CHAPTER-IV

PYROELECTRIC MEASUREMENTS

4.1 INTRODUCTION

The pyroelectricity is defined as the change in electrical spontaneous polarization (P_s) of the material when it undergoes a variation in its temperature. As ferroelectrics have a very large temperature dependent P_s, they are strongly pyroelectric materials. The pyroelectric effect shown by polar materials has been known since ancient times. The primary pyroelectricity in ferroelectric ceramics can arise from two factors: (i) the primary effect of aligned domains and (ii) switching of of domains by 180°. The ferroelectric crystal while heating shows pyroelectric effect creating electrical charges on the faces of the crystal. As it is well known that crystallographically, out of thirty two, ten crystal classes are noncentrosymmetric and are called pyroelectric crystals. These pyroelectric materials show change in the direction of the spontaneous polarization, when electric field is applied to them and hence they are called ferroelectric materials. So all ferroelectrics show phenomenon of pyroelectricity. The pyroelectric effect is first defined by Cady (1946). The pyroelectric current measurement technique can be regarded as complementary to hysteresis loop measurements and applied to a study of the Curie point transition in the ferroelectric materials. Chynoweth (1956) devised a dynamic method for pyroelectric measurements and deduced an equation,

$$i = A \left(\frac{dPs}{dt}\right) \qquad \ldots\ 4.1$$

or

$$i = A \left(\frac{dPs}{dT}\right) \left(\frac{dT}{dt}\right)$$

where, i the pyroelectric current, A electroded area, P_s spontaneous polarization, t time, T temperature, $\frac{dT}{dt}$ the rate of heating and $\frac{dPs}{dT}$ the pyroelectric coefficient. The equation reveals us that at a given temperature the pyroelectric current is proportional to the polarization of the material.

Ackermann (1915) suggested the static method for pyroelectric measrurements and it was used only at discrete temperature points. Chynoweth (1956) used his dynamic method for the study of pyroelectricity in $BaTiO_3$. The temperature dependence of pyroelectric current for $NaNO_2$ crystal was observed by Sawada et al (1961). A method for measuring the pyroelectric coefficients of a polar material over a wide range of temperature was described by Lang and Steckel (1965). Lang et al (1969) studied the pyroelectric effect in $BaTiO_3$ in ceramic form. Byer and Roundy (1972) introduced a direct method for measuring pyroelectric coefficients and application to nanoseccond response time detector(Sr_x-Ba_{1-x}) Nb_2O_6. Midorikawa et al (1980) were studied dielectric and pyroelectric properties of $Pb_3(Vo_4)_2$ crystals in the lowest temperature phase-Dielectric permittivity and pyroelectric coefficients of mixed crystals of TGS and TGFB were reported by Mathur et al (1981). Chaves et al (1982) measured pyroelectric current in the crystal of $SbSe_xS_{1-x}I$ by measuring the potential difference across a short-circuiting resistance while heating the sample with uniform rate and studied the variation of pyroelectric coefficients with temperature. Khan et al (1983) reported dielectric and pyroelectric properties of ferroelectric $NaVO_3$ in ceramic form. Mansing and Sreenivas (1983) were studied similar properties of TGS polysterene

composite. The pyroelectric properties of the ferroelectric single crystal series $(K_x\text{-}Na_{1-x})_{0.2}$ $(Sr_yBa_{1-y})_{0.8}$ Nb_2O_6 were reported by Yuhan et al (1984). The pyroelectric poperties of (Na-Bi) titanate ceramic were reported by Hagiyev et al (1984), Reddy et al (1986) studied pyroelectricity in polymer films for infra-red detection by using direct method. The similar properties of poled samples of lead-barium titanate and lead-strontium titanate investigated by Jamadar et al (1987). The effect of rare earth ions (La^{3+},Nd^{3+},Gd^{3+} and Sm^{3+}) doping on ferroelectric properties of (Sr-Ba)Nb_2O_6 ceramics modified with Na^+ and K^+ was observed by Umakantham et al (1987). The pyroelectric properties for ferroelectric $NaVO_3$,KVO_3, $LiVO_3$ and their solid solutions were studied by Patil et al (1988). Recently, the pyroelectric properties of KVO_3 doped with Gd_2O_3 and doped with Dy_2O_3 have studied by Kashid et al and Patil et al (1989) respectively.

