Chapter

General Introduction to Ferroelectrics

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Abstract

In this chapter “General introduction to ferroelectrics” we contribute the basic idea of the fundamental properties of ferroelectrics. We focus on the following properties in the chapter such as basic introduction, classification, ferroelectric phase transitions, spontaneous polarization, local field, dielectric properties, polarizability, thermodynamics of ferroelectricity and applications of ferroelectrics. Ferroelectric materials are unusual dielectric which possesses reversible spontaneous electric polarization which can be reversed by application of stress or electric field which exhibit a range of properties. These properties are widely used in the today’s scientific and industrial technology. The large number of areas due to their peculiar and interesting properties such as high permittivity capacitors, ferroelectric non-volatile FeRAM memories, pyroelectric sensors, piezoelectric and transducers, electrooptic and optoelectronic devices, etc.

Keywords: dielectrics, ferroelectrics, polarization, piezoelectric, pyroelectric, hysteresis loop, phase transitions

1. Introduction

The investigations of dielectrics, ferroelectrics, sensor, dipolar glasses and composite materials have attracted great attention in solid-state physics and material science in recent years. These studies reveal inter-and intra-molecular interactions and encourage increasing applications of these materials in modern technology. Dielectric substances are insulators or poor conductor of electricity. In these materials, the electrostatic field persists for a long time. These materials do not have free electrons, but the application of the electric field changes their behaviour. They have the ability to be polarized under the action of the electric field [1]. Dielectric materials are classified into two main categories (i) Non-ferroelectric (called normal dielectric or paraelectric) materials and (ii) Ferroelectric materials. The non-ferroelectric materials are divided into three categories according to the prevailing polarization mechanism as (i) non-polar dielectrics, (ii) polar dielectrics and (iii) dipolar dielectrics [1]. The non-polar dielectric materials consist of one type of atoms. These types of dielectric materials become polarized in an external electric field due to the relative displacement of electric charge with respect to the nucleus. The polar dielectric materials are made up of molecules without a permanent dipole moment, and dipolar dielectrics include materials whose molecules possess a permanent dipole moment.

Ferroelectric materials are unusual dielectrics that possess reversible spontaneous electric polarization, which can be reversed by applying stress or electric field. This property of showing spontaneous polarization persists over a certain temperature interval [2]. Above the critical temperature, called Curie temperature or transition temperature, the substance loses its property of spontaneous polarization and becomes paraelectric. This change of phase property, i.e., ferroelectric phase to paraelectric phase, is associated with anomalous behaviour of many physical properties along with a change of crystal structure from low to a high symmetry. The alignment of the electric dipoles may extend only over a region of the crystal, while in another region, the direction of spontaneous polarization may be reversed. Such regions of uniform polarization are called domains, a term acquired from ferromagnetism. If we first applied a small uniform electric field (E), directed, (say) in the positive direction, we will induce uniform polarization P (a linear relationship between P and E) because the field is not larger enough to switch any of the domains with the unfavorable direction of polarization and the crystal will behave like the normal dielectric [2, 3].

A material can be either piezoelectric, pyroelectric or ferroelectric, only if its crystalline symmetry is inherent (i.e., it lacks an inversion centre). A basic principle due to Neumann is that any physical property exhibited by a crystal must have at least the symmetry of the point group of the crystal. Thus, the above properties, which are inherently asymmetric, can only arise in asymmetric crystals. All crystal structures can be divided into 32 crystal classes. Of the 32 crystallographic point groups, 11 exhibit centre symmetry, leaving 21 non-centrosymmetric point groups. One of the 21 groups, however, have an inversion centre, causing it to lose its non-centrosymmetric nature, leaving 20 non-centrosymmetric point groups which have asymmetric properties. All the crystals in these 20 classes are piezoelectric [3, 4]. When such a non-centrosymmetric crystal is subjected to mechanical stress, the ions are displaced from each other in an asymmetric manner, and the crystal becomes electrically polarized. This is called the piezoelectric effect. The inverse effect of it, i.e., an applied electric field produces strain (causes the material to either expand or contract, depending on the field direction) has also been observed. The piezoelectric effect is often used to convert electrical energy into mechanical energy and vice-versa. Quartz is the best example of piezoelectric material and the one most frequently used in transducers. Out of the 20 piezoelectric point groups, only 10 have a unique polar-axis responsible for the appearance of a spontaneous electric polarization even in the absence of an applied electric field [3, 4]. If a piezoelectric material also shows the change in spontaneous polarization (P_s) upon a change in temperature, according to the relation, $\Delta P_s = \lambda \Delta T$, where λ is the pyroelectric coefficient. This is called the pyroelectric effect. A pyroelectric material changes its unit cell dimensions up to temperature change. This causes the unit cell to either expand or contract, including a temperature-dependent polarization. The simplest example of a pyroelectric material is Wurtzite (hexagonal ZnS). In some pyroelectric materials, the spontaneous polarization can be reversed by an externally applied electric field, giving a dielectric hysteresis loop. Such materials are called ferroelectric materials, and the phenomenon of reversing the direction of polarity is called the ferroelectric effect. It is to be noted that both piezoelectric and pyroelectric are inherent properties of a material. On the other hand, ferroelectricity is an effect produced in a pyroelectric material by the application of an external electric field. Classification of these materials based on symmetry is shown schematically in **Figure 1**. The occurrence of ferroelectricity may be understood in terms of either (i) polarization catastrophe or (ii) transverse optical phonon mode [5, 6].

The relationship between the piezoelectric, pyroelectric and ferroelectric materials is shown schematically in **Figure 2**. A dielectric material is an electrical

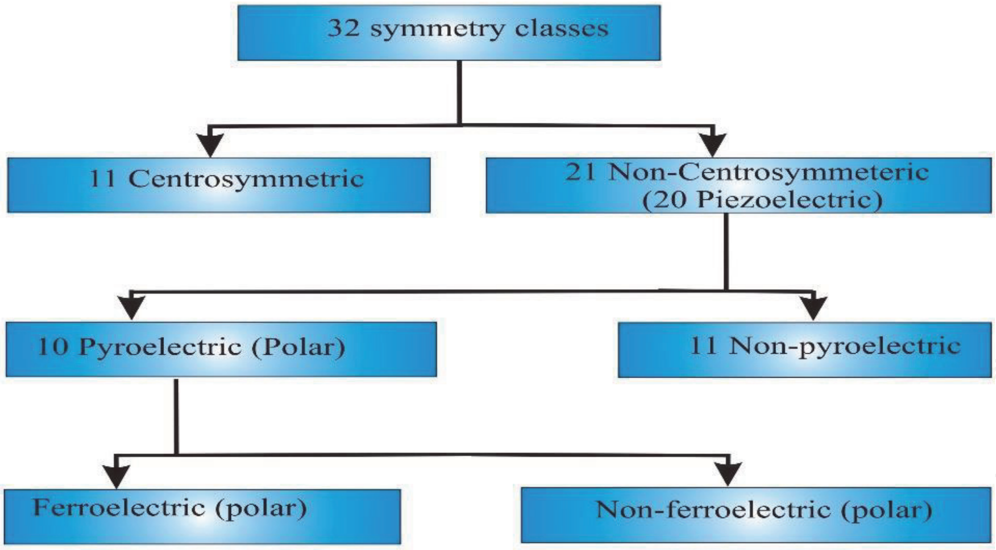

Figure 1.
Classification of piezoelectric and pyroelectric materials [6].

