Electromechanical Coupling in the Novel 2–2 Parallel-Connected PMN–0.33PT Single-Domain Crystal/Polymer Composite

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This paper considers effective electromechanical properties of the relaxor-ferroelectric crystal/polymer composite with 2–2 connectivity. A single-domain 0.67Pb(Mg1/3Nb2/3)O3−0.33PbTiO3 crystal/polymer composite is proposed in which the polarisation vectors of components are tailored to optimise the electromechanical coupling factors $k^*_j$ and $k^*_h$. A strong correlation between the hydrostatic electromechanical coupling factor $k^*_h$ and the hydrostatic piezoelectric coefficient $d^*_h$ is observed near min $k^*_h$ and max $k^*_h$. Examples of the condition $k^*_{31} = k^*_{32}$ are also considered. The specific advantages and potential of the 2–2 composite in terms of its considerable $d^*_h$ and $k^*_h$ values are discussed in connection with the studied orientation effect.

Keywords 2–2 crystal/polymer composite; piezoelectric coefficient; electromechanical coupling factor

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1. Introduction

Single crystals (SCs) of perovskite-type relaxor-ferroelectric solid solutions of $(1-x)$Pb(Mg1/3Nb2/3)O3−xPbTiO3 (PMN-xPT) and $(1-x)$Pb(Zn1/3Nb2/3)O3−xPbTiO3 (PZN-xPT) represent a new generation of high-performance piezoelectric materials. These materials with so-called ‘engineered domain structures’ and compositions near the morphotropic phase boundary exhibit remarkable electromechanical properties at room temperature (see, e.g., papers [1–3]). In the last decade novel piezo-active composites based...
on these SCs have been manufactured and studied in a series of papers. Among the composites studied experimentally are PZN–0.08PT/polymer [4], PMN–0.33PT/epoxy [5] and PMN–0.30PT/epoxy [6] composites with 1–3 connectivity. Effective electromechanical properties and related parameters of the relaxor-ferroelectric SC/polymer composites with 1–3, 2–2 and 0–3 connectivities have also been modeled and analysed [7–10]. The high performance of composites based on either PMN–xPT or PZN–xPT is important for modern piezotechnical applications [4–6, 10], including active elements of modern sensors, actuators, transducers, hydrophones, and other devices. Potential changes in the domain structures or the poling direction of the aforementioned SCs can lead to appreciable changes in their electromechanical properties [3, 11–13]. Currently PMN–0.33PT is the only relaxor-ferroelectric SC for which full sets of the electromechanical constants have been measured in both the single-domain (3 m symmetry) [11, 12] and polydomain (or domain engineered, 4 mm symmetry) [1] states at room temperature. The piezoelectric properties of the single-domain PMN–0.33PT SC were analysed for various orientations of its main crystallographic axes [12, 14], and these results were taken into account at the study on the piezoelectric response of a novel 2–2 composite [15] based on this single-domain SC.

In earlier work no attempt was made to analyse features of the electromechanical coupling of the composite based on the single-domain PMN–0.33PT SC. To the best of our knowledge, electromechanical coupling factors of composites based on relaxor-ferroelectric SCs have only been considered to a limited extent and for the 1–3-type composites only [16, 17]. Based on experimental room-temperature data [12], the PMN–0.33PT SC is of interest due to a combination of the large piezoelectric coefficients $d^{(1)}_{31}$ and $d^{(1)}_{33}$ and the moderate piezoelectric coefficients $d^{(1)}_{15}$ and $d^{(1)}_{22}$ (Table 1). These interesting properties stimulate a study of the performance of composites whereby the single-domain PMN–0.33PT SC can exhibit various electromechanical properties as a result of changes in the orientation of the crystallographic axes. The aim of this paper is to analyse features of electromechanical coupling of the 2–2 single-domain PMN–0.33PT/polymer composite.

