
CHAPTER - V

PYROELECTRICITY

CHAPTER - VPYROELECTRICITY5.1 Introduction :

When the polarization is altered by a small change in the temperature, the material is exhibiting its pyroelectric property. Pyroelectrics have finite polarization even at zero external fields and stresses, and this polarization is referred to as spontaneous polarization. If spontaneous polarization exists, then the material is pyroelectric, that is, that spontaneous polarization will change with temperature. This is why materials with spontaneous polarization are called pyro-electrics. As is well known, dielectric materials are classified by the point group symmetry, and the crystals belonging to 10 out of 32 point groups can be pyroelectric. Usually the surface charge due to the spontaneous polarization is neutralized by adsorbed ions. But, if the spontaneous polarization changes with temperature, a part of the surface charge can be observed on heating the crystal as a result of interruption of the neutralization. This is pyroelectricity. When the temperature of dielectric is changed, the spontaneous polarization changes so that an excess of free charge appears on one of the faces of the dielectric material which gives rise to current flow in the material and external circuit. The sense of current depends

upon the direction of the polarization change. The pyroelectric technique can be regarded as complementary to hysteresis loop measurements and applied to a study of the curie point transition in the materials.

The pyroelectric effect is determined by measuring the charge at the electrodes by a change in temperature, with an electrometer; a method which is neither accurate nor reliable. However, another, dynamic method devised by Chynoweth (1956), for pyroelectric measurements and deduced an equation,

$$\begin{aligned}
 i &= A \frac{dP_s}{dt} \\
 &= A \left[\frac{dP_s}{dT} \right] \left[\frac{dT}{dt} \right] \quad (5.1)
 \end{aligned}$$

where, A the area of the crystal, P_s the spontaneous polarization, t the time and T the temperature. The term $\frac{dT}{dt}$ is the rate of change of temperature and is independent of the initial crystal temperature, provided the specific heat at constant stress is assumed to be constant in the temperature range under consideration. As the pyroelectric coefficient $\left[\frac{dP_s}{dT} \right]$ changes, then the pyroelectric current also changes at a given temperature, therefore pyroelectric current is proportional to some approximate average polarization of the material.

Ackermann (1915) represented the static method for

measuring the pyroelectric coefficient and this method used only at discrete temperature points. Chynoweth (1956) devised a dynamical method for the study of pyroelectric effect in barium titanate. The pyroelectric current variation with temperature for NaVO_2 crystal was observed by Sawada et al (1961). Lang and Steckel (1965) described a method for measuring the pyroelectric coefficients of a polar material over a broad temperature range. The pyroelectric effect in barium titanate ceramic was studied by Lang et al (1969). Byer and Roundy (1972) introduced a direct method for measuring pyroelectric coefficients and application to a n sec response time detector $(\text{Sr}_x\text{-Ba}_{1-x})\text{Nb}_2\text{O}_6$. Dielectric and pyroelectric measurements were carried out for $\text{Pb}_3(\text{VO}_4)_2$ crystals in the lowest temperature phase (Phase III) by Midorikawa et al (1980). 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 $\text{Sb Se}_x\text{S}_{1-x}\text{I}$ 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. Dielectric and pyroelectric studies of ferroelectric ceramic NaVO_2 was reported by Khan et al (1983). Similar properties were studied by Mansingh and Sreenivas

(1983) for triglycine sulphate polystyrene composite. The pyroelectric properties of the ferroelectric single crystal series $(K_x Na_{1-x})_{0.4} (Sr_y Ba_{1-y})_{0.8} Nb_2O_6$ were reported by Yuhan et al (1984). The similar properties of poled samples of lead-barium titanate and lead-strontium titanate investigated by Jamadar et al (1987). The pyroelectric properties for ferroelectric $NaVO_3$, KVO_3 , $LiVO_3$ and their solid solutions studied by Patil et al (1988).