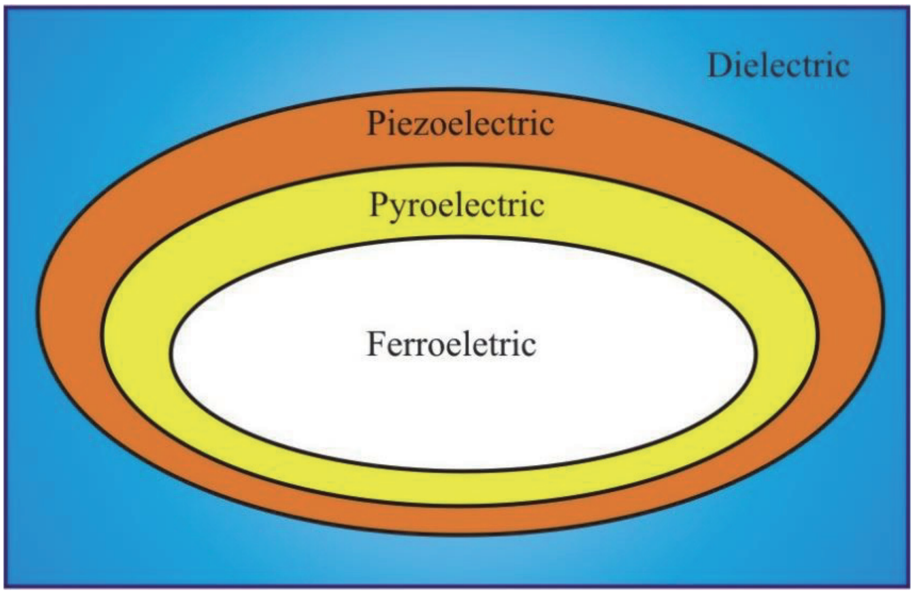

Figure 2.
Venn diagram showing the relationship between various types of dielectric materials [8].

insulator that can be polarized under an external applied electric field. Dielectric materials are often characterized by their dielectric permittivity, which describes the material's resistance against polarization by an external electric field [7, 8]. A group of dielectrics that show a change of strain or stress due to an applied external electric field or conversely to the change of the polarization due to a mechanical excitation are called piezoelectrics. Pyroelectrics are a group of piezoelectrics that show a change of polarization due to a change in temperature. Ferroelectric materials have both pyroelectric and piezoelectric properties.

Ferroelectricity is the phenomenon that refers to the state of spontaneous polarization, usually vanishes above a certain temperature called Curie or transition temperature (T_c). At the T_c, the crystal undergoes a phase transition from the polar state to the non-polar state. Three well-known characteristics of ferroelectrics are (i) their reversible polarization, (ii) their anomalous properties and (iii) their nonlinearities. Above the transition temperature (T_c), the crystal is said to be the paraelectric state. The term paraelectric is analogous with paramagnetism; similarly, there is usually a rapid drop in the dielectric constant (ε) as the temperature increases [5–9]. In ferroelectrics, the temperature dependence of dielectric constant above the Curie point can be explained by the simple law called Curie–Weiss law

$$\varepsilon = \varepsilon_0 + \frac{C}{(T - T_0)} \tag{1}$$

where ε_0 is the part of dielectric constant independent of temperature, C is the Curie constant and T_0 the Curie–Weiss temperature and it is different from the Curie point T_c (contributed by electronic polarization). The phase transition at T_c can be first-order or of the higher (second) order. In the case of a first-order phase transition, $T_0 < T_c$, while for the second-order phase transition $T_0 = T_c$. Usually, the temperature-independent term ε_0 can be neglected since it is much smaller than the term $\frac{C}{(T-T_0)}$ when T is near T_0.

2. Ferroelectric phase transitions

A phase transition is the transformation of the thermodynamic system from one phase or state of matter to another. It is a collective phenomenon in which critical behaviour depends on a small number of parameters and is universal for many systems. During a phase transition of a given medium, certain properties of the medium change, often discontinuously, as a result of some external condition, such as temperature, pressure, etc. Phase transition involves some change of symmetry. According to Paul Ehrenfest, phase transitions can be divided into two groups known as first- and second-order phase transitions, depending on whether the transition is discontinuous or continuous, respectively. Paul Ehrenfest classified phase transitions based on the behaviour of the thermodynamic Gibbs free energy as a function of other thermodynamic variables. Under this scheme, phase transitions were labeled by the lowest derivative of the Gibbs free energy that is discontinuous at the transition. First-order phase transitions exhibit a discontinuity in the first derivative of the Gibbs free energy with respect to the thermodynamic variable [10]. Second-order phase transitions are continuous in the first derivative but exhibit discontinuity in a second derivative of the Gibbs free energy with respect to a thermodynamic variable [10]. In the first-order phase transition, volume, entropy and polarization of the crystal change discontinuously at the transition point. In the second-order phase transition, the specific heat changes discontinuously, ‘whereas volume, entropy and polarization change continuously at the phase transition point. In the first-order phase transition, the energy appearing as latent heat in an infinitely narrow temperature range interval, while in the second-order phase transition, there is no release of the latent heat but the expansion of the coefficient exhibits anomalous behaviour over a finite range of temperature [11, 12].

In ferroelectrics, two common types of phase transition are identified. These are named depending on how the order parameter (polarization) changes during the transition. It is common to observe that as the temperature is raised, the bulk polarization decreases and vanishes abruptly at a Curie temperature (T_c). This is a phase transition, just as in a ferromagnet raised above its Curie temperature or a solid raised above its melting point. It arises microscopically because as the temperature is raised, the thermal vibrations of the atoms in the solid cause fluctuations, which overcome the potential barrier between the two (or more) wells. For example, in a molecular crystal such as $NaNO_2$, where we imagine that each molecule can fluctuate between two configurations. Each of which has a double potential well, as shown in **Figure 3** and some interactions between the dipoles that tend to align them [13].

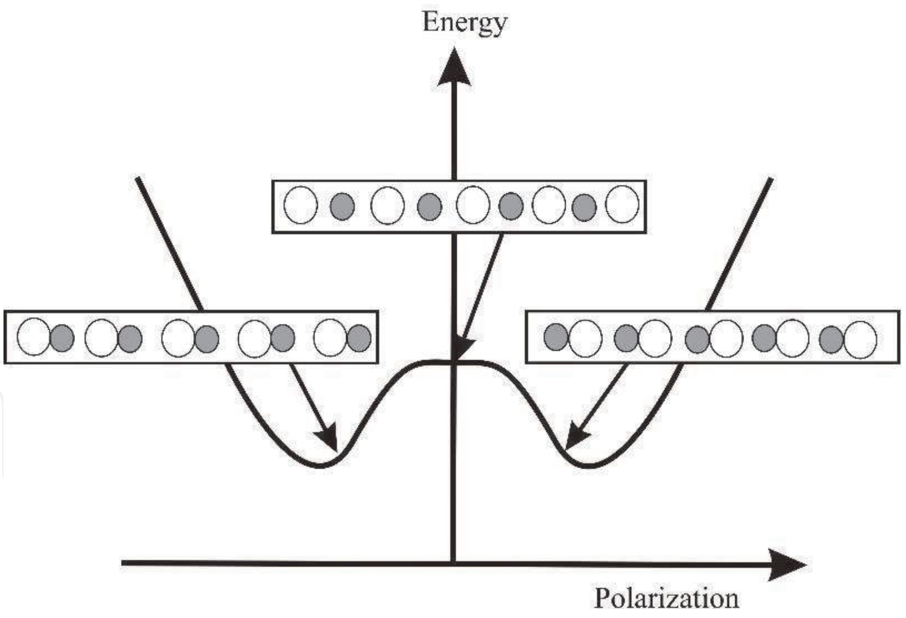

Figure 3.
Schematic potential well [13].

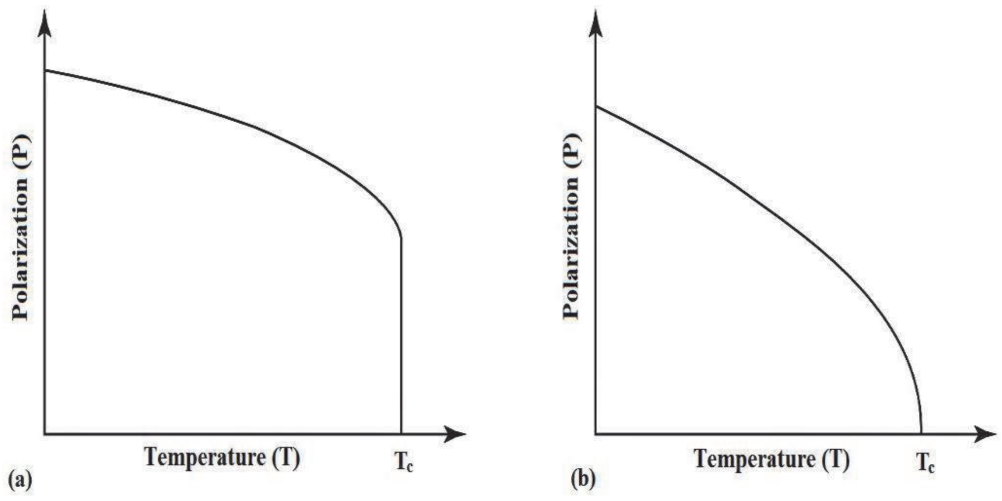

Figure 4.
Plots of spontaneous polarization versus temperature: (a) first-order transition (b) second order transition [13].

