# CHAPTER III

## DIELECTRIC HYSTERESIS

# C H A P T E R - I I I

## DIELECTRIC HYSTERESIS

### 3.1  Introduction :

For an ideal dielectric the relationship of the polarization P and the electric field E is linear and reversible, showing no dielectric loss. But the relationship between P and E is a square-like hysteresis loop for ferroelectric materials. If the applied field E is decreased from high positive value, the dielectric polarization decreases linearly. At zero applied field, there is a nonzero value of polarization. If the field E is increased in the negative direction the polarization decreases and switches to a negative value at a particular value of applied field E. The reverse effect is observed when the applied field E is decreased from high negative value. This effect is referred to as dielectric hysteresis. This type of dielectric behavior is an ideal response of a homogeneous ferroelectric crystal. The dielectrics do not exhibit dielectric hysteresis, since the dipole moments are rotated or oriented freely and follow the applied field, no work being required to be done during reversal.

### 3.1,a  Hysteresis loop :

The observed hysteresis loop for a ferroelectric crystal is more commonly continuous as shown in Fig.1.1. The deviation from the ideal behavior is attributed to the

multidomain structure of the crystal. The dipole moments are not parallel and hence the electric field and displacement field in the substance are not uniform. The dipole moments have parallel and anti-parallel orientations if the material has one ferroelectric axis. More complicated configurations occur if there is more than one ferroelectric axis. The net result is a rounding off of the ideal hysteresis loop.

The domains have all possible orientations. Therefore, the overall polarization is zero. When the field is applied, the polarization increases. The effect of field on the domains is quite different than that in ferromagnetics. In a ferroelectric, the nucleation and growth of domains of reversed polarity occur . When a small electric field is applied, the polarization P increases linearly with E, as shown by portion OA (Fig.1.1), because the field is not large enough to switch any of the domains and the crystal behaves as normal dielectric. When the electric field strength is increased, the domains switch over in the field direction and the polarization increases rapidly (portion AB), until all the domains are aligned in the field direction. This is a state of saturation (portion BC) and the crystal consists now of a single domain. The extrapolation of saturation portion gives spontaneous polarization $P_s$.

When the field is reduced to zero the polarization will not generally return to zero but rather follows the

path CD, exhibiting a remanent polarization OD. In order to annihilate the overall polarization, it is necessary to apply an electric field in the opposite direction. The value of the field at which half the polarization has reversed is called as <u>coercive field</u> (OF). Further increase in the field will produce complete alignment of domains in this direction and the cycle (CDFGHIC) can be completed by reversing the field once again (GHIC). Thus for a ferro-electric material the relation between P and E is a non-linear one in contrast to that for dielectric material. The shape of hysteresis loop depends mostly on the properties of the material and also does depend on the rate of change of externally applied field. The hysteresis loop is used to measure $P_s$, $E_c$ and susceptibility. These parameters become zero as the temperature approaches $T_c$ where the transition occurs from ferroelectric to the paraelectric phase.

The field, at which the polarization reverses its direction, depends upon the time that it is permitted to take for the reversal. Thus the shape of the hysteresis loop depends on the rate at which the loop is traversed. On the basis of exponential law found experimentally by Merz (1954), the rate at which polarization is reversed may be given by the formula :

$$\frac{dP}{dt} = F(P)e^{-\alpha/E(t)} \qquad \qquad \ldots (3.1)$$

where the function F(P) takes into account the fact that the switching rate depends on the extent to which the crystal has already reversed its polarization.

### 3.1.b  Coercive field :

The coercive field defined, by Fig. 1.1 as the field at which half the polarization has reversed, is also a function of the frequency of alternating field since there is some switching time associated with polarization reversal.

The coercive field of a ferroelectric crystal is defined as the external field required for the discontinuous transition from a metastable state to a stable one, through domain reversal or domain wall motion. In $BaTiO_3$, for example, the coercive field is expressed in terms of the movement of domain walls, since it has $180^O$ domains. The coercive field depends on the applied field, thickness, impurities and temperature of the substance.

### 3.1.c  Experimental reports on dielectric behavior of ferroelectrics :

The first quantitative experiments to determine the time and field dependence of polarization were carried out by Merz (1954) for $BaTiO_3$. The dependence of coercive field on frequency and amplitude of the applied field was studied by Landauer et al (1956). A theoretical explanation of coercive field was given by Janovec (1958) for $BaTiO_3$ and by Abe (1960). Dielectric and pyroelectric properties of $NaVO_3$ were investigated by Khan et al (1983).

Kurchatov and Eremeev (1933) were the first to study the dielectric and piezoelectric properties of mixed crystals

of sodium-potassium and isomorphous amonium-potassium-tartrate.
In recent years considerable advances have been made in
investigations on the effect of impurities on the ferro-
electric properties. Ferroelectric properties have been
greately influenced by impurity nature, its content, parti-
cle size and grain size. Mazdyasni and Brown (1971) found
that a small addition of $La_2O_3$ enormously increased the
dielectric constant and the Curie point was depressed to
below room temperature. Yamaji et al (1977) studied the
system of Dy-doped $BaTiO_3$ and concluded that the dielectric
properties depend strongly on grain size in the ferroele-
ctric state, where it is almost independent of grain size
in the paraelectric state. The decrease in $E_c$, $T_c$, $P_s$ and $\varepsilon$
for Cu, Cr and Fe as dopants were reported by J.Stankowska
(1983).

