

# Some specificities of the pyro- and piezoelectric phenomena in heterogeneous ferroelectric materials

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**Abstract** A system of equations has been constructed in order to find effective pyroelectric, dielectric, piezoelectric, elastic and thermoelastic constants of heterogeneous materials using the method of self-consistency. By means of these equations the characteristics are simulated of the electrically depoled piezoceramics and of composites with antiparallel polarization of the components. Such a composite, being a mixture of BaTiO<sub>3</sub> and PZT-19 ceramic particles, manifests at a certain concentration of PZT-19 high pyroelectric properties but does not practically possess the piezoeffect. But at another concentration it is a strong piezoelectric without any pyroeffect.

**Keywords** Ferroelectric · Piezoelectric · Pyroeffect · Composite

## 1 Introduction

In recent years the heterogeneous ferroelectric materials in the form of piezoceramics and composites have occupied and, apparently, will still long time occupy a leading position in the piezotechnology. For that reason an ever-increasing number of publications are devoted to the question of prediction of characteristics for these materials

[1–13]. A particular interest is attracted by the pyro- and piezoelectric phenomena which underlie quite a few practical applications. Effective properties of a heterogeneous material essentially depend on its micro-geometry. Definition of these properties is a difficult and important problem. Therefore exact solutions which have been found by authors [1–4] for some special cases inhomogeneous piezoelectric and pyroelectric materials cause the big interest. However, for many real situations such solutions are not applicable. As a rule, a self-consistent scheme has been used for practical calculations which was developed as a method of effective medium and a method of effective field [5–13].

The ferroelectric ceramics is characterized by some specific properties. It possesses domain structure with mobile domain walls which give the additional contribution to the linear macroscopic response. From experimental investigation it is well known that effective properties of ferroelectric ceramics cannot be understood without taking into account the domain wall motions. Besides, domains are switched under the influence of strong electric field and mechanical stress that leads to the hysteresis phenomena. For this reason some models which consider specific aspects of effective behavior of ferroelectric ceramics, have been developed [14–20].

The method of effective medium has been employed in the present work for theoretical prediction of effective pyroelectric, dielectric, piezoelectric, elastic and thermoelastic properties of piezoceramics and composites. An appropriate set of equations has been constructed allowing one to carry out necessary calculations, the relationship between the pyro- and piezoelectric characteristics is studied and the results are compared with experiment. The purpose of this work has been to show the possibility of creating active heterogeneous ferroelectric materials with preset pyro- or piezoelectric properties.

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### 2 A spherical inclusion into the pyroactive medium

A solution of the problem of interaction between a spherical inclusion and the homogeneous anisotropic piezoactive medium was presented in [5, 12]. It has been shown that if in the medium (away from the inclusion) homogeneous electric  $E^0$ ,  $D^0$  and elastic  $\sigma^0$ ,  $S^0$  fields are given, the corresponding fields inside the inclusion are also homogeneous and they are related to the fields  $E^0$ ,  $D^0$ ,  $\sigma^0$  and  $S^0$  by the linear equations

$$\begin{aligned} E &= E^0 + A'(D^0 - D) + H'(S^0 - S), \\ \sigma &= \sigma^0 + H'_t(D^0 - D) + B'(S^0 - S), \end{aligned} \tag{1}$$

where  $\sigma$ ,  $S$  are the tensors of stress and strain and  $E$ ,  $D$  are the electric field and the electric displacement field. The superscript “0” denotes here and in the following the values of the fields operative in the medium. The matrices  $A'$ ,  $H'$  and  $B'$  in Eq. 1 depend on the medium’s properties only and are determined by the relationships

$$\begin{aligned} A' &= -(\epsilon^{*S} + a)^{-1}, \quad H' = -A'(e^* + g), \\ B' &= b - c^{*E} - (e^* + g)_t H' \end{aligned} \tag{2}$$

where  $\epsilon^{*S}$  is the dielectric permittivity of the medium at a fixed strain,  $e^*$  are the piezoelectric constants,  $c^{*E}$  are the elastic moduli at a fixed field, the transposed matrices are designated by the letter  $t$  and the elements of the matrices  $a$ ,  $g$  and  $b$  were calculated in [5, 12].

Note that the Eq. 1 do not impose any restrictions on the relations between the fields  $E$ ,  $D$ ,  $\sigma$  and  $S$  inside the inclusion, they merely reflect the “elastic” linear character of the interaction between the inclusion and the medium. They have a very general form and do not contain in explicit form relations between  $E^0$ ,  $D^0$ ,  $\sigma^0$  and  $S^0$  (naturally assuming that these relations should be linear). Although the relationships 1 were obtained for the piezoelectric medium under isothermal external conditions, they remain valid also when homogeneous temperature effects are present. In this case, the electric and elastic fields  $E^0$ ,  $D^0$ ,  $\sigma^0$  and  $S^0$  may contain contributions produced by linear pyroelectric and thermoelastic processes.

