

Chapter 1

The Piezoelectric Medium and Its Characteristics

An effect that links a mechanical action (mechanical stress or strain) with an electrical response (electric field, electric displacement or polarisation) is the piezoelectric effect or, more exactly, the *direct piezoelectric effect*. This effect was first studied by brothers P. Curie and J. Curie in experimental work (1880) on the behaviour of quartz single crystals (SCs) subjected to an external mechanical stress. The *converse piezoelectric effect* was later revealed in acentric dielectric SCs wherein an external electric field generated a mechanical response, i.e., a stress or strain of the sample, and this effect is similar to electrostriction. The piezoelectric effect follows a linear relationship between electric and mechanical variables and originates from the displacement of ions of an acentric SC under an applied electric field [1–4]. This relationship leads to a change in the sign of the piezoelectric effect when the direction of the external electric field is switched in the piezo-active medium. Such a medium is of interest due to the potential for a significant electromechanical coupling and conversion of energy from a mechanical form into electric one and vice versa.

In contrast to the *converse* piezoelectric effect, an electrostrictive strain (or stress) in any dielectric material follows a quadratic effect [3, 4] and does not switch sign under an alternating electric field. Electrostriction is caused by the electric field and cannot be represented as a direct or converse effect. It should be added that electrostriction is observed in any dielectric media, irrespective of the crystal symmetry and aggregate states (gas, liquid, SC, or amorphous).

Numerous experimental data show that, despite the linear character between electric and mechanical fields, the piezoelectric response of a SC sample is often intricate owing to various interconnections between the piezoelectric and other properties such as the elastic, dielectric (including pyro- and ferroelectric), magnetic and thermal properties [3]. The piezoelectric effect in poled ferroelectric ceramic (FC) and composite samples based on SCs or FCs is even more complex in comparison to the piezoelectric effect in ferroelectric SCs due to the influence of microstructure, domain orientations, intrinsic and extrinsic contributions, hetero-phase structures, etc. [5–11].

In this chapter we consider some important characteristics of the piezoelectric medium in the context of its electromechanical coupling and energy-harvesting applications. We add that energy harvesting is currently of interest to both academia and industry since it provides a route for the development of autonomous and self-powered low-power electronic devices, e.g. for wireless sensor networks or consumable electronics.

1.1 Piezoelectric Coefficients

A general consideration of the piezoelectric effect in dielectric SCs is carried out in terms of thermodynamic functions, such as Helmholtz free energy, Gibbs free energy, elastic Gibbs energy, and electric Gibbs energy [2–4]. Each of these functions has at least three arguments that characterise the mechanical, electric and thermal states of the SC. The first argument can be either mechanical stress σ_{kl} or mechanical strain ζ_{jr} , the second argument can be either electric field \mathbf{E} or electric displacement (electric flux density) \mathbf{D} , and the third argument can be either temperature T or entropy S . Obviously, these arguments are represented as second-rank (σ_{kl} and ζ_{jr}), first-rank (E_k and D_j) and zeroth-rank (scalars T and S) tensors. We may also develop additional arguments concerned, for instance, with an external magnetic field \mathbf{H} or magnetic induction \mathbf{B} [5].

Based on the thermodynamic functions and relations between the arguments of the mechanical, electric and thermal states [2, 3], one can describe the linked ‘response–actions’ in terms of ζ_{jr} , E_i and T as follows:

$$\sigma_{kl} = c_{kljr}^E \zeta_{jr} - e_{ikl} E_i + \beta_{kl} \Delta T \quad (1.1)$$

$$D_i = e_{ikl} \zeta_{kl} + \varepsilon_{if}^E E_f + p_i \Delta T \quad (1.2)$$

$$\Delta S = \beta_{jr} \zeta_{jr} + p_i E_i + (\rho/T_0) c \Delta T \quad (1.3)$$

In (1.1)–(1.3) the constants are elastic moduli at constant electric field (c_{kljr}^E , fourth-rank tensor), piezoelectric coefficients (e_{ikl} , third-rank tensor), coefficients of thermal stress (β_{kl} , second-rank tensor), dielectric permittivities at constant mechanical strain (ε_{if}^E , second-rank tensor), pyroelectric coefficients (p_i , first-rank tensor, i.e., vector). In (1.1)–(1.3) density (ρ) and specific heat (c) of the SC are zeroth-rank tensors, i.e., scalars. Summing over the repeated subscripts [e.g., j , r and i in (1.1)] is to be performed from 1 to 3. The increments ΔT and ΔS in (1.1)–(1.3) denote differences $T - T_0$ and $S - S_0$, respectively, where T_0 is the initial temperature and S_0 is the initial entropy of the SC.

Linear relations from (1.1)–(1.3) hold in the case of relatively weak external fields [2–4]. For example, the linear dependence $\sigma_{kl}(\zeta_{jr})$ from (1.1) obeys Hooke’s law in an anisotropic medium [12] at small (<1 %) strains ζ_{jr} . The linear

dependence $D_i(E_f)$ from (1.2) is valid at relatively low levels of electric field E_f applied to a dielectric SC. In the case of an acentric dielectric SC, a low level of electric field is one in which the E_f value is much smaller than the electric breakdown field. With regard to a ferroelectric SC that exhibit a piezoelectric performance due to the acentric crystal structure and spontaneous polarisation axis, similar requirements concerning the linear dependences $\sigma_{kl}(\xi_{jr})$ and $D_i(E_f)$ are possible, but the E_f range becomes narrower than that in the acentric linear dielectric SC. It is well known that in the presence of a low electric field E , the polarisation of a ferroelectric SC linearly depends on E [3, 4] so that domain-wall displacements are reversible and no nuclei of reoriented domains are formed. In this connection the electric field E_f is usually regarded to be a few times lower than the coercive field E_c which is determined from a ferroelectric hysteresis loop [3, 4].

Using (1.1)–(1.3), one can determine a set of isothermal constants (at $T = \text{const}$) of a piezoelectric SC. An analogous set of adiabatic constants (at $S = \text{const}$) can also be derived using thermodynamic functions and a combination of three arguments including ΔS (for example, ξ_{jr} , E_i and ΔS). According to experimental data, the difference between the related isothermic and adiabatic constants of the piezoelectric SCs is approximately 1 % or less [3, 5]. Based on this observation, the effect of thermal fields on the elastic and electric responses of the piezoelectric SCs is often neglected, and the description of the piezoelectric effect is carried out in terms of (1.1) and (1.2) at $\Delta T = 0$. Equations (1.1) and (1.2) are often represented in the following matrix form [2, 3]:

$$\sigma_p = c_{pq}^E \xi_q - e_{fp} E_f \quad (1.4)$$

$$D_k = e_{kl} \xi_l + \varepsilon_{kr}^E E_r \quad (1.5)$$

Equations (1.4) and (1.5) are written taking into account a conventional transition from two subscripts to one subscript in accordance with the well-known Vogt's rule [2–4, 12].