Aim of this topic is to study pyroelectricity in KVO_3 doped with different concentrations(0.025 to 3 mol%) of Er_2O_3.

4.2 EXPERIMENTAL DETAILS

The experimental arrangement for pyroelectric measurements of these samples consists of a digital d.c. microvoltmeter VMV-15, a picoammeter adaptor for VMV-15, an electrically heated furnace and a digital millivoltmeter as shown in Fig. 4.1. The sintered pellets of the samples of 1 cm diameter and about 1 mm thickness were used for experimental purpose. The two sides of these pellets were coated with thin layer of conducting silver paste to achieve good electrical contact. The pellet of the samples was slowly heated inside the furnace and the pyroelectric

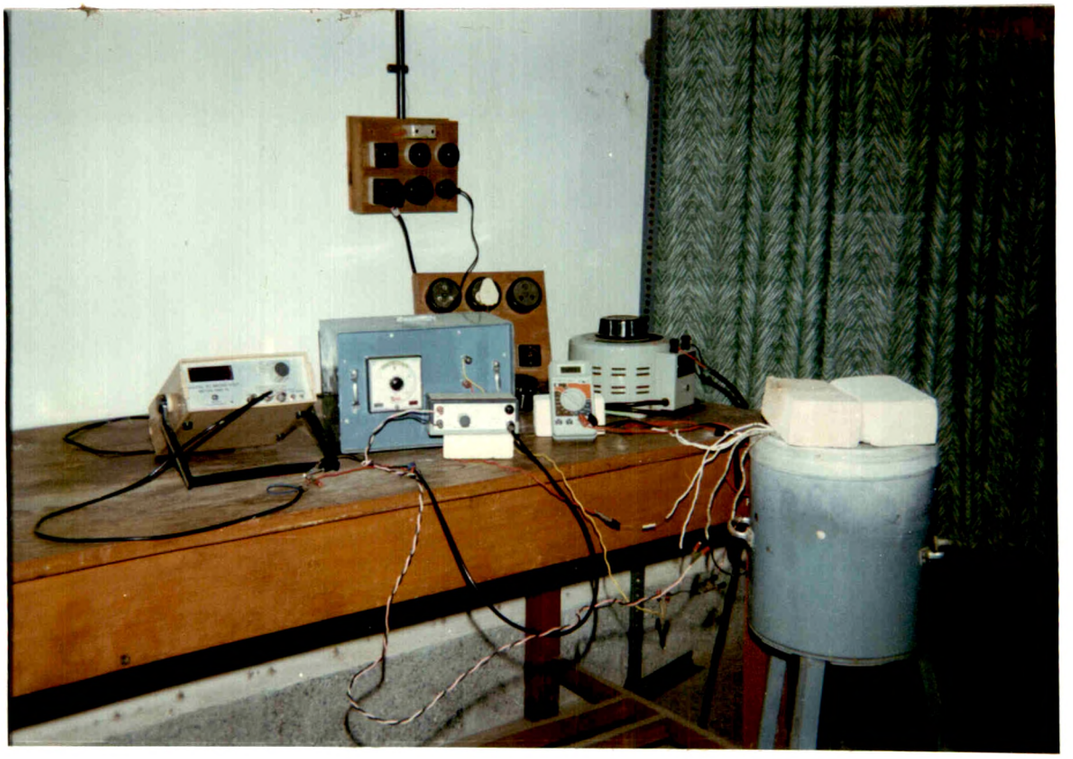

Fig. 4.1 : Experimental set-up to study the pyroelectric measurements.

current was measured with a digital d.c. microvoltmeter (VMV-15) at various temperatures. The rate of heating was calculated by measuring the corresponding time and plotting temperature vs time(Fig.4.2) and that was observed to be 2.5^0c/min. By knowing this rate of heating and the pyroelectric current the pyroelectric coefficients were calculated.

