Domain-engineered single crystals (SCs) of relaxor-ferroelectric \((1-x)\text{Pb}(\text{Mg\textsubscript{1/3}\text{Nb\textsubscript{2/3}}})\text{O}_3-x\text{PbTiO}_3\) (PMN-xPT) and \((1-y)\text{Pb}(\text{Zn\textsubscript{1/3}\text{Nb\textsubscript{2/3}}})\text{O}_3-y\text{PbTiO}_3\) (PZN-yPT) solid solutions are advanced materials that exhibit a range of intriguing properties such as high piezoelectric activity, large electromechanical coupling factors, and dielectric permittivities near the morphotropic phase boundary. The aforementioned SCs are used as highly effective components of modern piezo-composites that are applied in piezotechnical devices for applications including hydroacoustic, transducer and energy-harvesting applications.

Among the piezo-composites based on either PMN-xPT or PZN-yPT SCs, of specific interest are two-component (SC/polymer) materials\(^{3-5}\) with 1–3 and 2–2 connectivity patterns in terms of Ref. 6. Examples of the 1–3-type three-component composites and their improved effective characteristics in comparison to the conventional 1–3 systems were studied in Refs. 5, 7, 8. Despite a relatively simple 2–2 composite architecture (i.e., a system of alternating layers of two components only), approaches to modify this architecture to enhance the piezoelectric performance are yet to be studied in detail. Recently samples of a 2–2-type PZT ceramic / heterogeneous polymer composite were prepared\(^9\) by adding an inorganic component (graphite, silicon or strontium ferrite in the powder form) to each polymer layer. This use of such additives promoted an improvement in specific effective parameters of the composites. For instance, in the PZT-based composite containing strontium ferrite in the polymer layers,\(^9\) larger values of the ECF \(k_E\) at the thickness oscillation mode were achieved. It is therefore probable that an improvement of the piezoelectric response and related parameters of the 2–2-type composites can be achieved by employing a system of 0–3 ceramic / polymer layers as a counterpart to the main piezo-active component. The aim of the present report is to describe the influence of ferroelectric ceramic inclusions in the 0–3 layer on the performance of the 2–2-type composites based on relaxor-ferroelectric SCs.

We assume that the 2–2-type composite to be studied consists of the system of parallel-connected layers of two types (Fig. 1), and these layers are arranged regularly along the \(OX_1\) axis. The first type is represented by the domain-engineered SC with the spontaneous polarisation \(P_s^{(0)}\) and main crystallographic axes \(X||OX_1\), \(Y||OX_2\) and \(Z||P_s^{(0)}||OX_3\).
The second stage of the layers is regarded as a ferroelectric ceramic / polymer medium that is characterised by 0–3 connectivity in terms of Ref. 6. The shape of each ceramic inclusion (see inset in Fig. 1) obeys the equation \((x_1/a_1)^2+(x_2/a_2)^2+(x_3/a_3)^2=1\) relative to the axes of the coordinate system \((X_1X_2X_3)\), and \(\rho=a_1/a_3\) is the aspect ratio of the inclusion. The linear sizes of the inclusion are much smaller than the thickness of each layer as measured along \(OX_3\). The ceramic inclusions occupy sites of a simple tetragonal lattice with unit-cell vectors parallel to the \(OX_3\) axes. As a whole, the composite (Fig. 1) is characterised by 2–0–2 connectivity.

Effective electromechanical properties of the 2–0–2 composite can be evaluated as follows. At the first stage, the effective properties of the 0–3 ceramic / polymer matrix are determined using the effective field method\(^5\) that takes into consideration an interaction between the inclusions. At the second stage, the effective properties of the 2–0–2 composite are evaluated using the matrix method\(^5\) and represented as functions of the volume fraction of SC \(m\), volume fraction of ceramic inclusions \(m_i\) in the 0–3 layer and aspect ratio of these inclusions \(\rho\). Hereafter we analyse the following hydrostatic parameters of the composite: its piezoelectric coefficients

\[
d_{33}^* = d_{33}^* + d_{12}^* + d_{31}^*, \quad e_{33}^* = e_{33}^* + e_{12}^* + e_{31}^*,
\]

squared figure of merit (SFM)

\[
(Q_f)^2 = d_{33}^* g_{33}^*,
\]

and ECF

\[
k_h^* = d_{33}^*/(e_{33}^* s_{33}^* E)^{1/2}.
\]

In Eq.(2), \(g_{33}^* + g_{12}^* + g_{31}^*\) is the hydrostatic piezoelectric coefficient. In Eq.(3), \(e_{33}^*\) is dielectric permittivity at mechanical stress \(\sigma=\) const, and

\[
s_{33}^* = \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} e_{\alpha \beta}^* E_{\alpha \beta}
\]

is hydrostatic elastic compliance at electric field \(E=\) const.

