

# 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, heterophase 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  $\sigma_{kl}$  or mechanical strain  $\xi_{jr}$ , 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 ( $\sigma_{kl}$  and  $\xi_{jr}$ ), 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  $\xi_{jr}$ ,  $E_i$  and  $T$  as follows:

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

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

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

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 ( $\beta_{kl}$ , second-rank tensor), dielectric permittivities at constant mechanical strain ( $\varepsilon_{if}^E$ , second-rank tensor), pyroelectric coefficients ( $p_i$ , first-rank tensor, i.e., vector). In (1.1)–(1.3) density ( $\rho$ ) 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  $\Delta T$  and  $\Delta S$  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  $\sigma_{kl}(\xi_{jr})$  from (1.1) obeys Hooke’s law in an anisotropic medium [12] at small ( $<1\%$ ) strains  $\xi_{jr}$ . 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  $\Delta S$  (for example,  $\xi_{jr}$ ,  $E_i$  and  $\Delta S$ ). 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  $\xi$  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  $\sigma$  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  $\sigma$  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  $\zeta$  and electric displacement  $D$ . Superscripts  $\sigma$  and  $D$  denote measurement conditions at  $\sigma = \text{const}$  and  $D = \text{const}$ , respectively. Dielectric impermeabilities  $\beta_{kr}^\sigma$  (at  $\sigma = \text{const}$ ) and  $\beta_{kr}^\zeta$  (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  $\delta_{kv}$  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

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

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

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

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

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  $3 \times 6$  or  $6 \times 3$  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  $\infty$ ,  $\infty mm$  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  $\mathbf{P}_r \parallel OX_3$  ( $\infty mm$  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:

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

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

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

(ECF at the transverse oscillation mode) and

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

(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  $k_{15} = d_{15} / (e_{11}^\sigma s_{44}^E)^{1/2}$ . For various piezo-active materials the ECF is represented in the general form as  $k_{ij} = d_{ij} / (e_{ij}^\sigma s_{ij}^E)^{1/2}$ , 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  $\infty mm$  symmetry:

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

(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)  $\sigma_E$  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  $\rho$  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  $\epsilon_{jj}^\sigma$  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:  $\text{B}_1$  (or  $\text{B}_1'$ ) = Mg, Zn, Ni, Fe, Sc, Yb, and In (low-valence metals) and  $\text{B}_2$  (or  $\text{B}_2'$ ) = 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  $\text{PbTiO}_3$ ,  $\text{BaTiO}_3$  or  $\text{KNbO}_3$ . 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- $180^\circ$  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  $\epsilon_{pp}^\sigma$  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  $\text{PbTiO}_3$  SC [40] and conventional FC based on  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  [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  $\text{BaTiO}_3$  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  $\text{BaTiO}_3$  FC, the electromechanical properties in the  $\text{PbTiO}_3$  FC are determined [42, 53] in the absence of  $90^\circ$  domain-wall displacements within grains. According to results [53, 54], the  $90^\circ$  domain structure of the grains has a strong influence on the piezoelectric coefficients  $d_{fp}$  and their anisotropy  $d_{33}/d_{31}$  in  $\text{PbTiO}_3$ -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  $90^\circ$  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  $90^\circ$  domain-wall displacements ( $\text{BaTiO}_3$ ) or assuming that the  $90^\circ$  domain walls are motionless ( $\text{PbTiO}_3$ ) [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  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ , it is possible to identify materials which are stable with regard to electric and mechanical loads, materials with high dielectric permittivity  $\epsilon_{33}^\sigma$ , 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  $\epsilon_{33}^\sigma$ , and high-temperature materials (high Curie temperature  $T_C$ ). From the classification method proposed in monograph [9], the  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ -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 $^{-1}$ )<sup>a</sup>, piezoelectric coefficients  $d_{ij}$  (in pC/N) and dielectric permittivities  $\epsilon_{kk}^\sigma$  of perovskite-type FCs at room temperature