4.3 MEASUREMENT OF PYRO-PARAMETERS OF UNDOPED KVO_3 AND DOPED KVO_3 WITH Er_2O_3

The sample of undoped KVO_3 was slowly heated inside the furnace and pyroelectric current was recorded at different temperatures. During the heating the time was also noted to determine the rate of heating. The slope of the graph of temperature vs time(Fig. 4.2) was found to be 2.5^0c/min giving the rate of heating. The temperature dependent pyroelectric current and rate of heating of the sample were used to calculate the pyroelectric coefficient of undoped KVO_3. The different samples of KVO_3 doped with Er_2O_3 (varying from 0.025 to 3 mol%) were used further to measure there pyroelectric current w.r.t.temperature. The pyroelectric coefficients for these samples were calculated by using equation 4.1. The variation of pyroelectric current w.r.t. temperature for different samples of KVO_3 doped with Er_2O_3 is shown in Fig. 4.3, whereas dependence of pyroelectric coefficient on temperature for various samples is shown in Fig. 4.4.

4.4 RESULTS AND DISCUSSION

The temperature dependence of pyroelectric current and coefficient is shown in Fig. 4.3 and Fig. 4.4 respectively. These figures reveals us that these samples show peak values of pyroelectric current and coefficient

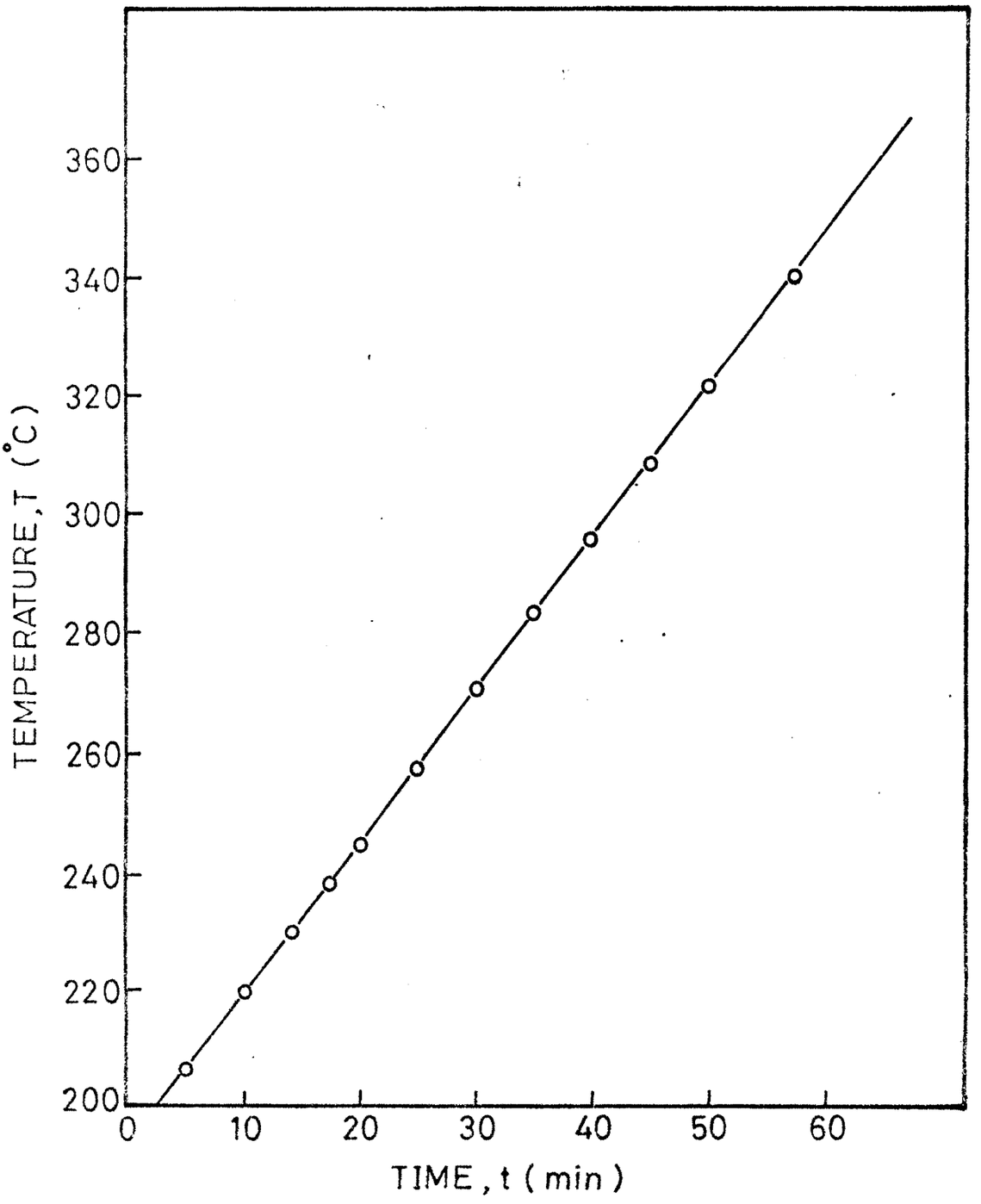

Fig. 4·2 PLOT OF TEMPERATURE VS TIME FOR UNDOPED KVO_3.

