PROGNOSTICATION OF EFFECTIVE ELECTROMECHANICAL PROPERTIES OF NOVEL COMPOSITES CONTAINING RELAXOR – FERROELECTRIC SINGLE CRYSTALS

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Abstract

In this paper we first calculate and analyze effective piezoelectric coefficients and figures of merit of a novel smart 0-1-3 composite "$0.67Pb(Mg_{1/3}Nb_{2/3})O_3 – 0.33PbTiO_3$ single crystal – PCR-7M ferroelectric ceramic – elastomer" at various volume concentrations of piezoactive components. The role of the single-crystalline relaxor-ferroelectric component in forming the considerable piezoelectric response is emphasized and discussed.

Introduction

The problem of creation of novel piezoactive composites (PCs), prognostication and optimization of their effective electromechanical properties remains one of the important problems in modern smart materials science. Various PCs are studied and developed as highly effective elements being suitable for acoustic, medical, piezotechnical, and other devices. As is known, the overwhelming majority of modern PCs are two-component ceramic / polymer materials [1-3]. Three-component PCs were earlier considered in a few works only (see, *e.g.*, [4,5]). Recent papers on the new class of PCs "single crystal – ceramic" [6,7] and interest in synthesis and further applications of highly piezoactive perovskite-type relaxor-ferroelectric solid solutions of the $Pb(A_{1/3}B_{2/3})O_3$ – $PbTiO_3$ type [8-10] stimulate our study of the related PCs and determination of their effective physical properties. The aim of this paper is to analyze piezoelectric properties and sensitivity of a novel PC based on two perovskite-type components, namely, on the $0.67Pb(Mg_{1/3}Nb_{2/3})O_3 – 0.33PbTiO_3$ (PMN-PT) single crystal and soft ferroelectric PCR-7M ceramic.

Model and Methods of Averaging

In the model we put forward, the PC consists of rods "single crystal – ceramic" surrounded by a lengthy polymer matrix (Fig. 1). Connectivity of these rods is 0-3 whereas connectivity of the PC as a whole is 0-1-3 in terms of works by Newnham *et al.* [1,11]. Single-crystalline spheroidal inclusions $(x_1/a_1)^2 + (x_2/a_1)^2 + (x_3/a_3)^2 = 1$ with semiaxes $a_1 = a_2$ and x_3 are uniformly aligned in each rod so that main crystallographic (or perovskite) axes of each inclusion are assumed to be oriented along the OX_j axes (Fig.1).

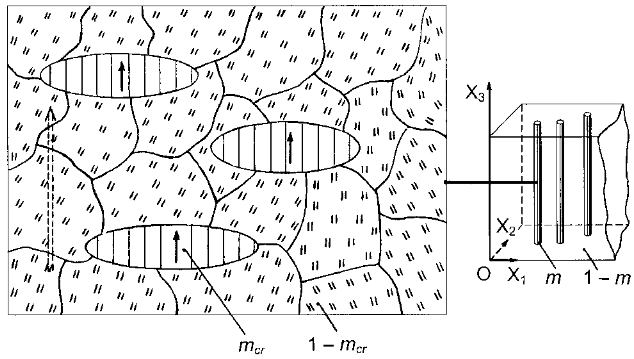


Figure 1: Schematic diagram of the 0-1-3 PC containing single-crystalline (n = 1), ceramic (n = 2) and polymer (n = 3) components. ($X_1X_2X_3$), the rectangular coordinate system, m_{cr}, volume concentration of the single-crystalline spheroidal inclusions in the rod, m, volume concentration of the rods in the matrix. The directions of the spontaneous polarization vector $\boldsymbol{P_s} \parallel OX_3$ of the single-crystalline inclusion and of the remanent polarization vector $\boldsymbol{P_R} \parallel OX_3$ of the surrounding ceramic matrix in the rod are indicated by arrows.

The nth component of the PC is characterized by sets of the elastic moduli $c_{ij}^{(n),E}$, piezoelectric coefficients $e_{kl}^{(n)}$ and dielectric permittivities $\varepsilon_{pq}^{(n),\xi}$, where the superscripts E and ξ denote measurement conditions at the constant electric field strength E and the constant mechanical strain ξ. In the first stage of our averaging procedure the electromechanical properties of the rods are determined in dependence on the volume concentration m_{cr} by the matrix method [7,12,13] being applied for 0-3 connectivity. This method, based on the Eshelby's concept on the equivalent spheroidal inclusion [14], enables us to determine a matrix of the effective electromechanical constants of the rod "single crystal - ceramic"

$$|| C^r || = || C^r(m_{cr}) || =$$

$$= \begin{pmatrix} ||c^{r,E}|| & || e^r||^T \\ ||e^r|| & -||\varepsilon^{r,\xi}|| \end{pmatrix} \quad (1)$$

