C H A P T E R - I

FERROELECTRICS

1.1 Introductory : Historical

Ferroelectrics are the substances which display spontaneous polarization whose direction can be reversed under an external electric field and other influences. These materials exhibit a hysteresis loop, which is the basic feature that makes them amenable to applications in computer memory devices just as ferromagnets and they offer considerable scope for the production of solid state integrated versions of memory devices.The reversible non-linear behavior of ferroelectrics makes them useful in dielectric amplifiers, voltage regulators and in automatic equipments and these interesting applications render them attractive to research workers.

The major events in the historical development of the field of ferroelectrics are shown in Table 1.1.

Table 1.1 : The major events in the historical development.

Sr.No.	Authors	Event	Remarks
1)	Seignette(France) (1655)	Discovery of first ferroelectric, $NaKC_4H_4O_6:4H_2O$	-
2)	Pockels (1894)	Dielectric, piezo-electric and electro-optic properties.	Unusual
3)	Valaseck (1920,1921)	Analogy between ferroelectrics and ferromagnetics	Origin of nomenclature
4)	Busch and Scherrer (Switzerland) (1935)	Discovery of KH_2PO_4 and its iso-morsphous salts	Creating inter-est in the study of ferro-electrics
5)	Onsagar and Slater (1939)	Ferroelectric transition is linked with ordering of hydrogen ions	First molecular theory of ferro-electricity based on crystal structure
6)	Mueller (1940)	Piezoelectric, elastic and electro-optic anomalies are consequence of unusual dlelectric behavior.	Interaction theory and coining the term ferro-electricity.
7)	Wainer and Salo-man (USA), Wul and Goldman (Russia),Ogawa (Japan),1943.	Discovery of diele-ctric properties of $BaTiO_3$	Anomalous
8)	Von Hipple, Wul and Goldman, (1945)	Confirmation of ferroelectricity in $BaTiO_3$	-
9)	Devonshire (1949)	Phenomenological theory of $BaTiO_3$	Remarkable success.

Sr.No.	Authors	Event	Remarks
10)	Kittle (1951)	Phenomenological theory of anti-ferro-electricity	-
11)	Shirane et al (1951)	Discovery of first antiferroelectric, $PbZrO_3$	-
12)	Jona and Shirane (1961)	Table of 76 ferroelectric crystals	Known upto Jan.1961
13)	Cochran (1961)	Lattice dynamical theory	Most successful
14)	Mitsui et al (1969)	Compilation of nearly 450 ferro-electric compounds	upto date
15)	Glasso (1969)	Structural data of a large number of ferroelectrics	Useful reference
16)	Subbarao (1972) and	Data on Curie temp. spontaneous polari-zation of a large number of ferro-electrics and antiferroelectrics	Useful for applications.
17)	Mitsui et al (1975)	Identification of almost 700 ferro-electrics and their solid solutions	Upto date

1.2 Characteristic Features :

The dielectric materials exhibit polarization under the influence of electric field. The polarization is affected by the physical properties such as elastic, optical, thermal, etc. Just as ferromagnetic materials exhibit spontaneous magnetization and hysteresis effects in relationship between M and H, ferroelectrics show spontaneous polarization and hysteresis effects

in relation between dielectric displacement D and applied electric field E. This behavior is observed in certain temperature regions only. Above a certain temperature called as transition (or Curie) temperature the crystals are no longer ferroelectric and show normal dielectric behaviour. Spontaneous polarization in ferroelectrics is experimentally observed as a normal hysteresis loop shown in Fig. (1.1),wherein domain structure plays an important role. Domains are regions of homogeneous polarization that differ only in the direction of the polarization. Using the language of the mineralogist the domain formation may be called as "Twinning".

The reversible polarization, the anomalous dielectric properties and the non-linearities are the prominent features of the ferroelectrics. The ferroelectric materials cease to be ferroelectric above the transition temperature T_c. The anomalous behavior near transition temperature is probably as significant as the reversible polarization, but it is not definitive of a ferroelectric. The permittivity rises sharply to a very high peak value at the temperature T_c and the very high values of dielectric constant in this neighbourhood are referred to as anomalous.

