Maxima of Effective Parameters of Novel Piezo-Composites Based on Relaxor-Ferroelectric Single Crystals

VITALY YU. TOPOLOV,1,2,* ANDREY V. KRIVORUCHKO,1 AND CHRISTOPHER R. BOWEN2

1Department of Physics, Rostov State University, 5 Zorge Street, 344090 Rostov-on-Don, Russia
2Materials Research Centre, Department of Mechanical Engineering, University of Bath, BA2 7AY Bath, United Kingdom

This paper is devoted to the analysis of effective electromechanical properties and their maxima in 0–3-type composites based on \((1 - x)\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3\) single crystals. It is shown that the electromechanical interaction between the single-crystal and polymer components with the anisotropy of their piezoelectric coefficients \(e_{33}^0 / |e_{31}^0| \geq 5\) results in relations \(d_{33}^* \approx e_{33}^*, s_{33}^* \approx h_{33}^* s_{33}^h, g_{33}^* \approx h_{33}^* s_{33}^h, \) and \(k_{33}^* \approx k_{33}^h\) for the electromechanical constants. These relations hold in a wide range of volume fraction and aspect ratio of the spheroidal inclusions in the 0–3 composite. An increase in the maximum values of different effective parameters is expected by forming a system of oblate air pores in the matrix.

Keywords Composite; relaxor-ferroelectric single crystal; polymer; piezoelectric coefficients; electromechanical coupling

PACS: 77.65.-j; Piezoelectricity and electromechanical effects; 77.84.Lf; Composite materials; 77.84.-s; Dielectric; piezoelectric; ferroelectric; and antiferroelectric materials

1. Introduction

Piezo-active composites are smart materials for sensor and actuator applications that act to convert electrical energy into mechanical energy and vice versa. This conversion is related to their effective electromechanical properties that are highly dependent on factors such as microstructure, connectivity and poling conditions. In the last decade, attempts have been made to create novel two-component composites combining single crystals (SCs) of relaxor-ferroelectric solid solutions with polymers [1, 2] and to predict the effective properties of these materials [3, 4]. The relevant application of piezo-composites, based on high-performance SCs of relaxor-ferroelectric \((1 - x)\text{Pb(A}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3\) solid solutions (A = Mg and Zn) with the composition chosen near the morphotropic phase boundary, has been discussed in recent papers [3, 4], where hydrostatic piezoelectric coefficients, figures.
of merit, and other parameters have been considered. The role of SC relaxor-ferroelectric as a component in 1–3-type composites was analysed and their electromechanical properties discussed [4] to demonstrate the ranges in which effective composite parameters are most sensitive to material properties and composite architecture, with particular emphasis on where their maximum values are attained. The related 0–3 composites based on relaxor-ferroelectric ceramics have only been studied in experimental work [5, 6] which examined their piezo-, pyro- and dielectric properties. However, it is not yet fully understood how the SC component influences the piezoelectric response of the 0–3 composite and the appropriate composite microgeometry to optimise its parameters. This paper is concerned with solving this problem for \((1 - x)\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3\) (PMN – xPT) SC-based composites. The aim is to study features of dependences of the effective electromechanical properties on both the volume fraction and the shape of the SC inclusions.

2. Modelling of Effective Properties of the 0–3 Composite

According to the model proposed, the 0–3-type composite consists of spheroidal SC inclusions surrounded by a polymer matrix, as shown in Fig. 1. The shape of the SC inclusions is described by the equation \((x_1/a_1)^2 + (x_2/a_1)^2 + (x_3/a_3)^2 = 1\) relative to the axes of the rectangular co-ordinate system \((X_1X_2X_3)\), where the semi-axes of the spheroid are \(a_1 = a_2\) and \(a_3\) and \(\rho = a_1/a_3\) is the aspect ratio. The inclusions are uniformly aligned in the matrix so that main crystallographic axes \((x, y, z)\) of the SCs are oriented as follows: \(x || OX_1\), \(y || OX_2\), and \(z || OX_3\). The spontaneous polarisation vector of each inclusion is oriented along the \(OX_3\) axis (Fig. 1), which is the poling axis of the sample as a whole. The polymer matrix can be either ferroelectric (piezo-active in the poled state) or simply dielectric (piezo-passive). It is assumed that surface charges appearing owing to the ferroelectric polarisation of the inclusions are to be fully screened by free charge carriers that would flow to interfaces separating the components. The above-described composite with \(\rho > 0\) is characterised by the 0–3 connectivity.

