Research Article

Hydrostatic Parameters and Domain Effects in Novel 2-2 Composites Based on PZN-0.12PT Single Crystals

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A novel 0.88Pb(Zn_{1/3}Nb_{2/3})O₃-0.12PbTiO₃ crystal/polymer composite with 2-2 connectivity is studied at variable orientations of spontaneous polarisation vector of the crystal component. Orientation and volume-fraction dependences of the hydrostatic piezoelectric coefficients d_h^* , e_h^* , and g_h^* and hydrostatic electromechanical coupling factor k_h^* are related to the important role of the piezoelectric and elastic anisotropy of single-domain layers of the 2-2 composite. The record value of $|e_h^*| \approx 77$ C/m² near the absolute-minimum point and the correlation between the hydrostatic (e_h^*) and piezoelectric (e_{3j}^*) coefficients and between the hydrostatic (g_h^*) and piezoelectric (g_{3j}^*) coefficients are first established. This discovery is of value for hydrostatic and piezotechnical applications. The hydrostatic performance of the composite based on the single-domain 0.88Pb(Zn_{1/3}Nb_{2/3})O₃-0.12PbTiO₃ crystal is compared to the performance of the 2-2 composites based on either the same polydomain crystal or the related single-domain crystal.

1. Introduction

The polarisation orientation effect in advanced piezo-active composites based on relaxor-ferroelectric single crystals (SCs) of $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ (PZN- x PT) [1–3] and $(1-y)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $y\text{PbTiO}_3$ (PMN- y PT) [3, 4] opens up new possibilities of the variation of effective parameters of the composites that are of value for modern hydroacoustic and piezotechnical applications. The anisotropic SC component with large piezoelectric coefficients (e.g., $d_{3j}^{(1)} \sim 10^3$ pC/N, hereafter we use superscript “(1)” to denote electromechanical constants of the SC component) [5, 6] plays an important role in forming the piezoelectric effect of the composite and its hydrostatic piezoelectric response, as shown in recent papers on the 2-2 [1, 3, 4] and 1-3 [2] SC/polymer composites. The 2-2 parallel-connected composite based on the single-domain PMN-0.33PT SC [4] is an example of a piezoelectric material whereby large hydrostatic piezoelectric coefficients are achieved at specific orientations of the

crystallographic axes and SC volume fraction. As is known, the chemical composition of PMN-0.33PT is located near the morphotropic phase boundary, and the PMN-0.33PT SC in the single-domain state is described by 3m symmetry at room temperature [7]. Along with electromechanical constants of PMN-0.33PT, there are complete sets of room-temperature electromechanical constants (Table 1) measured on the single-domain PMN-0.42PT [5] and PZN-0.12PT [8] SCs with 4mm symmetry. We see the difference between the piezoelectric coefficients $d_{ij}^{(1)}$ of PMN-0.42PT and PZN-0.12PT SCs, for which the order of magnitude of $d_{ij}^{(1)}$ remains 10^2 pC/N (Table 1). We note that the single-domain PZN-0.12PT SC exhibits a distinctive elastic anisotropy in comparison to that of the single-domain PMN-0.42PT SC: according to data from Table 1, ratios

$$\frac{s_{33}^{(1),E}}{s_{11}^{(1),E}} = 2.71, \quad \frac{s_{11}^{(1),E}}{|s_{13}^{(1),E}|} = 1.10 \quad (1)$$

TABLE 1: Elastic compliances $s_{ab}^{(n),E}$ (in 10^{-12} Pa $^{-1}$), piezoelectric coefficients $d_{ij}^{(n)}$ (in pC/N), and relative dielectric permittivity $\epsilon_{pp}^{(n),\sigma}/\epsilon_0$ of single-domain SC and polymer components at room temperature.

