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CHAPTER - I

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**FERROELECTRICS**

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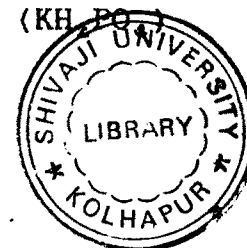
### FERROELECTRICS

#### 1.1 Introduction :

The ferroelectricity is one of the most interdisciplinary, and hence challenging of subjects. Ferroelectrics belong to pyroelectrics with additional property of reversibility of polarization by an external electric field. The scope of ferroelectricity is even further broadened because of the significance of related phenomena such as electro-optics, magneto-electricity, nonlinear dielectrics, ferroelasticity, liquid crystals, piezoelectricity and pyroelectricity.

Rochelle Salt was the first crystal known to be ferroelectric of chemical composition ( $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ) sodium potassium tartrate tetrahydrate. Rochelle Salt was prepared in seventeenth century by Seignette in La Rochelle (France). Pockel (1894) reported anomalously large piezoelectric constants of Rochelle Salt. Valasek (1920) discovered ferroelectricity in Rochelle Salt. Muller (1940) proposed a phenomenological theory, which first brought us systematic understanding of the relations between anomalous dielectric, piezoelectric and elastic behaviour of this crystal.

The second ferroelectric crystal discovered, by Bush and Scherrer (1935), was potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ )



and other compounds isomorphous with  $\text{KH}_2\text{PO}_4$  also were found to be ferroelectric. Slater (1941) published a theory of the phase transition of  $\text{KH}_2\text{PO}_4$ .

Wainer and Solomon (1943) in united states, Ogawa (1943) in Japan, and Wul and Goldman (1945) in Russia discovered independently the anomalous dielectric properties of  $\text{BaTiO}_3$ . The ferroelectric properties of  $\text{BaTiO}_3$  were reported by Wul and Goldman (1945 a,b) and Von Hippel et al (1946). After the discovery of ferroelectricity in  $\text{BaTiO}_3$ , compounds with the perovskite structure were studied extensively.

Jona and Shirane (1962) gave a useful table of seventy six ferroelectric crystals. Number of ferroelectrics and anti-ferroelectrics including solid solutions was given by Mitsui et al (1969). Recently, Subbarao (1972) provided comprehensive compilation of ferroelectric and antiferroelectric materials known upto (1971). This provides an excellent source of data on the spontaneous polarization and Curie temperature of ferroelectric and antiferroelectric materials.

Major sources of bibliographic information on polar materials are provided by Mitsui (1969), Lang (1973,1974), Toyoda (1970) Corolly et al (1970, 1974). Recently, Mitsui et al (1975) have been indentified almost seven hundred ferroelectric pure compounds and solid solutions.

## 1.2 Characteristic Properties of Ferroelectric Materials :

Ferroelectrics are all solids, and all are non-metallic. The properties of a ferroelectric are most simply studied when the material is in a single crystal form. Ferroelectrics are materials which possess spontaneous electric polarization which can be reversed by applying a suitable electric field. The process is known as switching and is accompanied by hysteresis loop as shown in fig. (1.1).

Ferroelectrics should not be confused with ferrites, which are non-metallic ferromagnetic materials.

The temperature dependence of the dielectric constant in some ferroelectrics can be described by the Curie-Weiss law from its ferromagnetic analogy as

$$\epsilon = \epsilon_0 + \frac{C}{T-T_C} \quad (1.1)$$

where  $C$  the Curie constant,  $T_C$  the Curie-Weiss temperature and  $\epsilon_0$  the part of dielectric constant independent of temperature.

With increasing temperature, ferroelectricity usually disappears above a certain temperature called the 'transition temperature'. The crystal undergoes a transition from the polar state to the non polar state at the transition temperature. The phase transition can be of the first order or of the higher (usually second) order.

