Ferroelectric, Piezoelectric Mechanism and Applications

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ABSTRACT
The features of ferroelectric materials and their applications are presented. State-of-the-art employment of characterization techniques, and the properties of ferroelectric materials are described. Classification of ferroelectric materials, phase transitions, and diffuse phase transition (DPT) have been discussed. Properties of ferroelectrics, polarization-field hysteresis, dielectric hysteresis, reversal of spontaneous polarization, and dielectric properties have been explained. Besides these, piezoelectric and pyroelectric properties of materials have also been demonstrated. The applications of ferroelectric thin films have been discussed with a specific focus on acousto-optic (AO) properties and their applications.

1. Introduction—nature of ferroelectricity
Polarization of charges is the displacement of electric charges when a dielectric is subjected to an electric field. There are numerous mechanisms taking place at atomic levels that can cause the polarization in dielectrics[1], and the dipole moment $p$ induced by the electric field varies in direct relation to the local electric field $E_{loc}$

$$p = aE_{loc}$$

(1)

The net polarizability $a$ can be expressed as the summation of four expressions denoting the most significant mechanisms contributing to the polarization:

$$a = a_e + a_i + a_d + a_s$$

(2)

where the electronic polarizability $a_e$ is generated by the relative shift of the nucleus and the cloud of atomic electrons, the ionic polarizability $a_i$ results from the comparative shifts of the negative and positive ions, the dipolar polarizability $a_d$ is attributed to the alteration in the direction of the permanent dipoles within a solid, while the space-charge polarizability $a_s$ originates from the charge carriers that migrate within the dielectric. The availability of numerous types of excitations of such polarizable charges in crystals makes them exclusive polar crystals fitting to the class of ferroelectric materials [2]. An example of the creation of such a dipole moment in a solid material is illustrated in Figure 1, where the unit cell of the common perovskite structure is shown.

The polarization is enhanced in the ferroelectric materials because of the absence of symmetry in the crystallographic structure of the unit cell as illustrated in Figure 1. This unit cell is in fact, the building block in the perovskite-type of ferroelectric materials where, in some range of pressure and temperature, spontaneous polarization can occur, and this electrical polarization can be reoriented between its different equilibrium states of orientation by applying an electric field. This generates a loop, corresponding to dielectric hysteresis, between the change of polarization and applied electric field as illustrated in Figure 2, together with the important hysteresis loop parameters.

1.1. Classification of ferroelectric materials
The symmetry elements are used to describe symmetry about a point in space, and employing these elements of symmetry, all crystals can be separated into 32 diverse point groups or classes [3]. These 32-point groups are subcategories of the seven basic crystal systems, the crystal system is a grouping of crystal structures that are categorized according to the axial system used to describe their “lattice”. A crystal’s lattice is a three dimensional network of atoms that are arranged in a symmetrical pattern. Each crystal system consists of a set of three axes in a particular geometrical arrangement. The seven unique crystal systems, listed in order of decreasing symmetry, are: 1. Isometric System, 2. Hexagonal System, 3. Tetragonal System, 4. Rhombohedral (Trigonal) System, 5. Orthorhombic System, 6. Monoclinic System, 7. Triclinic System. Twenty-one out of the 32-point groups lack a center of symmetry, and 20 exhibit piezoelectricity as they become polarized on the application of mechanical stress. The remaining one point group out of the 21

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Figure 1. The perovskite unit cell structure. The opposite shift of the anions and cations with regard to their equilibrium positions causes the generation of an electric dipole.

Figure 2. Ferroelectric hysteresis loop, showing properties of coercive field ($E_C$) and remanent polarization ($P_R$).

does not exhibit piezoelectricity, even though it lacks a center of symmetry, due to the combination of symmetry elements. Ten out of the 20 piezoelectric point groups display a polarization that has a finite and permanent value, termed as spontaneous polarization, which exists when the applied stress or field is zero, and such dielectric materials are known as polar materials or pyroelectric materials.

Materials exhibiting ferroelectricity are those polar dielectrics which when subjected to an external electric field reverse and reorient their spontaneous polarization. An organic pyroelectric crystal will be a ferroelectric if it satisfies the structural conditions that no atom within the unit cell can be displaced by more than about 1 Å from the position that it would occupy in the non-ferroelectric phase and that the displacement is greater than about 0.1 Å [4]. The first report on ferroelectricity was first published on Rochelle salt in 1921; the second was on KDP in 1935, and after that on BaTiO$_3$ in 1944. Since then, there has been a steady addition to this list, and at present, there are over 200 materials known to show ferroelectricity [5]. Initially, the name ferroelectric was not common, and this phenomenon was known as Seignette electricity.

Materials exhibiting ferroelectricity are a subcategory of pyroelectric materials, which further are a subcategory of piezoelectric materials [6]. Consequently, the ferroelectric materials own both the pyro and piezoelectric attributes in addition to their exclusive ferroelectric characteristics. Ferroelectric properties have a distinctive temperature, known as the temperature of transition, and at this temperature, the material goes from the polar-ferroelectric phase to the nonpolar-paraelectric phase.

Crystallography which is the experimental technique to determine arrangement of atoms in a crystal, can be used to predict whether a given material is pyroelectric or piezoelectric, but is unable to predict the ferroelectric nature. The ferroelectric property of a material can only be determined by electrical measurements. Ferroelectrics have been classified according to the following:

(i) Crystal chemical classification,
(ii) The permitted number of orientations of the spontaneous polarization, and
(iii) The existence of lack of symmetry in the non-polar phase [7].