2. Model of the 2–2 SC/Polymer Composite and its Effective Properties

The model considers a 2–2 parallel-connected SC/polymer composite with a regular distribution of layers on the $OX_1$ direction (Fig. 1). The SC and polymer layers are assumed to be lengthy on the $OX_2$ and $OX_3$ directions. An orientation of the spontaneous polarisation vector $P_s^{(1)}$ of each SC layer is described using Euler angles $\phi$, $\psi$ and $\theta$ (Fig. 1, inset 1). The polymer layers of the composite are ferroelectric (poled along a specific direction) and piezoelectric. It is assumed that the remanent polarisation vector $P_r^{(2)}$ of ferroelectric polymer over the whole composite sample is characterised by one of the following orientations: $P_r^{(2)} \uparrow \uparrow OX_3$ or $P_r^{(2)} \uparrow \downarrow OX_3$ (Fig. 1, insets 2 and 3). The manufacture of such 2–2 SC/polymer composites with various orientations of the $P_s^{(1)}$ and $P_r^{(2)}$ vectors can be achieved by poling of the individual components. In this work the composite comprising PMN–0.33PT and polyvinylidene fluoride (PVDF) is studied. As is known from experimental data, coercive fields $E_c^{(n)}$ of the single-domain PMN–0.33PT SC (hereafter with superscript $n = 1$) and PVDF ($n = 2$) obey the condition [13, 18] $E_c^{(1)} << E_c^{(2)}$, which favours the poling of the components of the 2–2 composite proposed.

Effective electromechanical constants and other parameters of the 2–2 composite (Fig. 1) are evaluated with use of full sets of elastic compliances $||s^{(n)}||$ (measured at electric field $E = \text{constant}$), piezoelectric coefficients $||d^{(n)}||$ and dielectric permittivities $||\varepsilon^{(n)}||$
Table 1

Room-temperature elastic compliances $s_{ab}^{(n),E}$ (in $10^{-12}$ Pa$^{-1}$), piezoelectric coefficients $d_{ij}^{(n)}$ (in pC N$^{-1}$) and relative dielectric permittivity $\varepsilon_{pp}^{(n),\sigma}/\varepsilon_0$ of the single-domain PMN–0.33PT SC [12] and poled PVDF [20]

<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>$s_{14}^{(n),E}$</th>
<th>$s_{33}^{(n),E}$</th>
<th>$s_{34}^{(n),E}$</th>
<th>$s_{44}^{(n),E}$</th>
<th>$s_{66}^{(n),E}$</th>
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<tr>
<td>PMN–0.33PT SC</td>
<td>62.2</td>
<td>-53.8</td>
<td>-5.6</td>
<td>-166.2</td>
<td>13.3</td>
<td>511.0</td>
<td>232.0</td>
<td></td>
</tr>
<tr>
<td>PVDF with $P_r^{(2)} \uparrow \uparrow OX_3$</td>
<td>333</td>
<td>-148</td>
<td>-87.5</td>
<td>0</td>
<td>299</td>
<td>1.90.10$^4$</td>
<td>943</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Components</th>
<th>$d_{15}^{(n)}$</th>
<th>$d_{22}^{(n)}$</th>
<th>$d_{31}^{(n)}$</th>
<th>$d_{33}^{(n)}$</th>
<th>$\varepsilon_{11}^{(n),\sigma}/\varepsilon_0$</th>
<th>$\varepsilon_{33}^{(n),\sigma}/\varepsilon_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN–0.33PT SC</td>
<td>4100</td>
<td>1340</td>
<td>-90</td>
<td>190</td>
<td>3950</td>
<td>640</td>
</tr>
<tr>
<td>PVDF with $P_r^{(2)} \uparrow \uparrow OX_3$</td>
<td>-38</td>
<td>0</td>
<td>10.42</td>
<td>-33.64</td>
<td>7.513</td>
<td>8.431</td>
</tr>
</tbody>
</table>
Figure 1. Schematic of the 2–2 SC/polymer composite with parallel-connected layers. (X1X2X3) is the rectangular co-ordinate system, m and 1—m are volume fractions of SC and polymer, respectively, \( P_s^{(1)} \) and \( P_r^{(2)} \) are the spontaneous polarisation vector of SC and the remanent polarisation vector of polymer, respectively. In inset 1 \( \phi, \psi, \) and \( \theta \) are Euler angles that characterise the rotation of the main crystallographic axes \((X_o 1 X_o 2 X_o 3) = (X'_1 X'_2 X'_3))\) and the orientation of the \( P_s^{(1)} \) vector in each single-domain SC layer. Orientations \( P_r^{(2)} \uparrow \uparrow OX_3 \) and \( P_r^{(2)} \uparrow \downarrow OX_3 \) are shown in insets 2 and 3, respectively.