Equations (1.4) and (1.5) represent the first pair of piezoelectric equations that links two variables, mechanical strain ξ and electric field E . The first term in the right part of (1.5), $P_k = e_{kl} \xi_l$, describes the piezoelectric polarisation produced by an external mechanical strain as a result of the *direct* piezoelectric effect. In contrast to this, the *converse* piezoelectric effect is described by the $e_{fp} E_f$ term in (1.4), and the sequence of subscripts (fp , f) differs from the sequence (kl , l) at the direct piezoelectric effect.

From the thermodynamic treatment of the interrelations between the electric and elastic fields [2, 3], the converse and direct piezoelectric effects can also be described by the three following pairs of equations:

$$\xi_p = s_{pq}^E \sigma_q + d_{fp} E_f \quad (1.6)$$

$$D_k = d_{kl}\sigma_l + \varepsilon_{kr}^\sigma E_r \quad (1.7)$$

in variables of mechanical stress σ and electric field E ,

$$\zeta_p = s_{pq}^D \sigma_q + g_{fp} D_f \quad (1.8)$$

$$E_k = -g_{kl}\sigma_l + \beta_{kr}^\sigma D_r \quad (1.9)$$

in variables of mechanical stress σ and electric displacement D , and

$$\sigma_p = c_{pq}^D \zeta_q - h_{fp} D_f \quad (1.10)$$

$$E_k = -h_{kl}\zeta_l + \beta_{kr}^\zeta D_r \quad (1.11)$$

in variables of mechanical strain ζ and electric displacement D . Superscripts σ and D denote measurement conditions at $\sigma = \text{const}$ and $D = \text{const}$, respectively. Dielectric impermeabilities β_{kr}^σ (at $\sigma = \text{const}$) and β_{kr}^ζ (at $\zeta = \text{const}$) from (1.9) and (1.11) are determined [2, 3] using relations $\beta_{kr}^\sigma \varepsilon_{rv}^\sigma = \delta_{kv}$ and $\beta_{kr}^\zeta \varepsilon_{rv}^\zeta = \delta_{kv}$. Elastic moduli c_{pq}^E or c_{pq}^D and elastic compliances s_{pq}^E or s_{pq}^D are related by conditions $c_{pq}^E s_{qr}^E = \delta_{pr}$ and $c_{pq}^D s_{qr}^D = \delta_{pr}$, where δ_{kv} is the Kronecker symbol.

Equations (1.4)–(1.11) contain four types of the piezoelectric coefficients, namely e_{kb} , d_{kl} , g_{kl} , and h_{kl} , and in each pair of (1.4)–(1.11), there is a term corresponding to the direct piezoelectric effect and a term corresponding to the converse piezoelectric effect. Each piezoelectric coefficient characterises the relationship between components of two fields that are described by first- and second-rank tensors, and all the piezoelectric coefficients from (1.4)–(1.11) are components of the third-rank tensors, but written in the matrix form (i.e., with two subscripts) [2–5].

The piezoelectric coefficients e_{kb} , d_{kl} , g_{kl} , and h_{kl} can be used as an aid in the selection of piezoelectric materials for various piezotechnical applications. For example, for an actuator application [4], it may be necessary to select materials with a high strain per unit applied electric field (i.e., with large values of $|d_{kl}|$). For a pressure sensor, the electric field generated per unit mechanical stress is more likely to be important (i.e., with large values of $|g_{kl}|$).

The interrelationships of the piezoelectric coefficients d_{kl} , e_{kl} , g_{kl} , and h_{kl} follow from the thermodynamic description [2, 3] and are given by

$$d_{fp} = \varepsilon_{fk}^\sigma g_{kp} = e_{fq} s_{qp}^E \quad (1.12)$$

$$e_{fp} = \varepsilon_{fk}^\zeta h_{kp} = d_{fq} c_{qp}^E \quad (1.13)$$

$$g_{fp} = \beta_{fk}^\sigma d_{kp} = h_{fq} s_{qp}^D \quad (1.14)$$

$$h_{fp} = \beta_{fk}^{\xi} e_{kp} = g_{fq} c_{qp}^D \quad (1.15)$$

The piezoelectric coefficients from (1.12)–(1.15) are also involved in relations [2, 3] between dielectric or elastic constants measured on different conditions:

$$\varepsilon_{kr}^{\sigma} - \varepsilon_{kr}^{\xi} = d_{kf} e_{rf} \quad (1.16)$$

$$\beta_{kr}^{\xi} - \beta_{kr}^{\sigma} = g_{kf} e_{rf} \quad (1.17)$$

$$c_{pq}^D - c_{pq}^E = e_{fp} h_{fq} \quad (1.18)$$

$$s_{pq}^D - s_{pq}^E = d_{fp} g_{fq} \quad (1.19)$$

As is seen from (1.12)–(1.19), there are close connections between the elastic, piezoelectric and dielectric constants of a piezoelectric medium. These connections enable us to term the sets of the elastic, piezoelectric and dielectric constants as electromechanical constants. These constants characterise electromechanical properties in a variety of materials, such as piezoelectric or ferroelectric SCs, poled FCs, thin ferroelectric films, piezo-active composites, etc.

As follows from (1.1), (1.2) and (1.4)–(1.11), the piezoelectric properties are described by third-rank tensors and are represented in the matrix form, as 3×6 or 6×3 matrices. Tables of the matrices of the piezoelectric coefficients related to acentric SCs, poled FCs, composites, and piezoelectric textures (i.e., to various piezoelectric media) have been collected in a series of monographs [2–5, 12]. As is known from crystallographic studies [1–3], the piezoelectric effect is found in 20 symmetry classes (or point groups) and 3 limiting symmetry classes (or Curie groups). The symmetry classes that obey the conditions for the piezoelectric effect [3, 12] are 1 (triclinic system), 2 and m (monoclinic system), 222 and $mm2$ (orthorhombic system), 3, 32 and $3m$ (trigonal or rhombohedral system), 4, 422, $4mm$, $\bar{4}$, and $\bar{4}2m$ (tetragonal system), 6, 622, $\bar{6}$, and $\bar{6}m2$ (hexagonal system), and 23 and $\bar{4}3m$ (cubic system). The Curie groups that satisfy conditions for the piezoelectric texture [3, 12] are ∞ , ∞mm and $\infty/2$. For instance, in the 1 class, the $\|d\|$ matrix comprises the largest number of independent constants, i.e., d_{11} , d_{12} , ..., d_{16} , d_{21} , d_{22} , ..., d_{26} , d_{31} , d_{32} , ..., d_{36} , or 18 piezoelectric coefficients. These piezoelectric coefficients are written in the form as shown in (1.12) and (1.13).

