FIGURES OF MERIT AND PROBLEMS OF PIEZOELECTRIC SENSITIVITY OF COMPOSITES BASED ON FERROELECTRIC CERAMICS

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Abstract

The present work generalizes recent results on modeling of novel piezocomposites and prediction of their effective parameters that describe the piezoelectric sensitivity. Of particular interest are data on squared figures of merit $d_{33}*g_{33}*$ and d_h*g_h* of the three-component ceramic-based piezocomposites with α-β-γ connectivity, where $d_{33}*$, ... , and g_h* are effective piezoelectric coefficients. It is established that in different piezoactive composites with a porous polymer matrix these figures of merit can exceed 10^6 $(\mathrm{PPa})^{-1}$ whereas typical values of the analogous squared figures of merit of ferroelectric ceramics are $d_{33}{}^{FC}g_{33}{}^{FC} \sim (10^3 \ldots 10^4)$ $(\mathrm{PPa})^{-1}$ and $d_h{}^{FC}g_h{}^{FC} \sim (10 \ldots 10^2)$ $(\mathrm{PPa})^{-1}$. The role of physical and microgeometrical factors in achieving the large figures of merit and related parameters of the α-β-γ piezocomposites is analyzed.

Introduction

For the past decades, various heterogeneous smart materials have attracted much interest because of performance limitations of single-phase crystals and ceramics. A variety of such materials, being piezoelectric composites (PCs), is made by combining the ferroelectric ceramic (FC) and polymer and taking into account features of microgeometry or connectivity [1]. Of two-component PCs, "FC rods – polymer matrix" materials with 1–3 connectivity offer many physical properties of practical value [1-4] and are most commonly used as active elements of hydrophones, sensors, transducers, medical diagnostic imaging devices, *etc.* Numerous experiments and theoretical studies suggest that such the PCs exhibit a nonmonotonic concentration dependence of all four types of piezoelectric coefficients $d_{3j}*$, $e_{3j}*$, $g_{3j}*$, and $h_{3j}*$ [2,5-9], planar and thickness electromechanical coupling coefficients [5-8,10], figures of merit (FOMs) [2,3], and other effective parameters. For the PC poled along the OX_3 axis (∞mm symmetry), the squared FOMs are determined as

$$(Q_{33}*)^2 = d_{33}*g_{33}* \text{ and } (Q_h*)^2 = d_h*g_h*, \qquad (1)$$

where $d_h* = d_{33}* + d_{32}* + d_{31}* = d_{33}* + 2d_{31}*$ and $g_h* = g_{33}* + g_{32}* + g_{31}* = g_{33}* + 2g_{31}* = d_h* / \varepsilon_{33}{}^{*\sigma}$ are hydrostatic piezoelectric coefficients, $\varepsilon_{33}{}^{*\sigma}$ is dielectric permittivity measured on the free sample along the poling axis. It should be additionally mentioned that Q_h* is often called "hydrostatic FOM" or "hydrophone FOM" [2-4,9,10]. The hydrostatic voltage coefficient g_h* relates the electric field appearing across a piezoactive element (transducer, hydrophone, sensor, *etc.*) to the applied hydrostatic stress. The hydrostatic strain coefficient d_h* links the piezoelectric polarization as a result of a change in the hydrostatic stress. The FOMs from Eq. (1) as products of the piezoelectric coefficients are related [1,4] to the power densities and the signal-to-noise ratios of piezoelectric elements and, therefore, used to characterize their piezoelectric sensitivity.

Many works, that have garnered considerable attention for the last decade, deal with the problem of optimization of electromechanical properties of different PCs [12-14]. One of the important items in this optimization is the analysis of opportunities for achieving the high piezoelectric sensitivity. In this connection the present paper represents a review of some recent results on large FOMs and high piezoelectric sensitivity of the FC-based PCs.

Figures of Merit and Their Maximal Values

As follows from results of numerous works (see, *e.g.*, [2,3,9,11-13]), peaks of the concentration dependences $(Q_{33}*)^2(m)$ and $(Q_h*)^2(m)$ of 1-3 PCs "Pb(Zr, Ti)O_3 FC rods – polymer matrix" (Fig. 1, central part) are several tens of times higher than those related to the same ceramic components. In the 1-3 PCs suitable for various applications, $\max(Q_{33}*)^2(m) = 20000 \ldots 50000$ $(\mathrm{PPa})^{-1}$ and $\max(Q_h*)^2(m) = 2000 \ldots 9500$ $(\mathrm{PPa})^{-1}$. Applications of these materials require a certain improvement in their performances, including the FOMs. A change in microgeometry of the PC may raise the piezoelectric voltage coefficients g_h* and $g_{33}*$ by more than one order of magnitude above $g_{33}{}^{FC} + 2g_{31}{}^{FC}$ and $g_{33}{}^{FC}$, respectively [9,17], where the superscript *FC* is assigned to the electromechanical constants of the FC rods. Such enhancement of the piezoelectric response results in increasing the FOMs.

