

CHAPTER-VID.C. ELECTRICAL CONDUCTIVITY6.1 INTRODUCTION

Electrical conductivity is an intrinsic or inherent property of the polar materials. The conduction can not occur unless the charge carriers are able to cross the potential well and for this purpose they need to be 'activated' by some external agency. Activation can be effected by thermal and electrical energies. The variation of conductivity ( $\sigma$ ) with temperature (T) can be represented by the general exponential law,

$$\sigma = \sigma_0 \exp(-\Delta E/KT) \quad \dots\dots 6.1$$

where  $\Delta E$  is the activation energy,  $\sigma_0$  the constant and K the Boltzmann constant. Most polar dielectric materials show only a gradual increase in conductivity with increasing temperature. However, sudden changes have been observed in certain ferroelectric materials near their Curie point. The electrical conductivity of ferroelectrics with perovskite structure is not well understood, but, it is found that the point defects are responsible for many electrical properties of  $ABO_3$  (A=Na,K,Li,Cs; B=V) oxides belonging to perovskite family. The conduction mechanism in ferroelectrics can be ionic and/ or electronic in nature, and it is the first step in the understanding of electrical transport in ferroelectrics. Type of conduction strongly depends on the temperature and the parity of the

material. The nature of conductivity can be determined by several ways, one of which is to measure d.c. conductivity as a function of time using electrodes blocking an ionic conduction. It is found that d.c. conductivity is time dependent for purely ionic type and it is independent of time for purely electronic type. For mixed conduction initially it decreases with time but remains constant at some finite value.

Lead titanate was discovered by Shirane et al ( 1950) and it has already been widely used for obtaining piezoelectric and other materials. Weise et al (1953) were studied the electrical resistivity of strontium titanate ceramics. The interesting behaviour of electrical conductivity of barium titanate was reported by Inuishi et al ( 1958). Grawford et al (1959) reported that almost all ferroelectric materials which possess a high Curie temperature 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. The dependence of electrical conductivity in  $\text{PbTiO}_3$  ceramics on temperature was studied by Fedulov et al (1961, 1962). The study of conductivity in  $\text{BaTiO}_3$  was carried out by Glower et al (1964). Fesenko et al (1974) were investigated that lead titanate is a semiconductor with considerable electrical conductivity. Roberts (1974) discussed in detail the important role of electrodes in the measurement of conductivity and suggested that Ohmic contact is the first stringent requirement for such measurement. Electrical conductivity and slow

polarization process in  $\text{PbTiO}_3$  ceramics was studied by Prokopalo ( 1974). Mott (1975) suggested that charge transport in lanthanum vanadate may be characterised by a degenerate gas of small polarons. The electrical conductivity of the rare-earth vanadates,  $\text{RVO}_3$  ( R = Ln, La, Lu and Y ) compounds was measured by Sakai et al ( 1976). Electrical transport studies on heavy rare-earth tungstates were reported by Verma and Lal (1981), wherein they have predicted that these materials are mixed ionic-electronic conductors. Lal et al(1982) reported the electrical transport in heavy rare-earth iron garnets. The transition from semiconductor to the semi-metal state in  $\text{LaVO}_4$  was studied by Kanchan Gaur et al (1984) by electrical transport phenomenon. Yadav et al (1985) were studied electrical conduction in  $\text{PrVO}_4$  single crystal and concluded that  $\text{PrVO}_4$  is a semiconductor with an energy gap of 1.5 eV. Electrical transport properties of iron vanadate were studied by Gupta et al (1986) where in they have related dielectric constant variations with electrical conductivity. Experimental and theoretical investigations of energy levels of intrinsic defects in  $\text{ABO}_3$  oxides belonging to the perovskite family have been carried out by Maksimov et al (1985). The effects of polarization in an external field on properties of  $\text{BaTiO}_3$  and  $\text{KNbO}_3$  semiconducting ferroelectric ceramics were studied by Raevskii et al (1985). Gaur and Lal (1985, 1986) studied the electrical transport in the light and heavy rare earth vanadates. Hyperfine interaction in the mixed conductor  $\text{LiV}_2\text{O}_5$  was studied by Bose et al (1987). Patil et al (1987) studied electrical conductivity of ferroelectric  $\text{KVO}_3$ ,  $\text{NaVO}_3$ ,  $\text{LiVO}_3$  and their solid solutions. Jamadar et al (1988) also studied electrical conductivity of solid solutions lead-barium titanate and lead-