Components	$s_{11}^{(n),E}$	$s_{12}^{(n),E}$	$s_{13}^{(n),E}$	$s_{33}^{(n),E}$	$s_{44}^{(n),E}$	$s_{66}^{(n),E}$
PZN-0.12PT SC [8]	20.1	-4.6	-18.2	54.5	19.5	17.2
PMN-0.42PT SC [5]	9.43	-1.68	-6.13	19.21	35.09	12.5
Polyurethane [11]	400	-148	-148	400	1100	1100
Components	$d_{31}^{(n)}$	$d_{33}^{(n)}$	$d_{15}^{(n)}$	$\epsilon_{11}^{(n),\sigma}/\epsilon_0$	$\epsilon_{33}^{(n),\sigma}/\epsilon_0$	
PZN-0.12PT SC [8]	-207	541	653	10000	750	
PMN-0.42PT SC [5]	-91	260	131	8627	660	
Polyurethane [11]	0	0	0	3.5	3.5	

are valid for PZN-0.12PT. At the same time, the single-domain SCs are characterised by the almost equal anisotropy of $d_{3j}^{(1)}$: as follows from Table 1,

$$\begin{aligned} \frac{d_{33}^{(1)}}{d_{31}^{(1)}} &= 2.61(\text{PZN-0.12PT}), \\ \frac{d_{33}^{(1)}}{d_{31}^{(1)}} &= 2.86(\text{PMN-0.42PT}). \end{aligned} \quad (2)$$

The distinctions shown in (1) could influence the piezoelectric effect and hydrostatic response of the composite, and such an effect has not been considered in detail in earlier studies. In this work, we first study the domain effects concerned with the polarisation orientation and the hydrostatic response of the 2-2 SC/polymer composite in a wide volume fraction and orientation ranges. The aim of the present paper is to show the role of the domain effects and the electromechanical properties of SCs in developing a considerable hydrostatic response of the 2-2 composite (with either single-domain or polydomain layers). Below we discuss some advantages concerned with the hydrostatic piezoelectric coefficients of the composite based on the single-domain PZN-0.12PT SC.

2. Structure and Effective Electromechanical Properties of the 2-2 Composite

It is assumed that the composite represents a system of the parallel-connected SC and polymer layers which form the regular laminar structure (Figure 1) with 2-2 connectivity (in terms of [9]). The crystallographic axes X , Y , and Z of the single-domain SC in the initial state ($\alpha = 0$ or $\beta = 0$; see insets 1 and 2 in Figure 1) are parallel to the following perovskite unit-cell directions: $X \parallel [100] \parallel OX_1$, $Y \parallel [010] \parallel OX_2$, and $Z \parallel [001] \parallel OX_3$. In this case, the spontaneous polarization vector in each SC layer is $\mathbf{P}_s^{(1)} \parallel OX_3$. We consider rotations of the $\mathbf{P}_s^{(1)}$ vector around one of the coordinate axes— OX_1 or OX_2 (see insets 1 and 2 in Figure 1), and all the SC layers in the composite sample have the same orientation of $\mathbf{P}_s^{(1)}$. Thus, a system of SC cuts with a fixed orientation of the crystallographic axes X , Y , and Z is to be

prepared before manufacturing the 2-2 composite sample. The orientation of the crystallographic axes in the aligned cuts can be checked by means of X-ray technique, and the further poling procedure is assumed to be performed at the fixed orientation of the composite sample as a whole. The single-domain state of the SC layers (cuts) in the sample can be stabilised under bias. In a polydomain SC layer, the rotation of the effective spontaneous polarisation vector $\mathbf{P}_s^{(1,\text{polyd})} = m_d \mathbf{P}_{s,1} + (1 - m_d) \mathbf{P}_{s,2}$ in the ($X_2 OX_3$) plane is caused by changes in the volume fraction m_d of the laminar 90° domains (inset 3 in Figure 1), and these changes can be caused by an external electric field that is initially applied to the SC layers.

The effective electromechanical properties of the 2-2 composite are studied within the framework of the matrix approach [10] that is applied to composite materials with planar microgeometry. The 9×9 matrix of the effective properties of the composite in the rectangular co-ordinate system ($X_1 X_2 X_3$)

$$\|C^*\| = \begin{pmatrix} \|s^{*E}\| & \|d^{*}\|^t \\ \|d^{*}\| & \|\epsilon^{*\sigma}\| \end{pmatrix} \quad (3)$$

is written in terms of $\|s^{*E}\|$ (6×6 matrix of elastic compliances at constant electric field), $\|d^{*}\|$ (3×6 matrix of piezoelectric charge coefficients), and $\|\epsilon^{*\sigma}\|$ (3×3 matrix of dielectric permittivities measured at constant stress), where superscript “ t ” denotes the transposed matrix. The $\|C^*\|$ matrix from (3) is determined from averaging the electromechanical properties of components on the volume fraction m and is given by

