CHAPTER - I

FERROELECTRICS

1.1 INTRODUCTION

Ferroelectricity is one of the most interesting and interdisciplinary subject, which encompasses Physics, Chemistry, Crystallography, Biology, Ceramics, Computer Science,Mathematics, Statistics, Communications, Mechanical and Electrical Engineering. In our sphere of interest ferroelectrics have a large number of applications in various fields. Applications involving switching-complex operation are piezoelectric devices, optic devices and TANDEL. While applications involving switching - complex structure are electroluminescent devices, photoconductor devices and semiconductor devices.Similarly non-switching applications are capacitors, thermisters, artificial gems and electrooptic, non-linear optic, photorefractive, pyroelectric, piezoelectric, elastooptic applications. Due to this variety of applications, the Physicist, the Crystallographer, the Ceramicist, the Chemist, the Mechanical and Electrical Engineers all have a vital interest in ferroelectrics.

The ferroelectricity is having word 'ferro' which had been borrowed from ferromagnetism. Ferro means iron, but there is no iron in ferroelectrics. Theories of ferroelectricity and ferromagnetism are totally different, but there is analogy between them, e.g. both materials possess domains, exhibit hysteresis loops and show Curie-Weiss behaviour near their phase transition temperatures. Ferroelectrics are defined by different ways as :-

- They are non-mettalic, non-magnetic and non-centrosymmetric solids, whose direction of spontaneous polarization (Ps) can be changed by an applied electric field.
- They are piezoelectrics, pyroelectrics.
- They are insulators, but doping has added semiconduction to their properties.
- They are H-bonded crystals or double. oxides.
- Either they are having spontaneous polarization along single axis or along several axes.
- They are either order-disorder type or displacive type.

1.2 HISTORICAL DEVELOPMENT

Historically, the first ferroelectric crystal discovered, has been the Rochelle salt i.e. sodium-- potassium tartrate tetrahydrate ($NaKc_4H_4O_6$-$4H_2O$). Rochelle salt was prepared by Seignette (1655) at La Rochelle in France. So it is also known as 'Seignette Salt.' Curie brothers(1880) studied piezoelectric property of Rochelle salt. The piezoelectric and electro-optic effects were observed by Pockels (1894). Valasek (1921) found analogy between ferroelectricity and ferromagnetism and because of that he recognized ferroelectric property of Rochelle salt. Mueller (1935) named the phenomenon as ferroelectricity. Busch and

Scherrer (1935) discovered ferroelectricity in potassium dihydrogen phosphate (KH_2PO_4). The properties of KH_2PO_4 were then studied by the Zurich group. Slater (1941) published a theory of the phase transition of KH_2PO_4, which stimulated interest and inspiration in ferroelectricity for many scientists. Wainer and Saloman (1942) in the United States, Wul and Goldman (1943) in U.S.S.R and Ogawa (1944) in Japan independently discovered the anomalous dielectric properties of barium titanate ($BaTiO_3$). The ferroelectric activity of $BaTiO_3$ was confirmed independently by Von-Hippel and his co-workers (1944) and Wul and Goldman (1945 a,b). Since the discovery of ferroelectricity in $BaTiO_3$ compounds with perovskite structure have been studied extensively, these studies have resulted in the discovery of several ferroelectric titanates ,niobates and tantalates particularly by Matthias (1949). The ferroelectricity in lead titanate ($PbTiO_3$)was reported independently by Shirane et al (1950) and Smolenskii (1950). Lead titanate and several ceramics of isomorphous oxides possess some of the most interesting properties such as dielectric, piezoelectric and electrical, which are more significant from the application point of view.

Jona and Shirane (1962) have given an 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 known upto 1968 in Landolt-Bornstein tables. The structure and property data on a large number of perovskite type compounds is provided by Galasso (1969). Subbarao (1972), has compiled in concise form ferroelectrics and antiferroelectrics known upto 1971. This provides an excellent source of data on the spontaneous polarization and Curie temperature of ferroelectrics and antiferroelectrics. Mitsui et al (1975) have been identified almost seven hundred ferroelectric pure compounds and solid solutions. Major sources of bibliographic information on polar materials are provided by Mitsui (1969, 1975), Toyoda (1970), Conolly et al,(1970, 1974) and Lang (1973, 1974).

1.3 CHARACTERISTIC PROPERTIES

The characteristic properties of ferroelectrics are their reversible polarization, their anomalous properties and their non-linearities. Most of the ferroelectrics cease to be ferroelectric above a temperature, Tc, known as the transition temperature. The anomalous behaviour near Tc is probably as significant as the reversible polarization, but it is not definitive of a ferroelectric. The high values of permittivity (ε) and susceptibility (η) near Tc are referred as an anomalous values. The dielectric non-linearity is a significant characteristic of ferroelectrics. The polarization created by an applied field does not remain proportional to electric field, E, this gives non-linear property of the ferroelectrics. Most of the ferroelectrics possess the following properties.

1. They possess a spontaneous electric polarization Ps, which can be reversed by applying a suitable electric field E. This process is known as switching and is accompanied by hysteresis loop, as shown in Fig. 1.1

2. They are non-metallic, non-magnetic solids. The properties of ferroelectrics are most simply studied when material is in a single crystal form.

3. As the temperature of the ferroelectric increases the magnitude of the permanent polarization decreases, until finally at critical temperature, it disappears. This temperature is known as 'Curie temperature'.

4. They have a high dielectric constant along the polar axis, which is a function of temperature and rises to a maximum peak value at the Curie temperature.