### 3 The method of effective medium; basic equations

This method is actually a self-consistent scheme for finding the effective constants of heterogeneous materials in which the individual crystallite is considered as an isolated inclusion in a certain medium whose properties are to be

determined. These properties coincide with the effective properties of the material as a whole.

In order to determine the effective constants consider the Eq. 1 together with the linear relationships for the inclusion

$$\begin{aligned} E &= -hs + \eta^S D - q^S \theta, \\ \sigma &= c^D S - h_t D - \beta^D \theta, \end{aligned} \tag{3}$$

where  $\theta = T - T_0$  is the deviation of the sample’s temperature  $T$  from a certain given temperature  $T_0$ ,  $\eta^S = (\epsilon^S)^{-1}$  is the dielectric stiffness at a fixed strain,  $c^D = c^E + e_t \eta^S e$  are the elastic moduli at a fixed electric displacement,  $h = \eta^S e$  are the piezoelectric constants,  $q^S$  and  $\beta^D$  are the pyroelectric coefficients and the coefficients of thermal stresses at a fixed strain and electric displacement. The Eq. 3 can be written in a compact form

$$\begin{pmatrix} E \\ \sigma \end{pmatrix} = L \begin{pmatrix} D \\ S \end{pmatrix} - \Gamma \theta, \quad L = \begin{pmatrix} \eta^S & -h \\ -h_t & c^D \end{pmatrix}, \quad \Gamma = \begin{pmatrix} q^S \\ \beta^D \end{pmatrix}. \tag{4}$$

The corresponding set of linear equations for the medium is as follows

$$\begin{aligned} \begin{pmatrix} D^0 \\ S^0 \end{pmatrix} &= L^* \begin{pmatrix} E^0 \\ \sigma^0 \end{pmatrix} + \Gamma^* \theta, \\ L^* &= \begin{pmatrix} \epsilon^{*\sigma} & d^* \\ d_t^* & s^{*E} \end{pmatrix}, \quad \Gamma^* = \begin{pmatrix} p^{*\sigma} \\ \alpha^{*E} \end{pmatrix}, \end{aligned} \tag{5}$$

where  $\epsilon^{*\sigma} = \epsilon^{*S} + e^*(c^{*E})^{-1} e_t^*$  are the dielectric permittivity at a fixed stress,  $d^* = e^*(c^{*E})^{-1}$  are the piezomoduli,  $s^{*E} = (c^{*E})^{-1}$  are the elastic compliances at a fixed field,  $p^{*\sigma}$  are the pyroelectric coefficients at a fixed mechanical stress,  $\alpha^{*E}$  are the coefficients of thermal expansion at a fixed field. By substituting Eq. 3 into Eq. 1 we obtain a set of equations for determining the electric displacement  $D$  and the strain  $S$  inside the inclusion. A solution to this system can be presented in the following form

$$\begin{pmatrix} D \\ S \end{pmatrix} = \Delta^{-1} (I + P^0 L^*) \begin{pmatrix} E^0 \\ \sigma^0 \end{pmatrix} + \Delta^{-1} (\Gamma + P^0 \Gamma^*) \theta, \tag{6}$$

where  $\Delta = P^0 + L$  is the symmetrical matrix of the system,  $I$  is the unit matrix of the ninth order. The matrix  $P^0$  defined as follows

$$P^0 = \begin{pmatrix} A' & H' \\ H'_t & B' \end{pmatrix}. \tag{7}$$

By averaging  $D$  and  $S$  given by the expression 6 over the volume, we get the sought-for system of 13 equations for

finding the effective pyroelectric, dielectric, piezoelectric, elastic and thermoelastic constants

$$\begin{aligned} L^* &= \left\langle (P^0 + L)^{-1} (I + P^0 L^*) \right\rangle, \\ \Gamma^* &= \left\langle (P^0 + L)^{-1} (\Gamma + P^0 \Gamma^*) \right\rangle. \end{aligned} \quad (8)$$

The Eq. 8 represent the most general and rigorous formulation of the effective medium; the averaging in Eq. 8 is performed over all components of the material and all orientations.

