

Effective Electromechanical Properties in Piezo-composites

2.1 Piezoelectric Medium and Its Properties

The appearance of an electric polarisation in quartz single crystals that were subjected to a mechanical load was first reported by brothers P. Curie and J. Curie in experimental work in 1880 [1]. The effect that links a mechanical action (stress or strain) with an electric response (electric field, displacement or polarisation) is called *the piezoelectric effect* or, more exactly, the *direct piezoelectric effect*. At a later date, it was experimentally established that the *converse piezoelectric effect* is also observed in acentric single crystals in that an external electric field generates a mechanical response, *i.e.*, a stress or strain of the sample [2, 3], similar to the electrostriction of dielectrics [3, 4].

It is generally realised that the piezoelectric effect reflects a linear relationship between electric and mechanical variables and originates from the displacement of ions of an acentric single crystal under an applied electrical field [1–4]. This relationship enables a change in the sign of the effect by switching the external electric field, unlike electrostriction that always exhibits a quadratic effect [3, 4] and does not undergo switching. Despite the linear character, the piezoelectric response of a single crystal is often intricate owing to various interconnections between the piezoelectric and other properties such as the elastic, dielectric and thermal properties [3].

A general consideration of the piezoelectric effect in single crystals is undertaken using 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 single crystal. The first argument can be either mechanical stress σ_{kl} or mechanical strain ξ_{jrs} , the second argument can be electric field \mathbf{E} or electric displacement (electric flux density) \mathbf{D} , and the third argument can be temperature T or entropy S . In addition, it is possible to develop additional arguments in terms of magnetic field \mathbf{H} or magnetic induction \mathbf{B} [5]. Based on knowledge of the thermodynamic functions and relations between the arguments of

the mechanical, electric and thermal states, it is possible to describe the linked “response – actions” in terms of ξ_{jr} , E_i and T as follows:

$$\sigma_{kl} = c_{kljr}^E \xi_{jr} - e_{ikl} E_i + \beta_{kl} \Delta T \quad (2.1)$$

$$D_i = e_{ikl} \xi_{kl} + \varepsilon_{if}^E E_f + p_i \Delta T \quad (2.2)$$

$$\Delta S = \beta_{jr} \xi_{jr} + p_i E_i + (\rho / T_0) c \Delta T \quad (2.3)$$

In Equations 2.1–2.3 the constants written in the tensor form are elastic moduli at constant electric field (c_{kljr}^E), piezoelectric coefficients (e_{ikl}), coefficients of thermal stress (β_{kl}), dielectric permittivities at constant mechanical strain (ε_{if}^E), pyroelectric coefficients (p_i), density (ρ), and specific heat (c). The increments ΔT and ΔS 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 single crystal. It is assumed that the linear relations in Equations 2.1 – 2.3 hold in the case of relatively weak external fields. For example, the dependence $\sigma_{kl}(\xi_{jr})$ from Equation 2.1 obeys Hooke’s law in an anisotropic medium at small strains ξ_{jr} . The dependence $D_i(E_f)$ from Equation 2.2 is linear at relatively low levels of the electric field E_f applied to the single crystal. With regard to ferroelectric single crystals, 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 acentric linear dielectric single crystals. It is well known that in the presence of a low electric field, the polarisation of ferroelectric single crystals linearly depends on field [3, 4] so that domain-wall displacements are reversible and no nuclei of reoriented domains will form. 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, 6].

Equations 2.1 – 2.3 enable the determination of a set of isothermal constants for a single crystal. An analogous set of adiabatic constants can also be derived using the 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 single crystals is approximately 1% or less [3, 5].

The effect of thermal fields on the elastic and electric responses of piezoelectrics is often neglected, and the description of the piezoelectric effect is carried out on the basis of Equations 2.1 and 2.2 at $\Delta T = 0$. These equations written in the matrix form then reduce to [2, 3]

$$\sigma_p = c_{pq}^E \xi_q - e_{fp} E_f \quad (2.4)$$

$$D_k = e_{kl} \xi_l + \varepsilon_{kr}^E E_r \quad (2.5)$$

and represents the first pair of piezoelectric equations linking the variables of strain

and field (ξ, E). The first term in the right part of Equation 2.5, $P_k = e_{kl}\xi_l$, describes the piezoelectric polarisation produced by an external strain as a result of the *direct* piezoelectric effect. In addition, the *converse* piezoelectric effect is described by the $e_{fp} E_f$ term in Equation 2.4. 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:

$$\xi_p = s_{pq}^E \sigma_q + d_{fp} E_f \quad (2.6)$$

$$D_k = d_{kl} \sigma_l + \varepsilon_{kr}^\sigma E_r \quad (2.7)$$

in variables (σ, E),

$$\xi_p = s_{pq}^D \sigma_q + g_{fp} D_f \quad (2.8)$$

$$E_k = -g_{kl} \sigma_l + \beta_{kr}^\sigma D_r \quad (2.9)$$

in variables (σ, D) and

$$\sigma_p = c_{pq}^D \xi_q - h_{fp} D_f \quad (2.10)$$

$$E_k = -h_{kl} \xi_l + \beta_{kr}^\xi D_r \quad (2.11)$$

in variables (ξ, D). Superscripts σ and D denote measurement conditions at $\sigma = \text{const}$ and $D = \text{const}$, respectively, constants β_{kr}^σ and β_{kr}^ξ are determined using equalities $\beta_{kr}^\sigma \varepsilon_{rv}^\sigma = \delta_{kv}$ and $\beta_{kr}^\xi \varepsilon_{rv}^\xi = \delta_{kv}$, and 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. It should be noted that Equations 2.4–2.11 contain four types of piezoelectric coefficients, namely e_{kl} , d_{kl} , g_{kl} , and h_{kl} .

The piezoelectric coefficient e_{kl} (stress coefficient) relates the electric field to the mechanical stress (Equation 2.4) and the mechanical strain to the electric displacement (Equation 2.5). The piezoelectric coefficient d_{kl} (charge coefficient) characterises the relation between the electric field and the mechanical strain (Equation 2.6) and the relation between the mechanical stress and the electric displacement (Equation 2.7). The piezoelectric coefficient g_{kl} (voltage coefficient) is introduced to relate the electric displacement to the mechanical strain (Equation 2.8) and the mechanical stress to the electric field (Equation 2.9). Finally, the piezoelectric coefficient h_{kl} (strain coefficient) relates the electric displacement to the mechanical stress (Equation 2.10) and the mechanical strain to the electric field (Equation 2.11). In general, 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 introduced in Equations 2.4–2.11 are defined to be components of the third-rank tensors, but written in the

matrix form (with two subscripts) [2–6] only. These individual piezoelectric coefficients can be used to aid in the selection of piezoelectric materials for specific 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.*, a high d_{kl}). For a pressure sensor, the electric field generated per unit mechanical stress is likely to be important (*i.e.*, a high g_{kl}).

The interrelationships of the piezoelectric coefficients follow from the thermodynamic description [2, 3] and are expressed by a set of equalities

$$d_{fp} = \varepsilon_{jk}^{\sigma} g_{kp} = e_{fq} s_{qp}^E \quad (2.12)$$

$$e_{fp} = \varepsilon_{jk}^{\xi} h_{kp} = d_{fq} c_{qp}^E \quad (2.13)$$

$$g_{fp} = \beta_{jk}^{\sigma} d_{kp} = h_{fq} s_{qp}^D \quad (2.14)$$

$$h_{fp} = \beta_{jk}^{\xi} e_{kp} = g_{fq} c_{qp}^D \quad (2.15)$$

All four types of piezoelectric coefficients from Equations 2.12–2.15 are also involved in relations [2] between dielectric or elastic constants measured on different conditions:

$$\varepsilon_{kr}^{\sigma} - \varepsilon_{kr}^{\xi} = d_{kf} e_{rf} \quad (2.16)$$

$$\beta_{kr}^{\xi} - \beta_{kr}^{\sigma} = g_{kf} e_{rf} \quad (2.17)$$

$$c_{pq}^D - c_{pq}^E = e_{fp} h_{fq} \quad (2.18)$$

$$s_{pq}^D - s_{pq}^E = d_{fp} g_{fq} \quad (2.19)$$

The close connections between the elastic, piezoelectric and dielectric constants of a single crystal (see Equations 2.12–2.19) or a piezoelectric medium enable them to be collectively described as *electromechanical constants*. These constants characterise *electromechanical properties* in a variety of piezo-active materials, such as piezoelectric or ferroelectric single crystals, poled ferroelectric ceramics, thin ferroelectric films, piezo-composites, *etc.*

It follows from Equations 2.1, 2.2 and 2.4–2.11 that the piezoelectric properties are described by third-rank tensors and are represented in the matrix form. Tables of matrices of the piezoelectric coefficients of the different symmetry classes have been collected in a series of monographs [2–5]. It should be noted that the matrices of the piezoelectric coefficients $\|d\|$ and $\|g\|$ differ from the matrices of the piezoelectric coefficients $\|e\|$ and $\|h\|$ for 3, 32, $3m\bar{6}$, and $\bar{6}m2$ classes [2, 3]. The conditions for measuring the piezoelectric coefficients are concerned with the electric and mechanical variables that are fixed for the direct or converse piezoelectric effect. For example, if the direct piezoelectric effect is considered, then the corresponding piezoelectric coefficients are measured under the following conditions [3]: $\xi = 0$ and $E = 0$ (for d_{kl}), $\xi = 0$ and $D = 0$ (for g_{kl}), $\sigma = 0$ and $D = 0$ (for h_{kl}), and $\sigma = 0$ and $E = 0$ (for e_{kl}). In the case of the converse piezoelectric

effect, the following conditions should be used: $\sigma = 0$ and $E = \text{const}$ (for d_{kl}), $\sigma = 0$ and $D = \text{const}$ (for g_{kl}), $\xi = 0$ and $D = \text{const}$ (for h_{kl}), and $\xi = 0$ and $E = \text{const}$ (for e_{kl}). The above-given conditions are determined on the basis of Equations 2.4–2.11 for the four types of piezoelectric coefficients.