5 They have ferroelectric domain structure which may be visible in polarized light.

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

7. They have phase transition at the Curie temperature to form the structure of higher symmetry.

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

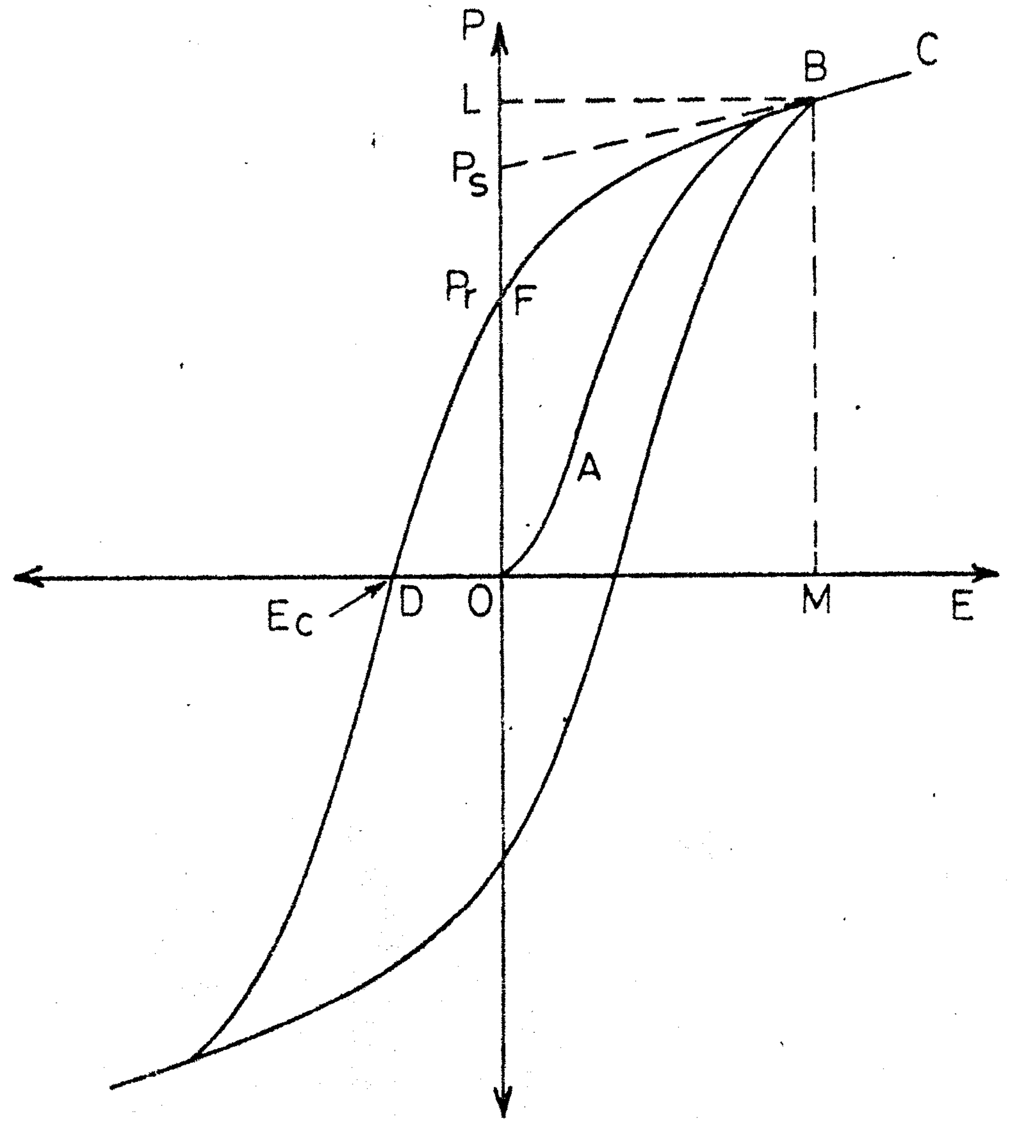

Fig. 1·1 Schematic representation of ferroelectric hysteresis loop.

9. They show piezoelectric and pyroelectric properties below the Curie temperature.

10. They show a sudden appearance of surface charge at the transition.

1.4 DIELECTRIC BAHAVIOUR, POLARIZABILITY AND SPONTANEOUS POLARIZATION

1.4 (a) Field In Dielectric Between Capacitor Plates

The macroscopic electric field intensity E of Maxwell's equations is defined as the spatial average of the electric field in the material, averaged over a volume at least as large as an unit cell. The displacement D is defined as,

$$D = E + 4\pi P \qquad \ldots\ldots 1.1$$

Measurements of the polarization P or of dielectric constant, $\varepsilon = \frac{D}{E}$, are usually made by measuring the capacitance, $C = \frac{Q}{V}$ of a capacitor filled with the dielectric as shown in Fig. 1.2. In the absence of the dielectric, we suppose that the field between the plates of the capacitor is E', so that the surface charge density on each plate is $\pm E'/4\pi$. When the dielectric is inserted, polarization surface charge density $\pm P$ are induced on the surface of the dielectric and these charges are neutralized by a flow of charge around the circuit to the capacitor plates. The space-average field E inside the dielectric is the sum of a field $E_1 = -4\pi P$ from the polarization charges on the dielectric and $E_0 = E' + 4\pi P$ from the original and the neutralization charges on the plates. Thus for the capacitor

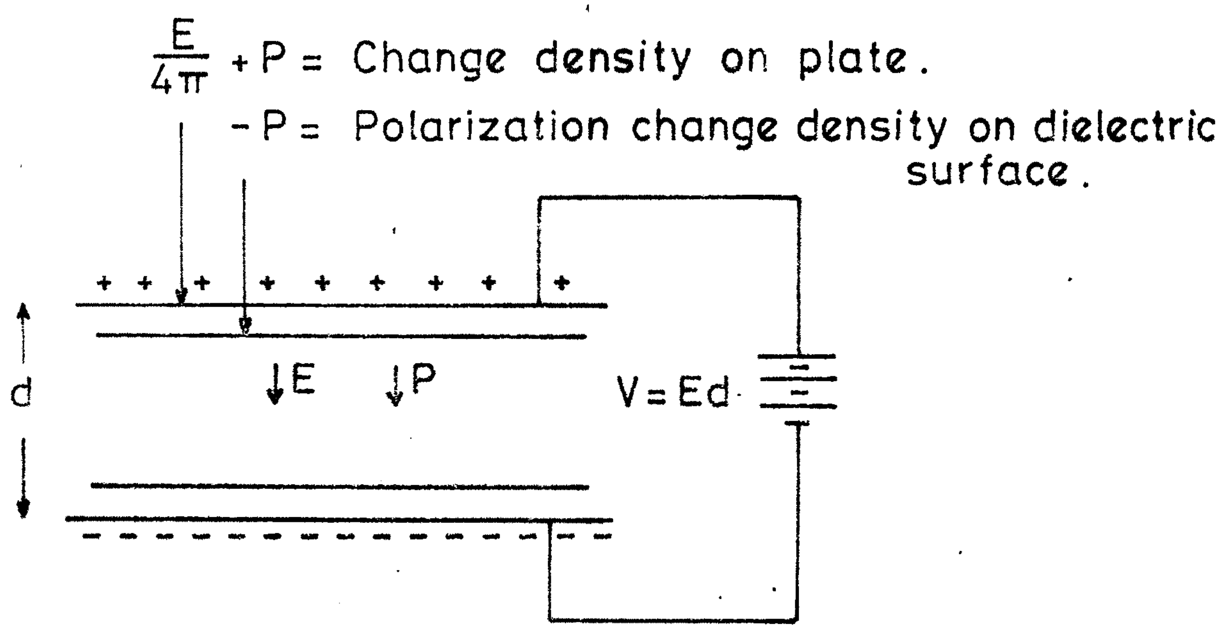

Fig. 1·1: DIELECTRIC BETWEEN CAPACITOR PLATES.

