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CHAPTER - I

: FERROELECTRICS :

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## C H A P T E R - I

### FERROELECTRICS

#### 1.1 Introduction:

The ferroelectricity is an interesting and recent branch of dielectrics. A number of physicists tried to investigate new phenomena during last few years in this branch. The ferroelectrics are the materials which possess the spontaneous electric polarization. The ferroelectrics can be studied only when they are in the form of single crystals. Many of the ferroelectric materials such as barium titanate, Rochelle salt, triglycine sulfate etc., can be used in optical devices, electronic devices and second harmonic generation. Usually the ferroelectric crystal belongs to the pyroelectric family and of which the direction of spontaneous polarization can be reversed by an electric field.

The first ferroelectric material that was discovered is Rochelle salt i.e. Sodium-Potassium tartrate tetrahydrate ( $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ). Pockels (1894) reported the anomalously large piezoelectric constants of Rochelle salt. Valasek (1920) observed the ferroelectric hysteresis loop in this crystal. After the invention of hysteresis loop, the studies on the properties of this crystal were made in several countries. Mueller (1940) proposed a phenomenological theory which first brought us to systematic understanding of the relations

between anomalous dielectric, piezoelectric and elastic behaviours of this crystal.

Busch and Scherrer (1935) discovered ferroelectricity in potassium dihydrogen phosphate,  $\text{KH}_2\text{PO}_4$  (KDP) and its properties were studied by the Zurich group. Slater (1941) published a theory of the phase transition of  $\text{KH}_2\text{PO}_4$ , which stimulated interest and inspiration in ferroelectricity for many physicists.

Ogawa (1943) in Japan, Wainer and Solomon (1943) in the U.S.A., and Mul and Goldman (1945) in the U.S.S.R. discovered independently the anomalous dielectric properties of  $\text{Ba TiO}_3$ , and later Von Hippel et al (1946) and Mul and Goldman (1945) confirmed that  $\text{Ba TiO}_3$  is ferroelectric.  $\text{Ba TiO}_3$  and several ceramics of isomorphous oxides show large dielectric constants and because of this fact ferroelectric materials became very useful in applications.

Shirane, Sawaguchi and Takagi (1951) reported anti-ferroelectric behaviour of  $\text{PbZrO}_3$ . After one or two years many new ferroelectrics were discovered and it was revealed that ferroelectricity is not so isolated a phenomenon as had been considered. Large discoveries of ferroelectrics were done since 1950. The rate of discovering ferroelectrics decreased to some extent about 1965, but recently again there are many reports on new ferroelectrics. Now a days, a number

of ferroelectrics accurate research techniques have been developed and, as a result, the researches on these materials have come across the boundary which is beyond the stage of phenomenological theory. These researches have also reached the stage of precise physics of the solid state. Much of the research work is done on  $\text{Ba TiO}_3$ , triglycine sulfate and  $\text{NaN}_2$ .

The useful table of seventy six ferroelectric crystals was given by Jona and Shirane (1962). Recently Subbarao (1972) provided comprehensive compilation of ferroelectrics and antiferroelectrics known upto (1971). This provides a useful source of data on the spontaneous polarization and curie temperature of ferroelectric and antiferroelectric materials.

## 1.2 Dielectric Properties of Crystals:

According to electromagnetic theory, when the electric field at a point is  $E$ , a small change  $dD$  in electric displacement  $D$  gives rise to a change of electric energy density by an amount of  $(1/4\pi) EdD$ . This is of course applicable to the case of ferroelectrics. The relation between  $D$  and a polarization  $P$  is:

$$D = E + 4\pi P \quad \text{---} \quad (1.1)$$

The first term has nothing to do with the existence of dielectrics and can be regarded as the change of electric energy density stored in vacuum. The second term of this

equation is due to the change of polarization of dielectrics.

Above equation can be also written as:

$$\vec{D} = \epsilon \vec{E} = \epsilon_0 \vec{E}_0 \quad - - - - \quad (1.2)$$

Where  $\vec{E}_0$  and  $\vec{E}$  are the field strengths outside and in the dielectric.  $\epsilon_0$  and  $\epsilon$  are the dielectric constants of the surrounding medium and of the dielectric respectively. Since the surrounding medium is usually air or vacuum,  $\epsilon_0$  is taken to be unity.

The dielectric constant of an isotropic medium can be defined as:

$$\epsilon = \frac{D}{E} = \frac{E + 4\pi P}{E} = 1 + 4\pi \eta \quad - - - - \quad (1.3)$$

$$\text{Where } \eta = \frac{P}{E} = \frac{\epsilon - 1}{4\pi} \quad - - - - \quad (1.4)$$

Here  $\eta$  is the dielectric susceptibility.

Equation (1.4) gives relation between  $\eta$  and  $\epsilon$ .

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

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

$$\epsilon_{jk} = 1 + 4\pi \eta_{jk} \quad - - - - \quad (1.6)$$

From equation (1.5), we can write following equations due to Kelvin:

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

Corresponding to (1.7), we have the following equations for components of displacement:

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

$$D_i = \epsilon_{i1} E_1 + \epsilon_{i2} E_2 + \epsilon_{i3} E_3$$

The subscripts 1, 2, 3 refer to the orthogonal crystallographic X, Y, Z axes respectively.