There are three classes of transitions that fall under structural phase transitions – reconstructive, displacive, and order-disorder. As the name suggests, the reconstructive phase transition involves the disintegration of bonds followed by their suitable rebonding in the other phase, resulting in different bond orientations (polar and non-polar) in the two phases. Thus, the two phases may exhibit radically transformed topology of the link configuration of the bonds. The reformation
of bonds is a slow process as it involves diffusion of atoms from a specific group of sites to a different set of locations, and therefore the reconstructive phase transitions are known to be time-taking (seconds to $10^{-9}$ s). If in the first phase, the material is in single crystal form, the latter phase may have smaller crystallites arising from the short-range systematic orientations of the bonds. Consequently, in several sections of the crystal, the orientations of restructured bonds are mismatched with those in the former phase.

The displacive phase transition involves a small (in comparison to internuclear distances) relative shift of atoms rather than bond disintegration. Therefore, in this phase transition, same topology of the link configuration is followed in both the phases. The time consumed in this phase transition is small ($10^{-11}$ to $10^{-15}$ s) owing to the small atomic displacements requiring time of the order of a phonon period (a lattice vibration).

The order-disorder phase transition can be further classified into two classes – substitutional/positional and orientational. In the former, the atoms may diffuse during the phase change, but the relation between the bond orientations in both the phases is close or remains the same. The time taken by this phase transition to occur is similar to that of reconstructive phase transition. Alteration in orientation of small groups of atoms by a small degree so that the material’s fundamental bonding remains undisturbed, is exhibited in the orientational order-disorder phase transition. As this phase transition does not require long-range diffusion, thus it generally takes less time than the reconstructive phase transition. The high temperature phase in both the order-disorder phase transitions exhibits disorder to some degree, either orientational or substitutional (positional).

The “order-disorder” class of ferroelectrics has permanent dipoles, which are disordered in the paraelectric phase, and on cooling through the transition temperature, they get ordered into domains. This ferroelectrics class contains crystals having H_2-bonds in which the movement of protons is mainly responsible for the ferroelectricity, e.g. Rochelle salt, TGS, and KDP. The second class of ferroelectrics, “displacive”, on the other hand, does not possess permanent dipoles in the paraelectric phase, and the transition is associated with the displacement of ions from the nonpolar paraelectric structure unit cell, and the dipoles are ordered into domains. This group of ferroelectrics involves ionic crystals. All the compounds in this group, with the exception of SbSI, have a perovskite structure.

A series of IV–VI semiconductor compounds which have a narrow bandgap, i.e GeTe, SnTe, and a solid solution of GeTe–SnTe and PbTe–GeTe, exhibit ferroelectricity, but because of their high dc conductivity, polarization reversal and dielectric constant anomaly cannot be measured. The differential capacitance measurement of Pb_{1−x}Ga_xTe junction diode under various conditions of temperature and bias shows an increase in the capacitance at the temperature of transition [8]. The ferroelectric phase transition in SnTe has been studied using the Raman scattering technique [9] and by the neutron diffraction method [10].

The solid solutions of BaTiO_3–BaSnO_3 and other disordered structures show the diffuse type of phase transition [11]. The transition from ferro-to-paraelectric phase in these systems is distinguished not by a sudden transition of structures but rather by a slow, diffuse transition occurring over a range of temperature.

1.2. Phase transitions

The shift in the state of the crystal from para-to-ferroelectric is accompanied by the slight atomic displacement, generating electric-dipole moments in the crystal [12]. According to phase transitions theory by Landau, the following types of alterations can occur in a crystal.

(i) Continual alteration with unvarying symmetry. This particular type of alteration involves no phase transition (e.g. changeover among the normal and the superconducting state)

(ii) A sudden alteration in the phase transition of first order and coexistence of two phases in equilibrium with each other at the temperature of transition. Such a transition of the phase of first order is feasible between any two phases, the solitary constraint being that the free energies of the phases become equal at the temperature of transition. The manifestation of first-order phase transition does not have any symmetry requirements.

(iii) The transition of phase of second order involves gradual modification in the crystal properties until a specific temperature of transition, when the modification is accomplished. Only one phase exists at each temperature, even at the point of transition; therefore, a transition of second order is within one phase and not between two phases. According to Aizu [13], the phase transition in the ferroelectric phase is based on the symmetry group, and in relation to the Landau’s theory of phase transition, there are three types of phase transitions: (i) primitive, (ii) complex, and (iii) others.

(i) Primitive: The paraelectric phase symmetry group includes the elements of symmetry of the ferroelectric phase in addition to the F-operation, which brings the alteration in the polarization sign. In this case, the ferroelectric phase space group will be a subgroup of the paraelectric phase space group, with 50% of elements of symmetry (second-order transition can occur).

(ii) Complex: The symmetry group of the paraelectric phase includes the ferroelectric phase symmetry group, the F-operation, and one or more independent extra
observed at a temperature well above the dielectric anomaly, in contrast to the simple perovskite, which becomes centrosymmetric at a temperature above the dielectric constant peak. The switch to the paraelectric phase from ferroelectric phase in such materials is not by a sudden structural transition but rather by a slow diffuse transition, which takes place over a range of temperature generally termed as the Curie range.

At a temperature beneath this Curie range, the material belongs to a pyroelectric state and behaves as a normal ferroelectric. Though, within the Curie range, the crystal exhibits uncommon behavior, the temperature corresponding to the maxima of dielectric constant is frequency dependent, and it is different from the temperature at which the maxima of dielectric loss and pyroelectric coefficients are obtained. The spontaneous polarization and other ferroelectric characteristics, for instance, refractive index, optical absorption edge, electro-optic properties, and specific heat anomaly, fluctuate gradually within the Curie range instead of exhibiting the drastic alterations typically anticipated at a ferroelectric transition [14].