The possibility of producing the three-component PCs involving the FC rods has been discussed in several papers [9,10]. Based on a series of calculation procedures it has been first shown [18] that the $(Q_h*)^2$ value exceeds 10000 $(\mathrm{PPa})^{-1}$ for 1-0-3 connectivity

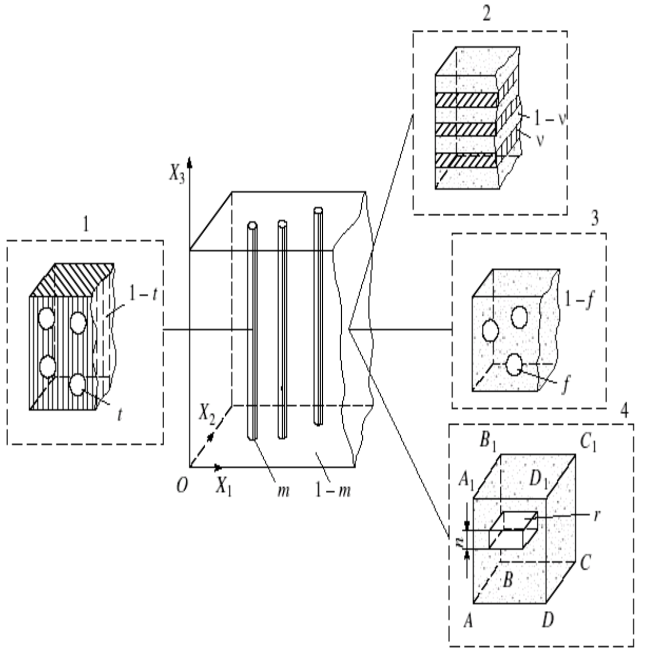

Figure 1: Schematic diagram of three-component piezoactive composites (insets 1 to 3) [15]. m, volume concentration of cylindrical FC rods, $1 - m$, volume concentration of the polymer component in a piezopassive lengthy matrix. Volume concentration of spherical pores in the rods is t and in the surrounding matrix it equals f (spherical pores shown in inset 3) or nr (parallelepiped-like pores arranged within the Banno cubic cell [16] $ABCDA_1B_1C_1D_1$ as shown in inset 4), where n and r are concentration parameters: n equals the ratio of the parallelepiped height to the cube edge $|AA_1|$ and r is the ratio of the parallelepiped base area to the cube face area $|AB|\cdot|BC|$. In inset 2, ν and 1 – ν are the volume concentrations of the layers of the first and second types, respectively.

and $(Q_h^*)^2$ attains 50500 $(\text{PPa})^{-1}$ for 1-2-2 connectivity (Fig. 1, inset 2). The last hydrostatic FOM exceeds the value $(Q_h^*)^2 = 50000$ $(\text{PPa})^{-1}$ that is related to 2-2-0 connectivity and known to be very large for the three-component composites [4,9].

In our recent work [15], devoted to modeling of the high-sensitive α-β-3 PCs, different combinations of the porous components have been first considered. The corresponding piezoelectric response of the PCs has been modeled for two cases: porous 0-3 rods surrounding by a homogeneous matrix (Fig. 1, inset 1, PC with 0-1-3 connectivity) and rods surrounding by a porous 0-3 matrix (Fig. 1, insets 3 and 4, PC with 1-0-3 connectivity). In the last case the matrix is supposed to be cellular with air-filled pores in the form of a sphere or a parallelepiped.

The effective elastic moduli c_{ij}^{*E} at the constant electric field, piezoelectric coefficients e_{kl}^* and dielectric permittivities $\varepsilon_{pp}^{*\xi}$ at the constant strain have been determined for the porous 0-1-3 and 1-0-3 PCs in two steps, as described in details in Ref. 15. Based on these electromechanical constants, the concentration dependences $(Q_{33}^*)^2(m)$ and $(Q_h^*)^2(m)$ have been calculated, where m is the volume concentration of the FC rods embedded in the polymer matrix. It has been established that these FOMs have maximal values at $m << 1$ independently of microgeometry of pores. For the small volume concentrations m and the considerable piezoelectric anisotropy $|e_{33}^* / e_{31}^*| >> 1$ (that is characteristic of 1-3-type FC-based PCs) [5,6,11], Eq. (1) can be rewritten as follows:

$$(Q_h^*)^2 \approx \eta_{elas,h}^*(e_{33}^*/c_{33}^{*E})^2/\varepsilon_{33}^{*\sigma} \approx \eta_{elas,h}^*(\gamma^{FC})^2 \times (m\varepsilon_{33}^{FC,\sigma}) \text{ and } (Q_{33}^*)^2 \approx (\eta_{elas,33}^* / \eta_{elas,h}^*)(Q_h^*)^2, \quad (2)$$