The piezoelectric coefficients \(d_{ij}^*\) and \(g_{ij}^*\) from Eqs. (1) and (2) describe the piezoelectric activity and sensitivity, respectively, under hydrostatic loading. The piezoelectric coefficient \(e_{33}^*\) from Eq.(1) is of interest to take into account sound propagation from an acoustic antenna in water. The ECF \(k_h^*\) from Eq.(3) describes the effectiveness of the energy conversion under hydrostatic loading.

Among the components of interest of manufacturing such a system, we consider [001]-poled domain-engineered PMN–0.33PT and PZN–0.08PT as SC layers with high piezoelectric activity, modified PbTiO\(_3\) ceramic with the large piezoelectric anisotropy and moderate piezoelectric activity for the ceramic inclusion, and piezo-passive polyethylene for the polymer matrix. To predict volume-fraction \((m, m_i)\) and aspect-ratio \((\rho)\) dependences of the effective parameters (1)–(3) of the 2–0–2 composite, we use electromechanical constants of the PMN–0.33PT\(^{10}\) and PZN–0.08PT\(^{11}\) SCs, modified PbTiO\(_3\) ceramic\(^{12}\) and polyethylene\(^{13,14}\) at the Poisson’s ratio 0.20. As follows from our evaluations, the 0–3 layer exhibits a low piezoelectric activity\(^8\) due to the isolated ceramic inclusions at \(0< m \leq 0.3\) and \(0.01 \leq \rho \leq 0.1\). Even though it is assumed that the level of electric poling of the 0–3 layer is ideal, the absolute values of its piezoelectric coefficients would be \(|d_{ij}^*|< 10\) pC/N.\(^8\) Hereafter we neglect the piezoelectric properties of the 0–3 layers in the studied 2–0–2 composites.

Examples of the hydrostatic piezoelectric response (Figs. 2 and 3) suggest that ceramic inclusions in the 0–3 layer strongly influence the parameters (1)–(3) even in the non-poled state and at relatively small volume fractions \(m_i\). A simple comparison of values of max\(d_{ij}^*\) of the 2–0–2 composite (Fig. 2a, curves 1–8 and 2a) and max\(d_{ij}^*\) of the 2–0–2 composite analog (Fig. 2a, curve 9) testifies to the active role of the elastic properties of the 0–3 layer in forming the piezoelectric response. The value of max\(d_{ij}^*\) increases with increasing the aspect ratio \(\rho\) at \(m=\) const (cf. curves 1 and 8 in Fig. 2a). In the presence of heavily oblate ceramic inclusions (\(\rho=100\)), we obtain max\(d_{ij}^*\) \(≈ 1000\) pC/N for both the 2–0–2 composites (Fig. 3a and 3b). As follows from experimental data\(^{10,11}\), \(d_{ij}^{\text{pol}} = -20\) pC/N and 160 pC/N for PZN–0.08PT SC and PMN–0.33PT SC, respectively. Despite this large difference, we observe a relatively small...
Remarkable hydrostatic piezoelectric response of novel 2–0–2 composites

**Fig. 2.** Volume-fraction ($m$) dependence of the hydrostatic piezoelectric coefficient $d'_{ii}$ (a, in pC/N), hydrostatic SFM ($Q'_{ii}$) (b, in $10^{-12}$ Pa$^{-1}$) and hydrostatic piezoelectric coefficient $d''_{ii}$ (c, in C/m$^2$) of the 2–0–2 PMN–0.33PT SC / modified PbTiO$_3$ ceramic / polyethylene composite. Curve 9 in graph (a) is related to the 2–2 PMN–0.33PT SC / polyethylene composite. The difference between maxima $d''_{ii}$ in Fig. 3a and 3b. Moreover, these maxima at $\rho_i > 1$ are achieved at $m_i = 0.19$. As follows from our results on the 0–3 layer, its elastic compliances $s_{ii}^{(2)}$ at $m_i = 0.19$ and $\rho_i = 100$ exhibit a large degree of anisotropy: e.g., $s_{11}^{(2)} / s_{12}^{(2)} = -5.68$, $s_{13}^{(2)} / s_{44}^{(2)} = -4.30$ and $s_{11}^{(2)} / s_{33}^{(2)} = 0.104$. The elastic compliances $s_{ab}^{(1)E}$ of the PZN–0.08PT$^{11}$ and PMN–0.33PT$^{10}$ SCs lead to ratios $s_{11}^{(1)E} / s_{12}^{(1)E} \approx s_{12}^{(1)E} / s_{22}^{(1)E} \approx 1.3–1.7$ and $s_{33}^{(1)E} / s_{33}^{(2)} \approx 0.11–0.13$, and these ratios favour large values of both $d'_{ii}$ and $d''_{ij}$. The large piezoelectric coefficient $d'_{ii}$ leads to large values of the

