

C H A P T E R - V

D. C. ELECTRICAL CONDUCTIVITY

5.1 Introduction :

Electrical conductivity is an important physical property of dielectric materials and its studies are not only useful for practical applications but also for the understanding of the various physical phenomena. The conductivity of a material denotes its ability to conduct electric charge. Electrons are usually the charge carriers in solids but ionic conduction can also be important for materials with ionic bonds. The conductivity of a solid dielectric depends upon the mobility of charge carriers and on their concentration. The major factors affecting the electrical conductivity of a material are conduction electrons or ion density and the nature of the inter-atomic bonds. The conduction, however, cannot occur unless the charge carriers are made available for the process through activation by some external agency like thermal and electrical energies. The variation of conductivity (σ) with temperature (T) can be expressed by the general exponential relation

$$\sigma = \sigma_0 \exp (-\Delta E/kT) \quad \dots (5.1)$$

where ΔE is the activation energy, σ_0 the constant and k the Boltzmann constant.

It was reported (Grawford 1959) that almost all ferroelectric materials which possess high Curie temperatures lose their piezoelectric properties at temperatures considerably below their Curie points. Guruvich and Rez (1960) showed that the loss of piezoelectric properties of these materials was due to the increase in electrical conductivity at high temperatures. Electrical transport studies on the heavy rare-earth tungstates were reported by Verma et al (1981) showing their ionic-electronic conductivity. Again, the rare-earth samarium, gadolinium and holmium were introduced singly into BaTiO_3 and the resistivity was measured (Tennery et al 1961) as a function of temperature. The conductivity, Hall effect, optical properties and luminescence of rare-earth ion (Gd^{3+} , Sm^{3+})-doped BaTiO_3 single crystal were also studied by Murakami et al (1973).

Temperature dependence of the conductivity of single crystal of ammonium dihydrogen phosphate and the change in conductivity due to Ba^{++} and SO_4^{--} impurities were described by Murphy (1964). Electrical transport properties of iron vanadates were studied by Gupta et al (1986). Kanchan Gaur et al (1984, 1985) have reported the electrical transport properties in light and heavy rare-earth vanadates. The electrical conductivity of Gd-doped BaTiO_3 single crystal was studied by Takeda et al (1966). Electrical conduction anomaly in Sm-doped BaTiO_3 was reported by Goodman (1963). Heyne (1977) discussed the electrical

transport in solids and several ways of determination of nature of conductivity, whether it is ionic, electronic or mixed were also dealt with.

Effect of Fe_2O_3 of different atomic percentage on conductivity of BaTiO_3 was studied by Nishioka et al (1956). The resistivity was found to be minimum at 4.95 atomic percentage of iron. Temperature dependence of electrical conductivity of BaTiO_3 containing iron and cobalt impurities was investigated by Matsonashvili (1967) and an anomalous temperature dependence of σ was observed at the Curie point. The conductivity was found to be depending on Fe or Co concentration. Effect of Fe or Cr impurities on electrical conductivity of SrTiO_3 was studied by Matsonashvili (1968) and it was shown that σ for a weakly reduced SrTiO_3 crystal was substantially greater than for unreduced sample but the law $\log \sigma = \phi (1/T)$ as a rule was very little altered. For weakly reduced crystals with Fe impurities σ decreases somewhat, while the slope of the curve $\log \sigma = \phi (1/T)$ was practically unchanged.

In the present work we have studied the variation with temperature of d.c. electrical conductivity of sodium vanadate and its Fe_2O_3 -doped compositions with a view to understand the following, directly or indirectly.

- 1) Understanding the relation between conduction and disappearance of piezoelectric properties of some ferro-electrics.

2) The role of magnetic impurities in affecting ferroelectric properties and positive temperature coefficient of resistivity.

5.2 Experimental Details :

The experimental set up used for the measurement of d.c. electrical conductivity of the samples is shown in Fig.5.1. It consists of an electrically heated furnace, a power supply unit to provide d.c. electrical field, a digital DC microvolt Meter (VMV 15), a Pico Ammeter Adaptor for VMV 15 and temperature controller. The pellets of the samples were sintered, polished and coated on two sides with a thin layer of air-drying silver paste for good electrical contact. To investigate the nature of the contact, the d.c. current density (J) through the pellets was measured as a function of applied electric field (E) for a constant temperature with stainless steel electrodes. The measurements of d.c. conductivity were carried by two probe method, at a constant 10 V d.c. electric field, after ensuring ohmic contact. The pellets were heated in a global furnace and resistivity was determined while heating, in the temperature region covering the transition point. The resistivity data were used to calculate the d.c. conductivity.

In order to investigate the nature of conductivity (ionic, electronic or mixed) the current through the pellet was measured as a function of time at a constant tempera-