$$\begin{aligned} \|C^*\| &= [\|C^{(1)}\| \cdot \|M\|m + \|C^{(2)}\|(1 - m)] \\ &\cdot [\|M\|m + \|I\|(1 - m)]^{-1}, \end{aligned} \quad (4)$$

where $\|C^{(1)}\|$ and $\|C^{(2)}\|$ are matrices of the electromechanical properties of SC and polymer, respectively, $\|M\|$ is concerned with the electric and mechanical boundary conditions [10] at interfaces $x_1 = \text{const}$ (Figure 1), and $\|I\|$ is the identity 9×9 matrix. Elements of the $\|C^{(1)}\|$ matrix are written taking into account the orientation of $\mathbf{P}_s^{(1)}$ in the single-domain SC layer (insets 1 and 2 in Figure 1) or the volume fraction m_d of the 90° domains (inset 3 in Figure 1).

FIGURE 1: Schematic of the 2-2 parallel-connected SC/polymer composite. $(X_1X_2X_3)$ is the rectangular co-ordinate system of the composite sample α and β are angles of rotation of the spontaneous polarisation vector $\mathbf{P}_s^{(1)} \parallel OX_3'$ of the single-domain SC layer around the OX_1 axis (inset 1) or around the OX_2 axis (inset 2). In inset 3 the 90° domain structure in the SC layer is schematically shown, where m_d and $1 - m_d$ are volume fractions of the 90° domains in the SC layer, and their spontaneous polarisation vectors are shown with arrows.

In case of the single-domain SC layer, the elements of $\|C^{(1)}\|$ are represented in the tensor form as $\varepsilon_{np}^{(1),\sigma} = r_{nk}r_{pl}(\varepsilon_{kl}^{(1),\sigma})_T$, $d_{ifg}^{(1)} = r_{it}r_{fu}r_{gv}(d_{tuv}^{(1)})_T$, and $s_{pqvw}^{(1),E} = r_{pc}r_{ql}r_{vh}r_{wn}(s_{clhn}^{(1),E})_T$, where r_{nk} is the element of the matrix that describes the rotation of the $\mathbf{P}_s^{(1)}$ vector and the co-ordinate axes, and subscript “ T ” means that the electromechanical constant is given in the main crystallographic axes, that is, taken from Table 1. The aforementioned rotation is shown in either inset 1 in Figure 1 (then r_{nk} is represented in the general form as $r_{nk} = r_{nk}(\alpha)$) or inset 2 in Figure 1 (then in the general form $r_{nk} = r_{nk}(\beta)$). In the case of a polydomain SC layer (inset 3 in Figure 1), the rotation of the co-ordinate axes by $\alpha = \pm 45^\circ$ in the adjacent domains is to be taken into account in the matrix elements r_{nk} , r_{pl} , and so forth. The effective electromechanical properties of the polydomain SC layer in the co-ordinate system $(X_1X_2X_3)$ are determined by analogy with (4)

$$\|C^{(1)}\| = \left[\|C^{(d1)}\| \cdot \|M_d\|m_d + \|C^{(d2)}\|(1 - m_d) \right] \cdot [\|M_d\|m_d + \|I\|(1 - m_d)]^{-1}, \quad (5)$$

where $\|C^{(d1)}\|$ and $\|C^{(d2)}\|$ are matrices of electromechanical constants of the 90° domains with the volume fractions m_d and $1 - m_d$, respectively, and $\|M_d\|$ is the matrix concerned

with the boundary conditions [10] for elastic and electric fields at the domain wall $x_3 = \text{const}$. The matrix from (5) is represented in the general form by