Voltage across plates V = Exd

E = Microscopic field E is the average over the volume of the microscopic electric field.

arrangement the space-average field in the dielectric is,

$$E = E_0 + E_1 = E' + 4\pi P - 4\pi P = E' \qquad \ldots\ldots \ 1.2$$

and

$$E_{loc} = E_0 + E_1 + E_2 + E_3$$

$$= (E + 4\pi P) + (-4\pi P) + \left(\frac{4\pi P}{3}\right) + 0 \qquad \ldots\ldots \ 1.3$$

at atom sites for which $E_3 = 0$. Thus for the cubic site,

$$E_{loc} = E + \frac{4\pi}{3} P \qquad \ldots\ldots \ 1.4$$

where the coefficient of P is know as the Lorentz local field factor. Here E is the space-average field inside the dielectric. The above relation is the the Lorentz relation, the field acting at the center of an atom, E, plus a contribution $\frac{4\pi}{3}P$ from the field produced by the polarization of the other atoms in the specimen, where the value of the macroscopic average field E is the same as the field existing between the capacitor plates before the dielectric was inserted. Evidence of this in ionic crystals is given by Tessman, Kahn and Shockley (1953).

1.4 (b) Dielectric Constant And Polarizability

The dielectric constant, ε, of an isotropic or cubic medium is defined as,

$$\varepsilon = \frac{D}{E} = 1 + 4\pi \frac{P}{E} = 1 + 4\pi \chi \qquad \ldots\ldots \ 1.5$$

where $\chi = \frac{p}{E}$, is the electric susceptilibity and E is the macroscopic average field. The polarizability, α , of an atom is defined as

$$\alpha = \frac{P}{Eloc} \qquad .... \ 1.6$$

where p is the dipole moment per unit volume of the atom and Eloc is the local electric field at the atom. The polarizability, α , is known as an atomic or ionic property, where χ and ϵ will also depend on the manner in which the atoms are assembled in the crystal, because E is not in general equal to Eloc. For an anisotropic molecule the polarizability is a tensor, with components $\alpha\mu v$ defined by,

$$P\mu = \alpha\mu\, v\, Ev \qquad ..... \ 1.7$$

where v is summed over x, y, z.

The polarization is given by,

$$P = \sum_i Ni\,\alpha i \ \ Eloc(i) \qquad ..... \ 1.8$$

where Ni is the number of atoms per unit volume, having polarizability αi and Eloc(i) is the local field at atoms of type i. If the local field is connected with the applied field by the Lorentz relation, we have,

$$\frac{P}{E} = \frac{Ni\,\alpha i}{1 - \frac{4\pi}{3}\sum_i Ni\,\alpha i} = \frac{\varepsilon - 1}{4\pi} \qquad ..... \ 1.9$$

which may be solved for Σ Ni αi, to give,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \sum_i Ni\ \alpha i \qquad .... \ 1.10$$

This is the Clausius-Mossottii relation.

The total polarizability is usually devided into three parts,

i) Electronic polarizability (αe), which is produced by opposite displacement of positive nuclei and negative electrons within the same atom.

ii) Atomic or Ionic Polarizability (αi), which is observed by opposite displacements of positive and negative ions in the substance and

iii) Dipolar or orientation Polarizability (αd), which arises from molecules with permanent electric dipole moment that can change orientation in an applied electric field. Therefore, the total polarizability is given by the relation,

$$\alpha = \alpha_e + \alpha_i + \alpha_d \qquad ..... \ 1.11$$

The contribution to the polarization made by αe and αi called distortion polarization. α_e and αi are independent of temperature and hence the part of the dielectric constant depending on them is essentially independent of the temperature. But the orientation polarization is a function of temperature.

Each type of polarizability is a function of frequency of the applied electric field. All types of polarization are equal to the value in steady field at low frequency. As the frequency of the applied field is increased, polarization no longer has time to reach its steady value. The orientational polarizability is almost damped for frequencies greater than

10^{10} c.p.s.The resonant frequency for the ionic polarization lies in the range 10^{13} c.p.s., whereas the electronic polarization is observed in the range 10^{15} c.p.s. The entire frequency response of a dielectric is shown in Fig.1.3

In the optical frequency range the dielectric constant arises entirely from the electronic polarizability. At high frequencies the dipolar and ionic contributions are small because of the inertia of the molecules and ions. In the optical range above equation reduces to,

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3} \sum_i N_i \alpha_i(\text{ electronic}) \qquad ....1.12$$

where n is the refractive index of the medium which is related to the dielectric constant by the relation,

$$n^2 = \epsilon \qquad ..... 1.13$$

If the effect of the frequency on the polarizability is taken into account, the result is progressive decrease in dielectric constant with increasing frequency. In each of the regions, where dielectric dispersion occurs, there is certain characteristic frequency $\frac{W_o}{2\pi}$,defined by the relation,

$$W_o = \frac{2KT}{b} = \frac{1}{T} \qquad .... 1.14$$

where, K is the Boltzman's constant, T is the absolute temperature, b is the frictional constant and T the relaxation time. The dielectric constant