In first order transition, volume and energy of a

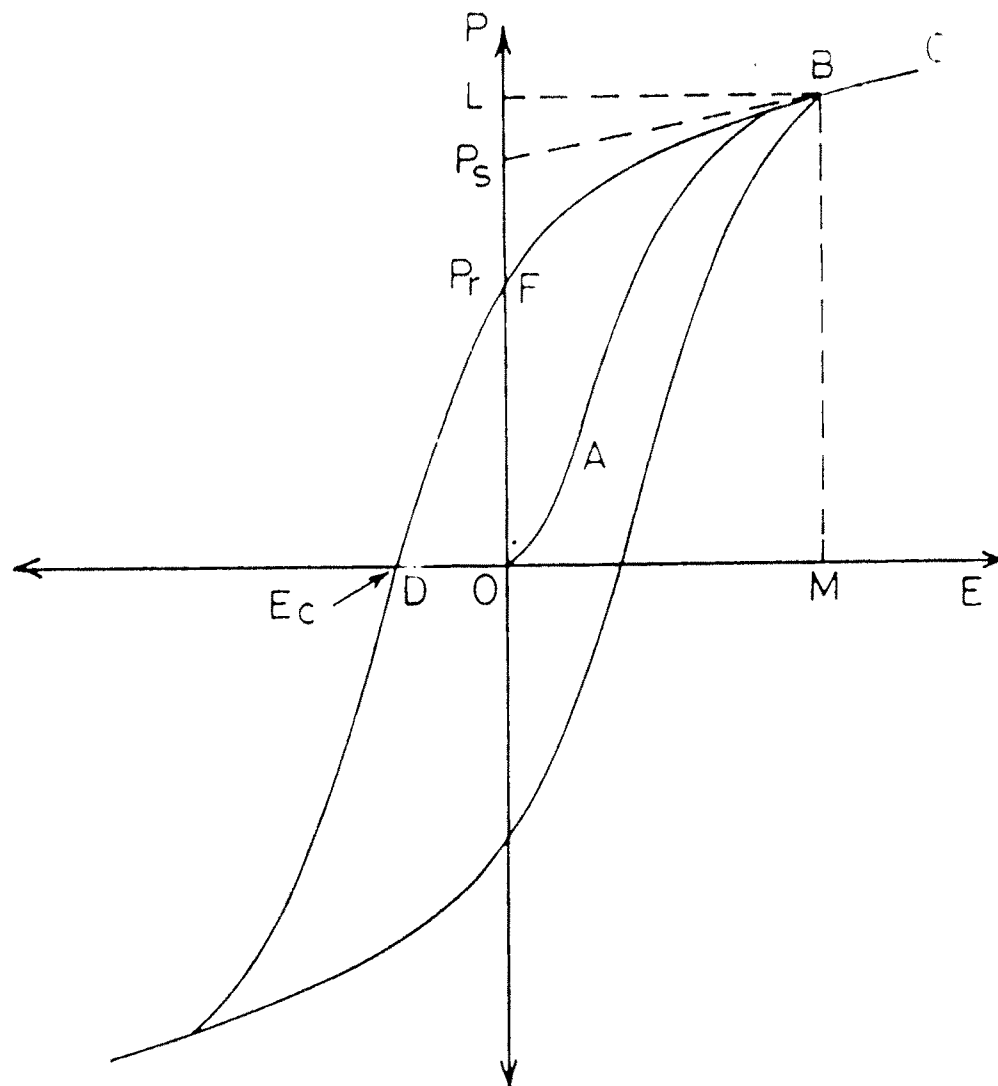


Fig.1.1 Schematic representation of ferroelectric hysteresis loop.

crystal change discontinuously at the transition point, the energy appearing as 'Latent heat' in an infinitely narrow temperature range. In the second order transition, volume and energy change continuously at the transition point. Therefore, in the second order transition there is no release of 'Latent heat' but the expansion coefficient and specific heat show anomalies extending over a finite range of temperature.

Ferroelectric materials possess the following properties:

- i) They exhibit a dielectric hysteresis loop between polarization and applied electric field below a certain critical temperature. This temperature is called ferroelectric transition temperature.
- ii) They have a high dielectric constant along the polar axis which is a function of temperature and rises to a peak value at the Curie temperature.
- iii) They possess a pseudosymmetric structure. In the ferroelectric state the structure belongs to the polar class.
- iv) They have a ferroelectric domain structure which may be visible in polarized light.
- v) They have a transition at the Curie temperature to form structure of higher symmetry.
- vi) The Curie temperature is raised by application of a

biasing field or a hydrostatic pressure.

- vii) There is a sudden appearance of surface charge at the transition.
- viii) They show piezoelectric and pyroelectric properties below the curie temperature.

### 1.3 Dielectric Properties and Polarizability :

When a flat slab of any solid dielectric is placed in a uniform field  $\vec{E}_0$ , with its normal parallel to the field the dielectric displacement  $\vec{D}$  in CGS system of units is given by

$$\vec{D} = \epsilon_0 \vec{E}_0 = \epsilon \vec{E} = E + 4\pi P \quad (1.2)$$

where  $\vec{E}_0$  and  $\vec{E}$  are field strengths outside and in the dielectric,  $\epsilon_0$  and  $\epsilon$  are dielectric constants of surrounding medium and of the dielectric respectively, and  $P$  is the polarization.

Usually, the surrounding medium is air or vacuum. hence  $\epsilon_0$  is taken to be unity and ignoring spontaneous polarization, the relation between  $\vec{P}$  and  $\vec{E}$  can be written as

$$\vec{P} = \eta \vec{E} \quad (1.3)$$

where  $\eta$  is dielectric susceptibility.

In an isotropic cubic system  $\vec{P}$  is parallel to  $\vec{E}$ , hence all quantities in the above equation are written as scalars.

The dielectric constant of an isotropic medium, from equation (1.2), is defined as

$$\epsilon = \frac{D}{E} = \frac{E + 4\pi P}{E} \quad (1.4)$$

But  $\frac{P}{E} = \eta$ , therefore  $\epsilon = 1 + 4\pi\eta$

$$\text{or} \quad \eta = \frac{\epsilon - 1}{4\pi} \quad (1.5)$$

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

$$P_j = \eta_{jk} E_k \quad (1.6)$$

$$\text{and} \quad \epsilon_{jk} = 1 + 4\pi\eta_{jk} \quad (1.7)$$

The dielectric behaviour of ferroelectric crystals depend on polarizability and internal field. The actual field in the dielectric varies from point to point, over distances comparable with molecular dimensions. The internal field  $\vec{F}$  is also called the local or molecular field. It is defined as that field in a very small spherical cavity from which atom or molecule have been removed. Local field can be written as

$$\vec{F} = \vec{E}_0 + \vec{E}_1 + \vec{E}_2 + \vec{E}_3 \quad (1.8)$$

where  $\vec{E}_0$  is external electric field from external charges =  $(E + 4\pi P)$ ,  $\vec{E}$  the macroscopic average field over the volume of



the specimen known as electric field of Maxwell's equation =  $(\vec{E}_0 + \vec{E}_1)$ ,  $E_1$  is depolarization field from polarization charges on the outer surface of the specimen =  $-4\pi P$ ,  $\vec{E}_2$  the Lorentz cavity field from polarization charges on inside of a spherical cavity cut out of the specimen with reference atom as centre =  $\frac{4\pi P}{3}$  and  $\vec{E}_3$  the field of atoms inside the cavity = 0 at atom sites. Therefore,

$$F = (E + 4\pi P) + (-4\pi P) + \left(\frac{4\pi P}{3}\right) + 0$$

Thus for a cubic site,

$$F = E + \frac{4\pi}{3} P \quad (1.9)$$

where the coefficient of  $P$  is known as the Lorentz local field factor.

The polarizability  $\alpha$  of an atom is defined as

$$p = \alpha F \quad (1.10)$$

where  $p$  is the dipole moment of the atom and  $F$  is the local electric field at the atom.

The polarization in the crystal may expressed as (Kittel 1971).

$$P = \sum_j N_j p_j = \sum_j N_j \alpha_j F_{(j)} \quad (1.11)$$

where  $N_j$  is the number of atoms per unit volume of polarizability  $\alpha_j$  and  $F_{(j)}$  the local field at atoms of type  $j$ .