$$\|C^{(1)}\| = \begin{bmatrix} s_{11}^{(1),E} & s_{12}^{(1),E} & s_{13}^{(1),E} & s_{14}^{(1),E} & 0 & 0 & 0 & d_{21}^{(1)} & d_{31}^{(1)} \\ s_{12}^{(1),E} & s_{22}^{(1),E} & s_{23}^{(1),E} & s_{24}^{(1),E} & 0 & 0 & 0 & d_{22}^{(1)} & d_{32}^{(1)} \\ s_{13}^{(1),E} & s_{23}^{(1),E} & s_{33}^{(1),E} & s_{34}^{(1),E} & 0 & 0 & 0 & d_{23}^{(1)} & d_{33}^{(1)} \\ s_{14}^{(1),E} & s_{24}^{(1),E} & s_{34}^{(1),E} & s_{44}^{(1),E} & 0 & 0 & 0 & d_{24}^{(1)} & d_{34}^{(1)} \\ 0 & 0 & 0 & 0 & s_{55}^{(1),E} & s_{56}^{(1),E} & d_{15}^{(1)} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{56}^{(1),E} & s_{66}^{(1),E} & d_{16}^{(1)} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{15}^{(1)} & d_{16}^{(1)} & \varepsilon_{11}^{(1),\sigma} & 0 & 0 \\ d_{21}^{(1)} & d_{22}^{(1)} & d_{23}^{(1)} & d_{24}^{(1)} & 0 & 0 & 0 & \varepsilon_{22}^{(1),\sigma} & \varepsilon_{23}^{(1),\sigma} \\ d_{31}^{(1)} & d_{32}^{(1)} & d_{33}^{(1)} & d_{34}^{(1)} & 0 & 0 & 0 & \varepsilon_{23}^{(1),\sigma} & \varepsilon_{33}^{(1),\sigma} \end{bmatrix}. \quad (6)$$

It should be added that the electromechanical properties of the polydomain PZN-0.12PT SC were also calculated in [8].

The $\|M\|$ matrix from (4) is determined [10] with due regard for the boundary conditions at the layer interfaces $x_1 = \text{const}$ as follows: $\|M\| = \|W_1\|^{-1} \cdot \|W_2\|$, where

$$\|W_n\| = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ s_{12}^{(n),E} & s_{22}^{(n),E} & s_{23}^{(n),E} & s_{24}^{(n),E} & s_{25}^{(n),E} & s_{26}^{(n),E} & d_{12}^{(n)} & d_{22}^{(n)} & d_{32}^{(n)} \\ s_{13}^{(n),E} & s_{23}^{(n),E} & s_{33}^{(n),E} & s_{34}^{(n),E} & s_{35}^{(n),E} & s_{36}^{(n),E} & d_{13}^{(n)} & d_{23}^{(n)} & d_{33}^{(n)} \\ s_{14}^{(n),E} & s_{24}^{(n),E} & s_{34}^{(n),E} & s_{44}^{(n),E} & s_{45}^{(n),E} & s_{46}^{(n),E} & d_{14}^{(n)} & d_{24}^{(n)} & d_{34}^{(n)} \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ d_{11}^{(n)} & d_{12}^{(n)} & d_{13}^{(n)} & d_{14}^{(n)} & d_{15}^{(n)} & d_{16}^{(n)} & \varepsilon_{11}^{(n),\sigma} & \varepsilon_{12}^{(n),\sigma} & \varepsilon_{13}^{(n),\sigma} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \quad (7)$$

$n = 1$ is related to SC, and $n = 2$ is related to polymer. The effective electromechanical properties of the composite ($\|C^*\|$ from (4)) and the polydomain layer ($\|C^{(1)}\|$ from (5)) are determined on an assumption that the wavelengths of acoustic waves propagated are considerably longer than the thickness of each layer in the composite sample (Figure 1), and the thickness of each domain (see inset 3 in Figure 1) is much less than the height of the polydomain layer.

Based on matrix elements of $\|C^*\|$ from (4), we study the volume fraction and orientation dependences of the hydrostatic piezoelectric coefficients

$$\begin{aligned} d_h^* &= d_{31}^* + d_{32}^* + d_{33}^*, \\ g_h^* &= g_{31}^* + g_{32}^* + g_{33}^*, \\ e_h^* &= e_{31}^* + e_{32}^* + e_{33}^*, \end{aligned} \quad (8)$$

and hydrostatic electromechanical coupling factor of the composite

$$k_h^* = \frac{d_h^*}{\sqrt{s_h^{*E} \varepsilon_{33}^{*\sigma}}}. \quad (9)$$

The piezoelectric coefficients g_{ij}^* from (8) are determined from the matrix $\|g^*\| = \|d^*\| \cdot \|\varepsilon^{*\sigma}\|^{-1}$ the piezoelectric coefficients e_{ij}^* from (8) are determined from the matrix $\|e^*\| = \|d^*\| \cdot \|s^{*E}\|^{-1}$. Hydrostatic compliance s_h^{*E} of the composite at $E = \text{const}$ (see (9)) is defined as follows: $s_h^{*E} = \sum_{a=1}^3 \sum_{b=1}^3 s_{ab}^{*E}$. The hydrostatic parameters Φ_h^* from (8) and (9) characterise the performance of the composite sample (Figure 1) with electrodes that are parallel to the (X_1OX_2) plane. The effective electromechanical properties of the polydomain SC layer (inset 3, Figure 1), the composite as a whole (see (4)), and its hydrostatic parameters (see (8)