In some ferroelectrics, the temperature dependence of the dielectric constant above the transition temperature can be described fairly accurately by Curie-Weiss law
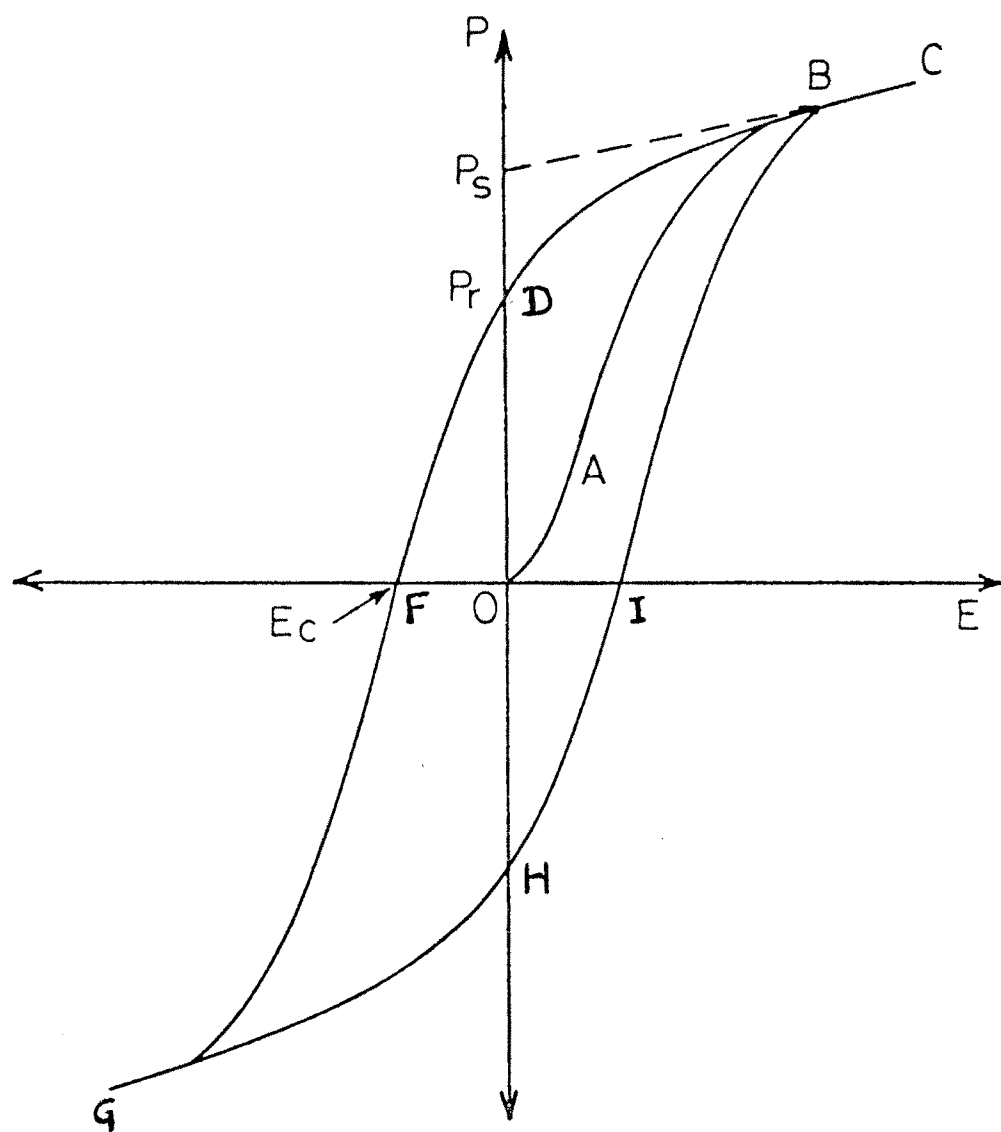
Fig.1·1   Schematic representation of
ferroelectric hysteresis loop

i.e.

$$\varepsilon = \varepsilon_o + \frac{C}{T-T_c} \qquad \qquad \dots \qquad (1.1)$$

where C = Curie constant

T_c = Curie-Weiss temperature

ε_o = The part of dielectric constant independent of temperature.

In the vicinity of Curie-Weiss temperature the dielectric constant becomes very large. The crystal undergoes a transition from the polar to the non-polar state at the transition temperature.

In addition, most of the ferroelectric crystals show the following properties also :

1)   They possess a pseudo-symmetric structure. In the ferroelectric phase the structure belongs to the polar class.

2)   The Curie temperature is raised by application of a biasing field or a hydrostatic pressure.

3)   They show piezoelectric and pyroelectric properties below T_c.

4)   The ferroelectric transition at the Curie temperature is associated with either the latent heat phenomenon or specific heat anomaly.

1.3 Ferroelectric Polarizability :

1.3(a) Dielectric properties :

When a flat slab of any solid dielectric is placed in a uniform field E_o with its normal parallel to the

field, the dielectric displacement D in CGS system of units is given by

$$D = \varepsilon_o E_o = \varepsilon E = E + 4\pi P \qquad \ldots \qquad (1.2)$$

Where E_o and E are field strengths outside and in the dielectric, ε_o and ε are dielectric constants of the surrounding medium and of the dielectric respectively and P is the polarization. Usually surrounding medium is air or vacuum. Therefore, ε_o is taken to be unity. Ignoring spontaneous polarization, the relation between field strength E and polarization P can be written as

$$P = \eta E \qquad \ldots \qquad (1.3)$$

where η is dielectric susceptibility.

In an isotropic cubic system P is always parallel to E, and therefore, all quantities in the above equations are written as scalars. From equation (1.2) the dielectric constant of an isotropic medium is defined as

$$\varepsilon = \frac{D}{E} = \frac{E + 4\pi P}{E}$$

$$= 1 + 4\pi\eta \qquad \ldots \qquad (1.4)$$

or

$$\eta = \frac{\varepsilon - 1}{4\pi} \qquad \ldots \qquad (1.5)$$

Equation (1.5) gives relation between η and ε .

In non-cubic crystal the dielectric response is described by the components of the susceptibility tensor or of the dielectric constant tensor,

$$P_i = \eta_{jk}E_k \qquad \qquad \cdots (1.6)$$

$$\varepsilon_{jk} = 1 + 4\pi\eta_{jk} \qquad \qquad \cdots (1.7)$$

1.3(b) Polarizability :

The dielectric behavior of ferroelectric crystals depends on polarizability and internal field. The actual field in a dielectric varies greatly from point to point, over a distance comparable with molecular dimensions. The internal field F, also called as local field or molecular field is defined as the field at the centre of a small spherical cavity taking into consideration the applied field, depolarization field, Lorentz cavity field and field due to dipoles inside the cavity.

According to Lorentz equation,

$$F = E + \gamma P = E(1 + \gamma\eta) \qquad \qquad \cdots (1.8)$$

Where E is the statistical field in the dielectric, P is the polarization and γ is the internal field constant. In an isotropic medium $\gamma = 4\pi/3$. The internal field constant γ differs from $4\pi/3$ in the crystal of lower symmetry. It is usually considered as independent of temperature.

In the field F, each molecule becomes polarized and acquires the dipole moment p. The polarizability of an atom is defined by

$$p = \alpha F \qquad \qquad \cdots (1.9)$$

where α is the polarizability, which is an atomic property.