where

$$\eta_{elas,h}^* = \{[1 + (\beta_{12}^*)^{-1} - 2(\beta_{13}^*)^{-1}] / [1 + (\beta_{12}^*)^{-1} - 2(\beta_{13}^*)^{-1}(\beta_{33}^* / \beta_{13}^*)]\}^2, \ \eta_{elas,33}^* = \{[1+ (\beta_{12}^*)^{-1}] / [1 + (\beta_{12}^*)^{-1} - 2(\beta_{13}^*)^{-1}(\beta_{33}^* / \beta_{13}^*)]\}^2, \ \gamma^{FC} = me_{33}^{FC} \times (mc_{33}^{FC,E} + c_{33}^{M})^{-1}, \quad (3)$$

and $\beta_{ab}^* = c_{11}^{*E} / c_{ab}^{*E}$ are factors depending on the electromechanical constants of the PC and its components, and c_{33}^M is the elastic modulus of the matrix.

Among the perovskite-type FCs [19,20], the soft-ceramic composition PCR-7M (one of so-called "piezoceramics from Rostov-on-Don") has the highest ratio $e_{33}^{FC} / c_{33}^{FC,E}$ at room temperature and, hence, large γ^{FC} values from Eq. (3) at $m << 1$ independently of the microgeometry of pores. As compared to the case of 1-2-2 connectivity [18], the elastomer-araldite laminated structure (Fig. 1, inset 2) features a large difference between the ratios c_{11}^M / c_{33}^M and c_{12}^M / c_{13}^M [15], so that the terms $\eta_{elas,h}^*$ and $\eta_{elas,33}^*$ from Eqs. (2) – (3) become appreciable.

Some examples of concentration dependences $(Q_h^*)^2(m)$ (Fig. 2, a, c) indicate how the spherical pores in the polymer matrix (Fig. 1, inset 3) favor the high piezoelectric sensitivity of the PCs. Changes in the ratios $c_{11}^M / c_{12}^M = c_{11}^M / c_{13}^M = c_{33}^M / c_{13}^M$ of the elastic moduli of the isotropic porous matrix undoubtedly influence $\eta_{elas,h}^*$ from Eq. (3) and $(Q_h^*)^2$ from Eq. (2) because the factor $\eta_{elas,h}^*$ considerably depends on the ratio $\beta_{33}^* / \beta_{13}^* \approx c_{13}^M / c_{33}^M$ at $m << 1$ and f = const. It would be additionally noted that positions of $\max(Q_{33}^*)^2(m)$ and $\max(Q_h^*)^2(m)$ in graphs of Fig. 2 take place in a fairly narrow range of the volume concentrations m.

The very large values of $\max(Q_{33}^*)^2(m) \approx \max(Q_h^*)^2(m) \approx (4 \ldots 7)\cdot 10^6$ $(\text{PPa})^{-1}$ calculated [15] for the 1-0-3 PC „FC rods – elastomer with plane-parallel pores" at $n = 0.01 \ldots 0.10$ and $r = 0.90 \ldots 0.99$ (Fig. 1, inset 4) are much larger than those in Fig. 2, b, c

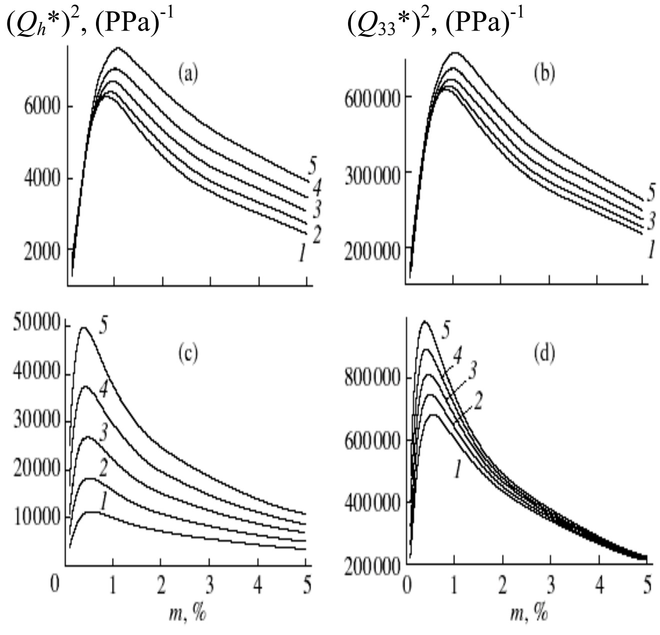

Figure 2: Concentration dependences of the squared hydrostatic FOM $(Q_h^*)^2(m)$ (a, c) and $(Q_{33}^*)^2(m)$ (b, d) calculated [15] for the 0-1-3 PC „FC rods with spherical pores – elastomer“ (a, b) and the 1-0-3 PC „FC rods – elastomer with spherical pores“ (c, d) shown in Fig. 1.