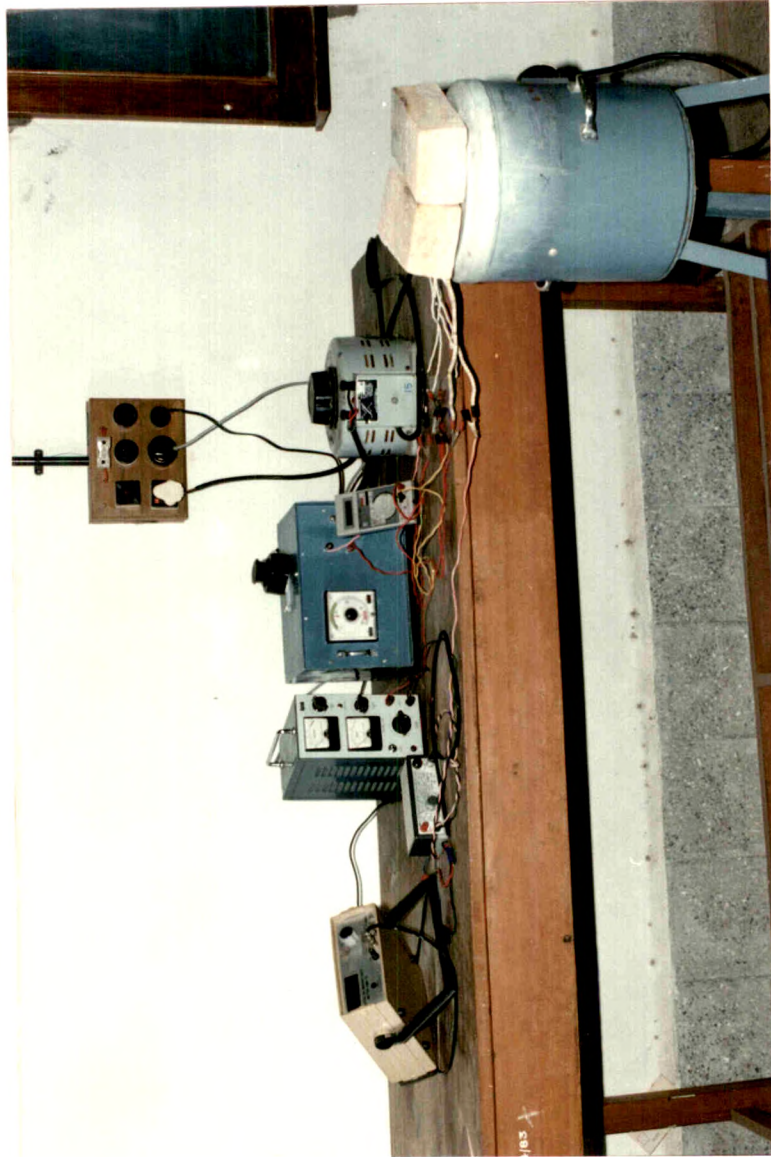


FIG. 5.1 : EXPERIMENTAL SET UP FOR MEASUREMENT OF D.C. ELECTRICAL CONDUCTIVITY

ture and biasing voltage of the sample and $\log \sigma$ was plotted against time.

5.3 Results and Discussion :

The estimated values of current density J for the samples were plotted as a function of applied electric field E . These plots are represented in Fig. 5.2 and 5.3. It is seen that the J - E characteristics are linear up to a critical field and above this the increase of J with E becomes faster. In the linear variation range, the contact between pellet and electrode interfaces remains ohmic around $E = 50 \text{ V/cm}$. Therefore, the 10 V d.c. electric field was applied to each sample for the conductivity measurements.

From the estimated values, the conductivity variation with temperature for the samples are represented in Fig.5.4 as plots of $\log \sigma$ vs T^{-1} . It is seen from the Fig.5.4 that $\log \sigma$ vs T^{-1} plots are linear, but a change in the slope of the straight lines occurs at a knee point (break temperature). The break temperature at the knee point corresponds to the phase transition point of the respective sample. The Curie temperatures of the samples obtained from the d.c. conductivity measurements are in agreement with those obtained from hysteresis studies or dielectric constant measurements. The typical variation of $\log \sigma$ with T^{-1} can be expressed by the equation (5.1). The activation energies