The statements concerning the polarizability and internal field are summarized 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:

$$F = E + \gamma p + \vec{E} ( 1 + \gamma \eta ) \quad - - - - \quad (1.9)$$

Where,  $E$  is statistical field in the dielectric,  $p$  is polarization and  $\gamma$  is internal field constant in an isotropic medium,  $\gamma = 4\pi/3$ . But in the crystals of the lower symmetry,  $\gamma$  differs from  $4\pi/3$  but the magnitude is the same. This  $\gamma$  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:

$$P = \alpha F \quad - - - - \quad (1.10)$$

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:

$$P = \sum_j N_j P_j = \sum_j N_j \alpha_j F(j) \quad - - - - \quad (1.11)$$

Where,  $N_j$  is concentration,  $\alpha_j$  is polarizability of the atoms  $j$  and  $F(j)$  is the local field at atom sites  $j$ .

Taking local field as:

$$F = E + 4\pi/3 P \quad - - - - \quad (1.12),$$

$$\text{We get } P = \sum_j N_j \alpha_j ( E + 4\pi/3 P ) \quad - - - - \quad (1.13)$$

Therefore dielectric susceptibility  $\eta$  is:

$$\eta = P/E = \frac{\sum N_j \alpha_j}{1 - \frac{4\pi}{3} \sum N_j \alpha_j} \quad \text{---} \quad (1.14)$$

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

in CGS units, we get,

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \sum N_j \alpha_j \quad \text{---} \quad (1.15)$$

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

I) Electronic Polarizability ( $\alpha_e$ ):

This is due to displacements of electrons within the atoms or ions.

II) Atomic Polarizability ( $\alpha_a$ ):

This is due to displacement of atoms or ions within the molecules.

III) Dipolar Polarizability ( $\alpha_d$ ):

This arises from molecules with a permanent electric dipole moment that can change orientation in an applied field. The contributions to the total polarizability are shown in the Fig. (1.1).



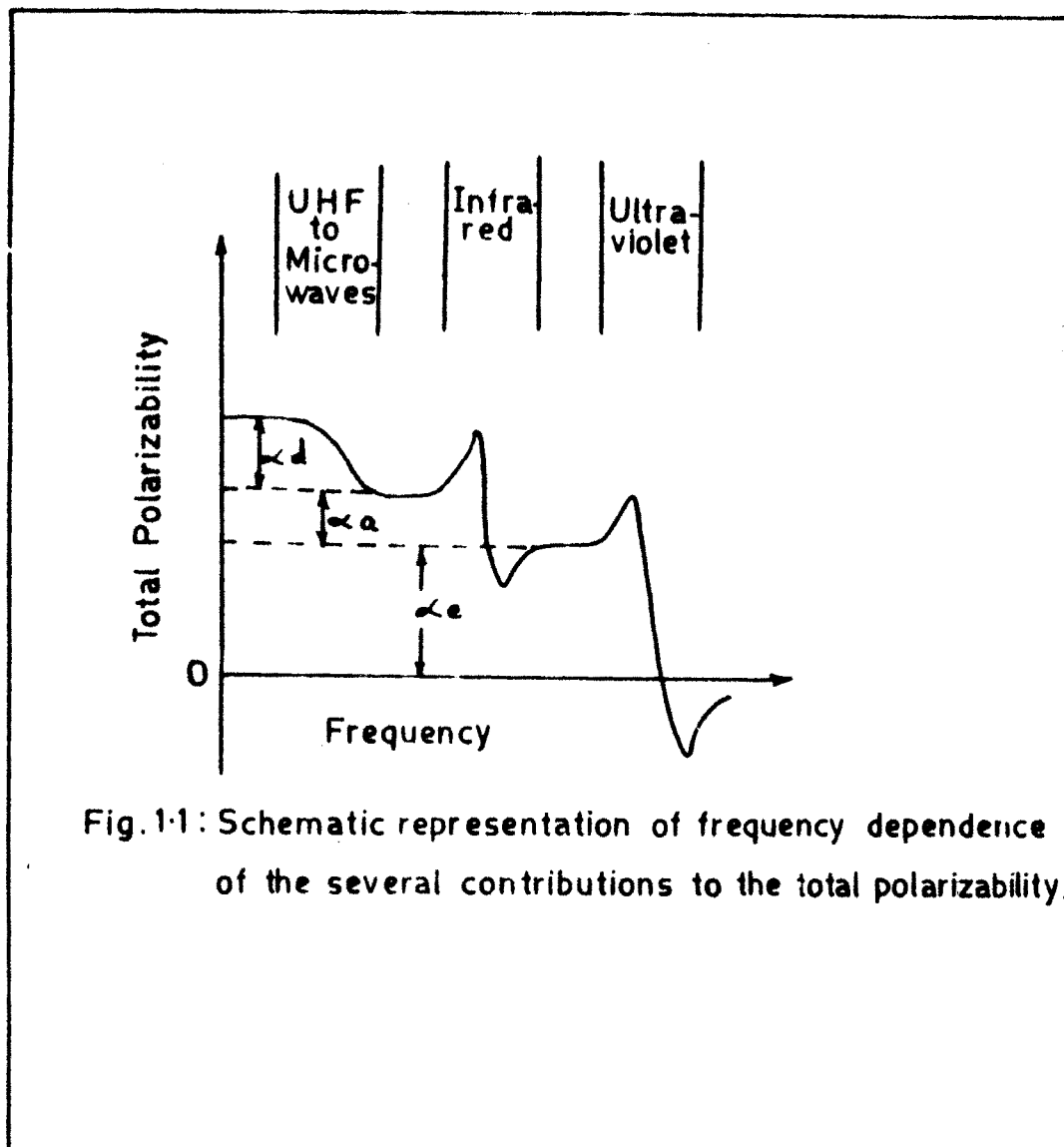


Fig. 1-1: Schematic representation of frequency dependence of the several contributions to the total polarizability.

The dielectric constant at optical frequencies is entirely due to the electronic polarizability. The atomic and dipolar contributions are small at high frequencies.