It has been shown that there are close connections between the variety of electromechanical constants, and two groups of these constants (*i.e.*, piezoelectric / dielectric and elastic / piezoelectric) are described by Equations 2.12–2.19. The elastic, piezoelectric and dielectric constants are factors that ultimately measure the effectiveness of the conversion of electric energy into mechanical energy and vice versa. From the analysis of energy conversion [6], the effectiveness strongly depends on differences between dielectric permittivities from Equation 2.16 or differences between elastic compliances from Equation 2.19, and these differences stem from the piezoelectric properties in the medium. In a general form, the effectiveness of the energy conversion is described by an electromechanical coupling factor [3, 5, 6]

$$k = w_{\text{piezo}} / \sqrt{w_{\text{el}} w_{\text{mech}}} \quad (2.20)$$

and is expressed in terms of volume densities of piezoelectric (or mutual) energy $w_{\text{piezo}} = \sigma_i d_{mi} E_m / 2$, electric energy $w_{\text{el}} = E_k \epsilon_{kr}^\sigma E_r / 2$, and mechanical energy $w_{\text{mech}} = \sigma_p s_{pq}^E \sigma_q / 2$. The k^2 value determined using Equation 2.20 characterises [2–6] a ratio of stored mechanical energy to electric energy input or a ratio of stored electric energy to mechanical energy input. The absolute value of the electromechanical coupling factor depends [2, 4, 6] on the vibration mode, measurement methodology, sample shape, and the electromechanical constants of the piezoelectric material.

To date, we have considered the constitutive equations and the electromechanical properties in linear piezo-active media. Equations 2.4–2.11 are often used to describe the linear behaviour of ferroelectric single crystals (single-domain, polydomain or unipolar) [3, 4] poled ferroelectric ceramics (piezo-ceramics) [6, 7] and piezo-active composites [5] under weak electric and mechanical fields. As discussed by Hall [7], the linear description provides a reasonable approximation of the functional characteristics of piezo-ceramics at low levels of the applied electric field and stress, but becomes increasingly inaccurate as these levels increase. Non-linear behaviour of the electromechanical properties in various perovskite-type ferroelectric ceramics is observed above the *threshold* values [7] of the electric field E_{thr} and mechanical stress σ_{thr} . According to data [7], the typical values equal $E_{\text{thr}} \approx 10 \text{ kV / m}$ for “soft” PZT ceramics (*i.e.*, Pb(Zr, Ti)O₃-type ceramics with low coercive field E_c) and $E_{\text{thr}} \approx 300 \text{ kV / m}$ for well-aged “hard” PZT ceramics (*i.e.*, having high E_c values). Similarly, non-linearity of mechanical properties in both the “soft” and “hard” PZT ceramics becomes evident as mechanical stress exceeds $\sigma_{\text{thr}} \approx 20 \text{ MPa}$ [7].

The hysteresis and non-linear behaviour of electromechanical properties in ferroelectric single crystals and ceramics are associated with the reorientation of the spontaneous polarisation vectors \mathbf{P}_s of domains under the external electric field

[3, 4, 6, 7]. The domain structure of ferroelectrics is of interest due to the significant influence of both the domain arrangement and reorientations on the electromechanical properties in these materials. Ferroelectric single crystals with the perovskite-type structure represent the vast group of multiaxial ferroelectrics and have various 180° and non- 180° domain structures in ferroelectric phases [3, 4]. Many examples of complicated domain structures have also been studied [4] in related perovskite-type ferroelectric ceramics. An effect of the domain structure on the electromechanical properties in the well-known perovskite-type single crystals has been studied for cases of the 180° (BaTiO_3 [8]) and 90° (BaTiO_3 [9], PbTiO_3 [10]) domains in the ferroelectric $4mm$ phase. The domain structures are characterised [8–10] as regular laminar structures (Figure 2.1) with planar domain walls that are motionless under weak external fields.

An orientation contribution caused by the elastic (or reversible) 90° domain-wall displacements under applied electric fields has been determined [11] for BaTiO_3 single crystals separated into 90° domains. The contribution of domain orientation to the electromechanical constants of a single crystal strongly depends on the mobility of the 90° domain walls within the material. The important role of the 60° , 90° and 120° domain-wall displacements on the piezoelectric coefficient d_{33} of the polydomain KNbO_3 single crystal ($mm2$ phase) has been analysed in ref. [12]. The contributions of domain-wall displacements to the d_{33} under an electric field correlate with some crystallographic characteristics of the non- 180° domain structures.

Full sets of the electromechanical constants of polydomain single crystals are used to study the relationships between electromechanical properties in a single grain and a poled ceramic [10, 13–15] consisting of a large number of grains with different orientations of main crystallographic axes. This study is based on solving a problem [13, 14] 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 [13, 14] that takes into account not only the piezoelectric effect but also the anisotropy of the piezoelectric properties in the grain and the ceramic medium. This anisotropy can be considerable, particularly in the presence of non- 180° domain reorientations in the grains [16]. Modelling of the 180° and 90° reorientations under an electric field results in the full set of the electromechanical constants, calculated for the BaTiO_3 ceramic [16] at various values of P_r / P_s , where P_r is the remanent polarisation of the ceramic and P_s is the spontaneous polarisation of the separate domain. In addition, the effect of the 90° domain-wall displacements within the grains on the electromechanical properties in poled BaTiO_3 ceramic was studied in [11, 17, 18] where contributions from these domain-wall displacements to a variety of constants for the ceramic were evaluated. Of particular interest is the significant contribution of domain-wall displacements (37–72%) to the piezoelectric coefficients d_{3j} [17, 18]. The analogous contribution to the elastic compliances s_{pq}^E is evaluated to be in a range from 11 to 43 % [18]. Differences between the experimental [6] and averaged [13] constants of the BaTiO_3 ceramic were accounted for by the evaluated contributions [11, 17, 18] from the 90° domain-wall displacements.

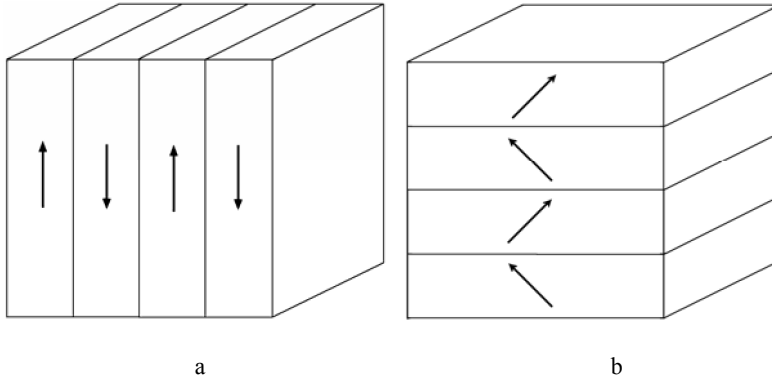


Figure 2.1. Schematic representation of the polydomain single crystal with the 180° (a) or 90° (b) domain structure. Spontaneous polarisation vectors of the domains are shown by arrows

In contrast to BaTiO₃ ceramics, the electromechanical properties in the PbTiO₃ ceramic are determined [10, 15] in the absence of 90° domain-wall displacements within the grains. According to results [15, 19], 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 the PbTiO₃-type ceramics. In particular, it is possible to attain large piezoelectric anisotropy (*i.e.*, $d_{33} / |d_{31}| \gg 1$) by doping the ceramic [20], varying temperature [15] and by changing the volume fractions of the 90° domains [15] within the ceramic grains.