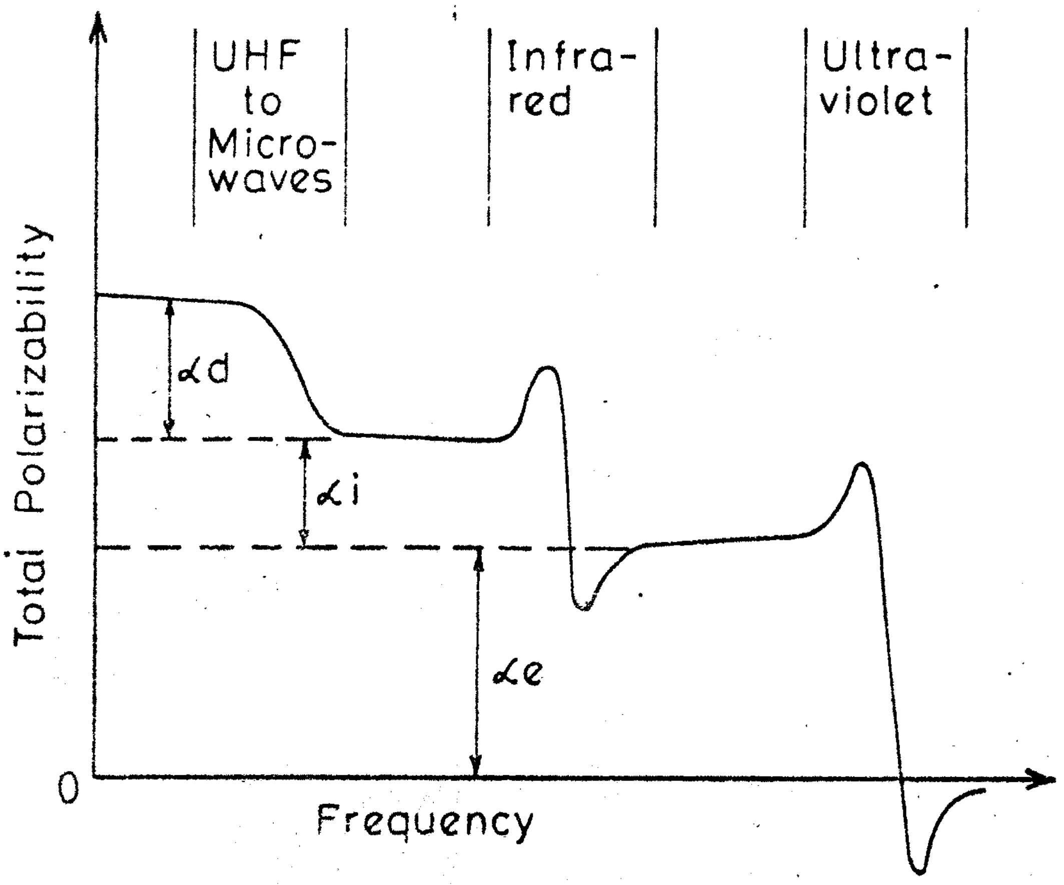

Fig. 1·3 Schematic representation of frequency dependence of the several contributions to the total polarizability.

shows anomalous changes in the vicinity of W_0. Absorption of energy in the infra-red and optical regions is due to the natural vibrations of electrons,molecules or crystal lattice.

1.4 (c) SPONTANEOUS POLARIZATION(Ps)

Due to application of an external applied electric field each atom or molecule of the dielectric becomes an 'electric dipole' and dielectric is said to be polarized. This displacement of charges or the reorientation of the polar molecules in the isotropic medium is propertional to the electric force and takes place in the direction of this force. The phenomenonis called the electric polarization and the medium is said to be polarized.

The word 'spontaneous' is used because polarization exists in presence or even in absence of the electric field. The existence of dielectric hysteresis loop indicates spontaneous polarization(Ps). The experimental methods for observation of the hysteresis loop on the screen of a Cathode Ray Oscilloscope are based on the modified Sawyer and Tower circuit. Linear extrapolation from the saturation region to zero field gives the spontaneous polarization (Ps). The intercept on polarization axis is remenant polarization (Pr) and the intercept OD 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 as shown in Fig.1.1. Other methods which are commonly used for measuring the P_s are, polarity reversal technique (Camlible, 1969), charge integration technique (Glass, 1969) and pyroelectric measurement using calibration for scaling (Glass, 1969).

The type of phase transition governs the nature of the temperature dependence of P_s. The P_s, suddenly falls to zero in a ferroelectric material which undergoes the first-order phase transition e.g. $BaTiO_3$(Merz,1953). While in second order phase transition, P_s decreases continuously to zero at the transition temperature e.g. triglycine sulphate (Jona and Shirane,1962).

1.5 CLASSIFICATION OF FERROELECTRICS

Today, ferroelectricity is becoming a more common phenomenon. As the number of ferroelectrics discovered, is very large, their classification according to different criteria is as given below.

i) Crystal Chemical Classification:

The first group of ferroelectrics according to this type of classification consists of hydrogen bonded crystals, such as KH_2PO_4, Rochelle salt,TGS etc, while the second group includes the double oxides, such as $BaTiO_3$, $KNbO_3$, $PbTa_2O_6$ etc.

ii) The Classification According To The Number Of Directions Allowed To Spontaneous Polarization :

Here, first group includes those ferroelectrics that can polarize along only one axis, e.g. Rochelle salt, KH_2PO_4, $(NH_4)_2SO_4$, colemanite, thiourea,TGS etc. The second group includes those ferroelectric that can polarize along several axes that are equivalent in non-polar phase, e.g. $BaTiO_3$ type, $Cd_2Nb_2O_7$, $Pb_2Nb_2O_6$ etc. Both classes show piezoelectric effect in the polarized phase. The ferroelectrics of second class often 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 Existance Or Lack Of Center Of Symmetry In The Point Group Of Their Non-Polar Phases :

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 $BaTiO_3$, $Cd_2Nb_2O_7$, $PbNb_2O_6$, Colemanite, H_2O etc. This classification is particularly useful for the thermodynamic treatment of the ferroelectric transitions.

iv) Classification According To The Nature Of Phase Change At the Curie Point :

According to this, ferroelectrics are divided into order-disorder group and displacive group. The order-disorder group includes crystals with hydrogen bonds e.g. KH_2PO_4 and isomorphous salts, TGS etc. In these crystals the motion of the protons is related to their ferroelectric properties, as in KH_2PO_4 (Bush and Scherrer in 1935 and Mayer and Bjorktan in 1962). The displacive group of ferroelectrics includes ionic crystals, whose structures are closely related to the perovskite and ilmenite structures e.g. $BaTiO_3$ and double oxide ferroelectrics. The simplest ferroelectric crystal of this type is GeTe (Pawley et al, 1966) with NaCl structure. This classifiication is practically equivalent to that which is done on the basis of the existence of permanent or induced dipoles in the non-polar phase of the crystals.

v) Classification According To Predominant Nature Of Atomic Displacements Required By Polarity Reversal :

Abrahams and Keve (1971) have divided ferroelectrics into three groups:

a) The one dimensional group includes those ferroelectric crystals in which the atomic displacement vectors ($\vec{\Lambda}$) and all Loci (L) followed by the atoms during reversal, are linear and parallel to the polar axis. The ferroelectrics of this group are restricted to the point groups, 2, 2mm, 3, 3m, 4, 4mm, 6 and 6mm, e.g. $BaTiO_3$ type, $KNbO_3$ type, SbSi etc.

b) The two dimensional group includes those ferroelectric crystals in which the atomic displacement vector($\vec{\Lambda}$)and Loci(L) followed by atoms during reversal lie in the parallel planes containing the polar direction. The point groups which satisfy the strict symmetry requirements for this are m, 2mm, 3m, 4mm and 6mm, e.g. HCl,HBr, $NaNO_2$, $BaCoF_4$ etc.

c) The three dimensional group includes those ferroelectric crystals in which the individual displacement vector ($\vec{\Delta}$) and the Loci(L) followed by atoms during reversal, have essentially random orientations. The ferroelectrics in this group contain one or more of the following structural features- a discrete tetrahedral or molecular ions, hydrogen bond or proton-oxygen frame works, e.g. $(NH_4)_2SO_4$, KH_2PO_4 etc.

