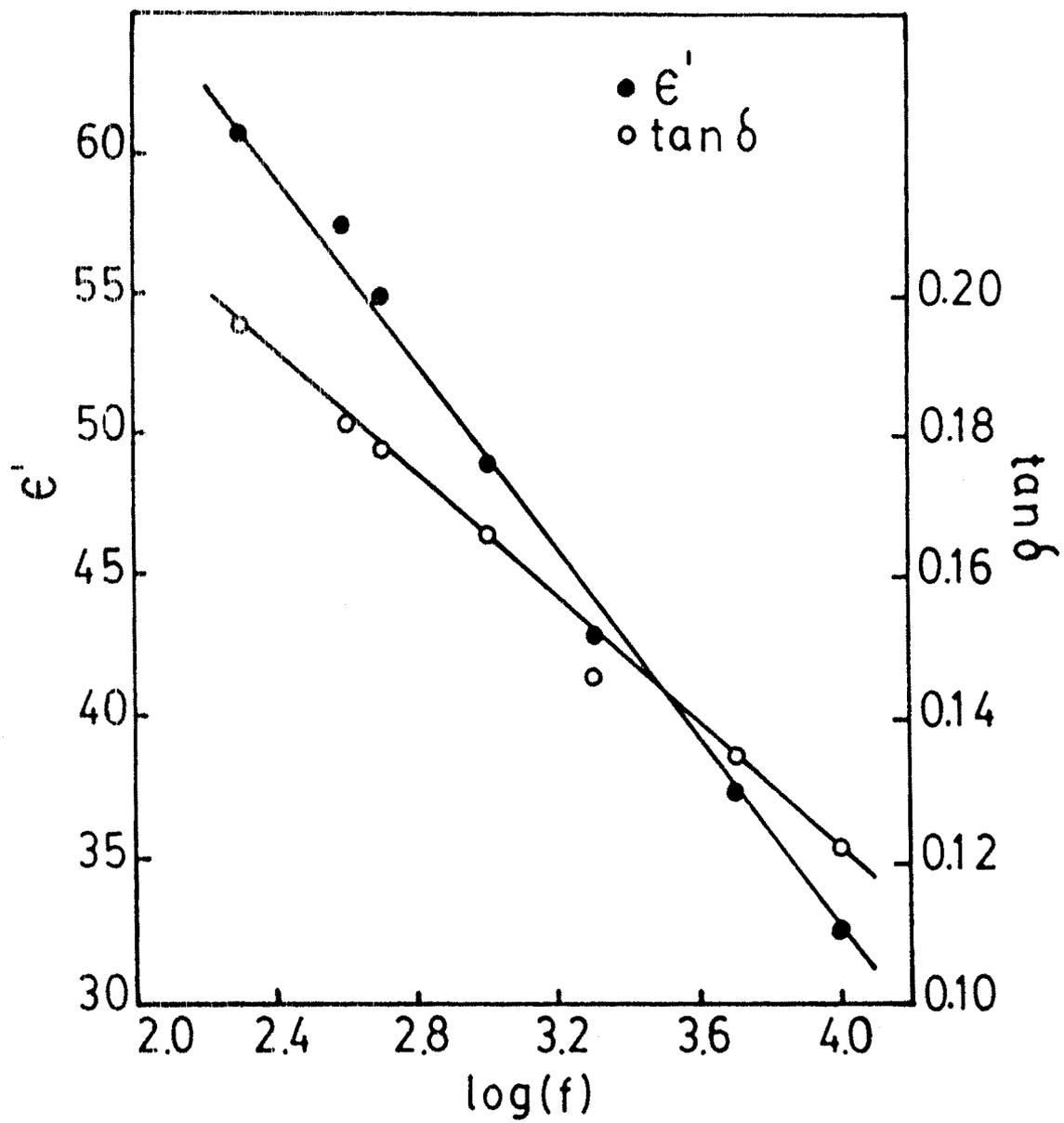   Assembly for dielectric measurements.