The widening of the phase transition can be accredited to disorder in the structure and fluctuations in the composition of the solid solution. Systems with perfect structural order have sharp phase transitions. However, above the Curie temperature, the paraelectric phase may have some characteristics of the ferroelectric phase, but within a critically small volume, the ensemble average will be of the paraelectric phase. In compositionally disordered systems, broadening of the phase transition may occur depending on the microscopic details. A crystal can be represented as a collection of small regions with a conventional ferroelectric behavior with different modes and parameters.

The macroscopic properties of such a mixed system will be an average of such micro-regions in the crystal. These micro-regions may also have compositional fluctuations, which in turn may have different Curie temperature as well as ferroelectric and dielectric attributes. On the macroscopic scale, the dielectric and the ferroelectric behavior will be an extensive envelope of the behavior of the discrete regions. The extent of the curie region depends both on the sensitivity of the Curie temperature to the range of the compositional variations and other properties as the composition changes.

The factors that make the ferroelectric phase transitions as DPT are as follows:

(i) macroscopic inhomogeneities due to the preparation technique,
(ii) submicroscopic inhomogeneities (scale 50–1000 Å) due to compositional thermal polarization fluctuations,
(iii) hetero-phase fluctuations and defects,

1.3. Diffuse phase transition: (DPT)

Broad phase transition in ferroelectrics was first discovered in solid solutions of the perovskite BaTiO$_3$-BaSnO$_3$ [11], in which the piezoelectric behavior was

![Figure 3. Three types of ferroelectric–paraelectric phase transitions.](image)
(IV) internal stress effects generated by the size of the grain (scale analogous with size of domain), and
(V) relaxation polarization.

The total polarization is the contribution of the following:

(i) Relaxation polarization, which is produced by the reorientation of the electric moments of the polar micro-regions under a weak electric (alternating) field
(ii) Induced (electron-ion) polarization, and it comprises the involvement of a ferroelectric phase transition.

The characteristic features of the ferroelectrics with diffuse phase transition are summarized below [15–19].

(a) The variation in the dielectric constant ($\varepsilon'$) is rounded, i.e. there is no divergence but only a maximum value of the dielectric constant exists at Curie temperature $T_c$, and the transition is not sharp but broadened. see Fig.4.
(b) The polarization as a function of temperature $[dP/dT]$ exhibits an inflection point at the temperature $T_p$, which is lower than $T_c$.
(c) Polarization ($P$) goes to zero at the temperature $T_p$, which does not coincide with $T_c$ see Fig.4.

(d) The dielectric polarization of relaxation type and related phenomena is the reason why the peaks of dielectric constant $\varepsilon'$ and dielectric loss $\varepsilon''$ do not coincide. Broadening is accompanied by a considerable frequency dispersion of the dielectric constant, and the maxima of the $\varepsilon'(T)$ and $\varepsilon''(T)$ curves shift to higher temperatures with increasing frequency.

(e) Domain structure exhibits extra peculiarities in comparison to the classical ferroelectrics.

(f) Coexistence of nonpolar and polar micro-regions; the polar micro-regions have distinct local curie temperatures.

(g) The variation of refractive index, $n$, with temperature is different from the ordinary displacive ferroelectrics, and this difference is due to the local disorder.

The basic ferroelectric properties are generally considered to be spontaneous polarization, $P_s$, pyroelectric coefficient, $P_p$, and dielectric anomaly. Figure 4 shows the different transition temperatures for these parameters in case of the diffuse phase transition, as discussed earlier in the text. Figure 5 shows the sketches of the diffuse and normal domain wall.

2. Theories of ferroelectricity

Theoretically, the nonlinear dielectric behavior of ferroelectrics can be predicted from the knowledge of the laws of electrostatics. A brief description of some important theories of ferroelectricity is presented in the succeeding sections.

2.1. Thermodynamic theory

The foundation of the thermodynamic theory is based on the postulate of the existence of a unique free energy function depending upon the external conditions. Devonshire [20] proposed that the dielectric data can be correlated by expanding the free energy as
a series expansion of polarization and temperature and stress as parameters. The Gibbs energy, $G$, can be expressed as a power series of $P$.

$$G = G_0 + \frac{1}{2} g_2 P^2 + \frac{1}{4} g_4 P^4 + \frac{1}{6} g_6 P^6 + O(P^8)$$  \hspace{1cm} (3)$$

The series lacks odd powered terms of $P$ because the unpolarized crystal has a center of inversion symmetry (as the paraelectric state is centrosymmetric).

### 2.2. Lattice dynamics theory

Cochran [21,22] analyzed the static and dynamic properties of the displacive ferroelectrics in terms of the classical lattice dynamics theory. The phenomenon of ferroelectricity has been considered a result of the instabilities of certain normal modes of vibrations. The frequency of the transverse optic mode for which the crystal becomes unstable can be derived from the difference between two terms, one of which arises from the short-range interaction between the nearest neighbors and the other originates from the long-range electric dipole interactions. It was pointed out that in most of the ferroelectric materials, both of these frequencies correspond to infrared frequencies. However, the frequency which arises from the short-range interaction is generally much larger than the other. Under certain conditions, these two terms can be very nearly equal. The frequency $\omega_T$ of this mode, generally called the ferroelectric mode or soft mode, is assumed to have a temperature dependence of the form,

$$\omega_T^2 = T - T_c$$  \hspace{1cm} (4)$$

At $T = T_c$, $\omega_T$ becomes zero and the ferroelectric mode in a crystal becomes unstable.

