Chapter - I

FERROELECTRIC

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1.1 Introduction

Ferroelectrics are certain materials that exhibit even in the absence of an electric field small microscopic regions, which are polarized in several directions. The intrinsic polarization of these regions is specified by the magnitude known as the spontaneous polarization and denoted by P_s. The magnitude of the vector $\overrightarrow{P_s}$ is representative of many properties of ferroelectrics. Dielectric constant of ferroelectric materials are usually large and depend to a great degree on the intensity of the electric field. Curie point T_c is the temperature at which, the chosen ferroelectric material does not exhibit the ferroelectric properties when the temperature exceeds the value of T_c.

Ferroelectrics are materials which posses a spontaneous electric polarization. However, it can be oriented in a specific direction by the application of a suitable electric field. Ferroelectrics show a hysteresis relation in the spontaneous polarization (P_s) and Electric field (E).

The first ferroelectric phenomenon was observed in the Rochelle salt i.e. sodium-potassium tartrate tetrahydrate [$NaKC_4H_4O_6$; $4H_2O$]. Rochelle salt was prepared around 1655 by

Seigrette in La Rochelle (France). Ferroelectrics of Rochelle salt was affiramitively established by Valasek (1). He was the first to point out the analogy between the dielectric properties of Rochelle salt and the magnetic properties of ferromagnetic material. Mueller (2) called this phenomenon as ferroelectricity because of its analogy with ferromagnetism. In 1935, the ferroelectric activity of potassium dihydrogen phosphate (KH_2PO_4) was discovered by Busch and Scherrer (3). Further they reported that a number of isomorphous compound of potassium dihydrogen phosphate are ferroelectric. Slater (4) published a theory of the phase transition of KH_2PO_4, in the year (1941).

The anomalous dielectric properties of ceramic barium titanate was discovered by Wainer and Saloman (5) (1942) in united states, Ogawa (6) (1944) in Japan, and Wula and Goldman (7) (1945) in Russia. Later on the ferroelectric activity of $BaTiO_3$ was confirred by Von Hipple (8) and his co-workers and independently by Wu and Goldman (9). Since the discovery of ferroelectricity in $BaTiO_3$ compounds with perovskite structure (ABO_3), they are being studied extensively. Matthias (10) discovered ferroelectricity in potassium niobates. Shirane (11) et al studied the various dielectric and opticel properties of $KNbO_3$.

Jona and Shirane (12) have given an useful table of seventy six ferroelectric crystals a collection made up-to January 1961. Mitsul (13) et al, have listed nearly 450 pure compounds and solid solutions of,ferroelectric character known to them from various sources. Galasso (14) provided the structure and property data on a large number of perovskite-type compounds.

1.2 Ferroelectric Materials and their characteristic properties

Ferroelectrics are usually solids but they are also the ones which are non-metallic. The properties of ferroelectrics are most simply studied, when the material is in a single crystal form. While in a ceramic form or as solid solutions, they offer wide practical importance. Ferroelectrics are materials which posses spontaneous electric polarization (P_s), that can be reversed by applying a sutable electric field (E_c). The process is known as switching and thus is characterized by a hysteresis behaviour as shown in Fig. (1.1).

The dielectric displacement (D) is related both to the electric field (E) and to the polarization (P) and is given by