A comparative analysis of the linear and non-linear effective properties in BaTiO₃ ceramics was carried out within the framework of the model of a polydomain grain in an effective medium [21, 22]. Results on the modelling of the piezoelectric behaviour of the ceramic and on the electromechanical properties determined using the effective medium method demonstrates that the non-linear behaviour is a result of 90° domain-wall displacements in the grains. These displacements in the presence of an externally applied field become an important extrinsic factor that influences the piezoelectric coefficients d_{fp} of the ceramic at different poling states. For the fully poled BaTiO₃ ceramic, the aforementioned contributions from the 90° domain-wall displacements to d_{fp} attain 68 % and 64 % [22] for $fp = 31$ and 33, respectively.

Therefore, subsequent averaging procedures facilitate the consideration of the hierarchy-of-properties chain of “single-domain single crystal – polydomain single crystal – ceramic” in the presence of the 90° domain-wall displacements (BaTiO₃) or on condition of the motionless 90° domain walls (PbTiO₃) [10, 13, 15, 19, 20]. The main aims are to analyse factors that influence the piezoelectric properties in the related ferroelectric materials and to study the correlation between the microstructure, domain-wall displacements and electromechanical properties in the ferroelectric ceramic. Knowledge of the full sets of the electromechanical constants of ferroelectric ceramics enables appropriate material selection for various piezotechnical applications and offers a route to using the ceramics as piezo-active components for composite materials.

At present, there is a limited number of full sets of electromechanical constants available in the literature for poled ferroelectric ceramics, primarily due to the effort involved in manufacturing and poling a variety of test samples. Electromechanical constants are often measured using standard methods [23, 24] at room temperature and with weak electric fields. The majority of the ferroelectric ceramics are manufactured as perovskite-type solid solutions [3–5, 25–27] with compositions varied and tailored to improve specific properties. Attempts to classify the ferroelectric ceramics have been made in different papers [25–27]. From the classification scheme [25] 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 that are stable with regard to electric and mechanical actions, materials with high dielectric permittivity ε_{33}^σ , materials having high sensitivity with respect to mechanical stress fields (high piezoelectric coefficients g_{fp}), materials with the large piezoelectric anisotropy d_{33} / d_{31} , materials with high stability to the 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 [26], the $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ -based ceramics are divided into four groups with specific performances. These groups are related to molar concentrations of Ti from 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 are mentioned [26] in connection with a variety of piezotechnical applications.

Examples of the ferroelectric ceramics and full sets of their room-temperature electromechanical constants used in Equations 2.4 and 2.5 are listed in Table 2.1. Analogous sets related to the advanced relaxor-ferroelectric single crystals with engineered domain structures are also shown in Table 2.2 for comparison. Differences between the individual constants of the materials with the same composition (e.g., BaTiO_3 and $(\text{Pb}_{0.9625}\text{La}_{0.025})(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ ceramics from Table 2.1 or the $0.70\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.30\text{PbTiO}_3$ single crystals from Table 2.2) are the result of technological, microstructural and poling factors, the selection of a composition in the proximity of the MPB, fluctuations of the composition over samples and a variable mobility of the domain walls. These factors can influence the domain structures [44], heterophase states [45, 46] and electromechanical properties [47]. For example, changes in volume fractions of the 90° domains or in the mobility of the 90° domain walls in the grains of the PbTiO_3 -type ceramics affect their piezoelectric and other properties [15, 19, 26, 47]. Furthermore, in the presence of an external electric field \mathbf{E} , displacements of interfaces separating morphotropic phases in the $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.08\text{PbTiO}_3$ single crystal promote an appreciable contribution to the piezoelectric coefficient d_{33} [46]. This contribution can exceed 50 % in a wide E range. The full sets of experimental electromechanical constants from Tables 2.1 and 2.2 have been used in our study on the piezo-composites, and we will analyse and discuss the results in Chapters 3–6.

In the next section we consider some of the physical factors that influence the effective properties of two-component composites based on ferroelectrics.

Table 2.1. Experimental room-temperature values of elastic moduli c_{pq}^E (in 10^{10} Pa),^a piezoelectric coefficients e_{fp} (in C / m²) and dielectric permittivities ϵ_{ff}^ϵ of ferroelectric ceramics

	BaTiO₃ [28]^b	BaTiO₃ [6]^b	(Ba_{0.917}Ca_{0.083}) ·TiO₃ [6, 29]	(Pb_{0.9625}La_{0.025}) ·(Ti_{0.99}Mn_{0.01})O₃ (I) [30]^b	(Pb_{0.855}Nd_{0.11}) ·(Ti_{0.94}Mn_{0.02} ·In_{0.04})O₃ [31]	
c_{11}^E	16.6	15.0	15.8	14.33	17.3	
c_{12}^E	7.66	6.6	6.91	3.220	5.31	
c_{13}^E	7.75	6.6	6.75	2.413	5.68	
c_{33}^E	16.2	14.6	15.0	13.16	16.6	
c_{44}^E	4.29	4.4	4.51	5.587	6.09	
e_{31}	-4.34	-4.35	-3.14	0.4584	2.00	
e_{33}	18.6	17.5	13.5	6.499	8.81	
e_{15}	11.6	11.4	10.9	5.923	4.84	
$\epsilon_{11}^\epsilon / \epsilon_0$	1270	1115	1000	210	270	
$\epsilon_{33}^\epsilon / \epsilon_0$	1420	1260	910	140	198	
	(Pb_{0.9625}La_{0.025}) ·(Ti_{0.99}Mn_{0.01})O₃ (II) [31]^b		(Pb_{0.85}Nd_{0.10}) ·(Ti_{0.99}Mn_{0.01})O₃ [31]	(Pb, Ca)TiO₃ [32]	TBK-3 [5]^c	TBK5 [5]^d
c_{11}^E	15.8		17.5	15.05	15.7	14.6
c_{12}^E	4.20		5.49	3.68	6.3	5.18
c_{13}^E	4.55		5.65	3.09	6.2	5.06
c_{33}^E	15.2		16.5	12.78	15.3	14.2
c_{44}^E	6.32		6.26	1.20	4.4	4.9
e_{31}	1.32		1.80	1.71	-3.2	-0.68
e_{33}	6.80		8.83	8.8	12.5	7.71
e_{15}	3.35		5.41	0.33	9.1	4.56
$\epsilon_{11}^\epsilon / \epsilon_0$	203		265	170	950	410
$\epsilon_{33}^\epsilon / \epsilon_0$	133		193	140	950	336
	NBS-1 [5]^e	ZTBS-3 [5]^f	ZTS-19 [5]^g	PZT-4 [6]^g	PZT-5 [6]	PZT-5A [32]
c_{11}^E	11.0	15.1	10.9	13.9	12.1	12.04
c_{12}^E	4.22	7.9	6.1	7.78	7.54	7.52
c_{13}^E	4.12	8.0	5.4	7.43	7.52	7.51
c_{33}^E	10.0	13.6	9.3	11.5	11.1	11.09
c_{44}^E	3.45	2.9	2.4	2.56	2.11	2.3
e_{31}	-3.3	-7.9	-4.9	-5.2	-5.4	-5.4
e_{33}	14.8	17.7	14.9	15.1	15.8	15.8
e_{15}	7.7	15.4	10.6	12.7	12.3	12.3
$\epsilon_{11}^\epsilon / \epsilon_0$	900	1610	820	730	916	540
$\epsilon_{33}^\epsilon / \epsilon_0$	890	1280	840	635	830	830

Table 2.1 (*continued*)

	PZ 27 [33]	PZ 34 [33]	PCR-1 [25]^h	PCR-7 [25]	PCR-7M [25]	PCR-8 [25]
c_{11}^E	14.28	18.84	16.0	12.5	13.3	14.4
c_{12}^E	9.98	8.02	10.1	8.4	9.2	8.5
c_{13}^E	9.22	8.23	9.6	8.1	9.1	7.7
c_{33}^E	11.45	12.72	13.3	12.1	12.5	11.6
c_{44}^E	2.28	5.89	2.58	2.36	2.28	2.83
e_{31}	-3.71	3.81	-3.7	-9.0	-9.5	-7.5
e_{33}	15.77	6.87	11.1	28.3	31.1	13.6
e_{15}	11.74	2.31	10.8	17.9	20.0	11.6
$\varepsilon_{11}^s/\varepsilon_0$	1121	181	570	1430	1980	830
$\varepsilon_{33}^s/\varepsilon_0$	878	154	300	1350	1810	740
	PCR-13 [25]	PCR-21 [25]	PCR-62 [25]	PCR-63 [25]	PCR-73 [25]	
c_{11}^E	11.9	13.4	12.7	14.1	17.3	
c_{12}^E	4.8	7.3	4.5	6.6	13.3	
c_{13}^E	3.1	6.2	0.8	5.6	12.5	
c_{33}^E	10.0	11.8	11.3	11.2	14.4	
c_{44}^E	3.50	2.45	4.70	4.15	2.29	
e_{31}	-6.0	-7.3	-6.6	-4.6	-9.1	
e_{33}	10.4	16.2	8.9	11.8	29.2	
e_{15}	7.1	12.0	6.0	6.9	22.4	
$\varepsilon_{11}^s/\varepsilon_0$	710	890	560	830	2220	
$\varepsilon_{33}^s/\varepsilon_0$	710	890	590	1000	2380	