The detailed microscopic theory of how this happens will be different from material to material, but the macroscopic properties of the phase transition will be similar across many different classes of materials. A first-order phase transition is one that has a discontinuity in the order parameter itself, while a second-order phase transition is one that has a discontinuity in the first derivative of the order-parameter. In a first-order transition, the polarization varies continuously until the Curie temperature, at which there is a discontinuity shown in **Figure 4a**. In a second-order transition, the order parameter itself is a continuous function of temperature, but there is a discontinuity in its first derivative at Curie temperature shown in **Figure 4b** [13].

3. Spontaneous polarization

The intensity of polarization (P) is defined as the electric dipole moment per unit volume of the dielectric material. Spontaneous polarization (P_s) is a polarization that occurs under the influence of an internal process in a dielectric, without the effect of external factors. A ferroelectric crystal generally consists of regions called domains of homogeneous polarization, within each of which the polarization is in the same direction, but in the adjacent domains, the polarization is in different directions so that the net polarization of the specimen is equal to zero in the beginning when no electric field ($E = 0$) is applied. The polarization varies in a non-linear configuration with an electric field (E). This non-linear relation exhibits the closed curve called the hysteresis loop in the polarization when an electric field is applied, as shown in **Figure 5** [2–6]. When the electric field ($E = 0$) is zero, the spontaneous polarization (P_s) in a single domain specimen is either positive or negative in sign. As an applied electric field strength gradually increases in the direction of spontaneous polarization (P_s), the polarization (P) increases due to induced polarization such as electronic, ionic and dipolar types. As the electric field is increased further, more and more domains rotate along the direction of the electric field (E) until the polarization reaches a maximum value called the saturation value.

At this stage, the whole specimen represents a single domain. This is usually accompanied by a distortion in the crystal along the polarization direction. The extrapolation of the saturation value to zero field gives the magnitude of the spontaneous polarization (P_s). This value of P_s is the same as possessed by each domain before the application of the electric field. However, if the applied electric field decreases, the polarization also decreases but follows another path and does not become zero for zero electric field. The remaining polarization at this stage is called remnant polarization ($\pm P_r$) and the intercept on the E-axis, where P_r refers to the whole crystal block. In order to destroy the remnant polarization (P_r), the polarization of nearly half of the crystal is to be reversed by reversing the direction of the field, the electric field required to make the polarization zero is called the coercive field (E_c). Furthermore, an increase in the reverse field results in the saturation of polarization in the reverse direction. Reversing the electric field again, the hysteresis curve will be obtained. The relation between polarization (P) and applied electric field (E) is thus represented by a hysteresis loop (BDFGHB) which is the most important characteristic of the ferroelectric crystals. The most important feature of a ferroelectric is thus not the fact that it has a spontaneous polarization (P_s) but rather the fact that this spontaneous polarization can be reversed by means of an electric field [2–14].

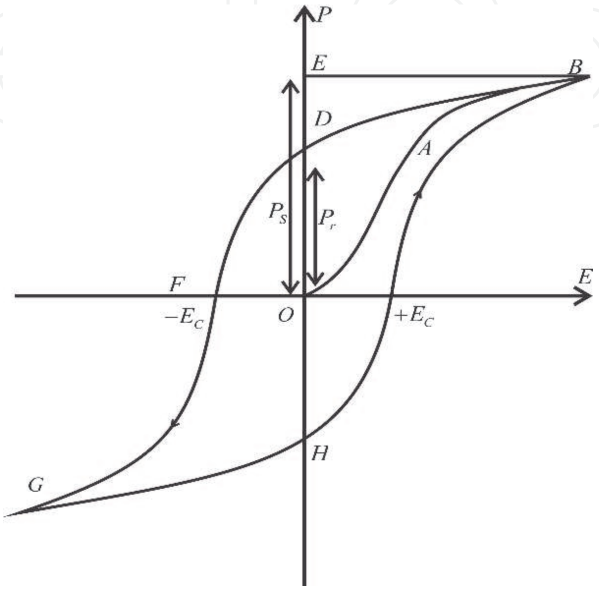

Figure 5.
Ferroelectric (P-E) hysteresis loop [13].

4. Dielectric properties

4.1 Local field

The electric field acting at the site of atom or molecule is, in general, significantly different from the macroscopic filed E and is known as the local field (E_{loc}). This field is responsible for the polarization of each atom or molecule of a material [5, 6]. For an atomic site with cubic crystal symmetry, the local field (E_{loc}) is expressed by the Lorentz-relation as

$$E_{loc} = E_0 + E_P + \frac{P}{3\varepsilon_0} = E + \frac{P}{3\varepsilon_0} \tag{2}$$

where $E = E_0 + E_P$. The field E_P is called the polarization field as it tends to oppose the external applied field E_0. Thus, apart from the macroscopic field (E), the local field also contains a term called Lorentz field (E_{loc}). The difference between the macroscopic field (E) and the Lorentz field (E_{loc}) may be understood as follows. The macroscopic field is macroscopic in nature, is an average value and is constant throughout the medium. On the other hand, the Lorentz field (E_{loc}) is a microscopic field and is periodic in nature. This is quite large at molecular sites representing that the molecules are more effectively polarized than they are under the average field.

4.2 Polarization and dielectric susceptibility

Generally, at ordinary electric fields, the magnitude of polarization (P) is directly proportional to the macroscopic electric field (E) at a given point of a dielectric [5–15]. It is expressed as

$$P \propto E \Rightarrow P = \varepsilon_0 \chi_e E \tag{3}$$

where ε_0 is the permittivity of free space and χ_e is the dielectric susceptibility. Thus, except for a constant factor (ε_0), the dielectric susceptibility is a measure of the polarization produced in the material per unit electric field. If the dielectric material slab is placed in a uniform electric field (E) with its normal parallel to the field. The dielectric displacement vector (D) for an isotropic or cubic medium relative to vacuum is defined in terms of the macroscopic field (E) as

$$D = \varepsilon_0 \varepsilon_r E = \varepsilon E = \varepsilon_0 E + P \tag{4}$$

where ε_r is called the relative permittivity or dielectric constant of medium and ε_0 is the permittivity or dielectric constant of free space, and P is the polarization. It is a scalar quantity for an isotropic medium and is always dimensionless. The dielectric constant (also called as permittivity of medium) is a measure of the degree to which a medium can resist the flow of charge, defined as the ratio of the dielectric displacement D to the macroscopic field intensity (E) as

$$\varepsilon_r = \frac{D}{\varepsilon_0 E} = \frac{\varepsilon_0 E + P}{\varepsilon_0 E} = 1 + \frac{P}{\varepsilon_0 E} = 1 + \chi_e \tag{5}$$

Eq. (5) gives the dielectric constant of an isotropic medium or cubic medium. This is represented by a scalar quantity. The dielectric susceptibility (χ_e) is related to the dielectric constant defined as

$$\chi_e = \frac{P}{\varepsilon_0 E} = \varepsilon_r - 1 \tag{6}$$

Thus, like susceptibility, the dielectric constant (ε_r) is also a measure of the polarization (P) of the material. The larger the polarization per unit resultant macroscopic field, the greater will be the dielectric constant of the dielectric medium. However, for anisotropic medium, the dielectric response ($\varepsilon_r$or χ_e) depends on the direction of the field and described by the components of the susceptibility tensor or of the dielectric tensor of the second rank

$$P_\mu = \chi_{\mu\nu}\varepsilon_0 E_\nu; \varepsilon_{\mu\nu} = \delta_{\mu\nu} + \chi_{\mu\nu} \tag{7}$$