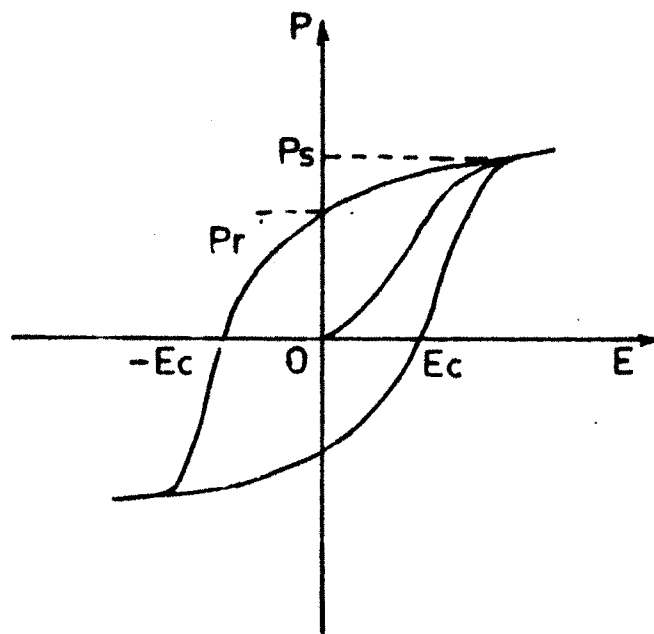
Polarizability is the function of frequency of the applied field. At low frequency of the applied field all types of polarization are equal to the value in the steady field.

### 1.3 Ferroelectric Materials and Their Properties:

Ferroelectrics are all solids and all are non-metallic, 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 non-metallic ferromagnetic materials.

A ferroelectric crystal is defined as a crystal which belongs to the pyroelectric family ( i.e. shows a spontaneous electric polarization), and the direction of spontaneous polarization of which can be reversed by an electric field. Experimentally the reversal of the spontaneous polarization in ferroelectrics is observed as a normal hysteresis loop shown in Fig. (1.2).

Three prominent properties of ferroelectrics are, their reversible polarization, their 'anomalous' properties and their non-linearities. Most of the ferroelectrics cease



**Fig.1.2:** Schematic representation of ferroelectric hysteresis loop.

$P_s$ : Spontaneous polarization.

$P_r$ : Remanent polarization.

$E_c$ : Coercive field.

to be ferroelectric above a temperature,  $T_0$  known as the transition temperature. The anomalous behavior near  $T_0$  is probably as significant as the reversible polarization, but it is not definitive of a ferroelectric. The permittivity rises sharply to a very high peak value at the temperature  $T_0$ ; the very high values in this neighbourhood are referred to as anomalous values.

The permittivity values can be calculated as:

$$\begin{array}{l} \epsilon = 1 + 4\pi \eta \quad \text{in e.s.u.} \\ \epsilon = \epsilon_0 + \eta \quad \text{in MKS units} \end{array} \quad \left. \vphantom{\begin{array}{l} \epsilon = 1 + 4\pi \eta \\ \epsilon = \epsilon_0 + \eta \end{array}} \right\} \text{---} \quad (1.16)$$

Where,  $\epsilon_0$  is permittivity of free space.

Above the transition temperature  $T_0$ , the anomaly is frequently of the Curie - Weiss form:

$$\begin{array}{l} \epsilon = \frac{4\pi C}{T - T_C} \\ \epsilon = \frac{C}{T - T_C} \quad \text{MK S} \end{array} \quad \left. \vphantom{\begin{array}{l} \epsilon = \frac{4\pi C}{T - T_C} \\ \epsilon = \frac{C}{T - T_C} \end{array}} \right\} \text{---} \quad (1.17)$$

Where  $C$  is known as the Curie constant and  $T_C$  is Curie temperature.

With increasing temperature, ferroelectricity usually 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.

The phase transition can be of the first order or of a higher (usually second) order.

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 show anomalies extending over a finite temperature range. Other properties such as polarization show discontinuity in a first order change but not in a second order change.

The properties possessed by the most of the ferroelectric materials 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 the 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 Pseudo Symmetric structure. In the ferroelectric phase 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:

Polarization  $P$  is defined as dipole moment per unit volume. Dipole moment may be measured in debyes; a debye is,  $10^{-18}$  e.s.u. or  $1/3 \times 10^{-29}$  MKS.

The existence of dielectric hysteresis loop indicates reversible spontaneous polarization  $P_S$ . The experimental methods for observation of the hysteresis loop on the screen of a Cathode Ray Oscillograph are based on the Sawyer and Tower circuit. The hysteresis loop schematically represented is as shown in the Fig.1.2. The linear extrapolation from the saturation region to zero field gives the spontaneous polarization  $P_S$ . The intercept on the polarization axis is  $P_R$  (remanent

polarization) and the intercept on the  $E$  - axis gives the coercive field.

The main defect of the Sawyer and Tower circuit is the phase difference introduced between the applied field and the polarization of the crystal, because the impedance of the crystal is variable.

The nature of the 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. Merz (1953) had reported that the transition in  $BaTiO_3$  is an example of the first order transition. In a ferroelectric crystal which undergoes the second-order phase transition,  $P_s$  decreases continuously to zero at the transition temperature. The transition in triglycine sulfate (Jona and Shirane, 1962) is an example of the second-order transition.