In the diatomic ionic crystal having one type of dipole, the Lyddane-Sachs-Teller (LST) theory gives a correlation between lattice vibrations, and the dielectric constant is expressed as

$$\varepsilon_\infty = \frac{\omega_T^2}{\omega_\infty}$$ \hspace{1cm} (5)$$

where $\omega_\infty$ is the frequency corresponding to phonon longitudinal vibrations, $\omega_T$ is the frequency corresponding to phonon transverse vibrations, $\varepsilon_\infty$ is the static value of the dielectric constant (zero frequency dielectric constant), and $\varepsilon_\infty$ is the high-frequency limit of the dielectric constant (square of the refractive index). The dielectric constant, $\varepsilon'$, behaves as

$$\varepsilon' \propto \frac{1}{\omega_T^2 - \omega^2}$$  \hspace{1cm} (6)$$

Thus, the low-frequency dielectric constant has a temperature dependence of the form

$$\varepsilon_\infty \propto \frac{1}{T - T_c}$$  \hspace{1cm} (7)$$

which is in accordance with the experimentally observed Curie–Weiss law.

Burns and Scott [19] measured the lattice vibrational modes in PbLaTiO$_3$ perovskite solid solution using the Raman technique and have shown that the Lyddane–Sachs–Teller LST equation, which correlates the optical modes corresponding to transverse and longitudinal vibrations, is not valid for exceedingly disordered mixed system perovskite ferroelectrics. Table 1 shows the possible values of $\omega_T$ with corresponding values of temperature and Curie temperature of the ferroelectric materials.

### 2.3. Properties of ferroelectrics

The ferroelectric materials are a subcategory of polar materials. These materials show spontaneous polarization, whose orientation changes with application of an electric field. The ferroelectric properties vanish beyond a specific temperature called the temperature of transition ($T_c$), as the ferroelectric material undergoes a phase change from ferroelectric to non-ferroelectric phase known as paraelectric. They also show pyroelectricity, piezoelectricity, electro-optic effect, and acousto-optic effect. Three types of phase transition may be identified, first-order, second-order, and diffused-order phase transition. These transitions are designated on the basis of the change of order as the transition takes place. In ferroelectrics, the polarization is known as the order parameter. The first- and second-order phase transitions can be easily distinguished as the former generates discontinuity in the order parameter, while the latter exhibits discontinuity in the first derivative of the order parameter. The first- or second-order structural transition at curie point, $T_c$, involves the complete changing of the ferroelectric phase into the paraelectric phase above $T_c$. The third category is the broad-phase transition, which is diffused at $T_c$, i.e., $P$, decreases gradually with increasing temperature. Phase coexistence (ferro- and paraelectric) is observed above Curie point up to a particular temperature range, and no obvious proof of structure transition is detected.

| S.No. | Ferroelectrics         | $\omega_T$ | Temperature | Curie temperature | Reference |
|-------|------------------------|------------|-------------|-------------------|----------|
| 1     | Barium Titanate, BaTiO$_3$ | 63.0 cm$^{-1}$ | 673.15 °C  | 131°C            | [23]     |
| 2     | Lead Titanate, PbTiO$_3$ | 161.45 cm$^{-1}$ | 570°C      | 493°C            | [24]     |
| 3     | SrTiO$_3$              | 95 cm$^{-1}$  | 300 K       | 26 K              | [25]     |
2.3.1. Polarization field hysteresis

The nonlinear variation of polarization with an applied oscillating electric field generates a ferroelectric hysteresis loop, which is a unique property of ferroelectric materials. Typical hysteresis loops are obtained by plotting polarization (P) vs electric field (E). Three important physical parameters of a ferroelectric material viz remnant polarization (P_r), coercive field (E_c), and spontaneous polarization (P_s) can be established from the hysteresis loop as shown in figure 2 & figure 7. The spontaneous polarization is described as the saturation value of the polarization. The remnant polarization is defined as the polarization at zero applied electric field. The electric field at which the polarization vanishes is defined as the coercive field, which is the apparent threshold field required to reverse the polarization. The parameters P_r, P_s, and E_c vary with change in temperature. Particularly, they attain zero value as the temperature advances toward T_c. The type of phase transition is indicated by the rate at which the reduction in polarization takes place. The transition can be the first order (I) or second order (II) as in single crystals and certain ceramics [26,27] or the diffuse phase transition (II) as is generally observed in ceramics and thin films.

2.3.2. Features of ferroelectrics

The transition of phase in a ferroelectric material is described as a modification in structure of the crystal, normally happening at a definite temperature, which changes the magnitude or direction or both of the electric polarization. This temperature of structural phase transition is termed as the ferroelectric Curie point, T_c. Beyond the Curie point, the crystal is no longer polar, although it might still be piezoelectric. Small signal permittivity or a dielectric constant along the direction of spontaneous polarization is usually large and exhibits a tall peak at the ferroelectric Curie point, at which the spontaneous polarization vanishes. The phase above this Curie point is called the paraelectric phase, while that below it is termed as the ferroelectric phase. However, for T > T_c, the dielectric constant falls quite swiftly in accordance with a relation similar to the Curie-Weiss law in case of ferromagnetism.

\[ \varepsilon = C/(T - \theta) = C/(T - T_0) \]  \hspace{1cm} (8)