The dielectric susceptibility is given by

$$\eta = \frac{P}{E} = \frac{P}{F - \frac{4\pi}{3} P} = \frac{\sum N_j \alpha_j}{1 - \frac{4\pi}{3} \sum N_j \alpha_j} \quad (1.12)$$

But  $\epsilon = 1 + 4\pi\eta$ , hence in CGS units we get,

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \sum N_j \alpha_j \quad (1.13)$$

This is the Clausius - Mossotti relation.

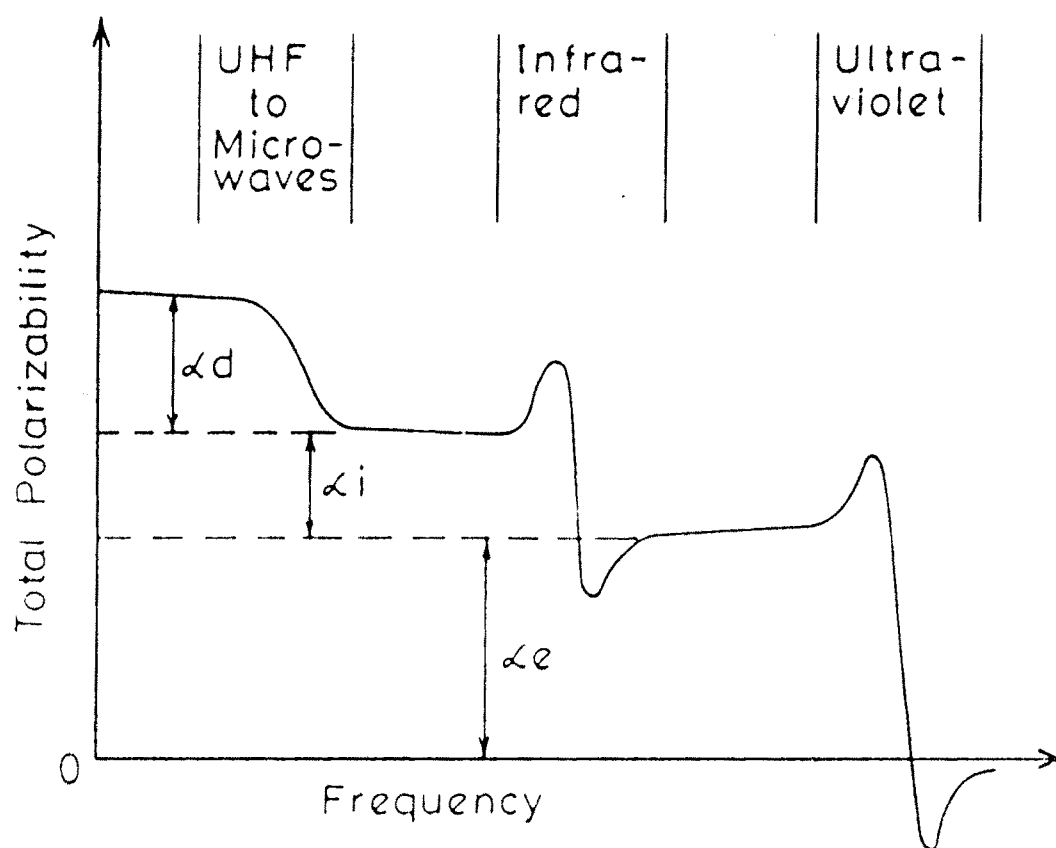
The total polarizability may be divided into three parts :

- i) Electronic polarizability ( $\alpha_e$ ) :- This is due to the displacements of electrons within the atoms or ions.
- ii) Atomic or ionic polarizability ( $\alpha_a$ ) :- This is due to the displacements of atoms or ions within the molecules.
- iii) Dipolar polarizability ( $\alpha_d$ ) :- This arises from molecules with a permanent electric dipole moment that can change orientations in an applied field.

The contributions to the total polarizability are shown in fig. (1.2).

The dielectric constant at optical frequencies arises from the electronic polarizability. The dipolar and ionic contributions are small at high frequencies because of the inertia of the molecules and ions. In optical range equation (1.13) reduces to,

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \sum N_j \alpha_j \quad (\text{electronic}) \quad (1.14)$$



**Fig.1.2** Schematic representation of frequency dependence of the several contributions to the total polarizability.

Here, we have used the relation  $n^2 = \epsilon$ , where  $n$  is the refractive index. By applying equation (1.14) to large number of crystals we determine empirical values of the electronic polarizabilities that are consistent with observed values of the refractive index. The scheme is not entirely selfconsistent because the electronic polarizability of an ion depends somewhat on the environment in which it is placed. The negative ions are highly polarizable because they are large.

#### 1.4 Classification of Ferroelectrics :

The phenomenon of ferroelectricity has been discovered in a large number of crystals or materials. Therefore, it is difficult to classify the ferroelectric materials. However, the ferroelectrics have been classified according to different criteria as follows :

##### i) Crystal chemical classification :

According to this classification the ferroelectric compounds are divided into two groups. The first group includes hydrogenbonded crystals, such as  $\text{KH}_2\text{PO}_4$ , Rochelle Salt, friglycine sulfacte etc. The second group includes the double oxides, such as  $\text{BaTiO}_3$ ,  $\text{KNbO}_3$ ,  $\text{Cd}_2\text{Nb}_2\text{O}_7$ ,  $\text{PbNb}_2\text{O}_6$  etc.

##### ii) Classification according to the number of directions allowed to the spontaneous polarization :

This classification also divides the ferroelectric

crystals into two groups. The first group includes those ferroelectrics that can polarize along only one axis, such as Rochelle Salt;  $\text{KH}_2\text{PO}_4$  type ferroelectrics,  $(\text{NH}_4)_2\text{SO}_4$ , thiourea etc. The second group includes those compounds that can polarize along several axes that are equivalent in nonpolar phases i.e.  $\text{BaTiO}_3$  type,  $\text{Cd}_2\text{Nb}_2\text{O}_7$ ,  $\text{PbNb}_2\text{O}_6$  etc.