**Fig. 3.** Behaviour of the hydrostatic piezoelectric coefficient $d'_{ii}$ (a and b, in pC/N) and hydrostatic ECF $k''_{ij}$ (c and d) of the 2–0–2 PMN–0.33PT SC / modified PbTiO$_3$ ceramic / polyethylene composite (a and c) and 2–2 PMN–0.08PT SC / modified PbTiO$_3$ ceramic / polyethylene composite (b and d) near maxima of the parameters at $\rho_i = 100$. 
SFM \((Q_e^0)^2 \) (Fig. 2b) and ECF \(k'\) (Fig. 3c and d), and a correlation between \(\max d'_e, \max[(Q_e^0)^2]\) and \(\max k'_\parallel\) is observed. For comparison we add that the PMN–0.33PT SC\(^{10}\) is characterised by \((Q_e^0)^2= 3.53 \times 10^{-13} \text{ Pa}^{-1}, k'_\parallel = 0.167\) and \(e'_s = 15.5 \text{ C/m}^2\), and the PZN–0.08PT SC\(^{11}\) is characterised by \((Q_e^0)^2= 5.87 \times 10^{-15} \text{ Pa}^{-1}, k'_\parallel = -0.0258\) and \(e'_s = 6.71 \text{ C/m}^2\). A displacement of max\([(Q_e^0)^2]\) to smaller \(m\) values in comparison to \(\max d'_e\) (cf. Fig. 2a and 2b) is caused by a sharp max \(g'_e\) at \(m<0.01\). Such a behaviour is a result of the strong influence of relatively small values of \(e'_s^m\) on \(g'_e\) at \(m<<1\). The sharp max \(g'_e\) is also typical of the 2–2 SC/polymer composite.\(^{4,5}\)

In contrast to max \(d'_e\) and max \(g'_e\), max \(e'_s\) is achieved at large volume fractions of SC \(m\) (Fig. 2c), and non-oblite ceramic inclusions promote larger values of \(e'_s\) at \(m=\text{const}\). The system of interfaces \(x=\text{const}\) (Fig. 1) and prolate ceramic inclusions in the 0–3 layers leads to decreasing \(|e'_s|\) and \(|e'_s^m|\) in the wide \(m\) range. As a consequence, \(e'_s^m\) becomes the largest contribution into \(e'_s\), and max \(e'_s\) appears at large \(m\) values. This effect is mainly accounted for by the specific elastic anisotropy of the SC component while the piezoelectric coefficients \(d'_e\) of the composite at \(m\geq 0.9\) slowly approach \(d'^{\infty}_e\) of SC.

Due to the large hydrostatic parameters, the 2–0–2 composites have advantages over some composites based on relaxor-ferroelectric SCs. For instance, in a 1–0–3 PZN–0.08PT SC / modified PbTiO\(_3\) ceramic / polyurethane composite,\(^{8}\) values of \(d'_s\sim 10^2 \text{ pC/N, (Q_{e^0}}^2\sim 10^{-11} \text{ Pa}^{-1},\) and \(k'_\parallel\sim 0.5–0.6\) are less than those of the studied 2–0–2 composites. Such a performance of the 1–0–3 composite is linked with its architecture, namely, with one direction of the continuous distribution of the piezo-active SC component\(^{5,7,8}\) only. For a 2–2 composite based on the [011]-poled PMN–xPT SC, values of \(d'_s = 337 \text{ pC/N and (Q_{e^0}}^2= 1.6 \times 10^{-11} \text{ Pa}^{-1}\) are achieved.\(^{1}\) These values are smaller than those of the 2–0–2 composites (see data in Figs. 2 and 3) because of a less pronounced influence of the isotropic polymer layers on the hydrostatic performance of the 2–2 composite. We add that the value of \(e'_s\sim 20 \text{ C/m}^2\) (Fig. 2c) is about 1.5–4 times larger than \(e'_s\) of widespread poled ferroelectric ceramics.\(^{5,12}\)

In the present report we have analysed the hydrostatic parameters (1)–(3) of novel 2–0–2 composites. Taking into account the contrasting properties of their components, we conclude as follows. First, the relaxor-ferroelectric SC component plays the dominating role in forming the piezoelectric performance of the 2–0–2 composite irrespective of its piezo-passive components. Second, the 0–3 ceramic/polymer layer exhibits a considerable level of elastic anisotropy and plays a key role in forming the pronounced hydrostatic piezoelectric response of the 2–0–2 composite. Third, due to the distinct correlation between \(d'_e^*, (Q_e^0)^2\) and \(g'_e\) in the presence of the 0–3 layers with specific microgeometry, it is possible to select volume-fraction \(m\) ranges wherein maxima of these three parameters are predicted. The large values of \(d'_e^*, (Q_e^0)^2\) and \(g'_e\) (Figs. 2 and 3) of the 2–0–2 composites examined here make them attractive for hydroacoustic and transducer applications.

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