It may be seen from the above that no systematic
connection has yet been established between the nature and
content of dopant and the $E_c$, $P_s$ or $\varepsilon$ of the host material.
Notwithstanding, it appears that doping might lower the $E_c$
to useful range of memory devices. Therefore, the studies
on $NaVO_3$ doped with $Fe_2O_3$ have been carried out with this
orientation of purpose.

## 3.2 Experimental Details :

The application of a large sine wave voltage to a
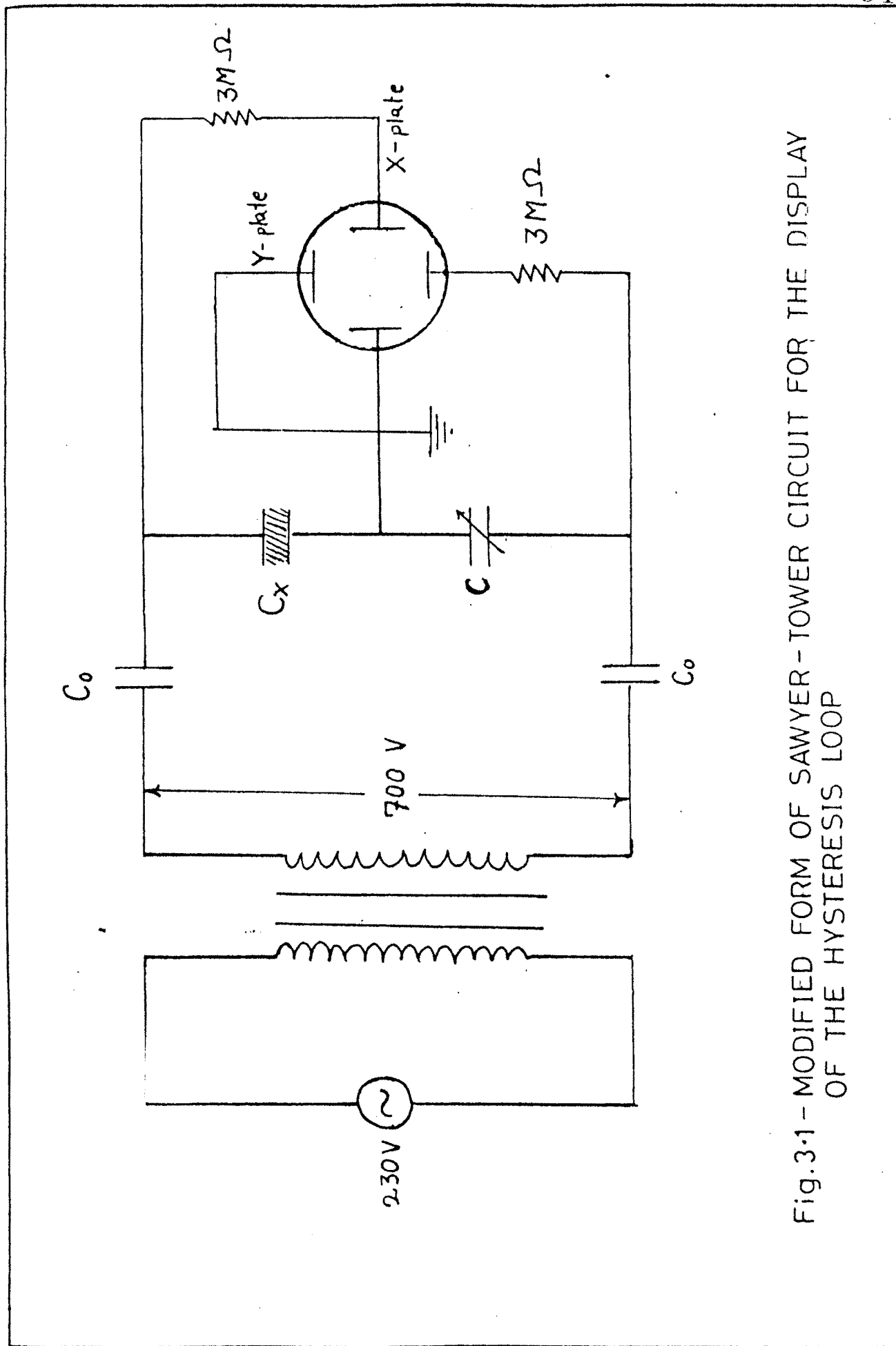dielectric material results in a current flow which varies

Fig. 3·1 – MODIFIED FORM OF SAWYER-TOWER CIRCUIT FOR THE DISPLAY OF THE HYSTERESIS LOOP

sinusoidally with time. The electrical non-linearity is often displayed as a function of time. This is done by using a Sawyer and Tower circuit (1930) as shown in the Fig. 3.1. It consists of a step up transformer which gives output voltage of 700 volts, two oil filled condensers $C_o$ and a gang condenser C in series with the sample $C_x$. In order to avoid damage to CRO, the resistances each of 3 MegOhm are connected in series with X- and Y-plates of the CRO. The voltage used across the sample was about 4 KV/cm and of frequency 50 Hz. A specially designed sample holder having stainless steel electrodes and a temperature controller arrangement was used while observing the dielectric hysteresis. The experimental set up used to observe the hysteresis loop is shown in Fig. 3.2.