1.6 THEORETICAL APPROACH TO FERROELECTRICITY

Many theories and theoretical models were suggested by different scientists to study the ferroelectricity. But neither model nor a theory is useful to explain in general the ferroelectric behaviour. A brief description of the thermodynamic theory, lattice dynamic theory and short review of model theories of ferroelectricity are given below :

1.6 (a) Thermodynamic Theory :-

This theory is very general in its scope and independent of any particular model. Though this theory does not provide physical mechanism, 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 Mueller (1940,a,b,c,d) and Cady (1946). The theory can be applied to KH_2PO_4 type ferroelectrics. The thermodynamic treatment of $BaTiO_3$ type ferroelectrics is some what different, since these crystals have more than one ferroelectric axis and are not piezoelectric in paraelectric phase. A thermodynamic theory of such ferroelectrics has been developed mainly by Devonshire (1949, 1951, 1954) and Ginzburg (1945, 1949). This theory is based upon the following assumptions.

i) The free energy of a ferroelectric crystal is regarded as a 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 behaviour. Thus the coefficients of P^2, in the free energy functions bear the significant temperature dependence.

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

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

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

$$Gi = U - Ts + \sum_{i=1}^{3} Xixi \qquad ..... 1.15$$

where U is an internal energy of the crystal under external stress, T is the temperature, S is the entropy, Xi is the ith component of mechanical stress. The differential form of this function is,

$$dG_1 = -sdT + \sum_{i=1}^{3} xidXi + Edp \qquad ..... 1.16$$

here 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_{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 X = 0 is given by the equation,

$$G_1 - G_{10} = \frac{1}{2}\chi' P^2 + \frac{1}{4}\beta' P^4 + \frac{1}{6} r' P^6 \qquad .....1.17$$

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 w.r.t. P is the externally applied electrical stress. The significant temperature dependence is contained in the coefficient χ^1. The meaning of χ' can be seen from the following consideration. Let a small electric field E be applied to the crystal. Then under zero pressure, equation 1.16 gives,

$$dG_1 = -sdT + Edp \qquad \text{.....1.18}$$

or

$$E = \frac{\delta G1}{\delta P} \; T \qquad \text{..... 1.19}$$

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

$$E = \frac{\delta G_1}{\delta P} = \chi' P \qquad \text{..... 1.20}$$

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

$$\frac{\delta E}{\delta P} = \frac{4\pi}{\epsilon - 1} = \frac{1}{\eta} \qquad \text{..... 1.21}$$

From 1.20 and 1.21, we have,

$$\chi^1 = \frac{4\pi}{\epsilon - 1} = \frac{1}{\eta} \qquad \text{..... 1.22}$$

This equation shows that the coefficient χ^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,

$$\eta = \frac{\epsilon - 1}{4\pi} = \frac{C}{T - T_0} \qquad \text{..... 1.23}$$

so that,

$$\chi^1 = \frac{T - T_0}{C} \qquad \text{..... 1.24}$$

where C is the Curie constant and T_o is the Curie-Weiss temperature. Hence equation 1.17 may be written as follows,

$$G_1 - G_{10} = \frac{1}{2}\left(\frac{T - T_o}{C}\right) P^2 + \frac{1}{4}\beta' P^4 + \frac{1}{6} r' P^6 \qquad \text{..... 1.25}$$

From equations 1.20 and 1.25, we obtain the following equations for the applied field and the dielectric constant,

$$E = \left(\frac{\delta G_1}{\delta P}\right)_T = \left(\frac{T - T_o}{C}\right) P + \beta' P^3 + r' P^5 \qquad \text{..... 1.26}$$

$$\frac{1}{\eta} = \frac{4\pi}{\varepsilon - 1} = \left(\frac{T - T_o}{C}\right) + 3\beta' P^2 + 5r' P^4 \qquad \text{..... 1.27}$$

1. <u>Spontaneous Polarization:</u>

In the thermal equilibrium $\left(\frac{\delta G_1}{\delta P}\right) = 0$, so that the spontaneous polarization (P_s) for zero electric field satisfies the equation,

$$0 = \chi' P_s + \beta' P_s^3 + r' P_s^5 \qquad \text{.....1.28}$$

It follows that the value of P_s which gives extremum of G_1 is given by $P_s = o$

$$X' + \beta' P_s^2 + r' P_s^4 = 0 \qquad \text{...... 1.29}$$

from equation 1.17 we have,

$$\frac{\delta^2 G_1}{\delta P^2} = X' + 3\beta' P^2 + 5r' P^4 \qquad \text{...... 1.30}$$

If χ^1, β^1 and r' are all positive, $P_s = 0$ gives a positive value of $\frac{\delta^2 G_1}{\delta P^2}$. 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 coefficient χ^1 becomes negative, G_1 would maximum for $P_s = 0$. Because, in this case $\frac{\delta^2 G_1}{\delta P^2}$ is a negative quantity. When is negative, the equation 1.17 gives atleast one non-vanishing value of P_s for which $\frac{\delta^2 G_1}{\delta P^2}$ 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 χ^1 from positive to negative value changes a stable paraelectric state ($\chi^1 > o$) to a stable ferroelectric state ($\chi^1 < o$). At the transition temperature, T_c, between these states, we have, $\chi^1 = 0$. Two particular cases are considered below, for discussing the properties in the vicinity of the transition temperature.