$$D = E + 4\pi P \tag{1.1}$$

Differentiating with respect to E, we get

$$\frac{dD}{dE} = 1 + 4\pi \frac{dp}{dE}$$

or as

$$\epsilon = 1 + 4\pi\eta \tag{1.2}$$

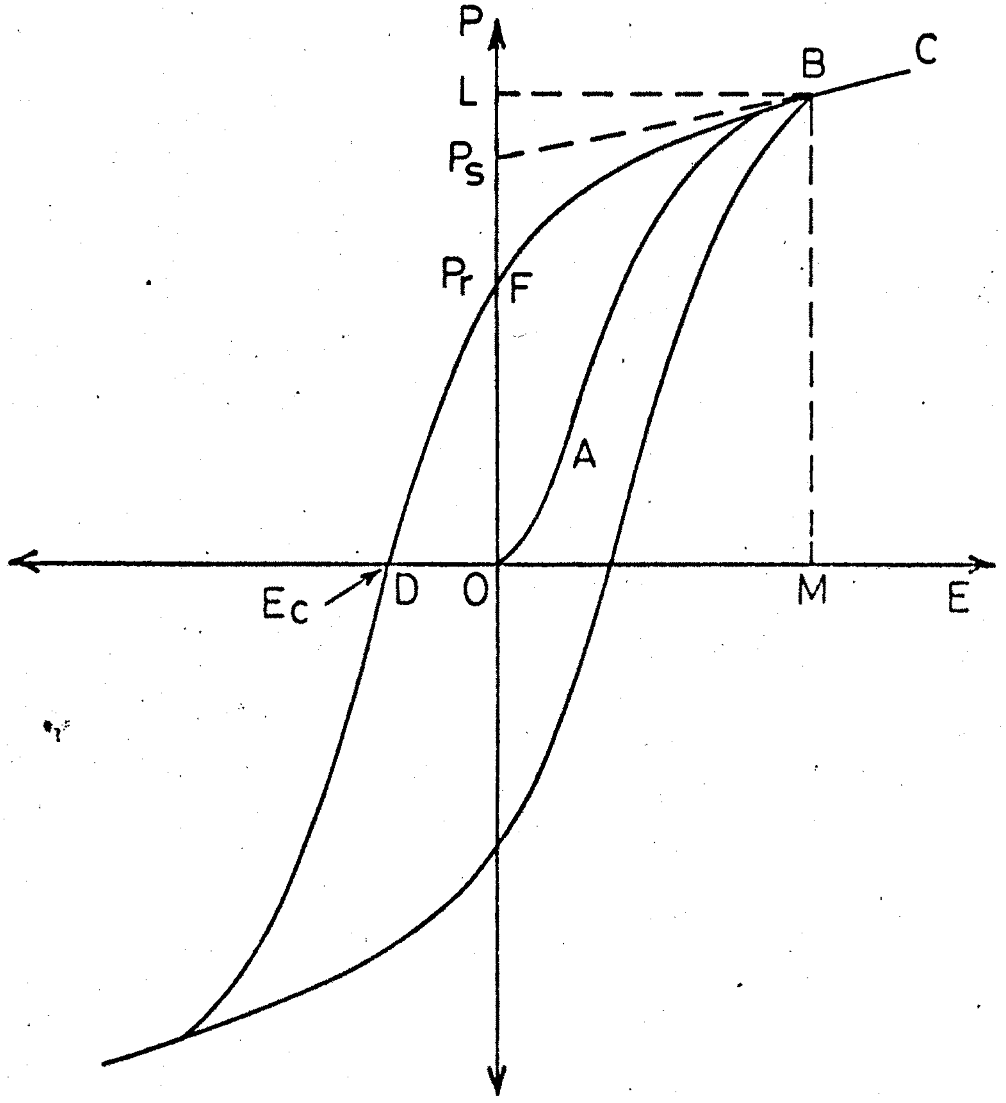

Fig. 1·1: Schematic representation of ferroelectric hysteresis loop.

where $\epsilon = \frac{dD}{dE}$ = the dielectric constant,

and $\eta = \frac{dD}{dE}$ = the dielectric susceptibility.

In some ferroelectrics, the temperature dependence of the dielectric constant above the transition temperature (T_o) can be described fairly by a simple law called the Curie-Wiess law (from its ferromagnetic analogue). This law states that,

$$\epsilon = \epsilon_o + \frac{C}{T-T_o} \qquad (1.3)$$

where C = Curie constant,

T_o = Curie-Wiess transition temperature,

and ϵ_o = the temperature independent part.

The dielectric constant becomes very large in the vicinity of the Curie-Wiess transition temperature and at such temperatures the relation between the dielectric constant and the susceptibility can be approximated by

$$\frac{\epsilon}{4\pi} \cong \eta \qquad (1.4)$$

With increasing temperature ferroelectricity disappears above a certain temperature and that temperature is known as the "Curie" transition temperature (T_C). At the transition temperature the material undergoes a transition from a polar state to a non-polar state. As a rule, the lower temperature phase is a polar phase and the high temperature phase is a non- polar phase.

The first-order transition is that in which there is a discontinuous change of volume and energy, the energy appearing as latent heat in an infinitely narrow temperature range. A second-order transition is that in which there is no discontinuity in the change in volume and energy. Therefore, in the second-order transition there is no release of latent heat but the expansion coefficient and the specific heat show anomalies extending over a finite range of temperature. Other properties, such as the spontaneous polarization, show discontinuity in a first-order transition but not in a second-order transition.

The following properties are in general possesed by most of the ferroelectric materials :

1) They exhibit a dielectric hysteresis loop below a certain critical temperature. This temperature is called ferroelectric transition temperature.
2) They have a ferroelectric domain structure which may be yet times visible in polarized light.
3) They have a high dielectric constant along the polar axis, which is a function of temperature and it rises to a peak value at the curie temperature.
4) They posses usually a pseudo-symmetric structure, in the ferroelectric state.
5) The curie temperature may be raised to a higher value by application of a biasing field, or a hydrostatic

pressure.

6) They show piezoelectric and pyroelectric properties below the curie temperature.

7) There is a sudden appearance of surface charge at the transition.

1.3 Classification of ferroelectrics

For a number of years,the phenomenon of ferroelectricity was known to occur in a rather limited number of crystals. Investigations, in recent years, have revealed that ferroelectricity is a more common phenomenon, than that has been thought for a long time. Satisfactory classification of all the materials has become very difficult, however, classifications of some ferroelectrics have been proposed, according to different criteria, certain of which are enumerated below.

(1) Crystal - chemical classification

This classification sorts ferroelectric compounds into two groups. The first group comprises of hydrogen bonded crystals, such as Rochelle salt, triglycine sulfate potassium dihydrogen phosphate etc. The second group includes the double oxides, such as $BaTiO_3$, $PbTiO_3$, $Cd_2Nb_2O_7$ etc.

(2) Classification according to the number of directions allowed to the spontaneous polarization

This classification also sorts the ferroelectric materials into two groups. The first group includes those ferroelectrics which can polarize along only one axis, such as Rochelle salt, KH_2PO_4, $PbTa_2O_6$, colemanite etc. The second group includes those ferroelectrics which can polarize along several axes, (that are equivalent in non-polar phase) eg. $BaTiO_3$, $PbNb_2O_6$, ferroelectric alums etc. These ferroelectrics are found best suited for the study of ferroelectric domains.

(3) Classification according to the existence of lack of centre of symmetry in the point group of their non-polar phase

This classification also divides the ferroelectrics into two groups. The first group includes those ferroelectrics that are piezoelectric in the non-polar phase, such as Rochelle salt, KH_2PO_4, and isomorphous compounds. The second group includes those ferroelectrics, which are not piezoelectric in the non- polar phase such as $BaTiO_3$, $Cd_2Nb_2O_7$, $PbNb_2O_4$ etc. This classification is particularly useful for the thermodynamic description of the ferroelectric transitions.

