

Chapter 2

Dielectric, Mechanical, and Electromechanical Properties of Ferroelectrics and Piezoelectrics

2.1 Dielectric Response

In this section, dielectric properties of materials are considered in the case where they are not coupled with their elastic properties. The case of coupled properties will be treated in [Sect. 2.3](#).

2.1.1 General

Dielectric properties of insulating materials are customarily characterized by a relationship between the vectors of electric field, \vec{E} , and electrical displacement, \vec{D} . In the case of an isotropic dielectric, the material is characterized with the dielectric permittivity defined as

$$\varepsilon = \left. \frac{dD}{dE} \right|_{E=0} \quad (2.1)$$

It has a physical meaning of the permittivity measured with a small AC electric field. The dielectric permittivity can also be defined under a DC bias electric field. Typically, AC and DC fields are parallel. In this case, one defines

$$\varepsilon(E_o) = \left. \frac{dD}{dE} \right|_{E=E_o} \quad (2.2)$$

This derivative has a clear physical meaning: the sample is under a DC bias electric field, whereas the dielectric response is tested with a small AC field. For description of the field dependence of the dielectric permittivity, two parameters are used: tuneability

$$n = \frac{\varepsilon(0)}{\varepsilon(E_o)} \quad (2.3)$$

and relative tuneability

$$T_\varepsilon = \frac{\varepsilon(0) - \varepsilon(E_o)}{\varepsilon(0)} = \frac{n - 1}{n} \quad (2.4)$$

If the material is dielectrically anisotropic, the directions of vectors \vec{E} and \vec{D} may not necessarily coincide and the dielectric permittivity becomes dependent on the direction of the measuring AC field. In this case, the dielectric permittivity is defined as a second rank tensor,

$$\varepsilon_{ij} = \left. \frac{dD_i}{dE_j} \right|_{E=0} \quad (2.5)$$

where suffixes i and j take on values from 1 to 3, denoting Cartesian components. Thermodynamics requires this tensor to be symmetric, that is, $\varepsilon_{ij} = \varepsilon_{ji}$ (Nye 1985). If the dielectric permittivity is field independent, (2.5) can be presented in the form:

$$D_i = \varepsilon_{ij} E_j \quad (2.6)$$

Hereafter, the Einstein dummy suffix summation convention is adopted, that is, summation from 1 to 3 is implied in the case of repeating suffixes, unless specified otherwise. A useful dielectric characteristic of a material is the relative dielectric permittivity (or dielectric constant) defined as

$$\varepsilon_{rij} = \frac{\varepsilon_{ij}}{\varepsilon_o} \quad (2.7)$$

Here, $\varepsilon_o = 0.885 \times 10^{-11}$ F/m is the dielectric constant of vacuum.

The structure of the tensor (matrix) depends on the symmetry of the material. In the case of isotropic materials (e.g., non-poled ceramics), the tensor of the dielectric permittivity has a simple form

$$\begin{pmatrix} \varepsilon_r & 0 & 0 \\ 0 & \varepsilon_r & 0 \\ 0 & 0 & \varepsilon_r \end{pmatrix} \quad (2.8)$$

For vacuum, $\varepsilon_r = 1$. For materials of cubic symmetry (e.g., crystals of SrTiO₃ at room temperature), the structure of ε_{rij} is also given by (2.8) but with $\varepsilon_r > 1$. Since, in view of (2.7), the tensor ε_{rij} is symmetric (as tensor ε_{ij} is), one can always find a reference frame where it is diagonal. Generally when diagonalized, it may have, in addition to the form given by (2.8), two more generic forms:

$$\begin{pmatrix} \varepsilon_{r1} & 0 & 0 \\ 0 & \varepsilon_{r1} & 0 \\ 0 & 0 & \varepsilon_{r3} \end{pmatrix} \quad (2.9)$$

and

$$\begin{pmatrix} \varepsilon_{r1} & 0 & 0 \\ 0 & \varepsilon_{r2} & 0 \\ 0 & 0 & \varepsilon_{r3} \end{pmatrix} \quad (2.10)$$

The components of the diagonalized tensor are called principal components. Directions of the corresponding axes of the reference frame are respectively principal axes. Materials where ε_{rij} has the form (2.9) (with two equal principal components) and where ε_{rij} has the form (2.10) (with three different principal components) are called uniaxial and biaxial, respectively. Examples of uniaxial materials are BaTiO₃ at room temperature, SrTiO₃ at temperature below 100 K, AlN, and ZnO. From Table 2.1, the reader can have an idea about typical values of the relative dielectric permittivity in dielectrics.

The capacitance of a parallel plate capacitor (Fig. 2.1) depends on the dielectric permittivity of the materials occupying the space between the plates.

Let us examine this, keeping in mind that the relationship between the electric field and electrostatic potential is given as

Table 2.1 Material parameters of some dielectrics. For all materials, components of tensors not included in the table are zero, except $c_{66} = (c_{11} - c_{12})/2$

Parameter material	Al ₂ O ₃	AlN	BaTiO ₃ (poled ceramics)
$c_{11}^E = c_{22}^E, 10^{11} \text{ N/m}^2$	5.0	3.5	1.7
c_{33}^E	5.0	4.0	1.6
c_{12}^E	1.6	1.3	0.77
$c_{13}^E = c_{23}^E$	1.1	1.2	0.78
$c_{44}^E = c_{55}^E$	10.5	1.2	0.43
$c_{14}^E = -c_{24}^E = c_{56}^E/2$	-0.2	0	0
$c_{11}^D = c_{22}^D$	c_{11}^E	3.5	1.7
c_{33}^D	c_{33}^E	4.2	1.9
c_{12}^D	c_{12}^E	1.3	0.78
$c_{13}^D = c_{23}^D$	c_{13}^E	1.1	0.71
$c_{44}^D = c_{55}^D$	c_{44}^E	1.2	0.55
$c_{14}^D = -c_{24}^D = c_{56}^D/2$	c_{14}^E	0	0
$\varepsilon_{r1}^S = \varepsilon_{r2}^S$	9.4	9.0	1268
ε_{r3}^S	11.5	10.7	1419
$\varepsilon_{r1}^T = \varepsilon_{r2}^T$	ε_{r1}^S	9.2	1622
ε_{r3}^T	ε_{r3}^S	11.9	1898
$e_{33}, \text{C/m}^2$	0	1.6	18.6
$e_{31} = e_{32}$	0	-0.6	-4.4
$e_{15} = e_{14}$	0	-0.5	11.6

Fig. 2.1 Schematic of a parallel plate capacitor

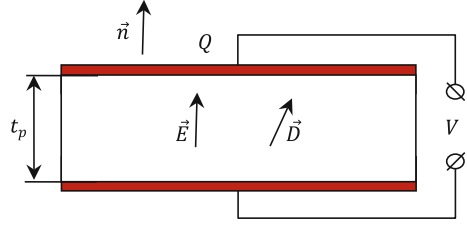
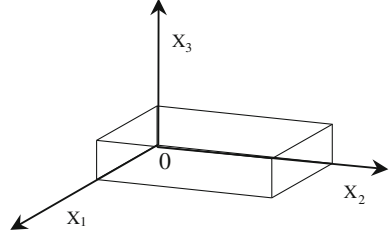


Fig. 2.2 Axis notations



$$E_i = -\frac{\partial \phi}{\partial x_i} \quad (2.11)$$

(x_i are Cartesian components of the spatial coordinates, Fig. 2.2), and the electric field should be normal to the electrodes. The voltage applied to the capacitor and the electric field is related as

$$V = Et_p \quad (2.12)$$

where t_p is the thickness of the dielectric, Fig. 2.1. Then, the charge density per unit area of the electrode, σ , is equal to the normal component of the electrical displacement in the dielectric (Gauss law),

$$\sigma = -\vec{D}\vec{n}, \quad (2.13)$$

the charge on the capacitor, Q , the electrical displacement, and the area of the capacitor plate, A_p , and they are linked as follows:

$$Q = A_p |\vec{D}\vec{n}| \quad (2.14)$$

Finally, the capacitance, C , of a parallel plate capacitor containing a dielectric with the tensor of the dielectric permittivity ϵ_{ijr} is found using (2.6, 2.7, 2.12), and (2.14):

$$C = \frac{Q}{V} = \frac{A_p}{t_p \epsilon_o} n_i \epsilon_{rij} n_j = C_o n_i \epsilon_{rij} n_j \quad (2.15)$$

where C_o is the capacitance of the empty capacitor. In the case of an isotropic dielectric using (2.8), one may present (2.15) in the form

$$\frac{C}{C_o} = \varepsilon_r \quad (2.16)$$

This form elucidates the physical meaning of the dielectric permittivity of an isotropic material, ε_r : filling a capacitor with such material leads to a ε_r times increase of its capacitance. In the case of anisotropic materials, if the dielectric filling of the space between the capacitor plates is cut normal to one of the principal axes of the tensor, as is clear from (2.15), the relationship (2.16) still holds but with the corresponding principle component of the tensor.

2.1.2 Nonlinear Dielectrics and Ferroelectrics

2.1.2.1 Regular Dielectrics and Ferroelectrics

For most dielectrics, the permittivity (or the principle components of ε_{rij} tensor) is in the range of few tenths or smaller. In these dielectrics, the permittivity is characterized by weak temperature dependence. The dielectric nonlinearity of these dielectrics is also very weak, which implies that the variation of the dielectric permittivity under a DC bias field of realistic values is very small. These materials will be referred to as “regular” *dielectrics*. There exists, however, materials where the dielectric permittivity attains much higher values (up to 60 000) in combination with its strong dependence on temperature and appreciable dielectric nonlinearity. These materials are classified as *ferroelectrics* (“regular” or incipient). These notions will be briefly introduced below, in a most elementary way, aiming to give the reader a tool for a simple phenomenological description of dielectric properties of such materials. First, the notion of dielectric polarization, $P_j^{(t)}$, is introduced and is defined as

$$D_i - \varepsilon_o E_i = P_j^{(t)} \quad (2.17)$$

Dielectric Polarization induced by a certain external perturbation (e.g., by application of an electric field, mechanical stress or temperature variation) can be related to the charge redistribution in the material caused by this perturbation. If the material is treated as a system of point charges $e^{(n)}$ (suffix n numerates the charges), displaced by the perturbation by vectors $\delta r_j^{(n)}$, the variation of the Polarization generated by this perturbation can be written as

$$P_j^{(t)} = \frac{1}{V} \sum_V e^{(n)} \delta r_j^{(n)} \quad (2.18)$$

where the summation is done over volume, V , of the material. If the material is inhomogeneous and/or the charge displacements are inhomogeneous, to find the Polarization at a given point of the material, the summation should be carried out

over a small (but still macroscopic, that is, occupied by many charges) volume containing this point.

There are a number of mechanisms contributing to the Polarization response. In ionic solids, the most important contribution is associated with the displacement of ions. Another contribution comes from displacements in the shells of valence electrons with respect to the atomic cores. If a material contains ions or defects hopping (in their thermal motion) between two and more local energy minima, the application of an electric field may redistribute the ions among these minima; this effect also contributes to the induced Polarization. If the dielectric permittivity of a material is very high, it usually implies that its structure allows for a mode of ionic displacements, which is very sensitive to external poling perturbations.