The polarization in the crystal may be expressed as (Kittle, 1971)

$$P = \sum_j N_j p_j = \sum_j N_j \alpha_j F_j \qquad \ldots (1.10)$$

Where N_j is the concentration, α the polarizability of atoms j and F_j the local field at atomic site j.

Taking local field as

$$F = E + \frac{4\pi}{3} P \qquad \ldots (1.11)$$

We get

$$P = N_j \alpha_j (E + \frac{4\pi}{3} P) \qquad \ldots (1.12)$$

Hence the dielectric susceptibility is given by

$$\eta = \frac{P}{E} = \frac{\sum N_j \alpha_j}{1 - 4\pi/3(\sum N_j \alpha_j)} \qquad \ldots (1.13)$$

Since, $\varepsilon = 1 + 4\pi\eta$

in CGS system we get,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \sum N_j \alpha_j \qquad \ldots (1.14)$$

This is the well known Clausius-Mossotti relation.

Types of polarizability : Dielectric polarizability may be classified under three basic types. i) Electronic polarizability (α_e) : It represents the displacement of electron orbits about the nuclei in an electric field. This polarization arises in the atoms of any substance. Electronic polarization sets in within a very short time on

applying an electric field; the set up time is about 10^{-14} to 10^{-15} s, which is comparable to the light oscillation period. This is why electronic polarization shows up in a very wide frequency range, upto the optical region.

ii) Ionic polarizability (α_a) : It arises from the displacement of ions of unlike charges relative to one another in substances displaying ionic bonding. The ionic polarization takes a short time to set in, about 10^{-13} to 10^{-14}s. Ionic polarizability is higher in substances where the ionic bond strength is weak and ions carry large charges.

iii) Dipolar polarizability (α_d) : It arises due to orentation of molecular dipoles in the field direction. The dipolar polarization takes to set in, a short time of about 10^{-6} to 10^{-10} s.

The electronic and ionic polarizabilities are independent of temperature and hence the portion of the dielectric constant dependent on them is essentially independent of temperature. The dipolar polarizability is a function of temperature. According to Debye's theory (1954) the dipolar polarizability per molecule in a weak field is given by

$$\alpha_d = p^2/3\ kT \qquad \qquad \dots (1.15)$$

where p is dipole moment of a polar molecule, k Boltzman constant and T absolute temperature.

The contributions to the total polarizability are shown in Fig. (1.2). The dielectric constant at optical frequencies is entirely due to the electronic polarizability. The ionic and dipolar contributions are small at high frequencies because of the inertia of the molecules and ions. Polarizability is the function of frequency of the applied field. At low frequency of the applied field all types of polarization are equal to the value in the steady field.

1.3(c) Polarization Relaxation :

The phenomena occuring in materials containing permanent dipoles are quite distinct from those occuring in materials containing no permanent dipoles. The principal effect in the polar solids is termed as dipole relaxation or polarization relaxation. In this case, E and P are not in phase.

When a periodic field E of arbitrary frequency ω is applied to the dielectric, the dipoles take some time in attaining equilibrium polarization. This time delay is expressed in terms of relaxation time τ . If $\omega \geqslant 1/\tau$ the dipoles can not orient themselves with the field direction and the polarization dies off. The dipole moment rises towards its equilibrium value exponentially, governed by the following equation

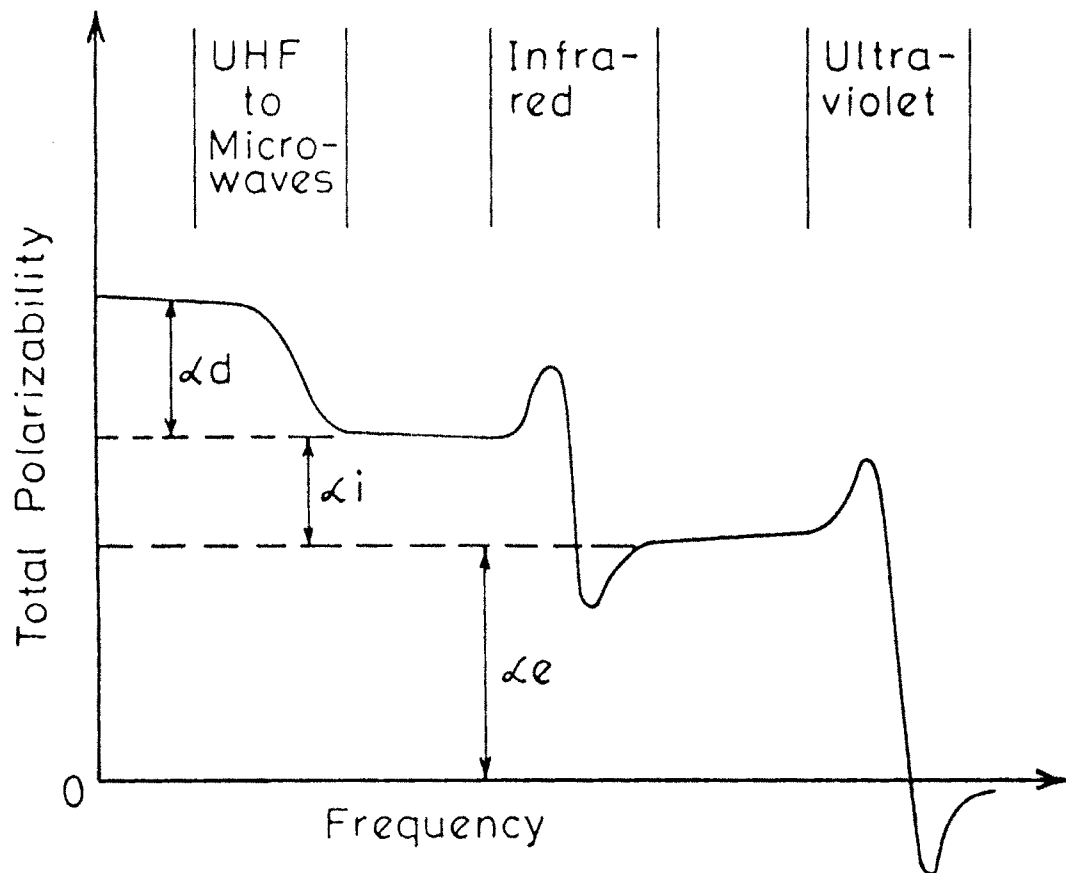$$P = P_s (1 - e^{-t/\tau}) \qquad \qquad \ldots (1.16)$$