by the self-consistency method [15] with allowance for the electromechanical interaction between the laminated rods and the laminated matrix where the superscripts r and T denote rod and transposition, respectively. Matrix (1) is written in accordance with formulas [13] as

$$\| C^r \| = \| C^{(2)} \| + m_{cr} (\| C^{(1)} \| - \| C^{(2)} \|) [\| K_{id} \| + (1 - m_{cr})\| S \| \| C^{(2)} \|^{-1} (\| C^{(1)} \| - \| C^{(2)} \|)]^{-1}, \quad (2)$$

where the matrices of the electromechanical constants of components $\| C^{(n)} \|$ with n = 1; 2 have the form similar to that shown in Eq. (1), $\| K_{id} \|$ is the identity matrix, and $\| S \|$ is the matrix of Eshelby coefficients depending on the $\| C^{(2)} \|$ elements and the shape of inclusions [12] (in our case on the ratio of semiaxes of spheroids $\rho = a_1 / a_3$).

In the second stage the effective elastic moduli $c_{ij}{}^{*E} = c_{ij}{}^{*E}(m, m_{cr})$, piezoelectric coefficients $e_{kl}{}^* = e_{kl}{}^*(m, m_{cr})$ and dielectric permittivities $\varepsilon_{pq}{}^{*\xi} = \varepsilon_{pq}{}^{*\xi}(m, m_{cr})$ of the PC shown in Fig. 1 are calculated on the basis of the same method, but for 1-3 connectivity only. It implies use of the matrix $\| S \|$ for the rods (*i.e.* in the limiting case of $\rho \to \infty$) and modification of Eq. (2) as follows:

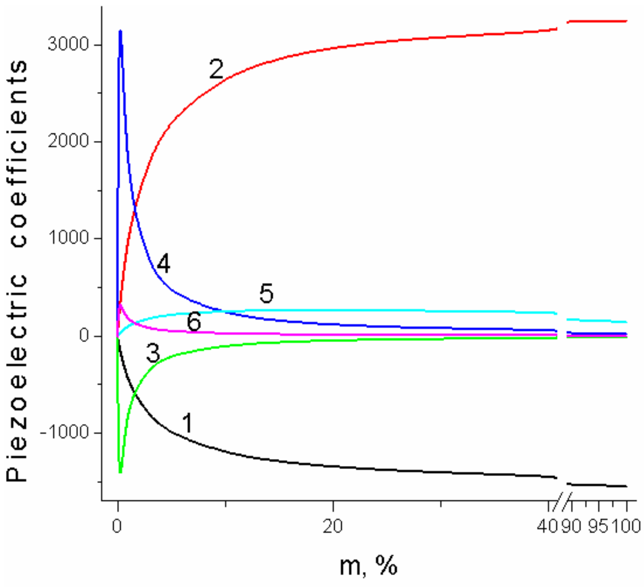
$$\| C^* \| = \| C^*(m, m_{cr}) \| = \| C^{(3)} \| + m(\| C^{(r)} \| - \| C^{(3)} \|) [\| K_{id} \| + (1 - m)\| S \| \| C^{(3)} \|^{-1} (\| C^{(r)} \| - \| C^{(3)} \|)]^{-1}. \quad (3)$$

Based on the effective electromechanical constants from Eq. (3), the piezoelectric coefficients $\| d^* \| = \| e^* \| \cdot \| c^{*E} \|^{-1}$, $\| g^* \| = \| d^* \| \cdot \| \varepsilon^{*\sigma} \|^{-1}$ as well as the hydrostatic piezoelectric coefficients $d_h{}^* = d_{33}{}^* + d_{32}{}^* + d_{31}{}^*$, $g_h{}^* = g_{33}{}^* + g_{32}{}^* + g_{31}{}^*$, squared figure of merit $(Q_{33}{}^*)^2 = d_{33}{}^* g_{33}{}^*$, and squared hydrostatic figure of merit $(Q_h{}^*)^2 = d_h{}^* g_h{}^*$ are determined as functions of m and m_{cr}, where the superscripts σ and D mean measurement conditions at the constant mechanical stress σ and the constant electric displacement D. The parameters $(Q_{33}{}^*)^2$ and $(Q_h{}^*)^2$, related [1,16,17] to power densities and signal-to-noise ratios of the piezoelectric element, are often used for characterization of piezoelectric sensitivity of the material.