$\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ is a classical material used in microwave technology due to its high dielectric permittivity and appreciable dielectric nonlinearity. In this material, one of the polar optical phonon modes is responsible for its enhanced dielectric properties (Strukov and Levanyuk 1998). A polar optical phonon mode refers to a mode of relative ionic displacements in the unit cell of a crystal associated with a variation of its dipole moment.

The term *ferroelectric contribution to the polarization* will be used for the contribution to polarization corresponding to the aforementioned sensitive mode of ionic displacements; this contribution is denoted as P_i . The rest of the contributions to polarisation leads to a linear dielectric response—as in the case of regular dielectrics. The corresponding contributions to the electrical displacement will be described by introducing dielectric permittivity associated with these contributions, ε_{ij}^b , which will be refer to as *background permittivity*. Thus, the electrical displacement is presented in the following form:

$$D_i = \varepsilon_{ij}^b E_j + P_i \quad (2.19)$$

Hereafter, as a shorthand, the term *polarization* for the ferroelectric contribution to the polarization, P_i , will be often used, unless it becomes confusion.

A simple and efficient approach to describe the properties of ferroelectrics (at this instance, their dielectric properties are considered) is using the Landau theory. In this theory, one considers the free energy density,¹ F , (hereafter as shorthand, the term free energy is used for it) as a series in even powers of P_i :

$$F = F_0 + \frac{\alpha_{ij}}{2} P_i P_j + \frac{\beta_{ijkl}}{4} P_i P_j P_k P_l - P_i E_i \quad (2.20)$$

The structures (components) of tensors α_{ij} and β_{ijkl} are controlled by the symmetry of the material. Here, F_0 is the part of F independent of P . In order to find P_i as a function of E_i , one uses the condition of the minimum for F :

¹ Here, this function is called « free energy density » as often done in literature. However, this is a proper name for $F + P_i E_i$.

$$\frac{\partial F}{\partial P_i} = 0 \quad (2.21)$$

Here, a reservation concerning the Landau theory framework should be done. This chapter does not provide the comprehensive Landau theory enabling description of properties for all kinds of ferroelectrics. It may be found, for example, in an excellent monograph by Strukov and Levanyuk (Strukov and Levanyuk 1998). Here, the key elements of this theory are introduced for the so-called proper ferroelectrics/non-ferroelectrics. It is suitable for the description of properties of perovskite ferroelectrics—the only type of ferroelectric materials of interest for technical applications addressed in the present book.

The set of equations (2.19, 2.20), and (2.21) fully define the dielectric response of the material (D_i as a function of E_i). In (2.20), the terms up to the 4th power in P_i are kept. For most problems, this is sufficient. For some problems, however, higher terms in this expansion are needed. The analysis that takes into account these terms can readily be carried out on the lines of the treatment given in this sub-section.

In ferroelectrics, at least one of the principle components of α_{ij} either changes its sign at a certain temperature or, if positive at any temperature, acquires very small positive values when the temperature tends to zero Kelvin. *Regular ferroelectrics* (simply called *ferroelectrics*) correspond to the first, while *incipient ferroelectrics* to the second situation. Once α_{ij} behaves this way, the second term of expansion (2.20) often plays an essential role in the description of properties of ferroelectrics.

The set of Eqs. (2.19, 2.20), and (2.21) can formally describe the dielectric response of regular dielectrics. In this case, one neglects the P^4 —term in (2.20). Then, using (2.19, 2.20, 2.21), and (2.5), one finds the dielectric permittivity of a regular dielectric in the form:

$$\varepsilon_{ij} = \varepsilon_{ij}^b + \alpha_{ij}^{-1} \quad (2.22)$$

where α_{ij}^{-1} denotes a matrix inverse to α_{ij} .

Let us discuss the properties of ferroelectrics in the simplest situation where only one component of the polarization and one of the field are involved. Now, the suffixes may be dropped and (2.20) rewritten as

$$F = F_0 + \frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 - PE \quad (2.23)$$

Setting $\alpha = a(T - T_o)$ with $a > 0$ and $\beta > 0$ (T stands for the temperature), the Landau theory describes a ferroelectric exhibiting a ferroelectric phase transition at the temperature T_o , and this temperature is also known as the Curie–Weiss temperature. One distinguishes between the paraelectric phase at $T > T_o$ and the ferroelectric phase at $T < T_o$. In the paraelectric phase, in the absence of an electric field, the material is not poled, that is, at $E = 0$, $P = 0$. Contrarily, in the ferroelectric phase, in the absence of an electric field, the material is poled (one says

that it is spontaneously poled), that is, at δT , $P \neq 0$. Such behaviour can be demonstrated by using (2.21) and (2.23). From these equations, one finds the following equation of state for the ferroelectric:

$$\alpha P + \beta P^3 = E \quad (2.24)$$

In the absence of an electric field, formally, this equation has two solutions:

$$\begin{aligned} (P) \quad & P = 0 \\ (F) \quad & P^2 = -\alpha/\beta \end{aligned} \quad (2.25)$$

In the paraelectric phase, that is, at $T > T_o$, where $\alpha > 0$ only the P -solution is a real. Thus, in the paraelectric phase at $E = 0$, the framework yields $P = 0$. In the ferroelectric phase, that is, at δS where $\alpha < 0$, both solutions are real. However, only the F -solution corresponds to an energy minimum, whereas the P -solution is unstable (corresponds to $\partial^2 F / \partial P^2 < 0$). This means that, in the ferroelectric phase, the material exhibits polarization in the absence of an electric field. In the one-component case discussed, it can acquire two values: P_o and $-P_o$ where

$$P_o = \sqrt{\frac{-\alpha}{\beta}} \quad (2.26)$$

is the so-called *spontaneous polarization*.

The formal treatment, in terms of the Landau theory given above, can be illustrated using the BaTiO_3 crystal as an example. At temperatures higher than $T_C = 120^\circ\text{C}$, the unit cell of this material has a structure shown in Fig. 2.3a. It is the so-called cubic perovskite structure. Here, the Ba^{+2} ions are at the corners of the cubic cell (A-site ions), the Ti^{+4} is at the center of the cube (B-site ions), whereas the oxygen O^{-2} ions are at the middle of the faces. Due to the central symmetry of this structure, no polarization can be attributed to it in the absence of a DC electric field. One can induce polarization in this structure by an application

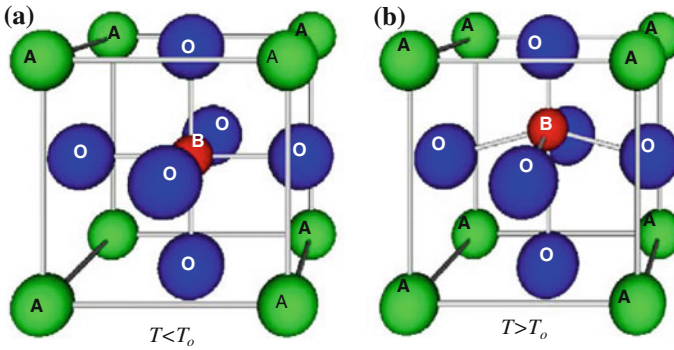


Fig. 2.3 Schematic structure of a unit cell of BaTiO_3 in paraelectric (a) and ferroelectric (b) phases. Notations for ions: A Barium, B Titanium, and O Oxygen

of a DC bias or by cooling it below $T_C = 120^\circ\text{C}$, Fig. 2.3b. In a simple model, the ferroelectric part of the polarization P_i can be associated with a displacement of the B-site ion from its central position, ξ_i , and can be written as

$$P_i = \frac{e^{(B)}}{v} \xi_i \quad (2.27)$$

where v is the unit cell volume, and $e^{(B)}$ is the charge of the B-site ion.

In this model, at temperatures higher than $T_C = 120^\circ\text{C}$, $\xi_i = 0$, whereas at temperatures below $T_C = 120^\circ\text{C}$, $\xi_i \neq 0$. Thus, in the framework used above, setting T_o equal to T_C , one qualitatively describes the evolution of the structure of BaTiO_3 while cooling from the paraelectric to ferroelectric phase. It occurs that the Landau theory enables a quite good qualitative description of many properties of ferroelectrics. However, in some cases, the scheme needs the involvement of more terms than given by (2.23) and (2.24). What follows in this chapter, the Landau framework given by these or more advanced forms of these equations will be used repeatedly.

The Landau theory provides a description for the polarization response of ferroelectrics. Using (2.2), (2.19), and (2.24), one finds the dielectric permittivity of a ferroelectric under DC bias, E , given by the following expression:

$$\varepsilon(E) = \varepsilon_b + \frac{1}{\alpha + 3\beta P^2} \quad (2.28)$$

where P should be calculated from (2.24).

2.1.2.2 Paraelectric Phase

In the paraelectric phase ($T > T_o$) in the absence of a DC field, $P = 0$ and (2.28) yield the dielectric permittivity of the ferroelectric as

$$\varepsilon = \varepsilon_b + \frac{1}{\alpha} \quad (2.29)$$

with

$$\alpha = a(T - T_o) \equiv \frac{T - T_o}{\varepsilon_o C} \quad (2.30)$$

where the parameter C is called *Curie–Weiss constant*. Its value in perovskite ferroelectrics is about 10^5 K. Since ε_b is typically about $10 \varepsilon_o$, one readily verifies that in perovskite ferroelectrics, the ferroelectric contribution to the polarization typically dominates the polarization response so that

$$\varepsilon_r = \frac{C}{T - T_o}. \quad (2.31)$$

In the temperature range $T > T_o$, the dependence (2.31) is referred to as Curie–Weiss law for the paraelectric phase. For the ferroelectric which is the most interesting for microwave applications, $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$, the parameters of the Curie–Weiss law are functions of the Ba content, x , specifically: $C = 10^5(0.86 + 1.1x^2)$ K and $T_o = 42 + 440x - 100x^2$ K (Vendik et al. 1999). Additionally, for $x < 0.7$, the β coefficient can be approximated as: $\beta = 8 \times 10^9(1 - x)$ JC^{-4}m^5 (Tagantsev et al. 2003). One should note that the coefficient β of a material is sensitive to the mechanical boundary condition (cf (2.57)). Its value in a clamped film can essentially differ from that in a bulk material.

As clear from (2.28), the application of a DC electric field makes the polarization non-zero and reduces the value of the dielectric permittivity. To find the field dependence of the dielectric permittivity, one should, first, solve the cubic equation, (2.24), and then insert the value of the polarization found into (2.28). A convenient form for calculation of the dependence of the permittivity on the temperature and DC bias field is suggested by Vendik and Zubko (1997). Alternatively, this field dependence of the permittivity can be presented in the form

$$\varepsilon_r(E) = \frac{\varepsilon_r(0)}{2 \cosh\left[\frac{2}{3} \operatorname{arsinh}\left(2 \frac{E}{E_{1/2}}\right)\right] - 1} \quad (2.32)$$

where

$$E_{1/2} = \frac{4}{3\sqrt{3}} \frac{1}{\beta^{1/2}(\varepsilon_0 \varepsilon_r(0))^{3/2}} \quad (2.33)$$

is the value of the field inducing a twofold reduction of the permittivity (Chase et al. 2005), and $\varepsilon_r(0)_r(0)$ is the relative permittivity at zero DC bias. The temperature dependence of $\varepsilon_r(0)$ may be given by (2.31).