Fig. 1·2 Schematic representation of frequency
dependence of the several contributions
to the total polarizability

Consequently, the dielectric constant may have an in-phase component and an out-of-phase component. It may then be represented by a complex number. Let

$$D = \varepsilon^* E \qquad \qquad \dots (1.17)$$

where ε^* may be complex; i.e.,

$$\varepsilon^* = \varepsilon_{real} - i\varepsilon_{jmag} \qquad \qquad \dots (1.18)$$

The real and imaginary parts of a complex dielectric constant will be given by

$$\varepsilon_{real} = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2} \qquad \qquad \dots (1.19)$$

$$\varepsilon_{imag} = \frac{(\varepsilon_s - \varepsilon_\infty)\,\omega\tau}{1 + \omega^2\,\tau^2} \qquad \qquad \dots (1.20)$$

These are known as Debye's equations. The factor ε_s is the static dielectric constant and ε_∞ corresponds to the high frequency dielectric constant. At very low frequencies, i.e., those frequencies for which $\omega \ll 1/\tau$, ε_{real} is closely the same as ε_s. At high frequencies ($\omega \gg 1/\tau$), ε_{real} has the value ε_∞ , as expected. The existence of an out-of-phase term in D leads to energy dissipation in the dielectric. The dielectric loss is maximum at $\omega\tau = 1$.

1.4 Classification of Ferroelectrics :

As investigations in recent years have shown that ferroelectricity is a more common phenomenon than had been considered for a long time and a large number of materials exhibit this phenomenon, it has become very

TABLE 1.2 : Classification of Ferroelectrics

Sr. No.	Basic feature by classification	Groups	Groups typified by	Remakrs
1	Chemical bond	i) Hydrogen bond ii) Ionic bond	KH_2PO_4 $BaTiO_3$	Obvious
2	Polarization direction	i) Undirectional ii) Multidirectional	Rochelle salt $BaTiO_3$	Useful for study of domains
3	Crystallographic cum piezoelectric	i) Non-centrosymmetric in unpolarized phase ii) Centrosymmetric in unpolarized phase	Piezoelectric e.g. Rochelle salt Non-piezoelectric e.g. $PbNb_2O_7$	Goes beyond ferroelectricity
4	Phase transition	i) Order-disorder ii) Displacive	TGS $BaTiO_3$, GeTe	Illucidates origin of spontaneous polarization
5	Nature of displacement vector and motion during its reversal	i) One dimentional ii) Two dimentional iii) Three dimentional	$PbTiO_3$ HCl, HBr $(NH_4)_2SO_4$	Characterises reversal

difficult to classify these materials. However, classification of ferroelectrics has been proposed according to different criteria as shown in table 1.2.

The different classifications shown in table 1.2 are not at all independent and therefore neither do we come across new traits or aspects of ferroelectrics nor do we add new types by discussing various classifications. However, the classification types enrich our understanding of the distinction between the two major types of ferroelectrics.

1.5 Spontaneous Polarization :

In ferroelectric crystals every unit cell might be visualised to carry a dipole moment and this dipole moment cannot be attributed to the specific pair of atoms in the unit cell without making arbitrary assumptions about the interatomic forces.

Electric moment is therefore,

$$\iiint \rho(r).r.dV \neq 0$$

where $\rho(r)$ is the combined nuclear and electric charge distribution with respect to any origin.

Such crystals posses spontaneous electric polarization P_s in the absence of external field, which can be reversed by electric field. The value of P_s can be obtained from the dielectric hysteresis loop (Fig.1.1) by extrapo-

lating the saturation region to zero field axis P_s. Spontaneous polarization depends on temperature and other factors such as stress etc. Spontaneous polarization refers to single domain (Polarization of each domain under no external influence) and not the overall polarization of the crystal.

The experimental method for observation of the hysteresis loop on the screen of a CRO is based on the Sawyer and Tower circuit (1930). The hysteresis loop is schematically shown in fig. 1.1. The intercept on the polarization axis is remanent polarization Pr and the intercept OD on the E-axis gives the coercive field.

Other methods which are commonly used for measuring the magnitude of Ps are polarity reversal technique (Camlible, 1969), charge integration technique (Glass, 1969) and pyroelectric measurement using calibration for scaling (Glass, 1969).

1.6 Ferroelectric Domains :

A ferroelectric crystal in equilibrium consists of domains which are regions of homogeneous polarization that differ only in direction of the polarization. All the spontaneously polarized unit cells within a domain in a ferroelectric crystal are oriented identically due to alignment. Consequently, each domain has a macroscopic spontaneous polarization. The directions of spontaneous

polarization of neighbouring domains make definite angles with one another. A boundary separating two neighbouring domains is called as domain wall. A domain wall is usually found to be so thin that it has a much smaller volume than the bulk material in the domains. A domain wall is electrically neutral and corresponds to minimum of the free energy. Consequently, the dipoles in the neighbouring domains are oriented in such a way that at a wall the projection of the polarization vector of one domain is equal in magnitude and opposite in sign to the projection of polarization vector of the neighbouring domain.

A single crystal may contain a number of domains although by definition it cannot contain more than one crystallite. A single crystal has domain walls but no grain boundaries. In a polycrystalline material there may be several domains in each crystallite.

