CHAPTER-I

: FERROELECTRICS :

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CHAPTER I

FERROELECTRICS

1.1 Introduction:

The ferroelectricity is a new field of dielectrics. Dielectrics are the crystals in which electric fields persist. They offer very high resistance to the flow of electric current. During the last few years, ferroelectricity is expanding fast and extensive investigations on the properties of ferroelectrics have been carried out especially on single crystals. Many of the ferroelectrics like Rochelle Salt, barium titanate, potassium dihydrogen phosphate, triglycine sulfate etc., have a number of properties which make them attractive for use in optical devices, dielectric amplifiers and second harmonic generation.

Historically, the first ferroelectric crystal discovered, has been the Rochelle salt i.e. Sodium-potassium tartrate tetrahydrate, $NaK C_4 H_4 O_6, 4H_2O$, which was known as ' sel de seignette ' after its discoverer. Rochelle salt was reported to have unusual dielectric, piezoelectric and electrooptic properties, Pockel,(1894). Till the end of the first world war no further work on the properties of the material was carried out. Ferroelectricity of Rochelle salt was established by detailed studies by Valasek (1924), who was the first to point out the analogy between the dielectric properties of ferromagnetic materials. It was due to this analogy with ferromagnetism that the phenomenon was named ferroelectricity by Muller (1935).

The second ferroelectric crystal discovered by Bush and Scherrer (1935), was potassium dihydrogen phosphate (KH_2PO_4) considered to be the only ferroelectric crystal. But it was showed that other compounds isomorphous with KH_2PO_4 also were found to be ferroelectric.

Wainer and Salomen,(1943) in United States, Wul and Goldman,(1943) in Russia and Ogawa,(1943) in Japan independently discovered the anamolous dielectric properties of barium titanate ($BaTiO_3$). The ferroelectric properties of this substance were reported simultaneously by Van Hippel and his co-workers (1944) in the United States, and Wul and Goldman (1945 a,b) in Russia. Since the discovery of ferroelectricity in $BaTiO_3$ compounds with the perovskite structure have been studied extensively. These studies have resulted in the discovery of many new ferroelectric materials.

Jona and Shivane (1962) have given a useful table of seventy six ferroelectric crystals which were known upto January 1961. Mitsui et al (1969) have given comprehensive compilation of ferroelectrics and antiferroelectrics, including solid solutions. Structure and property data on a large number of perovskite - type compounds is provided by Glasso (1969).

Recently Subbarao (1972) has compiled in concise form ferroelectric and antiferroelectric materials, known upto 1971. The compilation provides an excellent source of data on the spontaneous polarization and curie temperature of ferroelectric and antiferroelectric materials.

Regarding progress in the theoretical field a number of theories of ferroelectricity have been proposed, but none of them is satisfactory. The first theoretical explanation of properties of Rochelle salt was proposed by Kurchatov (1933). The first molecular theory of ferroelectricity based on the actual crystal structure, to explain the ferroelectric transition in KH_2PO_4, was proposed by Slater (1941), Muller (1935) but forward two phenomenological treatments of Rochelle salt which have proved very successful in correlating its properties and have contributed much to the subsequent theories of ferroelectricit Devonshire (1941, 1951, 1954) has proposed a phenomenological theory of $BaTiO_3$, which explains its behaviour with remarkable success. A general theory of ferroelectricity has not yet been established, although Cochran's lattice dynamical theory (1960, 1961) and Lines statistical theory (1969) have provided for major understanding of ferroelectric phenomena.

1.2 Dielectric Properties of Crystals:

When a flat slab of any solid dielectric is placed in a uniform field E_0, with its normal parallel to the field, the dielectric displacement D in CGS system of units is given by.

$$D = \epsilon_0 E_0 = \epsilon E = E + 4\pi P \qquad ---- \qquad (1.1)$$

Where E_0 and E are field streughts outside and in dielectric.

ϵ_o, ϵ are dielectric constants of surrounding medium and of the dielectric respectively. P is the polarization (electric dipole moment per unit volume). Since the surrounding medium is usually air or vacuum, ϵ_o is taken to be unity. Ignoring spontaneous polarization, the general relation between E and P is,

$$P = n \quad E \qquad ---- \qquad (1.2)$$

Where n is dielectric susceptibility.
In an isotropic cubic system p is always parallel to E.
Then all quantities in above equation are written as scalars.
From equation (1.1), the dielectric constant of an isotropic medium is defined as

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

$$= 1 + 4\pi n \qquad ---- \qquad (1.3)$$

From above equation the susceptibility is related to dielectric constant by

$$n = \frac{\epsilon - 1}{4\pi} \qquad ---- \qquad (1.4)$$

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

$$P_j = n_{jk} \quad E_k \qquad ---- \qquad (1.5)$$

$$_{jk} = 1 + 4\pi n_{jk} \qquad ---- \qquad (1.6)$$

From equation (1.5) we have the following equations due to Kelvin.

$$\left.\begin{aligned} P_1 &= n_{11} E_1 + n_{12} E_2 + n_{13} E_3 \\ P_2 &= n_{21} E_1 + n_{22} E_2 + n_{23} E_3 \\ P_3 &= n_{31} E_1 + n_{32} E_2 + n_{33} E_3 \end{aligned}\right) \text{- - - -} \quad (1.7)$$

corresponding to equation (1.7) we have the following equations for components of displacement.

$$\left.\begin{aligned} D_1 &= \epsilon_{11} E_1 + \epsilon_{12} E_2 + \epsilon_{13} E_3 \\ D_2 &= \epsilon_{21} E_1 + \epsilon_{22} E_2 + \epsilon_{23} E_3 \\ D_3 &= \epsilon_{31} E_1 + \epsilon_{32} E_2 + \epsilon_{33} E_3 \end{aligned}\right) \text{- - - -} \quad (1.8)$$

The subscripts 1, 2, 3 refer to the orthogonal crystallographic X, Y, Z axes respectively. The statements concerning the polarizability and internal field are summerized below. The dielectric behaviour of ferroelectric crystals depends on polarizability and internal field. The actual field in a dielectric varies greatly from point to point, over distances comparable with molecular dimensions. The internal field F, also called the local or molecular field, is defined as that field in a very small spherical cavity from which the molecules have been removed.