4.3 Dielectric constant and polarizability

The polarizability (α) of an atom is defined in terms of the local electric field (Lorentz field) at the atom. The induced dipoles of moments (p) are proportional to the local field (E_{loc}) can be expressed as

$$p = \alpha E_{loc} \tag{8}$$

where α is known as the polarizability of an atom. For a non-spherical atom or isotropic medium, α will be a tensor quantity [6–16]. Thus, polarizability is an atomic property, whereas dielectric constant is a macroscopic property that depends upon the arrangement of atoms within the crystal. If all the atoms have the same polarizability (α) and there are N number of atoms per unit volume, the total polarization of the crystal may be expressed as the product of the polarizabilities of the atoms times the local field

$$P = \sum_j N_j p_j = \sum_j N_j \alpha_j E_{loc}(j) \tag{9}$$

where the summation is over all the atoms or atomic sites. N_j is the concentration and α_j is the polarizability of atom j and $E_{loc}(j)$ is the local field at atom sites j. For an isotropic dielectric medium, the local field given by the Lorentz relation Eq. (2) inside the crystal is everywhere the same so that it can be taken out of the summation sign from Eq. (9). Substituting the value of the local field from Eq. (2), the Eq. (9) becomes

$$P = \left(E + \frac{P}{3\varepsilon_0}\right)\sum_j N_j \alpha_j \tag{10}$$

On rearranging the terms and making use of Eq. (5) gives

$$\chi_e = \frac{P}{\varepsilon_0 E} = \frac{\sum_j N_j \alpha_j}{\left(\varepsilon_0 - \frac{1}{3}\sum_j N_j \alpha_j\right)} \tag{11}$$

Using Eq. (6), we get

$$\varepsilon_r = 1 + \frac{\frac{\sum_j N_j \alpha_j}{\varepsilon_0}}{1 - \frac{1}{3\varepsilon_0}\sum_j N_j \alpha_j} = \frac{1 + \frac{2}{3\varepsilon_0}\sum_j N_j \alpha_j}{1 - \frac{1}{3\varepsilon_0}\sum_j N_j \alpha_j} \tag{12}$$

Solving for $\sum_j N_j \alpha_j$ we get

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{1}{3\varepsilon_0} \sum_j N_j \alpha_j \tag{13}$$

This is known as the Clausius-Mossotti relation. It relates the dielectric constant to the atomic polarizability, but only for crystal structures for which the Lorentz field Eq. (2) obtains. The total polarization (α) can be expressed as the sum of three types of basic polarizability representing the most important contributions to the polarization [2–17] given as

$$\alpha = \alpha_e + \alpha_i + \alpha_d \tag{14}$$

where α_e, α_i and α_d are the electronic, ionic and dipolar polarizabilities, respectively shown in **Figure 6**.

i. Electronic polarizability (α_e): The electronic polarizability (α_e) arises due to the displacement of electrons in an atom relative to the atomic nucleus in the external electric field, as shown in **Figure 6a**. The polarization, as well as the dielectric constant of a material at optical frequencies, results mainly from the electronic polarizability (α_e). The optical range Eq. (13) reduces as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3\varepsilon_0} \sum_j N_j \alpha_j (\text{electronic}) \tag{15}$$

where n being the refractive index which is related to the dielectric constant (ε_r) by the relation

$$n^2 = \varepsilon_r \tag{16}$$

ii. Ionic polarizability (α_i): The ionic polarizability (α_i) arises due to the relative displacement of positive and negative ions from their equilibrium positions to a distance less than the distance between adjacent ions. The cations are displaced parallel to the Lorentz field, and the anions are displaced in the opposite direction, as shown in **Figure 6b** [5–18].

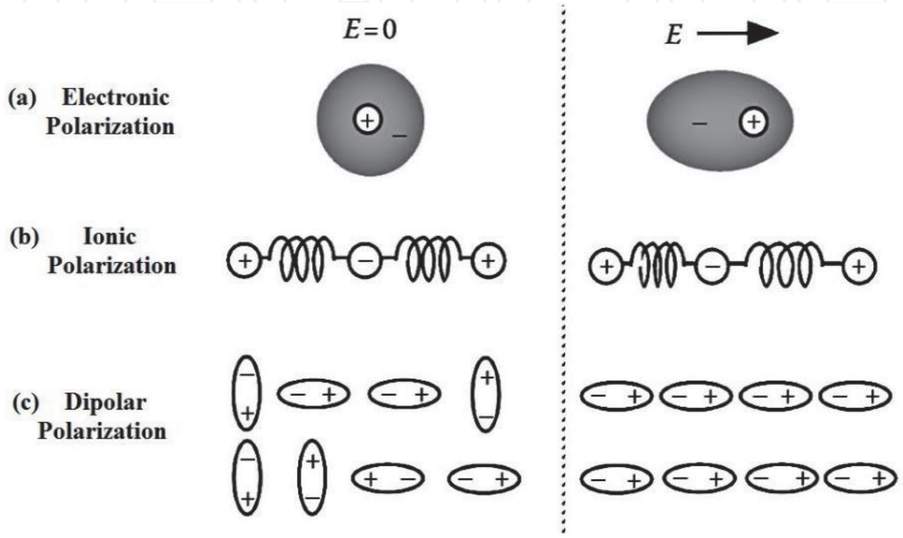

Figure 6.
Atomic contributions to electric polarization [18].

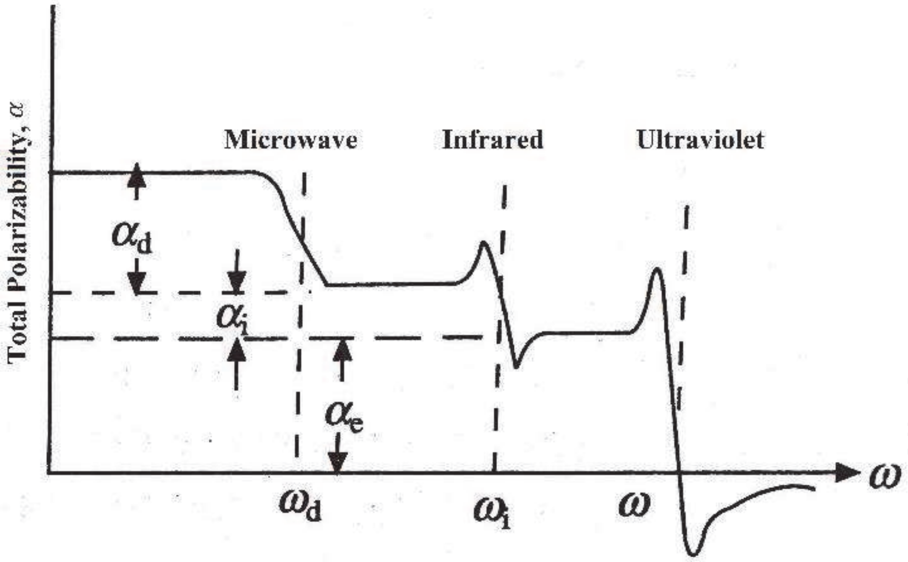

Figure 7.
Frequency dependence of the various contributions to the polarizability [6].

If the relative displacement of the positive and negative ions is d and the charge on each ion is q, then the dipole moment per molecule is $\bar{p} = qd$ and the ionic polarization becomes

$$P_{ion} = Nqd \tag{17}$$

where N is the number of atoms per unit volume.

iii. Dipolar polarizability (α_d): The dipolar polarizability, also called orientational polarizability, is important only in materials that contain complex ions having permanent dipole moment. In the absence of an external electric field, the dipoles have random orientations, and there is no net polarization. However, when the electric field is applied, the dipoles orient themselves along the direction of the field and produce dipolar or orientational polarization, as shown in **Figure 6c**. Such an orientation is opposed by the thermal agitation which tends. According to Debye's quantum theory, dipolar polarizability (α_d) per dipole is given by

$$\alpha_d = \frac{\bar{p}}{E} = \frac{p^2}{3kT} \tag{18}$$

where k is the Boltzmann's constant, T is the absolute temperature, and p is the dipole moment of the atom. The polarization contributed by electronic polarizability (α_e) and ionic polarizability (α_i) is called distortion polarization. Since α_e and α_i are temperature independent, the part of dielectric constant depending on them is essentially independent of the temperature. The contribution to the polarization made by dipolar polarizability (α_d) which is a function of temperature in accordance with Eq. (18). The contributions to the total polarizability (polarizability versus frequency curve) are shown in **Figure 7** [2–17].