Both classes show piezoelectric effect in the polarized phase. In the second group they have transition points below their curie temperature at which the spontaneous polarization changes in magnitude and direction. This classification is particularly useful for the study of ferroelectric domains.

iii) Classification according to the existence of centre of symmetry in the point group of their non-polar phase :

This classification also divides into two groups. The first group includes those ferroelectrics that are piezoelectric in the unpolarized phase such as Rochelle Salt and related tartrates,  $\text{KH}_2\text{PO}_4$  type ferroelectrics. The second group includes those ferroelectrics which are not piezoelectric in unpolarized phase, such as  $\text{BaTiO}_3$ ,  $\text{Cd}_2\text{Nb}_2\text{O}_7$ ,  $\text{PbNb}_2\text{O}_6$ ,  $\text{CaB}_3\text{O}_4(\text{OH})_2\text{H}_2\text{O}$  etc. This classification is useful for the thermodynamic treatment of the ferroelectric transition.

iv) Classification according to the nature of the phase change at the curie point :

According to this classification ferroelectric crystals are divided into two groups. (a) Order-disorder group (b) Displacive group.

The first group includes crystals with hydrogen bonds such as  $\text{KH}_2\text{PO}_4$  and isomorphous salts. In these crystals the motion of the protons is related to their ferroelectric properties such as  $\text{KH}_2\text{PO}_4$ .

The displacive group of ferroelectrics includes ionic crystals whose structures are closely related to the perovskite and ilmenite structures, such as those of  $\text{BaTiO}_3$  and most of the double oxide ferroelectrics.

v) Classification according to the predominant nature of atomic displacements required by polarity reversal :

According to this classification ferroelectric crystals are divided into three classes.

The one dimensional class includes those ferroelectrics in which the atomic displacement vector ( $\vec{\Delta}$ ) and all loci followed by the atoms during reversal are linear and parallel to their polar axis. Examples are,  $\text{BaTiO}_3$ ,  $\text{KNbO}_3$ ,  $\text{LiNbO}_3$  etc.

The two dimensional class includes those ferroelectric crystals in which the atomic displacement vector ( $\vec{\Delta}$ ) or the

actual Locii (L) followed by atoms during reversal lie in parallel phases containing the same polar direction. Examples are, HCl, HBr,  $\text{NaNO}_2$ ,  $\text{BaZnF}_4$  etc.

The three dimensional class includes those ferroelectric crystals in which the individual displacement vector ( $\vec{\Delta}$ ) and the Locii followed by the atoms during reversal have random orientations. Examples are,  $(\text{NH}_4)\text{SO}_4$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{B-GD}_2(\text{NO}_4)_3$  etc.

### 1.5 Theories of Ferroelectricity :

Many attempts were made to explain ferroelectricity in crystals and proposed a number of theories, but non of them is satisfactory. The first theoretical explanation of properties of Rochelle salt was proposed by Kurchatov (1933). Salter (1941) proposed the molecular theory of ferroelectricity based on the actual crystal structure, to explain the ferroelectric transition in  $\text{KH}_2\text{PO}_4$ . A general theory of ferroelectricity has not yet been established, although Cochran's lattice dynamic theory (1960,1961) and Lines statistical theory (1969) have provided for major understanding of ferroelectric phenomena.

We would discuss thermodynamic theory, model theories of ferroelectricity and Cochran's lattice dynamic theory in brief as follows :

#### 1.5 (a) Thermodynamic Theory :

Thermodynamic theory is very general in its scope and

independent of any particular model. The pioneering work in formulating a thermodynamic theory for the case of Rochelle Salt has been done by Muller (1940, a,b,c,d) and Cady (1946). The theory can be applied to  $\text{KH}_2\text{PO}_4$  type ferroelectric.

A thermodynamic theory of  $\text{BaTiO}_3$  type crystals has been developed by Devonshire (1949, 1951, 1954) and Ginzburg (1945, 1949). This theory is based on the following assumptions :

- (1) The free energy of a ferroelectric crystal is regarded as a function of temperature, stress and polarization.
- (2) The polarized phase is regarded as a slightly distorted unpolarized phase, therefore, in the polarized phase the crystal is described by the same free energy function.
- (3) The anomalous piezoelectric and elastic properties are considered to be a result of the anomalous dielectric behaviour. Thus the coefficients of  $P^2$  in the free energy functions bear the significant temperature dependence.
- (4) The second order piezoelectric coefficients are of main importance because the crystal is not piezoelectric in the unpolarized state.
- (5) The free energy functions contain three components of the polarization vector.



Thus free energy of the crystal is expressed by the Gibb's function :

$$G_i = U - T S + X_i x_i + E_m P_m \quad (1.15)$$

where  $U$  is the internal energy of the crystal under external stress,  $T$  is the temperature,  $S$  is the entropy  $X_i$  is the  $i$ th component of mechanical stress,  $P_m$  is  $m$ th component of electrical strain (polarization).

The differential form of this function is

$$d(G_i) = - S dT + X_i dx_i + E_m dP_m \quad (1.16)$$

The index  $i$  can take six values,  $i = 1, 2, 3$  for compression or expansion and  $i = 4, 5, 6$  for shear.

For a crystal free from stress ( $X = 0$ ), the function  $G_i$  can be expanded in powers of polarization with temperature dependent coefficients. Let the crystal be ferroelectric for temperature below the transition temperature  $T_c$ . For simplicity it is assumed that in the ferroelectric region the spontaneous polarization occurs along only one axis. Let  $G_{i,0}$  be the free energy of the unpolarized crystal. Devonshire found that it was necessary to consider terms upto  $P^6$ . Thus an expansion of the free energy for  $X = 0$  is given by the equation,

$$G_i - G_{i,0} = \frac{1}{2} x' P^2 + \frac{1}{4} \beta' P^4 + \frac{1}{6} \gamma' P^6 \quad (1.17)$$

where dashes indicate that the coefficients apply only to stress free condition. It is assumed that  $P$  is total

polarization and derivative of  $G_1$  with respect to  $P$  is the externally applied electrical stress. The significant temperature dependence is contained in the coefficient  $\chi'$ .

The meaning of  $\chi'$  can be seen from the following consideration. Let a small electric field  $E$  be applied to the crystal.