According to Lorentz equation

$$F = E + r P + E (1 + \gamma n) \quad \text{- - - -} \quad (1.9)$$

Where E = statistical field in the dielectric

P = polarization.

r = internal field constant in an isotropic medium.

$r = \frac{4\pi}{3}$

But in the crystal of the lower symmetry r differs from $4\pi/3$, the magnitude is the same. This r is independent of temperature. In the field, F, each molecule becomes polarized and acquires the dipole moment P. The polarizability of the atom is defined by

$$p = \alpha F \qquad - - - - \qquad (1.10)$$

The polarizability is the 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

$$P = \sum_j N_j P_j = \sum_j N_j \;{}_j F_j \qquad - - - - \qquad (1.11)$$

Where

N_j = concentration of atoms j

α_j = polarizability of the atoms j and

F_j = the local electric field at atoms sites j.

Taking local field as

$$F = E + \frac{4\pi}{3} P \qquad - - - - \qquad (1.12)$$

We get

$$P = \sum_j N_j \alpha_j \left(E + \frac{4\pi}{3} P \right) \qquad - - - - \qquad (1.13)$$

$\therefore$ dielectric susceptibility

$$n = \frac{P}{E} = \frac{\sum_j N_j \alpha_j}{1 - \frac{4\pi}{3} \sum_j N_j \alpha_j} \qquad ---- \qquad (1.14)$$

Since $= 1 + 4\pi \, n$

in CGS units we get

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \sum_j N_j \alpha_j \qquad ---- \qquad (1.15)$$

This is well known Clausicus- Mossotti relation. This equation relates the dielectric constant to the electronic polarizability. The total polarizability is usually separated into three parts:

i) Electronic polarizability (α_e) :- This is due to displacement of electrons within the atoms or ions.

ii) Atomic or ionic polarizability (α_a):- This is due to displacements of atoms or ions within the molecules.

iii) Dipolar polarizability (α_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. (1.1).

At frequencies to the electronic transition between different energy levels in the atom i.e. at visible, ultraviolet and X-ray frequencies, there is a fall of α_e. The dielectric constant at optical frequencies is entirely due tc the electronic polarizability. The atomic and dipolar contributions are small at high frequencies. In the optical frequency range the dielectric constant is given by

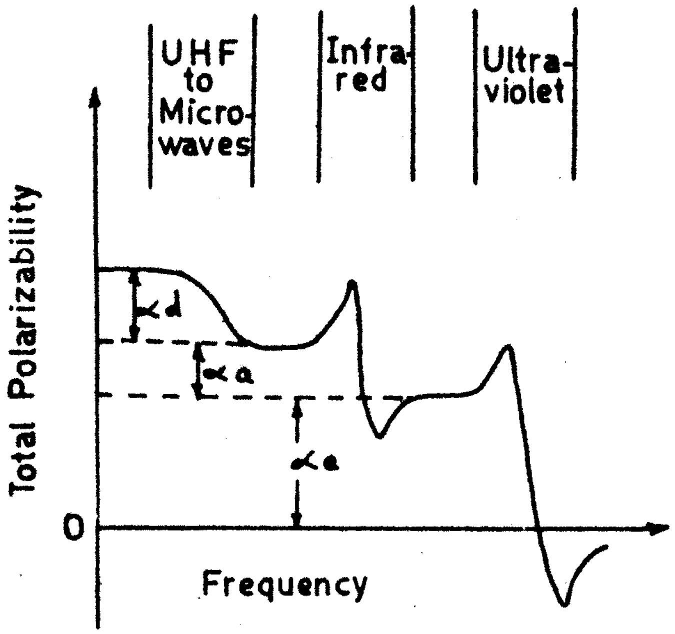

Fig. 1·1 : Schematic representation of frequency dependence of the several contributions to the total polarizability.

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \sum_j N_j \alpha_j \quad \text{(Electronic)} \quad - \quad (1.16)$$

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 Ferroelectric Materials and Their Characteristic Properties:

Ferroelectrics are materials which possess spontaneous electric polarization P_s which can be reversed by applying a suitable electric field (E). The process is known as switching and is accompanied by hysteresis as shown in Fig. (1. 2).

In many ways these materials are electrical analogues of ferromagnetics in which the magnetisation I may be varied by a magnetic field H . In some practical ways ferroelectrics differ from ferromagnetics and also in their fundamental mechanisms.