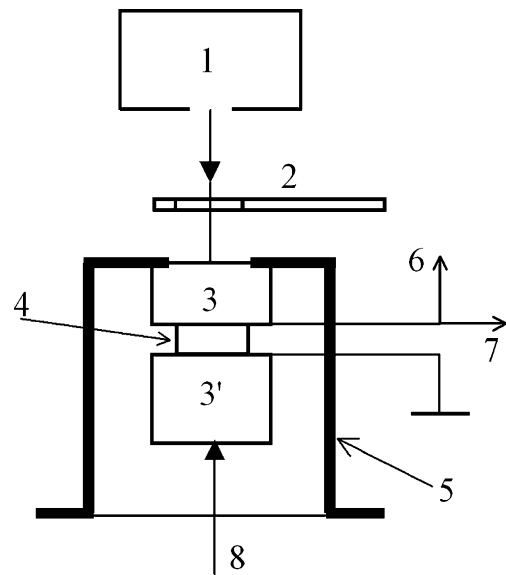
We wish to note that the matrices  $a$ ,  $g$  and  $b$  in Eq. 2 may also be calculated by means of the Eshelby matrix  $E_s$  the explicit form of which for the ellipsoidal inclusion was determined in [9, 10].

$$\begin{aligned} \begin{pmatrix} B & -H_t \\ -H & A \end{pmatrix} &= E_s \begin{pmatrix} c^{*E} & e_t^* \\ e^* & -\varepsilon^{*S} \end{pmatrix}^{-1}, \\ a &= A^{-1} + A^{-1} H b H_t A^{-1}, \quad b = (B - H_t A^{-1} H)^{-1}, \quad g = -A^{-1} H b. \end{aligned} \quad (9)$$

#### 4 Experimental procedure

The piezoelectric characteristics were measured by the resonance–antiresonance method [21]. When the piezoactivity of the samples was weak, the necessary constants were calculated by the technique described in [22]. Measurements were carried out on thin discs (with the diameter-to-thickness ratio being about 10) of the BaTiO<sub>3</sub> ceramics as well as of the “ferrosoft” tetragonal ceramics Pb<sub>0.95</sub>Sr<sub>0.05</sub>(Zr<sub>0.53</sub>Ti<sub>0.47</sub>)O<sub>3</sub>+1%Nb<sub>2</sub>O<sub>5</sub> (the commercial designation PZT-19) manufactured by the conventional technique in conditions of serial production. Prior to measurements the samples were annealed at a temperature manifestly exceeding the Curie point. The remanent polarization was measured by the Hamano technique [23] and the pyroelectric response by the dynamic method of Chynoweth [24].

So as to measure the piezoelectric response in the quasistatic regime a set-up was used analogous to that described by Damjanovic in [25]. A special measuring cell (Fig. 1) allowed one to simultaneously observe the piezo- and pyroelectric responses of the sample to the action of the sinusoidal load (frequency of 78 Hz) and of the modulated thermal stream. Before the measurements the sample was poled up to saturation. Then, in order to change the polarization in accordance with the pre-set value, an electric field of inverse polarity was applied to it whose strength and duration of action were appropriately chosen. The experimental data presented correspond to the stabilized values measured 5 to 10 min after the removal of the field.



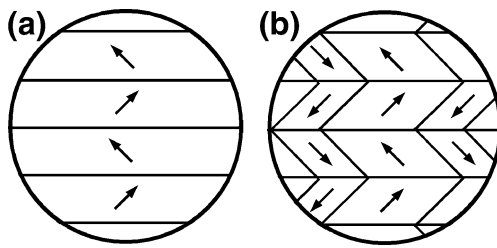
**Fig. 1** The scheme showing the setup of a measuring cell for simultaneous observation of the sample’s pyroelectric and piezoelectric responses. 1—Source of thermal irradiation, 2—mechanical interruptor, 3—a washer made of melted quartz, 3’—a steel washer, 4—sample, 5—thermostat, 6—to voltmeter (piezoelectric voltage), 7—to oscillograph (pyroelectric voltage), 8—the measuring load  $F = F_0 \cos 2\pi ft$  ( $f = 78$  Hz)

#### 5 Effective constants of piezoceramics

Using Eq. 8, the dependence of the effective constants of electrically depolarized BaTiO<sub>3</sub> piezoceramics on the value of polarization was calculated. We took into account the rearrangement of the 180° domain structure under the action of an electric field as well as the reversible shift of the 90° domain walls. The following model of the electrically depolarized piezoceramics was used [20]. It was assumed that in the initial state the sample was polarized up to saturation in the direction of the axis  $X_3^*$  of the laboratory system of coordinates. In this state all the crystallites, regardless of their orientation, have the same domain structure [Fig. 2(a)], and the maximum value of the remanent polarization  $P_r$  of the sample  $P_r^{\max} = \sqrt{2}P_s/4 \approx 0.35P_s$ , where  $P_s$  is the spontaneous polarization.

The electric field applied in the opposite direction causes a partial (or complete if it is big enough) depolarization of the sample due to the appearance of the 180° domains with the volume concentrations  $m$  and  $1-m$  corresponding to the reciprocally inverse orientation of  $P_s$  [Fig. 2(b)]. The value of  $m$  and, consequently, the constants of the crystallite depend on its orientation and on the value of the depoling field [20]. We assume that the relative volume concentration of the 90° domains in each crystallite is equal 1/2 [Figs. 2(a), (b)] and does not change in the course of repolarization.