Fig. 8.2

Fig. 8.3   The graphical variation of dielectric
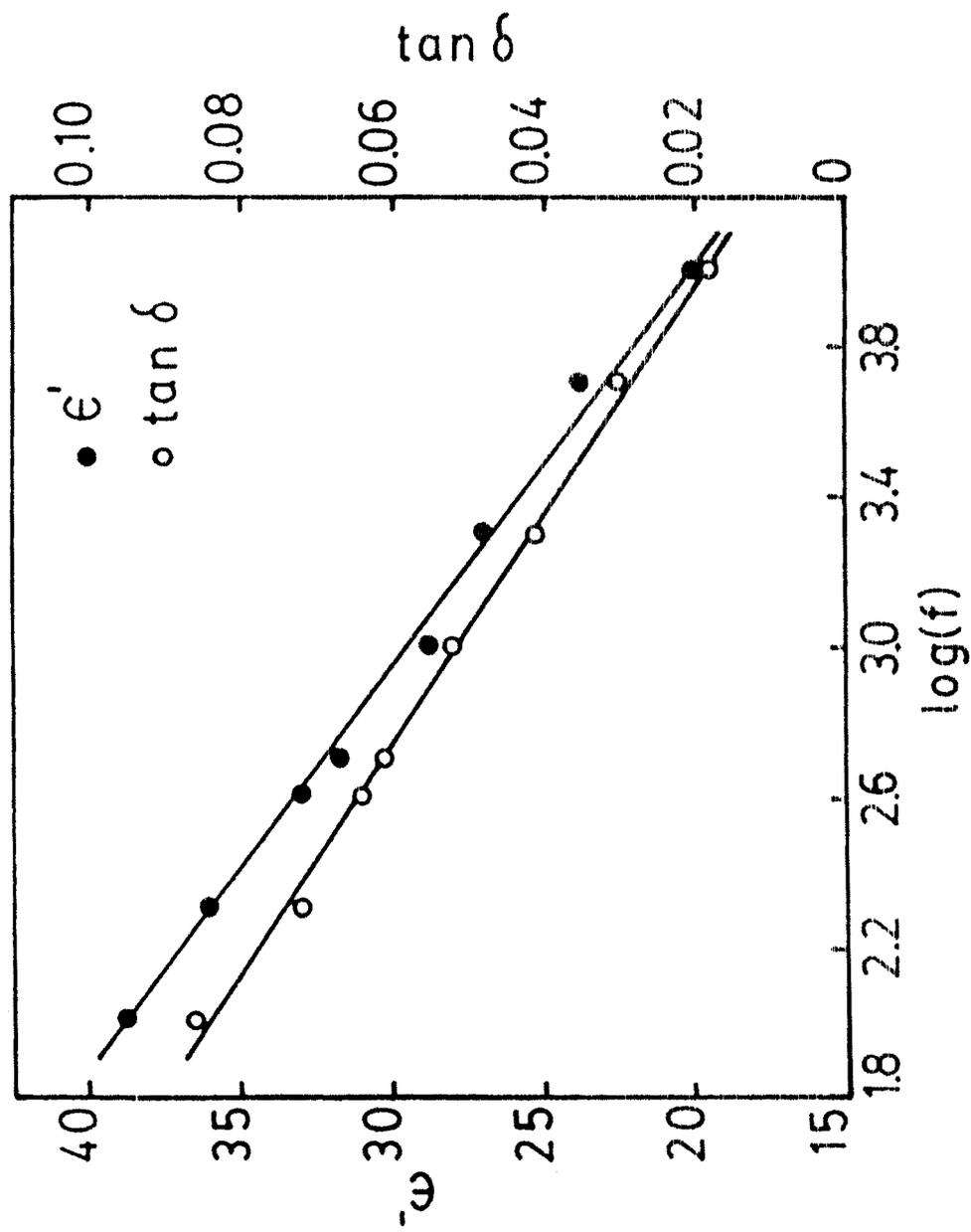constant and losses of pelletised samples
as a function of frequency.