strontium titanate. Recently, Patil et al (1989) studied electrical conductivity of  $\text{NaVO}_3$ ,  $\text{RbVO}_3$ ,  $\text{CsVO}_3$  and their solid solutions.

Tennery and Cook (1961) were studied electrical conductivity of  $\text{BaTiO}_3$  ceramics doped with rare-earth oxides. Dongier and Casalot (1970) and Sayer et al (1975) were studied extensively the electrical transport in strontium doped lanthanum vanadate. The interesting behaviour of electrical conductivity of  $\text{KNbO}_3$  crystals with Ce, La, V and Al as impurities was reported by Yanovskii (1980). Recently, Patil et al (1990) have studied d.c. electrical conductivity of undoped and  $\text{Nd}_2\text{O}_3$  doped  $\text{KVO}_3$  ceramics and Kashid et al (1990) also have studied d.c. electrical conductivity of undoped and  $\text{Gd}_2\text{O}_3$  doped  $\text{KVO}_3$ .

In this work, attempt is made to study d.c. electrical conductivity of undoped and doped  $\text{KVO}_3$  with  $\text{Er}_2\text{O}_3$  varying from 0.025 to 3.00 mol %.

## 6.2 EXPERIMENTAL

The experimental set-up used for the study of d.c. conductivity of ferroelectric undoped and doped  $\text{KVO}_3$  with  $\text{Er}_2\text{O}_3$  varying from 0.025 mol % to 3 mol %, is shown in Fig. 6.1. It consists of an electrically heated furnace, a transistorised power supply unit to provide d.c. electric field, a digital d.c. microvoltmeter (VMV-15) with a picoammeter adaptor and a temperature controller. The pellets of the above samples were sintered, polished and coated on two sides by air-drying silver paste, for good electrical contact. At a constant temperature of the pellet current flowing through the pellet was measured which was a function of applied d.c. field  $E$  and current density  $J$  was plotted against the applied electric field  $E$ . (Fig.6.2). The graph shows linearity upto