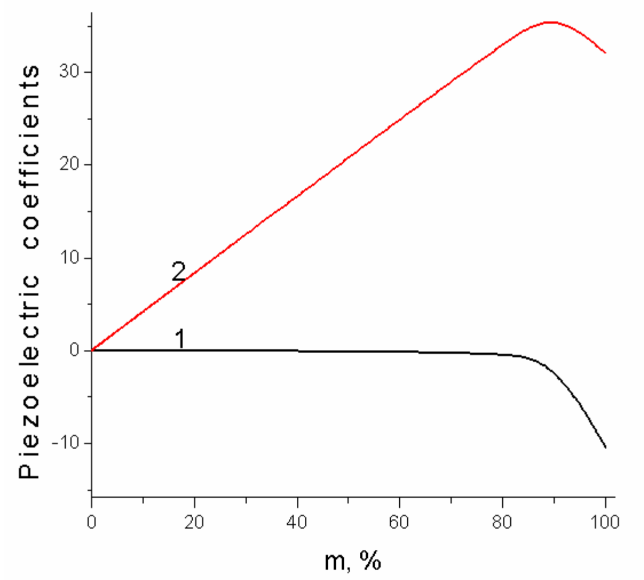
Features of Piezoelectric Effect and Hydrostatic Response

Components of the 0-1-3 PC are mainly distinguished by the piezoelectric coefficients and symmetry. Among these components of particular interest is the relaxor-based polydomain $0.67Pb(Mg_{1/3}Nb_{2/3})O_3 - 0.33PbTiO_3$ (PMN-PT) single crystal being used as the $(001)_c$ cut in perovskite axes. At room temperature this composition of the PMN-PT single crystal is related to the morphotropic phase boundary, and the domain structure after poling the $(001)_c$ cut is represented by four types of 71° (109°) rhombohedral (3*m*) domains [18]. It results in the very high piezoelectric activity of the PMN-PT $(001)_c$ cuts, especially along the OX_3 axis, and in 4*mm* symmetry of these cuts at an uniform distribution of the above-mentioned domains. Symmetry of the poled perovskite-type PCR-7M ceramic (named "piezoelectric ceramic from Rostov-on-Don" [19]) is ∞*mm*, and this composition is based on ferroelectric $Pb(Zr,Ti)O_3$ solid solutions near the morphotropic phase boundary. The recent results [5,17] show that the soft PCR-7M is the ceramic component promoting the very high piezoelectric sensitivity of the 1-2-2 PC. Elastomer is the piezopassive and isotropic material [16,17]. The PC as a whole is characterized by 4*mm* symmetry where the poling axis is parallel to OX_3 (Fig. 1). Experimental room-temperature elastic $c_{ij}{}^{(n),E}$, piezoelectric $e_{kl}{}^{(n)}$ and dielectric constants $\varepsilon_{pq}{}^{(n),\xi}$ of the components are taken for calculations from works [16-19].

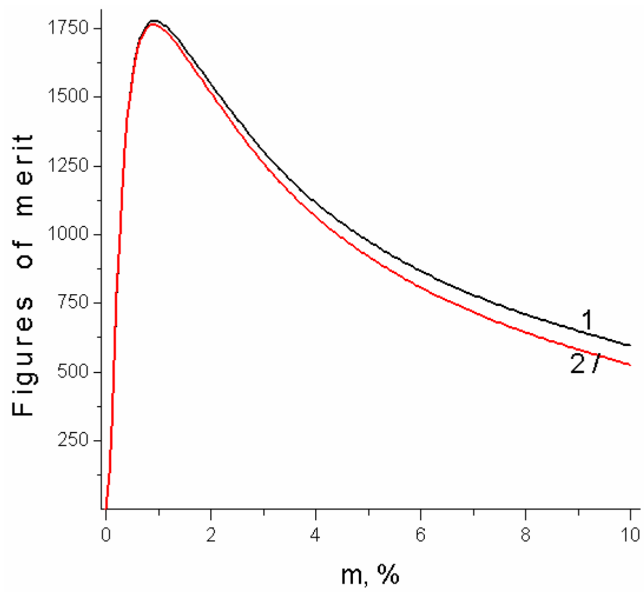
Now we consider some concentration dependences of the effective parameters of the 0-1-3 PC (Fig. 2). The evaluated effective electromechanical constants of the 0-3 rods were used in further procedures for search for extreme points and optimization of the properties of the 0-1-3 PC. The largest values of $(Q_{33}{}^*)^2$ and $(Q_h{}^*)^2$ corresponding the highest piezoelectric sensitivity take place in the presence of needle-shaped single-crystalline inclusions within the rods (Fig. 2, c). The value of $\max(Q_h{}^*)^2$ at m_{cr} = 0.50 is about 3-8 times larger than that known [1,17,20,21] for the 1-3 PCs "ferroelectric ceramic – polymer". For example, in the 1-3 PCs "PCR-7M ceramic – elastomer", $\max(Q_h{}^*)^2 = 6.24 \cdot 10^{-12}$ Pa^{-1} and $\max(Q_{33}{}^*)^2 = 6.24 \cdot 10^{-10}$ Pa^{-1} take place. Increasing the piezoelectric sensitivity in the case of the novel 0-1-3 PC is explained by the high piezoelectric activity of the interacting components (n = 1; 2) of the rod, the large values [17] of the ratio $e_{33}{}^r / c_{33}{}^{r,E}$ at small volume concentrations of the rods and the large anisotropy of the piezoelectric coefficients $e_{33}{}^* / e_{31}{}^*$ of the PC (Fig. 2, b) in the wide concentration range. The configuration of curves of concentration dependences of different piezoelectric coefficients (Fig. 2, a, b), that describe the response of this PC along the poling OX_3 axis, is typical of the 1-3-type PC (see, *e.g.*, [16,17,20,21]) due to the presence of the piezoactive rods (Fig. 1) running parallel to the same axis. However, in comparison with data [16,17,20] on the 1-3 ceramic-based PCs, our 0-1-3 PC exhibits considerable values of both $d_h{}^*$ and $g_h{}^*$ (see curves 5 and 6 in Fig. 2, a). It should be also noted that no changes in orders-of-magnitude of $\max g_h{}^*$, $\max(Q_{33}{}^*)^2$ and $\max(Q_h{}^*)^2$ are established for the volume concentrations of the rods $m \le 5$ ... 7 % even as the sharp maxima of the above-mentioned parameters correspond to $m \approx 1$ % (Fig. 2, a, c). This