(measured at mechanical stress \( \sigma = \text{constant} \)) of components (Table 1). We describe the rotation of the main crystallographic axes of SC \((X_o 1 X_o 2 X_o 3) \rightarrow (X'_1 X'_2 X'_3)\) (Fig. 1, inset 1) with the rotation matrix given by

\[
||r|| = \begin{pmatrix}
\cos \psi \cos \theta & \cos \psi \sin \phi & \sin \phi \\
-\sin \psi \cos \phi & \cos \psi \cos \phi & \sin \phi \\
\sin \psi & -\sin \theta & \cos \phi
\end{pmatrix}.
\]

Using the elements of the above rotation matrix ||\( r ||\), we determine the full set of electromechanical constants of the single-domain SC in the \((x'_1 x'_2 x'_3)\) system as follows:

\[
s_{qtu}^{(1),E} = r_{qa} \cdot r_{tb} \cdot r_{uc} \cdot r_{vd} (S_{abcd}^E)_0, \quad d_{efg}^{(1)} = r_{ej} r_{fk} r_{gl} (d_{ijkl})_0 \quad \text{and} \quad \epsilon_{mp}^{(1),\sigma} = r_{mh} r_{pi} (\epsilon_{hi}^\sigma)_0,
\]

where \((S_{abcd})_0, (d_{ijkl})_0\) and \((\epsilon_{hi}^\sigma)_0\) are electromechanical constants related to the \((X'_1 X'_2 X'_3)\) system. Hereafter we use the conventional two-index form [19] of electromechanical constants from Eqs. (1) and consider effective parameters with respect to the \((X_1X_2X_3)\) system of the composite sample (Fig. 1). The electromechanical properties of the \(n\)th component of the composite in the \((X_1X_2X_3)\) system are described using the Van Dyke matrix [19]

\[
||C^{(n)}|| = \begin{pmatrix}
\|s^{(n),E}\| & \|d^{(n)}\| \|T
\end{pmatrix},
\]

where \(n = 1\) and 2, and superscript \(T\) denotes the transposed matrix.

A procedure for averaging the electromechanical properties from Eq. (2) is achieved along the \(OX_1\) axis by taking into consideration the nine boundary conditions [8, 10, 15] for electric and mechanical fields in the adjacent layers of the composite (Fig. 1). These
Electromechanical Coupling in 2–2 Composite

boundary conditions at \(x_1 = \text{const}\) involve the continuity of three normal components of the mechanical stress (i.e., \(\sigma_{11}, \sigma_{12}\) and \(\sigma_{13}\)), three tangential components of the mechanical strain (i.e., \(\xi_{22}, \xi_{23}\) and \(\xi_{33}\)), one normal component of the electric displacement (i.e., \(D_1\)), and two tangential components of the electric field (i.e., \(E_2\) and \(E_3\)). Following this procedure for averaging, the effective electromechanical properties of the 2–2 composite are determined from a matrix

\[
\|C^*\| = [\|C^{(1)}\|] \cdot \|M\| m + [\|C^{(2)}\|](1 - m)\] \(1\) \|M\| m + \|I\|(1 - m)^{-1}
\]

that is represented in the form similar to that shown in Eq. (2). In Eq. (3) \(\|M\|\) is the 9 \times 9 matrix that describes the aforementioned boundary conditions at \(x_1 = \text{const}\), \(\|I\|\) is the identity 9 \times 9 matrix, \(m\) is the volume fraction of SC, and \(\|C^{(n)}\|\) is taken from Eq. (2). The full set of effective constants of the composite \(s_{ab}^{*E}, d_{ij}^*\) and \(e_{ij}^{*E}\) is determined from matrix (3). These constants are determined in the longwave approximation, i.e. the wavelength of an external acoustic field is assumed to be much greater than the width of each layer of the composite (Fig. 1).

Based on the elements of the \(\|C^*\|\) matrix from Eq. (3), we analyse the volume-fraction \((m)\) and orientation \((\phi, \psi, \theta)\) dependences of effective electromechanical coupling factors

\[
k_{3j}^* = d_{3j}^* / (\epsilon_{33}^{*E} s_{3j}^{*E})^{1/2}
\]

\((j = 1, 2 \text{ and } 3)\) and hydrostatic electromechanical coupling factor

\[
k_{h}^* = d_{h}^* / (\epsilon_{33}^{*E} s_{h}^{*E})^{1/2}
\]

of the 2–2 composite based on the single-domain PMN–0.33PT SC. In Eq. (5) the hydrostatic piezoelectric coefficient and elastic compliance of the composite

\[
d_{h}^* = \sum_{i=1}^{3} \sum_{j=1}^{3} d_{ij}^* \quad \text{and} \quad s_{h}^{*E} = \sum_{a=1}^{3} \sum_{b=1}^{3} s_{ab}^{*E}
\]

are expressed in terms of effective electromechanical constants \(d_{ij}^*\) and \(s_{ab}^{*E}\), respectively. Calculations of electromechanical coupling factors from Eqs. (4) and (5) are performed using the full sets of the electromechanical constants of the SC and polymer components (Table 1).