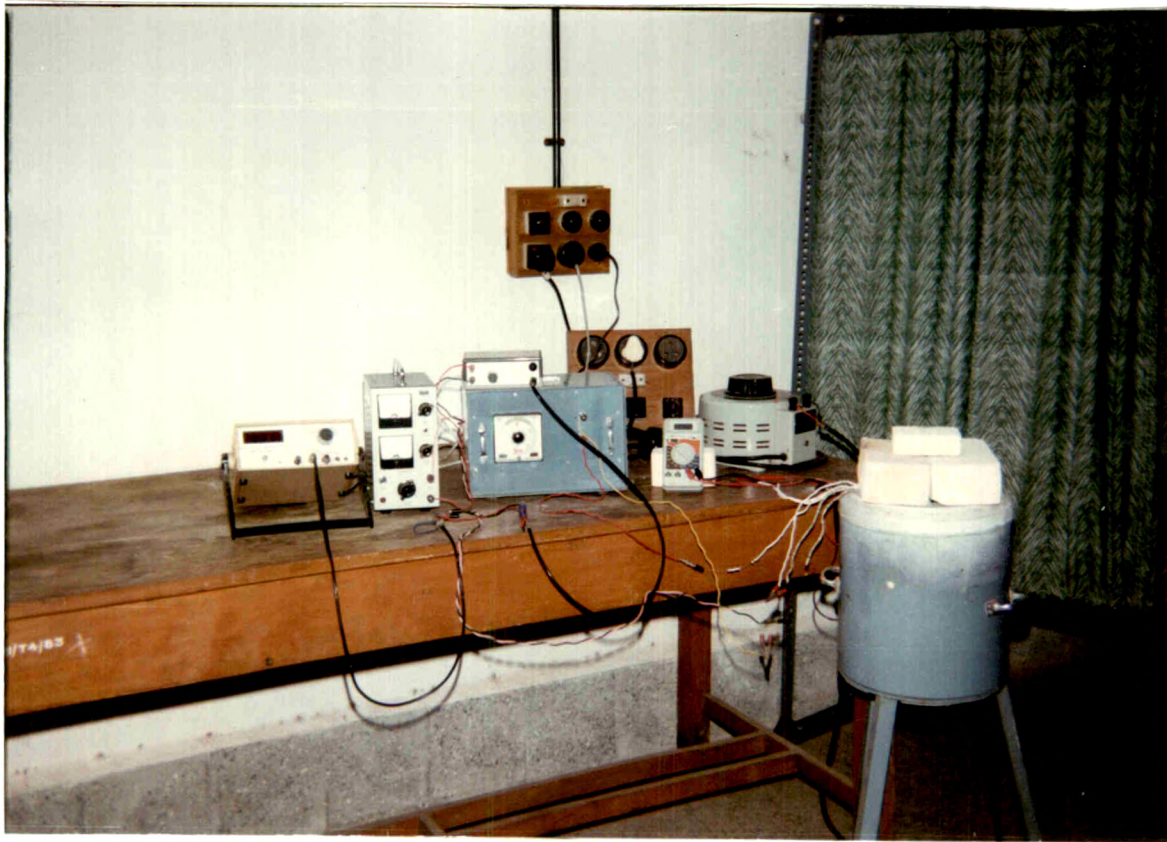


Fig. 6.1 : Experimental set-up for measurement of d.c. conductivity.



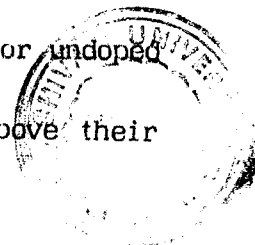
12 volts (critical field) and beyond that it shows non-linearity. For further study of d.c. conductivity the value of d.c. electric field was chosen (12 V) to fall within the critical field of the samples. The two-probe method was used to measure the resistivity and hence the d.c. conductivity of the samples in the temperature regions covering their transition temperatures.