2. Second-Order Transition :

If the coefficients β^1 and r^1 are positive and χ^1 varies from positive to negative as the temperature is lowered, we obtain free energy curves as shown in Fig 1.4(a). The corresponding spontaneous polarization, as a function of temperature, is shown in Fig 1.4(b). For $T<T_c$, the spontaneous polarization is given by,

$$P_s = \left(\frac{T_c - T}{C\beta^1}\right)^{1/2} \qquad \ldots.1.31$$

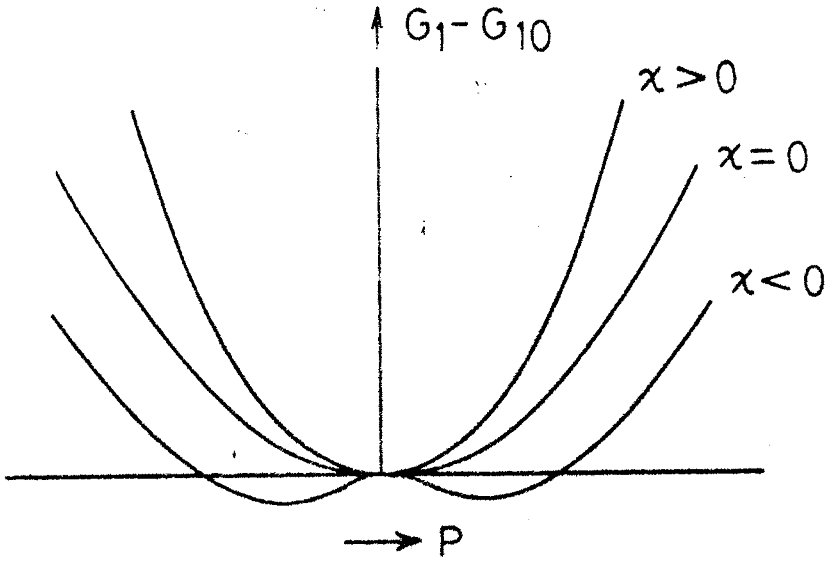

Fig. 1·4(a) Schematic representation of the free energy as function of polarization for various values of χ for a second-order transition.

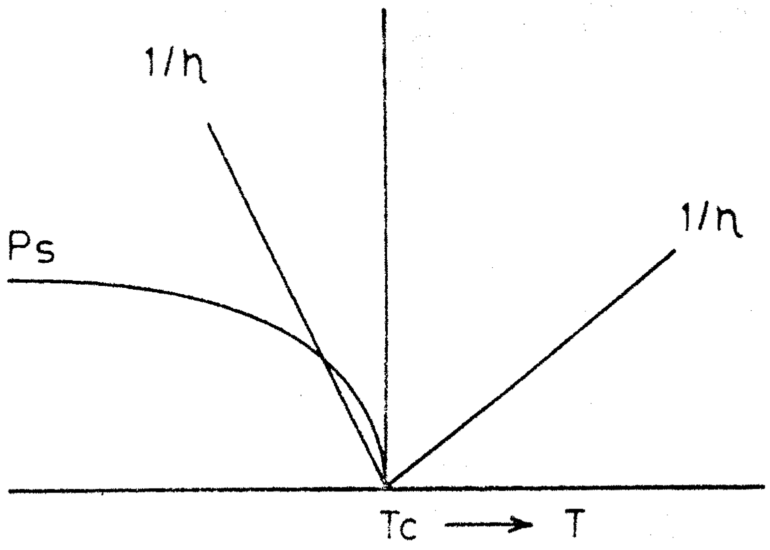

Fig. 1·4(b) Schematic representation of the spontaneous polarization and reciprocal susceptibility near the transition temperature Tc for a second-order transition.

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. 1.4(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 second-order phase transition are given by,

$$\eta = \frac{\epsilon-1}{4\pi} = \frac{C}{T-T_c} \qquad \text{..... 1.32}$$

Below the transition temperature an expression for the susceptibility and the dielectric constant is obtained as follows. Assuming that the term r^1 in equation 1.26 and 1.27, is negligible, we obtain,

$$E = \frac{T-T_o}{C} P + \beta' P^3 \qquad \text{..... 1.33}$$

$$\frac{1}{\eta} = \frac{4\pi}{\epsilon-1} = \frac{T-T_o}{C} + 3\beta' P^2 \qquad \text{..... 1.34}$$

For small applied fields the total polarization is nearly equal to spontaneous Polarization P_s i.e. $P \simeq P_s$, so that according to equation 1.31, we have,

$$\beta' P^2 = -\frac{T-T_o}{C} \qquad \text{.....1.35}$$

Now from 1.34 and 1.35, we obtain,

$$\frac{1}{\eta} = \frac{4\pi}{\varepsilon-1} = -2\left(\frac{T-T_o}{C}\right)$$

since for second-order transition, $T_o=T_c$,

we have,

$$\frac{1}{\eta} = \frac{4\pi}{\varepsilon-1} = -2\left(\frac{T-T_c}{c}\right)$$

or

$$\eta = \frac{\varepsilon-1}{4\pi} = \frac{c}{2(T_c-T)} \qquad \text{.....} \; 1.36$$

The temperature dependence of the reciprocal of the susceptibility on both sides of T_c, as given by equations 1.32 and 1.36, is shown in Fig. 1.4(b).

3. <u>First-Order Transition</u>

It has been seen that the condition for the occurrence of spontaneous polarization is that χ' should be negative. If β' is positive at the same time ,then, there is a second order transition. Let us consider the case for which β' is negative as the temperature is lowered. In this case the free energy curves are shown in fig.1.5(a). A transition from the non-polarized state to a spontaneously polarized state will now occur, when the minimum of the free energy corresponding to $P_s = 0$ becomes equal to the minimum associated with $P_s= 0$. In the absence of an external field the spontaneous polarization satisfies equation 1.28

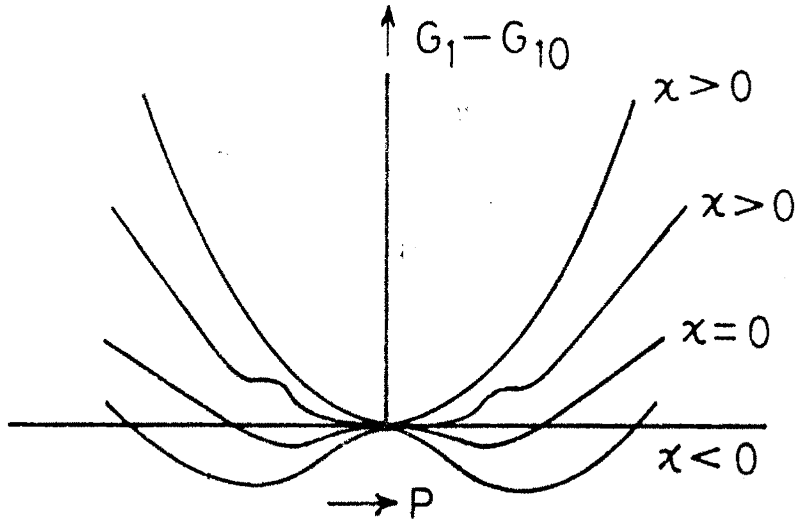

Fig.1·5(a) Schematic representation of the free energy as function of polarization for various values of χ for a first-order transition.