When the dielectric permittivity of a ferroelectric is large, the application of a DC electric field can substantially modify it. The field dependence of the dielectric permittivity given by (2.32) and (2.33) can be represented as a relationship between the tuneability, n , given by (2.3), and the bias field being applied to obtain such value of n , E_n (Tagantsev et al. 2003):

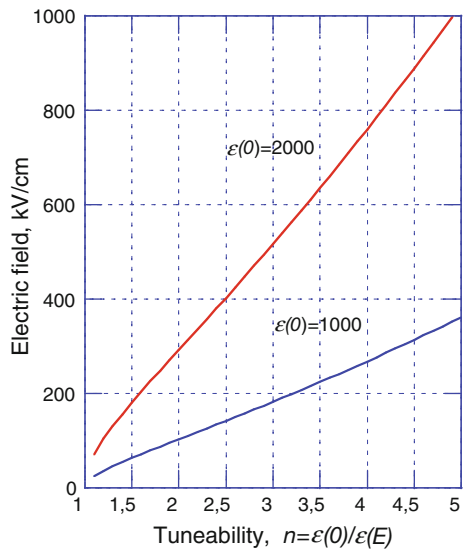
$$E_n = \frac{\sqrt{n-1}(2+n)}{\sqrt{27}\beta} \frac{1}{[\varepsilon_0 \varepsilon_r(0)]^{3/2}} \quad (2.34)$$

As it is seen from Fig. 2.4 for a higher tuneability, one needs a ferroelectric which has higher permittivity at zero DC bias.

2.1.2.3 Ferroelectric Phase

In the ferroelectric phase ($T < T_o$) in the absence of DC field, using (2.28) with P coming from (2.26), one finds the dielectric permittivity of the ferroelectric as

Fig. 2.4 Dependence of the electric field on the required tuneability, n , according to (2.34) $\beta = 8 \times 10^9 \text{ Vm}^5/\text{c}^3$



$$\epsilon = \epsilon_b + \frac{1}{2|\alpha|} \quad (2.35)$$

Like in the paraelectric phase, the contribution of the background permittivity can typically be neglected. This way one arrives at the so-called Curie–Weiss law for the ferroelectric phase:

$$\epsilon_r = \frac{C/2}{T_0 - T} \quad (2.36)$$

By putting together the dependence (2.31) and (2.36), it can be seen that the dielectric permittivity of ferroelectrics exhibits a strong increase when approaching the transition temperature. This prediction of an elementary Landau theory provides a qualitatively correct description on the temperature dependence of the dielectric permittivity in ferroelectrics at phase transition. This is illustrated by Fig. 2.5 where the temperature dependence of the dielectric permittivity in (Ba, Sr)TiO₃ ceramics is shown. The dielectric permittivity reaches its maximum at the transition temperature.

Here, the following should be noted: the Landau theory based description for the dielectric permittivity in the paraelectric phase is usually satisfactory. As for the ferroelectric phase, normally one can discuss only a qualitative agreement between (2.35) and experiment. There are two reasons for that. First, in many ferroelectrics, the quantitative description of the polarization response requires higher powers of polarization in the Landau expansion (2.20). This results in a certain modification of (2.35). Second, the Landau scheme presented above is directly applicable to only the so-called single-domain configuration, that is, the state where spontaneous polarization has the same value over the entire sample,

Fig. 2.5 Temperature dependence of the dielectric permittivity in $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ceramics (Smolenskii and Isupov 1954). The numbers indicate concentration of Ba

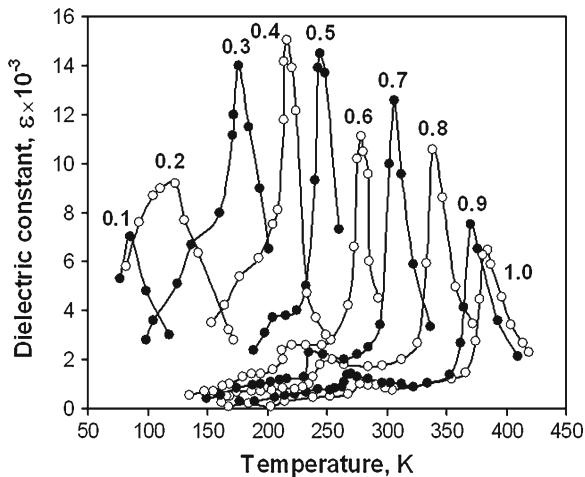


Fig. 2.6 Single-domain (a) and multi-domain (b) configurations

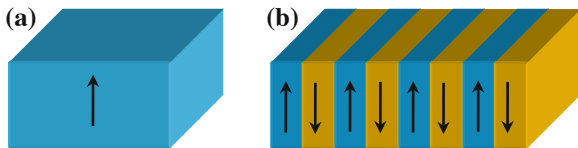


Fig. 2.6a. In the situation discussed above, this implies that the polarization should be either P_o or $-P_o$ throughout the whole sample. Very often this is not the case and the material occurs in the so-called *multi-domain configuration* where the sample is split into areas (domains) exhibiting one of the possible polarization states. Such a configuration² is schematically shown in Fig. 2.6b.

When the polarization response of the sample with such a configuration is tested with an AC field, the borders between domains (the so-called domain walls) are oscillating. This motion contributes to the dielectric response. This contribution can be comparable to that given by the Landau theory. The following terminology is used to distinguish the corresponding contributions to the dielectric permittivity. For the Landau theory contribution, discussed above, one uses the terms *lattice* or *intrinsic* contribution, whereas for the contribution related to the domain wall motion, one uses the terms *domain* or *extrinsic* contribution.

The polarization response to a relatively large periodic electric field is qualitatively different in the paraelectric and ferroelectric phases. In both cases, the dependence of polarization on the field is a nonlinear function. However, in the paraelectric phase, it is a “normal” single-valued function, Fig. 2.7a, whereas in

² Here, a ferroelectric exhibiting two domain states is considered. Hence, Fig. 2.6b gives an example of a multi-domain configuration consisting of two domain states. Often, ferroelectrics exhibit more than two domain states. In this case, the domain configurations can consist of more than two domain states.

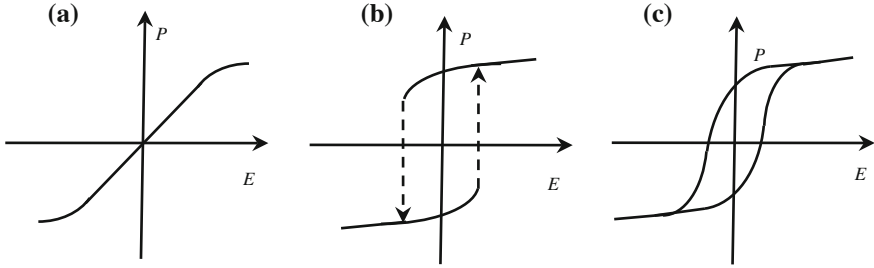


Fig. 2.7 Schematic P - E dependence for ferroelectrics according to Landau theory at $T > T_o$ (a) and $T < T_o$ (b and c)

the ferroelectric phase, it has a “hysteretic” dependence, Fig. 2.7b. The latter means that there is an interval of fields where for one value of the field, there exist two stable values of polarization. Equation (2.24) readily reproduces these situations for $\alpha > 0$ and $\alpha < 0$, respectively, as shown in Figs. 2.7a, b. The dependence, shown in Fig. 2.7b, is called *polarization hysteresis*. The maximum value of the electric field, at which the polarization bi-stability is possible, is called *coercive field*. The coercive field, predicted by the Landau theory, is called *thermodynamic coercive field*, E_{th} . Considered here is a version of this theory (with the equation of state given by (2.24))

$$E_{th} = \frac{2}{3\sqrt{3}} \frac{|\alpha|^{3/2}}{\beta^{1/2}} \quad (2.37)$$

Figure 2.8 shows, schematically, the dependence of free energy, (2.23), on the polarization for the ferroelectric phase (i.e., $\alpha < 0$). It illustrates the polarization bi-stability of the system. Figure 2.8a, b, c corresponds to the values of the electric field $E = 0$, $|E| < E_{th}$, and $E = E_{th}$, respectively.

In practice, in ferroelectrics, the real coercive field is at least one order of magnitude (often 2–3 orders of magnitude) smaller than the thermodynamic coercive field. The reason for this is that for any field smaller than E_{th} , as clear from Fig. 2.8b, the state with polarization antiparallel to the field is metastable, which makes the transition energetically favorable. However, to do this, the system should overcome an energy barrier between the metastable and ground states. This process is kinetic and is typically defect assisted, happening at $|E| < E_{th}$. In view of the kinetic nature of this process, the value of the coercive field depends on the frequency of the measuring field; usually this is a weak logarithmic dependence. The switching between the metastable and ground polarization states in real materials often happens over an interval of fields rather than at one value of the field, as suggested by the Landau theory. An example of measured hysteresis of a real ferroelectric is shown in Fig. 2.7c.

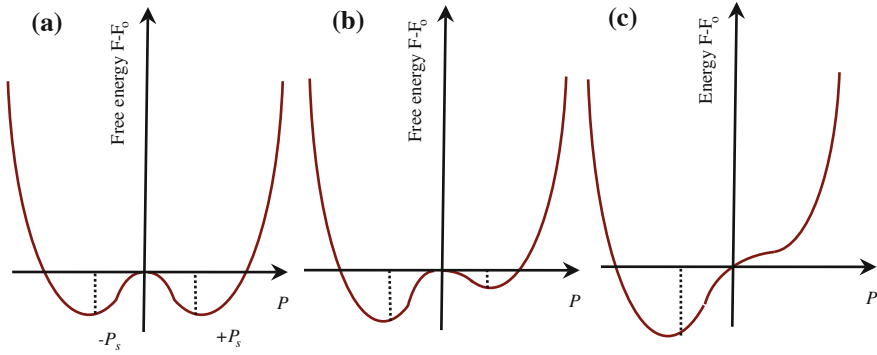


Fig. 2.8 Schematic dependence of free energy (2.23) on the Polarization for the ferroelectric phase for $E = 0$ (a), $|E| < E_{th}$, (b), and $|E| = E_{th}$ (c). In (b) and (c), the sign of the electric field is negative

2.1.2.4 Incipient Ferroelectrics

In some materials, a very high dielectric permittivity is observed which, in a wide temperature range, follows the Curie–Weiss law in the paraelectric phase (2.31) with a small value of T_o (smaller than 50 K). However, upon further cooling, no phase transition to the ferroelectric phase takes place. These dielectrics are known as *incipient ferroelectrics*. At very low temperatures (typically below 50 K), the temperature dependence of the permittivity, $\epsilon_r(T)$, essentially deviates from the Curie–Weiss law. The dielectric properties of incipient ferroelectrics can be modeled using (2.24), but with the α having a more complex rather than a linear temperature dependence (see e.g., (Vendik and Zubko 1997)). It is useful to note that the relationship for tuneability, (2.34), holds for incipient ferroelectrics. Typical incipient ferroelectrics are SrTiO_3 and KTaO_3 .

2.2 Elastic Properties

In this section, the elastic properties of the materials are treated for the situation where they are not coupled with the polarization response of the materials. The situation where this is not the case will be addressed in Sect. 2.3.