Ferroelectrics are all solids and are nonmetallic, the properties of ferroelectrics are most simply studied when the material is in a single crystal form. Ferroelectrics should not be confused with ferrites which are nonmetallic ferromagnetic materials. We know the well known relations between D, E and P.

$$D = E + 4\pi P \quad ---- \quad (1.17)$$

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

$$\epsilon = 1 + 4\pi n \quad ---- \quad (1.18)$$

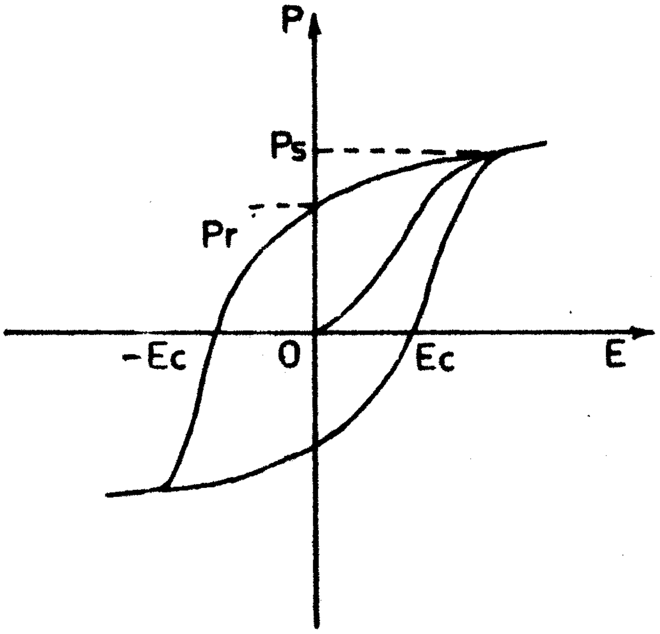

Fig.1·2: Schematic representation of ferroelectric hysteresis loop.

Ps: Spontaneous polarization.

Pr: Remanent polarization.

Ec: Coercive field.

Where

ϵ = dielectric constant

n = dielectric susceptibility.

In some ferroelectrics the temperature dependence of the dielectric constant above the transition temperature can be described fairly by a simple law called the Curie-Weiss law, from its ferromagnetic analogue

$$\epsilon = \epsilon_0 + \frac{C}{T - T_C} \qquad ---- \qquad (1.19)$$

Where C = Curie constant

T_C = Curie-Weiss temperature.

In the vicinity of Curie-Weiss temperature, the dielectric constant becomes very large and the relation between dielectric constant and susceptibility can be approximated by

$$\frac{\epsilon}{4\pi} \simeq n \qquad ---- \qquad (1.20)$$

Polar constants have the property that

$$\int\int\int \rho(\vec{r}) \quad \vec{r} \quad dx \quad dy \quad dz \quad \neq 0$$

Where (r) is the combined nuclear and electronic charge density. Such crystals possess spontaneous electric polarization P_S in the absence of an electric field.

Ferroelectric crystals possess an additional property that the polarization can be reversed by the application of an electric field. Thus ferroelectric crystals can be considered as a subgroup of pyroelectrics. Therefore, it is a necessary condition for a ferroelectric crystal to belong to any one of the ten polar classes in its ferroelectric phase, but not a sufficient condition as a reversibility of the polarity must also occur.

A ferroelectric crystal is thus defined as a pyroelectric crystal with reversible polarization. The polar structure of a ferroelectric crystal is a slightly distored non-polar structure, and this fact gives rise to reversibility of the polarization. The relation between polarization and applied field shows hysteresis effects.

With increasing temperature ferroelectricity disappears above a certain temperature called the transition temperature. At the transition temperature the crystal undergoes a transition from the polar state to the non-polar state. As a rule, the low temperature phase is a polar phase and high temperature phase is a nonpolar phase. The phase transition can be of the first order or of a higher order (usually second). 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 or energy. Thus in the second order transition there is no release of 'Latent heat'; but the expansion coefficient and the specific heat shows anomaly extending over a finite temperature range. Other properties such as the polarization, shows discontinuity in a first order change but not in a second order change.

The properties presented by the most of the ferroelectrics are as follows.

1) They exhibit a dielectric hysteresis loop between polarization and applied electric field below a certain critical temperature. This temperature is called ferroelectric transition temperature.

2) They have a ferroelectric domain structure which may be visible in polarized light.

3) 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.

4) They possess a pseudosymmetric structure. In the ferroelectric state the structure belongs to the polar class.

5) They have a transition at the Curie temperature to form structure of higher symmetry.

6) The curie temperature is raised by application of a biasing field or a hydrostatic pressure.

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

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

1.4 Spontaneous Polarization:

The existence of dielectric hysteresis loop indicates spontaneous polarization P_s. The experimental methods for observation of hysteresis on the screen of a cathode ray oscilloscope are based on the Sawyer and Tower circuit. The hysteresis loop is shown in Fig. (1.2). The linear extrapolation from the saturation region to zero field gives the spontaneous polarization P_s. The intercept on polarization axis is P_r called remanent polarization and the intercept on the E - axis gives the coercive field. The total polarization of the ferroelectric in the saturation field OM is represented by the intercept OL. The main defect of the Sawyer and Tower (1939) circuit is the phase difference introduced between the applied field and polarization of the crystal. Because the impedance of the crystal is variable. The circuit has been modified by Muller. Other methods which are commonly used for measuring the magnitude of P_s are polarity reversal techniques, charge integration techniques, pyroelectric measurement using calibration for scaling. The last technique is also used to study the temperature dependence of P_s. The nature of temperature dependence of P_s is governed by the type of phase transition. In a ferroelectric crystal which undergoes the first order phase transition, P_s suddenly falls to zero at the transition temperature. The transition in $BaTiO_3$ is an example of the first order transition. In a ferroelectric crystal which undergoes second order phase transition, P_s decreases continuously to zero at the transition temperature. The transition in triglycine sulfate is an example of the second order transition.