The conditions for measuring the piezoelectric coefficients are associated with the electric and mechanical variables from (1.4)–(1.11). If the direct piezoelectric effect is considered, then the piezoelectric coefficients of the medium are measured [3] using the following relations for the electric polarisation P_k and field E_k :

- (i) $P_k = d_{kl} \sigma_l$ (for d_{kl}),
- (ii) $E_k = -g_{kl} \sigma_l$ (for g_{kl}),
- (iii) $E_k = -h_{kl} \xi_l$ (for h_{kl}), and
- (iv) $P_k = e_{kl} \xi_l$ and $E = 0$ (for e_{kl}).

We remind that $P_k = D_k$ at $E_k = 0$, and the polarisation P_k is determined from a surface density of electric charge on a sample face [3]. At the converse piezoelectric effect, the following relations are taken into account:

- (i) $\xi_p = d_{fp} E_f$ (for d_{fp}),
- (ii) $\xi_p = g_{fp} D_f$ (for g_{fp}),
- (iii) $\sigma_p = -h_{fp} D_f$ (for h_{fp}), and
- (iv) $\sigma_p = -e_{fp} E_f$ (for e_{fp}).

As follows from the above-given conditions, it is relatively easy to find e_{kl} and h_{kl} as constants of the direct piezoelectric effect and d_{kl} as a constant of the converse piezoelectric effect [3].

1.2 Electromechanical Coupling at Various Oscillation Modes

1.2.1 Energy Conversion

Full sets of elastic, piezoelectric and dielectric constants from (1.4)–(1.11) enable us to estimate the effectiveness of the conversion of electric energy into mechanical energy and vice versa. As follows from the analysis of the energy conversion [2, 13] in a piezoelectric medium, this effectiveness depends on differences between dielectric permittivities from (1.16) or differences between elastic compliances from (1.19), and these differences strongly depend on the piezoelectric effect. In a general form, the effectiveness of the energy conversion is described by an electromechanical coupling factor (ECF) [2, 3, 5, 6, 13]

$$k = w_{piezo} / \sqrt{w_{el} w_{mech}} \quad (1.20)$$

and is expressed in terms of volume densities of piezoelectric (or mutual) energy $w_{piezo} = \sigma_i d_{mi} E_m / 2$, electric energy $w_{el} = E_l \varepsilon_{lr}^{\sigma} E_r / 2$, and mechanical energy $w_{mech} = \sigma_p s_{pq}^E \sigma_q / 2$. The k^2 value calculated from (1.20) characterises [2–5, 9, 13] a ratio of stored mechanical energy to electric energy input (when a portion of electric energy is applied to the piezoelectric sample) or a ratio of stored electric energy to mechanical energy input (when a portion of mechanical energy is applied to the piezoelectric sample). The k^2 value also characterises a measure of the magnitude of the piezoelectric transducer bandwidth [2]. The absolute ECF value depends [2, 4, 9, 13] on the vibration mode, measurement methodology, sample shape, and the electromechanical constants of the piezoelectric medium. As a rule, two kinds of ECFs are considered as follows: the static ECF determined from equations of the state of the piezoelectric medium and the dynamic (effective) ECF related to the individual piezoelectric element [9, 13]. It is obvious that the ECFs strongly depend on the orientation of the external electric or mechanical field applied to the piezoelectric element and on the symmetry of its properties.

1.2.2 Examples of Electromechanical Coupling Factors

A poled FC element with a remanent polarisation vector $\mathbf{P}_r \parallel OX_3$ (∞mm symmetry) is characterised [2–5] by three independent piezoelectric coefficients, namely, d_{31} , d_{33} and d_{15} . These piezoelectric coefficients are linked to the ECFs as follows:

$$k_{33} = d_{33}/(\epsilon_{33}^\sigma s_{33}^E)^{1/2} \quad (1.21)$$

(ECF at the longitudinal oscillation mode, or simply, longitudinal ECF),

$$k_{31} = d_{31}/(\epsilon_{33}^\sigma s_{11}^E)^{1/2} \quad (1.22)$$

(ECF at the transverse oscillation mode) and

$$k_{15} = d_{15}/(\epsilon_{11}^\sigma s_{55}^E)^{1/2} \quad (1.23)$$

(ECF at the shear oscillation mode). Since an equality $s_{55}^E = s_{44}^E$ holds [2–5] in a poled FC medium, expression (1.23) is often given by $k_{15} = d_{15}/(\epsilon_{11}^\sigma s_{44}^E)^{1/2}$. For various piezo-active materials the ECF is represented in the general form as $k_{ij} = d_{ij}/(\epsilon_{ij}^\sigma s_{ij}^E)^{1/2}$, and hereby it is sufficient to require $d_{ij} \neq 0$ at a specific oscillation mode. Due to equalities $s_{22}^E = s_{11}^E$ and $d_{24} = d_{15}$, which are valid for any FC poled along the OX_3 axis [2–5], the relations

$$k_{32} = k_{31} \text{ and } k_{24} = k_{15} \quad (1.24)$$

are also valid. It should be noted that a violation of conditions (1.24) may be accounted for by peculiarities of symmetry of the piezoelectric medium. For example, in a piezoelectric material belonging to the $mm2$ class, we should distinguish [3] s_{22}^E and s_{11}^E , d_{24} and d_{15} , etc. As a consequence, inequalities $k_{32} \neq k_{31}$ and $k_{24} \neq d_{15}$ hold.

Along with the ECFs from (1.21)–(1.24), the following ECFs are considered widely [2, 4, 9, 10, 13] and often measured on poled FC and piezo-active composite samples with ∞mm symmetry:

$$k_t = e_{33}/(c_{33}^D \epsilon_{33}^\xi)^{1/2} \quad (1.25)$$

(ECF at the thickness oscillation mode, or simply, thickness ECF),

$$k_p = k_{31}[2/(1-\sigma_E)]^{1/2} \quad (1.26)$$

(ECF at the planar oscillation mode, or simply, planar ECF) and

$$k_h = d_h / (\epsilon_{33}^\sigma s_h^E)^{1/2} \quad (1.27)$$

(hydrostatic ECF). In (1.26) σ_E is the Poisson's ratio at electric field $E = \text{const}$, and in (1.27) d_h and s_h^E are the hydrostatic piezoelectric coefficient and hydrostatic elastic compliance at $E = \text{const}$, respectively. Tables of ECFs measured on the FC elements at specific oscillation modes are given in work [2, 4, 13]. Data on the ECFs from (1.21)–(1.27) along with the piezoelectric coefficients from (1.12)–(1.15) are useful in the selection of piezoelectric materials for active elements of electromechanical transducers, hydrophones and piezoelectric energy harvesters [10, 13–24].

It should be added that examples of ECFs and their anisotropy in piezoelectric materials will be discussed in Chap. 2.