Thermal properties of $BaTiO_3$ crystals doped with cobalt were studied by Peraza et al (1976). The effect of DY_2O_3 doping and sintering parameters on dielectric properties of $BaTiO_3$ ceramics were studied by Yamaji et al (1977). Kuroda and Kubota (1980) studied the diffuse phase transition of a rare-earth ion doped $(Ba_x-Sr_{1-x})Nb_2O_6$ by measuring the spontaneous polarization and dielectric constant. The dielectric constant of barium titanate doped with ytterbium oxide with different concentrations were investigated at different temperatures by Molokhia et al (1984). Similar properties for barium titanate doped with Gd_2O_3 with different concentrations were studied by Issa et al (1984). 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).

Dielectric and ferroelectric properties of modified ferroelectric $\text{Ba}_4\text{Na}_2\text{Nb}_{10}\text{O}_{30}$ ceramics doped with La^{3+} and Pr^{3+} were studied by Subba Rao et al (1987).

The aim of the present investigation is to study the variation of pyroelectric current and coefficients with temperature of undoped sodium vanadate and doped with different concentrations of Nd_2O_3 .

5.2 Experimental :

The experimental set-up consisted of a Digital DC Micro Volt Meter VMV 15, a Pico Ammeter Adaptor for VMV 15, an electrically heated furnace and a digital millivoltmeter is shown in fig(5.1). The sintered pellets of the samples were used for pyroelectric measurements. The two sides of these pellets were coated with thin layer of air-drying silver paste for good electrical contact. The pellets of the samples were slowly heated inside the global furnace and pyroelectric current measurements were recorded at various temperatures. For calculating the rate of heating the corresponding time was noted. The pyroelectric coefficients were calculated from the pyroelectric current measurements and the rate of heating.

5.3 Pyroelectric Current And Coefficients Of Undoped NaVO_3 And Doped With Different Concentrations of Nd_2O_3 :

The samples of the mixtures of undoped NaVO_3 and doped with different concentrations (0.025 to 1 mol%) of Nd_2O_3 were

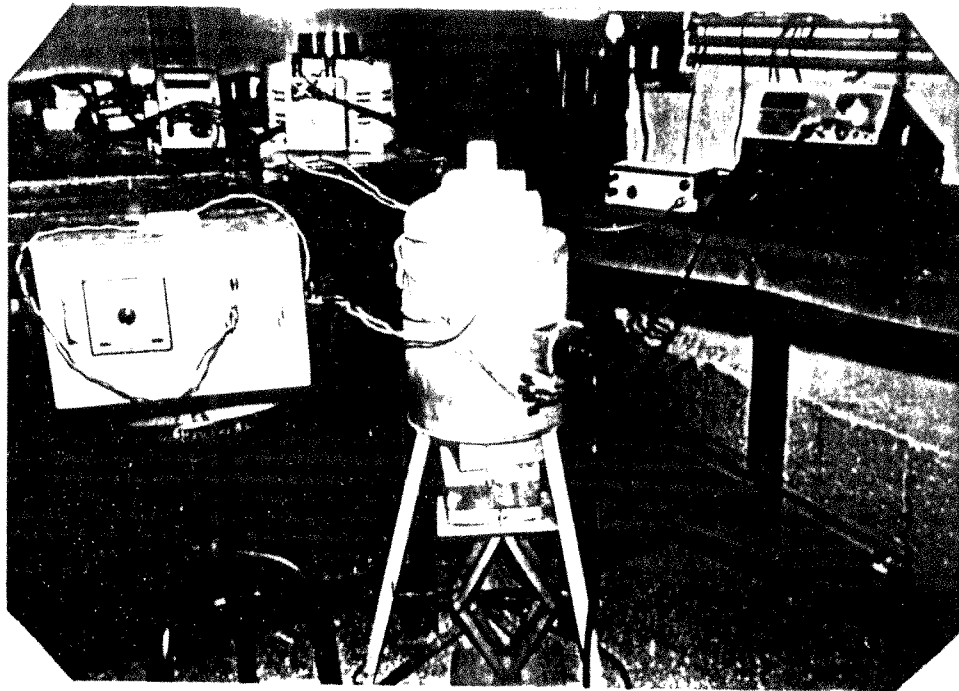


Fig. 5.1— Experimental set-up to study
the pyroelectric measurements.