In the above expression, the dielectric constant is denoted by \( \varepsilon \), C stands for the Curie constant, and \( \theta \) or \( T_0 \) is the Curie Weiss temperature, which defines the paraelectric phase. The display of anomaly in the dielectric behavior as a function of temperature is a distinguishing attribute of materials with ferroelectricity. Indeed, the thermodynamic theory of transition predicts both the Curie–Weiss law and the dielectric anomaly. The presence of ferroelectricity needs a hysteresis loop for its verification, and it cannot be determined alone on the basis of the existence of a dielectric anomaly. Based on the dielectric anomalies, the relation between the dielectric constants and temperature can be expressed via the modified Curie–Weiss law as follows:

\[ \frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = C'(T - T_m)^\gamma \] \hspace{1cm} (9)

In the above expression, C’ is a Curie–Weiss-like constant, and \( \gamma \) represents the critical exponent, signifying the degree of diffuseness of the transition. \( \varepsilon_m \) is the maximum dielectric constant at the temperature of transition peak \( T_m \). For normal ferroelectrics, \( \gamma = 1 \), which results in a sharp transition. For \( \gamma \) lying in the range of 1–2, a diffuse transition occurs, while for \( \gamma = 2 \), the material corresponds to the alleged “complete” diffuse phase. For the case of \( \gamma > 2 \), the materials make a diffuse phase transition from ferroelectric to antiferroelectric or antiferroelectric to paraelectric phase.

2.3.3. Dielectric hysteresis-reversal of spontaneous polarization

If we apply an AC electric field in the circuit shown in Figure 6, the polarization charge of the crystal gives a current, and the voltage developed across the integrating capacitor is proportional to polarization. When the polarization saturates, the voltage across the capacitor saturates. As can be seen in Figure 7, in a ferroelectric, the polarization remains (OD), even when the field becomes zero. At a higher negative voltage, the dipoles switch into the other direction, and a hysteresis loop is obtained. When applied field is zero, the polarization is not zero,

![Figure 6](image-url). A typical schematic set-up for observing ferroelectric hysteresis loops.
but it has a finite value known as the remnant polarization, $P_r$. Extension of the linear segment BC of the loop of hysteresis back to the y axis gives the measure of spontaneous polarization, $P_s$ (O'E'). To eradicate the remnant polarization, $P_r$, application of electric field in the opposite (negative) direction of the coercive field, $E_c$. Increasing the field further in the negative direction leads to realignment of the dipoles.

3. Dielectric properties

3.1. Dielectric permittivity

Dielectric permittivity, $\varepsilon$, also known as dielectric constant, is the most frequently determined small signal electrical attribute. As discussed below and in other chapters, $\varepsilon'$ in polar materials is seldom a constant and fluctuates with the variation in temperature, stress, applied field, and other factors. In the SI system, $\varepsilon$ is defined by the expression:

$$\varepsilon = \varepsilon_0 + \eta$$  \hspace{1cm} (10)$$

In the above expression, permittivity of free space is denoted by $\varepsilon_0$ and has a value of $8.85 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$, and $\eta$ is the electric susceptibility, which in turn is defined by the expression:

$$\eta = P/E$$  \hspace{1cm} (11)$$

Many authors use a relative permittivity, $\varepsilon_r$, defined by $\varepsilon = \varepsilon_0 \varepsilon_r \text{ C V}^{-1} \text{ m}^{-1}$. Relative permittivity $\varepsilon_r$ would have the same value as the permittivity $\varepsilon$ if c.g.s. units are used; $\varepsilon_r$ is normally greater than 1. In equation (12), the polarization, $P$, is estimated from

$$P = q/a$$  \hspace{1cm} (12)$$

Here, $q$ is the charge produced at the electrodes and “a” is the area of electrode of the dielectric material, and the electric field, $E$, is determined by

$$E = V/d$$  \hspace{1cm} (13)$$

where $V$ is the applied voltage and $d$ is the thickness of the dielectric material. Measurement of $\varepsilon$ (and $\eta$) is usually made on an A.C. bridge circuit using applied field E of less than 1 kV m$^{-1}$. It is particularly important to use a low E to avoid irreversible domain switching effects, which can occur in certain polar materials, e.g. ferroelectrics. The $\varepsilon$ value, in comparison to nonpolar dielectrics (in the range of 1–10), is typically quite large for polar dielectrics (in the range 100–10,000). Moreover, the majority of polar materials exhibit an immense rise in $\varepsilon$ value at a temperature close to the transition of crystal phase. Figure 8 is typical; in this case, it shows the temperature dependence of $\varepsilon$ of BaTiO$_3$ single crystal with a ferroelectric (tetragonal) to a paraelectric (cubic) phase transition. Like the c axis of the lattice, the a axis also exhibits a linear response to an applied electric field. Yet, both the responses are different: the application of the electric
field results in the expansion of the c axis in contrast to the shrinkage of the a axis, which results in a positive and negative piezoelectric coefficient, respectively.