(4) Classification according to the nature of the phase exchange at the curie point

According to this classification the ferroelectric crystal are divided into two groups, (1) order-disorder group and (2) displacive group. The order-disorder group of ferroelectrics includes crystals with hydrogen bonds, such as KH_2PO_4 and isomorphous salts, triglycine sulfate. The ferroelectrics in this group undergo transition of the ordered-disordered type.

The displacive group of ferroelectrics include ionic crystals whose structures are closely related to the perovskite, such as those of $BaTiO_3$ and most of the double oxide ferroelectrics.

(5) <u>Classification according to the predominant nature of atomic displacements required by polority reversal</u> :

According to the predominant nature of the atomic displacement required by polarity reversal, Abrahams and Keve (15) have divided ferroelectric crystals into three groups.

The one-dimensional class includes those feroelectric crystals, in which, the atomic displacement vectors $(\vec{\Delta})$, and loci (L) followed by the atoms during reversal, are linear and parallel to the polar axis, $BaTiO_3$, $PbTiO_3$, $KNbO_3$,.

The two-dimensional class includes those ferroelectric crystals, in which, the atomic displacement vector $(\vec{\Delta})$ and actual Loci (L) followed by atoms during reversal, lie in a set of parallel planes containing the polar direction. Examples of this group are $BaCOF_4$, HCl, HBr, $NaNO_2$.

The three-dimensional class includes those ferroelectric crystals, in which, the displacement vector $(\vec{\Delta})$ and the

Looi(L) followed by atoms during reversal, have essentially random orientations for example, such crystals such as $(NH_4)_2SO_4$, KH_2PO_4 etc.

1.4 Ferroelectric Domains

The ferroelectric phase of KH_2PO_4, directly related with the domains, was first given by de Quervain (16). Zwicker and Seherier (17) have made the direct optical observation of these domain using a polarized light. Kay (18) and Blatter (19) et al were the first to report the domain structure in single crystals of $BaTiO_3$.

In general, a ferroelectric crystal consists of domains, which are regions of homogenous polarization that differ only in a direction of the polarization. All the spontaneously polarised unit cells, within a domain, in a ferroelectric crystal are oriented identically, consequently, each domain has a microscopic spontaneous polarization, and such polarizations of neighbouring domains in a ferroelectric crystal make definite angles with one another. A line of separation between two neighbouring domains, is called, a domain wall. The domain wall is usually 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 a minimum of the energy of a crystal. 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-domain crystal is difficult to obtain, a crystal generally consists of a mixture of domains with different orientations of polar axis. The fundamental problem is then that of describing property of a ceramic below the curie temperature in terms of physical constants of a single crystal. Ceramic bodies are aggregates of crystallites which in a turn may consist of several domains. We have little knowledge of the forces that are working among the crystallites and of the mechanical strains created around the boundaries.

A single crystal may contain a number of domain regions although, by definition, it cannot contain more than one crystalliate. In a polycrystalline material, there may be several domains in each crystallite. In paraelectric phase i.e. above the curie temperature the direction along which the polarization is to occur cannot be a unique direction. Even in a ferroelectric phase, there must be at least two equivalent directions along which polarization can occur with the same probability. The paraelectric crystal consists of uniformly polarized regions, because at the curie temperature different regions of the crystal can occur polarized in different directions. Below T_c the crystal must belong, by its symmetry, to one of the paraelectric classes and the domains differ in the direction of spontaneous polarization. Therefore, when a ferroelectric is cooled below the curie-temperature, in the absence of external electrical and mechanical stress, it exhibits domains of different orientations. From a crystallographic point of view, the domain structure may be said to be identical with the twinning structure. Twin operations of ferroelectric domains have been discussed by Zheludev and Scuvalov (20).

1.5 Spontaneous Polarization

The existence of a dielectric hysteresis loop serves as a measure for spontaneous polarization (P_s). This is defined as the dipole moment per unit volume. The experimental methods of observation of the hysistersis loop are generally based on the Sawyer and Tower circuit (21). The hysteresis loop is shown in Fig.1.1. Linear extrapolation from the saturation region to zero field gives spontaneous polarization (P_s). The intercept on polarization axis is P_r (ramenant polarization) and the intercept OD on the E-axis gives coercive field. (See Fig 1.1). The total polarization of the ferroelectric in the saturation field OM is represented by the intercept OL.

The main defect of Sawyer and Tower circuit is the phase difference introduced between the applied field and the polarization of the ferroelectric crystal, that arises as the impedance of the crystal is variable. Sinha (22) proposed a modified Sawyer and Tower circuit. Other methods which are commonly adopted for measuring the magnitude of the P_s are (I) polarity reversal techniques (Camlibel) (23), (II) charge intergration technique (Glass) (24) and (III) pyroelectric measurement using calibration for scaling (Glass) (24).

The spontaneous polarization depends upon the temperature. The spontaneous polarization P_s suddenly falls to zero in ferroelectrics, which undergoes the first-order phase transition. The transition in $BaTiO_3$, is an example of first order transition (Merz) (25). In second-order phase transition P_s decreases continuously to zero at the transition temperature. The example of second-order transition type ferroelectric is triglycine sulfate (Jona and Shirane) (12).

1.6 Dielectric Properties and Polarizability

1.6.1 Dielectric properties

A flat slab of any solid dielectric when placed in a uniform electric field $\vec{E}_0$ and has a dielectric displacement ($\vec{D}$), which is normally parallel to the electric field. The dielectric displacement $\vec{D}$ is given in C.G.S system as :

$$\overrightarrow{D} = f_o \overrightarrow{E_o} = \epsilon \overrightarrow{E} = \overrightarrow{E} + 4\pi\overrightarrow{P} \qquad (1.5)$$

where $\overrightarrow{E}$ = the applied electric field strength,

$\overrightarrow{E_o}$ = the electric field inside the dielectric,

ϵ_o = the dielectric constant of the surrounding medium,

ϵ = the dielectric constent of the solid dielectric,

and $\overrightarrow{P}$ = the polarization.