and (9)) are calculated using the full sets of experimental electromechanical constants from Table 1.

3. Hydrostatic Parameters and Advantages

Examples of the calculated volume-fraction and orientation dependences of the hydrostatic parameters Φ_h^* of the composite based on the single-domain PZN-0.12PT SC are shown in Figures 2 and 3. The presence of SC with 4mm symmetry and polymer with ∞ mm symmetry enables us to establish the periodic dependence of the hydrostatic parameters on the rotation angles α and β . For any value of m from the range $0 < m < 1$, the equalities $\Phi_h^*(m, \alpha) = \Phi_h^*(m, 180^\circ - \alpha)$ and $\Phi_h^*(m, \beta) = \Phi_h^*(m, -\beta)$ hold, where $0^\circ \leq \alpha < 90^\circ$ and $0^\circ \leq \beta < 90^\circ$.

Changes in the orientation of the $\mathbf{P}_s^{(1)}$ vector of the SC layer in the (X_2OX_3) plane (inset 1 in Figure 1) mean changes in projections of $\mathbf{P}_s^{(1)}$ on the OX_2 and OX_3 axes, along which both the components of the composite are distributed continuously. Such a mode of rotation of the $\mathbf{P}_s^{(1)}$ vector leads to a relatively smooth dependence of the hydrostatic parameters Φ_h^* on α (Figure 2). The hydrostatic piezoelectric coefficient d_h^* of the composite (Figure 2(a)) remains less than $d_h^{(1)}$ of the single-domain SC. A combination of the piezoelectric (d_{ij}^*) and dielectric ($\varepsilon_{pp}^{*\sigma}$) properties gives rise to the pronounced maxima of g_h^* at $\alpha = \text{const}$ (Figure 2(b)) however, these maxima take place at a small volume fraction m . In (Figure 2(b)), we omit the volume-fraction range $0.1 < m < 1$ where g_h^* monotonically decreases at $\alpha = \text{const}$. Combining the piezoelectric (d_{ij}^*) and elastic (s_{ab}^{*E}) properties, one can attain the nonmonotonic volume-fraction behaviour of the hydrostatic piezoelectric coefficient e_h^* (Figure 2(c)) however, values of e_h^* near the local maximum points are relatively small. The complicated shape of the surface of $k_h^*(m, \alpha)$ (Figure 2(d)) is a result of the active influence of the dielectric properties at $0 < m < 0.1$ and of the elastic properties at $0.4 < m < 0.9$. As follows from the comparison of the $k_h^*(m, \alpha)$ and $d_h^*(m, \alpha)$ dependences, there is a correlation between them in certain ranges of m and α . It should be noted that this correlation stems from (9) and is concerned with the relatively smooth dependence of s_h^{*E} and $\varepsilon_{33}^{*\sigma}$ on m and α .

The related composite based on the polydomain SC (see inset 3 in Figure 1) is characterised by the hydrostatic parameters varying in the fairly narrow ranges (Table 2). The polydomain SC layers have fixed orientations and volume fractions (m_d and $1 - m_d$) of the 90° domains over the whole composite sample, and a change in m_d means a rotation of the effective spontaneous polarisation vector $\mathbf{P}_s^{(1, \text{polyd})}$ in the (X_2OX_3) plane. As in the previous case of the single-domain SC layer, this rotation does not lead to considerable hydrostatic parameters. In our evaluations, the 90° domain walls of the polydomain SC layer are assumed to be motionless. A contribution from the 90° domain-wall displacements [12] provides a contribution into electromechanical constants of SC. Our estimations show that this domain-wall contribution might give rise to

FIGURE 2: Hydrostatic piezoelectric coefficients (a)–(c) and electromechanical coupling factor (d) of the PZN-0.12PT SC/polyurethane composite at the rotation of the spontaneous polarisation vector $\mathbf{P}_s^{(1)}$ of the single-domain SC layer around the OX_1 axis (see inset 1 in Figure 1): (a) d_h^* (in pC/N), (b) g_h^* (in mV·m/N), (c) e_h^* (in C/m²), and (d) k_h^* .

increasing the upper bounds on Φ_h^* (Table 2) by about 1.5–2 times.