1.3 Figures of Merit

According to Uchino and Ishii [19], there are three major stages that are concerned with piezoelectric energy harvesting in electromechanical systems. These stages are characterised as follows:

- (i) mechanical-mechanical energy transfer, including the mechanical stability of the piezoelectric transducer under a large mechanical stress, and mechanical impedance matching,
- (ii) mechanical-electric energy transduction due to electromechanical coupling in a piezoelectric element (SC, ceramic or composite) and
- (iii) electric-electric energy transfer, including electric impedance matching, for instance, in the presence of a DC/DC converter to accumulate the energy into an electric rechargeable battery.

Mechanical (acoustic) impedance matching is one of the important factors to be taken into account at the first stage [19]. The mechanical impedance of a material is given by $Z = (\rho c_{ij})^{1/2}$, where ρ is its density, and c_{ij} is its elastic modulus. At the second stage, a portion of mechanical energy that reaches the piezoelectric transducer is converted into electric energy due to electromechanical coupling. Hereby a voltage induced in this transducer is written in the general form as

$$V = g_{ij} F t / A \quad (1.28)$$

In (1.28) g_{ij} is the piezoelectric coefficient, F is the applied force, t is the thickness of the piezoelectric element, and A is the area of the surface on which the force acts. As a result of mechanical loading and due to the piezoelectric effect, an output electric power is

$$P = (CV^2/2)f \quad (1.29)$$

In (1.29) C is the electric capacitance of the piezoelectric element, and f is frequency of its vibration. We note that the capacitance C is proportional to dielectric permittivity ϵ_{jj}^σ for a flat large electric condenser, and f is chosen in a low-frequency range far from a resonance frequency of this piezoelectric element.

When the mechanical loading is along the poling axis OX_3 (as is conventional for FCs [2–5]) with electrodes that are perpendicular to OX_3 , the output electric power is $P_{out} \sim d_{33}g_{33}$, and

$$(Q_{33})^2 = d_{33}g_{33} \quad (1.30)$$

is the squared figure of merit [10, 14, 19, 24] concerned with the oscillation ‘33’ (or longitudinal) mode. Taking into account (1.28) and (1.30), one can represent energy generated in the piezoelectric transducer at the applied force F as $W_{gen} = (Q_{33})^2 F^2 t / (2lw)$, where l is the length, and w is the width of the transducer in the form of the rectangular parallelepiped.

Along with $(Q_{33})^2$ related to the longitudinal piezoelectric effect, we introduce squared figures of merit

$$(Q_{31})^2 = d_{31}g_{31} \text{ and } (Q_{32})^2 = d_{32}g_{32} \quad (1.31)$$

which are related to the transverse piezoelectric effect and oscillation ‘31’ and ‘32’ modes, respectively, and

$$(Q_h)^2 = d_h g_h \quad (1.32)$$

that is a hydrostatic analog of the squared figure of merit from (1.30).

Squared figures of merit (1.30)–(1.32) are often used to characterise the sensor signal-to-noise ratio of the piezoelectric material and its sensitivity [10, 25]. A piezoelectric element with a large value of $(Q_{3j})^2$ from (1.30) or (1.31) will generate high voltage and power when this element is exploited for energy harvesting and sensing applications. It should be added that the electrical damping plays an important role in affecting the performance of the piezoelectric element. Taking into account dielectric losses ($\tan \delta$) in the low-frequency region, the squared figure of merit in an off-resonance region may be represented [24] as $(Q_{31})^2 = d_{31}g_{31}/\tan \delta$ (for a 3–1 mode of the transducer), $(Q_{32})^2 = d_{32}g_{32}/\tan \delta$ (for a 3–2 mode of the transducer) or $(Q_{33})^2 = d_{33}g_{33}/\tan \delta$ (for a 3–3 mode of the transducer). The criteria for maximising the $(Q_{33})^2$ in poled FCs and trends in optimising the FC composition for energy-harvesting related applications were considered in works [20, 23].

Numerous examples of figures of merit and related parameters of piezoelectric materials will be discussed in Chap. 3.

1.4 Hydrostatic Parameters Concerned with Electromechanical Coupling

In Sects. 1.2.2 and 1.3 we introduced some of the hydrostatic parameters of a piezoelectric medium, for instance, the hydrostatic piezoelectric coefficients d_h and g_h , electromechanical coupling factor k_h and squared figure of merit $(Q_h)^2$. Taking into account the symmetry features of a piezoelectric element and specific orientations of its electrode structure, we may consider different relationships for d_h :

- (i) $d_h = d_{33} + d_{32} + d_{31}$ at electrodes perpendicular to OX_3 ,
- (ii) $d_h = d_{23} + d_{22} + d_{21}$ at electrodes perpendicular to OX_2 and
- (iii) $d_h = d_{13} + d_{12} + d_{11}$ at electrodes perpendicular to OX_1 .

Similar relationships are valid for the hydrostatic piezoelectric coefficients d_h and e_h . A complicated system of electrodes can lead to an increase in d_h due to positive contributions from different co-ordinate directions OX_j . An additional route for increasing d_h , g_h and e_h is the use of piezo-active composites [26] wherein microgeometric factors and polarisation orientation effects can promote favourable relations between the piezoelectric coefficients related to the response along the OX_j axes. Finally, the hydrostatic elastic compliance s_h^E from (1.27) characterises an elastic response of the piezoelectric element under a hydrostatic pressure. In general form s_h^E is represented as $s_h^E = s_{11}^E + s_{22}^E + s_{33}^E + 2(s_{12}^E + s_{13}^E + s_{23}^E)$, where s_{ab}^E is the elastic compliance at $E = \text{const}$.

1.5 Effective Electromechanical Properties in Heterogeneous Piezoelectric Media

1.5.1 Relaxor-Ferroelectric Domain-Engineered Single Crystals

Relaxor-ferroelectric perovskite-type solid solutions are materials with one of the following general formulae: $(1-x)\text{Pb}(\text{B}_1, \text{B}_2)\text{O}_3 - x\text{PbTiO}_3$ or $(1-x-y)\text{Pb}(\text{B}_1, \text{B}_2)\text{O}_3 - x\text{Pb}(\text{B}_1', \text{B}_2')\text{O}_3 - y\text{PbTiO}_3$. The complex perovskites described with the general formula $\text{Pb}(\text{B}_1, \text{B}_2)\text{O}_3$ [or $\text{Pb}(\text{B}_1', \text{B}_2')\text{O}_3$] are disordered dielectric compounds that contain ions of metals from the following groups: B_1 (or B_1') = Mg, Zn, Ni, Fe, Sc, Yb, and In (low-valence metals) and B_2 (or B_2') = Nb, Ta and W (high-valence metals) [27, 28]. A combination of metal ions with low and high valences results in physical properties that distinguish $\text{Pb}(\text{B}_1, \text{B}_2)\text{O}_3$ from 'normal' (ordered or regular) perovskite-type ferroelectrics such as PbTiO_3 , BaTiO_3 or KNbO_3 . The complex perovskites $\text{Pb}(\text{B}_1, \text{B}_2)\text{O}_3$ exhibit a broad and frequency-dispersive dielectric maxima and contain polar nanoregions (with ferroelectric or antiferroelectric ordering) in a non-polar phase over a wide temperature

range. These materials are characterised by a relaxation dielectric polarisation and are often termed *relaxors* or *ferroelectric relaxors* [27–29].