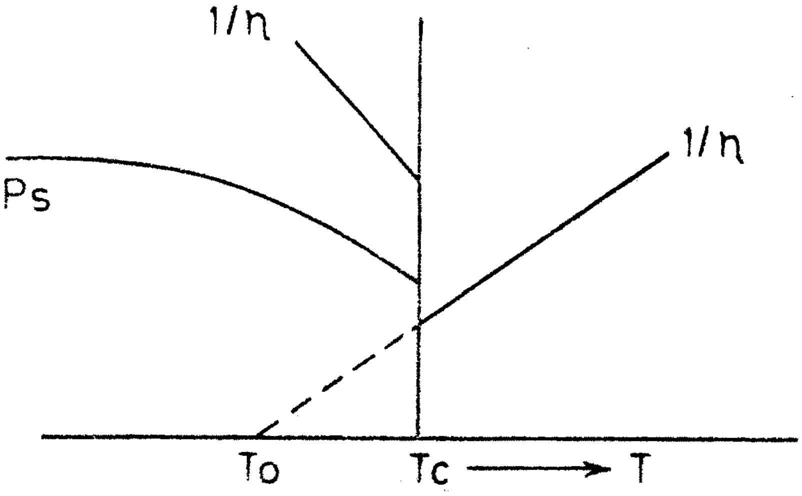

Fig.1·5(b) Schematic representation of the spontaneous polarization and reciprocal susceptibility near the transition temperature Tc for a first-order transition.

and also the condition $G_1 = G_{10}$. Therefore, from equation 1.25, we have ,

$$\frac{1}{2}\chi' P_s^2 + \frac{1}{4}\beta' P_s^4 + \frac{1}{6} r' P_s^6 = 0 \qquad \ldots\ldots 1.37$$

from equations 1.28 and 1.37, we have,

$$P_s^2 = -\frac{3}{4}\left(\frac{\beta'}{r'}\right) \qquad \ldots\ldots 1.38$$

$$\chi' = \frac{3}{16}\left(\frac{\beta'^2}{r'}\right) \qquad \ldots\ldots 1.39$$

$$P_s^4 = 3\left(\frac{\chi'}{r'}\right) \qquad \ldots\ldots 1.40$$

The equation 1.38 shows that the spontaneous polarization is discontinuous at the transition temperature as shown in fig. 1.5(b)

Let us consider the susceptibility and the dielectric constant on both sides of the transition temperature. As in the case of second-order transition the susceptibility and dielectric constant in the region above T_c again follow the Curie-Weiss law;

$$\eta = \frac{\varepsilon - 1}{4\pi} = \frac{c}{T - T_0} \qquad \ldots . 1.41$$

If we consider first-order transition, then below T_c, an expression for susceptibility and the dielectric constant is,

$$\eta = \frac{\varepsilon - 1}{4\pi} = \frac{c}{4(T - T_0)} \qquad \ldots\ldots 1.42$$

From equations 1.41 and 1.42, it is seen that the reciprocal of the susceptibility in a first order transition is not zero at T_c, but it is positive quantity. Its temperature variation just above and just below T_c shown in fig.1.5(b).

1.6 (b) Model Theories Of Ferroelectricity

i) Masson and Matthias (1948) proposed model theory of $BaTiO_3$ in which stable position for Ti^{4+} ion is not at the center of the oxygen octahedron. Instead, it is at any of the six positions, which correspond to slight displacement from the center towards the oxygen ions. When the Ti^{4+} ion is at any of these position, the unit cell would have a dipole moment. This theory is not in good agreement with experimental results.

ii) Jaynes (1950) proposed a model in which oxygen ions are displaced rather than Ti^{4+} ions. Jaynes (1953) has also proposed a theory in which dipole moments are not attributed to atomic displacements. Only the electronic states of TiO_6 octahedron are considered. The theory is satisfactory for determining the entropy change, but it predicts infra-red absorption line at $\sim 10\mu$, which is not detected.

iii) Devonshire 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.

iv) Slater (1950) has also proposed a model which is similar to that of Devonshire. He assumed in addition that each atom has an electronic polarization and Ti^{4+} ion has an ionic polarization. The theory predicts that the direction of spontaneous polarization is along the z-axis, but this is a disadvantage when it is applied to some other structure.

1.6 (c) Cochran's Theory

Different theories have met with partial success and one which is most promising is due to Cochran (1960, 61), based on lattice dynamics. It provides a microscopic theory of ferroelectricity for certain crystals.This theory is based on following assumptions.

i) Ferroelectric transitions are the results of the instability of crystal lattice with respect to one of the homogeneous (K=0) transverse optical mode.

ii) If a crystal is wholly or partly ionic, lattice vibrations are accompanied by polarization oscillations of equal frequencies which creat a local field interacting with the ions through long range coulomb forces.

iii) For one particular mode of vibration, long range force is equal to short range force, the crystal becomes unstable.

iv) Dielectric constant ϵ , which is connected to the frequency of critical mode becomes extremely large, as happens at T_C.

The ferroelectric properties of crystals and the thermodynamical properties are connected by the relation known as Lyddane-Sachs-Teller (LST) relation (1941). For diatomic crystals, LST relation gives the ratio of the frequencies of the longitudinal optical(W_L) and transverse optical modes (W_T) of infinite wavelength in terms of the ratio of the static dielectric constant (ϵ_s) of the crystal to the high frequency dielectric constant (ϵ_e)

$$\frac{W_L^2}{W_T^2} = \frac{\epsilon_s}{\epsilon_e} \qquad \text{..... 1.43}$$

In a ferroelectric crystal, the static dielectric constant folows a Curie-Weiss law above the transition temperature,

$$\epsilon_s = \epsilon^{1} + \frac{4\pi C}{T-T_c}, \quad T > T_c \qquad \text{.... 1.44}$$

where ϵ is part of dielectric constant independent of temperature. This equation 1.44 through (1.43) implies that the transverse optical modes of infinite wavelength have an anomalous temperature dependence given by

$$W_T^2 = A\,(T - T_c), \quad T > T_c \qquad \text{.... 1.45}$$

where A is coefficient to be determined. The generalization of the LST relation to any diagonally cubic crystal containing n ions in a primitive unit cell, according to Cochran (1959, 1960), is given by,

$$\frac{\epsilon_s}{\epsilon_e} = \prod_{j=2}^{n} \frac{(W^2)_L}{(W_j)^2_T} \qquad \text{..... 1.46}$$

when $W_T^2 = 0$, we have static dielectric constant $\epsilon_s = \infty$, because ϵ_e is equal to the square of refractive index.

Cochran (1953) estimated $\epsilon = 1.4 \times 10^4$ and $P_s = 19.5\ \mu c/cm^2$ for

$BaTiO_3$ at T_C which are very close to the experimental values. The most interesting new result of the theory is the prediction of the absolute value of the frequency W_T of the transverse optical mode with $k=0$ for perovskite materials. This frequency has been estimated to be 2×10^{11} cps for $BaTiO_3$. Similar results have also been reported in other perovskites.