Varying the angle β means the crossing of the spontaneous polarisation vector $\mathbf{P}_s^{(1)}$ of the single-domain SC layer and the interface $x_1 = \text{const}$ (see inset 2 in Figure 1). This mode of rotation of $\mathbf{P}_s^{(1)}$ becomes favourable to achieve large values of hydrostatic parameters $\Phi_h^*(m, \beta)$ (Figure 3). In addition to the aforementioned combination of the electromechanical properties, the anisotropy of elastic compliances $s_{ab}^{(1),E}$ of SC leads to increasing Φ_h^* in different volume-fraction ranges. Of particular interest is the hydrostatic piezoelectric coefficient $e_h^*(m, \beta)$ (Figure 3(c)) with the deep absolute minimum. Recently [4], absolute $\min e_h^* = -44.4 \text{ C/m}^2$ was found for the 2-2 PMN-0.33PT SC/polyvinylidene fluoride composite with the single-domain SC and piezo-active polymer layers. Distinctions between PMN-0.33PT and PZN-0.12PT (both SCs in the single-domain state) are associated with both symmetry

[7, 8] and anisotropy of the electromechanical properties. As follows from experimental data on single-domain PMN-0.33PT SCs with 3m symmetry [7], the ratios $s_{11}^{(1),E}/s_{13}^{(1),E} = -11.1$, $s_{11}^{(1),E}/s_{33}^{(1),E} = 4.68$, and $d_{22}^{(1)}/d_{33}^{(1)} = 7.05$ hold in the main crystallographic axes. The above circumstances are to be taken into account when comparing the composite performance. Undoubtedly, values of $|e_h^*| \approx 77 \text{ C/m}^2$ (Figure 3(c)) enable us to regard the studied 2-2 composite as an outstanding piezoelectric material for hydroacoustic applications. To the best of our knowledge, in various ferroelectric ceramic/polymer composites [10], the typical e_h^* values do not exceed 14 C/m^2 , and values of $e_h^* \approx 10 \text{ C/m}^2$ are peculiar to conventional poled ferroelectric ceramics at room temperature [10, 13].

Our comparison of the performance of the composites based on single-domain SCs of PZN-0.12PT and PMN-0.42PT SCs (Table 3) suggests that the main difference between the hydrostatic parameters of these composites is associated with the piezoelectric coefficients of the SCs

FIGURE 3: Hydrostatic piezoelectric coefficients (a)–(c) and electromechanical coupling factor (d) of the PZN-0.12PT SC/polyurethane composite at the rotation of the spontaneous polarisation vector $\mathbf{P}_s^{(1)}$ of the single-domain SC layer around the OX_2 axis (see inset 2 in Figure 1): (a) d_h^* (in pC/N), (b) g_h^* (in mV·m/N), (c) e_h^* (in C/m²), and (d) k_h^* .

TABLE 2: Lower and upper bounds on hydrostatic parameters $\Phi_h^*(m, m_d)$ of the PZN-0.12PT SC/polyurethane composite with polydomain SC layers (see inset 3 in Figure 1) at $0 < m < 1$ and $m_d = \text{const}$.

Φ_h^*	$m_d = 0.1$ and $m_d = 0.9$	$m_d = 0.3$ and $m_d = 0.7$	$m_d = 0.5$
d_h^* (in pC/N)	$0 < d_h^* < 89.8$	$0 < d_h^* < 89.8$	$0 < d_h^* < 89.8$
g_h^* (in mV·m/N)	$0 < g_h^* < 10.6$	$0 < g_h^* < 4.68$	$0 < g_h^* < 1.89$
e_h^* (in C/m ²)	$-0.816 < e_h^* < 0.763$	$0 < e_h^* < 7.81$	$0 < e_h^* < 10.5$
k_h^*	$0 < k_h^* < 0.115$	$0 < k_h^* < 0.115$	$0 < k_h^* < 0.115$