Then under zero pressure from equation (1.16)

$$dG_1 = -s dT + E dP \quad (1.18)$$

$$\text{or} \quad E = \left[ \frac{\partial}{\partial P} G_1 \right]_T$$

Above the transition temperature, the polarization is small for small applied fields. Therefore  $T < T_c$  all terms except first on the right hand side of equation (1.17) may be neglected. Therefore, we have

$$E = \left[ \frac{\partial}{\partial P} G_1 \right]_T = \chi' P \quad (1.19)$$

The dielectric constant and susceptibility along the polar axis is given by

$$\frac{\partial}{\partial P} E = \frac{4\pi}{\epsilon - 1} = \frac{1}{\chi} \quad (1.20)$$

$$\therefore \chi' = \frac{4\pi}{\epsilon - 1} = \frac{1}{\chi}$$

This equation shows that the coefficient  $\chi'$  is equal to reciprocal of the susceptibility. However in this temperature range the susceptibility and dielectric constant along the

polar axis are given by the Curie-Weiss law.

$$\eta = \frac{\epsilon - 1}{4\pi} = \frac{C}{T - T_0}$$

$$\text{so that } \chi' = \frac{T - T_0}{C} \quad (1.21)$$

where  $C$  is the curie constant and  $T_0$  is the Curie-Weiss temperature.

Hence the equation (1.17) may be written as follows,

$$G_1 - G_{10} = \frac{1}{2} \left[ \frac{T - T_0}{C} \right] P^2 + \frac{1}{4} \beta' P^4 + \frac{1}{6} \gamma' P^6 \quad (1.22)$$

From equation (1.19) and (1.22), we obtain the following equations for the applied field and the dielectric constant.

$$E = \left[ \frac{\partial}{\partial P} G_1 \right]_T = \left[ \frac{T - T_0}{C} \right] P + \beta' P^3 + \gamma' P^5 \quad (1.23)$$

$$\frac{1}{\eta} = \frac{4\pi}{\epsilon - 1} = \left[ \frac{T - T_0}{C} \right] + 3\beta' P^2 + 5\gamma' P^4 \quad (1.24)$$

#### 1.5 (b) Spontaneous Polarization :

In the thermal equilibrium  $\left[ \frac{\partial}{\partial P} G_1 \right]_T = 0$ , so that the

spontaneous polarization  $P_S$  for zero applied field satisfies the equation

$$0 = \chi' P_S + \beta' P_S^3 + \gamma' P_S^5 \quad (1.25)$$

It follows that the value of  $P_S$  which gives extremum of  $G_1$ , are given by  $P_S = 0$ ,

$$\chi' + \beta' P_S^2 + \gamma' P_S^4 = 0 \quad (1.26)$$

From equation (1.23), we have

$$\left[ \frac{\partial^2}{\partial P^2} G_1 \right]_T = \chi' + 3 \beta' P^2 + 5 \gamma' P^4 \quad (1.27)$$

If  $\chi'$ ,  $\beta'$ ,  $\gamma'$  are all positive,  $P_S = 0$  gives a positive value of  $\left[ \frac{\partial^2}{\partial P^2} G_1 \right]_T$ . Therefore  $P_S = 0$  will correspond to

the only minimum of free energy and in this case spontaneous polarization would not occur.

However, if as a result of temperature dependence the coefficient  $\chi'$  becomes negative,  $G_1$  would be maximum for  $P_S = 0$ ,

because in this case  $\left[ \frac{\partial^2}{\partial P^2} G_1 \right]_T$  is a negative quantity. When  $\chi'$

is negative, the equation (1.17) gives at least one nonvanishing value of  $P_S$  for which  $\left[ \frac{\partial^2}{\partial P^2} G_1 \right]_T$  would be positive

quantity. This shows that in this case  $G_1$  would be minimum and spontaneous polarization would occur.

### 1.5 (c) Second-Order Transition :

If the coefficients  $\beta'$  and  $\gamma'$  are positive and  $\chi'$  varies from positive to negative as the temperature is lowered. We obtain free energy curve as shown in fig [1.3(a)]. The corresponding spontaneous polarization as a function

temperature is shown in fig [1.3(b)]. Assuming that  $\gamma'$  is negligible the spontaneous polarization is obtained from the equation (1.25), which becomes,

$$\chi' P_S + \beta' P_S^3 = 0 \quad (1.28)$$

so that either  $P_S = 0$  or

$$P_S^2 = -\frac{\chi'}{\beta'} = -\frac{T - T_0}{C \beta'} = \frac{T_0 - T}{C \beta'} \quad (1.29)$$

For  $T \geq T_0$ , the only real root of equation (1.28) is at  $P_S = 0$ , because  $C$  and  $\beta'$  are positive. Thus the curie temperature  $T_0 = T_0$ . For  $T < T_0$  the  $P_S$  is given by

$$P_S = \left[ \frac{T_0 - T}{C \beta'} \right]^{1/2} \quad (1.30)$$

This equation shows that  $P_S$  is a continuous function of temperature below  $T_0$  and it decreases continuously to zero at  $T_0$ .

A transition of this type is not associated with Latent heat but with a discontinuity in the specific heat and is called a second order phase transition. For this transition the susceptibility and dielectric constant above curie temperature  $T_0$  are given by

$$\chi = \frac{\epsilon - 1}{4\pi} = \frac{C}{T - T_0} \quad (1.31)$$

Below the transition temperature the susceptibility is obtained as follows. From equation (1.24), neglecting the