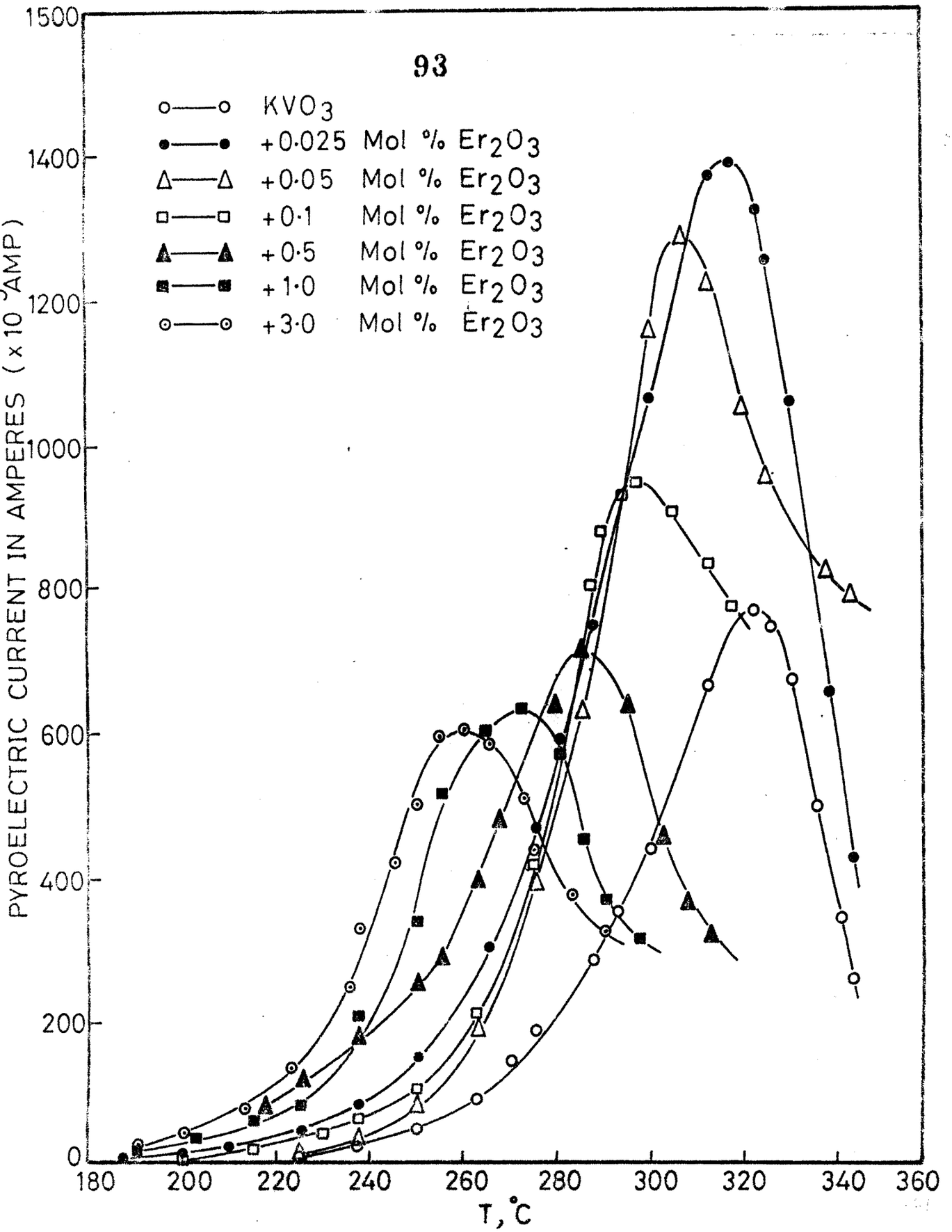

Fig. 4·3 TEMPERATURE DEPENDENCE OF THE PYROELECTRIC CURRENT OF UNDOPED AND DOPED KVO_3 WITH Er_2O_3.