![Figure 1](image)

**Figure 1.** Schematic of the 0–3 composite with spheroidal inclusions. The spontaneous polarisation vector \(P\) of the inclusion is denoted by an arrow. \(X_1X_2X_3\) is the rectangular coordinate system. \(a_i\) are semiaxes of the spheroid, \(m\) is the inclusion volume fraction, and \(1 - m\) is the matrix volume fraction.
The effective electromechanical properties of the 0–3 composite are determined by means of the effective field method, i.e. the Mori-Tanaka method [7] generalised for heterogeneous piezoelectric media [8, 9]. In the calculation procedure we take into account the electromechanical interaction between the piezo-active inclusions in the matrix and related coupled effects and assume that wavelengths of an external acoustic field are much longer than the size of the inclusion. A matrix characterising the effective properties of the 0–3 composite is written in accordance with formulas [9] as

$$\| C^* \| = \| C^*(m, \rho) \| = \left( \| e^{sE} \| \| e^s \|', \| e^{sE} \|-\| e^{sE} \| \right),$$

where the superscript “t” denotes the transposition, $\| e^{sE} \|$, $\| e^s \|$, and $\| e^{sE} \|$ are matrices of elastic moduli, piezoelectric coefficients, and dielectric permittivities, respectively. These matrices depend on both $m$ and $\rho$. The calculation procedure requires complete sets of the electromechanical constants $c_{ij}^{(m,E)}$, $e_{ij}^{(m)}$, and $\varepsilon_{pq}^{(m,E)}$ of the components where the superscripts $n = 1$ and 2 are related to the inclusion and the matrix, respectively. Based on elements of $\| C^* \|$, it is possible to determine the effective piezoelectric coefficients $e_{ij}^*$, $d_{ij}^*$, $g_{ij}^*$, and $h_{ij}^*$, electromechanical coupling factors $k_{ij}^*$, and other parameters of the composite. As is well known [10], relations between the four types of the piezoelectric coefficients are written in the form $d_{ij}^* = e_{ij}^* s_{ij}^{E}$ and $g_{ij}^* = h_{ij}^* s_{ij}^{D}$, where $s_{ij}^{E}$ and $s_{ij}^{D}$ are elastic compliances.

3. $\Phi_{33}(\rho)$ Dependences Calculated for PMN–xPT-Based Composites

All calculations were carried out using room-temperature electromechanical constants of the PMN–xPT SCs ($x = 0.30, 0.33$ and 0.42) [11, 12] and 75/25 mol.% copolymer of vinylidene fluoride and trifluoroethylene (VDF–TrFE) [13]. This polymer component is characterised by the piezoelectric coefficients with $\text{sgn} e_{3j}^{(2)} = -\text{sgn} e_{3j}^{(1)}$ and $\text{sgn} d_{3j}^{(2)} = -\text{sgn} d_{3j}^{(1)}$ ($j = 1$ and 3), whereas the higher piezoelectric activity of the composite would take place under conditions $\text{sgn} e_{3j}^{(2)} = \text{sgn} e_{3j}^{(1)}$ and $\text{sgn} d_{3j}^{(2)} = \text{sgn} d_{3j}^{(1)}$. To increase the piezoelectric activity, we assume that the SC and polymer components are poled in opposite directions, i.e. the SC inclusions are poled parallel to the OX3 axis (see Fig. 1) and the polymer matrix is poled antiparallel to the OX3 axis. Such a variance of poling is possible due to the considerable difference [12, 14] between the coercive fields of the two materials. Moreover, the opposite poling directions allow improved piezoelectric performance of the related 0–3 composites based on the PMN–0.35PT [5] or PZT ceramics.