#### 1.5 Classification of Ferroelectrics:

The phenomenon of ferroelectricity has been discovered in a large number of crystals or materials and therefore it is become a more common phenomenon than had been considered for a long time. Therefore, it is difficult to classify the ferroelectric materials. However, the ferroelectrics have been classified according to different criteria as follows -

1) Crystal Chemical Classification:

This classification divides ferroelectric compounds into two groups: The first group includes hydrogen-bonded crystal, such as potassium dihydrogen phosphate, Rochelle Salt, triglycine sulfate etc. The second group includes the double oxides, such as  $\text{Ba TiO}_3$ ,  $\text{KNbO}_3$ ,  $\text{Cd}_2\text{Nb}_2\text{O}_7$ ,  $\text{PbNb}_2\text{O}_6$ ,  $\text{PbTa}_2\text{O}_6$  etc.

2) Classification According to the Number of Directions Allowed to the Spontaneous Polarization:

This kind of classification also divides the ferroelectrics into two groups. The first group consists of such type of ferroelectric materials that can polarize along only one axis like potassium dihydrogen phosphate type ferroelectrics, Rochelle Salt, ammonium sulfate, thiourea, triglycine sulfate and triglycine selenate. The second group includes those ferroelectrics that can polarize along several axes that are equivalent in non-polar phase such as  $\text{Ba TiO}_3$  type ferroelectrics,  $\text{Cd}_2\text{Nb}_2\text{O}_7$ ,  $\text{PbNb}_2\text{O}_6$  etc.

Both groups show piezoelectric effect in the polarized phase. Ferroelectrics of the second group often have transition points below their Curie temperature, at which the spontaneous polarization changes in magnitude and direction. This type of classification is particularly useful for the study of ferroelectric domains.



3) Classification According to the Existence or Lack of Centre of Symmetry in the Point group of their non-polar Phase:

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

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

This classification divides ferroelectrics into two groups, order-disorder group and displacive group. The order-disorder group of ferroelectrics includes crystals with hydrogen bonds, such as  $\text{KH}_2\text{PO}_4$  and isomorphous salts, triglycine sulfate. The ferroelectrics in this group undergo a transition of the order-disorder type.

The displacive group of ferroelectrics includes ionic crystals, whose structures are closely related to the Perovskite and ilmenite structures, like  $\text{BaTiO}_3$  and most of the double oxides which are ferroelectrics. The simplest ferroelectric crystal of this group is  $\text{GeTe}$  (Fawley et al, 1966) with sodium chloride structure.

5) Classification According to the Predominant Nature of Atomic Displacements Required by Polarity Reversal:

Abrahams and Keve (1971) examined the properties of ferroelectric materials. They classified ferroelectrics 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 vectors ( $\vec{A}$ ) and all Loci (L) followed by the atoms during reversal, are linear and parallel to the polar axis, Examples of this groups are  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{KMnO}_3$  and  $\text{SbSI}$ .

The two - dimensional class includes those ferroelectrics in which the atomic displacement Vector ( $\vec{A}$ ) or the actual Loci (L) followed by atoms during reversal lie in parallel planes containing the polar direction. e.g.  $\text{BaCoF}_4$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{NaN}_2$  etc.

The three - dimensional class includes those ferroelectric crystals in which the displacement Vector ( $\vec{A}$ ) and the Loci (L) followed by atoms during reversal, have essentially random orientations. Examples are  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{KH}_2\text{PO}_4$ .

1.6 Theories of Ferroelectricity:

Many physicists tried to explain the phenomenon of ferroelectricity in crystals and proposed a number of theories

but no any one theory was found to be satisfactory. The most promising and challenging theory due to Cochran is based on the lattice dynamics. We shall discuss thermodynamic theory and model theories of ferroelectricity in brief as follows:

#### 1.6(a) Thermodynamic Theory:

This theory is general 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) and Cady (1946). This theory can be also applied to  $\text{KH}_2\text{PO}_4$  type ferroelectrics.

The thermodynamic theory is not applicable to  $\text{BaTiO}_3$  type of ferroelectrics; because these crystals have more than one ferroelectric axis and are not piezoelectric in paraelectric phase. A thermodynamic theory of such ferroelectrics was developed by Devonshire (1948, 1949). This theory is based on the following assumptions:-

- 1) The free energy of the ferroelectric crystal is regarded as a function of temperature, stress and polarization.
- 2) The polarized phase is regarded as a slightly distorted unpolarized phase. Therefore, in the polarized phase the crystal is described by the same free energy function.

- 3) The anomalous piezoelectric and elastic properties are considered to be a result of the anomalous dielectric behaviour.
- 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 functions contain three components of the polarization vector.

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

$$G_1 = U - T S + \sum_i X_i X_i + \sum_m E_m P_m \quad - - - - \quad (1.18)$$

where,  $U$  is the internal energy of the crystal under external stress,  $T$  is the temperature,  $S$  is the entropy and  $X_i$  is the  $i$  th component of mechanical stress.  $P_m$  is the  $m$  th component of electrical strain (Polarization). The differential form of this function is:

$$d(G_1) = - S dT + \sum_i X_i dX_i + \sum_m E_m dP_m \quad - - - - \quad (1.19)$$

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  $G_1$  can be expanded in powers of polarization with temperature

dependent coefficients. Let us consider that crystal is ferroelectric below the transition temperature  $T_0$ . For the sake of simplicity it is assumed that in the ferroelectric region, the spontaneous polarization occurs along only one axis. Let us consider that  $G_{10}$  is the free energy of the unpolarized crystal. Devonshire found that it was necessary to consider terms upto  $P^6$ . Thus on expansion of the free energy for  $X = 0$ , is given by the equation:

$$G_1 - G_{10} = \frac{1}{2} \chi^{\dagger} P^2 + \frac{1}{4} \beta^{\dagger} P^4 + \frac{1}{6} \gamma^{\dagger} P^6 \quad (1.20)$$