Notes to Table 2.1

- a. Ferroelectric ceramics poled along the OX_3 axis are characterised [2–6] by ∞mm symmetry and a relation $c_{66} = (c_{11}^E - c_{12}^E) / 2$
- b. Different processing conditions lead to different sets of the electromechanical constants as shown for the BaTiO_3 and $(\text{Pb}_{0.9625}\text{La}_{0.025})(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ ceramics
- c. Based on $(\text{Ba}_x\text{Ca}_{1-x})\text{TiO}_3$
- d. Based on $(\text{Ba}_x\text{Ca}_{1-x-y}\text{Pb}_y)\text{TiO}_3$
- e. Based on $(\text{Ba}_{1-x}\text{Pb}_x)\text{Nb}_2\text{O}_6$
- f. Based on $(\text{Ba}_{1-x}\text{Pb}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$
- g. Based on $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$
- h. PCR is the abbreviation for the group “piezoelectric ceramics from Rostov-on-Don”. These materials based mainly on $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ are manufactured [25] by the conventional method (PCR-13 and PCR-62) or by means of hot pressing (PCR-1, PCR-7, PCR-7M, PCR-8, PCR-21, PCR-63, and PCR-73)

Table 2.2. Experimental room-temperature values of elastic moduli c_{pq}^E (in 10^{10} Pa), piezoelectric coefficients e_{jp} (in C / m²) and dielectric permittivities ϵ_{jj}^E of (1 - x)Pb(A_{1/3}Nb_{2/3})O₃ - xPbTiO₃ single crystals (4mm symmetry)

	A= Mg, x= 0.30 [34]	A= Mg, x= 0.30 [35]	A= Mg, x= 0.33 [36]	A= Mg, x= 0.38 [37]	A= Mg, x= 0.42 [38]	A= Zn, x= 0.045 [39]	A= Zn, x= 0.07 [40]
c_{11}^E	11.7	16.04	11.5	21.25	17.51	11.1	11.3
c_{12}^E	10.3	14.96	10.3	14.33	8.51	10.2	10.3
c_{13}^E	10.1	7.51	10.2	13.51	8.3	10.1	10.5
c_{33}^E	10.8	12.0	10.3	9.92 ^a	10.5	10.5	10.91
c_{44}^E	7.1	5.38	6.9	5.56	2.85	6.4	6.30
c_{66}^E	6.6	2.87	6.6	6.95	8.0	6.3	7.10
e_{31}	-2.4	-5.22	-3.9	-3.26	-2.1	-3.7	-2.3
e_{33}	27.1	30.4	20.3	11.46	12.2	15.0	15.1
e_{15}	13.6	31.84	10.1	21.12	37.50 ^c	8.9	11.1
$\epsilon_{11}^E / \epsilon_0$	3307	4963	1434	2171 ^b	3054	3000	2779
$\epsilon_{33}^E / \epsilon_0$	1242	1386	680	255	259	1000	823

	A = Zn, x = 0.08 [41]	A = Zn, x = 0.08 [42]	A = Zn, x = 0.08 [43]
c_{11}^E	11.5	11.1	11.47
c_{12}^E	10.5	10.2	10.30
c_{13}^E	10.9	9.97	10.37
c_{33}^E	11.51	10.2	10.71
c_{44}^E	6.34	6.1	6.70
c_{66}^E	6.50	6.56	3.05
e_{31}	-5.1	-9.15	-5.83
e_{33}	15.4	12.2	12.60
e_{15}	10.1	9.39	6.22
$\epsilon_{11}^E / \epsilon_0$	2720	2848	1415
$\epsilon_{33}^E / \epsilon_0$	984	620	560

Notes to Table 2.2

a. According to our calculations based on formula [2] $c_{pq}^E s_{qr}^E = \delta_{pr}$ and values $s_{11}^E = 11.73$, $s_{12}^E = -2.71$, $s_{13}^E = -8.17$, and $s_{33}^E = 21.53$ (in 10^{-12} Pa⁻¹) [37], it would be $c_{33}^E = 14.89 \times 10^{10}$ Pa instead of 9.92×10^{10} Pa

b. According to our calculations based on formula [2] $\epsilon_{kr}^E = \epsilon_{kr}^\sigma (1 - k_{15}^2)$ and experimental values $\epsilon_{11}^\sigma / \epsilon_0 = 4301$ and $k_{15} = 0.459$ [37], it would be $\epsilon_{11}^E / \epsilon_0 = 3395$ instead of 2171. The value $\epsilon_{11}^E / \epsilon_0 = 3395$ would also be attained using Equation 2.16, $\epsilon_{11}^\sigma / \epsilon_0 = 4301$, $d_{15} = 380$ pC / N, and $e_{15} = 21.12$ C / m² from ref. [37]

c. According to our calculations based on Equation 2.13 and experimental values $d_{15} = 131$ pC / N and $c_{44}^E = 2.85 \times 10^{10}$ Pa [38], it would be $e_{15} = 3.73$ C / m² instead of 37.50 C / m²

2.2 Sum, Combination and Product Properties

Ferroelectrics and related piezo-active materials are characterised by the full sets of electromechanical constants that are listed in Tables 2.1 and 2.2. Ferroelectric ceramics and single crystals are used as components of piezo-composites and actively influence the effective properties of the composites. Each physical property of a piezo-composite is analytically determined using specific formulae or procedures of averaging (see, *e.g.*, [5, 32, 33]). The physical property can also be studied by experimental methods and characterisation. In the case of piezo-composites, results on averaging depend on the volume fractions of components and their properties, microstructure and connectivity [5, 33, 48, 49]. Numerous theoretical and experimental results point out that there are three main effects [48, 49] related to forming the effective properties in the piezo-composites, namely

- (i) the effect of the addition of the properties (forming the *sum* properties),
- (ii) the effect of the combination of the properties (forming the *combination* properties) and
- (iii) the effect of the generation of the properties (forming the *product* properties).

2.2.1 Sum Properties

For example, the effective property Y^* of a two-component piezo-composite¹ obeys a condition $Y^{(1)} < Y^* < Y^{(2)}$, where $Y^{(n)}$ is the analogous property of the n th component, $n = 1$ and 2 . Y^* belongs to the sum properties when it is characterised by a monotonic dependence (Figure 2.2a) on the volume fraction m of one of the components. It is the simplest example of the volume-fraction dependence of the effective property, that is determined by a general formula $Y^*(m) = Y^{(1)}m + Y^{(2)}(1 - m) + \Delta Y$, where ΔY depends on $Y^{(n)}$ and m and characterises deviations of $Y^*(m)$ from the linear dependence (compare solid and dotted lines in Figure 2.2a). Such behaviour is typical of elastic moduli c_{ab}^{*E} , piezoelectric coefficients d_{ij}^* and dielectric permittivities $\epsilon_{pr}^{*\sigma}$ of 0–3 or 1–3 composites [5, 50–54] comprising a PZT-type ceramic and a piezo-passive polymer.

2.2.2 Combination Properties

In this case, the properties $Y^{(n)}$ and $Z^{(n)}$ of the components ($n = 1$ and 2) form the effective properties $Y^*(m)$ and $Z^*(m)$ that are monotonic dependences (Figures 2.2a and b). It is assumed that $\Phi^{(n)}$ is expressed in terms of $Y^{(n)}$ and $Z^{(n)}$ and also

¹ Hereafter, we denote all of the effective constants and parameters of composites by an asterisk. Following Equations 2.6 and 2.7, the full set of effective constants is written as s_{pq}^{*E} , d_{jp}^* and $\epsilon_{kr}^{*\sigma}$. The similar set of the constants s_{pq}^{*D} , g_{jp}^* and $\beta_{kr}^{*\sigma}$ is derived from Equations 2.8 and 2.9. Finally, the full set of the effective constants c_{pq}^{*D} , h_{jp}^* and $\beta_{kr}^{*\epsilon}$ can be determined using Equations 2.10 and 2.11.