The constants of the single domain BaTiO<sub>3</sub> crystal were taken from [21]. Since there are no data in the literature on



**Fig. 2** The domain structure used in the calculation of effective constants of the BaTiO<sub>3</sub> piezoceramics. (a) The poled ceramics,  $P_r^{\max} = \sqrt{2}P_s/4$ , (b) the electrically depoled ceramics. Arrows show the direction of polarization in domains

the coefficients of thermal expansion  $\alpha_{11}^E$  and  $\alpha_{33}^E$  for single domain crystal we used corresponding values for the poled ceramics BaTiO<sub>3</sub> [26]. Note that the varying of numerical values of these constants within a quite broad range does not affect the essence of conclusions drawn from an analysis of results of subsequent calculations. For the pyrocoefficient the value  $-200$  is given in [24], while in [27] this value is  $-700 \mu\text{C}/\text{m}^2\text{K}$ . In the present work we used in calculations the value  $p_3^\sigma = -450 \mu\text{C}/\text{m}^2\text{K}$ .

The effective constants of a polydomain crystallite have, at a given value of  $m$ , two components: the intrinsic (lattice) component and the domain-orientational component produced by the reversible shift of the 90° domain walls. The technique of calculation of these components was described in [20]. All crystallites in the sample were assumed to possess the same mobility of the 90° domain walls which is characterized by the value  $\gamma = (Hc)^{-1} \times 10^6 \text{ N}/\text{m}^2$  ( $H$  is the average width of the domain and  $1/c$  is the so-called coefficient of the quasielastic force).

The set of Eq. 8 were solved numerically by the iteration method. The orientation of the crystallite’s main system of coordinates relative to the laboratory system was determined with the aid of the Euler angles. So as to carry out the averaging over the orientations of the matrix of the crystallite constants,  $L$  and  $\Gamma$  in Eq. 8 are transformed into the laboratory system of coordinates.

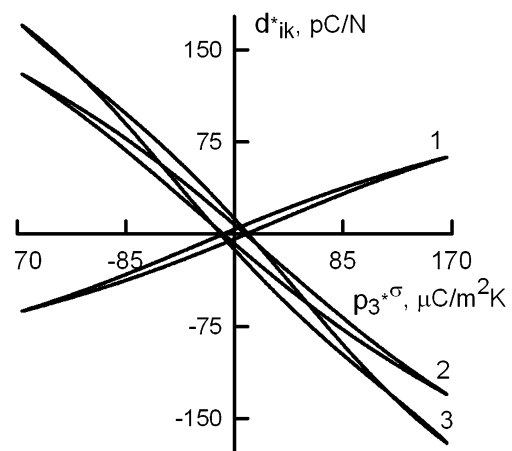
**6 Piezoceramics; results and discussion**

Calculations have shown that the values of all constants are largely determined by the domain mechanism. With a very low mobility of the 90° domain walls ( $\gamma=10^{-3}$ ) for the BaTiO<sub>3</sub> ceramics poled up to the limit  $d_{31}^* = -25.7$ ,  $d_{33}^* = 55.8$  and  $d_{15}^* = 89.0 \text{ pC}/\text{N}$ . But when the mobility is high ( $\gamma=10^3$ ), the piezomoduli are as follows:  $d_{31}^* = -70.3$ ,  $d_{33}^* = 145.5$ ,  $d_{15}^* = 185.5 \text{ pC}/\text{N}$ . Thus, for the upper limit of the value of a contribution to, e.g.,  $d_{33}^*$  produced by the reversible shift of 90° walls we obtain  $145.5-55.8 = 89.7 \text{ pC}/\text{N}$ . This estimate is consistent with the results obtained in [28].

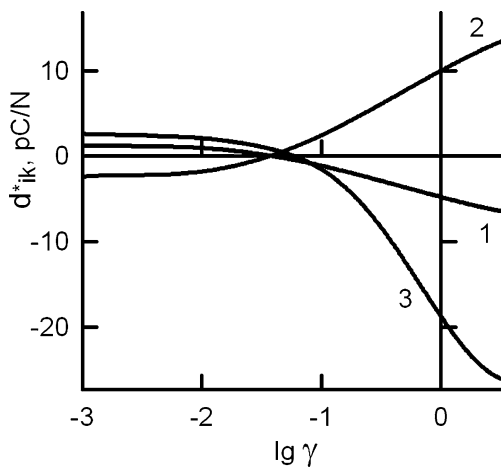
Figure 3 shows the dependence calculated at  $\gamma=0.5$  of the piezomoduli of the BaTiO<sub>3</sub> ceramics on the value of the pyrocoefficient. It is evident from this Figure that in the ferroelectric ceramics a state can be brought about in which this material will be piezoelectric without having pyroelectric properties. This conclusion is of crucial importance since it has been commonly assumed that such a state is typical, for example, of the piezoelectric crystals of non-polar classes, but not of the piezoceramic materials.