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 meaning of  $\chi^{\dagger}$  can be seen from the following consideration. Let a small electric field  $E$  be applied to the crystal; then under zero pressure from equation (1.18),

$$dG_1 = - SdT + E dP \quad - - - - \quad (1.21)$$

$$\text{or } E = \left( \frac{\delta G_1}{\delta P} \right)_T \quad - - - - \quad (1.22)$$

Above the transition temperature, the polarization is small for small applied fields. Therefore for  $T < T_0$  all terms except first on the right hand side of equation (1.20) may be neglected. Hence we have,

$$E = \left( \frac{\delta G_1}{\delta F} \right) \chi^{\dagger} P \quad \text{---} \quad (1.23)$$

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

$$\frac{\delta E}{\delta P} = \frac{4\pi}{\epsilon - 1} = 1/\eta \quad \text{---} \quad (1.24)$$

From equations (1.23) and (1.24) we have

$$\chi^{\dagger} = \frac{4\pi}{\epsilon - 1} = \frac{1}{\eta} \quad \text{---} \quad (1.25)$$

This equation shows that coefficient  $\chi^{\dagger}$  is equal to reciprocal of the susceptibility  $\eta$ . However, in this temperature range, the susceptibility and the dielectric constant along the polar axis are given by Curie-Weiss law:

$$\eta = \frac{\epsilon - 1}{4\pi} = \frac{C}{T - T_0} \quad \text{---} \quad (1.26)$$

So that  $\chi^{\dagger} = \frac{T - T_0}{C}$

where,  $C$  is Curie constant and  $T_0$  is Curie-Weiss temperature. Hence equation (1.20) may be written as follows:

$$G_1 - G_{10} = \frac{1}{2} \left( \frac{T - T_0}{C} \right) P^2 + \frac{1}{4} \beta^{\dagger} P^4 + \frac{1}{8} \gamma^{\dagger} P^6 \quad (1.27)$$

From equations (1.23) and (1.27), we obtain the following equations for the applied field and the dielectric constant:

$$E = \left( \frac{\delta G_1}{\delta P} \right) P = \left( \frac{T - T_0}{C} \right) P + \beta^{\dagger} P^3 + \gamma^{\dagger} P^5 \quad (1.28)$$

$$\frac{1}{\eta} = \frac{4\pi}{\epsilon - 1} = \frac{T - T_0}{C} + 3\beta^{\dagger} P^2 + 5\gamma^{\dagger} P^4 \quad (1.29)$$

1.6(b) Spontaneous Polarization:

For the thermal equilibrium,  $(\frac{\delta G_1}{\delta P}) = 0$ . Therefore spontaneous polarization  $P_S$  for zero applied electric field satisfies the equation:

$$0 = \chi^1 P_S + \beta^1 P_S^3 + \gamma^1 P_S^5 \quad \text{--- -- (1.30)}$$

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

$$\chi^1 + \beta^1 P_S^2 + \gamma^1 P_S^4 = 0 \quad \text{--- -- (1.31)}$$

From equation (1.20) we can also write,

$$\frac{\delta^2 G_1}{\delta P^2} = \chi^1 + 3\beta^1 P^2 + 5\gamma^1 P^4 \quad \text{--- -- (1.32)}$$

If  $\chi^1$ ,  $\beta^1$  and  $\gamma^1$  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 the coefficient  $\chi^1$  becomes negative,  $G_1$  would be maximum for  $P_S = 0$ , because in this case  $\frac{\delta^2 G_1}{\delta P^2}$

is a negative quantity. When  $\chi^1$  is negative, the equation (1.20) gives at least 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.

### 1.6(c) Second Order Transition:

If the coefficients  $\beta^{\downarrow}$  and  $\gamma^{\downarrow}$  are positive and  $\chi^{\downarrow}$  varies from positive to negative as the temperature is lowered, we obtain free energy curves as shown in Fig. 1.3 (a). The corresponding spontaneous polarization, as a function of temperature is shown in Fig. 1.3(b).

For  $T < T_c$ , the spontaneous polarization is given by,

$$P_s = \left( \frac{T_c - T}{C \beta^{\downarrow}} \right)^{1/2} \quad \text{---} \quad (1.33)$$

This equation shows that  $P_s$  is a continuous function of temperature below  $T_c$  and it decreases continuously to zero at  $T_c$  as shown in Fig. 1.3(b). A transition of this type is not associated with latent heat but with a discontinuity in the specific heat and is called a second-order transition.

For second-order transition the susceptibility and dielectric constant above the Curie temperature  $T_c$  are given by

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

Below the transition temperature an expression for the susceptibility and the dielectric constant is obtained as follows:

Assuming that the term  $\gamma^{\downarrow}$  in equation (1.28) and (1.29) is negligible, we obtain -



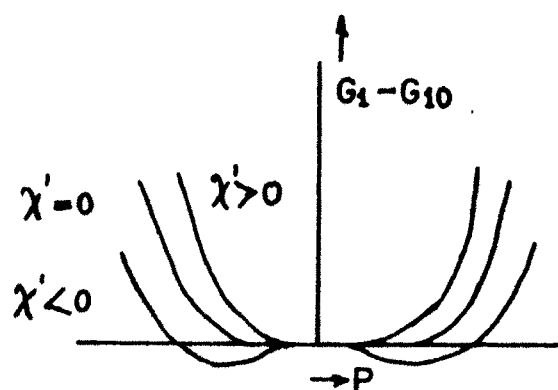


Fig.13(a): Schematic representation of the free energy as function of polarization for various values of  $\chi'$  for a second-order transition.