Below T_c the crystal belongs by its symmetry to one of the pyroelectric classes and the domains differ in the directioins of P_s. Therefore, when ferro-electric crystal is cooled below the Curie temperature, in the absence of external electrical and mechanical stress it breaks up into domains of different orientations. It means that from the crystallographic point of view, the domain structure is anologous with the twinning structure. Twin operations of ferroelectric

domains have been discussed by Zhelhdev and Shuvalov (1956,57). Domains have been observed by using etching method, charged powder method, polarized light micro-scopy and electro-optical method in case of KH_2PO_4 (Zwicker and Scherrer, 1944), $BaTiO_3$ (Kay, 1948) and Rochelle salt (Marutake, 1952).

1.7 Theoretical Review :

Many physicists tried to explain the phenomenon of ferroelectricity in crystals and proposed a number of theories. None of the early attempts is satisfactory. The most promising and challenging theory due to Cochran (1960,1961) is based on the lattice dynamics. A description of the thermodynamic and lattice dynamic theory of ferroelectricity and brief review of model theories are given below.

1.7(a) Thermodynamic Theory :

One would like to investigate the behavior of a ferroelectric in the vicinity of its transition tempe-rature T_c on the basis of thermodynamic arguments. Although such a theory does not provide the physical mechanism responsible for the ferroelectric properties of a given material, it does point to certain features one should look for in atomic models. The thermodynamic theory of ferroelectricity was developed by Devonshire (1948, 1949), based on the following assumptions.

1) The free energy of the ferroelectric crystal is regarded as a function of temperature, stress and polarization.

2) The polarized phase is regarded as a slightly distorted unpolarized phase and they are described by the same free energy function.

The free energy F of the polarized crystal may then be expanded as a power series in the polarization. It is assumed that the crystal is ferroelectric below the transition temperature T_O and P_S occurs along only one axis. If F_O be the free energy of the unpolarized crystal then

$$F = F_O + \frac{1}{2} C_1 P^2 + \frac{1}{4} C_2 P^4 + \frac{1}{6} C_3 P^6 + \ldots \quad (1.21)$$

The coefficients C's are temperature dependent. Again the requirement of the same free energy for positive and negative polarization along the polar axis is met by including only even powers of P. In thermal equilibrium ($\partial F/\partial P)_T = 0$, so that the spontaneous polarization satisfies the equation

$$0 = C_1 P_S + C_2 P_S^3 + C_3 P_S^5 + \ldots \quad \ldots (1.22)$$

$P_S = 0$ is always a root of this equation and that will correspond to a minimum of the free energy if C_1 is positive. If C_1, C_2 and C_3 are all positive, the root $P_S = 0$ will correspond to the only minimum of the free energy and thus spontaneous polarization would not

occur. However, should C_1 become negative, F would have a maximum for $P_s = 0$ and there would be at least one nonvanishing value for P_s for which F would be a minimum i.e. spontaneous polarization would occur. Consequently, if C_1 changes continuously with temperature from a positive to a negative value, the equilibrium of the crystal changes from an unpolarized to a spontaneously polarized state. There are two cases of particular interest viz. second order transition and first order transition.

1.7(b) Second-order transition :

If the coefficients C_2, C_3 .... are all positive and the value of C_1 varies from positive to negative as the temperature is lowered, one obtains free energy curve illustrated in Fig.1.3(a). The corresponding spontaneous polarization as function of temperature is indicated in Fig. 1.3(b). The transition temperature corresponds to $C_1 = 0$. Assuming that the term with C_3 in (1.22) is negligible, one obtains for the spontaneous polarization

$$P_s^2 = - C_1 / C_2 \qquad \qquad ... (1.23)$$

It is to be noted that P_s is a continuous function of temperature and isothermal changes at the transition temperature are absent. A transition of this type is not associated with a latent heat but with a discontinuity in the specific heat and is called a second-order transition.
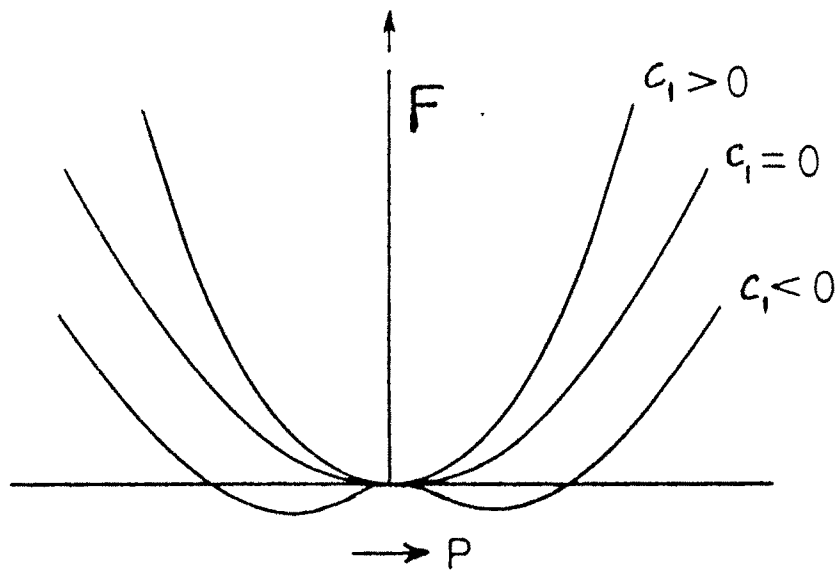
Fig.1·3(a) Schematic representation of the free energy
as function of polarization for various values
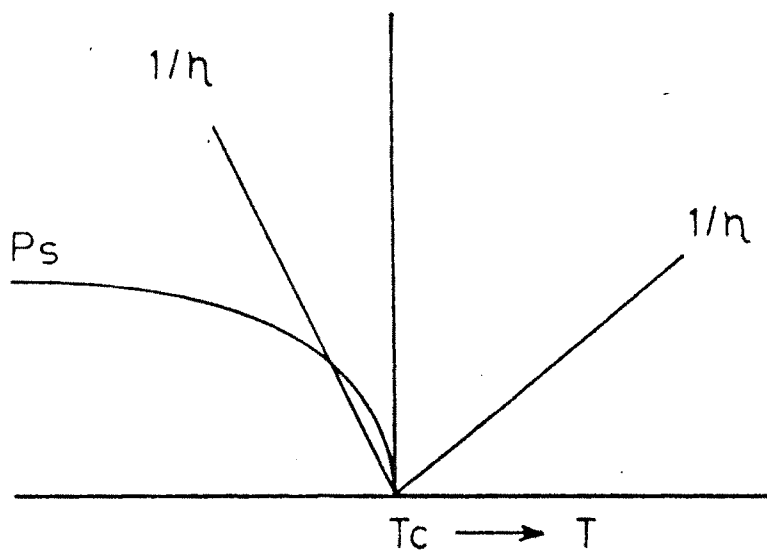of c_i for a second-order transition