Fig. 8.4 The graphical variation of dielectric constant and losses of single crystals as a function of frequency.
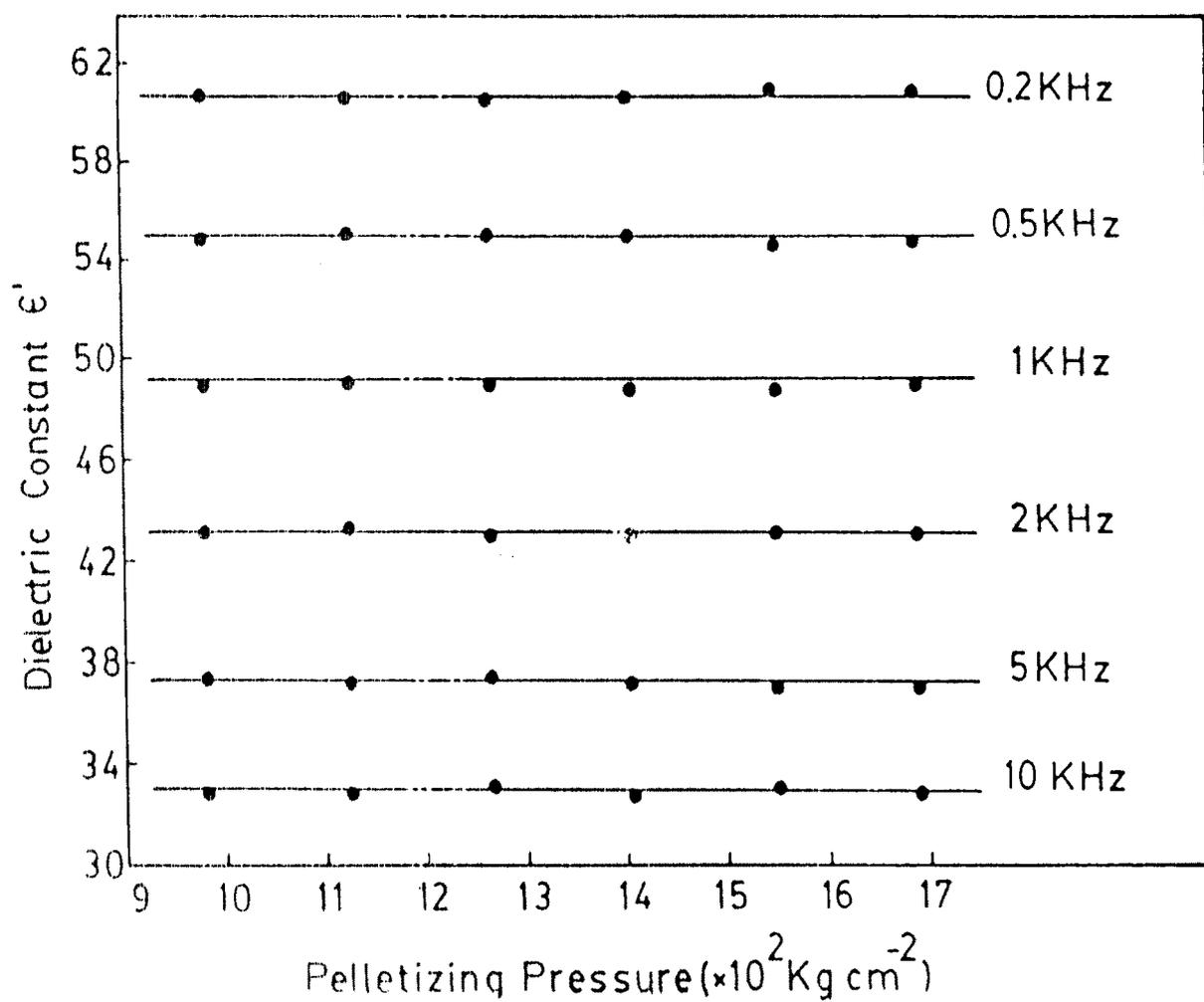