1.5 Classification of Ferroelectrics:

In recent years the phenomenon of ferroelectricity has been discovered in a large number of crystals. As investigations in recent years have shown that ferroelectricity is a more common phenomenon that had been considered for a long time. Hence the classification of these materials has become very difficult. However, classification of ferroelectrics has been proposed according to different criteria as follows.

1) Crystal Chemical Classification:

According to this classification the ferroelectric compounds are divided into two groups. The first group comprises hydrogen bonded crystals, such as KH_2PO_4, Rochelle salt, triglycine sulfate. The second group comprises the double oxides, such as $BaTiO_3$, $KNbO_3$, $cd_2Nb_2O_7$, $PbNb_2O_6$ etc.

2) Classification according to the Number of Directions allowed to the Spontaneous Polarization:

This classification also divides the ferroelectric crystals into two groups:

i) The first group includes those ferroelectrics that can polarize along only one axis, such as Rochelle Salt,

KH_2PO_4 type ferroelectrics, $(NH_4)_2SO_4$, $(NH_4)_2BeF_4$, colemanite, $CaB_3O_4(OH)_3H_2O$, thiourea etc.

ii) The second group includes those materials that can polarize along several axes that are equivalent in nonpolar phases. e.g. $BaTiO_3$ type, $Cd_2Nb_2O_7$ $PbNb_2O_6$ 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.

3) Classification According to the Existence of Centre of Summetry in the Point Group of their Nonpolar 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, KH_2PO_4 type ferroelectrics. The second group includes those ferroelectrics which are not piezoelectric in unpolarized phase, such as $BaTiO_3$, $CdNb_2O_7$, $PbNb_2O_4$, $CaB_3O_4(OH)_3H_2O$ etc.

This classification is particularly useful for the theromodynamic treatment of the ferroelectric transition.

4) Classification According to the Nature of the Phase Change at the Curie Point:

According to this classification ferroelectric crystals are divided into two groups. (i) order - disorder group (ii) dispacirie group.

The first group includes crystals with hydrogen bonds such as $KH_2 PO_4$ and isomorphous salts, triglycine sulpate and probably some of the alums. The ferroelectrics in this group undergo a transition of order disorder type. In these crystals the motion of the protons is related to their ferroelectric properties such as $KH_2 PO_4$.

The displacive group of ferroelectrics includes ionic crystals whose structures are closely related to the perovskite and ilmenite structures, such as those of $Ba TiO_3$ and most of the double oxide ferroelectrics. The simplest ferroelectric crystal of this group is $G_e T_e$ with sodium chloride structure. This classification is practically equivalent to that which is done on the basis of the existence of permanent or induced dipoles in the nonpolar phase of the crystals.

5) Classification According to the Predominant Nature of atomic Displacements required by polarity reversal:

Abrahms and Keve (1971) have examined the properties of ferroelectric crystals and have divided into three classes according to the predominant nature of the atomic displacements required by polarity reversal.

The one dimensional class includes those ferroelectric crystals in which the atomic displacement vector (Δ) and all Locii followed by the atoms during reversal, are linear and parallel to their polar axis. One dimensional ferroelectric are restricted to the point groups 2, 2 mm, 3, 3 m, 4, 4 mm etc. Examples are, $Ba TiO_3$, $Pb TiO_3$, $K NbO_3$, $Li NbO_3$, $Sb SI$ etc. The two dimensional class includes those ferroelectric crystals in which the atomic displacement vector (Δ) or the actual Locii (L) followed by atoms during reversal lie in parallel phases containing the same polar direction. These are four point groups that satisfy the strict symmetry requirements for this class; m, mm2 , 4 mm, 3 m and 6 mm. Examples are, $Ba COF_4$, $Ba ZnF_4$, HCl, HBr, $NaNO_2$.

The three dimensional class includes those ferroelectric crystals in which the individual displacement vector (Δ) and the locii followed by atoms during reversal, have essentially random orientations. Examples are, $B - Gd_2 (NO_4)_3$, $(NH_4)_2 SO_4$, KH_2PO_4 , $Ca B_3 O_4 (OH)_3 H_2O$ etc.

1.6 Theories of Ferroelectricity:

Many attempts were made to explain ferroelectricity in crystals. The theories proposed so far are completely satisfactory and the one which is most promising is due to Cochran based on the lattice dynamics. A description of the thermodynamic theory of ferroelectricity and a brief review of the model theories are given below.

1.6 (a) Thermodynamic Theory:

Thermodynamic theory is very general in its scope and is independent of any particular model. Thus it leads to quite general conclusions. Although such a theory does not provide physical mechanism which gives rise to ferroelectric properties of a given material. It provides a framework which can be used in connection with any particular model. The pioneering work in formulating a thermodynamic theory for the case of Rochelle Salt has been done by Muller and Cady (1935). The theory can be applied to $KH_2 PO_4$ type ferroelectrics.

The thermodynamic treatment of $Ba TiO_3$ type ferroelectrics is somewhat different, since these crystals have more than one ferroelectric axis and are not piezoelectric in paraelectric phase. A thermodynamic theory of such crystals has been developed mainly by Devonshire (1954) and Ginzburg. The 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 state. Therefore, in the polarized phase the crystal is described by the same free energy function.

3) The anomolous piezoelectric and electric properties are considered to be a result of the anamolous dielectric behaviour. Thus the coefficient of P^2 in the free energy functions bear the significant temperature dependence.