### 3.2.a  Hysteresis loop of $NaVO_3$ and its compositions doped with $Fe_2O_3$ :

The ferroelectric hysteresis loops of different samples were observed on the CRO screen by using modified Sawyer and Tower (1930) circuit. The pellets were coated on both sides with a thin layer of silver paste for good electrical contact. The hysteresis loops of the samples were observed at different temperatures. The hysteresis loop of undoped $NaVO_3$ at different temperatures is shown in Fig.3.3. As representative samples, the hysteresis loops of $NaVO_3$ doped with 0.5 mol% and 5.0 mol% of $Fe_2O_3$ are shown in Fig.3.4 and 3.5 respectively.
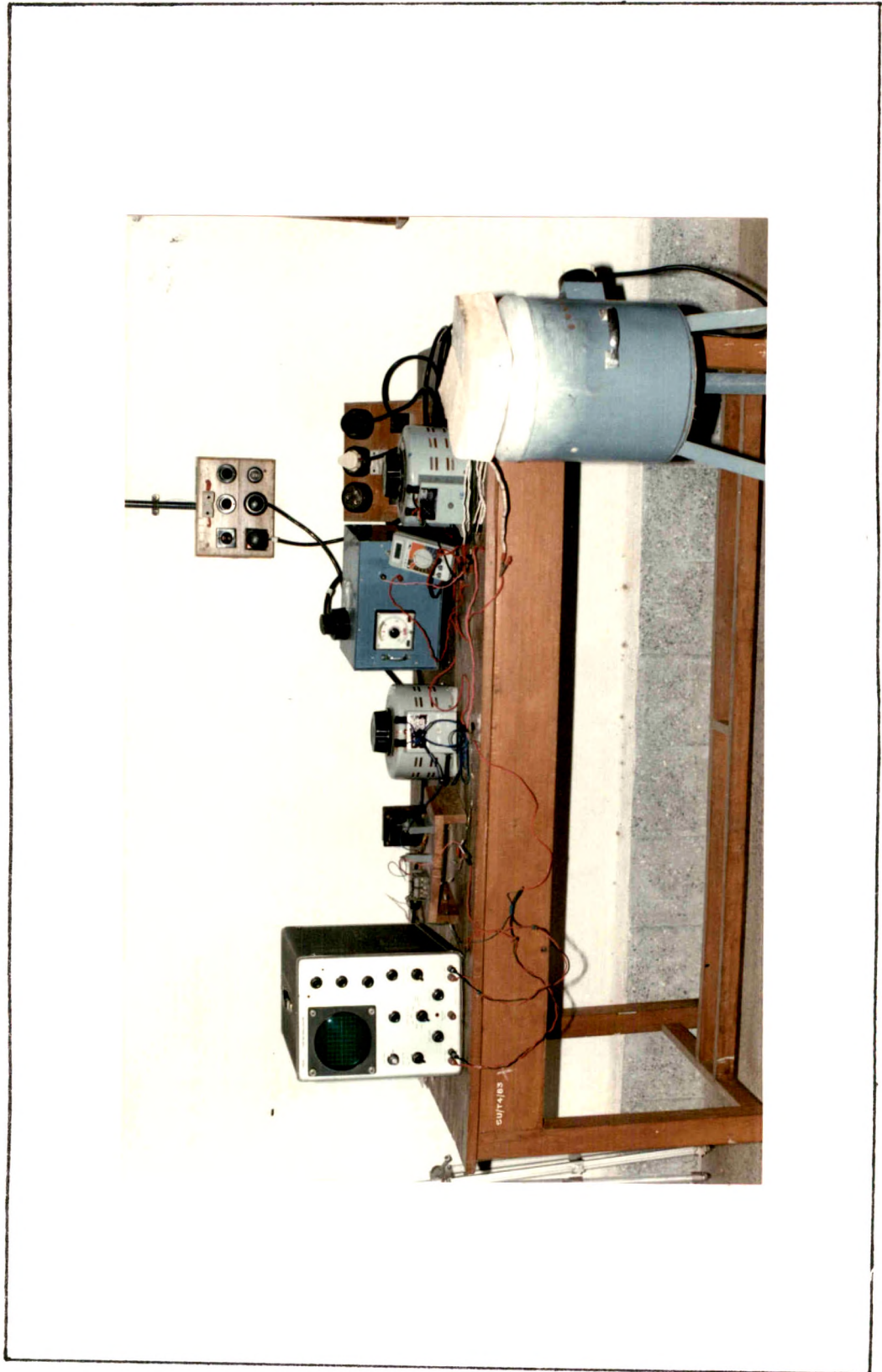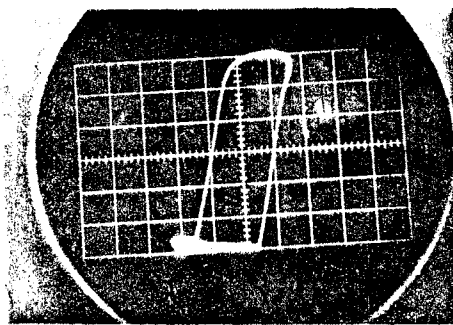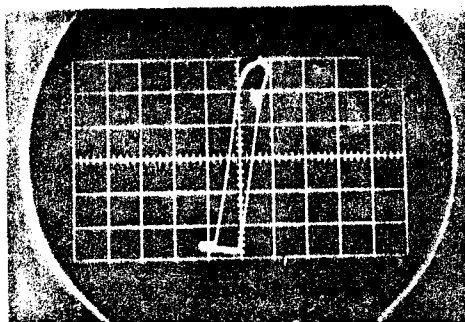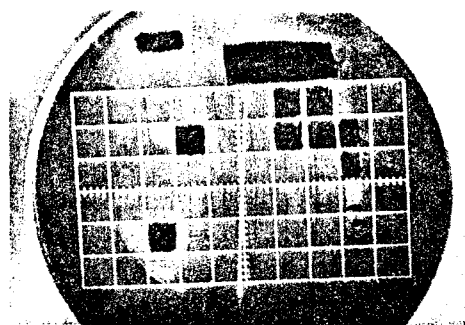
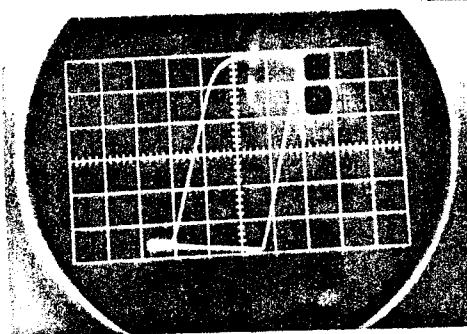FIG. 3.2 : EXPERIMENTAL SET UP TO STUDY THE DIELECTRIC HYSTERESIS
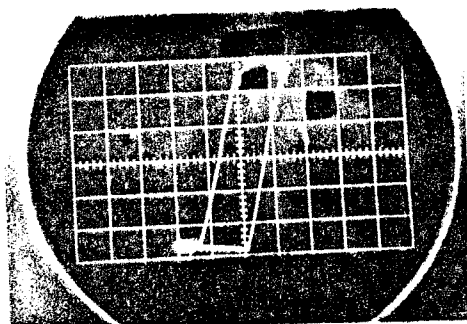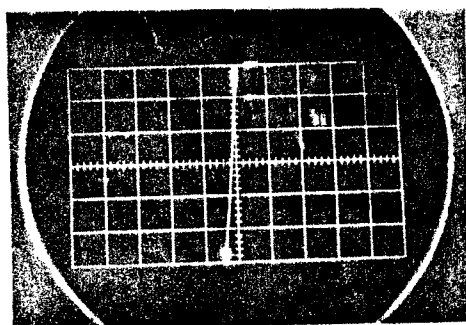
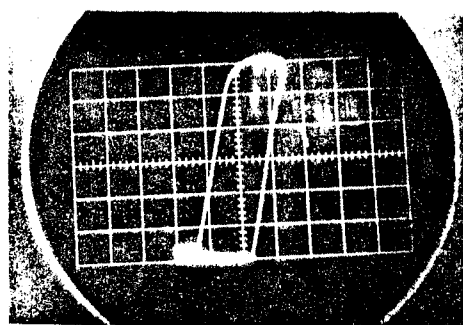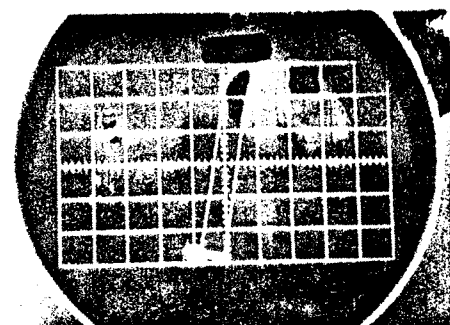100°C