Fig.8.5 The graphical variation of dielectric constant of the pelletised samples prepared at different pelletising pressures.
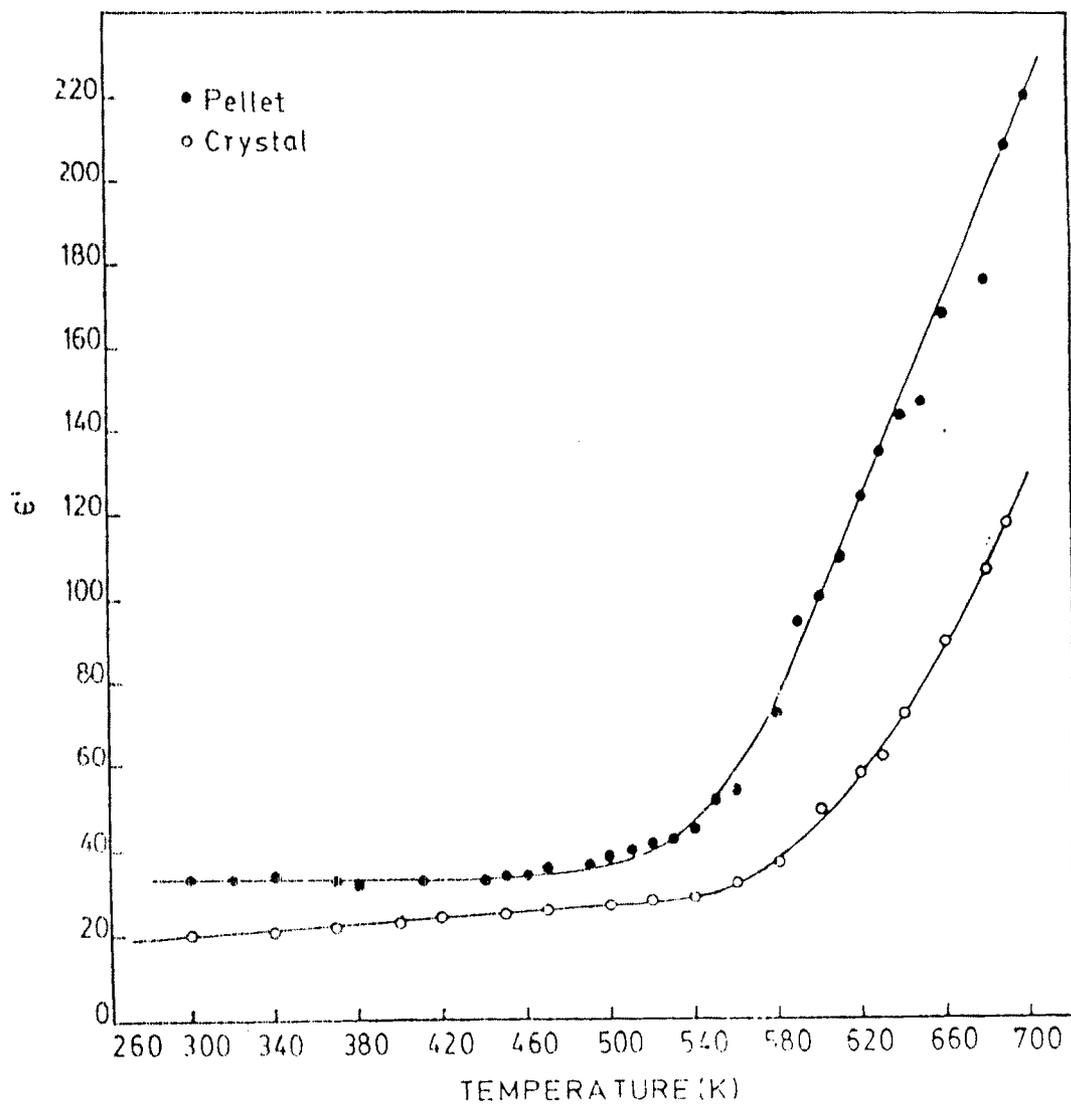