We find that in the optical frequency range, the dielectric constant (ε_0) arises entirely due to the electronic polarizability. The ionic and dipolar contributions are small at high frequencies because of the inertia of the ions and molecules.

5. Classification of ferroelectrics

Ferroelectric crystals have been classified into the following types [1–6].

1. According to the chemical composition of the crystal.
   a. Hydrogen bonded and its isomorphs such as KH_2PO_4 (KDP), triglycine sulphate (TGS), Rochelle salt (RS) and lead hydrogen phosphate (LHP) etc.
   b. Double oxides such as $BaTiO_3$, potassium niobite ($KNbO_3$) and lithium niobate ($LiNbO_3$) etc.
2. Based on the number of directions allowed to the spontaneous polarization are of two types.
   a. Single-axis of polarization such as Rochelle salt, KDP etc.
   b. Several-axes of polarization such as $BaTiO_3$ etc.
3. According to the existence or lack of centre of symmetry in non-polar phase.
   a. Non-centre of symmetrical non-polar phase such as KDP and Rochelle salt.
   b. Centre of symmetrical non-polar phase such as $BaTiO_3$ and TGS crystals, etc.
4. According to the nature of the phase change.
   a. Order–disorder type such as KDP, RS, TGS, LHP and CsH_2PO_4 (CDP) etc.
   b. Displacive type such as $BaTiO_3$, $LiNbO_3$ and $KNbO_3$ etc.

In the order–disorder group of ferroelectrics, the ferroelectric phase transition is associated with an individual ordering of ions. These are the crystals that contain H-bonds and in which the motion of protons is related to the ferroelectric properties. The examples are KH_2PO_4, RS, TGS, CsH_2PO_4, $PbHPO_4$ and RbH_2PO_4, etc. The displacive group of ferroelectrics is the one in which the ferroelectric phase transition is associated with the displacement of a whole sublattice of ions of one type relative to a sublattice of another type. The displacive type ferroelectrics possess perovskite ABO_3 type structures. Examples are $BaTiO_3$, $LiNbO_3$ and $KNbO_3$, etc. Consider the case of $BaTiO_3$ crystal, as shown in **Figure 8**. The unit cell is cubic with Ba^{2+} ions occupying at the corners, O^{2-} ions occupying the face centres and Ti^{4+} ion occupying the body centre of the cube. Thus, each Ti^{4+} ion is surrounded by six O^{2-} ions in an octahedral configuration. Above the Curie temperature ($T > T_c$), the prototype crystal structure is cubic, the centres of gravity of positive and negative charges exactly coincide with each other to produce a net dipole moment is zero. Below the Curie temperature ($T < T_c$), the structure is slightly deformed with Ti^{4+} at the body centre while Ba^{2+} ions at cube corners slightly move upwards, and the structure becomes tetragonal with centres of the positive $(+)$ and negative $(-)$ charges not coinciding with each other.

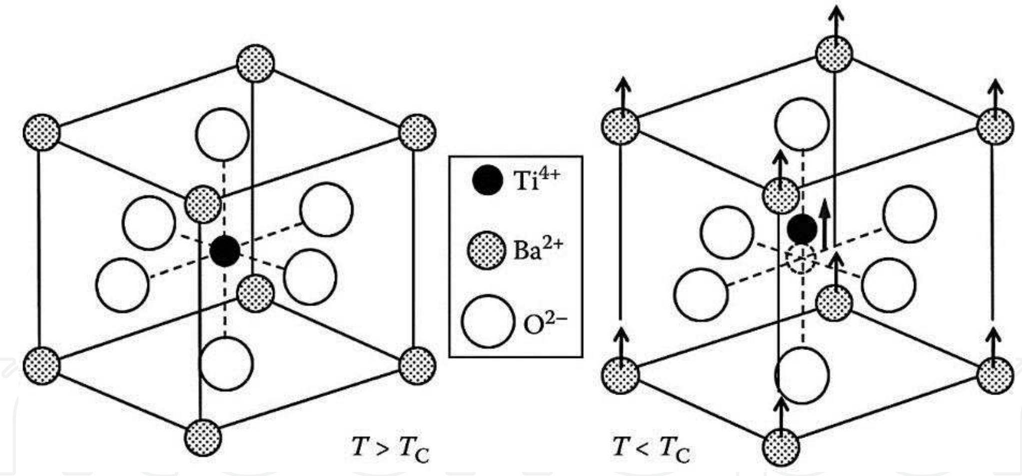

Figure 8.
Structures of BaTiO$_3$: $T > T_c$ left and $T < T_c$ right [18].

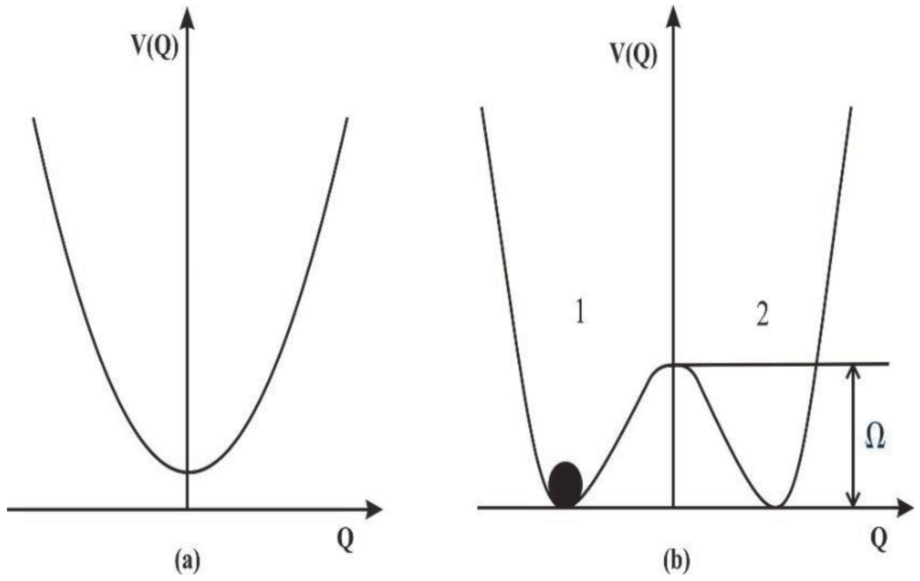

Figure 9.
Single cell potential for (a) displacive (b) order–disorder ferroelectrics [19].

This situation leads to net dipole moment and hence produces the spontaneous polarization (P_s) of the crystal [6–18]. **Figure 9** shows that in displacive ferroelectrics active atom has a single potential, while in the order–disorder ferroelectrics, the active atom has a double-well potential [19]. In the order–disorder systems, the proton can tunnel through the barrier, which separates the two minima of the potential energy in the hydrogen bond, and the ground state of the system splits into two levels separated by an energy Ω. The magnitude of Ω depends on the overlap of the wave functions appropriate to a proton located in each of the two separated minima.

6. Thermodynamics of ferroelectricity

Many of the experimental results on the macroscopic properties of ferroelectrics such as polarization and dielectric constant as well as their temperature, electric field and pressure dependence, etc. In 1920, Valasek [20] was discovered ferroelectricity in Rochelle salt. Thereafter, for about twenty years, the mechanism of ferroelectricity remained a mystery. In the period between 1935 and 1938, ferroelectricity in KDP crystal and its isostructural crystals was observed [21]. In order to explain ferroelectricity in KDP, a microscopic model Hamiltonian of disordered proton compositions was proposed, based on which a pseudospin model was developed by Slater [22] and Takagi [23] later independently. Ferroelectricity in Barium titanate ($BaTiO_3$) was reported in 1945–1946 [24, 25], and a microscopic model of Ti^{4+} ion displacement was proposed by Slater in 1950 [26]. Devonshire [27] developed a phenomenological approach based on Landu-Ginburg phase transition theories [28, 29] to explain ferroelectric phase transitions. Later on, the thermodynamic theories of piezoelectricity were summarized by Cady [30] and Mason [31] independently. The most important concept in the theory of solid-state phase transitions is the concept of a "soft mode", which was developed on the basis of lattice dynamics by Cochran [32, 33] and Anderson [34]. According to the concept of a "soft mode", ferroelectric order stems from the instability of a transverse vibrational mode or a ferroelectric mode. Detailed lattice dynamic calculations for ferroelectric crystals and more rigorous mathematical treatments of the soft mode in ferroelectrics and anti-ferroelectrics have been made by Blinc and Zeks [35] and others [36]. Later on, ten years ago, it was believed that there were two different types of ferroelectric phase transition mechanism: displacement type and order–disorder type. However, several ferroelectric phenomena discovered that could be explained neither by a displacement type mechanism nor by an order–disorder type mechanism unequivocally. Therefore, several unified models based on a combination of both mechanisms have been proposed [37], such as in the general model developed by Stamenkovic et al. [38], two basic ordering parameters associated with the motion of active atoms etc. Based on the theory of phase transition of Landau-Ginzburg [28, 29] and Devonshire [27], developed the phenomenological theory of ferroelectricity by choosing the polarization as an order parameter. The most convenient treatment of the ferroelectric phase transition by using the elastic Gibbs function G_1 as a state function of the ferroelectric system and the temperature (T), stress (Λ) and polarization (P) as independent variables [39, 40]. The Gibb's free energy function is expressed as

