Hydrostatic Piezoelectric Coefficients of the 2–2 Composite Based on [011]-poled 0.71Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-0.29PbTiO\textsubscript{3} Single Crystal

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The effect of the polarisation orientation of [011]-poled polydomain PMN-0.29PT single crystal on the hydrostatic piezoelectric coefficients $d^h_*$ and $e^h_*$ of a parallel-connected 2–2 composite has been analysed. Orientation and volume-fraction dependences of the piezoelectric coefficients of the 2–2 PMN-0.29PT/polymer composite have been studied to determine extreme points of $d^h_*$ and $e^h_*$ in three cases of rotations of the main crystallographic axes of the PMN-0.29PT single crystal. The largest values of the hydrostatic piezoelectric coefficients $|d^h_*|=444$ pC/N and $e^h_*=33.1$ C/m$^2$ are of interest for hydroacoustic applications. Important contributions from the piezoelectric coefficients $d^*_{3j}$ and $e^*_{3j}$ into $d^h_*$ and $e^h_*$, respectively, have been determined near the extreme points of the hydrostatic parameters.

Keywords Composite; relaxor-ferroelectric single crystal; piezoelectric coefficients; hydrostatic parameters; domains

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1. Introduction

The polarisation orientation effect in novel 2–2 \cite{1–3} and 1–3 \cite{4} composites based on relaxor-ferroelectric single crystals (SCs) of $(1-x)$Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} - xPbTiO\textsubscript{3} (PZN-\textit{xPT}) and $(1-y)$Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} - yPbTiO\textsubscript{3} (PMN-\textit{yPT}) is of interest for hydrophone and piezotechnical applications. The highly piezo-active SC components and their anisotropy have a strong influence on the electromechanical properties and hydrostatic piezoelectric response of the SC/polymer composites. Recently the piezoelectric performance was discussed for the 2–2 SC/polymer composite in which the SC component was either polydomain ([001]- or [011]-poled) \cite{1–3} or single-domain \cite{3}. Large hydrostatic piezoelectric

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coefficients of 2–2 single-domain PMN-0.29PT SC/polymer composite [3] with parallel-connected layers were attained by rotation of the main crystallographic axes of SC (3m symmetry) with respect to the co-ordinate system of the composite sample. However, the dependence of effective parameters on three rotation angles has not been studied for composites based on [011]-poled SCs with two domain types.

In the present paper we analyse the effect of the polarisation orientation on the hydrostatic piezoelectric coefficients $d_{ij}^*$ and $e_{ij}^*$ in the parallel-connected 2–2 composite based on polydomain [011]-poled PMN-0.29PT SC with macroscopic $mm_2$ symmetry. The SC composition at $y = 0.29$ with the rhombohedral distortion of the perovskite unit cell was chosen near the morphotropic phase boundary [5]. In the presence of a laminar 71° domain structure, there is considerable anisotropy of elastic and piezoelectric properties (Table 1) and high piezoelectric activity of SC. Below we show the role of these and other factors in forming the large hydrostatic piezoelectric response of the 2–2 PMN-0.29PT SC/polymer composite.

2. Structure of the 2–2 Composite and Its Effective Electromechanical Properties

Consider a parallel connection of anisotropic SC layers and transversely isotropic polymer layers which form the regular laminar structure (Fig. 1) with 2–2 connectivity (in terms of Ref. 8). The main crystallographic axes $X$, $Y$, and $Z$ of [011] poled PMN-0.29PT SC with $mm_2$ symmetry are parallel to the following perovskite unit-cell directions [6]: $X \parallel [0\bar{1}1]$, $Y \parallel [100]$ and $Z \parallel [0\bar{1}1]$, and spontaneous polarisation vectors of domains (Fig. 1) are denoted as $P_{s,1}$ and $P_{s,2}$. The orientation of the axes $X$, $Y$, and $Z$ is characterised by rotation angles $\alpha$, $\beta$, and $\gamma$ (Fig. 1), where an equality $\alpha = \beta = \gamma = 0^\circ$ means $X \parallel OX_1$,