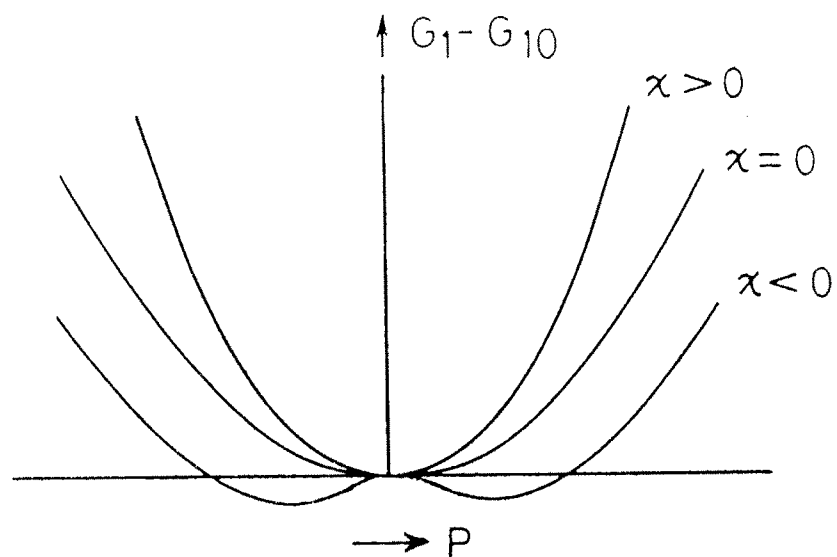


Fig.1.3(a) Schematic representation of the free energy as function of polarization for various values of  $\chi$  for a second-order transition.

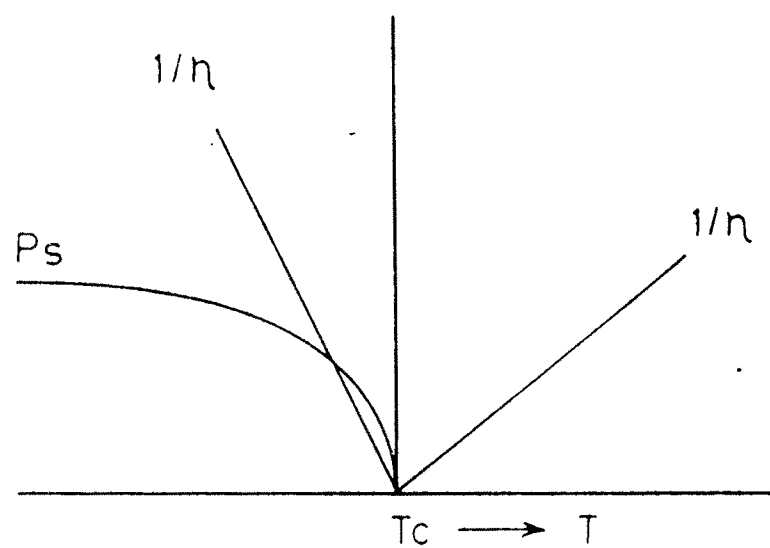


Fig.1.3(b) Schematic representation of the spontaneous polarization and reciprocal susceptibility near the transition temperature  $T_c$  for a second-order transition.

last term and since  $P \approx P_S$  for small  $E$ , we have,

$$\frac{1}{\eta} = \frac{4\pi}{\epsilon - 1} = \frac{T - T_0}{C} + 3 \rho' P_S^2 \quad (1.32)$$

Putting values of  $\rho' P_S^2$  from equation (1.29)

$$\frac{1}{\eta} = \frac{4\pi}{\epsilon - 1} = \frac{T - T_0}{C} + 3 \left[ \frac{T_0 - T}{C} \right] = 2 \left[ \frac{T_0 - T}{C} \right] \quad (1.33)$$

For second-order transition we have  $T_0 = T_C$ ,

$$\frac{1}{\eta} = \frac{\epsilon - 1}{4\pi} = \frac{C}{2(T_C - T)} \quad (1.34)$$

Temperature dependence of the reciprocal of the susceptibility on both sides of transition temperature, as given by equation (1.31) and (1.34), is shown in the fig [1.3(b)].

#### 1.5 (d) First-Order Transition :

It has been seen that the condition for the occurrence of spontaneous polarization is that  $\chi'$  should be negative. If  $\rho'$  is positive at the same time then there is a second-order transition. Let us consider the case for which  $\rho'$  is negative as temperature is lowered. In this case free energy curves are shown in fig. [1.4(a)] and spontaneous polarization is shown in fig. [1.4(b)]. A transition from the nonpolarized state to a spontaneously polarized state will now occur when the minimum of the free energy corresponding to  $P_S = 0$  becomes equal to minimum associated with  $P_S \neq 0$ . In the absence of an external field the spontaneous polarization

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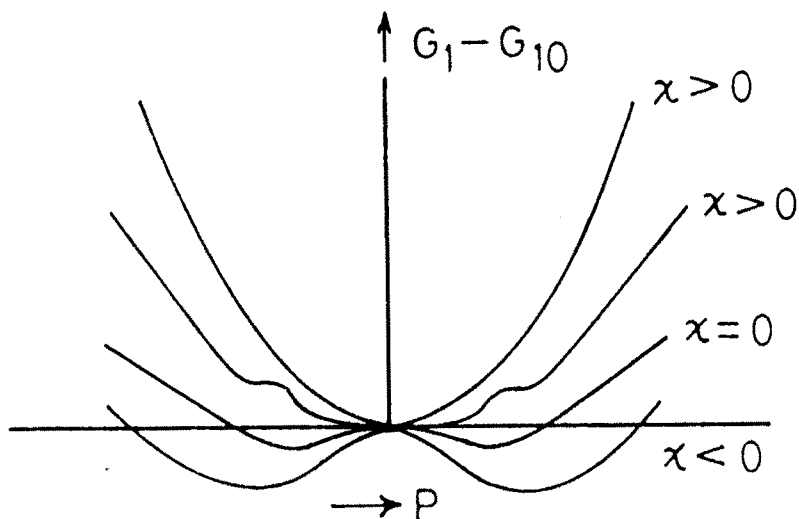


Fig.1.4 (a) Schematic representation of the free energy as function of polarization for various values of  $\chi$  for a first-order transition.