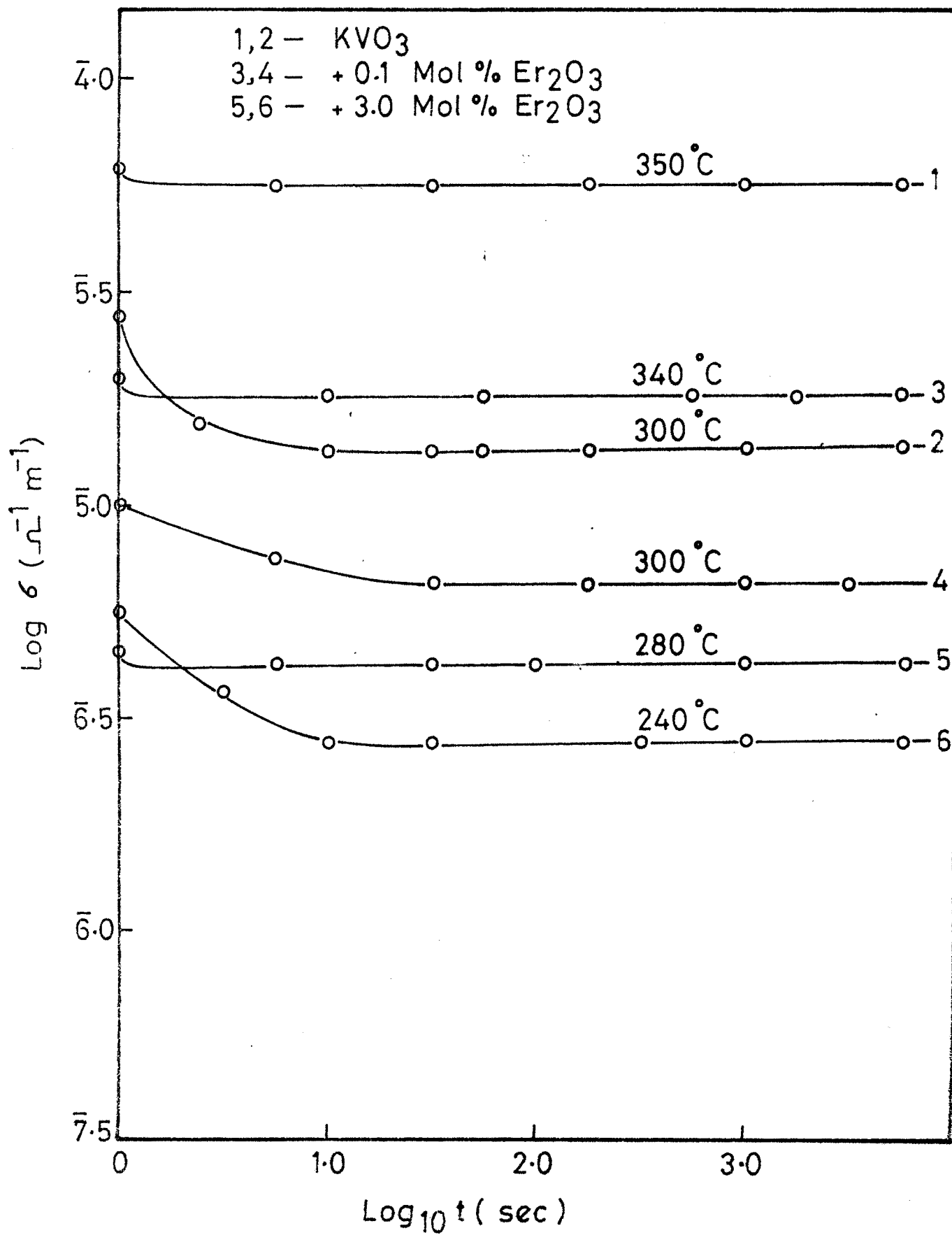
To ensure whether conductivity is ionic, electronic or mixed, the variation of d.c. conductivity with time at a constant temperature was studied both in the ferroelectric and paraelectric states. Such plots for undoped and doped  $\text{KVO}_3$  with different concentrations of  $\text{Er}_2\text{O}_3$ , are shown in Fig. 6.3.

\* CONDUCTIVITY MEASUREMENTS IN UNDOPED AND DOPED  $\text{KVO}_3$  WITH  $\text{Er}_2\text{O}_3$   
(0.025 to 3 mol%)

The sintered pellet of the sample was placed in a pellet holder with stainless steel electrodes. The d.c. voltage of 12V was applied across the pellet holder in series with picoammeter and this pellet holder was heated slowly in furnace. The d.c. resistivity measurements were taken by two-probe method in the temperature covering their transition points. The d.c. conductivity was obtained from resistivity data. The variation of  $\log \sigma$  with  $1/T$  for undoped and doped  $\text{KVO}_3$  with 0.025 to 3 mol % of  $\text{Er}_2\text{O}_3$  is shown in Fig. 6.4.

In order to detect the type of conduction, d.c. conductivity of pellet was measured at constant temperature as a function of time and  $\log \sigma$  was plotted against  $\log t$ . Three such plots were obtained for undoped  $\text{KVO}_3$  and  $\text{Er}_2\text{O}_3$  doped (0.025 and 3.00 mol %)  $\text{KVO}_3$  below and above their



Fig. 6.3 PLOT OF LOG  $\bar{\epsilon}$  VS LOG  $t$ .