<table>
<thead>
<tr>
<th>Components</th>
<th>$s_{11}^{(n),E}$</th>
<th>$s_{12}^{(n),E}$</th>
<th>$s_{13}^{(n),E}$</th>
<th>$s_{22}^{(n),E}$</th>
<th>$s_{23}^{(n),E}$</th>
<th>$s_{33}^{(n),E}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-0.29PT SC$^a$ poled along [011]</td>
<td>18.0</td>
<td>-31.1</td>
<td>8.4</td>
<td>112</td>
<td>-61.9</td>
<td>49.6</td>
</tr>
<tr>
<td>PVDF$^b$</td>
<td>333</td>
<td>-148</td>
<td>-87.5</td>
<td>333</td>
<td>-87.5</td>
<td>299</td>
</tr>
<tr>
<td>Components</td>
<td></td>
<td>$s_{44}^{(n),E}$</td>
<td>$s_{55}^{(n),E}$</td>
<td>$s_{66}^{(n),E}$</td>
<td>$d_{31}^{(n)}$</td>
<td>$d_{32}^{(n)}$</td>
</tr>
<tr>
<td>PMN-0.29PT SC$^a$ poled along [011]</td>
<td>14.9</td>
<td>69.4</td>
<td>13.0</td>
<td>610</td>
<td>-1883</td>
<td>1020</td>
</tr>
<tr>
<td>PVDF$^b$</td>
<td>1.90.10$^4$</td>
<td>1.90.10$^4$</td>
<td>943</td>
<td>10.4</td>
<td>10.4</td>
<td>-33.6</td>
</tr>
<tr>
<td>Components</td>
<td>$d_{15}^{(n)}$</td>
<td>$d_{24}^{(n)}$</td>
<td>$e_{11}^{(n),\sigma} l_{\varepsilon_0}$</td>
<td>$e_{22}^{(n),\sigma} l_{\varepsilon_0}$</td>
<td>$e_{33}^{(n),\sigma} l_{\varepsilon_0}$</td>
<td></td>
</tr>
<tr>
<td>PMN-0.29PT SC$^a$ poled along [011]</td>
<td>1188</td>
<td>167</td>
<td>3564</td>
<td>1127</td>
<td>4033</td>
<td></td>
</tr>
<tr>
<td>PVDF$^b$</td>
<td>-38</td>
<td>167</td>
<td>7.51</td>
<td>7.51</td>
<td>8.43</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Data from Ref. 6, macroscopic symmetry $mm_2$.

$^b$PVDF with $P_r^{(2)} \uparrow \uparrow OX_3$, data from Ref. 7, macroscopic symmetry $\infty mm$. 

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 $\varepsilon_{pp}^{(n),\sigma} / \varepsilon_0$ of poled SC and polymer components at room temperature.
Figure 1. Schematic of the 2–2 parallel-connected composite. $(X_1, X_2, X_3)$ is the rectangular coordinate system, $m$ and $1-m$ are volume fractions of SC and polymer, respectively. $P_{s,1}$ and $P_{s,2}$ are spontaneous polarisation vectors of $71^\circ$ domains in each SC layer, $X$, $Y$, and $Z$ are main crystallographic axes of polydomain SC, and $\alpha$, $\beta$ and $\gamma$ are rotation angles.