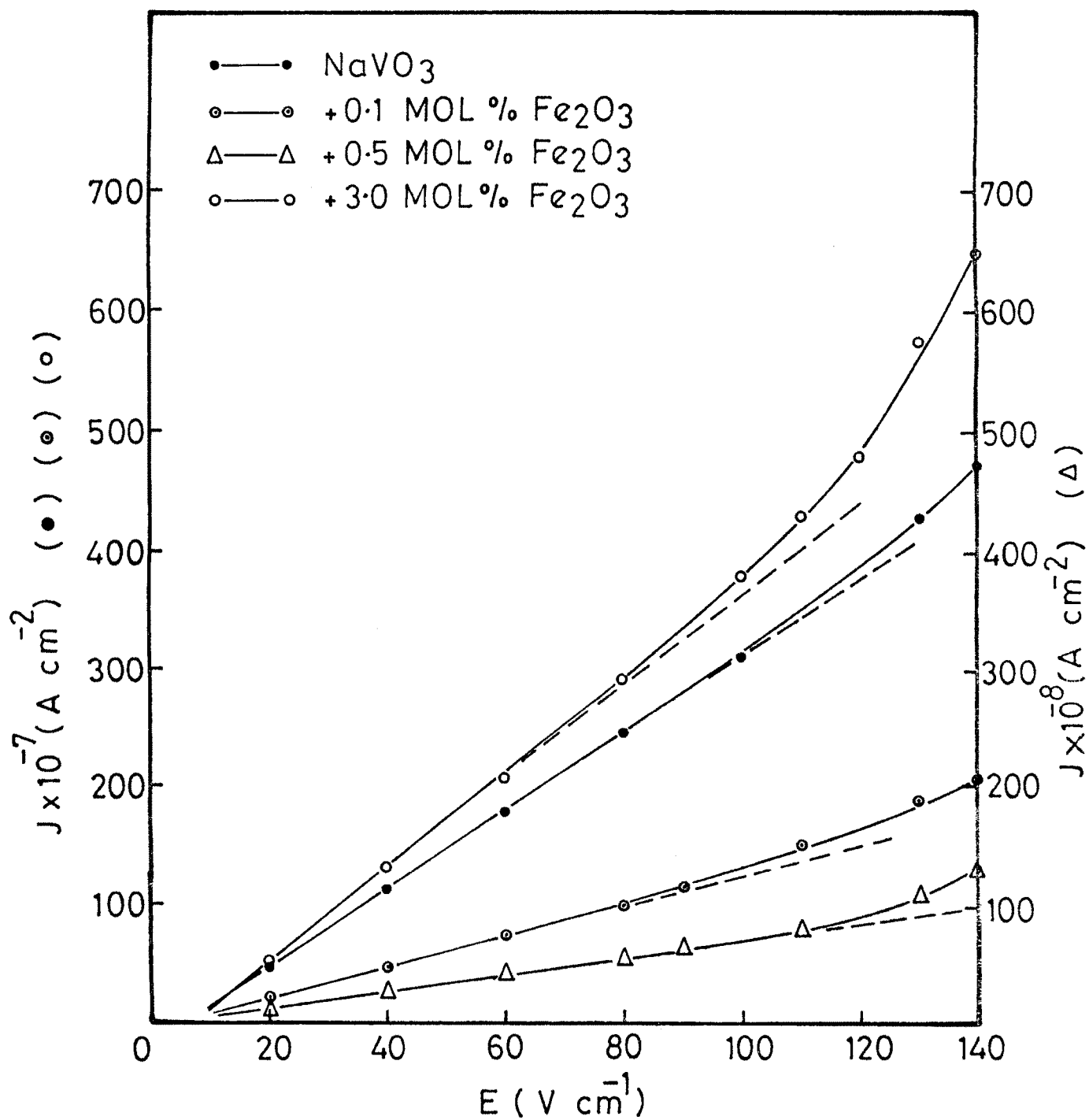


Fig.5.2 — PLOT OF CURRENT DENSITY VS APPLIED ELECTRIC FIELD

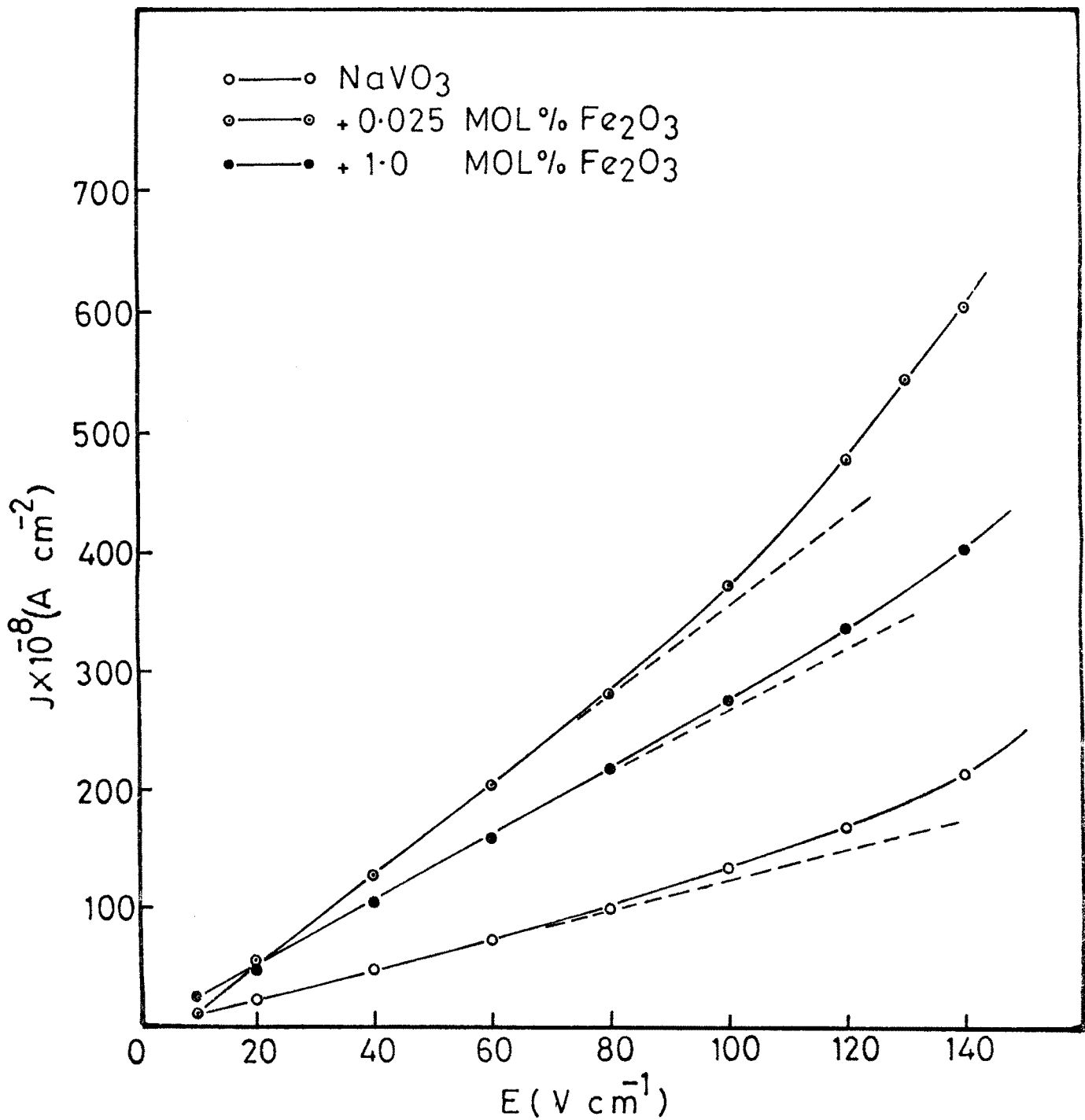


Fig. 5.3 - PLOT OF CURRENT DENSITY VS APPLIED ELECTRIC FIELD



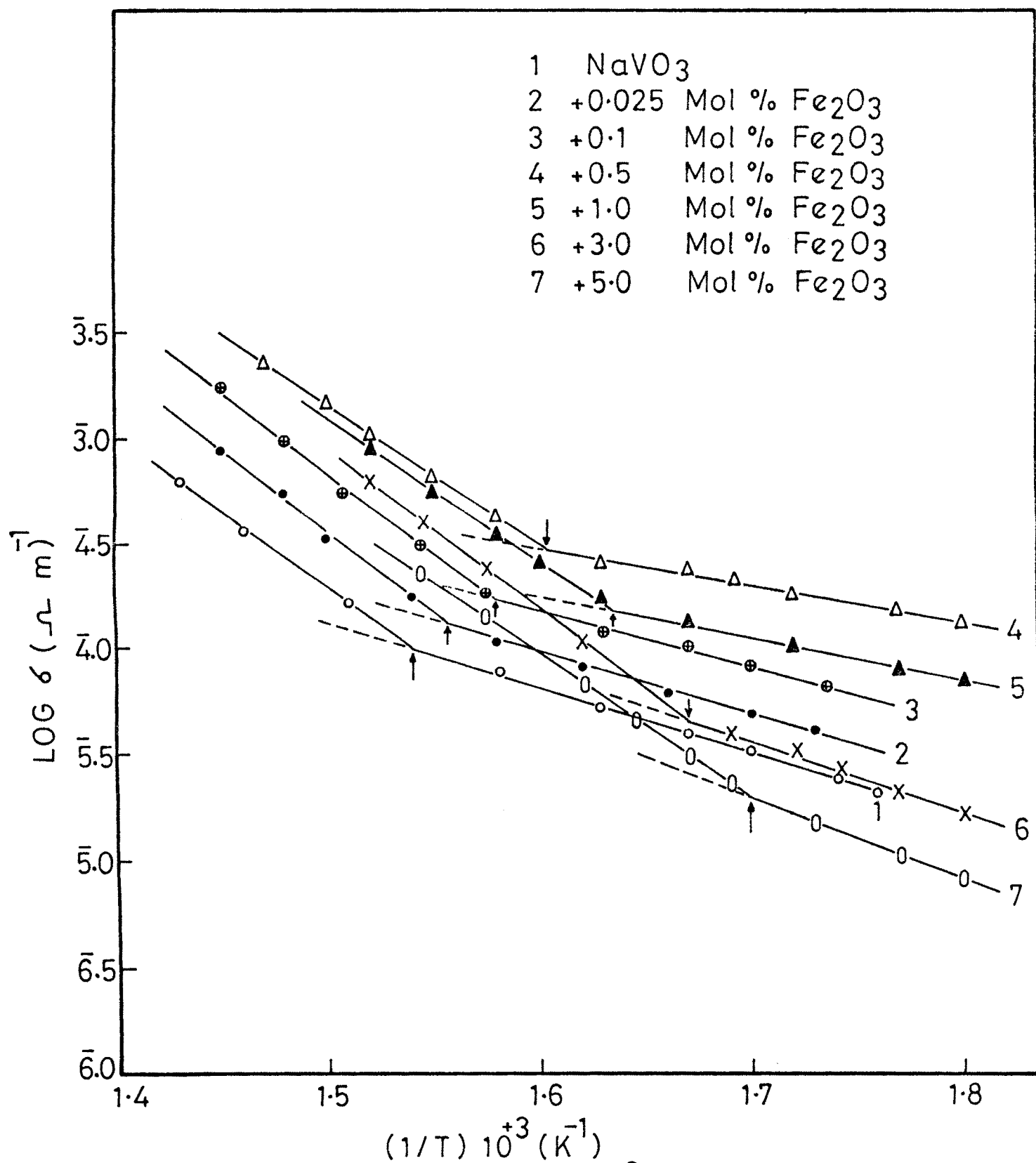


Fig.5.4 - PLOT OF LOG σ VS $(1/T)10^3$ FOR NaVO₃ AND ITS Fe₂O₃-DOPED COMPOSITIONS

are calculated, for each sample from the slopes of the plots of $\log \sigma$ against T^{-1} both in paraelectric and ferroelectric regions. The activation energies are listed in Table 5.1.

TABLE - 5.1

Activation energy and Curie temperature for NaVO_3
and its doped compositions.

Fe_2O_3 content (mol%)	Activation Energy (eV)		T_c ($^{\circ}\text{C}$)
	Ferro-state	Para-state	
0.0	0.56	1.49	376
0.025	0.59	1.52	370
0.1	0.53	1.48	360
0.5	0.35	1.32	350
1.0	0.41	1.35	338.6
3.0	0.68	1.51	325.8
5.0	0.76	1.36	315.2

For each sample it is found that the activation energy is larger in the paraelectric state than that in the ferroelectric state. It is also seen that the activation energy decreases approximately, in the ferroelectric state for increasing Fe_2O_3 content upto 0.5 mol%. While the activation energy increases for higher concentrations of Fe_2O_3 , from 1.0 to 5.0 mol % (Fig.5.5). It may be noted that the conductivity of NaVO_3 increases with increasing concentration of Fe_2O_3 upto 0.5 mol %. For higher doping concentra-