Elastic properties of a solid dielectric are controlled by Hook’s law written as

$$T_{ij} = c_{ijkl}S_{lk}, \quad i, j, k, l = 1 - 3, \quad (2.38)$$

where T_{ij} , S_{lk} , and c_{ijkl} are, respectively, tensors of stress, strain, and elastic stiffness. The stress and strain tensors are symmetric with respect to the permutation of their suffixes. This enables us to introduce the Voigt notation form for this equation:

$$T_n = c_{nm}S_m, \quad n, m = 1 - 6, \quad (2.39)$$

where the Voigt notations for T_{ij} and c_{ijkl} tensors are introduced as

$$T_n = T_{ij} \text{ and } c_{nm} = c_{ijkl} \quad (2.40)$$

with the correspondence of a pair of Cartesian suffixes to one respective Voigt suffix: $11 \Rightarrow 1$, $22 \Rightarrow 2$, $33 \Rightarrow 3$, $23, 32 \Rightarrow 4$, $13, 31 \Rightarrow 5$, and $12, 21 \Rightarrow 6$. For the strain tensor

$$S_n = S_{ij} \text{ for } n = 1 - 3 \text{ and } S_n = 2S_{ij} \text{ for } n = 4 - 6 \quad (2.41)$$

with the same correspondence rule for the suffixes.

Hook's law can also be obtained using the free energy density of the material written as

$$F = F_0 + \frac{c_{ijkl}}{2} S_{ij} S_{kl} \text{ or } F = F_0 + \frac{c_{nm}}{2} S_n S_m \quad (2.42)$$

(where F_0 is the part of the free energy independent of strain) with the equation of state

$$T_{ij} = \frac{\partial F}{\partial S_{ij}} \text{ or } T_n = \frac{\partial F}{\partial S_n} \quad (2.43)$$

One readily checks that (2.42) and (2.43) yield Hook's law. This thermodynamic formulation of Hook's law also implies that the tensor of elastic stiffness, written in Voigt notations, is symmetric with respect to the permutation of its suffixes (Nye 1985). The number of its independent components depends on the symmetry of the material. From Table 2.1, the reader can have an idea about typical values of elastic stiffness in solids.

The description of the elastic response of a material in terms of Hook's law, given by (2.38) with the same stiffness tensor for any distribution of strain, is possible for non-piezoelectric materials. For piezoelectric materials, it holds in the case where mechanical deformation does not create an electric field. In general in piezoelectric materials, to cover all possible situations, one introduces three kinds of elastic stiffnesses: at fixed polarization, fixed electrical displacement, and fixed electric field. This issue is addressed in detail in the next section.

2.3 Electromechanical Phenomena

In this section, the elastic, dielectric, and piezoelectric properties of the materials are considered taking into account the coupling between elastic deformation and electric polarization. More precisely what is considered is the linear electromechanical response, in other words—the linear relationships between the “elastic” and “electric” variables characterizing the state of the material. Such equations are

called linearized constitutive electromechanical equations. Hereafter, when this is not confusing, the term “constitutive equations” will be used as shorthand. The standard form for such equations is a set of linear equations relating components of the electric displacement and mechanical stress on one hand and components of electric field and strain on the other. The combination of these constitutive equations with the field equations (Maxwell’s equations and the equation of motion for elastic continuum) provides a full set of equations describing electro-mechanical devices.

2.3.1 Linear Piezoelectrics

Solid materials can be divided into two classes: centrosymmetric and non-centrosymmetric. In a centrosymmetric material, any direction can be changed by applying an operation of its macroscopic symmetry. For example, for a material of the cubic symmetry, the direction of the OX_1 axis can be inverted by application of the 180° rotation about the OX_2 axis (see Fig. 2.2). In a non-centrosymmetric material, this is only possible for some directions. This difference in the symmetry of materials has a great impact on their electromechanical properties.

In non-centrosymmetric materials, the application of a mechanical stress may induce dielectric polarization, whereas in centrosymmetric materials, it is not the case (Nye 1985). Such a response is called *piezoelectric response*. This phenomenon is also known as *piezoelectric effect*. Materials exhibiting this effect are called *piezoelectrics* (or *piezoelectric materials*). Term *linear piezoelectrics* applies to *piezoelectrics* exhibiting only weak (negligible for practical applications) nonlinearity of their electromechanical properties. In practice, *linear piezoelectrics* are *piezoelectrics* which are not ferroelectrics at the same time. In this sub-section, linear piezoelectrics are addressed and ferroelectrics will be considered in the next sub-section.

In piezoelectrics, the constitutive equation for electrical displacement, (2.6), should be modified by adding the contribution of the piezoelectric effect, leading to a new constitutive equation which reads

$$D_i = e_{ijl}S_{jl} + \epsilon_{ij}^S E_j \quad (2.44)$$

Here, the piezoelectric response is controlled by the piezoelectric tensor e_{ijl} . This is a third rank tensor. In contrast to the permittivity tensor (second rank tensor) and the tensor of elastic stiffness (second rank tensor), not in all materials, the structural symmetry allows a non-zero piezoelectric tensor. Thus, not all materials are piezoelectrics. The upper suffix “S” is added to the dielectric permittivity tensor to emphasize that it corresponds to the dielectric response of a material measured under the condition of constant strain (i.e., the material is mechanically clamped during the application of the measuring electric field).

As it is demonstrated using thermodynamics (Nye 1985), materials exhibiting piezoelectric response must exhibit *converse piezoelectric response* consisting of a linear response of mechanical strain (or stress) to the applied electric field. The converse effect is controlled by the same piezoelectric tensor as that controlling the direct effect. This implies a modification of the constitutive equation for mechanical stress, (2.38), and leads to a new constitutive equation which reads

$$T_{ij} = c_{ijkl}^E S_{kl} - e_{ijl} E_l \quad (2.45)$$

Here, the upper suffix “E” is added to the elastic stiffness tensor to emphasize that it corresponds to the elastic response of the material measured under the condition of constant electric field (e.g., the material is under short-circuited electrical conditions).

The piezoelectric tensor is symmetric with respect to the permutation of the last two suffixes (Nye 1985). This enables us to introduce Voigt notations for the modified constitutive equations, (2.44) and (2.45), which can now be represented in the form:

$$\begin{aligned} D_i &= e_{in} S_n + \varepsilon_{ij}^S E_j \\ T_m &= c_{mn}^E S_n - e_{lm} E_l \end{aligned} \quad i, j, l = 1 - 3, \quad n, m = 1 - 6 \quad (2.46)$$

where the Voigt notations for the piezoelectric tensor are introduced as

$$e_{im} = e_{ijl} \quad i, j, l = 1 - 3, \quad m = 1 - 6. \quad (2.47)$$

A change in mechanical conditions can substantially influence the dielectric response of piezoelectrics. The dielectric permittivity of a mechanically free material, ε_{ij}^T , can be found using (2.46) where $T_m = 0$. Specifically,

$$\varepsilon_{ij}^T = \left. \frac{\partial D_i}{\partial E_j} \right|_{T, E=0} = \varepsilon_{ij}^S + e_{in} \frac{dS_n}{dE_j} = \varepsilon_{ij}^S + e_{in} s_{nm}^E e_{jm} \quad (2.48)$$

Here, s_{nm}^E is the inverse of the matrix c_{nm}^E , also known as *elastic compliance*, and the derivative dS_n/dE_j is calculated using the second equation of (2.46). The renormalization of the dielectric response occurs since the electric field does not only directly affect the electric displacement but also deforms the sample through the direct piezoelectric effect. The resulting deformation, in turn, contributes to the electrical displacement through the converse piezoelectric effect.

A similar effect occurs with the elastic response. The elastic stiffness, measured under the open circuit electrical conditions, c_{mn}^D , can essentially differ from c_{mn}^E . Calculations analogous to those presented above for the dielectric permittivity yield

$$c_{mn}^D = c_{mn}^E + \frac{\partial T_m}{\partial S_n} \Big|_{D=0} = c_{mn}^E + e_{in} (\varepsilon_S^{-1})_{ij} e_{jm} \quad (2.49)$$

Here, $(\epsilon_S^{-1})_{ij}$ is the inverse of the matrix ϵ_{ij}^S . It should be noted that the electrical and mechanical conditions often do not correspond to the “ideal” mechanically clamped, free and electrically open, or short-circuited samples. In this case, the dielectric permittivity and elastic stiffness of the material should be determined using (2.46) appended with the proper additional conditions. The resulting tensors will be different from those obtained for ideal conditions.

Thin piezoelectric films deposited onto thick substrates provide a good example of such behavior. In this case, in the film normal to the OX_3 direction (Fig. 2.2), $T_3 = T_4 = T_5 = 0$ and $S_1 = S_2 = S_6 = 0$. These mixed mechanical conditions together with (2.46) enables calculation of the out-of-plane dielectric permittivity of the film ϵ_{33}^{film} . For films of materials with hexagonal symmetry (like AlN and ZnO), where the hexagonal axis is normal to the plane of the substrate, one finds

$$\epsilon_{33}^{film} = \epsilon_{33}^S + \frac{e_{33}^2}{c_{33}^E}. \quad (2.50)$$

In obtaining this result, it is that some of the components of c_{mn}^E and e_{inz} are equal to zero.

The reader can have an idea about the strength of electromechanical effect by comparing the values of the dielectric permittivity and elastic stiffness corresponding to different mechanical and electrical conditions, which are given in Table 2.1.

2.3.2 Ferroelectrics

A description of electromechanical properties of a ferroelectric is readily available in terms of the Landau theory expansion (2.20) appended with elastic energy (2.42) and the energy of electrometrical coupling:

$$F = F_0 + \frac{\alpha_{ij}}{2} P_i P_j + \frac{\beta_{ijkl}}{4} P_i P_j P_k P_l + \frac{c_{ijkl}}{2} S_{ij} S_{kl} - q_{ijkl} P_i P_j S_{kl} - P_i E_i \quad (2.51)$$

Here, F_0 is independent of both polarization and strain, and c_{ijkl} is the elastic stiffness tensor in the paraelectric phase. In this equation, the electrometrical coupling is described by the *electrostrictive contribution* to the free energy density, which contains the tensor of *electrostrictive coefficients* q_{ijkl} . Applying condition (2.21) and (2.43), one obtains equations of the state for ferroelectrics taking into account the mechanical degree of freedom:

$$E_i = \alpha_{ij} P_j + \beta_{ijkl} P_j P_k P_l - 2q_{ijkl} P_j S_{kl} \quad (2.52)$$

$$T_{ij} = c_{ijkl} S_{kl} - q_{lkij} P_l P_k \quad (2.53)$$

These equations fully describe the electromechanical response of a ferroelectric. As seen from these equations, in general, this response is nonlinear. However, it can be shown that in case of primary practical interest, if the deviations of the variables entering (2.52) and (2.53) around their equilibrium values are small, these equations lead to linearized constitutive equations in the form given by (2.46).