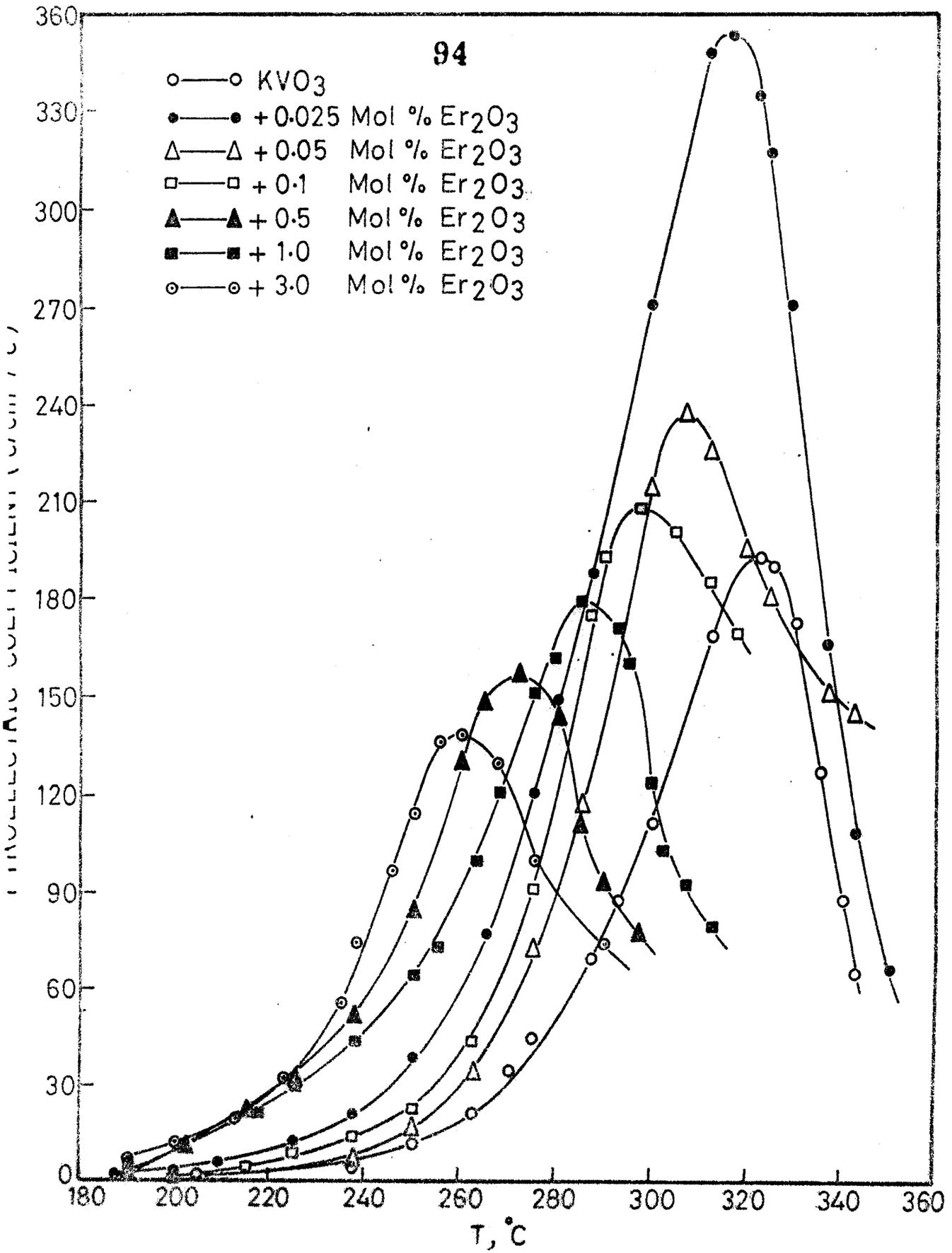

Fig. 4 TEMPERATURE DEPENDENCE OF PYROELECTRIC COEFFICIENT OF UNDOPED AND DOPED KVO_3 WITH Er_2O_3.

at their Curie temperatures. It is also observed that Curie temperature of KVO_3 sample changes as the dopant concentration (Er_2O_3) in KVO_3 varies from 0.025 to 3 mol%. As Er_2O_3 content in KVO_3 increases, Curie temperature of KVO_3 decreases. The Curie temperature of undoped KVO_3 is observed to be 322.5^0c which is in good agreement with that confirmed by Kashid et al in their DTA studies of undoped KVO_3.The peak values of pyroelectric parameters of different samples of KVO_3 doped with Er_2O_3 alongwith their densities and Curie temperatures are summarised in Table No. 4.1

TABLE NO.4.1

PEAK VALUES OF PYROELECTRIC PARAMETERS OF UNDOPED AND Er_2O_3 DOPED KVO_3

Er_2O_3 content (mole%)	Density gm/cc	T_c ^0c	I pyro (10^{-9}A)	pyro (10^{-7} c/cm ^{0}c
0.000	2.50	322.5	758.06	192.89
0.025	2.61	317.5	1387.00	352.93
0.050	2.58	307.5	1283.50	236.81
0.100	2.51	297.5	941.50	206.47
0.500	2.47	285.0	713.40	177.90
1.000	2.43	272.5	630.00	157.10
3.000	2.40	260.0	601.02	136.60

The Table 4.1 reveals us that peak values of pyroelectric parameters are higher for doping concentrations 0.025, 0.05 and 0.1 of Er_2O_3 in KVO_3 and they are smaller for doping concentrations 0.5, 1 and 3 mol% of Er_2O_3 in KVO_3 as compared to parameters of undoped KVO_3 .This result might be due to their respective change in densities as given in