The dielectric constant ($\varepsilon$) of a ferroelectric is a function of the field strength at which it is computed; this is a result of the nonlinear association between polarization and electric field. Above the transition temperature, $\varepsilon$ obeys the Curie–Weiss law. The process of phase transition involves four characteristic temperatures: Curie temperature $T_C$, Curie–Weiss temperature $T_0$, ferroelectric limit temperature $T_r$, and limit temperature of field-induced phase transition $T_p$. Using the Curie–Weiss law of dielectric constant ($\varepsilon$) in the paraelectric phase, one can easily determine the Curie–Weiss temperature experimentally.

$$\varepsilon = \frac{C}{T - T_0}$$

In the given equation, C denotes the Curie–Weiss constant, and the paraelectric phase is represented by the subscript p to $\varepsilon$. Though it is not so easy to experimentally determine the Curie temperature. Curie temperature assesses the balance between the ferro- and paraelectric phases. This temperature corresponds to the equal free energy in both phases. The ferroelectric phase becomes stable, while the paraelectric phase becomes meta-stable for temperature between $T_0$ and $T_c$. The ferroelectric phase becomes meta-stable, while the paraelectric phase becomes stable for temperature between $T_c$ and $T_f$. The ferroelectric phase vanishes for temperatures higher than $T_f$. Usually, it is the temperature $T_f$ and not $T_c$, which corresponds to the peak temperature of the dielectric constant when measured in the heating cycle. Ferroelectricity can still be stimulated between $T_1$ and $T_2$ by the application of an external electric field. The curve corresponding to electric polarization vs the electric field is a double hysteresis loop, which is very identical to that of antiferroelectrics. Only paraelectric phase exists for temperatures exceeding $T_p$. The relative permittivity is very large in the vicinity of transition temperature. At a certain temperature, the dielectric constant shows a dielectric anomaly peak. The dielectric anomaly peak is sharp for single crystals showing first- or second-order phase transition, while the peak is broad in the case of ceramics, which suggests diffused phase transition. The peak is also much wider in the case of thin films as shown in Figure 9.

3.2. Piezoelectricity and pyroelectricity

3.2.1. Piezoelectricity

Piezoelectricity is the potential of specific crystalline materials to generate an electric charge proportionate to the applied mechanical stress. This is the direct effect of piezoelectricity. It was observed by the Curie brothers in 1880. Conversely, on applying an electric field along particular directions in a piezoelectric crystal, the crystal is strained by an amount proportionate to the applied electric field. This is called the converse effect of piezoelectricity. If the resulting strain varies as the square of the field function, it is acknowledged as the electrostrictive effect.

In the direct piezoelectric effect, the strain produced, $S$, is proportional to stress $T$, and is represented as-

$$T = S \ast Y$$

where Y is the modulus of elasticity. T and S are tensors. Y is a matrix. Additionally, there is a certain amount of charge $Q$ produced by the applied stress, which varies in direct proportion with the force, and consequently, the sign of $Q$ for tension and compression is opposite. In terms of stress, T, and the dielectric displacement, D, which is defined as charge $Q$/unit area, the following expression is obtained,

$$D = Q \ast A^{-1} = T \ast d$$

Where d is the piezoelectric charge constant expressed in C/N. In the inverse or converse piezoelectric effect, a strain S is generated on applying an electric field E, that can cause contraction or expansion, which is determined by the polarity,

$$S = E \ast d$$

here d is the coefficient of piezoelectric strain with units of m/volt. The piezoelectric charge constant is equal to the piezoelectric strain coefficient. Hence, the

![Figure 9](image-url)
constant of proportionality, for both direct and converse effects, is \( d \), and its value is identical for both the effects.

\[
d = SE^{-1} = DT^{-1}
\]

(ratio of the strain generated along one direction to the strength of electric field along a different or same direction).

The materials employed for the fabrication of devices meant to generate vibration or motion, for instance, in sonar or ultrasonic cleaner transducers, need to possess a high \( d \) constant. In addition to \( d \), there is another recurrently employed piezoelectric constant, which provides the field generated by applied stress. Its typical units are m-V/N, derived from (volts/m)/(Newton/m²). This constant is given by

\[
g = d/\varepsilon = d/K\varepsilon_0
\]

The materials employed in the fabrication of devices meant for generating voltages on application of mechanical stress are required to have a high \( g \) constant, for instance, in phonograph pick up, which receives mechanical vibrations from a phonograph record via the needle and converts the vibrations into electrical impulses, which are amplified and sent to the speaker.

The factor of electromechanical coupling, \( k \) is probably the finest solitary parameter to know the intensity of the piezoelectric effect. The coupling factors of piezoelectric materials having significantly dissimilar compliance and dielectric constants may thus be evaluated directly.

The factor of piezoelectric coupling, \( k \) may be described as the square root of the ratio of the energy obtained in electrical form to net energy supplied in mechanical form (direct effect) or the square root of the ratio of the energy obtained in mechanical form to net energy supplied in electric form (converse effect), i.e., on applying an electric field, it determines the percentage of the energy transformed from electrical to mechanical form (or alternatively on applying stress to a ceramic or crystal). The actual relationships in terms of \( k^2 \)

\[
k^2 = \frac{\text{Energy in electrical form converted to energy in mechanical form/Supplied energy in electrical form}}{\text{or}}
\]

\[
k^2 = \frac{\text{Energy in mechanical form converted to energy in electrical form/Supplied energy in mechanical form}}
\]

As the transformation of energy from mechanical to electrical form is always imperfect, the value of \( k^2 \) is always less than one, and therefore \( k \) is also less than one.

The conventional values of \( k \) are 0.1, 0.4, and 0.5–0.7 for quartz, BaTiO3, and PZT, respectively. The property of piezoelectricity is exhibited by several of the compounds in single crystal form, for instance, ammonium dihydrogen phosphate (ADP), Rochelle salt, quartz, etc. All these materials have many uses based on these properties.

More recently, with development in the technology of electronic ceramics, polycrystalline materials such as BaTiO3, lead zirconate titanate (PZT), and lead titanate have been widely developed for their piezoelectric properties. In fact, PZT and its varied compositions with different dopants are now widely used in most of the commercial piezoelectric applications.