$Y \parallel OX_2$, and $Z \parallel OX_3$. It is assumed that the $71^\circ$ domains in SC are characterised by equal volume fractions and, therefore, the spontaneous polarisation vector of each SC layer is $P_{s}^{(1)} = (P_{s,1} + P_{s,2})/2$. Hereafter we consider rotations of the main crystallographic axes of SC around one of the co-ordinate axes — $OX_1$, $OX_2$, or $OX_3$ (see Fig. 1, right side). We assume that at these rotations, the spontaneous polarisation vectors of domains $P_{s,1}$ and $P_{s,2}$ remain situated either over the $(X_1,OX_2)$ plane or at this plane. Taking into account the mutual orientations of the $P_{s,i}$ vectors and the $OX_j$ axes (Fig. 1), we determine the following ranges in which the orientation angles are varied: $-\arcsin(1/\sqrt{3}) \leq \alpha \leq \arcsin(1/\sqrt{3})$, $-45^\circ \leq \beta \leq 45^\circ$, and $0^\circ \leq \gamma \leq 360^\circ$.

The polymer layers are made of polyvinylidene fluoride (PVDF), a ferroelectric, and can be poled so that the remanent polarisation vector $P_{r}^{(2)}$ in each polymer layer would be $P_{r}^{(2)} \uparrow \downarrow OX_3$. At such an orientation of $P_{r}^{(2)}$, signs of the piezoelectric coefficients [7] of PVDF obey the condition $\text{sgn}d_{31} = -\text{sgn}d_{33} = -\text{sgn}d_{15} < 0$ that is typical of conventional poled ferroelectric ceramics of the lead zirconate titanate (PZT) type [9]. Different mutual orientations of the $P_{s,i}$ and $P_{r}^{(2)}$ vectors in the 2–2 composite can be attained on poling the composite sample in an electric field due to a significant difference between the coercive fields $E_{c}^{(1)}$ and $E_{c}^{(2)}$ of SC and polymer: e.g., according to experimental data [10, 11] on related components, $E_{c}^{(2)} \gg E_{c}^{(1)}$.

The effective elastic, piezoelectric and dielectric (i.e., electromechanical) properties of the 2–2 composite are determined within the framework of the matrix approach [1, 12] and expressed by the $9 \times 9$ matrix

$$
||C^*|| = \begin{pmatrix}
||s^{*E}|| & ||d^{*}||^t \\
||d^{*}|| & ||\varepsilon^{*\sigma}||
\end{pmatrix},
$$

(1)

where $||s^{*E}||$ is the $6 \times 6$ matrix of elastic compliances at constant electric field, $||d^{*}||$ is the $3 \times 6$ matrix of piezoelectric charge coefficients, $||\varepsilon^{*\sigma}||$ is the $3 \times 3$ matrix of dielectric permittivities measured at constant stress, and superscript $t$ denotes the transposed matrix. As a result of averaging on the volume fraction $m$, the matrix $||C^*||$ from Eq. (1) is
given by
\[
\|C^e\| = [\|C^{(1)}\| \cdot \|M\| m + \|C^{(2)}\||(1 - m))] \cdot [\|M\| m + \|I\|(1 - m)]^{-1},
\]
where \(\|C^{(1)}\|\) and \(\|C^{(2)}\|\) are matrices of the electromechanical properties of polydomain SC and polymer, respectively, \(\|M\|\) is concerned with the electric and mechanical boundary conditions \([12]\) at interfaces \(x_1 = \text{const}\) (Fig. 1), and \(\|I\|\) is the identity matrix. Matrices \(\|C^{(i)}\|\) \((i = 1 \text{ and } 2)\) from Eq. (2) have a structure similar to that shown in Eq. (1), and \(\|C^{(1)}\|\) is calculated as a function of the rotation angle \((\alpha, \beta \text{ or } \gamma)\) before averaging of \(m\). The effective electromechanical properties from Eq. (2) are determined on an assumption that the wavelengths of acoustic waves propagated are considerably longer than the thickness of each layer in the 2–2 composite (Fig. 1).