a



b



c

Figure 2 : Concentration dependences calculated for the 0-1-3 PC "PMN-PT single crystal - PCR-7M ceramic - elastomer" at volume concentration of the single-crystalline inclusion in the rods $m_{cr} = 0.50$:
a) piezoelectric coefficients $d_{31}^*(m)$ (curve 1, in pC/N), $d_{33}^*(m)$ (curve 2, in pC/N), $g_{31}^*(m)$ (curve 3, in mV·m/N), $g_{33}^*(m)$ (curve 4, in mV·m/N), $d_h^*(m)$ (curve 5, in pC/N), and $g_h^*(m)$ (curve 6, in mV·m/N);
b) piezoelectric coefficients $e_{31}^*(m)$ (curve 1, in C/m^2) and $e_{31}^*(m)$ (curve 2, in C/m^2);
c) squared figures of merit $(Q_{33}^*)^2$ (curve 1, in 10^{-12} Pa^{-1}) and $(Q_h^*)^2$ (curve 2, in 10^{-14} Pa^{-1}).

In all the above-given cases inclusions in the rods are assumed to be spheroids with the ratio of semiaxes $\rho = 0.02$.

circumstance is associated with a certain balance between elastic moduli $c_{ij}^{r,E}$ of the rods and $c_{ij}^{(3),E}$ of the surrounding matrix as well as with fairly low dielectric permittivity of such the PC at $m < 10$ %.

Summary

The novel PC, that is described by 0-1-3 connectivity and based on two piezoactive components "relaxor-ferroelectric single crystal – ceramic", has been considered in this paper. The proper procedures have been applied for calculation of its effective electromechanical constants (3) on dependence of the volume concentrations of the single-crystalline and ceramic components. It has been shown that the piezoelectric coefficients $|g_{3j}^*|$, the hydrostatic piezoelectric coefficients d_h^* and g_h^* as well as figures of merit Q_{33}^* and Q_h^* reach considerable maximal values due to the relaxor-ferroelectric single-crystalline inclusions within the ceramic rods. Such microgeometry and the needle-like shape of the inclusions result in increasing the high piezoelectric sensitivity, and it becomes a few orders-of-magnitude higher than that in known ferroelectric ceramics or relaxor-ferroelectric single crystals. The above-mentioned results of our study offer a promising approach for prediction of the effective electromechanical properties in three-component PCs needed for advanced hydrophone, ultrasonic and other piezotechnical devices.

Acknowledgments

We would like to thank Prof. Dr. A. V. Turik and Dr. V. V. Eremkin (Russia) and Dr. M. Kamlah (Germany) for their constant interest in the research problems. The work was partially supported by the administration of the Rostov State University (Grant-in-aid No. 11.01.03 f on basic researches), and this support is acknowledged. Financial support by the Research Centre Karlsruhe (Germany) and by the Organizing Committee of the Fifth World Congress on Ultrasonics (Paris, France, 2003) during the stay of one of the authors (V. Yu. T.) at the Research Institute IMF II of the above-mentioned Centre is also gratefully acknowledged.

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