Next, this will be demonstrated for the simplest case where only one component of each variable entering (2.52) and (2.53) is non-zero. These components will be denoted as E , P , T , and S , respectively, while α , β , q , and c will be used for the corresponding components of the material tensors. Thus, (2.52) and (2.53) may be rewritten as

$$E = \alpha P + \beta P^3 - 2qPS \quad (2.54)$$

$$T = cS - qP^2 \quad (2.55)$$

To be specific, consider a ferroelectric in the initial equilibrium state where the stress and the electric field in it are equal to zero, that is, $T = 0$ and $E = 0$ (note that in a ferroelectric, this does not necessarily mean that $S = 0$ and $P = 0$). For this situation, the following problem is addressed: at a point in a sample, where a small variation of the strain δS and that of the electric field δE occurs, the corresponding variation in stress, δT , and that of electric displacement, $\delta D = \epsilon_0 \delta E + \delta P$ are considered. As a first step, the initial state of the ferroelectric is determined by solving (2.54) and (2.55) for $T = 0$ and $E = 0$. In the paraelectric state (at $\alpha > 0$), one finds $P = 0$ and $S = 0$, whereas in the ferroelectric state (at $\alpha < 0$), the non-zero spontaneous values for polarization and strain are found to be

$$\begin{aligned} P &= \pm P_o & P_o &= \sqrt{-\alpha/\beta^*} \\ S &= S_o & S_o &= qP_o^2/c \end{aligned} \quad (2.56)$$

where

$$\beta^* = \beta - 2q^2/c, \quad (2.57)$$

then E , P , T , and S are presented as the sum of their values in the initial state and small deviations from these values: δE , δP , δT , and δS . Inserting E , P , T , and S presented this way into (2.54) and (2.55) and keeping the linear terms with respect to δE , δP , δT , and δS , one arrives at the following equations:

$$\delta E = \alpha \delta P \quad (2.60)$$

$$\delta T = c \delta S \quad (2.61)$$

in the paraelectric phase and

$$\delta E = (\alpha + 3\beta^* P_o^2) \delta P - 2qP_o \delta S \quad (2.62)$$

$$\delta T = c \delta S - 2qP_o \delta P \quad (2.63)$$

for the ferroelectric phase. Using (2.19), these equations can be rewritten in the form of linearized constitutive equations specified by (2.46):

$$\begin{aligned} D &= eS + \varepsilon^S E \\ T &= c^E S - eE \end{aligned} \quad (2.64)$$

where

$$\varepsilon^S = \varepsilon_b + 1/\alpha, \quad c^E = c, \quad \text{and} \quad e = 0 \quad (2.65)$$

for the paraelectric phase and

$$\varepsilon^S = \varepsilon_b + 1/|2\alpha|, \quad c^E = c - 2q^2 P_0^2 / |2\alpha| \quad \text{and} \quad e = 2qP_0 / |2\alpha| \quad (2.66)$$

for the ferroelectric phase. To simplify notations, the δ' s in front of the variables are dropped.

Next, the obtained results are analyzed. It is seen that in the paraelectric phase, the ferroelectric is not piezoelectric. This corresponds to the fact that ferroelectrics described by free energy (2.51) are centrosymmetric in the paraelectric phase. However, they become piezoelectric in the ferroelectric phase. This happens due to the appearance of spontaneous polarization which makes the structure non-centrosymmetric. One states that the piezoelectricity is a result of “linearization” of electrostriction with spontaneous polarization. Since $P_o \propto \sqrt{T_o - T}$ and $|2\alpha| \propto T_o - T$, according to (2.66), the piezoelectric coefficient strongly increases on approach to the transition temperature from the ferroelectric phase: $e \propto 1/\sqrt{T_o - T}$. In the considered simplified model, it diverges when approaching T_o .

In more advanced models, the divergence may be absent but the qualitative prediction of the model concerning the strong increase always holds. Another feature which is clear from this consideration is that the electric stiffness measured at zero electric field exhibits a step-like reduction in variation at the transition point. This is a general qualitative feature of ferroelectrics. In real materials, this variation can be essential (up to tens of percent).

The above consideration explains how the linearized constitutive electromechanical equations written in standard form (2.46) can be, in principle, derived from Landau expansion (2.51). In a particular real problem of the linear electro-mechanical response of a ferroelectric, the calculations are analogous to those given above. The new features, which may appear in such a problem, are as follows:

- First, the calculations may involve more than one component of the variables;
- Second, the mechanical and electrical conditions in the initial state can be different from those treated above, for example, mechanical stress and electrical field may not be zero in the original state.

For example, mechanical conditions can be mixed as in the case of thin ferroelectric films on a relatively thick substrate discussed earlier in the Sect. 2.3.1. To

determine the initial state for a thin ferroelectric film on a substrate normal to the OX_3 axis, Fig. 2.2, one should solve (2.52) and (2.53) setting $T_3 = T_4 = T_5 = 0$ and $S_1 = S_{1m}, S_2 = S_{2m}, S_6 = S_{6m}$, where S_{1m}, S_{2m} , and S_{6m} are the in-plane components of the strain controlled by the substrate (Pertsev et al. 1998). Then, the linearized constitutive equations can be derived by the linearization of (2.52) and (2.53) with respect to the solutions obtained. Of particular interest is the situation where a ferroelectric in the initial state is loaded with a DC bias electric field. This situation will be treated in the next sub-section.

To concluding this sub-section, a remark is to be made. Strictly speaking, the above analysis of electromechanical properties applies only to ferroelectrics in single-domain configurations. In multi-domain configurations, domains may influence the electromechanical response. However, the domain-related effects do not seem to be relevant to the applications addressed in this book. For this reason, this issue is not covered here.

2.3.3 *Modification of Elastic and Piezoelectric Properties of Ferroelectrics Under Bias Electric Field and Higher Order Electromechanical Effects*

As pointed out in Sect. 2.1.2, the dielectric permittivity of ferroelectrics can be substantially changed by applying an external electric bias field. However, an external bias field can essentially affect the elastic and piezoelectric properties of ferroelectrics as well. These effects are elucidated below using the one-component framework, (2.54) and (2.55), employed in the previous sub-section. As in the previous sub-section, the stress-free initial state of the ferroelectric is considered ($T = 0$). However, it is assumed that the material is loaded with an external electric bias field, E_{DC} . Thus, the values of the polarization and strain in the initial state of the ferroelectric (denoted as P_{DC} and S_{DC}) can be found from the solution to the following set of equations:

$$E_{DC} = \alpha P + \beta P^3 - 2qPS \quad (2.67)$$

$$0 = cS - qP^2 \quad (2.68)$$

One can readily check that P_{DC} satisfies the equation

$$E_{DC} = \alpha P_{DC} + \beta^* P_{DC}^3 \quad (2.69)$$

where β^* is given by (2.57) and $S_{DC} = qP_{DC}^2/c$. The derivation of the linearized constitutive equations can be carried out as in the previous sub-section. The parameters E, P, T , and S are represented as a sum of their values in the initial state and small deviations from these values, $\delta E, \delta P, \delta T$, and δS . Then, E, P, T , and S presented this way are inserted into (2.54) and (2.55). Keeping linear terms with

respect to δE , δP , δT , and δS , one finally arrives at the standard set of constitutive equations (to simplify notations, the δ' in front of the variables are dropped)

$$\begin{aligned} D &= eS + \varepsilon^S E \\ T &= c^E S - eE \end{aligned} \quad (2.70)$$

where all coefficients can be presented as functions of P_{DC}

$$\varepsilon^S = \varepsilon_b + \chi_f, \quad \chi_f = \frac{1}{\alpha + 3\beta^* P_{\text{DC}}^3} \quad (2.71)$$

$$c^E = c - 2q^2 P_{\text{DC}}^2 \chi_f \quad (2.72)$$

$$e = 2q P_{\text{DC}} \chi_f \quad (2.73)$$

Since the DC bias always induces polarization, equation (2.69) has a non-zero stable solution for any sign of α . This implies that (2.71–2.73) with non-zero P_{DC} hold for both paraelectric and ferroelectric phases.

Let us examine the new features introduced into the elastic and piezoelectric properties of the ferroelectric due to application of the DC bias field, starting with the DC bias–induced piezoelectricity in the paraelectric phase. On the level of symmetry, it reflects the fact that the DC bias lowers the symmetry of the material in the paraelectric phase from centrosymmetric to non-centrosymmetric. Thus, by switching the DC bias on and off, the piezoelectric coupling can turn on and off. In addition, by changing the DC bias, it is possible to tune the values of the piezoelectric coefficient $e = 2q P_{\text{DC}} \chi_f$ and elastic stiffness $c^E = c - 2q^2 P_{\text{DC}}^2 \chi_f$ via DC field–induced variations of P_{DC} and χ_f . An essential feature of ferroelectrics is the strong polarization response so that the DC field–induced polarization can be appreciable. This means that $e = 2q P_{\text{DC}} \chi_f$ can be substantially changed by the application of an external electric field. On the practical level, this implies a possibility of an appreciable DC field–induced change in the piezoelectric and elastic properties of the material. Thus, one can discuss not only the tuning of the dielectric properties of ferroelectrics by a DC external field (see Sect. 2.1.2) but also the tuning of their piezoelectric and elastic properties.

To enable tuning of the elastic properties, another relevant effect needs to be introduced: *nonlinear electrostriction*. In terms of one-component model used above, this effect can be introduced by including an additional term in yet not linearized constitutive equation (2.55) as follows:

$$T = cS - qP^2 - mSP^2 \quad (2.74)$$

The new term in this equation is usually neglected in the phenomenological theory of ferroelectrics. Typically, it provides effects that are beyond the accuracy of the Landau theory. However, for the problem of tuning the elastic properties of ferroelectrics (Noeth et al. 2007), this may not be the case. Then, the *nonlinear electrostriction* should be taken into account.

The full treatment of the impact from *nonlinear electrostriction* on the properties of ferroelectrics is beyond the scope of this book. Only the result of the analysis will be given.

When determining the initial state of the ferroelectric (getting the values of P_{DC} and S_{DC}), one can readily neglect m in (2.74). At the same time, in calculations of the elastic stiffness entering (2.70), one should take m into account. Then, the full expression for the elastic stiffness will read as

$$c^E = c - 2q^2 P_{DC}^2 \chi_f - m P_{DC}^2 \quad (2.75)$$

It is clear from (2.74) that the nonlinear electrostriction will also modify the values of the piezoelectric coefficient. However, it can show that this effect may be neglected without appreciable loss in accuracy.

The consideration presented in this sub-section explains the principle of tuning of the piezoelectric and elastic properties of ferroelectrics with an external DC electric field. For the sake of transparency, the presentation is done in terms of the simplest model which deals with only one component of each variable and mechanically free system. As discussed in the previous sub-section, the consideration of a more realistic situation, though more cumbersome, is still straightforward. However, to get the full description of electrical tuning of electromechanical properties of ferroelectrics, one should start from the Landau expansion which incorporates nonlinear electrostriction. Thus, (2.51) should be generalized into the form:

$$\begin{aligned} F = & F_0 + \frac{\alpha_{ij}}{2} P_i P_j + \frac{\beta_{ijkl}}{4} P_i P_j P_k P_l \\ & + \frac{c_{ijkl}}{2} S_{ij} S_{kl} - q_{ijkl} P_i P_j S_{kl} - \frac{1}{2} m_{ijklpg} P_i P_j S_{kl} S_{pq} - P_i E_i \end{aligned} \quad (2.76)$$

In the general case, one uses (2.21) and (2.43) to obtain the equations of state of the type (2.52) and (2.53). Then, the values of the polarization vector and strain tensor in the initial state can be determined from these equations, taking into account the mechanical conditions. At this stage, the nonlinear electrostriction can be ignored (by setting $m_{ijklpg} = 0$) without loss of appreciable accuracy. Further calculations are analogous to those performed in deriving (2.70). At this stage, one should take into account the nonlinear electrostriction when calculating the components for the elastic stiffness tensor. An example of such calculations is given later in the book where the modeling of tuneable FBARs is addressed.