Fig.1·3(b) Schematic representation of the spontaneous
polarization and reciprocal susceptibility near
the transition temperature Tc for a second-order
transition

For small applied field and under zero pressure, we may write

$$dF = - SdT + EdP \qquad \ldots(1.24)$$

Hence

$$E = - (\partial F/\partial P)_T \qquad \ldots (1.25)$$

For $T > T_c$, and for small applied fields we can get

$$\frac{1}{\eta} = \frac{dE}{dP} = C_1 \qquad \ldots (1.26)$$

where η is the susceptibility above the critical tempe-rature. However, in this temperature range suscepti-bility is given by Curie-Weiss law i.e.

$$\eta = \frac{C}{T-T_o} \qquad \ldots (1.27)$$

But, $T_o = T_c$ for second order transition. Hence

$$\frac{1}{\eta} = \frac{T-T_c}{C} \qquad \ldots (1.28)$$

In the ferroelectric region we obtain likewise from (1.21) and (1.26)

$$\frac{1}{\eta} = \frac{dE}{dP} = C_1 + 3 C_2 P^2 \qquad \ldots (1.29)$$

For small applied field, $P \simeq P_s$ in this region so that the susceptibility in this region is given by

$$\frac{1}{\eta} = \frac{2(T_c-T)}{C} \qquad \ldots (1.30)$$

The temperature dependance of the reciprocal of the susceptibility on both sides of the transition tempe-rature as given by (1.28) and (1.30) is illustrated in Fig. 1.3(b).

Let us consider the entropy associated with the spontaneous polarization. According to (1.24) and (1.21) the entropy is given by

$$S = - (\partial F / \partial T)_p$$

$$= S_o - \frac{1}{2} P^2 \left(\frac{\partial C_1}{\partial T}\right) - \frac{1}{4} P^2 \left(\frac{\partial C_2}{\partial T}\right) + \ldots$$

Where S_o is the entropy of the nonpolarized crystal. To a first approximation we may then write

$$S - S_o \simeq - \frac{1}{2} P^2 \left(\frac{\partial C_1}{\partial T}\right) \qquad \ldots (1.31)$$

Since P is a continuous function of temperature for case under consideration and since the the slope of P^2 has a discontinuity at $T = T_c$, there should be a discontinuity in the specific heat, but **exhibiting no latent heat i.e. the transition is of** second order.

1.7(c) First-Order Transition :

It has been found that spontaneous polarization requires the coefficient C_1 to be negative. If C_2 is negative, a first order transition results. Let C_2 be negative and C_3 positive. Assuming that C_1 varies from positive to negative value as temperature is lowered, one obtains free energy curves of the type illustrated in Fig. 1.4(a). A transition from the unpolarized state to a spontaneously polarized state will now occur when the minimum of free energy corresponding to $P_s = 0$ becomes equal to the minimum associated with a nonzero
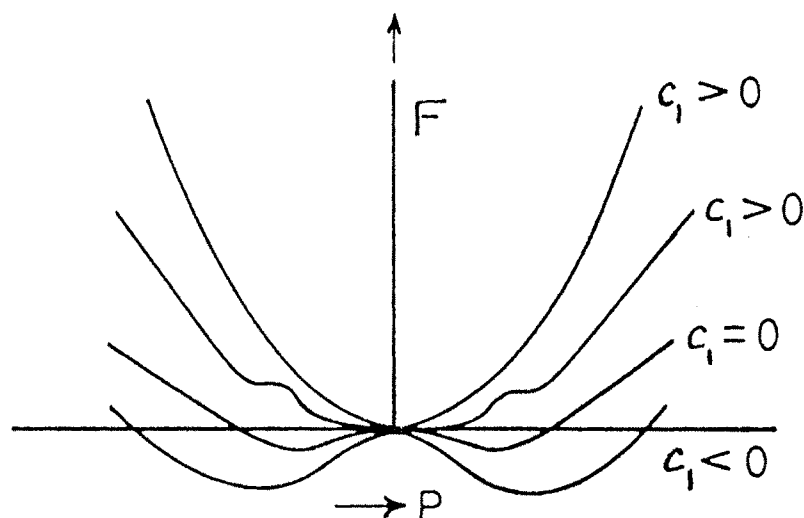
Fig.1·4 (a)   Schematic representation of the free energy
as function of polarization for various values
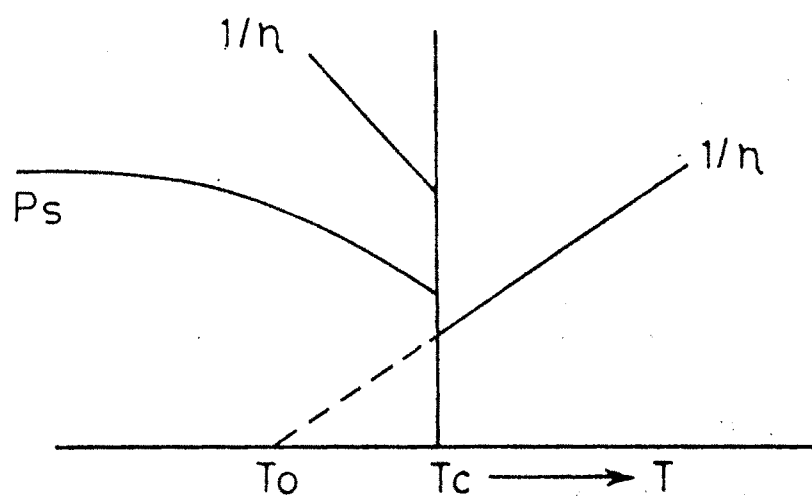of c_i for a first-order transition