The perovskite-type solid solutions of $(1-x)\text{Pb}(\text{B}_1, \text{B}_2)\text{O}_3 - x\text{PbTiO}_3$ combine the physical properties of the relaxor-type and ‘normal’ ferroelectric components, and, as a rule, excellent electromechanical properties are observed near the morphotropic phase boundary [27, 30, 31]. To achieve a high piezoelectric activity in SC samples, the relaxor-ferroelectric solid solutions are often engineered by compositional adjustment with a corresponding decrease in Curie temperature of the paraelectric-to-ferroelectric phase transition [27, 31, 32], and specific domain-engineered structures are formed in an electric field [31, 32].

Since the 2000s, domain-engineered SCs of $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3$ (PMN- x PT) and $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - y\text{PbTiO}_3$ (PZN- y PT) have been in the focus of many experimental and theoretical studies. Of particular interest are compositions taken in the vicinity of the morphotropic phase boundary, with intricate domain/heterophase states [33] etc. Results of numerous studies show that the engineered non- 180° domain structures [31, 32, 34], intermediate ferroelectric phases [30, 33, 35] and domain-orientation processes [36–39] play an important role in forming outstanding electromechanical properties in the aforementioned relaxor-ferroelectric SCs. Due to these and other phenomena, the domain-engineered PMN- x PT and PZN- y PT SCs poled along the certain crystallographic directions (often along [001], [011] or [111] of the perovskite unit cell) [27, 31] exhibit very high piezoelectric activity and significant electromechanical coupling [28, 31, 34, 36], which is of benefit for energy-harvesting applications.

Full sets of electromechanical constants of domain-engineered relaxor-ferroelectric SCs with compositions near the morphotropic phase boundary are given in Table 1.1. We note that the electromechanical properties are regarded as effective, i.e., averaged over a macroscopic volume of a SC sample with fixed orientations of domains and domain walls separating them. Typical absolute values

Table 1.1 Experimental values of elastic compliances s_{ab}^E (in 10^{-12} Pa $^{-1}$), piezoelectric coefficients d_{ij} (in pC/N) and dielectric permittivities ϵ_{pp}^σ of [001]-poled domain-engineered PMN- x PT and PZN- y PT SCs ($4mm$ symmetry) at room temperature

SC	s_{11}^E	s_{12}^E	s_{13}^E	s_{33}^E	s_{44}^E	s_{66}^E	d_{31}	d_{33}	d_{15}	$\epsilon_{11}^\sigma / \epsilon_0$	$\epsilon_{33}^\sigma / \epsilon_0$
PMN-0.33PT [59]	69.0	-11.1	-55.7	119.6	14.5	15.2	-1330	2820	146	1600	8200
PMN-0.30PT [60]	52.0	-18.9	-31.1	67.7	14.0	15.2	-921	1981	190	3600	7800
PMN-0.28PT [61]	44.57	-28.91	-13.91	34.38	15.22	16.34	-569	1182	122	1672	5479
PZN-0.045PT [62]	82.0	-28.5	-51.0	108	15.6	15.9	-970	2000	140	3100	5200
PZN-0.07PT [63]	85.9	-14.1	-69.0	142	15.9	14.1	-1204	2455	176	3000	5622
PZN-0.08PT [63]	87.0	-13.1	-70.0	141	15.8	15.4	-1455	2890	158	2900	7700

of piezoelectric coefficients $|d_{3j}| \sim 10^3$ pC/N in the domain-engineered PMN- x PT and PZN- y PT SCs (Table 1.1) are larger than the $|d_{3j}|$ of regular ferroelectric single-domain PbTiO₃ SC [40] and conventional FC based on Pb(Zr_{1- x} Ti _{x})O₃ [4, 5, 9, 10, 13]. Moreover, the piezoelectric coefficient d_{33} in the [001]-poled heterophase PZN-0.08PT SC can be approximately 12,000 pC/N [35] due to the electric-field-induced phase transition and the presence of an intermediate monoclinic phase.

Experimental results [28, 32] suggest that relatively high piezoelectric strains (over 0.5 %) are achieved in the [001]-poled domain-engineered PZN- y PT SCs under an electric field $\mathbf{E} \parallel [001]$. At room temperature these SCs are characterised by $3m$ symmetry in the single-domain state and by $4mm$ symmetry in the poly-domain state wherein the spontaneous polarisation vectors of the non-180° domains are parallel to the following perovskite unit-cell directions: [111], $[\bar{1} \ 11]$, $[1 \ \bar{1} \ 1]$, and $[\bar{1} \ \bar{1} \ 1]$ [27, 31, 41].

Important interconnections between the structure and properties in the PMN- x PT and PZN- y PT SCs have been reviewed by Noheda [30]. The high piezoelectric activity in these SCs is associated with a polarisation rotation in the electric field \mathbf{E} [36, 38]. This rotation between the single-domain states in the tetragonal ($4mm$) and rhombohedral ($3m$) phases can be implemented in different ways that form the intermediate monoclinic phases [30] and complex heterophase states [33, 35] near the morphotropic phase boundary.

The relaxor-ferroelectric SCs are used as active elements of energy harvesters [42–45] and as piezoelectric components of advanced composites [46] that are suitable for energy-harvesting devices due to the large piezoelectric coefficients d_{3j} , ECF k_t and other parameters.

1.5.2 Poled Ferroelectric Ceramics

Full sets of the electromechanical constants of ferroelectric polydomain SCs are used to study the relationships between electromechanical properties in a single grain and a poled FC [9] consisting of a large number of grains with different orientations of main crystallographic axes. This study is based on solving a problem [7, 9, 47–49] of the electromechanical interaction between a spherical piezo-active grain and a piezo-ceramic medium surrounding this grain. Such an interaction is considered within the framework of the effective medium method [48, 49] that takes into account not only the piezoelectric effect but also the anisotropy of the piezoelectric properties within the grain and the FC medium. This anisotropy can be considerable, particularly in the presence of non-180° domain reorientations in the grains [50]. The effect of the 90° domain-wall displacements within the grains on the electromechanical properties in the poled BaTiO₃ FC has been studied [7, 51, 52], and contributions from these domain-wall displacements to a variety of constants for the FC medium were evaluated.