255°C



375°C

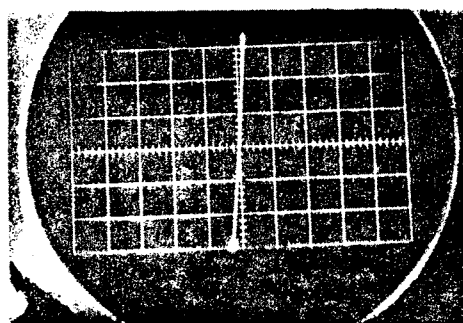FIG. 3.3 : HYSTERESIS LOOPS OF NaVO$_3$

100°C



300°C



350°C

FIG. 3.4 : HYSTERESIS LOOPS OF NaVO₃ DOPED WITH 0.5 MOL % Fe₂O₃

100°C

265°C

315°C

FIG. 3.5 : HYSTERESIS LOOPS OF NaVO$_3$ DOPED WITH 5.0 MOL % Fe$_2$O$_3$

### 3.2.b  Coercive field measurements :

The half width of the hysteresis loop on the CRO is the measure of coercive field. At increasing temperature up to $T_c$, the coercive fields are measured for all the samples at various temperatures.

### 3.3  Results and Discussion :

The observed hysteresis loop for any of the samples implies irreversible process taking place in the sample. The shape of the hysteresis loop is rectangular in nature and the area of the loop indicates the energy loss during a cycle. This is clear indication of the ferroelectric nature of the samples. Also it is observed that practically the height and shape of the hysteresis loop remains unchanged with increasing temperature of the sample. The loop width decreases with temperature and vanishes at $T_c$, indicating the phase change from ferroelectric to paraelectric state. The square like shape of the hysteresis loop is not affected much due to the addition of $Fe_2O_3$ of different mol%. However the coercive field of $NaVO_3$ is affected due to $Fe_2O_3$-doping. Fig. 3.6 shows the variation of $E_c$ with temperature for all the samples. The hysteresis loop width of $NaVO_3$ vanishes at $375^{\circ}C$ indicating its Curie temperature. This result is in good agreement with the results obtained by Sawada and Nomura (1951) and Patil et al (1988b). The Curie temperature of $NaVO_3$ decreases as the doping concentration of $Fe_2O_3$ increases from 0.025 to 5.0 mol%  (Fig. 3.6).       ......
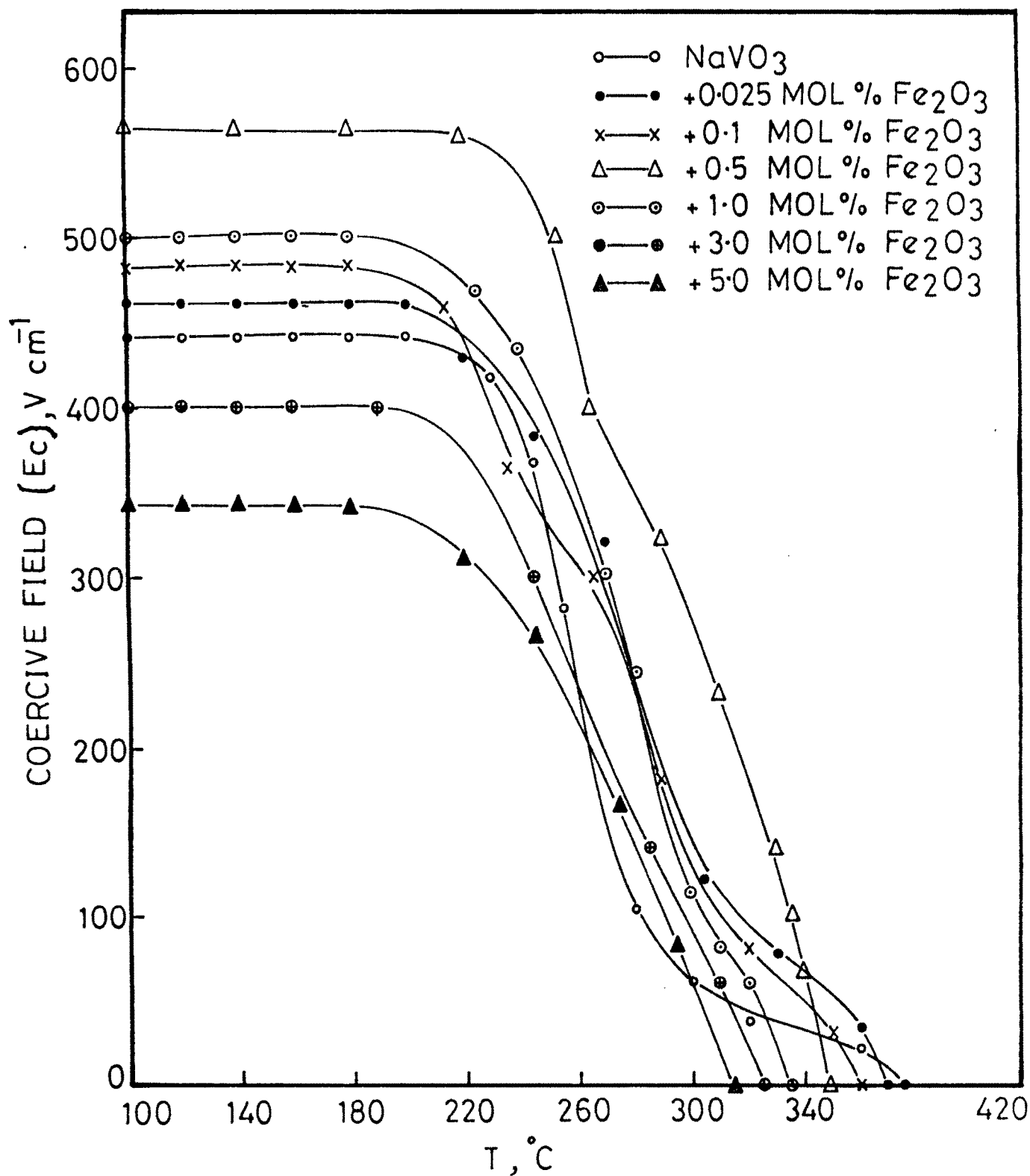
Fig. 3·6 — VARIATION OF COERCIVE FIELD WITH
TEMPERATURE FOR NaVO₃ AND ITS Fe₂O₃
DOPED COMPOSITIONS

Similar results have been obtained by Nishioka et al (1956) and Hagemann (1978) for $Fe_2O_3$-doped $BaTiO_3$. The Curie temperature of $Fe_2O_3$-doped $NaVO_3$ samples are indicated in Table 3.1

TABLE 3.1

Peak values of coercive field and Curie temperatures for $NaVO_3$ and its $Fe_2O_3$ doped compositions.