2.4 Dissipation Effects

Dielectric, elastic, and electromechanical responses of insulating solids, addressed in the previous Sections, are related to the so-called quasi-static approximation. The response of polarization and strain of a system is considered to follow

instantaneously with any variation in the external AC perturbation (e.g., electric field or stress). Typically, the perturbation is an AC signal changing with time as $\cos \omega t$, where ω is the angular frequency of the signal. The quasi-static approximation in this case implies that the response is in phase with the perturbation, that is, all components of the response variables are proportional to $\cos \omega t$. Such an approximation is suitable for a rough treatment to basically all problems related to the response in question. However, very often a comprehensive treatment of a problem requires taking into account the fact that the response is always lagging behind the perturbation. This means that the components of the response should be delayed in phase, with respect to the perturbation, being proportional to $\cos(\omega t - \varphi)$ where φ is the phase shift which is, in general, different for different components of the response. In any material of interest for practical application, $\varphi < \pi$ and the phase shift itself does not essentially affect the performance of the device using this material. However, a non-zero value of φ implies energy dissipation (losses) in the system, which can heavily affect the performance of a device using this material. Typical examples of parameters sensitive to the losses are power consumption in devices and the quality factor of resonators.

In the following sub-sections, the loss associated with the dielectric, elastic, and electromechanical responses are discussed.

2.4.1 Dielectric Losses

In the case of the dielectric response, the effect of the phase shift between the electric field (as the perturbation) and the electric displacement (as the response) is customarily described by introducing the so-called complex approach. In this approach, the AC electric field and displacement are both presented as the real parts of the complex fields \tilde{E} and \tilde{D} :

$$E = \text{Re}[\tilde{E}] \quad D = \text{Re}[\tilde{D}] \quad (2.77)$$

$$\tilde{E} = \tilde{E}_o e^{j\omega t} \quad \tilde{D} = \tilde{D}_o e^{j\omega t} \quad (2.78)$$

where \tilde{E}_o and \tilde{D}_o are the complex amplitudes.

In the case of an isotropic dielectric response, where electric field and displacement are always parallel, the complex permittivity is introduced as

$$\varepsilon' - j\varepsilon'' = \tilde{D}_o / \tilde{E}_o \quad (2.79)$$

where ε' and ε'' are the real and imaginary parts of complex permittivity. Note that, by convention, the imaginary part of the complex permittivity is introduced with an additional factor of “ -1 .” If $\varepsilon'' = 0$, the Eqs. (2.77–2.79) imply the relationship for the quasi-static polarization response introduced in Sect. 2.1, $D = \varepsilon' E$, with ε' playing the role of dielectric permittivity introduced there. With $\varepsilon'' \neq 0$, the

Eqs (2.77–2.79) describe an AC signal of D shifted in phase with respect to that of E . Indeed, consider an AC electric field equal $E_o \cos \omega t$, which corresponds to the complex form with $\tilde{E}_o = E_o$. Then, using (2.77–2.79), one finds

$$D = \text{Re}[(\epsilon' - j\epsilon'')E_o e^{i\omega t}] = \sqrt{\epsilon'^2 + \epsilon''^2} E_o \cos(\omega t - \delta) \quad (2.80)$$

where

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (2.81)$$

The angle δ is often called *loss angle*, whereas the ratio ϵ''/ϵ' —*loss tangent*.

The values of the imaginary part of the complex permittivity and loss tangent can readily be attributed to energy dissipation in the system. Specifically, the energy dissipated (per unit volume) during one cycle of the AC field can be found as the electrostatic work (per unit volume), A , executed over the system during this time. According to the foundations of electrostatics, this work can be presented as an integral along a closed counter in the $D - E$ plane, corresponding to a cycle,

$$A = \oint E dD. \quad (2.82)$$

It has a simple geometrical meaning: it equals the area of the loop in the $D - E$ coordinates corresponding to the AC cycling (see Fig. 2.9).

Calculating the integral (2.82) with T and $E = E_o \cos \omega t$, one finds

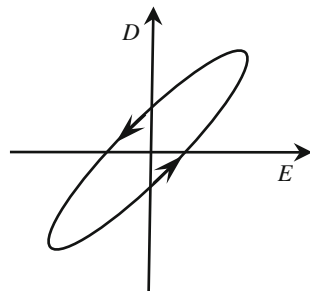
$$A = \left(\frac{2\pi}{\omega}\right) \epsilon' \tan \delta \frac{\omega}{2} E_o^2 = T \epsilon'' \frac{\omega}{2} E_o^2 \quad (2.83)$$

where $T = 2\pi/\omega$ is the period of the AC field. This relationship implies the following dissipation rate of the electrostatic energy density:

$$\frac{dW}{dt} = -\epsilon'' \frac{\omega}{2} E_o^2 \quad (2.84)$$

The energy dissipation related to the phase shift between the electric field and displacement is referred to as *dielectric loss*.

Fig. 2.9 Loop on the $D - E$ plane corresponding to AC cycling of lossy dielectric



Generally, ε' and ε'' are functions of the AC field frequency. It can be shown that $\varepsilon'/\varepsilon_o$ should either be larger than 1 or negative (Landau et al. 1984). Practically, for frequencies up to the THz range $\varepsilon'/\varepsilon_o > 1$. The imaginary part of the permittivity must be positive; this ensures that (2.84) describes energy dissipation.

All relationships presented above can be generalized for the case of anisotropic materials. In anisotropic materials, complex permittivity is introduced as a complex tensor by the relationship:

$$\tilde{D}_{oi} = (\varepsilon'_{ij} - j\varepsilon''_{ij})\tilde{E}_{oj} \quad (2.85)$$

whereas the relationship of the energy dissipation, (2.84), can be generalized into the form

$$\frac{dW}{dt} = -\varepsilon''_{ij} \frac{\omega}{2} E_{oi} E_{oj} \quad (2.86)$$

Thermodynamics requires that both tensors ε'_{ij} and ε''_{ij} are symmetric, the principal components of ε'_{ij} are larger than ε_o or negative, and the principal components of ε''_{ij} are positive (Landau et al. 1984); this ensures that (2.86) does describe energy dissipation.

2.4.2 Mechanical and Piezoelectric Losses

Energy dissipation in a material subjected to AC electrical and mechanical perturbations is not fully conditioned by the phase shift between the electric field and displacement, described in terms of the complex dielectric permittivity. At a finite frequency of the AC perturbation, elastic and piezoelectric responses also contain off-phase components. In terms of the complex approach, this effect is incorporated into the theory by introducing complex elastic stiffness and piezoelectric tensors in the constitutive equations for complex amplitudes of the electric field, \tilde{E}_{oi} , electric displacement, \tilde{D}_{oi} , strain, \tilde{S}_{0n} , and stress, \tilde{T}_{0n} (Holland 1967):

$$\begin{aligned} \tilde{D}_{0i} &= (e'_{in} - je''_{in})\tilde{S}_{0n} + (\varepsilon'^S_{ij} - j\varepsilon''^S_{ij})\tilde{E}_{0j} \\ \tilde{T}_{0m} &= (c'^E_{nm} + jc''^E_{nm})\tilde{S}_{0n} - (e'_{in} - je''_{in})\tilde{E}_{0i} \end{aligned} \quad i, j, l = 1 - 3, \quad n, m = 1 - 6 \quad (2.87)$$

Using thermodynamic arguments, one can demonstrate that, similarly to the quasi-static regime, the same complex piezoelectric tensor $e'_{in} - je''_{in}$ controls the direct and converse piezoelectric response in the dynamic case (Gurevich 1986). Based on thermodynamic arguments, one can also show that the imaginary part of the tensor of elastic stiffness is also symmetric (in Voigt notations), having the principal components positive.

In the case where both dielectric and elastic variables are involved, the rate of energy dissipation per unit volume of the system can be presented in terms of complex amplitudes of the electromechanical variables (Holland 1967):

$$\frac{dW}{dt} = -\frac{\omega}{2} \text{Im} [\tilde{E}_{oi} \tilde{D}_{oi}^* + \tilde{T}_{0n} \tilde{S}_{0n}^*]. \quad (2.88)$$

where the asterisk means complex conjugation. Using this relationship and (2.87), one can readily express the rate of energy dissipation in terms of the complex material tensors of the system as follows:

$$\frac{dW}{dt} = -\frac{\omega}{2} \text{Im} [\tilde{E}_{oi} \epsilon_{ij}^{S*} \tilde{E}_{oj}^* + \tilde{S}_{0n} c_{nm}^{E*} \tilde{S}_{on}^* + \tilde{E}_{oi} e_{in}^* \tilde{S}_{on}^* + \tilde{E}_{oi}^* e_{in}^* \tilde{S}_{on}^*] \quad (2.89)$$

One can readily check that in this expression, the first term in the square brackets is consistent with (2.86) and describes the dielectric losses. Similarly, the second term in the square brackets describes the *mechanical loss*. It can also be expressed in terms of real amplitudes of stress components, S_{0n} , and the imaginary part of the elastic stiffness:

$$\frac{dW}{dt} = -\frac{\omega}{2} c_{nm}^{\prime\prime E} S_{on} S_{om} \quad (2.90)$$

The principal components of $c_{nm}^{\prime\prime E}$ are positive ensures that (2.90) does describe energy dissipation. The last term in the square brackets in (2.90) describes the so-called *piezoelectric loss*. Thermodynamics sets no restrictions on the sign of components of the complex piezoelectric tensor (Holland 1967).

For a non-piezoelectric material energy, dissipation is controlled solely by the dielectric losses in the case of an electrical excitation and solely by mechanical loss in the case of a mechanical excitation. In contrast, for piezoelectric material, energy dissipation is governed, disregarding the type of the excitation, by the whole set of contributions: dielectric, mechanical, and piezoelectric losses.

Mechanical losses control the attenuation of an acoustic wave traveling in a medium. Typically, the amplitude of the wave decays exponentially with the distance so that the displacement of the medium in such a wave, u , can be cast in the form

$$\tilde{u} = u_0 e^{i\omega t - \gamma x} \quad (2.91)$$

where γ is the complex propagation constant:

$$\gamma = \alpha + j\beta \quad (2.92)$$

In the case where the dissipation is neglected, the imaginary part, β , of the complex propagation constant introduced this way corresponds to the *propagation constant* of the wave (also wavenumber). The real part, α , of the complex propagation is called *amplitude attenuation constant*. Typically, $\alpha \ll \beta$ so that $1/\alpha$ can be interpreted as a distance on which the acoustic wave amplitude decays e times.