FC	$s_{11}^E$	$s_{12}^E$	$s_{13}^E$	$s_{33}^E$	$s_{44}^E$	$d_{31}$	$d_{33}$	$d_{15}$	$\frac{\epsilon_{11}^\sigma}{\epsilon_0}$	$\frac{\epsilon_{33}^\sigma}{\epsilon_0}$
BaTiO <sub>3</sub> (I) [70]	8.55	-2.61	-2.85	8.93	23.3	-79	191	270	1623	1900
BaTiO <sub>3</sub> (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 <sup>b</sup> [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 <sub>0.54</sub> Ti <sub>0.46</sub> )O <sub>3</sub> [13]	11.6	-3.33	-4.97	14.8	45.0	-60.2	152	440	990	450
Pb(Zr <sub>0.52</sub> Ti <sub>0.48</sub> )O <sub>3</sub> [75]	13.8	-4.07	-5.80	17.1	48.2	-93.5	223	494	1180	730
(Pb <sub>0.94</sub> Sr <sub>0.06</sub> )(Ti <sub>0.47</sub> Zr <sub>0.53</sub> )O <sub>3</sub> [75]	12.3	-4.05	-5.31	15.5	39.0	-123	289	496	1475	1300
Modified PbTiO <sub>3</sub> (I) [76]	7.50	-1.51	-1.10	8.00	17.9	-4.40	51.0	53.0	228	177
Modified PbTiO <sub>3</sub> (II) [77]	7.7	-1.7	-1.2	8.2	19	-6.8	56	68	240	190
(Pb <sub>0.9625</sub> La <sub>0.025</sub> )· (Ti <sub>0.99</sub> Mn <sub>0.01</sub> )O <sub>3</sub> [78]	7.20	-1.42	-1.73	7.62	15.8	-4.15	47.2	53.0	223	168
(Pb <sub>0.85</sub> Nd <sub>0.10</sub> )(Ti <sub>0.99</sub> Mn <sub>0.01</sub> )· O <sub>3</sub> [78]	6.84	-1.50	-1.83	7.27	16.4	-5.42	56.8	79.5	313	252
(Pb <sub>0.855</sub> Nd <sub>0.11</sub> )· (Ti <sub>0.94</sub> Mn <sub>0.02</sub> In <sub>0.04</sub> )O <sub>3</sub> [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

<sup>a</sup>In the poled state of any FC ( $\infty mm$  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:  $s_{66} = 2(s_{11}^E - s_{12}^E)$

<sup>b</sup>FC 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-PbZrO<sub>3</sub>-PbTiO<sub>3</sub> 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  $10^{-12} \text{ Pa}^{-1}$ ) 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 <sub>3</sub> (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  $\alpha$ – $\beta$  where the connectivity of the piezoelectric or most piezo-active component takes the first position ( $\alpha$ ). 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  $\langle \xi_q \rangle$  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 piezo-electric medium can be written for the piezo-active composite in the following form:

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

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

In (1.33) and (1.34) elastic moduli  $c_{pq}^{*E}$ , piezoelectric coefficients  $e_{fp}^*$  and dielectric permittivities  $\varepsilon_{kr}^{*\xi}$  constitute the full set of effective electromechanical constants<sup>1</sup> 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,  $\xi_q$ ,  $E_f$ ,  $\sigma_p$ , and  $D_k$ . This averaging is performed on

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<sup>1</sup>Hereafter 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.  $c_{pq}^{(n),E}$ ,  $e_{fp}^{(n)}$  and  $\varepsilon_{kr}^{(n),\xi}$  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 piezo-electric 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.