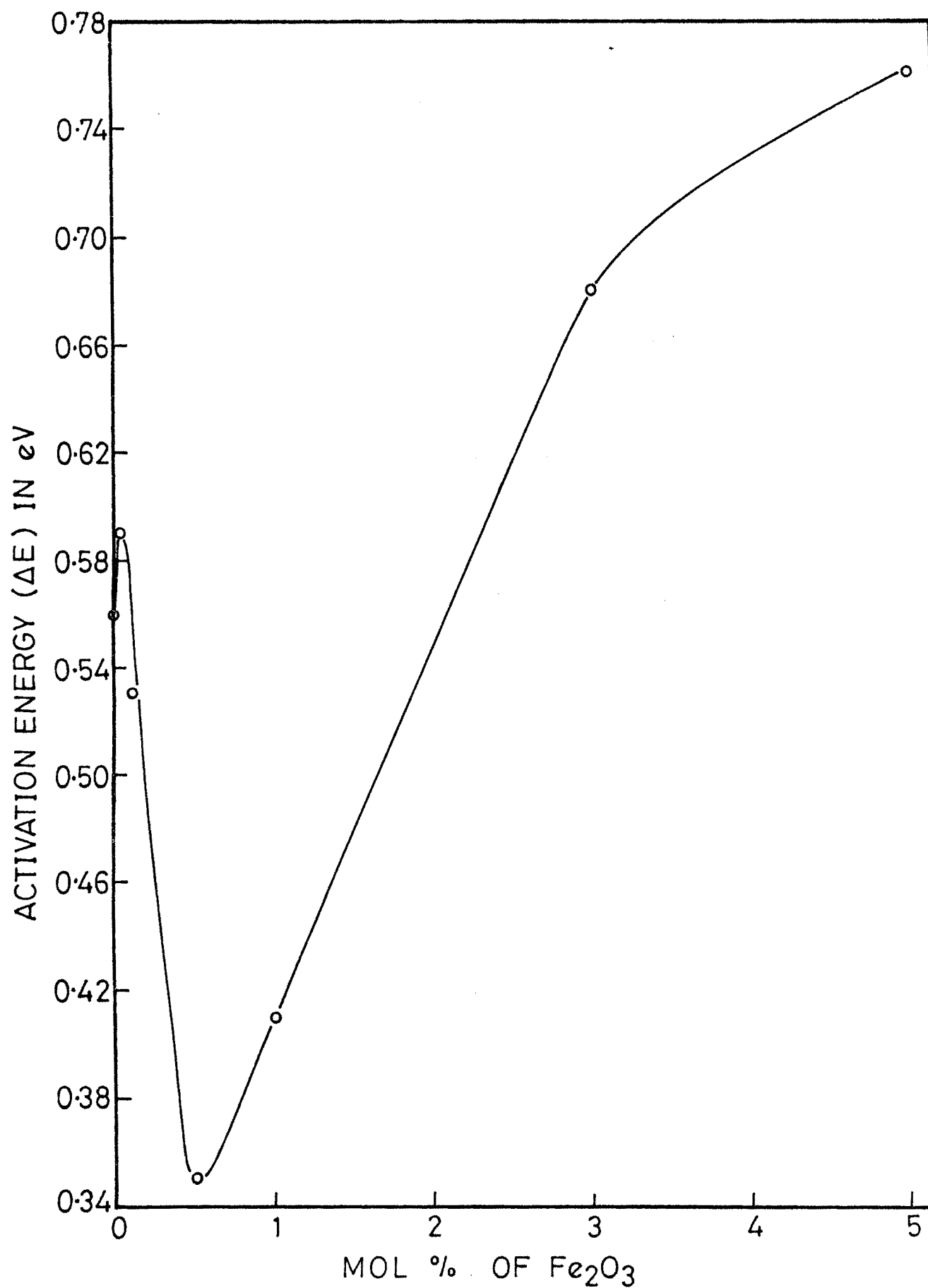


Fig. 5.5 - ACTIVATION ENERGY (ΔE) AS A FUNCTION OF Fe_2O_3 CONTENT