$$G_1 = U - T\sigma + \sum_{i,j} S_i \Lambda_j \tag{19}$$

where U is the internal energy of the system, T is the temperature and σ is the entropy, S_i and Λ_j are the i^{th} and j^{th} component of mechanical strain and stress. Making the use of a differential form of the internal energy

$$dU = Td\sigma - \sum_{i,j} \Lambda_j dS_i + \sum_{n,m} E_n dP_m \tag{20}$$

where E_n is the components of the electric field. Therefore, we can write the differential form of elastic Gibbs function

$$dG_1 = -\sigma dT + \sum_{i,j} S_i d\Lambda_j + \sum_{n,m} E_n dP_m (i, j = 1, 2, \ldots 6; m, n = 1, 2, 3) \tag{21}$$

where E_n is the components of the electric field, we have $E_n = \left(\frac{dG_1}{dP_n}\right)_{T,\Lambda}$ and $S_i = -\left(\frac{dG_1}{d\Lambda_i}\right)_{T,P}$. Since the Gibbs free energy density $G = G_1 - E_n P_m$, the stable state of the system can be determined by the minimum of Gibb's free energy (G). If T and Λ_i are constants, G_1 is a function of the polarization P (if G_1 and P_n are known, then E_n are entirely determined).

6.1 Equation of state

We consider a ferroelectric crystal having an intrinsic spontaneous polarization (P_s) along a specific-axis in the space coordinate system and assume that the external pressure is constant (say one atmosphere). As G_1 of the system is not changed by reversing the direction of the axes of space coordinate system, G_1 is independent of the direction of polarization (P). Thus, G_1 is an even function of P. Therefore, we can expand G_1 as a power series, in even powers of polarization P and neglecting the odd powers of P for symmetry reasons

$$G_1(T,P) = G_{10}(T) + \frac{1}{2}\beta(T)P^2 + \frac{1}{4}\xi_1(T)P^4 + \frac{1}{6}\xi_2(T)P^6 + \ldots \tag{22}$$

where $G_{10}(T)$ is the value of elastic Gibb's free energy (G_1) of the system at $P = 0$ and in general, the coefficients G_{10}, β, ξ_1 and $\xi_2 \ldots$, are the functions of temperature (T). A stable state of a thermodynamic system is characterized by a minimum value of the Gibbs free energy G. We have $G_1 = G$ when $E = 0$, G can be replaced by G_1. When a crystal exhibits a stable spontaneous polarization (P_s) at a certain temperature, the conditions for a minimum of G_1 are

$$\left(\frac{\partial G_1}{\partial P}\right)_{P_s} = 0, \left(\frac{\partial^2 G_1}{\partial P^2}\right)_{P_s} > 0 \; or \; \left(\frac{\partial E}{\partial P}\right)_{P_s} = \chi^{-1} > 0 \tag{23}$$

Using Eq. (22) into (23), we obtained the equation of state for the ferroelectric system of the form

$$P_s\left(\beta + \xi_1 {P_s}^2 + \xi_2 {P_s}^4\right) = 0 \tag{24}$$

$$\chi^{-1} = \left(\beta + 3\xi_1 {P_s}^2 + 5\xi_2 {P_s}^4\right) > 0 \tag{25}$$

Eq. (24) has two roots: (i) the first root $P_s = 0$ corresponds to a paraelectric phase and (ii) the second root $P_s \neq 0$ corresponds to a ferroelectric phase.

6.2 Paraelectric phase

Suppose spontaneous polarization $P_s = 0$; from Eq. (25), the reciprocal of the dielectric susceptibility can be explained as.

$$\chi^{-1} = \beta(T) > 0 \tag{26}$$

It is obvious that the value of β have a positive value when a stable state of the crystal is a paraelectric phase. Therefore, the boundary conditions at the critical temperature is $(\beta(T))_{T_0} \geq 0$. Expanding $\beta(T)$ as a Taylor's series in $(T - T_0)$ and taking into account only the first-order term in $(T - T_0)$, we have

$$\beta(T) = \frac{(T - T_0)}{C} \tag{27}$$

By combining Eqs. (26) and (27) we get

$$\chi = \frac{C}{(T - T_0)} \tag{28}$$

where C is the Curie–Weiss constant. This is the Curie–Weiss law, which applies to the dielectric susceptibility in a paraelectric phase. In the case of spontaneous polarization $P_s \neq 0$, we will see that the one result corresponds to a second-order phase transition when $\xi_1 > 0$, and that the other result to a first-order phase transition when $\xi_1 < 0$.

6.3 Second-order phase transitions

Consider first case $\xi_1 > 0$. The roots of Eq. (24) for ${P_s}^2 \neq 0$ are

$${P_s}^2 = \frac{\left[-\xi_1 \pm \left({\xi_1}^2 - 4\beta\xi_2\right)^{1/2}\right]}{2\xi_2} (\xi_1, \xi_2 > 0, \beta < 0) \tag{29}$$

One of the two roots of ${P_s}^2$ is always negative and corresponding to an imaginary value of P_s. When $\beta < 0$, we may get a positive root of ${P_s}^2$ and corresponding to a real value of P_s. However, for a real ferroelectric crystal $|\beta|\xi_2 \ll {\xi_1}^2$.

6.4 Susceptibility

When the temperature is below T_c. From Eq. (26), we get reciprocal of the dielectric susceptibility

$$\chi^{-1} = \left(\frac{\partial E}{\partial P}\right)_{P=P_s} = \beta + 3\xi_1{P_s}^2 + 5\xi_2{P_s}^4 \tag{30}$$

The term of $\xi_2{P_s}^4$ can be neglected when the temperature is below and near T_c because then P_s is very small and using the relation ${P_s}^2 = -\frac{\beta}{\xi_1}, (\beta < 0, \xi_1 > 0\ )$ into Eq. (30) we have.

$$\chi^{-1} = -2\beta = -2\frac{(T - T_c)}{C}, (T < T_c) \tag{31}$$

We plot the reciprocal of the susceptibility as a function of temperature in **Figure 10a**. This theoretical plot agrees well with the experimental data; the slope of the χ^{-1} curve in the ferroelectric phase is twice that of the χ^{-1} curve in the paraelectric phase.

6.5 Free energy

For $\xi_1 > 0$, using Eq. (22), $G_1 - G_{10}$ is plotted as a function of the polarization (P) at several temperatures ($T_{c1} < T_c < T_{c2}$) in **Figure 10b**. Since the sign of β, positive at $T = T_c$ and at T_{c2}, turns negative at T_{c1}, the curve representing $(G_1 - G_{10})$ changes from a minimum at T_{c2} to maximum at T_{c1} at $P = 0$. At T_{c1}, the two minima of the free energy ($P \neq 0$) corresponds to stable ferroelectric states.