Figure 2 shows examples of the $\Phi_{33}(\rho)$ dependences, namely $e_{33}^*$, $d_{33}^*$, $g_{33}^*$, $\varepsilon_{33}^*$, $\varepsilon_{33}^E$, $s_{33}^{E}$, $s_{33}^{D}$, $k_{33}^*$, and $k_s^*$, which have been calculated at fixed $m$ values and characterising the response of the composite along the poling axis. It is revealed that the prolate SC inclusions with a molar concentration in the morphotropic region ($x = 0.30$ or 0.42) do not significantly affect the curves of Fig. 2 which are for $x = 0.33$; changes in the $\Phi_{33}$ values calculated for $0.01 \leq \rho \leq 1$ and $0.05 \leq m \leq 0.5$ are under 5% for $x = 0.30 - 0.42$. All the four piezoelectric coefficients (Figs. 2a, b, c, and d) show non-monotonous behaviour owing to factors, such as internal electric and stress fields, strong dependence of the internal fields, depolarization effects, and stress-relief conditions on the aspect ratio $\rho$, etc. One can see that the monotonous $\varepsilon_{33}^E (\rho)$ dependence (Fig. 2c) would not significantly influence the configuration of the curves as compared $e_{33}^*(\rho)$ (Fig. 2a) with $h_{33}^*(\rho)$ (Fig. 2c). Contrary to this, the non-monotonous $\varepsilon_{33}^E (\rho)$ dependence comprising a contribution [10] from the
piezoelectric coefficients is responsible for changes in the configuration of the curves $d_{33}^\ast(\rho) \rightarrow g_{33}^\ast(\rho)$ (compare Figs. 2b and 2, d).

A careful comparison of the $\Phi_{33}^\ast(\rho)$ curves enables us to find a series of interconnections between all the graphs in Fig. 2. Due to a considerable anisotropy of the

Figure 2. Effective parameters $\Phi_{33}^\ast(\rho, m)$ calculated for the 0–3 PMN–0.33PT SC/75/25 mol.% VDF–TrFE composite: piezoelectric coefficients $e_{33}^\ast$ (a, in C/m$^2$), $d_{33}^\ast$ (b, in pC/N), $h_{33}^\ast$ (c, in 10$^8$ V/m), and $g_{33}^\ast$ (d, in mV m/N), relative dielectric permittivities $\varepsilon_{33}^\ast/\varepsilon_0$ (e) and $\varepsilon_{33}^\sigma/\varepsilon_0$ (f), elastic compliances $s_{33}^E$ (g, in 10$^{-12}$ Pa$^{-1}$) and $s_{33}^D$ (h, in 10$^{-12}$ Pa$^{-1}$), and electromechanical coupling factors $k_{33}^\ast = d_{33}^\ast/(\varepsilon_{33}^\ast s_{33}^E)^{1/2}$ (i) and $k_t^\ast = e_{33}^\ast/(\varepsilon_{33}^\sigma s_{33}^D)^{1/2}$ (j). The components are assumed to be poled along the OX$_3$ axis in opposite directions. In all graphs, curves 1, 2, 3, 4, and 5 are related to $m = 0.1, 0.2, 0.3, 0.4$, and 0.5, respectively. (Continued)
piezoelectric coefficients $e^{(2)}_{33}/|e^{(2)}_{31}| \approx 32$ (polymer) and $e^{(1)}_{33}/|e^{(1)}_{31}| \approx 5 - 11$ (SCs), it is surprising that electromechanical coupling between the OX$_3$ and OX$_1$ (or OX$_3$ and OX$_2$) directions is practically eliminated. As a consequence, in the aforementioned $\rho$ and $m$ ranges, equalities

\[ d^{*}_{33} = e^{*}_{33} s^{*}_{33} E^{*}_{33} \quad (1) \]

and

\[ g^{*}_{33} = h^{*}_{33} s^{*}_{33} \quad (2) \]

are fulfilled with an accuracy up to 5\%, i.e. items $e^{*}_{31} s^{*}_{13}$ or $h^{*}_{31} s^{*}_{13}$ can be omitted. Considering the known formulas [10] for piezoelectric media

\[ h^{*}_{33} = e^{*}_{33}/\varepsilon^{*}_{33} \quad (3) \]

\[ g^{*}_{33} = d^{*}_{33}/\varepsilon^{*}_{33} \quad (4) \]

\[ s^{*}_{33} = s^{*}_{33} (1 - k^{*2}_{33}) \quad (5) \]

and

\[ \varepsilon^{*}_{33} = \varepsilon^{*}_{33} (1 - k^{*2}) \quad (6) \]
one can prove that an interrelation between the thickness-mode and longitudinal electromechanical coupling factors