One can also link α the complex elastic stiffness. Let us demonstrate this for an idealized case of a longitudinal wave, that is, where the medium displacement in the wave, u , is parallel to the direction of its propagation (so that $S = \partial u / \partial x$) and only one longitudinal component of stress, T , is involved. By combining the equation of motion in an elastic medium

$$\rho \ddot{u} = \frac{\partial T}{\partial x} \quad (2.93)$$

(ρ is the mass density, kg/m^3) with the elastic constitutive equation³

$$\tilde{T}_0 = (c' + jc'')\tilde{S}_0 \quad (2.94)$$

and taking the medium displacement in the complex form, one finds the equation linking the frequency with the propagation constant:

$$-\rho\omega^2 = (c' + jc'')\gamma^2 \quad (2.95)$$

Typically, $c'' \ll c'$. Under this condition, the solution to this equation can be cast in the form

$$\gamma = j\beta \left(1 - j \frac{c''}{2c'} \right) \quad (2.96)$$

$$\beta = \sqrt{\frac{\rho}{c'}}\omega \quad (2.97)$$

Thus, the sought relationship between the imaginary part of the propagating constant (attenuation constant) and the complex elastic stiffness reads

$$\alpha = \frac{c''}{2c'} \sqrt{\frac{\rho}{c'}}\omega \quad (2.98)$$

To characterize the mechanical loss, one also introduces the notion of the acoustic *loss tangent* defined as

$$\tan \delta_{ac} = \frac{c''}{c'}. \quad (2.99)$$

The notions of complex elastic stiffness, acoustic damping constant, and acoustic loss tangent have been introduced above for the case of the dissipation of the acoustic wave energy (into the heat). However, the amplitude of the wave can decrease as a result of its partial scattering from defects or other inhomogeneities of the medium. In fact, the scattering is not energy dissipation. However, the

³ Such equation is valid for piezoelectrics as well. In this case, it should be derived from the set of electromechanical constitutive equations (2.87) by eliminating the electrical variables E and D . The additional relationship between these variables needed for such procedure is controlled by the electrical conditions in the medium (e.g., short-circuit).

related reduction of the wave amplitude can still be described in terms of relationships (2.91–2.99). The notion of complex elastic stiffness, acoustic damping constant, and acoustic loss tangent can still be used even though the physics behind them is very different from that of true mechanical loss. This approach is useful when it comes to analysis and modeling of the Q-factors of the FBARs.

2.4.3 Mechanisms of Energy Dissipation

In a perfectly insulating material, one distinguishes two types of contributions to the losses: the so-called *intrinsic and extrinsic losses or contributions*. The intrinsic loss is related to the interaction of an AC perturbation (e.g., electric field or stress) with phonons (lattice vibrations) in an ideal crystalline lattice. The extrinsic one corresponds to the energy dissipation mechanisms assisted with lattice imperfections or domains. This can be a defect assisted interaction of AC electric field with phonons or a direct interaction of AC electric field with “hopping impurities” and domain walls. The energy dissipation due to a finite DC conduction of a material can also be termed as an extrinsic loss, in view of the fact that any appreciable conduction of a dielectric is usually conditioned by a high concentration of impurities.

Comprehensive treatments of the matter can be found in review papers (Gurevich and Tagantsev 1991; Tagantsev et al. 2003) and textbooks (Gurevich 1986; Damjanovic 2005). Detailed discussions of the losses are beyond the scope of this book. Below only some basic issues are briefly addressed.

2.4.3.1 Acoustic Losses

When it comes to intrinsic losses, one always means properties of crystalline materials where lattice vibrations at all frequencies can be viewed as weakly damped waves of atomic displacements. Thus, the following discussion is not relevant to non-crystalline materials. The theoretical results of the intrinsic loss have been obtained using quantum mechanics and statistical physics of phonons. When presenting theoretical results (temperature and frequency dependence of the imaginary parts of dielectric permittivity, elastic stiffness, and piezoelectric coefficients), one distinguishes high-frequency and low-frequency ranges. In terms of temperature, one also distinguishes low temperature and high temperature ranges. The border between the high-frequency and low-frequency ranges is the so-called thermal phonon damping Γ , whereas the border between the low temperatures and high temperature ranges is the Debye temperature θ . Typically, in dielectrics, the Debye temperature θ is of the order of room temperature (with some exceptions like sapphire where $\theta \cong 1,000$ K). As for the parameter Γ , it is a pronounced function of the temperature; at room temperature, it is typically in the range of hundreds of GHz. In this book, the microwave frequency range about

room temperature is considered. For this reason, all theoretical results presented hereafter will correspond to low-frequency and high temperature ranges with respect to the definitions introduced above.

There are a number of features typical for intrinsic contributions to the loss. The most general feature is that the intrinsic contributions to the imaginary parts of the dielectric permittivity, elastic stiffness, and piezoelectric coefficients scale as the frequency of the AC perturbation. Here, for mechanical and piezoelectric loss in regular dielectrics, a rough order of magnitude estimate reads (Gurevich 1986)

$$\frac{c''}{c'} \cong \left| \frac{e''}{e'} \right| \cong \frac{f}{f_o} \quad (2.100)$$

where $f = \omega/2\pi$ is the frequency of the AC perturbation, and the characteristic frequency f_o is about a few THz, being weakly temperature dependent. Note that (2.100) implies that for intrinsic losses $\tan \delta_{ac} \propto f$. For mechanical losses, this estimate is not far from the real parameters of high quality dielectrics. For example, for AlN at $f_o = 2$ GHz and room temperature, the experiment gives $c''_{33}/c'_{33} = 0.4 \times 10^{-3}$ (Muralt et al. 2009), whereas setting $f_o = 5$ THz and using (2.90), one finds $c''/c' = 0.2 \times 10^{-3}$.

Dependence $\tan \delta_{ac} \propto f$ is often documented experimentally. For this reason, the mechanical Q-factor, $Q_m = 1/\tan \delta_{ac}$, is customarily extrapolated in frequency using the relation $Q_m \times f = \text{const}$. Figure 2.10 depicts the frequency dependence of single crystal SrTiO₃ where available low-frequency experimental data is extrapolated up to 7 GHz (Vorobiev and Gevorgian 2010). It is seen that the mechanical Q-factor of SrTiO₃ based FBAR operating at 5 GHz may be as high as 1,000.

Fig. 2.10 Estimated mechanical Q-factor for single crystal SrTiO₃ versus frequency at room temperature

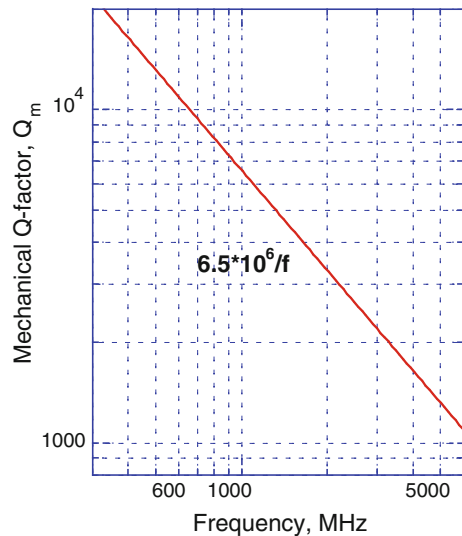


Table 2.2 Estimated mechanical Q-factors at 1.0 GHz and room temperature

Material	Q-factor for longitudinal waves
Ag	400
Al	1,250
AlN	2,000
Au	480
Ba _x Sr _{1-x} TiO ₃ (cubic)	>1,000
BiFeO ₃	~ 500
LiNbO ₃	10 ⁵
Mo	1,500
Pt	520
Si	1,000
Si ₃ N ₄	2,500
SiO ₂	20,000
Fused silica	2,700
SrTiO ₃ (cubic)	6,500
Ti	430
TiO ₂ (rutile)	10 ⁵
PMN28 %-PT	60
W	300

Information about acoustic losses (mechanical Q-factor) in materials of interest is very sparse and disparate. In most cases, the losses are given without specifying the propagation direction of the acoustic waves. However, the measurements in thin films are performed by using longitudinal waves in parallel plate FBARs. The available experimental results are extrapolated to 1.0 GHz assuming $Q_m \times f = \text{const}$. Table 2.2 summarizes the mechanical Q-factors of some materials found by averaging and extrapolating. Thus, these values should be regarded as order of magnitude estimates keeping in mind that the same thin film, that is, SiO₂, fabricated using different deposition routes may have drastically different acoustic parameters and losses. The relationship between the mechanical Q-factor and amplitude attenuation constant α is given by

$$Q_m = \frac{\beta}{2\alpha} \quad (2.101)$$

where β is the propagation constant. For practical applications, the acoustic attenuation is often characterized by the power attenuation constant defined as $\alpha_P = 10 \log (\text{power at } x / \text{power at } 0) / x = 20 \log e \alpha$ which is typically measured in dB/m. In terms of the acoustic wave, wavelength, $\lambda = 2\pi / \beta$, and α_P relationship (2.101) can be rewritten as

$$Q_m = \frac{27.3}{\alpha_P \lambda}. \quad (2.101a)$$

2.4.3.2 Intrinsic Dielectric Losses

Intrinsic dielectric losses are extensively addressed theoretically. Here, three types of contributions are distinguished: quasi-Debye, 4-quantum, and 3-quantum.

For *regular dielectrics*, the following estimates are available for these contributions (Gurevich and Tagantsev 1991; Tagantsev et al. 2003):

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \cong \frac{f}{f_o} \quad (2.102)$$

for the quasi-Debye contribution,

$$\tan \delta \cong \frac{f}{f_o} B^2 \quad (2.103)$$

for the 4-quantum contribution. At room temperature $B \cong 10^{-2}$ and scales linearly with temperature (in Kelvin) at higher temperatures.

As for the 3-quantum contribution, in the low-frequency range, one can only distinguish it in the case where it exceeds the 4-quantum one. When this is the case, for the 3-quantum contribution, typically

$$\tan \delta \cong b \frac{f}{f_o} B^2 \quad (2.104)$$

where b has values in the range 10–100, being weekly temperature dependent. In some very rare cases, this contribution follows an estimate

$$\tan \delta \cong \frac{f}{f_o} B \quad (2.105)$$

The dielectric losses are very sensitive to the crystalline symmetry of materials. Among the three aforementioned contributions, only the weakest 4-quantum contribution is allowed by the symmetry in any material. The strongest quasi-Debye contribution is only allowed in non-centrosymmetric materials. In such materials, the 3-quantum and 4-quantum contributions are expected to be negligible compared to the quasi-Debye one. In a centrosymmetric material, depending on its crystalline symmetry and the orientation of the measuring AC electric field, the dielectric losses are controlled either by the dominating 3-quantum contribution [given by (2.104) or (2.105)] or by the 4-quantum contribution.

The presented estimates imply an important conclusion: in regular centrosymmetric dielectrics, in the common GHz frequency range, the intrinsic contribution to the loss tangent is very small. Estimating the 4-quantum contribution, for $f = 2$ GHz, $f_o = 5$ THz, and $B = 10^{-2}$, one finds with the aid of (2.103) that $\tan \delta = 0.2 \times 10^{-7}$. For the 3-quantum contribution, the estimate would be 1–2 orders of magnitude larger, which still corresponds to the losses much lower than that typically reported for real materials. Thus, typically in a centrosymmetric crystal of regular dielectrics, the intrinsic mechanism cannot account for the level

of dielectric losses measured. As an example where that is not the case, one can indicate high quality sapphire crystals (Gurevich and Tagantsev 1991).

The estimates presented above are not applicable to the case of ferroelectrics. Theoretically, the problem of losses (dielectric, mechanical, and piezoelectric) in ferroelectrics is only partially addressed in literature. Only the issues that are the most relevant in the context of applications of ferroelectrics at microwaves are discussed below, specifically (1) dielectric losses in incipient ferroelectrics and centrosymmetric paraelectric phases of regular ferroelectrics and (2) losses where the material is subjected to an additional DC electric field.

In the absence of a DC electric field for the aforementioned materials, the intrinsic dielectric losses are controlled by the 3-quantum contribution, corresponding to the loss tangent (Tagantsev 1984):

$$\tan \delta = M f T^2 \epsilon^{3/2} \quad (2.106)$$

where T is the absolute temperature, and parameter M is a weakly temperature-dependent parameter. In the microwave frequency range, this result was found to be in a good agreement with experimental data for SrTiO_3 (both for frequency and temperatures dependence). For the temperature dependence, this is illustrated by Fig. 2.11. Thus, in contrast to regular dielectrics, in ferroelectrics, the intrinsic contribution can readily dominate the dielectric losses in the microwave frequency range. This is due to the fact that, in ferroelectrics, dielectric losses scale as a power function of dielectric permittivity, cf (2.106), which is strongly enhanced in these materials.

