

2. Ferroelectricity and piezoelectricity

2.1 General

Ferroelectrics are polar materials that possess at least two equilibrium orientations of the spontaneous polarization vector in the absence of an external electric field, and in which the polarization may be switched between those orientations by means of an electric field. The electric displacement takes the form (using the Einstein summation convention):

$$D_i = \varepsilon_0 E_i + P_i = \varepsilon_0 E_i + \varepsilon_0 \chi_{ij} E_j + P_{Si} = \varepsilon_{ij} E_j + P_{Si} \quad \text{Eq. 1}$$

where χ_{ij} is tensor of the susceptibilities, ε_{ij} is the linear dielectric tensor and P and P_S are the total and spontaneous ferroelectric polarization, respectively. Most ferroelectric materials undergo a structural phase transition from a high-temperature nonferroelectric (or paraelectric) phase into a low-temperature ferroelectric phase, of a lower crystal symmetry. The phase transition temperature is usually called the Curie point (T_c). In most cases, the dielectric constant above this temperature obeys the Curie-Weiss law: $\varepsilon = C(T - T_0)^{-1}$, where C is the Curie constant and T_0 the Curie temperature*.

Using a thermodynamic approach, it is possible to describe the important features of ferroelectric materials without taking into account the microscopic mechanisms of ferroelectricity. In this way, starting from the symmetry of the paraelectric phase**, it is possible to deduce the stable ferroelectric phase(s), the possible orientations of the polarization, and even to predict the possible orientations of domain walls inside the crystal in the ferroelectric phase^[1,2,3]. From the basic thermodynamic relations it follows that the stable phase under a given set of independent variables is the one which minimizes the corresponding free energy^[4]. Expressions that relate dependent and independent variables may be obtained using the usual thermodynamic formalism. Under isothermal conditions, with the electric displacement D , the elastic stress X , and the temperature T as independent variables, which is the situation in most of the experimental cases, the *elastic Gibbs free energy* function should be used^[3,5]:

$$G_1(T, X, D) = U - TS - X_{ij} x_{ij} \quad \text{and} \quad dG_1 = -SdT - x_{ij} dX_{ij} + E_i dD_i \quad \text{Eq. 2}$$

For small changes in D , X and T , the elastic Gibbs free energy can be expanded into a Taylor series around the equilibrium state $G_{10}(T)$ (in which $D = 0$, and $X = 0$), in terms of the independent variables T , X and D . Usually, the elastic Gibbs free energy is expressed with respect to the energy of the paraelectric state which is considered to be nonpolar, assuming that the same analytical function describes both the paraelectric and ferroelectric phases^[5].

* In the case of first order phase transitions the Curie point and the Curie temperature do not coincide. For more details, see Ref. 5.

** If a paraelectric phase does not exist, the higher symmetry prototype (from which the ferroelectric modification is derived) is used.

$$\begin{aligned}
 G_1(T, X, E) - G_{10}(T, X, E) = & \frac{\partial G_1}{\partial T} \Delta T + \frac{\partial G_1}{\partial D_i} D_i + \frac{\partial G_1}{\partial X_{ij}} X_{ij} + \frac{1}{2} \frac{\partial^2 G_1}{\partial T^2} \Delta T^2 + \\
 & + \frac{1}{2} \frac{\partial^2 G_1}{\partial D_i \partial D_j} D_i D_j + \frac{1}{2} \frac{\partial^2 G_1}{\partial X_{ij} \partial X_{kl}} X_{ij} X_{kl} + \frac{\partial^2 G_1}{\partial T \partial D_i} \Delta T D_i + \frac{\partial^2 G_1}{\partial D_i \partial X_{kl}} D_i X_{kl} + \\
 & + \frac{\partial^2 G_1}{\partial T \partial X_{kl}} \Delta T X_{kl} + \dots \text{higher order terms}
 \end{aligned} \quad \text{Eq. 3}$$

Each of the partial derivatives of the elastic Gibbs free energy (coefficients in the Taylor expansion) identifies a physical effect ^[6]. For instance, $g_{ijk} = (\partial^2 G_1 / \partial X_{ij} \partial D_k)$ is denominated strain- or voltage-related piezoelectric coefficient. Also, coefficients in the Taylor expansion transform as components of the associated tensor. For example, the piezoelectric coefficients like g_{ijk} transform as third-rank tensors when changing the system of coordinates. In most ferroelectric materials of interest the paraelectric phase is centrosymmetric, implying that all coefficients associated with odd-rank tensors are zero. This significantly reduces the number of terms that must be considered in Eq. 3. In the case of the elasto-electric coupling (piezoelectric effects), this means that all the piezoelectric coefficients derived from the linear terms (as g_{ijk} above) are zero. Since the terms in the expansion represent correction terms, it is usually sufficient to expand the elastic free energy up to the fourth- or sixth-order terms.