Based on matrix elements of \(\|C^e\|\) from Eq. (2), we study the volume-fraction \((m)\) and orientation \((\alpha, \beta \text{ or } \gamma)\) dependences of the hydrostatic piezoelectric charge and stress coefficients
\[
d^k_h = \sum_{i=1}^{3}(d^k_{i1} + d^k_{i2} + d^k_{i3}) \text{ and } e^k_h = \sum_{i=1}^{3}(e^k_{i1} + e^k_{i2} + e^k_{i3}),
\]
respectively, where the piezoelectric coefficients \(e^k_{ij}\) are determined from the matrix \(\|e^k\| = \|d^k\| \|s^{E}\|^{-1}\). The effective parameters (2) and (3) of the 2–2 composite are calculated using the full sets of experimental electromechanical constants listed in Table 1.

### 3. Results and Discussion

The hydrostatic piezoelectric coefficients \(d^k_h\) and \(e^k_h\) from Eqs. (3) are characterised by various orientation \((\alpha, \beta, \gamma)\) dependences. To study the volume-fraction dependence of the effective properties, we vary the volume fraction of SC in a range \(0 < m \leq 0.9\). The presence of SC with \(\text{mm}2\) symmetry and polymer with \(\infty\text{mm}\) symmetry enables us to establish the periodic dependence of the hydrostatic parameters on \(\gamma\). For any value of \(m\) the equalities \(d^k_h(m, \gamma) = d^k_h(m, 180^\circ - \gamma)\) and \(e^k_h(m, \gamma) = e^k_h(m, 180^\circ - \gamma)\) hold. This feature is concerned with the rotation of the main crystallographic axes \(X\) and \(Y\) around \(Z\parallel OX_3\) (Fig. 1, right side) so that the spontaneous polarisation vector of polydomain SC \(P_s^{(1)}\) remains parallel to \(OX_3\) at any \(\gamma\).

When varying the angle \(\alpha\), we change projections of spontaneous polarisation vectors \(P_{s,1}\) on the \(OX_3\) direction (Fig. 1, right side). As a consequence, a balance of the piezoelectric coefficients \(d^k_{3j}\) is varied in a wide range. At \(\alpha \approx 52^\circ\), the lowest hydrostatic piezoelectric coefficient \(d^k_{3j}(m, \alpha) = -444 \text{ pC/N}\) is attained at \(m \approx 0.43–0.44\) (cf. Figs. 2, a and 2, c) due to \(d^k_{22}(m, \alpha) < 0\) and \(d^k_{33}(m, \alpha) < 0\). At the same time, changes in \(\alpha\) lead to moderate values of \(e^k_{3j}\); as follows from our evaluations, \(\text{min}e^k_{3j}(m, \alpha) = -17.3 \text{ C/m}^2\) at \(m = 0.81\) and \(\alpha = 45^\circ\) and \(\text{max}e^k_{3j}(m, \alpha) = 3.02 \text{ C/m}^2\) at \(m = 0.81\) and \(\alpha = -54.7^\circ\). The relatively large volume fractions \(m \approx 0.8\) suggest that the elastic anisotropy of the SC has a strong influence on the piezoelectric coefficients \(e^k_{3j}(m, \alpha)\) and \(e^k_{3j}(m, \alpha)\), however, the rotation by \(\alpha\) does not lead to the favourable balance of \(e^k_{3j}(m, \alpha)\).

Varying the angle \(\beta\) means the simultaneous rotation of the \(P_{s,1}\) and \(P_{s,2}\) vectors of domains of SC around \(OX_2\) (Fig. 1, right side), and this mode of rotation of the main crystallographic axes of PMN-0.29PT is less favourable to attain large values of both \(d^k_{3j}\)
Figure 2. Volume-fraction and orientation dependences of effective piezoelectric coefficients of the 2–2 PMN-0.29PT SC/PVDF composite: $d^*_h(m, \alpha)$ (a), $e^*_h(m, \gamma)$ (b), contributions from $d^*_{3j}$ into $d^*_h$ near absolute min $d^*_h(m, \alpha)$ (c), and contributions from $e^*_{3j}$ into $e^*_h$ near absolute max $e^*_h(m, \gamma)$ (d). (See Color Plate LXIII)

and $|e^*_h|$ in the 2–2 composite. Our evaluations suggest that inequalities $-12.3 \text{ C/m}^2 \leq e^*_h(m, \beta) \leq 5.35 \text{ C/m}^2$ and $-243 \text{ pC/N} \leq d^*_h(m, \beta) \leq 13.0 \text{ pC/N}$ hold at various values of $\beta$.