| $Fe_2O_3$ content Mol % | Peak Coercive Field V/cm | Curie temperature $T^oC$ |
|---|---|---|
| 0 | 440 | 375 |
| 0.025 | 460 | 370 |
| 0.1 | 480 | 360 |
| 0.5 | 563 | 350 |
| 1.0 | 500 | 335 |
| 3.0 | 400 | 325 |
| 5.0 | 344 | 315 |

The Curie temperature and peak coercive field are plotted as a function of $Fe_2O_3$ content in $NaVO_3$. The plots are shown in Fig. 3.7 and 3.8, from which it can be seen that samples up to 1.0 mol % fall in a group wherein $T_c$ decreases at a faster rate than for a group of the samples having 3.0 to 5.0% of $Fe_2O_3$ content. However, the behavior with respect to $E_c$ is different. $E_c$ increases up to 0.5 mol% $Fe_2O_3$ content and then decreases. From this we conclude that the effect
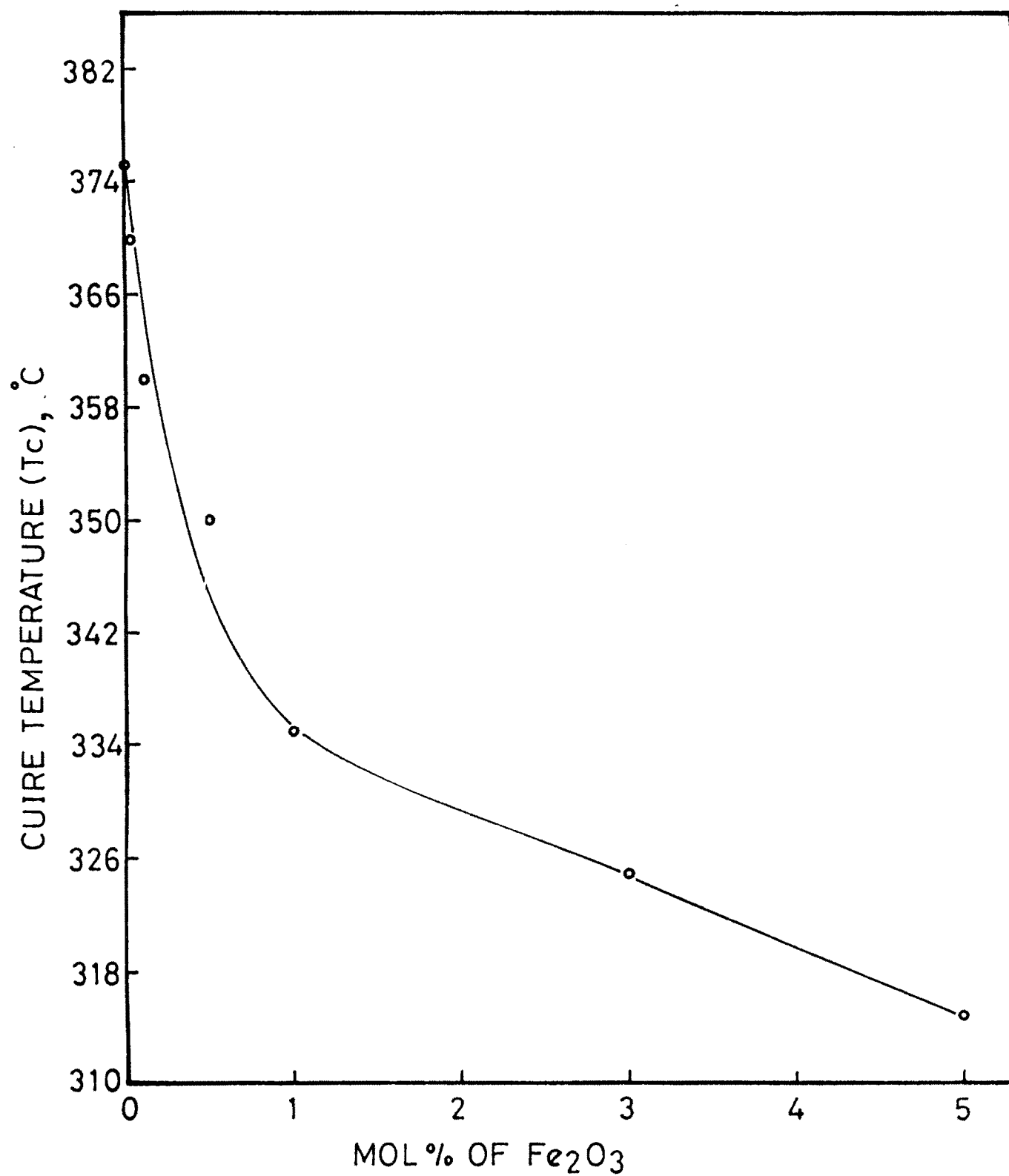
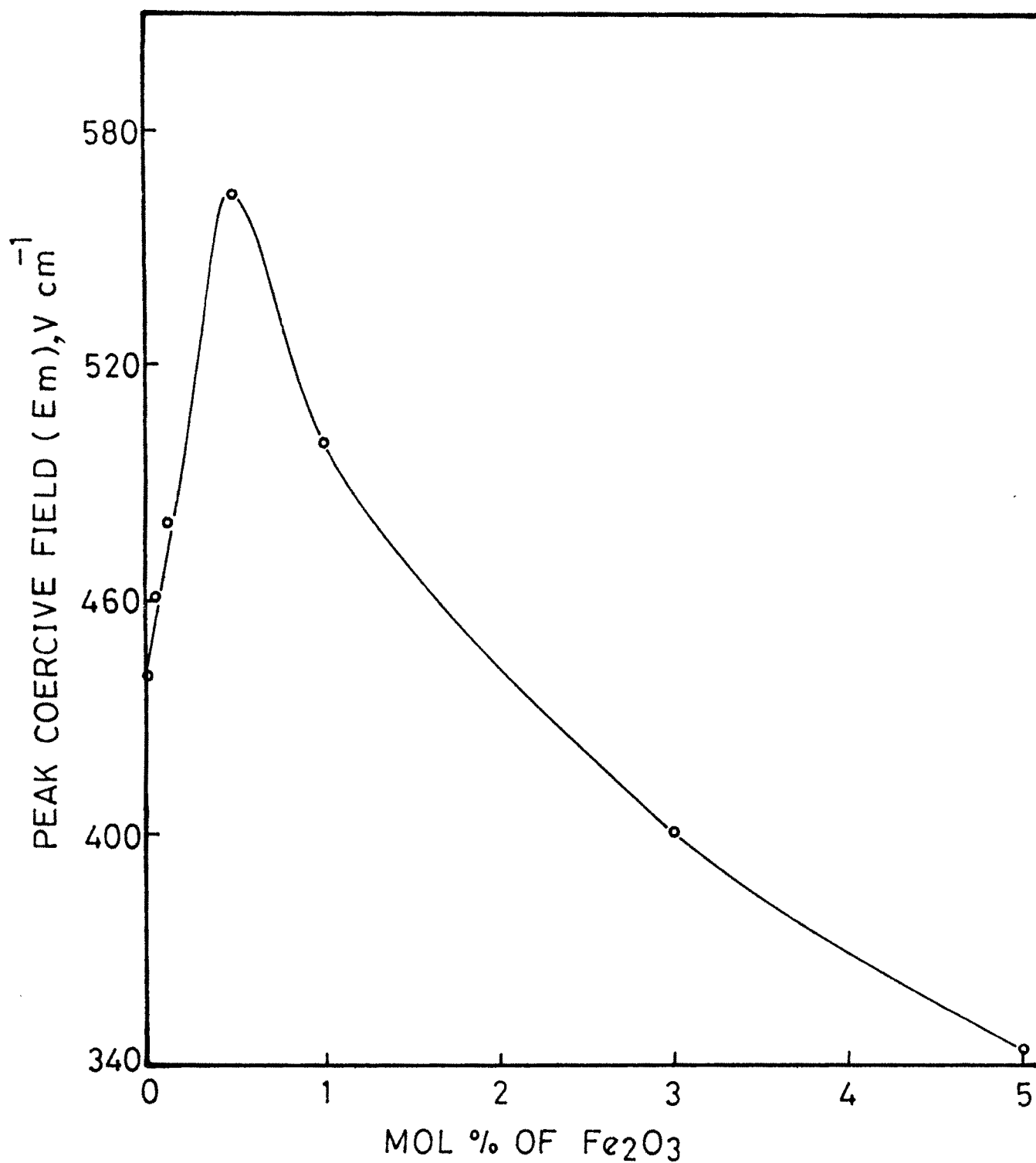Fig. 3·7 — CURIE TEMPERATURE OF NAVO$_3$ AS A
FUNCTION OF Fe$_2$O$_3$ CONTENT