The piezomoduli that correspond to a sample’s state in which it does not manifest any pyroelectric activity ( $p_3^{*\sigma} = 0$ ) also depend in large measure on the value of mobility of the 90° domain walls (Fig. 4). The character of these dependences is not consistent with the habitual ideas concerning the role of the domain mechanism in ferroelectrics—in electrically depolarized piezoceramics this mechanism may weaken rather than enhance the piezoelectric activity of the sample. Indeed, at a very low mobility of the 90° walls ( $\gamma=10^{-3}$ ) the piezomoduli are determined by the intrinsic piezoeffect of the crystallites as is evident from the Figures, with the increasing  $\gamma$  the piezoelectric activity of the sample grows weaker, all components of the tensor of the piezomoduli decrease in absolute value. At a certain, comparatively minor mobility of the walls the intrinsic piezoeffect in the crystallites is compensated by a contribution produced by the reversible displacement of the domain walls and the piezoelectric properties of the sample are lost. Note that a more detailed discussion of the questions relating to the effect of the domain walls’ mobility on properties of the piezoceramics lies outside the framework of this paper and will be the subject of separate publications in which, for example, the behavior of the ceramics’ effective constants at  $\gamma \rightarrow \infty$  could be dealt with.

The piezoelectric response of the sample which does not manifest the pyroelectric activity is clearly revealed in



**Fig. 3** Calculated piezomoduli of the BaTiO<sub>3</sub> ceramics dependent on the pyroelectric coefficient with the mobility of the 90° domain walls  $\gamma=0.5$  (the temperature was 25° C). 1— $d_{31}^*$ , 2— $d_{33}^*$ , 3— $d_{15}^*$

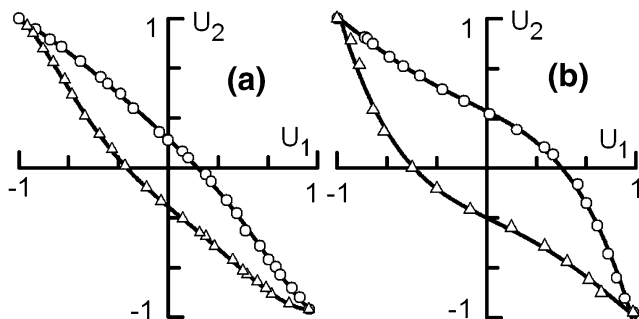


**Fig. 4** The dependence of the piezomoduli (1— $d_{31}^*$ , 2— $d_{33}^*$ , 3— $d_{15}^*$ ) that correspond to a state of the BaTiO<sub>3</sub> ceramic sample in which it does not manifest pyroelectric activity on the value  $\lg \gamma$  which characterizes mobility of the 90° domain walls at the temperature of 25 °C

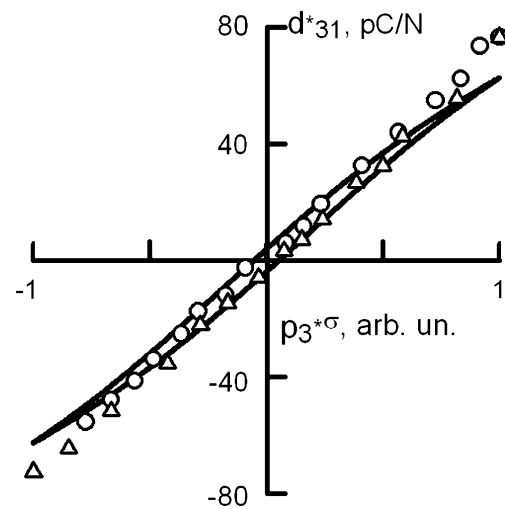
quasi-static measurements when a small sign-variable mechanical force acts on the sample along its polar axis (Fig. 5). However, an interpretation of the measurement results in this case is not easy since the mechanical stresses and the temperature are not uniform in the bulk of the sample.

The calculated absolute value of the transverse piezomodulus  $d_{31}^*$  corresponding to  $p_3^{*\sigma} = 0$  equals at  $\gamma=0.5$  about 3.8 pC/N, while the measured value, as is evident from Figs. 3 and 6, amounts to approximately 2–3 pC/N.