OF MOL % IN $NaVO_3$

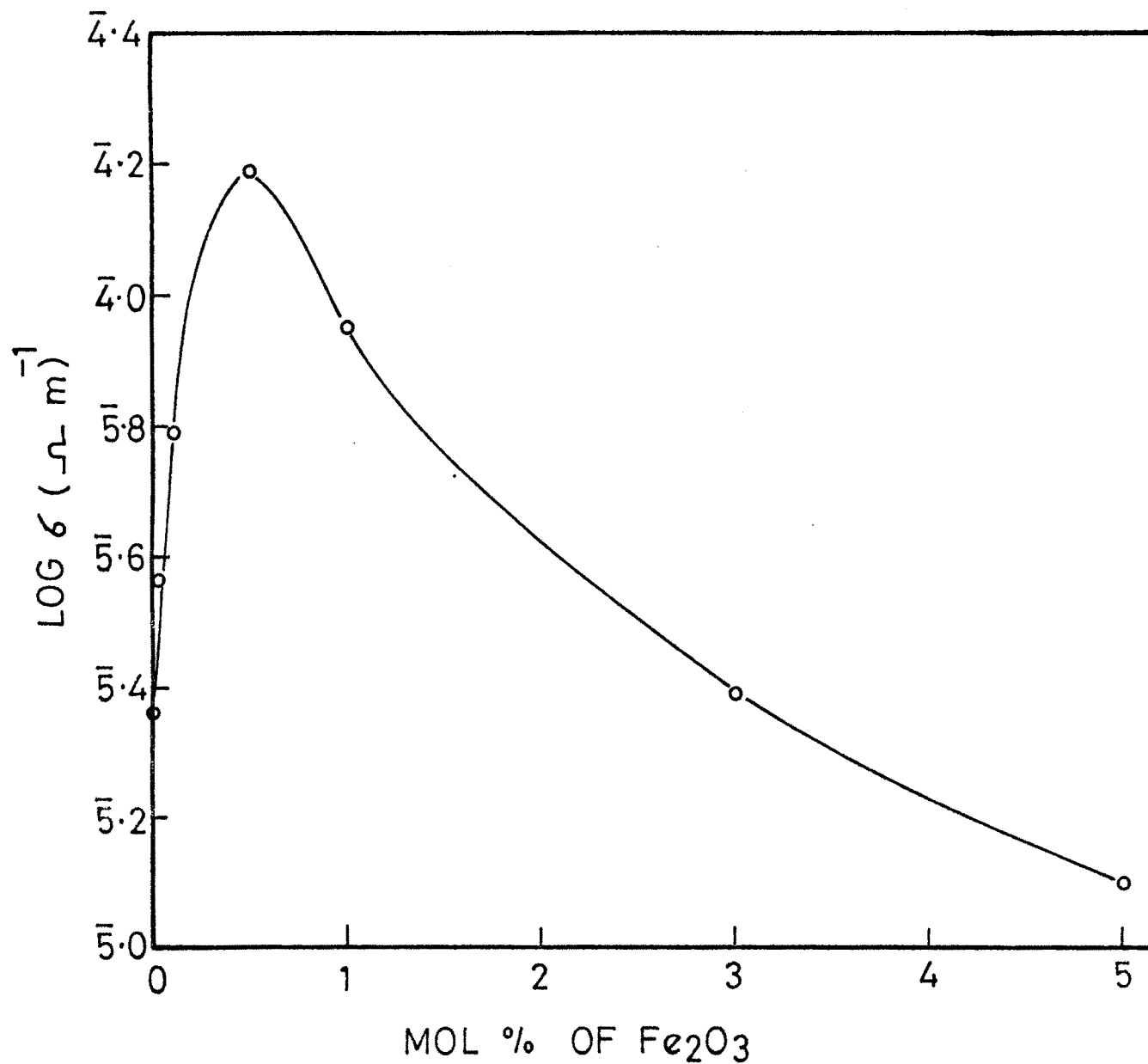
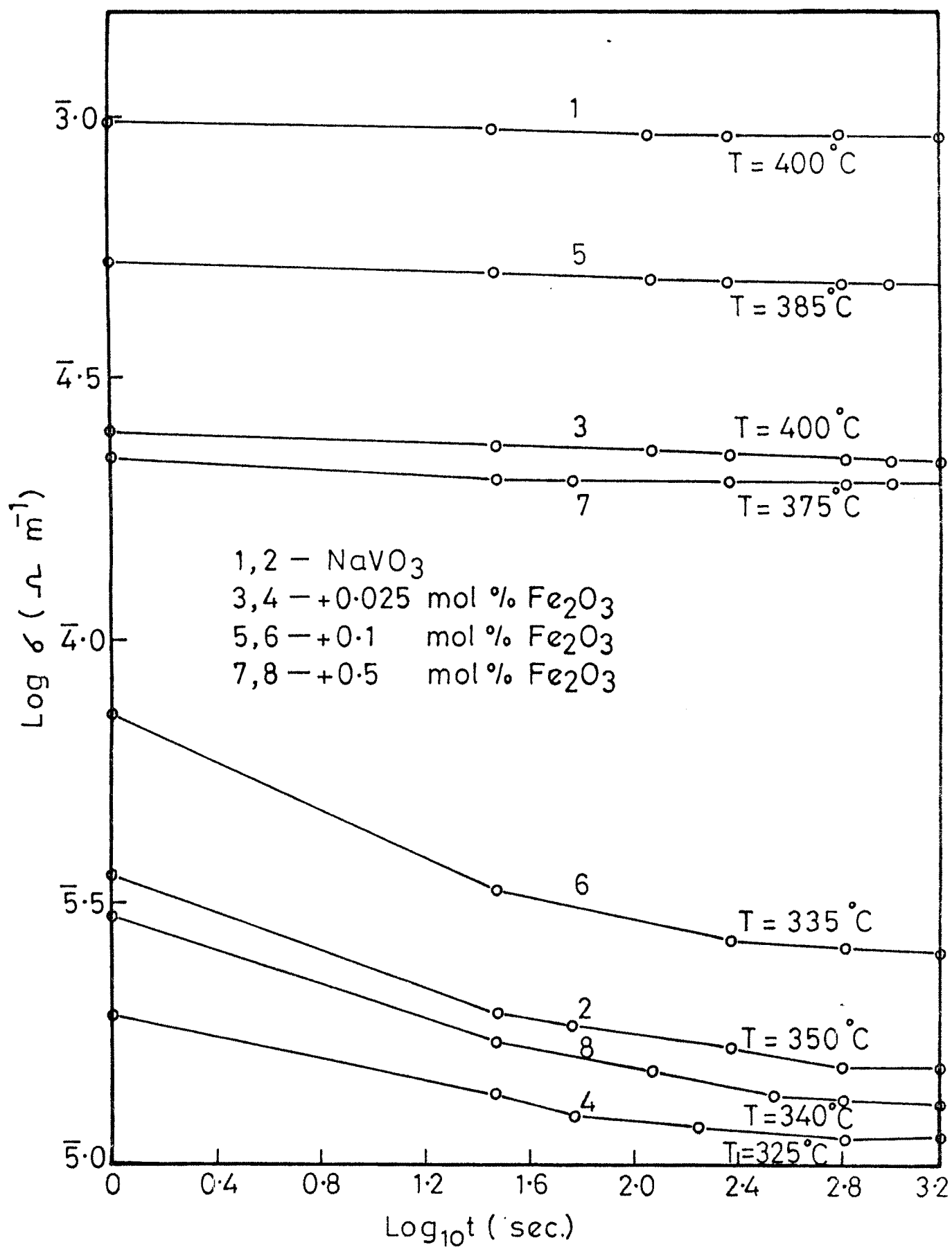