### 3. Results and Discussion

#### 3.1. Hydrostatic Electromechanical Coupling Factor \(k_{h}^*\)

The volume-fraction dependence of the hydrostatic electromechanical coupling factor \(k_{h}^*\) was first predicted and analysed [17] for a 1–2–2 composite based on a polydomain PMN–0.33PT SC poled along the [001] perovskite unit-cell direction. The electromechanical interaction between the highly piezo-active SC rods and the laminar polymer matrix leads to very high \(k_{h}^*\) values in a wide volume-fraction range. For example, in the 1–2–2 polydomain PMN–0.33PT/araldite/elastomer composite, \(\text{max}k_{h}^* = 0.473\) was attained whereas the SC component has \(k_{h}^{(1)} = 0.167\) only and is surrounded by two piezo-passive polymers [17].
In this paper we consider the electromechanical coupling of the composite that contains PVDF with $P_r(2) \uparrow \downarrow OX_3$ (Fig. 1, inset 3). Such an orientation of the $P_r(2)$ vector in all the polymer layers is preferable due to signs of the piezoelectric coefficients $d_{ij}^{(2)}$ in the $(X_1X_2X_3)$ system condition $\text{sgn}d_{33}^{(2)} = -\text{sgn}d_{31}^{(2)} = \text{sgn}d_{15}^{(2)} > 0$ holds. Similar signs of the piezoelectric coefficients are attained in a wide variety of PZT-type ferroelectric ceramics [21] poled parallel to $OX_3$. Euler angles $\phi$, $\psi$ and $\theta$ (inset 1 in Fig. 1) are varied in the following ranges: $0^\circ \leq \phi \leq 360^\circ$, $0^\circ \leq \psi \leq 360^\circ$ and $0^\circ \leq \theta \leq 180^\circ$. However in case of the single-domain SC with $3m$ symmetry [12, 14] the $\phi$ angle can be varied in a narrower range, i.e., $0^\circ \leq \phi \leq 120^\circ$.

The present results show that the 2–2 composite based on the single-domain PMN–0.33PT SC with $k_h^{(1)} = 0.048$ is characterised by the strong hydrostatic electromechanical coupling (Figs. 2 and 3) in the presence of the piezo-active polymer component. Figure 2 shows changes in values of local $\max k_h^*(m, \phi, \psi, \theta)$ at a fixed angle $\theta$. The specific sensitivity of $k_h^*$ to changes in the angle $\theta$ is the result of the considerable dependence of the $P_s(1)$ orientation (inset 1 in Fig. 1) and the piezoelectric properties of SC on the angle $\theta$.

The largest values of hydrostatic electromechanical coupling factor ($k_h^* \approx 0.8$) are attained in ranges of $0.1 < m < 0.2$ and $10^\circ < \theta < 20^\circ$ at a series of combinations of $\phi$ and $\psi$. Due to a complicated dependence of $k_h^*$ on Euler angles $\phi$, $\psi$ and $\theta$, a number of local $\max k_h^*$ values appear in the aforementioned ranges (Fig. 3, a–c). The smallest values of $k_h^* \approx -0.8$ can be found in ranges of $0.1 < m < 0.2$ and $160^\circ < \theta < 170^\circ$, and a similar orientation dependence of $k_h^*$ is observed (Fig. 3, d). Small differences between absolute values of extreme of $k_h^*$ found for the related composites with different orientations of $P_r(2)$ in the PVDF layers (see insets 2 and 3 in Fig. 1) are accounted for by the volume fraction of SC $m > 0.1$. In this volume-fraction range the piezoelectric properties of SC play a significant role in forming the hydrostatic piezoelectric coefficient $d_h^*$ (see Eqs. (5) and (6)) and, therefore, the hydrostatic electromechanical coupling of the composite. It should be mentioned for comparison that a 1–3-type PZT ceramic/porous polyurethane composite [22] has a $k_h^*$ value from approximately 0.11 to 0.57, depending of the elastic properties of