\[ k_1^* \approx k_{33}^* \]  

holds true (compare Figs. 2i and 2j). The fulfilment of Eqs. (1)–(7) becomes obvious after comparing graphs from Fig. 2 using a generalized scheme shown in Fig. 3. It should be noted that the maximum \( \varepsilon_{33}^{**} \) and \( d_{33}^* \) values calculated for \( \rho \approx 1 \) and \( m = 0.4 – 0.5 \) (see curves 4 and 5 in Figs. 2b and f) are approximately equal to those experimentally measured [5, 6] on the 0–3 PMN–0.35PT ceramic/70/30 mol. VDF–TrFE composite. This composite with components poled in opposite directions, for example, is characterized by such values as \( \varepsilon_{33}^{**} / \varepsilon_0 = 37.3 \) and \( d_{33}^* = 31 \) pC/N at \( m = 0.4 \). The presence of the isolated spherical ceramic grains embedded in the polymer media is unable to provide a high level of piezoelectric activity, and this tendency is also observed in the 0–3 composites (Fig. 2b) based on the PMN–xPT SCs with a SC piezoelectric coefficient \( d_{33}^{(1)} \sim 10^3 \) pC/N [11, 12]. As for the prolate SC inclusions, they promote increasing the piezoelectric activity, but in a restricted range only.

A further improvement of the performance of the proposed 0–3 composites may be attained with the formation of a porous structure in the polymer matrix. Such the structure would not only promote changes in the \( e_{33}^{(2)}/|e_{31}^{(2)}| \) ratio, but also provide conditions for increasing the piezoelectric activity and/or sensitivity. Recently, a system of the oblate air pores was considered in paper [4] to show advantages of the 1–3-type composites based on the same PMN–xPT SCs. If such the regular porous structure is formed in the VDF–TrFE matrix, then the \( e_{33}^{(2)}/|e_{31}^{(2)}| \) ratio considerably changes in dependence on both the porosity...
### Table 1

<table>
<thead>
<tr>
<th>Parameters of the porous matrix</th>
<th>max $d_{33}^*$ (in pC/N)</th>
<th>max $e_{33}^*$ (in C/m$^2$)</th>
<th>max $g_{33}^*$ (in mV m/N)</th>
<th>max $h_{33}^*$ (in $10^8$ V/m)</th>
<th>max $k_{33}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix I, $\rho_p = 24$ and $m_p = 0.1$</td>
<td>240</td>
<td>2.16</td>
<td>759</td>
<td>162</td>
<td>0.881</td>
</tr>
<tr>
<td>(\rho = 0.09)</td>
<td>(\rho = 0.17)</td>
<td>(\rho = 0.001)</td>
<td>(\rho = 0.03)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Matrix II, $\rho_p = 3.75$ and $m_p = 0.1$</td>
<td>129</td>
<td>1.28</td>
<td>837</td>
<td>129</td>
<td>0.777</td>
</tr>
<tr>
<td>(\rho = 0.30)</td>
<td>(\rho = 0.45)</td>
<td>(\rho = 0.08)</td>
<td>(\rho = 0.22)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note. The piezoelectric coefficients of the matrix I are characterised by the equality $e_{33}^{(2)} = |e_{31}^{(2)}|$. The matrix II is related to the case when the equality $e_{33}^{(2)}/|e_{31}^{(2)}| = e_{33}^{(1)}/|e_{31}^{(1)}|$ holds.

$m_p$ and the aspect ratio $\rho_p$ of the air pore. The parameters $m_p$ and $\rho_p$ are introduced similarly to $m$ and $\rho$ as shown in Section 2, and such a composite having closed pores in the matrix is described by the 0–0–3 connectivity. It is also assumed that the size of the pore is much less than the size of the SC inclusion in the composite sample. Results of finding the maximum $\Phi_{33}^*(\rho)$ values at $m = 0.5$ are shown in Table 1 for comparison. As seen from Table 1, the porous matrix I improves better the piezoelectric activity ($d_{33}^*$) and electromechanical coupling, whereas the porous matrix II mainly favours an increase in the piezoelectric sensitivity ($g_{33}^*$) of the composite. Thus, microgeometry of the pores becomes an important factor to control the piezoelectric response of the 0–3-type composites based on the relaxor-ferroelectric SCs. A more detailed consideration of this problem could be a subject of the further study.