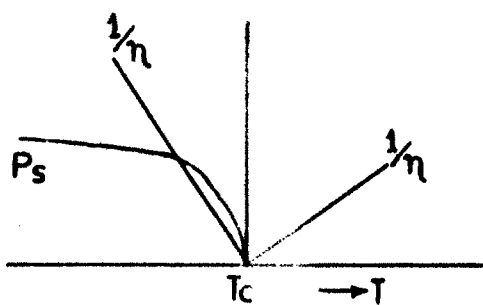


Fig.13(b): Schematic representation of the spontaneous polarization and reciprocal susceptibility near the transition temperature  $T_c$  for a second-order transition.

$$E = \left( \frac{T-T_0}{C} \right) P + \beta^1 P^3 \quad \text{---} \quad (1.35)$$

and  $\frac{1}{\bar{\chi}} = \frac{4\pi}{\epsilon - 1} = \left( \frac{T-T_0}{C} \right) + 3 \beta^1 P^2 \quad \text{---} \quad (1.36)$

For small applied fields the total polarization is nearly equal to the spontaneous polarization. i.e.  $P = P_S$ , so that according to equation (1.33), we have

$$\beta^1 P_S^2 = - \left( \frac{T-T_0}{C} \right) \quad \text{---} \quad (1.37)$$

From the equations (1.36) and (1.37) we obtain,

$$\frac{1}{\bar{\chi}} = \frac{4\pi}{\epsilon - 1} = - 2 \left( \frac{T - T_0}{C} \right).$$

Since for second-order transition

$$T_0 = T_C, \text{ we have } \frac{1}{\bar{\chi}} = \frac{4\pi}{\epsilon - 1} = - 2 \left( \frac{T - T_C}{C} \right).$$

or  $\bar{\chi} = \frac{\epsilon - 1}{4\pi} = \frac{C}{2 (T_C - T)} \quad \text{---} \quad (1.38)$

The temperature dependence of the reciprocal of the susceptibility on both sides of the transition temperature, as given by equations (1.34) and (1.38) is shown in Fig.1.3(b).

1.6(d) First Order Transition:

We know that for the occurrence of spontaneous polarization,  $\chi^1$  should be negative. If at the same time  $\beta^1$  is positive, there is a second-order transition. Let us consider the case for which  $\beta^1$  is negative as the temperature is lowered.

In this case the free energy curves are shown in Fig.1.4(a).

A transition from the non-polarized state to a spontaneously polarized state will now occur when the minimum of the free energy corresponding to  $P_S = 0$  becomes equal to the minimum associated with  $P_S \neq 0$ .

In the absence of an external field the spontaneous polarization satisfies equation:

$$0 = \chi P_S + \beta P_S^3 + \gamma P_S^5 \quad \text{---} \quad (1.39)$$

From equation (1.20) we get,

$$\frac{1}{2} \chi P_S^2 + \frac{1}{4} \beta P_S^4 + \frac{1}{6} \gamma P_S^6 = 0 \quad (1.40)$$

From equations (1.39) and (1.40), we can find the relations:-

$$P_S^2 = -3/4 \left( \beta / \gamma \right) \quad \text{---} \quad (1.41)$$

$$\chi^2 = 3/16 \left( \beta^2 / \gamma \right) \quad \text{---} \quad (1.42)$$

$$P_S^4 = 3 \left( \chi^2 / \beta^2 \right) \quad \text{---} \quad (1.43)$$

The equation (1.41) shows that the spontaneous polarization is discontinuous at the transition temperature as shown in Fig.1.4(b). According to equation (1.38), the entropy will also be discontinuous at  $T_C$  and there will be latent heat. i.e. the transition is of the first order.

Let us take into consideration the susceptibility and the dielectric constant on both sides of the transition

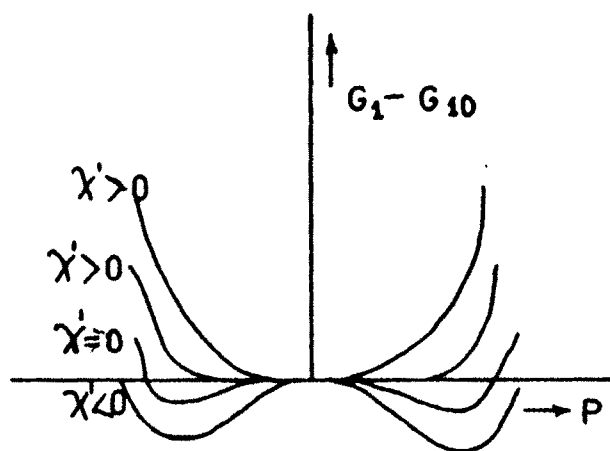


Fig.1-4(a): Schematic representation of the free energy as function of polarization for various values of  $\chi'$  for a first order transition.

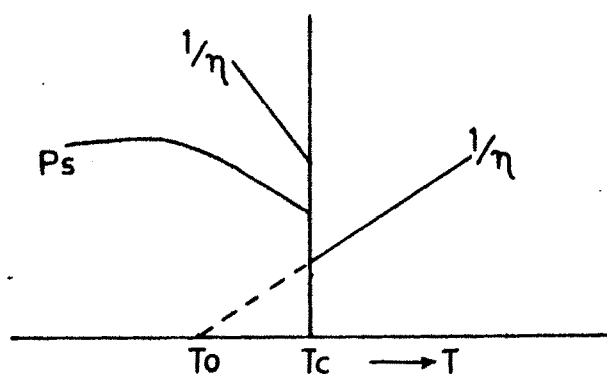


Fig.1-4(b): Schematic representation of the spontaneous polarization and reciprocal susceptibility near the transition temp.  $T_c$  for a first order transition.