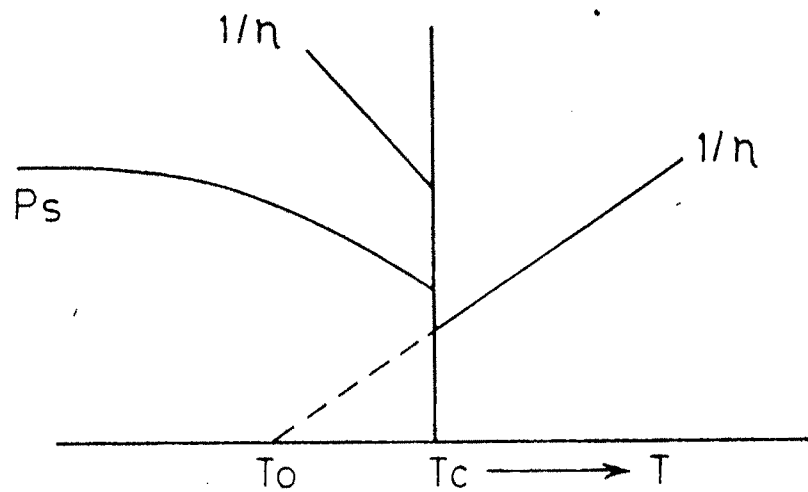


Fig.1.4(b) Schematic representation of the spontaneous polarization and reciprocal susceptibility near the transition temperature  $T_c$  for a first-order transition.



satisfies the equation (1.25) and also the condition  $G_1 = G_{1c}$ .

Therefore from equation (1.22)

$$\frac{1}{2} \chi' P_S^2 + \frac{1}{4} \beta' P_S^4 + \frac{1}{6} \gamma' P_S^6 = 0 \quad (1.35)$$

From this equation and equation (1.25) we can find the relations,

$$P_S^2 = \frac{3}{4} \left[ \frac{\beta'}{\gamma'} \right] \quad (1.36)$$

$$\chi' = \frac{3}{16} \left[ \frac{\beta'^2}{\gamma'} \right] \quad (1.37)$$

$$P_S^4 = 3 \left[ \frac{\chi'}{\gamma'} \right] \quad (1.38)$$

Equation (1.35) shows that the spontaneous polarization is discontinuous at the transition temperature as shown in fig. [1.4(b)].

If we consider first order transition, then below the transition temperature, using relation (1.24) with  $P \approx P_S$  for small  $E$  and equations (1.36), (1.37) and (1.38), the susceptibility  $\chi$  can also be obtained as,

$$\begin{aligned} \frac{1}{\chi} &= \frac{4\pi}{\epsilon - 1} = \left[ \frac{T - T_c}{C} \right] - 12 \left[ \frac{T - T_c}{C} \right] + 15 \left[ \frac{T - T_c}{C} \right] \\ \chi &= \frac{\epsilon - 1}{4\pi} = \frac{C}{4(T - T_c)} \end{aligned} \quad (1.39)$$

From this equation it is seen that the reciprocal of the susceptibility in the first-order transition is not zero at the transition temperature  $T_c$ , but it is positive quantity.

Its temperature variation just above and just below  $T_c$  is shown in fig. [1.4(b)].

#### 1.5 (e) Model Theories of Ferroelectricity :

In order to explain spontaneous polarization in general it is necessary to have physical model in which the dipole moments of the different unit cells are oriented along a common direction. Since a ferroelectric crystal is a very complicated molecular system, a rigorous theoretical treatment of realistic model is very difficult. A number of workers have proposed model theories for ferroelectricity.

Mason and Mathies (1948) gave model theory for  $\text{BaTiO}_3$  crystal, they have suggested that stable position for the  $\text{Ti}^{+4}$  ion is not at the centre of the oxygen octahedron. Instead, it is at any of the six positions which correspond to slight displacement from the centre towards the oxygen ions. When  $\text{Ti}^{+4}$  is in any of these positions, the unit cell would have a dipole moment.

Jaynes (1950) proposed a model in which oxygen ions are displaced rather than titanium ions. He proposed a theory in which dipole moments are not attributed to atomic displacements. Only the electronic states of  $\text{TiO}_6$  Octahedra are considered. The theory is satisfactory for determining the entropy change, but it predicts infra-red absorption line at nearly  $10\mu$ , wavelength, which is not detected.

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

Slater (1950) has also proposed a model in which he assumes in addition to Devonshire's model that each atom has an electric polarization and titanium ion has an ionic polarization.

Megaw (1952,54) has suggested that directional covalent bonding is of primary importance in the ferroelectricity of  $\text{PbTiO}_3$  and antiferroelectricity of  $\text{PbZrO}_3$ . The [110] displacements of Pb in  $\text{PbZrO}_3$  indicate that the Pb ion can get displaced in directions other than a four fold axis. While in  $\text{PbTiO}_3$  the Pb ions get displaced along the four fold axis at all temperatures from the curie point ( $490^\circ\text{C}$ ) to that of liquid helium temperature.

#### 1.5 (f) Cochran's Theory :

Cochran (1960-61) has proposed a lattice dynamical theory of ferroelectricity for certain crystals. The theory is based on the assumptions that the ferroelectric phase transitions are the results of the instability of the crystal lattice with respect to one of the homogeneous transverse optical models. If the crystal is wholly or partly ionic, lattice vibrations are accompanied by polarization

oscillations of equal frequency which gives rise to a local electric field interacting with the ions through long range coulomb forces. If for one particular mode of vibration, these long range forces are equal in magnitude but opposite in sign to the short range forces, the crystal becomes unstable for that 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 theory provides an explanation of ferroelectric phase transition in diatomic crystals of the NaCl - type. Cochran has used the data on the lattice dynamics of diatomic crystals and his own experimental data on the dielectric properties of cubic crystals in an analysis of some characteristics of transitions of  $\text{BaTiO}_3$ . He has estimated the dielectric crystal constant and the spontaneous polarization,  $P_S$  of  $\text{BaTiO}_3$  at the curie temperature as  $\epsilon = 1.4 \times 10^4$  and  $P_S = 19.5 \mu \text{ coulomb/cm}^2$  respectively, which are very close to the experimental values. The temperature dependence of the spontaneous polarization, calculated by Cochran is very close to experimentally determined variation. These results indicate that Cochran's theory explains satisfactory, many problems of  $\text{BaTiO}_3$ .

The most interesting new result of the theory is the prediction of the absolute value of the frequency of the

transverse optical mode with wave vector zero for perovskite materials.