For the surrounding medium of air or vaccum the value of dielectric constant ϵ_o is taken to be unity. The total polarization $(\overrightarrow{P})$ is proportional to the electric field of strength, $(\overrightarrow{E})$

$$\overrightarrow{P} = \eta \overrightarrow{E} \qquad (1.6)$$

where η is the dielectric susceptibility.

In an isotropic cubic system $\overrightarrow{P}$ is parallel to $\overrightarrow{E}$, then all quantities in the above equations are written as scalars. But from equation (1.5) the dielectric constant of an isotropic medium is defined as

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

$$= 1 + 4\pi\eta \qquad (1.7)$$

$$\therefore \quad \eta = \frac{\epsilon - 1}{4\pi} \qquad (1.8)$$

The equation (1.8) is a relation between dielectric susceptibility and the dielectric constant.

In a non-cubic crystal, the dielectric response is described by the components of the susceptibility tensor η_{jk} or the dielectric constant tensor E_{jk} .

$$P_j = n_{jk} E_k \quad (1.9)$$

$$E_{jk} = 1 + 4\pi \eta_{jk} \quad (1.10)$$

1.6.2 (b) Polarizability

The dielectric behaviour of ferroelectric crystals depends on polarizability and internal field. The internal field is also called the local field E_{loc} .

According to Lorentz equation the internal field is given by

$$E_{loc} = E_1 + E_2 + E_3 + E_4 \quad (1.11)$$

where E_1 = field due to the charges on the plate,

E_2 = field due to the charges on the surface of the dielectric,

E_3 = field due to the charges on the surface of the spherical cavity,

and E_4 = field due to the dipole interaction of the material with the sphere.

The effect of plate charges is given directly by the Gauss theorem.

$$E_1 = \frac{Q}{\epsilon_0}$$

Since the surface charges on the dielectric are given by the polarization P and their electric field, which is oppositely directed to E_1, we get,

$$\therefore \quad E_2 = \frac{P}{\epsilon_0}$$

The field due to charges on the surface of the spherical cavity is given

$$E_3 = \int_0^{\pi} \frac{P \cos^2 \theta}{4\pi \; \epsilon_0 \; r^2} \; 2\pi \; r^2 \sin \theta \, d \, \theta$$

$$= \frac{P}{3\epsilon_\theta}$$

If the material is assumed to have cubic symmetry, then effect of dipole intercations averages to zero,

$$E_4 = 0.$$

The magnitude of the total internal field is given by

$$E_{loc} = \frac{Q}{\epsilon_0} - \frac{P}{\epsilon_0} + \frac{P}{3\epsilon_0} .$$

But $Q = D = E + 4\pi P.$

Therefore, equation (1.11) becomes

$$E_{loc} = E + \frac{P}{3\epsilon_0} \qquad (1.12)$$

In the local field E_{loc} each molecule becomes polarized and acquires the dipole moment p. The polarizability of an atom is defined as,

$$p = \alpha E_{loc} \qquad (1.13)$$

where α is the polarizability.

The polarizability is an atomic property, but the dielectric constant will depend on the manner in which the atoms are assembled to form a crystal.

The polarization in the crystal may be expressed as

$$P = \sum_j N_j p_j = \sum_j N_j \alpha_j E_{loc}(j) \qquad (1.14)$$

Where N_j is the concentration and α_j the polarizability of atoms j and $E_{loc}(j)$ is the local field at atom sites j.

$$\therefore \quad P = \sum_j \alpha_j N_j \left(E + \frac{4\pi P}{3}\right) \qquad (1.15)$$

$\therefore$ the dielectric susceptibility is given by

$$\chi = \frac{P}{E} = \frac{\Sigma N_j \alpha_j}{1-(4\pi/3)\Sigma N_j \alpha_j} \qquad (1.16)$$

Since $\epsilon = 1 + 4\pi\chi$ in C.G.S. unit

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{3} \Sigma N_j \alpha_j \qquad (1.17)$$

This equation is known as Clausius-Mossotti relation. The total polarizability is usually separated into three parts.

(1) Electric ploarizability (α_e) it is arises due to displacement of electron and nucleus within the atom.

(2) Atomic [illegible] ionic polarizability (α_a) : it arises due to

displacement of atoms or ions within the same molecules.

(3) Dipolar polarizability (α_d) : it arises from molecules with a permanant electric dipole moment that can change orientation in an applied field.

The electronic and atomic polarizabilities are independent of temperature. Hence, in this region, the dielectric constant α_d is essentially independent of temperature. The dipolar polarizability, is a function of temperature. But from the Debye's theory (26) the dipolar polarizability per molecule in a weak field is given by

$$\alpha_d = \frac{p^2}{3KT} \tag{1.18}$$

Where p is dipole moment of a polar molecule, k is Boltzman constant and T is the absolute temperature. The contributions to the total probability are shown in Fig.1.2. The dielectric constant at optical frequercies, is entirely due to the electronic polarizability. The atomic and dipolar contributions are small at high frequencies, because of the inertia of the molecules and ions. Polarizability is a function of frequency of the applied field.