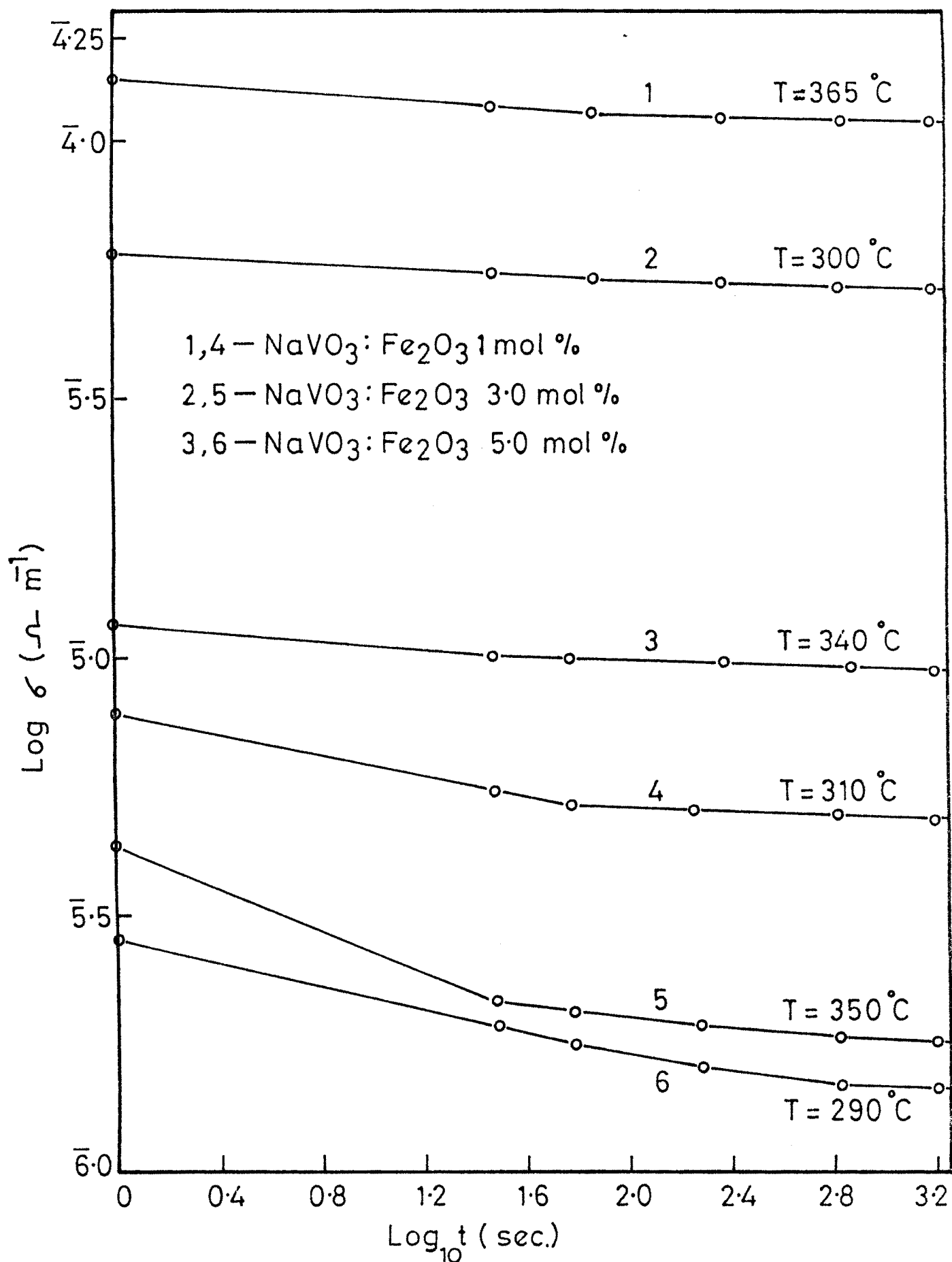
FIG. 5.6 — LOG DC CONDUCTIVITY OF NaVO₃ AS A FUNCTION OF MOL % Fe₂O₃ CONTENT

tion (from 1.0 to 5.0 mol%) of Fe_2O_3 , the conductivity of NaVO_3 decreases with increasing percentage. The maximum of the conductivity was observed for 0.5 mol % Fe_2O_3 -doping (Fig.5.6). To investigate the nature of conductivity, $\log \sigma$ was plotted against $\log t$ (Fig.5.7 and 5.8) for all the samples.

J(E) Characteristics and Ohmic Contact :

The additive trivalent metal ion Fe^{3+} is regarded as acceptor type dope, which generally occurs in perovskite structure (Hennings et al 1974). The charge deficit is compensated by creation of oxygen vacancies, giving rise to trapping centres for electrons. When a d.c. field is applied to the sample, both the electrons generated in the sample and the electrons injected contribute to conductivity. If the applied field is low, the number of electrons generated in the sample is large than the number injected from the electrodes, then the J(E) dependence according to Ohm's law is valid. Yet when the charge introduced from the electrodes under the influence of an E has greater density than the charge density corresponding to thermal equilibrium, then the conductivity current depends on E in accordance with Child's law for solids. When there is no trapping, the conductivity follows child's law which in turn is valid as long as thermal effects control current flow or until electrical breakdown occurs. On other hand, when trapping plays the major role in the conduction process,

Fig.5.7 - PLOT OF LOG δ vs LOG t

Fig.5.8 - PLOT OF LOG σ vs LOG t

then the injected charge is being stored in traps and consequently does not contribute to the conductivity. Thus Ohm's is valid upto a certain field above which current increases rapidly (Fig. 5.2 and 5.3). This increase of current is associated with the collapse of an electric field due to release of the trapped charge (Rose 1955, Lampert 1956).