Fig. 8.6   The temperature variation of dielectric
           constant of pelletised sample and single
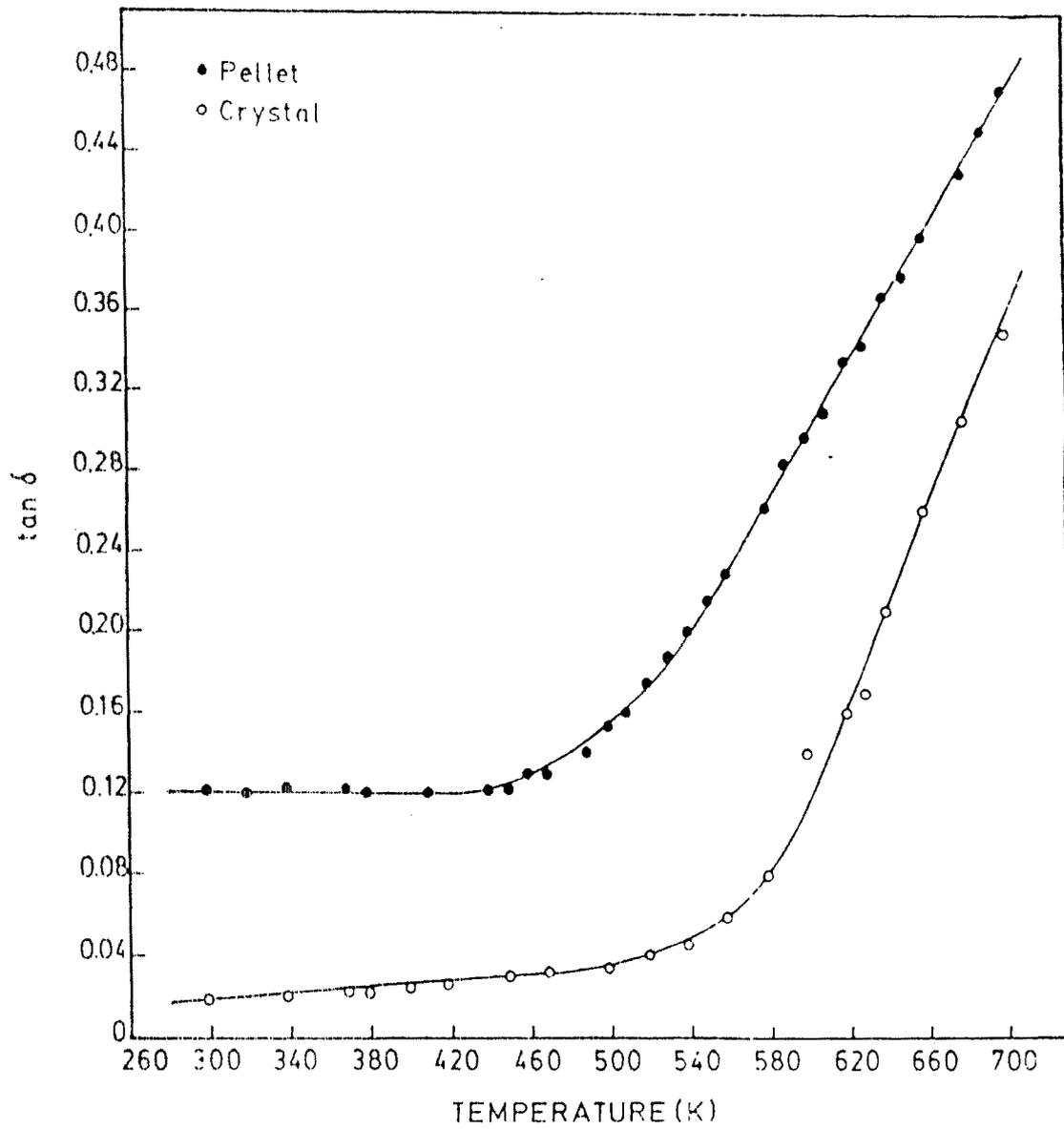   crystal.