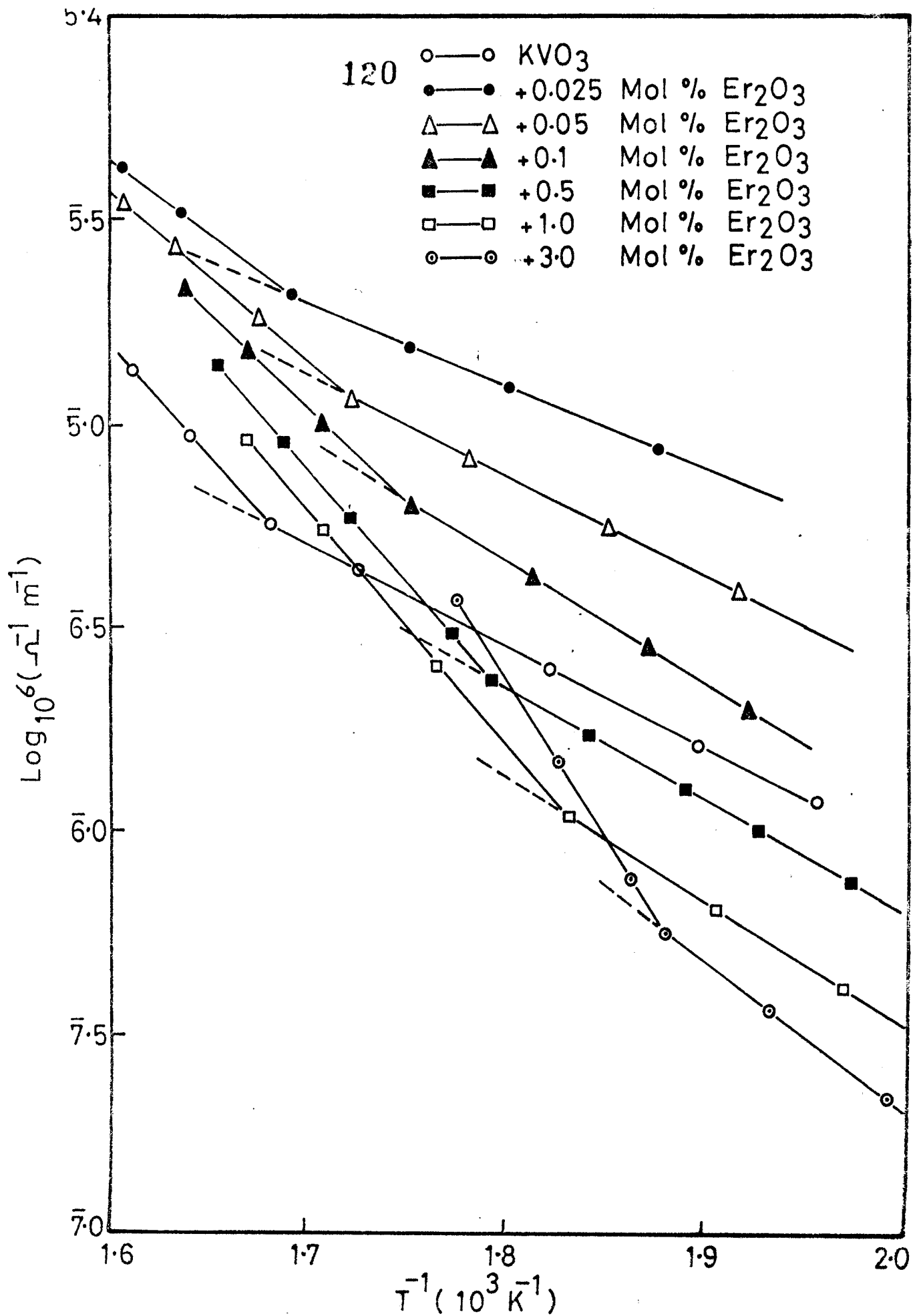


Fig. 6.4 PLOT OF LOG  $\epsilon$  VS  $(1/T)10^3$  FOR UNDOPED AND DOPED KVO<sub>3</sub> WITH Er<sub>2</sub>O<sub>3</sub>.