**Figure 2.** Local maxima of hydrostatic electromechanical coupling factor $(k_h^*)_m = \max k_h^*(m, \phi, \psi, \theta)|_{\theta=\text{const}}$ of the 2–2 single-domain PMN–0.33PT / PVDF composite with $P_r(2) \uparrow \downarrow OX_3$. The $\theta$ range is shown where the inequality $(k_h^*)_m > 0.5$ holds.
Figure 3. Volume fraction ($m$) and orientation ($\phi$, $\psi$, $\theta$) dependences of hydrostatic electromechanical coupling factors $k_h^*$ (a–d) and hydrostatic piezoelectric coefficients $d_h^*$ (e and f, in pC / N) of the 2–2 single-domain PMN–0.33PT / PVDF composite with $P_r^{(2)} \uparrow\downarrow OX_3$. (See Color Plate I)
3.2. Electromechanical Coupling Factors $k^*_j$ and the Orientation Effect

An interesting example of the electromechanical coupling in the 2–2 composite based on the PMN–0.33PT SC is shown in Table 2 wherein values of $k^*_j$ correspond to $m = 0.15$, $\theta = 15^\circ$. We find possible orientations of the main crystallographic axes (inset 1 in Fig. 1) that obey condition

$$k^*_3 \equiv k^*_1. \tag{7}$$

Condition (7) is known to be fulfilled in poled ferroelectric ceramics [21]. According to Eqs. (4) and (7), effective electromechanical constants of the composite satisfy an equality $d^*_3/s^*_{33}^{E} = d^*_1/s^*_{11}^{E}$. It is seen that the electromechanical coupling factor $k^*_3$ is varied in a narrow range ($0.63 < k^*_3 \leq 0.67$) while $k^*_1$ and $k^*_2$ change more appreciably.

The reason of these changes is associated with microgeometry of the 2–2 composite (Fig. 1), mainly with the presence of the piezo-active layers poled along the $OX_3$ axis. Moreover,
Table 2
Fulfilment of condition $k_{31}^* = k_{32}^*$ for the 2–2 single-domain PMN–0.33PT/PVDF composite at $m = 0.15$, $\theta = 15^\circ$ and $P_r^{(2)} \uparrow \downarrow OX_3$

<table>
<thead>
<tr>
<th>$\phi$, deg</th>
<th>$\psi$, deg</th>
<th>$k_{31}^*$</th>
<th>$k_{32}^*$</th>
<th>$k_{33}^*$</th>
<th>$\phi$, deg</th>
<th>$k_{31}^*$</th>
<th>$k_{32}^*$</th>
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<td>-0.197</td>
<td>0.664</td>
<td>60</td>
<td>9 or 189</td>
<td>-0.220</td>
<td>-0.226</td>
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<tr>
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<td>49, 131, 229, or 311</td>
<td>-0.184</td>
<td>-0.176</td>
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<td>-0.220</td>
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</tr>
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<td>-0.202</td>
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<td>172 or 352</td>
<td>-0.222</td>
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<tr>
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<td>-0.170</td>
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<td>151 or 331</td>
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<td>-0.172</td>
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<td>0.631</td>
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<td>-0.215</td>
<td>0.633</td>
<td>105</td>
<td>145 or 325</td>
<td>-0.201</td>
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</tr>
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</table>
the complicated orientation dependence of \( d_{3j}^* \) and \( s_{jj}^{E*} \) leads to a set of angles \((\phi, \psi)\) for which Eq. (7) holds true.

4. Conclusion

This paper is concerned with the study on electromechanical coupling factors \( k_3^* \) and \( k_{3j}^* \) of the 2–2 composite based on single-domain PMN–0.33PT SC. The volume-fraction and orientation behaviour of electromechanical coupling has been analysed for the low-symmetry composite with a variable poling direction of the SC component. The results point out opportunities associated with use of the single-domain SC component with preferable orientations of its main crystallographic axes. The present study shows that these orientations can be optimised to obtain large values of \(|k_{3j}^*|\) and \(|k_h^*|\). A ratio of \( k_h^* / k_h^{(1)} \) calculated for the 2–2 single-domain PMN–0.33PT / PVDF composite is varied from -16.5 to 13, and such a range has no analogues among the piezo-active composites studied earlier. The strong correlation between \( k_h^* \) and \( d_h^* \) has been revealed for the 2–2 composite based on the relaxor-ferroelectric SC. The results of our study can be of interest for the design of composite structures for transducer and hydroacoustic applications of the advanced 2–2 composites. It is believed that high performance of the single-domain PMN–0.33PT SC and the composite based thereon can stimulate the manufacturing of novel piezo-active composites with considerable electromechanical coupling factors.

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