1.7 FERROELECTRIC DOMAINS

Zwicker and Scherrer (1944) first made direct optical observation of domains in KH_2PO_4; with polarized light. The domain structure in single crystals of $BaTiO_3$ was first reported, almost simultaneously, by Kay (1948), Blattner et al (1948), Matthias and Von Hippel (1948) and Mitsui and Furuchi (1953). Domain structure in Rochelle salt was observed by Marutake (1952). Broad survey of domain observation and domain walls are given in the publications of Megaw (1957), Kanzig (1957), Jona and Shirane (1962), Sachse (1956) and Zheludev (1971).

The ferroelectric domains are the regions of homogeneous polarization that differ only in the direction of the polarization. Within a domain in a ferroelectric crystal, all the spontaneously polarized unit cells are oriented identically. Consequently, each domain has macroscopic spontaneous polarization. The directions of spontaneous polarization of neighbouring domains in a ferroelectric crystal make definite angles with one another. The demarkation between the two domains is called 'domain wall.' A domain is usually considered so thin that it has 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 diploes 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.

The reasons for the occurrence of domains in a ferroelectric crystal are now well-understood. Above Curie temperature i.e. in the para-electric phase the direction along which the polarization is to be occured can not be a unique direction. But even in ferroelectric phase, there must be atleast two equivalent 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 symmetry, to one of the pyroelectric classes and the domains differ in the direction of P_s. So, when a ferroelectric crystal is cooled below the Curie temperature in the absence of the external electrical and mechanical stress; it breaks up into domains of different orientations. It means that from the crystallographic point of view, the domain structure is identical with the twinning structure. Twin operations of ferroelectric domains have been discussed by Zheludev (1971).

The equilibrium arrangement of domains in a ferroelectric crystal is that in which the free energy of the crystal is least. So free energy can be reduced by the formation of domains.

i) Electrostatic self energy,

ii) Energy of strain fields around imperfections,

iii) Domain wall energy and elastic energy,

iv) The anisotropic energy,

v) External mechanical stress,

vi) External applied electric field and,

vii) Phase transition; these are the factors governing the free energy and hence the domain structure. Similarly, there exist different types of walls.

i) W_∞ walls with arbitrary orientation,

ii) Crystallographically prominent w_f walls and

iii) S-walls whose indices depend upon P_s and electromechanical coefficients.

Ferroelectric domain structure can be observed by different methods such as,

i) optical method using polarized light,

ii) Optical method using multiple beam interferrometric technique,

iii) X-ray method,

iv) Etching method,

v) Charged powder method,

vi) Electron-optical method and,

vii) Electroluminescence method.

1.8 APPLICATIONS

Ferroelectricity is having number of practical applications in day to day life. Some of them are simple and others are sophisticated. Ferroelectrics are the materials with strong anomalies in their physical properties. These properties are used to build special devices. Similarly their linearities and non-linearities are useful in number of applications. Ferroelectrics are mainly studied at high temperatures 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).

a) Applications Related With Anomalies

For ferroelectrics the anomalies observed are large dielectric constant, piezoelectric and pyroelectric coefficients. The large dielectric constant of some ferroelectrics make them useful in ceramic form to make high value condensers, while their large piezoelectric coefficients make them particularly suitable as transducers. They are used in frequency controls, filters, miniature capacitors, modulating devices, thermal meters, switches and modulators for laser light.

b) Linear Properties

Ferroelectric transducers have high coupling constant, but comparatively high dielectric losses. In some cases they change electrical energy into mechanical energy e.g. ultraviolet generators, loud speakers or pulse generators for use with atomic delay lines and in other cases they are used to convert mechanical into electrical energy e.g. ultrosonic detectors, strain gauges, microphones, pickups and devices to measure the extent of vibrations. They have been used as bolometers for infra-red detectors, since they have a response over a wide spectral region.

c) Non-Linear Properties

The non-linearities are most marked at low frequencies and near T_c. Ferroelectrics can be replaced by varacter diodes which are expensive often the loss lower than varacter diodes. In 1962, barium strontium titanate could be used for harmonic microwave generation and also for harmonic microwave generation at millimeter wavelength at 3 to 9 x 10^9 cps. A Prague team has reported the use of TGS as thermoautostatic, non-linear dielectric element (TANDEL). Non-linear piezoelectric properties can be used in direct amplification of sound and in computer circuits. It can be used as dielectric amplifier, which is low power amplifier. This type of amplifier is used for remote controls, servo systems, stabilization of supplies, audio frequency amplification and for d.c amplifer.The non-linearity at optical frequencies results in a large electro-optics effect which makes ferroelectrics attractive for control of the beams of coherent light from lasers. The presence of a hysteresis loop makes it possible to use ferroelectrics as memory elements in computers.

1.9 ORIENTATION OF THE PRESENT WORK

Ferroelectricity is one of the interesting 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 five decades owing to their important device applications they continue 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 of ferroelectrics 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.

Among the ferroelectric materials, vanadates of alkali metals are not extensively studied yet. These are high temperature ferroelectrics and they can be obtained in the ceramic forms. Ferroelectricity in sodium vanadate was first reported by Sawada and Nomura (1951), Baughman (1970), K.Ramani and Viswamitra (1974). They studied the crystal structure, dielectric hysteresis, thermal expansion, phase transition of sodium vanadate. Dielectric dispersion in $NaVO_3$ was reported by Matsuda (1974). Recently dielectric and pyroelectric properties of $NaVO_3$, in ceramic form, were reported by Khan et al (1983). Electrical second harmonic generation by $NaVO_3$ and KVO_3 was studied by Chavan et al (1986). Patil et al(1988) studied dielectric and pyroelectric properties of $NaVO_3$ and KVO_3

and their solid solutions. Patil et al and Kashid et al (1989) studied effect of rate earth doping on KVO_3 and reported pyroelectric measurements of KVO_3 ceramics doped with Dysprosium and Gadolinium.

In the present investigation an attempt has been made to study the ferroelectricity in undoped KVO_3 and doped with erbium oxide (Er_2O_3) having different molear concentrations of Er_2O_3 varying from 0.025 mol% to 3 mol%. This study gives better understanding of ferroelectric phenomenon of KVO_3. Therefore, the aim of our present work is to prepare KVO_3 and to dope it with Er_2O_3 and to study the following properties.

i) X-ray diffraction and E.P.R.
ii) Dielectric hysteresis and coercive field.
iii) Pyroelectricity.
iv) Dielectric constant.
v) D.C. electrical conductivity.

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