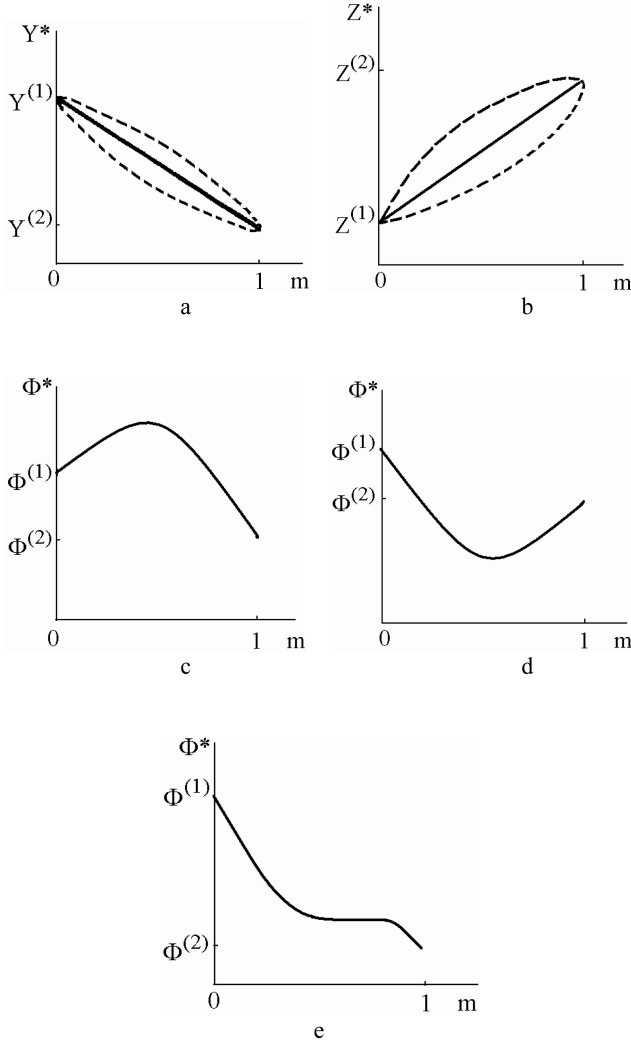


Figure 2.2. Sum properties $Y^*(m)$ and $Z^*(m)$ (a and b) and combinations properties $\Phi^*(m)$ (c–e) in two-component composites. m is the volume fraction of the first component. In graphs a and b, possible versions of the volume-fraction dependence are shown with dotted lines

characterises some property of the n th component. The monotonic character of $Y^*(m)$ and $Z^*(m)$ does not imply a monotonic volume-fraction behaviour of the effective property Φ^* . In this case a non-monotonic $\Phi^*(m)$ dependence (often with values $|\Phi^*(m)| > |\Phi^{(n)}|$, Figures 2.2c and d) is concerned with the effect of combination of the properties. This effect is important, for example, when considering the piezoelectric coefficients $g_{3j}^* = d_{3j}^* / \varepsilon_{33}^{*\sigma}$ and $h_{3j}^* = e_{3j}^* / \varepsilon_{33}^\varepsilon$ ($j = 1$ and 3) of various piezo-composites [50, 52, 54] (see also Sections 3.1–3.3 and 5.4).

Furthermore, the combination property $\Phi^*(m)$ can be described by a monotonic volume-fraction dependence (Figure 2.2e), but a configuration of the $\Phi^*(m)$ curve differs from both the $Y^*(m)$ and $Z^*(m)$ curves. The effect of combination of three properties (*i.e.*, elastic, piezoelectric and dielectric properties) is concerned with the volume-fraction dependence of electromechanical coupling factors of the 1–3 ceramic / polymer composites [32, 51].

2.2.3 Product Properties

The effect of generation of properties in a two-component composite is described as follows. It is assumed that a response V_1 of the first component is the result of an external action X . Simultaneously, the second component does not show a response on the action X , but generates only a response V_2 in response to V_1 . This implies that the internal action V_1 from the first component due to the external action X is the reason for the new response V_2 . As a result, the formation of product properties is associated with two different responses, V_1 and V_2 . Such an effect takes place, for example, in composites [55, 56] comprising one magnetostrictive (CoFe_2O_4 or other ferrites) and one piezoelectric (BaTiO_3 , PbTiO_3 or PZT-type) ceramics. In the presence of an external magnetic field, a mechanical strain is generated in the magnetostrictive ceramic. This strain is transferred into the piezoelectric component of the composite that generates an electric field in the piezoelectric ceramic. Thus, the magnetic field applied to the composite sample generates an electric field due to the combination of the magnetostrictive (but piezo-passive) and piezo-active (but showing no magnetostriction) components. In this composite the role of both the electromechanical and electromagnetic interactions between the components is obviously of importance.

In general, the product property appears due to the interaction of two components that have different properties being mutually complementary. Other examples of the product properties [49] in the composites based on ferroelectrics are concerned with pyroelectricity (taking into account piezoelectricity of the first component and thermal expansion of the second component) and photostriction (taking into account the photovoltaic effect in the first component and electrostriction in the second component).

Recent work [57–59] has been devoted to the study of more complicated effects in the piezo-composites and disordered piezo-active heterogeneous materials. Taking into account electric conductivities of the components, it is possible to achieve giant dielectric permittivity [57], giant piezoelectric and dielectric enhancement [58].

Our further consideration of the effective electromechanical properties is closely connected with examples of non-monotonic dependences of these properties that are often caused by the effect of the combination of properties. A transition to an analysis of the properties would be impossible without a characterisation of methods for determination of the effective properties in the piezo-composites with different connectivity patterns and components. These will now be described.

2.3 Methods for Evaluation of Effective Parameters

It is well known [2–6, 26, 29] that Equations 2.4–2.19 are valid not only for piezoelectric single crystals, but also for poled ferroelectric polydomain single crystals, ferroelectric ceramics and composites containing at least one piezo-active component. The applicability of Equations 2.4–2.19 to describe the electromechanical properties of piezo-composites is reasonable in cases when these properties can be regarded as effective (or overall), *i.e.*, characterising the response of the composite sample as a whole. The effective electromechanical properties and related parameters enable us to move away from the properties of the individual components, the specifics of microgeometry and other features of heterogeneous materials and to estimate the potential advantages and applications of these materials.

The problem of prediction of the effective physical properties in advanced 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 the piezo-composite is given in ref. [5]. Equations 2.4 and 2.5 are examples of constitutive equations that describe the behaviour of the piezo-active material under electric and mechanical fields. If averaged components of the electric field $\langle E_f \rangle$ and the mechanical strain $\langle \xi_q \rangle$ in a macroscopic region of the piezo-composite are independent of coordinates x_j ($j = 1, 2$ and 3), then Equations 2.4 and 2.5 can be rewritten as follows:

$$\langle \sigma_p \rangle = c_{pq}^{*E} \langle \xi_q \rangle - e_{fp}^* \langle E_f \rangle \quad (2.21)$$

$$\langle D_k \rangle = e_{kl}^* \langle \xi_l \rangle + \varepsilon_{kr}^{*\xi} \langle E_r \rangle \quad (2.22)$$

In Equations 2.21 and 2.22 elastic moduli c_{pq}^{*E} , piezoelectric coefficients e_{fp}^* and dielectric permittivities $\varepsilon_{kr}^{*\xi}$ constitute the full set of effective electromechanical constants of the piezo-composite. These constants are determined [5] taking into account equations of electric and mechanical equilibrium and boundary conditions at the surface of the macroscopic region in the heterogeneous medium. Calculations of the effective electromechanical constants of the piezo-composite are closely connected with averaging a series of vector and tensor components of the electric and mechanical fields, for example, ξ_q , E_f , σ_p , and D_k (see Equations 2.4–2.11). This averaging is performed on volume fractions of the composite components² ($n = 1, 2, \dots$) for which the full sets of electromechanical constants, such as $c_{pq}^{(n),E}$, $e_{fp}^{(n)}$ and $\varepsilon_{kr}^{(n),\xi}$ or other constants involved in Equations 2.6–2.11, are known. The formulation of the problem allows the development of a variety of methodologies for the determination of the full sets of electromechanical constants and various methods of numerical realisation for specific connectivity patterns and arrangement, *etc.* [5, 32, 33, 51–54, 60–63].

² In order to avoid confusion owing to vector (tensor) components and composite components, the latter are also called *constituents*.

The central aspect of this problem is a method of homogenisation of the electromechanical properties [33, 63]. It is clear that the effective properties are to be regarded as properties in a material at distances exceeding the linear dimensions of an individual inclusion or the thickness of a separate layer in a composite sample. However, the same inclusions can be inhomogeneous (for example, ferroelectric ceramic particles that are split into domains or are heterophase). It is therefore necessary to attain an additional homogenisation of the properties in these inclusions. Such a situation needs a compromise. For example, the effective electromechanical properties in the 2–2 piezo-composite are determined [64, 65] by assuming that their components are characterised by an equivalent homogeneity [66]. The authors of refs. [67, 68] have considered a variety of applications of the approach developed with attention to piezo-composite and biological materials. It is also noted that homogenisation methods are applicable [67] to media with periodic and quasi-periodic structures.

Based on the detailed analysis of results concerning composite materials and their effective properties, Khoroshun *et al.* [5] placed emphasis on two main scientific directions in modern mechanics of composites. The first direction represents the mechanics of the composites having regular (periodic) structures. The second direction is related to the mechanics of stochastically heterogeneous materials, including the composites with arbitrary connectivity, shape and distribution of structural elements.