The requirement of the procedure of poling, in piezoelectric ceramics, for the appearance of the phenomenon of piezoelectricity by generation of polar axis is the only difference between piezoelectric ceramics and crystals. Each piezoelectric material is defined by its unique Curie temperature. Beyond this temperature, the intrinsic electric dipoles have arbitrary orientations.

On application of an intense electric field, these dipoles orient themselves along the field direction and stay partly oriented even on removing the field, given that initially the sample is cooled beneath its Curie temperature. In this poled state, when a small electric field is applied to the ceramic, the dipoles act together to generate a further microscopic extension in the direction of axis of poling, while the contraction occurs perpendicular to it, or vice-versa, if the polarity of the applied field is reversed (Figure 10).

Ceramic piezoelectric materials can be formed into a wide assortment of sizes and shapes by modern ceramic processing techniques. The application of electrodes can also be given in different configurations to provide poling in desired directions. Typical configurations include disks, plates, rings, and tubes as shown in Figure 11. To understand the properties attributed to specific shapes of piezoelectric ceramics, it is best to consider a plain block of the piezoelectric element with bottom and top surfaces having electrodes (Figure 12).

The numerical subscripts here indicate the \( x, y, z \) directions of the cartesian coordinates. By rule, the numerical 3 indicates the direction of polarization, directing from the positive to the negative electrode.

**Figure 10.** Dimensional changes of ceramics because of poling: (a) before poling and (b) after poling.
The general equation connecting the applied electric field \( E \) and the generated vector of strain, \( S \), in the piezoelectric block is

\[
S = E \times d
\]  
(20)

For strain measured along the direction 3, with polarization also along direction 3 the above equation can be written as,

\[
\Delta t = V \times d_{33}
\]  
(21)

using \( E = V/t \) and \( S = \Delta t/t \), where \( t \) is thickness of material along direction 3 and \( \Delta t \) is the change in dimensions along direction 3. For strains \( S = \Delta l/l \) measured along either 1 or equivalent 2 directions, the given expression is written as

\[
\Delta l/l = d_{33} V/t
\]  
(22)

where \( l \) is thickness along direction 1 or 2. The former subscript on the \( d \) constant or any other piezoelectric constant refers to the applied stress or electric field direction and the latter refers to the induced strain’s direction.

The piezoelectric coupling factors in the ceramics measure the intensity of the piezoelectricity and are used as a figure of merit. The \( k_{33} \) and \( k_{31} \) are the coupling coefficients when the field is applied along directions-3, and the coupling of the transducer is affected along directions-3 and direction-1, respectively. In addition, the planar coupling factor \( k_p \), indicates the concurrent application of identical stress along 1 and 2 axes (two dimension or in a plane), which is comparable to uniform radial compression or tension in the plane perpendicular to the axis of poling. Similarly, the thickness coupling factor \( k_t \) indicates that this coupling pertains to the vibration of longitudinal thickness of lateral clamped plates. The shear effects are specified by the subscripts 4, 5, and 6.

Thus, conclusively, it may be said about specifying the piezoelectric directional properties that, coefficients which relate two variables (e.g. \( d \) coefficient), are indicated by two subscripts, the former of which specifies the direction of dielectric displacement or electric field and the latter specifies the direction of strain or stress. Also, when a particular property is being measured while holding another quantity constant, a superscript symbol is used to indicate the quantity held constant. Typical examples of often-used symbols of constants with subscripts and superscripts and their usual meaning are given below.

\[
d = \text{piezoelectric strain coefficient (piezoelectric charge constant)}
\]

[Short circuit charge density developed per unit applied stress]

\[
d_{31} = \text{where the first subscript, i.e. 3, is a displacement or electric field}
\]

| Axes | Desired Electromechanical effect | Piezoelectric elastic and dielectric constants |
|------|----------------------------------|---------------------------------------------|
| ![Diagram 1](image1.png) | ![Diagram 2](image2.png) | \( d_{33} \), \( d_{33} \), \( k_{33} \) |
| ![Diagram 3](image3.png) | ![Diagram 4](image4.png) | \( \gamma_{13}, \rho_k \) |

Figure 11. Piezoelectric ceramics: basic shapes, electromechanical effects, and various constants.
3.2.2. Pyroelectricity

In pyroelectric materials, a variation in temperature modifies the spacing of lattice of non-symmetrically positioned atoms, which alters the spontaneous polarization of the material. This alteration of spontaneous polarization generates a displacement current (I) along the polar axis and is defined as

\[ I = A \frac{dP}{dT} \frac{dT}{dt} \]  

(23)

In the above expression, \( A \frac{dP}{dT} \) is the coefficient of pyroelectricity determined at temperature T, A denotes the surface area perpendicular to the polar axis, and \( P \) is the polarization t denotes time.

3.3. Applications of ferroelectrics

There are a number of properties of ferroelectric materials, which are found useful for various device applications, and a few of them are listed below [31].

(i) High dielectric constant
(ii) High piezoelectric constant
(iii) Moderately low dielectric loss
(iv) High electrical resistivity
(v) Moisture insensitivity
(vi) High electromechanical coupling
(vii) Medium hardness
(viii) High pyroelectric coefficient
(ix) High optical transparency
(x) High electro-optic coefficients

Interest in ferroelectric materials is due to their various device applications, both in the bulk and thin film forms. Table 2 shows the applications of ferroelectrics, which are grouped into two categories: one based on the switching properties of ferroelectrics and the other on the non-switching properties of ferroelectrics. The major application of ferroelectric materials is in the form of ceramics.