Curie temperatures as shown in Fig. 6.3.

### 6.3 RESULTS AND DISCUSSION

The variation of  $\log \sigma$  with  $1/T$  for undoped  $\text{KVO}_3$  and doped with different concentrations of  $\text{Er}_2\text{O}_3$  (0.025, 0.05, 0.1, 0.5, 1 and 3 mol %) is shown in Fig. 6.4. It is clear from the Fig. 6.4 that the d.c. conductivity increases exponentially with increasing temperature which is attributed to the hopping of cations due to thermal agitation. A change in conductivity is observed at  $T_c$ . This transition temperature of undoped  $\text{KVO}_3$  is the ferroelectric curie temperature (322.5<sup>0</sup>c) which was confirmed by our earlier properties and which was reported previously by Chavan and Suryavanshi (1985) and Patil et al (1988). The measurement of d.c. electrical conductivity for undoped and doped  $\text{KVO}_3$  with  $\text{Er}_2\text{O}_3$  obeys the exponential law given by the equation 6.1 Fig. 6.4 also exhibits a maximum conductivity at a particular content (0.025 mol %) of  $\text{Er}_2\text{O}_3$  in  $\text{KVO}_3$ . This increase in d.c. electrical conductivity for  $\text{KVO}_3$  ceramic doped with 0.025 mol %  $\text{Er}_2\text{O}_3$  is might be due to a rather more solid state interaction that takes place in the material. Our sample containing 0.025 mol %  $\text{Er}_2\text{O}_3$  is more dense because, doping with  $\text{Er}_2\text{O}_3$  may keep grain size small. This also indicates that 0.025 mol %  $\text{Er}_2\text{O}_3$  content in  $\text{KVO}_3$  may represent the solubility limit of  $\text{Er}_2\text{O}_3$  in  $\text{KVO}_3$  lattice. Here  $\text{K}^{1+}$  ions are assumed to be mobile ions due to their low atomic weights compared to  $\text{Er}^{3+}$ . Replacement of  $\text{K}^{1+}$  by  $\text{Er}^{3+}$  produces vacancies because of which defects created are

playing an important role for the d.c. electrical conductivity of the samples. The activation energies both in the ferroelectric and paraelectric states are evaluated from the slope of  $\log \sigma$  vs  $1/T$  plots and are summarised along with ceramic density and  $T_c$  in Table 6.1.

TABLE NO.6.1

ACTIVATION ENERGIES, DENSITY OF UNDOPED AND DOPED  $KVO_3$  WITH  $Er_2O_3$

$Er_2O_3$ mol%	Activation Energy(eV)		Ceramic density ( $gm/cm^3$ )	$T_c$ $^{\circ}C$
	Ferro-state	Para-state		
0.000	0.496	1.090	2.50	322.5
0.025	0.372	0.744	2.61	317.5
0.050	0.495	0.818	2.54	307.5
0.100	0.595	0.893	2.51	297.5
0.500	0.546	1.116	2.47	285.0
1.000	0.596	1.141	2.43	275.5
3.000	0.744	1.488	2.40	260.0

From Table 6.1 it is observed that the activation energy in the ferroelectric state is smaller than that in paraelectric state.

The electrical conductivity for the samples is observed due to migration of ions or electrons or both. The nature of electrical conductivity can be investigated by knowing the principal charge carriers. It is well known that for ions as a charge carriers, d.c. conductivity of a conductor decreases with time and tends to zero after very long time. In the case of electrons as the charge carriers, d.c. electrical conductivity of a conductor is independent of time, while in mixed charge carriers, the d.c. conductivity first decreases with time and then acquires a constant value after a long time. For the samples of undoped and  $\text{Er}_2\text{O}_3$  doped  $\text{KVO}_3$ , the graphical variation of  $\log \sigma$  with  $\log t$  at a constant temperature are shown in Fig 6.3. It also indicates that the d.c. conductivity below  $T_c$  is of mixed type ( ionic + electronic), while above  $T_c$ , it is electronic.