## References

1. Levanyuk AP, Sannikov DG (1994) Piezoelectrics. In: Prokhorov AM (ed) Physics encyclopaedia. Bolshaya Rossiyskaya Entsiklopedia, vol 4. Moscow (in Russian), pp 188–189
2. Ikeda T (1990) Fundamentals of piezoelectricity. Oxford University Press, Oxford
3. Zheludev IS (1971) Physics of crystalline dielectrics. Electrical properties, vol. 2. Plenum, New York
4. Uchino K (1997) Piezoelectric actuators and ultrasonic motors. Kluwer, Boston
5. Khoroshun LP, Maslov BP, Leshchenko PV (1989) Prediction of effective properties of piezo-active composite materials. Naukova Dumka, Kiev (in Russian)
6. Turik AV (1970) Elastic, piezoelectric, and dielectric properties of single crystals of BaTiO<sub>3</sub> with a laminar domain structure. Soviet Phys—Solid State 12:688–693
7. Aleshin VI (1990) Domain-orientation contribution into constants of ferroelectric polydomain single crystal. Zh Tekh Fiz 60:179–183 (in Russian)
8. Topolov VYu (2003) Domain wall displacements and piezoelectric activity of KNbO<sub>3</sub> single crystals. J Phys: Condens Matter 15:561–565
9. Gorish AV, Dudkevich VP, Kupriyanov MF, Panich AE, Turik AV (1999) Piezoelectric device-making. Physics of ferroelectric ceramics, vol. 1. Radiotekhnika, Moscow (in Russian)
10. Topolov VYu, Bowen CR (2009) Electromechanical properties in composites based on ferroelectrics. Springer, London
11. Siffert P (2008) Foreword. In: Heywang W, Lubitz K, Wersing W (eds) Piezoelectricity. Evolution and future of a technology. Springer, Berlin, p V
12. Newnham RE (2005) Properties of materials. Anisotropy, symmetry, structure. Oxford University Press, New York
13. Berlincourt DA, Cerran DR, Jaffe H (1964) Piezoelectric and piezomagnetic materials and their function in transducers. In: Mason W (ed) Physical acoustics. Principles and methods. Methods and devices. vol 1, Pt A. Academic Press, New York, pp 169–270
14. Kim H, Tadesse Y, Priya S (2009) Piezoelectric energy harvesting. In: Priya S, Inman DJ (eds) Energy harvesting technologies. Springer, New York, pp 3–39