Fig. 8.7 The temperature variation of dielectric loss
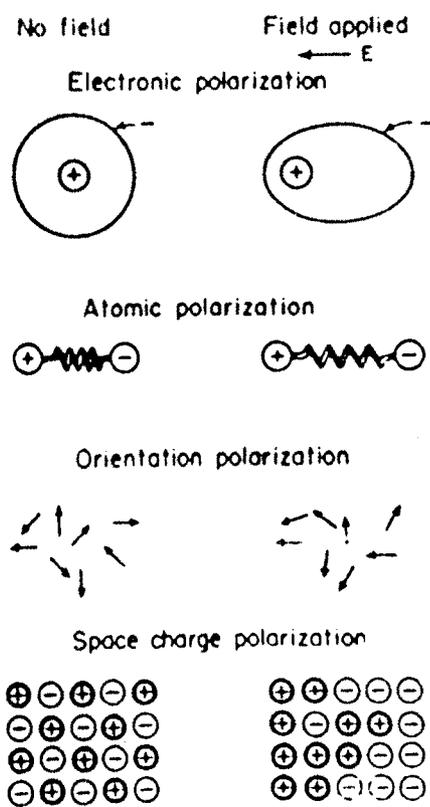for pelletised sample and single crystal.

No field   Field applied

$\longleftarrow$ E

Electronic polarization

Atomic polarization

Orientation polarization

Space charge polarization

Fig. 8.8 Schematic diagram of different
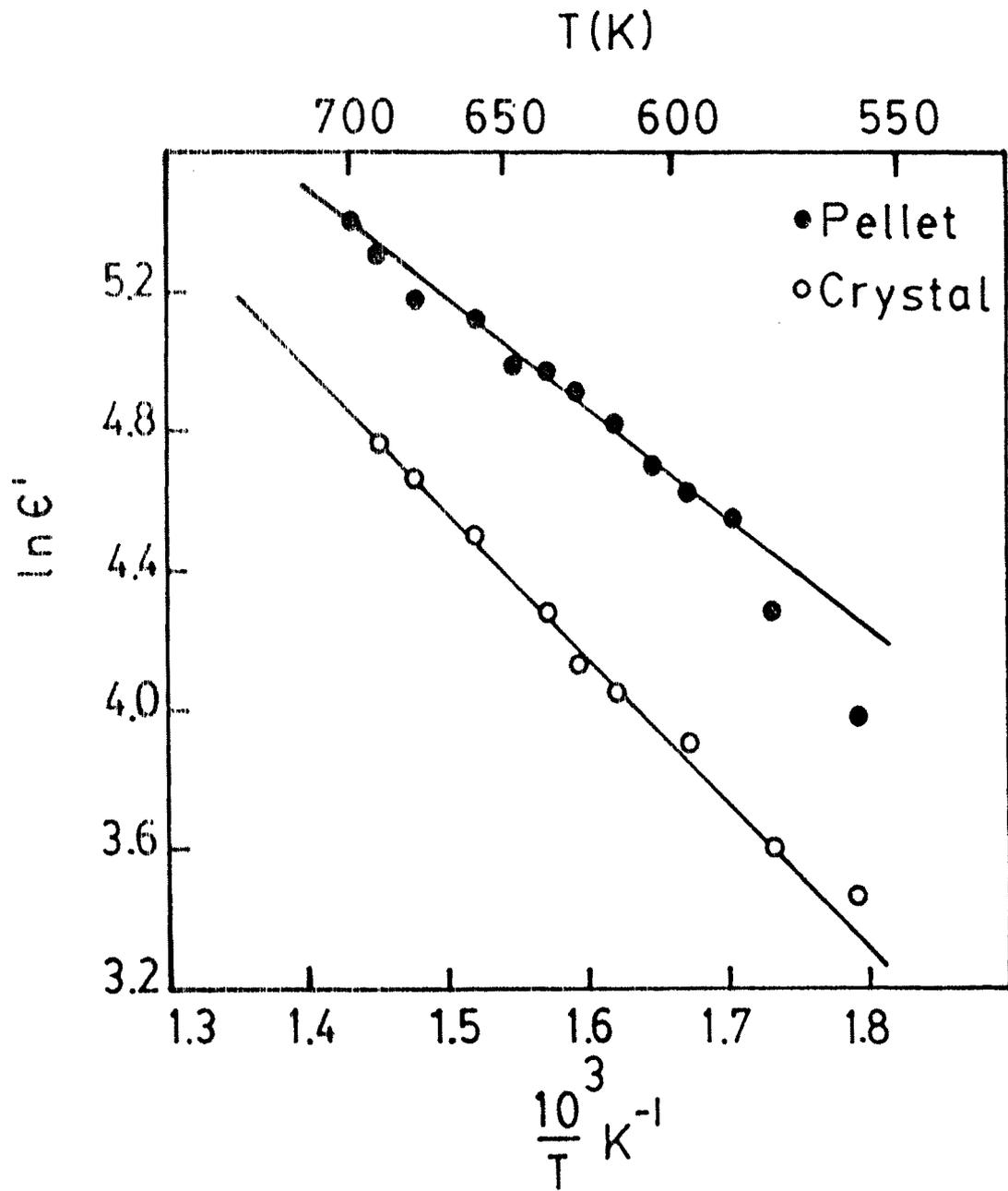mechanism of polarization.

Fig. 8.9 The variation of ln ϵ' versus inverse
of temperature for pelletised sample and
single crystal.