Fig. 3·8 — PEAK COERCIVE FIELD OF NAVO$_3$ AS A
FUNCTION OF Fe$_2$O$_3$ CONTENT

of $Fe_2O_3$ doping with respect to change in $T_c$ is more pronounced for the smaller contents than for higher contents. Similar effects have been observed by Tein et al (1962) for Ca-F addition in $PbTiO_3$.

The early workers Nassan and Lines (1970) suggested the bond strength effect in lowering the Curie temperature of $LiNbO_3$ and $LiTaO_3$. In the present work Curie temperature of $NaVO_3$ decreases with increasing addition of $Fe_2O_3$. The decrease in Curie temperature is attributed to a greater degree of co-valent bonding between Fe and O than that formed between V and O, the iron being substitutional or interstitial.

The other possibility is that of rattling of central ion, of oxygen polyhedra which is an important effect in ferroelectricity of perovskites. A similar situation would arise for substitution of V by Fe in $NaVO_3$, wherein Fe is smaller than V. Consequently, it would provide more of rattling space for the central ion. In anology with the behavior of perovskites as discussed by Jona and Shirane ( 1962), one will have to expect increase in $T_c$, which is not the case.

The decrease in $T_c$ of $NaVO_3$ doped with $Fe_2O_3$ can be due to the carrier electrons contributed by $Fe^{3+} \rightleftharpoons Fe^{2+}$. According to Kristoffel and Konisin (1971) theory, due to addition of impurity ($Fe_2O_3$), the carrier electrons, as discussed earlier, would add to the stiffness of the lattice and hence

to the (quartic) anharmonicity. These effects make a lattice more resistant to ordering, reducing thereby Curie temperature of $NaVO_3$.