In contrast to the BaTiO₃ FC, the electromechanical properties in the PbTiO₃ FC are determined [42, 53] in the absence of 90° domain-wall displacements within grains. According to results [53, 54], the 90° domain structure of the grains has a strong influence on the piezoelectric coefficients d_{fp} and their anisotropy d_{33}/d_{31} in PbTiO₃-type FCs. In particular, it is possible to attain a large piezoelectric anisotropy (i.e., $d_{33}/|d_{31}| \gg 1$) by doping the FC, varying the temperature and by changing the volume fractions of the 90° domains within ceramic grains [54].

Subsequent averaging procedures facilitate consideration of the hierarchy-of-properties chain of ‘single-domain SC—polydomain SC—poled FC’ in the presence of the 90° domain-wall displacements (BaTiO₃) or assuming that the 90° domain walls are motionless (PbTiO₃) [42, 53, 54]. Knowledge of the full sets of the electromechanical constants of ferroelectric ceramics enables appropriate material selection for various piezotechnical applications, such as energy harvesting, and offers a route to using poled FCs as piezo-active components for composite materials.

The electromechanical constants of poled FC materials are often measured using standard methods [55, 56] at weak electric fields. The majority of the FCs are manufactured as perovskite-type solid solutions [3–5, 9, 13, 57, 58] with compositions varied and tailored to improve specific properties. Attempts to classify the FCs have been made in a variety of papers [9, 57, 58]. From the classification scheme [57] and by considering the conventional perovskite-type ceramics based on Pb(Zr_{1-x}Ti_x)O₃, it is possible to identify materials which are stable with regard to electric and mechanical loads, materials with high dielectric permittivity ϵ_{33}^{σ} , materials having high sensitivity with respect to mechanical stress fields (large absolute values of piezoelectric coefficients g_{fp}), materials with the large piezoelectric anisotropy d_{33}/d_{31} , materials with high stability with regard to resonance frequency, materials with low dielectric permittivity ϵ_{33}^{σ} , and high-temperature materials (high Curie temperature T_C). From the classification method proposed in monograph [9], the Pb(Zr_{1-x}Ti_x)O₃-based FCs are divided into four groups with specific performances. These groups are related to molar concentrations of Ti from molar-concentration ranges $0 \leq x \leq 0.1$, $0.1 \leq x \leq 0.4$, $0.4 \leq x \leq 0.6$, and $0.6 \leq x \leq 1$, and some advantages of each group of poled FC materials have been discussed [9] in the context of piezotechnical applications.

Examples of the full sets of electromechanical constants of poled FC materials are given in Table 1.2. It is seen that the piezoelectric coefficients d_{3j} of the listed FCs are considerably smaller than the piezoelectric coefficients d_{3j} of well-known domain-engineered relaxor-ferroelectric SCs (Table 1.1), i.e., piezoelectric activity of the FC medium along the poling axis is less pronounced. This feature can be associated with the grain microstructure of the FC, with internal mechanical stress fields in each grain and with restricted possibilities of domain reorientations therein.

We now compare some parameters of relaxor-ferroelectric SCs to the related parameters of poled FCs. Among the parameters of interest for energy harvesters, we mention ECFs k_{3j} and squared figures of merit $(Q_{3j})^2$. Published data from Table 1.3 suggests that the electromechanical properties of the PMN- x PT and

Table 1.2 Experimental values of elastic compliances s_{pq}^E (in 10^{-12} Pa $^{-1}$)^a, piezoelectric coefficients d_{ij} (in pC/N) and dielectric permittivities ϵ_{kk}^σ of perovskite-type FCs at room temperature

FC	s_{11}^E	s_{12}^E	s_{13}^E	s_{53}^E	s_{44}^E	d_{31}	d_{33}	d_{15}	$\frac{\epsilon_{11}^\sigma}{\epsilon_0}$	$\frac{\epsilon_{33}^\sigma}{\epsilon_0}$
BaTiO ₃ (I) [70]	8.55	-2.61	-2.85	8.93	23.3	-79	191	270	1623	1900
BaTiO ₃ (II) [13]	9.1	-2.7	-2.9	9.5	22.8	-78	190	260	1450	1700
ZTS-19 [5]	15.1	-5.76	-5.41	17.0	41.7	-126	307	442	1350	1500
PZT-4 [13]	12.3	-4.03	-5.35	15.6	39.1	-124	291	496	1440	1280
PZT-5 [13]	16.3	-5.67	-7.17	18.7	47.4	-170	373	583	1730	1700
PZT-5H [71]	10.8	-3.28	-3.41	11.6	28.3	-128	315	482	2640	2490
PZT-7A [72]	10.7	-3.22	-4.62	13.9	39.5	-60.2	151	364	843	427
PZ 27 [73, 74]	16.9	-6.32	-8.56	22.5	43.9	-174	419	515	1800	1770
PZ 34 [73, 74]	7.71	-1.54	-3.99	13.0	17.0	-3.92	59.1	39.2	191	196
PCR-1, hp ^b [57]	12.5	-4.4	-5.8	15.9	38.8	-95	220	420	1130	650
PCR-7, hp [57]	17.2	-7.2	-6.7	17.3	42.4	-280	610	760	2970	3500
PCR-7M, hp [57]	17.5	-6.7	-7.9	19.6	43.8	-350	760	880	3990	5000
PCR-8, hp [57]	12.5	-4.6	-5.2	15.6	35.3	-130	290	410	1380	1400
PCR-8, ct [57]	13.3	-4.8	-4.4	14.5	39.5	-125	280	458	1320	1300
PCR-13, ct [57]	10.4	-3.7	-2.1	11.3	28.5	-65	140	200	870	780
PCR-21, hp [57]	11.8	-4.5	-3.9	12.6	40.8	-109	250	370	1400	1350
PCR-63, hp [57]	9.8	-3.5	-2.7	9.8	24.1	-60	140	166	960	1170
PCR-73, hp [57]	17.9	-6.8	-9.6	23.5	43.7	-380	860	980	4750	6000
Pb(Zr _{0.54} Ti _{0.46})O ₃ [13]	11.6	-3.33	-4.97	14.8	45.0	-60.2	152	440	990	450
Pb(Zr _{0.52} Ti _{0.48})O ₃ [75]	13.8	-4.07	-5.80	17.1	48.2	-93.5	223	494	1180	730
(Pb _{0.94} Sr _{0.06})(Ti _{0.47} Zr _{0.53})O ₃ [75]	12.3	-4.05	-5.31	15.5	39.0	-123	289	496	1475	1300
Modified PbTiO ₃ (I) [76]	7.50	-1.51	-1.10	8.00	17.9	-4.40	51.0	53.0	228	177
Modified PbTiO ₃ (II) [77]	7.7	-1.7	-1.2	8.2	19	-6.8	56	68	240	190
(Pb _{0.9623} La _{0.025})· (Ti _{0.99} Mn _{0.01})O ₃ [78]	7.20	-1.42	-1.73	7.62	15.8	-4.15	47.2	53.0	223	168
(Pb _{0.85} Nd _{0.10})(Ti _{0.99} Mn _{0.01})· O ₃ [78]	6.84	-1.50	-1.83	7.27	16.4	-5.42	56.8	79.5	313	252
(Pb _{0.855} Nd _{0.11})· (Ti _{0.94} Mn _{0.02} In _{0.04})O ₃ [78]	6.77	-1.55	-1.79	7.29	16.0	-6.40	57.9	86.4	318	248
PMN-0.35PT [79]	13.2	-3.96	-6.05	14.7	33.4	-133	270	936	4610	3270