1.7 Theories of Ferroelectricity

Many attempts were made to explain the property of ferroelectricity in crystals. The theories proposed so far have only a partial success, and but one of which is most the promising is that due to Cochran. His theory is based on the

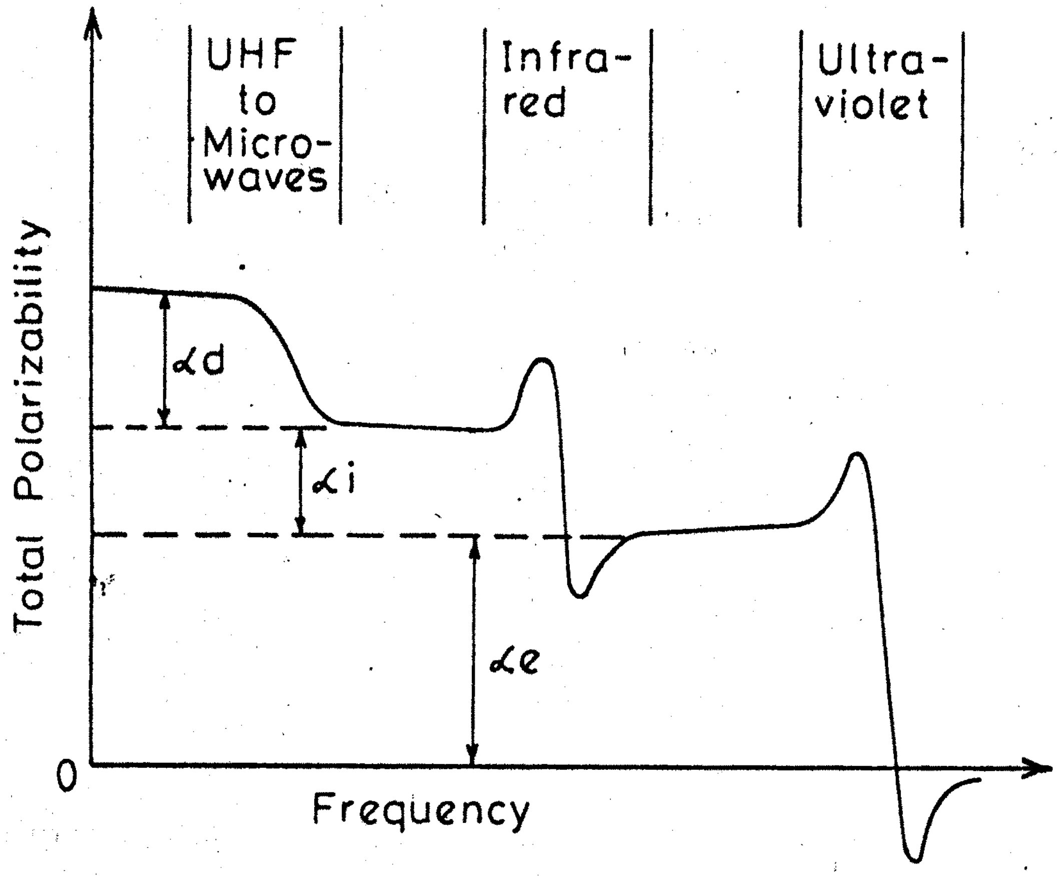

Fig. 1·2: Schematic representation of frequency dependence of the several contributions to the total polarizability.

lattice dynamics. A description of thermodynamic theory is given below.

1.7.1 Thermodynamic Theory

Mueller (27) and Cady (28) formulated a thermodynamic theory for the Rochelle salt. This theory can be applied to KH_2PO_4 type ferroelectrics. The thermodynamical teatment of $BaTiO_3$ type ferroelectric is some what different, since these crystals have more than one ferroelectric axis and are not piezoelectric in paraelectric phase. Devonshire (29) and Ginzburg (30) developed a thermodynamic theory for such type of ferroelectrics.

The thermodynamic theory is based on the following assumptions :

i) The free energy of a ferroelectric crystal is unique function of temperature, stress, and polarization.

ii) 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.

iii) The anomalous piezoelectric and elastic properties are considered to be a result of the anomalous dielectric behaviouor. Therefore the coefficients of P^2, in the free energy functions, exhibit the significant temperature dependence.

iv) The free energy functions contain three components of the polarization vector.

v) The second-order piezoelectric coefficients i.e. the electrostrictive coefficients are of main importance because the crystal is not piezoelectric in the unpolarized state.

The free energy of the crystal is expressed in terms of Gibb's function.

$$G_i = U - T S + \chi_i X - T S - E_m P_m \qquad (1.19)$$

where U is the internal energy of the crystal under external stress, χ_i is the ith component of mechanical stress. X_i is the ith component of the mechanical strain, T is the temperature, S is entropy and P_m is the mth component of electrical polarization.

The differential form of this Gibbs function is

$$dG_i = - SdT + \chi_i dX_i + E_m dP_m . \qquad (1.20)$$

The index i can take six values, for compression or expansion i = 1,2,3 and for shear i = 4,5,6. For fixed temperature T, stress (χ) and field (E) are zero, the G_i can be expanded in powers of polarization. For simplicity it is assumed, that in the ferroelectric region, the spontaneous polarization occurs along only one axis. Let G_{io} be the free energy of the unpolarized crystal. Devonshire found that it was necessary to consider terms upto p^6. The expression for the free energy is given by

$$G_1 - G_{10} = 1/2\ \chi'\ P^2 + 1/4\ \beta'\ P^4 + 1/6\ \gamma'\ P^6, \quad (1.21)$$

where dashes indicate that the coefficients are taken at fixed stress.