6.6 Ferroelectric hysteresis loop

Using the value of $\beta = \frac{(T - T_c)}{C}$ and $E_i = \left(\frac{\partial G_1}{\partial P_i}\right)_{T,\Lambda}$ impiles

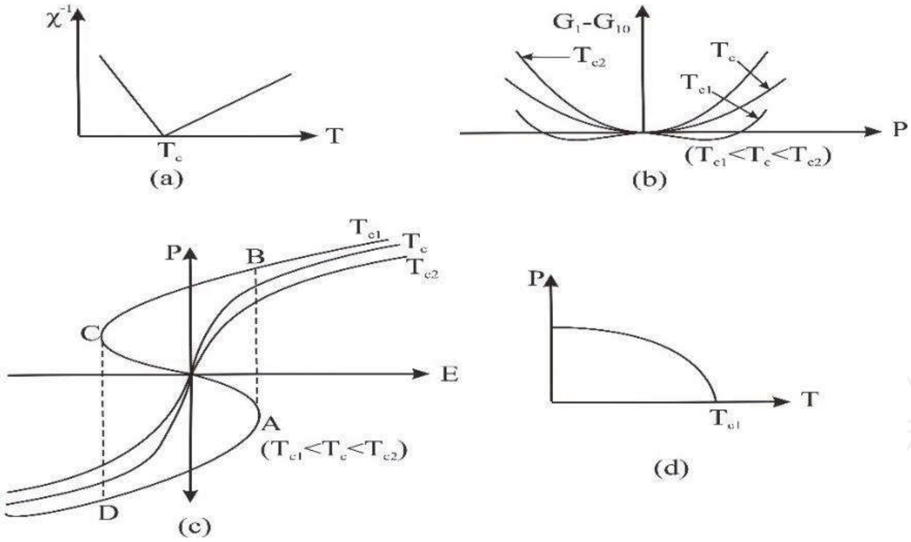

Figure 10.
Functional relations of (a) χ^{-1} *versus* T; *(b)* $G_1 - G_{10}$ *versus* P; *(c)* P *versus* E *and (d)* P *versus* T *near the second-order phase transition [40].*

$$E = \beta P + \xi_1 P^3 + \xi_2 P^5 \tag{32}$$

We get $(P - E)$ curve at different temperatures corresponding to different β values are displayed in **Figure 10c**. In fact, at temperature $T_{c1}(<T_c)$, the segment in the curve from point A to point C corresponds to an unstable state, since the slope in this segment corresponds to $\beta > 0$. The experimental curves always jump directly from the state A to the state B and also directly from C to D. Thus, the observed results are hysteresis loop.

6.7 Spontaneous polarization

When $E = 0$, we putting Eq. (27) into relation $P_s^2 = -\frac{\beta}{\xi_1}$, $(\beta < 0, \xi_1 > 0)$, we get

$$P_s^2 = \frac{(T_c - T)}{\xi_1 C} \tag{33}$$

The function P_s changes continuously with temperature and becomes zero at T_c as shown in **Figure 10d**. This theoretical curve agrees with the experimental results in ferroelectric crystals exhibiting second-order phase transitions.

6.8 First order phase transitions ($\xi_1 < 0$)

As explained above the condition for the occurrence of spontaneous polarization (P_s) is that β should be negative while ξ_1 should be positive and there is second-order transition, for first-order transition, the coefficient β is negative and also ξ_1 is negative as temperature is lowered. The Gibbs free energy curves with function of polarization (P) at different temperatures for this transition are shown in **Figure 11a**. It is obvious that the polarization state $(P \neq 0)$ is stable at the temperature $T_{c1}(<T_c)$ in the **Figure 11b**. The P-E curves at various temperatures are plotted in **Figure 11b** from the hysteresis loop occurs at $T_{c1}(<T_c)$. For $E = 0$, the spontaneous polarization (P_s) satisfies the Eq. (28) and from the Eq. (22), using the condition $G_1 = G_{10}$ we get the following relations given by.

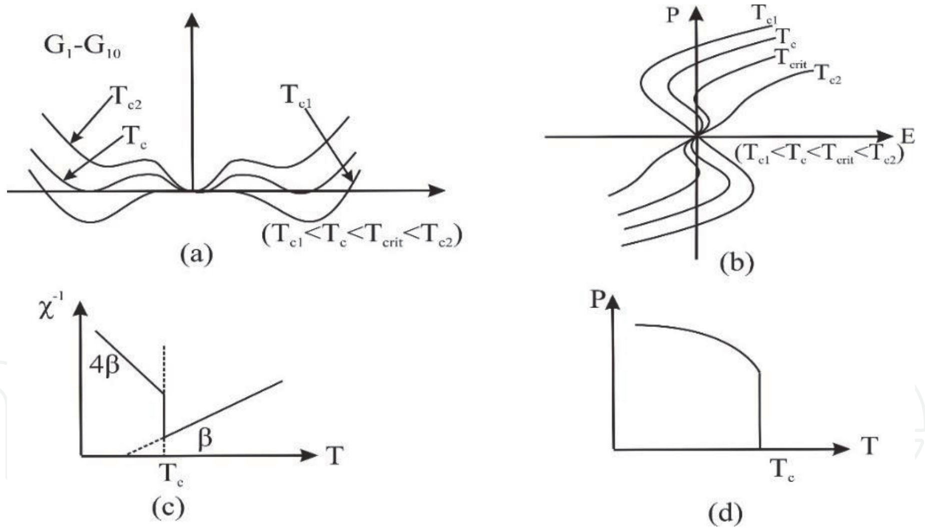

Figure 11.
Functional relations of (a) $G_1 - G_{10}$ versus P; (b) P versus E; (c) χ^{-1} versus T and (d) P versus T near the first-order phase transition [40].

$$P_s^2(T_c) = \frac{3|\xi_1|}{4\xi_2}, \beta = \frac{3{\xi_1}^2}{16\xi_2}, P_s^4(T_c) = \frac{3\beta}{\xi_2} \tag{34}$$

Combing the Eq. (30) with Eq. (34) and keeping in the mind that $\xi_1 < 0$ in the second term of Eq. (30) we get.

$$\chi^{-1} = 4\beta = 4\frac{(T - T_c)}{C} \tag{35}$$

At the transition temperature (T_c), the χ^{-1} in a first order transition is not zero but it is positive quantity as can be seen from Eq. (35). The variation of temperature dependence of inverse (χ^{-1}) above and below the transition temperature (T_c) is shown in **Figure 11c**. The χ^{-1} at a temperature just below T_c is four times that at a temperature above T_c. The curve for the polarization (P) with temperature (T) is shown in **Figure 11d**.

7. Model theories of ferroelectricity

Various physicists have developed model theories of ferroelectricity. An introductory idea of model theories that have been developed to explain the phenomenon of ferroelectricity is given below. Many experimental and theoretical attempts were made to explain the phenomenon of ferroelectricity in single and polycrystals and proposed a number of theories. The first theoretical explanation of the ferroelectric properties of Rochelle salt was proposed by Kurchatov [41]. Slater [22] put forward the first molecular theory of ferroelectricity and suggested that the ferroelectric behaviour in KDP and Rochelle salt is principally due to the ordering of H-bonds. A general theory of ferroelectricity established at that time by Cochran's lattice dynamic theory [33] and Lines statistical theory [42] have provided for major understanding of the ferroelectric phenomena of ferroelectricity.

A simple order–disorder model Hamiltonian was proposed by Mason [43]. In this model, a proton motion along an H-bond. A proton may transfer from one-well to another, and vice versa, stochastically over a potential barrier, and this model does not explain the isotope effect. Blinc [44] introduced the concept of proton tunneling motion between the two equilibrium sites in the double-well minimum O-H–O bond potential. The Blinc's [44] concept was quickly put into the simple formalism of the pseudospin-model by De Gennes [45] and independently by Matsubara [46]. De Gennes [45] showed that the proton in a double minimum type potential has described by a one-half pseudospin. The pseudospin model Hamiltonian developed to explain the proton system and the triggering of phase transition can be ascribed to the ordering of the proton in the double-well potential. The dipoles formed by the proton ordering make a small contribution to the spontaneous polarization (P_s) which is the result of heavy atoms displacements along the ferroelectric axis. The major contribution to the spontaneous polarization (P_s) is the displacement of heavy atoms projected on c-axis. To account for the displacement of the heavy atoms, Kobayashi [47] included pseudospin lattice interaction into the pseudospin model. The net result of this approach was to enhance the effective dipolar proton-proton interaction.