Varying the angle $\gamma$, we attain large values of $e^*_h$ (Fig. 2, b) and $d^*_h$: for example, $d^*_h(m, \gamma)$ changes from $-243 \text{ pC/N}$ ($m = 0.90$ and $\gamma = 0^\circ$) to $337 \text{ pC/N}$ ($m = 0.25$ and $\gamma = 90^\circ$). This behaviour is accounted for by appreciable changes in $e^*_{31}(m, \gamma)$ and $e^*_{32}(m, \gamma)$ as well as in $d^*_{31}(m, \gamma)$ and $d^*_{32}(m, \gamma)$ at the volume fraction $m = \text{const}$, and these changes are caused by the piezoelectric and elastic anisotropy of the PMN-0.29PT SC (see data from Table 1). Near absolute max $e^*_h(m, \gamma) = 33.1 \text{ C/m}^2$ (Fig. 2, b), the piezoelectric coefficients $e^*_{33}(m, \gamma) > 0$ and $e^*_{32}(m, \gamma) > 0$ pass maximum points on changing $m$ (Fig. 2, d). It is noteworthy that values of $e^*_h \approx 33 \text{ C/m}^2$ can be of great interest for hydroacoustic applications. To the best of our knowledge, in the studied two-component ferroelectric ceramic/polymer composites [12], the typical $e^*_h$ values do not exceed $14 \text{ C/m}^2$.

Finally, it should be mentioned that the orientation and volume-fraction dependences of its piezoelectric coefficients have recently been determined for the 2–2 composite based on single-domain PMN-0.33PT SC [3]. According to results [3], inequalities $-44.4 \text{ C/m}^2 \leq e^*_h \leq 42.6 \text{ C/m}^2$ and $-413 \text{ pC/N} \leq d^*_h \leq 309 \text{ pC/N}$ hold when a large anisotropy of elastic
and piezoelectric properties of SC is observed. As follows from data on electromechanical constants of single-domain PMN-0.33PT SC [3], in its main crystallographic axes the ratios $s_{11}^{(1)E}/s_{13}^{(1)E} = -11.1$, $s_{11}^{(1)E}/s_{33}^{(1)E} = 4.68$ and $d_{33}^{(1)}/d_{31}^{(1)} = 7.05$ hold. As follows from Table 1, electromechanical constants of polydomain [011]-poled PMN-0.29PT SC satisfy conditions $s_{22}^{(1)E}/s_{11}^{(1)E} = 6.2$ and $d_{33}^{(1)}/d_{31}^{(1)} \approx |d_{32}^{(1)}|/d_{33}^{(1)}$, and the role of the anisotropy of the SC properties in forming the hydrostatic response of the studied 2–2 composite cannot be ignored.

4. Conclusion

In this paper we studied the effective piezoelectric properties and features of the hydrostatic piezoelectric response of the 2–2 [011]-poled PMN-0.29PT SC/PVDF composite with the parallel-connected layers. The behaviour of the hydrostatic piezoelectric coefficients $d_{h}^*$ and $e_{h}^*$ has been modelled and analysed for different modes of rotation of the main crystallographic axes of the SC. The large hydrostatic piezoelectric coefficients $|d_{h}^*| = 444$ pC/N and $e_{h}^* = 33.1$ C/m$^2$ indicate the potential of 2–2 composites with specified orientations of the SC crystallographic axes for a variety of hydroacoustic and piezotechnical applications. The high piezoelectric performance of this composite is of value for specialists using relaxor-ferroelectric SCs as a component in novel 2–2 SC/polymer composites and optimising their effective piezoelectric properties and related hydrostatic parameters.

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