Let a small electric field E be applied to the crystal. Then under zero pressure. The equation yields,

$$dG_1 = -\ SdT + EdP \quad (1.22)$$

$$\therefore \quad E = \left[\frac{\partial G_1}{\partial P}\right]_T \quad (1.23)$$

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

$$E = \left[\frac{\partial G_1}{\partial P}\right] = \chi'\ P \quad (1.24)$$

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

$$\frac{\partial E}{\partial P} = \frac{4\pi}{\epsilon - 1} = 1/\eta\ . \quad (1.25)$$

From equations (1.23) and (1.25), we have

$$\chi' = \frac{4\pi}{\epsilon - 1} = 1/\eta\ . \quad (1.26)$$

From this equation the coefficient χ' is seen equal to the reciprocal susceptibility. However, in this temperature range, the susceptibility and the dielectric constant along the polar axis are given by the Curie-Weiss law,

$$\eta = \frac{\epsilon-1}{4\pi} = \frac{C}{T-T_c} , \qquad (1.27)$$

so that

$$\chi' = \frac{T-T_0}{C} \qquad (1.28)$$

where C is the Curie contant, and T_0 is the Curie-Weiss temperature.

Hence the equation (1.21) becomes

$$G_1-G_{10} = 1/2(\frac{T-T_0}{C})P^2 + 1/4\ \beta'\ P^4 + 1/6\ \gamma'\ P^6 . \qquad (1.29)$$

From equation (1.24) and (1.29) we obtain equation for the applied field and the dielectric constant.

$$E = (\frac{\partial G}{\partial P})_T = (\frac{T-T_0}{C})\ P + \beta'\ P^3 + \gamma'\ P^5 \qquad (1.30)$$

and

$$\eta = \frac{4\pi}{C} = (\frac{T-T_0}{C}) + 3\ \beta' P^2 + 5\ \gamma' P^4 \qquad (1.31)$$

1.7.2 Spontaneous Polarization

In the thermal equlibrium $(\frac{\partial G_1}{\partial P}) = 0$, since spontaneous polarization P_s for zero electric field satisfies the equation,

$$0 = \chi' P_s + \beta' P_s + \gamma'\ P_s^5 , \qquad (1.32)$$

it follows the values of P_s which give extremum of G_1

are given by

$$P_s = 0,$$

$$\chi' P_s + \beta' P_s^3 + \gamma' P_s^5 = 0. \qquad (1.33)$$

From equation (1.32), we have,

$$\frac{\partial^2 G}{\partial P^2} = \chi' + 3\,\beta'\,\chi^2 + 5\,\gamma'\,P^4\,. \qquad (1.34)$$

If χ', β', and γ' are positive, $P_s = 0$ gives a positive $\frac{\partial^2 G}{\partial P^2}$. Therefore $P_s = 0$ will correspond to the only minimum of free energy, and in this event spontaneous polarization would not occur. However, if as a result of temperature dependence, the coefficient χ' becomes negative, G_1 would be maximum for $P_s = 0$. Because in this case $\frac{\partial^2 G}{\partial P^2}$ is negative quantity. When χ' is negative, the equation (1.34) gives at least one non-vanishing value of P_s for which $\frac{\partial^2 G}{\partial P^2}$ would be a positive quantity. This shows that in this case G_1 would be a minimum i.e. spontaneous polarization would occur. Consequently, continuous variation of χ' from positive to negative values changes a stable paraelectric state ($\chi' > 0$) to a stable ferroelectric state ($\chi' < 0$). At the transition temperature T_c between these states we have $\chi' = 0$.

1.7.3 Second-Order Transision

If the coefficent β' and γ' are positive and χ' changes from positive to negative, as the temperature is lowered, we obtain free energy curves, as shown in Fig.1.3(a). The corresponding spontaneous polarization, as a function of temperature is shown in Fig.1.3(b).

The electric field can be written as upto 4th order

$$E = \frac{\partial G_1}{\partial p} = \chi' P_s + \beta' P_s^3 \qquad (1.35)$$

If $E = 0$ in the above equation (1.35), then spontaneous polarization for $T < T_c$ is given by,

$$P_s = \chi'/\beta' \ ; \qquad P_s = \left(\frac{T_c - T}{c\beta'}\right)^{1/2} . \qquad (1.36)$$

This equation shows that P_s is a continuous function of temperature below T_c and it decreases continuously to zero at T_c as shown in Fig.1.3(b). 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 transition. The susceptibility and dielectric constant above the curie temperature for the second-order phase transition are given by

$$\eta = \frac{\varepsilon - 1}{4\pi} = \frac{C}{T - T_c} \qquad (1.37)$$

The susceptibility and dielectric constant below the transition temperature is obtained as follows. Assuming that the term γ' in equations (1.30) and (1.31) is negligible,

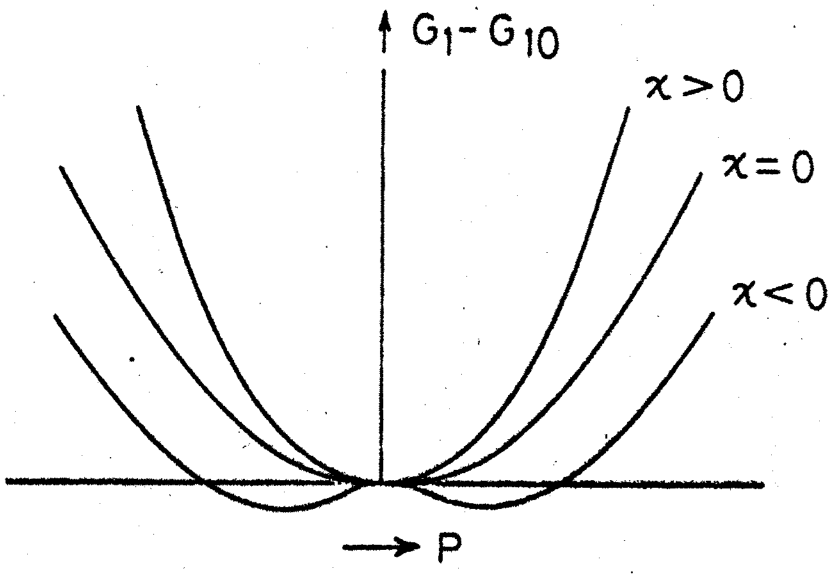

Fig. 1·3(a) Schematic representation of the free energy as function of polarization for various values of χ for a second-order transition.