Figures 6, 7, and 8 show that the calculation results reproduce quite well the typical experimental dependences. The extreme character of the behavior of the dielectric permittivity dependent on the pyrocoefficient (Fig. 7) is due to the electromechanical interaction. When  $p_3^{*\sigma}$  attains a certain value close to zero, the domains in crystallites take on an “antiparallel” orientation and, owing to the piezoelect-



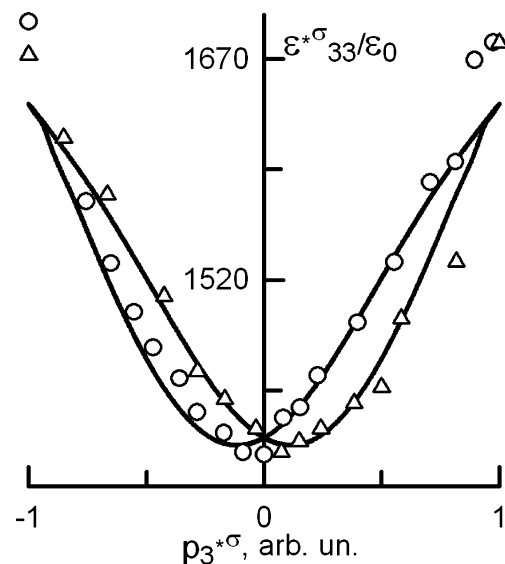
**Fig. 5** Relationship between the pyroelectric  $U_1$  and piezoelectric  $U_2$  voltage arising at the sample’s electrodes (diameter 10 mm, thickness 0.5 mm) subjected to an intensity-modulated thermal irradiation and a weak sign-variable force acting along the polar axis. (a) BaTiO<sub>3</sub> ceramics at 25 °C, (b) PZT-19 ceramics at 25 °C. Solid lines represent approximations of experimental data (circles and triangles)



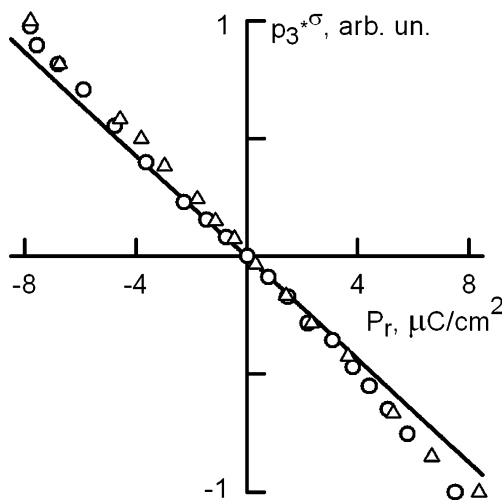
**Fig. 6** The dependence of the transverse piezomodulus of the BaTiO<sub>3</sub> ceramics on the pyroelectric coefficient at 25 °C. Solid lines represent values calculated by means of Eqs. 8 while circles and triangles indicate the experimental data

fect, the crystallites and domains actively “clamp” each other. With the changing polarity of the sample this clamping is gradually removed and, accordingly, the dielectric permittivity increases.

When the mobility of the 90° domain walls is moderate ( $\gamma=0.5$ ), the dependence of the pyroelectric coefficient  $p_3^{*\sigma}$  on the remanent polarization  $P_r$  calculated for the BaTiO<sub>3</sub> ceramics is practically linear and single-valued, which agrees satisfactorily with the experiment (Fig. 8). At a high enough value of  $\gamma$ , the calculated dependence  $p_3^{*\sigma} = f(P_r)$  is characterized by the hysteresis.



**Fig. 7** Dependence of the relative dielectric permittivity of BaTiO<sub>3</sub> ceramics on the pyroelectric coefficient at 25 °C. Solid lines represent values calculated from Eqs. 8 and circles and triangles are the data of experiment



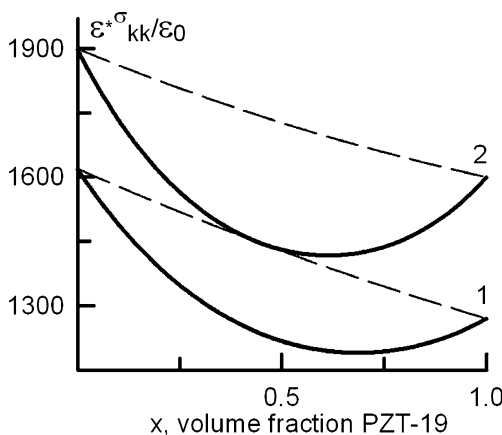
**Fig. 8** The dependence of the pyroelectric coefficient of the BaTiO<sub>3</sub> ceramics on the remanent polarization of the sample at the temperature of 25 °C. The *solid line* represents the calculation results with the mobility of the 90° domain walls  $\gamma=0.5$  while the *circles and triangles* denote the experimental data

**7 The effective constants of mixture composites**

The piezoactivity of the electrically depolarized BaTiO<sub>3</sub> ceramics in the state when it is not a pyroelectric is relatively minor as has been shown by the results presented in Section 6. One may expect that the composites represent in this respect more promising materials.