Finally, a stable state of the system under the conditions of fixed temperature, stress and electric field is obtained when the elastic Gibbs free energy G_1 is minimal.

$$G = G_1 - \vec{E} \cdot \vec{D} \quad \text{Eq. 4}$$

This is the starting point that allows the deduction of all main features of a ferroelectric system. Imposing the first derivative of Eq. 4 to be zero (conditions of stability) results in a set of equations that yield the polarization and the strains developed in a ferroelectric by a set of boundary conditions and external fields.

2.2 The piezoelectric effect in ferroelectric materials

“Piezo” originates from the Greek word *piezein*, meaning to press or to squeeze. In 1880, the Curie brothers found that quartz changed its dimensions when subjected to an electric field and conversely generated an electric charge when it was pressed.

Piezoelectric materials are a class of materials that can be polarized by applying a mechanical stress or an electric field. The class of the piezoelectric materials includes ferroelectrics. The direct piezoelectric effect is equivalent to the appearance of charges when the material is subject to a stress ^[7]. It is described by a linear relationship between the stress X_{ik} applied to a piezoelectric material and the resulting charge density D_i :

$$D_i = d_{ijk}^{\text{direct}} X_{jk}$$

where d_{ijk} is the third-rank tensor of piezoelectric coefficients, measured in [C/N].

Also the reverse effect is always present: Piezoelectric materials change their dimensions (they contract or expand) when subject to an electric field ^[7]. The converse piezoelectric effect is described by a linear relationship between the strain x_{ij} developed in a piezoelectric material and the applied electric field E_k :

$$x_{ij} = d_{kij}^{\text{converse}} E_k = (d_{ijk}^{\text{direct}})^t E_k$$

where t denotes the transposed “matrix”. The unit of the converse piezoelectric coefficient is [m/V]. The piezoelectric coefficients for the direct and converse piezoelectric effects are thermodynamically identical i.e. $d^{converse} = d^{direct}$. Because the strain and the stress are symmetrical tensors, the tensor of the piezoelectric coefficients is symmetrical with respect to the corresponding indices, $d_{ijk} = d_{ikj}$. The number of independent piezoelectric coefficients is thus reduced from 27 to 18. The number of independent elements of d_{ijk} may be further reduced by the symmetry of the material.

The piezoelectric coefficient measured in the direction of the applied field is usually called the *longitudinal* coefficient, and that measured in the direction perpendicular to the field is known as the *transverse* coefficient [7]. Other piezoelectric coefficients are denominated shear coefficients. It is worth mentioning that the piezoelectric coefficient d can be either positive or negative. Using the usual thermodynamic formalism (like the one described in the previous section), depending on the set of independent variables chosen, four sets of isothermal piezoelectric constitutive equations can be obtained (for the matrix notation used, see Appendix D):

$$\begin{cases} D_i = d_{im}^{T,E} X_m + \varepsilon_{ij}^{T,X} E_j \\ x_m = s_{mn}^{T,E} X_n + d_{im}^{T,X} E_i \end{cases} \quad \text{Eq. 5a}$$

$$\begin{cases} D_i = e_{im}^{T,E} X_m + \varepsilon_{ij}^{T,x} E_j \\ X_m = c_{mn}^{T,E} x_n - e_{im}^{T,x} E_i \end{cases} \quad \text{Eq. 5b}$$

$$\begin{cases} E_i = -h_{im}^{T,D} x_m + \beta_{ij}^{T,x} D_j \\ X_m = c_{mn}^{T,D} x_n - h_{im}^{T,x} D_i \end{cases} \quad \text{Eq. 5c}$$

$$\begin{cases} E_i = -g_{im}^{T,D} X_m + \beta_{ij}^{T,X} D_j \\ x_m = s_{mn}^{T,D} X_n + g_{im}^{T,X} D_i \end{cases} \quad \text{Eq. 5d}$$