The first direction deals with periodic solutions of equations of mechanics of microinhomogeneous media in which the regular distribution of the structural elements is present. As a rule, such solutions are applicable to the matrix piezo-composites with inclusions having the appropriate shape, *e.g.*, spheroids. The accompanying method, called *the method of regularisation of structure* [5], is applied to the composites [32, 33, 60, 63, 69] with a certain disorder in the shape and distribution of the structural elements. This method makes it possible to substitute the real composite by a model material with regularly distributed structural elements having the appropriate shape only. In such a model material, a periodic representative volume element (similar to unit cells in single crystals, as shown, for example, in the Banno cube model [69]) is chosen and analysed using micromechanical methods including the finite-element method (FEM). A representative volume element used for a prediction of effective parameters of the porous piezo-ceramic [70] with 3–3 connectivity is shown in Figure 2.3.

The second direction implies using random functions to describe the properties in the composite with a stochastic structure. These properties are regarded as randomly varied ones over the composite sample, and the homogenisation can be performed with regard to mathematical features of the random functions. This approach is suitable for the prediction of the effective properties in the piezo-composites without restrictions on the shape and distribution of inclusions and connectivity.

A considerable amount of research is devoted to the 0–3 piezo-composites [5, 33, 50, 53, 60–62] that contain a system of isolated inclusions embedded in a matrix. The inclusion is often made from a ferroelectric ceramic, and the matrix is regarded as a polymer medium being either piezoelectric or piezo-passive. Such piezo-composites are manufactured using a variety of techniques (see, *e.g.*, reviews

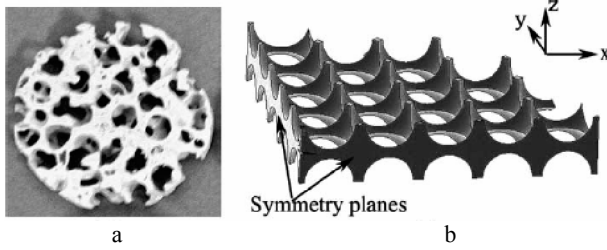


Figure 2.3. Micrograph of the porous PZT ceramic (a) and example of the representative FEM image (b) that is used for calculations of the effective electromechanical properties. x , y and z are co-ordinate axes (reprinted from Ramesh *et al.* [70], with permission from Elsevier)

[48, 71, 72]) and studied using a series of experimental methods [73–79]. Theoretical studies of 0–3 piezo-composites are focused on the effective electromechanical properties that are strongly dependent on the properties and volume fractions of the components [5, 33, 50, 61], on the shape of the inclusions and features of their distribution in the matrix [5, 60, 80] as well as on poling conditions [75, 77] for the composite sample as a whole. In these studies, it is often assumed that the inclusions have the shape of a spheroid [53, 81] or a rectangular parallelepiped [33] and aligned regularly in the matrix. An electromechanical interaction between each inclusion and the surrounding matrix is taken into account [5, 60, 61] in connection with internal electric and mechanical fields and boundary conditions for the specific shape of the inclusion.

An approach developed by Banno [69, 82, 83] stems from concepts [84] initially applied to 2–2 composites. Based on these concepts, the 0–3 composite is represented [83] by the Banno unit cell (or the representative volume element) that comprises the parallelepiped-like inclusion and the surrounding matrix. The effective electromechanical properties in this composite are determined by direct averaging of the properties in the components. In this averaging procedure, the shape of the parallelepiped (*i.e.*, a ratio of their edges), but not the interaction between the components plays an important role.

In an alternative matrix method [33] proposed for the prediction of the electromechanical properties in the 0–3 composite, the theoretical description is based on the matrix approach [64, 85] previously applied to the 2–2 composite. This approach enabled the authors of ref. [33] to perform the averaging procedure for the 0–3 composite with a regular distribution of the parallelepiped-like inclusions. The method developed by Levassort *et al.* [33] has been extended to 3–3 and 1–3 ceramic / polymer piezo-composites [86, 87] with planar interfaces. In refs. [33, 86, 87], the electromechanical constants of the components $c_{pq}^{(n),E}$, $e_{jp}^{(n)}$ and $\varepsilon_{kr}^{(n),\xi}$ are involved in matrices of the properties (9×9) and boundary conditions. To avoid mathematical complications concerned with the presence of the matrix elements with strongly differing degrees of values (*e.g.*, $c_{pq}^{(n),E} \sim (10^{10} - 10^{11})$ Pa and $e_{jp}^{(n)} \sim (1-10)$ C / m² for the n th component), the matrix approach has been modified and successfully applied to the 1– β piezo-composites with $\beta = 1, 2$

and 3 [88, 89]. The matrices describing the electromechanical properties in the components comprise elastic compliances $s_{pq}^{(n),E} \sim (10^{-11} - 10^{-10}) \text{ Pa}^{-1}$, piezoelectric coefficients $d_{jp}^{(n)} \sim (10^{-11} - 10^{-9}) \text{ pC / N}$ and dielectric permittivities $\epsilon_{kr}^{(n),\sigma} \sim (10^{-11} - 10^{-8}) \text{ F / m}$, and use of such a set of electromechanical constants [88, 89] avoids the aforementioned significant differences in the degrees of the values of the electromechanical constants.

Many publications on 0–3 composites are concerned with a piezoelectric ellipsoidal inclusion problem [5, 53, 60, 90–95]. This problem stems from the classical Eshelby analysis [96, 97] of the stress and strain fields in and around an elastic ellipsoidal inclusion. Results [96, 97] on the uniform stress and strain fields in such inclusions and the equivalent inclusion method stimulated intensive investigations into heterogeneous media and their effective physical properties [98]. Work on the coupled electric and mechanical fields in heterogeneous materials implied the application of the equivalent inclusion method [96, 97] for the description of the piezo-composites, poled ferroelectric ceramics and piezo-active materials with pores or cracks [94, 95, 99–101]. The inclusion can be either piezo-active or piezo-passive, and no restrictions on its symmetry are introduced. The matrix can be either piezo-active (transversely isotropic) or piezo-passive (isotropic) [91–95, 99, 101].

The analysis of the coupled electromechanical behaviour of an “inclusions – matrix” system is based on knowledge of the Eshelby tensors. These tensors represent the strain and electric fields that are induced in the inclusion due to a constraint of the matrix in the external fields. The Eshelby tensors are expressed in the explicit form for the following inclusion shapes [101, 102]: spheroid, elliptic cylinder, rod, penny, and ribbon-like. All of the inclusions are assumed to be aligned along the axis of anisotropy, *i.e.*, along the poling axis in the transversely isotropic medium. As in the work on elastic inclusions in an elastic matrix [96, 97], the Eshelby tensors depend on the shape of the inclusion and on the properties in the matrix. Further averaging of the electromechanical properties is often carried out according to a self-consistent scheme. The main variants of this scheme are concerned with the effective medium method [94, 103, 104] and the effective field method (or the mean field method) [53, 94, 95, 104–106].

In the *effective medium method*, the inclusion is regarded as a region in a continuous medium (*i.e.*, in a matrix containing an ensemble of similar inclusions). The effective properties in this medium are found using the Eshelby tensors for the specified shape of the inclusions, and calculations are performed within the framework of iterative (self-consistent) procedures.

The *effective field method* (EFM) stems from the Mori – Tanaka method [107] based on the concept of an average stress in the matrix containing the inclusions with so-called *eigenstrains*. The eigenstrains represent the strains appearing in a stress-free region, similar to the spontaneous strains in ferroelectric or ferroelastic phases. In the EFM, the inclusion interacts with the matrix subjected to an action of an external electric and mechanical field. Due to the presence of the ensemble of similar inclusions in the matrix, the field can be regarded as the effective field

that acts on each inclusion therein. This means that the effective (or average) electric and mechanical fields in the composite sample (see Equations 2.21 and 2.22) play a significant role in forming the overall effective electromechanical properties. The EFM is one of the most powerful and most suitable methods [105] for studying the overall behaviour of piezo-composites and for predicting their effective electromechanical properties. Moreover, the EFM is known to produce physically realistic results with regard to the effective properties in the piezo-composites [53, 104, 106] in a wide range of inclusion volume fractions. This method has been applied to determine the effective electromechanical properties in the 0–3 ferroelectric ceramic / polymer [53, 80], ceramic / ceramic [61, 105] and single crystal / ceramic [108] composites.

In addition to the above approaches, the effective electromechanical properties in a piezo-composite with spheroidal inclusions have also been determined using the dilute concentration limit (or dilute solution) [94, 106, 109], the differential scheme [94] and the conditional moments method [5]. These methods are based on different averaging procedures and take into account features of the arrangement of the inclusions and their electromechanical interaction.