15. Ayed SB, Abdelkefi A, Najar F, Hajj MR (2014) Design and performance of variable-shaped piezoelectric energy harvesters. *J Intell Mater Syst Struct* 25:174–186
16. Tang G, Yang B, Liu J-Q, Xu B, Zhu H-Y, Yang C-S (2014) Development of high performance piezoelectric  $d_{33}$  mode MEMS vibration energy harvester based on PMN-PT single crystal thick film. *Sensors Actuators A* 205:150–155
17. Chae M-S, Koh J-H (2014) Piezoelectric behavior of  $(1 - x)(\text{PbMgNbO}_3\text{--PbZrTiO}_3) - x(\text{BaTiO}_3)$  ceramics for energy harvester applications. *Ceram Int* 40:2551–2555
18. Maiwa H, Sakamoto W (2013) Vibrational energy harvesting using a unimorph with PZT- or BT-based ceramics. *Ferroelectrics* 446:67–77
19. Uchino K, Ishii T (2010) Energy flow analysis in piezoelectric energy harvesting systems. *Ferroelectrics* 400:305–320
20. Yoon M-S, Mahmud I, Ur S-C (2013) Phase-formation, microstructure, and piezoelectric/dielectric properties of  $\text{BiYO}_3$ -doped  $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$  for piezoelectric energy harvesting devices. *Ceram Int* 39:8581–8588
21. Gusarova E, Gusarov B, Zakharov D, Bousquet M, Viala B, Cugat O, Delamare J, Gimeno L (2013) An improved method for piezoelectric characterization of polymers for energy harvesting applications. *J Phys: Conf Ser* 476:012061
22. Yan Y, Cho K-H, Maurya D, Kumar A, Kalinin S, Khachaturyan A, Priya S (2013) Giant energy density in  $[001]$ -textured  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - \text{PbZrO}_3 - \text{PbTiO}_3$  piezoelectric ceramics. *Appl Phys Lett* 102:042903
23. Islam RA, Priya S (2006) Realization of high-energy density polycrystalline piezoelectric ceramics. *Appl Phys Lett* 88:032903
24. Priya S (2010) Criterion for material selection in design of bulk piezoelectric energy harvesters. *IEEE Trans Ultrason Ferroelectr Freq Control* 57:2610–2612
25. Grekov AA, Kramarov SO, Kuprienko AA (1989) Effective properties of a transversely isotropic piezoelectric composite with cylindrical inclusions. *Mech Compos Mater* 25:54–61
26. Topolov VYu, Bisegna P, Bowen CR (2014) Piezo-active composites. Orientation effects and anisotropy factors. Springer, Berlin Heidelberg
27. Cross LE (2008) Relaxor ferroelectrics. In: Heywang W, Lubitz K, Wersing W (eds) *Piezoelectricity. Evolution and future of a technology*. Springer, Berlin, pp 131–156
28. Park S-E, Hackenberger W (2002) High performance single crystal piezoelectrics: applications and issues. *Curr Opin Solid State Mater Sci* 6:11–18
29. Smolensky GA, Bokov VA, Isupov VA, Krainik NN, Pasynkov RE, Sokolov AI, Yushin NK (1985) *Physics of ferroelectric phenomena*. Nauka, Leningrad (in Russian)
30. Noheda B (2002) Structure and high-piezoelectricity in lead oxide solid solutions. *Curr Opin Solid State Mater Sci* 6:27–34
31. Park S-E, Shrout TR (1997) Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals. *J Appl Phys* 82:1804–1811
32. Park S-E, Shrout TR (1997) Relaxor based ferroelectric single crystals for electro-mechanical actuators. *Mater Res Innovations* 1:20–25
33. Topolov VYu (2012) *Heterogeneous ferroelectric solid solutions. Phases and Domain States*. Springer, Berlin
34. Dammak H, Renault A-É, Gaucher P, Thi MP, Calvarin G (2003) Origin of the giant piezoelectric properties in the  $[001]$  domain engineered relaxor single crystals. *Japan J Appl Phys* 42(42):6477–6482
35. Topolov VYu, Turik AV (2002) An intermediate monoclinic phase and electromechanical interactions in  $x\text{PbTiO}_3 - (1 - x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  crystals. *Phys Solid State* 44:1355–1362
36. Fu H, Cohen RE (2000) Polarization rotation mechanism for ultrahigh electromechanical response in single-crystal piezoelectrics. *Nature* 403:281–283
37. Davis M (2007) Picturing the elephant: Giant piezoelectric activity and the monoclinic phases of relaxor-ferroelectric single crystals. *J Electroceram* 19:23–45
38. Noheda B, Cox DE, Shirane G, Park S-E, Cross LE, Zhong Z (2001) Polarization rotation via a monoclinic phase in the piezoelectric  $92\% \text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ -8%  $\text{PbTiO}_3$ . *Phys Rev Lett* 86:3891–3894