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

5) The free energy of the crystal is expressed by the Gibb's function.

$$G_i = U - T_B + X_i S_1 + E m P m - - - \qquad (1.21)$$

Where U is the internal energy of the crystal under external stress, T the temperature, S the entropy, $_i$ the $_i$ the component of mechanical stress, P_m is the m th component of electrical polarization. The differential form of this function is

$$d (G_i) = - S dT + X_i d s , + E_m d P_m \qquad (1.22)$$

The index i can take six values. For compressions or expansions i = 1, 2, 3 and for shear, i = 4, 5, 6. For a stress free crystal ($X * _0$), 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_{10} 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 $= o$ is given by the equation.

$$G_1 - G_{10} = \frac{1}{2} \chi^1 P^2 + \frac{1}{4} \beta' P^4 + \frac{1}{6} \gamma' P^6 \qquad (1.23)$$

Where dashes indicate that the coefficients apply only to stress free crystal 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 X^1. The meaning of X' can be seen from the following consideration. Let a small electric field be applied to the crystal.

Then under zero pressure, from equation (1.23)

$$d G_1 = - s \, dT + E \, dP$$

$$\text{or} \quad E = \left(\frac{\partial G_1}{\partial P} \right)_T \qquad ---- \qquad (1.24)$$

Above the transition temperature, the polarization is small, for small electric fields. Therefore, for T T_c all terms except first on the right hand side of the equation may be neglected, then

$$E = \left(\frac{\partial G_1}{\partial P} \right)_T \equiv \chi^1 P \qquad ---- \qquad (1.25)$$

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

$$\frac{\delta E}{\delta P} = \frac{4\pi}{\epsilon - 1} = \frac{1}{n} \qquad ---- \qquad (1.25)$$

$$\therefore \quad \chi^1 = \frac{4\pi}{\epsilon - 1} = \frac{1}{n}$$

This equation shows the coefficient X^1 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.

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

So that $\chi^1 = \dfrac{T - T_0}{C}$ ---- (1.27)

Where C is the Curie constant and

T_0 - the Curie-Weiss temperature.

Hence equation (1.23) can be written as

$$G_1 - G_{10} = \frac{1}{2} \left(\frac{T - T_0}{C} \right) P^2 + \frac{1}{4} \beta^1 P^4 + \frac{1}{6} \gamma' P^6 \quad (1.28)$$

From differentiation, We obtain the equations for applied field and dielectric constant

$$E = \left(\frac{\partial G_1}{\partial P} \right)_T = \left(\frac{T - T_0}{C} \right) P + \beta^1 P^3 + \gamma^1 P^5 \quad (1.29)$$

and

$$\frac{1}{n} = \frac{4\pi}{\epsilon - 1} = \left(\frac{T - T_0}{C} \right) \text{[illegible]} + 3\beta^1 P^2 + 5 \gamma^1 P^4 \quad (1.30)$$

<u>Spontaneous polarization:</u>

In the thermal equilibrium $\left(\dfrac{\partial G_1}{\partial P} \right)_T = 0$ so that spontaneous polarization P_s for zero applied field satisfies the equation

$$0 = \chi^1 P_s + \beta^1 P_s^3 + \gamma^1 P_s^5 \quad \text{-- --} \quad (1.31)$$

it follows that the value of P_s which gives extremum of G_1, are given by

$$P_s = 0$$

$$x^1 + \beta^1 P_s^2 + \gamma^1 P_s^4 = 0 \quad \text{- - - -} \quad (1.32)$$

From equation (1.29) we have

$$\left(\frac{\partial^2 G_1}{\partial P^2}\right)_T = X^1 + 3\,\beta^1 P^2 + 5\,\gamma^1 P^4 \qquad (1.33)$$

If X^1 , β^1 , ^{1} are all positive, $P_s = 0$ gives a positive value of $\left(\frac{\partial^2 G_1}{\partial P^2}\right)_T$. 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 X^1 becomes negative, G_1 would b be maximum for $P_s = 0$ because in this case $\left(\frac{\partial^2 G_1}{\partial P^2}\right)_T$ is a negative quantity. When X^1 is negative, the equation (1.23) gives at least one nonvanishing value of P_s for which $\frac{\partial^2 G^1}{\partial P^2}$ would be positive quantity.

This shows that in this case G_1 would be minimum i.e. spontaneous polarization would occur. Consequently continuous variation of X^1 from positive to negative values changes a stable paraelectric state ($X^1 > o$) to a stable ferroelectric state ($X^1 < o$) . At the transition temperature T_C between these states we have $X^1 = o$. Two palar cases in the vicinity of transition temperature can be considered.

1) <u>Second Order Transition:</u>

If the coefficients β^1 and γ^1 are positive and X^1 varies from positive to negative as the temperature is lowered. We obtain free energy curve as shown in Fig. (1.3b). The corresponding

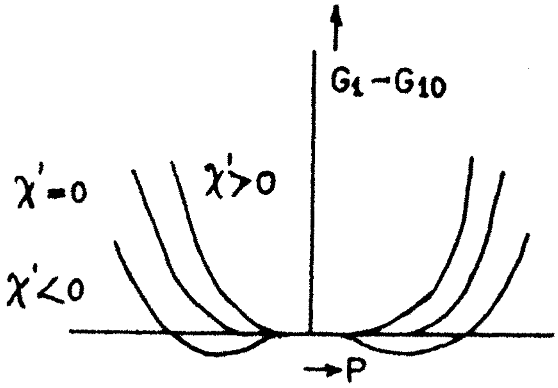

Fig.1·3(a): Schematic representation of the free energy as function of polarization for various values of χ' for a second-order transion.