The four types of coefficients are denominated as follows: d is either charge or strain coefficient, e is either charge or stress coefficient, h is either voltage or stress coefficient, and g is either voltage or strain coefficient [8], depending on the physical quantity that is calculated. For simplicity, d and g are usually called piezoelectric strain-coefficients, and e and h are called piezoelectric stress-coefficients [9]. The superscripts of the coefficients in Eq. 5 indicate the variables held constant during the partial derivation of the thermodynamic potential. The coefficients are mutually related by:

$$d_{im} = e_{in} s_{nm}^E = \varepsilon_{ij}^X g_{jm} \quad [m/V] \text{ or } [C/N] \quad \text{Eq. 6a}$$

$$e_{im} = d_{in} c_{nm}^E = \varepsilon_{ij}^x h_{jm} \quad [C/m^2] \text{ or } [V/N] \quad \text{Eq. 6b}$$

$$g_{im} = h_{in} s_{nm}^D = \beta_{ij}^X d_{jm} \quad [m^2/C] \text{ or } [N/V] \quad \text{Eq. 6c}$$

$$h_{im} = g_{in} c_{nm}^D = \beta_{ij}^x e_{jm} \quad [N/C] \text{ or } [V/m] \quad \text{Eq. 6d}$$

It is of practical interest to relate the piezoelectric coefficients to the spontaneous polarization. As already mentioned, if the paraelectric phase is centrosymmetric, then the resulting linear piezoelectric coefficients are zero. Because ferroelectrics are nonlinear

materials, higher order terms have to be taken into account in Eq. 3. The first term (with non-zero coefficient) that includes the elastic-electric coupling is the electrostrictive term, which for $E = 0$ takes the form:

$$\Delta G_1^{estr} = Q_{ijkl} X_{ij} P_{Sk} P_{Sl} \quad \text{Eq. 7}$$

where Q_{ijkl} are the polarization-related electrostrictive coefficients, components of the fourth rank electrostrictive tensor. First, this term implies that in ferroelectric materials the existence of the spontaneous polarization \mathbf{P}_S is always associated to a spontaneous strain x_S . This results from the differential form of Eq. 2 (containing the electrostrictive term) and the condition of stability $dG_I = 0$:

$$x_{Sij} = \left(\frac{\partial G_1}{\partial X_{ij}} \right) = Q_{ijkl} P_{Sk} P_{Sl} \quad \text{Eq. 8}$$

The spontaneous strain plays an important role in the process of the formation of stable ferroelectric domains and also in their switching.

If we now consider the (electrostrictive) spontaneous strain in Eq. 8 as a piezoelectric strain, it follows (index m in matrix notation):

$$x_m = \left(\frac{\partial G_1}{\partial X_m} \right) = Q_{mkl} P_{Sk} P_{Sl}$$

From Eq. 5d in the case of $X = 0$ and $E = 0$ we obtain:

$$g_{im} = \left(\frac{\partial E_i}{\partial X_m} \right) = \left(\frac{\partial^2 G_1}{\partial X_m \partial P_i} \right) = \frac{\partial}{\partial P_i} \left(\frac{\partial G_1}{\partial X_m} \right) = 2Q_{mik} P_{Sk}$$

Inserting g_{im} in Eq. 6a, it follows that:

$$d_{im} = \varepsilon_{ij} Q_{mjk} P_{Sk} \quad \text{Eq. 9}$$

In the particular case of the tetragonal symmetry (axis “3” is the polar axis), Eq. 9 reduces to* (as also deduced by Devonshire for barium titanate^[10]):

$$d_{33} = 2\varepsilon_{33} Q_{33} P_{S3} \quad \text{Eq. 10a}$$

$$d_{31} = 2\varepsilon_{33} Q_{13} P_{S3} \quad \text{Eq. 10b}$$

$$d_{15} = 2\varepsilon_{11} Q_{44} P_{S3} \quad \text{Eq. 10c}$$

It should be kept in mind that all the above statements are valid only for a ferroelectric single crystal in the monodomain state. This hypothesis is underlying the thermodynamic approach, and was set when the possible orientations of spontaneous polarization were established.

* The symmetry imposes $P_{S1} = P_{S2} = 0$, $\varepsilon_{11} = \varepsilon_{22}$, $\varepsilon_{ij} = 0$ for $i \neq j$, and the only non-zero electrostrictive coefficients are $Q_{11} = Q_{22}$, $Q_{12} = Q_{21}$, $Q_{13} = Q_{23}$, $Q_{31} = Q_{32}$, Q_{33} , $Q_{44} = Q_{55}$, Q_{66} .