a, b) Curves 1, 2, 3, 4, and 5 have been calculated for the volume concentration of pores in the FC rods $t = 0.05$, 0.10, 0.15, 0.20, and 0.25, respectively.

c, d) Curves 1, 2, 3, 4, and 5 have been calculated for the volume concentration of pores in the elastomer matrix $f = 0.05$, 0.10, 0.15, 0.20, and 0.25, respectively.

because the ratios c_{11}^M / c_{12}^M, c_{11}^M / c_{13}^M and c_{33}^M / c_{13}^M differ. The like behavior has been established in the case [18] of the laminated elastomer–araldite matrix in the 1-2-2 PC, but the lack of the pores in this matrix impedes further increasing the FOMs.

The advanced modeling of novel PC structures enabled us to reach $\max(Q_{33}^*)^2(m)$ and $\max(Q_h^*)^2(m)$ in a range of $(10^5 \ldots 10^6)$ $(\mathrm{PPa})^{-1}$. Corresponding calculations have been first made for the 1-0-1 PC „PCR-7M – araldite with plane-parallel pores“ [21,22] with microgeometry of pores shown in inset 4 of Fig.1. This circumstance, as well as analogous concentration behavior of the piezoelectric coefficients d_{3j}^*, e_{3j}^*, and g_{3j}^*, calculated for the 1-3-type [6,8,11,15] and 1-1-type [21] PCs, can be associated with the similarity in the boundary conditions for the electric and mechanical fields. It can be probably one of consequences of a similar redistribution of the internal electric and mechanical fields in structures with FC – polymer interfaces oriented parallel to the poling axis OX_3.

All the calculated data for $\max(Q_{33}^*)^2(m)$ and $\max(Q_h^*)^2(m)$ indicate that the corresponding volume concentrations of the FC rods in the 1-3 [11], 1-2-2 [18], 0-1-3, 1-0-3 [15], and 1-0-1 [21,22] PCs on the basis of PCR-7M or other perovskite-type FCs are small ($m < 5$ %). This seems likely to retard the use of such piezoactive materials as potential elements of hydrophones. However, the squared FOMs (1) calculated for the 1-0-3 [15] and 1-0-1 [21] PCs with the porous polymer matrix remain roughly one order-of-magnitude higher than those evaluated for the 1-3 PC [2,9,11,12] even at $m \approx 10$ %. Such performance of the PCs with the porous polymer matrices can be effectively exploited in various acoustic and other applications.

Conclusions

1. The squared FOMs $(Q_{33}^*)^2$ and $(Q_h^*)^2$ and their concentration behavior have been studied in order to describe the piezoelectric sensitivity of different PCs based on FC materials. It has been shown that $\max(Q_{33}^*)^2$ and $\max(Q_h^*)^2$ calculated for the 1-0-γ PCs (γ = 1; 3) strongly depend on ratios $e_{33}^{FC} / c_{33}^{FC,E}$ (FC properties) c_{11}^M / c_{j3}^M (polymer matrix properties, $j = 1$; 3). These parameters depend to a lesser extent on dielectric properties of the components and on differences between elastic moduli of the components.

2. The factors $\eta_{elas,h}^*$ and $\eta_{elas,33}^*$ introduced for the 1-0-3 PCs can be used for characterization of redistribution of internal electric and mechanical fields as well as for prediction of extreme values of the parameters describing the piezoelectric response of this and related materials. The correlation between c_{11}^M / c_{i3}^M, $\eta_{elas,h}^*$ and $\max(Q_h^*)^2$ or $\max(Q_{33}^*)^2$ is regarded as an important step in prediction of the FOMs, related parameters and further design of the PC.

3. A comparison of performance data on the 1-3 and 1-0-3 PCs sheds light on some advantages of the 1-0-3 and related PC structures owing to the porous polymer matrix with low dielectric permittivity and elastic moduli c_{ab}^M as well as with certain ratios c_{11}^M / c_{j3}^M. For both the 1-3 and 1-0-3 PCs the maxima of the concentration dependences $(Q_{33}^*)^2(m)$ and $(Q_h^*)^2(m)$ take place at small volume concentrations of the FC rods. In every case it would be found a compromise settlement in the fairly wide concentration range (about 10 %) where smooth decreasing the FOMs is realized.

4. The correlation between concentration behavior of the FOMs and ratios of several electromechanical constants of the components have been studied for different combinations of perovskite-type FCs and piezopassive polymers. Due to the known ratio $e_{33}^{FC} / c_{33}^{FC,E}$, related to the rods in the 1-3-type PCs, the FC components can be chosen for various acoustic, hydrophone, transducer, and other applications.

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