slowly heated inside the furnace and the pyroelectric current measurements were recorded at different temperatures. The corresponding time was also noted to determine the rate of heating. The rate of heating was determined from the graph of temperature VS time and was found to be about $3^{\circ}\text{C}/\text{min}$. The temperature dependence of pyroelectric current for undoped and Nd doped NaVO_3 are shown in fig(5.2). The pyroelectric coefficients were calculated by using equation (5.1) and the temperature dependence of pyroelectric coefficients for undoped and Nd doped NaVO_3 are shown in fig(5.3).

5.4 Results and discussion :

It is observed from figures (5.2) and (5.3) that all the samples have the pyroelectric current and coefficients. The pyroelectric current and coefficients increase with temperature and reach a peak value at the curie temperature, and then decrease. The mixtures with concentrations of additives of Nd_2O_3 from 0.025 to 1 mol% exhibit a pronounced curie peak. The curie temperature of undoped NaVO_3 is found to be 380°C which is in good agreement with those reported by Sawada et al (1951) and Patil et al (1988).

It is also observed from figures (5.2) and (5.3) that the pyroelectric current and pyroelectric coefficients show maximum values at the curie temperatures 330°C , 320°C , 310°C ,

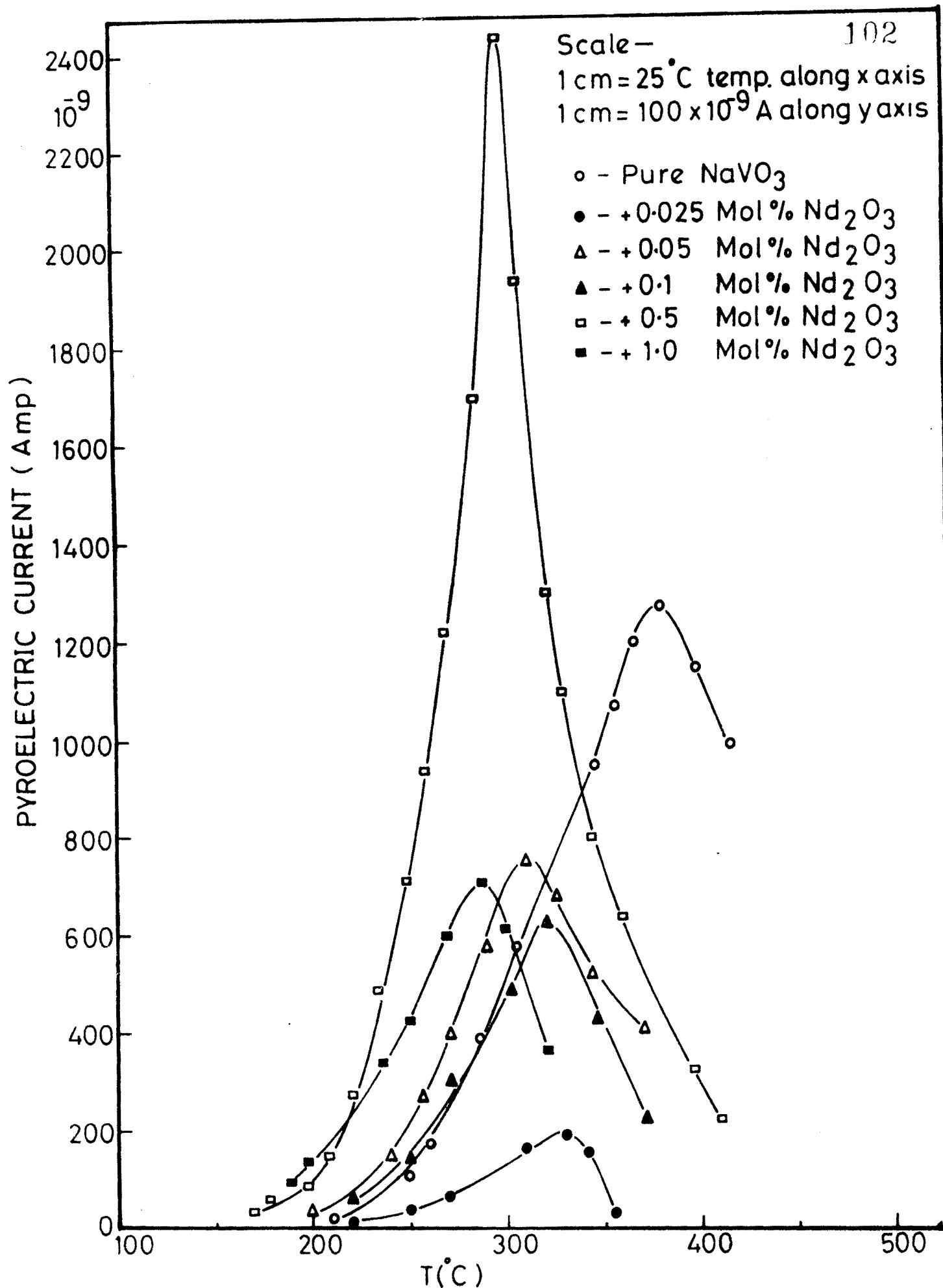


Fig. 5.2 — VARIATION OF PYROELECTRIC CURRENT WITH TEMPERATURE FOR DIFFERENT CONCENTRATIONS.