^aIn the poled state of any FC (∞mm symmetry, the poling axis is parallel to the co-ordinate axis OX_3), elastic compliance s_{66} is determined [2, 3, 9, 12, 13] as follows: $s_{66} = 2(s_{11}^E - s_{12}^E)$

^bFC samples of the PCR type have been manufactured using either the conventional technology (ct) or hot pressing (hp). PCR is the abbreviation for the group ‘piezoelectric ceramics from Rostov-on-Don’ (Russia) [57]

PZN- y PT SCs lead to larger values of k_{33} , $|k_{31}|$ and $(Q_{3j})^2$ in comparison to those of various FCs. This is a result of the high piezoelectric activity of the relaxor-ferroelectric SCs and the key role of the piezoelectric coefficients d_{3j} in the formation of k_{3j} and $(Q_{3j})^2$ [see (1.21), (1.22), (1.30), and (1.31)]. It should be added for a further comparison that textured PMN-PbZrO₃-PbTiO₃ FC samples studied in work [22] are characterised by $(Q_{33})^2 = 59.18 \cdot 10^{-12}$ Pa $^{-1}$, and this value

Table 1.3 ECFs k_{3j} and squared figures of merit $(Q_{3j})^2$ (in 10^{-12} Pa^{-1}) of some relaxor-ferroelectric SCs and poled FCs (evaluated using data from Tables 1.1 and 1.2)

Material	k_{31}	k_{33}	$(Q_{31})^2$	$(Q_{33})^2$
<i>Domain-engineered SCs</i>				
PMN–0.33PT	–0.594	0.957	24.4	110
PMN–0.30PT	–0.486	0.916	12.3	56.9
PMN–0.28PT	–0.387	0.915	6.66	28.8
PZN–0.045PT	–0.499	0.897	20.4	86.9
PZN–0.07PT	–0.582	0.924	29.1	121
PZN–0.08PT	–0.598	0.932	31.1	123
<i>Poled FCs</i>				
PZT-5	–0.343	0.703	1.92	9.25
PZT-5H	–0.262	0.623	0.743	4.50
PZT-7A	–0.299	0.659	0.959	6.03
PCR-1	–0.126	0.727	1.57	8.41
PCR-7	–0.384	0.833	2.53	12.0
PCR-7M	–0.398	0.816	2.77	13.1
Modified PbTiO ₃ (I)	–0.0406	0.456	0.0124	1.66

is comparable to that related to the domain-engineered PMN–0.30PT SC and much more than $(Q_{33})^2$ of conventional FCs (see Table 1.3). We add that examples of the squared figures of merit $(Q_{3j})^2$ and $(Q_h)^2$ of poled perovskite-type FCs are also discussed in Sect. 3.1.

The piezoelectric and elastic anisotropy of FCs leads to larger ratios of $k_{33}/|k_{31}|$ and $(Q_{33})^2/(Q_{31})^2$ which are of particular importance for energy-harvesting applications. The relevant piezoelectric element will enable us to transform energy on the specific direction, and the main energy flow, its transformation and piezoelectric sensitivity of this element will be along the poling axis OX_3 .

1.5.3 Piezo-Active Composites

Composites are heterogeneous systems that consist of two or more components that differ in chemical composition and properties and are separated by distinct interfaces [5]. Each composite material is characterised by the following features [5, 10]:

- (i) the typical size of the separate structural elements are small in comparison with the whole composite sample (i.e., there is an element of micro-inhomogeneity) and
- (ii) the typical sizes of the structural elements are greater than the size of their individual atoms or molecules so that each component of the composite sample is regarded as a continuous medium. As a result, to describe the composite properties, it is possible to consider the physical laws and equations suitable for continuous media.

The piezo-active composites (often termed *piezo-composites*) form an important group of modern smart materials. This group is vast due to the large number of components that may be involved in the design of the composites. Among the wide range of piezo-active components to be considered, ferroelectrics (FCs and SCs) play an important role [4, 5, 10, 26]. Moreover, modern processing technologies enable the synthesis of a variety of ferroelectric SCs, FCs, ferroelectric films, and nano-sized ferroelectrics. The ferroelectric properties of these systems are generally related to the change of the spontaneous polarisation vector in an external electric field (domain switching).

Piezo-active composites are of great interest due to the ability to vary and tailor the microgeometry, effective physical properties, their anisotropy, and hydrostatic and other parameters across a wide range [5, 10, 26]. These significant variations appear upon combining different components [5, 10], for example,

- (i) FC and polymer (the latter can be either piezo-passive or piezo-active),
- (ii) ferroelectric SC and FC, or
- (iii) ferroelectric SC and polymer.

In various compositions (i)–(iii) at least one of the components always exhibits some piezoelectric properties. The presence of one or more piezoelectric components enables a set of parameters or properties to be attained that are not specific to the separate components, and this synergy is important for piezoelectric transducer, hydroacoustic and other applications [10, 26]. The piezo-active composites based on ferroelectrics form the final (and very important) link in hierarchy-of-properties chains [10, 26, 54] of ‘single-domain SC \rightarrow polydomain SC \rightarrow FC \rightarrow composite’ and ‘single-domain SC \rightarrow polydomain SC \rightarrow heterophase SC \rightarrow composite’. We add that since the 1980s, FCs have been of interest as piezoelectric components of composites [4, 5, 10]. However since the 2000s, relaxor-ferroelectric SCs with high piezoelectric activity [59–63] are also used as components of modern piezo-composites (see, for instance, [19, 26, 46]). Due to their remarkable electromechanical properties, the piezo-active composites form an important group of modern smart materials [10], i.e., materials that undergo transformations through physical interactions, and these transformations lead to changes in the physical properties that are of value for piezotechnical applications.