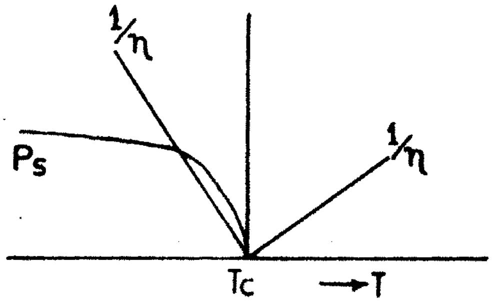

Fig.1·3(b): Schematic representation of the spontaneous polarization and reciprocal susceptibility near the transition temperature T_c for a second-order transition.

spontaneous polarization as a function of temperature is shown in Fig.(1.3b). Assuming that γ^1 is negligible the spontaneous polarization is obtained from equation (1.31) which becomes

$$X^1 P_s + \beta^1 P_s^3 = o \qquad - - - - \qquad (1.34)$$

So that either $P_s = o$ or

$$P_s^2 = \frac{-X^1}{\beta^1} = \frac{T - T_o}{C\beta^1} = \frac{T_o - T}{C\beta^1} \qquad (1.35)$$

For $T \gg T_c$ the only real root of equation (1.34) is at $P_s = \rho$, because C and β^1 are positive. Thus T_o the curie temperature is equal to T_c. For $T < T_c$ the spontaneous polarization is given by

$$P_s = \left(\frac{T_c - T}{C\beta^1}\right)^{\frac{1}{2}} \qquad - - - - \qquad (1.36)$$

This equation shows that P_s is a continuous function of temperature below T_c and it decreases continucusly to zero at T_c (see Fig.1.3a). A transitim of this type is not associated with Latent heat but with a discontinuity in the specific head and is called a second order phase transition. For second order phase transition the susceptibility and dielectric constant above the curie temperature T_c are given by

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

The entropy associated with spontaneous polarization can also be found as follows:

$$S = -\left(\frac{\delta G_1}{\delta T}\right)_P = S_o - \frac{1}{2} P^2 \left(\frac{\delta X^1}{\delta T}\right) - \frac{1}{4} P^4 \left(\frac{\delta X^1}{\delta T}\right) \qquad (1.38)$$

Where S_o is the entropy of the unpolarized state. Assuming that the third term in above equation is negligible, we obtain,

$$S = S_o = -\frac{1}{2} P^2 \left(\frac{\delta X^1}{\delta T}\right) = -\frac{1}{2} P^2 \frac{\delta}{\delta T}\left(\frac{T - T_o}{C}\right)$$

$$S - S_o = -\frac{1}{2}\left(\frac{P_s^2}{C}\right) \qquad ---- \qquad (1.39)$$

Since P_s is a continuous function of temperature in a second order transition and since the slope of P_s^2 has a discontinuity at $T - T_o$, there should be a discontinuity in the specific heat at the transition temperature.

First Order Transition:

It has been seen that the condition for the occurance of spontaneous polarization is that X^1 should be negative. If at the same time β^1 is positive, there is a second order transition. Let us consider the case for which β^1 is negative as temperature is lowered. In this case free energy curves are shown in Fig. (1.4a) and the spontaneow polarization is shown in Fig. (1.4b). A transition from the nonpolarized state to a spontaneously polarized state will now occur when the minimum at the free energy corresponding to $P_s = o$ becomes equal to minimum associated with $P_s \neq 0$. In the absence of an external field the spontaneous polarization satisfies the equation and also the condition,

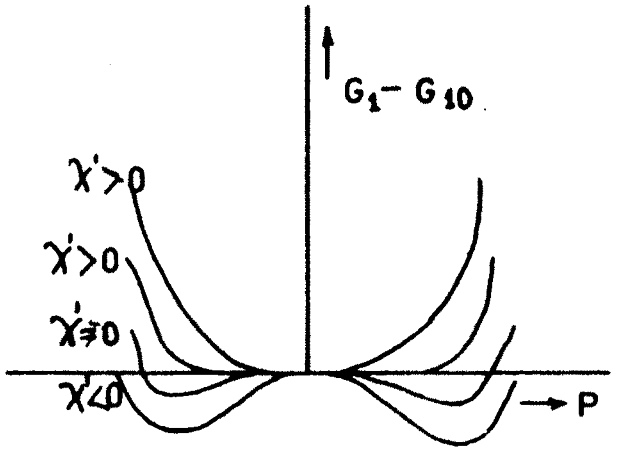

Fig.1·4 : Schematic repesentation of the free energy as function of polarization for various values of χ' for a first order transition.

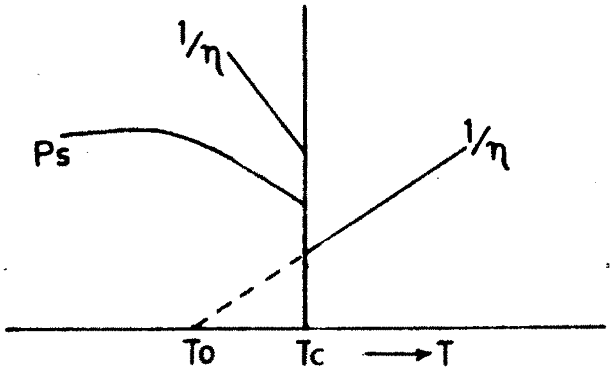

Fig.1·4(b): Schematic representation of the spontaneous polarization and reciprocal susceptibility near the transition temp. Tc for a first order transition.

$$G_1 = G_{10}$$

Therefore we have

$$\frac{1}{2} X^1 \; P_s^2 + \frac{1}{4} \; \beta^1 \; P_s^4 \; + \frac{1}{6} \gamma^1 \; P_s^6 \quad = 0 \qquad (1.40)$$