Fig.1·4(b)   Schematic representation of the spontaneous
polarization and reciprocal susceptibility near
the transition temperature Tc for a first-order
transition

value for P_s. In this case the polarization jumps, at
the critical temperature, from zero to some nonzero
value, i.e. the polarization as a function of tempera-
ture exhibits a discontinuity at $T = T_c$ as shown in
Fig.1.4(b). According to (1.31) the entropy will also
be discontinuous at $T = T_c$ and there will be a latent
heat, i.e. the transition is of the first order.

In the absence of an external field we obtain
from the equilibrium condition $(\partial F/\partial P)_T = 0$ and from
(1.21) for the nonvanishing value of the spontaneous
polarization, the euqation

$$0 = C_1 + C_2 P_s^2 + C_3 P_s^4 + \ldots \qquad \ldots (1.32)$$

At the critical temperature T_c the quantity $P_s(T_c)$
should satisfy (1.32) as well as the condition mentioned
above, i.e. $F(T_c) = F_o(T)$. According to (1.21) we have

$$0 = \frac{1}{2}C_1 P_s^2(T_c) + \frac{1}{4}C_2 P_s^4(T_c) + \frac{1}{6}C_3 P_s^6(T_c) + \ldots \qquad \ldots (1.33)$$

From this equation and (1.32) as applied to the criti-
cal temperature, one finds the relations

$$P_s^2(T_c) = -\frac{3}{4}(C_2/C_3) \qquad \ldots (1.34a)$$

$$C_1 = \frac{3}{16}(C_2^2/C_3) \qquad \ldots (1.34b)$$

$$P_s^4(T_c) = 3 C_1/C_3 \qquad \ldots (1.34c)$$

Thus it has been found that the polarization is discon-
tinuous at the critical temperature (Fig. 1.4b).

In the region above T_c, susceptibility follows the Curie-Weiss law, so that

$$\eta = \frac{C}{T-T_o} \qquad \dots (1.35)$$

Where T_o is smaller than T_c. Susceptibility below the critical temperature is given by

$$\frac{1}{\eta} = \frac{4(T-T_o)}{C} \qquad \dots (1.36)$$

The reciprocal susceptibility as one passes through the transition temperature is illustrated in Fig.1.4(b).

1.7(d) Model Theories of Ferroelectricity :

Masson and Matthias (1948) suggested a model theory for $BaTiO_3$. According to this, Ti^{4+} ion is not at the centre of the oxygen octahedron. Instead, it is at any of the six positions, which corresponds to slight displacement from the centre towards the oxygen ions. When Ti^{4+} ion is at any of these positions, the unit cell would have a dipole moment. The disadvantage of this theory is that it is not possible to obtain a good agreement with the experimental results.

Jaynes (1950) proposed a model theory in which oxygen ions are displaced rather than Ti^{4+} ions and the dipole moments are not attributed to atomic displacements. Only the electronic states of TiO_6 octahedra are considered to give rise to spontaneous polarization. This is satisfactory for determining the entropy changes,

but it predicts infra-red absorption line at 10 μ which is not detected.

Devonshire's model theory (1949) considered the atomic dipole vibrating in the field of its neighbours. The dipole moment is not fixed in magnitude, but depends on the displacement from the equilibrium position.

Slater (1950) proposed a similar model theory. He introduced that each atom has electronic polarization and spontaneous polarization is directed only along the Z-axis, but this has disadvantage when it is applied to some other structures.

Megaw (1952,1954) has suggested that directional covalent bonding is of primary importance in ferroelectricity of $PbTiO_3$ and antiferroelectricity of $PbZrO_3$. Megaw pointed out that Zr ion may have directional covalency which would certainly influence the behavior of Pb. The disadvantage of this theory is that the origin of ferroelectricity is attributed to abrupt changes at each transition in the character of bonds which is rather difficult to estimate and the explanation tends to be intuitive.

1.7(e) Cochran's Theory :

Cochran's (1960,1961) lattice dynamical model provides a microscopic theory of ferroelectricity for certain crystals. The theory is based on the assumption

that the ferroelectric transition is the result of the instability of the crystal lattice with respect to one of the homogeneous (wave vector q=0) transverse optical mode (w_T). Essentially the theory is based on the assumption that if a crystal is wholly or partly ionic, lattice vibrations are accompanied by polarization oscillations of equal frequency which create a local field interacting with the ions through the long range coulomb forces. If, for one particular mode of vibration these long range forces, have the magnitude equal but opposite in sign as the short range forces, the crystal becomes unstable for this mode. The dielectric constant which is connected to the frequency of the critical mode becomes extremely large as it happens at the Curie temperature.