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 -

$$\chi = \frac{\epsilon - 1}{4\pi} = \frac{C}{T - T_0} \quad \text{--- (1.44)}$$

If we consider first order transition, then below the transition temperature, an expression for the susceptibility and the dielectric constant is given by:

$$\chi = \frac{\epsilon - 1}{4\pi} = \frac{C}{4(T - T_0)} \quad \text{--- (1.45)}$$

From equations (1.44) and (1.45) it is seen that the reciprocal of the susceptibility in a first order transition is not negative at the transition temperature  $T_C$ , but it is positive quantity. Its temperature variation just above and just below  $T_C$  is shown in Fig.1.4 (b).

#### 1.6(c) Model Theories of Ferroelectricity:

The physical models consisting of dipole moments of different unit cells oriented along the common direction are essential to explain the occurrence of spontaneous polarization. A number of physicists have proposed model theories of ferroelectricity. An introductory idea of these model theories is given below:

Mason and Mathies (1948) proposed the model theory of  $\text{BaTiO}_3$ . In their model theory, they suggested that stable

position for the  $Ti^{4+}$  ion is not at the centre of the oxygen octahedron but it is at any of the six positions which correspond to slight displacement from the centre towards the oxygen ions. The unit cell will have dipole moment only when  $Ti^{4+}$  is in any one of these six positions. Such a dipole can not be compared with that in polar liquids; because alignment of dipoles in liquids would be expected to give rise to ferroelectric liquids. The disadvantage of this theory is that experimental and theoretical results are quite different.

Jaynes (1950) proposed a model in which oxygen ions are displaced rather than titanium ions. This theory is satisfactory for determining the entropy change, but it predicts infra-red absorption line at  $\sim 10\mu$  which is not detected.

Devonshire's model theory (1949) consists of 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 positions.

Another model similar to that of Devonshire was proposed by Stater (1950). The only difference between these two models is that each atom has an electronic polarization and titanium ion has an ionic polarization.

Megaw (1952,54) has suggested that directional covalent bonding is of primary importance in the ferroelectricity of  $PbTiO_3$  and antiferroelectricity of  $PbZrO_3$ . Megaw pointed out

that Zr ion may have directional covalency which would certainly influence the behaviour of Pb. The drawback of Megaw's theory is that the origin of ferroelectricity is attributed to abrupt changes at each transition in the character of bonds which is rather difficult to estimate.

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

Cochran (1960-61) has proposed a lattice dynamical theory of ferroelectricity for certain crystals. The theory is based on the assumption 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 partially ionic, lattice vibrations are accompanied by polarization oscillations of equal frequency which give rise to a local field interacting with the ions through long range Coulomb forces. If for one particular mode of vibration, these long range forces are equal in magnitude but opposite in sign to the short range forces, the crystal becomes unstable for that mode. The dielectric constant, which is connected to the frequency of the critical mode becomes extremely large, as it happens at the Curie temperature.

The theory provides an explanation of ferroelectric phase transition in diatomic crystals of the NaCl-type. Cochran has used the data on the lattice dynamics of diatomic crystals and his own experimental data on the dielectric

properties of cubic crystals in an analysis of some characteristics of transition in  $\text{BaTiO}_3$ . He has estimated the dielectric constant and the spontaneous polarization. Cochran calculated the  $P_s$  of  $\text{BaTiO}_3$  at the Curie temperature as:

$$\epsilon = 1.4 \times 10^4 \text{ and } P_s = 19.5 \mu\text{coulomb/cm}^3.$$

These are very close to the experimental values. These results indicate that Cochran's theory explains quite satisfactorily many problems of  $\text{BaTiO}_3$ .

The most interesting new result of the theory is the prediction of the absolute value of the frequency  $\omega_T$  of the transverse optical mode with wave-vector zero for perovskite materials. This frequency has been estimated to be:

$$\omega_T = (2 - 3) \times 10^{11} \text{ cps for } \text{BaTiO}_3$$

The frequency lies in the millimeter wavelength range. For this reason an experimental verification of the theory is difficult.

### 1.7 Ferroelectric Domains:

The first direct optical observation of domains in  $\text{KH}_2\text{F}_4$  with polarized light was made by Zwicker and Schesser (1944). The domain structure in single crystals of  $\text{BaTiO}_3$  was reported for the first time almost simultaneously by Matthias and Van Hippel and Mitsui and Furuchi. Marutake made direct observations of the domain structure in Rochelle Salt.



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 a macroscopic spontaneous polarization. The directions of spontaneous polarizations of neighbouring domains in a ferroelectric crystal make definite angles with one-another. The demarcation between 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 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.

The reasons for the occurrence 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 be occurred cannot be a unique direction. But even in ferroelectric phase, there must be at least 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  $P_S$ . Therefore, when a ferroelectric crystal is cooled below the Curie temperature, in the absence of external electrical and mechanical stress, it breaks up into domains of different orientations. It means that from the crystallographic point of view, the domain structure is identical with the twinning structure. Twin operations of ferroelectric domains have been discussed by Zheluder and Scudalov (1956,57).