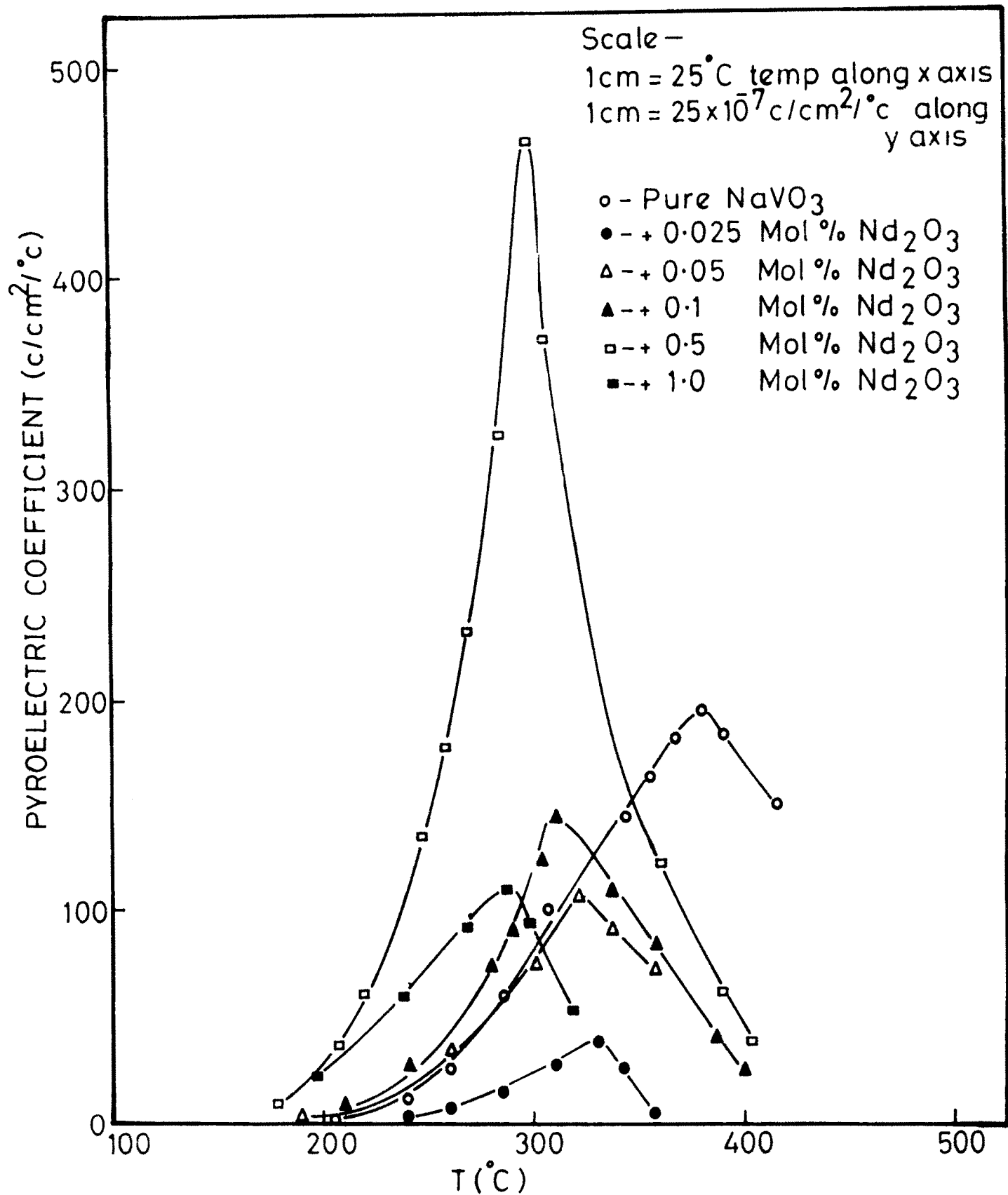


Fig. 5.3 - VARIATION OF PYROELECTRIC COEFFICIENT WITH TEMPERATURE FOR DIFFERENT CONCENTRATIONS.

300°C and 290°C for NaVO₃ doped with different concentrations (0.025, 0.05, 0.1, 0.5, 1 mol%) of Nd₂O₃ respectively. The addition of Nd₂O₃ to NaVO₃ shows change in the curie temperature. It is similar with the results obtained for (Ba_x-Sr_{1-x}) Nb₂O₆ doped with praseodymium (Pr³⁺) and Neodymium (Nd³⁺) by Kuroda and Kubota (1980).

The peak value observations of pyroelectric current and coefficients at curie temperature for undoped NaVO₃ and doped with different concentrations (0.025 to 1 mol%) of Nd₂O₃ are summarized in table (5.1).

Table (5.1) : Peak values of various parameters, curie temperatures and densities of material NaVO₃ :

Nd ₂ O ₃ content mol %	Pyroelectric current (10 ⁻⁹ Amp)	Pyroelectric coefficient (10 ⁻⁷ c/cm ² /°C)	Curie Temp. (°C)	Density (g/cm ³)
0	1273	194.5	380	2.78
0.025	190	30.9	330	2.61
0.05	628	109.0	320	2.65
0.1	752	143.0	310	2.69
0.5	2430	464.0	300	2.75
1	716	109.4	290	2.68

The table (5.1) reveals that the pyroelectric current and pyroelectric coefficients are maximum at 0.5 mol% doping



of Nd_2O_3 in NaVO_3 . The peak values indicate ferroelectric curie temperatures of the respective materials which are consistent with the curie temperatures determined by the hysteresis loop method as discussed in previous Chapter-III. Table (5.1) reveals that the curie temperatures of doping mixtures are different with respect to undoped sodium vanadate and also shows that the curie temperatures of doping mixtures are different with each other. The effect of Nd_2O_3 doping on the pyroelectric current and coefficients of NaVO_3 ceramic indicates that the maximum pyroelectric current and coefficients of NaVO_3 containing 0.5 mol% Nd_2O_3 was attributed to a rather more solid state interaction that takes place in the materials. This can be studied from the pronounced increase of density with addition of Nd_2O_3 . The maximum densification is observed at 0.5 mol% doping of Nd_2O_3 . Thus in this investigation the dielectric saturation states are attained at 0.5 mol% Nd_2O_3 addition, which may represent the solubility limit of Nd_2O_3 in NaVO_3 lattices.