### 4. Conclusion

In this paper we have analysed the effective electromechanical properties of the 0–3 and 0–0–3 composites based on PMN–$x$PT SCs. The dependences of electromechanical properties on the aspect ratio $\rho$ and volume fraction $m$ of the spheroidal SC inclusions do not undergo considerable changes at variations of the molar concentration $x$ in the morphotropic region ($x = 0.30 – 0.42$). Predicted values are in agreement with those experimentally measured [5, 6] on the 0–3 PMN–0.35PT ceramic/70/30 mol. VDF–TrFE composite. Maximum values of the effective piezoelectric coefficients $d_{33}^*$, $e_{33}^*$, $g_{33}^*$, and $h_{33}^*$ as well as the electromechanical coupling factors $k_{33}^*$ and $k_{t}^*$ have been determined for the 0–3-type composites at $m = \text{const}$ from the range $0 < m \leq 0.5$. It has been shown that the considerable anisotropy of the piezoelectric coefficients $e_{3j}^{(n)}$ of both the components promotes the fulfillment of Eqs. (1)–(7), and such behaviour has no analogs among the piezo-composites studied earlier. The increase of the aforementioned maximum values is expected at forming the porous structure in the polymer matrix, namely, a system of oblate air pores distributed regularly in the matrix and changing a balance of the $e_{3j}^{(2)}$ values.

The results of the present work can be taken into account for the manufacture and design of the novel 0–3-type piezo-composites which can be used as elements of sensors, actuators, hydrophones, transducers, etc. Calculated dependences of the effective parameters $\Phi_{33}^*(\rho, m)$ allow determination of the ranges of $\rho$ in which the maxima of different piezoelectric coefficients and electromechanical coupling factors take place. The information concerning
the maxima and non-monotonous behaviour of the effective parameters is of benefit for the
optimisation and exploitation of the piezo-composite properties.

Acknowledgments

The authors would like to thank Prof. Dr. A. V. Turik, Prof. Dr. V. G. Gavrilyachenko
(Rostov-on-Don, Russia), and Prof. Dr. R. Stevens (Bath, UK) for their interest in the
research problems. Financial support by the Royal Society (London, UK, International
short visits) for the stay of one of the authors (V. Yu. T.) at the University of Bath is also
gratefully acknowledged.

References

1. T. Ritter, X. Geng, K. K. Shung, P. D. Lopath, S.-E. Park, and T. R. Shrout, Single crystal PZN/PT-
2. K. C. Cheng, H. L. W. Chan, C. L. Choy, Y. Qingrui, L. Hasou, and Y. Zhiwen, Single crystal
PMN-0.33PT/epoxy 1–3 composites for ultrasonic transducer applications. *IEEE Trans. Ultrason.
3. V. Yu Topolov, S. V. Glushanin, and A. E. Panich, Features of the piezoelectric response for a
4. S. V. Bezus, V. Yu Topolov, and C. R. Bowen, High-performance 1–3-type composites based on
\((1 - x)Pb(A_{1/3}Nb_{2/3})O_3 - xPbTiO_3\) single crystals \((A = \text{Mg, Zn})\). *J. Phys. D: Appl. Phys.* **39**, 
5. K. H. Lam and H. L. W. Chan, Piezoelectric and pyroelectric properties of 65PMN-35PT/P(VDF-
7. T. Mori and K. Tanaka, Average stress in matrix and average elastic energy of materials with
8. M. Levin, M. I. Rakovskaja, and W. S. Kreher, The effective thermoelectroelastic properties of
9. V. Yu Topolov and M. Kamla, Piezoelectric properties of PbTiO$_3$-based 0–3 and 0–1–3 com-
11. R. Zhang, B. Jiang, and W. Cao, Elastic, piezoelectric and dielectric properties of multidomain
properties of 0.58Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ – 0.42PbTiO$_3$ single crystal. *J. Appl. Phys.* **96**, 549–554 
(2004).
14. K. L. Ng, H. L. W. Chan, and C. L. Choy, Piezoelectric and pyroelectric properties of PZT/P(VDF-
TrFE) composites with constituent phases poled in parallel or antiparallel directions. *IEEE Trans.