In the presence of an additional DC electric field, the so-called field-induced quasi-Debye contribution is activated. Its appearance can be elucidated as follows. In the absence of DC bias, the quasi-Debye contribution is forbidden by the symmetry (since the material is centrosymmetric). Under a DC bias field, this mechanism becomes active due to the breaking of the central symmetry by the

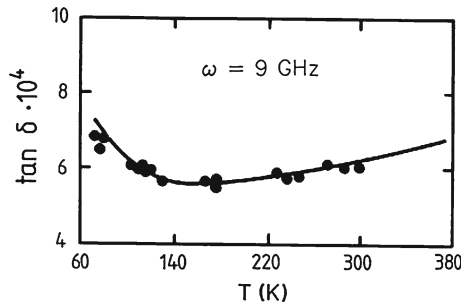


Fig. 2.11 Temperature dependence of the dielectric loss tangent in SrTiO_3 crystals at the AC electric field frequency of 9 GHz: points—experimental data, curve—the prediction of the theory: $\tan \delta \propto f T^2 \epsilon^{1.5}$. The theory also correctly predicts the order of magnitude for the proportionality coefficient in this relationship, after the study by Tagantsev et al. (Tagantsev 1982)

field. Since, in general, the quasi-Debye mechanism is strong, even a relatively weak DC bias leads to an appreciable contribution by this mechanism to the total loss tangent of the material. It was shown that, in the microwave frequency range, the field-induced quasi-Debye contribution to the loss tangent can be presented in the form (Tagantsev et al. 2003):

$$\tan \delta_{QD}(E_o) = AfI(E_o)T_e \quad (2.107)$$

where T_e is relative tuneability of dielectric permittivity under DC bias E_o defined by (2.4). Here, the function $I(E_o) \rightarrow 1$ in the limit of $T_e < 1$, and parameter A is temperature dependent but field independent.

The theory predicts that it is a realistic situation where in a ferroelectric, under a DC bias field, the field-induced quasi-Debye contribution dominates the losses, being a pronounced increasing function of S . This prediction is in a good agreement with experimental data for incipient ferroelectrics such as SrTiO_3 and KTaO_3 . This is illustrated in Fig. 2.12 where the Q-factors of the resonators with superconducting electrodes are plotted versus DC bias. Since the losses in the superconducting electrodes are negligible, the loss tangent relates to the Q-factor as $\tan \delta \approx 1/Q$, where $\tan \delta$ is the dielectric loss tangent of the dielectric filling of the resonator. Shown in Fig. 2.4b is also the DC bias dependence of the resonant frequency. The DC field applied to the samples resulted in a small (<20 %) variation of the dielectric permittivity of the material. A more detailed discussion of this loss mechanism can be found in a review paper (Tagantsev et al. 2003).

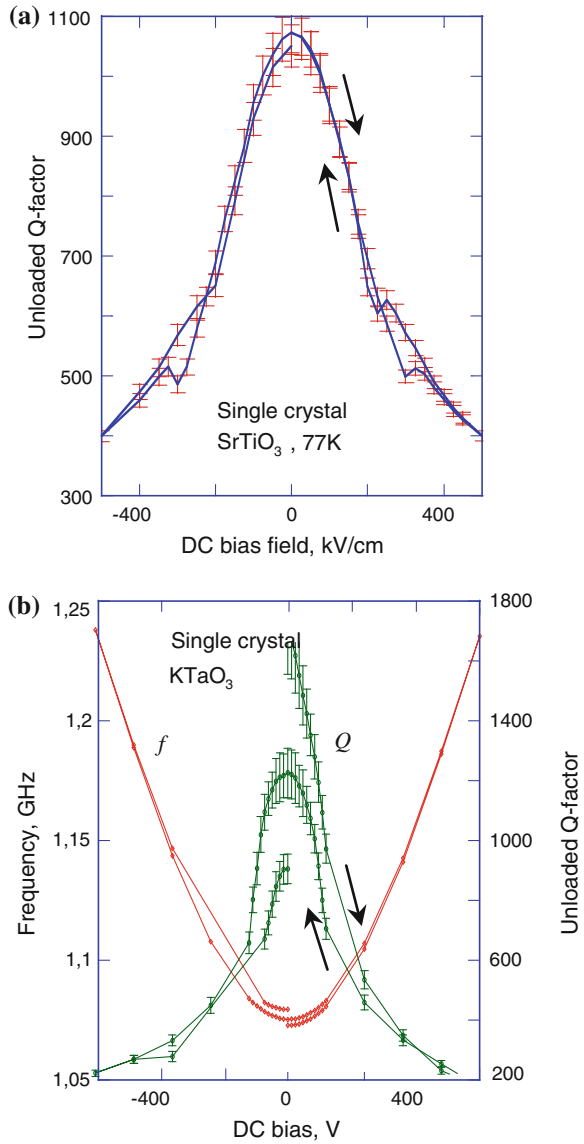
2.4.3.3 Extrinsic Dielectric Losses

The negative impact of crystalline defects on energy dissipation in dielectrics has been recognized for a long time. A large body of theoretical results on mechanical losses has been obtained. A comprehensive discussion on this matter can be found in Gurevich's book (Gurevich 1986). In this book, mainly the extrinsic dielectric losses are considered. The reason for that is that the intrinsic dielectric losses are typically too small to dominate the total balance of dielectric losses. As pointed out above in this chapter, in single crystals of SrTiO_3 , the contribution of intrinsic losses is essential. However, in thin films, the experimentally measured loss levels are too high to be attributed to intrinsic mechanisms (Tagantsev et al. 2003). Thus, the understanding or at least the ability to give a phenomenological description, of extrinsic dielectric losses, is vital. Below a number of extrinsic dielectric loss mechanisms are addressed.

Losses owing to Charged Defects

The motion of charged defects caused by an AC electric field results in the generation of acoustic waves at the frequency of the applied field. The contribution of this mechanism to the loss tangent can be approximated as follows (Tagantsev et al. 2003):

Fig. 2.12 Field dependence of the quality factors of SrTiO_3 - (a) and KTaO_3 - (b) based bulk resonators with lossless superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ electrodes. The arrows indicate the direction of changes in the DC bias. Error bars indicate the accuracy of measurements



$$\tan \delta = F \varepsilon_r \frac{n_d}{\rho v_t^3} \frac{Z^2}{4\pi \varepsilon_0} \omega \cdot \left[1 - \frac{1}{(1 + \omega^2/\omega_c^2)^2} \right] \quad (2.108)$$

where Z and n_d are the effective charge of the defects and their atomic concentration; ρ and v_t are density and average transversal sound velocity of the material; F is a material-dependent numerical constant of the order of unity; $\omega_c = v_t/r_c$ where r_c is the correlation length of charge distribution in the material. The

physical meaning of r_c is the minimum distance at which electroneutrality is maintained. For Schottky defects, r_c is of the order of the typical distance between the positively and negatively charged defects. This mechanism may play an essential role in ferroelectric thin films where an elevated defect concentration compared to bulk materials is expected. An essential feature of this mechanism is that its contribution to the loss tangent is proportional to the permittivity of the material.

Universal Relaxation Law Mechanism

For all of the loss mechanisms discussed above, a linear frequency dependence of the loss tangent is typical, at least for microwave frequencies and below. In reality, this dependence is usually observed at the microwave and higher frequencies. Much weaker frequency dependence is usually observed at lower frequencies, which is consistent with the so-called universal relaxation law characterized by the following complex dielectric permittivity ε (Jonscher 1996):

$$\varepsilon = G(j\omega)^{n-1} = G(\cos(n\pi/2) - j \sin(n\pi/2))(\omega)^{n-1} \quad (2.109)$$

where G is a frequency-independent constant and $0 < n < 1$. In perovskite thin films both in frequency and time domains, dielectric relaxation, corresponding to this equation (for n close to but smaller than unity), has been reported up to the microwave frequency range, for example, in (Ba,Sr)TiO₃ (Baniecki et al. 1998). The physical origin of this behavior is attributed to a variation in charge transport barriers, for example, at the grain boundaries (Waser 1995), or to boundary creep of electrode-adjacent depletion layers (Fukuda et al. 1996). No information is available on the dependence of G on the dielectric permittivity of the material.

Impact of local polar regions

Typically, centrosymmetric ferroelectric materials may have local polar regions induced by various defects and structural imperfections. In all these polar inclusions, the quasi-Debye mechanism is expected to be active. Though the volume fraction of the polar phase is typically small, this “defect-induced” quasi-Debye mechanism may be important due to its large (compared to other intrinsic loss mechanisms) contribution per unit of volume. According to (Tagantsev et al. 2003) the contribution of this mechanism to the loss, tangent is very sensitive to the dielectric permittivity of the material and the dimensionality of the defects, d :

$$\tan \delta \propto \omega \varepsilon^{4.5-d} \quad (2.110)$$

where $d = 2$ for planar defects like grain boundaries, $d = 1$ for the linear defects, and $d = 0$ for point defects.

DC Conductivity and Domain Wall Motion

The role of DC conductivity in the measured complex dielectric permittivity of a material, $\varepsilon_m = \varepsilon'_m - j\varepsilon''_m$, (we will further term it as effective dielectric permittivity) can be elucidated by considering the situation in a parallel plate capacitor. For simplicity, the case of an isotropic material is considered. In this case, the

effective dielectric permittivity can be expressed in terms of the amplitude, \tilde{Q}_{m0} , of the complex charge, $\tilde{Q} = \tilde{Q}_{m0}e^{j\omega t}$, on the capacitor as follows:

$$\varepsilon_m = \frac{\tilde{D}_o}{\tilde{E}_o} = \frac{\tilde{Q}_o}{A\tilde{E}_o}. \quad (2.111)$$

where A_p is the capacitor plate area. In a real dielectric, the charge on the capacitor is controlled not only by the dielectric response, corresponding to the complex charge amplitude $\tilde{Q}_{do} = A_p\varepsilon\tilde{E}_o$, but also by the DC conduction, corresponding to the complex charge amplitude $\tilde{Q}_{co} = -jA_p\frac{\sigma}{\omega}\tilde{E}_o$ where σ is the conductivity of the material. Thus, with $\tilde{Q}_o = \tilde{Q}_{co} + \tilde{Q}_{do}$, the definition (2.111) yields the imaginary part of the effective dielectric permittivity:

$$\varepsilon_m'' = \varepsilon'' + \frac{\sigma}{\omega}. \quad (2.112)$$

A remarkable feature of the conductivity-related contribution to the imaginary part of the effective dielectric permittivity is that, in contact to the behavior of ε'' , it increases with decreasing frequency. This kind of behavior is also typical for the contribution of domain wall motion to the imaginary part of the dielectric permittivity. As mentioned above in this chapter, in an electric field, a ferroelectric domain wall exhibits a force. This force causes a motion of the wall. For the “viscose” regime of motion, where the wall velocity is proportional to the electric field at the wall, the wall motion contributes to the imaginary part of the dielectric permittivity and is inversely proportional to the AC field frequency (Tagantsev et al. 2010) similar to the effect of DC conductivity.

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