39. Wada S, Tsurumi T (2002) Domain switching properties in PZN-PT single crystals with engineered domain configurations. *Key Eng Mater* 214–215:9–14
40. Fesenko EG, Gavrilyachenko VG, Semenchov AF (1990) Domain structure of multiaxial ferroelectric crystals. Rostov University Press, Rostov-on-Don (in Russian)
41. Liu T, Lynch CS (2003) Ferroelectric properties of [110], [001] and [111] poled relaxor single crystals: measurements and modeling. *Acta Mater* 51:407–416
42. Hong YK, Moon KS (2005) Single crystal piezoelectric transducers to harvest vibration energy. *Proc SPIE Optomechatronic Actuators Manipulation* 6048:60480E
43. Sun C, Qin L, Li F, Wang Q-M (2009) Piezoelectric energy harvesting using single crystal  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$  (PMN-PT) device. *J Intell Mater Syst Struct* 20:559–568
44. Moon SE, Lee SQ, Lee S-K, Lee Y-G, Yang YS, Park K-H, Kim J (2009) Sustainable vibration energy harvesting based on Zr-doped PMN-PT piezoelectric single crystal cantilevers. *ETRI J* 31:688–694
45. Song HJ, Choi YT, Wang G, Wereley NM (2009) Energy harvesting utilizing single crystal PMN-PT material and application to a self-powered accelerometer. *J Mech Des* 131:091008
46. Ren K, Liu Y, Geng X, Hofmann HF, Zhang QM (2006) Single crystal PMN-PT/epoxy 1–3 composite for energy-harvesting application. *IEEE Trans Ultrason Ferroelectr Freq Control* 53:631–638
47. Turik AV, Topolov VYu, Aleshin VI (2000) On a correlation between remanent polarization and piezoelectric coefficients of perovskite-type ferroelectric ceramics. *J Phys D Appl Phys* 33:738–743
48. Turik AV, Chernobabov AI (1977) On an orientation contribution in dielectric, piezoelectric and elastic constants of ferroelectric ceramics. *Zh Tekh Fiz* 47:1944–1948 (in Russian)
49. Aleshin VI (1991) Spherical inclusion in an anisotropic piezo-active medium. *Kristallografiya* 36:1352–1357 (in Russian)
50. Aleshin VI (1987) Properties of textures being formed on the basis of non-180° reorientations. *Kristallografiya* 32:422–426 (in Russian)
51. Bondarenko EI, Topolov VYu, Turik AV (1990) The effect of 90° domain wall displacements on piezoelectric and dielectric constants of perovskite ceramics. *Ferroelectrics* 110:53–56
52. Bondarenko EI, Topolov VYu, Turik AV (1991) The role of 90° domain wall displacements in forming physical properties of perovskite ferroelectric ceramics. *Ferroelectr Lett Sect* 13: 13–19
53. Topolov VYu, Bondarenko EI, Turik AV, Chernobabov AI (1993) The effect of domain structure on electromechanical properties of  $\text{PbTiO}_3$ -based ferroelectrics. *Ferroelectrics* 140:175–181
54. Turik AV, Topolov VYu (1997) Ferroelectric ceramics with a large piezoelectric anisotropy. *J Phys D Appl Phys* 30:1541–1549
55. Ruschmeyer K, Helke G, Koch J, Lubitz K, Möckl T, Petersen A, Riedel M, Schönecker A (1995) *Piezokeramik: Grundlagen, Werkstoffe, Applikationen*. Expert-Verlag, Renningen-Malmsheim
56. Algueró M, Alemany C, Pardo L, González AM (2004) Method for obtaining the full set of linear electric, mechanical and electromechanical coefficients and all related losses of a piezoelectric ceramic. *J Am Ceram Soc* 87:209–215
57. Dantsiger AYa, Razumovskaya ON, Reznitchenko LA, Grineva LD, Devlikanova RU, Dudkina SI, Gavrilyachenko SV, Dergunova NV, Klevtsov AN (1994) Highly effective piezoceramic materials (Handbook). *Kniga*, Rostov-on-Don (in Russian)
58. Haertling G (1999) Ferroelectric ceramics: history and technology. *J Am Ceram Soc* 82: 797–818
59. Zhang R, Jiang B, Cao W (2001) Elastic, piezoelectric, and dielectric properties of multidomain  $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $0.33\text{PbTiO}_3$  single crystals. *J Appl Phys* 90:3471–3475
60. Zhang R, Jiang W, Jiang B, Cao W (2002) Elastic, dielectric and piezoelectric coefficients of domain engineered  $0.70\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $0.30\text{PbTiO}_3$  single crystal. In: Cohen RE (ed) *Fundamental physics of ferroelectrics*. Melville, American Institute of Physics, pp 188–197