As a result of this investigation the following conclusions may be drawn.

- (1) Maximum value of current and coefficients gives ferroelectric curie temperatures of the respective materials.

- (2) The ferroelectric curie temperatures determined by pyroelectric measurements for undoped and doped materials are in good agreement with those investigated by hysteresis loop method.
- (3) Pyroelectric current and pyroelectric coefficients are high for 0.5 mol% of Nd_2O_3 .
- (4) It was found that the curie temperatures of doping mixtures are different with respect to undoped NaVO_3 and also curie temperatures of doping mixtures are different.
- (5) The peak values of pyroelectric current and coefficients increase with increase of Nd_2O_3 concentrations upto 0.5 mol% and then decrease for higher concentrations.
- (6) These materials can be used for pyroelectric detector applications.

REFERENCES

- Ackermann W. (1915), Ann.Physik 46, 217.
- Byer R.L. and Roundy C.B. (1972), Ferroelectrics 3, 333.
- Chaves R. (1982), Phys. Stat.Sol. (a) 73, 367.
 Amaral H. Levelut A.
 Ziolkowich S.
 Balkanski M. Teng M.
 Vittori J. and
 Stone H.
- Chynoweth A.G. (1956), J.Appl.Phys. 27, 78.
- Issa MAA, Molokhia N.M. and Nasser S.A. (1984), J.Phys.D:Appl.Phys. 17, 571.
- Jamadar V.M. (1987), Bull.Mater.Sci. 9, 249.
 Patil T.A. and
 Chavan S.H.
- Kuroda S. and Kubota K. (1980), J.Phys.Chem. solids 42, 573.
- Khan A. Ghare D. (1983), Bull.Mater,Sci. 5, 133.
 and Narayanan P.
- Lang S.B. and Steckel F. (1965), Rev.Sci.Instr. 36, 929.
- Lang S.B. Rice L.H. (1969), J.Appl.Phys. 40, 4335.
 and Shaw S.A.
- Mathur S.C. (1981), Ferroelectrics, 39, 1197.
 Baria A.Y. and
 Singh H.
- Mansingh A. and Sreenivas K. (1983), Ferroelectr.Lett.Sec. 1, 67.
- Midorikawa M. (1980), J.Phys.Soc.Jpn. 49, 1095.
 Kashida H.
 Sawada A. and
 Ishibashi Y.

- Molokhia N.M. (1984), J. Am. Ceram. Soc. 67, 289.
Issa MAA and
Nasser S.A.
- Patil T.A. (1988), Indian J. Phys. 62A, 341.
Jamadar V.M. and
Chavan S.H.
- Peraza J. (1976), Mater. Res. Bull. 11, 981.
Bocanegra E. Tello M.
and Fernandez J.
- Sawada S. Nomura S. (1961), I. Phys. Soc. Jpn. 16, 2466.
and Asao Y.
- Subba Rao P.S.V. (1987), J. Mater. Sci. Lett. 6, 299.
Sambasiva Rao K. and
Bhanumathi A.
- Umakantham K. (1987), J. Mater. Sci. Lett. 6, 565.
Narayana Murthy S.
Sambasiva Rao K. and
Bhanumathi A.
- Yamaji A. Enomoto Y. (1977), J. Am. Ceram. Soc. 60, 97.
Kinoshita K. and
Murakami T.
- Yuhan Xu, (1984), Ferroelectr. Lett. Sec. 2, 189.
Huanchu Chen and
Cross L.E.