The study of d.c. electrical conductivity for undoped and doped  $\text{KVO}_3$  with  $\text{Er}_2\text{O}_3$  concludes.

1. The d.c. electrical conductivity of all samples increases with temperature exponentially, both in the ferroelectric and paraelectric regions.
2. The temperature at which the electrical conductivity of the sample changes is the Curie temperature of the sample.
3. The Curie temperature of  $\text{KVO}_3$  decreases as the  $\text{Er}_2\text{O}_3$  content in

$KVO_3$  increases and they are in good agreement with Curie temperatures observed in various properties in previous chapters.

4. Activation energy in para-state is higher than that in ferro-state of the material.
5. For all the samples, below Curie temperature conduction is of mixed type (ionic + electronic), while above  $T_c$  it is purely electronic.

REFERENCES

- Bose M. and Bose A. (1987), *Hyperfine Interactions (Switz)*  
34, 463.
- Chavan S.H, and Suryavanshi S.G. (1985), *Ind. J.Phys.A-59*, 555.
- Dougier P.and Casalot A (1970), *J.Solid State Chem.2*, 396.
- Glower and Others (1964), *Kri.Akad.Nacik.SSSR-7*,408.
- Crawford A.E. (1959), *Brit. Com.and Ele.6*, 516.
- Guruvich V.M. and Rez I. (1960), *Sov.Phys.Sol. State. 2*,824.
- Fedulov and Others (1961,1962),*Fizika, Tverdog Tela Akad.Nauk. SSSR. 3*, 959.
- Jamadar V.V.,Patil T.A. and Chavan S.H. (1988), *Ind. J.Phys. 62A*. 341.
- Kanchan Gaur and Lal H.B (1984) *J.Mat.Sci. 19*, 3325.
- Kanchan Gaur and Lal H.B (1985) *J.Mat.Sci. 20*, 3167.
- Kashid A.P., Patil V.v. and Chavan S.H. (1990)*Ind.J.Pure and Appl.Phys.(Communicated)*
- Lal H., Verma B and Yadav V (1982),*J.Mat.Sci. 17*, 3317.
- Maksimov S.M. and others (1985), *Sov. Phy.S.S. 27*,562.
- Mott. (1975), *Proc. R.Soc.A. 345*, 169.
- Patil R.T., Patil N.B.and Chavan S.H. (1990), *Ferroelectrics (Accepted)*.
- Patil T.A., Jamadar V.M. and Chavan S.H. (1987), *Ind. J.Phys. 62A*, 341.
- Prokopalo O.T. (1974), *Ferroelectrics. 7*, 333.

- Raevskii I.P. and Others (1985), Sov. Phys. Tech. Phys. 30, 351.
- Roberts G.G. (1974), Transfer and Storage of energy  
by moles. 41 (J.W. New York)
- Sakai t. and Others (1976), Mat. Res. Bull. 11, 1295.
- Sayer M. and Others (1975), J.Phys. Chem.8, 2059.
- Shirane A. and Others (1950), Phys. rev. 80, 1105.
- Tennery V.J. and Cook R.L. (1961), J.Am. Cer. Soc. 44, 187.
- Verma B.K. and Lal H.B. (1981), Mat. Ros.Bull. (USA) 16, 1579.
- Weise E. and Lesk I. (1953), J.Chem. Phys. 21, 801.
- Yadav Y. ,Singh R. and  
Wanklyn B. (1985), J.Mat. Sci. Lett. 4, 224.
- Yanovskii V.K. (1980), Sov. Phys. Sol. State. 22, 1284.