For the effective constants of a two-phase composite which is a mixture of particles with the antiparallel polarization of the phases we have

$$\Delta^{-1} = x\Delta_1^{-1} + (1 - x)\Delta_2^{-1}, \tag{10}$$



**Fig. 9** Dependence of relative dielectric permittivities ( $1-\epsilon_{11}^{*\sigma}/\epsilon_0$ ,  $2-\epsilon_{33}^{*\sigma}/\epsilon_0$ ) of a pyroelectric composite, which is a mixture of the BaTO<sub>3</sub> and PZT-19 ceramic particles on the PZT-19 concentration. *Solid lines* represent the BaTO<sub>3</sub> and the PZT-19 particles with the opposite polarization. *Broken lines* show the particles partially polarized in the same direction

where  $x$  is the relative volume concentration of the components. The subscripts in Eq. 10 indicate the first and second component, respectively.

The effective pyroelectric coefficients  $p^{*\sigma}$  and the coefficients of thermal expansion  $\alpha^{*E}$  of the composite

$$\begin{pmatrix} p^{*\sigma} \\ \alpha^{*E} \end{pmatrix} = x\Delta_1^{-1}G_1 + (1 - x)\Delta_2^{-1}G_2, \tag{11}$$

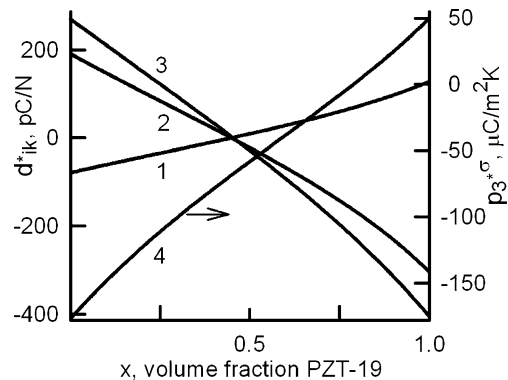
where the following notation has been introduced

$$G = \begin{pmatrix} q^S + A'p^{*\sigma} + H'\alpha^{*E} \\ \beta^D + H_t p^{*\sigma} + B'\alpha^{*E} \end{pmatrix}. \tag{12}$$

Calculations have been carried out for a composite that consists of the ceramic BaTiO<sub>3</sub> and PZT-19 particles. It was assumed that BaTiO<sub>3</sub> particles were poled in the direction of the sample’s polar axis and the PZT-19 particles in the opposite direction. Practically, such a composite may be manufactured by the mixing and subsequent sintering of two ceramic powders previously ground to the necessary size. When a strong poling field is applied to such a composite it will obviously lead to such a situation that the remanent polarization will in each particle be directed strictly parallel to the field. Since the coercive fields of the chosen materials are different, the application of an opposite and weaker electric field will result in the antiparallel polarization of the components.

The constants for BaTiO<sub>3</sub> ceramic were borrowed from [21, 26] and the pyrocoefficient  $p^\sigma$  for PZT-19 from [29]. It was assumed that the coefficients  $\alpha^E$  for PZT-19 were equal to the corresponding value for BaTiO<sub>3</sub>. The remaining constants for PZT-19 were measured by us using the resonance–antiresonance method [21].

As may be seen from Fig. 9, with the antiparallel polarization of the components there occur nonmonotonic dependences of dielectric permittivities on the PZT-19 concentration. Similarly to the case of ceramics (Fig. 7), the electromechanical interaction between the structural



**Fig. 10** The dependence of the piezomoduli ( $1-d_{31}^*$ ,  $2-d_{33}^*$ ,  $3-d_{15}^*$ ) and the pyrocoefficient (Eq. 4) of a composite that consists of a mixture of the BaTO<sub>3</sub> and PZT-19 ceramic particles on the PZT-19 concentration. The particles are poled in reciprocally opposite directions

elements brings about the “clamping” effect: at a certain concentration  $x$ , the dielectric permittivity of the composite as a whole turns out to be less than the permittivities of both components. In a composite with the parallel orientation of the polarization in the components (broken lines in Fig. 9), the minimum of  $\varepsilon_{kk}^{*\sigma} = f(x)$  is not observed: the dielectric permittivities decrease monotonically with the growing concentration of PZT-19.

Figure 10 illustrates the fact that some properties can be totally absent in the composite whereas each component separately does have them. We can see in the Figure that there are two characteristic points on the concentration dependences  $d_{ik}^{*\sigma} = f(x)$  and  $p_3^{*\sigma} = f(x)$ . At  $x \approx 0.45$  the composite practically loses its piezoactivity, even though either component possesses a strong piezoeffect. At the same time the composite retains a high pyroelectric activity and the pyrocoefficient  $p_3^{*\sigma}$  is at the given concentration greater in absolute value than for the PZT-19 ceramics attaining  $-68 \mu\text{C}/\text{m}^2\text{K}$ . At the concentration  $x \approx 0.8$ , the composite loses its pyroactivity but manifests fairly high piezoelectric properties ( $d_{31}^* \approx 70$ ,  $d_{33}^* \approx -160$  and  $d_{15}^* \approx -220 \text{ pC}/\text{N}$ ).