(Table 1). In addition, the hydrostatic piezoelectric coefficient g_h^* (see Table 3 and Figures 2(b) and 3(b)) at small volume fractions ($0 < m < 0.1$) strongly depends on the dielectric properties of components, while the hydrostatic piezoelectric coefficient e_h^* mainly depends on the anisotropy of the elastic properties of SC. It is clear that the anisotropy of elastic compliances $s_{ab}^{(1),E}$ of the single-domain PMN-0.42PT SC is less pronounced (Table 1) and therefore do not lead to

the very large $|e_h^*|$ values in the composite based on this SC. As for the extreme values of g_h^* , they are achieved at small volume fractions m and are of the same order of magnitude as those studied in earlier papers [1, 3, 4, 10].

We also reveal an interesting correlation between the volume-fraction dependences of the hydrostatic piezoelectric coefficients and the piezoelectric coefficients that contribute to the hydrostatic response of the composite based on

TABLE 3: Extreme values of hydrostatic parameters $\Phi_h^*(m, \beta)$ of 2-2 composites with single-domain SC layers (see inset 2 in Figure 1) at $0 < m < 1$ and $0^\circ \leq \beta \leq 90^\circ$.

Parameter	Single-domain PZN-0.12PT SC/polyurethane composite		Single-domain PMN-0.42PT SC/polyurethane composite	
	Absolute minima	Absolute maxima	Absolute minima	Absolute maxima
d_h^*	-161 pC/N at $m = 0.090$ and $\beta = 78^\circ$	214 pC/N at $m = 0.972$ and $\beta = 72^\circ$	-69.9 pC/N at $m = 0.081$ and $\beta = 78^\circ$	130 pC/N at $m = 0.968$ and $\beta = 72^\circ$
g_h^*	-261 mV·m/N at $m = 0.005$ and $\beta = 71^\circ$	215 mV·m/N at $m = 0.028$ and $\beta = 0^\circ$	-821 mV·m/N at $m = 0.005$ and $\beta = 70^\circ$	197 mV·m/N at $m = 0.017$ and $\beta = 0^\circ$
e_h^*	-77.2 C/m ² at $m = 0.825$ and $\beta = 83^\circ$	7.78 C/m ² at $m = 0.768$ and $\beta = 35^\circ$	-28.6 C/m ² at $m = 0.725$ and $\beta = 79^\circ$	10.2 C/m ² at $m = 0.931$ and $\beta = 0^\circ$
k_h^*	-0.237 at $m = 0.020$ and $\beta = 74^\circ$	— ^a	-0.100 at $m = 0.025$ and $\beta = 74^\circ$	0.144 at $m = 0.063$ and $\beta = 0^\circ$

^aThe largest value of k_h^* corresponds to SC ($m = 1$).

FIGURE 4: Correlation between piezoelectric coefficients e_{3j}^* and e_h^* (in C/m²) of the PZN-0.12PT SC/polyurethane composite near absolute min e_h^* . The spontaneous polarisation vector $\mathbf{P}_s^{(1)}$ of the single-domain SC layer is oriented as shown in inset 2 in Figure 1, the rotation angle $\beta = 80^\circ$ (a), 83° (b) and 86° (c).

FIGURE 5: Correlation between piezoelectric coefficients g_{3j}^* and g_h^* (in $\text{mV} \cdot \text{m/N}$) of the PZN-0.12PT SC/polyurethane composite near absolute min g_h^* . The spontaneous polarisation vector $\mathbf{P}_s^{(1)}$ of the single-domain SC layer is oriented as shown in inset 2 in Figure 1, the rotation angle $\beta = 69^\circ$ (a), 71° (b) and 73° (c).