Later on, Arefev et al. [48] and Brout et al. [49] suggested that essentially the same concept could also be applied such that KDP etc. In this case, where the permanent electric dipoles move-in a potential with more than one equilibrium position and the soft mode collective excitations are not phonons but rather the unstable pseudospin phonon coupled-wave. Kaminow [50] experimentally confirmed the existence of soft mode in KDP crystal, and the other investigators also confirmed the soft mode in other ferroelectric crystals. It is now well recognized that the several interesting properties of ferroelectrics are associated with the high-temperature dependence of the soft mode. Cowely [51] has given a microscopic theory of ferroelectricity in which the temperature dependence of the normal mode (soft mode) arises from anharmonic interactions between normal modes. These anharmonic interactions in a crystal are quite small, at least at low temperatures, so that an anharmonic crystal provides an example of the many-body system in which interactions between the elementary excitations are both small and non-singular. In the harmonic approximation, the equations of motion of the shell model can be obtained from a quadratic function of the displacements of the ions and of the electronic dipoles produced on the ions during the lattice vibrations. The anharmonic interactions arise from the cubic and higher terms in potential function, and in general, there will be anharmonic interactions between all the displacements and all the dipoles. In the ferroelectrics, the root at wave vector $\vec{k} = 0$ is imaginary in the harmonic approximation showing the instability of the lattice [51]. This indicates that the harmonic forces alone are not sufficient to stabilize the system at any temperature. The stabilization of the mode can only be brought about by a consideration of anharmonic interactions terms. The anharmonic interactions thus play a fundamental role as regards the stability of the crystal system. A number of physical properties of solids could be well explained by considering the effects of phonon anharmonic interactions.

A very successful attempt has been made to give a microscopic theory of ferroelectric crystals given by Cochran [33, 52]. This lattice dynamical theory is based on the hypothesis that the ferroelectric transitions are the results of the instability of the crystal lattice with respect to one of the homogeneous (wave number $k = \frac{2\pi}{\lambda} = 0$) transverse optic mode. If a crystal is fully or partly ionic, lattice vibrations are accompanied by polarization oscillations having an equal frequency which provide a Lorentz field called local field interacting with the ions through long-range Coulomb forces. The crystal becomes unstable for one particular mode of vibration at which the long-range forces are equal and opposite to the short-range forces. A relation given by Lyddane et al. [53] explains the relation between the ferroelectric properties and the thermodynamic properties of the crystals. For $k = 0$ modes of diatomic crystal, Lyddane et al. [53] relation gives the ratio of the static dielectric constant (ε_s) of the crystal to the high-frequency dielectric constant (ε_e) in terms of the frequencies of the longitudinal optical (ω_L) and transverse optical (ω_T) of infinite wavelength

$$\frac{\varepsilon_s}{\varepsilon_e} = \frac{{\omega_L}^2}{{\omega_T}^2} \tag{36}$$

When ${\omega_T}^2 = 0$, we get $\varepsilon_s = \infty$. Cochran [32] developed a more general case in which there are n atoms in the elementary cell as

$$\frac{\varepsilon_s}{\varepsilon_e} = \prod_j^n \frac{\left({\omega_j}^2\right)_L}{\left({\omega_j}^2\right)_T} \tag{37}$$

This Eq. (36) produces one essential anomaly needed to explain a ferroelectric transition. In order to complete understanding the ferroelectric behaviour, it is necessary to investigate the temperature of ${\omega_T}^2$. In the ferroelectric crystal, the static dielectric constant (ε_s) obeys Curie–Weiss law above $T_c(T > T_c)$. Eq. (37) was derived for harmonic forces. In order to derive the temperature dependence of ${\omega_T}^2$ it will be necessary to introduce anharmonic interaction, which shows little effect on any mode other than$k = 0$ mode, and only that mode exhibits any anomalous behaviour. Thus Eq. (37) through (36) implies that the transverse optical mode ${\omega_T}^2$ have anomalous temperature dependence given by the Curie–Weiss law by a relation ${\omega_T}^2 = K(T - T_c)$, where the coefficient K is constant related to the temperature dependence dielectric constant $\varepsilon(T)$ through the Lyddane et al. [53] relation.

8. Applications of ferroelectrics

Ferroelectric materials have been extensive applications [3, 54] in a large number of areas due to their peculiar and interesting properties such as high permittivity capacitors ($BaTiO_3$), ferroelectric non-volatile FeRAM memories (due to bi-stable polarization in modulation and deflector), pyroelectric sensors, piezoelectric and electrostrictive transducers (TGS crystal), electrooptic and optoelectronic devices (due to their non-linear polarizability), thermistors, storage and laser devices, sensors, resonators and actuators which have revolutionized consumer electronics, automobile industry, biomedical diagnosis, underwater acoustic technology, defense-related sectors, gas sensing devices and surface acoustic wave technology, etc. The major areas of applications [3, 54] of ferroelectrics have received a great deal of attention amongst all the above capacitors, ferroelectric memories, pyroelectric sensors, piezoelectric, electrostrictive transducers, electrooptic devices and thermistors. The basic specifications required for capacitors are small size, large capacitance (materials with a large dielectric constant are desired). High frequency characteristics (ferroelectrics with a high dielectric constant are sometimes associated with dielectric dispersions, which must be taken into account for practical applications). Ferroelectric relaxors such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Pb(Zn_{1/3}Nb_{2/3})O_3$ are some examples of these applications.

The bi-stable polarization of ferroelectrics makes them useful for binary memory systems. There are volatile and non-volatile memory devices in erasable semiconductor memories. Non-volatile memory does not require a holding voltage. Dynamic random-access memory (DRAM), which is widely used because of its high integration capability, is an example of volatile memory. Data stored in these memories are lost when the electric power is shut off. To record information of polarization may be reversed or reoriented by application of an electric field greater than the coercive field. For erasure, the polarization can be returned to its original state with an applied field of opposite polarity. To read the stored information, it is retrieved by electrical or optical means. Optical memory is an electrically addressed light valve. For example, $BaTiO_3$, $(Pb,La)(Zr,Ti)O_3$ and $Pb_5Ge_3O_{11}$ single crystals are extensively used as light values. When a ferroelectric thin film with a large polarization-electric field hysteresis is used as the memory capacitor, non-volatile memory is realized. When a voltage is applied to the gate and the field-effect transistor (FET) assumes the "on" state, a pulse voltage to the drain generates a drain current dependent on the remanent polarization state. A large electric field is applied to a ferroelectric film in every process in the ferroelectric RAM (FeRAM), the polarization hysteresis characteristic degrades with increasing cycles. This problem of ferroelectric films needs to be overcome for non-volatile memory applications. The development of the ferroelectric memory started with DRAMs is composed of a FET and memory capacitor, then moved into FeRAMs and is now focused on metal ferroelectric semiconductor field-effect transistors (MFSFETs). $BaTiO_3$, $LiNbO_3$ and KH_2PO_4 crystals, etc., are some examples of these applications.

The pyroelectric properties of polar materials were studied a long time ago, and such materials were belonged as electric stones, measuring the current or voltage response of a crystal to a temperature change, either by continuous heating or by the absorption of sinusoidally modulated radiation. This is basically due to the temperature dependence of the spontaneous polarization of a polar material. The pyroelectric sensors are widely used for monitoring temperature or infrared radiation (IR). Practical applications of the pyroelectric material in temperature sensors and infrared (IR) light detectors lead to some commercial making of ferroelectric ceramics. Pyroelectric detectors can be used to record infrared images. The converse effect is called the electrocaloric effect, which may be a future cooling system. Materials such as TGS, $LiTaO_3$, $Sr_{1/2}Ba_{1/2}Nb_2O_6$ etc. are some examples. Another important application of piezoelectric devices. Certain materials produce electric charges on their surfaces when mechanical stress is applied. The induced charges are proportional to the mechanical stress. This is called the piezoelectric effect, which was discovered in Quartz by Pierre and Jacques Curie in 1880. Materials showing this phenomenon also conversely have a geometric strain proportional to an applied electric field showing the converse piezoelectric effect, discovered by Gabriel Lippmann in 1881. The root of the word "piezo" means "pressure" in Greek. Hence the original meaning of the word piezoelectricity implied "pressure electricity". The phenomenon of Piezoelectricity is widely utilized in the fabrication of various devices such as sensors, transducers, actuators, surface acoustic wave (SAW) devices, frequency control devices etc. Quartz, $BaTiO_3$, $(Pb, Sm)TiO_3$, $LiNbO_3$, and $LiTaO_3$ etc., are some materials that can be used for these applications.

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