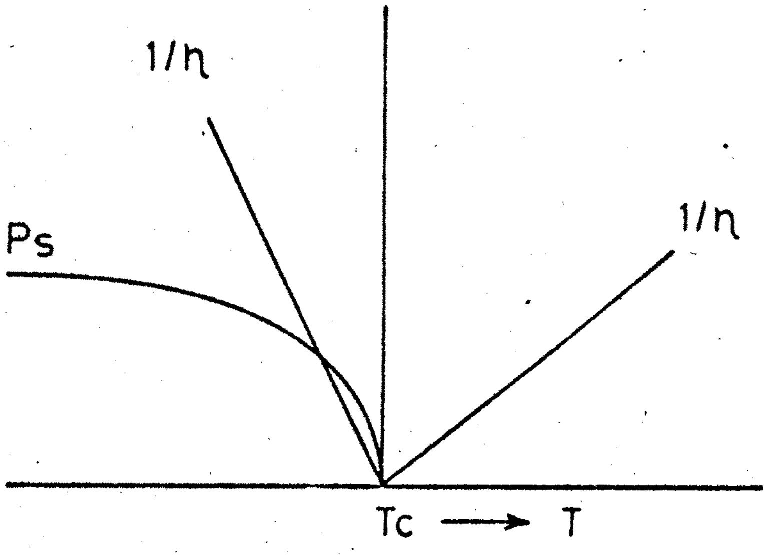

Fig. 1·3(b) Schematic representation of the spontaneous polarization and reciprocal susceptibility near the transition temperature Tc for a second-order transition.

we obtain

$$E = (\frac{T-T_c}{C})\ P + \beta' P^3 \qquad (1.38)$$

and
$$1/\eta = \frac{4\pi}{\epsilon-1} = (\frac{T-T_o}{C}) + 3\ \beta' P^2\ . \qquad (1.39)$$

For small aplied fields the total polarization is nearly equal to spontaneous polarization P_s i.e. $P = P_s$.

$$\therefore \quad \beta' P^2 = -\ (\frac{T-T_o}{C}) \qquad (1.40)$$

Now from equation (1.36) and 1.37 we obtain

$$1/\eta = \frac{4\pi}{\epsilon-1} - \alpha/2(\frac{T-T_o}{C})$$

Since for second order transition $T_o = T_c$, we have

$$1/\eta = \frac{4\pi}{\epsilon-1} - 2(\frac{T-T_c}{C}).$$

$$\therefore \quad \eta = \frac{\epsilon-1}{4\pi} = -\ 1/2(\frac{T-T_o}{C}) \qquad (1.41)$$

The temperature dependence of the reciprocal of the susceptibility on either sides of the transition temperature is shown Fig.1.4(b).

1.7.4 First order Transition

The condition for the occurance of spontaneous polarization is that χ' should be negative. If β' is positive at the same time as well then the transition is a secohd-order type transition. Let us consider the case for which β' is negative, as the temperature is lowered. For this case, the free energy curves are shown in Fig. 1.4 (a). A transition from the non-polarized state to a spontaneously polarized state occurs when the minimum of the free energy corresponding to $P_s = 0$ becomes equal to the minimum associated with $P_s \neq 0$. In the absence of an external field the spontaneous polarization satisfies equation (1.21) and also the condition $G_1 = G_{10}$. Therefore,

$$1/2\ \chi'\ P_s^2 + 1/4\ \beta' P_s^4 + 1/6\ \gamma' P_s^6 = 0 \qquad (1.42)$$

from equation (1.32) and (1.42), we get

$$P_s^2 = -\ 3/4\ \left(\frac{\beta'}{\gamma'}\right), \qquad (1.43)$$

$$P_s^2 = -\ 3/16\ \left(\frac{\beta'}{\gamma'}\right)^2, \qquad (1.44)$$

and

$$P_s^4 = 3\ \left(\frac{\chi'}{\beta'}\right). \qquad (1.45)$$

The equation (1.43) shows that the spontaneous polarization is discontinuous at the transition temperature as is shown in Fig.1.4 (b). The susceptibility and dielectric constant in the region above T_c can also be written as

$$\eta = \frac{\epsilon-1}{4\pi} = \frac{C}{T-T_o} \qquad (1.46)$$

For first-order transition $T_o < T_c$. The expressions for susceptibility and dielectric constant below transition temperature are now given by

$$\eta = \frac{\epsilon-1}{4\pi} = \frac{C}{4(T-T_o)}\ . \qquad (1.47)$$

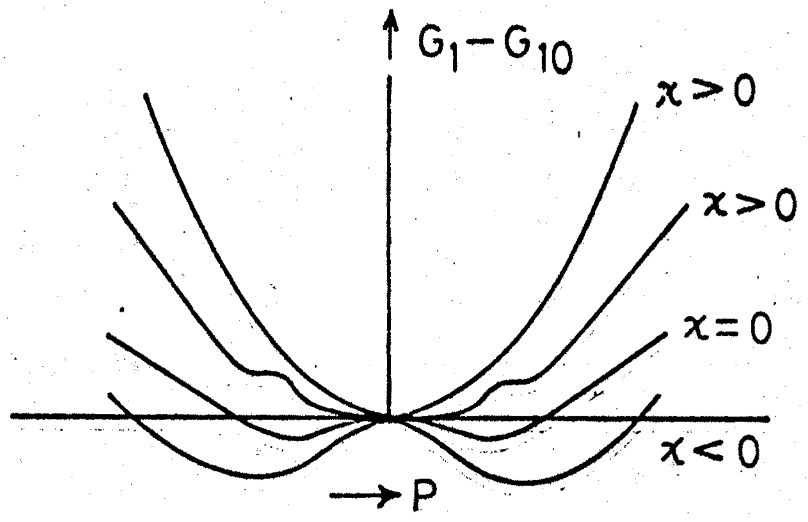

Fig. 1·4 (a) Schematic representation of the free energy as function of polarization for various values of χ for a first-order transition.