61. Liu G, Jiang W, Zhu J, Cao W (2011) Electromechanical properties and anisotropy of single- and multi-domain  $0.72\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $0.28\text{PbTiO}_3$  single crystals. *Appl Phys Lett* 99:162901–162903
62. Yin J, Jiang B, Cao W (2000) Elastic, piezoelectric, and dielectric properties of  $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $0.045\text{PbTiO}_3$  single crystals. *IEEE Trans Ultrason Ferroelectr Freq Control* 47:285–291
63. Zhang R, Jiang B, Cao W, Amin A (2002) Complete set of material constants of  $0.93\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $0.07\text{PbTiO}_3$  domain engineered single crystal. *J Mater Sci Lett* 21: 1877–1879
64. Newnham RE, Skinner DP, Cross LE (1978) Connectivity and piezoelectric-pyroelectric composites. *Mater Res Bull* 13:525–536
65. Gururaja TR, Safari A, Newnham RE, Cross LE (1988) Piezoelectric ceramic-polymer composites for transducer applications. In: Levinson LM (ed) *Electronic ceramics: properties, devices, and applications*. Marcel Dekker, New York, pp 92–128
66. Topolov VYu, Glushanin SV (2002) Evolution of connectivity patterns and links between interfaces and piezoelectric properties of two-component composites. *J Phys D Appl Phys* 35:2008–2014
67. Swallow LM, Luo JK, Siores E, Patel I, Dodds D (2008) A piezoelectric fibre composite based energy harvesting device for potential wearable applications. *Smart Mater Struct* 17:025017
68. Qi Y, McAlpine MC (2010) Nanotechnology-enabled flexible and biocompatible energy harvesting. *Energy Environ Sci* 3:1275–1285
69. Guyomar D, Lallart M (2011) Recent progress in piezoelectric conversion and energy harvesting using nonlinear electronic interfaces and issues in small scale implementation. *Micromachines* 2:274–294
70. Bechmann R (1956) Elastic, piezoelectric, and dielectric constants of polarized barium titanate ceramics and some applications of the piezoelectric equations. *J Acoust Soc Am* 28:347–350
71. Huang JH, Kuo W-S (1996) Micromechanics determination of the effective properties of piezoelectric composites containing spatially oriented short fibers. *Acta Mater* 44:4889–4898
72. Dunn ML, Taya M (1993) Electromechanical properties of porous piezoelectric ceramics. *J Am Ceram Soc* 76:1697–1706
73. Levassort F, Lethiecq M, Millar C, Pourcelot L (1998) Modeling of highly loaded 0–3 piezoelectric composites using a matrix method. *IEEE Trans Ultrason Ferroelectr Freq Control* 45:1497–1505
74. Levassort F, Lethiecq M, Certon D, Patat F (1997) A matrix method for modeling electroelastic moduli of 0–3 piezo-composites. *IEEE Trans Ultrason Ferroelectr Freq Control* 44:445–452
75. Jaffe B, Cook WR, Jaffe H (1971) *Piezoelectric ceramics*. Academic Press, London
76. Ikegami S, Ueda I, Nagata T (1971) Electromechanical properties of  $\text{PbTiO}_3$  ceramics containing La and Mn. *J Acoust Soc Am* 50:1060–1066
77. Xu Y (1991) *Ferroelectric materials and their applications*. North-Holland, Amsterdam
78. Nagatsuma K, Ito Y, Jyomura S, Takeuchi H, Ashida S (1985) Elastic properties of modified  $\text{PbTiO}_3$  ceramics with zero temperature coefficients. In: Taylor GW (ed) *Ferroelectricity and related phenomena*, vol 4. Piezoelectricity. Gordon and Breach Science Publishers, New York, pp 167–176
79. Levassort F, Thi MP, Hemery H, Marechal P, Tran-Huu-Hue L-P, Lethiecq M (2006) Piezoelectric textured ceramics: effective properties and application to ultrasonic transducers. *Ultrasonics* 441(Suppl. 1):e621–e626

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