2.3 Ferroelectric domains

In the absence of an external force, the direction of the spontaneous polarization in an ideal ferroelectric crystal can arise with equal probability along several crystallographic directions of the prototype (paraelectric) phase. Accordingly, after the transition to a ferroelectric state the crystal breaks up into separate regions that differ in the direction of the spontaneous polarization. The regions of the crystal with uniformly oriented spontaneous polarization are called ferroelectric domains. The region between two domains is called a domain wall. Domain walls that separate different orientations of the spontaneous polarization vector are called ferroelectric domain walls and those which separate different orientations of the spontaneous strain are called ferroelastic domain walls.

Ferroelectric domains form to minimize the electrostatic energy of the depolarizing fields and the elastic energy associated with mechanical constraints to which the ferroelectric material is subjected during the transition from the paraelectric to the ferroelectric phase. Depolarizing fields develop whenever a nonhomogeneous distribution of the spontaneous polarization appears, for instance, during the formation of the ferroelectric phase. Also, the fall-off of the polarization at a grain boundary usually causes strong depolarizing fields of the order of 10 kV/cm. Due to these high values, the depolarizing fields cause the single-domain state of a ferroelectric to be energetically unfavorable. As a consequence, the electrostatic energy associated is minimized by splitting the ferroelectric into domains with opposite polarization. Alternatively, the charges associated with the depolarizing fields may be neutralized by conduction of free charges through the crystal or coming from the surrounding of the material.

Regarding the domain formation, Fousek and Janovec^[2] have established a criterion to predict the possible domain wall orientations between two allowed polarization directions in a perfect infinite single crystal:

- During the transition to the polarized state, the crystal distorts. This distortion can be predicted from the magnitude and direction of the spontaneous polarization, and from the piezoelectric and electrostrictive coefficients in the paraelectric phase.
- Two domains having different orientations of the spontaneous polarization will have a common domain wall only along the planes for which the two distortions of the lattice match exactly. These planes are therefore possible domain walls for the crystal.

Another condition that should be fulfilled at the domain wall is the *electric neutrality*. Unless the crystal is conductive, the normal component of the spontaneous polarization should be continuous through the domain wall; otherwise, the electrostatic energy will make it very unstable.

The domain structure that develops in single crystal perovskites is well known. The spontaneous polarization can be oriented only along three mutually perpendicular crystallographic directions (in the tetragonal phase). This gives rise to two types of domain walls: walls that separate domains with oppositely oriented polarization (called *180°-walls*), and those which separate regions with mutually perpendicular polarization (called *90°-walls*). The *90°-walls* are both ferroelectric and ferroelastic domain walls, because they separate regions with different orientation of the polarization and of the strain.

The application of the above criteria applied to tetragonal perovskites shows that the 180° domain walls can be any cylindrical surface separating regions with the spontaneous polarization parallel to the polar axis. No other restrictions are limiting their position or orientation. The allowed 90° domain walls are parallel to the $\{110\}_{\text{tet}}$ family of crystal planes. The continuity of the normal component of the spontaneous polarization results in the so-called head-to-tail configuration, as depicted in Figure 1.

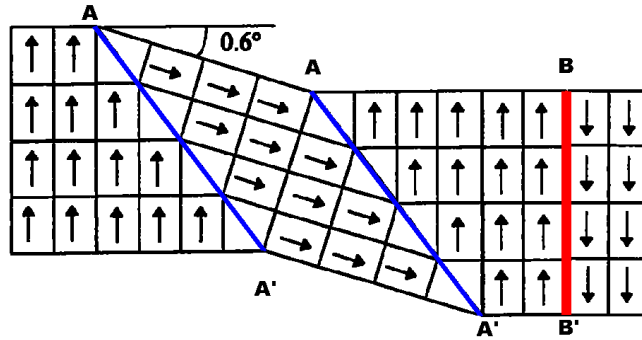


Figure 1 Ferroelectric domain walls in a perovskite ferroelectric. A-A' lines represent 90° domain walls, and the B-B' line a 180° domain wall (the tetragonality is highly exaggerated).

The ferroelectric domain structure is the most important factor that determines the ferroelectric properties of a ferroelectric material, together with domain nucleation and domain wall mobility. The way how the material splits up into domains at the formation of the ferroelectric phase depends very much on the mechanical and electrical boundary conditions imposed on the sample, as well as on the nature of the sample itself.