Conductivity :

Conductivity of pure NaVO_3 is partly intrinsic and partly due to other impurities present. For Fe_2O_3 -doped NaVO_3 it is assumed that each Fe^{3+} ion contributes one electron (Yamashita 1961). It is likely that the conduction mechanism in Fe_2O_3 -doped NaVO_3 occurs through the electron hopping from one Fe^{3+} ion to Fe^{2+} ion via changing valence of V. The increase in conductivity of NaVO_3 (Fig. 5.6) due to addition of Fe_2O_3 from 0.025-0.5 mol% is due to the increase in charge carriers as more and more Fe^{3+} and Fe^{2+} ions get embedded in the structure of the host material. However, the conductivity decreases with increasing Fe_2O_3 content from 1.0-5.0 mol%. This is probably due to the fact that at higher concentrations of Fe_2O_3 (1.0 to 5.0 mol%) the inclusions (Refer to Chapter II, Section 2.6) act as the scattering centres for the charge carriers causing decrease in conductivity.

Activation Energy :

Having explained the increased conductivity of Fe_2O_3 -doped NaVO_3 in terms of the electron hopping between Fe^{3+} and Fe^{2+} ions via vanadium ions, it is but natural to try to explain alike, the decreasing activation energy of the samples with increasing Fe_2O_3 content upto 0.5 mol%. As more and more number of Fe^{3+} and Fe^{2+} ions are to be distributed in the crystal structure of the host, the average distance between them decreases. In the limiting circumstances the activation energy then drops to the characteristic value of $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ exchange mechanism which is ≈ 0.3 eV reported for ferrites. In order to account for the increase in the activation energy for higher Fe_2O_3 contents wherein the Fe^{3+} and Fe^{2+} ions distribution remains the same but form the inclusions from additional Fe_2O_3 that is brought in, one has to invent a mechanism of increasing the activation energy. The new surface of inclusions that is being created has certain surface structure. It is likely that either Fe^{3+} or Fe^{2+} might prefer these sites on the surface of the inclusions, leaving a deficiency in the solid solution of the said ion. This would make the hopping difficult through a larger region and other sequence of ions changing valence. Hence the activation energy is likely to increase with Fe_2O_3 content beyond 0.5 mol %.

An abrupt change in $\sigma(T^{-1})$ dependence at a phase transition point can occur either through a change in σ_0 as

a result of a sudden change in the geometrical factor governing hopping probability or through a sudden change in barrier. As the slope of the straight line in Fig.5.4 appears higher in the paraelectric region, we conclude that there is an increase in ΔE above T_c and also an increase in σ_0 indicating an increase in the hopping probability.

Nature of Conductivity :

The contribution to electrical conductivity is due to migration of ions or electrons or both. The theories for ionic conduction and electronic conduction are significantly different. Hence to present any meaningful discussion of electrical conduction, one has to distinguish the principle charge carriers. In order to distinguish whether the conductivity is predominantly electronic or ionic, one has to measure σ_{dc} as a function of time with an electrode that blocks ionic conduction but not electronic conduction. Such measurements were carried out for all Fe_2O_3 -doped $NaVO_3$ samples, below the Curie temperature as well as above it. The Fig. 5.7 and 5.8 represent the variation of $\log \sigma$ versus $\log t$ at a constant temperature both in paraelectric and ferroelectric states. It is seen from these figures that in ferroelectric state at a constant temperature and constant d.c. applied voltage, σ_{dc} decreases with time and after some time tends to become constant. In paraelectric state, σ_{dc} attains a constant value within a short time. It is well known that pure electronic conductors do not

show any time dependence for electrical conductivity. A time-dependent electrical conductivity normally occurs in solids with permanent dipoles (either intrinsic or produced by defects, impurities, etc.) A d.c. current in a pure ionic solid decreases with time and tends to become zero after a very long time if the electrodes used for this measurements were capable for blocking the flow of ions. In case of a mixed ionic electronic conductor, one expects a continuous decrease in current which should tend to acquire a constant value after a sufficiently long time.

In view of the fact that d.c. current of our samples initially decreases with time and tends to become constant, we conclude that the materials are mixed conductors having both electronic and ionic conductivity in ferroelectric state and these materials are mostly electronic conductors in the paraelectric state. In oxide ceramics and other ionic-covalent solids that are not ferroelectric, the conduction at high temperatures acquires more and more ionic component as creation and migration energies of ion vacancies are large (1.00 eV). However, in the present case of ferroelectric NaVO_3 , the ionic component of conduction below T_c is not likely to involve creation and migration of ions via ion vacancies. Therefore, the only mechanism to which the phenomenon of ionic conduction can be ascribed is that of the rotation of dipoles and of domain wall motion. In d.c. conductivity measurements in paraelectric

state, which is electronically conducting according to the explanation reckoned, the transient appears most probably due to redistribution and readjustment of surface charges.

Conclusions :

1) D.C. electrical conductivity of all the samples increases exponentially with temperature both in paraelectric and ferroelectric state.

2) Knee point in the plot of $\log \sigma$ against T^{-1} corresponds to the Curie point of the respective sample.

3) The addition of Fe_2O_3 into NaVO_3 effects the shift in phase transition point to a lower temperature.

4) In paraelectric state the activation energy is found to be larger than that in the ferroelectric state.

5) The conduction in undoped and doped NaVO_3 in the paraelectric state is electronic while it is of mixed (ionic-electronic) type in the ferroelectric state.

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