From this equation and equation (1.31) we can find the relations:

$$P_s^2 = - \frac{3}{4} \left(\frac{\beta^1}{\gamma 1} \right) \qquad ---- \qquad (1.41)$$

$$X^1 = \frac{3}{16} \left(\frac{\beta^{12}}{\gamma 1} \right) \qquad ---- \qquad (1.42)$$

$$P_s^4 = 3 \left(\frac{X^1}{\beta^1} \right) \qquad ---- \qquad (1.43)$$

Equation (1.40) shows that the spontaneous polarization is discontinuous at the transition temperature. According to equation (1.18) the entropy will also be discontinuous at T_c and there will be latent heat i.e. the transition is of the first order. By the way of calculation n , the susceptibility can also be obtained as

$$n = \frac{\epsilon - 1}{4\pi} = \frac{C}{4(\,T - T_o)} \qquad ---- \qquad (1.44)$$

The reciprocal of susceptibility is not zero in a first order transition, but it is a positive quantity. Its temperature variation just above and just below T_c is shown in Fig.(1.4).

1.6(b) 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 regorous 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 $Ba\ TiO_3$ crystal, they have suggested that stable position for the 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 Ti^{+4} is in any of these positions, the unit cell would have a dipole moment.

Taynes (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 $Ti\ O_6$ octahedra are considered. The theory is satisfactory for determining the entropy change, but it predicts infra-red absorption line at nearly 10 μ, wavelength, which is not detected.

Devonshire's model theory (1949) considered the dipole of an atom vibrating in the field of its neighbours. 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 electronic polarization and titanium ion has an ionic polarization.

Megaw (1952, 1954) has suggested that directional covalent bonding is of primary importance in the ferroelectricity of Pb TiO_3 and autiferroelectricity of $PbZrO_3$. The (110) displacement of Pb in $PbZrO_3$ indicate that the Pb ion can get displaced in directions other than a four fold axis, while in Pb TiO_3 the Pb ions get displaced along the four fold axis at all temperatures from the Curie point (490°C) to that of liquid helium temperature.

1.6(c) 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 modes. 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 thro' 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 Ba TiO_3 . He has estimated the dielectric crystal constant and the spontaneous polarization, calculated by Cochran, P_s of Ba TiO_3 at the Curie temperature as $= 1.4 \times 10^4$ and $P_s = 19.5\ \mu$ coulomb/cm^2 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 quite satisfactory, many problems of Ba TiO_3. The interesting new result of the theory is the prediction of the absolute value of the frequency WT of the fransverse optical mode with wave vector zero for perovskite materials.

$$T = (2 - 3) \times 10^{11} \text{ cps for Ba } TiO_3$$

The frequency lies in the millimeter wavelength range. For this reason an experimental verification of the theory is difficult. Recently, investigations have been made in the infra-red part of the spectrum. Infra-red studies by Ballantyne (1964) on Ba TiO_3 above the Curie temperature, show that within the experimental error, the results are in agreement with Cochran's theory. Similar results also have been reported in other perovskite ferroelectrics. Cochran's theory is supported along by experimental observations that there is fall of the frequency of the transverse optical mode as the curie temperature is reached from above, and that no dielectric relaxation occurs for several perovskite ferroelectrics upto 10^{11} cps.

1.7 Ferroelectric Domains:

The early evidence of ferroelectric domains was based on indirect method which are now of historical importance only. The first direct optical observation of domains in KH_2PO_4 with polarized light, was made by Zwicker and Schesser (1944). The domain structure in single crystals of Ba TiO_3 was reported for the first time almost simultaneously by Kay (1948), Blattner et al (1948), Mathias and Van Hipple (1948), and Mitsui and Furuchi (1953). Marutalae (1952) made direct observations of the domain structure in Rochelle Salt. Broad surveys of domain observation and domain walls are given in the publications of Megaw (1957), Kanzig (1957). Jona and Shirane (1962) Sachse (1956) and Zheluder (1971).

In general, a ferroelectric crystal consists of domains, which are regions of homogeneous polarization that differ only in the direction of the polarization. Within a domain in a ferrelectric crystal all the spontaneously polarized unit cells are oriented indentically. Consequently, each domain has a macroscopic spontaneous polarization. The directions of spontaneous polarization of neighbouring domains in a ferroelectric crystal make definite angles with one another. The demarkation between two domains is called a domain wall. A domain wall is usually considered to be so thin that it has a much smaller valume 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 crystal may contain a number of domain regions 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. The crystal lattice remains coherent through a wall, although it may be distorted by wall. In spite of this coherence, the directions with walls of a particular type, depends on the crystal summetry. Adjacent ferroelectric domains are related in a manner which is quite similar to the relationship of crystallographic twins, and hence the domain formation may be called "twining".

The reasons for the occurance of domains in a ferroelectric crystal are now fairly well understood. Above the Curie temperature, i.e. in the paraelectric phase the direction along which the polarization is to occur cannot be a unique direction. But even in the ferroelectric phase, there must be at least two equivalent directions directions along which P_s can occur with the same probability. Since at the curie temperature different regions of the crystal can polarize in different directions, the paraelectric crystal consists of uniformly polarized regions. Below T_c the crystal must belong by its summetry, to one of the pyroelectric casses, and the domains differ in the direction of P_s. Therefore, when a ferroelectric crystal is cooled below the curie temperature, in the absence of an external electrical and mechanical stress, it breaks up into domains of different orientation. If means that from the crystallographic point of view, the domain structure is identical with twining structure. In contrast to ordinary twining, twining in the case of ferroelectrics arises from a common and uniform paraelectric phase. Twining determines the nature of the polarization reversal process, and it influences some of the crystal properties by the pressure of walls between individual domains. The mutual relationship between two components of a twinned crystal is described by (a) the twin operation which determines the mutual orientation of the components and (b) the orientation of the composition plane, which in ferroelectrics is identical with domain wall.