The well-known classification of the two-component composites with planar interfaces was first put forward by Newnham et al. [64]. This classification is concerned with the so-called *connectivity* of each component. Connectivity is regarded as one of the main characteristics of the microstructure and expressed by the numbers of dimensions (or co-ordinate axes) in which each component is continuously distributed between limiting surfaces of the composite sample. The distribution of a self-connected state of a component can take place along zero, one, two, or three co-ordinate axes, i.e., connectivity $\alpha = 0, 1, 2,$ or 3 for component 1 and connectivity $\beta = 0, 1, 2,$ or 3 for component 2. The connectivity of a two-component composite is written in a general form [10, 64] of α – β where the connectivity of the piezoelectric or most piezo-active component takes the first position (α). In the case of $\alpha \leq \beta$, the n -component composites are described by

$(n + 3)!/(3! n!)$ connectivities [64], and for instance, the number of connectivities is 10 for $n = 2$. It is also possible to introduce 10 alternative connectivities $\alpha\text{-}\beta$ at $\alpha \geq \beta$ and $n = 2$.

The concept of connectivity [64] is fundamental in developing an understanding of the electromechanical interaction between components within piezo-composites, in the study of the distribution of internal electric and mechanical fields and in the interpretation of experimental or calculated data related to composites with specific connectivity. The connectivity, of the piezo-active composites is crucial in influencing the piezoelectric response and electromechanical coupling of these materials [10, 26, 65, 66].

The entire complex of the $\alpha\text{-}\beta$ connectivity patterns, their evolution and inter-connections between them in the two-component composites with planar interfaces were analysed in work [10]. To describe the evolution and determine the effective electromechanical properties in the $\alpha\text{-}\beta$ piezo-composite with planar interfaces, a group of so-called *junction* connectivity patterns (1–1, 1–3, 2–2, and 3–1) was introduced. Knowledge of the evolution of the connectivity patterns enables the analysis of the $\alpha\text{-}\beta$ piezo-composites and their effective electromechanical properties [10].

The problem of predicting the effective physical properties in piezo-active composites is of interest to many specialists undertaking theoretical and experimental studies of these heterogeneous materials. A formulation of the related problem on the effective electromechanical properties in a piezo-active composite is given in monograph [5]. If the averaged components of the electric field $\langle E_f \rangle$ and the mechanical strain $\langle \zeta_q \rangle$ in a macroscopic region of the composite sample are independent of co-ordinates x_j ($j = 1, 2$ and 3), then (1.4) and (1.5) for the piezoelectric medium can be written for the piezo-active composite in the following form:

$$\langle \sigma_p \rangle = c_{pq}^{*E} \langle \zeta_q \rangle - e_{fp}^* \langle E_f \rangle \quad (1.33)$$

$$\langle D_k \rangle = e_{kl}^* \langle \zeta_l \rangle + \varepsilon_{kr}^{*\zeta} \langle E_r \rangle \quad (1.34)$$

In (1.33) and (1.34) elastic moduli c_{pq}^{*E} , piezoelectric coefficients e_{fp}^* and dielectric permittivities $\varepsilon_{kr}^{*\zeta}$ constitute the full set of effective electromechanical constants¹ that are found [5] by taking into account equations of electric and mechanical equilibrium and boundary conditions at the surface of the macroscopic region in the heterogeneous medium. The determination of the effective electromechanical properties of the piezo-active composite is concerned with an averaging of a series of vector and tensor components of the electric and mechanical fields, for example, ζ_q , E_f , σ_p , and D_k . This averaging is performed on

¹Hereafter we use asterisk (*) to denote the effective properties and related parameters of the composite.

volume fractions of the composite components ($n = 1, 2, \dots$), for which the full sets of electromechanical constants, e.g. $c_{pq}^{(n),E}$, $e_{jp}^{(n)}$ and $\varepsilon_{kr}^{(n),\zeta}$ are known.

Taking into consideration volume-fraction dependences of the effective electromechanical properties of a composite [5, 10] with a specific microgeometry [66], one can predict the behaviour of the ECFs, figures of merit and other parameters that are of interest for energy-harvesting applications [46, 67–69].

The next step in studying the piezo-composites is concerned with the orientations effects [26]. The orientation effects broaden our outlook in the field of *composition—structure—properties* relations [10, 12]. Examination of the orientation effects can promote an improvement of the performance of the piezo-composites, the anisotropy of their piezoelectric coefficients and ECFs, the hydrostatic piezoelectric response, etc. Fundamental links between the domain orientations and electromechanical properties in relaxor-ferroelectric SCs with high piezoelectric activity represent a considerable opportunity for improving the piezoelectric performance of the SC/polymer and SC/porous polymer composites. In comparison to the composites based on relaxor-ferroelectric SCs, the orientation effects in the conventional FC-based composites are less pronounced [26], but should be taken into account when predicting the piezoelectric properties and related parameters.

1.6 Conclusion

This chapter has been devoted to the introduction and description of the electromechanical properties and related characteristics of piezoelectric media and the consideration of the piezoelectric performance of modern piezoelectric materials. In the last decades the most important piezoelectric materials have been poled FCs, relaxor-ferroelectric, SCs with engineered domain structures and piezo-active composites with at least one of the aforementioned components. The use of highly-effective relaxor-ferroelectric SCs with compositions near the morphotropic phase boundary is of significant interest due to their electromechanical properties compared to those of the conventional FCs. The excellent electromechanical properties of the relaxor-ferroelectric PMN- x PT and PZN- y PT SCs (Table 1.1) in the domain-engineered/heterophase states are a result of their large values of piezoelectric coefficients d_{ij} , elastic compliances s_{ab}^E , ECFs k_{ij} , and squared figures of merit $(Q_{3j})^2$. The ECFs k_{ij} and squared figures of merit $(Q_{3j})^2$ are parameters that are specifically related to the energy-harvesting characteristics of the piezoelectric material, and these characteristics strongly depend on its piezoelectric activity.

The electromechanical properties and related characteristics of the poled FCs (Table 1.2) vary in a wide range as a result of the strong dependence of these properties on microstructure, composition, poling conditions and technological factors such as a range of sintering temperatures, hot-pressure parameters, etc. The lower piezoelectric activity of the poled FCs in comparison to the aforementioned

relaxor-ferroelectric SCs leads to smaller values of $|k_{ij}|$ and $(Q_{3j})^2$ (Table 1.3), and this interconnection is to be taken into account when selecting potential piezoelectric energy-harvesting materials.

In general the electromechanical properties of the domain-engineered SCs, poled FC and piezo-active composite materials are regarded as ‘effective properties’ in accordance with features of the microstructure, domain structure, arrangement of components and connectivity. The piezo-active composites based on ferroelectrics are the final link in the hierarchy-of-properties chains of ‘single-domain SC \rightarrow polydomain SC \rightarrow FC \rightarrow composite’ and ‘single-domain SC \rightarrow polydomain SC \rightarrow heterophase SC \rightarrow composite’, and this makes the piezo-active composites a unique range of modern functional materials whose effective properties can be tailored in wide ranges due to a range of factors (physical, chemical, microgeometric, technological, etc.) Variations of the effective electromechanical properties and related parameters in the piezo-active composites open up new possibilities for piezoelectric energy-harvesting applications of these materials.

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