Finally, it must be noted that the conventional ferroelectric piezomaterials are also, as a rule, good pyroelectrics. It is well-known that in technological applications materials are required with definite preset pyro- or piezoelectric properties that would correspond to the concrete use of the material. In electro-mechanical transducers, the presence of pyroelectric properties is in some cases undesirable or even, inadmissible. As opposed to that case, for pyroelectric receivers of the thermal irradiation materials are needed with weak piezoelectric properties.

The above-presented discussion has shown that the composite materials can be quite strong piezoelectrics and have at the same time the weakest possible pyroelectric properties. Such heterogeneous materials are analogs of the piezoelectric crystals of non-polar classes, a typical representative of which is quartz. On the other hand, a composite may be a good pyroelectric but have near-zero piezoelectric properties.

## 8 Conclusion

A set of equations have been proposed for calculating the effective pyroelectric, dielectric, piezoelectric, elastic and thermoelastic constants of heterogeneous materials. This

system represent the most comprehensive and most rigorous formulation of the effective medium method and allows one to simulate characteristics of the electrically depoled piezoceramics in a satisfactory agreement with experiment.

A possibility has been established in principle of creating two types of active heterogeneous materials: (1) pyroactive materials which practically do not possess piezoelectric properties; (2) piezoactive materials without pyroelectric properties.

## References

1. K. Schulgasser, *J. Mech. Phys. Solids* **40**, 473 (1992)
2. Y. Benveniste, G.J. Dvorak, *J. Mech. Phys. Solids* **40**, 1295 (1992)
3. Y. Benveniste, *J. Appl. Mech.* **60**, 265 (1993)
4. J. Yu Li, M.L. Dunn, H. Ledbetter, *J. Appl. Phys.* **86**, 4626 (1999)
5. V.I. Aleshin, *Crystallography* **36**, 1352 (1991)(in Russian)
6. T. Olson, M. Avellaneda, *J. Appl. Phys.* **71**, 4455 (1992)
7. C.-W. Nan, *J. Appl. Phys.* **76**, 1155 (1994)
8. V.M. Levin, *PMM* **60**, 313 (1996)(in Russian)
9. J.H. Huang, W.-S. Kuo, *Acta Mater.* **44**, 4889 (1996)
10. M.L. Dunn, H.A. Wienecke, *Int. J. Solids Struct.* **34**, 3571 (1997)
11. N.A. Pertsev, A.G. Zembilgotov, R. Waser, *J. Appl. Phys.* **84**, 1524 (1998)
12. V.I. Aleshin, *J. Appl. Phys.* **88**, 3587 (2000)
13. V.M. Levin, T. Michelitsch, I. Sevostianov, *Arch. Appl. Mech.* **70**, 673 (2000)
14. V.I. Aleshin, *J. Tech. Phys.* **60**, 179 (1990)(in Russian)
15. G. Arlt, *Ferroelectrics* **189**, 103 (1996)
16. X. Chen, D.N. Fang, K.C. Hwang, *Acta Mater.* **45**, 3181 (1997)
17. S.C. Hwang, J.E. Huber, R.M. McMeeking, N.A. Fleck, *J. Appl. Phys.* **84**, 1530 (1998)
18. J.E. Huber, N.A. Fleck, C.M. Landis, R.M. McMeeking, *J. Mech. Phys. Solids* **47**, 1663 (1999)
19. J.R. Rödel, W.S. Kreher, *Proc. SPIE* **3992**, 353 (2000)
20. V.I. Aleshin, A.G. Luchaninov, *Ferroelectrics* **266**, 111 (2002)
21. B. Jaffe, W. Cook, H. Jaffe, *Piezoelectric Ceramics* (Nauka, Moscow, 1974)
22. K. Shibayama, *J. Acoust. Soc. Am.* **43**, 1883 (1962)
23. K. Hamano, *J. Phys. Soc. Jpn.* **35**, 157 (1973)
24. M.E. Lines, A.M. Glass, *Ferroelectrics and Related Materials* (Mir, Moscow, 1981)
25. D. Damjanovic, *J. Appl. Phys.* **82**, 1788 (1997)
26. W.S. Kreher, J. Rödel, in *EUROMECH 373 Colloquium* (Magdeburg, 1998)
27. J.C. Burfoot, G.W. Taylor, *Polar Dielectrics and Their Applications* (Mir, Moscow, 1981)
28. A.G. Luchaninov, V.I. Aleshin, L.A. Shuvalov, *Phys. Solid. State* **43**, 1080 (1999)(in Russian)
29. L.S. Kremenchugskii, O.V. Roitsina, *Pyroelectric Irradiation Receivers* (Naukova Dumka, Kiev, 1979)