The connection between the ferroelectric properties of crystal and the thermodynamical properties is obtained through Lyddane-Sachs-Teller (LST) relation, i.e.

$$\prod \frac{w_L^2}{w_T^2} = \frac{\varepsilon_s}{\varepsilon_o} \qquad \qquad \ldots (1.37)$$

For the wave vector q=0 mode of a crystal i.e. $w_T^2 = 0$, we have static dielectric constant $\varepsilon_s = \infty$, because ε_o is equal to the square of refractive index.

In a ferroelectric crystal ε_s follows Curie-Weiss law above T_c,

$$\epsilon_s = \epsilon + \frac{4\pi C}{T-T_c} \qquad , \quad T > T_C \qquad \cdots \quad (1.38)$$

Where ϵ is part of dielectric constant independent of temperature. This equation (1.38) through (1.37) implies that the transverse optical modes of infinite wavelength have an anomalous temperature dependence given by

$$W_T^2 = G(T-T_c), \qquad T > T_C \qquad \cdots \quad (1.39)$$

Where G depends on the short range force constant.

The softening of the transverse optical mode W_T, by polarization (1.39) and the rapid rise of static dielectric constant (1.38) offers an explanation for the onset of ferroelectricity. The temperature dependence of W_T follows the Curie-Weiss law (1.38) and is related to $\epsilon(T)$ through LST relation (1.37). Moreover, the IR and Raman studies have shown the role of ferrodistortive soft modes during the transition. ·

1.8 Applications of Ferroelectrics :

Historically the study of ferroelectricity has been closely linked with device applications. The discovery of the first ferroelectric viz. Rochelle salt, seen to be unusual in piezoelectric effect, itself resulted in wide usage of Rochelle salt in phonograph pick-ups and microphones. Although it is now obsolete as the transducer material, other ferroelectrics - perticularly ceramics in which the electrical and mechanical

impedances can be effectively matched for efficient power conversion, serve several useful functions in this field.

Linear Properties : Ferroelectrics are used as transducers because of high coupling constant. The purpose of a transducer is in some cases to convert a.c. fields or sudden changes of field into corresponding mechanical motions as in ultrasonic generators, loud-speakers or pulse generators for use with sonic delay lines. In other cases a transducer uses the piezoelectric effects to convert small motions into electric changes as in ultrasonic detectors, strain-gauges, microphones and devices to measure the extent of vibrations.

Non-linear properties : These properties of ferroelectrics are mostly marked at low frequencies and near the transition temperature. Ferroelectric condensers have been used for tuning in superhets. They are used as dielectric amplifiers for remote controls, servo-systems stabilization of supplies, varactor diodes, auto-frequency amplification and for d.c. amplifiers.

Some polar materials, particularly ferroelectrics show increase in resistivity with increasing temperature. This property is utilised for fabricating PTC switching thermistors. PTC thermistors are used mostly in control applications such as in TV set, in single phase electric motors, as overcharge protection devices in batteries,

the automatic control for the electric choices of auto-
mobiles, control elements for slowly turning off lights
and time delay fuses.

Some of the devices mentioned above such as capa-
citors and piezoelectric transducers are of commercial
importance and may prove to be significant in future.

1.9 Orientation of the Present Work :

Ferroelectricity is one of the interdisciplinary
fields of research which has spin-offs in physical
sciences, engineering and technology. Although an exten-
sive study of ferroelectrics in theory and experiment
has been carried out during the last few decades owing
to their important device applications, they still
continue to arouse interest among the research workers
especially because of the promise in diverse new areas
of technology (SHG, TANDEL, Dielectric amplifier etc.)
and their understanding is yet not satisfactory. The
scope of ferroelectrics is even further broadened in
view of the applications such as laser communications,
memory and display applications such as video discs
(laser beam operated) etc.

In the work of various workers in twentieth century
before Devonshire the term "Ferroelectricity" was coined
by Muller and the seeds of molecular interaction theories
and the role of crystal structure were already developed.

The discovery of $BaTiO_3$ and its ferroelectric properties, however, created a new wave of interest in the field of ferroelectricity and by 1969 Mitsui et al could already give a compilation of a very large number of ferroelectric compounds. Notwithstanding the availability of a most successful lattice dynamic theory of Cochran, the understanding of the phenomenon and the ferroelectric materials remained incomplete. Therefore, further data acquisition on T_c, P_s and studies of soft mode, its role and other physical properties were carried out in the recent past [e.g. Glasso 1969, Subbarao 1972, Mitsui 1975] and data on structure, T_c and P_s has been obtained. Having convinced ourselves of the significant applicability of ferroelectrics as mentioned in the first paragraph, the brief review presented herein adds to the significance of ferroelectrics also from the cognitive point of view.

In the oxide family of ferrolectrics besides perovskites new oxide structures have been shown to be ferroelectrics. Among these, alkali metal vanadates assume importance in view of the fact that they are chain structures. It will be worthwhile to study how these structural differences of alkali metal vanadates affect various ferroelectric properties.

Ferroelectric properties in sodium vanadate were first reported by Sawada and Nomura (1975). Its crystal

structure and phase transition were reported respectively by Ramani et al (1975) and Shaikh et al (1978). Despite considerable effort that has gone into ferroelectrics in the form of single crystals and solid solutions, very little attention has been paid to study the effect of impurities on the ferroelectric properties of vanadates. If the ferroelectric crystals and the materials contain impurities or imperfections, the properties are expected to change. Therefore, in addition to the structural factor involving chains, the impurity content could provide for tailor-making of materials with desired properties.

Keeping in view the above requirements we have undertaken to investigate the ferrolectric properties of $NaVO_3$ doped with Fe_2O_3 by ceramic method of preparation. Our aim of the present problem is to study the following properties of $NaVO_3$ doped with Fe_2O_3 after characterizing it.

1) Dielectric hysteresis and determination of coercive field.

2) Measurement of dielectric constant.

3) D.C. electrical conductivity.

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