Table 4.1. The maximum values of parameters are observed for KVO_3 sample doped with 0.025 mol% of Er_2O_3 and it is due to a rather greater solid state interaction that takes place in the material. This might be due to the high value of density with the addition of 0.025 mol % Er_2O_3 in KVO_3. Thus 0.025 mol % doping may represent the maximum solubility of Er_2O_3 in KVO_3. Similarly Table 4.1 shows that Curie temperature of KVO_3 decreases from 322.5^oc to 260^oc due to doping of Er_2O_3 (0.025 to 3 mol%) in KVO_3. As a result of this pyroelectric measurements of KVO_3 samples doped with Er_2O_3 the following conclusions could be drawn.

1. The pyroelectric current and coefficient for different samples of KVO_3 doped with Er_2O_3 are temperature dependent.
2. The every sample of KVO_3 doped with Er_2O_3 shows peak values of pyroelectric current and coefficient.
3. The variation of pyroelectric parameters is related with the variation of the density of the sample.
4. The peak value of pyroelectric parameters represents ferroelectric Curie temperature of the sample.
5. The Curie temperatures determined by pyroelectric measurements of different samples are in good agreement with those obtained by hysteresis loop method.

6. As concentration of Er_2O_3 increases in KVO_3 its Curie temperature decreases.

7. The Curie temperature of undoped KVO_3 is in good agreement with that reported by earlier authors.

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