High transparency can be achieved only by special processing techniques and by adding dopants (e.g., lanthanum in PZT) [32], which makes them useful for electro-optic applications. In the following section, we will discuss the applications of ferroelectrics thin films for devices.

Thin films of ferroelectrics are of great interest for engineering innovative devices. Thin films of ferroelectrics not only shrink the size of devices and save the source material but also enhance the device operation efficiency due to their properties resulting from reduced scale and configuration [33,34,35].

3.3.1. Application in memory devices

Therefore, The solid-state dynamics, random access memory (DRAM) is a one-transistor cell, which contains a sole capacitor storing the charge and a switching transistor to separate the capacitor. Ferroelectric materials have a high dielectric constant.
and high breakdown field, so they are used as a storage capacitor. Because of the large variation in the material characteristics, in crystal form it is necessary to employ the material whose temperature of transition is above the usual operating temperature of semiconductor chips, and for this particular application, ferroelectric materials in amorphous form are desirable. The amorphous ferroelectric materials do not show substantial variation in the dielectric constant with temperature and exhibit high breakdown field and high charge storage capacity, which makes them useful materials for DRAM [51–57].

Conventionally, a metal–ferroelectric–semiconductor (MFS) thin film structure can be used as a nonvolatile memory device [36,37]. These devices utilize the basic characteristics of the remnant polarization of the ferroelectrics. The gate oxide of a MOS device is substituted by a ferroelectric film, and on applying voltage, an inversion/depletion layer is created, which stays unaffected even after the removal of the gate voltage due to the persistence of charges at the interface of film and semiconductor caused by the remanent polarization of the ferroelectric film [38]. The flat band shift and large interface state are created during the sputtering process, which makes the true ferroelectric field effect transistor difficult to realize. In the modified structure, a ferroelectric capacitor is used with a JFET (junction field effect transistor). Figure 13 illustrates the structure of the nonvolatile memory on GaAs substrate. The ferroelectric capacitor is used to bias the gate of the JFET, and even after the removal of the biasing voltage, the gate bias is non-zero because of the remanent polarization of the ferroelectric capacitor [39]. Many ferroelectrics like LiNbO3 and PZT have high electro-optic coefficients.

### 3.3.2. Applications in electro-optic (EO) and acousto-optic (AO)

The electro-optic effect can be employed in optical modulators and display systems. A thin film, electro-optic light modulators is shown in Figure 13 (c) [33]. The light is coupled with the film by using a prism coupling (not shown in the figure). The small separation between electrodes across the optical

![Figure 13. Various applications of ferroelectric films.](image-url)
wave guide enables the application of large electric fields at relatively low voltages. The change in polarization depends on the applied field and the length of the waveguide. An applied ac signal can produce intensity variations in a polarized light beam when seen through an analyzer.

Since the beginning of the 1970s, thin film technology has become a prime interest to researchers worldwide for SAW and acousto-optic (AO) device applications. This technique utilizes a piezoelectric thin film on a piezoelectric substrate to generate surface waves. The acoustic wave can be generated in piezoelectric materials by applying an external ac electrical signal. The utmost significant application of ferroelectrics is based on their high coefficients of piezoelectricity. Surface acoustic wave devices use the piezoelectric property of the ferroelectric films. A delay line is a device, which causes the output to lag behind the input by a finite delay time. A simple delay line is shown in Figure 13. An Inter Digital Transducer Electrode (IDT) transforms the incident electromagnetic wave into a Rayleigh surface acoustic wave, which propagates on the piezoelectric crystal/film surface. After the required delay, another transducer at the output reconverts the acoustic wave back into an electromagnetic signal [40,41]. In layered structures, there exists more than one way of locating the IDTs on the piezoelectric surface as shown in Figure 14. For an AO device, a thin film layer that can be utilized as a waveguide medium is required. This waveguide layer itself can be piezoelectric in nature so as to generate surface acoustic wave, or another piezoelectric layer is required to generate SAW. The configuration of such an AO device is illustrated in Figure 15.

3.3.3. Advantages of ferroelectric thin films
Thin film-based devices possess a variety of advantages over the bulk piezoelectric substrate such as the following:

- Possibility for direct integration with GaAs and Si-SiO$_2$ substrates exists
- High-temperature stable devices can be obtained by a combination of the layer having proper temperature coefficient of delay TCD values
- Enhanced electromechanical coupling and higher sensitivity can be achieved by combining layers with suitable material properties

![Figure 14. Different IDT configurations on layered structures.](image)

![Figure 15. Thin film-based AO device.](image)
4. Conclusion

In the present work, a systematic review on fundamentals of ferroelectric materials has been attempted. The review broadly explores the ferroelectric, electro-mechanical piezoelectric, and dielectric properties of these materials. Classification of ferroelectric materials, phase transitions, diffuse phase transition (DPT) has been deliberated. Properties of ferroelectrics, polarization field hysteresis, dielectric hysteresis-reversal of spontaneous polarization, and dielectric properties have been discoursed. Besides these, piezoelectricity and pyroelectricity properties of materials have also been discussed. The key features of ferroelectric materials like high dielectric constant, high piezoelectric constant, moderately low dielectric loss, high electrical resistivity, moisture insensitivity, high electromechanical coupling, medium hardness, high pyroelectric coefficient, high optical transparency, high electro-optic coefficients have been discussed. The applications of ferroelectric thin films have been discussed, with specific focus on the use of acousto-optic (AO) properties.

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