$\nu_T = (2-3) \times 10^{11}$  cps for  $\text{BaTiO}_3$ . The frequency lines in the millimeter wavelength range. For this reason an experimental verification of the theory is difficult.

#### 1.6 Applications :

Many applications have been and are being found for ferroelectric materials. Some of these applications are simple, others sophisticated. Some have widespread use and are of great economic importance, while others are of a specialised nature.

Later, the existing and forthcoming applications are widespread, but many of them are component parts of computer and communication systems. These applications include memories, displays, printers, logic circuits, light modulators and deflectors, frequency changers and detectors. Displays can be considered a special type of memory in which reading is done optically in the visible spectrum. In some displays the primary reading mechanism is electrical and this is converted to visible light by means of suitable electrical-optical transducer.

##### i) Applications Involving Switching-Simple Operation :

It deals with simple operation, that is, devices which utilise only the polarization reversal properties of the

material. There are four types of 'Simple Operation' devices. They are Matrix-addressed Memories, Shift registers, Transchargers and some applications based on the Self-reversal effect.

ii) Applications Involving Switching-Complex Operation :

It is concerned with ferroelectric devices that simultaneously utilise the polarization reversal and one of the other associated properties of the ferroelectric material. There are three groups of 'Complex Operation' devices. They are the ferroelectric piezoelectric devices; the ferroelectric optic devices and the TANDEL type devices.

The ferroelectric-piezoelectric devices depend on a particular geometry and the material used. Most of the elastic constants of a ferroelectric material are functions of the polarization state of the material. They have been used as filters; which are very useful for remote control of television receivers. The ferroelectric-optic devices are divided into three groups. The first group utilises single light valves and includes modulators and deflectors. The second group requires a small quantity of light valves and include alpha-numeric and bargraphs. The third group requires a large number of light valves and includes displays, optical memories and pattern generators. The TANDEL effect can be used for building miniature thermostats to control temperature accurately. It can be used as a frequency

multiplier, electromechanical transducer and dielectric amplifier.

iii) Applications Involving Switching-Complex Structure :

It contains ferroelectric materials in combination with other active materials. Three such types of complex structures are ferroelectric - electroluminescent devices, ferroelectric - photoconductor devices, and ferroelectric - semiconductor devices. These devices are used to store electrically the 'Video' information. They can also be used as projection displays, adaptive resistors and transistors.

iv) Non-Switching Applications :

It includes the devices based on the following properties (a) the dielectric electro-optical and related linear and non-linear properties (b) the pyroelectric properties (c) the piezoelectric and related elasto-optic properties.

Ferroelectrics can be used as capacitors, thermistors, modulator and light deflector. In other cases, a transducer uses the piezoelectric effect to convert small motions into electrical changes, in an ultrasonic detectors; strain-gauges and microphones.

Ferroelectric condensers have been used for tuning in superhets. The non-linearities are most marked at low frequencies and near transition temperature. The pyroelectric

properties of ferroelectric materials make them very suitable for thermal detectors. The elasto-optic effect can be used for the electrical deflection and modulation of light.

Some ferroelectrics show increase in resistivity with increase in temperature. However, dramatic changes have been observed in certain ferroelectric materials near their curie point. These large increase in resistivity have been successfully utilised for fabricating PTC (positive temperature coefficient) switching thermistors. Some polar materials and ferroelectrics have the largest positive temperature coefficients, and also can be most easily fabricated as thermistors, are  $\text{SrTiO}_3$ , and the ferroelectrics  $\text{BaTiO}_3$ , and  $\text{PbTiO}_3$  doped with certain rare earth elements and solid solutions of lead-barium titanate (Kuwabara, et al. 1983; Nagata, et al. 1985; Kuwabara, et al. 1986). PTC thermistors are used mostly in control applications such as TV set, in single phase electric motors etc. In addition, PTC thermistors can be used as over-charge protection devices in batteries, thermal overload protection devices, control elements for slowly turning off lights and time delay fuses. The thermistor is in most instances smaller and cheaper than its electromechanical and mechanical counterparts. PTC thermistors are also used for measuring devices. Because of their resistance-temperature characteristic they have been



used to sense liquid levels and measure the flow rates of gases.

Some devices mentioned above such as capacitors and piezoelectric transducers, are of great commercial importance. Others, such as optical holographic storage media and colour projection TV system (Marie 1976), are still at a developmental stage but may prove to be economically very significant in future.

#### 1.7 Orientation of the Present Work :

Ferroelectricity is one of the important and interdisciplinary research fields which needs to be tackled in physical sciences, engineering and technology. The electronic and computer applications of ferroelectrics aroused interest among a number of research workers. The scope for ferroelectrics is even further broadened in view of the significance of the related phenomena such as piezoelectricity, electro-optics, pyroelectricity, electro-striction, non-linear dielectrics and liquid crystals.

Among the ferroelectric materials, sodium vanadate doped with different concentrations of Neodymium Oxide are not extensively studied yet. Therefore it is difficult to understand the origin of ferroelectricity in them. These ferroelectrics are high temperature ferroelectrics and they can be obtained in the ceramic forms. Kuroda and Kubota

(1980) studied the diffuse phase transition of  $(\text{Ba}_x \text{Sr}_{1-x})\text{Nb}_2\text{O}_6$  doped with  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  by measuring the spontaneous polarization and dielectric constant. Sawada and Nomura (1951) studied the ferroelectric activity of  $\text{NaVO}_3$  below  $380^\circ\text{C}$ . Chavan and Suryawanshi (1985) reported the ferroelectric activity of  $\text{NaVO}_3$  and  $\text{KVO}_3$ . The ferroelectric activity of  $\text{LiVO}_3$  was investigated by Patil et al. (1988).

Therefore, the aim of the present research work is to prepare ferroelectric sodium vanadate ( $\text{NaVO}_3$ ) doped with different concentrations of Neodymium Oxide ( $\text{Nd}_2\text{O}_3$ ) and the following studies are undertaken :

- 1) X-ray diffraction.
- 2) Dielectric hysteresis and determination of coercive field.
- 3) D.C. electrical conductivity.
- 4) Pyroelectricity.

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