Twin operations of ferroelectric domains have been discussed by Zheludev and Scuvalov (1956,1957).

The free energy of a crystal is regarded as a function of temperature, stress and polarization. When a ferroelectric crystal is cooled below the curie temperature in the absence of the external mechanical and electrical stresses, it splits up into domains of different orientation. Therefore, the free energy of the crystal with domains is lower than the free energy of the crystal with a single domain. Thus the equilibrium arrangement of domains in a ferroelectric crystal is that in which the free energy of the crystal is least. The contributions to the free energy that can be reduced by the formation of domains are many in number. The condition for minimum depolarization energy with respect to a wall may be used to determine the stable orientation of the domain wall. A calculation based on simplification shows that the stable orientation of the wall is in the direction of the adjacent domain. The orientation of domain walls can be investigated by many methods. Recently, Fousek and Janovec (1969) have formulated mathematical conditions for determining the orientations of domain walls in twin ferroelectric crystals. The mathematical treatment makes it possible to find all permissible walls in any infinite ferroelectric crystal.

1.8 Applications:

Ferroelectrics have been used for many years in devices requiring piezo-electricity such as transducers. Ferroelectrics are often better than other materials even for piezoelectric purposes, because the high permitivity values allow the electromechanical coupling factor to approach unity. Ferroelectrics are also used in capacitors because of their high permitivity values. They are used in frequency controls, filters, miniature capacitors, thermal meters, modulating devices, frequency multipliers and dielectric amplifiers and as switches and modulators for Laser light.

It is not always convenient to keep the ferroelectric crystal in an oven or crystal in order to maintain the required value of a given property. Therefore, the efforts have been made to build materials such that the required value of the property occurs at room temperature. This control of properties can be achieved by varying the proportions in solid solutions. We know that similar control of properties may be achieved by means of suitable additives during the manufacture of ceramics. This view was given by Mcquarrie (1955). Nonlinear piezoelectric properties can be used in direct amplification of sound, and in computer circuits. Ferroelectrics can be made use of matrix stores as stores with ultrasonic readout and in switches, counters and other bistable elements.

(a) Linear Properties:

Ferroelectric transducers have high coupling constant, but comparatively high dielectric losses. 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 atomic delay lines. In other cases, a transducer uses the piezoelectric effects to convert small motions into electric changes, an in ultrasonic detectors, straingauges, microphones, pickups and devices to measure the extent of vibrations. Such devices can be small, with linear dimensions of 1 mm or less.

Ferroelectrics have been suggested as bolometers for infra-red detectors since they have a response over a wide spectral region.

(b) Non-Linear Properties:

Ferroelectric condensers have been used for tuning in superhets and for frequency modulation. The nonlinerities are most marked at low frequencies and near the transition temperature. Ferroelectrics can be replaced by Varactor diodes. Barium strontium titanates could be used for harmonic generation at millimeter wavelength also for microwave harmonic generation at 3 to 9 X 10^9 cps.

A Prague team has reported the use of TGS (Triglycine sulfate) as thermoaltostic, nonlinear dielectric element (Tandel).

It can be used as dielectric amplifier and as low frequency power amplifier. This type of amplifier could be used for remote controls, servo-systems, stabilization of supplies and auto frequency amplification. KH_2PO_4 has been used for large electro-optic effects. Generation of harmonics has been carried out with red-laster light incident on potassium dihydrogen phosphate. Considerable intensities has been reached in certain directions (Maker et al, 1962).

1.9 Orientation of the Present Work:

Ferroelectricity is one of the interdisciplinary fields of research which needs to be tackled in physical sciences, engineering and technology. Although ferroelectrics have been extensively studied in theory and in experiment, during the last six decades owing to their important device applications. The theory of ferroelectricity continues to arouse interest among the research workers especially because they hold promise in diverse new areas of technology and their understanding is not yet complete. The scope for ferroelectrics is even further broadened in view of the significance of the related phenomena such as ferroelasticity, magnetoelesticity, electro-optics, nonlinear dielectrics and liquid crystals.

Barium titanate is the most extensively investigated ferroelectric material. Barium titanate has been studied by using various techniques such as X-ray diffraction, neutron diffraction, infra-red spectroscopy, Raman spectroscopy, N.M.R., E.P.R. electron microscopy and their characteristic properties have been investigated by various research workers.

Lead titanate, calcium titanate, strontium titanate are the materials belonging to the perovskite family of ferroelectrics similar to barium titanate. It is interesting to study these crystals and their solid solutions from the view point of physicists, because the structure is far simpler than the other ferroelectrics. Thus the study of these solid solutions offers a great promise for a better understanding of the ferroelectric phenomena. Also from chemical and mechanical view point they are very stable as regards their practical applications. Since they exhibit ferroelectric properties at and above room temperature and can be prepared and used in the ceramic form.

Therefore, the aim of our present work is to prepare solid solutions of (Pb TiO_3 and Sr TiO_3), and (Pb TiO_3 and Ca TiO_3) and to study the following properties.

1) Dielectric hysteresis loop.
2) Solid state battery formation.
3) Second harmonic generation and Tandel effect.

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