### 1.3 Applications:

Ferroelectrics have been used for many years in devices requiring piezoelectricity such as transducers. Ferroelectrics are often better than other materials for piezoelectric purposes, because the high permittivity values allow the electromechanical coupling factor to approach unity. Ferroelectrics are also used in capacitors; because they have high permittivity values. The large piezoelectric values of ferroelectric materials, especially near the transition temperature, make ferroelectrics attractive in piezoelectric applications. The ferroelectrics can be used in frequency controls, filters, miniature capacitors, thermal meters, modulating devices, frequency multipliers and dielectric amplifiers. Ferroelectrics can be also used as matrix stores, counters and other bistable elements.

a) Linear Properties:

Ferroelectric transducers have larger values of piezoelectric coefficients near the transition temperature. The purpose of transducer is in some cases, to convert a.c. fields, or sudden changes of field, into corresponding mechanical motions, as in ultrasonic generators, loudspeakers or pulse generators for use with sonic delay lines. In some other cases, the piezoelectric effects to convert small motions into electric changes, as in ultrasonic detectors, strain-gauges, microphones, pickups and devices to measure the extent of vibrations. Such devices can be quite small, with linear dimensions of a millimeter or less. A Vibration strain-gauge has been reported to give 100 mV for a movement of  $L/10^6$ , where  $L$  is its size in centimeters.

In microphones and pickups, a narrow resonance is unwanted. For matching into air 'blenders' and 'twisters' are used. These have lower mechanical impedance and undergo greater motion.

b) Non-Linear Properties:

The non-linear properties of the ferroelectrics are mostly marked at low frequencies and near the transition temperature. Ferroelectrics can replace varactor diodes, which are expensive. The loss is lower than in varactor diodes, and it has been said (Johnson, 1962) that barium

strontium titanates could be used for harmonic generation to the third harmonic at millimeter wavelengths.

The dielectric amplifier is a low frequency power amplifier. It is cheap and needs no heater supplies. This type of amplifier can be used for remote controls, servo systems, stabilization of supplies, audio-frequency amplification and for d.c. amplifier.

#### 1.9 Orientation of the Present Work:

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

Among the ferroelectric materials, vanadates of sodium and potassium are not extensively studied yet. Therefore it is difficult to understand the origin of ferroelectricity in them. These ferroelectrics are high temperature ferroelectrics and they can be obtained in the ceramic forms. A very less work is done on the vanadates of sodium and potassium by Sawada S. and Nomura (1951), Baughman (1970), K. Ramani and Viswamitra (1974). They studied the crystal structures, dielectric

hysteresis, thermal expansion, phase transition of  $\text{NaVO}_3$  and  $\text{KVO}_3$ .  $\text{NaVO}_3$  shows the irregular shape of dielectric hysteresis ( Sawada and Nomura, 1951). These vanadates of sodium and potassium are doubtful ferroelectrics.

Therefore our aim of the present problem is to prepare the ferroelectric materials of  $\text{NaVO}_3$  and  $\text{KVO}_3$  and to study the following properties of ferroelectrics:-

- 1) Dielectric hysteresis loop.
- 2) solid- State battery formation.
- 3) Second harmonic generation and ~~TA~~ANDEL effect.

REFERENCES

- Abrahams S. C. and  
Reve E. T. : (1971) Ferroelectrics, Vol.2,  
129, Gordon and Breech Science  
Publishers.
- Busch G., and  
Scherrer P. : (1935). Naturwiss, 23,737.
- Cady, W. G. : (1964). Piezoelectricity, Vol.I,  
Dover Publication, New York.
- Cochran, W. : (1960), Adv.in Physics, 9,387.
- Cochran, W. : (1961). Adv.in Physics, 10,401.
- Devonshire, A. F. : (1949). USP. Fiz. Nauk, 38,490.
- Jaynes, E. T. : (1950). Phys. Rev. 79, 1008.
- Jona E. and  
Shirane G. : (1962). Ferroelectric Crystals,  
Pergamon Press, London.
- Kittel, C. : (1971). Introduction to solid  
State Phys. 4th Edition, Wiley  
& Sons, New York.
- Mason, W. P. and  
Matthias, B. T. : (1948). Phys. Rev. 74, 1622.
- Megaw, H. D. : (1957). Ferroelectricity in  
Crystals, Methuen, London.
- Merz, W. J. : (1953). Phys. Rev. 91, 513.

- Mitsui, T. and Furuichi, J. : (1953). Phys. Rev. 90, 193.
- Mueller, H. : (1940). Ann. New York, Acad-Sci, 40, 321.
- Pawley, G. S. : (1966). Phys. Rev. Letters, 17, 753.
- Cochran, W. Cowley R. A., and Dolling, G.
- Pockel, F. : (1894). Abhandl., Göttingen, 39, 1-204.
- Ramanik, and Viswamitra, A. : (1975). Ferroelectrics, Vol. 9, 9-56.
- Sawyer, C. B. and Tower, C. H. : (1930). Phys. Rev. 35, 269.
- Sawada, S. and Monura, S. : (1951). J. Phys. Soc. Japan, 6, 192.
- Slater, J. C. : (1941). J. Chem. Phys. 9, 16.
- Slater, J. C. : (1950). Phys. Rev. 78, 748.
- Shirane, G., Sawaguchi E., and Takagi, Y. : (1951). Phys. Rev. 84, 476.
- Subbarao, E. C. : (1972). Ferroelectric and Antiferroelectric Materials, Deptt. Metallurgical Engineering, I. I. T., Kanpur, India.

- Valasek, J. : (1920). Phys. Rev. 15, 537.
- Van Hippel, A., : (1946). Ind. Eng. Chem., 38, 1097.  
Erekenridge R. G.,  
Chesley F. G., & Tisza L.
- Wil, S., and : (1945). C. R. Acad. Sc. U. S. S. R.  
Goldman, I. M. 46, 139.
- Zheludev, I. S., and : (1956). Kristallografiya, 1, 681.  
Shuvalova L. A.
- Zwicker, B., and : (1944). Helv. Phys. Acta. 17, 346.  
Scherrer, P.