The variation of coercive field with temperature for all the samples is shown in Fig.3.6. It is observed that the coercive field strongly depends upon the temperature and $Fe_2O_3$ content. For any of the samples, the coercive field remains constant over the wide range of temperature and then decreases with further increase of temperature vanishing finally at a certain temperature indicating the transition temperature $T_c$ of the sample under consideration. Similar dielectric hysteresis behavior was observed by Ismailzade et al (1981), for rare earth vanadates. The value of peak coercive field increases as $Fe_2O_3$ content increases from 0.025 to 0.5 mol% and then it decreases as $Fe_2O_3$ content increases from 1.0 to 5.0 mol% (Table 3.1). The increase in $E_c$ with $Fe_2O_3$ content is due to increase in the structural rigidity caused by probable substitution of V by Fe. The maximum coercive field corresponds to the solubility limit of $Fe_2O_3$ of 0.5 mole% in $NaVO_3$. However, the decrease in coercive field for $Fe_2O_3$ content from 1.0 to 5.0 mol% is due to the defects created near the domain walls. Boser (1987) suggested that the lattice defects such as vacancies, interstitials, pairs of positively and negatively charged defects and dislocations present will interact with the domain walls. Because of random fluctuations in the number of positions of the obstacles with respect to the domain wall, it experiences a randomly

varying force as the domain wall is displaced by an applied electric field. The model of randomly distributed obstacles that interact with the domain walls provides a way to interpret the change in properties. This will be the reason for the decrease in $E_c$ of $NaVO_3$ for $Fe_2O_3$ content from 1.0 to 5.0 mol%. Similar effects (decrease in $T_c$, increase in $\varepsilon$) are observed by Hagemann (1978) and G.Godefroy et al (1981) for Fe-doped $BaTiO_3$. They showed that Fe additions can act as obstacles to domain wall motion. Further study is required to give a qualitative explanation for the observed effects.

Conclusions :

1) Ferroelectric properties are influenced by $Fe_2O_3$-doping in $NaVO_3$.

2) Curie temperature of $NaVO_3$ continuously decreases with increasing $Fe_2O_3$ content.

3) Coercive field depends on both the temperature and $Fe_2O_3$ content.

4) Properties of $NaVO_3$ are greatly influenced by first instalments (< 1.0 mol%) of $Fe_2O_3$-doping.

5) Usual explanations of change in $T_c$ and $E_c$ are rather simplistic to account for the present case, wherein the detailed structural considerations would need to be made. The chain structure involving $VO_4$ tetrahedera (with two of the oxygens double bonded) might receive structural rigidity when the group is replaced by $FeO_2$.

## REFERENCES

| | |
|---|---|
| Abe R. | J. Phys. Soc. Japan, $\underline{15}$,795 (1960). |
| Boser O. | J.Appl.Phys., $\underline{62}$(4), 1344 (1987). |
| Godefroy G.,Dumas C. Lompre P. and Perrot A. | Ferroelectrics, $\underline{37}$(1-4), 725 (1981). |
| Hagemann H.J. | J.Phys.C., $\underline{11}$, 3333 (1978). |
| Ismailzade I.H., Iskenderov R.N., Alekberov A.I., Ismailov R.M., Habibov A.M. and Salyev F.M. | Ferroelectrics, $\underline{31}$, 45 (1981). |
| Janovec V. | Czechoslov J. Phys., $\underline{8}$, 3 (1958). |
| Jona F. and Shirane G. | Ferroelectric crystals, Pergamon Press, London (1962). |
| Khan A., Ghare D. and Narayanan P. | Bull.Mat.Sci. (Ind), $\underline{5}$, 133 (1983). |
| Kristoffel N.N. and Konisin P.I. | Sov.Phys.-Solid St., $\underline{13}$, 2969 (1971). |
| Kurchatov B. and Eremeev M. | Phys. Zs. Sow. Union, $\underline{1}$, 140 (1932). and $\underline{3}$, 304 (1933). |
| Landauer R., Young D.R. and Drougard M.E. | J.Appl.Phys., $\underline{27}$, 752 (1956). |
| Mazdyasni K.S. and Brown L.M. | J.Am.Ceram.Soc., $\underline{54}$(11), 539 (1971). |
| Merz W.J. | Phys. Rev., $\underline{95}$, 690 (1954). |
| Nassau K. and Lines M.E. | J.Appl.Phys., $\underline{41}$, 533 (1970). |

Nishioka A., Sekikawa        J.Phys.Soc.Japan, <u>11</u>, 180 (1956).
K. and Owaki M.

Patil T.A., Jamadar          Indian J. Pure and Appl. Phys.,
V.M. and Chavan S.H.         <u>26</u>, 456 (1988b).

Sawada S. and                J.Phys.Soc.Japan, <u>6</u>, 192 (1951).
Nomura S.

Sawyer C.B. and              Phys.Rev. (USA), <u>35</u>, 269 (1930).
Tower C.H.

Stankowska J.                Acta. Phys. (Poland), <u>64</u>(1),
                             115 (1983).

Tein T.Y. and Carlson W.G.   J.Am.Ceram.Soc., <u>45</u>(12),
                             566 (1962).

Yamaji A., Enomoto Y.,       J.Amer.Ceram.Soc., <u>60</u>, 97 (1977).
Kinoshita K. and
Marakami T.