PZN-0.12PT SC (see (8) and Figures 4 and 5). Graphs in Figure 4 show that, near the absolute minimum of e_h^* , the piezoelectric coefficients e_{3j}^* from (8) obey conditions

$$e_{32}^* \approx e_{33}^*, \quad |e_{33}^*| \gg e_{31}^*, \quad (10)$$

that is, the presence of interfaces $x_1 = \text{const}$ weakens the electromechanical interaction between the SC layers (Figure 1) and strongly influences the anisotropy of e_{3j}^* . Contrary to e_{3j}^* from Figure 4, the piezoelectric coefficients g_{3j}^* from Figure 5 obey conditions

$$g_{31}^* \approx |g_{32}^*|, \quad g_{33}^* \approx g_h^*. \quad (11)$$

In our opinion, the distinctions between conditions (10) and (11) are associated with the different volume-fraction ranges of validity (e.g., large m values for e_{3j}^* and small m values for g_{3j}^*) and with the combination of the properties in the 2-2 parallel-connected composite. In case of e_{3j}^* , the combination of the piezoelectric and elastic properties plays the leading role, whereas behaviour of g_{3j}^* is accounted for by the combination of the piezoelectric and dielectric properties. Graphs in Figure 5 suggest that large $|g_h^*|$ values can be attained at volume fractions of SC $m \approx 0.04-0.07$, and this range is to be taken into consideration when manufacturing the composite sample with high piezoelectric sensitivity. Our analysis of behaviour of the piezoelectric coefficients near the absolute maxima (Figures 4 and 5) enables us to conclude

that not only the elastic and dielectric anisotropy, but also the parallel interfaces $x_1 = \text{const}$ in the composite sample influence validity of conditions (10) and (11) in certain volume-fraction and orientation ranges.

4. Conclusion

In this paper, we first studied features of the hydrostatic piezoelectric response of the novel 2-2 PZN-0.12PT SC/polyurethane composite with parallel-connected layers. The considerable hydrostatic parameters and the anisotropy of the piezoelectric coefficients (see conditions (10) and (11)) in the composite based on the single-domain PZN-0.12PT SC are strongly connected with peculiarities of its elastic and piezoelectric properties as well as with the orientation of the spontaneous polarisation vector $\mathbf{P}_s^{(1)}$ with respect to the interface $x_1 = \text{const}$ (Figure 1). The correlation between the piezoelectric coefficients near the absolute minima of the hydrostatic parameters (Figures 4 and 5) is observed at different conditions for the piezoelectric coefficients (cf. (10) and (11)), and such behaviour has no analogs among other piezo-active composites. In our opinion, the anisotropy of the piezoelectric and elastic properties of the single-domain SC indirectly could influence the volume-fraction dependence of the piezoelectric coefficients shown in Figures 4 and 5.

The orientation effect studied in this paper enables us to conclude that the mutual arrangement of the interfaces and the spontaneous polarisation vectors of the SC layers (Figure 1) plays an important role in forming the significant hydrostatic response of the 2-2 parallel-connected composite. The single-domain SC layers in the 2-2 composite studied have advantages over the polydomain layers mainly as the result of the large hydrostatic piezoelectric coefficients from (8). According to data from Table 3 and Figure 3, and values of $d_h^* \approx 200 \text{ pC/N}$ are expected at $0.90 < m < 0.98$ and $70^\circ < \beta < 75^\circ$, values of $|g_h^*| \approx 200 \text{ mV} \cdot \text{m/N}$ are predicted for $m \approx 0.04\text{--}0.07$ and $70^\circ < \beta < 75^\circ$ (more preferable) or for $m \approx 0.03\text{--}0.04$ and $\beta = 0^\circ$ (less preferable because of the lower volume fraction m of SC). It is remarkable that these hydrostatic parameters attain the extreme values in the same narrow range of the orientation angle β . The value of absolute $\min e_h^* = -77.2 \text{ C/m}^2$ is achieved at $m = 0.825$ and $\beta = 83^\circ$. Moreover, near this minimum point, conditions (10) are valid for the piezoelectric coefficients e_{3j}^* (Figure 4) that bring contributions into e_h^* from (8). As for the variation of the α angle (inset 1 in Figure 1) and the volume fraction m_d of the 90° domains shown in inset 3 in Figure 1, it leads to the smaller extreme values of the effective hydrostatic parameters from (8) and (9). In our opinion, such a suppression of the hydrostatic response in comparison with that at the variation of the β angle is directly connected with peculiarities of the elastic and piezoelectric anisotropy of the single-domain PZN-0.12PT SC.

The hydrostatic piezoelectric performance and the piezoelectric anisotropy of the studied composite based on the single-domain PZN-0.12PT SC is of value for specialists manufacturing the advanced composites with pronounced

domain effects. The results reported and discussed in the present paper may stimulate new studies on interrelations between the electromechanical properties of anisotropic components and the performance of the novel piezo-active composites.

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