In addition to the piezoelectric effect in the composites studied, the piezomagnetic and magnetoelectric effects have also been examined in 0–3 composite systems [110–112]. These coupled effects are of interest due to the involvement of three subsystems (*e.g.*, electric, magnetic and mechanical) in materials whereby an interaction between piezoelectric and piezomagnetic components [110, 111] occur. The study of these effects is based on knowing the magneto-electro-elastic Eshelby tensors for spheroidal inclusions [112]. The authors of refs. [110–112] generalised earlier results [101] for the case of a 0–3 piezoelectric–piezomagnetic composite.

The determination of the effective properties in piezo-composites with arbitrary connectivity is often carried out by means of the FEM [63, 113–118]. This method employs numerical modelling techniques that take into account boundary conditions for electric and mechanical fields in a composite system. The model of the composite is based on the unit cell being the periodic representative volume element, and this element is assumed to be characteristic of the whole composite structure. An important advantage of the FEM is that there are no restrictions on connectivity of the composite, sizes of the inclusions and their spatial distribution, the number of the components and their properties. Interesting examples of the numerical realisation of the FEM for evaluating the effective electromechanical constants are given in refs. [116, 117] (0–3 connectivity), [63, 68, 113, 118] (1–3 connectivity) and [114, 115] (3–0, 3–3 and mixed connectivity patterns). Trends in the study of the piezo-composites and other piezo-active materials show that the FEM and related finite-element software becomes increasingly more widespread in mechanical-engineering, smart-materials and piezotechnical applications (transducers, sensors, actuators, hydrophones, acoustic antennae, *etc.*). However, advances in numerical techniques do not exclude the development of analytical methods for connectivity patterns such as 0–3, 1–3 and 2–2.

2.4 Evolution of α - β Connectivity Patterns

An example of the evolution of the connectivity patterns in the two-component composites becomes clear with reference to the problem of a piezo-composite with ellipsoidal inclusions (see Section 2.3). In a general case, a composite containing isolated ellipsoidal inclusion is characterised by 0-3 or 3-0 connectivity, where the index 3 refers to the number of co-ordinate axes along which the matrix of the composite is distributed continuously. In the case of 0-3 connectivity, this corresponds to a ferroelectric ceramic / polymer composite with ceramic inclusions. Infinite elongation of one of the axes of the ellipsoid enables us to consider the inclusions having the shape of the elliptic cylinder or a lengthy rod, and this microgeometry results in 1-3 or 3-1 connectivity of the composite. However, the structure of the 0-3 composite containing penny-shaped inclusions approaches a structure of the 2-2 composite. These changes in connectivity are accompanied by changes in the Eshelby tensors [101] so that they can be utilised to predict the effective properties in the 1-3, 3-1 or 2-2 composites with one or two piezoelectric components.

Another example of the evolution of the connectivity patterns is associated with various modifications of the 2-2 composite structure. According to Levassort *et al.* [33, 86, 87], the modified patterns are described by 0-3, 1-3 or 3-3 connectivity. The effective properties in the corresponding piezo-composites are determined by means of the matrix method [33, 64].

It can be seen from the examples above that some connectivities of the two-component composite can be associated with slight modifications of the initial connectivity pattern. In this section, we consider the entire complex of the α - β connectivity patterns (Figure 1.1), their evolution and interconnections between them [89] in the two-component composites with planar interfaces.

It is assumed that there is a group of *junction* connectivity patterns and that their combination can form new connectivity patterns. Each composite with a regular arrangement of components is represented by the Banno unit cell (or representative volume element) [82, 83]. The presence of planar interfaces and their certain hierarchy inherent in the α - β composite suggest that the 2-2 connectivity pattern (*i.e.*, a system of series or parallel layers) may be regarded as one of the *junction* connectivity patterns. For example, a simple multiplication of the 2-2 connectivity pattern results in the 1-1 connectivity pattern [88], see Figure 2.4 and the connection between the 2-2 and 1-1 structure. A further simplification of the 1-1 connectivity pattern enables us to obtain the 1-3 or 3-1 connectivity pattern.³ It should be noted that this simplification has similarities to the formation or rearrangement of ferroelectric domain structures, in which not all domain types are present even though these types are predicted [119] in accordance with symmetry changes at phase transitions.

³ It is seen from Figure 2.4 that the above-mentioned 2-2, 1-1, 1-3, and 3-1 connectivity patterns make up the full set of the junction connectivity patterns. These patterns show numerous interconnections between the structures of the two-component composites from Figure 1.1.

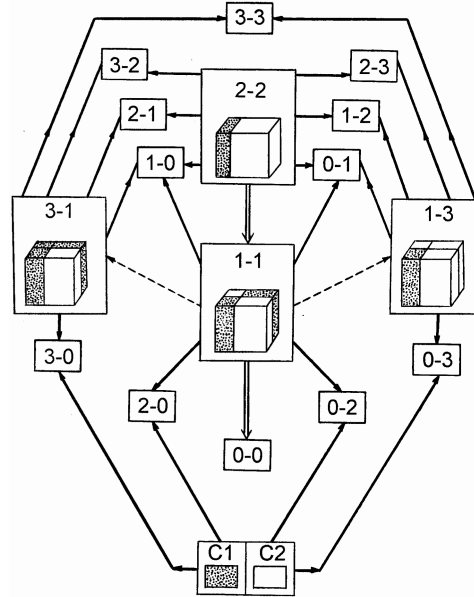


Figure 2.4. Links between the α - β connectivity patterns. C1 and C2 denote components 1 and 2, respectively. Double lines connecting the 2-2 and 1-1 connectivity patterns as well as the 1-1 and 0-0 connectivity patterns denote a multiplication of structural elements at transformations $2-2 \rightarrow 1-1$ and $1-1 \rightarrow 0-0$. Dashed lines connecting the 1-1 and 1-3 connectivity patterns as well as the 1-1 and 3-1 connectivity patterns denote a simplification of the 1-1 structure at transformations $1-1 \rightarrow 3-1$ and $1-1 \rightarrow 1-3$ (reprinted from Topolov and Glushanin [89], with permission from IOP Publishing)

The main interconnections between the α - β connectivity patterns are shown in the schematic in Figure 2.4 that contains links between the junction connectivity patterns and other connectivity patterns in the α - β composites. All the α - β composite structures can be generated by systems of the layers. These layers are either homogeneous (see components C1 and C2 at the base of Figure 2.4) or heterogeneous. The heterogeneous layers are characterised by the junction connectivity pattern, by the combination of the junction connectivity patterns or by the combination of the junction connectivity pattern and one of the components.

The evolution of the connectivity patterns demonstrates the important role of the junction connectivity patterns. The main features of this evolution are described as follows.

1. From the symmetrical arrangement of the junction connectivity patterns and other elements in the scheme (Figure 2.4), it can be concluded that the evolution of the connectivity patterns is primarily caused by a motion along the symmetry axis (*i.e.*, the line that mentally connects the connectivity patterns with $\alpha = \beta$) and adjacent branches.

2. The structures of the interfaces are rather complicated for 0-1 and 1-2 connectivity patterns (Figure 1.1) that are generated by three or two junction connectivity patterns. The 0-0 connectivity pattern is situated at a dead-end

between the 1–1 connectivity pattern and the component C_i ($i = 1$ or 2). As a consequence, the 0–0 connectivity pattern does not influence the formation of the 0– β structures with $\beta = 1, 2$ and 3 .

3. The maximum distance between the 3–3 connectivity pattern and the components C_i , along with the lack of direct links between them are also typical of the evolution of the connectivity patterns. It is shown in Figure 2.4 that the remaining connectivity patterns are located in between 3–3 and C_i . The continuous distribution of the C_1 or C_2 component or each component in the 3–3 connectivity pattern along three co-ordinate axes represents two extreme cases of the arrangement in the scheme (see upper and bottom parts of Figure 2.4).

4. The number of systems of the interfaces decreases at $\alpha = 3$ or $\beta = 3$. Such a decrease is a result of a continuous distribution of one (at $\alpha = 3 \neq \beta$ or $\beta = 3 \neq \alpha$) or two (at $\alpha = \beta = 3$) components along three co-ordinate axes. In fact, any introduction of an additional type of interface would destroy this continuity.

Knowledge of the evolution of the connectivity patterns enables the analysis of the α – β piezo-composites with planar interfaces as well as understanding the resulting effective electromechanical properties in these heterogeneous materials. The concepts developed in this section can ease both the modelling and optimisation of the effective electromechanical properties, especially in the piezo-composites with complicated connectivity patterns. An example of the 1–2 composite and a series of parameters introduced for determination of its effective electromechanical properties are considered below.