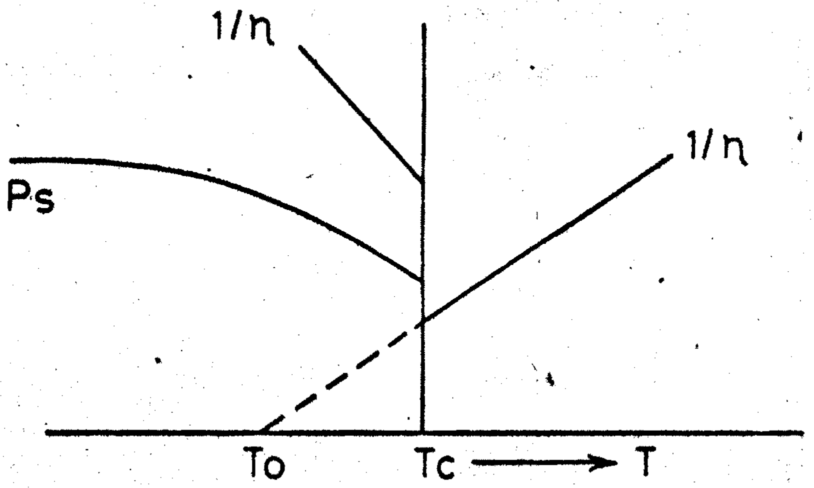

Fig. 1·4(b) Schematic representation of the spontaneous polarization and reciprocal susceptibility near the transition temperature Tc for a first-order transition.

From equation (1.46) and (1.47) it is seen that the reciprocal of the susceptibility in a first-order transition is not zero at the transition temperature T_C, but is a positive

quantity.. Its temperature variation just above and just below the T_C is schematically shown in Fig.1.4(b).

1.8 Applications

Ferroelectric materials have many applications. These materials have strong anomalies in may of their physical properties such as large dielectric constant, piezoelectric and pyroelectric coefficient. The large piezoelectric coefficent make them particularly suitable as transducers. Ferroelectrics have large dielectric constant makes them useful, in ceramic form to make high capacitance and sansors. Ferroelectrics are often better than other materials even for piezoelectric purposes, because the high permitivity values allow the electro-mechanical coupling factor to approach unity. They are used in frequency controls, filters, minature capacity, dielectric amplifers, as slow switches and modulators for laser light.

Non-linear piezoelectric properties can be used in direct amplification of sound and in computer circuits. Ferroelectrics can also be used as matrix stores, as stores with ultrasonic readout systems counters and other bistable elements. The pyroelectric properties of ferroelectric materials make them very suitable for thermal detectors.

1.8.1 Linear properties

Ferroelectric transducere have high coupling constant but comparatively high dielectric losses. The purpose of a transducere is in some case to convert a.c.fields into corresponding mechanical motions, as in ultrasonic generators, loud-speakers or pulse generators for use with some delay lines. In other cases, a transducer uses the piezoelectric effects to convert small motions into electric charges, as in ultrasonic detectors, sprain-gauges, microphones, pickups and devices to measure the extent of vibrations.

1.8.2 Non-Linear Properties

The non-linearities are most marked at low frequencies and near the transition temperature. Ferroelectrics can be used as dielectric amplifer as a low frequency power amplifier. This type of amplifer could be used for remote controls, sterio-system, stabilizer of supplies, audio-frequency amplifers and for d.c. amplifer. Potassium dihydrogen phosphate has large electric-optic effects. Generation of optical harmonics has been therefore carried out with red-laser light incident on KH_2PO_4 (Maker et al) (31).

1.9 Orientation of the present work

Ferroelectrics assume importance since they find applications in electronic and electrical fields. Although ferroelectrics have been extensively studied in theory and in experiment during the last five decads owing to their important devices applications, they continue to arouse interest among the research workers. The scope for ferroelectric is even further broadened in view of the significance of the related phenomena such as piezoelectricity. Electro-optics, pyroelectricity, non-linear dielectrics and liquid-crystals.

Potassium niobates have been studied by using various techniques and reports are available in literature. Data on these materials such as X-ray diffraction, infra-red spectroscopy, E.P.R. and their characteristic dielectric properties are available made by various research workers.

The present work is prompted by the fact that potassium niobate doped with various elements gives rise to new type of ferroelectrics. Also from a chemical and mechanical view point, they are very stable. As regards their practical applications, they exhibit ferroelectric property above room temperature and can be best used in the form of both ceramic crystalline and polycrystalline samples.

An object of the present research investigations on potassium niobates is to prepare these with specifically chosen molar proportions of dopant nickel and iron oxides. The significance of dopants are highlighted by the following studies.

(1) X-ray diffraction and lattice planes determination for the ferroelectric phase of the ceramics at room temperature.

(2) Dielectric hysteresis and determination of coercive field at different temperatures.

(3) Measurement of dielectric constant at different temperatures.

(4) Measurement of d.c conductivity at different temperatures.

(5) Thermoelectric powers and nature of seeback coefficient at different temperatures.

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