2.5 Modelling of Effective Properties in Piezo-composites with Planar Interfaces

An important step following the analysis of the evolution of the connectivity patterns is the *synthesis*, i.e., a combination of parts to form a connected composite. An approach developed in ref. [89] is based on the assumption that different α – β composite structures with planar interfaces can be generated using a system of layers (Figure 2.5). It is assumed that the layers with specified connectivity regularly alternate along the OX_3 axis that represents the poling direction. The C_1 component is shown as the dotted area in all cross-sections (Figure 2.5) of the α – β connectivity patterns ($\alpha \leq \beta$) and in the schematic arrangement of the 1–2 composite (Figure 2.5, see bottom right). In order to determine the effective electromechanical properties of the 1–2 composite, one can introduce a series of concentration parameters [89], for example, $t = |AC| / |AE|$, $n = |FH| / |FL|$, $t' = |AB| / |AC|$, $n' = |FG| / |FH|$, and $v = |MN| / |MP|$. These parameters⁴ characterise volume

⁴ The concentration parameters t , n and t' , which are related to the 0–0 and 0–1 connectivity patterns (Figure 2.5), are introduced by analogy with the concentration parameters related to the 1–2 composite. The α – β connectivity patterns obeying the condition $\alpha \geq \beta$ are depicted by the similar schemes wherein the dotted areas shown in Figure 2.5 become white and the white areas become dotted.

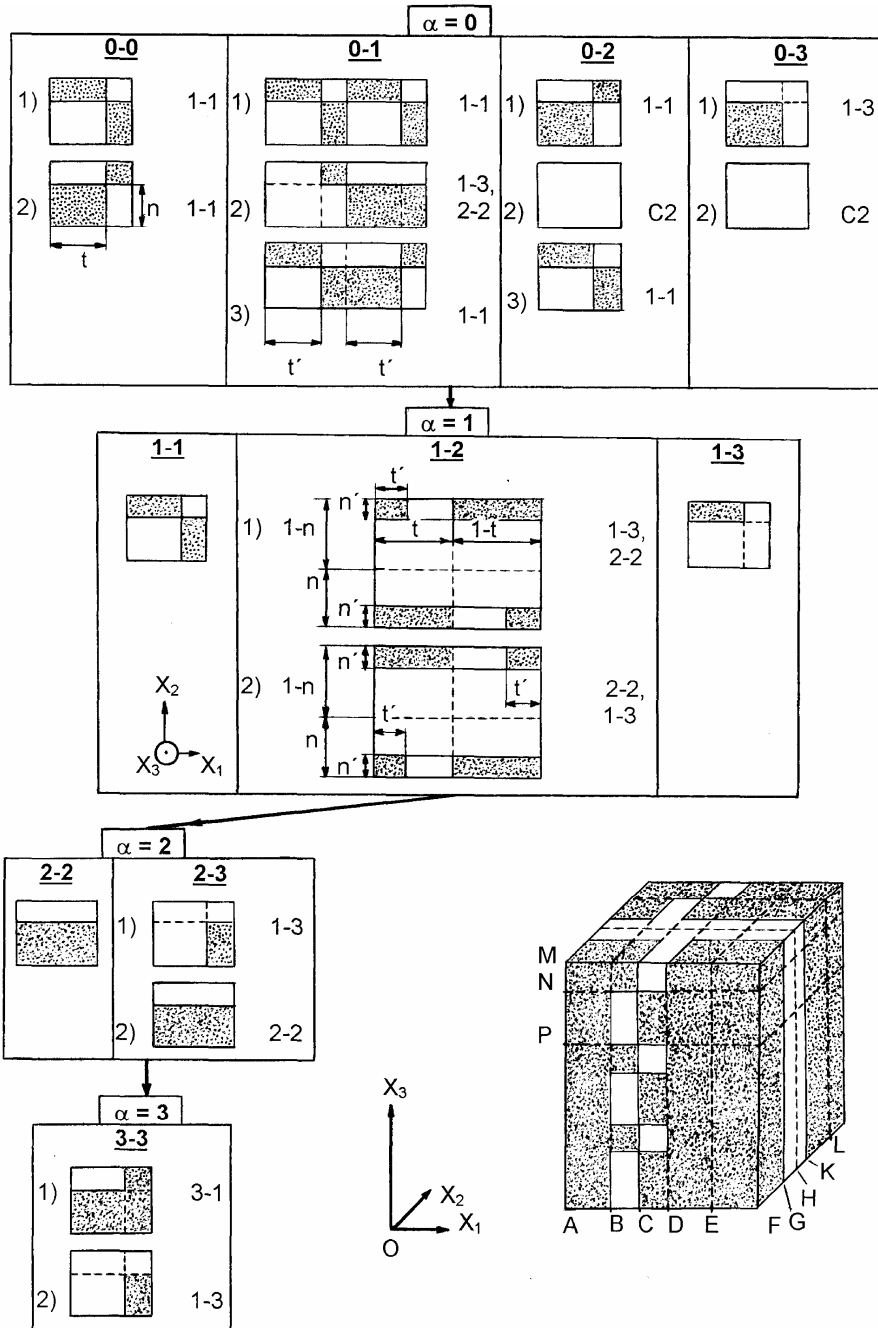


Figure 2.5. Systems of layers forming the α - β connectivity patterns (reprinted from Topolov and Glushanin [89], with permission from IOP Publishing)

fractions of the C1 and C2 components in the 1–2 composite and are assumed to be constant over the composite sample. Any variations of the concentration parameters mean that relative widths (or lengths) of several parallelepipeds are simultaneously varied in all the layers of the composite. The layers forming the α – β composites are parallel to the (X_1OX_2) plane as shown for the 1–2 composite (Figure 2.5, see bottom right).

The calculation of the effective electromechanical constants of the α – β composites can be performed by means of the matrix method [64] (as shown for the 1–1, 1–2 and 1–3 ferroelectric ceramic / polymer composites [88, 89]) or the FEM. In these methods the electromechanical interaction between the adjacent regions is taken into account in averaging procedures. For this calculation, full sets of electromechanical constants of both components are required. The effective properties in the aforementioned 1– β composites with $\beta = 1, 2$ and 3 are determined [88, 89], for example, using elastic compliances $s_{pq}^{(n),E}$, piezoelectric coefficients $d_{jp}^{(n)}$ and dielectric permittivities $\varepsilon_{kk}^{(n),\sigma}$ of the ferroelectric ceramic ($n = 1$) and polymer ($n = 2$).

In a general case, the matrix method [64] is applied to predict the effective electromechanical properties in the periodically layered 2–2 composite or the ferroelectric single crystal with a laminar domain structure [120, 121]. This approach can be applied, providing the wavelength of an incident acoustic field is much longer than the thickness of the separate layer. In a range of low frequencies ω of the AC electric field, the condition $\omega\tau \ll 1$ holds (where τ is the Maxwell–Wagner relaxation time) and the electric conductivities of the layers are to be taken into account [57] for the correct prediction of the effective electromechanical properties in the 2–2-type piezo-composite. The matrix method [64], which does not take into account the electric conductivities, can be applied at frequencies that are considerably more than those where the Maxwell–Wagner relaxation is in progress. At the same time, the frequency of the electric field should be well below a piezoelectric resonant frequency of the composite sample for specific oscillation modes.

The modelling of the effective properties in the piezo-composites is closely connected with their potential applications. Clearly, for successful and optimum piezotechnical applications, the piezo-composites with different connectivity patterns, volume fractions of the components and other parameters are required. The optimisation of the effective properties and related parameters as well as manufacturing the appropriate piezo-composites are of independent interest. It should be noted that *structure – processing – property* relations in the ferroelectric ceramic / polymer composites are described using connectivity as the unifying central concept [71]. Computer-aided design-based fabrication methods have advanced in recent years [72]. In particular, novel processing technologies make it possible to attain unprecedented structural complexity [71] as compared to the traditional methods [48, 69] for manufacturing the ceramic / polymer composites.

2.6 Connectivity – Links – Properties

Chapter 2 has been devoted to the description of the electromechanical properties in piezo-active materials. An emphasis has been placed on the piezo-composites, their connectivity and trends in forming their effective electromechanical properties. Three types of effective properties (*i.e.*, sum, combination and product properties) have been considered and applied to the two-component composites based on ferroelectrics. Results on the evolution of the α - β connectivity patterns and the role of systems of planar interfaces inherent in the α - β piezo-composites have been discussed. A scheme demonstrating the links between the α - β connectivity patterns has been put forward for the modelling of the effective properties in the piezo-composites with planar interfaces. In general, Chapter 2 can be regarded as a transition from the connectivity concept to determination of the volume-fraction dependences of the effective properties in different groups of piezo-composites, such as ferroelectric ceramic / polymer, ferroelectric single crystal / polymer, ferroelectric single crystal / ferroelectric ceramic, with two or more piezoelectric components, *etc.* Further discussion will examine the determination and interpretation of calculated data relating to specific connectivity patterns and the aforementioned groups of the piezo-composites. In Chapter 3 we will consider the most important α - β connectivity patterns as well as features of the effective electromechanical properties and applications of the two-component composites based on ferroelectric ceramics.

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